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Safety of toys —

Part 11: Chemical toys (sets) other than experimental sets

Sécurité des jouets —

Partie 11: Jouets chimiques (coffrets) autres que les coffrets d'expériences

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 181, *Safety of toys*.

A list of all parts in the ISO 8124 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document is intended to reduce the risks and health hazards to children when chemical toys are used as intended or in a foreseeable way, bearing in mind the behaviour of children.

When using these chemical toys, potential risks should be kept to a minimum by the inclusion of appropriate information drawing attention to possible hazards, risks and other problems.

The Chemical Abstract Service Registry Numbers (CAS) and European Inventory of Existing Chemical Substances Numbers (EINECS) given in various tables are provided for information purposes only.

Products covered by this document may be subject to legal requirements specific to the jurisdiction in which they are sold and conformity with the requirements in this document cannot be relied on to ensure compliance with those requirements.

Safety of toys —

Part 11:
Chemical toys (sets) other than experimental sets

1 Scope

This document specifies requirements and test methods for the substances and materials used in chemical toys (sets) other than experimental sets. These substances and mixtures are:

— those classified as dangerous by the Globally Harmonized System of Classification and Labelling of Chemicals (GHS)[1];

— substances and mixtures which in excessive amounts could harm the health of the children using them and which are not classified as dangerous by the GHS; and

— any other chemical substance(s) and mixture(s) delivered with the chemical toy.

Additionally, requirements are specified for markings, warnings, safety rules, contents lists, instructions for use and first aid information.

This document applies to:

— plaster of Paris (gypsum) moulding sets;

— oven-hardening plasticised PVC modelling clay sets;

— polystyrene granules sets;

— embedding sets;

— adhesives, paints, lacquers, varnishes, thinners and cleaning agents (solvents) supplied or recommended in model sets.

2 Normative references

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

ISO 3104, *Petroleum products — Transparent and opaque liquids — Determination of kinematic viscosity and calculation of dynamic viscosity*

ISO 3219, *Plastics — Polymers/resins in the liquid state or as emulsions or dispersions — Determination of viscosity using a rotational viscometer with defined shear rate*

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 22854, *Liquid petroleum products — Determination of hydrocarbon types and oxygenates in automotive-motor gasoline and in ethanol (E85) automotive fuel — Multidimensional gas chromatography method*

3 Terms and definitions

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

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

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
chemical toy
toy intended for the direct handling of chemical substances and mixtures and which is used in a manner appropriate to a given age-group and under the supervision of an adult

[SOURCE: ISO 8124-2:2014, 3.1]

3.2
experimental set
chemical toy (3.1) in which the experimental and explorative character in playing with single chemical substances and mixtures is guided by strict instructions that dominate over the creative ideas of the user

3.3
plaster of Paris (gypsum) moulding set
toy containing moulds into which a mixture of water and gypsum is poured and allowed to harden

Note 1 to entry: The gypsum consists predominantly of calcium sulfate hemihydrate $CaSO4 \cdot 0{,}5\ H_2O$.

Note 2 to entry: Plaster of Paris (gypsum) moulding sets are used, for example, for preparing figures and plates.

3.4
oven-hardening plasticised PVC modelling clay set
toy to be used for creating all kinds of figures, brooches and fashion jewellery, prepared by hardening in the oven at temperatures of 100 °C to 130 °C

3.5
polystyrene granules set
toy to be used in substitution of ceramic materials to create decorative articles or models by fusion of a polymer by heating in an oven up to a maximum of 180 °C

3.6
embedding set
toy to be used to preserve certain products in a transparent material

3.7
model set
product used to assemble and coat models which are supplied with or recommend *adhesives* (3.8), *paints or lacquers* (3.9 and 3.10), *varnishes* (3.11), *thinners and cleaning agents* (3.12)

Note 1 to entry: Examples for these models include motorcars, aeroplanes, houses and ships.

3.8
adhesive
non-metallic substance capable of joining materials by surface bonding (adhesion) and the bond possessing adequate internal strength (cohesion)

3.9
water-based paint or lacquer
water-based pigmented material which, when applied in a liquid form to a surface, eventually forms a dry adherent film or coating

3.10
solvent-based paint or lacquer
solvent-based pigmented material which, when applied in a liquid form to a surface, eventually forms a dry adherent film or coating

3.11
varnish
low-viscosity lacquer

3.12
thinners and cleaning agents
solvents
products which are intended to obtain the required viscosity of paints and lacquers and to clean tools and brushes

4 Plaster of Paris (gypsum) moulding sets

4.1 Marking

See D.2 and D.3.

The primary packaging shall, in addition to the marking required in Clause 9, bear the following:

"Warning! Not suitable for children under (*) years. For use under adult supervision. Read the instructions before use, follow them and keep them for reference."

(*) The age is to be specified by the manufacturer, authorized representative or importer. It shall not be below 5 years.

4.2 First aid information

The instructions for use shall, in addition to the general first aid information in 9.2 d), contain the following:

— "In case of eye contact: Wash out eye with plenty of water, holding eye open. Seek immediate medical advice."

— "If swallowed: Wash out mouth with water, drink some fresh water. Do not induce vomiting. Seek immediate medical advice."

4.3 Safety rules

The instructions for use shall, in addition to the rules required in 9.4, contain the following safety rules:

— "Do not place the material in the mouth."

— "Do not inhale dust or powder."

— "Do not apply to the body."

5 Oven-hardening plasticised PVC modelling clay sets

5.1 Chemical substances

See D.4.

These modelling clay sets shall consist of PVC (polyvinylchloride) and plasticisers and may contain modifiers, fillers (e.g. China clay) and colourants. Only plasticisers given in Table 1 shall be used.

The mass fraction of plasticisers in the mixture shall not exceed 30 %.

The vinyl chloride monomer content shall be below 1 mg/kg.

Table 1 — Plasticisers in oven-hardening plasticised PVC modelling clay sets

Chemical substance	CAS number
Adipic acid polyesters	various
Alkylsulfonic acid esters (C_{12} to C_{20}) of phenol	91082–17–6
Di(isononyl) cyclohexane-1,2-dicarboxylate (DINCH)	166412–78–8
Tributyl acetylcitrate	77–90–7
Tris(2-ethylhexyl) acetylcitrate	144–15–0

During heating of these materials at the maximum permitted temperature and duration, the limits given in Table 2 shall not be exceeded for the emission of the listed toxic substances when tested according to 10.3.

Table 2 — Limits for the emission of substances from oven-hardening plasticised PVC modelling clay sets and polystyrene granules sets during heating

Substance	Limit mg/kg
Benzene	5
Toluene	15
Xylenes	25

5.2 Marking

See D.2 and D.3.

The primary packaging shall, in addition to the marking required in Clause 9, bear the following warning:

"Warning! Not suitable for children under (*) years. For use under adult supervision. Read the instructions before use, follow them and keep them for reference."

(*) The age is to be specified by the manufacturer, authorized representative or importer. It shall not be below 8 years.

5.3 First aid information

The instructions for use shall, in addition to the general first aid information in 9.2 d), contain the following:

— "In case of accidental overheating and inhalation of poisonous gases: Remove person to fresh air and seek immediate medical advice."

5.4 Safety rules

The instructions for use shall, in addition to the rules required in 9.4, contain the following safety rules:

— "Do not place the material in the mouth."

— "Do not exceed a hardening temperature of 130 °C or harmful gases may be produced."

— "Do not exceed a hardening time of 30 minutes."

— "The hardening process is not part of the function of the toy and should be carried out by the supervising adult."

— "Use a domestic oven thermometer, e.g. bimetal, to measure the temperature."

— "Do not use a glass thermometer."

— "Do not heat the material and cook food at the same time in a domestic oven."

— "Do not use a microwave oven."

6 Moulding sets

6.1 Polystyrene granules sets

6.1.1 Chemical substances

These sets shall contain uncoloured and coloured polystyrene granules in accordance with Table 3.

Table 3 — Polystyrene

Chemical substance	CAS number	EINECS number
Polystyrene with monomer content of styrene ≤ 500 mg/kg	9003-53-6	—

6.1.2 Marking

See D.2 and D.3.

The primary packaging shall, in addition to the marking required in Clause 9, bear the following warnings:

"Warning! Not suitable for children under (*) years. For use under adult supervision. Read the instructions before use, follow them and keep them for reference."

(*) The age is to be specified by the manufacturer, authorized representative or importer. It shall not be below 10 years.

6.1.3 First aid information

The instructions for use shall, in addition to the general first aid information in 9.2 d), contain the following:

— "In case of accidental overheating and inhalation of poisonous gases: Remove person to fresh air and seek immediate medical advice."

6.1.4 Safety rules

The instructions for use shall, in addition to the rules required in 9.4, contain the following safety rules:

— "Do not exceed a melting temperature of 180 °C."

— "The melting process is not part of the function of the toy and should be carried out by the supervising adult."

— "Use a domestic oven thermometer, e.g. bimetal, to measure the temperature."

— "Do not swallow material."

— "Do not heat the material and cook food at the same time in a domestic oven."

— "Do not use a glass thermometer."

— "Do not exceed the maximum recommended processing period."

— "Do not use a microwave oven."

6.2 Embedding sets

6.2.1 General

See D.5.

Only preservatives permitted in foodstuffs and/or cosmetics, except those preservatives which are only allowed in cosmetic products that are rinsed off after use, shall be used.

NOTE 1 Examples of information on preservatives permitted in cosmetics in Europe and the United States are provided in References [4] and [5].

Other substances classified as dangerous substances (see Reference [1]) shall not be used in embedding sets.

NOTE 2 Substances such as gelatine or agar could be utilized with suitable preservation.

6.2.2 Packaging

See D.2.

The name(s) of any preservative(s) used shall be indicated on the primary packaging.

6.2.3 Marking

See D.3.

The packaging shall, in addition to the marking required in Clause 9, bear the following warnings:

"Warning! Not suitable for children under (*) years. For use under adult supervision. Read the instructions before use, follow them and keep them for reference."

(*) The age is to be specified by the manufacturer, authorized representative or importer. It shall not be below 5 years.

6.2.4 First aid information

The instructions for use shall, in addition to the general first aid information in 9.2 d), contain the following:

— "If swallowed: Wash out mouth with water, drink some fresh water. Do not induce vomiting. Seek immediate medical advice."

6.2.5 Safety rules

The instructions for use shall, in addition to the rules required in 9.4, contain the following safety rule:

— "Do not place the preserved material in the mouth."

7 Adhesives, paints, lacquers, varnishes, thinners and cleaning agents (solvents) supplied or recommended in model sets

7.1 General

Adhesives, paints, lacquers, varnishes, thinners and cleaning agents (solvents) supplied in model sets shall conform with the requirements in Clause 7. The instructions included in the set shall mention only adhesives, paints, lacquers, varnishes, thinners and cleaning agents (solvents) that conform with the requirements in Clause 7.

7.2 Adhesives

7.2.1 Water-based adhesives

7.2.1.1 General

See D.5.

Water-based adhesives shall consist of water and basic materials. Only basic materials given in Table 4 shall be used. Additionally, water-based adhesives may contain special materials given in Table 5 or Table 7, preservatives, fillers and modifiers.

Only preservatives permitted in foodstuffs and/or cosmetics, except those preservatives which are only allowed in cosmetic products that are rinsed off after use, shall be used.

NOTE Examples of information on preservatives permitted in cosmetics in Europe and the United States are provided in References [4] and [5].

Table 4 — Basic materials for water-based adhesives and water-based paints or lacquers

Chemical substance	CAS number	EINECS number
Acrylic homo and copolymers	—	—
Hydrophilic polyurethane containing neither free isocyanate groups nor aromatic amino-compounds	—	—
Polymers and copolymers of monomers permitted for materials intended to come into contact with foodstuffs	—	—
Polyvinyl homo and copolymers	—	—
Poly(vinyl alcohol)	9002–89–5	209–183–3
Polyvinylpyrrolidone homo and copolymers	—	—

The basic materials shall be appropriate for food contact. The migration solvent shall be water, grade 3 according to ISO 3696. The contact time shall be approximately 60 min at approximately 40 °C.

7.2.1.2 Liquid adhesives for paper and wood

7.2.1.2.1 General

Special materials for adhesives for paper and wood shall be in accordance with Table 5.

Table 5 — Special materials for adhesives for paper and wood and water-based paints and lacquers

Chemical substance	CAS number	EINECS number
Cellulose ethers (e.g. carboxymethylcellulose, methylcellulose)	9004–67–5	—
Dextrin	9004–53–9	232–675–4
Gum arabic	9000–01–5	232–519–5
Starch or modified starch	9005–25–8	232–679–6

Special additives for adhesives for paper and wood shall be in accordance with Table 6.

