SLOVENSKI STANDARD
SIST EN 16521:2014

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Kozmetika - Analizne metode - Metoda GC/MS za identifikacijo in analizo 12 ftalatov v kozmetičnih vzorcih, pripravljenih za neposredno injeciranje

Cosmetics - Analytical methods - GC/MS method for the identification and assay of 12 phthalates in cosmetic samples ready for analytical injection

Kosmetische Mittel - Analysenmethoden - GC/MS-Methode für die Identifizierung und die Prüfung von 12 Phthalaten in kosmetischen Proben für die analytische Injektion

Cosmétiques - Méthodes analytiques - Méthode GC-MS pour l'identification et le dosage de 12 phtalates dans les produits cosmétiques prêts à être injecté dans un système analytique

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English Version

Cosmetics - Analytical methods - GC/MS method for the identification and assay of 12 phthalates in cosmetic samples ready for analytical injection

Cosmétiques - Méthodes analytiques - Méthode CG-SM pour l'identification et l'analyse de 12 phtalates dans des échantillons de produits cosmétiques prêts à être injectés dans un système analytique

Kosmetische Mittel - Analysenmethoden - GC/MS-Methode für die Identifizierung und die Quantifizierung von 12 Phthalaten in zur direkten Injektion geeigneten Proben kosmetischer Mittel

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Foreword

This document (EN 16521:2014) has been prepared by Technical Committee CEN/TC 392 “Cosmetics”, the secretariat of which is held by AFNOR.

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of an identical text or by endorsement, at the latest by November 2014 and conflicting national standards shall be withdrawn at the latest by November 2014.

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Introduction

Phthalates are esters of phthalic acid (Figure 1). About 80 % of all phthalates manufactured are used as “plasticizers” to make plastics flexible without sacrificing strength or durability. These compounds are present in cosmetic products like perfumes and toiletries. Some phthalates, particularly those of low molecular weight, are introduced into cosmetics as ingredients, for examples DEP and DMP are used as solvents and perfume fixatives [1-3] or DEP can be used as alcohol denaturing [2, 4]. Their presence in such products may come from their use as ingredients during the manufacturing process or may come from the migration of phthalates from packaging when plastic is used. Their presence as contaminant could also be due to the manufacturing process or raw materials used. Some analytical methods are proposed in the literature for the determination of phthalates in cosmetic products [1, 4-12].

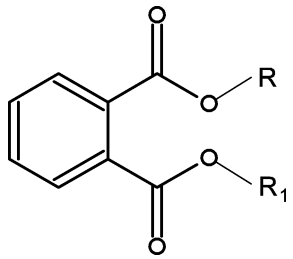

Figure 1 — Esters of phthalic acid

This standard proposes a GC/MS method for a simultaneous assay in cosmetic samples ready for analytical injection of 12 phthalates listed in Table 1. These chromatographic conditions are not suitable for the quantification of di-isononyl phthalate (DiNP) or di-isodecyl phthalate (DiDP). According to SCCP [13], the possible presence of DiNP or DiDP in cosmetics does not seem to be a problem for human health. A GC/MS method using positive chemical ionisation with ammonia as collision gas is proposed in literature for the determinations of those compounds in cosmetic products [14].

Analyses are carried out on a GC/MS system with electron impact ionization mode (Ei). The separation of phthalates is obtained on a cross-linked 5 %-phenyl/95 %-dimethylpolysiloxane capillary column 30 m × 0,25 mm (i. d.) × 0,25 µm film thickness using a temperature gradient. Phthalate quantification is performed by external calibration using an internal standard or by the standard addition. Cosmetic samples are analyzed directly or after a previous dilution in ethanol [15].

1 Scope

This European Standard describes a GC/MS method for the assay of 12 phthalates, amongst which the 8 phthalates regulated by the European cosmetic regulation 1223/2009 [16]. This method is given for the analysis of samples ready for analytical injection from cosmetic products or raw materials used in cosmetic products. Samples should be compatible with GC analysis possibly after dilution. This method does not include requirements for the preparation of samples in cosmetic matrices for which direct injection in GC is not feasible.

2 Reagents

If not otherwise specified, analytical-grade chemicals shall be used.

2.1 Phthalates considered

Table 1 — Phthalates considered

Phthalates	CAS	Manufacturer[b]	Quality
DBP [a] (dibutyl phthalate)	84–74–2	ALDRICH	97,0 %
DEHP [a] (diethylhexyl phthalate)	117–81–7	ALDRICH	99,8 %
BBP [a] (butylbenzyl phthalate)	85–68–7	ALDRICH	97,0 %
DMEP [a] (di(2-methoxyethyl) phthalate)	117–82–8	ALDRICH	97,0 %
DnPP [a] (di-n-pentyl phthalate)	131–18–0	CIL CLUZEAU	99,0 %
DiPP [a] (diisopentyl phthalate)	605–50–5	CIL CLUZEAU	95,0 %
DPP [a] (n-pentyl isopentyl phthalate)	84777–06–0	CIL CLUZEAU	95,0 %*
DiBP [a] (diisobutyl phthalate)	84–69–5	ACROS	98,0 %
DCHP (dicyclohexyl phthalate)	84–61–7	ALDRICH	98,0 %
DEP (diethyl phthalate)	84–66–2	ACROS	98,0 %
DMP (dimethyl phthalate)	131–11–3	ACROS	98,0 %
DnOP (di-n-octyl phthalate)	117–84–0	ALDRICH	98,0 %

a Regulated phthalates.

b This 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 CEN of this product.

