



BSI Standards Publication

Safety of toys

Part 3: Migration of certain elements

National foreword

This British Standard is the UK implementation of EN 71-3:2019. It supersedes BS EN 71-3:2013+A3:2018, which is withdrawn.

BSI, as a member of CEN, is obliged to publish EN 71-3:2019 as a British Standard. However, attention is drawn to the fact that during the development of this European Standard, the UK committee voted against its approval.

The UK committee voted negatively during the formal voting stage of EN 71-3:2019 because clause 7 of the standard does not clarify whether or not test portions can be made up of more than one material before the migration and analysis stages of the test. In the opinion of the UK committee, the omission of this information could cause users of the standard to interpret it as a reason for allowing combined test portions at the migration or analysis stage – a practice that was identified in EN 71-3:1994 as ‘not satisfactory because from a theoretical viewpoint it can result in the reduction in the migration of toxic elements that would otherwise occur.’

The UK participation in its preparation was entrusted to Technical Committee CW/15, Safety of toys.

A list of organizations represented on this committee can be obtained on request to its secretary.

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

© The British Standards Institution 2019
Published by BSI Standards Limited 2019

ISBN 978 0 580 51882 9

ICS 97.200.50

Compliance with a British Standard cannot confer immunity from legal obligations.

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 April 2019.

Amendments/corrigenda issued since publication

Date	Text affected
------	---------------

EUROPEAN STANDARD

EN 71-3

NORME EUROPÉENNE

EUROPÄISCHE NORM

April 2019

ICS 97.200.50

Supersedes EN 71-3:2013+A3:2018

English Version

Safety of toys - Part 3: Migration of certain elements

Sécurité des jouets - Partie 3: Migration de certains
élémentsSicherheit von Spielzeug - Teil 3: Migration bestimmter
Elemente

This European Standard was approved by CEN on 8 April 2019.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the CEN-CENELEC Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the CEN-CENELEC Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG**CEN-CENELEC Management Centre: Rue de la Science 23, B-1040 Brussels**

Contents		Page
European foreword		5
Introduction		7
1	Scope	8
2	Normative references	8
3	Terms and definitions	8
4	Requirements	9
5	Principle	11
6	Reagents and apparatus	12
7	Sampling and sample preparation	12
8	Migration methodology	16
9	Stabilization and analysis of migration solutions	19
10	Calculation of results	20
11	Method performance	21
12	Test report	24
Annex A (informative) Significant technical changes between this document and the previous version		25
Annex B (informative) Information on method validation		26
B.1	General	26
B.2	Samples of interlaboratory comparison	26
B.3	Selection of material category/element combinations	27
Annex C (informative) Estimation of reproducibility		28
Annex D (informative) Toy material visual particle size comparison materials		30
Annex E (normative) Method of analysis for general elements		32
E.1	Principle	32
E.2	Working solutions	32
E.2.1	Stock solution (M_1)	32
E.2.2	Diluted stock solution (M_2)	33
E.2.3	Working solutions	33
E.2.4	Internal standard stock solution	33
E.3	Procedure	33
E.4	Analysis	33
E.5	Calculation	34
E.5.1	Calibration curve	34

E.5.2	Calculation of migration	34
Annex F	(normative) Method of analysis for Chromium (VI)	35
F.1	Principle	35
F.2	Reagents	35
F.3	Apparatus	36
F.4	Procedure	37
F.5	Analysis	37
F.5.1	General	37
F.5.2	Chromatographic conditions	37
F.5.3	Limit of detection and quantification	38
F.5.3.1	General	38
F.5.3.2	Example of chromatogram	38
F.6	Calculation	38
F.6.1	Calibration curve	38
F.6.2	Calculation of migration	39
Annex G	(normative) Method of analysis for organic tin (see H.9)	40
G.1	Principle	40
G.2	Reagents	41
G.3	Apparatus	44
G.4	Procedure	44
G.4.1	Sample derivatisation	44
G.4.1.1	Derivatisation	44
G.4.1.2	Category I and III materials	45
G.4.1.3	Category II materials	45
G.4.1.4	Standard addition method	45
G.4.2	Calibration standards	46
G.5	Analysis	46
G.5.1	General	46
G.5.2	Example of GC conditions	48
G.5.3	Example of MS conditions	48
G.5.4	Limit of detection and quantification	48
G.5.5	Example of a GC-MS chromatogram	49
G.6	Calculation	50
G.6.1	Calibration curve	50
G.6.2	Standard addition	50
G.6.3	Calculation of migration of organic tin	50

Annex H (informative) Rationale	52
H.1 General	52
H.2 Mouthing behaviour of children (see Clause 1)	52
H.3 Skin contact (see Clause 1)	53
H.4 Toy categories (see 4.1)	53
H.5 Test portions (see Clause 7)	53
H.6 Size of test pieces (see 7.2)	53
H.7 Stability of Chromium (VI) in the migration solution (see 9.3)	54
H.8 Filtration of migration solutions (see 8.3.2)	54
H.9 Organic tin (see Annex G)	54
H.10 pH value (see 8.2 and 8.3.1.2)	56
H.11 De-waxing (see 7.2.3)	56
Annex ZA (informative) Relationship between this European Standard and the essential requirements of EU Directive 2009/48/EC aimed to be covered	57
Bibliography	58

European foreword

This document (EN 71-3:2019) has been prepared by Technical Committee CEN/TC 52 “Safety of toys”, the secretariat of which is held by DS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by October 2019, and conflicting national standards shall be withdrawn at the latest by October 2019.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. CEN shall not be held responsible for identifying any or all such patent rights.

This document supersedes EN 71-3:2013+A3:2018.

This document has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association, and supports essential requirements of EU Directive 2009/48/EC.

For relationship with EU Directive 2009/48/EC, see informative Annex ZA, which is an integral part of this document.

The significant changes from the previous edition of this standard are detailed in Annex A.

EN 71, *Safety of toys*, consists of the following parts:

- *Part 1: Mechanical and physical properties;*
- *Part 2: Flammability;*
- *Part 3: Migration of certain elements (this document);*
- *Part 4: Experimental sets for chemistry and related activities;*
- *Part 5: Chemical toys (sets) other than experimental sets;*
- *Part 7: Finger paints — Requirements and test methods;*
- *Part 8: Activity toys for domestic use;*
- *Part 9: Organic chemical compounds — Requirements;*
- *Part 10: Organic chemical compounds — Sample preparation and extraction;*
- *Part 11: Organic chemical compounds — Methods of analysis;*
- *Part 12: N-Nitrosamines and N-nitrosatable substances;*
- *Part 13: Olfactory board games, cosmetic kits and gustative games;*
- *Part 14: Trampolines for domestic use.*

NOTE 1 In addition to the above parts of EN 71, the following guidance documents have been published: CEN/TR 15071, *Safety of toys — National translations of warnings and instructions for use in EN 71*, and CEN/TR 15371 (all parts), *Safety of toys — Interpretations*.

NOTE 2 Words in *italics* are defined in Clause 3 (Terms and definitions).

According to the CEN-CENELEC Internal Regulations, the national standards organisations of the following countries are bound to implement this European Standard: Austria, Belgium, Bulgaria, Croatia, Cyprus, Czech Republic, Denmark, Estonia, Finland, Former Yugoslav Republic of Macedonia, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxembourg, Malta, Netherlands, Norway, Poland, Portugal, Romania, Serbia, Slovakia, Slovenia, Spain, Sweden, Switzerland, Turkey and the United Kingdom.

Introduction

The Toy Safety Directive (2009/48/EC) [1] specifies maximum migration limits for three categories of *toy materials*. Certain limit values have been amended (see [4, 5, 6, 7]). The limits for the migration of certain elements are expressed in milligram per kilogram *toy material* and are detailed in Table 2. The purpose of the limits is to minimize children's exposure to certain potentially toxic elements.

1 Scope

This document specifies requirements and test methods for the migration of aluminium, antimony, arsenic, barium, boron, cadmium, Chromium (III), Chromium (VI), cobalt, copper, lead, manganese, mercury, nickel, selenium, strontium, tin, organic tin and zinc from *toy materials* and from parts of toys.

Packaging materials are not considered to be part of the toy unless they have intended play value.

NOTE 1 See the European Commission guidance document no. 12 on the application of the Directive on the safety of toys – packaging [2].

The standard contains requirements for the migration of certain elements from the following categories of *toy materials*:

- Category I: Dry, brittle, powder like or pliable materials;
- Category II: Liquid or sticky materials;
- Category III: Scraped-off materials.

The requirements of this document do not apply to toys or parts of toys which, due to their accessibility, function, volume or mass, clearly exclude any hazard due to sucking, licking or swallowing or prolonged skin contact when the toy or part of toy is used as intended or in a foreseeable way, bearing in mind the behaviour of children.

NOTE 2 For the purposes of this document, for the following toys and parts of toys the likelihood of sucking, licking or swallowing toys is considered significant (see H.2 and H.3):

- All toys intended to be put in the mouth or to the mouth, cosmetics toys and writing instruments categorized as toys can be considered to be sucked, licked or swallowed;
- All the accessible parts and components of toys intended for children up to 6 years of age can be considered to come into contact with the mouth. The likelihood of mouth contact with parts of toys intended for older children is not considered significant in most cases (see H.2).

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 71-1:2014+A1:2018, *Safety of toys — Part 1: Mechanical and physical properties*

3 Terms and definitions

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

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

3.1

base material

material upon which *coatings* can be formed or deposited

3.2
coating

layer of material formed or deposited on a *base material* which can be removed by *scraping*

Note 1 to entry: *Coatings* can include paints, varnishes, lacquers, inks, polymeric *coatings* or other substances of a similar nature, whether they contain metallic particles or not, and irrespective of the manner of application.

3.3
paper

sheet formed by irregularly intervened fibres with a mass per unit area of 400 g/m² or less

3.4
paper board

sheet formed by irregularly intervened fibres with a mass per unit area over 400 g/m²

Note 1 to entry: The term *paper board* also includes materials commonly referred to as card or cardboard with a mass per unit area over 400 g/m².

3.5
scraping

mechanical removal of *coatings* down to but not including the *base material*

3.6
toy material

material present in toys and accessible as determined in accordance with EN 71-1:2014+A1:2018, 8.10

3.7
sample

toy or material subject to testing

3.8
laboratory sample

material taken from a *sample*

4 Requirements

4.1 Toy material categories (see H.4)

Table 1 contains a list of common *toy materials* and their respective categories. *Toy materials* not specifically listed in Table 1 shall be assigned to one of the categories.

Table 1 — Cross-reference table for determining category

Toy Material	Category I	Category II	Category III
<i>Coatings</i> of paints, varnishes, lacquers, printing inks, polymers, foams and similar <i>coatings</i>			X
Polymeric and similar materials, including laminates, whether textile reinforced or not, but excluding other textiles			X
<i>Paper</i> and <i>paper board</i>			X
Textiles, whether natural or synthetic			X
Glass, ceramic, metallic materials			X
Wood, fibre board, hard board, bone, leather and other solid materials			X
Compressed paint tablets, materials intended to leave a trace or similar materials in solid form appearing as such in the toy (e.g. the cores of colouring pencils, chalk, crayons)	X		
Pliable modelling materials, including modelling clays and plaster	X		
Liquid paints, including finger paints, varnishes, lacquers, liquid ink in pens and similar materials in liquid form appearing as such in the toy (e.g. slimes, bubble solution)		X	
Glue sticks		X	

4.2 Specific requirements

The migration of elements from *toy materials* categorized in accordance with 4.1 shall not exceed the migration limits given in Table 2 when tested in accordance with Clause 7 (sampling and sample preparation), Clause 8 (migration procedure) and Clause 9 (stabilization and analysis of migration solutions).

Table 2 — Migration limits from toy materials

Element	Migration limit		
	Category I mg/kg	Category II mg/kg	Category III mg/kg
Aluminium	5 625	1 406	70 000
Antimony	45	11,3	560
Arsenic	3,8	0,9	47
Barium	1 500	375	18 750
Boron	1 200	300	15 000
Cadmium	1,3	0,3	17
Chromium (III)	37,5	9,4	460
Chromium (VI)	0,02	0,005	0,2 / 0,053 ^a
Cobalt	10,5	2,6	130
Copper	622,5	156	7 700
Lead	2,0	0,5	23
Manganese	1 200	300	15 000
Mercury	7,5	1,9	94
Nickel	75	18,8	930
Selenium	37,5	9,4	460
Strontium	4 500	1 125	56 000
Tin	15 000	3 750	180 000
Organic tin	0,9	0,2	12
Zinc	3 750	938	46 000

^a The migration limit for Chromium (VI) for Category III toy material (scraped-off toy material) has been amended by Commission Directive (EU) 2018/725 [7]. The new limit value (0,053 mg/kg) applies from 2019-11-18. Before this date the limit value 0,2 mg/kg applies.

5 Principle

Soluble elements are extracted from *toy materials* using conditions which simulate the material remaining in contact with gastric juices for a period of time after swallowing. The concentrations of the soluble elements are determined quantitatively by three different methods:

- method for determining general elements: Aluminium, Antimony, Arsenic, Barium, Boron, Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Mercury, Nickel, Selenium, Strontium, Tin and Zinc;
- method for determining Chromium (VI);
- method for determining organic tin.

6 Reagents and apparatus

6.1 Reagents

All reagents, including water, used for analysis shall be of analytical grade or, if unavailable, technical grade reagents which have been determined to have acceptably low levels of impurity to allow the analysis to be performed.

- 6.1.1 **Hydrochloric acid solution**, $c(\text{HCl}) = (0,07 \pm 0,005) \text{ mol/l}$.
- 6.1.2 **Hydrochloric acid solution**, $c(\text{HCl}) = (0,14 \pm 0,010) \text{ mol/l}$.
- 6.1.3 **Hydrochloric acid solution**, $c(\text{HCl}) = \text{approximately } 1 \text{ mol/l}$.
- 6.1.4 **Hydrochloric acid solution**, $c(\text{HCl}) = \text{approximately } 2 \text{ mol/l}$.
- 6.1.5 **Hydrochloric acid solution**, $c(\text{HCl}) = \text{approximately } 6 \text{ mol/l}$.
- 6.1.6 **Isooctane, (C₈H₁₈), 99 %**.

6.2 Apparatus

Standard laboratory equipment and the following shall be used.

6.2.1 Equipment for measuring pH, calibrated and sufficiently accurate for the purposes of this European Standard.

NOTE H.10 contains additional information on equipment for measuring pH.

- 6.2.2 **Centrifuge**, capable of centrifuging at high speed to separate the solids (see H.8).
- 6.2.3 **A means to agitate the mixture**, at a temperature of $(37 \pm 2) \text{ }^\circ\text{C}$.

An orbital or linear shaker or shaking water bath capable of maintaining the migration solution in constant motion relative to the *sample*.

- 6.2.4 **Plastic containers** of gross volume, between 1,6 times and 5,0 times the volume of hydrochloric acid extract.
- 6.2.5 **High retention filter-paper**, ashless filter paper, particle retention in liquids 2,5 μm .
- 6.2.6 **Membrane filters** with pore sizes of 0,45 μm and 0,02 μm .

