BS EN 71-7:2014

BSI Standards Publication

Safety of toys

Part 7: Finger paints — Requirements and test methods

...making excellence a habit.™

National foreword

This British Standard is the UK implementation of EN 71-7:2014. It supersedes BS EN 71-7:2002 which is withdrawn.

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

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

ISBN 978 0 580 78517 7

ICS 87.040; 97.200.50

This British Standard was published under the authority of the Standards Policy and Strategy Committee on 30 April 2014.

Amendments issued since publication

Date	Text affected

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

EN 71-7

April 2014

ICS 97.200.50

Supersedes EN 71-7:2002

English Version

Safety of toys - Part 7: Finger paints - Requirements and test methods

Sécurité des jouets - Partie 7: Peintures au doigt - Exigences et méthodes d'essai

Sicherheit von Spielzeug - Fingermalfarben - Teil 7: Anforderungen und Prüfverfahren

This European Standard was approved by CEN on 8 February 2014.

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

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

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

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

CEN-CENELEC Management Centre: Avenue Marnix 17, B-1000 Brussels

Ref. No. EN 71-7:2014 E

Contents

Page

Foreword

This document (EN 71-7:2014) has been prepared by Technical Committee CEN/TC 52 “Safety of toys”, the secretariat of which is held by DS.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by October 2014 and conflicting national standards shall be withdrawn at the latest by October 2014.

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

This document supersedes EN 71-7:2002.

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

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

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

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

NOTE 1 In addition to the above parts of EN 71, the following guidance documents have been published: CEN Report, CR 14379:2002, *Classification of toys - Guidelines*, CEN Technical Report CEN/TR 15071:2005, *Safety of toys - National translations of warnings and instructions for use in* EN 71 and CEN/TR 15371:2013, *Safety of toys - Replies to requests for interpretation of* EN 71-1, EN 71-2*, and* EN 71-8.

This part 7 of the EN 71 series is intended to be read in conjunction with EN 71, part 1.

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

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

Introduction

This European Standard contains requirements which are intended to reduce the risks to children when *finger paints* are used as intended or in a foreseeable way, bearing in mind the behaviour of children. It is intended to complete the essential safety requirements of Directive 2009/48/EC by providing special requirements for *finger paints*.

It is recognized that *finger paints* when compared to other toy products present different risks because of the intended use by fingers or hands and the age of the child. For example, prolonged skin contact or possible ingestion of paint material cannot be ruled out. Therefore, the safety requirements outlined in other parts of EN 71 needed to be expanded upon for *finger paints*. In order to address the risks associated with the use of *finger paints* by children, this part of EN 71 contains requirements relating to preservatives as well as other ingredients that may be used in the manufacture of *finger paints* and requirements relating to impurities, migration of certain elements and other attributes.

Chemical Abstract Service Registry Number (CAS), European Inventory of Existing Chemical Substances Number (EINECS) or Colour Index Number given in the tables are provided for information purposes only.

1 Scope

This part of EN 71 specifies requirements for the substances and materials used in *finger paints* and applies to *finger paints* only.

Additional requirements are specified for markings, labelling and containers.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

EN 71-3, *Safety of toys - Part 3: Migration of certain elements*

EN 71-12, *Safety of toys - Part 12: N-Nitrosamines and N-nitrosatable substances*

EN ISO 787-9, *General methods of test for pigments and extenders - Part 9: Determination of pH value of aqueous suspension (ISO 787-9)*

3 Terms and definitions

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

3.1
finger paint
aqueous semi-solid or liquid, coloured mixture specially designed for children to apply directly to suitable surfaces with the fingers and hands

3.2
colourant
pigment or dyestuff

Note 1 to entry: For definitions of pigment and dyestuff, see EN ISO 4618.

3.3
extender
material in granular or powder form, insoluble in the medium and used to modify or influence certain physical properties

[SOURCE: EN ISO 4618:2006, 2.98]

3.4
humectant
substance that delays the drying process

3.5
binding agent
water soluble or miscible, non-volatile component that binds the paint to the surface to which it has been applied

3.6
preservative
substance that prevents the growth of undesirable micro-organisms

3.7
surfactant
surface active substance

3.8
embittering agent
substance that gives the product a bitter taste

4 Requirements

NOTE The requirements of this standard apply to *finger paints* in the form used by the child. In the case of powdered *finger paints* (for example to which water might be added before use) the requirements apply to the *finger paint* prepared according to the manufacturer's instructions.

4.1 General

Finger paints shall not contain dangerous substances or mixtures in amounts which can harm the health of children using them.

NOTE 1 For more information, see Directive 1999/45/EC [2] and Regulation No. (EC) 1272/2008 [1].

Finger paints shall not fulfil the criteria of any of the following hazard classes:

- "acute toxicity" (hazard class 3.1),
- "Skin corrosion/irritation" (hazard class 3.2),
- "Serious eye damage/eye irritation" (hazard class 3.3),
- "Respiratory or skin sensitisation" (hazard class 3.4),
- "Germ cell mutagenicity" (hazard class 3.5),
- "Carcinogenicity" (hazard class 3.6),
- "Reproductive toxicity" (hazard class 3.7),
- "Specific target organ toxicity — single exposure" (hazard class 3.8),
- "Specific target organ toxicity — repeated exposure" (hazard class 3.9),
- "Aspiration hazard" (hazard class 3.10).

NOTE 2 The classification is detailed in Regulation (EC) No. 1272/2008 [1] (Annex I, Part 3: Health Hazards).

4.2 *Colourants*

4.2.1 Only *colourants* and colouring materials which are not fulfilling the hazard criteria in 4.1 shall be used in *finger paints*.

NOTE A non-exhaustive list of commonly used *colourants*, subject to meeting purity requirements, is given in Annex A consisting of *colourants* falling in one or more of the following categories: *Colourants* permitted for use in food and/or cosmetics and other pigments which meet the general requirements of 4.1.

4.2.2 *Finger paints* shall not contain azo *colourants* that by cleavage of one or more azo groups can produce the primary aromatic amines listed in Tables 1 and 2 when tested in accordance with the test method specified in Annex D.

4.3 Preservatives

Finger paints shall be preserved using only the *preservatives* listed in Annex B. The determination of preservatives shall be in accordance with the methods approved under EU Cosmetics Legislation, where available (see Directive 82/434/EEC [6], Directive 83/514/EEC [7], Directive 85/490/EEC [8], Directive 93/73/EEC [9], Directive 95/32/EC [10], Directive 96/45/EC [11]). When tested in accordance with these methods, the maximum concentrations specified in the column ”maximum allowed concentration” of Table B.1 and the limitations and requirements specified in the column ”Limitations and requirements” of Table B.1 shall be observed.

4.4 Migration of certain elements

When tested in accordance with EN 71-3 the concentration of elements shall not exceed the limit values specified in EN 71-3.

4.5 Limits for impurities

4.5.1 Limits for primary aromatic amines

4.5.1.1 The primary aromatic amines listed in Table 1 shall not be determinable when tested in accordance with the test method in Annex D.

Table 1 — Primary aromatic amines

Primary aromatic amines	CAS number
Benzidine	92–87–5
2-Naphthylamine	91–59–8
4-Chloro-2-methyl-aniline (4-Chloro-*o*-toluidine)	95–69–2
4-Aminobiphenyl	92–67–1

4.5.1.2 *Finger paints* shall not contain carcinogenic primary aromatic amines (see Table 2 for a non-exhaustive list of relevant substances) in a total amount exceeding 20 mg/kg, with no individual primary aromatic amine exceeding 10 mg/kg, when tested in accordance with Annex D. The limitation does not apply to aromatic aminocarboxylic acids or aminosulfonic acids.

Table 2 — Other carcinogenic primary aromatic amines (non-exhaustive list)

Carcinogenic primary aromatic amine	CAS number
o-Aminoazotoluene (4-*o*-tolyazo-o-toluidine)	97–56–3
2-Amino-4-nitro-toluene (5-Nitro-*o*-toluidine)	99–55–8
4-Chloroaniline	106–47–8
2,4-Diaminoanisole	615–05–4
4,4'-Diaminodiphenylmethane (4,4'-Methylenedianiline)	101–77–9
3.3'-Dichlorobenzidine[a]	91–94–1
3,3'-Dimethoxybenzidine	119–90–4
3.3'-Dimethylbenzidine	119–93–7
3,3'-Dimethyl-4,4'-diaminodiphenylmethane	838–88–0
p-Cresidine (6-Methoxy-m-toluidine)	120–71–8

Carcinogenic primary aromatic amine	CAS number
2,2’-Dichloro-4,4’-methylenedianiline (4,4'-Methylene-bis-2-chloroaniline)	101–14–4
4,4'-Oxydianiline	101–80–4
4,4'-Thiodianiline	139–65–1
o-Toluidine	95–53–4
2,4-Xylidine	95–68–1
2,6-Xylidine	87–62–7
4-Amino-3-fluorophenol	399–95–1
6-Amino-2-ethoxynaphthalene	293733–21–8
2-Methoxyaniline (*o*-anisidine)	90–04–0
4-Aminoazobenzene	60–09–3
4-Methyl-*m*-phenylenediamine (Toluene-2,4-diamine)	95–80–7
2,4,5-Trimethylaniline	137–17–7
Aniline	62–53–3
[a] For certain pigments limit values for 3,3’-Dichlorobenzidine are given Annex A.	

4.5.2 Limits for other impurities

Finger paints shall not contain the impurities specified in Table 3, column 1 above the limits specified in column 2 when *colourants* specified in Table 3, column 3 are used, when tested in accordance with Annex E.

Table 3 — Impurities in *finger paints*

Impurity	Limit mg/kg	*Finger paints* of concern
Polychlorinated biphenyls	2	*Finger paints* containing *colourant* products containing chlorine or manufactured in chlorinated solvents
Hexachlorobenzene	5	*Finger paints* containing *colourant* products containing chlorine or manufactured in chlorinated solvents
Benzo (a) pyrene	0,05	Only for *finger paints* containing carbon black

4.6 Taste and smell

Finger paints shall not be sweetened, flavoured or fragranced.

An *embittering agent* in accordance with the following list (see Table 4) shall be added in order to discourage and minimize the ingestion of paint. The bitterness shall stay in the product during product lifetime.

The bitterness should be sensorically detectable in a dilution with water 1:100.

Table 4 — Embittering agents

Embittering agent	CAS number
Naringin	CAS 10236–47–2
denatonium benzoate	CAS 3734–33–6

NOTE The relative bitterness of these substances is approximately 1:3000 (naringin : denatonium benzoate). The following levels have been found suitable: naringin 1 %; denatonium benzoate 0,0004 % (4 mg/kg).

4.7 pH-value

The pH-value of the *finger paint* shall be between 4,0 and 10,0 when tested in accordance with EN ISO 787-9.

4.8 Binding agents, extenders, humectants and surfactants

Only *binding agents*, *extenders*, *humectants* and *surfactants* which are not fulfilling the hazard criteria in 4.1 shall be used in *finger paints*.

NOTE 1 See Annex C for a list of compounds known to be commonly used.

NOTE 2 The classification is detailed in Regulation (EC) No. 1272/2008 [1] (Annex I, Part 3: Health Hazards).

4.9 N-Nitrosamines

When tested in accordance with EN 71-12 the concentration of N-nitrosamines shall not exceed the limit values specified in EN 71-12.

4.10 Containers

The containers used for *finger paints* shall not possess a form, odour, colour, appearance, packaging, labelling, volume or size, such that it is likely that consumers, especially children, will confuse them with foodstuffs and in consequence place them or the *finger paints* in their mouths, or suck or ingest them.

5 Product information

5.1 General

Markings shall be clearly visible, easily legible, indelible, understandable and accurate. All markings shall be in the national language(s) of the country(ies) of sale.

NOTE EN 71–1 contains further marking requirements.

If the container is also the primary packaging all information under 5.2.1 shall also be given on the container. All information shall draw the attention of users or their supervisors to the inherent hazards and risks of harm involved in using the *finger paint* and to the way of avoiding such hazards and risks.

5.2 Marking

5.2.1 Primary packaging

NOTE Primary packaging is referred to as consumer packaging in Directive 2009/48/EC or as outer packaging in Regulation EC No. 1272/2008.

5.2.1.1 Manufacturer's identification

The primary packaging shall bear the name, trade name and/or trade mark and the address of the manufacturer, his authorized representative or the importer.

5.2.1.2 Labelling phrases

The primary packaging shall carry the following warning:

“Warning. Children under 3 years of age should be supervised by adults.”

The word “Warning” may be followed by, e.g. an exclamation mark or other punctuation marks. The word “Warning” may be written in capital letters.

Finger paints supplied in powder form shall additionally bear the following warning:

“Warning. Mix with water in accordance with the instructions before giving to a child.”

Finger paints supplied in powder form should bear instructions that indicate how to mix with water and in particular, the correct ratio of water to powder. This information may alternatively be placed in documentation supplied with the toy.

Additionally there shall be information included for *finger paints* supplied as a powder to avoid inhalation of the powder.

5.2.1.3 Indication of preservative(s) and embittering agent(s)

The primary packaging shall be labelled with an indication of the *preservative(s)* and *embittering agent(s)* used.

Preservatives shall be identified by their chemical name or INCI (name) or E-number, where available.

5.2.2 Container

The container shall bear the name, trade name and/or trade mark and the address of the manufacturer, his authorized representative or the importer.

Manufacturers shall ensure that their toys bear a type, batch, serial or model number or other element allowing their identification, or, where the size or nature of the toy does not allow it, that the required information is provided on the packaging or in a document accompanying the toy.

Annex A
(informative)

Non-exhaustive list of *colourants* which are commonly used in *finger paints*, and need to be in compliance with both the general and specified purity requirements

General Requirements

The *colourants* used in the manufacture of *finger paints* should be of technical quality and a purity suitable for the intended use. The composition of the *colourant* shall be known to the manufacturer of the *finger paint* and made available to the competent authorities on request.

Specific Requirements

When using the *colourants* of Table A.1 in *finger paints* it is important to apply the restrictions and specifications set out in column 6 of this table.

Table A.1 — Organic *colourants* which are commonly used in *finger paints*

No.	Colour	C.I. Generic Name[a]	CI number	CAS number	Restrictions, specifications and information
1	Yellow	Pigment Yellow 1	11680	2512–29–0	See footnote [b] Amine limits. Excess coupling component [e] less than 1 000 ppm
2		Pigment Yellow 3	11710	6486–23–3	See footnote [b] Amine limits. Excess coupling component [e] less than 1 000 ppm
3		Pigment Yellow 12	21090	6358–85–6	3,3’-dichlorobenzidine ≤ 5 mg/kg
4		Pigment Yellow 13	21100	5102–83–0	See footnote [d] 3,3’-dichlorobenzidine ≤ 5 mg/kg
5		Pigment Yellow 14	21095	5468–75–7	3,3’-dichlorobenzidine ≤ 5 mg/kg
6		Pigment Yellow 17	21105	4531–49–1	3,3’-dichlorobenzidine ≤ 5 mg/kg
7		Pigment Yellow 74	11741	6358–31–2	Amine limits. Excess coupling component [e] less than 1 000 ppm
8		Pigment Yellow 138	56300	30125–47–4	
9	Yellow	Pigment Yellow 139	56298	36888–99–0	
10		Pigment Yellow 151	13980		
11		Pigment Yellow 154	11781	68134–22–5	Amine limits. Excess coupling component [e] less than 1 000 ppm
12		Pigment Yellow 155	200310	68516–73–4	
13		Pigment Yellow 185	56290	76199–85–4	

14		Natural Yellow 3	75300	458–37–7	E 100 Food grade, see current European legislation (Directive 2008/128/EC [15])
15		Natural Yellow 6	75100	27876–94–4	
16		Natural Yellow 26 “Food Orange 5”	75130		E 160 a Food grade, see current European legislation (Directive 2008/128/EC [15])
17		Natural Yellow 27	75135	502–65–8	E 160 d Food grade, see current European legislation (Directive 2008/128/EC [15])
18	Orange	Pigment Orange 13	21110	3520–72–7	Amine limits and coupling component [e] limits Combinations with Pigment Black 7 shall be checked for release of 3,3’ dichlorobenzene 3,3’-dichlorobenzidine ≤ 5 mg/kg
19		Pigment Orange 34	21115	15793–73–4	Amine limits and coupling component [e] limits Combinations with Pigment Black 7 shall be checked for release of 3,3’ dichlorobenzene 3,3’-dichlorobenzidine ≤ 5 mg/kg
20	Orange	Pigment Orange 43	71105	4424–06–0	See footnote [b]
21		Pigment Orange 71	561200	86432–50–8	
22		Pigment Orange 73	56117	84632–59–7	
23		Natural Orange 4	75120	1393–63–1	E 160 b Food grade, see current European legislation (Directive 2008/128/EC [15])
24	Red	Pigment Red 48:2	15865:2 [c]	7023–61–2	
25		Pigment Red 57:1	15850:1 [c]	5281–04–9	
26		Pigment Red 63:1	15880:1	6417–83–0	
27		Pigment Red 68	15525	5850–80–6	
28		Pigment Red 83	58000:1	104074–25–1	
29		Pigment Red 122	73915	980–26–7	See footnote [d]
30		Pigment Red 181	73360	2379–74–0	
31		Pigment Red 214	200660	82643–43–4	
32		Pigment Red 242	20067	52238–92–3	
33		Pigment Red 254	56110	84632–65–5	
34		Pigment Red 255	561050	54660–00–3	
35		Pigment Red 264	561300		
36		Pigment Red 272	561150		

37		Natural Red 4	75470	1390–65–4, 1260–17–9	E 120 Food grade, see current European legislation (Directive 2008/128/EC [15])
38	Violet	Pigment Violet 19	73900	1047–16–1	See footnote [d]
39		Pigment Violet 23	51319	215247–95–3, 6358–30–1	See footnote [d]
40	Blue	Pigment Blue 15	74160	147–14–8, 12239–87–1, 27614–71–7, 68987–63–3, 16040–69–0	Limits as specified in existing chemical regulations in EU (see reg. (EC) No. 1709/2006 “REACH, Annex XVII) respectively EU member states Pigment Blue 15:2 and 15:4 are surface treated. Before using surface treated substances, manufacturers are well advised to contact their suppliers regarding composition and hazards.
41		Pigment Blue 16	74100	574–93–6	See footnote [d]
42		Pigment Blue 60	69800	81–77–6	
43	Green	Pigment Green 7	74260	1328–53–6	See footnote [b]
44		Pigment Green 36	74265	14302–13–7	
45		Natural Green 3	75810	8049–84–1, 11006–34–1	E 140 and E 141 Food grade, see current European legislation (Directive 2008/128/EC [15])

[a] The Colour Index is published by The Society of Dyers and Colourists, PO Box 244, Perkin House 82 Grattan Road, Bradford, West Yorkshire BD1 2JB, United Kingdom, www.colour-index.org. *Colourants* are classified using both their CI Generic name and their constitution number. These relate only to the “essential *colourant*” as defined by the Colour Index. The CAS numbers given are also taken from this database and again refer only to the “essential *colourant*”.

