
International Standard



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Rubber and latex — Determination of copper content — Photometric method

Caoutchouc et latex — Dosage du cuivre — Méthode photométrique

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established 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. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 8053 was prepared by Technical Committee ISO/TC 45, *Rubber and rubber products*.

It cancels and replaces International Standard ISO 1396-1975 and ISO Recommendation R 1654-1971, of which it constitutes a technical revision.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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Rubber and latex — Determination of copper content — 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 even in relatively large amounts, without degradation taking place, but in these cases there is always the possibility that under the influence of some chemicals, notably the unsaturated acids, the copper could assume a more aggressive oxidative catalytic 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 but to determine the total amount of copper in the rubber. The method described here is a combination of ISO/R 1654-1971 and ISO 1396-1975.

The method specified in this International Standard is applicable to all the commonly used elastomers, including those containing chlorine.

1 Scope and field of application

This International Standard specifies a photometric method for the determination of trace amounts of copper in raw rubber, latices and compounded rubber, both natural and synthetic.

This method may be applied to rubbers containing silica, provided that treatment with hydrofluoric acid is included in the procedure.

The method is sensitive down to 1 mg/kg copper.

2 References

ISO 123, *Rubber latex — Sampling.*

ISO 124, *Rubber latices — Determination of total solids content.*

ISO 247, *Rubber — Determination of ash.*

ISO 648, *Laboratory glassware — One-mark pipettes.*

ISO 1042, *Laboratory glassware — One-mark volumetric flasks.*

ISO 1795, *Raw rubber in bales — Sampling.*

ISO 1796, *Rubber, raw — Sample preparation.*

ISO 4661/2, *Rubber, vulcanized — Preparation of test pieces — Part 2: Chemical tests.*

3 Principle

The rubber sample is subjected to ashing or digestion in a mixture of concentrated sulfuric and nitric acids, followed by removal of excessive amounts of calcium (if present) and complexing of any iron present with ammonium citrate. After making alkaline, the aqueous solution is shaken with a solution of diethyldithiocarbamate in 1,1,1-trichloroethane to form and extract the yellow copper complex. Spectrophotometric measurement of this solution, and comparison of the result with those for standard matching solutions, permit the quantitative determination of copper.

4 Reagents

All precautions and safeguards for carrying out trace metal analysis shall be observed. All recognized health and safety precautions shall be observed when carrying out the procedures specified in this International Standard.

For the analysis, only reagents of recognized analytical grade and only distilled water or water of equivalent purity shall be used.

4.1 Sodium sulfate, anhydrous.

4.2 Sulfuric acid, concentrated, $\rho = 1,84 \text{ g/cm}^3$.¹⁾

1) The term millilitre (ml) is commonly used as a special name for the cubic centimetre (cm³), in accordance with a decision of the 12th Conférence Générale des Poids et Mesures. Glassware with either designation is acceptable for use in this International Standard.

4.3 Nitric acid, concentrated, $\rho = 1,42 \text{ g/cm}^3$.

4.4 Hydrochloric acid/nitric acid mixture, prepared as follows:

Mix together

- 2 volumes of hydrochloric acid, $\rho = 1,18 \text{ g/cm}^3$
- 1 volume of nitric acid, $\rho = 1,42 \text{ g/cm}^3$
- 3 volumes of water

4.5 Hydrogen peroxide, 30 %.

4.6 Ammonia solution, $\rho = 0,890 \text{ g/cm}^3$.

4.7 Hydrochloric acid, $c(\text{HCl}) = 5 \text{ mol/l}$.

4.8 Hydrofluoric acid, $\rho = 1,13 \text{ g/cm}^3$.

4.9 Citric acid solution.

Dissolve 50 g of citric acid in 100 cm³ of water.

4.10 Zinc diethyldithiocarbamate reagent

Dissolve 1 g of solid zinc diethyldithiocarbamate in 1 000 cm³ of 1,1,1-trichloroethane. 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 sulfate heptahydrate. Extract the resulting zinc diethyldithiocarbamate by shaking with 100 cm³ of 1,1,1-trichloroethane in a separating flask. Separate the 1,1,1-trichloroethane layer and dilute to 1 000 cm³ with 1,1,1-trichloroethane.

This reagent is stable for at least 6 months when stored in a bottle of non-actinic glass.

