SLOVENSKI STANDARD

SIST EN 71-5:1995/A1:2006

01-marec-2006

Varnost igraļ - 5. del: Kemijske igraļ e (kompleti), razen kompletov za kemijske poskuse ï Dopolnilo A1

Safety of toys - Part 5: Chemical toys (sets) other than experimental sets - Amendment A1

Sicherheit von Spielzeug - Teil 5: Chemisches Spielzeug (Sets) ausgenommen Experimentierkästen

Sécurité des jouets - Partie 5: Jouets chimiques (coffrets) autres que les coffrets d'expériences chimiques

Ta slovenski standard je istoveten z: EN 71-5:1993/A1:2006

ICS:

97.200.50 Igraļ e Toys

SIST EN 71-5:1995/A1:2006 **en,fr,de**

EUROPEAN STANDARD

NORME EUROPÉENNE

EUROPÄISCHE NORM

EN 71-5:1993/A1

January 2006

ICS 97.200.50

English Version

Safety of toys - Part 5: Chemical toys (sets) other than experimental sets

Sécurité des jouets - Partie 5: Jeux chimiques (coffrets) autres que les coffres d'expériences chimiques

Sicherheit von Spielzeug - Teil 5: Chemisches Spielzeug (Sets) ausgenommen Experimentierkästen

This amendment A1 modifies the European Standard EN 71-5:1993; it was approved by CEN on 7 December 2005.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for inclusion of this amendment into the relevant national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

This amendment 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.

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

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

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

Ref. No. EN 71-5:1993/A1:2006: E

Contents

Page

Foreword

This European Standard (EN 71-5:1993/A1:2006) has been prepared by Technical Committee CEN/TC 52 “Safety of toys”, the secretariat of which is held by DS.

This Amendment to the European Standard EN 71-5:1993 shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by July 2006, and conflicting national standards shall be withdrawn at the latest by July 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.

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, Romania, Slovakia, Slovenia, Spain, Sweden, Switzerland and United Kingdom.

Add under "Introduction",

following the 1st paragraph:

Part 6: Graphical symbol 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

following the 6th paragraph:

Under a mandate given to CEN by the European Commission, test methods were developed to determine the migration and emission of the following substances or compounds, respectively:

- elements in ceramic and vitreous enamelling materials;
- plasticizers in oven hardening poly (vinyl chloride) (PVC) modelling clay sets;
- toluene, xylene and benzene in oven hardening plasticized PVC modelling clay sets and plastic moulding sets;
- styrene in plastic moulding sets;
- substances in photographic processing sets;
- organic solvents in adhesives, lacquers, paints etc. and
- modifiers, film builders and plasticizers in paints and lacquers.

Five lead laboratories worked out the relevant test methods. In a second step the developed test procedures were validated by the lead and peer review laboratories using specially manufactured or specially selected samples (see Annex D). All test methods have been supervised by CEN/TC 52/WG 5 which also developed EN 71-4.

The 7th to 12th paragraph in the "Introduction" shall be deleted.

Replace the 1st sentence under Clause 1 "Scope" by

This part of EN 71 specifies requirements and test methods for the substances and materials used in chemical toys (sets) other than experimental sets.

Amend the standard text in Clause 2 to read

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.

Add under Clause 2 "Normative references"

EN 14517:2004, *Liquid petroleum products — Determination of hydrocarbon types and oxygenates in petrol — Multidimensional gas chromatography method*

EN ISO 3696:1995, *Water for analytical laboratory use — Specification and test methods (ISO 3696:1987)*

Delete the following references

ISO 3696:1987, *Water for analytical laboratory use; specifications and test methods*

Add the following clause:

12 Test methods

12.1 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.

12.2 Determination of elements in ceramic and vitreous enamelling materials

12.2.1 Principle

The ceramic or enamel sample is submitted to a melting digestion using dilithium tetraborate. After the dissociation the fused product is extracted by means of diluted hydrochloric acid. The individual metals are determined by atomic emission spectrophotometry.

12.2.2 Standards and reagents

12.2.2.1 Standards

NOTE These elemental standard solutions are commercially available.