[b] This substance is restricted in Regulation (EC) No 1223/2009 [5] as follows: “Not to be used in eye products” or “Not to be used in products applied to mucous membranes”, as applicable.

[c] The insoluble barium, strontium and zirconium lakes, salts and pigments of these *colourants* are also permitted. According to Directive 2009/48/EC requirements on these elements need to be taken in consideration.

[d] This substance is restricted in Regulation (EC) No 1223/2009 [5] as follows: ” Rinse-off products”.

[e] Azo *colourants* are typically formed by a reaction sequence of diazotisation of a primary aromatic amine which is referred to as the diazo component, followed by reaction (aka coupling) with a compound having active methylene groups referred to as a coupling component.

Table A.2 — Non organic *colourants* which are commonly used in *finger paints*

No.	Colour	C.I. Generic Name[a]	CI number	CAS number	Restrictions, specifications and information
46	Yellow	Pigment Yellow 42	77492	51274–00–1	Iron oxide yellow E 172 Food grade, see current European legislation (Directive 2008/128/EC [15])
47	Red	Pigment Red 101	77491	1309–37–1	E 172 Food grade, see current European legislation (Directive 2008/128/EC [15])
48	Blue	Pigment Blue 29	77007	1317–97–1, 57455–37–5	Ultramarine
49	White	Pigment White 4	77947	1314–13–2	Zinc Oxide
50		Pigment White 6	77891	13463–67–7	E 171 Food grade, see current European legislation (Directive 2008/128/EC [15])
51		Pigment White 18	77220	207–439–9, 208–915–9	E 170 Chalk Food grade, see current European legislation (Directive 2008/128/EC [15]) Mixture Calcium carbonate, Magnesium carbonate
52		Pigment White 19	77004, 77005	8047–76–5	Aluminium silicate, hydrated
53		Silver	77820		E 174 Food grade, see current European legislation (Directive 2008/128/EC [15])
54		Pigment White 21	77120	7727–43–7	Blancfixe
55		Pigment White 25	77231	91315–45–6	Gypsum
56		Aluminium, zinc, magnesium and calcium stearates	-		
57	Black	Pigment Black 6	77266	1333–86–4	Carbon black food contact quality
58		Pigment Black 7	77266	1333–86–4	Carbon black food contact quality
59		Pigment Black 11	77499	12227–89–3	E 172 Food grade, see current European legislation (Directive 2008/128/EC [15])

60	Brown	Pigment Metal 3	77480	7440–57–5	E 175 Gold Food grade, see current European legislation (Directive 2008/128/EC [15])
61	Orange	Ferrous oxide	77489 Not in CI online	Ferrous oxide	E 172 (Mix) Food grade, see current European legislation (Directive 2008/128/EC [15])

[a] The Colour Index is published by The Society of Dyers and Colourists, PO Box 244, Perkin House 82 Grattan Road, Bradford, West Yorkshire BD1 2JB, United Kingdom, www.colour-index.org. *Colourants* are classified using both their CI Generic name and their constitution number. These relate only to the “essential *colourant*” as defined by the Colour Index. The CAS numbers given are also taken from this database and again refer only to the “essential *colourant*”.

Annex B
(normative)

List of preservatives allowed for use in *finger paints*

Table B.1 — Preservatives

Ref. nr.	**Substance**	**EC-Number**	**CAS-Number**	**Maximum allowed concentration**	**Limitations and requirements**
1	Benzoic acid sodium benzoate	200–618–2, 208–534–8	65–85–0, 532–32–1	0,5 % (acid)	
2	Ammonium benzoate, calcium benzoate, potassium benzoate, magnesium benzoate, MEA-benzoate, methyl benzoate, ethyl benzoate, propyl benzoate butyl benzoate, isobutyl benzoate, isopropyl benzoate, phenyl benzoate	217–468–9, 218–235–4, 209–481–3, 209–045–2, 224–387–2, 202–259–7, 202–284–3, 219–020–8, 205–252–7, 204–401–3, 213–361–6, 202–293–2	1863–63–4, 2090–05–3, 582–25–2, 553–70–8, 4337–66–0, 93–58–3, 93–89–0, 2315–68–6, 136–60–7, 120–50–3, 939–48–0, 93–99–2	0,5 % (acid)	
3	Propionic acid, ammonium propionate, calcium propionate, magnesium propionate, potassium propionate, sodium propionate	201–176–3, 241–503–7, 223–795–8, 209–166–0, 206–323–5, 205–290–4	79–09–4, 17496–08–1, 4075–81–4, 557–27–7, 327–62–8, 137–40–6	2 % (acid)	
4	Hexa-2,4-dienoic acid and its salts: Sorbic acid, calcium sorbate, sodium sorbate, potassium sorbate	203–768–7, 231–321–6, 231–819–3, 246–376–1	110–44–1, 7492–55–9, 7757–81–5, 24634–61–5	0,6 % (acid)	
5	Paraformaldehyde		30525–89–4	0,1 % (free formaldehyde)	Oral products limit
6	Biphenyl-2-ol (o-Phenylphenol) sodium o-phenylphenate, potassium o-phenylphenate, MEA o-phenylphenate	201–993–5 205–055–6, 237–243–9, 282–227–7	90–43–7, 132–27–4, 13707–65–8, 84145–04–0	0,2 % expressed as the phenol	
7	Pyrithione zinc	236–671–3	13463–41–7	0,5 %	
8	Inorganic sulphites and hydrogen-sulphites: Sodium sulfite, ammonium bisulfite, ammonium sulfite, potassium sulfite, potassium hydrogen sulfite, sodium bisulfite, sodium metabisulfite, potassium metabisulfite	231–821–4, 233–469–7, 233–484–9, 233–321–1, 231–870–1, 231–548–0, 231–673–0, 240–795–3	7757–83–7, 10192–30–0, 10196–04–0, 10117–38–1, 7773–03–7, 7631–90–5, 7681–57–4, 16731–55–8	0,2 % (as free SO_2)	
9	Chlorobutanol	200–317–6	57–15–8	0,5 %	
10	4-Hydroxybenzoic acid,	99–96–7,	202–804–9,	0,4 % (as acid)	

	methylparaben, potassium ethylparaben, potassium paraben, sodium methylparaben, sodium ethylparaben, ethylparaben, sodium paraben, potassium methylparaben, calcium paraben, phenylparaben	99–76–3, 36457–19–9, 16782–08–4, 5026–62–0, 35285–68–8, 120–47–8, 114–63–6, 2611–07–2, 69959–44–0, 17696–62–7	202–785–7, 253–048–1, 240–830–2, 225–714–1, 252–487–6, 204–399–4, 204–051–1, 247–464–2, 274–235–4, 241–698–9	for single ester, 0,8 % (as acid) for mixtures of esters	
11	3-Acetyl-6-methylpyran-2,4 (3H)-dione and its salts: Dehydroacetic acid, sodium dehydroacetate	208–293–9, 224–580–1	520–45–6, 4418–26–2, 16807–48–0	0,6 % (as acid)	
12	Formic acid, sodium formate	200–579–1, 205–488–0	64–18–6, 141–53–7	0,5 % (as acid)	
13	3,3’-Dibromo-4,4’-hexamethylenedioxydi-benzamidine and its salts (including isethionate) (Dibromohexamidine Isethionate)	299–116–4	93856–83–8	0,1 %	
14	Undec-10-enoic acid and its salts: Undecylenic acid, potassium undecylenate, sodium undecylenate, calcium undecylenate, TEA-undecylenate, MEA-undecylenate	203–965–8, 222–264–8, 215–331–8, 282–908–9, 260–247–7	112–38–9, 6159–41–7, 3398–33–2, 1322–14–1, 84471–25–0, 56532–40–2	0,2 % (as acid)	
15	5- Pyrimidinamine, 1,3-bis (2-ethylhexyl) hexahydro-5-methyl- (Hexetidine)	205–513–5	141–94–6	0,1 %	
16	2-Bromo-2-nitropropane-1,3-diol (Bronopol)	200–143–0	52–51–7	0,1 %	Avoid formation of nitrosamines
17	2,4-Dichlorobenzyl alcohol	217–210–5	1777–82–8	0,15 %	
18	1-(4-Chlorophenyl)-3-(3,4-dichlorophenyl) urea (Triclocarban)	202–924–1	101–20–2	0,2 %	Purity criteria:3,3’,4,4’-Tetrachloro-azobenzene < 1 ppm, 3,3’,4,4’-Tetrachloro-azoxybenzene < 1 ppm
19	5-Chloro-2- (2,4- dichlorophenoxy) phenol (Triclosan)	222–182–2	3380–34–5	0,3 %	
20	Chloroxylenol	201–793–8	88–04–0	0,5 %	
21	N,N″-methylenebis[N′-[3-(hydroxymethyl)-2,5-dioxoimidazolidin-4-yl]urea] (Imidazolidinyl urea)	254–372–6	39236–46–9	0,6 %	
22	Poly(methylene),.alpha.,.omega.-bis[[[(aminoiminomethyl)amino]iminomethyl] amino]-, dihydrochloride (Polyaminopropyl biguanide)		70170–61–5, 28757–47–3, 133029–32–0	0,3 %	
23	2-Phenoxyethanol	204–589–7	122–99–6	1,0 %	
24	Methenamine	100–97–0	202–905–8	0,15 %	
25	Methenamine 3-chloro-allylochloride (Quaternium-15)	223–805–0	4080–31–3	0,2 %	

26	1-(4-Chlorophenoxy)-1-(imidazol-1-yl)-3,3-dimethylbutan-2-one (Climbazole)	253–775–4	38083–17–9	0,5 %	
27	1,3-Bis (hydroxymethyl)-5,5-dimethylimidazolidine-2,4-dione (DMDM Hydantoin)	229–222–8	6440–58–0	0,6 %	
28	1-Hydroxy-4-methyl-6-(2,4,4-trimethylpentyl) 2-pyridon and its monoethanolamine salt (Piroctone Olamine)	272–574–2	50650–76–5, 68890–66–4	0,5 %	
29	2,2’-methylenebis(6-bromo-4-chlorophenol) (Bromochlorophene)	239–446–8	15435–29–7	0,1 %	
30	4-Isopropyl-m-cresol (o-Cymen-5-ol)	221–761–7	3228–02–2	0,1 %	
31	Mixture of 5-Chloro-2-methyl-isothiazol-3(2H)-one and 2-methylisothiazol-3(2H)-one with magnesium chloride and magnesium nitrate	247–500–7	26172–55–4, 2682–20–4, 55965–84–9	0,000 8 % (of a mixture in the ratio 3:1 of 5-chloro-2-methylisothiazol 3(2H)-one and 2-methylisothiazol-3 (2H)-one	a
32	2-methylisothiazol-3(2H)-one (MIT)	220–239–6	2682–20–4	0,01 %	[a]
33	2-Benzyl-4-chlorophenol (Chlorophene)	204–385–8	120–32–1	0,2 %	
34	2-Chloroacetamide	201–174–2	79–07–2	0,3 %	
35	N,N″-bis(4-chlorophenyl)-3,12-diimino-2,4,11,13-tetraazatetradecanediamidine and its digluconate, diacetate and dihydrochloride: Chlorhexidine, Chlorhexidine Diacetate, Chlorhexidine Digluconate, Chlorhexidine Dihydrochloride	200–238–7, 200–302–4, 242–354–0, 223–026–6	55–56–1, 56–95–1, 18472–51–0, 3697–42–5	0,3 % (as chlorhexidine)	
36	Alkyl (C 12–22) trimethyl ammonium bromide and chloride: Behentrimonium chloride, cetrimonium bromide, cetrimonium chloride, laurtrimonium bromide, laurtrimonium chloride, steartrimonium bromide, steartrimonium chloride	241–327–0, 200–311–3, 203–928–6, 214–290–3, 203–927–0, 214–294–5, 203–929–1	17301–53–0, 57–09–0, 112–02–7, 1119–94–4, 112–00–5, 1120–02–1, 112–03–8	0,1 %	
37	4,4-Dimethyl-1,3-oxazolidine	257–048–2	51200–87–4	0,1 %	The pH of the finished product may not be lower than 6.
38	N-(Hydroxymethyl)-N-(dihydroxymethyl-1,3-dioxo-2,5-imidazolidinyl-4)-N’-(hydroxymethyl) urea (Diazolidinyl Urea)	278–928–2	78491–02–8	0,5 %	
39	Benzenecarboximidamide, 4,4’-(1,6-hexanediylbis (oxy))bis- and its salts (including isethionate and p-hydroxybenzoate): Hexamidine, Hexamidine diisethionate, Hexamidine paraben	211–533–5, 299–055–3	3811–75–4, 659–40–5, 93841–83–9	0,1 %	
40	Pentane-1,5-dial (Glutaraldehyde,	203–856–5	111–30–8	0,1 %	

	Glutaral)				
41	3-(p-Chlorophenoxy)-propane-1,2 diol (Chlorphenesin)	203–192–6	104–29–0	0,3 %	
42	Sodium N-hydroxymethyl-glycinate	274–357–8	70161–44–3	0,5 %	
43	Benzenemethanaminium, N,N-dimethyl-N-[2-[2-[4-(1,1,3,3,-tetramethylbutyl)phenoxy] ethoxy] ethyl]-, chloride (Benzethonium Chloride)	204–479–9	121–54–0	0.1 %	

[a] For additional labelling requirements for mixtures containing substances with sensitizing properties, see Regulation (EC) No. 1272/2008 [1]. Mixtures containing substances with sensitizing properties in certain concentrations shall be labelled: “Contains (name of sensitising substance). May produce an allergic reaction”.