Syringe filters made with a cellulose acetate membrane are recommended for the 0,45 μm filter.

7 Sampling and sample preparation

7.1 Selection of test portions

A *sample* for testing shall consist of one toy in the form in which it will be marketed. Test portions shall be taken from *toy materials* of the single toy *sample*. Identical materials in the toy may be combined and treated as a single test portion but additional toy *samples* shall not be used to prepare larger test portions. Test portions are taken from each colour of each *toy material*. Test portions may be composed of more than one *toy material* or colour only when discrete specimens cannot be separated physically, e.g. dot printing, patterned textiles, multi-coloured printed surfaces etc. Such test portions shall be representative of the whole material.

NOTE This requirement does not preclude the preparation of test portions which represent the material and any *base material* upon which it is deposited.

Analysis of *toy materials* present in amounts less than 0,010 g is not required (see H.5).

The above does not preclude the testing of *toy materials* before they are used to manufacture a toy (raw materials). In these cases, the manufacturing process shall be assessed in order to ensure that it does not influence the migration of elements from the *toy materials*.

7.2 Sample preparation

7.2.1 General

Appropriate blank solutions shall be analysed so that appropriate corrections can be made when necessary (e.g. contamination of reagents and materials). If the blank result exceeds half of the lowest value the laboratory intends to report (laboratory's reporting limit) at least two blank solutions shall be analysed and the analytical result shall be corrected by the average value of the blank solutions.

7.2.2 Sampling

Whenever possible obtain a test portion of not less than 0,100 g of each *toy material* of the *laboratory sample* using the appropriate sampling method specified in Table 3.

Table 3 — Sampling methods

Toy material	Category (Table 1)	Sampling method
Liquid paints, including finger paints, varnishes, lacquers, liquid ink in pens and similar materials in liquid form appearing as such in the toy (e.g. slimes, bubble solutions)	II	Mix the <i>laboratory sample</i> . Ink in pens should be removed from the pen's refill before mixing.
<i>Coatings</i> of paints, varnishes, lacquers, printing ink, polymers, foams and similar <i>coatings</i>	III	<p>NOTE 1 <i>Paper or paper board samples</i> with paint, varnish, lacquer, printing ink, adhesive or similar material applied to their surfaces are not subjected to this sampling method but are treated according to the sampling method for <i>paper or paper board</i>.</p> <p>Remove the <i>coating</i> from the <i>laboratory sample</i> by <i>scraping</i> at room temperature, taking care to avoid the inclusion of the <i>base material</i>. Obtain particles of approximately 0,5 mm. The use of pre-prepared materials for visual size comparison is recommended (see Annex D).</p> <p>In case of a thick layer or one which is difficult to remove (e.g. pliable or plasticised layers), the <i>coating</i> can be cut off and tested as polymeric material.</p> <p>For <i>coatings</i> deposited on a non-polymeric <i>base material</i>, it is permissible to add a few drops of solvent, such as acetone/ethanol (1:1) mixture, methylene chloride or tetrahydrofuran to soften the <i>coating</i> and assist in its removal from the <i>base material</i>. If</p>

Toy material	Category (Table 1)	Sampling method
		<p>a solvent is used, remove the traces of solvent only by evaporation prior to migration. This procedure shall not be used if there are indications that the use of solvents can affect the migration of an element from the <i>coating</i>.</p> <p>NOTE 2 The use of <i>scraping</i> tools made of plastic materials helps to prevent the removal of <i>base material</i> after applying the solvent.</p> <p>This solvent assisted procedure may be used for verifying previous high results which might have been caused by the release of elements from scraped off <i>base materials</i> underlying the <i>coating</i>, e.g. high release of zinc from a <i>coating</i> scraped off from a <i>base material</i> containing zinc.</p>
<i>Paper and paper board</i>	III	<p>Prepare a test portion by cutting the <i>laboratory sample</i> using suitable tools. Take care to produce clean cut edges. Each dimension of the test pieces shall be as near to 6 mm as possible (see H.6). The use of pre-prepared materials for visual size comparison is recommended (see Annex D).</p> <p>If a <i>paper or paper board sample</i> has paint, varnish, lacquer, printing ink, adhesive or similar material applied to its surface, test portions of the <i>coating</i> shall not be taken separately. In such cases test portions shall be taken from the <i>toy material</i> so that they also include representative parts of the coated area.</p>
Toys and removable components which fit entirely within the small parts cylinder (see EN 71-1:2014+A1:2018, 8.2) containing accessible glass, ceramic, metallic materials	III	Apply the migration procedure to the whole component including any <i>coatings</i> . Components, the <i>coatings</i> of which have been removed for analysis, shall not be used. A separate unchanged component shall be used.
Compressed paint tablets, materials intended to leave a trace or similar materials in solid form appearing as such in the toy (e.g. the cores of colouring pencils, chalk, crayons)	I	<p>Prepare a test portion by cutting the <i>laboratory sample</i> using suitable tools. Take care to produce clean cut edges. Each dimension of the test pieces shall be as near to 6 mm as possible (see H.6). The use of pre-prepared materials for visual size comparison is recommended (see Annex D).</p>
Pliable modelling materials, including modelling clays and plaster	I	
Glue sticks	II	
Polymeric and similar materials, including laminates, whether textile reinforced or not, but excluding other textiles	III	

Toy material	Category (Table 1)	Sampling method
Textiles, whether natural or synthetic, including textile threads	III	
Wood, fibre board, hard board, bone, leather and other solid materials	III	

NOTE No sampling procedure for inaccessible *toy materials* or glass, ceramic and metallic toy components which do not fit within the small parts cylinder is specified as they are not within the scope of this European Standard. The exposure to certain elements from inaccessible materials and larger hard components, which cannot be swallowed, is not considered significant.

If a test portion of 0,1 g or more cannot be obtained, a test portion shall be obtained from each *toy material* present in the *sample* in a mass greater than 0,010 g. If the weight of the test portion obtained is between 0,010 g and 0,100 g, this shall be indicated in the report (see Clause 12 h)). In this case the analytical results shall be calculated as though 0,100 g of the test portion had been used ($W_{tp} = 0,100$ g, see H.5).

7.2.3 Dewaxing (see H.11)

7.2.3.1 General

If there are indications that the test portion contains grease, oil, wax or similar material dewax the test portion according to 7.2.3.2.

Category II test portions which can be dispersed in 0,07 mol/l HCL shall not be dewaxed.

De-waxing shall not be carried out on test portions prepared for organic tin analysis.

NOTE There are certain *sample* types known to contain grease, oil, wax or similar material. See H.11 for more information on which *samples* contain wax and, consequently, would need to be dewaxed.

7.2.3.2 Dewaxing procedure

Use a high-retention filter paper (see 6.2.5) which should be as small as possible without risking loss of the test portion during the de-waxing procedure. Weigh the test portion, to the nearest 0,001 g, onto the filter paper (W_{tp}). Use this mass of the test portion for the calculation of the results of the test. For category II *samples* containing grease, oil, wax or similar material, dry the test portion at (37 ± 2) °C for approximately 4 h. Fold the filter paper carefully to enclose the test portion without loss. Put the filter paper into the thimble of a Soxhlet extractor. Add an amount of isooctane appropriate for the equipment into the boiling flask of the extractor and extract for at least 60 min with no less than 10 reflux cycles per hour. If after 60 min there are indications of residual grease, oil, wax or similar material continue the extraction as necessary.

After extraction, dry the folded filter paper containing the dewaxed test portion at (80 ± 2) °C for approximately 1 h to remove the residual solvent. Weigh the dried filter paper parcel, to the nearest 0,001 g (W_{fp}). Use W_{fp} to calculate the volume of water and 0,14 mol/l HCl used in the migration procedure (see 8.1.2.1, samples containing grease, oil, wax or similar material).

The use of a dewaxing step shall be reported (see Clause 12 h)).

8 Migration methodology

8.1 Preparation of test portions before migration testing

8.1.1 General

For the purposes of the following subclauses the density of the water and hydrochloric acid solution can be assumed to be 1,0 g/ml and the solutions can be added volumetrically using suitable dispensers accurate to the nearest 0,05 ml.

The volume of simulant (V) added shall be recorded for the purpose of calculation of results.

8.1.2 Category I: Dry, brittle, powder like or pliable materials and Category II: Liquid or sticky materials

8.1.2.1 Samples containing grease, oil, wax or similar material

After dewaxing (see 7.2.3), weigh to the nearest 0,05 g $W_{fp} \times 25$ of water at (22 ± 3) °C into the appropriate sized container (see 6.2.4) containing the filter paper parcel.

Using a suitable mechanical means (e.g. a glass rod, a pestle or similar implement) homogenize the filter paper containing the dewaxed test portion in the water.

Add to the nearest 0,05 g $W_{fp} \times 25$ of 0,14 mol/l hydrochloric acid solution (see 6.1.2) at (22 ± 3) °C and mix.

Proceed without any delay with the appropriate pH adjustment procedure specified in 8.2 (pH adjustment).

8.1.2.2 Samples not containing grease, oil, wax or similar material

Weigh the test portion to the nearest 0,001 g (W_{tp}) into the appropriate sized container (see 6.2.4). Add to the nearest 0,05 g $W_{tp} \times 50$ of an aqueous solution of 0,07 mol/l HCl (see 6.1.1) at (22 ± 3) °C.

For test portions of mass between 0,010 g and 0,100 g, add 5,0 ml of 0,07 mol/l HCl (see 6.1.1) at (22 ± 3) °C.

Proceed without any delay with the appropriate pH adjustment procedure specified in 8.2 (pH adjustment).

8.1.3 Category III: Scraped-off materials

8.1.3.1 Glass, ceramic and metallic materials

Weigh the toy or component to the nearest 0,001 g (W_{tp}) into a 50 ml container with nominal height 60 mm and nominal diameter 40 mm.

Add sufficient amount of an aqueous solution of 0,07 mol/l HCl (see 6.1.1) at (22 ± 3) °C to just cover the toy or component.

NOTE This size of container can contain components/toys that fit inside the small parts cylinder.

Proceed without any delay with the appropriate pH adjustment procedure specified in 8.2 (pH adjustment).

8.1.3.2 Paper and paper board

Weigh the test portion to the nearest 0,001 g (W_{tp}) into the appropriate sized container (see 6.2.4).

Add to the nearest 0,05 g $W_{tp} \times 25$ g of water at (22 ± 3) °C.

Using a suitable mechanical means (e.g. a glass rod, a pestle or similar implement) homogenize the test portion in the water.

Add to the nearest 0,05 g Wtp × 25 g of 0,14 mol/l hydrochloric acid solution (see 6.1.2) at (22 ± 3) °C and mix.

Proceed without any delay with the appropriate pH adjustment procedure specified in 8.2 (pH adjustment).

8.1.3.3 Other materials

Weigh the test portion to the nearest 0,001 g (Wtp) into the appropriate sized container (see 6.2.4).

Add to the nearest 0,05 g Wtp × 50 g of an aqueous solution of 0,07 mol/l HCl (see 6.1.1) at (22 ± 3) °C.

For test portions of mass between 0,010 g and 0,100 g, add 5,0 ml of 0,07 mol/l HCl (see 6.1.1) at (22 ± 3) °C.

Proceed without any delay with the appropriate pH adjustment procedure specified in 8.2 (pH adjustment).

8.2 pH adjustment (see H.10)

8.2.1 General

Before starting the migration procedure adjust pH as specified in:

- 8.2.2 (pH adjustment – no buffering effect by toy material) if the test portion is not expected to contain a significant quantity of alkaline/buffering materials; or
- 8.2.3 (pH adjustment – buffering effect by toy material) if the test portion is expected to contain a significant quantity of alkaline/buffering materials.

Sample types for which close pH control is most important include chalk, finger paints, crayons, pigments, paints, solid paint tablets and, in particular, paper and paper board.

For each batch of test portions (i.e. test portions taken through the migration procedure at the same time), the pH control check measurement shall be performed on at least one solution from each material type within the batch. If the pH measured is less than 1,10 or more than 1,30 the remaining solutions in the batch for test portions of that type shall also be checked.

8.2.2 pH adjustment – no buffering effect by toy material

8.2.2.1 Following the addition of diluted of hydrochloric acid as specified in the relevant subclause of 8.1 (preparation of test portions before migration testing), shake the mixture gently for approximately 1 min to mix the contents.

8.2.2.2 Measure the pH of the mixture at (22 ± 3) °C.

8.2.2.3 If the pH is greater than 1,30 add 2 mol/l HCl (see 6.1.4) dropwise whilst mixing until the pH is within the range 1,10 to 1,30. Proceed to the migration steps (see 8.3, migration procedure).

8.2.3 pH adjustment – buffering effect by toy material

8.2.3.1 Shake the mixture gently to mix the contents.

8.2.3.2 Allow the mixture to stand at (22 ± 3) °C for 5₀⁺² min.

8.2.3.3 Measure the pH of the mixture at (22 ± 3) °C (pH_a).

If pH_a is within the range 1,10 – 1,20 proceed with the migration procedure (8.3, migration procedure).

If pH_a is greater than 1,20, add 6 mol/l HCl (see 6.1.5) dropwise whilst mixing until the pH is within the range 1,10 – 1,20.

8.2.3.4 Allow the mixture to stand at $(22 \pm 3)^\circ\text{C}$ for 5_0^{+2} min.

8.2.3.5 Measure the pH of the mixture at $(22 \pm 3)^\circ\text{C}$ (pH_b).

If pH_b is within the range 1,10 – 1,20 proceed with the migration procedure (8.3, migration procedure).

If pH_b is greater than 1,20, add 6 mol/l HCl (see 6.1.5) dropwise whilst mixing until the pH is within the range 1,10 – 1,20.

8.2.3.6 Allow the mixture to stand at $(22 \pm 3)^\circ\text{C}$ for 10_0^{+2} min.

8.2.3.7 Measure the pH of the mixture at $(22 \pm 3)^\circ\text{C}$ (pH_c).

If pH_c is within the range of 1,10 – 1,20 proceed with the migration procedure (8.3, migration procedure).

If pH_c is greater than 1,20, add 6 mol/l HCl (see 6.1.5) dropwise whilst mixing until the pH is within the range 1,10 – 1,20.

8.2.3.8 Allow the mixture to stand at $(22 \pm 3)^\circ\text{C}$ for 10_0^{+2} min.

8.2.3.9 Measure the pH of the mixture at $(22 \pm 3)^\circ\text{C}$ (pH_d).

If pH_d is within the range of 1,10 – 1,20 proceed with the migration procedure (8.3, migration procedure).

If pH_d is greater than 1,20, add 6 mol/l HCl (see 6.1.5) dropwise whilst mixing until the pH is within the range 1,10 – 1,20. Then proceed with the migration procedure (8.3, migration procedure).

8.3 Migration procedure

8.3.1 Migration

8.3.1.1 Migration conditions

For glass, ceramic and metallic materials, cover the container and allow the contents to stand for 120_0^{+10} min at $(37 \pm 2)^\circ\text{C}$.