Table 6 — Special additives for liquid adhesives for paper and wood

Chemical substance	CAS number	EINECS number
Butyl glycolate (Butyl hydroxyacetate)[a]	7397–62–8	230–991–7
Caprolactam[b]	105–60–2	203–313–2
Glycerol	56–81–5	200–289–5
Polyacrylamide	9003–05–8	—
Poly(acrylic acid)	9003–01–4	—
Polyethylene glycol	25322–68–3	—
Poly(methacrylic acid)	25087–27–7	—
Polypropylene glycol	25322–69–4	—
Sodium salts of fatty acids (C_{14} upwards)	—	—
Sorbitol	50–70–4	200–061–5
2-(2-Butoxyethoxy)ethyl acetate[c]	124–17–4	204–685–9
Xylitol	87–99–0	201–788–0

[a] The mass fraction of butyl glycolate shall not exceed 3 %.

[b] The mass fraction of caprolactam shall not exceed 5 %.

[c] The mass fraction of 2-(2-butoxyethoxy)ethyl acetate shall not exceed 3 %.

The polymers given in Table 6 shall be appropriate for food contact. The migration solvent shall be water grade 3 according to ISO 3696. The contact time shall be approximately 60 min at approximately 40 °C.

7.2.1.2.2 Packaging

See D.2.

The capacity of the containers for water-based adhesives in a set shall not be more than 100 ml. The name(s) of any preservative(s) used shall be indicated on the primary packaging.

7.2.1.2.3 Marking

See D.3.

The adhesive container shall, in addition to the marking required in Clause 9, bear the following warnings:

"Warning! Not suitable for children under (*) years. For use under adult supervision."

(*) The age is to be specified by the manufacturer, authorized representative or importer. It shall not be below 5 years.

7.2.1.2.4 First aid information

The instructions for use shall, in addition to the general first aid information in 9.2 d), contain the following:

— "In case of skin contact: Wash affected area with plenty of water.";

— "In case of eye contact: Wash out eye with plenty of water, holding eye open. Seek immediate medical advice."

7.2.1.3 Adhesive sticks and pastes for paper

7.2.1.3.1 General

Special materials for adhesive sticks and pastes for paper shall be in accordance with Tables 5, 6 and 7.

Table 7 — Special material for adhesive sticks and pastes for paper

Chemical substance	CAS number	EINECS number
Acrylic homo and copolymers	—	—
Hydrophilic polyurethane containing neither free isocyanate groups nor aromatic amino-compounds	—	—
Polymers and copolymers of monomers permitted for materials intended to come into contact with foodstuffs	—	—
Polyvinyl homo and copolymers	—	—
Poly(vinyl alcohol)	9002–89–5	209–183–3
Polyvinylpyrrolidone homo and copolymers	—	—
Dextrin	9004–53–9	232–675–4
Starch or modified starch	9005–25–8	232–679–6

The special materials shall be appropriate for food contact. The migration solvent shall be water grade 3 according to ISO 3696. The contact time shall be approximately 60 min at approximately 40 °C.

7.2.1.3.2 Packaging

The mass of the adhesive stick in a set shall not exceed 50 g.

7.2.1.3.3 Marking

See D.3.

The packaging, if any, or the adhesive stick container shall, in addition to the marking in Clause 9, bear the following warning:

"Warning! Not suitable for children under (*) years. For use under adult supervision."

(*) The age is to be specified by the manufacturer, authorized representative or importer. It shall not be below 3 years.

7.2.1.3.4 First aid information

The instructions for use shall, in addition to the general first aid information in 9.2 d), contain the following:

— "In case of skin contact: Wash affected area with plenty of water.";

— "In case of eye contact: Wash out eye with plenty of water, holding eye open. Seek immediate medical advice."

7.2.2 Solvent-based adhesives

7.2.2.1 General

Solvent-based adhesives consist of basic material specified in Tables 4, 5 and 7 and basic materials from the relevant subclauses under 7.2.2. Further, they consist of substances from Tables 6 and 11 with the limits given there and may additionally contain fillers, modifiers and plasticisers. Plasticisers shall be appropriate for food contact (or be in accordance with Table 12).

The mass fraction of plasticiser in these adhesives shall not exceed 8 %. The mass fraction of modifiers shall not exceed 3 %.

For solvent-based adhesives containing petroleum fractions, the mass fraction of *n*-hexane shall not exceed 0,5 %.

The final mixture containing petroleum fractions shall not be classified with H372.

NOTE The classifications are detailed in the GHS[1].

7.2.2.2 Multi-purpose adhesives

Basic materials for multi-purpose adhesives shall be in accordance with Table 8.

Table 8 — Basic materials for multi-purpose adhesives

Chemical substance	CAS number	EINECS number
Acrylic homo and copolymers	—	—
Cellulose nitrate	9004–70–0	—
Polyvinyl homo and copolymers	—	—
Vinyl acetate homo and copolymers	—	—

7.2.2.3 Contact adhesives

Basic materials for contact adhesives shall be in accordance with Table 9.

Table 9 — Basic materials for contact adhesives

Chemical substance	CAS number	EINECS number
Polymers and copolymers of monomers permitted for materials intended to come into contact with foodstuffs	—	—
Poly(chlorobutadiene)	9010–98–4	—
Polyurethane	73561–64–5	—

7.2.2.4 Special adhesives

See D.4.

Basic materials for special adhesives shall be in accordance with Table 10.

Table 10 — Basic materials for special adhesives

Chemical substance	CAS number	EINECS number
Acrylic homo and copolymers	—	—
Polymers and copolymers of monomers permitted for materials intended to come into contact with foodstuffs	—	—
Polystyrene	9003–53–6	—
Vinyl chloride copolymers	—	—

The basic materials shall be appropriate for food contact. The migration solvent shall be water, grade 3 according to ISO 3696. The contact time shall be approximately 60 min at approximately 40 °C.

Table 11 — Solvents in solvent-based adhesives

Chemical substance/mixture	CAS number	EINECS number
Acetone (Dimethyl ketone)	67–64–1	200–662–2
Cyclohexane[a]	110–82–7	203–806–2
Pentan-3-one (Diethyl ketone)	96–22–0	202–490–3
Ethyl acetate	141–78–6	205–500–4
Ethanol (Ethyl alcohol)	64–17–5	200–578–6
Isopropyl acetate	108–21–4	203–561–1
Propan-2-ol (Isopropyl alcohol)	67–63–0	200–661–7
Methyl acetate	79–20–9	201–185–2
Butan-2-one (Methyl ethyl ketone)	78–93–3	201–159–0
3-Methylbutan-2-one (Methyl isopropyl ketone)	563–80–4	209–264–3
n-Butyl acetate	123–86–4	204–658–1
n-Propyl acetate	109–60–4	203–686–1
1-Methoxypropan-2-ol[b]	107–98–2	203–539–1
1,1-Dimethoxyethane	534–15–6	208–589–8
Petroleum fraction (35 to 160) °C[c]	64742–89–8	265–192–2
Hydrocarbons, C9 –C16, hydrotreated, dearomatized	93763–35–0	297–854–1

[a] The mass fraction of cyclohexane shall not exceed 3 %.

[b] The mass fraction of 1-Methoxypropan-2-ol shall not exceed 20 %.

[c] The mass fraction of benzene shall not exceed 0,1 %.

If the product contains petroleum fraction (35 to 160) °C, the viscosity of the product shall exceed 20,5 mm^2/s when tested in accordance with ISO 3104 or ISO 3219.

Table 12 — Plasticisers in solvent-based adhesives and solvent-based paints, lacquers, thinners and cleaning solvents

Plasticiser	CAS number
Tributyl acetylcitrate	77–90–7
Tri(2-ethylhexyl) acetylcitrate	144–15–0
Alkyl sulfonic acid esters (C_{12} to C_{20}) of phenol	91082–17–6
Adipic acid polyesters	various
Di(isononyl) cyclohexane-1,2-dicarboxylate (DINCH)	166412–78–8

2,2-Bis(4-hydroxyphenyl)propane diglycidyl ether (BADGE), bis(hydroxyphenyl)methane diglycidyl ether (BFDGE) and Novolac glycidyl ethers (NOGE), together with their derivatives, shall not be used as modifiers for adhesives.

NOTE BADGE — 2,2-bis(4-hydroxyphenyl)propane diglycidyl ether, Bisphenol-A diglycidyl ether [1675–54–3];

BFDGE — bis(hydroxyphenyl)methane diglycidyl ether, Bisphenol-F diglycidyl ether [39817–09–9];

NOGE — Novolac glycidyl ethers [28064–14–4] and [9003–36–5].

7.2.2.5 Packaging

The content of the container in a set shall not exceed 15 g.

7.2.2.6 Marking

See D.2 and D.3.

The primary packaging of the set shall, in addition to the marking required in Clause 9, bear the following warnings:

"Warning! Not suitable for children under (*) years. For use under adult supervision. Read the instructions before use, follow them and keep them for reference."

(*) The age is to be specified by the manufacturer, authorized representative or importer. It shall not be below 8 years.

The individual container shall be marked according to 8.3.

7.2.2.7 First aid information

The instructions for use shall, in addition to the general first aid information in 9.2 d), contain the following:

— "In case of skin contact: Wash affected area with plenty of water.";

— "In case of eye contact: Wash out eye with plenty of water, holding eye open. Seek immediate medical advice.";

— "In case of inhalation: Remove person to fresh air."

7.2.2.8 Safety rules

The instructions for use shall, in addition to the rules required in 9.4, contain the following safety rules:

— "Keep away from ignition sources.";

— "Do not allow adhesive to come into contact with the skin, the eyes and the mouth.";

— "Do not swallow material.";

— "Do not inhale fumes."

7.3 Water-based paints or lacquers

7.3.1 General

See D.5.

Water-based paints or lacquers shall consist of water and basic materials. Only basic materials given in Table 4 shall be used. Additionally, water-based paints or lacquers may contain special materials given in Table 5 and organic solvents and film-forming agents given in Table 13 or Table 6, colouring agents, preservatives, fillers and modifiers.

The mass fraction of organic solvents and film-forming agents shall not exceed 6 %.

Only preservatives permitted in foodstuffs and/or cosmetics, except those preservatives which are only allowed in cosmetic products that are rinsed off after use, shall be used.

NOTE Examples of information on preservatives permitted in cosmetics in Europe and the United States are provided in References [4] and [5].

Table 13 — Organic solvents and film-forming agents

Chemical substance/mixture	CAS number	EINECS number
Di(2-methylpropyl)ester of aliphatic dicarboxylic acids (C_{20} to C_{33})[a]	—	—
Ethanol (Ethyl alcohol)	64–17–5	200–578–6
Mixture of aliphatic esters and alcohols (C_{12} to C_{14})[a]	—	—
1-Methoxypropan-2-ol	107–98–2	203–539–1
Propan-1,2-diol (Propylene glycol)	57–55–6	200–338–0
2-Methylpentane-2,4-diol (Hexylene glycol)	107–41–5	203–489–0
Propan-2-ol (Isopropyl alcohol)	67–63–0	200–661–7
[a] Maximum mass fraction of 2 % as film-forming agents.		

7.3.2 Packaging

See D.2.

The content of the container in a set shall not exceed 100 ml.

The name(s) of any preservative(s) used shall be indicated on the primary packaging.

7.3.3 Marking

See D.3.

The packaging or the container shall, in addition to the marking required in Clause 9, bear the following warning:

"Warning! Not suitable for children under (*) years. For use under adult supervision. Read the instructions before use, follow them and keep them for reference."

(*) The age is to be specified by the manufacturer, authorized representative or importer. It shall not be below 5 years.

7.3.4 First aid information

The instructions for use shall, in addition to the general first aid information in 9.2 d), contain the following:

— "In case of skin contact: Wash affected area with plenty of water.";

— "In case of eye contact: Wash out eye with plenty of water, holding eye open. Seek immediate medical advice.";

— "In case of inhalation: Remove person to fresh air."

7.3.5 Safety rules

The instructions for use shall, in addition to the rules required in 9.4, contain the following safety rules:

— "Do not allow material to come into contact with the eyes.";

— "Do not place material in the mouth.";

— "Do not inhale vapours."

7.4 Solvent-based paints, lacquers, thinners and cleaning solvents

7.4.1 General

Solvent-based paints and lacquers shall consist of solvents and basic materials. Only basic materials given in Table 14 and solvents given in Table 13 and Table 15 shall be used. Paints and lacquers shall not have a mass fraction of more than 2 % of 2-methylpropan-1-ol or *n*-butanol and not more than 20 % 1-Methoxypropan-2-ol. Additionally, solvent-based paints and lacquers may contain colourants, fillers and modifiers. The mass fraction of modifiers shall not exceed 3 %.

For solvent-based paints and lacquers prepared with nitrocellulose the mass fraction of plasticiser shall not exceed 5 %.

Plasticisers shall be appropriate for food contact (see Reference [9]) or be in accordance with Table 12.

Thinners and cleaning solvents shall contain only substances and mixtures given in Tables 13 and 15 except film-forming agents. 2-Methylpropan-1-ol, *n*-butanol and 1-Methoxypropan-2-ol shall not be used in thinners and cleaning agents.

For solvent-based paints, lacquers, thinners and cleaning solvents containing petroleum fractions the *n*-hexane mass fraction shall not exceed 0,5 %. *n*-hexane shall only occur in these solvents as a contaminant of petroleum fractions.

The final mixture containing petroleum fractions shall not be classified with H372.

NOTE The classifications are detailed in the GHS[1].