Annex C
(informative)

Ingredients used in the manufacture of *finger paints*

In accordance with current knowledge the following ingredients are used:

a) Binding agents:

- carboxymethylcellulose and its salts
- dextrins
- polyvinyl alcohol
- cellulose ethers
- starch
- tragacanth
- xanthan
- polyvinylpyrolidone
- casein
- alginates
- polyacrylates

b) Extenders:

- calcium carbonates (including whitening)
- calcium sulphate
- silicon dioxide
- magnesium oxide
- aluminium oxide (appropriate quality to meet toy migration limits for aluminium)
- magnesium silicate
- calcium silicate
- kaolin (china clay)
- bentonite
- barium sulphate, magnesium carbonate, aluminium trihydrate (appropriate quality to meet toy migration limits for aluminium), talc

c) Humectants:

- sodium polyphosphate
- fatty alcohol ethoxylates
- polyalkylene glycol ethers
- fatty acid taurid- sodium salt
- glycerols
- polyglycols
- propylene glycol
- capillaire syrup (commercial blends of soluble saccharides), provided they do not impart sweetness

d) Surfactants:

- sodium salts of edible fatty acids
- polyalkylene glycol ethers
- polywaxes

Annex D
(normative)

Method for the detection of certain azo *colourants* and determination of free primary aromatic amines

D.1 General

For the detection of certain azo *colourants*, the sample is treated with sodium dithionite in a citrate buffer (pH 6) at 70 °C in a sealed vessel. Upon reductive cleavage, the resultant amines are extracted with MTBE by means of a “kieselguhr” type SPE column, e.g. Chromabond® XTR, or equivalent[1]. The ether extract is carefully concentrated with a rotary evaporator or an equivalent sample concentrator and the residue is dissolved in acetonitrile or other suitable solvent, depending upon the detection/determination procedure to be used.

The detection/determination of amines resulting either from the reductive cleavage method or already present in the sample as free primary aromatic amines is performed by high performance liquid chromatography with a diode-array detector (HPLC/DAD) or by capillary gas chromatography with mass-selective detector (GC-MS).

The amines shall be identified by at least one of the chromatographic separation techniques described in this annex. Unless an unequivocal identification is achieved (e.g. by using GC-MS and comparing retention times with known standards), confirmation of positive results shall be achieved by a suitable alternative separation technique (to avoid possible misinterpretation from, for example, isomers of the amines to be identified).

NOTE 1 Some amines may be thermally unstable and cannot be determined by gas chromatography.

The quantification of the amines is performed by HPLC/DAD or GC-MS.

NOTE 2 Some of the amines are cleaved under the reductive conditions in D.6.2 according to Table D.1:

Table D.1

Amine compound	**Cleavage products**
o-Aminoazotoluene	*o*-Toluidine, 2-Methyl-*p*-phenylendiamine
2-Amino-4-nitrotoluene	4-Methyl-*m*-phenylenediamine
4-Amino-azo-benzene	*p*-Phenylenediamine, Aniline

4-Aminoazobenzene is reductively cleaved to *p*-phenylenediamine and aniline; *o*-aminoazotoluene is reductively cleaved to 2-methyl-*p*-phenylenediamine and *o*-toluidine; and 2-Amino-4-nitrotoluene is reduced to 4-methyl-*m*-phenylenediamine.

A prohibited azo *colourant* is deemed to be present in the *finger paint* if, on reductive cleavage, one or more of the amines listed in Tables 1 and 2 is present in a concentration exceeding 30 mg/kg.

Each primary aromatic amines listed in Table 1 is deemed to be determinable at levels exceeding 5 mg/kg.

---

[1] This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

D.2 Reagents

Reagent-grade chemicals are to be used, if nothing else is specified.

D.2.1 Methanol

D.2.2 Acetonitrile

D.2.3 *tert*-Butyl methyl ether (MTBE)

D.2.4 Citrate/sodium hydroxide buffer, *c*(trisodium citrate) = 0,06 mol/l, pH 6, preheated to 70 °C or 37 °C: Dissolve 12,6 g citric acid monohydrate and 6,4 g sodium hydroxide in 900 ml water. Adjust the volume to 1 L.

NOTE 'Ready-for-use' solution, Merck-Nr. 1.09437, has been found suitable[2].

D.2.5 Sodium dithionite solution, freshly dissolved in water, ρ = 200 mg/ml

D.2.6 Porous, granular “kieselguhr” SPE column

NOTE Chromabond® XTR has been found suitable[2].

D.2.7 Anhydrous sodium sulphate

D.2.8 Certified amine standards, primarily those listed in Tables 1 and 2

NOTE The amines in Tables 1 and 2 are human carcinogens or cancer suspect agents (Cat. 1A and 1B). The handling of these chemicals requires the utmost care and commensurate safety measures.

D.2.9 Internal standards (IS) for gas chromatography

D.2.9.1 IS 1: 2,4,5-Trichloroaniline, CAS No. 636-30-6

D.2.9.2 IS 2: 4-Amino-2-methylquinoline, CAS No. 6628-04-2

D.2.9.3 IS 3: Tributylphosphate, CAS No. 126-73-8

D.2.10 Standard solutions

D.2.10.1 Stock solution of aromatic amines

Prepare a stock solution containing 100 mg/l of each aromatic amine (D.2.8) in methanol (D.2.1). This solution shall be stored in the absence of light at (−18 ± 2) °C.

D.2.10.2 Calibration solutions

Prepare six calibration solutions in the range 0,1 mg/l to 5,0 mg/l by dilution of the aromatic amines stock solutions (D.2.10.1) into (100 ± 0,1) ml volumetric flasks using MBTE (D.2.3). Before making up to the final volume, add 0,1 ml of internal standard (D.2.10.3) to each calibration solution in order to obtain a final internal standard concentration of 1 mg/l. The calibration solutions are ready for GC-MS analysis.

D.2.10.3 Internal standard solution

---

[2] This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Prepare a stock solution of each internal standard (D.2.9.1 to D.2.9.3) at 10,0 mg/l in methanol (D.2.1).

D.2.10.4 Recovery solution of aromatic amines

Prepare a recovery solution containing 10 mg/l of each aromatic amine (D.2.10.1) in methanol (D.2.1). This solution shall be stored in the absence of light at (−18 ± 2) °C.

The stability of all calibration solutions should be checked regularly. These should be stable for up to 6 months when stored in the dark at (−18 ± 2) °C.

NOTE The solvent used will depend on the chromatographic method chosen for analysis.

D.3 Apparatus

Ordinary laboratory equipment, and

D.3.1 50 ml conical flask of temperature-resistant glass with tight-fitting cap

D.3.2 Water bath, capable of maintaining a temperature of (37 ± 2) °C and (70 ± 2) °C.

D.3.3 Column made from glass or polypropylene, 25 mm to 30 mm internal diameter, 140 mm to 150 mm length, filled with about 20 g porous, granular “kieselguhr” SPE material, fitted on the outlet with a glass fibre filter (or commercial SPE column).

NOTE Chromabond® XTR (Macherey-Nagel Catalogue No. 730 507) has been found suitable[3].

D.3.4 Vacuum rotary evaporator or equivalent low temperature sample concentration system

D.3.5 Pipettes 10 ml, 5 ml, 2 ml, 1 ml

D.4 Instrumentation

The analysis shall be performed using equipment selected from the following list

D.4.1 HPLC with gradient-elution and DAD

D.4.2 GC with MS

D.5 Sampling procedure

Homogenize the sample by stirring thoroughly.

D.6 Procedure

D.6.1 Sample preparation

For both the detection of certain azo *colourants*, and the determination of ‘free’ primary aromatic amines, a representative sample of approximately 1,0 g is weighed accurately into a 50 ml conical flask (D.3.1).

D.6.2 Reductive cleavage of azo *colourants*

---

[3] This information is given for the convenience of users of this European Standard and does not constitute an endorsement by CEN of the product named. Equivalent products may be used if they can be shown to lead to the same results.

Approximately, 15 ml of buffer (D.2.4), preheated to (70 ± 2) °C, is added to the sample. The conical flask is tightly closed and after brief vigorous shaking to homogenize the contents is kept at (70 ± 2) °C for (30 ± 2) min.

To achieve reductive cleavage of the azo *colourants* (3,0 ± 0,01) ml of sodium dithionite solution (D.2.5) is added to the conical flask. The conical flask is immediately tightly sealed, thoroughly shaken and kept again at (70 ± 2) °C for another (30 ± 2) min, and then cooled to ambient temperature within 2 min.

D.6.3 Extraction of soluble amines

For the determination of free aromatic amines (see 4.5.1.1 and 4.5.1.2), the reductive cleavage (D.6.2) is not carried out. Instead, approximately 20 ml of the buffer solution (D.2.4) preheated only to (37 ± 2) °C is added to the sample. The conical flask is tightly closed and after brief vigorous shaking to homogenize the contents is kept at (37 ± 2) °C about 30 min.

D.6.4 Solid phase extraction and concentration of amines

The solution from D.6.2 or D.6.3, as appropriate, is poured onto the SPE column without rinsing the conical flask with water or buffer. The aqueous phase is left for 30 min to absorb onto the column. The amines are then extracted twice with approximately 40 ml of MTBE as described below.

Before extracting the SPE column, the first 40 ml of MTBE is divided into portions of 2 × 10 ml and 1 × 20 ml for rinsing the conical flask. 10 ml of ether is added to the conical flask, it is closed and shaken vigorously. After allowing 30 min for the water phase to absorb onto the column, the MTBE is decanted from the conical flask onto the column leaving behind any residual water in the conical flask (Note: addition of 0,2 g of anhydrous sodium sulphate to dry the MTBE). The eluant is collected in a suitable glass container for evaporation. This operation is repeated with the remaining 10-ml and 20-ml portions of *MTBE*. Finally, the second 40 ml is poured directly onto the column.

The MTBE extract is carefully concentrated at a maximum temperature of 25 °C using a rotary evaporator with vacuum, or equivalent sample concentrator, to about 1 ml (do not allow the solution to go to dryness!). If MTBE is not the required chromatographic solvent, the remainder of the ether is carefully removed under a light flow of inert gas and the residue made up to 2,0 ml with acetonitrile in a graduated test tube. If MTBE is the required chromatographic solvent, the residue is quantitatively transferred to a small graduated tube and the volume made up to (2,0 ± 0,1) ml using washings from the container used in the rotary evaporator flask or sample concentrator.

During solvent removal, considerable losses of amines may occur if the process is not closely controlled (i.e. vacuum too high, temperature too high, high inert gas flow). The solvent removal should be performed under subdued light (avoid direct sunlight and if possible, direct fluorescent lightening).

If taken to dryness, each residue is immediately dissolved in (2,0 ± 0,1) ml of a suitable solvent, e.g. methanol in an amber glass flask, and subsequently analysed. If the analysis cannot be carried out immediately, the sample shall be stored at (–20 ± 2) °C.

The quantification of the amines is conducted using HPLC/DAD or GC-MS. If using GC-MS, internal standards shall be used.

NOTE Certain amines, e.g. 2,4-Toluenediamine and 2,4-Diaminoanisole, have a very low stability. If the extraction and concentration procedure is not carried out expediently, partial or total loss of amines can occur.

D.6.5 Chromatography

D.6.5.1 General

The following conditions have been found suitable for the detection/determination of primary aromatic amines. The analysis of *finger paints* shall be performed in accordance with the methods of analysis described in this

European Standard. Alternative methods of analysis or modifications to the procedures described 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.

NOTE It is reported that some amines are heat sensitive and may breakdown on heating when injected onto a GC column requiring an alternative detection technique to be used.

D.6.5.2 High pressure liquid chromatography (HPLC)

Eluent 1:	Acetonitrile
Eluent 2:	0,575 g ammonium dihydrogenphosphate + 0,7 g disodium hydrogenphosphate in 1 000 ml water, pH 6,9
Column:	HyPurity Advance 250 mm x 3 mm; 5 µm or equivalent ThermoQuest Catalogue No. 21005–0035
Flow rate:	0,5 ml/min
Gradient:	0 min 15 % eluent 1, within 45 min linear to 75 % eluent 1
Column temperature:	40 °C
Injection volume:	5,0 µl
Detection:	DAD, full spectral scan
Quantification:	at 240 nm, 280 nm and 305 nm

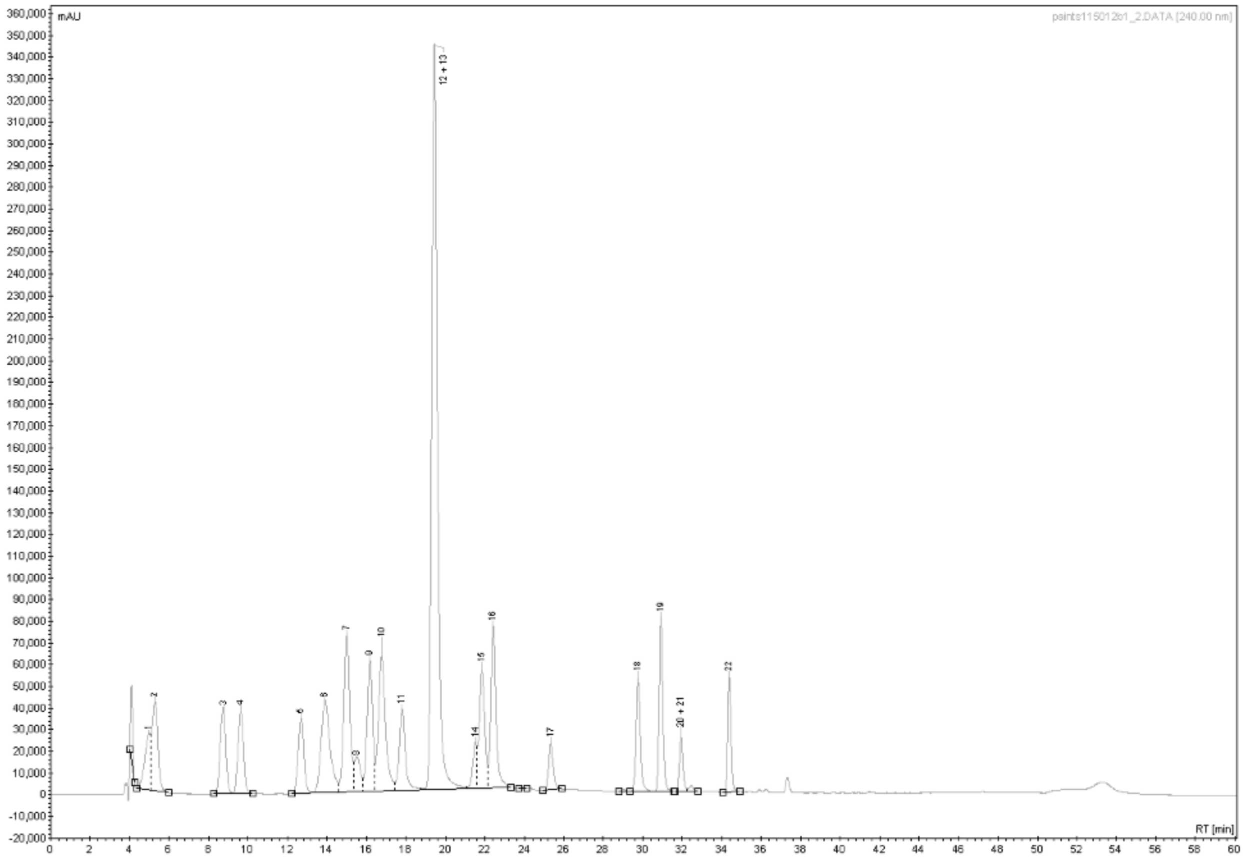

Figure D.1 — Example of HPLC-DAD chromatogram of 22 mixed aromatic amine standard at 240 nm using the conditions in D.6.5.2

