BRITISH STANDARD

BS EN
71-11:2005

Safety of toys —

Part 11: Organic chemical compounds — Methods of analysis

The European Standard EN 71-11:2005 has the status of a British Standard

ICS 97.200.50

BSI
British Standards

National foreword

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The UK participation in its preparation was entrusted to Technical Committee CW/15, Safety of toys, which has the responsibility to:

— aid enquirers to understand the text;

— present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep UK interests informed;

— monitor related international and European developments and promulgate them in the UK.

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English Version

Safety of toys - Part 11: Organic chemical compounds - Methods of analysis

Sécurité des jouets - Partie 11 : Composés chimiques organiques dans les jouets - Méthodes d'analyse

Sicherheit von Spielzeug - Teil 11: Organisch-chemische Verbindungen - Analysenverfahren

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EUROPEAN COMMITTEE FOR STANDARDIZATION
COMITÉ EUROPÉEN DE NORMALISATION
EUROPÄISCHES KOMITEE FÜR NORMUNG

Management Centre: rue de Stassart, 36 B-1050 Brussels

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Contents

Foreword

This European Standard (EN 71-11:2005) 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of an identical text or by endorsement, at the latest by May 2006, and conflicting national standards shall be withdrawn at the latest by May 2006.

This European Standard 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(s).

For relationship with EU Directive(s), see informative Annex ZA, which is an integral part of this European Standard.

This European Standard constitutes part 11 of the European Standard on Safety of Toys.

This part should be read in conjunction with parts 9 and 10.

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

Introduction

The European Standard EN 71 for “safety of toys” consists of the following parts:

Part 1: Mechanical and physical properties
Part 2: Flammability
Part 3: Migration of certain elements
Part 4: Experimental sets for chemistry and related activities
Part 5: Chemical toys (sets) other than experimental sets
Part 6: Graphical symbols for age warning labelling
Part 7: Finger paints – Requirements and test methods
Part 8: Swings, slides and similar activity toys for indoor and outdoor family 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

The European Standards EN 71-9, EN 71-10 and EN 71-11 were mandated by the European Commission (M/229) to address the risks presented by organic chemical compounds in toys by taking into account the potential exposure and toxicological effects of those substances considered to present the greatest risk to health.

This European Standard specifies methods of analysis to enable assessment of compliance with the chemical requirements specified in EN 71-9 when toy and *toy material* extracts have been prepared according to the sampling procedures in EN 71-10.

This part on methods of analysis should be read in conjunction with EN 71-9, which contains requirements for certain organic chemical compounds in toys, and EN 71-10, which describes sample preparation and extraction procedures.

This European Standard takes into account the opinion of the Toxicology Section of the Scientific Advisory Committee published in 1992 (EUR 13976), which recommended that certain groups of chemical compounds used in toys and *toy materials* need to be given special attention. In drafting this European Standard CEN/TC 52 has considered organic chemicals that can be classified within the following groups:

— Solvents
— Preservatives
— Plasticisers (excluding phthalate plasticisers)[1]
— Flame retardants
— Monomers
— Biocides (wood preservatives)
— Processing aids
— Colouring agents

[1] Phthalate plasticisers were specifically excluded from the scope of mandate M/229.

1 Scope

This Part 11 of the European Standard EN 71 for safety of toys specifies methods for the analysis of toy and *toy material* extracts prepared according to the sampling procedures in EN 71-10, to enable assessment of compliance with the chemical requirements specified in EN 71-9.

This European Standard specifies analytical methods for the identification and determination of the following groups of organic chemicals:

— Flame retardants
— Colourants
— Primary aromatic amines
— Monomers and solvents
— Wood preservatives
— Preservatives
— Plasticisers

NOTE 1 Methods for formaldehyde in accessible textile components of toys; accessible paper components of toys; and accessible resin-bonded wood components of toys are specified in EN 71-9.

NOTE 2 The method for free formaldehyde as a preservative is specified in EN 71-10.

2 Normative references

The following referenced documents are indispensable for the application of this European Standard. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 71-9:2005, *Safety of toys – Part 9: Organic chemical compounds – Requirements*

EN 71-10:2005, *Safety of toys – Part 10: Organic chemical compounds – Sample preparation and extraction*

EN ISO 3696*, Water for analytical laboratory use – Specification and test methods (ISO 3696:1987)*

3 Terms and definitions

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

3.1
action limit
routinely-achievable limit of quantification for a particular substance using the specified method of analysis

3.2
aqueous migrate
liquid obtained after extracting a *toy material* according to the procedure specified in Clause 6 of EN 71-10:2005

3.3
test portion
portion of the laboratory sample prepared for analysis

3.4
toy material
material from which toys and toy components are made

NOTE This definition differs from that given in EN 71-3

4 Environmental, health and safety precautions

When preparing this European Standard, consideration was given to the minimisation of environmental impacts caused by the use of the methods of analysis.

It is the users' responsibility to use safe and proper techniques in handling materials in the methods of analysis specified in this European Standard.

— Consult manufacturers for specific details such as material safety data sheets and other recommendations.

— Wear protective goggles and coats in all laboratory areas.

— Be careful about substances, which are toxic and/or human carcinogens.

— A fume cupboard shall be used during preparation of organic solvent solutions.

— Solvents shall be disposed of in accordance with environmental requirements.

5 Methods of analysis

5.1 General

All chemicals used for analysis shall be of analytical grade (pro analysis) or, if unavailable, the best technical grade. Water shall be of grade 3 according to EN ISO 3696 or of a comparable quality, and demonstrably free from analytes of interest.

The precision of volumetric glassware should be grade A.

The analysis of toys and *toy materials* for chemical compounds for which limits are given in Tables 2 A to 2 I of EN 71-9:2005 shall be performed in accordance with the sampling procedures specified in EN 71-10 and the methods of analysis described in this European Standard. Alternative methods of analysis are acceptable only if they are capable of achieving at least the accuracy and precision of the methods described in this European Standard; an adequate sensitivity; and have been validated to show that the results are equivalent to those of these standard methods.

5.2 Flame retardants

NOTE Methods are given for pentabromodiphenyl ether and octabromodiphenyl ether in order to enable compliance with Directive 2003/11/EC of the European Parliament and of the Council to be demonstrated for textile *toy materials*.

5.2.1 Principle

Flame retardants are determined in acetonitrile extracts of *toy materials* by liquid chromatography with diode-array and mass spectrometry detection (LC-DAD-MS) using the external standard method of calibration.

5.2.2 Standards, reagents and solvents

5.2.2.1 Standards

5.2.2.1.1 Pentabromodiphenyl ether[2*], CAS No. 32534-81-9

5.2.2.1.2 Octabromodiphenyl ether[3*] , CAS No. 32536-52-0

5.2.2.1.3 Tri-*o*-cresyl phosphate, CAS No. 78-30-8

5.2.2.1.4 Tris(2-chloroethyl) phosphate, CAS No. 115-96-8

5.2.2.2 Reagents and solvents

5.2.2.2.1 Acetonitrile

5.2.2.2.2 Dichloromethane

5.2.2.2.3 Ammonium acetate, anhydrous

5.2.2.2.4 Acetic acid, glacial

5.2.2.2.5 Ammonium acetate, 10 mmol/l aqueous solution, pH 3,6

Transfer (0,77 ± 0,01) g ammonium acetate (5.2.2.2.3) into a 1 000-ml volumetric flask, add 980 ml of water, adjust the pH to 3,6 ± 0,1 with glacial acetic acid and make up to the mark with water.

5.2.2.3 Stock standard solution (100 mg/l)

Weigh, to the nearest 0,1 mg, (10 ± 1) mg of each flame retardant (5.2.2.1) into a 100-ml volumetric flask. Add 25 ml of acetonitrile (5.2.2.2.1) and mix carefully to dissolve. Place in an ultrasonic bath for 10 min to ensure complete dissolution. Make up to the mark with acetonitrile.

The stability of the mixed stock standard solution should be checked regularly. It should be stable for up to 6 months when stored in the dark at (4 ± 2) °C.

5.2.3 Apparatus

Liquid chromatograph with diode-array and mass spectrometer detectors

The following LC-DAD-MS conditions for flame retardant determination have been found to be suitable:

Column:	C18, 80 Å, 3,5 µm, double endcapped, (Zorbax Eclipse XDB[4], or equivalent) 2,1 mm x 150 mm
Guard column:	C18, 80 Å, 4 mm x 2,0 mm,
Mobile phase A:	Ammonium acetate solution, 10 mmol/l, pH 3,6 (5.2.2.2.5)
Mobile phase B:	Acetonitrile
Gradient:	see Table 1

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[2] This substance is also known as pentabromodiphenyl oxide.

[*] There are no requirements in EN 71-9 for this substance.

[3] This substance is also known as octabromodiphenyl oxide.

[4] Zorbax Eclipse XDB is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

Injection volume: 5 µl
Run time: 45 min
Flow: 0,3 ml/min
DAD mode: 240 nm ± 20 nm
DAD range: 200 nm to 800 nm
Nebulizer: 200 Kpa
Dry gas: 10 l/min
MS range: 110 m/z to 500 m/z
MS mode: Scan positive
Ionisation: ESI+
Fragmentor: 80 V

Table 1 – Gradient program

Time min	**Mobile phase A** %	**Mobile phase B** %
0	60	40
7	40	60
17	2	98
35	2	98
45	60	40

5.2.4 Procedure

5.2.4.1 Calibration solutions

Prepare a series of mixed flame retardant calibration solutions from the stock standard solution (5.2.2.3) at 1,0 mg/l, 2,0 mg/l, 4,0 mg/l and 8,0 mg/l concentrations in acetonitrile.

5.2.4.2 Determination

Proceed to liquid chromatographic determination using the conditions described in **5.2.3**. Inject the calibration solutions (5.2.4.1) and the extract obtained at **8.1.1** of EN 71-10:2005.

5.2.4.3 Identification

For a positive identification, the peak purity factor should achieve a match of at least 85 %.

5.2.5 Calculation of analyte concentration

Determine the concentration of a flame retardant in the acetonitrile extract from a calibration graph produced from the calibration solutions.

Calculate the concentration of a flame retardant in the sample using the following equation:

$$Conc\ [mg\ /\ kg\ ] = \frac{\mathrm{C}_{\mathrm{comp,\ solvent}}\ [mg\ /\ l]}{A}\ x\ 10 \qquad (1)$$

where

$C_{comp, solvent}$ is the concentration of a flame retardant in acetonitrile extract

A is the mass in grams of the *test portion* taken for analysis (see **8.1.1** of EN 71-10:2005).

5.2.6 Limits and precision

Table 2 – Limits and precision

Component	Action limit mg/kg	RSD % at 5 mg/l (equivalent to 50 mg/kg in sample)	Recovery % at 100 mg/kg from fabric
Pentabromodiphenyl ether (total of 3 isomers)	[a]	2,0	103
Octabromodiphenyl ether (total of 4 isomers)	[a]	1,2	99
Tri-*o*-cresyl phosphate	50	2,4	69
Tris(2-chloroethyl) phosphate	50	2,6	102
[a] The limit in Directive 2003/11/EC is 0,1 % by mass (1 000 mg/kg)			

Correlation coefficient (r): > 0,995

5.2.7 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) identification of flame retardants in the extract of the *test portion*;

d) amount of each flame retardant identified expressed as a concentration (mg/kg) in the *toy material*;

e) any deviations from the test procedure specified;

f) date of test.

5.3 Colourants

5.3.1 Principle

Colourants are identified and semi-quantified in extracts of *toy materials* by liquid chromatography with diode-array detection (LC-DAD). If a positive identification is obtained, confirmation can be achieved using liquid chromatography with mass spectrometry detection (LC-MS).

5.3.2 Standards, reagents and solvents

NOTE Pure materials for these colourants are not readily available and their composition can vary. A supplier of a suitable colourant is indicated for each analyte.

5.3.2.1 Standards[5]

5.3.2.1.1 Disperse Blue 1, C.I. 64500

e.g. Sigma Aldrich 21 564-3

5.3.2.1.2 Disperse Blue 3, C.I. 61505

e.g. Sigma Aldrich 21 565-1

5.3.2.1.3 Disperse Blue 106

e.g. Fluka 28241

5.3.2.1.4 Disperse Blue 124

e.g. Fluka 21620

5.3.2.1.5 Disperse Yellow 3, C.I. 11855

e.g. Sigma Aldrich 21 568-6

5.3.2.1.6 Disperse Orange 3, C.I. 11005

e.g. Sigma Aldrich 36 479-7

5.3.2.1.7 Disperse Orange 37

e.g. Fluka 21603

5.3.2.1.8 Disperse Red 1, C.I. 11110

e.g. Sigma Aldrich 34 420-6

5.3.2.1.9 Solvent Yellow 1, C.I. 11000

e.g. Sigma Aldrich 18 636-8

5.3.2.1.10 Solvent Yellow 2, C.I. 11020

e.g. Sigma Aldrich 11 449-9

5.3.2.1.11 Solvent Yellow 3, C.I. 11160

e.g. Sigma Aldrich 12 156-8

5.3.2.1.12 Basic Red 9, C.I. 42500

e.g. Sigma Aldrich 21 559-7

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[5] The suppliers of the colourants mentioned in this subclause are examples of suppliers of suitable products available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN.

5.3.2.1.13 Basic Violet 1, C.I. 42535

e.g. Sigma Aldrich 19 809-9

5.3.2.1.14 Basic Violet 3, C.I.42555

e.g. Sigma Aldrich 86 099-9

5.3.2.1.15 Acid Red 26, C.I.16150

e.g. Sigma Aldrich 19 976-1

5.3.2.1.16 Acid Violet 49, C.I. 42640

e.g. Sigma Aldrich S334294

5.3.2.2 Reagents and solvents

5.3.2.2.1 Tetrabutylammonium hydroxide solution, 40 % in water

5.3.2.2.2 Citric acid

5.3.2.2.3 Ammonium acetate, anhydrous

5.3.2.2.4 Acetonitrile

5.3.2.2.5 Tetrahydrofuran

5.3.2.2.6 Ethanol, absolute

5.3.2.2.7 Ammonium hydroxide, approx. 35 % (*V/V*)

5.3.2.2.8 Acetic acid, glacial

5.3.2.2.9 Ammonium acetate, 10 mmol/l aqueous solution, pH 3,6

Transfer (0,77 ± 0,01) g ammonium acetate (5.3.2.2.3) into a 1 000-ml volumetric flask, add 980 ml of water, adjust the pH to 3,6 ± 0,1 with glacial acetic acid and make up to the mark with water.

5.3.2.2.10 Citrate-buffered tetrabutylammonium hydroxide solution

Transfer (13,6 ± 0,1) g tetrabutylammonium hydroxide solution (5.3.2.2.1) and (2,8 ± 0,1) g citric acid into a 1 000-ml volumetric flask, add 980 ml of water, adjust the pH to 9,0 ± 0,1 with ammonium hydroxide (5.3.2.2.7) and make up to the mark with water.