Pressurized containers (aerosols) shall not be used for paints, lacquers, thinners or cleaning solvents.

Table 14 — Basic materials

Chemical substance	CAS number	EINECS number
Acrylic polymers	—	—
Alkyd polymers	—	—
Nitrocellulose	9004–70–0	—

Table 15 — Solvents

Chemical substance/mixture	CAS number	EINECS number
Glycerol triacetate	102–76–1	203–051–9
2-Methylpropan-1-ol (isobutanol)	78–83–1	201–148–0
Butan-2-one (Methyl ethyl ketone)	78–93–3	201–159–0
1-Methoxypropan-2-ol	107–98–2	203–539–1
1-Methoxypropan-2-yl acetate	108–65–6	203–603–9
Butan-1-ol (*n*-butanol)	71–36–3	200–751–6
3-Methoxybutyl acetate	4435–53–4	224–644–9
Petroleum fraction (35 to 160) °C	64742–89–8	265–192–2
Hydrocarbons, C9 – C16, hydrotreated, dearomatized	93763–35–0	297–854–1

If the product contains petroleum fraction (35 to 160) °C, the viscosity of the product shall exceed 20,5 mm^2/s when tested in accordance with ISO 3104 or ISO 3219.

7.4.2 Packaging

The maximum content of the container in a set shall not exceed:

— 15 ml for liquids with a flash point < 23 °C and initial boiling point > 35 °C;

— 50 ml for liquids with a flash point ≥ 23 °C.

NOTE For information regarding packaging and labelling, including child-resistant fastenings, see References [1] and [3].

7.4.3 Marking

See D.2 and D.3.

The primary packaging shall, in addition to the marking required in Clause 9, bear the following warning:

"Warning! Not suitable for children under (*) years. For use under adult supervision. Read the instructions before use, follow them and keep them for reference."

(*) The age is to be specified by the manufacturer, authorized representative or importer. It shall not be below 8 years.

7.4.4 First aid information

The instructions for use shall, in addition to the general first aid information in 9.2 d), contain the following:

— "In case of skin contact: Wash affected area with plenty of water.";

— "In case of eye contact: Wash out eye with plenty of water, holding eye open. Seek immediate medical advice.";

— "If swallowed: Wash out mouth with water, drink some fresh water. Do not induce vomiting. Seek immediate medical advice."

7.4.5 Safety rules

The instructions for use shall, in addition to the rules required in 9.4, contain the following safety rules:

— "Keep away from ignition sources.";

— "Do not allow product to come into contact with the skin and the eyes.";

— "Do not place material in the mouth.";

— "Do not inhale vapours."

8 Marking

8.1 General

Markings shall be visible, easily legible, indelible and in the national language(s) of the country of sale.

If the container is too small to carry all the necessary information an additional instruction leaflet shall be supplied with the package.

8.2 Marking of the primary packaging

See D.2.

8.2.1 General

The primary packaging shall indicate any dangerous substances or dangerous mixtures (see Reference [1]) that are recommended but not included in the toy.

NOTE Examples of dangerous substances or dangerous mixtures that are recommended but not included in the toy are adhesives, paints or lacquers.

8.2.2 Manufacturer's identification

The primary packaging shall bear the name, registered trade name or registered trademark of the manufacturer or the importer and the address at which they can be contacted.

Chemical toys/toy sets shall bear a type, batch, serial or model number or other element allowing their identification.

8.2.3 Warning phrases

The primary packaging shall bear the relevant warning phrases in Clauses 4 to 7. An uppercase letter size of a minimum height of 7 mm shall be used for the word "Warning" (as recommended under "Marking" in Clauses 4 to 7) on primary packaging.

8.3 Marking of individual containers and any packaging

The individual containers and packaging (including primary packaging) shall bear the following information:

a) If the substance/mixture is classified as dangerous (see Reference [1]), the name of the chemical substance or mixture as given in the relevant table(s) and clause(s).

b) Where relevant, the required pictogram(s) and the required H- and P-phrases (see Reference [1]).

9 Instructions for use

9.1 General

The instructions for use shall be given in the national language(s) of the country of sale.

The marking of the primary packaging according to 8.2.3 shall be repeated on the cover of the instructions for use.

9.2 Contents list

The contents list shall contain the following information:

a) where relevant, the name(s) of the chemical(s) supplied;

b) where relevant, the H-and P-phrases specified in the GHS[1] appropriate to each particular substance and mixture;

c) where relevant, and if the substances/mixture is classified according to the GHS[1], an empty space shall be provided in which the telephone number of the local poison centre (central office for first aid information) or hospital, if possible, should be entered in case of intake by accident of dangerous substances;

d) general first aid information as follows:

   1) "In case of doubt seek medical advice without delay: Take the chemical and/or product together with the container with you.";

2) “In case of injury always seek medical advice.”;

NOTE First aid information can also be found in the instructions for carrying out the activity.

e) specific first aid information specified in Clauses 4 to 7 when appropriate.

9.3 Advice for adult supervision

Where appropriate, the advice for adults shall contain the following information:

a) This chemical toy is not suitable for children under (*) years. For use under adult supervision. Keep this chemical toy set out of reach of children under (*) years old.

b) Read and follow these instructions, the safety rules and the first aid information and keep them for reference.

c) Incorrect use of chemicals can cause injury and damage to health. Only carry out those activities which are listed in the instructions.

d) Because children’s abilities vary so much, even within age groups, supervising adults should exercise discretion as to which activities are suitable and safe for them. The instructions should enable supervisors to assess any activity to establish its suitability for a particular child.

e) The supervising adult should discuss the warnings, safety information and possible hazards with the child or children before commencing the activities. Particular attention should be paid to the safe handling of alkalis, acids and flammable liquids.

f) The area surrounding the activity should be kept clear of any obstructions and away from the storage of food. It should be well lit and ventilated and close to a water supply. A solid table with a heat-resistant top should be provided.

g) The working area should be cleaned immediately after carrying out the activity.

(*) The age is to be specified by the manufacturer, authorized representative or importer. It shall not be below the requirements for the age limits specified within Clauses 4 to 7.

9.4 Safety rules

The following safety rules shall be given:

— “Keep younger children under the specified age limit and animals away from the activity area.”;

— “Store chemical toys out of reach of young children.”;

— “Wash hands after carrying out activities.”;

— “Clean all equipment after use.”;

— “Do not use any equipment which has not been supplied with the set or recommended in the instructions for use.”;

— “Do not eat, drink or smoke in the activity area.”;

and, where appropriate, the special safety rules given in Clauses 4 to 7.

9.5 Instructions for carrying out the activities

Detailed information on how to perform each activity shall be given.

The activities, where relevant, should be evaluated by the manufacturer.

Any known hazards arising from the use of the toy should be detailed.

9.6 Spills and disposal of chemicals

Where relevant, information on the handling of spills and on the disposal of used chemicals shall be given.

10 Test methods

10.1 General

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

The precision of volumetric glassware should be grade A.

The analysis of chemical toys and chemical toy materials for chemical compounds shall be performed in accordance with the methods of analysis described in this document. 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 document, are of an adequate sensitivity and have been validated to show that the results are equivalent to those of these standard methods.

Information on the validation of the method in this document is provided in Annex C.

Environmental, health and safety precautions shall be followed as specified in Annex A.

10.2 Determination of plasticisers in oven-hardening polyvinyl chloride (PVC) modelling clay sets

10.2.1 Principle

The plasticiser content is determined by solvent extraction to quantitatively extract the plasticiser from a known weight of PVC material using a Soxhlet extractor. Hexane is used to extract citric acid esters and alkyl sulfonic acid esters. Methanol is used to extract adipic acid polyesters. Indicative plasticiser content can be determined by evaporating off the solvent and weighing the solvent residue and identifying the plasticiser by attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectrometry.

Determination of plasticiser(s) content is by gas chromatography-mass spectrometry (GC-MS) for alkyl sulfonic acid phenyl ester and citric acid esters. Adipic acid esters are quantified gravimetrically.

This method is also partly used for the determination of plasticisers in solvent-based adhesives and solvent-based paints or lacquers (see 10.6.4).

10.2.2 Standards and reagents

10.2.2.1 Standards

NOTE The given substances (except citrates) are examples for the requirements in Table 12.

Table 16 — Adipic acid polyesters

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

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

[a] Polymeric plasticiser derived from adipic acid and polyhydric alcohols.

[b] Polyester adipate.

Table 17 — Citric acid esters

Chemical	CAS number
Tributyl acetylcitrate	77–90–7
Tris(2-ethylhexyl) acetylcitrate	144–15–0

Table 18 — Alkyl sulfonic acid esters

Chemical	CAS number
Alkyl sulfonic phenyl ester	91082–17–6

10.2.2.2 Reagents

Table 19 — Solvents

Chemical	CAS number
Hexane, analytical grade	110–54–3
Methanol, analytical grade	67–56–1

10.2.3 Apparatus

10.2.3.1 Analytical balance, precision 0,1 mg.

10.2.3.2 Spark-proof heating mantle/water bath.

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

10.2.3.4 Desiccator chamber.

10.2.3.5 150-ml or 250-ml glass-stoppered flat-bottomed flask.

10.2.3.6 Soxhlet glass extractor with siphon cup.

10.2.3.7 Soxhlet cellulose thimble.

10.2.3.8 Water-cooled glass condenser.

10.2.3.9 Cotton wool.

10.2.3.10 Glass volumetric flask.

10.2.3.11 General volumetric glassware.

10.2.3.12 Stainless steel scalpel blade.

10.2.3.13 Attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectrometer.

10.2.3.14 Gas chromatograph with mass spectrometer detector (GC-MS).

Column: 50 % phenyl – 50 % dimethylpolysiloxane (ZB-50), 30 m × 0,25 mm (ID) × 0,25 µm (film thickness)

Carrier gas: helium

Flow rate: 0,8 ml/min

Injector temperature: 290 °C

Injection volume: 2 µl

Injection type: splitless

Transfer line temperature: 280 °C

Detector scan range: 50 m/z to 550 m/z

Run time: 37 min

Oven program: in accordance with Table 20

Table 20 — Oven programme for the determination of plasticisers in oven-hardening polyvinyl chloride (PVC) modelling clay sets

Ramp	Initial temperature °C	Hold time min	Rate °C/min	Final temperature °C	Final hold time min
1	60	1	10	290	
2	290	5	5	320	5

Quantification ions: Main target ion m/z

Citric acid esters 157

Alkyl sulfonic acid esters 94

10.2.4 Preparation of standard solutions

10.2.4.1 Stock solutions

Prepare stock solutions of the citric acid esters (Table 17) and the alkyl sulfonic acid esters (Table 18) dissolved in hexane (Table 19) in accordance with Table 21.

Table 21 — Stock solutions I

Stock solution	Solvent	Ester	Concentration µg/ml
Citric acid ester 3a	hexane	tributyl acetylcitrate	500
Citric acid ester 3b	hexane	tris(2-ethylhexyl) acetylcitrate	1 000
Alkyl sulfonic acid ester 4	hexane	Alkyl sulfonic acid phenyl ester	5 000

Prepare stock solutions of the adipic acid polyesters (Table 16) dissolved in methanol (Table 19) in accordance with Table 22.

Table 22 — Stock solutions II

Stock solution	Solvent	Ester	Concentration µg/ml
Adipic acid polyester 2a	methanol	Palamoll 632 or 636	5 000
Adipic acid polyester 2b	methanol	Palamoll 646	5 000
Adipic acid polyester 2c	methanol	Palamoll 652	5 000
Adipic acid polyester 2d	methanol	Palamoll 654 or 656	5 000
Adipic acid polyester 2e	methanol	Palamoll 858	5 000
Adipic acid polyester 2f	methanol	Paraplex G-40	5 000

NOTE Primarily the stock solutions for adipic acid polyesters are used for identification purposes.

10.2.4.2 Calibration solutions

Prepare calibration solutions (Std 1 to Std 5) containing a mixture of the components from the stock solutions by appropriate solvent dilutions using pipettes in 100-ml glass volumetric flasks and making up to the mark with hexane (Table 19). Table 23 shows the concentration of each analyte in the calibration solution.

Table 23 — Calibration solutions

	Concentrations µg/ml				
Stock solution	Std 1	Std 2	Std 3	Std 4	Std 5
Stock solution 3a	10	15	20	25	30
Stock solution 3b	50	100	150	200	250
Stock solution 4	10	15	20	25	30

10.2.4.3 Stability of standard solutions

Stability tests have shown that the plasticiser stock solutions and the calibration solutions can be stored for 6 months in a refrigerator at (4 ± 2) °C.

10.2.5 Sampling

Modelling clays are generally presented commercially as rectangular blocks presented in retail packs. Representative test portions of the modelling clay can be taken without further treatment.

10.2.6 Sample preparation

For each sample pre-heat two flat-bottomed flasks (10.2.3.5) marked A and B in an oven (10.2.3.3) at (105 ± 5) °C for (30 ± 5) min.

Remove the flasks from the oven and allow to cool in a desiccator for (30 ± 5) min.

After cooling, accurately weigh the flasks and record the masses.

Using a scalpel or other appropriate cutting equipment, cut small representative pieces (≤5 mm) from the centre and sides of the sample.