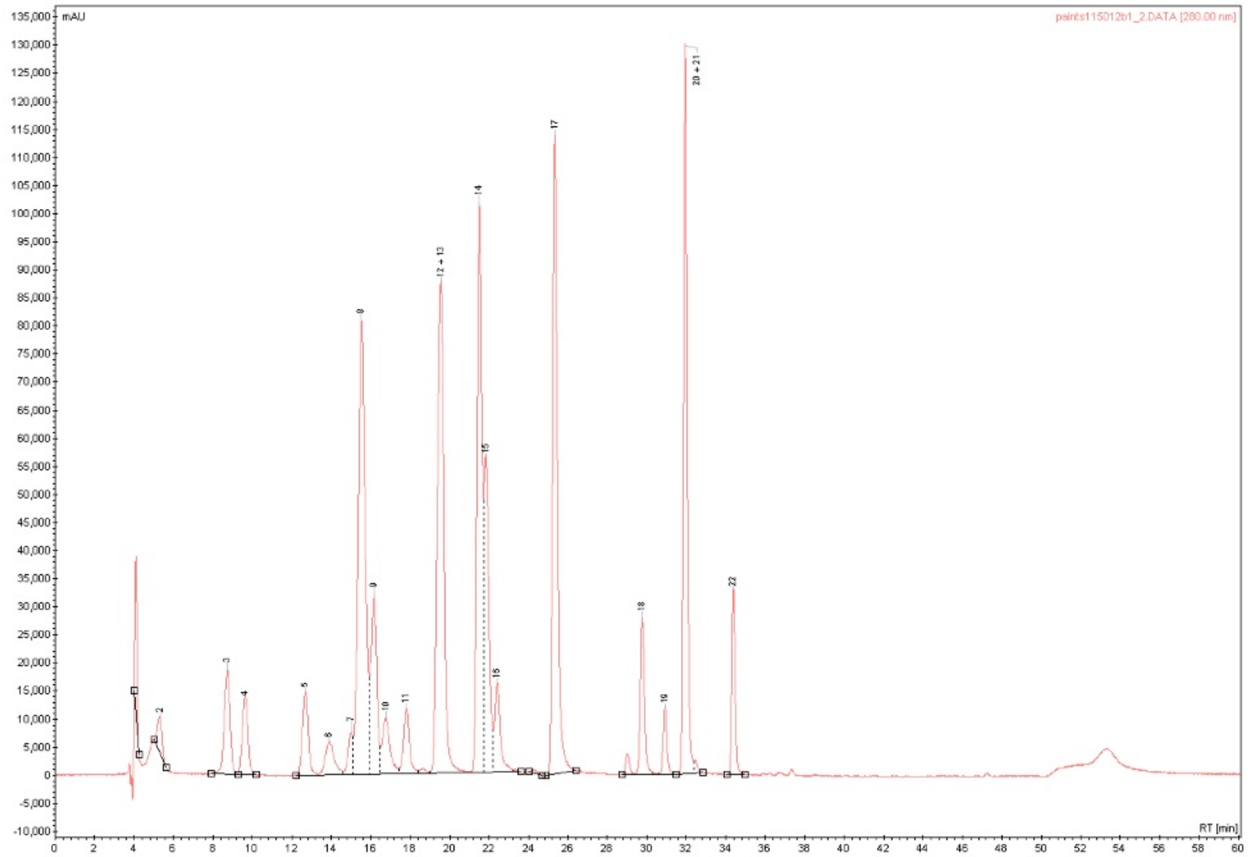

Figure D.2 — Example of HPLC-DAD chromatogram of 22 mixed aromatic amine standard at 280 nm using the conditions in D.6.5.2

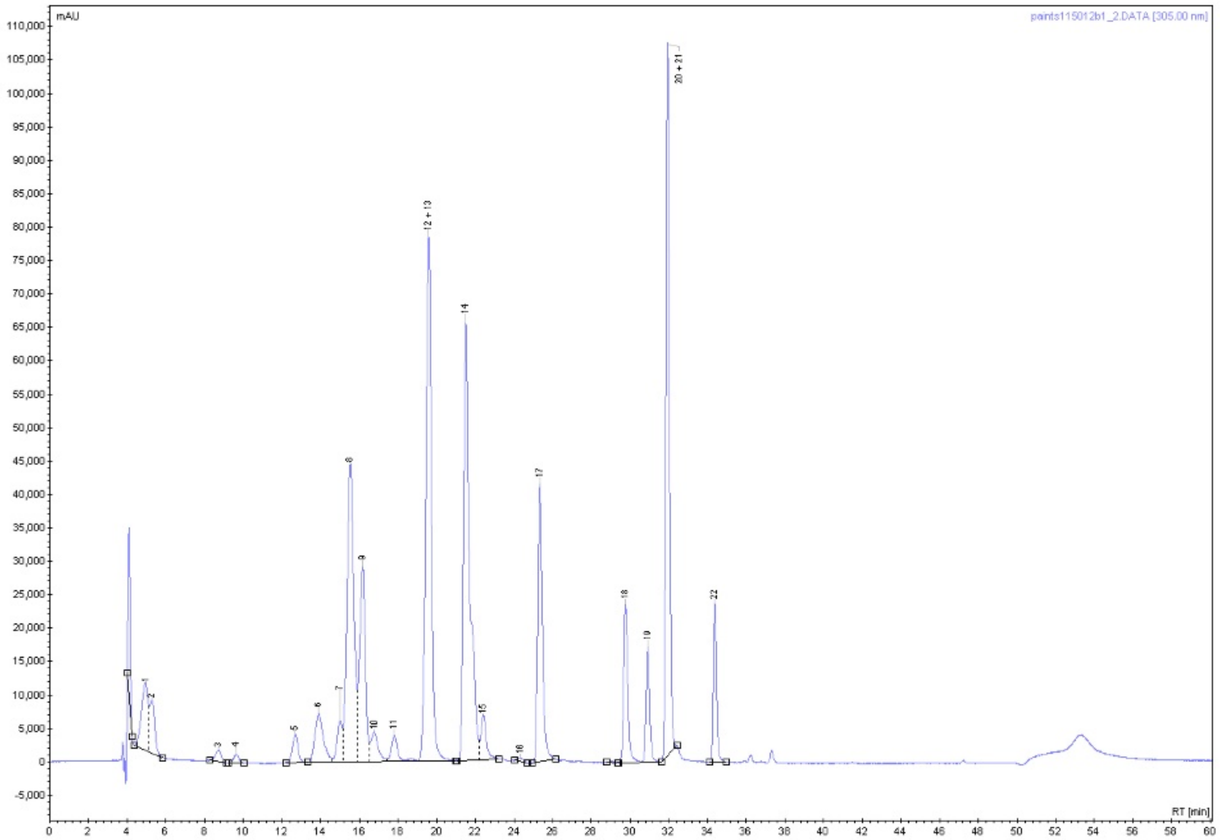

Figure D.3 — Example of HPLC-DAD chromatogram of 22 mixed aromatic amine standard at 305 nm using the conditions in D.6.5.2

Table D.2 — Key to retention time for LC-DAD at 280nm

No	Retention time min	Primary aromatic amine	No	Retention time min	Primary aromatic amine
1	4,97	4-Methoxy-m-phenylenediamine	12	19,4	4-Chloro-o-toluidine
2	5,29	4-Methyl-m-phenylenediamine	13	19,4	2-Naphthylamine
3	8,75	4-Methoxy-aniline	14	21,52	3,3'-Dimethoxybenzidine
4	9,64	o-Toluidine	15	21,85	3,3'-Dimethylbenzidine
5	12,69	6-Methoxy-m-toluidine	16	22,43	4,4'-Thiodianiline
6	13,89	4,4'-Oxydianiline	17	25,33	4,4-Methylenedi-o-toluidine
7	14,99	Benzidine	18	29,01	4-Aminobiphenyl
8	15,50	4-Chloroaniline	19	30,80	p-Aminoazobenzene
9	16,10	5-Nitro-o-toluidine	20	32,45	2,2'-Dichloro-4,4-methylenedianiline
10	16,7	4,4'-Methylenedianiline	21	32,45	3,3'-Dichlorobenzidine
11	17,8	2,4,5-Trimethylaniline	22	34,37	o-Aminoazotoluene

D.6.5.3 Gas Chromatography (GC) with mass spectrometry

Capillary column: RTX5 Amine or equivalent type, length: 30 m, internal diameter: 0,25 mm, film thickness: 0,25 µm, preferably deactivated for amines or equivalent

Injector: split/splitless

Injection temperature: 220 °C

Carrier: Helium

Temp. programme: 60 °C (3 min), 60 °C to 280 °C (7 °C/min), 280 °C (4 min),

280 °C to 300 °C (10 °C/min), 300 °C (2 min)

Injection volumes: 1,0 µl, split 1:15

A single quadrupole MS instrument is recommended with ionization by electronic impact at 70 eV.

GC interface temperature: 250 °C

Source temperature: 200 °C

In SIM mode, the fragment ions allow quantification by using one of the three ions as the target quantification ion and the remaining two ions as qualifiers identified in Table D.3.

NOTE T1 is considered as the target ion for quantification.

The time spent on each ion (dwell time) shall be the same for all ions within a given window. The m/z values are rounded. Exact values should be used as SIM parameters.

Table D.3 — List of ions for quantification

Primary aromatic amine	Target ion m/z	Qualifier 1 m/z	Qualifier 2 m/z
o-Toluidine	106	107	77
4-Chloroaniline	127	129	92
4-Methoxy aniline	108	123	80
6-Methoxy-m-toluidine	122	137	94
2,4,5-Trimethylaniline	135	120	134
4-Chloro-o-toluidine	106	141	140
4-Methyl-m-phenylendiamine	121	122	94
4-Methoxy-m-phenylenediamine	123	138	95
2-Naphthylamine	143	115	116
5-Nitro-o-toluidine	152	106	78
4-Aminobiphenyl	169	168	170
p-Aminoazobenzene	92	197	120
4,4'-Oxydianiline	200	108	171
Benzidine	184	183	185
4,4-Methylenedianiline	198	197	106
o-Aminoazotoluene	106	225	134
4,4-Methylenedi-o-toluidine	226	211	225
3,3-Dimethylbenzidine	212	213	106
4,4'-Thiodianiline	216	184	215
3,3'-Dichlorobenzidine	252	254	126
2,2-Dichloro-4,4-methylenedianiline	231	266	195
3,3-Dimethoxybenzidine	244	201	229
2,4,5-Trichloroaniline	195		
4-Amino-2-methylquinoline	158		
Tributyl phosphate	99		

D.6.5.4 Maximum permitted tolerances

The relative intensities of the ion for quantification against respectively the two qualifiers, expressed as a percentage of the intensity of the most intense ion, shall correspond to those of the calibration standard solutions, at comparable concentrations, measured under the same conditions, within the tolerances described Table D.4.

The calibration standard used as reference should be at the middle of the calibration curve.

Table D.4 — Maximum permitted tolerances for relative ion intensities

Relative intensity % of base ion intensity	**Relative range of the response**
> 50 %	±10 %
> 20 % - 50 %	±15 %
> 10 % - 20 %	±20 %
≤ 10 %	±50 %

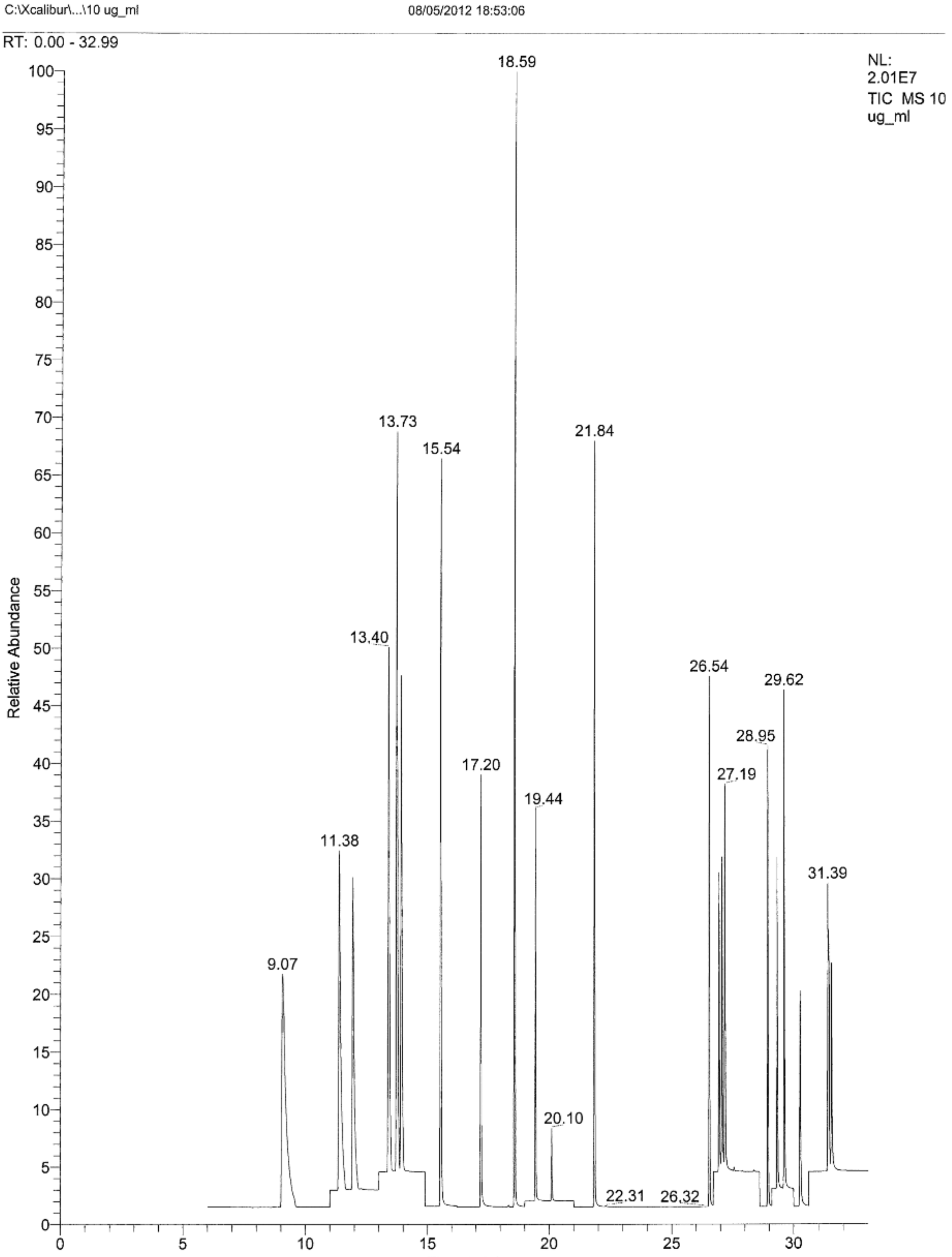

Figure D.4 — Example of GC-MS chromatogram of 22 mixed aromatic amines

Table D.5 — Key to retention time for GC-MS

No	Retention time (min)	Primary aromatic amine	No	Retention time (min)	Primary aromatic amine
1	9,07	o-Toluidine	12	26,54	p-Aminoazobenzene
2	11,38	4-Methoxy-aniline	13	26,94	4,4'-Oxydianiline
3	11,93	4-Chloroaniline	14	27,07	Benzidine
4	13,40	6-Methoxy-m-toluidine	15	27,19	4,4'-Methylenedianiline
5	13,73	2,4,5-Trimethylaniline	16	28,95	o-Aminoazotoluene
6	13,92	4-Chloro-o-toluidine	17	29,33	4,4-Methylenedi-o-toluidine
7	15,53	4-Methyl-m-phenylenediamine	18	29,62	3,3'-Dimethylbenzidine
8	17,20	4-Methoxy-m-phenylenediamine	19	30,26	4,4'-Thiodianiline
9	18,58	2-Naphthylamine	20	31,39	3,3'-Dichlorobenzidine
10	19,43	5-Nitro-o-toluidine	21	31,42	2,2'-Dichloro-4,4'-methylenedianiline
11	21,84	4-Aminobiphenyl	22	31,53	3,3'-Dimethoxybenzidine

D.6.6 Verification of analytical system

To check the analytical procedure, add (0,2 ± 0,01) ml of the recovery solution (D.2.10.4) and 1,0 ml methanol into a conical flask (D.3.1) containing approximately 15 ml buffer preheated to (70 ± 2) °C and follow the procedure from D.6.2 (second sentence). The recovery rate of the amines will normally be expected to be ≥ 70 % with the exception of 4-methyl-m-phenylenediamine, 4-methoxy-m-phenylenediamine, 2-naphthylamine, p-aminoazobenzene and o- aminoazotoluene where the recoveries have been found to be between 10 % and 50 %.

D.7 Calculation

The amine concentration is calculated from the area of each amine peak and is given as mass portion *w,* in mg/kg, of single amine component in test material according to Formula (D.1):

$$w = \frac{A_s \cdot C_c \cdot V_s}{A_c \cdot E_S} \tag{D.1}$$

where

A_s is the peak area of the amine in the sample solution in area units;

A_c is the peak area of the amine in the calibration solution in area units;

C_c is the concentration of the amine in the calibration solution (µg/ml);

E_s is the initial mass of sample in the end volume (g);

V_s is the volume of test solution obtained in D.6.4 used for chromatographic analysis (ml).

If an internal standard has been used, the mass portion of amine component (w) is given as:

$$w = \frac{A_{IS(S)}}{A_{IS(C)}} \tag{D.2}$$

where

w is the mass portion of a single amine component in test material, in mg/kg;

$A_{\mathrm{IS(S))}}$ is the peak area of the internal standard in the sample solution in area units;

$A_{\mathrm{IS(C))}}$ is the peak area of the internal standard in the calibration solution in area units.

D.8 Precision

D.8.1 Linearity

The correlation coefficient shall be > 0,990.

D.8.2 Limits of Detection (LOD) and Quantification (LOQ)

The LODs and the LOQs for method using GC-MS and LC-DAD instruments are shown in Tables D.6 and D.7.