Table 16 — Standards

Chemical	Concentration mg/l
Copper	1 000
Iron	1 000
Praseodymium	1 000
Cobalt	1 000
Zirconium	1 000
Vanadium	1 000
Tin	1 000

12.2.2.2 Reagents

Table 17 — Reagents

Chemical	Concentration
Di-lithium tetraborate ($Li_2B_4O_7$)	
Hydrochloric acid	ρ(HCl) = 1,12 g/ml

12.2.3 Apparatus

NOTE As there is no standardized equipment on the market only general detailed user's instructions could be provided.

12.2.3.1 Platinum crucible

12.2.3.2 **Muffle furnace,** or relevant equipment, temperature range: up to (1 000 ± 50) ºC

12.2.3.3 **Analytical balance,** precision 0,1 mg

12.2.3.4 Glassware (beaker, funnel, volumetric flask and pipettes)

Before use all glass equipment shall be cleaned using 10 % hydrochloric acid (per volume).

12.2.3.5 Atomic emission spectrometer

12.2.4 Preparation of standard solutions

12.2.4.1 Multi-element standard solution I

c (Cu, Fe, Pr, Co, Zr, V, Sn) = 10 mg/l

Pipette (1,0 ± 0,01) ml of each of the 1 000 mg/l standards (12.2.2.1) into a 100-ml volumetric flask. Add 10 ml of hydrochloric acid (12.2.2.2), mix and make up to the mark with water.

NOTE The multi-element standard solution I may be stored for a month in a refrigerator at (4 ± 2) ºC.

12.2.4.2 Multi-element standard solution II

c (Cu, Fe, Pr, Co, Zr, V, Sn) = 5,0 mg/l

Pipette (50 ± 0,05) ml of the multi-element standard solution I into a 100-ml volumetric flask. Add 10 ml of hydrochloric acid, mix and make up to the mark with water.

This solution shall be freshly prepared.

12.2.4.3 Multi-element standard solution III

c (Cu, Fe, Pr, Co, Zr, V, Sn) = 1,0 mg/l

Pipette (10 ± 0,02) ml of the multi-element standard solution I into a 100-ml volumetric flask. Add 10 ml of hydrochloric acid, mix and make up to the mark with water.

This solution shall be freshly prepared.

12.2.5 Blank solution

Add 10 ml hydrochloric acid to 90 ml water in a polyethene- or polytetrafluorethene (PTFE)-flask.

12.2.6 Sampling

Obtain three test portions from each colour of the material and treat them separately.

NOTE Homogenisation of the test portions is not necessary because the materials have been melted and are very finely ground.

12.2.7 Sample preparation

Weigh (0,1 ± 0,05) g to the nearest 0,001 g of each test portion in a platinum crucible. Add 1 g of dilithium tetraborate to the crucible and mix carefully. Heat the crucible in a muffle furnace to (1 000 ± 50) ºC for 120 min.

After cooling to approximately 500 ºC remove the crucible from the muffle furnace and transfer it into a glass of water. Add 20 ml of hydrochloric acid. Heat the solution to boiling point and let it boil until complete dissolution of the sample occurs. Transfer the solution into a 250-ml volumetric flask and filled up to the mark. If silicon dioxide is precipitated, remove it by filtration.

12.2.8 Procedure

Determine the elemental concentrations using the wavelengths according to Table 18. In case of spectral interference choose an alternative appropriate wavelength.

Table 18 — Wavelengths

Element	Wavelength nm
Copper (Cu)	324,752
Iron (Fe)	259,942
Praseodymium (Pr)	422,285
Cobalt (Co)	228,616
Zirconium (Zr)	339,198
Vanadium (V)	292,399
Tin (Sn)	189,932

After the verification of the calibration function the samples are measured.

Determine the blank solutions before analysing the solutions.

Recalibrate the analytical instruments frequently. To avoid memory effects perform also checks with the blank solution.

12.2.9 Evaluation of results

12.2.9.1 General

The mean value of three test portions shall be given.

