BS 5923 : Part 2 : 1980

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British Standard Methods for

Chemical analysis of rubber

Part 2. EDTA titrimetric method for determination of zinc content of rubber products

Méthodes d'analyse chimique du caoutchouc
Partie 2. Méthode titrimétrique à l'EDTA pour le dosage du zinc dans les produits en caoutchouc

Verfahren der chemischen Analyse von Kautschuk
Teil 2. EDTA-titrimetrisches Verfahren zur Bestimmung von Zink in Kautschukerzeugnissen

Foreword

This Part of BS 5923 has been prepared under the direction of the Rubber Standards Committee.

In the past, methods for the chemical analysis of different types of rubber were published, as appropriate, in the 'B series' of BS 903 'Methods of testing vulcanized rubber' and in BS 1673 'Methods for testing raw rubber and unvulcanized compounded rubber'. However, in many cases the methods for the various types of material are very similar. In the work of Technical Committee 45, Rubber and rubber products, of the International Organization for Standardization (ISO), this has led to the preparation of international standards for methods for the chemical analysis of rubber of general applicability; in order to facilitate the adoption of these as British Standards and to simplify the general presentation of methods for the chemical analysis of rubber, it has been decided to publish this new British Standard. As further Parts of BS 5923 are published, they will replace any corresponding methods in BS 903 and BS 1673, so that the BS 903 'B series' and the appropriate parts of BS 1673 will eventually be withdrawn completely. This Part supersedes section 4 of BS 903 : Part B13 'Determination of ash and zinc oxide'; the remaining sections of BS 903 : Part B13 are superseded by BS 5923 : Part 1.

This Part is based on ISO 2454-1976, with the inclusion of some technical and editorial changes in the text. The major changes are listed below and are indicated by a vertical line in the margin.

Clause reference	Textual change
6.1	In this British Standard, a reference to BS 5923 : Part 1 has been substituted for the reference to ISO 247-1978. BS 5923 : Part 1 is identical with ISO 247-1978.
4	In ISO 2454-1976 some of the reagents are listed in a different order as follows: **4.11** EDTA (*di*sodium salt) **4.12** Zinc chloride **4.13** Dithizone indicator
4.13	The note in this British Standard is not included in ISO 2454-1976.
6.2	The instructions in the first paragraph have been extended. In ISO 2454-1976, the end of the first paragraph reads: '. . . . . add 2 ml of the sulphuric acid (**4.4**) and ash in the muffle furnace (**5.1**), maintained at 550 ± 25 °C'. In the second sentence of the second paragraph, the words 'in a fume cupboard' have been added after 'Evaporate the hydrofluoric acid'. In the fourth sentence of the second paragraph, ISO 2454-1976 refers, incorrectly, to the evaporation of 'hydrochloric' acid.
6.3	In ISO 2454-1976, the second sentence of the third paragraph begins, incorrectly, with the word 'Acidity'.

The changes in clauses in **4**, **6.2** and **6.3** have been proposed by the United Kingdom as amendments to the ISO text.

The method described in BS 903 : Part B13 involved titration with EDTA solution but the procedure described in this revision differs substantially.

1. Scope and field of application

This British Standard specifies an EDTA titrimetric method for the determination of the zinc content of all rubber products.

Lead, magnesium, iron, titanium, antimony, silica, and silicates in the ash do not interfere. The method is not applicable, however, if cobalt is present.

2. References

The titles of the standards publications referred to in this standard are listed on page 3.

3. Principle

Incineration of a test portion and dissolution of the ash in hydrochloric acid. Extraction of silica by treatment with hydrofluoric and sulphuric acids. Addition of aluminium chloride and aluminium fluoride to precipitate calcium and magnesium as hexafluoroaluminates. Fluoride complexes iron, titanium and excess aluminium (interference from large amounts of iron is further reduced by addition of 2,4-pentanedione). Titration of the zinc with an EDTA (*di*sodium salt) standard volumetric solution in the presence of dithizone as indicator.

4. Reagents

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity. All recognized health and safety precautions must be observed in the handling of chemicals listed and in performing the analysis.

4.1 *Acetone.*

4.2 *2,4-Pentanedione*, 10 % (*V*/*V*) solution in the acetone (**4.1**).

4.3 *Hydrochloric acid* (ρ 1.18 g/ml).

4.4 *Sulphuric acid* (ρ 1.84 g/ml).

4.5 *Hydrofluoric acid*, 48 % (*m*/*m*) solution.

