

Determination of metals in textiles —

Part 1: Analysis by atomic absorption and colorimetric spectroscopy

Committees responsible for this British Standard

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- British Carpet Manufacturers' Association Ltd.
- Department of Trade and Industry (Laboratory of the Government Chemist)
- International Wool Secretariat
- Man-made Fibres Producers' Committee
- Ministry of Defence
- Textile Research Council

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Methods for determination of metals in textiles

Revised text

Foreword

In paragraph 7, lines 3 and 4, delete 'L. Bretherick (ed.), London' and 'third edition, 1981.' and substitute 'S. G. Luxon (ed.) Cambridge' and 'fifth edition, 1993' respectively.

After paragraph 7 insert the following.

'NOTE. Practical guidance in the application of COSHH regulations and broader aspects of health and safety in chemical laboratories are given in 'COSHH in laboratories' and 'Safe practices in chemical laboratories' : The Royal Society of Chemistry, London, 1989.'

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Clause 3.2 Equipment and reagents

In paragraph 1, delete the first sentence and substitute 'Water complying with grade 3 of BS 3978 shall be used.'

In the note, last line, delete 'BS 1051' and substitute 'BS EN 20139'.

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Publications referred to

Delete the entries for BS 1051 and BS 4404.

In the entry for BS 3978 delete the existing title and substitute 'Specification for water for laboratory use'.

After the entry for BS 4F 100 insert the following new entry.

'BS EN 20139 Textiles. Standard atmospheres for conditioning and testing'

In the entry for 'Hazards in the chemical laboratory' delete 'L. Bretherick (ed.) London' and 'third edition, 1981' and substitute 'S. G. Luxon (ed.) Cambridge' and 'fifth edition, 1993' respectively.

After the entry for 'Colour index' insert the following new entries.

'COSHH in laboratories', The Royal Society of Chemistry, London, 1989'

'Safe practices in chemical laboratories', The Royal Society of Chemistry, London, 1989'

AMD 8187/May 1994

Foreword

This Part of BS 6810-1 has been prepared by Technical Committee TCM/26.

BS 6810 has been prepared in the context of several test methods for the determination of metals in textiles by different analytical techniques. This Part of the standard covers the determination of metals in textiles by the colorimetric and atomic absorption spectroscopy techniques.

Part 2 of this standard covers the determination of metals in textiles by analysis using atomic emission spectroscopy.

Methods of test for the determination of relatively large proportions of metals in textiles, such as may be introduced for proofing purposes, are covered by BS 2087, and BS 4F 100 also includes methods for the determination of traces of iron and copper.

This standard covers methods for the determination, at levels of 0.1 % or less of the mass of the textile material, of a range of metals (antimony, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, and zinc), wider than formerly included in BS Handbook 11 (withdrawn 1984). It also extends the range of textile fibres in which these metals are to be determined, to include all those commonly encountered (as listed in BS 4815), with the exception of inorganic fibres. Methods for both soluble and total metals are included.

The methods for the determination of metals used to be based almost exclusively on colorimetry. It is recognized that today instrumental techniques such as atomic absorption spectrophotometry or a related technique is the preferred method for the final determination of metals, and that the appropriate instruments are available in most well-equipped laboratories.

Atomic absorption spectroscopy is therefore included in this Part, and other instrumental techniques appear in subsequent parts of this standard.

Attention is drawn to the standard addition method in Appendix B. Alternative colorimetric methods have been retained.

Metals in textile materials come from a variety of origins, and are consequently present at different concentration levels. For some metals, the significance of the particular level found in a sample will be determined by the toxicity of the metal, for other less toxic metals, textile considerations can determine this significance. As a general indication of the lower limits of applicability of the methods, it is suggested that, for those methods based on atomic absorption spectrophotometry; with the exception of antimony and arsenic for which the technique is less sensitive, an optimum concentration range of a few parts per million of metal can be realized in the sample.

With the exception of the methods for chromium, iron, manganese and nickel, for which the lower limit is in the range 10 parts per million to 50 parts per million, the colorimetric methods are of almost equal sensitivity when the assumption is of a sample mass of a few grams.

Chemical names in accordance with BS 2474:1993(1998) have been used, but deprecated names or other names used in industry are given, where applicable, in brackets.