For all other materials, close the container (see 6.2.4) and agitate the mixture at $(37 \pm 2)^\circ\text{C}$ for 60_0^{+5} min with a speed of $(150 \pm 10) \text{ min}^{-1}$. Stop the agitation and leave the containers to stand for a further 60_0^{+5} min at $(37 \pm 2)^\circ\text{C}$.

8.3.1.2 pH control after migration (see H.10)

After completing migration the pH shall be checked in order to ensure that the correct pH has been maintained throughout the migration procedure. If it is possible to demonstrate that there is no variation of the pH for certain materials (e.g. plastic) it is not necessary to control the pH for that material after migration.

Migration solutions with a pH less than 1,10 or greater than 1,30 which have been adjusted according to 8.2.2 (pH adjustment – no buffering effect by toy material) shall be discarded and a new test portion shall be analysed using the migration procedure for *toy materials* with high buffering capacity (see 8.2.3, pH adjustment – buffering effect by toy material).

For migration solutions with a pH less than 1,10 or greater than 1,30 which have been adjusted according to 8.2.3 (pH adjustment – buffering effect by toy material) the pH measured after migration shall be indicated in the test report.

It is sufficient to carry out the pH control check for one solution from each material type within a batch. If the pH measured is less than 1,10 or more than 1,30 the remaining solutions in the batch for test portions of that type shall also be checked.

8.3.2 Filtration (see H.8)

8.3.2.1 General

Without delay separate the solid matter from the solution by filtration through a membrane filter with a pore size of 0,45 µm (see 6.2.6). In case filtration is very slow, centrifugation (see H.8) may be used to remove particles before filtration.

For special concerns regarding high copper results see 8.3.2.2 (samples exceeding the copper limit value).

8.3.2.2 Samples exceeding the copper limit value

In some rare cases high copper results can be obtained due to minute particles of copper containing insoluble matter (normally indicated by e.g. a Tyndall beam or a blue or green coloured filtrate). When the migration limits for copper are exceeded repeat the migration and filtration steps using a membrane filter (see 6.2.6) with a pore size of 0,02 µm. It is recommended to centrifuge the migration mixture (see H.8) and filter it with a 0,45 µm filter before the final filtration with a 0,02 µm filter in order to remove insoluble copper containing particles.

9 Stabilization and analysis of migration solutions

9.1 General

The methods specified in 9.2 to 9.4 each require a certain volume of the prepared migration solution (see 8.3, migration procedure). Approximately 4 ml are required for the analysis for general elements, at least 2 ml for Chromium (VI) analysis and approximately 5 ml for organic Tin analysis.

Whilst it is acceptable to dilute migration solutions in order to provide sufficient volumes for the analyses, care should be taken to do this accurately and without compromising the laboratory's limit of detection and other analytical quality parameters.

9.2 General elements

If the migration solutions (see 8.3, migration procedure) are to be retained for more than 24 h prior to analysis, they shall be stabilized by the addition of a suitable amount of hydrochloric acid such that the concentration HCl of the stored solution is approximately 1 mol/l.

Analyse the migration solution according to Annex E.

Alternative methods of analysis or modifications to the methods of this European Standard are acceptable only if they are capable of achieving at least the accuracy and precision of the methods specified in Annex E. The sensitivity of any alternative methods or modifications shall be adequate and they shall have been validated to show that the results achieved are equivalent to those of the methods in this document. In particular, the limits of quantification (LOQ) shall not be greater than 50 % of the respective limit values specified in Table 2.

NOTE Experience has shown that the detection using ICP-OES is suitable for category III *toy materials*.

9.3 Chromium (VI)

Neutralize the migration solution (see 8.3, migration procedure) according to F.4 without delay. After neutralization the solution is stable for at least 4 h.

Alternative methods of analysis or modifications to the methods in this European Standard are acceptable only if they are capable of achieving at least the accuracy and precision of the methods specified in Annex F. The sensitivity of any alternative methods or modifications shall be adequate and they shall have been validated to show that the results achieved are equivalent to those of the methods in this European Standard. In particular, the limits of quantification (LOQ) shall not be greater than 50 % of the respective limit values specified in Table 2.

NOTE Experience has shown that the detection using IC with post-column derivatisation and UV/VIS detection is suitable for category III *toy materials*.

9.4 Organic tin

The migration solution (see 8.3, migration procedure) shall be analysed as quickly as possible, preferably within 24 h, according to Annex G.

Alternative methods of analysis or modifications to the methods in this European Standard are acceptable only if they are capable of achieving at least the accuracy and precision of the methods described in Annex G. The sensitivity of any alternative methods or modifications shall be adequate and they shall have been validated to show that the results achieved are equivalent to those of the methods in this Standard. In particular, the limits of quantification (LOQ) of individual organic tin compounds shall not be greater than approximately 15 % of the organic tin limit values specified in Table 2.

10 Calculation of results

10.1 Calculation of migration

10.1.1 General

Calculate the migration of elements from the *toy material* according to:

- E.5 for general elements (Aluminium, Antimony, Arsenic, Barium, Boron, Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Mercury, Nickel, Selenium, Strontium, Tin and Zinc);
- F.6 for Chromium (VI);
- G.6 for organic tin.

10.1.2 Calculation of Chromium (III)

Chromium (III) is calculated by the following formula:

$$C_{Cr(III)} = C_{Cr(total)} - C_{Cr(VI)} \quad (1)$$

where

- $C_{Cr(III)}$ is the concentration of Chromium (III), in mg/kg;
- $C_{Cr(total)}$ is the concentration of Chromium (all forms), in mg/kg;
- $C_{Cr(VI)}$ is the concentration of Chromium (VI), in mg/kg.

NOTE The concentration of Chromium (VI) in many cases is below 2 % of the total concentration and can usually be neglected in Formula (1).

10.2 Interpretation of results

When assessing whether or not *samples* comply with the migration limit requirements analytical results should be interpreted using the data in Clause 11 (method performance).

In accordance with normal analytical quality assurance measures, laboratories are required to determine their own method performance data, including measurement uncertainty (see Clause 11, method performance and Annex C).

NOTE Eurachem Guides [8, 9] give guidance on how to evaluate measurement uncertainty and how to use measurement uncertainty for interpretation of analytical results in relation to compliance assessment.

11 Method performance

11.1 Repeatability and reproducibility

Table 4, Table 5 and Table 6 show the results from an interlaboratory comparison performed during September 2017.

Table 4 — Results from interlaboratory comparison for general elements

Element	Material category	Material number ^a	l ^b	n ^c	x ^d mg/kg	CV _R ^e %	CV _r ^f %	CV _i ^g %
Al	I	1	18	17	7 122	7,6	2,7	5,7
Al	II	5	18	16	133,8	6,2	3,6	5,6
B	II	4	18	15	303,7	10,3	3,0	5,8
As	I	1	18	17	3,74	12,6	5,8	9,5
As	II	6	17	16	0,958	13,5	7,9	5,8
Cd	III	12	18	17	26,2	12,1	2,0	5,9
Ba	II	5	18	16	363,4	6,4	2,5	4,7
Ba	III	13	15	13	5 021	18,7	6,4	8,2
Co	III	12	18	17	223,4	10,8	2,9	5,0
Cr(III)	I	1	18	16	37,3	7,4	2,7	6,1
Cr(III)	II	9	18	17	7,25	8,0	2,4	5,8
Cr(III)	III	12	18	16	1 110	17,6	3,5	8,0
Cu	I	1	18	17	767,3	11,5	3,6	7,4
Cu	II	4	18	16	156,5	5,8	2,5	4,8
Hg	II	6	17	16	1,23	23,4	7,5	13,1
Mn	I	2	18	15	1 676	10,2	2,5	6,4
Mn	II	4	18	16	301	6,2	3,4	4,2
Ni	III	11	15	12	1 688	19,8	2,3	7,1
Pb	III	11	15	12	35,8	20,6	3,2	8,5
Pb	I	2	18	16	2,11	15,7	6,4	9,2
Pb	II	6	18	15	0,613	19,8	5,4	8,7
Sb	III	12	18	16	712,7	33,9	3,3	19,8

Element	Material category	Material number ^a	l ^b	n ^c	\bar{x} ^d mg/kg	CV _R ^e %	CV _r ^f %	CV _i ^g %
Se	II	6	18	16	9,53	8,5	4,1	7,7
Sn	III	13	15	14	2 864	47,7	9,9	13,5
Sr	III	12	18	16	10 017	10,3	2,2	6,7
Sr	I	2	18	16	5 310	14,8	2,3	5,6
Zn	III	12	18	15	9 236	12,4	1,9	9,4
Zn	II	4	18	16	108,6	16,1	10,0	11,1

^a See B.2 for more information about materials used in the interlaboratory comparison.

^b *l* is the number of laboratories reporting result for this parameter.

^c *n* is the number of results used in the statistical calculations after removal of outliers.

^d \bar{x} is the mean of the accepted results.

^e CV_R is the coefficient of variation of the reproducibility.

^f CV_r is the coefficient of variation of the repeatability (indicating the relative spread between duplicate measurements from the same migration).

^g CV_i is the relative intermediate standard deviation (indicating the relative spread between two migrations on different days in the same laboratory).

Table 5 — Results from interlaboratory comparison for Chromium (VI)

Element	Material category	Material number ^a	l ^b	n ^c	\bar{x} ^d mg/kg	CV _R ^e %	CV _r ^f %	CV _i ^g %
Cr(VI)	I	3	9	7	0,022	62,4	4,0	25,8
Cr(VI)	II	8	9	9	0,012	56,3	7,8	30,2
Cr(VI)	III	14	8	8	2,97	36,5	6,2	12,6

^a See B.2 for more information about materials used in the interlaboratory comparison.

^b *l* is the number of laboratories reporting result for this parameter.

^c *n* is the number of results used in the statistical calculations after removal of outliers.

^d \bar{x} is the mean of the accepted results.

^e CV_R is the coefficient of variation of the reproducibility.

^f CV_r is the coefficient of variation of the repeatability (indicating the relative spread between duplicate measurements from the same migration).

^g CV_i is the relative intermediate standard deviation (indicating the relative spread between two migrations on different days in the same laboratory).

Table 6 — Results from interlaboratory comparison for organic tin compounds

Element	Material category	Material number ^a	l ^b	n ^c	\bar{x} ^d mg/kg	CV_R ^e %	CV_r ^f %	CV_i ^g %
Butyl Tin	II	7	11	7	0,137	40,5	7,5	15,2
Butyl Tin	III	15	11	10	27,6	37,7	7,8	10,9
DiButyl Tin	II	7	11	8	0,072	55,5	7,9	10,8
DiButyl Tin	III	15	11	10	20,4	37,1	5,0	8,5
TriButyl Tin	III	15	11	10	7,64	71,7	4,3	14,0
Sum Butyl Tin+DiButyl Tin	II	7	11	8	0,205	41,0	8,1	9,5
Sum Butyl Tin+DiButyl Tin+TriButyl Tin	III	15	11	10	55,7	34,8	5,6	8,5

^a See B.2 for more information about materials used in the interlaboratory comparison.
^b l is the number of laboratories reporting result for this parameter.
^c n is the number of results used in the statistical calculations after removal of outliers.
^d \bar{x} is the mean of the accepted results.
^e CV_R is the coefficient of variation of the reproducibility.
^f CV_r is the coefficient of variation of the repeatability (indicating the relative spread between duplicate measurements from the same migration).
^g CV_i is the relative intermediate standard deviation (indicating the relative spread between two migrations on different days in the same laboratory).

More information on the interlaboratory comparison is available in Annex B.

11.2 Estimation of bias

In order to estimate the method bias, spiking experiments were performed during the interlaboratory comparison. Unknown to participant laboratories and for each analyte/matrix combination used the concentration of the migration solution was increased by a factor of approximately 3. The result of these spiking experiments showed recoveries close to 100 % for each analyte. The method bias was therefore minimal.

11.3 Limit of detection (LOD) and limit of quantification (LOQ)

The limits of detection (LOD) and the limits of quantification (LOQ) for Cr(VI) and organic tin are given in Annex F and Annex G, respectively. For the general elements the LOQ obtained with ICP-MS following the procedures specified in this standard are more than 50 times better than required for assessing compliance of the limit values for any of the material categories (see Table 2).

In the interlaboratory comparison a blank sample from material category II was tested for Chromium (VI). 5 out of 8 laboratories did not detect Chromium (VI) reporting LOQs below the limit value. 1 laboratory result exceeded the maximum migration limit. The method specified in this standard is therefore capable of achieving sufficiently low LOQ for *toy material* category II samples.

The results from the interlaboratory comparison also confirm that special care need to be taken to avoid any false positive findings of Chromium (VI) originating from reagents, solutions or materials used.

12 Test report

In accordance with normal laboratory practice, the test report shall contain at least:

- a) a title, e.g. Test report, Test Certificate;
- b) the name and address of the laboratory and the name and address of the client;
- c) a serial number or similar unique identification for the report which should appear on each page together with pagination in the form Page .. of ..;
- d) the client's identification details for the *samples* and the identifiers used by the laboratory, for example *sample* numbers;
- e) the date of receipt of the items and the date(s) of testing;
- f) identification of the analytical technique used;
- g) a reference to this document (i.e. EN 71-3:2019);
- h) a note of any deviations from the standard and any environmental conditions which can bear upon the results;
- i) a note to state that a *sample* was dewaxed;
- j) the pH after the migration if it was outside the range of 1,1 to 1,3;
- k) the test results themselves with units and the measurement uncertainty (if required to assist in the interpretation of the results);
- l) the name, position and signature or other identification of the person accepting responsibility for the report and the report's date of issue;
- m) a statement that the results only apply to the items tested.

Annex A (informative)

Significant technical changes between this document and the previous version

Table A.1 — Significant technical changes between this European Standard and the previous version

Clause/Paragraph/Table/Figure	Change
3	New terms and definitions for sample and laboratory sample added and terms and definitions on limit of detection, limit of quantification and other material (whether mass coloured or not) removed.
4	In Table 2 the limit value for Chromium (VI) for material category III adapted to new legal limit values.
6	The list of reagents and apparatus has been revised
7	Sampling and sample preparation have been revised and restructured to improve the user-friendliness of the standard. In particular sieving is no longer required and the corresponding annex with sieve requirements (former Annex C) has been deleted. Furthermore, the dewaxing procedure has been revised.
8	The migration procedure has been revised and more detailed procedures for checking the pH before and after migration has been introduced.
9	The stabilization of the migration solution has been revised. The status of test methods (included in Annex E, Annex F and Annex G) has been changed to normative. Performance requirements concerning the use of modifications to the annexes and alternatives to the specified test methods have been introduced.
10	The calculation has been revised, in particular Chromium (III) is now calculated by subtracting the Chromium (VI) concentration from the total chromium concentration.
11	Data on method performance have been introduced based on the results of test method validation and in particular the results of an interlaboratory comparison.
Annex B	A new informative annex containing information on the method development has been introduced.
Annex C	A new informative annex with estimations of reproducibility has been added.
Annex D	A new annex concerning the use of visual particle size comparison materials has been added.
Annex E	Minor revisions of the test method for general elements have been made.
Annex F	The test method for Chromium (III) and Chromium (VI) has been replaced by a test method for Chromium (VI) which is capable of determining Chromium (VI) at the limit values for all material categories.
Annex G	The test method for organic tin has been revised.
Annex H	Various rationales have been revised and new rationales concerning sampling and dewaxing have been added.