4.6 *Ammonium hydroxide solution* (ρ 0.01 g/ml).

4.7 *Buffer solution.* Dissolve 60 g of acetic acid (CH_3COOH) and 77 g of ammonium acetate (CH_3COONH_4) in water and dilute to 1000 ml* with water.

4.8 *Aluminium chloride*, 0.1M solution. Dissolve 2.42 g of aluminium chloride hexahydrate ($AlCl_3.6H_2O$) in water and dilute to 100 ml with water.

4.9 *Magnesium chloride*, 0.1M solution. Dissolve 2.03 g of magnesium chloride hexahydrate ($MgCl_2.6H_2O$) in water and dilute to 100 ml with water.

4.10 *Ammonium fluoride*, 3M solution. Dissolve 55.5 g of ammonium fluoride (NH_4F) in water and dilute to 500 ml with water. Store in a polyethylene or wax-coated bottle.

4.11 *Zinc chloride*, standard solution. Calcine zinc oxide in a porcelain crucible for 2 h in the furnace (**5.1**), maintained at 550 ± 25 °C, and cool in a desiccator. Dissolve about 1.0 g of the dried reagent, weighed to the nearest 0.000 1 g, in 50 ml of water and 20 ml of the hydrochloric acid (**4.3**). Transfer to a 1000 ml volumetric flask and dilute to the mark with water.

4.12 *Dithizone indicator.* Dissolve 0.01 g of dithizone [(phenylazo)thioformic acid, 2-phenylhydrazide] in 10 ml of the acetone (**4.1**). Prepare a fresh solution every 48 h.

4.13 *(Ethylenedinitrilo)tetraacetic acid disodium salt, dihydrate (ECTA disodium salt)*, 0.01M standard volumetric solution.

NOTE. This solution should be prepared and standardized as described in **4.13.1** to **4.13.3**. Standard solutions purchased from reagent suppliers may contain mercury salts, added as preservative, which will interfere with the dithizone indicator and possibly mask the end-point.

4.13.1 *Preparation.* Dissolve 3.72 g of EDTA (*di*sodium salt) in water and dilute to 1000 ml with water.

4.13.2 *Standardization.* Pipette 25 ml of the standard zinc chloride solution (**4.11**) into a 250 ml conical flask. Add 5 ml of the hydrochloric acid (**4.3**) and proceed according to **6.3** beginning with 'add 2 ml of the aluminium chloride solution'. Carry out the titration as described in **6.4**, using the 50 ml burette (**5.3**).

4.13.3 *Standardization factor.* The standardization factor, *T*, of the EDTA (*di*sodium salt) solution, expressed as grams of zinc oxide (ZnO) per millilitre, is given by the formula

$$T = \frac{m_1}{40\ V_1}$$

where

m_1 is the mass, in grams, of dried zinc oxide used in the preparation of the standard zinc chloride solution (**4.11**);

V_1 is the volume, in millilitres, of EDTA (*di*sodium salt) solution used in the titration of the standard zinc chloride solution (**4.11**).

4.14 *Universal indicator paper.*

5. Apparatus

Ordinary laboratory apparatus and

5.1 *Muffle furnace*, capable of being controlled at 550 ± 25 °C.

5.2 *Burette*, of capacity 10 ml, graduated in 0.02 ml divisions.

5.3 *Burette*, of capacity 50 ml, graduated in 0.1 ml divisions.

5.4 *Platinum crucibles*, of capacity 50 ml.

6. Procedure

6.1 Weigh, to the nearest 0.000 1 g, approximately 1 g of the sample. Place this test portion in one of the platinum crucibles (**5.4**) and reduce to ash according to method C specified in BS 5923 : Part 1.

Cool the crucible and add approximately 50 ml of the hydrochloric acid (**4.3**). Transfer the contents of the crucible to a 250 ml beaker with approximately 50 ml of water. Break up any large cakes of ash with a glass stirring rod. If any insoluble residue is present after cooling, proceed in accordance with **6.2**. If no insoluble material is present, proceed in accordance with **6.3**.

6.2 Filter the residue through an ashless filter paper. Retain the filtrate. Place the insoluble residue and the filter

*The term millilitre (ml) is commonly used for the cubic centimetre (cm^3), particularly to denote the capacity of laboratory glassware. Apparatus with either type of marking is satisfactory to use with this British Standard.

paper into a second platinum crucible (**5.4**), add 2 ml of the sulphuric acid (**4.4**) and then heat over a gas burner to volatilize the excess sulphuric acid. Transfer the crucible and its contents to the muffle furnace, maintained at 550 ± 25 °C, and heat until all the carbon is completely oxidized and a clean ash is obtained.