The presence of metallic elements in textile materials can arise in a variety of ways. Accidental or unforeseen contamination of textiles can occur, at any stage of manufacture or in use, by metals whose presence can pose a health hazard to humans or animals, particularly if the contamination is of such a nature that the metal is easily released. Some man-made fibres contain metals introduced in polymer manufacture (e.g. catalyst residues) or mass colouration (pigments). Animal fibres contain traces of copper, probably of biosynthetic origin. Metals can be deliberately introduced in subsequent processing (e.g. mordanting) or as components of metal-complex dyes. During textile processing, accidental contamination by materials of construction, notably copper and iron, is not uncommon, and may have a deleterious effect on quality.

Methods of test for metals in textiles can be required for a variety of reasons related to the origins detailed above, quality control, fault diagnosis or complaint investigation, textile research and development work, or hygienic considerations.

The methods for the determination of metals described in this standard are restricted to those which can be carried out in a well-equipped textile laboratory. Determination of metals in textile fibres, e.g. for general research purposes, for forensic investigations, and for the identification through the presence of traces of metals deliberately introduced, of specific brands of man-made fibres, might not be covered by this standard.

WARNING This British Standard calls for the use of substance and/or procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and does not absolve the user from legal obligations relating to health and safety at any stage. Sources of hazard, which require particular attention, include the use of compressed gases, the use of corrosive liquids at elevated temperatures, the handling of toxic substances, and the possibilities of explosive detonations in gases.

It has been assumed in the drafting of this British Standard that execution of its provisions is entrusted to qualified and experienced people.

NOTE Good practice in relation to safety procedures is defined in *Hazards in the chemical laboratory*. LUXON, S.G. (ed.) Cambridge: The Royal Society of Chemistry, fifth edition, 1993.

Practical guidance in the application of COSHH regulations and broader aspects of health and safety in chemical laboratories are given in *COSHH in laboratories* and *Safe practices in chemical laboratories*. The Royal Society of Chemistry, London, 1989.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

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Section one. General

0 Introduction

The presence of metallic elements in textile materials may arise in a variety of ways. Some man-made fibres contain metals introduced in polymer manufacture (e.g. catalyst residues) or mass colouration (pigments). Animal fibres contain traces of copper, probably of biosynthetic origin. Metals may be deliberately introduced in subsequent processing (e.g. mordanting) or as components of metal-complex dyes. During textile processing, accidental contamination by materials of construction, notably copper and iron, is not uncommon, and may have a deleterious effect on quality. Accidental or unforeseen contamination of textiles may occur, at any stage of manufacture or in use, by metals whose presence may pose a health hazard to humans or animals, particularly if the contamination is of such a nature that the metal is easily released.

Methods of test for metals in textiles may be required for a variety of reasons related to the origins detailed above, quality control, fault diagnosis or complaint investigation, textile research and development work, or hygienic considerations.

The methods for the determination of metals described in this standard are restricted to those which can be carried out in a well-equipped textile laboratory. Determination of metals in textile fibres, e.g. for general research purposes, for forensic investigations, and for the identification, through the presence of traces of metals deliberately introduced, of specific brands of man-made fibres, may not be covered by this standard.

1 Scope

This British Standard describes methods for the determination of the proportions present in commonly encountered textile fibres (excluding inorganic fibres) of the following metals: antimony, arsenic, barium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel and zinc. Methods are given for both soluble and total metals. This standard applies to textile materials in which the metal being determined constitutes not more than 0.1 % by mass of the material.

NOTE. The titles of the publications referred to in this standard are listed on the inside back cover.

2 Definitions

For the purposes of this British Standard, the definitions given in BS 4815 apply, together with the following.

2.1 soluble metal content of textile fibres. The content of a metal (excluding chromium) in the fibre that is soluble under specified conditions in hydrochloric acid, $c(\text{HCl}) = 0.07 \text{ mol/L}$.

2.2 soluble chromium content of textile fibres. The content of chromium in the fibre that is soluble under specified conditions in *d*/sodium tetraborate solution, $c(\text{Na}_2\text{B}_4\text{O}_7) = 0.05 \text{ mol/L}$.

3 General requirements

3.1 Choice and restrictions on the use of a method

3.1.1 Preliminary treatment (see section two). If barium is sought, wet ashing (see clause 5) employing sulphuric acid is not suitable, and dry ashing (see clause 6) shall be used. If barium is suspected to be present, dry ashing shall be used for the determination of other metals, except when mercury is the metal sought, when wet ashing shall be used.

NOTE. For the destruction of the organic material of textile fibres prior to the determination of metals, wet ashing is in general to be preferred, particularly when low levels of metals are being sought.

Dry ashing, when its use is appropriate, has the advantage that it minimizes operator attention and avoids the use of large quantities of reagents and the high blank values that can result from their use.

