SLOVENSKI STANDARD
SIST EN 71-11:2006

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Varnost igrač – 11. del: Organske kemijske spojine – Analizne metode

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

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

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

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

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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of an identical text or by endorsement, at the latest by May 2006, and conflicting national standards shall be withdrawn at the latest by May 2006.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.

5.2.3 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:

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

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 %.

[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.