Weigh (1 ± 0,2) g to the nearest 0,1 mg of the cut pieces of sample into a Soxhlet thimble and add approximately 0,2 g of cotton wool to the top of the thimble to form a plug to prevent any inorganic filler escaping from the thimble.

10.2.7 Procedure

10.2.7.1 General

It is essential to observe all safety precautions when handling chemicals and apparatus. The use of appropriate air extraction systems needs to be observed.

10.2.7.2 Extraction of citric acid esters and alkyl sulfonic acid esters

Add approximately (50 ± 1) ml of hexane into a flask A.

NOTE Depending on the size of the glassware, and in order to reach the overflow level and have a proper reflux, the volume of hexane can be adjusted.

Place the Soxhlet thimble into the Soxhlet extractor, connect flask A, Soxhlet extractor and condenser together and place onto a heating mantle.

Reflux gently for (6 ± 0,5) h.

After 6 h switch off the mantle and allow sufficient time for the hexane to cool.

Decant any excess hexane left in the Soxhlet extractor into flask A.

Collection of evaporated solvent for environmental protection is advised.

10.2.7.3 Extraction of adipic acid polyesters

Repeat 10.2.7.2 using the pre-weighed flask B and approximately (50 ± 1) ml of methanol.

NOTE Depending on the size of the glassware and in order to reach the overflow level and have a proper reflux, the volume of methanol can be adjusted.

10.2.7.4 Evaporation of the solvent and weighing

Place both flasks A and B on top of a steam bath and allow both the hexane and methanol to completely evaporate.

After the hexane and methanol have evaporated, transfer the flasks A and B to an oven (10.2.3.3) at (105 ± 5) °C.

After (30 ± 5) min remove both flasks A and B from the oven and cool in a desiccator.

After (30 ± 5) min cooling, accurately weigh both flasks A and B and record the masses.

Replace the flasks in the oven, dry to constant mass until the difference between two consecutive weighings for each flask is not more than 0,000 5 g.

Record the masses and determine the solvent extractable content for both hexane and methanol.

10.2.7.5 Blank determination

Determine the solvent blank residue content by evaporating 50 ml hexane and 50 ml methanol, respectively, in two pre-weighed flasks C and D following the steps in 10.2.6 (omitting the sample and extraction steps) and 10.2.7.2. If the calculated blank residue value for a solvent is ≥ 0,001 g, the analysis is repeated using a different batch of solvent until the value for the blank is < 0,001 g.

10.2.7.6 GC-MSD determination of citric acid esters and alkyl sulfonic acid esters

After completing weighing as described in 10.2.7.4, add (50 ± 2) ml of hexane to flask A.

Stopper flask A and swirl the hexane to completely dissolve the plasticiser extract.

Decant the solution into a 250-ml volumetric flask and by repeatedly rinsing the flask using hexane add to the 250-ml flask and make up to the mark.

Prepare (if necessary) further diluted solutions using hexane such that the final concentration in solution is within the linear calibration concentration for plasticiser present.

Transfer a portion of the hexane into a capped vial for GC-MS analysis (conditions as described in 10.2.3.14).

Compare the obtained GC-MS spectra with known spectra or ester standards to allow qualitative identification of plasticisers or any other compounds.

Plot a calibration graph of the response against the known standard concentrations.

From the calibration graph determine the response of ester found in the blank/sample and interpolate the concentration of ester in µg/ml, correcting for any dilutions.

10.2.7.7 ATR-FT-IR identification of adipic acid polyesters

After completing weighing as described in 10.2.7.4 add (50 ± 2) ml of methanol to flask B.

Stopper flask B and swirl the methanol to completely dissolve the plasticiser extract.

Decant the solution into a 250-ml volumetric flask and by repeatedly rinsing the flask using methanol add to the 250-ml flask and make up to the mark.

Compare the infrared spectra obtained with a suitable spectral database.

10.2.8 Evaluation of results

10.2.8.1 Calculation of solvent-extractable content containing plasticisers

10.2.8.1.1 Mass fraction of hexane extractable material, in %, identified as citric and alkyl sulfonic acid esters by GC-MS

The mass fraction of hexane extractable material is calculated according to Formula (1):

$$M_{\text{Hexane}} = \frac{W_{\text{A+E}} - W_{\text{A}}}{W_{\text{S}}} \times 100 \quad (1)$$

where

M_{Hexane} is the mass fraction of hexane extractable material, in %;

$W_{\text{A+E}}$ is the mass of flask A and extract, in g;

W_{A} is the mass of flask A, in g;

W_{S} is the mass of sample, in g.

10.2.8.1.2 Mass fraction of methanol extractable material, in %, identified as adipic acid polyester by ATR-FT-IR

The mass fraction of methanol extractable material is calculated according to Formula (2):

$$M_{\text{Methanol}} = \frac{W_{\text{B+E}} - W_{\text{B}}}{W_{\text{S}}} \times 100 \quad (2)$$

where

M_{Methanol} is the mass fraction of methanol extractable material, in %;

$W_{\text{B+E}}$ is the mass of flask B and extract, in g;

W_{B} is the mass of flask B, in g;

W_{S} is the mass of sample, in g.

10.2.8.1.3 Mass fraction of combined (hexane + methanol) extractable material, in %

The mass fraction of combined extractable material is calculated according to Formula (3):

$$M_{\text{te+p}} = (1) + (2) \quad (3)$$

where $M_{\text{te+p}}$ is the total mass fraction of extractable material including plasticiser, in %.

Values for combined mass fraction of (hexane + methanol) extractable material < 30 % will not require further characterization of individual plasticisers and should be reported as % total mass fraction of extractable material if it can be shown that only plasticisers in Table 15 are used.

10.2.8.2 Calculation and identification of the mass fraction of plasticiser by GC-MS analysis

10.2.8.2.1 Identification of plasticisers

Record the plasticisers identified according to 10.2.7.6 and 10.2.7.7.

10.2.8.2.2 Calculation of plasticisers content by GC-MS

10.2.8.2.2.1 Mass fraction of citric acid ester, in %, by GC-MS

The mass fraction of citric acid ester is calculated according to Formula (4):

$$M_{CAE} = \frac{c_{e2} \times 250 \times f}{W_S \times 10\,000} \quad (4)$$

where

M_{CAE} is the mass fraction of citric acid ester, in %;

c_{e2} is the concentration of citric acid ester in the extract solution, in µg/ml;

f is the dilution factor;

W_S is the mass of sample, in g.

The concentration of citric acid ester in the extract solution is calculated according to Formula (5):

$$c_{e2} = (W_{B+E}) - W_B \quad (5)$$

where

c_{e2} is the concentration of extract solution, in µg/ml;

W_{B+E} is the mass of flask B and extract, in g;

W_B is the mass of flask B, in g.

10.2.8.2.2.2 Mass fraction of alkyl sulfonic acid ester by GC-MS in %

The mass fraction of alkyl sulfonic acid ester is calculated according to Formula (6):

$$M_{AAE} = \frac{c_e \times 250 \times f}{W_S \times 10\,000} \quad (6)$$

where

M_{AAE} is the mass fraction of alkyl sulfonic acid ester, in %;

c_e is the concentration of alkylsulfonic acid ester in extract solution, in µg/ml;

f is the dilution factor;

W_S is the mass of sample, in g.

10.2.9 Test report

The test report shall contain, as a minimum, the following:

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

b) a reference to this document (i.e. ISO 8124-11);

c) the results of the tests expressed as:

1) identified plasticisers;

2) mass fraction of hexane-extractable material, in %;

3) mass fraction of methanol-extractable material identified as adipic acid polyester by ATR-FT-IR, in %;

4) mass fraction of combined (hexane + methanol) extractable material, in %;

5) mass fraction of citric acid ester by GC-MS, in %;

6) alkylsulfonic acid ester mass fraction by GC-MS, in %;

d) any deviation from the test procedure specified;

e) date of test.

10.3 Determination of the emission of benzene, toluene and xylenes from oven-hardening plasticised PVC modelling clay sets and polystyrene granules sets

10.3.1 Principle

The determination of the emission of benzene, toluene and xylenes from oven-hardening plasticised PVC modelling clay sets and polystyrene granules sets is performed by headspace gas chromatography with a mass spectrometer detector using the method of standard additions.

10.3.2 Standards and reagents

Table 24 — Standards

Chemical	CAS number
Toluene	108–88–3
Benzene	71–43–2
o-Xylene	95–47–6
m-Xylene	108–38–3
p-Xylene	106–42–3

Table 25 — Solvents

Chemical	CAS number
Methanol	67–56–1
NOTE Alternatively, a high-boiling solvent such as dodecane (free of the compounds to be analysed) will be used instead of methanol in order to reduce the vapour pressure in the head space vial. This is especially relevant when the head space vial is not pressurized (see headspace conditions 10.3.3.2).	

10.3.3 Apparatus

10.3.3.1 Gas chromatograph with mass spectrometer detector (GC-MS)

The measurement of benzene, toluene and xylenes requires a gas chromatograph equipped with a split/splitless injector system coupled with a mass spectrometer detector.

Column: crosslinked 5 % phenylmethylsiloxane, 95 % dimethylpolysiloxane (DB-VRX[1)]), 30 m × 0,25 mm (ID) × 0,25 µm (film thickness).

1) DB-VRX is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.

Injection temperature: 300 °C

Injection mode: split, splitless time, 0 min to 1,5 min

Interface temperature: 250 °C

Ion source temperature: 250 °C

Sampling time: from 2 min to 22 min

Mass range: from 30 m/z to 500 m/z

Acquisition data: 1 scan/s

Other conditions may be used, provided they give better or comparable results.

Carrier gas: helium

Oven program: in accordance with Table 26

Table 26 — Oven programme for the determination of the emission of benzene, toluene and xylenes

Ramp	Initial temperature °C	Hold time min	Rate °C/min	Final temperature °C	Final hold time min
1	35	10	7	150	
2	150	0	20	220	6

Table 27 provides typical retention times.

Table 27 — Typical retention times for benzene, toluene, *m*-xylene and *o*-xylene

Solvent	Typical retention time min	Solvent	Typical retention time min
Benzene	3,4	*m*-xylene	10,5
Toluene	5,6	*o*-xylene	12,3

Detector conditions for benzene, toluene and xylenes determination:

Quantification ions	**Main target ion m/z**
Benzene	78
Toluene	91
Xylenes	91

10.3.3.2 Headspace analysis conditions

Balanced-pressure system, the vial pressurized with a carrier gas. After equilibrium has been reached the valve is switched for a specific amount of time to transfer the volatiles of the sample into the column.

Pressure-loop system, the vial pressurized with a carrier gas. Then a valve is turned and the loop is filled with the sample. Then the valve is turned again to transfer the volatiles of the sample into the column.

Pressurization gas: He, set at 45 KPa

Thermostatting temperature: 130 °C for test material based on PVC; 180 °C for test material made of polystyrene

Needle temperature: 140 °C for test material based on PVC, 190 °C for test material made of polystyrene

Transfer line temperature: 140 °C for test material based on PVC, 190 °C for test material made of polystyrene

Injection time: 0,05 min

Pressurization time: 4 min

Thermostatting time: 30 min

Withdrawal time: 0,2 min

10.3.3.3 Other laboratory equipment

Glassware should be cleaned, preferably rinsed with a few millilitres of dichloromethane and dried before use to avoid contamination of benzene, toluene and xylenes.

10.3.3.3.1 Analytical balance, precision 0,1 mg.

10.3.3.3.2 Refrigerator, capable of maintaining a temperature of (4 ± 2) °C.

10.3.3.3.3 Brown glass vials for headspace sampling.

10.3.3.3.4 Volumetric glass pipettes, 0,5 ml, 1 ml, 2 ml, 10 ml and 20 ml capacity.

10.3.3.3.5 Brown glass volumetric flasks, 10 ml, 20 ml, 50 ml and 100 ml capacity.

10.3.3.3.6 Syringe, 1 000 µl capacity.

10.3.4 Preparation of standard solutions

Weigh accurately approximately 100 mg of each standard listed in Table 24 (benzene, toluene, *m*-, *p*-, *o*-xylene).

Dissolve in methanol and make up to 100 ml in a volumetric flask.

Dilute this stock standard solution with methanol (Table 25) to produce standard solutions with a concentration of 5 µg/ml, 10 µg/ml, 20 µg/ml, 50 µg/ml and 100 µg/ml.

Solutions shall be handled in a glass container (10.3.3.3.3 and 10.3.3.3.5) at (4 ± 2) °C. The stock standard solution shall be used within one month. The standard solutions shall be freshly prepared.

10.3.5 Sampling

The applicable sample for the method is PVC modelling clay and polystyrene granules. Representative portions of material are taken without further homogenization. Samples shall be stored in a sealed container before analysis in order to avoid losses of volatile substances.

10.3.6 Sample preparation

No specific sample preparation is necessary. For PVC material take each test portion as a single piece of similar shape and weight.

Obtain test portions from each colour of the material, where possible, and treat them separately.

