

Suitability of non-metallic products for use in contact with water intended for human consumption with regard to their effect on the quality of the water —

Part 4: Method for the GCMS identification of water leachable organic substances

ICS 13.060.20; 13.060.50

Committees responsible for this British Standard

The preparation of this British Standard was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/7, Effects of materials on water quality, upon which the following bodies were represented:

- Association of Manufacturers of Domestic Electrical Appliances
- Automatic Vending Association of Britain
- British Bathroom Council
- British Cement Association
- British Coatings Federation Ltd.
- British Malleable Tube Fittings Association
- British Non-Ferrous Metals Federation
- British Plastics Federation
- British Plumbing Fittings Manufacturers' Association
- British Precast Concrete Federation Ltd.
- British Rubber Manufacturers' Association
- British Valve and Actuator Manufacturers' Association
- British Water
- Department of the Environment for Northern Ireland
- The Drinking Water Inspectorate
- Galvanizers Association
- Laboratory of the Government Chemist
- Lead Development Association
- Pipeline Industries Guild
- UK Steel Association
- UK Water Byelaws Scheme
- Water Research Centre
- Water UK
- Zinc Development Association

This British Standard, having been prepared under the direction of the Health and Environment Sector Committee, was published under the authority of the Standards Committee and comes into effect on 15 July 2001

© BSI 07-2001

Amendments issued since publication

Amd. No.	Date	Comments

The following BSI references relate to the work on this standard:
Committee reference EH/3/7
Draft for comment 00/561599 DC

ISBN 0 580 33274 8

Contents

	Page
Committees responsible	Inside front cover
Foreword	ii
Introduction	1
1 Scope	1
2 Terms and definitions	1
3 Principle	3
4 Reagents	3
5 Apparatus	5
6 Leachate	6
7 Method of analysis	6
8 Expression of results	9
9 Test report	10
Annex A (informative) Procedure for preparing test leachates	12
Annex B (informative) Methods for sealing the ends of pipe sections	18
Annex C (informative) Suitable methods for preparing extracts from large diameter pipes	20
Annex D (informative) Additional procedural details	23
Bibliography	27
Figure A.1 — Test sequence — Factory made	13
Figure A.2 — Test sequence — Site applied products	14
Figure B.1 — Metal clamp to seal pipe sections	18
Figure C.1 — Test arrangement 1	21
Figure C.2 — Test arrangement 2	22
Table D.1 — Within-laboratory performance data for internal standards	25
Table D.2 — Summary of variation (% RSD) for internal standards in interlaboratory performance testing	26

Foreword

This part of this British Standard has been prepared by Subcommittee EH/3/7, Effects of materials on water quality. It is a revision of BS 6920-4:1997, which is now withdrawn.

This standard contains technical revisions to the test method, based upon experience of using this method. In addition, the main part of the (normative) text for leachate preparation (clause 8 in the 1997 edition) has been transferred to a new informative Annex A to allow variations in leachate preparation conditions to be specified by the National Regulator.

BS 6920 is published in several other parts, namely:

- Part 1: *Specification*;
- Part 2: *Methods of test*;
- Part 3: *High temperature tests*.

Part 2 is further sub-divided into a number of sections and subsections as follows:

Section 2.1	<i>Samples for testing;</i>
Section 2.2	<i>Odour and flavour of water;</i>
Subsection 2.2.1	<i>General method of test;</i>
Subsection 2.2.2	<i>Method of testing tastes imparted to water by hoses;</i>
Subsection 2.2.3	<i>Method of testing tastes imparted to water by hoses for conveying water for food and drink preparation;</i>
Section 2.3	<i>Appearance of water;</i>
Section 2.4	<i>Growth of aquatic micro-organisms;</i>
Section 2.5	<i>The extraction of substances that may be of concern to public health;</i>
Section 2.6	<i>The extraction of metals.</i>

Annex A, Annex B, Annex C and Annex D are informative.

This part of this British Standard describes methods of identification only, and should not be used or quoted as a specification. References to this standard should indicate that the methods of identification used are in accordance with BS 6920-4.

This British Standard calls for the use of substances 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.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

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

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 27 and a back cover.

The BSI copyright notice displayed in this document indicates when the document was last issued.

Introduction

Chemicals that leach from materials used in contact with public water supplies can cause health concerns for consumers. Potential health effects of these chemicals are assessed in three stages:

- 1) preparation of leachates by exposing a portion of the material to water under controlled conditions;
- 2) analysis of the leachates;
- 3) toxicological evaluation of the concentrations of substances identified.