5.3.3 Standard solutions

5.3.3.1 General

When preparing stock solutions of each colourant, purity values shall be taken into account. Store the stock standard solutions in a refrigerator at (4 ± 2) °C.

5.3.3.2 Stock standard solution (50 µg/ml), mix 1

Weigh, to the nearest 0,1 mg, (5 ± 1) mg of each colourant listed below into a 100-ml volumetric flask. Add 50 ml of ethanol (5.3.2.2.6) and mix carefully to dissolve. Place in an ultrasonic bath for 15 min to ensure complete dissolution. Make up to the mark with ethanol.

— Disperse Blue 1
— Disperse Blue 106
— Disperse Blue 124
— Disperse Orange 3
— Disperse Orange 37
— Solvent Yellow 1
— Solvent Yellow 2
— Solvent Yellow 3
— Basic Red 9
— Basic Violet 1
— Basic Violet 3

5.3.3.3 Stock standard solution (50 µg/ml), mix 2

Weigh, to the nearest 0,1 mg, (5 ± 1) mg of each colourant listed below into a 100-ml volumetric flask. Add 50 ml of ethanol and mix carefully to dissolve. Place in an ultrasonic bath for 15 min to ensure complete dissolution. Make up to the mark with ethanol.

— Disperse Blue 3
— Disperse Yellow 3
— Disperse Red 1
— Acid Red 26
— Acid Red 49

5.3.4 Apparatus

5.3.4.1 **PTFE membrane filter,** 0,45 µm

5.3.4.2 Ultrasonic bath

5.3.4.3 Liquid chromatograph with diode-array detector

The following LC-DAD conditions for colourant analysis have been found to be suitable:

Column: C18, 100 Å, 5 μm, endcapped, (Luna C18(2)[6], or equivalent), 250 mm x 4,6 mm
Guard column: 2 x C18, 100 Å, 5 μm, endcapped, (Luna C18(2)[6], or equivalent)
Column temperature: 25 °C
Mobile phase A: Citrate-buffered tetrabutylammonium hydroxide solution (5.3.2.2.10)
Mobile phase B: Tetrahydrofuran
Mobile phase C: Acetonitrile
Gradient: see Table 3
Run time: 45 min
Flow rate 0,8 ml/min
Injection volume: 5 μl to 50 μl
Analysis time: 35 min
Wavelength range: 275 nm to 760 nm
Resolution factor: 4,8 nm
Acquisition rate: 1 spectrum/second

Table 3 – Gradient program

Time min	**Mobile phase A** %	**Mobile phase B** %	**Mobile phase C** %
0	80,0	10,0	10,0
2,50	80,0	10,0	10,0
30,0	5,0	48,0	47,0
35,0	5,0	48,0	47,0
45,0	80,0	10,0	10,0

5.3.5 Procedure

5.3.5.1 Calibration solutions

Prepare two series of colourant calibration solutions from the stock standard solutions of mix 1 (5.3.3.2) and mix 2 (5.3.3.3) at 1 mg/l, 2 mg/l, 3 mg/l, 4 mg/l and 5 mg/l concentrations in ethanol.

5.3.5.2 Determination

Proceed to liquid chromatographic determination using the conditions described in **5.3.4.3**. Inject the calibration solutions of both mix 1 and mix 2 (5.3.5.1) and the ethanol phase obtained at **8.1.3**, **8.2.1**, **8.3.1**, **8.4.1**, **8.5.1**, **8.6.1**, **8.7.1**, **8.8.1** or **8.9.1** of EN 71-10:2005, as appropriate.

5.3.5.3 Identification

For a positive identification, the peak purity factor should achieve a match of at least 85 %.

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[6] Luna C18(2) is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

5.3.6 Calculation of analyte concentration

Determine the concentration of a colourant in the ethanolic extract from a calibration graph produced from the calibration solutions.

Calculate the concentration of a colourant in the sample using the following equation:

$$Conc\ [mg\ /\ kg\ ] = \frac{C_{comp,\ solvent}\ [mg\ /\ l]}{A} xD \qquad (2)$$

where

$C_{comp, solvent}$ is the concentration of a colourant in ethanolic extract

A is the mass in grams of the *test portion* taken for analysis (see **8.1.3**, **8.2.1**, **8.3.1**, **8.4.1**, **8.5.1**, **8.6.1**, **8.7.1**, **8.8.1** or **8.9.1** of EN 71-10:2005, as appropriate)

D is the dilution factor; generally 10, but see **8.5** of EN 71-10:2005 for aqueous liquid *toy material* samples.

5.3.7 Limits and precision

Table 4 – Limits and precision

Substance	**Action limit** mg/kg	**RSD** % at 5 mg/l (equivalent to 10 mg/kg in a sample)
Disperse Blue 1	10	1,8
Disperse Blue 3	10	4,9
Disperse Blue 106	10	4,4
Disperse Blue 124	10	2,2
Disperse Yellow 3	10	0,3
Disperse Orange 3	10	1,6
Disperse Orange 37	10	2,8
Disperse Red 1	10	1,6
Solvent Yellow 1	10	1,1
Solvent Yellow 2	10	1,1
Solvent Yellow 3	10	1,6
Basic Red 9	10	1,1
Basic Violet 1	10	1,5
Basic Violet 3	10	1,0
Acid Red 26	10	2,1
Acid Violet 49	10	1,4

Correlation coefficient (*r*): > 0,995

5.3.8 Additional information

5.3.8.1 LC-DAD spectral library

It is advisable to compile a spectral library of all colours listed in **5.3.2.1** using the processing software that is used to operate the liquid chromatograph. Details of retention times and Lambda max of each colourant should be recorded together with peak purity data, if available.

It has been observed that several of the colourants separated into two or more chromatographic peaks. The colourants concerned were C.I. Acid Red 26, C.I. Disperse Blue 3, C.I. Acid Violet 49 and C.I. Basic Violet 1. In an attempt to characterise these peaks, an LC-MS method was developed in tandem with the LC-DAD method. The conditions used for the LC-MS analysis are detailed in Annex C.

5.3.9 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) identification of colourants in the ethanolic extract of the *test portion;*

d) amount of each colourant identified expressed as a concentration (mg/kg) in the *toy material*;

e) whether a confirmation test has been carried out and, if so, the technique used and its result;

f) any deviations from the test procedure specified;

g) date of test.

5.4 Primary aromatic amines

5.4.1 Principle

Aromatic amines are determined in extracts of *toy materials* by gas chromatography with mass spectrometry detection (GC-MS) using the external standard method of calibration combined with appropriate internal standards.

5.4.2 Standards, reagents and solvents

5.4.2.1 Standards

5.4.2.1.1 Benzidine

5.4.2.1.2 Aniline

5.4.2.1.3 2-Naphthylamine

5.4.2.1.4 3,3'-Dichlorobenzidine

5.4.2.1.5 3,3'-Dimethoxybenzidine

5.4.2.1.6 3,3'-Dimethylbenzidine

5.4.2.1.7 2-Methoxyaniline

5.4.2.1.8 *o*-Toluidine

5.4.2.1.9 4-Chloroaniline

5.4.2.2 Reagents and solvents

5.4.2.2.1 Acetonitrile

5.4.2.2.2 *tert*-Butyl methyl ether

5.4.2.2.3 *n*-Hexane

5.4.2.2.4 Chromabond XTR (Porous granulated kieselguhr)[7]

5.4.2.3 Stock standard solution (100 mg/l)

Weigh, to the nearest 0,1 mg, (10 ± 1) mg of each aromatic amine (5.4.2.1) into a 100-ml volumetric flask. Add 25 ml of acetonitrile (5.4.2.2.1) and mix carefully to dissolve. Place in an ultrasonic bath for 10 min to ensure complete dissolution. Make up to the mark with acetonitrile.

The stability of the mixed stock standard solution should be checked regularly. It should be stable for up to 6 months when stored in the dark at (4 ± 2) °C.

[7] Chromabond XTR is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

5.4.3 Apparatus

5.4.3.1 Ultrasonic bath

5.4.3.2 Vortex® shaker

5.4.3.3 Centrifuge

5.4.3.4 Gas chromatograph with mass spectrometer detector

Ensure that the gas chromatograph has been fully cleaned before analysis, as the determination of aromatic amines by this technique is affected by other contaminants. It is recommended that the inlet sleeve is deactivated and an amine-specific column used.

The following GC-MS conditions for primary aromatic amine determination have been found to be suitable:

Injector:
Mode: Splitless 0,5 min
Carrier gas: Helium 0,8 ml/min
Injector temperature: 250 °C
Injection volume: 2 µl
Column: 5 % diphenylpolysiloxane / 95 % dimethylpolysiloxane, (RTX-5 Amine[8], or equivalent), 30 m x 0,25 mm (ID) x 0,25 µm (film thickness)
Oven program: 60 °C (3 min) – 7 °C/min – 280 °C (4 min) – 10 °C/min – 300 °C (2 min)
Detector: MSD
Transfer line temperature: 280 °C
Detector scan range: 70 m/z to 400 m/z

Quantification ions

Choose the molecular ion as the target ion for each of the aromatic amines followed by two qualifier ions for confirmation.

Table 5 – Target and qualifier ions

Substance	Target ion *m/z*	Qualifier 1 *m/z*	Qualifier 2 *m/z*
o-Toluidine	106	107	77
2-Methoxyaniline	108	123	80
4-Chloroaniline	127	129	92
2-Naphthylamine	143	115	116
Benzidine	184	183	185
Aniline	93	92	94
3,3'-Dimethylbenzidine	212	213	106
3,3'-Dichlorobenzidine	252	254	126
3,3'-Dimethoxybenzidine	244	201	229

[8] RTX-5 Amine is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

5.4.4 Procedure

5.4.4.1 Calibration solutions

Prepare a series of mixed aromatic amine calibration solutions from the stock standard solution (5.4.2.3) at 1 mg/l, 2,5 mg/l, 5 mg/l, 10 mg/l and 20 mg/l concentrations in *tert*-butyl methyl ether.

The calibration solutions should be freshly prepared on a daily basis.

5.4.4.2 Determination

Proceed to gas chromatographic determination using the conditions described in **5.4.3.4**. Inject the calibration solutions (5.4.4.1) and the *tert*-butyl methyl ether phase obtained at **8.1.4**, **8.2.2**, **8.3.2**, **8.4.2**, **8.5.2**, **8.6.2**, **8.7.2**, **8.8.2** or **8.9.2** of EN 71-10:2005, as appropriate.

5.4.5 Calculation of analyte concentration

Determine the concentration of a primary aromatic amine in the *tert*-butyl methyl ether extract from a calibration graph produced from the calibration solutions.

Calculate the concentration of a primary aromatic amine in the sample using the following equation:

$$Conc\,[mg/kg] = \frac{C_{comp,\ solvent}\,[mg/l] \times V[ml]}{A} \qquad (3)$$

where:

$C_{comp,\ solvent}$ is the concentration of a primary aromatic amine in *tert*-butyl methyl ether extract;

V is the volume in ml of *tert*-butyl methyl ether extract;

A is the mass in grams of the *test portion* taken for analysis (see 8.1.4, 8.2.2, 8.3.2, 8.4.2, 8.5.2, 8.6.2, 8.7.2, 8.8.2 or 8.9.2 of EN 71-10:2005, as appropriate).

5.4.6 Limits and precision

Table 6 – Limits and precision

Substance	**Action limit** mg/kg	**RSD** % at 5 mg/l (equivalent to 5 mg/kg in sample)	**Recovery** % at 2,5 mg/l
o-Toluidine	5	3,7	93
2-Methoxyaniline	5	3,2	95
4-Chloroaniline	5	3,8	87
2-Naphthylamine	5	2,3	84
Benzidine	5	3,2	85
Aniline	5	5,0	102
3,3'-Dimethylbenzidine	5	1,9	82
3,3'Dichlorobenzidine	5	2,6	81
3,3'Dimethoxybenzidine	5	3,0	77

Correlation coefficient (r): > 0,995

5.4.7 Additional information

Due to the polar nature of some amines, clean chromatographic conditions are essential. Derivitization of the *toy material* extract using trifluoroacetic anhydride (TFAA) or *N*-methyl-bis(trifluoroacetamide) (MBTFA) may help overcome this problem.

During sample preparation and extraction of a *toy material* for primary aromatic amines, the possibility exists of azo-dyes also being extracted. Such dyes can decompose to aromatic amines during GC analysis. If a result above the action limit for a primary aromatic amine specified in Table 6 is obtained from a *toy material* extract that is coloured, it is necessary to ascertain whether the amine has arisen from the decomposition of an azo-dye. Except for aniline, this could indicate the presence of an azo-dye prohibited from textile and leather toys under European legislation.

NOTE 1 Directive 2002/61/EC of the European Parliament and of the Council refers.

NOTE 2 Primary aromatic amines can also be determined using a suitably validated LC-DAD or LC-MS method.

5.4.8 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) identification of primary aromatic amines in the *tert*-butyl methyl ether extract of the *test portion*;

d) amount of each primary aromatic amine identified expressed as a concentration (mg/kg) in the *toy material*;

e) any deviations from the test procedure specified;

f) date of test.

5.5 Monomers and solvents

NOTE Monomers and solvents are covered by six methods in this European Standard (**5.5.1** to **5.5.6**).

5.5.1 Method for acrylamide

5.5.1.1 Principle

Acrylamide is determined in aqueous extracts of *toy materials*, without sample preparation and derivatization, by liquid chromatography with diode-array detection (LC-DAD).

5.5.1.2 Standards

5.5.1.2.1 Acrylamide

5.5.1.2.2 Acrylamide stock standard solution, 1 000 mg/l, in water

5.5.1.3 Apparatus

Liquid chromatograph with diode-array detector

The following LC-DAD conditions for acrylamide analysis have been found to be suitable:

Column:	C18, 100 Å; 5 µm, (Nucleosil 100-5 C_{18}[9], or equivalent), 250 mm x 3 mm
Column temperature:	25 °C
Eluent:	Deionized water
Flow:	0,85 ml/min
Injection volume:	100 µl
Run time:	10 min
DAD wavelength:	198 nm

5.5.1.4 Procedure

5.5.1.4.1 Calibration solutions

Prepare a series of acrylamide calibration solutions from the acrylamide stock standard solution (5.5.1.2.2) at 0,02 mg/l, 0,04 mg/l, 0,08 mg/l, 0,2 mg/l and 0,4 mg/l concentrations in water.

5.5.1.4.2 Determination

Transfer a portion of the *aqueous migrate* obtained at **6.4** of EN 71-10:2005 into a 2-ml vial and close with a crimping cap.

Proceed to liquid chromatographic determination using the conditions described in **5.5.1.3**. Inject the calibration solutions (5.5.1.4.1) and the *aqueous migrate*.