The metal contents are calculated according to Equation (1):

$$M_m = \frac{(c_{sample} - c_{blank}) \times V \times f}{W \times 10000} \qquad (1)$$

where

M_m is the content of the metal in the sample, in mass-%;

c_{sample} is the concentration of the metal in the analytical solution, in mg/l;

c_{blank} is the concentration of the metal in the blank value solution, in mg/l;

V is the volume of the sample solution, in ml;

f is the dilution factor;

W is the weighed portion of the sample, in g.

The calculated contents of elements are compared with the maximum permitted element concentrations in the compounds given in Table C.1. If these concentrations are not exceeded, the requirements of EN 71-5 are fulfilled.

If the concentrations are exceeded, the concentration of compounds have to be calculated according to Equation (2) and 12.2.9.2:

$$M_m = \frac{(c_{sample} - c_{blank}) \times V \times f \times f_m}{W \times 10000} \quad (2)$$

where

M_m is the content of the metal in the sample, in mass-%;

c_{sample} is the concentration of the metal in the analytical solution, in mg/l;

c_{blank} is the concentration of the metal in the blank value solution, in mg/l;

V is the volume of the sample solution, in ml;

f is the dilution factor;

W is the weighed portion of the sample, in g;

f_m is the calculation factor of metal to metal oxide.

For the conversion factor f as to the individual metals see Table 19.

Table 19 — Conversion factors

Compound	Element	Conversion factor
Copper oxide (CuO)	Cu	1,251 8
Di-iron trioxide (Fe_2O_3)	Fe	1,429 7
Dipraseodymium trioxide (Pr_2O_3)	Pr	1,170 3
Coblat oxide (CoO)	Co	1,271 5
Zirconium dioxide (ZrO_2)	Zr	1,350 8
Divanadium pentoxide (V_2O_5)	V	1,785 2
Tin dioxide (SnO_2)	Sn	1,269 6

12.2.9.2 Calculation of the pigment contents in the enamel samples

12.2.9.2.1 Calculation of the concentration of copper oxide (CuO) and tin dioxide (SnO_2)

The concentration of copper oxide and tin dioxide shall be calculated according to Equation (2).

12.2.9.2.2 Calculation of the concentration of aluminium cobalt oxide ($CoO.Al_2O_3$)

The concentration of aluminium cobalt oxide shall be calculated by multiplying the amount of CoO calculated according to Equation (2) by the factor 2,360 7.

$$\mathbf{CoO \times 2{,}360\ 7 = CoO.Al_2O_3} \quad (3)$$

12.2.9.2.3 Calculation of the concentration of praseodymium zirconium silicate ($Pr_2O_3 + ZrSiO_4$)

The concentration of praseodymium zirconium silicate shall be calculated by multiplying the amount of Pr_2O_3 calculated according to Equation (2) by the factor 1,555 8.

$$\mathbf{Pr_2O_3 \times 1{,}555\ 8 = Pr_2O_3 + ZrSiO_4} \quad (4)$$

12.2.9.2.4 Calculation of the concentration of vanadium zirconium silicate ($V_2O_4 + ZrSiO_4$)

The amount of vanadium zirconium silicate shall be calculated by multiplying the amount of V_2O_5 calculated according to Equation (2) by the factor 1,919 8.

$$\mathbf{V_2O_5 \times 1{,}9198 = V_2O_4 + ZrSiO_4} \quad (5)$$

12.2.9.2.5 Calculation of the concentration of di-iron oxide (Fe_2O_3), iron zirconium silicate ($Fe_2O_3 + ZrSiO_4$) and zirconium ortho silicate ($ZrSiO_4$)

Calculate the $Fe_2O_{3\ total}$, $V_2O_{5\ total}$, $Pr_2O_{3\ total}$ and $ZrO_{2\ total}$ concentration according to Equation (2).

If Pr_2O_3 is present, then the concentration of $(Pr_2O_3 + ZrSiO_4)$ shall be calculated according to Equation (4).

The amount of ZrO_2 (a) shall be calculated by multiplying the concentration of $(Pr_2O_3 + ZrSiO_4)$ by the factor 0,240 1.

$$\mathbf{(Pr_2O_3 + ZrSiO_4) \times 0{,}240\ 1 = ZrO_2\ (a)} \quad (6)$$

If V_2O_5 is present, the concentration of $(V_2O_4 + ZrSiO_4)$ shall be calculated according to Equation (5).