Analysis of organic substances present in the leachates usually involves two types of analytical method:

- a screening method which enables a qualitative and semi-quantitative assessment to be made of unspecified organic compounds;
- accurate quantitative methods for the determination of specific target compounds known to be present in the chemical formulations of the materials.

This part of BS 6920 describes the analytical procedures based upon gas chromatography and mass spectrometry (GCMS) used to screen leachates for unspecified organic compounds derived from finished products such as pipes, protective coatings, membranes, etc.

This method is suitable for leachates from all non-metallic materials that could be used in contact with water for human consumption, and which could be the subject of an application for approval by the National Regulator. In addition, Annex A gives general guidance on the preparation of test samples and their leachates.

NOTE 1 At the time of publication, products for use in contact with public water supply must be approved by the Secretary of State for the Environment under the provisions of regulation 25(1)(a) of the Water Supply (Water Quality) Regulations 1989 [1], unless any of the subsections 25(1)(b), (c) or (d) applies. The methods described in this section of BS 6920 may form the basis of leaching test specifications issued by the committee that advises the Secretary of State on the approval of substances and products for use in contact with public water supplies. Equivalent provisions apply in Scotland and Northern Ireland.

NOTE 2 The results of these tests are assessed by reference to existing toxicological data concerning the chemicals identified. Where little or no information exists, it might be necessary for the substance itself or the material leachate to be submitted for toxicity testing.

1 Scope

This part of BS 6920 describes a method for identifying organic chemicals that are amenable to GCMS analysis using the techniques described and which might leach from a product into water intended for human consumption. A method of calculating the concentrations of the organic substances identified is also provided.

This part of this British Standard is not applicable to the toxicological evaluation of chemicals.

NOTE The method to be used for the preparation of leachates will be specified by the National Regulator. Annex A provides a suitable method for preparing these leachates.

2 Terms and definitions

For the purposes of this British Standard, the following terms and definitions apply.

2.1

amu

atomic mass unit

defined as 1/12 of the mass of a single atom of carbon-12 in the gas phase (i.e. unbound), at rest and in its ground state

2.2**asymmetry factor** **A_s**

measure of the adsorption of a compound during gas chromatographic analysis

NOTE 1 It can be derived from the equation:

$$A_s = (a + b)/2b$$

where

a is the distance from the leading edge of the peak at the point on the baseline at which a perpendicular dropped from the peak maximum crosses it;

b is the corresponding distance from the trailing edge of the peak.

NOTE 2 Some manufacturer's GCMS software packages allow the calculation of peak asymmetries to be produced automatically.

2.3**electron impact ionization**

ionization by a beam of electrons

2.4**GCMS**

analytical instrument comprising a gas chromatograph (GC) linked to a mass spectrometer (MS)

2.5**GCMS general survey analysis**acquisition of a series of mass spectra (up to several thousand) during the course of a gas chromatographic run, by operating the mass spectrometer in a continuous cyclic scanning mode over a wide m/z range**2.6****internal standards**

organic compounds added to the leachate at a known concentration prior to the commencement of the analysis

NOTE Internal standards are added:

- to demonstrate that the analysis has been undertaken successfully; and
- to provide a reference to allow other substances detected to be quantified.

Ideally, the internal standards should not be present in the leachate; for this reason, isotopically labelled standards are preferred.

2.7**laboratory blank**

water sample known to contain negligible levels of contamination, to which internal standards have been added and which is then analysed in the same way as the leachate

NOTE Laboratory blanks are used to check for potential contamination of either leachates or solvent extracts which could occur within the laboratory during analysis.

2.8**leachate**

aqueous solution that results from leaving test water in contact with the test material under the specified test conditions

NOTE See Annex A.

2.9**mass spectrometric resolution**measure of the capability of the mass spectrometer to correctly distinguish two mass spectral peaks, having similar mass to charge m/z values, as separate peaksNOTE 1 When $z = 1$ this is generally denoted by $m_2/(m_2 - m_1)$ where m_2 has the higher m/z value and m_1 has the lower m/z value.NOTE 2 A mass spectrometer set up so that the resolution is 650 will satisfactorily resolve and assign the correct masses to mass spectral peaks at m/z 649 and m/z 650.