5.5.1.5 Calculation of analyte concentration

Determine the concentration of acrylamide in the *aqueous migrate* (mg/l) directly from a calibration graph produced from the calibration solutions.

5.5.1.6 Limit and precision

Table 7 – Limit and precision

Substance	**Action limit in the *aqueous migrate*** mg/l	**RSD** % at 0,02 mg/l
Acrylamide	0,02	0,6

— Correlation coefficient (r): > 0,995

[9] Nucleosil 100-5 C_{18} is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

5.5.1.7 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) result of the analysis for acrylamide expressed as a concentration (mg/l) in the *aqueous migrate* of the *toy material*;

d) any deviations from the test procedure specified;

e) date of test.

5.5.2 Method for phenol and bisphenol A

5.5.2.1 Principle

Phenol and bisphenol A are determined in aqueous extracts of *toy materials* by liquid chromatography with diode-array and fluorescence detection (LC-DAD-FLD).

5.5.2.2 Standards, reagents and solvents

5.5.2.2.1 Standards

5.5.2.2.1.1 Phenol

NOTE Phenol should be colourless or bright yellow. If the colour is pink, the substance should not be used.

5.5.2.2.1.2 Bisphenol A

5.5.2.2.2 Solvents

Methanol

5.5.2.2.3 Standard solutions

5.5.2.2.3.1 Phenol stock standard solution (1 000 mg/l)

Weigh to the nearest mg, (100 ± 10) mg of phenol into a 100-ml volumetric flask. Dissolve and make up to the mark with methanol.

5.5.2.2.3.2 Bisphenol A stock standard solution (1 000 mg/l)

Weigh to the nearest mg, (100 ± 10) mg of bisphenol A into a 100-ml volumetric flask. Dissolve and make up to the mark with methanol.

5.5.2.3 Apparatus

Liquid chromatograph with diode-array and fluorescence detector (FLD)

The following LC-DAD-FLD conditions for phenol and bisphenol A analysis have been found to be suitable:

Column:	C18, 100 Å; 5 µm, (Nucleosil 100-5 C_{18}[10], or equivalent), 250 mm x 4 mm
Column temperature:	20 °C
Mobile phase:	Methanol : water = 65 : 35; isocratic
Flow:	0,8 ml/min
Injection volume:	40 µl
Detectors:	
For phenol: DAD:	274 nm
For bisphenol A: FLD:	Excitation wavelength, Ex = 275 nm Emission wavelength, Em = 313 nm

NOTE Both detectors are connected in series, the DAD first.

5.5.2.4 Procedure

5.5.2.4.1 Calibration solutions

NOTE Aqueous solutions of phenol and bisphenol A should be stable for a period of up to 3 weeks when stored in the dark at (4 ± 2) °C.

5.5.2.4.1.1 Phenol

Prepare a series of phenol calibration solutions from the phenol stock standard solution (5.5.2.2.3.1) at 1 mg/l, 3 mg/l, 7,5 mg/l, 15 mg/l and 45 mg/l concentrations in water.

5.5.2.4.1.2 Bisphenol A

Prepare a series of bisphenol A calibration solutions from the bisphenol A stock standard solution (5.5.2.2.3.2) at 0,01 mg/l, 0,05 mg/l, 0,1 mg/l, 0,2 mg/l and 0,5 mg/l concentrations in water.

5.5.2.4.2 Determination

Transfer a portion of the *aqueous migrate* obtained at **6.4** of EN 71-10:2005 or the extract obtained at **8.2.3**, **8.5.3**, **8.7.3** or **8.9.3** of EN 71-10:2005, as appropriate, to a 2-ml vial and close with a crimping cap.

Proceed to liquid chromatographic determination using the conditions described in **5.5.2.3**. Inject the calibration solutions (5.5.2.4.1) and the *aqueous migrate*.

5.5.2.5 Calculation of analyte concentration

Determine the concentration of phenol and bisphenol A in the *aqueous migrate* (mg/l), or the concentration of phenol (as a preservative) in the extract (mg/l), directly from a calibration graph produced from the calibration solutions.

The mass concentration of phenol (as a preservative) in a sample can be calculated using the following equation:

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[10] Nucleosil 100-5 C_{18} is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

$$Conc\ [mg\ /kg\ ] = \frac{C_{comp,\ solvent}\ [mg\ /l\ ]}{A} x15 \quad (4)$$

where

$C_{comp, solvent}$ is the concentration of phenol in extract

A is the mass in grams of the *test portion* taken for analysis (see **8.2.3**, **8.5.3**, **8.7.3**, or **8.9.3** of EN 71-10:2005, as appropriate).

5.5.2.6 Limits and precision

Table 8 – Limits and precision

Substance	**Limit in *aqueous migrate*** mg/l	**RSD** %
Phenol (as a monomer)	15	0,3 at 15 mg/l
Phenol (as a preservative)	10 mg/kg (Action limit in *toy material*)	
Bisphenol A	0,1	1,5 at 0,03 mg/l

— Correlation coefficient (*r*): > 0,995

5.5.2.7 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) result of the analysis for phenol and bisphenol A expressed as a concentration (mg/l) in the *aqueous migrate* of the *toy material*; or

result of the analysis for phenol (as a preservative) expressed as a concentration (mg/kg) in the *toy material*;

d) any deviations from the test procedure specified;

e) date of test.

5.5.3 Method for formaldehyde

5.5.3.1 Principle

Formaldehyde reacts with pentane-2,4-dione (acetylacetone) in the presence of ammonium acetate to form 3,5-diacetyl-1,4-dihydrolutidine. The absorbance is measured at a wavelength of 410 nm. Ultraviolet (UV) spectroscopy is used for confirmation where the level of formaldehyde exceeds the limit specified in EN 71-9.

NOTE This method is based on the procedure specified in EN 1541.

5.5.3.2 Standards, reagents and solvents

5.5.3.2.1 Ammonium acetate, anhydrous

5.5.3.2.2 Acetic acid, glacial (d = 1,05)

5.5.3.2.3 Pentane-2,4-dione

5.5.3.2.4 Hydrochloric acid, 1 mol/l

5.5.3.2.5 Sodium hydroxide solution, 1 mol/l

5.5.3.2.6 Starch solution freshly prepared, 2 g/l

5.5.3.2.7 Formaldehyde solution, 370 g/l to 400 g/l

5.5.3.2.8 Standard iodine solution, 0,05 mol/l

5.5.3.2.9 Standard sodium thiosulphate solution, 0,1 mol/l

5.5.3.2.10 Pentane-2,4-dione reagent

In a 100-ml volumetric flask dissolve in 25 ml of water:

- 15,0 g anhydrous ammonium acetate;
- 0,3 ml glacial acetic acid;
- 0,2 ml pentane-2,4-dionex;.

Make up to 100,0 ml with water. This reagent shall be freshly prepared.

5.5.3.2.11 Reagent without pentane-2,4-dione

In a 100-ml volumetric flask dissolve in 25 ml of water:

- 15,0 g anhydrous ammonium acetate;
- 0,3 ml glacial acetic acid.

Make up to 100,0 ml with water.

5.5.3.3 Standard solutions

5.5.3.3.1 Standardised formaldehyde stock solution

Transfer 5,0 ml formaldehyde solution (5.5.3.2.7) into a 1 000-ml volumetric flask and make up to the mark with water.

Just before use determine the concentration of this solution as follows:

To standardise this stock solution transfer 10,0 ml into a conical flask, add 25,0 ml of a standard iodine solution (5.5.3.2.8) and 10,0 ml of sodium hydroxide solution (5.5.3.2.5). Allow to stand for 5 min.

Acidify with 11,0 ml of hydrochloric acid (5.5.3.2.4) and determine the excess iodine by titration with a standard sodium thiosulphate solution (5.5.3.2.9), using 0,1 ml of the starch solution (5.5.3.2.6) as indicator.

NOTE Add the starch solution when the solution being titrated has become a pale straw colour. Theoretically, 1,0 ml of 0,05 mol/l iodine consumed is equivalent to 1,5 mg formaldehyde.

5.5.3.3.2 Formaldehyde dilute standard solution

Using pipettes and volumetric flasks, dilute an aliquot of the standardised formaldehyde stock solution (5.5.3.3.1) to 20 times its volume with water, and then further dilute an aliquot of this second solution to 100 times its volume so that 1,0 ml of the final solution contains about 0,001 mg of formaldehyde.

Calculate the actual formaldehyde concentration (mg/l).

This solution shall be freshly prepared.

5.5.3.4 Apparatus

5.5.3.4.1 Spectrometer, capable of measuring absorbance at a wavelength of 410 nm with cells of an optical path length of 10 mm

5.5.3.4.2 Scanning ultraviolet (UV) spectrometer, capable of measuring in the range of 300 nm to 500 nm (Required for the confirmation steps)

5.5.3.4.3 Thermostatic water-bath, capable of maintaining a temperature of (60 ± 2) °C

5.5.3.5 Procedure

5.5.3.5.1 General

Two parallel determinations shall be carried out on the *aqueous migrate* within 24 h of extraction.

5.5.3.5.2 Calibration solutions

Into a series of 50-ml conical flasks add 5,0 ml, 10,0 ml, 15,0 ml, 20,0 ml and 25,0 ml, respectively, of the formaldehyde dilute standard solution (5.5.3.3.2). To each flask add 5,0 ml of pentane-2,4-dione reagent (5.5.3.2.10) and make up to 30,0 ml with water.

Calculate the concentration of formaldehyde (mg/l) in these solutions.

5.5.3.5.3 Sample solution

Into a 50-ml conical flask add 5,0 ml of the *aqueous migrate* obtained at **6.4** of EN 71-10:2005, 5,0 ml of pentane-2,4-dione reagent (5.5.3.2.10) and 20,0 ml water.

5.5.3.5.4 Reference solution

Into a 50-ml conical flask add of the 5,0 ml of the *aqueous migrate* obtained at **6.4** of EN 71-10:2005, 5,0 ml of the reagent without pentane-2,4-dione (5.5.3.2.11) and 20,0 ml water.

NOTE Possible interference due to coloured substances in the *aqueous migrate* is eliminated by the use of this reference solution.

5.5.3.5.5 Blank solution

Into a 50-ml conical flask add 25,0 ml water and 5,0 ml of pentane-2,4-dione reagent (5.5.3.2.10).

NOTE This solution is required in order to construct the calibration curve.

5.5.3.5.6 Determination

Shake the calibration solutions (5.5.3.5.2) for about 15 s and immerse the conical flasks in a thermostatic water-bath at (60 ± 2) °C for 10 min ± 10 s. Allow the flasks to cool for at least 2 min in a bath of iced water.

Transfer the solutions into the measuring cells (see 5.5.3.4.1). Measure the absorbance at 410 nm of each of the calibration solutions with water in the reference cell.

Shake the sample solution (5.5.3.5.2), the reference solution (5.5.3.5.4) and the blank solution (5.5.3.5.5) for about 15 s. Immerse the conical flasks in a thermostatic water-bath at (60 ± 2) °C for 10 min ± 10 s. Allow the flasks to cool for at least 2 min in a bath of iced water.

Transfer the solutions into the measuring cells (see 5.5.3.4.1). Measure the absorbance at 410 nm of the sample solution with the reference solution in the reference cell (A_1). If the absorbance obtained exceeds the range covered by the calibration solutions, the measurement shall be repeated with a more dilute sample solution and an equally diluted reference solution.

Measure the absorbance of the blank solution with water in the reference cell (A_2).

The absorbance measurements shall be made between 35 min and 60 min from the time when the conical flasks were placed in the water-bath at 60 °C.

5.5.3.6 Calculation of analyte concentration

Construct a calibration curve after subtraction of the blank solution value (A_2) from each of the absorbances obtained from the calibration solutions.

Subtract A_2 from A_1 and read off from the calibration curve the concentration (C) of formaldehyde in the sample solution.

Calculate the formaldehyde content of the *aqueous migrate*, C_s, using the following equation:

$$C_s \text{ [mg/l]} = C \times 5 \qquad (5)$$

where

C is the concentration of formaldehyde in the sample solution (mg/l)

5 is the dilution factor of the sample solution.

Report the results to two significant figures.

5.5.3.7 Confirmation

5.5.3.7.1 Requirement for confirmation

Where the level of formaldehyde in the *aqueous migrate* exceeds 2,5 mg/l (see Table 2 D of EN 71-9:2005), the determination shall be confirmed by scanning ultraviolet (UV) spectroscopy.

5.5.3.7.2 Standard spectrum

Whilst preparing the formaldehyde derivative (see 5.5.3.5.6), scan the 10,0-ml calibration solution from 300 nm to 500 nm. Record the position and absorbance value at the peak maximum and calculate the ratio of the measurements of the absorbance measured at 20 nm increments either side of the maximum.

The spectrum should satisfy the following conditions:

a) maximum absorbance in the range from 408 nm to 411 nm;

b) spectrum that tends to zero absorbance, i.e. less than 0,02 absorbance units, below 320 nm.

Examples of the absorbance ratios to be expected are listed in Table 9.

Maximum absorbance : 410 nm

Table 9 – Examples of absorbance ratios at corresponding wavelengths

Wavelength pair nm	Ratio
370/410	0,520 ± 0,02
390/410	0,843 ± 0,01
430/410	0,802 ± 0,01
450/410	0,386 ± 0,02

5.5.3.7.3 Sample spectrum

Record the spectrum of the sample solution between 300 nm and 500 nm and determine the absorption maxima and the absorption ratios. These ratios should agree with those found for the 10,0-ml calibration solution to within ± 5%. If this criterion is satisfied, the level of formaldehyde found is confirmed.

5.5.3.8 Validation and limit

This method has been validated in an inter-laboratory trial with both hot and cold water extracts of paper and board (see EN 1541). The limit for formaldehyde as a monomer is 2,5 mg/l in the *aqueous migrate* of a *toy material*.

5.5.3.9 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) mean result of the analysis for formaldehyde expressed as a concentration (mg/l) in the *aqueous migrate* of the *toy material*;

f) whether the confirmation test has been carried out and if so, its result;

d) any deviations from the test procedure specified;

g) date of sample extraction;

h) date of test.

5.5.4 Method for trichloroethylene and dichloromethane

5.5.4.1 Principle

Trichloroethylene and dichloromethane are determined in aqueous extracts of *toy materials* by headspace - gas chromatography with electron capture detection (HS-GC-ECD).

5.5.4.2 Standards, reagents and solvents

5.5.4.2.1 Standards

5.5.4.2.1.1 Trichloroethylene

5.5.4.2.1.2 Dichloromethane

5.5.4.2.2 Reagents and solvents

5.5.4.2.2.1 Acetone

5.5.4.2.2.2 Sodium chloride

5.5.4.2.3 Standard solution

Prepare a stock standard solution by diluting the volume of each substance listed in Table 10 in a 100-ml volumetric flask with acetone.