3.1.2 Determination of metals in the extract (see section three). For soluble metals other than chromium in the hexavalent state, the metal in the extract shall be determined either by atomic absorption spectrophotometry (see clause 7) or colorimetrically (see clause 8).

Soluble hexavalent chromium shall be determined colorimetrically. The total chromium in the extract shall be determined either by atomic absorption spectrophotometry or by colorimetry.

NOTE 1. The colorimetric methods described in clause 8 provide alternatives to the methods based on atomic absorption spectrophotometry. They are applicable to the determination of soluble metals extracted as described in clause 4, or of total metals following an appropriate pretreatment by wet or dry ashing. No colorimetric method is described for the determination of barium.

NOTE 2. Because of the volatility of mercury, a special apparatus and procedure is used for its determination by atomic absorption spectrophotometry.

3.2 Equipment and reagents

Water complying with BS 3978 shall be used. For atomic absorption spectrophotometric determinations, reagents of analytical grade, or the grade specified for the particular method, shall be used. This shall also apply to acids used for the wet ashing of textiles for atomic absorption spectrophotometric determinations.

The apparatus shall be sound and clean. Glassware shall be made of chemically resistant glass. For colorimetric determinations, a spectrophotometer or colorimeter capable of measuring absorbance in the appropriate spectral region shall be used.

Caution. Special attention needs to be paid to ensure cleanliness and the avoidance of contamination when carrying out the procedures described in this standard.

NOTE. For the determinations described in this standard, conditioning of samples before testing will not normally be necessary. If conditioning is agreed between the interested parties, it is recommended that the conditioning atmospheres defined in BS 1051 be used.

Section two. Preliminary treatments

4 Extraction of soluble metals

4.1 Principle

For all metals except chromium, the soluble portion of the metal in the sample is extracted under defined conditions with hydrochloric acid, $c(\text{HCl}) = 0.07 \text{ mol/L}$. Any buffering capacity that the sample may possess is compensated for by the addition of hydrochloric acid, $c(\text{HCl})$ approximately 2 mol/L , so that the pH of the extract does not exceed 1.5. For chromium, the soluble portion of the metal, which will be mostly in the hexavalent state, is extracted under defined conditions with disodium tetraborate solution, $c(\text{Na}_2\text{B}_4\text{O}_7) = 0.05 \text{ mol/L}$, pH 9.2. At this pH minimum reduction occurs.

NOTE. For the extraction of soluble metals, the ratios of mass of textile material to volume of extracting solution specified in 8.1.3 of BS 3266 : 1981 have been adopted.

4.2 Reagents

4.2.1 Hydrochloric acid, $c(\text{HCl}) = 0.07 \text{ mol/L}$.

4.2.2 Hydrochloric acid, $c(\text{HCl})$ approximately 2 mol/L . Dilute hydrochloric acid approximately 37 % (m/m), ρ approximately 1.18 g/mL , 1 + 5.

4.2.3 Buffer solution, for standardization of the pH meter before measurement. Potassium hydrogen phthalate, $c[\text{C}_6\text{H}_4(\text{COO})_2\text{HK}] = 0.05 \text{ mol/L}$, pH 4.000 at 15°C , 4.001 at 20°C , 4.005 at 25°C , 4.011 at 30°C .

4.2.4 Disodium tetraborate solution, $c(\text{Na}_2\text{B}_4\text{O}_7) = 0.05 \text{ mol/L}$, prepared by dissolving 19.07 g of disodium tetraborate in water and diluting to a volume of 1 L.

4.3 Apparatus

4.3.1 Conical flasks, capacity 100 mL or 250 mL, with ground glass joints and stoppers, as required.

4.3.2 pH meter, complying with BS 3145, used in conjunction with glass and reference electrodes complying with BS 2586.

4.3.3 Mechanical shaker, providing rotational or reciprocating movement sufficient to provide a ready exchange of liquid between the interior of the material and the extracting solution. A to-and-fro movement at a rate of 60 min^{-1} or a rotational frequency of 30 min^{-1} has been found satisfactory.