NOTE The technical changes referred to above are the significant changes to the previous version. The list is not an exhaustive list of all modifications to the previous version.

Annex B
(informative)

Information on method validation

B.1 General

The test methods specified in this standard have been validated by the technical project leader of the revision of EN 71-3:2013+A1:2014 and by a peer review laboratory as well as in a interlaboratory comparison. The results of the interlaboratory comparison are given in 11.1 (repeatability and reproducibility). The results of the technical project leader and peer review laboratory are in line with the results from the interlaboratory comparison and have been considered in the estimations provided in Annex C.

B.2 Samples of interlaboratory comparison

Table B.1 contains an overview of the *samples* tested in the interlaboratory comparison. The *samples* were specifically produced for the purpose of method validation. Although the *samples* covered the three material categories it was not possible to cover the whole variety of possible *toy materials* (which could cause various matrix effects). It was also not possible to produce *samples* covering all specific sample preparation steps specified in this standard such as dewaxing, *scraping-off* and pH adjustment of materials with buffering capacity.

Table B.1 — Samples of interlaboratory comparison

Material category	Material number	Elements	Base material
I	1	Al, As, Cr, Cu	Mixture of calcium sulfate and magnesium oxide
	2	Mn, Pb, Sr	Quartz powder
	3	Cr(VI)	Mixture of calcium sulfate and magnesium oxide
II	4	B, Cu, Mn, Zn	Water based paint
	5	Al, Ba	Water based paint
	6	As, Hg, Pb, Se	Water based paint
	7	Organic tin compounds	Finger paint
	8	Cr(VI)	Finger paint
	9	Cr	Finger paint
	10	None	Finger paint
III	11	Ni, Pb	Polymer material
	12	Co, Cd, Cr, Sb, Sr, Zn	Polymer material
	13	Ba, Sn	Polymer material
	14	Cr(VI)	Sol Gel, SiO ₂ -based
	15	Organic tin compounds	Polymer material

B.3 Selection of material category/element combinations

In accordance with Directive 2009/48/EC this European Standard specifies limit values for the migration of 19 elements for three different material categories, i.e. 57 limit values in total (see Table 2). Due to limited resources it was not possible to produce and test reference materials for all 57 element/material category combinations. Therefore, a prioritization of element/material category combinations was carried out when planning the revision of EN 71-3:2013+A1:2014. This prioritization was mainly based on the reported migration of elements in practice and on the relevance for the method development and validation.

The decision whether an element/material category combination was included in the reference materials for the revision of EN 71-3:2013+A1:2014 was based on the following:

- the priority of the element/material category combinations, i.e. combinations with high priority (reported migration of elements in the material category) were preferred;
- the representation of each element in at least one material category is considered as crucial for the purpose of method development/validation because this allows to have reference material(s) for all the elements in question;
- given the limitations in budget and time frame for the revision of EN 71-3 it was not possible to cover all element/material category combinations.

As the project focused on method development/validation the aspect of covering all elements in at least one material category had been considered as more important than to cover all element/material combinations with high/medium priority. Consequently, in order to limit the number of element/material category combinations only very few elements were included in all material categories.

In order to compensate for the missing data for certain element/material category combinations estimations for the reproducibility have been included in Annex C.

Annex C (informative)

Estimation of reproducibility

During the revision of EN 71-3:2013+A1:2014 a lot of data, e.g. from the technical project leader and the peer review laboratory as well as from the interlaboratory comparison, had been produced. Only a few data could be given in the standard. Based on the data and on the expertise of the experts involved, the responsible working group tried to summarize the results and knowledge obtained from the revision of this project (SA/CEN/2013-03 Migration of certain elements) in order to help the user of this standard in fulfilling the requirements of Directive 2009/48/EC.

In this process in particular the following aspects had been considered:

- the limited experience of laboratories participating in the interlaboratory comparison in particular with regard to the modified methods for organic tin and Chromium (VI) as these methods had been provided only shortly before the interlaboratory comparison;
- in order to facilitate the application of the standard, four balanced levels for relative reproducibility have been introduced which were derived from the data of the interlaboratory comparison and the data from the technical project leader and peer review laboratory;
- standard deviations especially on reproducibility are usually increasing when element concentrations get lower which had also been shown in the interlaboratory comparison. As a general rule this had been treated by a higher level of reproducibility generally below 10 mg/kg in Table C.1;
- bearing in mind the prioritization of element/material category combinations and the need to fill the gaps for combinations for which no reference materials had been available during the revision of the standard (see Annex B);
- applying the standard to a broad spectrum of toys with various compositions within the material categories but recognizing that the estimated reproducibility data does not intend to represent the worst case (e.g. higher reproducibilities than estimated in Table C.1 could result for certain *toy materials*);
- developing a guideline for principal equivalence of other methods in relation to the results with the given methods in this standard;
- recognizing that the estimated reproducibility data are not intended to replace the standard deviation (and measurement uncertainty) data which shall be prepared by each laboratory.

Table C.1 contains estimations of relative reproducibility for the elements for each material category at concentration at levels approximately at the limit value.

Table C.1 — Estimations of relative reproducibility at concentrations corresponding approximately to the limit values in Table 2

Element	Estimated coefficient of variation of the reproducibility (CV_R)		
	Material Category I	Material Category II	Material Category III
Aluminium	15	15	15
Antimony	30	30	30
Arsenic	20	20	20
Barium	20	15	30
Boron	15	15	15
Cadmium	20	20	15
Chromium (III)	15	20	15
Chromium (VI)	50	50	50
Cobalt	15	20	15
Copper	15	15	15
Lead	20	20	30
Manganese	15	15	15
Mercury	30	30	20
Nickel	20	20	20
Selenium	15	20	15
Strontium	15	15	15
Tin	20	20	30
Organic tin	50	50	50
Zinc	15	15	15

Annex D
(informative)

Toy material visual particle size comparison materials

When preparing test portions of *toy materials* for analysis it is important to control the particle size. Trials have shown that the benefits of sieving test portions to control the particle size are outweighed by the inconvenience and the loss of the test portions in some cases. For that reason, it is recommended that comparison materials are used against which test portions can be compared visually.

Visual comparison materials can conveniently be prepared from typical toys materials such as:

- Polymeric materials;
- *Paper and paper board*;
- Textile materials;
- Paints and *coatings*;
- Natural materials such as wood, fibre board, bone, leather etc.

This standard recommends that visual comparison materials be prepared in accordance with 7.2 (Table 3). Visual comparison materials can be prepared which fulfil the size criteria (see below) and which have been measured or sieved to ensure that they do. The comparison materials can be stored in transparent containers for ease of use and handled carefully so that the particle sizes do not alter significantly with time. They should be checked periodically.

Table D.1 — Toy material visual particle size comparison materials

Toy material	Category (Table 1)	Comparison material particle size
<i>Coatings</i> of paints, varnishes, lacquers, printing ink, polymers, foams and similar <i>coatings</i>	III	approximately 0,5 mm prepared by <i>scraping</i> materials and passing through a metal sieve of nominal aperture 0,500 mm
Polymeric and similar materials, including laminates, whether textile reinforced or not, but excluding other textiles	III	Approximately 6 mm in at least one dimension. The visual comparison materials shall show the analyst acceptable sized pieces from a variety of materials with different thicknesses, some with 3 dimensions of 6 mm and some with only 2 dimension of 6 mm (when they are thinner pieces).
<i>Paper and paper board</i>	III	Approximately 6 mm in at least one dimension. Prepare a variety of particles from materials of different thicknesses which demonstrate acceptable sizes of materials typically used in toys.

Toy material	Category (Table 1)	Comparison material particle size
Textiles, whether natural or synthetic	III	Approximately 6 mm in at least one dimension. Prepare a variety of particles from materials of different thicknesses which demonstrate acceptable sizes of materials typically used in toys.
Toys and removable components which fit entirely within the small parts cylinder (see EN 71-1:2014+A1:2018, 8.2) containing accessible glass, ceramic, metallic materials	III	Comparison material not required
Wood, fibre board, hard board, bone, leather and other solid materials	III	Approximately 6 mm in at least one dimension. The visual comparison materials shall show the analyst acceptable sized pieces from a variety of materials with different thicknesses, some with 3 dimensions of 6 mm and some with only 2 dimension of 6 mm (when they are thinner pieces).
Compressed paint tablets, materials intended to leave a trace or similar materials in solid form appearing as such in the toy (e.g. the cores of colouring pencils, chalk, crayons)	I	Approximately 6 mm in at least one dimension. The visual comparison materials shall show the analyst acceptable sized pieces from a variety of materials with different thicknesses, some with 3 dimensions of 6 mm and some with only 2 dimension of 6 mm (when they are thinner pieces).
Pliable modelling materials, including modelling clays and plaster	I	Approximately 6 mm in at least one dimension. The visual comparison materials shall show the analyst acceptable sized pieces from a variety of materials with different thicknesses, some with 3 dimensions of 6 mm and some with only 2 dimension of 6 mm (when they are thinner pieces).
Liquid paints, including finger paints, varnishes, lacquers, liquid ink in pens and similar materials in liquid form appearing as such in the toy (e.g. slimes, bubble solutions)	II	Comparison material not required.
Glue sticks	II	Approximately 6 mm in at least one dimension. The visual comparison materials shall show the analyst acceptable sized pieces from a variety of materials with different thicknesses, some with 3 dimensions of 6 mm and some with only 2 dimension of 6mm (when they are thinner pieces).

Annex E (normative)

Method of analysis for general elements

E.1 Principle

This method quantifies Aluminium, Antimony, Arsenic, Barium, Boron, Cadmium, Chromium, Cobalt, Copper, Lead, Manganese, Mercury, Nickel, Selenium, Strontium, Tin and Zinc in the migration solution (see 8.3, migration procedure). The migration solution and its dilutions are analysed directly by ICP-MS.

E.2 Working solutions

E.2.1 Stock solution (M_1)

Prepare a stock solution (M_1) diluting the commercial available stock solutions of the individual elements (concentration = 1 000 mg/l) in hydrochloric acid solution (see 6.1.1) to a volume of 50 ml, according to the scheme in Table E.1.

Table E.1 — Preparation scheme stock solution M_1

Element	Volume stock ml	Volume ml	Concentration mg/l
Aluminium	0,5	50,0	10,0
Antimony	0,5	50,0	10,0
Arsenic	0,5	50,0	10,0
Barium	0,5	50,0	10,0
Boron	0,5	50,0	10,0
Cadmium	0,5	50,0	10,0
Chromium	0,5	50,0	10,0
Cobalt	0,5	50,0	10,0
Copper	0,5	50,0	10,0
Lead	0,5	50,0	10,0
Manganese	0,5	50,0	10,0
Mercury	0,05	50,0	1,0
Nickel	0,5	50,0	10,0
Selenium	0,5	50,0	10,0
Strontium	0,5	50,0	10,0
Tin	0,5	50,0	10,0
Zinc	0,5	50,0	10,0

E.2.2 Diluted stock solution (M_2)

Dilute 0,5 ml of stock solution M_1 in hydrochloric acid (see 6.1.1) to 50 ml.

E.2.3 Working solutions

Sequentially dilute diluted stock solutions (M_1) and (M_2) with hydrochloric acid solution (see 6.1.1), in order to obtain standards to be used for calibration according to the scheme in Table E.2.

Table E.2 — Preparation scheme working solutions

Working solutions	Volume M_1 ml	Volume M_2 ml	Volume HCl (6.1.1) ml	Volume total ml	Concentration of each element $\mu\text{g/l}^a$
Working solution W_1		1,25	48,75	50,0	2,5
Working solution W_2		2,5	47,50	50,0	5,0
Working solution W_3		5,0	45,0	50,0	10,0
Working solution W_4	0,125		49,875	50,0	25,0
Working solution W_5	0,250		49,75	50,0	50,0
Working solution W_6	0,50		49,50	50,0	100,0

^a The concentration of mercury is respectively 0,25 $\mu\text{g/l}$, 0,50 $\mu\text{g/l}$, 1,00 $\mu\text{g/l}$, 2,5 $\mu\text{g/l}$, 5,0 $\mu\text{g/l}$ and 10,0 $\mu\text{g/l}$.

E.2.4 Internal standard stock solution

Prepare an Internal Standard stock solution diluting 250 μl of a commercial available stock solution containing at least one element, e.g. Bismuth, Indium, Lithium or Yttrium, (100 $\mu\text{g/ml}$ in 7 % HNO_3 (volume fraction)) to a volume of 500 ml. This solution can either be used to prepare the standard and sample solutions, or by mixing with these solutions using continuous flow before entering the spray chamber.

E.3 Procedure

Use the migration solution (see 8.3, migration procedure). The elements shall be within the range of the calibration curve and therefore dilutions of the migration solutions can be necessary. For example, a dilution range of 2, 20, 200 and 2 000 can be used.

E.4 Analysis

The migration solution can be analysed directly respectively after dilution using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) to determine the content of general elements (Aluminium, Antimony, Arsenic, Barium, Boron, Cadmium, Cobalt, Chromium, Copper, Lead, Manganese, Mercury, Nickel, Selenium, Strontium, Tin and Zinc).

Optimize the instrument according to the manufacturer's instructions. The quantification limit for each element should be well below the limits set in Table 2 divided by the dilution caused by the migration test (50). Dilution is often required when determining elements close to or above the migration limit (see Table 2).

Table E.3 contains recommended isotopes (m/z) for the determination of elements in the migration solution using ICP-MS.

Table E.3 — Recommended isotopes (m/z) for the determination of elements in the migration solution using ICP-MS

Element	Recommended Isotope	Element	Recommended Isotope
Aluminium	²⁷ Al	Lead	²⁰⁸ Pb
Antimony	¹²¹ Sb	Manganese	⁵⁵ Mn
Arsenic	⁷⁵ As	Mercury	²⁰² Hg
Barium	¹³⁷ Ba	Nickel	⁶⁰ Ni
Boron	¹¹ B	Selenium	⁸² Se
Cadmium	¹¹¹ Cd	Strontium	⁸⁷ Sr
Chromium	⁵² Cr	Tin	¹¹⁸ Sn
Cobalt	⁵⁹ Co	Zinc	⁶⁶ Zn
Copper	⁶⁵ Cu		

Care shall be taken to avoid the polyatomic and isobaric interference (e.g. from ArC⁺ when determining Chromium), meaning that the instrument should be equipped with either a collision/reaction system or a high resolution mass spectrometer.

E.5 Calculation

E.5.1 Calibration curve

Prepare calibration curves of each element of interest by plotting the concentration of the standards of the element of interest against the measuring signal.