Calculate the concentration of each substance in mg/ml using the appropriate density.

Table 10 – Concentration of substance in the stock standard solution

Substance	**Volume** µl	**Density** g/ml	**Concentration** mg/ml
Trichloroethylene	100	1,476	1,48
Dichloromethane	300	1,325	3,98

NOTE The aqueous solution can be stored in the dark at (4 ± 2) °C for a period of 3 weeks.

5.5.4.3 Apparatus

5.5.4.3.1 Headspace sampler

Oven temperature: 95 °C
Needle temperature: 95 °C
Transfer line temperature: 110 °C
Cycle time: 61 min
Thermostatic time: 120 min
Pressure increasing time: 2,0 min
Injection time: 0,04 min

5.5.4.3.2 Gas chromatograph with electron capture detector

The following GC-ECD conditions for trichloroethylene and dichloromethane analysis have been found to be suitable:

Injector:
Mode: Splitless 1 min
Carrier gas: Nitrogen
Injector temperature: 200 °C
Column: 6 % cyanopropylphenyl / 94 % dimethylpolysiloxane, (DB-624[11], or equivalent), 75 m x 0,53 mm (ID) x 3 µm (film thickness)
Oven program: 40 °C (5 min) – 2 °C/min – 65 °C – 0 min – 10 °C/min – 200 °C (5 min)
Detector: ECD
Detector temperature: 300 °C
Make up gas: Argon/methane
Typical run time: 36 min

5.5.4.4 Procedure

5.5.4.4.1 Calibration solutions

Prepare a series of working standard solutions from the stock standard solution (5.5.4.2.3) by diluting 0,5 ml, 1,0 ml, 2,0 ml, 5,0 ml and 10,0 ml, respectively, to 100 ml with acetone.

Then prepare a series of calibration solutions by diluting 50 µl of each working standard solution to 100 ml with water.

5.5.4.4.2 Determination

Transfer 10,0 ml of the *aqueous migrate* obtained at **6.4** of EN 71-10:2005 into a 20-ml glass vial and add 5 g sodium chloride. Immediately close the vial with a crimping cap, and shake to saturate the solution with salt. Treat the calibration solutions (5.5.4.4.1) in the same manner.

Proceed to HS-GC-ECD analysis using the conditions described in **5.5.4.3**.

5.5.4.5 Calculation of analyte concentration

Determine the concentration of the analyte(s) in the *aqueous migrate* (mg/l) directly from a calibration graph produced from the calibration solutions.

5.5.4.6 Limits and precision

Table 11 – Limits and precision

Substance	**Limit in *aqueous migrate*** mg/l	**RSD** %
Trichloroethylene	0,02 (Action limit)	1,4 at 0,013 mg/l
Dichloromethane	0,06	3,0 at 0,04 mg/l

— Correlation coefficient (*r*): > 0,995

[11] DB-624 is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

5.5.4.7 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) result of the analysis for trichloroethylene and dichloromethane expressed as a concentration (mg/l) in the *aqueous migrate* of the *toy material*;

d) any deviations from the test procedure specified;

e) date of test.

5.5.5 Method for methanol, toluene, ethyl benzene, xylene and cyclohexanone

5.5.5.1 Principle

Methanol, toluene, ethyl benzene, xylene (all isomers) and cyclohexanone are determined in aqueous extracts of *toy materials* by headspace - gas chromatography with mass spectrometry detection (HS-GC-MS).

5.5.5.2 Standards, reagents and solvents

5.5.5.2.1 Standards

5.5.5.2.1.1 Methanol

5.5.5.2.1.2 Toluene

5.5.5.2.1.3 Ethylbenzene

5.5.5.2.1.4 Xylenes (all isomers)

5.5.5.2.1.5 Cyclohexanone

5.5.5.2.2 Reagents and solvents

5.5.5.2.2.1 Sodium chloride

5.5.5.2.2.2 Acetone

5.5.5.2.3 Stock standard solutions

The analytes determined by this analytical method are divided into two groups. For each group, prepare a stock standard solution by diluting the volume of each relevant substance listed in Table 12 in a 100-ml volumetric flask with acetone. Calculate the concentration of each substance in mg/ml using the appropriate density.

Table 12 – Preparation of stock standard solutions

Substance	Volume ml	Density g/ml	Concentration mg/ml
Group 1: Toluene, ethylbenzene, *o*-xylene, *p*-xylene, *m*-xylene and cyclohexanone			
Toluene	3,0	0,865	25,9
Ethylbenzene	2,0	0,867	17,3
o-Xylene	2,0	0,870	17,4
m-Xylene	2,0	0,868	17,4
p-Xylene	2,0	0,866	17,3
Cyclohexanone	3,0	0,947	28,4
Group 2: Methanol			
Methanol	5,0	0,791	39,6

5.5.5.3 Apparatus

5.5.5.3.1 Headspace sampler

Oven temperature: 95 °C
Needle temperature: 95 °C
Transfer line temperature: 110 °C
Cycle time: 61 min
Thermostatic time: 120 min
Pressure increasing time: 2,0 min
Injection time: 0,04 min

5.5.5.3.2 Gas chromatograph with mass spectrometer detector

The following GC-MS conditions for methanol, aromatic hydrocarbons and cyclohexanone analysis have been found to be suitable:

Injector:
Mode: Split 1: 5
Carrier gas: Helium
Injector temperature: 220 °C
Column: Polyethylene glycol, (Supelco WAX-10[12], or equivalent),
60 m x 0,32 mm (ID) x 0,5 µm (film thickness)
Oven program: 40 °C (10 min) – 4 °C/min – 110 °C – 0 min – 8 °C/min – 230 °C (10 min)
Detector: MSD
Transfer line temperature: 250 °C
Mode: SIM
Typical run time: 52 min

[12] Supelco WAX-10 is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

Table 13 – Selected ions

Substance	Selected ions *m/z*
Methanol	29; 32; 31
Toluene	65; 91; 92
Ethylbenzene	71; 91; 106
o-Xylene	91; 105; 106;
m-Xylene	91; 105; 106;
p-Xylene	91; 105; 106;
Cyclohexanone	55; 69; 98

5.5.5.4 Procedure

5.5.5.4.1 Calibration solutions

5.5.5.4.1.1 Group 1: Toluene, ethylbenzene, *o*-xylene, *m*-xylene, *p*-xylene and cyclohexanone

Prepare a series of working standard solutions from the group 1 stock standard solution (5.5.5.2.3) by diluting 0,1 ml, 0,25 ml, 0,5 ml, 1,0 ml and 2,0 ml, respectively, to 10 ml with acetone.

Then prepare a series of calibration solutions by diluting 50 µl of each working standard solution to 100 ml with water.

5.5.5.4.1.2 Group 2: Methanol

Prepare a series of working standard solutions from the group 2 stock standard solution (5.5.5.2.3) by diluting 0,1 ml, 0,25 ml, 0,5 ml, 1,0 ml and 2,0 ml, respectively, to 10 ml with water.

Then prepare a series of calibration solutions by diluting 100 µl of each working standard solution to 100 ml with water.

5.5.5.4.2 Determination

Transfer 10,0 ml of the *aqueous migrate* obtained at **6.4** of EN 71-10:2005 into a 20-ml glass vial and add 5 g sodium chloride. Close the vial with a crimping cap, and shake to saturate the solution with salt. Treat the calibration solutions (5.5.5.4.1) in the same manner.

NOTE If a high concentration of cyclohexanone is present and/or the linear range of the calibration graph has been exceeded, dilution of the *aqueous migrate* will be required. In such cases, ensure that the volume of diluted *aqueous migrate* transferred to the glass vial is maintained at 10 ml.

Proceed to GC-MS headspace analysis using the conditions described in **5.5.5.3**.

5.5.5.5 Calculation of analyte concentration

Determine the concentration of the analyte(s) in the *aqueous migrate* (mg/l) directly from a calibration graph produced from the calibration solutions.

NOTE It is important to check that the linear range of the calibration solutions has not been exceeded.

5.5.5.6 Limits and precision

Table 14 – Limits and precision

Substance	Limit in *aqueous migrate* mg/l	RSD % at 0,9 mg/l
Toluene	2,0	9,0
Ethylbenzene	1,0	8,5
o-Xylene	2,0 (total)	7,9
m-Xylene		8,1
p-Xylene		8,0
Cyclohexanone	46	8,1
Methanol	5,0	4,2 (at 7,9 mg/l)

— Correlation coefficient (*r*): > 0,995

5.5.5.7 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) result of the analysis for methanol, toluene, ethyl benzene, xylene and cyclohexanone expressed as a concentration (mg/l) in the *aqueous migrate* of the *toy material*;

d) any deviations from the test procedure specified;

e) date of test.

5.5.6 Method for 2-methoxyethyl acetate, 2-ethoxyethanol, 2-ethoxyethyl acetate, bis(2-methoxyethyl) ether, 2-methoxypropyl acetate, styrene, 3,5,5-trimethyl-2-cyclohexene-1-one and nitrobenzene

5.5.6.1 Principle

2-Methoxyethyl acetate, 2-ethoxyethanol, 2-ethoxyethyl acetate, bis(2-methoxyethyl) ether, 2-methoxypropyl acetate, styrene, 3,5,5-trimethyl-2-cyclohexene-1-one and nitrobenzene are determined in aqueous extracts of *toy materials* by solid-phase extraction and gas chromatography with mass spectrometry detection (GC-MS).

NOTE The LC-DAD method for phenol and bisphenol A (5.5.2) is also suitable for the determination of 3,5,5-trimethyl-2-cyclohexene-1-one (isophorone).

5.5.6.2 Standards, reagents and solvents

5.5.6.2.1 Standards

5.5.6.2.1.1 2-Methoxyethyl acetate

5.5.6.2.1.2 2-Ethoxyethanol

5.5.6.2.1.3 2-Ethoxyethyl acetate

5.5.6.2.1.4 Bis(2-methoxyethyl) ether

5.5.6.2.1.5 2-Methoxypropyl acetate

5.5.6.2.1.6 Styrene

5.5.6.2.1.7 3,5,5-Trimethyl-2-cyclohexene-1-one (isophorone)

5.5.6.2.1.8 Nitrobenzene

5.5.6.2.2 Reagents and solvents

5.5.6.2.2.1 Acetone

5.5.6.2.2.2 Ethyl acetate

5.5.6.2.2.3 Sodium sulfate

5.5.6.2.3 Stock standard solution

Prepare a stock standard solution by diluting the volume of each substance listed in Table 15 in a 100-ml volumetric flask with acetone. Calculate the concentration of each substance in mg/ml by using the appropriate density.

Table 15 – Preparation of stock standard solution

Substance	**Volume** µl	**Density** g/ml	**Concentration** mg/ml
2-Methoxyethyl acetate	100	1,009	1,01
2-Ethoxyethanol	100	0,930	0,93
2-Ethoxyethyl acetate	100	0,975	0,97
Bis(2-methoxyethyl) ether	100	0,937	0,94
2-Methoxypropyl acetate	100	0,960	0.96
Styrene	200	0,909	1,82
3,5,5-Trimethyl-2-cyclohexene-1-one (isophorone)	600	0,923	5,54
Nitrobenzene	50	1,196	0,60

5.5.6.3 Apparatus

5.5.6.3.1 Solid-phase extraction tubes

Polar modified polystyrene-divinylbenzene copolymer, 6 ml / 500 mg, Chromabond - Easy[13], or equivalent.

5.5.6.3.2 Gas chromatography with mass spectrometry detector

The following GC-MS conditions have been found to be suitable:

Injector:	
Mode:	Splitless 1 min
Carrier gas:	Helium
Injector temperature:	250 °C
Injection volume:	(1 to 2) µl
Column:	Polyethylene glycol, (Supelco WAX-10[14], or equivalent), 60 m x 0,32 mm (ID) x 0,5 µm (film thickness)
Oven program:	50 °C (2 min) – 5 °C/min – 260 °C – 2 min
Detector:	MSD
Transfer line temperature:	260 °C
Mode:	SIM
Typical run time:	46 min

Table 16 – Selected ions

Substance	Selected ions *m/z*
2-Methoxyethyl acetate	43; 45; 58; 73
2-Ethoxyethanol	43; 59
2-Ethoxyethyl acetate	39; 43; 72; 87
Bis(2-methoxyethyl) ether	45; 58; 59; 73; 89
2-Methoxypropyl acetate	43; 45; 58; 72; 87
Styrene	51; 78; 104
3,5,5-Trimethyl-2-cyclohexene-1-one	82; 95; 138
Nitrobenzene	77; 93; 123

5.5.6.4 Procedure

5.5.6.4.1 Calibration solutions

Prepare a dilute stock standard solution by diluting 5 ml of the stock standard solution (5.5.6.2.3) to 100 ml with dichloromethane.

Prepare a series of calibration solutions from the dilute stock standard solution by diluting 0,1 ml, 0,25 ml, 0,5 ml, 1,0 ml and 2,0 ml, respectively, to 100 ml with dichloromethane.

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[13] Chromabond – Easy is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

[14] Supelco WAX-10 is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

5.5.6.4.2 Solid-phase extraction

Condition the cartridge with about 4 ml of water. Do not allow the cartridge to dry out prior to the next step.

Slowly pass 50 ml of the *aqueous migrate* obtained at **6.4** of EN 71-10:2005 through the conditioned SPE cartridge under vacuum. The flow rate should not exceed 5 ml/min. Do not blow dry the tube.

Rinse the cartridge five times with 1 ml of ethyl acetate. Each aliquot should be in contact with the packaging for 30 s to 1 min. Transfer the eluted solvent into a 50-ml volumetric flask and make up to the mark with dichloromethane.

Transfer a portion of this solvent extract to a glass vial and seal with a crimping cap.

5.5.6.4.3 Determination

Proceed to gas chromatographic determination using the conditions described in **5.5.6.3.2**. Inject the calibration solutions (5.5.6.4.1) and the sample solution prepared under **5.5.6.4.2**.

NOTE 1 The calibration solutions are not subjected to solid-phase extraction before analysis.

NOTE 2 Further dilution of the sample solution might be required, particularly if a high concentration of isophorone is present and/or the linear range of the calibration graph has been exceeded.

5.5.6.5 Calculation of analyte concentration

Determine the concentration of the analyte(s) in the solvent extract of the *aqueous migrate* (mg/l) directly from a calibration graph produced from the calibration solutions.

NOTE It is important to check that the linear range of the calibration graph has not been exceeded.