The amount of ZrO_2 (b) shall be calculated by multiplying the concentration of $(V_2O_4 + ZrSiO_4)$ by the factor 0,352 9.

$$\mathbf{(V_2O_4 + ZrSiO_4) \times 0{,}352\ 9 = ZrO_2\ (b)} \quad (7)$$

The ZrO_2 (a) and ZrO_2 (b) amounts shall be added and subtracted from $ZrO_{2\ total}$.

$$\mathbf{ZrO_{2\ total} - (ZrO_2\ (a) + ZrO_2\ (b)) = ZrO_2\ (c)} \quad (8)$$

The concentration of iron zirconium silicate $(Fe_2O_3 + ZrSiO_4)$ shall be calculated from the amount of Fe_2O_3 calculated according to Equation (2).

The amount of Fe_2O_3 shall be multiplied by the factor 2,147 8.

$$\mathbf{Fe_2O_3 * 2{,}147\ 8 = Fe_2O_3 + ZrSiO_4} \quad (9)$$

The amount of ZrO_2 (d) shall be calculated by multiplying the concentration of $(Fe_2O_3 + ZrSiO_4)$ by the factor 0,359 3.

$$\mathbf{(Fe_2O_3 + ZrSiO_4) \times 0{,}359\ 3 = ZrO_2\ (d)} \quad (10)$$

If ZrO_2 (c) > ZrO_2 (d) the difference ZrO_2 (c) - ZrO_2 (d) is used to calculate ZrO_2 (e).

$$\mathbf{ZrO_2\ (c) - ZrO_2\ (d) = ZrO_2\ (e)} \quad (11)$$

The amount of $ZrSiO_{4\ pure}$ is calculated by multiplying the ZrO_2 (e) concentration by the factor 1,487 6.

$$\mathbf{ZrO_2\ (e) \times 1{,}487\ 6 = ZrSiO_{4\ pure}} \quad (12)$$

If ZrO_2 (c) < ZrO_2 (d) the concentration of (Fe_2O_3 + $ZrSiO_4$) is calculated by multiplying the ZrO_2 (c) concentration by the factor 2,783 6.

$$\mathbf{ZrO_2\ (c) \times 2{,}783\ 6 = Fe_2O_3 + ZrSiO_4} \quad (13)$$

The amount of Fe_2O_3 (a) is calculated by multiplying the concentration of (Fe_2O_3 + $ZrSiO_4$) by the factor 0,465 6.

$$\mathbf{Fe_2O_3 + ZrSiO_4 \times 0{,}465\ 6 = Fe_2O_3\ (a)} \quad (14)$$

The concentration of the pure di-iron oxide ($Fe_2O_{3\ pure}$) is the difference between $(Fe_2O_3)_{total}$ and Fe_2O_3 (a).

$$\mathbf{Fe_2O_{3\ total} - Fe_2O_3\ (a) = Fe_2O_{3\ pure}} \quad (15)$$

12.2.10 Test report

The analytical report shall contain as a minimum the following information:

a) type and identification of the product and/or material tested;

b) a reference to this European Standard;

c) the results of the tests expressed as x % (*m/m*) pigment content rounded to 0,01 % (*m/m*), but not more than three significant digits;

d) any deviation from the test procedure specified;

e) date of test.

12.3 Determination of plasticizers in oven hardening polyvinyl chloride (PVC) modelling clay sets

12.3.1 Principle

The plasticizer content is determined by solvent extraction to quantitatively extract the plasticizer from a known weight of PVC material using a soxhlet extractor. Hexane is used to extract phthalic acid esters, citric acid esters and alkylsulfonic acid esters. Methanol is used to extract adipic acid polyesters. Indicative plasticizer content can be determined by evaporating off the solvent and weighing the solvent residue and identifying the plasticizer by Attenuated Total Reflectance-Fourier Transform-Infra Red (ATR-FT-IR) Spectrometry.