Weigh each test portion of (1 ± 0,05) g to the nearest 0,001 g into each of five headspace vials. Then, add 500 µl of the different standard solutions (10.3.4) to achieve standard additions of 2,5 µg, 5 µg, 10 µg, 25 µg and 50 µg, respectively.

Seal each vial quickly and store it at room temperature for 1 h.

10.3.7 Procedure

Prior to injection, heat each test portion in the head space GC system for (30 ± 1) min at 130 °C for analysis of test material based on PVC or 180 °C for analysis of test material made of polystyrene. Analyse also an empty vial as blank in order to determine if there is contamination from the ambient air.

Analyse the samples using the GC conditions in accordance with 10.3.3.1.

10.3.8 Evaluation of results

In a graph, plot the area for the individual component against the individual concentration added. The extrapolation of the straight line with the concentration axis in absolute value is the actual concentration of the analyte in the sample.

The regression coefficient (r) shall be better than 0,995.

10.3.9 Test report

The test report shall contain, as a minimum, the following:

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

b) a reference to this document (i.e. ISO 8124-11);

c) the results of the tests expressed as:

   1) benzene emitted from PVC or polystyrene, in mg/kg;

   2) toluene emitted from PVC or polystyrene, in mg/kg;

   3) xylene emitted from PVC or polystyrene, in mg/kg;

d) any deviation from the test procedure specified;

e) date of test.

10.3.10 Critical control points

The volume of the standard shall be added to the surface of the lower part of the vial. Due to the volatility of the organic compounds, the vial shall be immediately well sealed.

Heating time of the toy material shall be (30 ± 1) min for every test portion. The temperature of the headspace thermostatting compartment shall be controlled to (130 ± 3) °C for PVC-based modelling clays and (180 ± 5) °C for polystyrene granules.

The septum of the headspace vial shall have no influence on the result (inertness, no emissions, no adsorption).

10.4 Determination of styrene content in polystyrene granules

10.4.1 Principle

The amount of styrene in polystyrene is determined by gas chromatography using mass spectrometry as a detection system. Quantification is achieved using calibration with external standards of styrene monomer.

The method is appropriate for the quantitative determination of styrene in an approximate analyte concentration range of (50 to 3 000) mg/kg of polystyrene.

10.4.2 Standards and reagents

10.4.2.1 Standards

Table 28 — Standard

Chemical
Styrene, stored at (4 ± 2) °C

10.4.2.2 Reagents

Table 29 — Reagents

Chemical
Dichloromethane
Methanol

10.4.3 Apparatus

10.4.3.1 Gas chromatograph, equipped with split/splitless injector and mass spectrometer detector GC-column capable of separating styrene from the mixture of solvents and fully resolving the additives in polystyrene, for example:

Column: crosslinked 5 % phenylmethylsiloxane, 95 % dimethylpolysiloxane (DB-VRX), 30 m × 0,25 mm (ID) × 0,25 µm (film thickness) or equivalent.

Carrier gas: helium

Oven program: in accordance with Table 30

Table 30 — Oven programme for the determination of the styrene content

Ramp	Initial temperature °C	Hold time min	Rate °C/min	Final temperature °C	Final hold time min
1	35	10	7	150	
2	150	0	20	220	6

Using these conditions, typical retention time for styrene is about 12,5 min.

Injection conditions:

— Injection temperature: 250 °C

— Injection volume: 2 µl

— Injection mode: splitless, split valve closed from 0 min to 1,5 min

Detector conditions for styrene determination:

— Detection system: quadrupole mass spectrometer

— Mode: SIM (selected ion monitoring) focused on ions: 104 m/z and 78 m/z

— Interface temperature: 250 °C

— Ion source temperature: 250 °C

— Sampling time: from 3 min to 25 min

— Acquisition data: two scan/s

10.4.3.2 General equipment and glassware used in laboratory.

10.4.3.3 Analytical balance, precision 0,1 mg.

10.4.3.4 Centrifuge, able to maintain at least 2 300 g.

10.4.3.5 Refrigerator, capable of maintaining a temperature of (4 ± 2) °C.

10.4.3.6 Glass containers, equipped with a glass stopper.

Plastic equipment shall be avoided and glassware shall be cleaned, rinsed with a few millilitres of the mixture of solvents from Table 29 (dichloromethane and methanol) and dried before use.

10.4.3.7 Volumetric flask and volumetric pipettes.

10.4.4 Preparation of standard solutions

Prepare a stock standard solution by dissolving 80 mg of styrene (Table 28) in methanol (Table 29) and make up to 100 ml in a volumetric flask.

Dilute this stock standard solution with a mixture consisting of two parts dichloromethane and one part methanol measured by volume, to produce calibration solutions with a concentration of 0,4 µg/ml, 1 µg/ml, 5 µg/ml, 10 µg/ml and 20 µg/ml.

Standard solutions shall be stored at (4 ± 2) °C and used within 2 weeks of preparation.

10.4.5 Sampling

Each colour of granules shall be tested separately.

10.4.6 Sample preparation

No specific sample preparation is necessary.

10.4.7 Procedure

Weigh (1,5 ± 0,1) g to the nearest 0,001 g of the test portion into a 50-ml conical flask with a glass stopper. Add 10,0 ml of dichloromethane. Gently shake the solution until complete dissolution of the polymer (can take up to 24 h). Then add 5,0 ml of methanol and agitate in order to precipitate the polymer. In order to complete the separation between the phases, centrifuge the solution before analysis.

Analyse the calibration solutions by GC-MS using the conditions specified in 10.4.3.1. Construct a five-point calibration curve of response against styrene concentration (mg/ml), then analyse the test portion solution using identical conditions.

10.4.8 Evaluation of results

The concentration of styrene (mg/ml) in the sample solution is directly interpolated from the graph and the styrene content (mg/kg) in the sample calculated according to Formula (7):

$$M_{st} = \frac{c_{st} \times 15}{W_s \times 1\,000} \tag{7}$$

where

M_{st} is the content of free styrene in polystyrene sample, in mg/kg;

c_{st} is the concentration of styrene obtained from calibration graph, in mg/l;

W_s is the mass of the sample, in g.

The results expressed in mg styrene/kg polystyrene shall be reported as the average value from two or more determinations.

10.4.9 Test report

The test report shall contain, as a minimum, the following:

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

b) a reference to this document (i.e. ISO 8124-11);

c) results of the tests reported as:

   1) content of styrene, in mg/kg polystyrene;

d) any deviation from the test procedure specified;

e) date of test.

10.5 Determination of organic solvents

10.5.1 General

Only certain solvents are permitted for use in chemical toys and in certain cases these solvents should not be present in excess of a maximum limit. The 27 solvents listed in Table 31 require identification at a minimum detection level of 0,2 % mass fraction. Annex B, Table B.1 provides information on the technique required for each type of sample and solvent.

Table 31 — Solvents/identification

Solvent	Subclause(s) and associated table(s) containing requirement(s)
Acetone (Dimethyl ketone)	7.2.2, Table 11
Cyclohexane	7.2.2, Table 11
Pentan-3-one (Diethyl ketone)	7.2.2, Table 11
Ethyl acetate	7.2.2, Table 11
Ethanol (Ethyl alcohol)	7.2.2, Table 11; 7.3.1 and 7.3.1, Table 13
Isopropyl acetate	7.2.2, Table 11
Propan-2-ol (Isopropyl alcohol)	7.2.2, Table 11; 7.3.1 and 7.3.1, Table 13
Methyl acetate	7.2.2, Table 11
Butan-2-one (Methyl ethyl ketone)	7.2.2, Table 11; 7.4.1, Table 15

Table 31 *(continued)*

Solvent	Subclause(s) and associated table(s) containing requirement(s)
3-Methylbutan-2-one (Methyl isopropyl ketone)	7.2.2, Table 11
n-Butyl acetate	7.2.2, Table 11
n-Propyl acetate	7.2.2, Table 11
1-Methoxypropan-2-ol	7.2.2, Table 11; 7.3.1, Table 13; 7.4.1, Tables 14 and 15
1,1-Dimethoxyethane	7.2.2, Table 11
n-hexane	7.2.2, 7.4
Petroleum fraction (boiling range 35 °C to 160 °C)	7.2.2, Table 11; 7.4.1, Table 15
Hydrocarbons, C9 – C16, hydrotreated, dearomatized	7.2.2, Table 11; 7.4.1, Table 15
Propane-1,2-diol (Propylene glycol)	7.3 and 7.3.1, Table 13
2-Methylpentane-2,4-diol (Hexylene glycol)	7.3 and 7.3.1, Table 13
Butan-1-ol (*n*-Butyl alcohol)	7.4.1, Table 15
2-Methylpropan-1-ol (isobutanol)	7.4.1, Table 15
1-Methoxypropan-2-yl acetate	7.4.1, Table 15
3-Methoxybutyl acetate	7.4.1, Table 15
Butyl glycolate (Butyl hydroxyacetate)	7.2.1.2.1, Table 6
Caprolactam	7.2.1.2.1, Table 6
2-(2-Butoxyethoxy)ethyl acetate	7.2.1.2.1, Table 6
Glycerol triacetate	7.4.1, Table 15

The 12 solvents listed in Table 32 require determination at a minimum detection limit of 0,1 % mass fraction.

Table 32 — Solvents/determination

Solvent	Permitted maximum mass fraction
Butyl glycolate (Butyl hydroxyacetate)	3 %
Caprolactam	5 %
2-(2-Butoxyethoxy)ethyl acetate	3 %
n-hexane	0,5 %
2-Methylpropan-1-ol (Isobutyl alcohol)	2 %
Butan-1-ol (*n*-Butyl alcohol)	2 %
Ethanol (Ethyl alcohol)	10 % (total) in *water-based paints or lacquers*
Propan-2-ol (Isopropyl alcohol)	
Propane-1,2-diol (Propylene glycol)	
2-Methylpentane-2,4-diol (Hexylene glycol)	
1-Methoxypropan-2-ol	
1-Methoxypropan-2-ol	20 % in solvent-based paints
NOTE The permitted maximum concentrations are provided for information purposes only.	

10.5.2 Principle

Solvents are identified either by headspace gas chromatography with a flame ionization detector (HS-GC-FID) using two different columns for comparative identification, or by gas chromatography with a mass spectrometer detector (GC-MS).

Solvents are determined using one of the following techniques depending on the volatility of the solvent and the sample matrix:

1) headspace gas chromatography with a flame ionization detector (HS-GC-FID) for the determination of volatile solvents (boiling point ≤ 120 °C);

2) gas chromatography with a mass spectrometer detector (GC-MS) for the determination of non-volatile solvents (boiling point > 120 °C);

3) gas chromatography with a flame ionization detector (GC-FID) for the determination of propane-1,2-diol.

ISO 22854 shall be used for the confirmation of the identification of petroleum fractions.

10.5.3 Standards and reagents

10.5.3.1 Standards

Table 33 — Solvents

Chemical	CAS number	Density[a] g/ml
Acetone	67–64–1	0,791
Cyclohexane	110–82–7	0,778
Pentan-3-one	96–22–0	0,853
Ethyl acetate	141–78–6	0,902
Ethanol	64–17–5	0,785
Isopropyl acetate	108–21–4	0,872
Propan-2-ol	67–63–0	0,785
Methyl acetate	79–20–9	0,932
Butan-2-one	78–93–3	0,806
3-Methylbutan-2-one	563–80–4	0,805
Butyl acetate	123–86–4	0,872
Propyl acetate	109–60–4	0,888
1-Methoxypropan-2-ol	107–98–2	0,922
1,1-Dimethoxyethane	534–15–6	0,852
Propane-1,2-diol	57–55–6	1,036
2-Methylpentane-2,4-diol	107–41–5	0,925
1-Methoxypropan-2-yl acetate	108–65–6	0,969
3-Methoxybutyl acetate	4435–53–4	0,96
2-Methylpropan-1-ol	78–83–1	0,803
Butan-1-ol	71–36–3	0,810
n-hexane	110–54–3	0,659
Petroleum fraction (boiling range 35 °C to 160 °C)[b]	64742–89–8	—
Hydrocarbons, C9 – C16, hydrotreated, dearomatized	93763–35–0	—
Butyl glycolate	7397–62–8	1,019

[a] The density values are those of the pure substance.

[b] The relevant petroleum fractions are not commercially available; the closest match has been referenced.

Table 33 *(continued)*

Chemical	CAS number	Density[a] g/ml
Caprolactam	105–60–2	—
2-(2-Butoxyethoxy)ethyl acetate	124–17–4	0,978
Glycerol triacetate	102–76–1	1,155
[a] The density values are those of the pure substance.		
[b] The relevant petroleum fractions are not commercially available; the closest match has been referenced.		

10.5.3.2 Reagents

Table 34 — Reagents

Chemical	CAS number
Dimethylformamide (DMF)	68–12–2
Sodium chloride	7647–14–5
Dichloromethane	75–09–2
Methanol	67–56–1
NOTE Sodium chloride, 10 % aqueous solution mass fraction (saline).	