5.5.6.6 Limits and precision

Table 17 – Limits and precision

Substance	**Limit in *aqueous migrate*** mg/l	**RSD**[a] % at 0,05 mg/l
2-Methoxyethyl acetate	0,5 (total)[b]	4,9
2-Ethoxyethanol		4,1
2-Ethoxyethyl acetate		1,9
Bis(2-methoxyethyl) ether		3,4
2-Methoxypropyl acetate		3,4
Styrene	0,75	9,6
3.5-Trimethyl-2-cyclo-hexene-1-one (isophorone)	3,0	3,1
Nitrobenzene	0,02 (Action limit)	4,8 at 0,025 mg/l
a The RSD data were derived from experiments using 200 ml of aqueous extract at the solid-phase extraction stage.		
b Each individual glycol ether and glycol ether acetate listed should be determined if its concentration exceeds 0,05 mg/l.		

— Correlation coefficient (r): > 0,995

5.5.6.7 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) result of the analysis for glycol ethers, glycol ether acetates, styrene, 3,5,5-trimethyl-2-cyclohexene-1-one and nitrobenzene expressed as a concentration (mg/l) in the *aqueous migrate* of the *toy material*;

d) any deviations from the test procedure specified;

e) date of test.

5.6 Wood preservatives

5.6.1 Principle

Wood preservatives are determined in acetylated extracts of wooden *toy materials* by gas chromatography with electron capture detection (GC-ECD) using the internal standard method of calibration.

5.6.2 Standards, reagents and solvents

5.6.2.1 Standards

5.6.2.1.1 2,4-Dichlorophenol* (2,4-DCP)

5.6.2.1.2 2,3,4-Trichlorophenol (2,3,4-TCP), internal standard

5.6.2.1.3 2,4,6-Trichlorophenol* (2,4,6-TCP)

5.6.2.1.4 2,4,5-Trichlorophenol* (2,4,5-TCP)

5.6.2.1.5 2,3,4,6-Tetrachlorophenol* (2,3,4,6-TeCP)

5.6.2.1.6 Pentachlorophenol (PCP)

5.6.2.1.7 Lindane

5.6.2.1.8 Cyfluthrin, mixture of isomers

5.6.2.1.9 Cypermethrin, mixture of isomers

5.6.2.1.10 Deltamethrin

5.6.2.1.11 Permethrin, mixture of cis- and trans-isomer (1:3)

5.6.2.2 Reagents and solvents

5.6.2.2.1 Potassium carbonate

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* There are no requirements in EN 71-9 for this substance.

5.6.2.2.2 *ortho*-Phosphoric acid

5.6.2.2.3 *n*-Hexane

5.6.2.2.4 Acetic anhydride

5.6.2.2.5 Ethanol

5.6.2.2.6 Acetic acid, glacial

5.6.2.2.7 Ethanol/acetic acid solution (90:10, *V/V*)

Carefully mix 900 ml ethanol (5.6.2.2.5) and 100 ml acetic acid (5.6.2.2.6).

5.6.2.2.8 Potassium carbonate solution (0,1 M)

Weigh to nearest 0,1 g, approximately 13,8 g of potassium carbonate in a 1 000-ml volumetric flask and fill to the mark with water. Mix carefully.

5.6.3 Standard solutions

NOTE The concentrated and dilute stock solutions should be stable for two weeks when stored in brown glass containers at (4 ± 2) °C in the dark. Cyfluthrin, cypermethrin, deltamethrin and permethrin are unstable in daylight.

5.6.3.1 Concentrated stock standard 1

Weigh to nearest 0,1 mg, (14 ± 1) mg of cyfluthrin (5.6.2.1.8) and cypermethrin (5.6.2.1.9) and (25 ± 1) mg of deltamethrin (5.6.2.1.10) and permethrin (5.6.2.1.11) in a 50-ml volumetric flask. Fill to the mark with ethanol/acetic acid solution (5.6.2.2.7) and mix carefully.

5.6.3.2 Concentrated stock standard 2

Weigh to nearest 0,1 mg, (16 ± 1) mg 2,4-DCP (5.6.2.1.1) in a 100-ml volumetric flask. Fill to the mark with ethanol/acetic acid solution and mix carefully.

5.6.3.3 Concentrated stock standard 3

Weigh to nearest 0,1 mg, (17 ± 1) mg of 2,3,4,6-TeCP (5.6.2.1.5) and PCP (5.6.2.1.6) and (25 ± 1) mg of 2,4,6-TCP (5.6.2.1.3) and lindane (5.6.2.1.7) and (42 ± 1) mg of 2,4,5-TCP (5.6.2.1.4) in a 50-ml volumetric flask. Fill to the mark with ethanol/acetic acid solution and mix carefully.

5.6.3.4 Concentrated stock internal standard

Weigh to the nearest 0,1 mg, (10 ± 1) mg of 2,3,4-TCP (5.6.2.1.2) in a 50-ml volumetric flask. Fill to the mark with ethanol/acetic acid solution and mix carefully.

5.6.3.5 Diluted stock standard solution

Transfer by means of a volumetric glass pipette, 10 ml of solution 5.6.3.1, 5 ml of solution 5.6.3.2 and 1 ml of solution 5.6.3.3 in a 100-ml volumetric flask. Fill to the mark with ethanol/acetic acid solution and mix carefully.

5.6.3.6 Diluted internal standard solution

Transfer by means of a volumetric glass pipette, 2,5 ml of solution **5.6.3.4** into a 100-ml volumetric flask. Fill to the mark with ethanol/acetic acid solution and mix carefully.

Calculate the actual concentration of all the analytes in mg/l.

5.6.4 Apparatus

5.6.4.1 Ultrasonic bath

5.6.4.2 Calibrated pipettes

5.6.4.3 Vortex® shaker

5.6.4.4 Gas chromatograph with electron capture detector (ECD)

Injector:	
Mode:	Splitless 1 min
Carrier gas:	Nitrogen
Injector temperature:	250 °C
Injection volume:	2 µl
Column:	5 % phenylpolysiloxane / 95 % methylpolysiloxane,, (CPSil-8 CB-MS[15], or equivalent), 30 m x 0,25 mm (ID), 0,50 µm (film thickness)
Oven program:	80 °C (0 min) – 5 °C/min – 200 °C – 0 min – 10 °C/min – 300 °C (5 min)
Detector:	ECD
Detector temperature:	330 °C
Make up gas:	Argon/methane
O	

5.6.5 Procedure

5.6.5.1 Calibration solutions

To each of five 50-ml glass tubes with stoppers add 35 ml 0,1 M potassium carbonate solution (5.6.2.2.8). Using a calibrated pipette, transfer 0 µl, 15 µl, 30 µl, 45 µl and 60 µl, respectively, of the diluted stock standard solution (5.6.3.5) and 40 µl of diluted internal standard solution (5.6.3.6) to the tubes, holding the pipette in the potassium carbonate solution. Close each glass tube with a stopper and mix the solution with a mechanical shaker (5.6.4.3) for 30 s.

To each tube add 5 ml hexane and 1 ml acetic anhydride. Shake 5 times for (3 ± 1) s using a mechanical shaker. After each shaking period remove the stopper carefully to let the gas formed during the derivatization reaction escape. When almost no gas is likely to be developed, shake each tube 3 times for (30 ± 5) s, allowing the gas formed to escape by removing the stopper.

Allow sufficient time for the two phases to separate.

Calculate the actual concentrations (mg/l) of the preservatives in the upper, hexane layer.

5.6.5.2 Derivatization

To a 50-ml glass tube with stopper add 35 ml 0,1 M potassium carbonate solution. Using a calibrated pipette transfer 400 µl of the extract obtained at **8.3.3** of EN 71-10:2005 and 40 µl of the diluted internal standard solution (5.6.3.6) to the tube while holding the pipette in the potassium carbonate solution. Close the glass tube with a stopper and mix the solution with a mechanical shaker for 30 s.

Then add 5 ml hexane and 1 ml acetic anhydride. Shake 5 times for (3 ± 1) s using a mechanical shaker. After each shaking period remove the stopper carefully to let the gas formed during the derivatization reaction escape. When almost no gas is likely to be developed, shake 3 times for (30 ± 5) s, allowing the gas formed to escape by removing the stopper.

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[15] CPSil-8 CB-MS is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

Allow sufficient time for the two phases to separate.

5.6.5.3 Determination

Proceed to gas chromatographic determination as described in **5.6.4.4**. Inject the hexane phases obtained at **5.6.5.1** and **5.6.5.2**.

5.6.6 Calculation of analyte concentration

Calculate the peak area ratio for each of the calibration solutions by dividing the peak area of a component by the peak area of the internal standard.

Determine the concentration of a wood preservative in the hexane extract from a calibration graph produced from the calibration solutions.

Calculate the concentration of a wood preservative in the sample using the following equation:

$$Conc\ [mg\ /\ kg\ ] = \frac{C_{\text{comp, solvent}}\ [mg\ /\ l\ ] * 312\ ,5}{A} \qquad (6)$$

where

$C_{comp, solvent}$ is the concentration of a wood preservative in hexane extract

A is the mass in grams of the *test portion* taken for analysis (see **8.3.3** of EN 71-10:2005)

312,5 is the factor to calculate the concentration in mg/kg.

5.6.7 Limits and precision

Table 18 – Limits and precision

Substance	**Action limit** mg/kg	**RSD** % at the action limit	**Recovery** % at the action limit from beech wood
2,4-Dichlorophenol	(5)[a]	3,7	114
2,4,6-Trichlorophenol	(5)[a]	3,1	96
2,4,5-Trichlorophenol	(10)[a]	0,9	115
2,3,4,6-Tetrachlorophenol	(1)[a]	5,0	114
Pentachlorophenol	2	5,6	120
Lindane	2	5,0	102
Cyfluthrin	10	13,1	101
Cypermethrin	10	2,9	109
Deltamethrin	10	8,2	92
Permethrin	10	11,8	80,5
a There are no requirements in EN 71-9 for this substance but the value in parenthesis is achievable.			

— Correlation coefficient (*r*): > 0,995 (except 2,4,5-trichlorophenol = 0,992)

5.6.8 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) identification of wood preservatives in the extract of the *test portion*;

d) amount of each wood preservative identified expressed as a concentration (mg/kg) in the *toy material*;

e) any deviations from the test procedure specified;

f) date of test.

5.7 Preservatives

5.7.1 Principle

Preservatives are determined in extracts of *toy materials* by liquid chromatography with ultraviolet detection (LC-UV) using the external standard method of calibration.

NOTE Phenol is determined by the LC-DAD method specified at 5.5.2.

5.7.2 Standards, reagents and solvents

5.7.2.1 Standards

5.7.2.1.1 1,2-Benzylisothiazolin-3-one

5.7.2.1.2 2-Methyl-4-isothiazolin-3-one

5.7.2.1.3 5-Chloro-2-methyl-4-isothiazolin-3-one (≈1,2 %) / 2-methyl-4-isothiazolin-3-one (≈ 0,3 %)

NOTE The concentration of 5-chloro-2-methyl-4-isothiazolin-3-one (and 2-methyl-4-isothiazolin-3-one impurity) will depend on the supplier and the batch.

5.7.2.2 Solvents and reagents

5.7.2.2.1 Acetic acid, glacial

5.7.2.2.2 Methanol

5.7.2.2.3 Acetic acid, 0,4 % (*V/V*) aqueous solution.

5.7.3 Standard solutions

Store the stock standard solutions in the dark at (4 ± 2) °C and check their stability regularly.

5.7.3.1 1,2-Benzylisothiazolin-3-one stock standard solution (50 mg/l)

Weigh, to the nearest 0,1 mg, 10 mg of 1,2-benzylisothiazolin-3-one (5.7.2.1.1) into a 200-ml volumetric flask. Add 25 ml of mobile phase and mix carefully to dissolve. Place in an ultrasonic bath for 10 min to ensure complete dissolution. Make up to the mark with mobile phase.

5.7.3.2 2-Methyl-4-isothiazolin-3-one stock standard solution (100 mg/l)

Weigh, to the nearest 0,1 mg, 10 mg of 2-methyl-4-isothiazolin-3-one (5.7.2.1.2) into a 100-ml volumetric flask. Add 25 ml of mobile phase and mix carefully to dissolve. Place in an ultrasonic bath for 10 min to ensure complete dissolution. Make up to the mark with mobile phase (5.7.2.2.3).

5.7.3.3 5-Chloro-2-methyl-4-isothiazolin-3-one stock standard solution (120 mg/l)

Weigh 1,0 g of 5-chloro-2-methyl-4-isothiazolin-3-one (5.7.2.1.2) into a 100-ml volumetric flask. Add 25 ml of mobile phase and mix carefully to dissolve. Make up to the mark with mobile phase.

5.7.4 Apparatus

5.7.4.1 Ultrasonic bath

5.7.4.2 Calibrated pipettes

5.7.4.3 Vortex® shaker

5.7.4.4 Centrifuge

5.7.4.5 Liquid chromatograph with UV detector

The following LC-UV conditions for isothiazolinone determination have been found to be suitable:

Column:	C18, 120 Å, 18,5 µm, endcapped, (Hypersil RP[16], or equivalent), 25 cm x 0,46 cm
Mode:	Isocratic
Column temperature:	27 °C
Flow rate:	1,0 (ml/min)
Injection volume:	30 µl
Mobile phase:	Methanol : aqueous acetic acid, 0,4 % (20:80)
UV wavelengths:	280 nm for 5-chloro-2-methyl-4-isothiazolin-3-one and 2-methyl-4-isothiazolin-3-one 320 nm for 1,2-benzylisothiazolin-3-one

5.7.5 Procedure

5.7.5.1 Calibration solutions

NOTE Calibration solutions should be stored in the dark at (4 ± 2) °C and freshly prepared on a weekly basis.

5.7.5.1.1 1,2-Benzylisothiazolin-3-one calibration solutions

Prepare a series of 1,2-benzylisothiazolin-3-one calibration solutions from the 1,2-benzylisothiazolin-3-one stock standard solution (5.7.3.1) at 1,25 mg/l, 2,5 mg/l, 5,0 mg/l, 7,5 mg/l, and 10,0 mg/l concentrations in mobile phase (5.7.2.2.3).

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[16] Hypersil RP is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

5.7.5.1.2 2-Methyl-4-isothiazolin-3-one calibration solutions

Prepare a series of 2-methyl-4-isothiazolin-3-one calibration solutions from the 2-methyl-4-isothiazolin-3-one stock standard solution (5.7.3.2) at 2,5 mg/l, 5,0 mg/l, 10,0 mg/l, 15,0 mg/l and 20,0 mg/l concentrations in mobile phase.

5.7.5.1.3 5-Chloro-2-methyl-4-isothiazolin-3-one calibration solutions

Prepare a series of 5-chloro-2-methyl-4-isothiazolin-3-one calibration solutions from the 5-chloro-2-methyl-4-isothiazolin-3-one stock standard solution (5.7.3.2) at 3 mg/l, 6 mg/l, 12 mg/l, 18 mg/l and 24 mg/l concentrations of 5-chloro-2-methyl-4-isothiazolin-3-one in mobile phase.