Table D.6 — Limits of Detection (LOD) and Quantification (LOQ) Using GC-MS

Primary aromatic amine	LOD mg/L	LOQ mg/kg	Primary aromatic amine	LOD mg/L	LOQ mg/kg
o-Toluidine	0,02	0,5	p-Aminoazobenzene	0,02	0,5
4-Methoxy-aniline	0,02	0,5	4,4'-Oxydianiline	0,05	1,0
4-Chloroaniline	0,02	0,5	Benzidine[a]	0,05	0,5
6-Methoxy-m-toluidine	0,02	0,5	4,4'-Methylenedianiline	0,05	1,0
2,4,5-Trimethylaniline	0,02	0,2	o-Aminoazotoluene	0,02	0,5
4-Chloro-o-toluidine[a]	0,02	0,5	4,4-Methylenedi-o-toluidine	0,05	1,0
4-Methyl-m-phenylenediamine	0,02	0,2	3,3'-Dimethylbenzidine	0,04	1,0
4-Methoxy-m-phenylenediamine	0,05	0,5	4,4'-Thiodianiline	0,04	1,0
2-Naphthylamine[a]	0,01	0,2	3,3'-Dichlorobenzidine	0,05	1,0
5-Nitro-o-toluidine	0,05	1,0	2,2'-Dichloro-4,4-methylenedianiline	0,05	1,0
4-Aminobiphenyl[a]	0,01	0,2	3,3'-Dimethoxybenzidine	0,05	1,0

[a] Primary aromatic amines that shall not be determinable when tested in accordance with the test method in Annex D.

Table D.7 — Limits of Detection (LOD) and Quantification (LOQ) Using LC-DAD at 240nm

Primary aromatic amine	LOD mg/L	LOQ mg/kg	Primary aromatic amine	LOD mg/L	LOQ mg/kg
o-Toluidine	1,0	2,0	p-Aminoazobenzene	1,0	2,0
4-Methoxy-aniline	1,0	2,0	4,4'-Oxydianiline	1,0	2,0
4-Chloroaniline	1,0	2,0	Benzidine	-	-
6-Methoxy-m-toluidine	1,0	2,0	4,4'-Methylenedianiline	1,0	2,0
2,4,5-Trimethylaniline	1,0	2,0	o-Aminoazotoluene	1,0	2,0
4-Chloro-o-toluidine	-	-	4,4-Methylenedi-o-toluidine	1,0	2,0
4-Methyl-m-phenylenediamine	1,0	2,0	3,3'-Dimethylbenzidine	1,0	2,0
4-Methoxy-m-phenylenediamine	1,0	2,0	4,4'-Thiodianiline	1,0	2,0
2-Naphthylamine	-	-	3,3'-Dichlorobenzidine	1,0	2,0
5-Nitro-o-toluidine	1,0	2,0	2,2'-Dichloro-4,4-methylenedianiline	1,0	2,0
4-Aminobiphenyl	-	-	3,3'-Dimethoxybenzidine	1,0	2,0

D.8.3 Repeatability and reproducibility data for soluble aromatic amines

Each primary aromatic amine was determined in a single batch of *finger paint* containing twenty-two aromatic amines each spiked at a concentration of 1 mg/kg using D.6.3 by two independent laboratories on 6 replicate samples using GC-MS and shown in Table D.8.

Table D.8 — Repeatability and reproducibility data for soluble aromatic amines by GC-MS

Primary aromatic amine	Conc mg/kg	Lab 1 mg/kg	Lab 2 mg/kg
o-Toluidine	1,00	1,03 ± 0,17	0,81 ± 0,13
4-Methoxy-aniline	1,00	1,28 ± 0,16	0,68 ± 0,10
4-Chloroaniline	1,00	1,04 ± 0,13	0,63 ± 0,09
6-Methoxy-m-toluidine	1,00	1,17 ± 0.09	0,35 ± 0,07
2,4,5-Trimethylaniline	1,00	0.89 ± 0,14	0,44 ± 0,05
4-Chloro-o-toluidine	1,00	1,11 ± 0,18	0,87 ± 0,04
p-Aminoazobenzene	1,00	0,82 ± 0,10	0,16 ± 0,01
4,4'-Oxydianiline	1,00	0,83 ± 0,10	0,95 ± 0,07
Benzidine	1,00	0,72 ± 0,09	0,74 ± 0,06
4,4'-Methylenedianiline	1,00	0,72 ± 0,09	0,60 ± 0.06
o-Aminoazotoluene	1,00	0,99 ± 0,09	0,12 ± 0,01
4,4-Methylenedi-o-toluidine	1,00	1,02 ± 0,09	0,16 ± 0,01
4-Methyl-m-phenylenediamine	1,00	n.d.[a]	0,15 ± 0,05
4-Methoxy-m-phenylenediamine	1,00	n.d.[a]	0,11 ± 0,03
2-Naphthylamine	1,00	0,69 ± 0,03	0,18 ± 0,01

Primary aromatic amine	Conc mg/kg	Lab 1 mg/kg	Lab 2 mg/kg
5-Nitro-o-toluidine	1,00	1,62 ± 0,03	0,69 ± 0,03
4-Aminobiphenyl	1,00	0,80 ± 0,14	0,47 ± 0,02
3,3'-Dimethylbenzidine	1,00	0,91 ± 0,17	0,24 ± 0,01
4,4'-Thiodianiline	1,00	0,94 ± 0,07	0,22 ± 0,03
3,3'-Dichlorobenzidine	1,00	1,28 ± 0,15	0,83 ± 0,06
2,2'-Dichloro-4,4-methylenedianiline	1,00	1,33 ± 0,12	0,77 ± 0.06
3,3'-Dimethoxybenzidine	1,00	1,36 ± 0,21	0,24 ± 0,01
[a] n.d. = not detected.			

D.8.4 Repeatability and reproducibility data for reductively cleaved aromatic amines

Each cleaved aromatic amine was determined in a single batch of *finger paint* containing twenty-two aromatic amines each spiked at a concentration of 0,5 mg/kg using D.6.2 by two independent laboratories on six replicate samples using GC-MS and shown in Table D.9.

Table D.9 — Repeatability and reproducibility of cleaved aromatic amines by GC-MS

Reductively cleaved aromatic amine	Conc mg/kg	Lab 1 mg/kg	Lab 2 mg/kg
o-Toluidine	0,5	0,73 ± 0,09	0,33 ± 0,03
4-Methoxy-aniline	0,5	0,48 ± 0,02	0,32 ± 0.03
4-Chloroaniline	0,5	0,42 ± 0,03	0,30 ± 0.05
6-Methoxy-m-toluidine	0,5	0,51 ± 0,02	0,19 ± 0,02
2,4,5-Trimethylaniline	0,5	0,32 ± 0,04	0,24 ± 0,02
4-Chloro-o-toluidine	0,5	0,40 ± 0,03	0,41 ± 0,04
4-Methyl-m-phenylenediamine	0,5	n.d.	0,15 ± 0,02
4-Methoxy-m-phenylenediamine	0,5	n.d.	0,19 ± 0,02
2-Naphthylamine	0,5	0,28 ± 0,03	0,17 ± 0,01
5-Nitro-o-toluidine	0,5	n.d.	0,28 ± 0,02
4-Aminobiphenyl	0,5	0,36 ± 0,03	0,22 ± 0,01
p-Aminoazobenzene	0,5	n.d.	0,17 ± 0.01
4,4'-Oxydianiline	0,5	0,72 ± 0.05	0,78 ± 0,10
Benzidine	0,5	0,55 ± 0.03	0,53 ± 0.07
4,4'-Methylenedianiline	0,5	n.d.	0,34 ± 0.06
o-Aminoazotoluene	0,5	n.d.	0,14 ± 0,01
4,4-Methylenedi-o-toluidine	0,5	0,74 ± 0,04	0,20 ± 0,01
3,3'-Dimethylbenzidine	0,5	0,55 ± 0.04	0,24 ± 0,02
4,4'-Thiodianiline	0,5	0,77 ± 0.05	0,23 ± 0,01
3,3'-Dichlorobenzidine	0,5	0,71 ± 0.07	0,41 ± 0.04
2,2'-Dichloro-4,4'-methylenedianiline	0,5	0,78 ± 0.06	0,39 ± 0.04
3,3'-Dimethoxybenzidine	0,.5	0,83 ± 0.06	0,22 ± 0.02
n.d. not detected			

D.8.5 Recovery

D.8.5.1 Recovery of 22 soluble aromatic amines

Recovery was determined in a single batch of *finger paint* containing twenty-two aromatic amines each spiked at a concentration of 1,0 mg/kg using D.6.2 by two independent laboratories on replicate samples using GC-MS and shown in Table D.10.

Table D.10 — Recovery of 22 primary aromatic amines

Primary aromatic amine	% Recovery (Average of Lab 1 and 2)	Primary aromatic amine	% Recovery (Average of Lab 1 and 2)
o-Toluidine	92	p-Aminoazobenzene	49
4-Methoxy-aniline	98	4,4'-oxydianiline	89
4-Chloroaniline	84	Benzidine	73
6-Methoxy-m-toluidine	76	4,4'-Methylenedianiline	66
2,4,5-Trimethylaniline	67	o-Aminoazotoluene	56
4-Chloro-o-toluidine	99	4,4-Methylenedi-o-toluidine	59
4-Methyl-m-phenylenediamine	< 10	3,3'-Dimethylbenzidine	58
4-Methoxy-m-phenylenediamine	< 10	4,4'-Thiodianiline	58
2-Naphthylamine	44	3,3'-Dichlorobenzidine	106
5-Nitro-o-toluidine	116	2,2'-Dichloro-4,4'-methylenedianiline	105
4-Aminobiphenyl	64	3,3'-Dimethoxybenzidine	80

D.8.5.2 Verification data

Verification data was determined using D.6.6 (Verification of analytical system) for twenty-two primary aromatic amines as shown in Table D.11.

Table D.11 — Verification data

Primary aromatic amine	% Recovery	Primary aromatic amine	% Recovery
o-Toluidine	125	p-Aminoazobenzene	24
4-Methoxy-aniline	116	4,4'-Oxydianiline	112
4-Chloroaniline	112	Benzidine	97
6-Methoxy-m-toluidine	113	4,4'-Methylenedianiline	102
2,4,5-Trimethylaniline	102	o-Aminoazotoluene	42
4-Chloro-o-toluidine	107	4,4-Methylenedi-o-toluidine	109
4-Methyl-m-phenylenediamine	58	3,3'-Dimethylbenzidine	96
4-Methoxy-m-phenylenediamine	14	4,4'-Thiodianiline	109
2-Naphthylamine	68	3,3'-Dichlorobenzidine	104
5-Nitro-o-toluidine	117	2,2'-Dichloro-4,4'-methylenedianiline	100
4-Aminobiphenyl	86	3,3'-Dimethoxybenzidine	122

NOTE The data presented is based on a single laboratory.

D.9 Report

Any report of analysis shall refer to this method and include:

D.9.1 Precise sample description/identification/article number

D.9.2 Type and date of sampling

D.9.3 Date of submission and date of analysis

D.9.4 Data on procedure (separation and detection)

D.9.5 Data on quantification procedure

D.9.6 Calculated results

D.9.7 A statement as to whether or not a proscribed azo *colourant* has been detected (see 4.2.2)

D.9.8 A statement as to whether the requirements for primary aromatic amines have been met (see 4.5.1)

D.9.9 Measurement uncertainty (where relevant)

D.10 Additional Information

The effects of evaporation on amine recovery were studied by removing the extracting solvent, MTBE, to dryness at 50 °C. The resulting recoveries were less than 40 % for the target amines, giving an indication of the effects that evaporation to dryness has on amine recovery. The method requires the evaporation of the solvent to approximately 5 ml by rotary evaporation equivalent low temperature sample concentration system. This volume is transferred to a 10-ml test tube and reduced to a final extract volume of (1 ± 0,01) ml with nitrogen at room temperature.

Due to the polar nature of some amines, clean chromatography conditions are essential when undertaking this analysis.

Annex E
(normative)

Method for the determination of hexachlorobenzene, polychlorinated biphenyls and benzo[α]pyrene

E.1 Principle

Solvent extractable benzo[α]pyrene (B[α]P), hexachlorobenzene (HCB) and polychlorinated biphenyl (PCB) congeners are determined in *finger paints* by mixing with anhydrous sodium sulphate and extracting with either a 1:1 mixture of cyclohexane and acetone for HCB and PCBs or 2:1 mixture of toluene and acetone for B[α]P using a soxhlet extractor. The extract is cleaned up and concentrated prior to analysis using gas chromatography with a mass spectrometric detection (GC-MS) using the internal standard method of calibration.

E.2 Standards, reagents and solvents

Reagent-grade chemicals are to be used, unless otherwise specified.

The stability of all calibration solutions should be checked regularly. These should be stable for up to 6 months when stored in the dark at (5 ± 2) °C.

E.2.1 Hexane, analytical grade

E.2.2 Cyclohexane, analytical grade

E.2.3 Acetone, analytical grade

E.2.4 2,2,4-trimethylpentane, analytical grade

E.2.5 Toluene, analytical grade

E.2.6 Cyclohexane (E.2.2):acetone (E.2.3) 1:1 v/v mixture

E.2.7 Toluene (E.2.5):acetone (E.2.3) 2:1 v/v mixture

E.2.8 Anhydrous sodium sulphate

E.2.9 Standards

E.2.9.1 Hexachlorobenzene (HCB), CAS No 118-74-1, > 99 %

E.2.9.2 Certified PCB standard mixture or individual PCB congeners

PCB congener 11 (3,3'-Dichlorobiphenyl), CAS No: 2050-67-1

PCB congener 28 (2,4,4'-Trichlorobiphenyl), CAS No: 7012-37-5

PCB congener 52 (2,2',5,5'-Tetrachlorobiphenyl), CAS No: 35693-99-3

PCB congener 101 (2,2',4,5,5'-Pentachlorobiphenyl), CAS No: 37680-73-2

PCB congener 118 (2,3',4,4',5-Pentachlorobiphenyl), CAS No: 31508-00-6

PCB congener 138 (2,2',3,4,4',5'-Hexachlorobiphenyl), CAS No: 35065-28-2

PCB congener 153 (2,2',4,4',5,5'-Hexachlorobiphenyl), CAS No: 35065-27-1

PCB congener 180 (2,2',3,4,4',5,5'-Heptachlorobiphenyl), CAS No:35065-29-3

PCB congener 209 (Decachlorobiphenyl), CAS No: 2051-24-3

E.2.9.3 Benzo[α]pyrene (B[α]P), CAS No: 50-32-8, > 99 %

E.2.10 Internal standards

E.2.10.1 HCB $^{13}C_6$, CAS No: 118-74-1

E.2.10.2 PCB congener 101 $^{13}C_{12}$, CAS No: 37680-73-2

E.2.10.3 PCB congener 138 $^{13}C_{12}$, CAS No: 35065-28-2

E.2.10.4 B [α]P d_{12}, CAS No: 63466-71-7

E.2.11 Primary standard solutions

E.2.11.1 Prepare a 100 mg/L HCB primary standard solution (E.2.9.1) in 2,2,4-trimethylpentane (E.2.4).

E.2.11.2 Prepare a primary standard solution (E.2.9.2) containing the nine PCB congeners each at a concentration of 100 mg/l in 2,2,4-trimethylpentane (E.2.4).

E.2.11.3 Prepare a 200 mg/L B[α]P primary standard solution (E.2.9.3) in 2,2,4-trimethylpentane (E.2.4).

E.2.12 Internal standard solutions

E.2.12.1 HCB $^{13}C_6$

Prepare a stock solution of internal standard (E.2.10.1) at 10mg/l in 2,2,4-trimethylpentane (E.2.4).

E.2.12.2 PCB congener 101 $^{13}C_{12}$ and PCB congener 138 $^{13}C_{12}$

Prepare a stock solution of each internal standard (E.2.10.2) at 10mg/l in 2,2,4-trimethylpentane (E.2.4).

E.2.12.3 PCB congener 138 $^{13}C_{12}$

Prepare a stock solution of each internal standard (E.2.10.3) at 10mg/l in 2,2,4-trimethylpentane (E.2.4).

E.2.12.4 B[α]P d_{12}

Prepare a stock solution of internal standard (E.2.10.4) at 1mg/l in 2,2,4-trimethylpentane (E.2.4).