* Mixed isomers (DiPP, DnPP and DPP)

2.2 Ethanol

2.3 Internal standard, 4,4-Dibromodiphenyl from Fluka [1)] 97,0 % was used as internal standard (ISTD).

2.4 Internal standard stock solution (SM-ISTD), c = 1 000 µg/ml.

1) This 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 CEN of this product.

Weigh approximately 10 mg of 4,4-Dibromodiphenyl (2.3) into a 10 ml volumetric flask. Firstly, dissolve in a small amount of ethanol (2.2) and then fill to the calibration mark with ethanol. This stock solution is daily prepared.

2.5 Phthalates stock solution, c = 500 µg/ml (SM).

Weigh approximately 10 mg of each phthalate (2.1) into a 20 ml volumetric flask. Firstly, dissolve in a small amount of ethanol (2.2) and then fill to the calibration mark with ethanol. This stock solution has a shelf life of at least 2 weeks if stored in a refrigerator.

NOTE Due to the low amount of DIPP standard (sold in quantities of 10,0 mg), a stock solution of this phthalate is prepared independently from other phthalates. In this way, two intermediate stock solutions SM-1 and SM-2 at 1 000 µg/ml are prepared. SM-1 is prepared weighting approximately 10 mg of each phthalate (2.1), except DiPP, into a 10,0 ml volumetric flask, whereas SM-2 is prepared weighting approximately 5,0 mg of DiPP (2.1) into a 5,0 ml volumetric flask. The final stock solution SM is obtained mixing equal volumes of both standard solutions (c = 500 µg/ml). All these stock solutions have a shelf life of at least 2 weeks if stored in a refrigerator.

2.6 Calibration solutions (standard solutions)

1,0 ml of the phthalate stock solution SM (2.5) is transferred into a 10,0 ml volumetric flask and filled with ethanol (2.2) up to the calibration mark (c = 50 µg/ml). From this intermediate solution (S1), at least 5 calibration solutions are prepared by dilution in ethanol (2.2) after the addition of 100 µl of the internal standard stock solution (SM-ISTD). Phthalates concentrations on these calibration solutions ranges from 0,25 µg/ml to 5,0 µg/ml with an ISTD concentration fixed at 10,0 µg/ml. These calibration solutions are prepared extemporaneously and injected.

If cosmetic samples (perfume) are directly prepared in a 1,5 ml GC vial, according to 4.2, the preparation of calibration solutions have to be adapted. Calibration solutions, ranging from 0,25 µg/ml to 5,0 µg/ml, are prepared without internal standard and 10 µl of the internal standard stock solution (SM-ISTD) are added to 1,0 ml of each calibration solution directly in a 1,5 ml GC vial. These calibration solutions are prepared extemporaneously. Vials are shaken and the solution injected.

3 Apparatus and equipment

3.1 Standard laboratory equipment.

3.2 Gas chromatography/mass spectrometry apparatus.

3.3 Gas chromatography/FID (for standard purity).

3.4 Analytical separation column.

The following parameters have proved useful:

GC column, low bleeding phase: 5 %-Phenyl-95 %-dimethylpolysiloxane, 30 m × 0,25 mm (i. d.) × 0,25 µm or equivalent material.

4 Procedure

4.1 Standard purity

The purity of each standard and the internal standard and the respective percentages for geometrical isomers (n-pentyl isopentyl phthalate - DPP) shall be determined by GC-FID for further calculations.

4.2 Sample preparation

1,0 g of the cosmetic sample ready for analytical injection is transferred into a 10,0 ml volumetric flask and filled with ethanol (2.2) up to the calibration mark after the addition of 100 µl of the internal standard stock solution (SM-ISTD). This solution is injected. In case of excessive concentration of phthalates, an appropriate previous dilution of the sample is performed. The limit of quantification using this sample preparation was set at 5 ppm.

An alternative sample preparation consists to prepare the cosmetic sample directly in a 1,5 ml GC vial. 10 µl of the internal standard stock solution (SM-ISTD) are added to 1,0 ml of cosmetic samples (perfume). Vials are shaken and the solution injected. The limit of quantification obtained using this sample preparation was set at 0,5 ppm. Calibration solutions are prepared according to 2.6.

4.3 Gas chromatography (GC) measurement conditions

When using the apparatus (3.2) and column (3.4), the following conditions have shown to be useful:

Table 2 — GC/MS programme

Apparatus	Gas chromatography with mass selective detector (GC/MS) Autosampler		
Column	GC column, low bleeding phase: 5 %-Phenyl-95 %-dimethylpolysiloxane, 30 m × 0,25 mm × 0,25 µm (or equivalent)		
Oven programme	**Ramp**	**Temperature**	**Time**
		100 °C	0 min
	30 °C/min	200 °C	0 min
	3 °C/min	260 °C	0 min
	30 °C/min	320 °C	5 min
Injector T	300 °C		
Interface T	250 °C		
Source T	230 °C		
Injection time	30 min		
Gas / flow rate	He/1 ml/min		
Injection port	split/splitless		
Injection parameters :	1 µl/Constant pressure, Split 1/20		
Detection mode	Quadrupole		
Ionisation mode	EI (70 eV)		
Mass detection (Full/SIM)	Identification: full-scan (m/z 40 to 350) Quantification: SIM using 3 specific ions		
Internal standard	4,4-Dibromodiphenyl		
Calibration	0,25 µg/ml to 5,0 µg/ml		
Solvent used	Ethanol (injection)		