Calibration curves used to calculate analytical results shall have a correlation coefficient no less than 0,990.

E.5.2 Calculation of migration

Calculate the migration of the element from the test portion as follows (E.1):

$$M = \frac{C \cdot V \cdot f}{W_{tp} \cdot 1000} \tag{E.1}$$

where

- M* is the migration of an element from the toy material, in mg/kg;
- C* is the concentration of the element in the migration solution, in µg/l;
- V* is the volume of simulant added, in ml;
- W_{tp}* is the weight of the test portion, in g;
- f* is the dilution factor, appropriate for any dilutions made during the analysis.

Report the results to the number of significant figures appropriate for the precision of the analysis.

Annex F (normative)

Method of analysis for Chromium (VI)

F.1 Principle

This method quantifies Chromium (VI) in the migration solution (see 8.3, migration procedure).

To prevent interconversion of Chromium (III) and Chromium (VI), the migration solution is neutralized directly after the migration step. Experiments have shown that at a pH of 7 to 8 both species are stable. Chromium (VI) is separated from other Chromium species using an ion exchange column and detected by inductively coupled plasma – mass spectrometry (ICP-MS).

Other chromatographic systems (instrument, separation column, eluent, chromatographic conditions) as the one described here can be used as long as the method:

- uses an ion exchange separation mechanism,
- is able to achieve sufficient separation of Chromium (VI) from Chromium (III) (baseline separation; also when there is much more Chromium (III) than Chromium (VI) in the migration solution),

NOTE Peak tailing of Chromium (III) can significantly affect the LOQ and reproducibility of the Chromium (VI) determination if the Cr(VI) elutes after Cr(III), the Cr(III) concentrations is very high and the peaks are not baseline separated.

- ensures that there is no interconversion between Chromium (VI) and Chromium (III) during analysis,
- achieves a sufficient LOQ for the limit values specified in this standard.

Due to the very low concentrations which have to be measured special care should be taken to avoid any false positive findings of Chromium (VI) originating from reagents, solutions or materials used.

F.2 Reagents

All reagents, including water, used for analysis shall be of analytical grade or, if unavailable, technical grade reagents which have been determined to have acceptably low levels of impurity to allow the analysis to be performed.

F.2.1 Nitric acid, (65 % to 69 %) trace metal grade

F.2.2 Ammonia, NH₃ (25 % in water)

F.2.3 Ammonia solution, 0,7 mol/l

Add 5,3 ml of ammonia (see F.2.2) to a 100 ml volumetric flask. Make up to the mark with water and mix carefully.

F.2.4 Hydrochloric acid solution, 0,07 mol/l

F.2.5 Mobile phase, 75 mM HNO₃ (see F.2.1) adjusted to pH = 7,0 with ammonia (see F.2.2) and/or ammonia solution (see F.2.3)

F.2.6 Potassium dichromate (K₂Cr₂O₇), dried for (16 ± 2) h at (102 ± 2) °C

F.2.7 Chromium (VI) stock solution

Dissolve 2,829 g potassium dichromate ($K_2Cr_2O_7$) (see F.2.6) in water in a 1 000 ml volumetric flask and make up to the mark with water. Alternatively, a commercially available solution at 1 000 mg/l of hexavalent Chromium can be used. This solution will be stable for at least three months.

NOTE Information on the stability of commercial solution is usually provided by the supplier.

F.2.8 Chromium (VI) solution (M_1), 1 mg/l

Prepare a Chromium (VI) solution (M_1) by diluting 0,1 ml of the stock standard solution (see F.2.7) in mobile phase (see F.2.5) to a volume of 100 ml. Make up to the mark with mobile phase (see F.2.5) and mix. This solution will be stable for at least one week.

NOTE Information on the stability of commercial solutions is usually provided by the supplier.

F.2.9 Diluted Chromium (VI) solution (M_2), 1 μ g/l, freshly prepared

Dilute 0,05 ml of Chromium (VI) solution M_1 (see F.2.8) in mobile phase (see F.2.5) in a 50 ml volumetric flask. Make up to the mark with mobile phase (see F.2.5) and mix carefully.

F.2.10 Working solutions (Calibrating Standards), freshly prepared

Prepare 6 working solutions according to Table F.1.

After the addition of ammonia solution (see F.2.3) to the hydrochloric acid (see F.2.4) check pH and, if necessary, adjust the pH to $7,5 \pm 0,5$ using ammonia solution (see F.2.3) or hydrochloric acid (see F.2.4).

Table F.1 — Preparation scheme for working solutions

Working solutions	Volume M_2 (F.2.9) ml	Volume hydrochloric acid solution (F.2.4) ml	Volume ammonia solution (F.2.3) ml	Volume mobile phase (F.2.5)	Volume total ml	Concentration of Chromium (VI) μ g/l
W_1	0	4,0	0,4	amount needed in order to achieve a total volume of 10,0 ml	10,0	0
W_2	0,2	4,0	0,4		10,0	0,020
W_3	0,4	4,0	0,4		10,0	0,040
W_4	0,8	4,0	0,4		10,0	0,080
W_5	1,2	4,0	0,4		10,0	0,120
W_6	1,6	4,0	0,4		10,0	0,160

F.3 Apparatus

F.3.1 Variable pipettes with disposable tips, variable range

The tip ejector shall not be made of stainless steel.

F.3.2 Volumetric flasks Class A, plastic

F.3.3 Column packed with polymeric, non-porous, weak ion exchange phase

F.3.4 Chromatographic system suitable for trace metal analysis (e.g. Bio inert Liquid chromatograph, Ion Chromatograph)

F.3.5 Inductively coupled plasma mass spectrometer (ICP-MS) equipped with chromatographic system (see F.3.4). The instrument shall be able to determine ^{52}Cr with high sensitivity. This normally requires an ICP-MS with a collision/reaction system or a high resolution mass spectrometer.

F.3.6 Equipment for measuring pH in small volumes, calibrated and sufficiently accurate for the purposes of this European Standard.

F.4 Procedure

For the category I and II *sample*, pipette 2 ml (V_1) of migration solution (see 8.3, migration procedure) and 0,2 ml of ammonia solution (see F.2.3). Add 2,8 ml of mobile phase (see F.2.5) and mix thoroughly. Check the pH of the solution obtained and, if necessary, adjust the pH to $7,5 \pm 0,5$ using ammonia solution of suitable concentration or hydrochloric acid of suitable concentration. Record the final volume of the solution obtained after the pH adjustment, in ml (V_2).

NOTE For the adjustment of pH the following concentrations of ammonia solution have been found suitable:

- pH < 2: 2 mol/l ammonia solution;
- pH between 2 and 3: 0,4 mol/l ammonia solution;
- pH > 3: 0,1 mol/l ammonia solution.

For the category III *sample*, pipette 0,2 ml (V_1) of migration solution (see 8.3, migration procedure) and 0,02 ml of ammonia solution (see F.2.3). Add 4,78 ml of mobile phase (see F.2.5) and mix thoroughly. Check the pH of the solution obtained and, if necessary, adjust the pH to $7,5 \pm 0,5$ using ammonia solution (see F.2.3) or hydrochloric acid (see F.2.4). Record the final volume of the solution obtained after the pH adjustment, in ml (V_2).

F.5 Analysis

F.5.1 General

Optimize the ICP-MS for optimal detection of Chromium, normally at mass 52 according to the manufacturer's recommendations. The instrument settings shall give a sufficient reduction of the $^{40}\text{Ar}^{12}\text{C}$ signal to eliminate false-positive results. A suitable integration time for the MS is 1 s.

F.5.2 Chromatographic conditions

Table F.2 — Example of chromatographic settings

Parameter	Setting
Mobile phase	75 mM HNO_3 adjusted to pH = 7,0
Flow rate	0,8 ml/min
Column	Polymeric, non-porous, weak ion exchange phase 5 μm , 4,6 mm x 50 mm
Column temperature	Ambient
Injection volume	100 μl
Total analysis time	3 min

F.5.3 Limit of detection and quantification

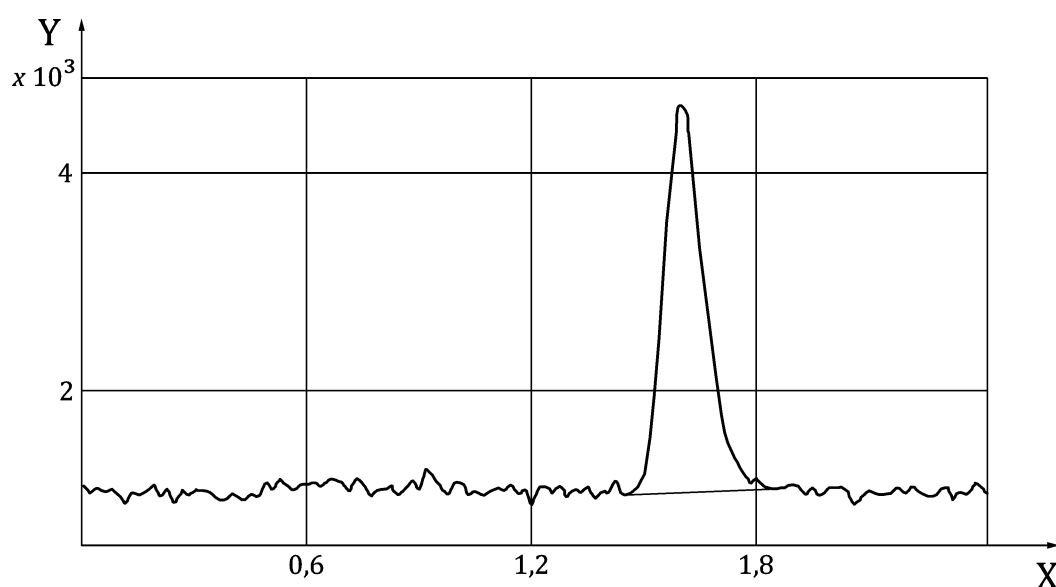
F.5.3.1 General

Table F.3 contains typical limits of detection (LOD) and quantification (LOQ) expressed in mg/kg toy material.

Table F.3 — Typical detection limit (LOD) and quantification limit (LOQ)

Element	LOD mg/kg	LOQ mg/kg
Chromium (VI)	0,000 75	0,002 5

F.5.3.2 Example of chromatogram



Key

- Y intensity, in cps
- X retention time, in min

Figure F.1 — Example of chromatogram of 0,08 µg/l Chromium (VI) using the conditions in Table F.2

F.6 Calculation

F.6.1 Calibration curve

Prepare calibration curves by plotting the concentration of the standards against the measuring signal. For quantification, the calibration curve shall have a correlation coefficient better or equal to 0,990.

F.6.2 Calculation of migration

Calculate the amount of migrated Chromium (VI) by Formula (F.1).

$$M = \frac{C \cdot V \cdot F}{W_{tp} \cdot 1000} \quad (\text{F.1})$$

where

Migration is the migration of Chromium (VI) from the toy material, in mg/kg;

C is the concentration of Chromium (VI) obtained from the regression curve, in µg/l;

V is the volume of simulant added for the migration procedure (see 8.3, migration procedure), in ml;

W_{tp} is the weight of the test portion, in g;

F is a correction factor calculated with Formula (F.2).

$$F = \frac{V_1}{V_2} \quad (\text{F.2})$$

where

V₁ is the volume after neutralization and final dilution with eluent, in ml.

V₂ is the volume of the solution from the migration procedure (see 8.3, migration procedure) used for Chromium (VI) determination, normally 0,2 or 2, in ml;

Report the results to the number of significant figures justified by the precision of the measurement.

Annex G (normative)

Method of analysis for organic tin (see H.9)

G.1 Principle

This method quantifies organic tin compounds and/or cations as mentioned in Table G.1 in the migration solution (see 8.3, migration procedure), and covers the main organic tin cation/compound additives which can be present in toys. The anionic part bound to the organic tin cation is mainly dependent on the chemical environment and is not determined using this method.

Table G.1 — Organic tin compounds and cations

$R_nSn(4-n)^+$	R	<i>n</i>	Name	Acronym
MeSn ³⁺	Methyl	1	Methyltin cation	MeT
Me ₂ Sn ²⁺	Methyl	2	Dimethyltin cation	DMT
BuSn ³⁺	Butyl	1	Butyltin cation	BuT
Bu ₂ Sn ²⁺	Butyl	2	Dibutyltin cation	DBT
Bu ₃ Sn ⁺	Butyl	3	Tributyltin cation	TBT
Bu ₄ Sn	Butyl	4	Tetrabutyltin	TeBT
OcSn ³⁺	Octyl	1	Monooctyltin cation	MOT
Oc ₂ Sn ²⁺	Octyl	2	Diocetyl tin cation	DOT
Pro ₂ Sn ²⁺	Propyl	2	Dipropyltin cation	DProT
Ph ₂ Sn ²⁺	Phenyl	2	Diphenyltin cation	DPhT
Ph ₃ Sn ⁺	Phenyl	3	Triphenyltin cation	TPhT

Most organic tin compounds are too polar to be analysed directly by gas-chromatography and shall be derivatised to form non-polar alkyltin compounds prior to analysis.

The per-alkylated organic tin compounds behave in a completely different way from their parent compounds. Tetra-alkylated organic tin compounds which are already per-alkylated, such as tetrabutyltin, are determined in the same analysis even if they are not affected by the derivatisation.

This standard method utilizes *in situ* derivatisation using tetraethylborate to produce ethyl organic tin derivatives. The ethylated derivatives are extracted with hexane and analysed by GC-MS. For quantification single ion mode should be used to achieve sufficiently low LOQ for quantification at the migration limits (see Table 2).

The concentration is determined by calibration of the total procedure using an internal standard mixture. The internal standards shall have chemical properties as similar as possible to the organic tin compound of interest. Table G.2 contains recommended internal standards.

Table G.2 — Recommended internal standards for organic tin compounds

Organic tin compound	Internal standard
Methyltin cation	Butyl tin (d9)
Dimethyltin cation	Butyl tin (d9)
Butyltin cation	Butyl tin (d9)
Dibutyltin cation	Butyl tin (d9)
Tributyltin cation	Tributyl tin (d27)
Tetrabutyltin	Tetrabutyl tin (d36)
Monooctyltin cation	Butyl tin (d9)
Dioctyltin cation	Butyl tin (d9)
Dipropyltin cation	Butyl tin (d9)
Diphenyltin cation	Triphenyl tin (d15)
Triphenyltin cation	Triphenyl tin (d15)

For matrices which cause a low recovery of the internal standard even after the procedure used in G.4.1.3 is applied, standard addition (see G.4.1.4) should be used for quantification.

G.2 Reagents

Use reagents of highest purity.

G.2.1 Hydrochloric acid, HCl (37 %).

G.2.2 Acetic acid, CH₃COOH, glacial.

G.2.3 Sodium acetate, CH₃COONa.

G.2.4 Methanol, CH₃OH.

G.2.5 Hexane, C₆H₁₄.

G.2.6 Sodium tetraethylborate, NaB(C₂H₅)₄, CAS# 15523-24-7.