NOTE 5-Chloro-2-methyl-4-isothiazolin-3-one calibration solutions will also contain 2-methyl-4-isothiazolin-3-one.

5.7.5.2 Determination

Proceed to LC-UV determination using the conditions described in **5.7.4.5**. Inject the calibration solutions (5.7.5.1) and the extract obtained at **8.2.3**, **8.5.3**, **8.7.3** or **8.9.3** of EN 71-10:2005, as appropriate.

5.7.6 Calculation of analyte concentration

Determine the concentration of a preservative in the extract from a calibration graph produced from the calibration solutions.

Calculate the concentration of a preservative in the sample using the following equation:

$$Conc\ [mg\ /\ kg\ ] = \frac{C_{comp,\ solvent}\ [mg\ /\ l]}{A} x15 \qquad (7)$$

where

$C_{comp,\ solvent}$ is the concentration of a preservative in the extract

A is the mass in grams of the *test portion* taken for analysis (see **8.2.3**, **8.5.3**, **8.7.3** or **8.9.3** of EN 71-10:2005, as appropriate).

5.7.7 Limits and precision

Table 19 – Limits and precision

Substance	**Limit in the *toy material*** mg/kg	**RSD** at 2,5 mg/l	**Recovery** % average of 2,5 mg/l, 5 mg/l and 20 mg/l from party bubble
1,2-Benzylisothiazolin-3-one	5 (Action limit)	2,2	80
2-Methyl-4-isothiazolin-3-one	10	3,8	86
5-Chloro-2-methyl-4-isothiazolin-3-one	10	3,0	89

— Correlation coefficient (*r*): > 0,995

5.7.8 Test report

The test report shall contain the following information:

a) description and identification of the product and material tested;

b) reference to this European Standard;

c) identification of preservatives in the extract of the *test portion*;

d) amount of each preservative identified expressed as a concentration (mg/kg) in the *toy material*;

e) any deviations from the test procedure specified;

f) date of test.

5.8 Plasticisers

5.8.1 Principle

Plasticisers are determined in aqueous extracts of *toy materials* by gas chromatography with mass spectrometery detection (GC-MS) using both the external and internal standard methods of calibration.

5.8.2 Standards, reagents and solvents

5.8.2.1 Standards

5.8.2.1.1 Triphenyl phosphate, CAS No. 115-86-6

5.8.2.1.2 Tri-*o*-cresyl phosphate (tri-*o*-tolyl phosphate), CAS No. 78-30-8

5.8.2.1.3 Tri-*m*-cresyl phosphate (tri-*m*-tolyl phosphate), CAS No. 563-04-2

5.8.2.1.4 Tri-*p*-cresyl phosphate (tri-*p*-tolyl phosphate), CAS No. 78-32-0

5.8.2.1.5 Benzyl butyl phthalate (internal standard), CAS No. 85-68-7

5.8.2.2 Reagents and solvents

5.8.2.2.1 Acetone

5.8.2.2.2 Toluene

5.8.2.2.3 Ethyl acetate

5.8.2.2.4 Solvent mixture: mixture containing 95 % toluene and 5 % ethyl acetate, by volume

5.8.3 Standard solutions

5.8.3.1 Stock standard solution (120 mg/l)

Weigh, to the nearest 0,1 mg, (12 $\pm$ 1) mg of each plasticiser (5.8.2.1.1 to 5.8.2.1.4) into a 100-ml volumetric flask. Add 25 ml of acetone and mix carefully to dissolve. Then make up to the mark with acetone, and mix.

5.8.3.2 Stock internal standard solution, 10 mg/ml, benzyl butyl phthalate in acetone

5.8.3.3 Dilute internal standard solution, 1 mg/ml, benzyl butyl phthalate in acetone

5.8.4 Apparatus

5.8.4.1 Gas chromatograph with mass spectrometer detector

Injector:
Mode: Splitless 1 min
Carrier gas: Helium
Injector temperature: 275 °C
Injection volume: 1 µl
Column: Optima delta-3[17], or equivalent, 30 m x 0,25 mm (ID) x 0,25 µm (film thickness)
Oven program: 100 °C (1 min) – 7 °C/min – 300 °C – 10 min
Detector: MSD
Transfer-line temperature: 290 °C
Mode: SIM

5.8.4.2 Quantification ions

For each substance, use the target ion for quantification. The qualifier ion is used for confirmation.

NOTE Typically the base ion is chosen as the target ion and the ion with the second highest peak in the mass spectrum as the qualifier. In the case of interference with other substances, other ions are chosen. The use of a qualifier ion reduces the risk of false positive results due to interfering signals. A deviation of 20 % from the expected response of the qualifier ion is acceptable.

Table 20 – Target and qualifier ions for plasticisers

Substance	Target ion *m/z*	Qualifier *m/z*
Triphenyl phosphate	325	169
Tri-*o*-cresyl phosphate; tri-*o*-tolyl phosphate	165	179
Tri-*m*-cresyl phosphate; tri-*m*-tolyl phosphate	368	165
Tri-*p*-cresyl phosphate; tri-*p*-tolyl phosphate	368	165

Table 21 – Target and qualifier ions for internal standard

Substance	Target ion *m/z*	Qualifier *m/z*
Benzyl butyl phthalate (internal standard)	149	206

[17] Optima delta-3 is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

Table 22 – Time windows of monitored ions

Start time min	**Monitored ions** *m/z*
27	149, 206
29	325, 169
31	165, 179, 368

5.8.5 Procedure

5.8.5.1 General

Rinse all glassware and other items in contact with the sample, standard or calibration solutions twice with acetone.

5.8.5.2 Calibration solutions

Prepare a series of mixed plasticiser calibration solutions, each containing 5 mg/l internal standard, from the stock standard solution (5.8.3.1) and the stock internal standard solution (5.8.3.2) at 0,3 mg/l, 0,6 mg/l, 1,2 mg/l, 1,8 mg/l and 2,4 mg/l concentrations of plasticisers in toluene.

5.8.5.3 Determination

Prepare a blank by adding 50 µl of stock internal standard solution (5.8.3.2) to 1 000 ml of water.

Add 50 µl of dilute internal standard solution (5.8.3.3) to 100 ml of the *aqueous migrate* obtained at **6.4** of EN 71-10:2005.

Extract 100 ml of both the internally-spiked blank and aqueous migrate by shaking with 10 ml of the solvent mixture (5.8.2.2.4) for 1 min. Allow the two phases to separate and draw off the upper layer.

Proceed to gas chromatographic determination using the conditions described in **5.8.4**. Inject the calibration solutions (5.8.5.2), the blank and the extract of the *aqueous migrate*.

After data collection is complete, establish calibration curves using the appropriate target and qualifier ions. The internal standard should be used.

5.8.6 Calculation of analyte concentration

Calculate the peak area ratio for each of the calibration solutions by dividing the peak area of a component by the peak area of the internal standard.

Determine the concentration of a plasticiser in the extract of the *aqueous migrate* directly from a calibration graph produced from the calibration solutions.

NOTE Content of plasticiser(s) determined in blank should not exceed 10 % of the content in the lowest calibration standard.

Calculate the concentration of a plasticiser in the *aqueous migrate* using the following equation:

$$Conc\ [mg\ /\ l] = \frac{C_{comp,\ solvent}\ [mg\ /\ l]}{10} \quad (8)$$

where

$C_{comp, solvent}$ is the concentration of plasticiser in the extract of the *aqueous migrate.*

5.8.7 Limits and precision

Table 23 – Limits and precision

Substance	**Action limit in *aqueous migrate*** mg/l	**RSD** % at 0,03 mg/l
Triphenyl phosphate	0,03	4,6
Tri-*o*-cresyl phosphate	0,03	5,9
Tri-*m*-cresyl phosphate	0,03	5,0
Tri-*p*-cresyl phosphate	0,03	3,7

— Correlation coefficient (*r*): > 0,995

5.8.8 Test report

The test report shall contain the following information:

f) description and identification of the product and material tested;

g) reference to this European Standard;

h) result of the analysis for plasticers expressed as a concentration (mg/l) in the *aqueous migrate* of the *toy material*;

i) any deviations from the test procedure specified;

j) date of test.

Annex A
(informative)

Methods of analysis for volatile solvents

A.1 Introduction

NOTE Since it was not possible in the time available to validate and peer-review the methods in this Annex A, the methods in this annex are informative rather than normative. A laboratory proposing to follow these methods should perform validation, adequate for the purpose to which the results are to be used.

A.1.1 General

Testing and assessment of chemical emissions are essential in order to identify safe materials. In general, the results of a suitable test method should allow for a conclusion on whether or not a toy is safe. Therefore, the method should deliver an exposure relevant outcome.

The assessment of inhalation exposure to volatile organic solvents can be addressed analytically by tiered testing:

1. The total amount of solvent present in a toy sample (tier 1).

2. The (initial) evaporation rate of a solvent from a toy sample (tier 2).

Tier 1 is based on a worst-case exposure scenario. It is assumed that any solvent evaporates instantaneously from a toy sample. For this reason, a static headspace method (A.2) with a high evaporation temperature (90°) has been chosen for estimating the 'total' amount of solvent present in a toy sample.

Tier 2 requires a test that mimics real-life conditions and distinguishes between short- and long-term emissions (reflecting acute and chronic health exposure). This can be achieved by measuring emissions from samples over longer periods with several sampling times. A dynamic, thermal desorption method (A.3) that measures volatile solvent concentrations has been adopted for the analysis of gaseous emissions from toys.

A.1.2 Tiered testing approach

Toy samples are analysed first by static headspace-GC-MS. The quantities are expressed as µg of volatile organic compounds (VOC) per gram toy material. If high concentrations are found by static headspace, the second test method, thermal desorption, is followed. The advantages of the second test method, which reflects real life conditions, are:

1. The sensitivity of the thermal desorption method is much higher than the sensitivity of the static headspace method at the same temperature. This is achieved by working under dynamic conditions with enrichment of VOC in the cooled injection system. Using this technique, emissions can be sampled at the preferred temperature of 40 ˚C.

2. The possibility exists of relating the emissions to a gas volume (the extraction gas volume) and of expressing the results in µg/m^3. The results can be compared with the limits given in Table 2 F of EN 71-9:2005.

A.2 Static headspace - GC/MS - method

A.2.1 Principle

Volatile organic compounds (VOC) in toys are identified and determined by headspace-GC/MS. Samples are heated in a sealed vial to 90 °C, allowing the volatile components to evaporate out of the sample to form a gaseous phase above the solid. This temperature is held for 45 min and the headspace gas is extracted from the vial and injected directly into a GC/MS-system. Quantification of VOC is achieved using toluene-d_8 as an internal standard.

A.2.2 Reagents

Table A.1 – Analytes and solvents

Substance	CAS-Number
Methanol (solvent)	67-56-1
Toluene-d_8 (internal standard)	108-88-3
Benzene	71-43-2
Toluene	108-88-3
Ethylbenzene	100-41-4
Xylene (all isomers)	106-42-3/5
1,3,5-Trimethylbenzene	108-67-8
Trichloroethylene	79-01-6
Dichloromethane	75-09-2
n-Hexane	110-54-3
Nitrobenzene	98-95-3
Cyclohexanone	108-94-1
3,5,5-Trimethyl-2-cyclohexene-1-one (Isophorone)	78-59-1

A.2.3 Standard solutions

A.2.3.1 General

For benzene, toluene, ethylbenzene, xylene (all isomers), 1,3,5-trimethylbenzene, trichloroethylene and dichloromethane a mixed stock standard solution is prepared. For *n*-hexane, nitrobenzene, cyclohexanone and 3,5,5-trimethyl-2-cyclohexene-1-one (isophorone) separate stock standard solutions are prepared. Store the stock standard solutions in a refrigerator at (4 ± 2) °C.

A.2.3.2 Stock standard solutions (approximately 2 mg/ml)

To prepare each stock standard solution weigh to the nearest mg, (200 ± 20) mg of the appropriate solvent(s) (see A.2.3.1) into a 100-ml volumetric flask. Fill to the mark with methanol and mix carefully.

When preparing the mixed stock standard solution start with the solvent of the lowest volatility/ highest boiling point.

A.2.3.3 Stock internal standard solution (approximately 2 mg/ml)

Weigh to the nearest 0,1 mg (200 ± 20) mg of toluene-d_8 into a 100-ml volumetric flask. Fill to the mark with methanol and mix carefully.

A.2.3.4 Calibration solutions I (approximately 0,2 mg/ml)

Transfer by means of a volumetric glass pipette, 10 ml of the appropriate stock standard solution (A.2.3.2) into a 100-ml volumetric flask. Fill to the mark with methanol and mix carefully.

A.2.3.5 Calibration solutions II (approximately 0,02 mg/ml)

Transfer by means of a volumetric glass pipette, 10 ml of the appropriate calibration solution I (A.2.3.4) into a 100-ml volumetric flask. Fill to the mark with methanol and mix carefully.

A.2.3.6 Dilute internal standard solution (approximately 0,02 mg/ml)

Transfer by means of a volumetric glass pipette, 1 ml of the stock internal standard solution (A.2.3.3) into a 100-ml volumetric flask. Fill to the mark with methanol and mix carefully.

A.2.4 Apparatus

A.2.4.1 Gas chromatograph with mass spectrometer detector and headspace sampler

A.2.4.2 Analytical conditions for headspace - GC - MS

Table A.2 – Static headspace: Analytical conditions

Injector:	
Mode:	Splitless 0,5 min
Carrier gas:	Helium
Injector temperature:	235 °C
Injection volume:	Loop 1 ml
Column:	DB-VRX[18]: 30 m x 0,25 mm (ID) x 1,45 µm (film thickness), or equivalent
Oven program:	40 °C (7 min) – 10 °C/min – 125 °C – 0 min - 15 °C/min – 250 °C (5 min)
Detector:	ITD
Mode:	SIM

A.2.5 Procedure

A.2.5.1 Sample preparation

Weigh to the nearest 0,1 mg, (10 ± 5) mg of the *test portion* into a 20-ml headspace vial and add 10 µl of the dilute internal standard solution (A.2.3.6). Seal the vial immediately. Prior to GC/MS analysis, heat the vial to 90 °C and maintain at this temperature for 45 min.

NOTE 1 If it is necessary to determine volatile solvents in samples with low concentrations of VOC, the sample size may be increased up to 300 mg.

NOTE 2 If the laboratory sample consists of several different materials (e.g. a tent for children with blue, red and yellow coloured materials), it is necessary to analyse these different materials separately.

[18] DB-VRX is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

NOTE 3 The mass share of the different materials with respect to the total mass of the sample is determined in order to be able to calculate the emissions of the whole sample correctly.