4.11 Copper, standard solution, containing 0,01 g of Cu per cubic decimetre.

Weigh 0,393 g of copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) into a small beaker and dissolve in water. Add 3 cm³ of the concentrated sulfuric acid (4.2), transfer the solution to a 1 000 cm³ volumetric flask (5.6) and dilute with water to the mark to form the stock solution. Pipette 10 cm³ of this stock solution into a 100 cm³ volumetric flask (5.6) and dilute with water up to the reference mark.

1 cm³ of this solution contains 0,01 mg of Cu.

Prepare freshly from the stock solution when required.

4.12 Magnesium oxide.

4.13 Litmus paper.

4.14 Filter paper (hardened paper, resistant to acids).

5 Apparatus

Ordinary laboratory apparatus and

5.1 Photometer or spectrophotometer, capable of measuring absorbance at approximately 435 nm, with matched cells, usually 10 mm path length.

5.2 Kjeldahl flask, of capacity 100 cm³, of silica or borosilicate glass.

5.3 Crucibles or dishes of porcelain, silica or platinum, of capacity 50 cm³ for small samples, appropriately larger for large samples.

Porcelain or silica ware, especially if etched, should be lined with about 0,1 g of magnesium oxide, distributed over the base and partly up the sides. This minimizes the possibility that copper will be adsorbed on the etched walls and on fillers (if present) and instead the copper will now be preferentially adsorbed on the magnesium oxide. Platinum ware need not be treated with magnesium oxide.

5.4 Pipette, 25 cm³, complying with the requirements of ISO 648.

5.5 Balance, accurate to 0,1 mg.

5.6 One-mark volumetric flasks, 100 cm³ and 1 000 cm³, complying with the requirements of ISO 1042.

5.7 Electric heating plate or gas burner with sand bath.

5.8 Platinum rod, as stirrer.

6 Sampling, sample preparation and selection of test portion

6.1 For raw rubber, carry out the sampling in accordance with ISO 1795 and prepare the sample in accordance with ISO 1796.

6.2 For latex, carry out the sampling in accordance with one of the methods specified in ISO 123 and sample preparation in accordance with ISO 124.

6.3 For rubber compounds, carry out the sampling to obtain as representative a sample of the compound as possible. See ISO 4661/2.

6.4 Weigh, to the nearest 0,001 g, a test portion of between 2 and 10 g, selected from 6.1, 6.2 or 6.3.

NOTE — The size of the test portion depends upon the amount of copper present. It should be selected to give an absorbance reading of 0,3 to 0,8 absorbance units, or in the case of very low amounts of copper, at least 10 times the absorbance reading of a blank. Appropriate test portion size will depend largely upon prior experience.

7 Determination

The determinations shall be carried out in duplicate.

7.1 Preparation of the test portion may be by milling (7.1.1) and/or by comminution (7.1.2).

7.1.1 Mill the sample by passing it 6 times between the cold rolls of a laboratory mill set to a nip of 0,5 mm, rolling the rubber into a cylinder after each pass and presenting the cylinder end-on to the rolls for the next pass.

7.1.2 Cut the sample into pieces of not more than 0,1 g.

7.2 Dissolution of the test portion for the measurement of copper may be by ashing (7.2.1) or by acid digestion (7.2.2). If the rubber contains chlorine, the acid digestion method (7.2.2) shall be used.

7.2.1 Ash the test portion in accordance with method A or method B of ISO 247. After ashing, moisten the contents of the crucible with 0,5 to 1 cm³ of water, then add 10 cm³ of the acid mixture (4.4), cover with a clock glass and heat at about 100 °C for 30 to 60 min. If the ash is totally dissolved, transfer the solution, quantitatively, to a small conical flask and proceed in accordance with 7.3.

If the ash is not totally dissolved, or if silicates are known to be present, proceed as follows.

Repeat the ashing in accordance with method A or method B of ISO 247, using a new test portion and a platinum crucible. After ashing, add a few drops of the sulfuric acid (4.2) and heat to fuming. Cool, and add a further 3 drops of the sulfuric acid and 5 cm³ of the hydrofluoric acid (4.8). Heat on the electric heating plate or sand bath (5.7) and evaporate to dryness while stirring with the platinum rod (5.8). Repeat this procedure twice or until all silicates have been removed as indicated by the absence of white fumes of silicon tetrafluoride.

Cool, moisten the contents of the crucible with 0,5 to 1 cm³ of water, add 10 cm³ of the acid mixture (4.4), cover with a clock glass and heat at about 100 °C for 30 to 60 min. Transfer the solution, quantitatively, to a small conical flask and proceed in accordance with 7.3.