4.3.4 Balance, accurate to $\pm 0.05 \text{ g}$.

4.3.5 Source of heat, controllable at $40 \pm 2^\circ\text{C}$, e.g. a water bath.

4.3.6 Coarse laboratory sintered filter, grade P250 complying with BS 1752.

4.3.7 One-mark volumetric flasks, capacities 100 mL and 250 mL, complying with BS 1792.

4.4 Procedure

4.4.1 General. If the amount of sample available permits, carry out the extraction in duplicate.

4.4.2 Soluble metals except chromium. Cut the sample into pieces of such a size that all parts are readily wetted out. Weigh a specimen of 2.5 g to an accuracy of $\pm 0.05 \text{ g}$, and transfer it to a glass stoppered conical flask (4.3.1). For all materials except

(a) wool in any textile form; and

(b) felts and loose fibres

use a 100 mL flask and add to the flask $50 \pm 0.2 \text{ mL}$ of hydrochloric acid (4.2.1); for (a) and (b) use a 250 mL flask and add to the flask $125 \pm 0.5 \text{ mL}$ of hydrochloric acid (4.2.1).

Agitate the flask by hand for a short period to ensure that the textile is properly wetted out. For samples containing wool or polyamide, ensure that the pH of the extracting solution does not rise above 1.5; do this by measuring the approximate pH of the solution after the preliminary wetting out and carefully adding hydrochloric acid solution (4.2.2) until the pH is 1.5 or less.

NOTE. If sufficient material is available, it may be more convenient to determine the quantity of additional acid required in a separate experiment.

Shake the flask with the mechanical shaker (4.3.3) for 1 h. Filter the extract through the coarse laboratory sintered filter (4.3.6). Rinse the filter and combine the rinsings and the extract.

4.4.3 Soluble chromium. Cut the sample into pieces of such a size that all parts are readily wetted out. Weigh a specimen of 2.5 g to an accuracy of $\pm 0.05 \text{ g}$, and transfer it to a 100 mL glass stoppered flask. Add 50 mL of disodium tetraborate solution (4.2.4). Agitate the flask by hand for a short period to ensure that the textile is properly wetted out. Heat the flask and maintain the temperature at $40 \pm 2^\circ\text{C}$ for 30 min, shaking the flask occasionally during this period. Allow the flask to cool. Filter the extract through the coarse laboratory sintered filter (4.3.6). Rinse the filter and combine the rinsings and the extract.

4.4.4 Preparation of the extract for analysis. Make up the extract to a suitable volume with the solution used to prepare the extract noting that, if either soluble barium or total soluble chromium is to be determined by atomic absorption spectrophotometry (see 7.1.4.2), the addition of other reagents is necessary before the test solution is made up to its final volume.

5 Wet ashing

5.1 Principle

The procedure involves the destruction of organic matter in the sample by controlled heating with a mixture of acids.

5.2 Procedure

Carry out wet ashing in accordance with BS 6648. Do not subject the material to a preliminary charring procedure with sulphuric acid alone if arsenic is to be determined.

Prepare a blank digest using the same quantities of reagents.

6 Dry ashing

6.1 Principle

An amount of the material, of known mass, is incinerated in a muffle furnace at a temperature preferably not exceeding 450 °C.

6.2 Apparatus

6.2.1 *Silica, porcelain or platinum dish or crucible of suitable size.*

6.2.2 *Temperature-controlled muffle furnace.*

6.2.3 *Balance, accurate to ± 0.001 g.*

6.3 Procedure

Place a suitable weighed quantity of the material in the dish or crucible (**6.2.1**). Burn the material cautiously at the front of the open muffle furnace (**6.2.2**), taking care to avoid draughts, and when the material has reached the glowing stage move the dish towards the rear of the furnace, close the door, and complete the ashing at a temperature preferably not exceeding 450 °C (see note 2).

Caution. Because of the possible evolution of toxic fumes in the slow ignition of some fibres, suitable ventilation should be provided.

NOTE 1. The mass of material used for the test is governed by the proportion present of the metal sought and the sensitivity of the method used for subsequent determination.

NOTE 2. This method is not suitable for the determination of mercury, which is lost under these conditions of heating. Losses of arsenic, cadmium, lead and zinc may occur if the temperature is much in excess of 450 °C.

NOTE 3. Losses of certain metals, especially antimony, zinc and lead, can occur when dry ashing is carried out in the presence of halogens (i.e. polyvinylchloride and polyvinylidene chloride fibres). In this case, the sample may be moistened with sodium carbonate solution (ρ 0.20 g/mL), which is evaporated to dryness before ashing is carried out.

NOTE 4. If difficulty is encountered in dry ashing samples completely, the use of an ashing aid, e.g. ammonium nitrate solution (ρ 0.50 g/mL) to moisten the sample should be considered.

NOTE 5. Silica and porcelain ware becomes etched during heating and cooling cycles over a prolonged period and fairly frequent replacement is recommended.