A.2.5.2 Calibration standards

Prepare a series of calibration standards containing approximately 0,1 µg, 0,2 µg, 0,5 µg, 1,0 µg and 3,0 µg of the analytes by transferring 5 µl, 10 µl, 25 µl, 50 µl and 150 µl, respectively, of each calibration solution II (A.2.3.5) and 10 µl of the dilute internal standard solution (A.2.3.6) into a series of 20-ml headspace vials. Seal each vial immediately after addition of the standards. Prior to GC/MS analysis, heat the vials to 90 °C and maintain at this temperature for 45 min.

A.2.5.3 Determination

Proceed to GC determination using the conditions described in A.2.4.2. Inject the gas extracted from the sample vial prepared at A.2.5.1. Treat the calibration standards (A.2.5.2) in the same manner.

VOCs are detected and quantified by GC/MS. Use the target ion for quantification and the qualifier ions for positive identification of the substance. The retention times and characteristic fragment ions of the selected volatile organic compounds for the headspace method are shown in Table A.3.

Table A.3 – Static headspace: Chromatographic identification

Substance	**Typical retention time** min	**Target ion** m/z	**Qualifier ions** m/z
Toluene-d_8 (internal standard)	11,4	98	100
Benzene	7,4	78	77/51
Toluene	11,5	91	92/89
Ethylbenzene	14,15	91	106/51
m- & *p*-Xylene	14,5	91	106/105
o-Xylene	15,1	91	106/78
1,3,5-Trimethylbenzene	16,8	105	120/119
Trichloroethylene	8,8	130	95/132
Dichloromethane	3,4	49	84/86
n-Hexane	4,7	57	85/43
Nitrobenzene	19,05	77	123/51
Cyclohexanone	15,0	98	55/42
Isophorone	19,6	82	39/138

Calculate the peak area ratio for each of the calibration standards by dividing the peak area of the target ion by the area of the internal standard (target ion 98). Construct the calibration curve by plotting the peak area ratio against the concentration of the component in µg.

A.2.6 Calculation of analyte concentration

Calculate the peak area ratio for the component in the sample by dividing the peak area of the component (target ion) by the internal standard (IS) area (target ion):

$$Peak\ area\ ratio = \frac{Peak\ area\ of\ the\ component\ (t.ion)}{Peak\ area\ of\ the\ IS.(t.ion)} \quad (A.1)$$

NOTE Internal Standard = Toluene-d_8 (target ion 98)

Calculate amounts of VOC (conc. (x) in µg) by plotting the peak area ratio in the current calibration function:

$$y = a \times x\ [\mu g\ ] + b \quad (A.2)$$

$$conc \times (x)\ in\ \mu g = \frac{(y(peak\ \ area\ \ ratio\ ) - b)}{a} \quad (A.3)$$

$$conc \times (x)\ in\ \mu g\ /\ g = \frac{\mu g\ (x)}{g\ (sample\ )\ per\ \ vial} \quad (A.4)$$

A.2.7 Validation, precision and limits

A.2.7.1 Limit of detection, limit of quantification and emission limit

Table A.4 – Limit of detection, limit of quantification and emission limit

Substance	Limit of detection µg absolute	Limit of quantification µg absolute	Emission limit from *toy material* [a] µg/g		
			Tent	Inflatable toy	Helmet
Benzene	0,03	0,09	–	–	–
Toluene	0,02	0,06	2	1	0,1
Ethylbenzene	0,04	0,11	10	5	0,5
m- & *p*-Xylene	0,03	0,09	10	5	0,5
o-Xylene	0,02	0,06			
1,3,5-Trimethylbenzene	0,01	0,04	2	1	0,1
Trichloroethylene	0,02	0,05	0,2	0,1	0,05
Dichloromethane	0,01	0,03	0,2	0,1	0,05
n-Hexane	0,03	0,09	20	10	1
Nitrobenzene	0,06	0,17	0,2	0,2	0,2
Cyclohexanone	0,03	0,07	0,5	0,25	0,1
Isophorone	0,04	0,12	10	5	0,5

a These limits have been derived from the results obtained on toy samples that were analysed by both this Static headspace method (A.2) and the Thermal desorption method (A.3). The following values were assumed for the mass of toy type and its reference volume: tent: 1 kg & 1 m^3; inflatable toy: 500 g & 25 m^3 (room volume, of which 10 % inhaled); helmet: 200 g & 0,01 m^3 (internal volume). The limits should be regarded as indicative and, where more accurate values can be substituted for the assumptions made, may be adjusted using the following formula [which is derived from the relative loading factor (see A.3.6.2)]:

Adjusted emission limit = $\frac{\text{emission limit x assumed mass of toy x substituted reference volume}}{\text{substituted mass of toy x assumed reference volume}}$

A.2.7.2 Repeatability/reproducibility

The repeatability of the static headspace method was determined by making five replicate measurements of the standard solutions and the emissions from three toy samples. The calibration levels for the standard solutions and the results for the relative standard deviations (RSD) are shown in Table A.5. The results for three toy samples and their relative standard deviations (RSD) are shown in Table A.6.

Table A.5 – Static headspace: Calibration levels for the standard solutions and their relative standard deviations (RSD)[a]

Substance	Relative standard deviation (%)					
	Level 1 0,1 µg	***Level 2 0,2 µg***	***Level 3 0,4 µg***	***Level 4 1 µg***	***Level 5 2 µg***	***Level 6 3 µg***
Benzene	2,4	3,8	0,8	14,0	6,0	
Toluene	5,1	3,5	2,2	4,7	0,5	
Ethylbenzene	10,1	7,3	4,7	14,4	5,2	
m- & *p*-Xylene	10,5	5,4	4,3	11,2	2,6	
o-Xylene	4,2	4,9	4,8	12,6	12,5	
1,3,5-Trimethylbenzene	3,3	3,9	6,4	11,2	6,1	
Trichloroethylene	7,5	3,3	1,3	7,2	8,4	3,4
Dichloromethane	2,4	9,4	1,7	3,4	6,9	
n-Hexane	7,1	8,5	0,5	0,1	0,4	
Nitrobenzene	12,4	6,8	3,5	3,4		
Cyclohexanone	4,7	4,8	5,7	3,9		6,5
Isophorone	7,9	9,0	7,8			0,2

[a]For each concentration five determinations were made

Table A.6 – Static headspace: Results for three toy samples

Substance	Sample analysis						
	1 µg/g	**2** µg/g	**3** µg/g	**4** µg/g	**5** µg/g	**Mean value** s	**RDS** %
Toy sample 1							
Toluene	0,30	0,20	0,26	0,31	0,35	0,29	20,2
n-Hexane	0,11	0,12	0,13	0,10	0,10	0,11	11,6
Cyclohexanone	21,9	19,6	17,2	17,3	13,5	17,9	17,4
Isophorone	43,4	48,4	44,6	37,0	36,1	41,9	12,5
Toy sample 2							
Toluene	2,35	2,65	2,25	2,93	2,28	2,56	11,9
n-Hexane	0,15	0,13	0,16	0,15	0,21	0,15	18,8
Cyclohexanone	9,4	9,0	7,2	10,3	13,4	9,9	23,3
Isophorone	15,1	15,1	30,6	20,4	15,9	19,4	34,0
Toy sample 3							
Toluene	0,85	0,72	0,74	0,82	0,90	0,81	9,3
Ethylbenzene	0,52	0,41	0,45	0,41	0,69	0,50	23,9
m- & *p*-Xylene	0,71	0,53	0,44	0,50	0,72	0,58	22,1
o-Xylene	0,43	0,45	0,37	0,39	0,71	0,47	29,3
n-Hexane	0,20	0,18	0,19	0,22	0,20	0,20	7,5
1,3,5-Trimethyl-benzene	0,16	0,13	0,14	0,09	0,12	0,13	20,2

A.2.7.3 Linearity

Linearity was determined using the data obtained for the determination of precision plus the blank value. The mean values for each concentration of the standard solutions were determined and used for the regression analysis. Calibration curves were constructed for five concentration levels. The data obtained for some solvents of interest are shown in Table A.7.

Table A.7 – Solvents of interest

Substance	Calibration function	R
Benzene	Y= 0,0250 + 3,5216 x	0,9992
Toluene	Y= 0,0922 + 4,6073 x	0,9991
Ethylbenzene	Y= 0,0661 + 4,1928 x	0,9978
m- & *p*-Xylene	Y= 0,3813 + 3,4990 x	0,9973
o-Xylene	Y= 0,2143 + 3,7119 x	0,9975
1,3,5-Trimethylbenzene	Y= 0,2786 + 3,3833 x	0,9966
Trichloroethylene	Y= -0,0989 + 1,6924 x	0,9990
Dichloromethane	Y= -0,0050 + 1,7835 x	0,9996
n-Hexane	Y= -0,2190 + 3,2625 x	0,9959
Nitrobenzene	Y= -0,0001 + 1,4090 x	0,9993
Cyclohexanone	Y= 0,0452 + 0,8614 x	0,9988
Isophorone	Y= 0,1055 + 2,0738 x	0,9998

A.3 Thermal desorption - GC/MS - method

A.3.1 Principle

Volatile organic compounds in toys are identified and determined by thermal desorption – GC/MS. Samples are first extracted in a thermal extractor unit at 40 °C for 15 min by trapping the volatiles onto an air sampling adsorbent tube. The tubes are then thermally desorbed and analytes are focused in the inlet of a GC/MS system by cold trapping and then injected for qualitative and quantitative analysis. Quantification of VOC is achieved using toluene-d_8 as an internal standard.

Determination of VOC is achieved by sampling on Tenax TA™ and then performing thermal desorption and gas chromatographic analysis in accordance with EN/ISO 16017-1 and ISO/DIS 16000-6.

A.3.2 Reagents

A.3.2.1 Sorbent material

Tenax TA™, (poly(2,6-diphenyl-*p*-phenylene oxide)), particle size 0,18 - 0,25 mm (60 - 80 mesh)

A.3.2.2 Analytes and solvents

see Table A.1

A.3.3 Standard solutions

see A.2.3

A.3.4 Apparatus

A.3.4.1 Gas chromatograph with mass spectrometer detector

A.3.4.2 Equipment for thermal desorption – GC/MS

A.3.4.2.1 Thermal extraction device

Device for heating the sample to 40 °C for 15 min in a controlled flow of pure air or inert gas.

A.3.4.2.2 Sorbent tube

Glass, stainless steel or silica-coated stainless steel tube packed with at least 200 mg of Tenax TA™ sorbent.

A stainless steel frit/gauze or unsilanised glass wool is used to retain the sorbent in the tube. Tubes should be packed and capped/sealed in accordance with EN/ISO 16017-1.

Two sorbent tubes connected together in series are used to collect the emitted vapours from the extraction device (A.3.4.2.1).

A.3.4.2.3 Tube calibration device

Device for introducing liquid or gas standards to the sampling ends of the sorbent tubes (A.3.4.2.2) in a flow of inert gas (as described in EN/ISO 16017-1).

A.3.4.2.4 Tube conditioning device

Devise for pre-conditioning the sorbent tubes before they are used for vapour collection, either the thermal desorption device (A.3.4.2.5) itself or separate apparatus capable of heating the tube in a flow of inert carrier gas.

A.3.4.2.5 Thermal desorption device

Device for thermal desorption meeting the requirements of EN/ISO 16017-1.

A.3.4.3 Flow-meter calibrator

A bubble flow -meter or appropriate instrument suitable for gas-flow calibration.

A.3.4.4 Analytical conditions for thermal desorption: Analytical conditions

Table A.8 – Thermal desorption: Analytical conditions

Apparatus	Analysis conditions	
Thermal desorption device	Sample mode sample remove	
	Flow-mode:	Splitless
	Initial temperature:	30 °C
	Delay time:	0,30 min
	1st rate:	60 °C/min
	1st final temperature.:	300 °C
	1st final time:	5 min
	Transfer line:	300 °C
Carrier gas	Helium 5,0	
Column	5% phenyl polysilphenylene-siloxane (HP-Ultra 2[19] or equivalent): 50 m, ID: 0,32 mm, coating: 0,25 µm	
Injector	Mode:	Splitless 1,5 min
	Equilibrium time:	0,5 min
Cold trap device	Initial temperature:	-150 °C
	1st rate:	10 °C/s
	1st final temperature:	300 °C
	1st final time:	3 min
	Glass liner:	filled with Tenax TA™
Detector	MSD	
	Scan-range:	35 m/z to 450 m/z

A.3.5 Procedure

A.3.5.1 Preparation of sorbent tubes

A.3.5.1.1 General

Preconditioning; storage of conditioned sorbent tubes; reconditioning; and the storage of loaded sampling tubes are performed in accordance with EN/ISO 16017-1.

A.3.5.1.2 Preconditioning of sorbent tubes

Prior to use, condition the sorbent tubes (A.3.4.2.2) for at least 18 h in a carrier gas flow of 100 ml/min at a temperature of 330 °C using the tube conditioning device (A.3.4.2.4).

A.3.5.1.3 Storage of conditioned sorbent tubes

Seal the conditioned sorbent tubes with caps and store in an emission-free container at ambient temperature.

A.3.5.1.4 Reconditioning the preconditioned sorbent tubes

Before using the preconditioned sorbent tubes, remove trace organic volatiles possibly trapped on the tube at a temperature of 300 °C for 10 min. Determine the tube blank level by analysing the unloaded tubes under

[19] HP-Ultra 2 is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

ordinary conditions. The sorbent tube blank level is acceptable if artefact peaks are less than 10 % of the areas of the analytes of interest (ENV 13999-1:2001). In this case, the peak areas should be less than 10 % of the areas of the lowest standard concentration. If the blank value is too high, repeat the conditioning procedure.

A.3.5.2 Sample preparation and desorption

Weigh to the nearest 0,1 mg (50 ± 5) mg of the *test portion* into the container for thermal extraction device (A.3.4.2.1). Extract the sample for 15 min at 40 °C with a 20 ml/min flow of nitrogen trapping the emitted volatiles onto two conditioned sorbent tubes (see A.2.5.1) connected together in series. Seal the tubes immediately after sampling. Analyse loaded sampling tubes as soon as possible to avoid possible losses, but not later than one month after collection (ENV 13999-1:2001)[20].

Prior to analysis, spike the loaded tubes with 10 µl of the dilute internal standard solution (A.1.3.6) using the tube calibration device (A.3.4.2.3) in a 100 ml/min flow of nitrogen. Reseal the tubes immediately after the addition of internal standard. Using the conditions specified in Table A.8, thermally desorb the tubes in the thermal desorption device (A.3.4.2.5), cold-trapping the volatiles in the inlet of the gas chromatograph. To ensure the complete desorption of volatiles trapped on sorbent tubes, perform a second desorption under the same conditions. Analyse the volatiles by GC/MS (see A.3.5.4).