7.2.2 Digest the test portion with 4 cm³ of the sulfuric acid (4.2) and 3 cm³ of the nitric acid (4.3), in a Kjeldahl flask (5.2). Warm the flask to start the reaction.

NOTE — The quantities of reagents in 7.2.2 are for a 2 g test portion. If a larger test portion is used, appropriately larger portions of acid will be required.

7.2.2.1 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 cm³ 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 cm³ of the sulfuric 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 cm³ of hydrogen peroxide (4.5) 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 cm³ of water and evaporate to fuming. Finally, cool the solution and add 5 cm³ of water.

7.2.2.2 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 cm³ portions of water which are also 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 cm³ of the hydrochloric acid (4.7) 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. Rinse the Kjeldahl flask with three 5 cm³ portions of water which are also added to the flask.

7.3 Add 5 cm³ of the citric acid solution (4.9) to the contents of the conical flask and if, on cooling, the solution remains clear, neutralize it by the drop by drop addition of the ammonia solution (4.6), using a small piece of litmus paper as indicator. If, however, calcium sulfate crystallizes out from the solution on cooling, chill the flask and contents to about 10 °C, filter into a second conical flask and wash and filter the contents with three 2 cm³ portions of ice-cold water before neutralizing with the ammonia solution (4.6). Cool the solution, for example by immersion in running water, transfer to a separating funnel, add a further 2 cm³ of ammonia solution, and then dilute to about 40 cm³ with water. Using a pipette add 25 cm³ of the zinc diethyldithiocarbamate reagent (4.10) to the solution and shake the funnel for 2 min. Immediately after separation, draw the 1,1,1-trichloroethane layer into a stoppered flask containing about 0,1 g of the anhydrous sodium sulfate (4.1). If turbidity persists after standing for about 30 min, make further small additions of anhydrous sodium sulfate until the solution becomes clear.

7.4 Filter the 1,1,1-trichloroethane solution through a plug of glass wool or a small filter paper into the cell of the photometer or spectrophotometer (5.1), and measure the absorbance at the wavelength used in preparing the calibration curve (see clause 8), using 1,1,1-trichloroethane in the reference cell. Correct the reading by subtracting the absorbance of the blank solution.

7.5 Carry out a blank determination by using the appropriate preparation and the appropriate quantity of reagents, but omitting the test portion (see 7.4). The blank shall be not greater than 2 ppm.

8 Preparation of calibration curves

8.1 Prepare a series of standard solutions each consisting of 5 cm³ of the sulfuric acid (4.2) diluted to 10 cm³ with water.

To these solutions add portions of the standard copper solution (4.11) ranging from 0 to 10 cm³, followed by 5 cm³ of the citric acid solution (4.9). Add the ammonia solution (4.6), drop by drop, until the solutions are just alkaline to the litmus paper (4.13). Cool the solutions, transfer individually to a separating

funnel and add to each a further 2 cm³ of the ammonia solution. Using a pipette (5.4), add to each solution 25 cm³ of the zinc diethyldithiocarbamate reagent (4.10) and shake for 2 min. Immediately after separation, draw the 1,1,1-trichloroethane layer into a stoppered flask containing about 0,1 g of the anhydrous sodium sulfate (4.1). If turbidity persists after standing for about 30 min, add further small quantities of the anhydrous sodium sulfate.

NOTE — If magnesium oxide was used to ash the test portion (see 5.3), the same quantity should be present in each standard solution.

8.2 Filter each 1,1,1-trichloroethane solution through a plug of glass wool or a small filter paper (4.14) into the cell of the photometer or spectrophotometer (5.1) and measure the absorbance at the wavelength of maximum absorption (about 435 nm) using 1,1,1-trichloroethane in the reference cell. Correct the readings by subtracting the absorbance of the solution containing no added copper.

8.3 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.

9 Expression of results

9.1 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.

9.2 Express the results as milligrams of copper per kilogram.

9.3 Take as the result the mean of the two determinations.

10 Test report

The test report shall include the following information:

- a) reference to this International Standard;
- b) identification of the sample;
- c) the results and the method of expression used;
- d) the method of ashing used;
- e) whether hydrogen fluoride treatment was carried out;
- f) any unusual features noted during the determination;
- g) any operation not included in this International Standard or in the International Standards to which reference is made, or regarded as optional.

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