Determination of plasticizer(s) content is by Gas Chromatography–Mass Spectrometry (GC-MS) for phthalic acid esters, alkylsulfonic acid phenyl ester and citric acid esters. Adipic acid esters are quantified gravimetrically.

This method is also partly used for the determination of plasticizers in solvent-based adhesives and solvent-based paints and lacquers (see 12.8.4).

12.3.2 Standards and reagents

12.3.2.1 Standards

NOTE The given substances (except citrates) are examples for the requirements in Table 17.

Table 20 — Phthalic acid esters

Chemical	CAS No.
bis(2-ethylhexyl) phthalate (DEHP)	*117-81-7*
di-isononyl phthalate (DINP)	*28553-12-0*
di-isodecyl phthalate (DIDP)	*26761-40-0*
benzyl butyl phthalate (BBP)	*85-68-7*
di-n-butyl phthalate (DBP)	*84-74-2*
di-n-hexyl phthalate (DNHP)	84-75-3
di-n-heptyl phthalate (DNHpP)	3648-21-3
di-n-octyl phthalate (DNOP)	117-84-0
di-n-nonyl phthalate (DNP)	84-76-4
di-n-decyl phthalate (DDP)	84-77-5
NOTE 1 The chemicals DEHP, DINP, DIDP, BBP and DBP can be used for analytical purposes for modelling clays. They are not permitted for the use in PVC modelling clays. However, they are examples for plasticizers according to the requirements in 9.2.2 and 9.4. NOTE 2 The technical grade of the substances DINP and DIDP is typically a mixture of isomers and homologues.	

Table 21 — Adipic acid polyesters

Chemical	Trade names	CAS No.
Hexanedioic acid, polymer with propane-1,2-diol, acetate	Palamoll [a] 632 & 636	55799-38-7
Hexanedioic acid, polymer with butane-1,3-diol and butane-1,4-diol, acetate	Palamoll [a] 646	150923-12-9
Hexanedioic acid, polymer with 2,2-dimethyl-propane-1,3-diol and propane-1,2-diol, isononyl ester	Palamoll [a] 652	208945-13-5
Hexanedioic acid, polymer with butane-1,4-diol and 2,2-dimethyl-propane-1,3-diol, isononyl ester	Palamoll [a] 654 & 656	208945-12-4
Hexanedioic acid, polymer with 2,2-dimethyl-propane-1,3-diol and 3-hydroxy-2,2-dimethylpropanoic acid, isononyl ester	Palamoll [a] 858	208945-11-3
No chemical inventory name available	Paraplex [b] G-40	39363-92-3

[a] Polymeric plasticizer derived from adipic acid and polyhydric alcohols.
[b] Polyester adipate.

NOTE Trade names for adipic acid polyesters are examples for those types of plasticizers.

Table 22 — Citric acid esters

Chemical	CAS No.
Tributyl acetylcitrate	77-89-4
Tris(2-ethylhexyl) acetylcitrate	144-15-0

Table 23 — Alkylsulfonic acid esters

Chemical	CAS No.
Alkylsulfonic phenyl ester	91082-17-6

12.3.2.2 Reagents

Table 24 — Solvents

Chemical	CAS No.
Hexane, analytical grade	110-54-3
Methanol, analytical grade	67-56-1

12.3.3 Apparatus

12.3.3.1 Analytical balance, precision 0,1 mg

12.3.3.2 Spark-proof heating mantle/water bath

12.3.3.3 Oven, capable of maintaining a temperature of (105 ± 5) °C

12.3.3.4 Desiccator chamber

12.3.3.5 150-ml or 250-ml glass stoppered flat bottomed flask

12.3.3.6 Soxhlet glass extractor with siphon cup

12.3.3.7 Soxhlet cellulose thimble (Whatman or equivalent)

12.3.3.8 Water-cooled glass condenser

12.3.3.9 Cotton wool

12.3.3.10 Glass volumetric flask

12.3.3.11 General volumetric glassware

12.3.3.12 Stainless steel scalpel blade

12.3.3.13 Attenuated Total Reflectance Fourier Transform Infra Red Spectrometer (ATR-FT-IR)