10.5.4 Apparatus

10.5.4.1 Analytical balance, precision 0,1 mg.

10.5.4.2 Headspace vial, glass, 22 ml with crimp cap.

10.5.4.3 Glass volumetric flask, 20 ml.

10.5.4.4 Volumetric flask, 50 ml.

10.5.4.5 Volumetric flask, 100 ml.

10.5.4.6 General volumetric glassware.

10.5.4.7 Variable positive displacement pipettes (range 0,02 ml to 10,00 ml).

10.5.4.8 Filter paper, general purpose laboratory, medium retention, medium/fast flow rate, pore size 11 µm.

10.5.4.9 Syringe filter, nylon membrane, 0,45 µm.

10.5.4.10 Syringe filter, surfactant-free cellulose acetate (SFCA) membrane, 0,45 µm.

10.5.4.11 Headspace gas chromatograph with flame ionization detector (HS-GC-FID).

Polar column: polyethylene glycol (ZB-Wax), 60 m × 0,32 mm (ID) × 0,5 µm (film thickness)

Non-polar column: dimethylpolysiloxane (ZB-1), 60 m × 0,32 mm (ID) × 1,0 µm (film thickness)

Carrier gas: helium

Split vent flow: 18 ml/min (GC without headspace)

Column flow: 1,19 ml/min at 50 °C

Small flow at 220 °C

Column head pressure: 72,4 kPa

Septum purge: 4 ml/min

Split vent flow: 51 ml/min (GC with headspace)

Equilibration time: 45 min

Equilibration temperature: 80 °C

Injection type: split

Transfer line temperature: 250 °C

Detector temperature: 250 °C

Run time: 35 min

Oven program: in accordance with Table 35

Table 35 — Oven programme for the determination of organic solvents (HS-GC-FID)

Ramp	Initial temperature °C	Hold time min	Rate °C/min	Final temperature °C	Final hold time Min
1	50	1	2,5	100	
2	100	0,5	10	220	5

10.5.4.12 Gas chromatograph with mass spectrometer detector (GC-MS).

Column: 50 % phenylmethylpolysiloxane (ZB-50), 30 m × 0,25 mm (ID) × 0,25 µm (film thickness)

Carrier gas: helium

Flow rate: 0,8 ml/min

Injector temperature: 290 °C

Injection volume: 2 µl

Injection type: split/splitless

Transfer line temperature: 280 °C

Detector scan range: 50 m/z to 550 m/z

Run time: 25 min

Oven program: In accordance with Table 36

Table 36 — Oven programme for the determination of organic solvents (GC-MS)

Ramp	Initial temperature °C	Hold time min	Rate °C/min	Final temperature °C	Final hold time Min
1	40	4	20	280	
2	280	4	20	300	2

10.5.4.13 Gas chromatograph with flame ionization detector (GC-FID).

Column: polyethylene glycol (ZB-Wax), 30 m × 0,32 mm (ID) × 0,25 µm (film thickness)

Carrier gas: helium

Flow rate: 1,6 ml/min

Injector temperature: 250 °C

Injection type: split (split ratio 100:1)

Injection volume: 0,2 µl

Transfer line temperature: 250 °C

Detector temperature: 250 °C

Run time: 35 min

Oven program: in accordance with Table 37

Table 37 — Oven programme for the determination of organic solvents (GC-FID)

Ramp	Initial temperature °C	Hold time min	Rate °C/min	Final temperature °C	Final hold time Min
1	50	0,55	7	75	
2	75	4	4	110	6

10.5.5 Preparation of the standard solutions

NOTE Stability tests have shown that the solvent stock solutions (>10 mg/ml) can be stored for 6 months in a refrigerator at (4 ± 2) °C.

10.5.5.1 Stock solutions for the identification and determination of solvents using HS-GC-FID

Prepare a 250 mg/ml stock standard solution for each solvent (Table 33) in Table 38 (except *n*-hexane) using a variable pipette (10.5.4.7) to deliver a calculated volume of solvent (equivalent to 12,5 g of solvent) into a 50-ml volumetric flask (10.5.4.4) and make up to the mark with DMF (Table 34).

The volume of each volatile organic solvent required for a 50-ml volumetric flask can be calculated according to Formula (8):

$$V_s = \frac{V_f \times d_s}{c_{sst}} \quad (8)$$

where

V_s is the volume of the solvent, in ml;

V_f is the volume of the flask, in ml;

c_{sst} is the concentration of the stock standard, in mg/ml;

d_s is the density of the solvent, in mg/ml.

For *n*-hexane prepare a 100-mg/ml stock standard solution due to the lower miscibility of *n*-hexane in DMF.

Table 38 — Organic solvents for analysis by HS-GC-FID

Organic solvent
Acetone
Cyclohexane
Pentan-3-one
Ethyl acetate
Ethanol
Isopropyl acetate
Propan-2-ol
Methyl acetate
Butan-2-one
3-Methylbutan-2-one
Butyl acetate
Propyl acetate
1-Methoxypropan-2-ol
1,1-Dimethoxyethane
2-Methylpropan-1-ol
Butan-1-ol
n-hexane

10.5.5.2 Stock solutions for the identification and determination of solvents using GC-MS

Prepare a 10-mg/ml stock standard solution for each organic solvent (Table 33) in Table 39 by weighing 1,00 g of solvent into a 100-ml volumetric flask (10.5.4.5) and making up to the mark with dichloromethane (Table 34).

Table 39 — Organic solvents for analysis by GC-MS

Organic solvent
Butyl acetate
1-Methoxypropan-2-yl acetate
2-Methylpentane-2,4-diol
3-Methoxybutyl acetate
Butyl glycolate
2-(2-Butoxyethoxy)ethyl acetate
Caprolactam
Glycerol triacetate
Petroleum fraction (boiling range 35 °C to 160 °C)
Hydrocarbons, C9 – C 16, hydrotreated, dearomatized

10.5.5.3 Stock solution for the identification and determination of propane-1,2-diol

Prepare a 10-mg/ml stock standard solution for propane-1,2-diol (Table 33) by weighing 1,00 g of propane-1,2-diol into a 100-ml volumetric flask and making up to the mark with dichloromethane (Table 34).

10.5.5.4 Calibration solutions

NOTE Stability tests have shown that the working solutions can be kept for 6 months in a refrigerator at (4 ± 2) °C.

10.5.5.4.1 Calibration solutions for the identification of solvents using HS-GC-FID

Table 40 — Working solution 1

Organic solvent	Stock standard	Working solution 1
Ethanol	250 mg/ml	50 mg/ml
Propan-2-ol	250 mg/ml	
1-Methoxypropan-2-ol	250 mg/ml	

Table 41 — Working solution 2

Organic solvent	Stock standard	Working solution 2
Acetone	250 mg/ml	50 mg/ml
Ethyl acetate	250 mg/ml	
3-Methylbutan-2-one	250 mg/ml	
2-Methylpropan-1-ol	250 mg/ml	

Table 42 — Working solution 3

Organic solvent	Stock standard	Working solution 3
1,1-Dimethoxyethane	250 mg/ml	50 mg/ml
Butan-2-one	250 mg/ml	
Propyl acetate	250 mg/ml	
Butan-1-ol	250 mg/ml	

Table 43 — Working solution 4

Organic solvent	Stock standard	Working solution 4
Methyl acetate	250 mg/ml	50 mg/ml
Cyclohexane	250 mg/ml	
Butyl acetate	250 mg/ml	
Pentan-3-one	250 mg/ml	
Isopropyl acetate	250 mg/ml	

Prepare a 50-mg/ml working solution for *n*-hexane (see Table 44) by pipetting 25,00 ml of the 100-mg/ml *n*-hexane stock standard solution into a 50-ml volumetric flask and making up to the mark with DMF.

Table 44 — Working solution 5

Organic solvent	Stock standard	Working solution 5
n-hexane	100 mg/ml	50 mg/ml

10.5.5.4.2 Calibration solutions for the identification of solvents in aqueous-based materials

Using a variable pipette, prepare calibration solutions (a and b) in saline (Table 34) for working solution 1 (Table 40) in headspace vials (10.5.4.2) according to Table 45. Crimp each headspace vial tightly to achieve a good seal and shake each vial to homogenize the solution.

NOTE The saline solution is used to increase detection sensitivity by decreasing the solubility of organic molecules in the aqueous phase (salting-out effect).

Table 45 — Calibration solutions in saline for aqueous-based materials

Calibration solution	Volume of 50 mg/ml working solution to be added	Volume of 10 % saline to be added	Total volume of working solution and saline	Mass of solvent in headspace vial	Equivalent mass fraction in sample
	ml	ml	ml	mg	%
a	0,40	4,60	5,00	20	2
b	0,04	4,96	5,00	2,0	0,2

10.5.5.4.3 Calibration solutions for the identification of solvents in solvent-based materials

Using a variable pipette, prepare calibration solutions (a and b) in DMF (Table 34) for each working solution 1 to 5 (Tables 41 through 44) in headspace vials according to Table 46. Crimp each headspace vial tightly to achieve a good seal and shake each vial to homogenize the solution.

Table 46 — Calibration solutions in DMF for solvent-based materials

Calibration solution	Volume of 50 mg/ml working solution to be added	Volume of DMF to be added	Total volume of working solution and DMF	Mass of solvent in headspace vial	Equivalent mass fraction in sample
	ml	ml	ml	mg	%
a	0,40	4,60	5,00	20	2
b	0,04	4,96	5,00	2,0	0,2

10.5.5.4.4 Calibration solutions for the determination of solvents using HS-GC-FID

Depending on the matrix and the solvent being determined, prepare calibration solutions (a to e) for butan-1-ol, 2-methylpropan-1-ol, *n*-hexane, 1-Methoxypropan-2-ol, ethanol and propan-2-ol by pipetting the specified amounts (according to Table 47 to Table 50) of DMF or saline (Table 34), as required, and the appropriate working solution (Table 40 through 44) or stock standard solution (10.5.5.1) into a

headspace vial. Crimp each headspace vial tightly to achieve a good seal and shake to homogenize the solution.

Table 47 — Calibration solutions in DMF for butan-1-ol and 2-methylpropan-1-ol

Calibration solution	Volume of working solution 2 or 3 to be added	Volume of DMF to be added	Total volume of working solution and DMF	Mass of solvent in headspace vial	Equivalent mass fraction in sample
	ml	ml	ml	mg	%
a	0,80	4,20	5,00	40	4,0
b	0,40	4,60	5,00	20	2,0
c	0,20	4,80	5,00	10	1,0
d	0,10	4,90	5,00	5,0	0,5
e	0,05	4,95	5,00	2,5	0,25

Table 48 — Calibration solutions in DMF for *n*-hexane

Calibration solution	Volume of 100 mg/ml stock standard solution to be added	Volume of DMF to be added	Total volume of stock standard solution and DMF	Mass of solvent in headspace vial	Equivalent mass fraction in sample
	ml	ml	ml	mg	%
a	1,00	4,00	5,00	100	10
b	0,80	4,20	5,00	80	8
c	0,50	4,50	5,00	50	5
d	0,20	4,80	5,00	20	2
e	0,10	4,90	5,00	10	1

Table 49 — Calibration solutions in DMF for 1-Methoxypropan-2-ol

Calibration solution	Volume of 250 mg/ml working solution to be added	Volume of DMF to be added	Total volume of stock standard solution and DMF	Mass of solvent in headspace vial	Equivalent mass fraction in sample
	ml	ml	ml	mg	%
a	1,20	3,80	5,00	300	30
b	1,00	4,00	5,00	250	25
c	0,60	4,40	5,00	150	15
d	0,40	4,60	5,00	100	10
e	0,20	4,80	5,00	50	5

Table 50 — Calibration solutions in saline for 1-Methoxypropan-2-ol, ethanol and propan-2-ol

Calibration solution	Volume of 250 mg/ml stock standard solution to be added	Volume of 10 % saline to be added	Total volume of stock standard solution and saline	Mass of solvent in headspace vial	Equivalent mass fraction in sample
	ml	ml	ml	mg	%
a	0,80	4,20	5,00	200	20
b	0,40	4,60	5,00	100	10
c	0,20	4,80	5,00	50	5
d	0,08	4,92	5,00	20	2
e	0,04	4,96	5,00	10	1

10.5.5.4.5 Calibration solutions for the identification of solvents using GC-MS

Prepare calibration solutions (a and b) for each set of solvents (A to E) as shown in Table 51 by pipetting appropriate volumes of the appropriate 10 mg/ml stock standard solutions (10.5.5.2) into a series of 100-ml volumetric flasks and making up to the mark with dichloromethane.

Table 51 — Calibration solutions for identification of solvents by GC-MS

Set	Organic solvent	Concentration of calibration solution (a) mg/ml	Concentration of calibration solution (b) mg/ml
A	Propane-1,2-diol	1,00	0,05
B	Butyl acetate 1-Methoxypropan-2-yl acetate 2-Methylpentane-2,4-diol 3-Methoxybutyl acetate	0,02	0,005
C	Butyl glycolate 2-(2-Butoxyethoxy)ethyl acetate	0,25	0,05
D	Caprolactam Glycerol triacetate	0,02	0,005
E	Petroleum fraction (boiling range 35 °C to 160 °C) Hydrocarbons, C9 –C16, hydrotreated, dearomatized	0,25	0,05

10.5.5.4.6 Calibration solution for the determination of solvents using GC-MS

Prepare calibration solutions (a to e) in Table 52 for 2-(2-butoxyethoxy)ethyl acetate, butyl glycolate, caprolactam and 2-Methylpentane-2,4-diol by pipetting the specified volume (according to Table 52 to Table 55) of the appropriate 10-mg/ml stock standard solution (10.5.5.2) into a series of 100-ml volumetric flasks and making up to the mark with dichloromethane.