E.2.13 Calibration standards

E.2.13.1 HCB and PCB congeners calibration standards

Prepare six calibration solutions in the concentration range 0,02 mg/L to 1 mg/L by dilution of the primary standard HCB (E.2.11.1) and PCB mixed congener (E.2.11.2) standard solutions in 2,2,4-trimethylpentane (E.2.4). Each calibration solution shall also contain 0,5 mg/l of the HCB $^{13}C_6$ (E.2.12.1), 0,25 mg/l PCB congener 101 $^{13}C_{12}$ (E.2.12.2) and PCB congener 138 $^{13}C_{12}$ (E.2.12.3) internal standards.

E.2.13.2 B[α]P calibration standard

Prepare six calibration solutions in the concentration range 0,005 mg/L to 0,02 mg/L by dilution of the primary B[α]P (E.2.11.3) standard solution in 2,2,4-trimethylpentane. Each calibration solution shall also contain 0,02 mg/L of the B[α]P d_{12} (E.2.12.4) internal standard.

E.2.14 Recovery solutions

E.2.14.1 HCB recovery solution

Prepare a recovery solution containing 10 mg/l of HCB in 2,2,4-trimethylpentane (E.2.4).

E.2.14.2 Mixed PCB congener recovery solution

Prepare a recovery solution containing 1 mg/l of each polychlorinated biphenyl congener in 2,2,4-trimethylpentane (E.2.4).

E.2.14.3 B [α]P recovery solution

Prepare a recovery solution containing 0,1 mg/l of B[α]P in 2,2,4-trimethylpentane (E.2.4).

E.3 Apparatus

Standard laboratory glassware and equipment and the following shall be used. Apparatus should be free from contamination before use. Glassware should be rinsed with acetone and then hexane before use and allowed to drain.

E.3.1 Amber coloured glass bottle approximately 40 mL volume with tight-fitting screw cap

E.3.2 Analytical balance, capable of weighing to 4 decimal places

E.3.3 Glass microfibre thimble, 33**Ø** x 100 mm

E.3.4 Soxhlet extractor with siphon cup to hold a 33**Ø** x 100 mm thimble

E.3.5 Water cooled condenser

E.3.6 250 ml round bottom flask

E.3.7 Spark proof heating mantle

E.3.8 Sample concentration system with nitrogen gas stream

E.3.9 Solid phase extraction column made from either glass or polypropylene, 25 mm to 30 mm internal diameter, 140 mm to 150 mm length, filled with about 20 g porous, granular “kieselguhr” SPE material (or commercial SPE column).

E.4 Instrumentation

E.4.1 A gas chromatograph-mass spectrometric system fitted with a capillary column and glass-lined injector, capable of operating in electron impact mode with selected ion monitoring which permits different groups of ions to be monitored at selected time intervals during the analysis.

E.4.2 Analytical capillary column, for example HT-8, 50 m length x 0,22 mm ID x 0,25 mm film thickness 8 % phenyl polysiloxane-carborane or equivalent

E.5 Sampling

The *finger paint* is mixed vigorously using a glass rod to ensure a homogeneous test portion can be sampled.

Finger paints are mainly water based and so once a container has been opened an immediate test portion should be taken. Also care in repeated sampling over time from a container shall be taken as the composition of the test portion may vary through loss of constituents to the atmosphere.

E.6 Procedure

E.6.1 General

The sample preparation is the same for all analytes using the solvent and solid phase extraction stages. However, to achieve the lower limits specified for B[α]P the concentration stage has been separately described to HCB and PCB congeners.

E.6.2 Sample preparation

A screw cap amber bottle (E.3.1) is filled with approximately 6 g of anhydrous sodium sulphate (E.2.8). Weigh accurately (1,0 ± 0,1) g of the test portion onto the surface of the anhydrous sodium sulphate and record the weight (M). Add an additional 6g of anhydrous sodium sulphate to cover the test portion and tightly close the screw cap.

Shake the bottle vigorously for (60 ± 5) s to mix the test portion and sodium sulphate. Remove the cap and allow the mixture to stand for 24 h ± 1 h under standard laboratory conditions ensuring the mixture will not come into contact with any possible contaminants.

After 24 h, replace the screw cap onto the amber bottle and shake vigorously again for a further (60 ± 5) s.

The mixture should consist of particles no larger than 1 mm to 5 mm, where larger particles have formed a glass rod can be used to break up the larger particles.

E.6.3 Solvent extraction

E.6.3.1 Solvent extraction of soluble HCB and PCBs

Transfer the mixture in E.6.2 into a glass microfibre thimble (E.3.3) and add a filter paper disc to the top of the thimble. Insert the thimble into a soxhlet extractor (E.3.4) and connect to a water cooled condenser (E.3.5). Add approximately 175 ml of cyclohexane/acetone (E.2.6) into a 250 ml round bottom flask (E.3.6) and connect to the soxhlet extractor, place on a heating mantle (E.3.7) and reflux gently for > 6 h.

Allow sufficient time for the cyclohexane/acetone to cool before disconnecting the soxhlet extractor and gently evaporate the cyclohexane/acetone extract to approximately 5-10 ml using a rotary evaporator or equivalent sample concentration system (E.3.8).

Transfer the cyclohexane/acetone extract into a graduated glass tube washing with 2 × 3 ml cyclohexane and evaporate the extract to approximately 3 ml under a gentle stream of nitrogen (E.3.8).

E.6.3.2 Solvent extraction of soluble B[α]P

Transfer the mixture in E.6.2 into a glass microfibre thimble (E.3.3) and add a filter paper disc to the top of the thimble. Insert the thimble into a soxhlet extractor (E.3.4) and connect to a water cooled condenser (E.3.5). Add approximately 200 ml of toluene/acetone (E.2.7) into a 250 ml round bottom flask (E.3.6) and connect to the soxhlet extractor, place on a heating mantle (E.3.7) and reflux gently for > 6 h.

Allow sufficient time for the toluene/acetone to cool before disconnecting the soxhlet extractor and gently evaporate the toluene/acetone extract to approximately 3 ml using a rotary evaporator or equivalent sample concentration system (E.3.8).

Transfer the toluene/acetone extract into a graduated glass tube washing with 1 ml toluene and evaporate the extract to approximately 3ml under a gentle stream of nitrogen (E.3.8).

E.6.4 Solid phase extraction

E.6.4.1 Solid phase extraction of HCB and PCBs

Transfer the extract obtained in E.6.3 onto a column containing kieselguhr (E.3.9) and leave to stand for approximately 1 h. Then wash the column with 3 × 5ml portions of cyclohexane (E.2.2) collecting the eluent into a suitable glass vessel. To the glass vessel and eluent add approximately 6 ml of 2,2,4-trimethylpentane (E.2.4).

E.6.4.2 Solid phase extraction of B[α]P

Transfer the extract obtained in E.6.3.2 onto a column containing kieselguhr (E.3.9) and leave to stand for approximately 1 h. Then wash the column with 3 × 5 ml portions of toluene (E.2.5) collecting the eluent into a suitable glass vessel.

E.6.5 Sample concentration for determining HCB and PCB congeners

Evaporate the eluent obtained in E.6.4 to approximately 3 ml using the sample concentrator (E.3.8) and quantitatively transfer into a graduated test tube and make to the 6 ml mark with 2,2,4-trimethylpentane. Transfer 1 ml to a sample vial and add 0,025 ml of the HCB internal standard solution (E.2.12.1) and 0,05 ml of each PCB internal standard solutions (E.2.12.2 and E.2.12.3) for quantitative determination by GC-MS.

E.6.6 Sample concentration for determining B[α]P

Evaporate the eluent obtained in E.6.4 to approximately 3 ml using the sample concentrator (E.3.8) and quantitatively transfer into a graduated test tube and make to the 4 ml mark with 2,2,4-trimethylpentane. Transfer 1 ml to a sample vial and add 0,05 ml of the B[α]P internal standard solution (E.2.12.4) for quantitative determination by GC-MS.

E.6.7 Gas chromatography conditions

Set up the gas chromatography-mass spectrometer detection system according to manufacturer's instructions, to monitor the selected mass fragmentation ions for HCB, PCB congeners, and B[α]P.

The following conditions have been shown to be suitable for HCB and PCB congeners.

Capillary column:	HT-8 or equivalent type, length: 50 m, internal diameter: 0,25 mm, film thickness: 0,22 µm,
Injector:	split/splitless
Injection temperature:	220 °C
Carrier:	Helium
Injection volumes:	1,0 µl, split 1:15
Detection:	Mass Spectrometry

Temp. Programme for

HCB and PCB congeners: 60 °C (hold 2 min), 60 °C to 170 °C (3,5 °C/min), 300 °C (12 min)

Temp. Programme for B[α]P: 60 °C (hold 1 min), 60 °C to 170 °C (30 °C/min), (hold 1 min), 170 °C to 300 °C (20 (30 °C/min), (hold 25 min)

E.6.8 Mass spectrometry

A single quadrupole MS instrument is recommended with ionization by electronic impact at 70eV.

E.6.9 SIM mode

E.6.9.1 General

In SIM mode, the fragment ions allow quantification by using one of the three ions as the target quantification ion and the remaining two ions as qualifiers identified in Tables E.1 and E.2.

NOTE Target ion 1 is considered as the target ion for quantification.

The time spent on each ion (dwell time) shall be the same for all ions within a given window. The m/z values are rounded. Exact values should be used as SIM parameters.

Table E.1 — List of ions for quantification

Component	Target ion (m/z)	Qualifier 1 (m/z)	Qualifier 2 (m/z)
HCB	284	249	286
PCB 11	222	224	152
PCB 28	256	258	186
PCB 52	292	290	294
PCB 101	326	328	324
PCB 118	326	328	324
PCB 153	360	362	290
PCB 138	360	362	290
PCB 180	396	394	324
PCB 209	498	500	496
HCB $^{13}C_6$	294		
PCB 101 $^{13}C_{12}$	338		
PCB 138 $^{13}C_{12}$	372		

Table E.2 — List of ions for quantification

Component	Target ion (m/z)	Qualifier 1 (m/z)	Qualifier 2 (m/z)
B[α]P	255	250	253
B[α] d_{12}	264		

E.6.9.2 Maximum permitted tolerances

The relative intensities of the ion for quantification against respectively the two qualifiers, expressed as a percentage of the intensity of the most intense ion, shall correspond to those of the calibration standard solutions, at comparable concentrations, measured under the same conditions, within the tolerances described Table E.3.

The calibration standard used as reference should be at the middle of the calibration curve.

Table E.3 — Maximum permitted tolerances for relative ion intensities

Relative intensity % of base ion intensity	**Relative range of the response**
> 50 %	±10 %
> 20 % - 50 %	±15 %
> 10 % - 20 %	±20 %
≤ 10 %	±50 %

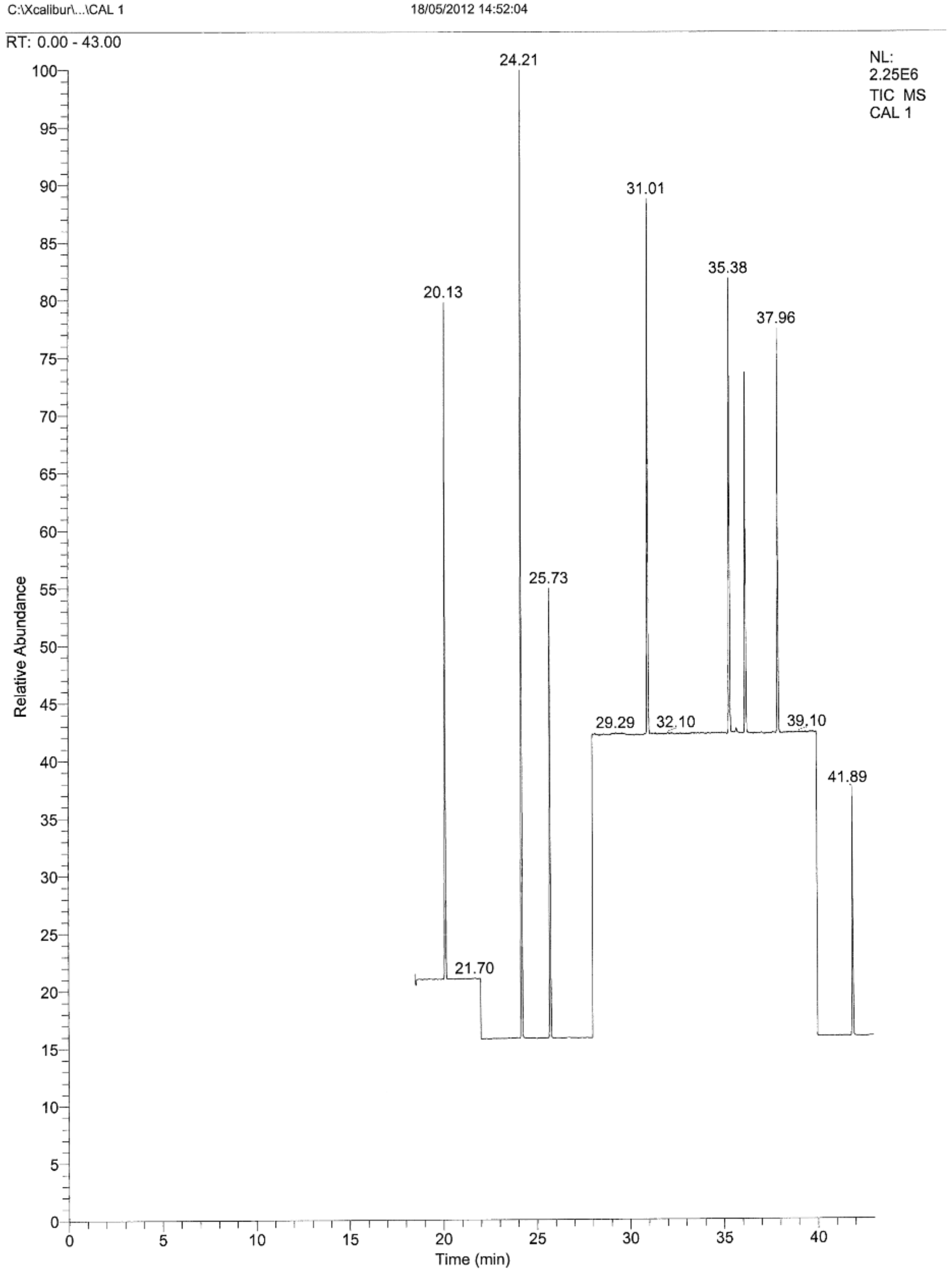

Figure E.1 — Example of chromatographic separation of HCB and 9 PCB Congeners

Table E.4 — Key to retention time for HCB and 9 PCB Congeners

Component	**Key retention time (min)**
HCB	19,65
PCB 11	20,76
PCB 28	23,57
PCB 52	25,03
PCB 101	30,14
PCB 118	34,43
PCB 153	35,28
PCB 138	36,98
PCB 180	40,87
PCB 209	49,00

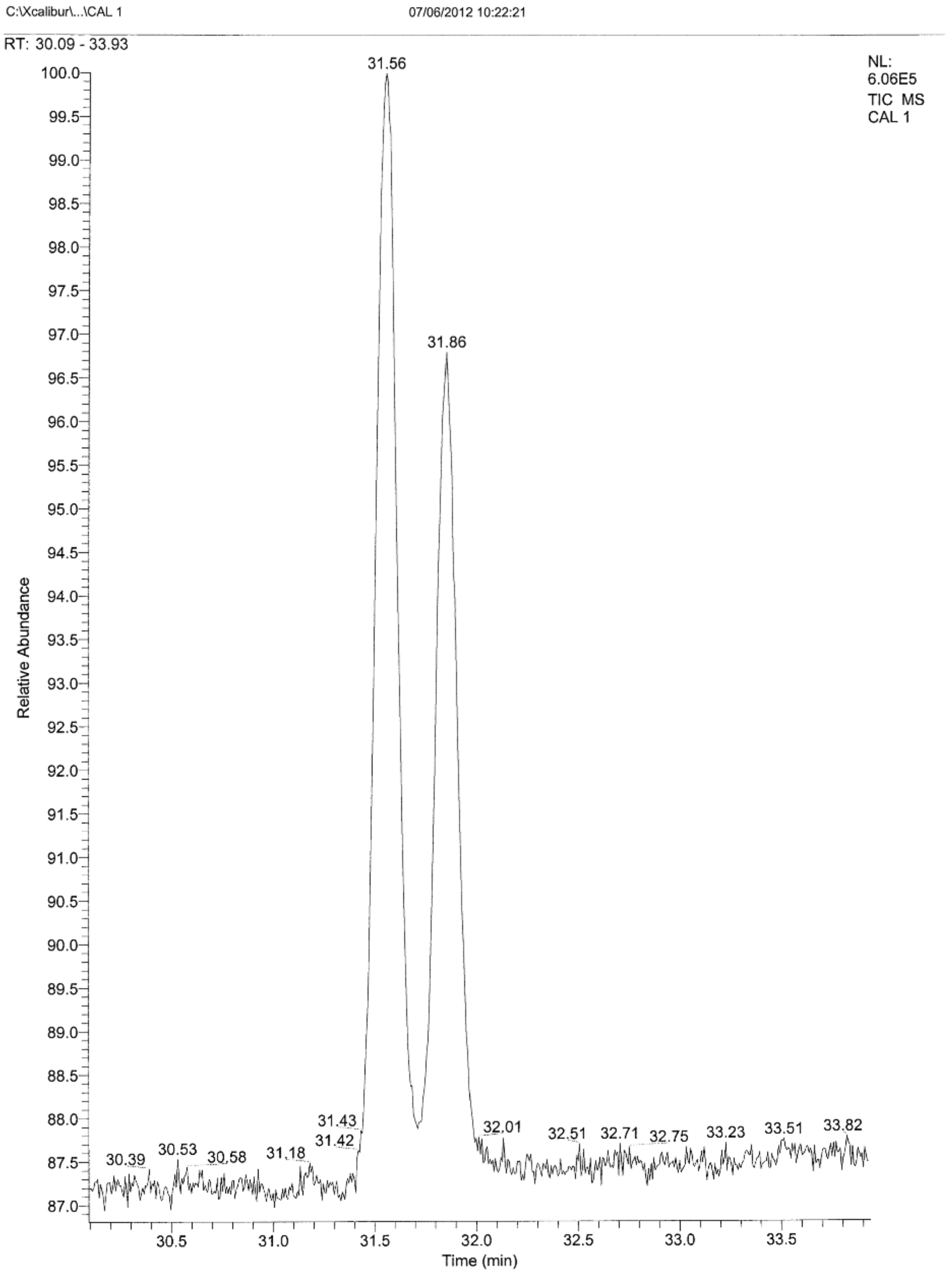

Figure E.2 — Example of chromatographic separation of B[α]P and B[α]P d12

Table E.5 — Key to retention time for benzo[α]pyrene and benzo[α]pyrene d12

Component	Key retention time (min)
B[α]P	31,86
B[α]P d12	31,56

E.6.9.3 Verification of analytical system

To check the analytical procedure for HCB, add 0,5 ml of a recovery solution (E.2.14.1) onto the sodium sulphate as described in E.6.2 and follow the relevant procedure from E.6.3 to E.6.6.