G.2.7 Methyltin trichloride, MeTCl, CH₃SnCl₃, CAS# 993-16-8.

G.2.8 Dimethyltin dichloride, DMTCl, (CH₃)₂SnCl₂, CAS# 753-73-1.

G.2.9 Butyltin trichloride, BuTCl, C₄H₉SnCl₃, CAS# 1118-46-3.

G.2.10 Dibutyltin dichloride, DBTCl, (C₄H₉)₂SnCl₂, CAS# 683-18-1.

G.2.11 Tributyltin chloride, TBTCl, (C₄H₉)₃SnCl, CAS# 1461-22-9.

G.2.12 Tetrabutyltin, TeBT, (C₄H₉)₄Sn, CAS# 1461-25-2.

G.2.13 Monoctyltin trichloride, MOTCl, $C_8H_{17}SnCl_3$, CAS# 3091-25-6.

G.2.14 Dioctyltin dichloride, DOTCl, $(C_8H_{17})_2SnCl_2$, CAS# 3542-36-7.

G.2.15 Dipropyltin dichloride, DProTCl, $(C_3H_7)_2SnCl_2$, CAS# 867-36-7.

G.2.16 Diphenyltin dichloride, DPhTCl, $(C_6H_5)_2SnCl_2$, CAS# 1135-99-5.

G.2.17 Triphenyltin chloride, TPhTCl, $(C_6H_5)_3SnCl$, CAS# 639-58-7.

G.2.18 Tributyl-d27-tin chloride, TBTCl (d27), $(C_4D_9)_3SnCl$, CAS# 1257647-76-9.

G.2.19 Tetrabutyl-d36-tin, TeBT (d36), $(C_4D_9)_4Sn$, CAS# 358731-92-7.

G.2.20 Monobutyl-d9-tin trichloride, BuTCl (d9), $C_4D_9SnCl_3$.

G.2.21 Triphenyl-d15-tin chloride, TPhTCl (d15), $(C_6D_5)_3SnCl$, CAS# 358731-94-9.

G.2.22 Tetrahydrofuran (THF), C_4H_8O , CAS# 109-99-9.

G.2.23 Sodium chloride, NaCl, CAS# 7647-14-5.

G.2.24 Dichloromethane (DCM), CH_2Cl_2 , CAS# 75-09-2.

G.2.25 Multi-component solutions and prepared reagents

G.2.25.1 Multi-component-standard solution in methanol, Stock solution A

For the preparation of 1 000 mg/l of organic tin cation stock solution, in TBT equivalents, weigh, to the nearest 0,1 mg, the amounts of organic tin compounds specified in Table G.3 into a 100 ml volumetric flask. Dissolve these compounds in a small amount of methanol (see G.2.4). Then make up to the mark with methanol (see G.2.4) and mix carefully.

If stored at 4 °C in the dark, the solution is stable for at least two months.

NOTE If using a commercial organic tin standard solution, information on the stability is usually provided by the supplier.

Table G.3 — Required portions of organic tin compounds, and their weighing factors, corresponding to 100 mg of organic tin cations (expressed as TBT cation)

Substance	Weighed portion <i>mg</i>	MW of substance <i>g/mol</i>	MW of organic tin cation <i>g/mol</i>	Weighing factor ^a	Organic tin cation	Relative molecular weight ^b
Methyl tin trichloride	82,8	240,1	133,7	0,557	MeT	2,169
Dimethyl tin dichloride	75,7	219,7	148,8	0,677	DMT	1,949
Di- <i>n</i> -propyl tin dichloride	95,1	275,8	204,9	0,743	DProT	1,416
Butyl tin trichloride	97,3	282,2	175,8	0,623	BuT	1,650
Dibutyl tin dichloride	104,8	303,8	232,9	0,767	DBT	1,245
Tributyl tin chloride	112,2	325,5	290,0	0,891	TBT	1,000
<i>n</i> -Octyl tin trichloride	116,6	338,3	231,9	0,686	MOT	1,251
Di- <i>n</i> -octyl tin dichloride	143,4	416,0	345,1	0,830	DOT	0,840
Tetrabutyl tin	119,7	347,2	347,1	1,000	TeBT	0,835
Diphenyl tin dichloride	118,5	343,8	272,9	0,794	DPhT	1,063
Triphenyl tin chloride	132,9	385,5	350,0	0,908	TPhT	0,829

^a Weighing factor = molar mass (organic tin cation)/molar mass (organic tin chloride).

^b Compared to tributyltin. Relative molecular weight = molar mass (tributyl tin cation) / molar mass (organic tin cation).

G.2.25.2 Calibration solution of organic tin cations, working solutions BI, BII and BIII

For working solution BIII (suitable for category III materials), dilute from the stock solution A (see G.2.25.1) to a concentration of 10 mg of each organic tin cation (expressed as TBT cation) per litre in methanol (see G.2.4, dilution factor 100, relative to stock solution A).

For working solution BII (suitable for category II materials), dilute from working solution BIII to a concentration of 0,25 mg (dilution factor 40, relative to working solution BIII) of each organic tin cation (expressed as TBT cation) per litre in methanol (see G.2.4.).

For working solution BI (suitable for category I materials), dilute from working solution BIII to a concentration of 1 mg (dilution factor 10, relative to working solution BIII) of each organic tin cation (expressed as TBT cation) per litre in methanol (see G.2.4.).

NOTE Working solution BI is only needed when applying standard addition to category I samples.

G.2.25.3 Mix solution of the internal standards in methanol, internal standard stock solution C

Weigh, to the nearest 0,1 mg, into a 100 ml volumetric flask, approximately 100 mg of tributyl-d27-tin chloride (see G.2.18), 100 mg of tetrabutyl-d36-tin (see G.2.19), 100 mg of triphenyl-d15-tin chloride (see G.2.21) and 100 mg of monobutyl-d9-tin trichloride (see G.2.20) and dissolve in a small amount of methanol (see G.2.4). Make up to the mark with methanol (see G.2.4) and mix carefully.

The solution is stable for up to one year when stored in the dark at 4 °C.

NOTE If using a commercial organic tin internal standard solution, information on the stability is usually provided by the supplier.

G.2.25.4 Working solution of the internal standards in methanol, internal standard working solution D (2 mg deuterated organic tin compound per litre in methanol)

Pipette 0,200 ml of the internal standard stock solution C into a 100 ml volumetric flask. Make up to the mark with methanol (see G.2.4) and mix carefully.

G.2.26 Hydrochloric acid solution, $c(\text{HCl}) = (0,070 \pm 0,005) \text{ mol/l}$.

G.2.27 Acetate buffer solution

Dissolve about 10,0 g sodium acetate (see G.2.3) in 250 ml of water into a 500 ml volumetric flask. Add 1,2 ml glacial acetic acid (see G.2.2). Make up to the mark with water and mix carefully.

G.2.28 Derivatisation agent

Under inert atmosphere, e.g. nitrogen, for preparation of 10 ml of derivatization reagent solution, weigh about 2 g of sodium tetraethylborate (see G.2.6) into a 10 ml volumetric flask and make up to volume with tetrahydrofuran (THF, G.2.22). This solution is stable for at least a week.

NOTE If using a commercial organic tin internal standard solution, information on the stability is usually provided by the supplier.

CAUTION — Derivatisation reagent is flammable and catches fire spontaneously if exposed to air.

G.3 Apparatus

NOTE 1 It is important to exercise care to avoid contamination. Therefore, it is essential that flasks, equipment and anything making contact with *samples* and extracts thereof, are dedicated. It is essential to avoid cleaning by dishwashers. Instead rinsing with ethanol and hexane (see G.2.5) is preferred.

NOTE 2 To minimize recovery losses by adsorption, the use of plastic vessels before derivatization, and glass vessels during and after derivatization is preferred.

NOTE 3 It is important to verify blank values.

G.3.1 Volumetric flasks.

G.3.2 Variable pipettes for organic fluids with disposable tips, with a volume range from 10 μl to 100 μl , 100 μl to 1 000 μl and 1 ml to 5 ml.

G.3.3 20 ml glass vials with gas-tight caps (e.g. headspace vials).

G.3.4 Shaker capable of vigorously agitating the mixture.

G.3.5 Gas chromatograph, equipped with split/splitless injector and mass spectrometer using electron impact (EI) mode.

G.4 Procedure

G.4.1 Sample derivatisation

G.4.1.1 Derivatisation

In a glass vial (see G.3.3), add 5,00 ml of migration solution (see 8.3, migration procedure). Add 0,100 ml internal standard solution D (see G.2.25.4). 5 ml of acetate buffer (see G.2.27) is added to the migration solution. Then 0,050 ml of 20 % sodium tetra ethyl borate (see G.2.28) and 2 ml of hexane (see G.2.5) are

added, and the vial is immediately closed to avoid evaporation of the most volatile derivatized organic tin compounds. The mixture is shaken for approximately 60 min with a shaker (see G.3.4) and subsequently left to stand until the phase separation is complete. The two phases should be completely clear. Depending on the material category of the *sample* proceed with G.4.1.2 or G.4.1.3.

NOTE Signs like cloudiness, gel formation, foam, precipitation or liquid droplets on the reaction vessel walls have been found to potentially severely decrease the extraction efficiency. Different organic tin compounds are in such case typically affected to highly different degree, more than can be corrected for by normalizing to the different internal standards. In case of doubt it is also possible to directly proceed with G.4.1.3 also for category I and III material *samples*.

G.4.1.2 Category I and III materials

For category I and III materials phases are usually well separated. In this case, the hexane fraction can be used for GC-MS analysis and the analytes can be quantified (after normalization to internal standard) from the external standard calibration (see G.4.2). If phase separation is poor proceed as specified in G.4.1.3.

After GC-analysis verify that internal standard recoveries are > 60 % (internal standard peak areas compared to internal standard peak areas in the calibration solutions), otherwise the derivatisation (see G.4.1.1) is performed again followed by the separation process in G.4.1.3.

G.4.1.3 Category II materials

NOTE 1 For category II *samples*, phases are often not well separated and it is essential to improve extraction efficiency, which is why special treatment is needed.

Add 3 g NaCl (s), 0,9 ml HCl (37 %) and 0,5 ml DCM (dichloromethane, G.2.24) to the solution after derivatization (see G.4.1.1) and mix, e.g. by vortexing, until the dissolution of the NaCl is complete or almost complete.

Leave to stand until the two phases have completely separated. If problems with phase separation occur ultrasonicate for 30 min and leave to stand until the two phases have completely separated. Analyse the organic fraction with GC-MS. If the responses of the internal standards are more than 50 % compared to the average responses in the calibration solutions, quantify according to G.4.2. If the recoveries of internal standards are lower than that, proceed according to G.4.1.4.

NOTE 2 50 % recovery corresponds to about 60 % recovery in G.4.1.2 since the organic phase is diluted.

G.4.1.4 Standard addition method

Repeat the procedure with another test portion (see G.4.1.1) but before acetate buffer is added, spike the migration solution with a concentration corresponding to 5 to 10 times the migration limit of the *sample* category (Table 2) of each organic tin cation (use 0,200 ml of the calibration standard, working solution BI, BII or BIII (see G.2.25.2) depending on the *sample* category).

After shaking for 60 min add 3 g NaCl (s), 0,9 mL HCl (37 %) and 0,5 ml DCM (dichloromethane, G.2.24) to the solution after derivatization and mix, e.g. by vortexing, until the dissolution of the NaCl is complete or almost complete.

Quantify by the standard addition according to G.6.2, using the spiked solution and the unspiked solution from G.4.1.3.

NOTE 1 If the response of tetrabutyltin-d36 is good, but the response of butyltin-d9, tributyltin-d27 or triphenyltin-d15 is low, and especially if it is also lower in the spiked solution than in the unspiked solution, this can be an indication of insufficient derivatization reagent. It is essential to repeat the procedure with another test portion with a higher amount of tetraethylborate.

NOTE 2 If the peak area of an analyte in the spiked solution is much less than 5 times the peak area in the unspiked solution, i.e. the concentration is much higher than the migration limit, higher spiking concentrations are necessary for reliable calculations.

G.4.2 Calibration standards

Take 6 20 ml glass vials (see G.3.3), add to each vial 5 ml hydrochloric acid solution (see G.2.26) and add to each vial with a pipette (see G.3.2), respectively 0,020 ml, 0,100 ml and 0,400 ml of working solution BII (see G.2.25.2) and 0,020 ml, 0,100 ml and 0,400 ml of working solution BIII (see G.2.25.2). Add 0,100 ml internal standard solution D (see G.2.25.4) and 5 ml of acetate buffer (see G.2.27). Then 0,050 ml of 20 % sodium tetra ethyl borate (see G.2.28) and 2 ml of hexane (see G.2.5) are added. The mixture is shaken for 60 min with a shaker (see G.3.4) and left to stand until the phase separation is complete. The hexane fraction is then analysed by GC-MS.

Table G.4 — Preparation scheme for calibrations standards

Calibrations standards	Working solution (G.2.25.2)	Volume Working solution µl	Volume hydrochloric acid solution (G.2.26) ml	Concentration of each organo tin compound (TBT equivalents) mg/l ^a
<i>Standard 1</i>	BII	20	5,0	0,001
<i>Standard 2</i>	BII	100	5,0	0,005
<i>Standard 3</i>	BII	400	5,0	0,02
<i>Standard 4</i>	BIII	20	5,0	0,04
<i>Standard 5</i>	BIII	100	5,0	0,2
<i>Standard 6</i>	BIII	400	5,0	0,8

^a mg/l refers to the equivalent concentration in the migration solution.

G.5 Analysis

G.5.1 General

Optimize the instrument (see G.3.5) according to the manufacturer's instructions.

Analyse the analytes in the Selective Ion Monitoring (SIM) mode (see Table G.5) or Multiple Reaction Monitoring (MRM) mode (see Table G.6). Generally, high mass fragment ions are preferable to minimize interference, but depend on the system used (column etc.). One quantifier and two qualifier ions should be used, whenever possible.

Table G.5 — Selected ion monitoring for organic tin cations

Organic tin Ethyl derivative	Abbreviation	m/z
Dimethyl tin	DMT	135, 151, 179
Methyl tin	MeT	163, 165, 191, 193
Butyl tin	BuT	121, 149, 179, 235
Di-n-propyl tin	DProT	191, 193, 233, 235
Dibutyl tin	DBT	205, 207, 261, 263
Tributyl tin	TBT	205, 207, 289, 291
n-Octyl tin	MOT	177, 179, 289, 291
Tetrabutyl tin	TeBT	177, 179, 289, 291
Diphenyl tin	DPhT	195, 301, 305
Di-n-octyl tin	DOT	261, 263, 375
Triphenyl tin	TPhT	347, 349, 351
Internal Standards		
Butyl tin (d9)	BuT (d9)	180, 242, 244
Tributyl tin (d27)	TBT (d27)	217, 281, 318
Tetrabutyl tin (d36)	TeBT (d36)	190, 254, 318
Triphenyl tin (d15)	TPhT (d15)	364, 366

Table G.6 — Example of MRM data

Analyte	Precursor ion	Quantification ion	Qualification ion 1
MeT	193	165	137
DProT	235	151	193
MBT-d9	244	152	180
MBT (BuT)	235	151	179
DBT	263	151	
TBT-d27	318	190	254
TBT	291	179	235
MOT	291	179	
	179		151
TeBT-d36	318	190	254
TeBT	291	179	235
DPhT	303	197	275
DOT	263	151	
TPhT-d15	366	201	
TPhT	351	197	
NOTE The interlaboratory comparison has shown that the qualification ion 123 might not be suitable for certain matrices. For this reason this ion has been deleted from the table. In case more qualifier ions are needed the precursor ion can be changed to another molecule based on a different tin isotope.			