2.10***m/z***

mass-to-charge ratio of an ion

NOTE As most ions produced by electron impact ionization are singly charged, this ratio usually corresponds to the mass of an ion. However, exceptionally, ions can possess multiple charges.

2.11**solvent extract**

solution containing compounds partitioned from the leachate into the extraction solvent

2.12**total ion current****TIC**

sum of all the separate ion currents carried by the individual ions contributing to a mass spectrum

2.13**TIC chromatogram**

graphical representation of the TIC versus time

3 Principle

A mixture of internal standards is added to each of the test leachates prior to solvent extraction with dichloromethane. The solvent extract is concentrated and analysed by GCMS to determine the identity and approximate concentrations of organic chemicals that could be present.

The mass spectrometer is used in a repetitive full-scan mode and the mass spectra produced are recorded by, and stored on, the GCMS data system.

Wherever possible, each compound detected is identified and may be quantified by reference to the responses obtained for the internal standards.

NOTE 1 The number and duration of leaching (migration) periods, the nature of the test sample(s) and the test surface area to volume ratio are specified by the National Regulator based upon the nature of the product and its proposed use. Annex A provides a typical "model" for the preparation of leachates based upon the current requirements of the National Regulator.

NOTE 2 The methods used to identify organic compounds from their mass spectra do not form part of this method, but further information on this subject is given in Annex D.

4 Reagents

4.1 Only reagents of analytical grade shall be used, except where otherwise specified. All reagents shall be of sufficient purity to ensure that they do not give rise to interferences during the GCMS analysis.

NOTE Contamination can arise from various sources, e.g. plastics or rubber materials. The use of procedural blanks and laboratory blanks assists in detecting and identifying the source of any contamination.

4.2 *Reagent water*, having a conductivity of <2 mS/m, a total organic carbon content of <0.2 mg/l carbon, and free from organic contaminants which would interfere with the GCMS analysis of the extracts.

NOTE Suitable water may be prepared by reverse osmosis, deionization or distillation.

4.3 *Hydrochloric acid*, concentrated (30 % *m/V*).

4.4 *Hydrochloric acid solution*, prepared as follows.

Slowly add (0.5 ± 0.01) l of concentrated hydrochloric acid (4.3) to (0.5 ± 0.01) l of reagent water (4.2).

NOTE 1 Care is needed in preparing this solution which can generate heat.

NOTE 2 This solution should be replaced on a monthly basis.

4.5 *Nitric acid*, concentrated (65 % *m/V*).

4.6 *Nitric acid solution*, prepared as follows.

Slowly add (0.5 ± 0.01) l of concentrated nitric acid (4.5) to (0.5 ± 0.01) l of reagent water (4.2).

NOTE Care is needed in preparing this solution which can generate heat.

4.7 Sulfuric acid, concentrated (98 % *m/V*).

4.8 Sulfuric acid solution (0.5 mol/l), prepared as follows.

Slowly add (14.0 ± 0.5) ml of sulfuric acid (4.7) to (300 ± 5) ml of reagent water (4.2) and make up to (500 ± 5) ml with reagent water.

NOTE Care is needed in preparing this solution which can generate heat.

4.9 Chromic acid (5 % *m/V*), prepared as follows.

Dissolve (50 ± 1) g of chromium(VI) oxide in (1 ± 0.02) l of sulfuric acid (4.7).

NOTE Chromic acid is a storage hazard; it can burst a sealed container due to carbon dioxide release. It is a powerful oxidant and can give potentially explosive reactions with oxidizable materials. It can ignite on contact with acetone or alcohols. When heated to decomposition, it emits acrid smoke and irritating fumes.

4.10 Sodium hydroxide solution (0.5 mol/l), prepared as follows.

Dissolve (20.0 ± 0.1) g of sodium hydroxide pellets in test water and make up to 1 l.

NOTE Replace this solution on a monthly basis.

4.11 Dichloromethane, glass distilled grade.

NOTE Other grades may be suitable but it is necessary to demonstrate that any impurities present do not interfere with the detection of compounds of interest or the internal standards, or introduce unacceptable contamination.

4.12 Acetone, glass distilled grade.

NOTE Other grades may be suitable but it is necessary to demonstrate that any impurities present do not interfere with the detection of compounds of interest or the internal standards, or introduce unacceptable contamination.