Moisten the residue with 5 to 10 drops of the sulphuric acid (**4.4**) and 5 ml of the hydrofluoric acid solution (**4.5**). Evaporate the hydrofluoric acid in a fume cupboard and stop heating as soon as the evolution of white fumes indicates sulphuric acid decomposition. When cool, add an additional 5 to 10 drops of the sulphuric acid and 5 ml of the hydrofluoric acid solution. Repeat the evaporation of the hydrofluoric acid and add 1 ml of the sulphuric acid and 5 ml of the hydrofluoric acid solution to the wet residue. Evaporate the hydrofluoric acid and stop heating as soon as white fumes appear.

Pour the contents of the crucible carefully into the retained filtrate, wash the crucible with distilled water and add the washings to the filtrate. Proceed according to **6.3**.

6.3 If necessary, evaporate the solution or filtrate to a volume of approximately 50 ml. Transfer the cooled solution to a 100 ml volumetric flask and make up to the mark with distilled water. Select an aliquot portion from the following table according to the expected zinc content and transfer to a 250 ml conical flask.

ZnO expected	Aliquot portion	Capacity of burette to be used
% (*m*/*m*)	ml	ml
0 to 3	25	10 (**5.2**)
3 to 8	10	10 (**5.2**)
more than 8	10	50 (**5.3**)

If necessary, dilute the aliquot portion to 25 ml, add 2 ml of the aluminium chloride solution (**4.8**), 5 ml of the magnesium chloride solution (**4.9**), and 10 ml of the ammonium fluoride solution (**4.10**).

Add ammonium hydroxide solution (**4.6**) until alkaline to the universal indicator paper (**4.14**). Acidify with approximately 1 ml of the sulphuric acid (**4.4**). Bring the solution to the boil, and then cool to room temperature. Add ammonium hydroxide solution (**4.6**) until just alkaline. Then add an additional 0.5 ml. Add 10 ml of the buffer solution (**4.7**), 60 ml of the acetone (**4.1**), 5 ml of the 2,4-pentanedione solution (**4.2**) and 5 drops of the dithizone indicator solution (**4.12**). Cool the solution in an ice bath.

6.4 Titrate with the EDTA (*di*sodium salt) standard volumetric solution (**4.13**), using the appropriate burette indicated in the table. The end-point is reached at a yellow-green colour, which does not change on the addition of a further drop of the EDTA (*di*sodium salt) standard volumetric solution.

7. Expression of results

The zinc content of the test portion, expressed as a percentage by mass of zinc oxide (ZnO), is given by the formula

$$\frac{T \times V_2 \times 100 \times 100}{V_3 \times m_2}$$

where

T is the standardization factor as calculated in **4.13.3**;

V_2 is the volume, in millilitres, of the EDTA (*di*sodium salt) standard volumetric solution (**4.13**) used in the titration of the aliquot portion of the test solution;

V_3 is the volume, in millilitres, of the aliquot portion;

m_2 is the mass, in grams, of the test portion.

8. Test report

The test report shall include the following particulars:

(a) a reference to this British Standard;

(b) the results and the method of expression used;

(c) any unusual features noted during the determination;

(d) any operation not included in this British Standard or in the British Standard to which reference is made, or regarded as optional.

Standards publications referred to

BS 903*	Methods of testing vulcanized rubber
BS 1673*	Methods for testing raw rubber and unvulcanized compounded rubber
BS 5923	Methods for chemical analysis of rubber Part 1 Determination of ash
ISO 247*	Rubber – Determination of ash
ISO 2454*	Rubber products – Determination of zinc content – EDTA titrimetric method

*Referred to in the foreword only.

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The following BSI references relate to the work on this standard:
Committee reference RUC/37 Draft for comment 78/55298 DC

Cooperating organizations

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

*British Association of Synthetic Rubber Manufacturers
*British Rubber Manufacturers' Association
Department of Industry (Chemicals and Textiles)
Medical Sterile Products Association
*Ministry of Defence
Plastics and Rubber Institute
*Rubber and Plastics Research Association of Great Britain
Rubber Growers' Association
Society of Motor Manufacturers and Traders Limited
*The Malaysian Rubber Producers' Research Association

The 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:

Chemical Society, Analytical Division
Electric Cable Makers' Confederation
Institution of Water Engineers and Scientists
National College of Rubber Technology
Individual expert

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