INTERNATIONAL STANDARD

ISO 8053

Second edition
1995-04-01

Rubber and latex — Determination of copper content — Photometric method

Caoutchouc et latex — Dosage du cuivre — Méthode photométrique

Reference number
ISO 8053:1995(E)

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. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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

This second edition cancels and replaces the first edition (ISO 8053:1986), of which it constitutes a minor revision.

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Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

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

Another method for the determination of the copper content of rubber and latex is given in ISO 6101-3:1988, *Rubber — Determination of metal content by atomic absorption spectrometry — Part 3: Determination of copper content*.

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Rubber and latex — Determination of copper content — Photometric method

WARNING — Persons using this International Standard shall be familiar with normal laboratory practice. This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

1 Scope

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 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 123:1985, *Rubber latex — Sampling.*

ISO 247:1990, *Rubber — Determination of ash.*

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 1042:1983, *Laboratory glassware — One-mark volumetric flasks.*

ISO 1795:1992, *Rubber, raw, natural and synthetic — Sampling and further preparative procedures.*

3 Principle

A test portion 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. Spectrometric measurement of this solution, and comparison of the result with those for standard matching solutions, permit the quantitative determination of copper.

4 Reagents and materials

WARNING — 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.

During the analysis, use only reagents of recognized analytical grade and only distilled water or water of equivalent purity.

4.1 Sodium sulfate, anhydrous.

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

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

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

Mix together

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

4.5 Hydrogen peroxide, 30 %(m/m).

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

4.7 Hydrochloric acid, $c(\text{HCl}) = 5\ \text{mol/dm}^3$.

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

4.9 Citric acid solution.

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

4.10 Zinc diethyldithiocarbamate reagent.

Dissolve 1 g of solid zinc diethyldithiocarbamate in 1 000 cm^3 of 1,1,1-trichloroethane. 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 sulfate heptahydrate. Extract the resulting zinc diethyldithiocarbamate by shaking with 100 cm^3 of 1,1,1-trichloroethane in a separating flask. Separate the 1,1,1-trichloroethane layer and dilute to 1 000 cm^3 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 ($CuSO_4 \cdot 5H_2O$) into a small beaker and dissolve in water. Add 3 cm^3 of concentrated sulfuric acid (4.2), transfer the solution to a 1 000 cm^3 volumetric flask (5.6), 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 (5.6), and dilute with water up to the reference mark.

1 cm^3 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, plus the following:

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

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

5.3 Crucibles or dishes of porcelain, silica or platinum, of capacity 50 cm^3 for small samples, appropriately larger for large samples.

Porcelain or silica ware, especially if etched, shall be lined with about 0,1 g of magnesium oxide (4.12), 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 cm^3, complying with the requirements of ISO 648.

5.5 Balance, accurate to 0,1 mg.

5.6 One-mark volumetric flasks, 100 cm^3 and 1 000 cm^3, 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

6.1 For raw rubber, carry out the sampling in accordance with ISO 1795.

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

6.3 For rubber compounds, carry out the sampling to obtain as representative a sample of the compound as possible.

7 Procedure

The determination shall be carried out in duplicate.

7.1 Preparation of solid test samples may be by milling (see 7.1.1) and/or by comminution (see 7.1.2).

7.1.1 Mill the test 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 test sample into pieces of not more than 0,1 g.

7.1.3 Weigh, to the nearest 1 mg, a test portion of between 2 g and 10 g from the sample taken as specified in 6.1, 6.2 or 6.3 and, in the case of solid samples, prepared as specified in 7.1.

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

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 247:1990. After ashing, moisten the contents of the crucible with 0,5 cm^3 to 1 cm^3 of water, then add 10 cm^3 of the acid mixture (4.4), cover with a watch glass and heat at about 100 °C for 30 min 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 fresh platinum crucible. After ashing, add a few drops of sulfuric acid (4.2) and heat to fuming. Cool, and add a further 3 drops of sulfuric acid and 5 cm^3 of 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 cm^3 to 1 cm^3 of water, add 10 cm^3 of the acid mixture (4.4), cover with a watch glass and heat at about 100 °C for 30 min 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 cm^3 of sulfuric acid (4.2) and 3 cm^3 of nitric acid (4.3) in a Kjeldahl flask (5.2). Warm the flask to start the reaction.

NOTE 1 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 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 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 cm^3 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 cm^3 of water and evaporate to fuming. Finally, cool the solution and add 5 cm^3 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 cm^3 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 cm^3 of 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 cm^3 portions of water which are also added to the flask.

7.3 Add 5 cm^3 of 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 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 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 (5.4), add 25 cm^3 of zinc diethyldithiocarbamate reagent (4.10) to the solution and shake the funnel for 2 min. Immediately after separation, draw the 1,1,1-tricholoroethane layer into a stoppered flask containing about 0,1 g of 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 spectrometer (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, using the appropriate preparation and the appropritе quantity of reagents, but omitting the test portion. The blank shall be not greater than 2 mg Cu/kg.

8 Preparation of calibration curves

8.1 Prepare a series of standard solutions each consisting of 5 cm^3 of sulfuric acid (4.2) diluted to 10 cm^3 with water.

To these solutions add portions of standard copper solutions (4.11) ranging from 0 cm^3 to 10 cm^3, followed by 5 cm^3 of citric acid solution (4.9). Add ammonia solution (4.6), drop by drop, until the solutions are just alkaline to litmus paper (4.13). Cool the solutions, transfer individually to a separating funnel and add to each a further 2 cm^3 of ammonia solution. Using a pipette (5.4), add to each solution 25 cm^3 of 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 mg of anhydrous sodium sulfate (4.1). If turbidity persists after standing for about 30 min, add further small quantities of anhydrous sodium sulfate.

If magnesium oxide was used to ash the test portion (see 5.3), the same quantity shall 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 spectrometer (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 concentation 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 two determinations.

10 Test report

The test report shall include the following information:

a) a reference to this International Standard;

b) all details necessary for complete identification of the sample;

c) the method of ashing used;

d) whether hydrogen fluoride treatment was carried out;

e) the results and the units in which they are expressed;

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, as well as any operation regarded as optional;

h) the date of the test.