To check the analytical procedure for PCB congeners, add 0,3 ml of a recovery solution (E.2.14.2) onto the sodium sulphate as described in E.6.2 and follow the relevant procedure from E.6.3 to E.6.6.

The recovery rate of the hexachlorobenzene and the PCB congeners should be at least 70 %.

To check the analytical procedure for B[α]P, add 0,2 ml of a recovery solution (E.2.14.3) onto the sodium sulphate as described in E.6.2 and follow the relevant procedure from E.6.3 to E.6.6.

The recovery rate of B[α]P shall be at least 70 %.

E.7 Calculation

E.7.1 General

For HCB, PCB congeners and B[α]P determination, the internal standard calibration method is used. An *R* value is determined, which is the ratio between the intensity from the ion used for quantification and the internal standard ion. Prepare a calibration curve by plotting the concentration of HCB, PCB and B[α]P calibration solutions against the corresponding *R* value. Determine the concentration C of each analyte in mg/l in the sample solution directly from the calibration curve.

E.7.2 The concentration of PCBs in the original sample at each level of chlorination is given by:

$$C_{LC} = \frac{C}{M} \cdot V mg kg^{-1} \qquad \text{(E.1)}$$

where

C_{LC} is the concentration of PCB congeners at each level of chlorination (where n is 1 to 7) in the sample, in mg/kg;

M is the mass of sample extracted, in g;

V is the volume of sample solution, in ml;

C is the concentration PCB congener in sample solution, in mg/l.

$$C_{Total} = \sum_{1}^{7} C_{Lc} \qquad \text{(E.2)}$$

where

C_{Total} is the concentration of all PCB congeners determined in the original sample, in mg/kg;

C_{LC} is the concentration of PCB congeners at each level of chlorination (where n is 1 to 7) in the sample, in mg/kg.

E.7.3 The concentration of HCB in the original sample is given by:

$$C_{HCB} = \frac{C}{M} \cdot V mgkg^{-1} \qquad \text{(E.3)}$$

where

C_{HCB} is the concentration of HCB in the original sample, in mg/kg;

M is the mass of sample extracted, in g;

V is the volume of sample solution, in ml;

C is the concentration HCB in sample solution, in mg/l.

E.7.4 The concentration of B[α]P in the original sample is given by:

$$C_{B[\alpha]P} = \frac{C}{M} \cdot V mgkg^{-1} \qquad \text{(E.4)}$$

where

$C_{\mathrm{B[\alpha]P}}$ is the concentration of B[α]P in the original sample, in mg/kg;

M is the mass of sample extracted, in g;

V is the volume of sample solution, in ml;

C is the concentration B[α]P in sample solution, in µg/ml.

The B[α]P concentration is calculated from the area of the B[α]P peak and is given as mass portion w, in mg/kg, of B[α]P in test material according to Formula (E.5):

$$w = \frac{A_S \cdot C_C \cdot V_S}{A_C \cdot E_S} \qquad \text{(E.5)}$$

where

w is the mass portion of B[α]P in test material, in mg/kg;

A_S is the peak area of the B[α]P in the sample solution, in area units;

A_C is the peak area of the B[α]P in the calibration solution, in area units;

C_C is the concentration of the B[α]P in the calibration solution (µg/ml);

V_S is the volume of test solution obtained in D.6.4 used for chromatographic analysis, in ml;

E_S is the initial mass of sample in the end volume, in g;

If an internal standard has been used, the mass portion of amine component (w) is given as;

$$w = \frac{A_{IS(S)}}{A_{IS(C)}} \qquad \text{(E.6)}$$

where

w is the mass portion of B[α]P;

$A_{IS(S}$ the peak area of the internal standard in the sample solution in area units;

$A_{IS(C)}$ is the peak area of the internal standard in the calibration solution in area units.

E.8 Precision

E.8.1 Linearity

The correlation coefficient shall be > 0,990.

E.8.2 Limits of detection (LOD) and Quantification (LOQ)

The LODs and the LOQs for the method using GC-MS are shown in Table E.6.

Table E.6 — Limits of Detection (LOD) and Quantification (LOQ) using GC-MS

Component	**LOD** mg/L	**LOQ** mg/kg
HCB	0,003	0,04
PCB-28	0,005	0,07
PCB-52	0,005	0,07
PCB-101	0,005	0,07
PCB-118	0,005	0,07
PCB-138	0,005	0,07
PCB-153	0,005	0,07
PCB-180	0,005	0,07
B[α]P	0,002	0,05

E.8.3 Repeatability and reproducibility data for HCB, PCB congeners and B[α]P

HCB, PCB congeners and B[α]P was determined in a single batch of *finger paint* spiked at the concentration limits of 5 mg/kg for HCB, 2 mg/kg for the sum of seven PCB congeners (~0,29 mg/kg individual PCB congener) and 0,05 mg/kg for B[α]P using 6 replicate samples by two independent laboratories using GC-MS and shown in Table E.7.

Table E.7 — Repeatability and Reproducibility data for HCB, PCB and B[α]P

Component	**Conc** mg/kg	**Lab 1** mg/kg	**Lab 2** mg/kg
HCB	5,00	3,40 ± 0,25	4.09 ± 0,13
(1) PCB-28	0,29	0,27 ± 0,01	0,22 ± 0,01
(2) PCB-52	0,29	0,25 ± 0,01	0,24 ± 0,01
(3) PCB-101	0,29	0,26 ± 0,01	0,26 ± 0,01
(4) PCB-118	0,29	0,28 ± 0,01	0,29 ± 0,01
(5) PCB-138	0,29	0,27 ± 0,01	0,26 ± 0,01
(6) PCB-153	0,29	0,26 ± 0,01	0,28 ± 0,01
(7) PCB 180	0,29	0,27 ± 0,01	0,36 ± 0,01
Sum of PCBs (1–7)	2,00	1,85 ± 0,07	1,91 ± 0,07
B[α]P	0,050	0,037 ± 0,002	0,039 ± 0,001

NOTE The repeatability data are a good indicator of the performance of the method within a laboratory. Although comparable values were obtained in the two laboratories, for reproducibility values this will require further verification.

E.8.4 Recovery

Recovery was determined in a single batch of *finger paint* spiked at the concentration limits of 5 mg/kg for HCB, 2 mg/kg for the sum of seven PCB congeners (0,28 mg/kg individual PCB congener) and 0,05 mg/kg for B[α]P using 6 replicate samples by two independent laboratories using GC-MS and shown in Table E.8.

Table E.8 — Recovery of HCB, PCB and B[α]P

Component	**% Recovery (Average of Lab 1 and 2)**
HCB	75
(1) PCB-28	86
(2) PCB-52	84
(3) PCB-101	89
(4) PCB-118	97
(5) PCB-138	91
(6) PCB-153	94
(7) PCB 180	108
(1–7) Sum of PCB Congeners	94
B[α]P	77

E.9 Report

Any report of analysis shall refer to this method and include:

E.9.1 Precise sample description/identification/article number

E.9.2 Type and date of sampling

E.9.3 Date of submission and date of analysis

E.9.4 Data on procedure (separation and detection)

E.9.5 Data on quantification procedure

E.9.6 Calculated results

E.9.7 Measurement uncertainty (where relevant)

E.10 Additional information

There are 209 congeners of polychlorinated biphenyls (PCB) possible but there is no information in the literature regarding the levels and the congeners likely to be present in *finger paints* and also little published data on the materials used in their formulations; that available for organic pigments suggests that the manufacturing conditions have a strong influence on the PCBs which may inadvertently be present. The method allows for the quantification of any of the potential congeners, by including, as far as possible, one member of each congener family as calibration standards. (see E.2.9.2). Table E.9 shows all other PCB-homologues.

Table E.9— Nomenclature of PCB-homologues according to IUPAC [14]

PCB No	Structure	PCB No	Structure
Monochlorobiphenyls		47	2,2',4,4'
1	2	48	2,2',4,5
2	3	49	2,2',4,5'
3	4	50	2,2',4,6
Dichlorobiphenyls		51	2,2',4,6'
4	2,2'	52	2,2',5,5'
5	2,3	53	2,2',5,6'
6	2,3’	54	2,2',6,6'
7	2,4	55	2,3,3',4
8	2,4'	56	2,3,3',4'
9	2.5	57	2,3,3',5
10	2,6	58	2,3,3',5'
11	3,3'	59	2,3,3',6
12	3,4	60	2,3,4,4'
13	3,4'	61	2,3,4,5
14	3,5	62	2,3,4,6
15	4,4'	63	2,3,4',5
Trichlorobiphenyls		64	2,3,4',6
16	2,2',3	65	2,3,5,6
17	2,2',4	66	2,3',4,4'
18	2,2',5	67	2,3',4,5
19	2,2’,6	68	2,3',4,5'
20	2,3,3'	69	2,3',4,6
21	2,3,4	70	2,3',4',5
22	2,3,4'	71	2,3,4',6
23	2,3,5	72	2,3',5,5'
24	2,3,6	73	2,3',5',6
25	2,3',4	74	2,4,4',5
26	2,3',5	75	2,4,4',6
27	2,3',6	76	2',3,4,5
28	2,4,4'	77	3,3',4,4'
29	2,4,5	78	3,3',4,5
30	2,4,6	79	3,3',4,5'
31	2,4',5	80	3,3',5,5'
32	2,4',6	81	3,4,4',5
33	2',3,4	**Pentachlorobiphenyls**	
34	2',3,5	82	2,2',3,3',4
35	3,3',4	83	2,2',3,3',5
36	3,3',5	84	2,2',3,3',6
37	3,4,4'	85	2,2',3,4,4'

38	3,4,5	86	2,2',3,4,5
39	3,4',5	87	2,2',3,4,5'
Tetrachlorobiphenyls		88	2,2',3,4,6
40	2,2',3,3'	89	2,2',3,4,6'
41	2,2',3,4	90	2,2',3,4',5
42	2,2',3,4'	91	2,2',3,4',6
43	2,2',3,5	92	2,2',3,5,5'
44	2,2,3,5'	93	2,2',3,5,6
45	2,2',3,6	94	2,2',3,5,6'
46	2,2',3,6'	95	2,2',3,5',6
Pentachlorobiphenyls		154	2,2',4,4,5,6'
96	2,2',3,6,6'	155	2,2',4,4',6,6'
97	2,2',3',4,5	156	2,3,3',4,4',5
98	2,2',3,4,6	157	2,3,3',4,4',5'
99	2,2',4,4',5	158	2,3,3',4,4',6
100	2,2',4,4',6	159	2,3,3',4,5,5'
101	2,2',4,5,5'	160	2,3,4',4,5,6
102	2,2',4,5,6'	161	2,3,3',4,5',6
103	2,2',4,5',6	162	2,3,3',4',5,5'
104	2,2',4,6,6'	163	2,3,3',4',5,6
105	2,3,3',4,4'	164	2,3,3',4',5',6
106	2,3,3',4,5	165	2,3,3',5,5',6
107	2,3,3',4',5	166	2,3,4,4',5,6
108	2,3,3',4,5'	167	2,3',4,4',5,5'
109	2,3,3',4,6	168	2,3',4,4',5',6
110	2,3,3',4',6	169	3,3',4,4',5,5'
111	2,3,3',5,5'	**Heptachlorobiphenyl**	
112	2,3,3',5,6	170	2,2',3,3',4,4',5
113	2,3,3',5',6	171	2,2',3,3',4,4',6
114	2,3,4,4',5	172	2,2',3,3',4,5,5'
115	2,3,4,4',6	173	2,2',3,3',4,5,6
116	2,3,4,5,6	174	2,2',3,3',4,5,6'
117	2,3,4',5,6	175	2,2',3,3',4,5',6
118	2,3',4,4',5	176	2,2',3,3',4,6,6'
119	2,3,4,4',6	177	2,2',3,3',4',5,6
120	2,3',4,5,5'	178	2,2',3,3',5,5',6
121	2,3',4,5',6	179	2,2',3,3',5,6,6'
122	2',3,3',4,5	180	2,2',3,4,4',5,5'
123	2',3,4,4',5	181	2,2',3,4,4',5,6
124	2',3,4,5,5'	182	2,2',3,4,4',5,6'
125	2',3,4,5,6'	183	2,2',3,4,4',5',6
126	3,3',4,4',5	184	2,2',3,4,4',6,6'
127	3,3',4,5,5'	185	2,2',3,4,5,5',6

Hexachlorobiphenyls		186	2,2',3,4,5,6,6'
128	2,2',3,3',4,4'	187	2,2',3,4',5,5',6
129	2,2',3,3',4,5	188	2,2',3,4',5,6,6'
130	2,2',3,3',4,5'	189	2,3,3',4,4',5,5'
131	2,2',3,3',4,6	190	2,3,3',4,4',5,6
132	2,2',3,3',4,6'	191	2,3,3',4,4',5',6
133	2,2',3,3',5,5'	192	2,3,3',4,5,5',6
134	2,2',3,3',5,6	193	2,3,3',4',5,5',6
135	2,2',3,3',5,6'	**Octachlorobiphenyls**	
136	2,2',3,3',6,6'	194	2,2',3,3',4,4',5,5'
137	2,2',3,4,4',5	195	2,2',3,3',4,4',5,6
138	2,2,3,4,4',5'	196	2,2',3,3',4,4',5',6
139	2,2',3,4,4',6	197	2,2',3,3',4,4',6,6'
140	2,2',3,4,4',6'	198	2,2',3,3',4,5,5',6
141	2,2',3,4,5,5'	199	2,2,3,3',4',5,5',6
142	2,2',3,4,5,6	200	2,2',3,3',4,5,6,6'
143	2,2',3,4,5,6'	201	2,2',3,3',4,5',6,6'
144	2,2',3,4,5',6	202	2,2',3,3',5,5',6,6'
145	2,2',3,4,6,6'	203	2,2',3,4,4',5,5',6
146	2,2',3,4',5,5'	204	2,2',3,4,4',5,6,6'
147	2,2',3,4',5,6	205	2,3,3',4,4',5,5',6'
148	2,2',3,4,5,6'	**Nonachlorobiphenyls**	
149	2,2',3,4',5’6	206	2,2',3,3',4,4',5,5',6
150	2,2',3,4',6,6'	207	2,2',3,3',4,4',5,6,6'
151	2,2',3,5,5',6	208	2,2',3,3',4,5,5',6,6'
152	2,2',3,5,6,6	**Decachlorobiphenyl**	
153	2,2',4,4',5,5'	209	2,2',3,3',4,4',5,5',6,6'

Annex F
(informative)

Rationale

F.1 *Finger paints* (see 3.1 and 3.2)

In addition to water, *finger paints* essentially consist of *colourants*, binders, preservatives, and embittering agent and may additionally contain extenders, humectants and surfactants. *Finger paints* may be coloured by using colouring substances or mixtures containing colouring and other ingredients which are incorporated into a *finger paint* to impart colour to the *finger paint*.