Table 52 — Calibration solutions for 2-(2-butoxyethoxy)ethyl acetate

Calibration solution	Volume of 10-mg/ml stock standard solution required ml	Concentration of calibration solution mg/ml	Equivalent mass fraction in sample[a,b] %
a	0,50	0,050	15
b	0,25	0,025	7,5
c	0,10	0,010	3
d	0,075	0,007 5	2,25
e	0,005	0,000 5	1,5

[a] Assuming 1,000 g of sample is taken for analysis and the dilution in 10.5.5.4.1 is applied.

[b] For information purposes only.

Table 53 — Calibration solutions for butyl glycolate

Calibration solution	Volume of 10-mg/ml stock standard solution required ml	Concentration of calibration solution mg/ml	Equivalent mass fraction in sample[a,b] %
a	2,50	0,25	5
b	2,00	0,20	4
c	1,50	0,15	3
d	1,00	0,10	2
e	0,50	0,05	1

[a] Assuming 1,000 g of sample is taken for analysis and the dilution in 10.5.5.4.1 is applied.

[b] For information purposes only.

Table 54 — Calibration solutions for caprolactam

Calibration solution	Volume of 10-mg/ml stock standard solution required ml	Concentration of calibration solution mg/ml	Equivalent mass fraction in sample[a,b] %
a	0,20	0,020	10
b	0,10	0,010	5
c	0,08	0,008	4
d	0,06	0,006	3
e	0,05	0,005	2,5

[a] Assuming 1,000 g of sample is taken for analysis and the dilution in 10.5.5.4.1 is applied.

[b] For information purposes only.

Table 55 — Calibration solutions for 2-Methylpentane-2,4-diol

Calibration solution	Volume of 10-mg/ml stock standard solution required ml	Concentration of calibration solution mg/ml	Equivalent mass fraction in sample[a,b] %
a	0,50	0,050	15
b	0,25	0,025	7,5
c	0,10	0,010	3
d	0,075	0,007 5	2,25
e	0,005	0,000 5	1,5

[a] Assuming 1,000 g of sample is taken for analysis and the dilution in 10.5.5.4.1 is applied.

[b] For information purposes only.

10.5.5.4.7 Calibration solutions for the determination of propane-1,2-diol using GC-FID

Prepare calibration solutions (a to e) for propane-1,2-diol by pipetting the specified volume (according to Table 56) of the 10-mg/ml propane-1,2-diol stock standard solution (10.5.5.3) into a series of 100-ml volumetric flasks and making up to the mark with dichloromethane.

Table 56 — Calibration solutions for the determination of propane-1,2-diol by GC-FID

Calibration solution	Volume of 10-mg/ml stock standard solution required	Concentration of calibration solution	Equivalent mass fraction in 1 g sample[a,b]
	ml	mg/ml	%
a	5,00	0,50	20
b	4,00	0,40	16
c	3,00	0,30	12
d	2,00	0,20	8
e	1,00	0,10	4

[a] Assuming 1,000 g of sample is taken for analysis and the dilution in 10.5.5.4.1 is applied.

[b] For information purposes only.

10.5.6 Sampling

For sampling the test portion is taken from the container. Samples are packaged in a variety of tubes and bottles that will release volatile components to the atmosphere on opening. On opening the container the sample should be stirred using a glass rod to homogenize the sample, whenever possible. For samples ≤ 1 g the whole sample should be transferred immediately into a sampling tube or vial.

10.5.7 Sample preparation

10.5.7.1 General

To minimize loss of solvent, the samples shall be cooled in a refrigerator at (4 ± 2) °C for 1 h before opening.

10.5.7.2 Sample preparation for identification and determination of solvents by HS-GC-FID

Weigh (1,0 ± 0,05) g to the nearest 0,001 g of the test portion into a headspace vial and record the mass. For aqueous samples add 5 ml of saline and for non-aqueous samples add 5 ml of DMF. Crimp the vial immediately, then shake the vial to homogenize the solution.

10.5.7.3 Sample preparation for identification of solvents by GC-MS

10.5.7.3.1 General

Direct injection of samples into a gas chromatograph is not advised; a suitable cleanup of the sample is necessary. As the solvents identified by this technique have low volatility, minimal losses are expected.

10.5.7.3.2 Solvent-based glue, thinner and paint samples

Weigh (1,0 ± 0,05) g to the nearest 0,001 g of the test portion into a 50-ml beaker and add 5 ml of dichloromethane. Dissolve the test portion by gentle swirling and filter into a 20-ml volumetric flask using filter paper (10.5.4.8), then make up to the mark using dichloromethane. Glue and the paint samples solutions might require additional filtering before injection into the GC-MS using a 0,45-µm nylon syringe filter (10.5.4.9). Pipette 1 ml of the sample solution into a crimped vial.

10.5.7.3.3 Aqueous-based glue samples

Weigh (1,0 ± 0,05) g to the nearest 0,001 g of the test portion into a 50-ml beaker and add 5 ml of water. Dissolve the test portion by gentle swirling and filter into a 20-ml volumetric flask using filter paper, then make up to the mark using methanol. Some solutions might require additional filtering before injection into the GC-MS using a 0,45-µm surfactant-free cellulose acetate (SFCA) syringe filter (10.5.4.10). Pipette 1 ml of the sample solution into a crimped vial.

10.5.7.3.4 Aqueous-based paint samples

Weigh (1,0 ± 0,05) g to the nearest 0,001 g of the test portion into a 50-ml beaker and add 5 ml of methanol. Dissolve the test portion by gentle swirling and filter into a 20-ml volumetric flask using filter paper (10.5.4.8), then make up to the mark using methanol. Some solutions might require additional filtering before injection into the GC-MS using a 0,45-µm SFCA syringe filter (10.5.4.10). Pipette 1 ml of the sample solution into a crimped vial.

10.5.7.4 Sample preparation for determination of certain solvents by GC-MS

Determination of 2-(2-butoxyethoxy)ethyl acetate, butyl glycolate, caprolactam and 2-Methylpentane-2,4-diol will require the sample solution prepared in 10.5.7.3 to be further diluted in dichloromethane or methanol, as appropriate, to ensure the concentration of the analyte is within the calibration range. The dilutions are shown in Table 57. Pipette 1 ml of the diluted sample solution into a crimped vial for analysis by GC-MS.

Table 57 — Dilution factors for the quantification of solvents by GC-MS and GC-FID

Solvent	Dilution	Dilution factor
2-(2-Butoxyethoxy)ethyl acetate	1 ml in 150 ml dichloromethane	150
Butyl glycolate	1 ml in 10 ml dichloromethane	10
Caprolactam	1 ml in 250 ml dichloromethane	250
2-Methylpentane-2,4-diol	1 ml in 150 ml dichloromethane	150
Propane-1,2-diol	1 ml in 20 ml dichloromethane	20

10.5.7.5 Sample preparation for determination of propane-1,2-diol using GC-FID

Determination of propane-1,2-diol will require the sample solution prepared in 10.5.7.2 to be further diluted with dichloromethane or methanol, as appropriate, to ensure the concentration of the analyte is within the calibration range. The appropriate dilution is shown in Table 57. Pipette 1 ml of the diluted sample solution into a crimped vial for analysis by GC-FID.

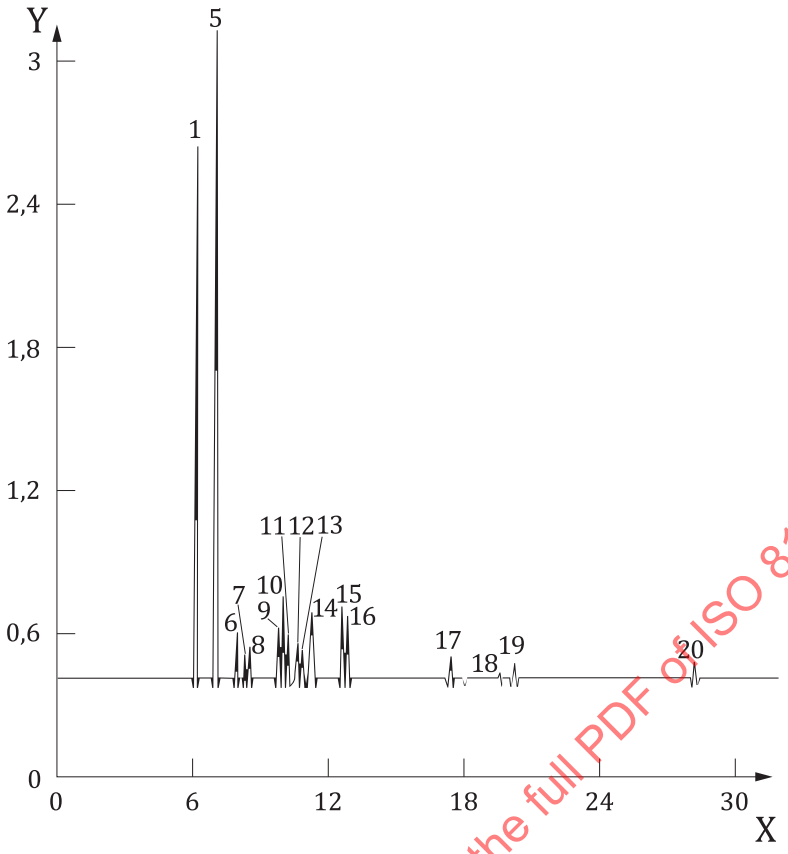
10.5.8 Procedure

10.5.8.1 Identification of solvents using HS-GC-FID

For the identification of solvents in aqueous-based materials, a two-point calibration graph is constructed by the calibration solutions prepared in 10.5.5.4.2.

For the identification of solvents in solvent-based materials, a two-point calibration graph is constructed by the calibration solutions prepared in 10.5.5.4.3.

Analyse the calibration solutions by HS-GC-FID using the conditions specified in 10.5.4.13. The order of elution for the solvents in the chromatogram using a 60 m × 0,32 mm × 0,50 µm polar column (ZB-WAX) is shown in Figure 1 and Table 58.



Key

Y response

X time, in min

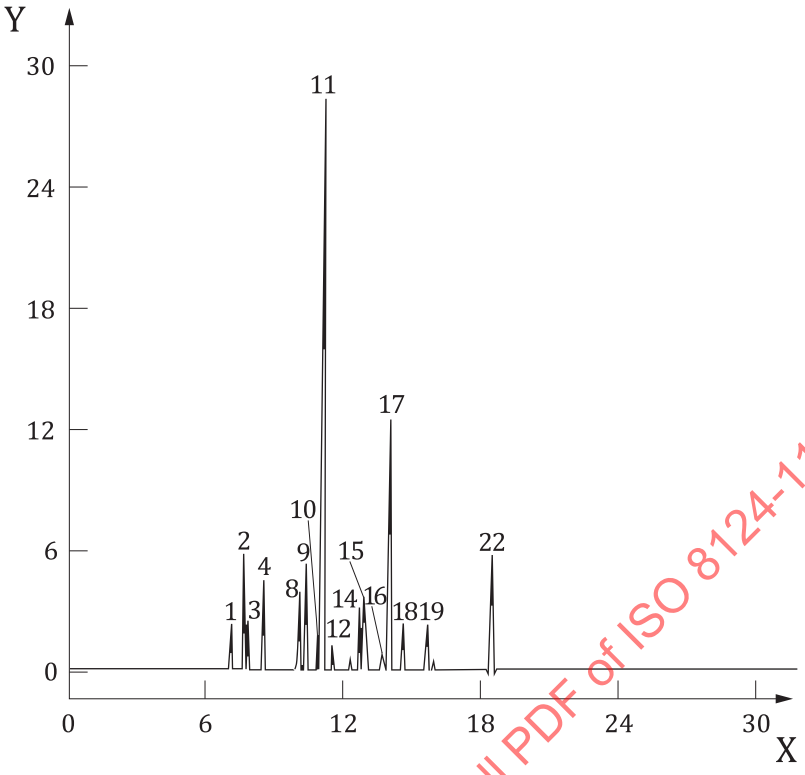
Figure 1 — Chromatogram of a mixture of organic solvents by HS-GC-FID using a 60 m × 0,32 mm × 0,50 µm polar column (ZB-WAX)

Table 58 — Typical retention times for solvents using the polar column (ZB-WAX)

Peak	Solvent	Retention time min	Peak	Solvent	Retention time min
1	*n*-hexane	6,18	13	Ethanol	11,0
5	Cyclohexane	7,07	14	3-Methylbutan-2-one	11,1
6	1,1-Dimethoxyethane	7,93	15	Propyl acetate	12,5
7	Acetone	8,28	16	Pentan-3-one	12,7
8	Methyl acetate	8,50	17	2-Methylpropan-1-ol	17,3
9	Ethyl acetate	9,75	18	1-Methoxypropan-2-ol	19,5
10	Isopropyl acetate	10,0	19	Butan-1-ol	20,1
11	Butan-2-one	10,2	20	Dimethylformamide	28,1
12	Propan-2-ol	10,7			

Analyse the sample headspace vial prepared in 10.5.7.2 by HS-GC-FID using identical conditions as those used for the calibration solutions. Compare the sample chromatogram with known reference standards to allow identification of solvents or any other compounds. Confirmation of solvent identity is by comparison of retention times on an alternative non-polar column (ZB-1).

The order of elution for the solvents in the chromatogram using a 60 m × 0,32 mm × 1,00 µm non-polar column (ZB-1) is shown in Figure 2 and Table 59.



Key

Y response

X time, in min

Figure 2 — Chromatogram of a mixture of organic solvents by HS-GC-FID using a 60 m × 0,32 mm × 1,00 µm non-polar column ZB-1

Table 59 — Typical retention times for solvents using the non-polar column (ZB-1)

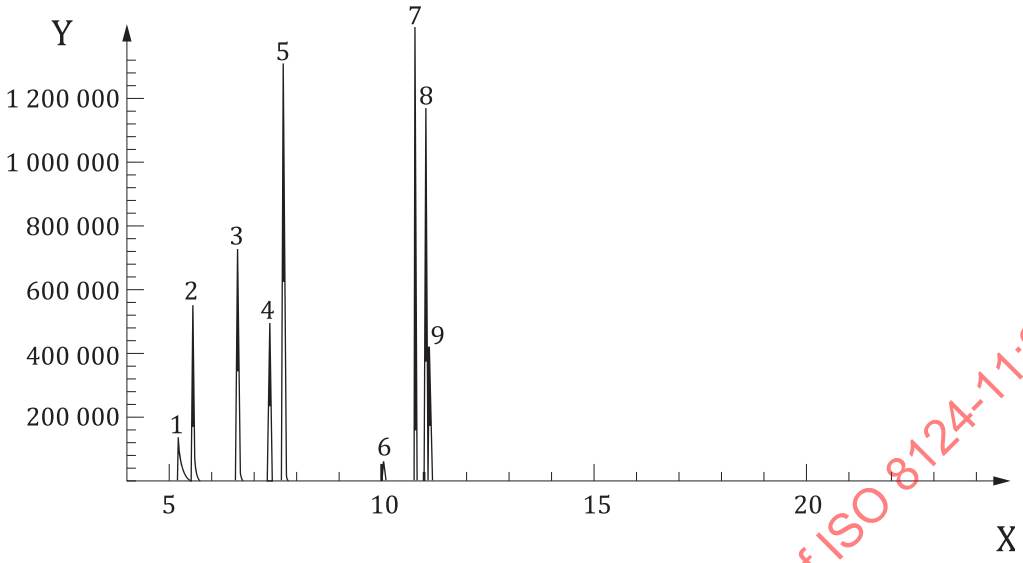
Peak	Solvent	Retention time min	Peak	Solvent	Retention time min
1	Ethanol	7,10	14	3-Methylbutan-2-one	12,8
2	Acetone	7,60	15	Butan-1-ol	13,0
3	Propan-2-ol	7,77	15	Isopropyl acetate	13,0
4	Methyl acetate	8,45	16	1-Methoxypropane-2-ol	13,7
8	Butan-2-one	10,1	17	Cyclohexane	14,1
9	1,1-Dimethoxyethane	10,4	18	Pentan-3-one	14,6
10	Ethyl acetate	10,9	19	Propyl acetate	15,6
11	*n*-hexane	11,1	22	Dimethylformamide	18,4
12	2-Methylpropan-1-ol	11,5			
NOTE On a non-polar column butan-1-ol and isopropyl acetate might not be separated when analysed in the same solution.					

Confirmation of the retention time and order of elution can be established by separately preparing and analysing directly the 250-mg/ml stock standard solutions (10.5.5.1).

10.5.8.2 Identification of solvents using GC-MS

Analyse each set of calibration solutions (a and b) prepared in 10.5.5.4.5 by GC-MS using the conditions specified in 10.5.4.12 and construct a two-point calibration graph. The order of elution for certain

solvents in the chromatogram is shown in Figure 3 and Table 60. For the identification of petroleum fraction [boiling range (35 to 160) °C] use a 60-m column.



Key

Y response

X time, in min

Figure 3 — Chromatogram: Total ion chromatogram of a mixture of organic solvents by GC-MSD

Table 60 — Typical retention times for certain solvents analysed by GC-MS

	Solvents	Retention time min	Ion m/z
1	Propane-1,2-diol	5,29	45
2	Butyl acetate	5,55	43
3	1-Methoxypropan-2-yl acetate	6,61	43
4	2-Methylpentane-2,4-diol	7,35	59/43
5	3-Methoxybutyl acetate	7,70	43/59
6	Butyl glycolate	10,0	57
7	2-(2-Butoxyethoxy)ethyl acetate	10,8	48/87/57
8	Glycerol triacetate	11,0	53
9	Caprolactam	11,2	113/55/85

Analyse the sample vial prepared in 10.5.7.3 by GC-MS using identical conditions as those used for the calibration solutions. Compare the sample chromatogram with known reference standards to allow identification of solvents or any other compounds.

10.5.8.3 Determination of solvent content by HS-GC-FID

For each solvent identified in 10.5.8.1 that requires quantification by HS-GC-FID, analyse the appropriate calibration solutions prepared in 10.5.5.4.5 using the conditions specified in 10.5.4.11. For each identified solvent construct a five-point calibration curve of response against solvent concentration (mg/vial).

Analyse the sample headspace vial prepared in 10.5.7.2 by HS-GC-FID using identical conditions as those used for the calibration solutions. From the calibration graph determine the solvent concentration in the sample vial (mg/vial) and calculate the percentage solvent content in the sample using Formula (9).

10.5.8.4 Determination of solvent content using GC-MS

For each solvent identified in 10.5.8.2 that requires quantification by GC-MS, analyse the appropriate calibration solutions prepared in 10.5.5.4.5 using the conditions specified in 10.5.4.12. For each identified solvent construct a five-point calibration curve of response against solvent concentration (mg/ml).

Analyse the diluted sample solution(s) prepared in 10.5.7.4 by GC-MS using identical conditions as those used for the calibration solutions. From the calibration graph determine the solvent concentration in the diluted sample solution (mg/ml) and calculate the percentage solvent content in the sample using Formula (10).

10.5.8.5 Determination of propane-1,2-diol by GC-FID

NOTE Propane-1,2-diol cannot be quantified on a non-polar column using the GC-MS conditions specified in 10.5.4.12 due to tailing effects of the chromatogram.

Analyse the calibration solutions prepared in 10.5.5.4.7 by GC-FID using the conditions specified in 10.5.4.13 and construct a five-point calibration curve of response against solvent concentration.

The retention time of propane-1,2-diol under these conditions is typically 16,5 min.

Analyse the diluted sample solution prepared in 10.5.7.5 by GC-FID using identical conditions as those used for the calibration solutions. From the calibration graph determine the propane-1,2-diol concentration in the diluted sample solution (mg/ml) and calculate the percentage propane-1,2-diol content in the sample using Formula (10).

10.5.8.6 Blank determination

10.5.8.6.1 HS-GS-FID blank determination

For each test, analyse a blank solution prepared in 10.5.7.2 by HS-GC-FID omitting the sample using the conditions specified in 10.5.4.11.

10.5.8.6.2 GS-MS and GC-FID blank determination

For each test, analyse a blank solution prepared in 10.5.7.3 by GC-MS or CC-FID omitting the sample using the conditions specified in 10.5.4.12 or 10.5.4.13, as appropriate.

10.5.9 Evaluation of results

10.5.9.1 Calculation of solvent content by HS-GC-FID

The concentration of each solvent (mg/ml) in the sample solution is directly interpolated from the graph and the mass fraction of each solvent (%) in the sample calculated according to Formula (9):

$$M_{\mathrm{sol}} = \frac{W_{\mathrm{s}}}{W \times 10} \tag{9}$$

where

M_{sol} is the mass fraction of solvent, in %;

W_S is the mass of solvent, in mg;

W is the mass of sample, in g.

10.5.9.2 Calculation of solvent content by GC-MS or GC-FID

The concentration of each solvent (mg/ml) in the sample solution is directly interpolated from the graph and the mass fraction of each solvent (%) in the sample calculated according to Formula (10):

$$M_{sol} = \frac{W_S \times f}{W \times 0,5} \quad (10)$$

where

M_{sol} is the mass fraction of solvent, in %;

W_S is the mass of solvent, in mg;

W is the mass of sample, in g;

f is the dilution factor.

10.5.10 Test report

The test report shall contain, as a minimum, the following:

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

b) a reference to this document (i.e. ISO 8124-11);

c) results of the tests recorded as:

1) identification of solvent and technique used to identify the solvent HS-GC-FID/GC-MS/GC-FID;

2) mass fraction of each solvent identified, in %;

3) the total solvent mass fraction, being the sum of the individual solvent mass fractions, in %;

d) any deviation from the test procedure specified;

e) date of test.

10.6 Combined approach for the determination of plasticisers in solvent-based adhesives and in solvent-based paints or lacquers, film-forming agents in paints and lacquers and modifiers in solvent-based paints or lacquers

10.6.1 Principle

This method describes a procedure that is suitable for the quantification of plasticisers, film-forming agents and modifiers in solvent-based adhesives and in solvent-based paints or lacquers.

The sample is extracted with diethyl ether and the total extract is determined gravimetrically. The content of plasticisers in this extract is determined according to 10.2 (determination of plasticisers in oven-hardening PVC modelling clay sets). The film-forming agents are determined by gas

chromatography with mass selective detector. The content of modifiers is calculated as the difference between the total extract and the amount of plasticisers and film-forming agents.

Nitrocellulose in solvent-based paints or lacquers is identified by IR-spectroscopy.

Test report, see 10.6.7.

10.6.2 Determination of total extract

10.6.2.1 Standards and reagents

10.6.2.1.1 Standards

None.

10.6.2.1.2 Reagents

Table 61 — Reagents

Chemical	CAS number
Diethyl ether	60–29–7
Methanol	67–56–1
Potassium hydrogen carbonate	298–14–6
Sand	

10.6.2.2 Apparatus

10.6.2.2.1 Centrifuge, capable of achieving at least 1 900 g.

10.6.2.2.2 Ultrasonic bath or shaker.

10.6.2.2.3 Rotary evaporator.

10.6.2.2.4 Oven, capable of maintaining a temperature of (110 ± 2) °C.

10.6.2.2.5 Analytical balance, precision 0,1 mg.

10.6.2.2.6 50-ml glass-stoppered flat-bottomed flasks.

10.6.2.2.7 General volumetric glassware.

10.6.2.2.8 Desiccator chamber.

10.6.2.2.9 Centrifuge tubes, min. 30 ml with caps.

10.6.2.3 Sampling

For sampling the test portion is taken from the container.

10.6.2.4 Sample procedure

Homogenize the sample of paint or lacquer by stirring with a glass rod or a spatula before extraction. The adhesives are analysed without treatment.

10.6.2.5 Procedure

Weigh (1,0 ± 0,1) g to the nearest 0,001 g of the test portion into a centrifuge tube, add a small amount of sand and 10 ml of diethyl ether (Table 61). Close the centrifuge tube and place it in an ultrasonic bath for 15 min.

Instead of the ultrasonic bath, an alternative extraction method may be used.

Centrifuge the tube for 5 min and transfer the supernatant liquid to a second centrifuge tube containing 10 ml of methanol (Table 61). If a precipitate forms within a few minutes, separate by centrifuging. Transfer the supernatant into a weighed 50-ml glass-stoppered flask and evaporate to dryness with a rotary evaporator. Dry the flask in an oven at (110 ± 2) °C. After drying, store the flask in a desiccator chamber till cooled. Then re-weigh and determine the amount of residue.

Reconstitute the residue in 50 ml of diethyl ether.

Use this solution for the determination of plasticisers and for the determination of film-forming agents.

10.6.2.6 Evaluation of results

The residue content in the sample is calculated according to Formula (11):

$$M_r = \frac{W_r \times 100}{1\,000 \times W} \tag{11}$$

where

M_r is the extractable material mass fraction, in %;

W_r is the mass of residue, in mg;

W is the mass of sample, in g.

10.6.3 Identification of nitrocellulose

10.6.3.1 Principle

Nitrocellulose in solvent-based paints or lacquers is identified by IR-spectroscopy.

10.6.3.2 Reagents

Table 62 — Solvents

Chemical	CAS number
Potassium bromide for IR-spectroscopy	7758–02–3

10.6.3.3 Apparatus

10.6.3.3.1 Oven, capable of maintaining a temperature of (105 ± 2) °C.

10.6.3.3.2 Press, for making potassium bromide (Table 62) pellets.

10.6.3.3.3 Fourier transform infrared spectrometer (FTIR-spectrometer), with attenuated total reflectance (ATR) cell.

Measurement range: 4 000 cm^{-1} to 400 cm^{-1}

Scans: 32