Section three. Determination of metals

7 Atomic absorption spectrophotometry and related methods

7.1 Determination of metals other than mercury by atomic absorption spectrophotometry

7.1.1 Principle. The solution containing the metal is aspirated into an air/acetylene or dinitrogen monoxide/acetylene flame. The absorption of characteristic radiation emitted by a hollow-cathode lamp or a discharge lamp containing the metal being sought is measured.

NOTE. This method is relatively insensitive for antimony and arsenic.

7.1.2 Reagents

7.1.2.1 Acetylene, commercial grade, in a steel cylinder.

7.1.2.2 Dinitrogen monoxide, commercial grade, in a steel cylinder.

7.1.2.3 Compressed air.

7.1.2.4 Standard matching solutions prepared in accordance with appendix A.

7.1.2.5 Hydrochloric acid, $c(\text{HCl})$ approximately 5 mol/L. Dilute hydrochloric acid, approximately 37 % (m/m), ρ approximately 1.18 g/mL, 1 + 1.

7.1.2.6 Hydrochloric acid, $c(\text{HCl})$ approximately 2 mol/L. Dilute hydrochloric acid (7.1.2.5), 2 + 3.

7.1.2.7 Hydrochloric acid, $c(\text{HCl}) = 0.07$ mol/L.

7.1.2.8 Disodium tetraborate solution, $c(\text{Na}_2\text{B}_4\text{O}_7) = 0.05$ mol/L, prepared by dissolving 19.07 g of disodium tetraborate decahydrate in water and diluting to a volume of 1 L.

7.1.2.9 Sodium chloride.

7.1.2.10 Sulphuric acid, approximately 98 % (m/m), ρ approximately 1.84 g/mL.

7.1.2.11 Potassium iodide.

7.1.3 Apparatus

7.1.3.1 Flame atomic absorption spectrophotometer, fitted with burners capable of being fed with

- (a) air and acetylene; and
- (b) dinitrogen monoxide and acetylene.

7.1.3.2 Hollow-cathode lamp or discharge lamp, containing the metal being sought.

7.1.3.3 One-mark volumetric flasks, capacity 100 mL, complying with BS 1792.

Caution. The exhaust gases from the operation of a flame atomic absorption spectrophotometer can contain significant quantities of toxic products, and the provision of an efficient extraction system is essential.

7.1.4 Procedure

7.1.4.1 Preparation of the calibration graph. Prepare standard matching solutions by introducing into a series of six 100 mL one-mark volumetric flasks the volumes of the

required standard matching solution (7.1.2.4) shown in table 1, and dilute each to the mark with the following solutions:

- (a) for the determination of soluble metals other than chromium, hydrochloric acid (7.1.2.7);
- (b) for the determination of soluble chromium, disodium tetraborate solution (7.1.2.8);
- (c) for the determination of total metals, an acidic solution approximating in composition to that of the diluted digest to be analysed.

If barium is being determined, add 0.5 g of sodium chloride to each standard matching solution.

If chromium is being determined, add 4.0 mL of sulphuric acid (7.1.2.10) and 0.40 g of potassium iodide (7.1.2.11) to each standard matching solution before making up to the final volume.

Prepare these solutions on the day of use.

Table 1. Standard matching solutions for atomic absorption spectrophotometry

Standard matching solution number	Volume of standard matching solution
	mL
0*	0
1	2
2	5
3	10
4	15
5	20
*Blank matching solution.	

Prepare either a calibration graph as described in the next paragraph or, alternatively, use a method of instrumental calibration of at least equivalent accuracy and precision.

Obtain measurements in accordance with 7.1.4.3 and plot a graph having the masses, in micrograms, of the metal being determined which are present in 1 mL of the standard matching solutions as abscissae and the corresponding values of the absorbances, reduced by the reading for the blank matching solution, as ordinates.

7.1.4.2 Preparation of the test solution. If soluble metals are being determined, use an extract prepared as described in clause 4. For total metals, dilute the digest obtained by the wet ashing procedure given in clause 5, so that acid concentrations which may give rise to interference effects (usually greater than $c(\text{H}^+) 0.5$ mol/L to 1.0 mol/L) are not exceeded.

If samples have been dry ashed for the determination of total metals, extract the ash with several small measured portions of hot hydrochloric acid (7.1.2.6). If lead or zinc are sought, use the stronger hydrochloric acid (7.1.2.5). Rinse the crucible or dish, combine the rinsings and the extract, and filter if necessary. Prepare blank solutions containing the same quantity of acid.