F.2 *Colourants* (see 4.2.1)

Annex A contains a list of *colourants* which are suitable for *finger paints*, subject to them meeting certain purity requirements. It includes *colourants* specific for *finger paints*, *colourants* allowed in food and *colourants* allowed in cosmetics. Available safety information show that the pigments are not classified according to CLP regulation.

More detailed requirements on aromatic amines are included in order to exclude risks which may derive from impurities in *colourants*.

F.3 Preservatives (see 4.3)

According to toy safety Directive 2009/48/EC, toys shall be designed and manufactured in such a way that they meet hygiene and cleanliness requirements in order to avoid any risk of infection, sickness or contamination. Preservation protects products in the long term against growth of bacteria, fungi and yeasts in water-based paint systems.

Finger paints present ideal growing conditions for microorganisms. Preservation of *finger paints* against microbiological spoilage is necessary to maintain the hygenic status. Preservatives suitable for *finger paints* are listed in Annex B. The following requirements have been considered: high efficacy with respect to microorganisms accompanied by suitable toxicological performance (e.g. low human toxicity, low volatility, low odour), suitable technical performance (e.g. solubility in water-based systems, stability against other ingredients, stability against chemical or physical influences) and suitable environmental performance (e.g. low AOX, low persistence). The list includes e.g. preservatives for cosmetic use or for food use.

F.4 Elements (see 4.4)

The limit values and test methods for the migration of certain elements in *finger paints* are specified in EN 71-3. The limit values in this standard derive from Directive 2009/48/EC.

F.5 Primary aromatic amines (see 4.5.1.2, Tables 1 and 2 and Annex D)

The limitation for primary aromatic amines does not apply to aromatic aminocarboxylic acids or aminosulfonic acids because they are considered to be harmless.

Table 1 lists the four primary aromatic amines which shall not be determinable in *finger paints* at the limit of quantification (LOQ) using the method described in Annex D using GC-MS as the detection technique. Table 2 lists 23 primary aromatic amines which were taken from Table 4 of EN 71-7:2002 entitled ‘Other primary aromatic amines of concern (examples)’. Therefore the listing of primary aromatic amines in Table 2 has been described as a non-exhaustive list and does not preclude other primary aromatic amines from being analysed.

The information provided in Chromatography (D.6.5) and Precision (D.8) includes the four primary aromatic amines listed in Table 1 and eighteen primary aromatic amines from Table 2. The inclusion of eighteen rather than all twenty-three primary aromatic amines in Table 2 reflects either the difficulty in obtaining the suitable commercial standards or difficulties in preparing samples containing all the listed primary aromatic amines in the time available. The information in D.6.5 and D.8 should provide the competent analyst with indicative information in the determination of other primary aromatic amines where calibration standards are available.

F.6 Limit for Benzo[α]Pyrene (see 4.5.2)

Benzo(a)Pyrene in *finger paints* is limited to the currently technically achievable analytical limit of quantitation (LOQ) of 0,02 mg/kg.

F.7 Embittering agents (see 4.6)

The requirements for *finger paints* provide sufficient risk minimization. But due to the easy and foreseeable availability during play the addition of *embittering agents* will reduce the risk of ingestion by most children.

It should be noted that products with added embittering agents show remarkable bitterness, which may remain for a while after putting it into the mouth.

In general, the bitterness in a *finger paint* was found to be appropriate for product life, if the bitterness of *finger paints* is detectable in a diluted product as given in 4.6 (1:100).

F.8 pH value (see 4.7)

The use of Calcium carbonate may raise the pH value as a result of more dissociation by dilution with water in accordance with EN ISO 787-9 up to 10.

Some types of formulations containing calcium carbonate show pH values higher than 10 because the dilution of the *finger paint* is made with distilled water. This may also be found for small amounts of calcium carbonate in *finger paint*. Such a high increase as an analytical artefact doesn’t happen when tap water is used to dilute the *finger paint*.

F.9 N-Nitrosamines (see 4.9)

The limit value and test method for N-nitrosamines in *finger paint*s are specified in EN 71-12. The present standard EN 71-12:2013 sets a limit of 0,02 mg/kg N-nitrosamines in *finger paint*s.

The formation of N-nitrosamines is possible when secondary amines and nitrosating agents are both present in the *finger paint* under certain conditions. It is known from studies on cosmetic products that NDELA can be formed by the reaction of diethanolamine with a nitrite source.

To avoid the possible formation of N-nitrosamines avoid using formulations that combine diethanolamine and triethanolamine (which is known to be often contaminated with diethanolamine or which can be decomposed to diethanolamine) with possible sources of nitrite that may be present in certain preservatives (e.g bronopol) and other raw materials.

F.10 Container (see 4.10)

Containers should be designed in a way that they will not encourage children to ingest or to taste the *finger paint* therein because of a possible confusion with containers intended for food.

This requirement is intended to minimize the potential for a child to confuse *finger paint* with a foodstuff or a drink. The requirement is one part of a bundle series of precautionary measures intended to discourage the ingestion of *finger paint*s (e.g. embittering agents, no flavour, no sweetening, no fragrance).

Since typical users of *finger paint*s are younger children, the bundle of measures set requirements of this clause are stricter than those described in Council Directive 87/357/EC [22], "…concerning products which, appearing to be other than they are, endanger the health or safety of consumers" which focuses specifically on factual endangerment confusion of consumers health.

F.11 Labelling phrases (see 5.2.1.2)

Young children have a propensity for exploring objects orally. The warning phrase recognizes the fact that children under 3 years may be tempted to taste or eat the *finger paint* and this is something that the supervisor would be expected to discourage or prevent. The warning requires that adults supervise children in order to minimize the possibility of ingestion. Even though *finger paints* that are in conformity with this standard may be considered to present a minimal risk, ingestion of repeated amounts of *finger paint* is not recommended.

F.12 List of polychlorinated biphenyl congeners (see Annex E)

There are potentially two hundred and nine (209) different polychlorinated biphenyl (PCB) congeners that could be present as consequence of contaminated pigments being present in a *finger paint*. In the absence of any specific information regarding PCB contamination of *finger paints*, it was decided to use compounds; 28, 52, 101, 118, 138, 153, and 180 representative of the range of PCB congeners as marker compounds. During discussion within the task group it was suggested that the two additional PCB congeners should be included to capture the chromatographic range and compounds 11 and 209 were added to the list of calibration standards.

The information provided in Procedure (E.6) includes the nine PCB congeners and in Precision (E.8) the seven PCB congeners. Information in E.6 and E.8 should provide the competent analyst with indicative information in the determination of any other PCB congeners where they are suspected of being present and calibration standards can be obtained.

F.13 Reference materials (see Annex D and E)

The availability of suitable certified reference materials are important in ensuring methods are being performed correctly. Unfortunately, the availability of reference materials especially for toy materials are currently limited, as a wide range of analytes at different concentration levels in different matrices are required to be covered. Where-ever possible suitable alternative reference materials (preferably certified), should be used but failing these materials being available, consideration should be made for controls on the method using techniques such as 'spiking' that is adding a solution with a compound of known concentration (which is similar in chemistry to the target analyte(s)) to the sample matrix and determining the precision data.

Consideration was made for inclusion in Annex D and E to describe spiking of samples but experience of the different *finger paints* matrices ranging from liquids, gels, semi-solids to solids that are available on the market indicated that the inclusion of a such a step could cause difficulties, particularly if the homogeneity of the spiked solution in the sample matrix has not been established. However, this should not deter the analyst in using this technique where appropriate.

F.14 PCB Analytical Method (see E.6)

The current method quantifies the solvent extractable PCB congeners in *Finger paints*, followed by a clean-up step and quantification by GC-MS.

The analytical procedure for PCB congeners is validated in a separate series of experiments by adding the recovery solution (E.2.14.2) onto the sodium sulphate as described in E.6.2 and following the relevant procedure from E.6.3 to E.6.6 .The recovery rate of the PCB congeners should be at least 70 %.

Alternatively the $^{13}C_{12}$ PCB congeners may be incorporated into the *finger paint* test portion prior to its addition onto the sodium sulphate. This variant would imply that separate recovery experiments are not needed; advantageously the recovery values would reflect the total analytical method. However the homogeneous incorporation of the spike into a viscous, maybe jelly like *finger paint*, is not without difficulties and low values (<70 %) need to be checked.

Annex G
(informative)

Significant technical changes between this European Standard and the previous version

Clause/Paragraph/Table/Figure	Change
General	The standard has been revised to reflect new particular safety requirements in Directive 2009/48/EC, in comparison to 88/378/EEC.
Clause 3	Terms and definitions of “*finger paint*”, “*colourant*”, “extender” and “binding agent” have been modified.
4.2	The requirements on *colourants* have been modified.
4.4	The limit values for certain elements are no longer specified in this standard. Instead, the standard refers to EN 71–3.
4.5	Table 2 (former Table 4) has been updated. Limit values for impurities in *finger paints* (polychlorinated biphenyls, hexachlorobenzene and benzo(a)pyrene) have been specified.
4.6	The list of embittering agents has been updated.
4.7	The range of the allowed pH value has been modified.
4.8	The requirements on “binding agents, extenders, humectants and surfactants” have been modified.
4.9	A new limit value and test methods for N-nitrosamines in *finger paints* has been included by referring to EN 71–12.
4.10	New requirements on containers have been included.
Former Clause 5 (“Test methods”)	The requirements in Clause 4 now directly refer to the test methods specified in Annexes or other standards. Consequently, the clause on test methods has been deleted.
Clause 5 (former Clause 6)	The requirements on product information have been modified.
Annex A	The *colourant* list has been updated and the status of the annex has been changed from normative to informative.
Annex B	The preservative list has been updated.
Annex C	The lists of extenders and surfactants have been modified.
Annex D	The test methods for the detection of certain azo *colourants* and determination of free primary aromatic amines have been modified and validated.
Annex E	Normative Annex E with test methods for the determination of hexachlorobenzene, polychlorinated biphenyls and benzo[α]pyrene has been included.
Annex F	A new informative Annex F with a rationale on the requirements of the standard has been included.
NOTE The technical changes referred include the significant technical changes from the EN revised but is not an exhaustive list of all modifications from the previous version.	

Annex ZA
(informative)

Relationship between this European Standard and the Essential Requirements of EU Directive 2009/48/EC

This European Standard has been prepared under a mandate given to CEN by the European Commission and the European Free Trade Association to provide a means of conforming to Essential Requirements of the New Approach Directive 2009/48/EC of the European Parliament and of the Council of 18 June 2009 on the safety of toys.

Once this standard is cited in the Official Journal of the European Union under that Directive and has been implemented as a national standard in at least one Member State, compliance with the clauses of this standard given in Table ZA.1 confers, within the limits of the scope of this standard, a presumption of conformity with the corresponding Essential Requirements of that Directive and associated EFTA regulations.

Table ZA.1 — Correspondence between this European Standard and Directive 2009/48/EC of the European Parliament and of the Council of 18 June 2009 on the safety of toys

Clause(s)/subclause(s) of this Part of EN-71	**Particular Safety Requirements of Directive 2009/48/EC, Annex II**	**Qualifying remarks/Notes**
Clause 4	III.1	
Clause 4	III.3, 8, 11, 13	
Clause(s)/subclause(s) of this Part of EN-71	**Provisions of Directive 2009/48/EC**	**Qualifying remarks/Notes**
Clause 5	Art. 11.2	

WARNING — Other requirements and other EU Directives may be applicable to the product(s) falling within the scope of this standard.

Bibliography

[1] Regulation (EC) No. 1272/2008 of the European Parliament and of the Council of 16 December 2008 on classification, labelling and packaging of substances and mixtures

[2] Directive 1999/45/EC of the European Parliament and of the Council of 31 May 1999 concerning the approximation of the laws, regulations and administrative provisions of the Member States relating to the classification, packaging and labelling of dangerous preparations

[3] European Parliament and Council Directive 94/34/EC of 30 June 1994 amending Directive 89/107/EEC on the approximation of the laws of Member States concerning food additives authorized for use in foodstuffs intended for human consumption

[4] European Parliament and Council Directive 95/2/EC of 20 February 1995 on food additives other than colours and sweeteners

[5] Regulation (EC) No 1223/2009 of the European Parliament and of the Council of 30 November 2009 on cosmetic products

[6] Second Commission Directive 82/434/EEC of 14 May 1982 on the approximation of the Laws of the Member States relating to methods of analysis necessary for checking the composition of cosmetic products

[7] Third Commission Directive 83/514/EEC of 27 September 1983 on the approximation of the laws of the Member States relating to methods of analysis necessary for checking the composition of cosmetic products

[8] Fourth Commission Directive 85/490/EEC of 11 October 1985 on the approximation of the laws of the Member States relating to methods of analysis necessary for checking the composition of cosmetic products

[9] Fifth Commission Directive 93/73/EEC of 9 September 1993 on the methods of analysis necessary for checking the composition of cosmetic products

[10] Sixth Commission Directive 95/32/EC of 7 July 1995 on the methods of analysis necessary for checking the composition of cosmetic products

[11] Seventh Commission Directive 96/45/EC of 2 July 1996 on the methods of analysis necessary for checking the composition of cosmetic products

[12] Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 concerning the placing of biocidal products on the market

[13] Commission Regulation (EC) No 1451/2007 of 4 December 2007 on the second phase of the 10-year work programme referred to in Article 16(2) of Directive 98/8/EC of the European Parliament and of the Council concerning the placing of biocidal products on the market

[14] BALLSCHMITER K., ZELL M. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius Z. Anal. Chem.* 1980, **302** pp. 20–31

[15] Commission Directive 2008/128/EC of 22 December 2008 laying down specific purity criteria concerning colours for use in foodstuffs

[16] Analytical method No. 212: Determination of unsulphonated primary aromatic amines in pigments and in solvent soluble dyestuffs intended for use in food packaging; Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD)

[17]. HPLC Method for the determination of aromatic amines released from water-colours under physiological conditions. *Mitt. Gebiete Lebensm. Hyg.* 1997, **88** pp. 305–320

[18] SCHNEIDER G. *Dtsch. Lebensmitt. Rundsch.* 1997, **93** pp. 69–74

[19] DEUTSCHE FORSCHUNGSGEMEINSCHAFT. MAK- und BAT-Werte-Liste 1995; Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe, Mitteilung 31, Abschnitt IIIA, VCH-Verlagsgesellschaft, Weinheim

[20] EN ISO 4618:2006, *Paints and varnishes - Terms and definitions (ISO 4618:2006)*

[21] EN 14362-1, *Textiles - Methods for determination of certain aromatic amines derived from azo colorants - Part 1: Detection of the use of certain azo colorants accessible with and without extracting the fibres*

[22] Council Directive 87/357/EEC of 25 June 1987 on the approximation of the laws of the Member States concerning products which, appearing to be other than they are, endanger the health or safety of consumers

This page deliberately left blank

British Standards Institution (BSI)

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

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

About us

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

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

Information on standards

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

Buying standards

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

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

Subscriptions

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

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

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

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

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

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

Revisions

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

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

Copyright

All the data, software and documentation set out in all British Standards and other BSI publications are the property of and copyrighted by BSI, or some person or entity that owns copyright in the information used (such as the international standardization bodies) and has formally licensed such information to BSI for commercial publication and use. Except as permitted under the Copyright, Designs and Patents Act 1988 no extract may be reproduced, stored in a retrieval system or transmitted in any form or by any means – electronic, photocopying, recording or otherwise – without prior written permission from BSI. Details and advice can be obtained from the Copyright & Licensing Department.

Useful Contacts:

Customer Services
Tel: +44 845 086 9001
Email (orders): orders@bsigroup.com
Email (enquiries): cservices@bsigroup.com

Subscriptions
Tel: +44 845 086 9001
Email: subscriptions@bsigroup.com

Knowledge Centre
Tel: +44 20 8996 7004
Email: knowledgecentre@bsigroup.com

Copyright & Licensing
Tel: +44 20 8996 7070
Email: copyright@bsigroup.com

BSI Group Headquarters

389 Chiswick High Road London W4 4AL UK

bsi.

...making excellence a habit.™