A.3.5.3 Calibration standards

Prepare a series of calibration standards containing approximately 0,1 µg, 0,2 µg, 0,5 µg, 1,0 µg and 3,0 µg of the analytes by spiking 5 µl, 10 µl, 25 µl, 50 µl and 150 µl, respectively, of each calibration solutions II (A.2.3.5) and 10 µl of the dilute internal standard solution (A.2.3.6) onto a series of conditioned sorbent tubes using the tube calibration device (A.3.4.2.3) and a 100 ml/min flow of nitrogen. Seal each tube immediately with caps after addition of the standards.

Thermally desorb the spiked sorbent tubes in the thermal desorption device, using identical conditions to those used for the sample analysis.

A.3.5.4 Detection and quantification

Perform VOC analysis by means of GC/MS (see Table A.8). Use the target ion for quantification and the qualifier ions for positive identification of the substance. In Table A.9, the retention times and characteristic fragment ions of the selected volatile organic compounds for the thermal desorption method are shown.

[20] The effects of storage are not known, although certain experiences (ECA, 1993) suggest that they may be stable over several months at room temperature (ENV 13999-1:2001).

Table A.9 – Thermal desorption: Chromatographic identification

Substance	Typical retention time min	Target ion m/z	Qualifier ions m/z
Toluene-d_8 (internal standard)	5,82	98	100
Benzene	4,57	78	77/51
Toluene	5,87	91	92/89
Ethylbenzene	7,13	91	106/51
m- & *p*-Xylene	7,23	91	106/105
o-Xylene	7,56	91	106/78
1,3,5-Trimethylbenzene	8,48	105	120/119
Trichloroethylene	4,98	130	95/132
Dichloromethane	4,02	49	84/86
n-Hexane	3,90	57	85/43
Nitrobenzene	9,97	77	123/51
Cyclohexanone	7,53	55	98/42
Isophorone	10,34	82	39/138

Calculate the peak area ratio for each of the calibration standards by dividing the peak area of the target ion by the area of the internal standard (target ion 98). Construct the calibration curve by plotting the peak area ratio against the concentration of the component in µg. Determine the linearity range for each of the analytes.

A.3.6 Calculation of analyte concentration

A.3.6.1 Calculation in µg/g

see A.2.6

A.3.6.2 Calculation in µg/m^3

Compare the results of the thermal desorption method (in µg/g) with the limits given in µg/m^3. The following parameters were used as the basis for these calculations:

Tents and similar — reference volume of play tent: 1 m^3,

Helmets and similar — reference volume: 0,01 m^3 (based on anthropometric data for the 97 percentile of a 12-year-old male's maximum head diameter of 25,6 cm);

Inflatable toys — reference volume: 25 m^3 (room volume) accepting that only 10 % of this will be inhaled.

First the loading factor L in g/m^3 is calculated and the loading factor is correlated to the volume of the glass extractor tube.

Example for tent-type products:

1. Loading factor children's room: mass of the tent in g / 1 m^3 (M_{toy} / 1 m^3);

2. Volume of sorbent tube: 0,00002361 m^3 (V_e).

Calculated loading factor of sorbent tube (L): M_{toy} / 1 m^3 → M_a / 0,00002361 m^3.

NOTE It is possible to choose this calculated mass for the analysis or it is possible to correlate another mass to the calculated mass.

With this (calculated) mass, it is possible to determine the emission of VOC ($M_{absolute}$) found under the expected conditions.

Furthermore, it is necessary to refer the emissions to the extraction gas volume (20 ml/min nitrogen flow for 15 min = 300 ml):

$$C_x\,[\mu g / m^3] \rightarrow \frac{M_{absolute}\,[\mu g] \times 1\,000}{V_{gas}\,[L]} \qquad \text{(A.5)}$$

Comprehensive, the amount of volatiles in µg/m^3 is calculated according to:

$$C_x = \frac{M_{absolute}\;\; V_e\;\; M_{toy}}{V_{gas}\;\; M_a\;\; V_{ref}} \times 1\,000 \;\; = \frac{M_{absolute}}{V_{gas}} \times L_{rel} \times 1\,000 \qquad \text{(A.6)}$$

Where

C_x is the concentration of volatiles in the sorbent tube [µg/m^3]

$M_{absolute}$ is the mass of volatiles absolute from the test specimen [µg]

V_e is the volume of sorbent tube [m^3]

V_{gas} is the extraction gas volume [L] (sampling time x nitrogen flow)

V_{ref} is the reference volume given [m^3]

M_{toy} is the total mass of the toy sample [g]

M_a is the mass of the *test portion* [g]

L is the loading factor = M_a / V_e [g/m^3]

L_{rel} is the relative loading factor = $M_{toy}\,V_e$ / $V_{ref}\,M_a$.

A.3.7 Validation, precision and limits

A.3.7.1 Limit of detection, limit of quantification and emission limit

The limit of detection and limit of quantification were determined by making five replicate injections of the lowest concentration standard directly into conditioned sorbent tubes and analysing and calculating the emissions in the same way as for the samples (see A.3.6.2).

Table A.10 – Limit of detection, limit of quantification and emission limit

Substance	Limit of detection [a] µg/m^3	Limit of quantification [a] µg/m^3	Emission limit from *toy material* µg/m^3
Benzene	7,9	24	–
Toluene	7,9	24	260
Ethylbenzene	6,3	19	5 000
m- & *p*-Xylene	3,1	9	870 (total)
o-Xylene	6,3	19	
1,3,5-Trimethylbenzene	7,9	24	2 500
Trichloroethylene	11,0	33	33 (Action limit)
Dichloromethane	11,0	33	3 000
n-Hexane	14,2	43	1 800
Nitrobenzene	11,0	33	33 (Action limit)
Cyclohexanone	9,4	28	136
Isophorone	9,4	28	200

a limits are for a tent and make the following assumptions:
V_e = 0,00002361 m^3, M_{toy} = 1 000 g, M_a = 0,050 g and V_{ref} = 1 m^3.

A.3.7.2 Repeatability and reproducibility

The calibration levels for the standard solutions and the relative standard deviations (RSD) are shown in Table A.11. The results for the samples are shown in Table A.12 and Table A.13.

Table A.11 – Thermal desorption: Calibration levels for the standard solutions and their relative standard deviations (RSD)[a]

Substance	Relative standard deviation (%)					
	Level 1 0,02 µg	**Level 2 0,04 µg**	**Level 3 0,1 µg**	**Level 4 0,2 µg**	**Level 5 1 µg**	**Level 6 2 µg**
Benzene	12,5	7,0	2,7	1,0	7,3	3,3
Toluene	13,6	7,2	10,6	0,8	12,9	14,8
Ethylbenzene	1,9	5,6	0,5	8,3	11,7	13,3
m- & *p*-Xylene		1,2	9,9	1,4	1,4[b]	13,0
o-Xylene	5,3	13,4	9,2	10,2	8,2	0,9
1,3,5-Trimethylbenzene	1,6	3,0	7,6	2,3	4,8	13,7
Trichloroethylene	3,3	4,1	6,9	8,6	12,4	
Dichloromethane	8,5	8,9	0,3	2,5	2,2	
n-Hexane	3,8	1,8	3,7		0,2	3,8
Nitrobenzene	8,4	2,7	3,4	1,3	1,0	
	Level 1 0,04 µg	**Level 2 0,1 µg**	**Level 3 0,4 µg**	**Level 4 1 µg**	**Level 5 3 µg**	**Level 6 5 µg**
Cyclohexanone	5,1	4,2	5,1	0,6	2,2	0,4
Isophorone	6,6	0,4	0,5	2,4	1,1	1,7
[a] For each concentration five determinations [b] Level 0,4 µg						

Table A.12 – Thermal desorption: Results of a toy sample with a high concentration level

Substance	Results of sample analysis						
	1 µg/m^3	**2** µg/m^3	**3** µg/m^3	**4** µg/m^3	**5** µg/m^3	**Mean value** s	**RSD** %
Toluene	209	215	252	355	235	253	23,5
Ethylbenzene	88	77	84	69	60	76	15
Xylene	148	142	167	148	152	151	6,2
1,3,5-Trimethylbenzene	13,1	8,4	13,6	13,8	12,5	12,3	18,1
Cyclohexanone	6 890	5 490	6 140	5 640	6 270	6 090	9,1
Isophorone	20 900	19 200	19 200	15 400	17 400	18 400	11,5
TVOC[a]	37 700	25 000	36 500	30 700	34 500	32 900	15,7
[a] TVOC = Total volatile organic compounds							

Table A.13 – Thermal desorption: Results of a toy sample with a low concentration level

Substance	Results of sample analysis						
	1 µg/m^3	**2** µg/m^3	**3** µg/m^3	**4** µg/m^3	**5** µg/m^3	**Mean value** s	**RSD** %
Toluene	13,1	10,9	15,3	13,5	13,0	13,2	11,9
Ethylbenzene	0,5	0,55	0,6	0,6	0,6	0,57	7,8
Xylene (all isomers)	0,85	1,0	0,8	0,8	0,8	0,85	10,2
1,3,5-Trimethylbenzene	0,2	0,2	0,2	0,3	0,2	0,22	20,3

A.3.7.3 Linearity

The data obtained for some solvents of interest are shown in Table A.14.

Table A.14 – Solvents of interest

Substance	Calibration function	R
Benzene	Y= 0,0655+ 4,4284 x	0,9998
Toluene	Y= 0,0742+ 4,4714 x	0,9996
Ethylbenzene	Y= 0,1104+ 5,0734 x	0,9986
m- & *p*-Xylene	Y= 0,0891+ 4,3747 x	0,9992
o-Xylene	Y= -0,0477+ 4,7417 x	1,0000
1,3,5-Trimethylbenzene	Y= 0,0350+ 4,8485 x	0,9996
Trichloroethylene	Y= 0,0120+ 0,9984 x	0,9998
Dichloromethane	Y= 0,0303+ 1,6393 x	0,9995
n-Hexane	Y= -0,0260+ 5,4802 x	0,9999
Nitrobenzene	Y= -0,0874+ 3,710 x	0,9964
Cyclohexanone	Y= -0,0881+ 2,7227 x	1,0000
Isophorone	Y= 0,2269+ 4,8978 x	0,9972

Annex B
(informative)

Validation of test methods

The methods described in this European Standard were developed and validated using a peer-review protocol based on that used by the AOAC International. The validation data obtained during the development of the methods met the repeatability limits (RSD repeatability) of acceptability based on the statistical experimental values derived by Horwitz. (The percentage recovery is required to fall within the range defined in the AOAC Peer-Verified Program).

However, it should be noted that validation data were mainly obtained using spiked solutions rather than extracts of toy materials. The exceptions were: flame retardants (spiked fabric); wood preservatives (spiked beach wood); and preservatives (spiked party bubble liquid).

Annex C
(informative)

Colourants – conformational analysis

C.1 LC-MS instrumental conditions for conformational analysis

Column: C12, 80 Å, TMS-endcapped (Phenomenex Max RP[21], or equivalent), 150 mm x 2 mm
Mobile phase A: Ammonium acetate 10 mmol/l to pH 3,6
Mobile phase B: Acetonitrile
Flow: 0,3 ml/min
Gradient: see Table C.1

Table C.1 – Gradient program

Time min	Mobile phase A %	Mobile phase B %
0	60,0	40,0
15,0	40,0	60,0
25,0	20,0	80,0
28,0	20,0	80,0
30,0	60,0	40,0
32,0	60,0	40,0

C.2 LC-MS and LC-MS-MS conformational analysis

When the mass ions were determined for each of the colourants, it was found that C.I. Solvent Yellow 2 and C.I. Solvent Yellow 3 shared an identical mass ion (M^+ 226,1). When the selective ion recording (SIR) chromatograms were examined, it was noted that there were two distinct, well-separated peaks in the chromatogram of M^+ 226,1.

It was also found that there were extra, unexpected peaks in the SIR chromatograms. This was attributed to contaminants in the colourant standards that were of similar masses to the colourants of interest.

Both of these issues were overcome with the use of LC-MS-MS. This technique has only been available commercially from the early 1990's, and has the ability to positively identify compounds. LC-MS alone does not usually fragment compounds in the way a GC-MS does, and often leaves the M^+ ion intact. With the introduction of MS-MS, the first MS can be used to screen out the M^+ ion of interest. This ion is then fragmented in a collision cell; the fragments (daughters) can be detected by the second MS operating in the SIM mode.

[21] Phenomenex Max RP is an example of a suitable product available commercially. This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of this product.

With the initial pre-screening of the M^+ ion, coupled with the unique fragmentation of the ion means that the uncertainty of identification is very low. Using this process, the two peaks in the SIR chromatogram of M^+ ion 226,1 could be assigned. This technique also shows little interference in the chromatograms from impurities.

NOTE The following conditions were found to be suitable for the analysis of the colourants:

Polarity:	Positive ion electrospray (ES^+)	Cone gas flow (l/h):	105
Capillary (kV):	3,00	Desolvation gas flow (l/h):	619
Source temperature (°C):	120	Multiplier (*V*):	650
Desolvation temperature (°C):	400		

Annex ZA
(informative)

Clauses of this European Standard addressing essential requirements or other provisions of EU Directives

This European Standard 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 88/378/EEC.

WARNING: Other requirements and other EU Directives may be applicable to the products falling within the scope of this standard.

The following clauses of this standard as detailed in table ZA.1 are likely to support requirements of Directive 88/378/EEC.

Compliance with this standard provides one means of conforming to the specific essential requirements of the Directive concerned and associated EFTA regulations.

Table ZA.1 – Correspondence between this European Standard and Directive 88/378/EEC

Requirements of Directive 88/378/EEC	Corresponding requirement clauses of this standard
ANNEX II. 3. 1 Chemical properties	Clause 5
ANNEX II. 3. 3 Chemical properties	Clause 5

Bibliography

[1] EN 71-3:1994, *Safety of toys – Part 3: Migration of certain elements*

[2] EN 1541, *Paper and board intended to come into contact with foodstuffs – Determination of formaldehyde in an aqueous extract*

[3] Directive 2003/11/EC of the European Parliament and of the Council of 6 February 2003 amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenyl ether, octabromodiphenyl ether) [Official Journal of the European Communities, No. L 42, 14.2.2003]

[4] Directive 2002/61/EC of the European Parliament and of the Council of 19 July 2002 amending for the nineteenth time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (azocolourants) [Official Journal of the European Communities, No. L 243, 11.9.2002]

[5] ECA-Report No. 13 (1993): Determination of VOCs emitted from indoor materials and products – Interlaboratory comparison of small chamber measurements, EUR 15054 EN, 1993

[6] ISO/DIS 16000-6, *Indoor air - Part 6: Determination of volatile organic compounds in indoor and chamber air by active sampling on TENAX TA sorbent, thermal desorption and gas chromatography using MSD/FID*

[7] ISO 16017-1*, Indoor, ambient and workplace air - Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography - Part 1: Pumped sampling*

[8] ENV 13999-1, *Adhesives - Short term method for measuring the emission properties of low-solvent or solvent-free adhesives after application - Part 1: General procedure*

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