4.13 Ascorbic acid solution, prepared as follows.

Dissolve (4.0 ± 0.1) g of ascorbic acid in (1.0 ± 0.01) l test water. Prior to use, extract this solution with dichloromethane (2 × 200 ml).

NOTE This solution should be replaced on a monthly basis.

4.14 Internal standards, use the following isotopically-labelled compounds:

- d₆-benzene;
- d₂₁-2,6-di-*t*-butyl-4-methylphenol (d₂₁-BHT);
- d₅-chlorobenzene;
- d₃₄-hexadecane;
- d₈-naphthalene;
- d₁₀-phenanthrene;
- d₅-phenol;
- d₆₂-squalane;
- d₁₀-*p*-xylene.

4.15 Internal standards stock solutions, prepared as follows.

Make up in acetone (4.12) as follows:

d ₆ -benzene	(2.0 ± 0.05) mg/ml;
d ₂₁ -BHT	(8.0 ± 0.20) mg/ml;
d ₅ -chlorobenzene	(2.0 ± 0.05) mg/ml;
d ₃₄ -hexadecane	(1.0 ± 0.02) mg/ml;
d ₈ -naphthalene	(1.0 ± 0.02) mg/ml;
d ₁₀ -phenanthrene	(2.0 ± 0.05) mg/ml;
d ₅ -phenol	(8.0 ± 0.20) mg/ml;
d ₁₀ - <i>p</i> -xylene	(1.0 ± 0.02) mg/ml.

NOTE 1 Due to its volatility, it is difficult to make standard solutions of d₆-benzene by weighing; it is recommended that suitable volumes (measured using micro-syringes) of d₆-benzene, based on its density (0.950), are used.

Make up the following stock solution in dichloromethane (4.11):

d_{62} -squalane (8.0 ± 0.20) mg/ml.

NOTE 2 The stock solutions are stable for at least six months, provided they are stored in the dark at (-18 ± 5) °C.

4.16 Internal standards intermediate solution, prepared as follows.

Place (2.5 ± 0.025) ml of the d_{62} -squalane stock solution in a 25 ml volumetric flask. Gently evaporate the dichloromethane until it is completely removed using nitrogen blow down. Verify the complete removal of the dichloromethane to incipient dryness.

NOTE 1 One way of verifying this is to evaporate to constant mass.

Then place (2.5 ± 0.025) ml of each of the remaining individual standard stock solutions (4.15) into the volumetric flask, ensuring that the d_6 -benzene stock solution is added last, and make up to the graduation mark with acetone (4.12).

NOTE 2 The d_6 -benzene stock solution is added last in order to minimize any potential evaporative losses of this standard.

NOTE 3 This solution is stable for at least six months provided it is stored in the dark at (-18 ± 5) °C.

4.17 Internal standards GC column test solution, prepared as follows.

Add (200 ± 5) µl of the internal standards intermediate solution (4.16) to (8 ± 0.5) ml of dichloromethane (4.14) in a 10 ml volumetric flask, then make up to the graduation mark with dichloromethane (4.11).

NOTE 1 To avoid potential losses of the most volatile internal standard (d_6 -benzene), it is recommended that a syringe, fitted with a needle of sufficient length to allow the tip to be introduced below the meniscus of the dichloromethane prior to expelling the syringe contents, is used.

NOTE 2 This solution should be renewed every three months or sooner if, during its use, an indication is obtained that the concentrations of any of the internal standards have changed.

4.18 Internal standards spiking solution, prepared as follows.

Add (1.00 ± 0.01) ml of the internal standards intermediate solution (4.16) to (8 ± 0.5) ml acetone (4.15) in a 10 ml volumetric flask, then make up to the graduation mark with acetone (4.12).

NOTE This solution should be renewed every three months or sooner if, during its use, any indication is obtained that the concentrations of any of the internal standards have changed.

4.19 Sodium sulfate (anhydrous), prepared as follows.

Remove any organic contaminants by heating at (500 ± 50) °C for ≥ 4 h, and store so that rehydration is minimized and re-contamination cannot occur.

5 Apparatus

5.1 Vessels and containers, constructed of a material such as glass or polytetrafluoroethylene (PTFE) that is inert under the specified test conditions.

5.2 Cleaning, in accordance with either the following procedure or with an alternative procedure demonstrated to be equally effective in removing all detectable traces of organic compounds from the apparatus.

Laboratory glassware shall be cleaned by washing with a biodegradable laboratory detergent specially designed for the removal of organic materials, followed by rinsing with hydrochloric acid solution (4.6) or chromic acid (4.9) and finally by thoroughly rinsing with reagent water (4.2).

NOTE Hydrochloric acid (4.4) should not be used to clean any stainless steel apparatus and equipment.

5.3 1 litre borosilicate glass bottles, of nominal capacity 1 l, fitted with either ground-glass stoppers or screw-top caps with PTFE or PTFE-faced liners.

5.4 Concentration apparatus, which is specifically designed to allow the solvent extract (2.11) to be reduced in volume from 200 ml to 50-500 µl.

NOTE Various commercial equipment, such as Kuderna-Danish or equivalent concentration apparatus, might be suitable. However, during this operation (which may proceed in several steps), it is essential that losses of volatile compounds are minimized. The response of the most volatile internal standard (d_6 -benzene) should be checked to ensure that losses of this compound in the concentration step do not exceed 50 %. One method of checking for losses is given in D.2.

5.5 Instrumental

5.5.1 Capillary gas chromatograph, with temperature gradient facility interfaced to a mass spectrometer (5.5.4).

5.5.2 GC capillary column, fused silica having a length of at least 50 m, with an internal diameter of 0.25 mm or 0.32 mm, coated with a non-polar bonded phase which performs equivalently to dimethylsilicone gum (e.g. DB-1 or BP-1).

NOTE Other column types capable of giving equivalent or better performance characteristics in this test may be used. Suitable validation data should be produced to justify the substitution.

5.5.3 Carrier gas (for GCMS system), helium (99.999 % purity, or better).

5.5.4 Mass spectrometer, which is capable of operating in the electron impact ionization mode covering the m/z range 20-650 provided that the mass spectrometric resolution (2.9) is sufficient to allow unit mass resolution at the highest mass recorded with a scan cycle of ≤ 1 s.

5.5.5 Mass spectrometry data system, which is capable of acquiring data from the mass spectrometer under the conditions in 5.5.4, and which can produce total ion current (TIC) chromatograms, background-subtracted averaged mass spectra and TIC peak areas. It shall also be capable of producing hard-copy outputs of TIC chromatograms and mass spectra.

5.5.6 Mass spectral library.

NOTE If a mass spectral library is not available on the mass spectrometry data system (5.5.5) alternative hard-copy documents shall be available. Examples of alternative hard-copy documents are the *Eight Peak Index of Mass Spectra* [2] or the *Registry of Mass Spectral Data* [3].

6 Leachate

NOTE The leachates for analysis may be prepared in accordance with Annex A or the specific requirements of the National Regulator.

6.1 Storage of test sample leachates

Start the analysis of leachate samples as soon as possible following collection. If necessary, store the leachate samples in the absence of light at $(4 \pm 2) ^\circ\text{C}$ for a maximum of 48 h before solvent extraction is undertaken.

6.2 Procedural blank tests

Carry out a blank test procedure with each batch of test samples using the same test conditions (test water, test temperature, leaching periods, type of test vessel, stoppers, etc.) as specified for the test samples (Annex A) but omitting the test sample(s).

When only glass stoppers or stainless steel plates are used to seal pipe test pieces, a glass container is suitable for the procedural blank; when other articles, such as stoppers, connectors or sealants are used (e.g. PTFE, silicone sealant, etc.) include these in the procedural blank at the same test surface area to volume (S/V) ratio as the exposure in the test containers.

7 Method of analysis

7.1 Extraction procedure

WARNING During the solvent extraction step, excess pressure (which can build up in the stoppered separating funnel) should be dissipated via the separating funnel tap when the separating funnel is inverted. As dichloromethane vapour is hazardous, dissipation of pressure should be undertaken with the separating funnel in a fume hood.

NOTE If any leachates have been prepared using chlorinated water the residual chlorine should be neutralized by the addition of ascorbic acid solution (4.13).

Transfer (1 ± 0.01) l of the leachate sample to a 2 l separating funnel.

Add (100 ± 2) μl of the internal standards spiking solution (4.18) into the sample using a syringe, ensuring that the tip of the syringe needle is below the surface of the sample. Insert the stopper and swirl the contents of the separating funnel to mix.

Check the pH of the sample and adjust to (2 ± 0.2) , if necessary, by dropwise addition of either sulfuric acid solution (4.8) or sodium hydroxide solution (4.10) as appropriate.