Quantify the gas chromatographic signals. The evaluation using peak areas is recommended.

A typical injection sequence is as follows:

- hexane;
- calibration solutions;
- blank extract;
- sample solutions (in replicate runs);
- quality control sample.

Examples of GC and MS conditions are given in G.5.2 and G.5.3 respectively.

G.5.2 Example of GC conditions

Injection conditions:	Pulsed splitless, pulse pressure = 30 kPa, pulse time = 0,5 min Purge flow = 50 ml/min, purge time = 2,00 min
Injection temperature:	275 °C
Carrier:	Helium; Constant flow: 1,7 ml/min
Column:	5 %-diphenyl-95 %-dimethyl polysiloxane copolymer, 30 m × 0,32 mm ID × 0,25 µm film thickness
Oven temperature program:	50 °C (1 min) – 20 °C/min – 325 °C (4 min)
Injection volume:	2 µl

G.5.3 Example of MS conditions

Transfer line:	280 °C
Electron impact:	70 eV
Electron multiplier:	source dependent
Selected ion monitoring mode:	choose at least three of the most intensive non-interfered fragment ions

NOTE The concentration of the organic tin compound is already expressed as TBT as this is how the working solutions are prepared (see Table G.3).

G.5.4 Limit of detection and quantification

In Table G.7 typical limits of detection (LOD) and quantification (LOQ) for organic tin compounds are given. In a *sample*, several organic tin compounds can be present, and the LOQ of a single compound should be under 1/3 of the migration limit (see Table 2).

Table G.7 — Typical detection limits (LOD) and quantification limits (LOQ) expressed in mg/kg toy material (as TBT equivalents)

Element	LOD mg/kg	LOQ mg/kg
Methyltin	0,02	0,06
Dimethyltin	0,02	0,05
Butyltin	0,02	0,06
Tributyltin	0,02	0,06
Monooctyltin	0,01	0,03
Diocyltin	0,01	0,04
Dibutyltin	0,02	0,06
Dipropyltin	0,02	0,06
Tetrabutyltin	0,02	0,05
Diphenyltin	0,02	0,06
Triphenyltin	0,01	0,04

G.5.5 Example of a GC-MS chromatogram

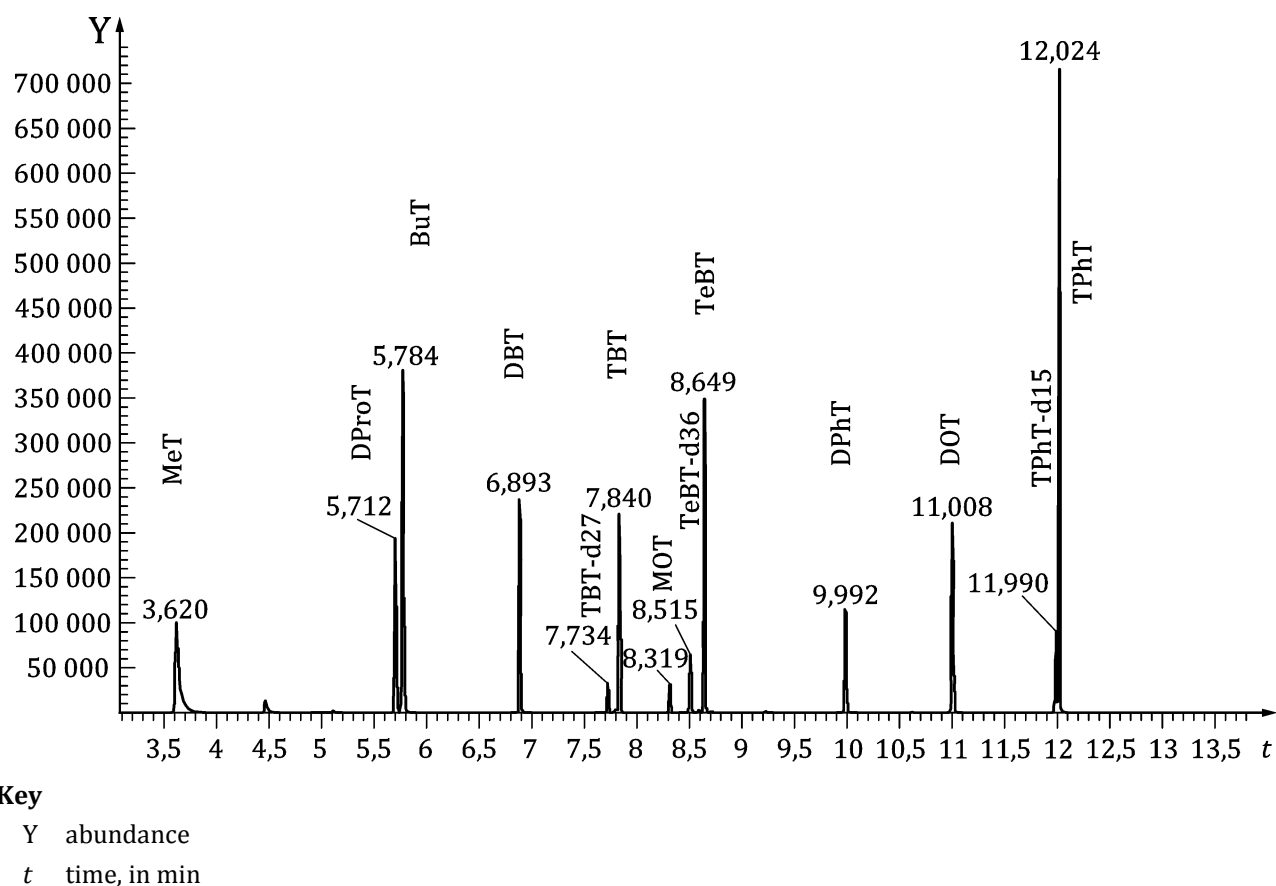


Figure G.1 — Example of a GC-MS chromatogram of ethylated organic tin compounds

G.6 Calculation

G.6.1 Calibration curve

The procedure shall be calibrated using internal standards that are comparable to the organic tin compound of interest. In the calibration curves the peak areas for the different organotin compounds divided by the peak area for the relevant internal standard (see Table G.2) is plotted against the concentration of the organotin substance. For quantification the calibration curve shall have a correlation coefficient better or equal to 0,990.

Using the calibration curve, the concentration of a compound in a migration solution (see *C* in G.6.3) is calculated from the peak area of the compound divided by the peak area from the relevant internal standard in the migration solution.

G.6.2 Standard addition

When using standard addition, the concentration of each detected organic tin cation in the migration solution, *C*, is calculated according to the following formula:

$$C = \frac{A_{sample}}{A_{IS, sample}} \cdot \left(\frac{C_{spike}}{\frac{A_{spiked sample}}{A_{IS, spiked sample}} - \frac{A_{sample}}{A_{IS, sample}}} \right) \quad (G.1)$$

where

<i>C</i>	is the concentration of the substance in the migration solution, in mg/l as TBT equivalents;
<i>C_{spike}</i>	is the concentration added to the migration solution by the spike, in mg/l as TBT equivalents;
<i>A_{sample}</i>	is the peak area for the substance in the chromatogram of the unspiked solution;
<i>A_{IS, sample}</i>	is the peak area for the relevant internal standard (see Table G.2) in the chromatogram of the unspiked solution;
<i>A_{spiked sample}</i>	is the peak area for the substance in the chromatogram of the spiked solution;
<i>A_{IS, spiked sample}</i>	is the peak area for the relevant internal standard (see Table G.2) in the chromatogram of the spiked solution;

G.6.3 Calculation of migration of organic tin

For each detected organic tin cation the migration shall be calculated according to the following formula:

$$M = \frac{C \cdot V}{W_{tp}} \quad (G.2)$$

where

M is the migration of an organic tin compound from the toy material, in mg/kg as TBT equivalents;

C is the concentration of the substance in the migration solution (from G.6.1 or G.6.2), in mg/l as TBT equivalents;

V is the volume of simulant added, in ml;

W_{tp} is the weight of the test portion, in g.

Organic tin compounds other than those specified in Table G.3 can also be present in toys and shall be included when calculating the organic tin concentration.

The migration of organic tin shall be calculated by adding the migration values expressed as tributyltin for all the single organic tin compounds (see also H.9).

Annex H (informative)

Rationale

H.1 General

Migration limits for certain elements in *toy materials* or parts of toys are given in Annex II, III.13 of the Toy Safety Directive 2009/48/EC [1]. The limits in the Toy Safety Directive have been influenced by an RIVM report according to the criteria of the relevant Scientific Committee, in order to ensure that these elements, if present, are at safe levels for children and in accordance with good manufacturing practice. The assessment includes a differentiation of toys into three toy categories, based on different assumed consumption. The migration limits do not apply to toys or components of toys which, due to their accessibility, function, volume or mass, clearly exclude any hazard due to sucking, licking, swallowing or prolonged contact with skin, bearing in mind the normal and foreseeable behaviour of children.

This standard specifies the sampling, sample preparation, migration procedure (Clause 6 to Clause 8) and three methods for quantifying the elements in the migration solution based on ICP-MS and GC-MS, respectively (Annex E, Annex F and Annex G). The migration procedure simulates contact of the *toy material* with gastric juices for a period of time after swallowing.

In Clause 11 performance criteria are given for the analytical techniques to determine the amount of a certain element in the resulting migration solution. These methods have been developed and validated in a project, funded by the European Commission (SA/CEN/2013-03 Migration of certain elements), by the technical project leader. They were confirmed by the peer review laboratory and finally validated by the results of an interlaboratory comparison. The results and background are given in Clause 11 and Annex B. The method performance is available for the prioritized elements for which reference materials were prepared during the revision work. In order to include all elements in all 3 material categories an estimation of the reproducibility data is given in the informative Annex C. Other standards preparation and analytical techniques may also be used, as long as they meet the requirements specified in Clause 11 and are in line with the expectations of Annex C.

This standard contains requirements and test methods for the migration of certain elements in a wide range of toys and *toy materials*. The compliance of toys with the element migration requirements of Directive 2009/48/EC [1] can be demonstrated by compliance with this standard.

H.2 Mouthing behaviour of children (see Clause 1)

Most studies on mouthing behaviour look at children under three years old. Only 3 studies are known that observe children over three years of age [11, 12, 13], of which only one presents mouthing duration data [11]. The mean mouthing time on toys for 4 years and 5 years old children was very low (3 min and 1 min per day, respectively) with a maximum observed mouthing time on toys of 20 min and 11 min per day.

By the age of 6 years, children do not mouth their toys to any significant degree.

H.3 Skin contact (see Clause 1)

The RIVM has conducted a study on the assessment methodology of chemical safety of toys with a focus on elements and identified the oral exposure to elements as the relevant route [10]. Most if not all toys or accessible parts of toys will come in contact with the skin, which can result in dermal exposure and via hand to mouth contact in additional oral exposure. For systemic exposure to elements, the dermal exposure route is less relevant than the oral exposure route, as the dermal absorption of elements is distinctly lower as their oral absorption. Therefore, as a worst case simulant hydrochloric acid was chosen as gastric simulant for migration, also covering other exposure routes.

H.4 Toy categories (see 4.1)

Directive 2009/48/EC [1] sets migration limits for certain elements in three different toy categories, based on the assumed ingestion of the materials. The assumed ingestion of the materials is based on an RIVM report [10] and a SCHER opinion [15]. Further explanation of the categories is given in the Explanatory Guidance Document [3].

Category I: Dry, brittle, powder like or pliable

Category I includes solid *toy material* from which powder-like material is released during play. The material can be ingested. Contamination of the hands with powder contributes to enhanced oral exposure. The assumed ingestion is 100 mg per day.

Category II: Liquid or sticky

Category II includes fluid or viscous *toy material* which can be ingested and/or to which dermal exposure occurs during playing. The assumed ingestion is 400 mg per day.

Category III: Scraped-off

Category III includes solid *toy material* with or without a *coating* which can be ingested as a result of biting, tooth scraping, sucking or licking. This category includes those materials which are not covered by category I and II. The assumed ingestion is 8 mg per day.

H.5 Test portions (see Clause 7)

It is not always possible, especially for category III toys (scraped off), to obtain 0,100 g of *toy material*.

If less than 0,010 g of *toy material* can be obtained, it is not required to analyse. From such a small amount of *toy material* the exposure to certain elements is considered to be negligible.

If 0,010 g to 0,100 g of *toy material* is available, the test is performed as if it were 100 mg of material. The migration is calculated as though 100 mg of the test portion had been used. This compensates for the low exposure to certain elements by migration from such low amounts of *toy material*.

H.6 Size of test pieces (see 7.2)

The results of the interlaboratory comparison (polymeric disk with high element content) showed that the particle size has a significant impact on the test results. It is therefore important to closely follow the instructions on particle size in 7.2 taking into account the Annex D.

The test pieces should have at least one dimension of approximately 6 mm, but preferably two or three dimensions. As an example, a *paper* sheet shall be cut in pieces of approximately 6 mm by 6 mm. A cord shall be cut in pieces of approximately 6 mm in length. The aim is to achieve comparable procedures for sample preparation and similar surface areas of the test portions prepared in different laboratories.

H.7 Stability of Chromium (VI) in the migration solution (see 9.3)

Interconversion of Chromium (III) and Chromium (VI) can occur. This equilibrium is influenced by the pH. Therefore, immediately after the migration procedure (including filtration) the migration solution shall be stabilized by performing a neutralization step. Experiments have shown that at a pH of 7 to 8 Chromium (VI) is sufficiently stable for 4 h, the approximate time it takes for analysis.

H.8 Filtration of migration solutions (see 8.3.2)

Experiments have shown that centrifuges which are capable of achieving at least 7 000 *g* are capable of separating insoluble material within a convenient time. Centrifugation at high speed for about 45 min at about 7 000 *g* (6.2.2) provides a migration solution that is significantly easier to filter. The time and acceleration may be adapted when using a more efficient centrifuge.

It is possible for small pigment particles to pass through a 0,45 µm membrane filter (6.2.6). This could lead, in certain cases, to falsely high results possibly due to elements chemically bound to the suspended particles.

Currently this phenomenon is known for copper phthalocyanines (e.g. Pigment blue 15, which can be used in finger paints and is permitted by EN 71-7). When not removed by a 0,02 µm pore size membrane filter (6.2.6) these pigments lead to an exaggerated copper result. These pigments give a green or blue coloured solution and the particles can cause a Tyndall beam.

