BRITISH STANDARD

METHODS OF TESTING VULCANIZED RUBBER

PART B 17. DETERMINATION OF TOTAL COPPER

B.S. 903 : Part B 17 : 1959

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THIS BRITISH STANDARD, having been approved by the Rubber Industry Standards Committee and endorsed by the Chairman of the Chemical Divisional Council, was published under the authority of the General Council on 20th February, 1959.

The following B.S.I. references relate to the work on this standard:
Committee references RUC 10, RUC 10/12
Draft for comment CY(RUC) 7974

CO-OPERATING ORGANIZATIONS

The Rubber Industry Standards Committee, under whose supervision this British Standard was prepared, consists of representatives from the following Government departments and scientific and industrial organizations:

*British Rubber Producers' Research Association
*Federation of British Rubber and Allied Manufacturers
*Institution of the Rubber Industry
*Ministry of Supply
Natural Rubber Development Board
*Research Association of British Rubber Manufacturers
*Rubber Growers' Association

The Government department and scientific and industrial organizations marked with an asterisk in the above list, together with the following, were directly represented on the committee entrusted with the preparation of this British Standard:

Admiralty
Air Ministry
Association of British Chemical Manufacturers
British Chemical Plant Manufacturers' Association
British Electrical and Allied Industries Research Association
British Railways, The British Transport Commission
British Rubber and Resin Adhesive Manufacturers' Association
Department of the Government Chemist
Institution of Chemical Engineers
Institution of Mechanical Engineers
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Ministry of Housing and Local Government
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Royal Institute of Chemistry
Rubber Trade Association of London
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BRITISH STANDARD

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Part B 17. Determination of Total Copper

FOREWORD

This British Standard Method has been prepared under the authority of the Rubber Industry Standards Committee, and replaces Part 8.2 of B.S. 903 : 1950 which relates to the determination of copper.

In the revision of B.S. 903 the methods are being published as separate parts, and chemical methods are distinguished by the letter B.

INTRODUCTION

It is assumed that determinations will be made by an analyst aware of all the precautions and safeguards required for the carrying out of trace metal analysis. Since a high standard of analytical skill and a suitable working environment are implied, no specific recommendations to that effect are made in the text. It must be realized, however, that unless these requirements are satisfied the results will not be dependable.

In reporting the copper content of the sample, it is recommended that the figure be returned as the nearest whole number in parts of copper per million parts of dry rubber. Results should be repeatable to within 0·5 p.p.m. Figures outside this range are usually indicative of abnormality in the sample.

SUMMARY

Two grammes of the sample are digested with concentrated sulphuric and nitric acids. Excessive amounts of calcium are removed as sulphate and any iron present is complexed with ammonium citrate. After making alkaline, the aqueous solution is shaken with a measured amount of a chloroform solution of zinc diethyldithiocarbamate to form and extract the yellow copper complex. The absorbence of this solution is measured photometrically and is proportional to the concentration of copper.

REAGENTS

All reagents shall be of recognized analytical reagent quality unless otherwise specified, and demineralized water shall be used whenever water is specified.

Sulphuric acid, sp. gr. 1·84 *Nitric acid*, sp. gr. 1·42	Acids of a grade suitable for foodstuffs analysis are satisfactory.
Hydrochloric acid, sp. gr. 1·18	
Hydrochloric acid, 5 N *solution*	
Hydrogen peroxide, 100 vol.	
Citric acid solution	Dissolve 50 g of solid citric acid in 100 ml of water.
Ammonia	Aqueous solution, sp. gr. 0·880.
Zinc diethyldithiocarbamate reagent	Dissolve 1 g of sodium diethyldithiocarbamate in water and then add 2 g of zinc sulphate ($ZnSO_4 7H_2O$). Extract the resulting zinc diethyldithiocarbamate by shaking with 100 ml of chloroform. Separate the chloroform solution and dilute to 1 litre. Store in an amber coloured bottle; in these conditions the reagent is stable for at least six months.
Sodium sulphate, anhydrous	
Standard copper solution	Weigh 0·393 g of copper sulphate ($CuSO_4 . 5H_2O$) into a small beaker and dissolve in water. Add 3 ml of sulphuric acid (sp. gr. 1·84). Transfer the solution to a 1000 ml one-mark graduated flask and dilute with water to the mark. Pipette 10 ml of this solution into a 100 ml one-mark graduated flask and dilute with water to the mark. The final solution contains the equivalent of 10 μg Cu per millilitre and should be made freshly.

PROCEDURE

All apparatus shall be thoroughly cleaned immediately before use with a hot mixture of dilute acids—1 part of hydrochloric acid (sp. gr. 1·18), 1 part of nitric acid (sp. gr. 1·42), and 3 parts of water—followed by a thorough washing with water.

Weigh out accurately about 2 g of the rubber compound* and cut into pieces weighing not more than 0·1 g to avoid prolonged wet digestion. Place the pieces in a 100 ml Kjeldahl flask of borosilicate glass or silica, and add 4·0 ml of sulphuric acid (sp. gr. 1·84) and 5·0 ml of nitric acid (sp. gr. 1·42). If the initial

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* The test portions should be prepared in such a way that contamination from copper (e.g. from rolls) is avoided.

reaction becomes too vigorous cool the flask in a beaker of cold water. As soon as any vigorous reaction has subsided heat gently until further vigorous reaction ceases and then heat for 30 minutes or until the mixture chars and darkens appreciably (any darkening of the solution can be seen even in the presence of carbon black by carefully observing the meniscus of the liquid). Add nitric acid (sp. gr. 1·42) in 1 ml portions, heating after each addition for a further 30 minutes or until darkening again takes place. Continue this treatment until the solution becomes colourless or pale yellow and fails to darken on prolonged heating. It may be found necessary to add a further 1 ml of sulphuric acid (sp. gr. 1·84) during the digestion to prevent the contents of the flask from solidifying. To destroy the last traces of organic matter, cool and add 0·5 ml of 100 vol. hydrogen peroxide and 2 drops of nitric acid (sp. gr. 1·42), heat to fuming and repeat these additions and heating until there is no further reduction in the colour of the solution. Cool, dilute with 10 ml of water and evaporate to fuming, cool, add a further 5 ml of water and again evaporate to fuming. Finally, cool and add 5 ml of water.

Carry out a reagent blank side by side with the test, using the same quantities of sulphuric acid, nitric acid and hydrogen peroxide as were used to decompose the sample, and continue with exactly the same procedure.

If the test solution is free from insoluble matter, transfer the acid digest to a 100 ml conical flask, rinse the Kjeldahl flask with three 5 ml portions of water and add these to the conical flask. If the test solution contains insoluble matter, filter the supernatant liquid through a 7 cm filter paper into a 100 ml conical flask, retaining as much of the insoluble residue as possible in the Kjeldahl flask. Add 5 ml of 5 N hydrochloric acid to the Kjeldahl flask, heat to incipient boiling, swirling vigorously to wash the sides of the flask, and drain the flask contents through the filter paper into the conical flask. Finally, wash the Kjeldahl flask with two 5 ml portions of water, passing the washings through the filter paper into the conical flask.

Add 5 ml of citric acid solution to the diluted acid digest or to the filtrate in the conical flask. If the solution remains clear neutralize by the dropwise addition of ammonia, using a small piece of litmus paper as indicator, but if calcium sulphate crystallizes out in the solution chill to about 10°C and filter through a fresh 7 cm filter paper, washing the flask and filter with three 2 ml portions of ice-cold water before neutralizing with ammonia. After cooling, if necessary, add a further 2 ml of ammonia and transfer to a 100 ml graduated separating funnel. Wash the conical flask with small portions of water, transferring the washings to the separating funnel, and bring the total volume of the solution to about 40 ml.

Pipette 25·0 ml of zinc diethyldithiocarbamate reagent into the solution and thoroughly shake for 2 minutes. After allowing sufficient time for separation, draw off the chloroform layer into a dry 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 solution through a plug of glass wool or a filter paper into the cell of a photoelectric absorptiometer and measure the optical density at approximately 435 mμ. Subtract the value of the optical density of the blank and from the corrected figure use the calibration curve of the instrument to obtain the concentration of copper in the test solution.

Prepare a calibration graph for the instrument as follows:

> Prepare a series of standard solutions containing a range of from 0–10 ml of the standard copper solution, followed by 5 ml of citric acid solution and a 2 ml excess of ammonia. Dilute each solution to 40 ml with water and extract with 25·0 ml of the zinc diethyldithiocarbamate reagent for 2 minutes. Separate the chloroform layers in each case into a dry flask containing 0·1 g of anhydrous sodium sulphate. If turbidity persists after standing for 30 minutes make further small additions of anhydrous sodium sulphate until the solution becomes clear.
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> Decant each solution through a plug of glass wool or a filter paper into the cell of a photoelectric absorptiometer and measure the optical density at approximately 435 mμ. Correct the reading for each standard solution by subtracting the value obtained for the solution containing no added standard copper solution.

Prepare the calibration graph by plotting microgrammes of copper as abscissae and optical densities as ordinates.

Check the calibration graph as necessary depending on local conditions and on the type of instrument used.

BRITISH STANDARDS INSTITUTION

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The principal objects of the Institution as set out in the charter are to co-ordinate the efforts of producers and users for the improvement, standardization and simplification of engineering and industrial materials; to simplify production and distribution; to eliminate the waste of time and material involved in the production of an unnecessary variety of patterns and sizes of articles for one and the same purpose; to set up standards of quality and dimensions, and to promote the general adoption of British Standards.

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