For this reason, the standard requires an additional filtration step with a 0,02 µm filter for migration solutions which:

- exceed the copper limit value and
- show the described characteristics (i.e. coloured solution, mostly blue or green; Tyndall beam)

in order to avoid too high results.

If the high copper concentration was caused by such pigments the solution should be colourless or the colour should have changed after filtration with a 0,02 µm pore size membrane filter (6.2.6) due to the removal of the green or blue colour portion of the total colour. The copper result should also be considerably lower after the filtration. The filtration may be conducted with the original 0,07 M hydrochloric acid solution or after dilution with 0,07 M hydrochloric acid or water (sometimes necessary to speed the filtration).

H.9 Organic tin (see Annex G)

The requirement in the Toy Safety Directive is for total migratable organic tin. The method in Annex G determines the migration of individual organic tin compounds. The method was validated using a list of organic tin compounds that was selected for this purpose by the working group responsible for this project (CEN/TC 52/WG 5 “Safety of toys – Chemical properties”). Selection was based on the toxicity and exposure (presence in toys). Other organic tin compounds can also be present in toys and have then also to be analysed and reported.

EFSA has published an opinion on oral exposure of consumers to organic tin compounds [14]. The group TDI for organic tin compounds is expressed either as Sn content or as TBT chloride. For this European Standard it was chosen to express the migration of individual organic tin compounds as TBT, as the chloride is removed during the derivatisation step.

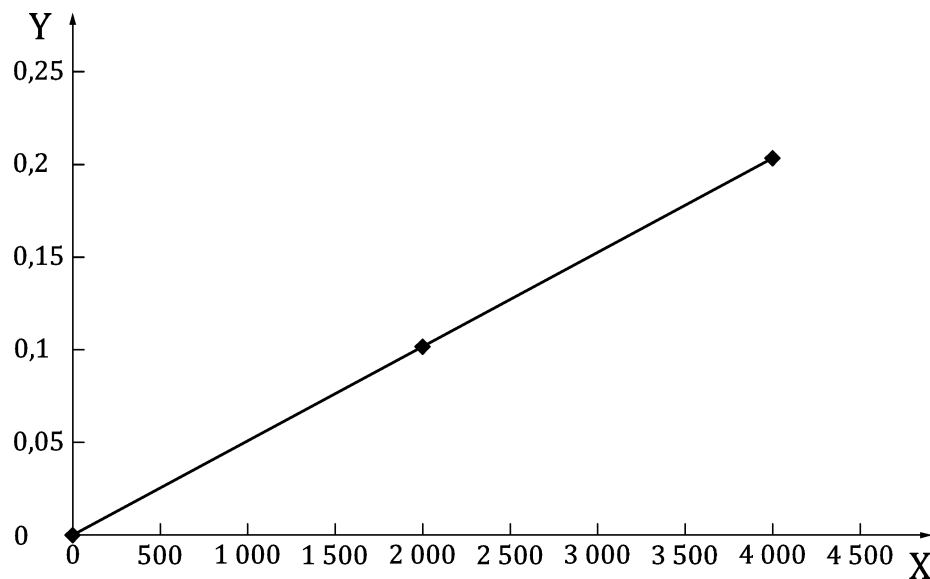
Recently it has been shown that inorganic tin substances can react under certain conditions with the derivatisation reagent sodium tetraethylborate (G.2.6) producing triethylmonomethyl tin, in addition to the expected product tetraethyl tin. This can lead to a false-positive result for methyl tin for example for

coated tin toys where test portions of the *coating* have been obtained by *scraping* off or for *samples* of wet oil paints that were stored in tinplate containers.

Experiments have shown that:

- with increasing concentration of inorganic tin, the detected methyl tin concentration increases as well (Figure H.1),
- the amount of the generated MeT is dependent on the quality of the derivatisation reagent.

These experimental results indicate that the methylation can be caused by an impurity in the derivatisation reagent which means that the impact of this effect on the methyl tin results shall be evaluated for each new batch of derivatisation reagent.



Key

- X concentration of inorganic tin in migration solution, in mg/l
- Y detected as MeSn^{3+} in migration solution, in mg TBT/l

Figure H.1 — False positive methyl tin relationship with concentration of inorganic tin

When methyl tin results are suspected to be false positive the following actions can be taken to check if the results are false positive and to get more correct results:

- repeat the scrape off process and avoid to scrape off metallic material from the *base material*;
- use a further organic tin method (e.g. ISO 22744);
- use another derivatization reagent, e.g. tetrapropylborate;
- prepare a blank sample with the same concentration of inorganic tin as in the test portion (normally known from analysis of general elements) and conduct the determination of organic tin according to Annex G. Estimate from this result the amount of false positive methyl tin and therefore its impact on the result. Possibly the methyl tin result of the *sample* can be corrected by the methyl tin result from the tin containing blank sample.

The method in Annex G has been optimized to ensure the correct pH value during derivatization.

H.10 pH value (see 8.2 and 8.3.1.2)

After sample preparation, a migration procedure under acidic conditions is performed. The concentration of the hydrochloric acid and the pH control are important parameters during this migration procedure. Therefore, it is important that the hydrochloric acid solutions used in the extraction step are carefully prepared and standardized before use. The hydrochloric acid solution has been shown to be stable for at least 3 months.

Experience has shown that deviations in the pH value during the migration procedure can have a significant impact on the results of the analysis. Therefore, it is important to follow the specified procedure precisely.

After adding the hydrochloric acid, it can take several minutes until a stable pH value is reached. In most cases the pH value will be stable. In some special cases (e.g. *paper samples*) the pH value can change throughout the migration and the effects of this have been investigated and addressed in this European Standard.

It is important that the equipment specified in 6.2.1 is capable of measuring pH with accuracy required by this European Standard. In practice, a pH meter with an accuracy of $\pm 0,02$ is sufficient. To accurately determine the pH at about 1,2 it is necessary to use pH buffers close to this pH when calibrating the electrode. Calibration buffers with pH 1,00 and 2,00 are recommended. It has been found that pH measurements without stirring improves the stability of the measurement.

H.11 De-waxing (see 7.2.3)

Every *sample* needs to be assessed to determine whether or not the de-waxing procedure specified in 7.2.3.2 is required. Indications that a *sample* contains grease, oil, wax or similar material could be:

- the declaration of the composition of the *toy material*,
- that the *sample* is hydrophobic,
- the smoothness of material.

Furthermore, the following *sample* types usually contain wax:

- Category 1: wax crayons, certain modelling clays, leads of coloured pencils, certain toy cosmetics (e.g. lipstick, eyeshadow);
- Category 2: certain toy cosmetics (e.g. lipgloss).

Different temperatures are used to dry the test portions before and after dewaxing. The lower temperature applied before dewaxing avoids melting of the wax and the higher temperature applied after reduces the drying time.

Annex ZA (informative)

Relationship between this European Standard and the essential requirements of EU Directive 2009/48/EC aimed to be covered

This European Standard has been prepared under a Commission's standardization request Mandate M/445 to provide one voluntary means of conforming to essential requirements of Directive 2009/48/EC.

Once this standard is cited in the Official Journal of the European Union under that Directive, compliance with the normative clauses of this standard given in Table ZA.1 confers, within the limits of the scope of this standard, a presumption of conformity with the corresponding essential requirements of that Directive, and associated EFTA regulations.

Table ZA.1 — Correspondence between this European Standard and Directive 2009/48/EC

Essential Requirements of Directive 2009/48/EC	Clause(s)/subclause(s) of this EN	Remarks/Notes
Annex II, III point 13	4.2 Specific requirements	Limit values have been amended by Commission Directive 2012/7/EU [4] (cadmium), Commission Regulation (EU) No 681/2013 [5] (barium), Council Directive (EU) 2017/738 [6] (lead) and Commission Directive (EU) 2018/725 [7] (Chromium (VI)).

WARNING 1 — Presumption of conformity stays valid only as long as a reference to this European Standard is maintained in the list published in the Official Journal of the European Union. Users of this standard should consult frequently the latest list published in the Official Journal of the European Union.

WARNING 2 — Other Union legislation may be applicable to the product(s) falling within the scope of this standard.

Bibliography

- [1] Directive 2009/48/EC of the European Parliament and of the Council of 18 June 2009 on the safety of toys
- [2] European Commission Guidance document No. 12 on the application of the Directive on the safety of toys – packaging
- [3] The European Commission, *An explanatory guidance document (to Directive 2009/48/EC)*
- [4] Commission Directive 2012/7/EU of 2 March 2012 amending, for the purpose of adaptation to technical progress, part III of Annex II to Directive 2009/48/EC of the European Parliament and of the Council relating to toy safety
- [5] Commission Regulation (EU) No 681/2013 of 17 July 2013 amending part III of Annex II to Directive 2009/48/EC of the European Parliament and of the Council on the safety of toys
- [6] Council Directive (EU) 2017/738 of 27 March 2017 amending, for the purpose of adapting to technical progress, Annex II to Directive 2009/48/EC of the European Parliament and of the Council on the safety of toys, as regards lead
- [7] Commission Directive (EU) 2018/725 of 16 May 2018 amending, for the purpose of adaptation to technical and scientific developments, point 13 of part III of Annex II to Directive 2009/48/EC of the European Parliament and of the Council on the safety of toys, as regards chromium VI
- [8] ELLISON S.L.R., WILLIAMS A., eds. Eurachem/CITAC guide: Quantifying Uncertainty in Analytical Measurement, Third edition, (2012), available from www.eurachem.org
- [9] ELLISON S.L.R., WILLIAMS A., eds. Eurachem/CITAC guide: Use of uncertainty information in compliance assessment. (First Edition (2007)), available from www.eurachem.org
- [10] Chemicals in toys. A general Methodology for assessment of safety of toys with a focus on elements. RIVM report 320003001/2008
- [11] SMITH S.A., NORRIS B.J. *Research into the mouthing behaviour of children up to 5 years old. Report URN 02/748, Consumer and Competition Policy Directorate.* Dept. of Trade and Industry, UK, 2002
- [12] TULVE N.S., SUGGS J.C., MCCURDY T., COHEN HUBAL E.A., MOYA J. Frequency of mouthing behavior in young children. *J. Expo. Anal. Environ. Epidemiol.* 2002, **12** pp. 259–264
- [13] BLACK K., SHALAT S.L., FREEMAN N.C.G., JIMENEZ M., DONNELLY K.C., CALVIN J.A. Children’s mouthing and food-handling behavior in an agricultural community on the US/Mexico border. *J. Expo. Anal. Environ. Epidemiol.* 2005, **15** pp. 244–251
- [14] Opinion of the Scientific panel on Contaminants in the Food Chain on a request from the Commission to assess the health risks to consumers associated with exposure to organotins in foodstuffs, 2004, *The EFSA Journal* 102, 1-119
- [15] Scientific Committee on Health and Environmental Risks (SCHER), Final Opinion on Estimates of the amount of toy materials ingested by children, adopted on 8 April 2016

- [16] Measurement of pH Definition, Standards and procedure IUPAC Recommendations 2002. *Pure Appl. Chem.* 2002, **74** (11) pp. 2169–2200
- [17] ISO 8124-3, *Safety of toys — Part 3: Migration of certain elements*
- [18] ISO 22744 (all parts), *Textiles and textile product — Critical substances potentially present in components of textile product materials — Determination of organotin compounds*

British Standards Institution (BSI)

BSI is the national body responsible for preparing British Standards and other standards-related publications, information and services.

BSI is incorporated by Royal Charter. British Standards and other standardization products are published by BSI Standards Limited.

About us

We bring together business, industry, government, consumers, innovators and others to shape their combined experience and expertise into standards-based solutions.

The knowledge embodied in our standards has been carefully assembled in a dependable format and refined through our open consultation process. Organizations of all sizes and across all sectors choose standards to help them achieve their goals.

Information on standards

We can provide you with the knowledge that your organization needs to succeed. Find out more about British Standards by visiting our website at bsigroup.com/standards or contacting our Customer Services team or Knowledge Centre.

Buying standards

You can buy and download PDF versions of BSI publications, including British and adopted European and international standards, through our website at bsigroup.com/shop, where hard copies can also be purchased.

If you need international and foreign standards from other Standards Development Organizations, hard copies can be ordered from our Customer Services team.

Copyright in BSI publications

All the content in BSI publications, including British Standards, is the property of and copyrighted by BSI or some person or entity that owns copyright in the information used (such as the international standardization bodies) and has formally licensed such information to BSI for commercial publication and use.

Save for the provisions below, you may not transfer, share or disseminate any portion of the standard to any other person. You may not adapt, distribute, commercially exploit, or publicly display the standard or any portion thereof in any manner whatsoever without BSI's prior written consent.

Storing and using standards

Standards purchased in soft copy format:

- A British Standard purchased in soft copy format is licensed to a sole named user for personal or internal company use only.
- The standard may be stored on more than 1 device provided that it is accessible by the sole named user only and that only 1 copy is accessed at any one time.
- A single paper copy may be printed for personal or internal company use only.
- Standards purchased in hard copy format:
- A British Standard purchased in hard copy format is for personal or internal company use only.
- It may not be further reproduced – in any format – to create an additional copy. This includes scanning of the document.

If you need more than 1 copy of the document, or if you wish to share the document on an internal network, you can save money by choosing a subscription product (see 'Subscriptions').

Reproducing extracts

For permission to reproduce content from BSI publications contact the BSI Copyright & Licensing team.

Subscriptions

Our range of subscription services are designed to make using standards easier for you. For further information on our subscription products go to bsigroup.com/subscriptions.

With **British Standards Online (BSOL)** you'll have instant access to over 55,000 British and adopted European and international standards from your desktop. It's available 24/7 and is refreshed daily so you'll always be up to date.

You can keep in touch with standards developments and receive substantial discounts on the purchase price of standards, both in single copy and subscription format, by becoming a **BSI Subscribing Member**.

PLUS is an updating service exclusive to BSI Subscribing Members. You will automatically receive the latest hard copy of your standards when they're revised or replaced.

To find out more about becoming a BSI Subscribing Member and the benefits of membership, please visit bsigroup.com/shop.

With a **Multi-User Network Licence (MUNL)** you are able to host standards publications on your intranet. Licences can cover as few or as many users as you wish. With updates supplied as soon as they're available, you can be sure your documentation is current. For further information, email subscriptions@bsigroup.com.

Revisions

Our British Standards and other publications are updated by amendment or revision.

We continually improve the quality of our products and services to benefit your business. If you find an inaccuracy or ambiguity within a British Standard or other BSI publication please inform the Knowledge Centre.

Useful Contacts

Customer Services

Tel: +44 345 086 9001

Email (orders): orders@bsigroup.com

Email (enquiries): cservices@bsigroup.com

Subscriptions

Tel: +44 345 086 9001

Email: subscriptions@bsigroup.com

Knowledge Centre

Tel: +44 20 8996 7004

Email: knowledgecentre@bsigroup.com

Copyright & Licensing

Tel: +44 20 8996 7070

Email: copyright@bsigroup.com

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK