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Interested committees:

Title: BS EN 62321-8 Determination of certain substances in electrotechnical products

Part 8: Phthalates in polymers by gas chromatography-mass spectrometry (GC-MS); gas chromatography-mass spectrometry using a pyrolyzer/thermal desorption accessory (Py-TD-GC-MS)

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Introduction

This draft standard is based on national and international discussions. Your comments on this draft are invited and will assist in the preparation of the consequent standard.

For international standards, comments will be reviewed by the relevant UK national committee before sending the consensus UK vote and comments to the international committee, which will then decide appropriate action. If the international standard is approved, it is usual for the text to be published as a British Standard.

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Template for comments and secretariat observations

Date: xx/xx/20xx	Document: ISO/DIS xxxx
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1	2	(3)	4	5	(6)	7
MB	Clause No./ Subclause No./Annex (e.g. 3.1)	Paragraph/Figure/ Table/Note	Type of comment	Commend (justification for change) by the MB	Proposed change by the MB	Secretariat observations on each comment submitted
	3.1	Definition 1	ed	Definition is ambiguous and needs clarifying.	Amend to read '...so that the mains connector to which no connection...'	
	6.4	Paragraph 2	te	The use of the UV photometer as an alternative cannot be supported as serious problems have been encountered in its use in the UK.	Delete reference to UV photometer.	



111/692/CD

COMMITTEE DRAFT (CD)

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2023-04-14

SUPERSEDES DOCUMENTS:

111/647/RR

IEC TC 111 : ENVIRONMENTAL STANDARDIZATION FOR ELECTRICAL AND ELECTRONIC PRODUCTS AND SYSTEMS	
SECRETARIAT: Italy	SECRETARY: Mr Alfonso Sturchio
OF INTEREST TO THE FOLLOWING COMMITTEES:	PROPOSED HORIZONTAL STANDARD: ☒ Other TC/SCs are requested to indicate their interest, if any, in this CD to the secretary.
FUNCTIONS CONCERNED: ☐ EMC ☒ ENVIRONMENT ☐ QUALITY ASSURANCE ☐ SAFETY	

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TITLE:

Determination of certain substances in electrotechnical products - Part 8: Phthalates in polymers by gas chromatography-mass spectrometry (GC-MS), gas chromatography-mass spectrometry using a pyrolyzer/thermal desorption accessory (Py-TD-GC-MS)

NOTE FROM TC/SC OFFICERS:

The CD is prepared by IEC TC111 WG3, which was approved by TC111 WG3 35th meeting held on November 7 and 8 2022.

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS –

Part 8: Phthalates in polymers by gas chromatography-mass spectrometry (GC-MS), gas chromatography-mass spectrometry using a pyrolyser/thermal desorption accessory (Py/TD-GC-MS)

FOREWORD

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International Standard IEC 62321-8 has been prepared by IEC technical committee 111: Environmental standardization for electrical and electronic products and systems.

It has the status of a horizontal standard in accordance with IEC Guide 108.

This second edition cancels and replaces the first edition published in 2017, which has been technically revised.

In this second edition, the main technical changes with respect to the previous edition are as follows :

- a) the test methods have been evaluated by the test of PVC, PE, paint, rubber, and adhesive in polymers of electrotechnical products.

b) determination of target phthalates in this second edition is expanded to 20 specific phthalates.

c) the GC-MS using a pyrolyser/thermal desorption (TD) accessory is used as quantitative determination analysis of specific phthalates as well as screening analysis.

The text of this second edition is based on that of the first edition and the following documents:

CDV	Report on voting

Full information on the voting for the approval of this International Standard can be found in the report on voting indicated in the above table.

This document has been drafted in accordance with the ISO/IEC Directives, Part 2.

A list of all parts in the IEC 62321 series, published under the general title: *Determination of certain substances in electrotechnical products*, can be found on the IEC website.

The committee has decided that the contents of this publication will remain unchanged until the stability date indicated on the IEC website under "<http://webstore.iec.ch>" in the data related to the specific publication. At this date, the publication will be

- reconfirmed,
- withdrawn,
- replaced by a revised edition, or
- amended.

INTRODUCTION

The widespread use of electrotechnical products has drawn increased attention to their impact on the environment. In many countries all over the world this has resulted in the adaptation of regulations affecting wastes, substances and energy use of electrotechnical products.

The use of certain substances (e.g. lead (Pb), cadmium (Cd), polybrominated diphenyl ethers (PBDEs) and specific phthalates) in electrotechnical products is a source of concern in current and proposed regional legislation.

The purpose of the IEC 62321 series is therefore to provide test methods that will allow the electrotechnical industry to determine the levels of certain substances of concern in electrotechnical products on a consistent global basis.

This second edition of IEC 62321-8 describes the test method for specific phthalates based on REACH Annex XVII, RoHS Directive and US CPSIA in electrotechnical products.

WARNING – Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS –

Part 8: Phthalates in polymers by gas chromatography-mass spectrometry (GC-MS), gas chromatography-mass spectrometry using a pyrolyser/thermal desorption accessory (Py/TD-GC-MS)

1 Scope

This part of IEC 62321 specifies two normative and two informative techniques for the determination of specific phthalates in polymers of electrotechnical products.

Normative techniques provide the test methods for the determination of 19 specific phthalates listed in Table 1. Test method for determination of dimethyl phthalate (DMP; Cas No. 131-11-3) and diethyl phthalate (DEP; Cas No. 84-66-2) are shown in Annex Q. Informative techniques provide the test methods for the determination of 7 phthalates.

Table 1 – List of phthalates

No.	Substance	Abbreviation	CAS No.
1	Diisobutyl phthalate	DIBP	84-69-5
2	Dibutyl phthalate	DBP	84-74-2
3	Bis(2-methoxyethyl) phthalate	DMEP	117-82-8
4	Diisopentyl phthalate	DIPP	605-50-5
5	N-pentyl-isopentyl phthalate	PIPP	776297-69-9
6	Dipentyl phthalate	DnPP	131-18-0
7	Benzyl butyl phthalate	BBP	85-68-7
8	Diisohexyl phthalate	DIHxP	71850-09-4
9	Dihexyl phthalate	DnHP	84-75-3
10	1,2-Benzenedicarboxylic acid, di-C6-8-branched alkyl esters, C7-rich	DIHP	71888-89-6
11	Dicyclohexyl phthalate	DCHP	84-61-7
12	Bis(2-ethylhexyl) phthalate	DEHP	117-81-7
13	Di-n-octyl phthalate	DNOP	117-84-0
14	Diisononyl phthalate	DINP	28553-12-0
15	Diisodecyl phthalate	DIDP	26761-40-0
16	1,2-Benzenedicarboxylic acid, dipentyl ester, branched and linear ^a	DPP	84777-06-0
17	1,2-Benzenedicarboxylic acid, dihexyl ester, branched and linear ^a	DHP	68515-50-4
18	1,2-benzenedicarboxylic acid, di-C6-10-alkyl esters; 1,2-benzenedicarboxylic acid, mixed decyl and hexyl and octyl diesters with ≥ 0,3 % of dihexyl phthalate ^a	-	68515-51-5 68648-93-1
19	1,2-Benzenedicarboxylic acid, di-C7-11-branched and linear alkyl esters ^a	DHNUP	68515-42-4
20	Didecyl phthalate ^b	DDP	84-77-5
21	Decyl hexyl phthalate ^b	DeHP	25724-58-7
22	Decyl octyl phthalate ^b	DOP	119-07-3
23	Hexyl octyl phthalate ^b	HOP	61827-62-1
24	Diheptyl phthalate ^b	DHpP	3648-21-3
25	Heptyl nonyl phthalate ^b	HNP	19295-81-9
26	Dinonyl phthalate ^b	DNP	80764

27	Heptyl undecyl phthalate ^b	HUP	65185-88-8
28	Nonyl undecyl phthalate ^b	NUP	65185-89-9
29	Diundecyl phthalate ^b	DUP	3648-20-2
^a These substances are UVCB (Unknown or Variable Composition, Complex Reaction Products, or Biological Materials)			
^b These substances are only used for monitoring phthalates for qualitative and quantitative analysis of UVCB.			

380

381 Gas chromatography-mass spectrometry (GC-MS) and the GC-MS using a pyrolyser/thermal
382 desorption (TD) techniques are described in the normative part of this document.

383 The GC-MS method is considered the referee technique for the quantitative determination of
384 specific phthalates in the range of 50 mg/kg to 2 000 mg/kg.

385 The GC-MS using a pyrolyser/thermal desorption (TD) accessory is suitable for screening and
386 quantitative determination of specific phthalates in polymers that are used as parts of the
387 electrotechnical products in the range of 100 mg/kg to 2 000 mg/kg.

388 The IAMS technique is suitable for screening and semi-quantitative analysis of DIBP, DBP,
389 BBP, DEHP, DNOP, DINP, and DIDP. Determination of DBP and DIBP, DEHP and DNOP by
390 IAMS has not been established due to peak and mass spectral resolution limitations.

391 The LC-MS technique is limited to the determination of of BBP, DEHP, DNOP, DINP, and
392 DIDP. Determination of DBP and DIBP by LC-MS has not been established due to peak and
393 mass spectral resolution limitations.

394 A flow chart depicting how the normative Py/TD-GC-MS and GC-MS methods can be used are
395 provided in annexes of this document.

396 These two test methods using GC-MS and Py/TD-GC-MS have been evaluated by the test of
397 polyethylene (PE), polyvinyl chloride (PVC), paint, rubber and adhesive materials containing
398 individual phthalates between ~450 mg/kg to 30 000 mg/kg as depicted in the parts of this
399 document. The use of the four methods described in this document for other polymer types,
400 phthalate compounds or concentration ranges other than those specified above has not been
401 specifically evaluated.

402 This document has the status of a horizontal standard in accordance with IEC Guide 108 [16].

403 2 Normative references

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

408 IEC 62321-1:2013, *Determination of certain substances in electrotechnical products – Part 1:*
409 *Introduction and overview*

410 3 Terms, definitions and abbreviated terms

411 3.1 Terms and definitions

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

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

- IEC Electropedia: available at <http://www.electropedia.org/>
- ISO Online browsing platform: available at <http://www.iso.org/obp>

3.1.1 reference material

material, sufficiently homogeneous and stable with reference to specified properties, which has been established to be fit for its intended use in measurement or in examination of nominal properties

[SOURCE: IEC 62321-1:2013, 3.1.7 [2]]

3.1.2 screening

analytical procedure to determine the presence or absence of substances in the representative part or section of a product, relative to the value or values chosen as the criterion for presence, absence or further testing

Note 1 to entry: If the screening method produces values that are not conclusive, then additional analysis or other follow-up actions may be necessary to make a final presence/absence decision.

[SOURCE: IEC 62321-1:2013, 3.1.10]

3.1.3 calibrant calibration standard

substance in solid or liquid form with known and stable concentration(s) of the analyte(s) of interest used to establish instrument response (calibration curve) with respect to analyte(s) concentration(s)

3.1.4 response factor RF

ratio between the mass of the compound being analysed and the peak area of that compound in Equation (1)

$$RF = A / m \quad (1)$$

where

RF is the response factor;

A is the peak area of a compound;

m is the mass of a compound

3.1.5 relative response factor RRF

ratio between the RFs of two compounds – compound A and compound B – in Equation (2)

$$RRF_{A/B} = RF_A / RF_B \quad (2)$$

where

$RRF_{A/B}$ is the relative response factor of compound A to compound B;

RRF_A is the response factor of compound A;

RRF_B is the response factor of compound B

3.1.6**substitute compound**

Compound used to normalize the RF of a target compound by dividing by its RF

Note 1 to entry: The role is the same as internal standards to correct the response factor. However, this is not included in test samples and is analysed before analysis of test samples. More than one compound can be selected as a substitute compound.

3.1.7**relative response factor database****RRF database**

database in which RRFs are registered

3.1.8**RRF database calibration**

calibration method for determining the RF of target compound using measured RF of substitute compound and RRF registered in RRF database (Equation (3))

$$RF_A = RF_B \times RRF_{A/B} \quad (3)$$

where

RF_A is the response factor of target compound A;

RF_B is the response factor of substitute compound B;

$RRF_{A/B}$ is the relative response factor of compound A to compound B registered in RRF database

3.2 Abbreviated terms

ACN	Acetonitrile
BSA	N,O-bis(trimethylsilyl)acetamide
BSTFA	N,O-bis(trimethylsilyl)trifluoroacetamide
CRM	Certified reference material
DIP	Direct injection probe
EGA	Evolved gas analysis
EI	Electron ionization
GC	Gas chromatography
GC-MS	Gas chromatography – mass spectrometry
IAMS	Ion attachment mass spectrometry
IS	Internal standard
LC-MS	Liquid chromatography – mass spectrometry
LOD	Limit of detection
LOQ	Limit of quantification
MDL	Method detection limit
MS	Mass spectrometry
PBMS	Performance-based measurement system
PE	Polyethylene
PS	Polystyrene
PVC	Polyvinyl chloride
Py/TD-GC-MS	Gas chromatography-mass spectrometry using a pyrolyser/thermal desorption accessory
QC	Quality control

500	RF	Response factor
501	RRF	Relative response factor
502	SIM	Selected ion monitoring
503	TD	Thermal desorption
504	THF	Tetrahydrofuran
505	UVCB	Unknown or Variable Composition, Complex Reaction Products, or
506		Biological Materials

507 NOTE See Table 1 for abbreviated terms of specific phthalates.

508 4 Principle

509 In the GC-MS method, phthalates are quantitatively determined using ultrasonic dissolution
510 and precipitation of the sample matrix or Soxhlet extraction from polymers with separation by
511 gas chromatography separation and mass spectrometry detection.

512 The Py/TD-GC-MS uses gas chromatography-mass spectrometry using a pyrolyser/thermal
513 desorption accessory (see Annex E, Figure E.2) to screen for the presence of phthalates and
514 to quantitatively determine phthalates in polymers. One-point calibration and RRF database
515 calibration are applied to the screening analysis of phthalates, and multi-point calibration is
516 applied to the quantitative analysis of phthalates. Any calibration method may be selected for
517 each compound.

518 NOTE 1 A full scan run using a total ion current ("full scan") MS method for each sample can be used in order to
519 check for the existence of negative matrix interference from other additives in the polymer. Negative matrix
520 interference causes ion suppression which provides lower concentration results. Scan/SIM measurement
521 (simultaneous measurements) is also applicable.

522 NOTE 2 When the accuracy satisfies the recovery rate between 70 % and 130 % by the test in xx, the RRF
523 database which were constructed by a different Py/TD-GC-MS system can be applied.

524 5 Reagents and materials

525 5.1 GC-MS method

526 All chemicals shall be tested for contamination and blank values prior to application, as
527 follows:

- 528 a) ACN (HPLC grade);
- 529 b) THF (GC grade or higher);
- 530 c) n-Hexane (GC grade or higher);
- 531 d) helium (purity of greater than a volume fraction of 99,999 %);
- 532 e) phthalates : refer to Table 1
- 533 f) surrogate and internal standards:
 - 534 – surrogate standard used to monitor analytes recovery according to 8.2.1.1, 8.2.1.3,
535 and 8.5.1.1, for example dibutyl phthalate-3,4,5,6-d₄ or di-(2-ethylhexyl)phthalate-
536 3,4,5,6-d₄ standard;
 - 537 – internal standard used to correct for injection errors, according to 8.2.1.1 and 8.5.1.2,
538 for example anthracene-d₁₀ or benzyl benzoate.

539 The standards are acceptable when using a quadruple-type mass spectrometer. A high-
540 resolution mass spectrometer will require the use of other suitable standard substances
541 having a mass and elution time similar to that of the analyte. Deuterium substituted DBP and
542 DEHP are recommended for specified phthalates.

5.2 Py/TD-GC-MS method

All reagent chemicals shall be tested for contamination and blank values prior to application as follows:

a) helium (purity of greater than a volume fraction of 99,999 %);

NOTE 1 The nitrogen gas can be used if it is confirmed that the required performance is satisfied.

b) phthalates: refer to Table 1;

NOTE 2 Commercially available reference materials can be used and are listed in Annex I

The following reagent chemicals, when used for preparing the polymer sample, shall be similarly tested as the above:

c) n-hexane for preparing the phthalate standard solution (GC grade or higher);

d) THF, or a solvent suitable for preparing the polymer sample (GC grade or higher).

6 Apparatus

6.1 GC-MS method

The following items shall be used for the analysis:

a) analytical balance capable of measuring accurately to 0,000 1 g;

b) cryogenic grinding/milling with liquid N₂ cooling;

c) 1 ml, 5 ml, 10 ml, 100 ml volumetric flasks;

d) Soxhlet extractors:

– 30 ml Soxhlet extractors;

– 250 ml round-bottomed flask;

– ground-in stopper NS 29/32;

– Dimroth condenser NS 29/32;

– boiling stones (e.g. glass pearls or Raschig rings);

e) extraction thimble (cellulose 30 ml, ID 22 mm, height 80 mm);

f) glass wool (for extraction thimble);

g) ultrasonic bath;

h) deactivated injector liner (for GC-MS);

i) heating jackets;

j) funnels;

k) aluminium foil;

l) cork rings;

m) 0,45 µm PTFE filter;

n) microlitre syringe or automatic pipettes;

o) rotary evaporator with vacuum capability;

p) Pasteur pipettes;

q) 1,5 ml sample vials and a screw cap with polytetrafluoroethylene (PTFE) gasket or, depending on the analytical system, a comparable sample receptacle;

r) mini-shaker (also known as vortexer or vortex mixer);

s) a gas chromatograph – mass spectrometer, split/splitless inlet and a programmable temperature controlled oven. The mass spectrometer shall be able to perform selected ion monitoring (SIM) and a total ion current (“full scan”). The ionization box shall be treated

for chemical stability, and controlled at 230 °C. A 70 eV energy shall be applied in electron ionization (EI) mode.

The use of an autosampler is strongly recommended to ensure repeatability.

t) a capillary column.

NOTE A liquid phase 100 % dimethyl polysiloxane or 5 % diphenyl, 95 % dimethyl polysiloxane has been found suitable. The preferred column dimension length is 30 m, internal diameter is 0,25 mm, and the film thickness is 0,25 µm (see Annex J).

6.2 Py/TD-GC-MS method

The following items shall be used for the analysis:

- a) analytical balance capable of measuring accurately to 0,000 01 g (0,01 mg);
- b) a gas chromatograph – mass spectrometer equipped with pyrolyser/thermal desorption accessory, a split/splitless inlet and a programmable temperature controlled oven. The mass spectrometer shall be able to perform selected ion monitoring (SIM) and a total ion current (“full scan”). The ionization box shall be treated for chemical stability. A 70 eV energy shall be applied in electron ionization (EI) mode.

NOTE 1 For example, the ion box is heated in a furnace at 400 °C for 1 h for the treatment of chemical stability.

- c) the pyrolyser/thermal desorption accessory shall be capable of rising temperature to the thermal desorption temperature of target phthalates (See Annex D, Figure D.1). The pyrolyser/thermal desorption sample cup shall be treated for chemical stability and capable of accommodating both liquid and solid samples. The use of an auto-sampler is strongly recommended to ensure repeatability.

- d) capillary column;

NOTE 2 Commercially available columns are listed in Annex J.

The following items should be used for sample preparation as necessary:

- e) cryogenic grinding/milling with liquid nitrogen cooling;
- f) polymer sample preparation tools to cut or file polymer such as nipper, micro spatula, tweezers, cutter, file, and micro puncher;
- g) micro syringe or automated pipettes.
- h) deactivated glass wool;

7 Sampling

7.1 General

As described in IEC 62321-2 unless otherwise indicated (e.g. “using a nipper.”), cryogenic grinding/milling with liquid nitrogen cooling shall be performed.

7.2 GC-MS method

The sample should be cut into small pieces (no dimension larger than 3 mm), or milled/ground into a representative powder to pass through a 500 µm sieve before extraction.

7.3 Py/TD-GC-MS method

The sample can either be cut into small pieces using a cutter or filed off.

NOTE See GC-MS method in 7.1 for the preparation of grinding/milling sample.

8 Procedure

8.1 General instructions for the analysis

8.1.1 Overview

The validation of the instrumentation should include testing of potential cross contaminations between sequential samples. Additional blanks or an inverted sequence of testing will help to identify cross contaminations.

See Annex K for guidance regarding labware cleaning procedures for phthalate testing and Annex M for recommended sample analysis sequence.

8.1.2 GC-MS method

The following general instructions shall be followed.

- a) In order to reduce blank values, ensure the cleanliness of all glass equipment. Glass wool (6.1 f)) shall be deactivated at 450 °C for at least 30 min before use.
- b) If the amount of phthalates in the sample is considerably above the 0,1 % range, it will be necessary to carry out the analysis using an adjusted sample size or by repeating the analysis using an extract that has been appropriately diluted prior to internal standard addition.

8.1.3 Py/TD-GC-MS method

The following general instructions should be followed.

- a) After analysis of test samples with high analyte concentration, blank samples should be analysed until the background level of individual phthalates is decreased to 30 mg/kg or less.

NOTE A blank polymer material or blank sample cup is used for blank-sample analysis.

- b) In order to reduce blank values, ensure the cleanliness of all tools used in sample preparation.

8.2 Sample preparation

8.2.1 GC-MS method

8.2.1.1 Stock solution

The following stock solutions shall be prepared.

- a) Deuterated surrogate standard (to monitor analyte recovery): 1 000 µg/ml in an organic solvent (e.g. dibutyl phthalate-3,4,5,6-d₄ or di-(2-ethylhexyl)phthalate-3,4,5,6-d₄).
- b) Internal standard (to correct for injection error): 1 000 µg/ml in n-hexane (e.g. anthracene-d₁₀ or benzyl benzoate).
- c) Each phthalate solution: 10 000 µg/ml in n-hexane.
- d) Each phthalate spiking solution: 100 mg/l in n-hexane.
- e) Internal standard solution (100 µg/ml of anthracene-d₁₀ or benzyl benzoate): Transfer 1,0 ml of internal standard (8.2.1.1 b)) solution (1 000 µg/ml) into a 10 ml volumetric flask and fill with solvent up to the mark.

8.2.1.2 Pre-extraction of the Soxhlet extractors

To clean the Soxhlet extractors (6.1 d)), a 2 h pre-extraction is carried out with 70 ml of n-hexane. The washing solvent is discarded.

8.2.1.3 Extraction

The following steps shall be followed for sample extraction.

- f) Quantitatively transfer 500 ± 10 mg of the sample into a cellulose extraction thimble for Soxhlet extraction. Record the mass to the nearest 0,1 mg.
- g) Allow the sample to be transferred through a funnel into the extraction thimble. To ensure a quantitative transfer, the funnel should be rinsed with approximately 10 ml of n-hexane.
- h) 25 μ l of the surrogate standard (8.2.1.1 a) (1 000 μ g/ml) is added.
- i) Cover the thimble with glass wool to prevent the sample from floating.
- j) Approximately 120 ml of n-hexane is used for extraction under reflux. Allow the sample to be extracted for at least six hours with 6 to 8 cycles per hour. Shorter extraction time may result in lower recoveries of the analytes.
- k) After six hours of reflux, concentrate the extract to about 10 ml using rotary evaporation under vacuum (or similar process), and then dilute with n-hexane to 50 ml.

8.2.1.4 Alternative extraction procedures

For an organic solvent (e.g. THF) soluble polymer sample (e.g. PVC), the following alternative extraction procedure may be applied.

- a) Weigh (300 ± 10) mg of sample and transfer it into a 40 ml vial. Record the mass to the nearest 0,1 mg.
- b) Transfer 10 ml of appropriate solvent such as THF and 15 μ l of the surrogate standard (8.2.1.1 a) (1 000 μ g/ml) to the vial, and record the weight of the mixture.
- c) Tightly cap the sample vial. Place it in an ultrasonic bath (6.1 g)) and sonicate for 30 min to 60 min until the sample has dissolved. A small piece of adhesive tape may be used to prevent the cap from loosening due to vibration.
- d) After the sample has dissolved, allow the vial to cool to ambient temperature and record the weight. Verify that the weight is the same as recorded in step b) above.
- e) Choose a non-solvent for the polymer that is a good solvent for phthalates. Accurately add 20 ml of the non-solvent dropwise into the vial to precipitate the sample matrix.
- f) Allow the resulting extracted solution to stand at room temperature for 30 min (the polymeric material will precipitate resulting in sedimentation at the bottom of the vial).
- g) Allow the polymer to settle or filter the mixture through a 0,45 μ m PTFE membrane.

For a insoluble polymer sample (e.g. NBR), the same procedure should be applied with minimum 90 min if it has been confirmed in advance that the percent recovery of phthalates is between 70 % and 130 % over time. See Annex P.

8.2.1.5 Addition of the internal standard (IS)

- a) Transfer a 1 ml portion of the extract (8.2.1.2 g) into a 2 ml GC sample/autosampler vial with PTFE coated seal, Add 10 μ l of internal standard solution (8.2.1.1.e)) to the sample vial and cap the vial. Invert the vial manually two times to mix.
- b) Inject 1 μ l of the sample solution into the GC-MS and analyse it according to the parameters described in Table 2.

8.2.2 Py/TD-GC-MS method**8.2.2.1 Polymer sample**

- a) Place approximately 0,5 mg of the cut or powdered sample into a pre-weighed sample cup using a micro spatula or tweezers.
- b) Record the total weight of the cup with the sample in it to the nearest 0,01 mg and record the sample weight by subtracting the weight of the sample cup from the total weight.
- c) Place an appropriate amount of deactivated glass wool into the sample cup to ensure that the sample powder will not spill out.

NOTE If the distribution of the analyte is not uniform and a sample mass of 0,5 mg is not guaranteed to represent the degree of concentration, the sample is taken from several locations and mixed well using a cryogenic mill or completely dissolved using an optimal solvent such as THF. Refer to IEC 62321-2 [14].

8.2.2.2 Polymer reference materials or stock solution

Polymer reference materials are recommended for the calibration and sensitivity check. A thinly stretched polymer reference sheet or film would be particularly convenient. When polymer reference materials are not available, the following stock solutions are to be prepared.

NOTE 1 Commercially available polymer reference materials are listed in Annex I.

a) Polymer solution: Dissolve a polymer such as PVC or PS using a suitable solvent such as THF in a concentration of 50 mg/ml.

b) Standard mixture solution: Prepare a standard mixture solution containing target phthalates in n-hexane at a concentration of 100 µg/ml.

The following solution is to be prepared for RRF database calibration:

c) Stock solution of substitute compound such as DEHP: 100 µg/ml in organics solvent such as hexane or toluene.

NOTE 2 When more than one compound is used as a substitute compound, each stock solution or mixture solution is prepared.

8.3 Instrumental parameters

8.3.1 GC-MS method

Different conditions may be necessary to optimize a specific GC-MS system to achieve effective separation of each phthalate and meet the QC and limits of detection (LOD) requirements.

The following parameters have been found suitable and are provided as an example (see Table 2 and Table 3). The total ion current chromatogram and the extracted ion chromatogram are shown in Annex C (see from Figure C.1).

Table 2 – Measurement condition of GC-MS

GC	
Injection volume	1,0 µl
Column	Non-polar (phenyl-arylene-polymer equivalent to 5 % diphenyl-dimethyl-polysiloxane), length 30 m; internal diameter 0,25 mm; film thickness 0,25 µm (See Annex J)
Injector liner	4 mm single bottom taper glass liner with glass wool at bottom (deactivated)
Injection port temperature	300 °C
Column temperature	80 °C (0,5 min) → (15 °C/min) → 300 °C (5min)
Injection mode	Splitless
Carrier gas	Helium (5.1.d)), 1,0 ml/min, constant flow
Transfer line	280 °C, direct
MS	
Ion source temperature	230 °C
Electron ionization (EI)	70 eV
Quad	150 °C
Dwell time	50 ms
Scan range	50 m/z to 1 000 m/z

NOTE 1 Additional deactivation of a purchased deactivated injector liner (6.1.h)) can be performed. An example of a chemical deactivation procedure is as follows: take a commercially available, factory-deactivated liner.

(split/splitless single-taper with glass wool at the bottom) and immerse it in 5 % dimethyldichlorosilane (DMDCS) in dichloromethane or toluene for 15 min. Pick it up with forceps and drain and immerse it three times in the DMDCS to make sure the glass wool has been thoroughly covered and flushed. Drain once more and blot the residue solution onto a clean wiper. Immerse the liner in methanol for 10 min to 15 min, and again drain/immerse three times. Rinse it inside and out with methanol from a squeeze bottle, followed by dichloromethane from a squeeze bottle. Transfer the liner to a vacuum oven purged with nitrogen and dry it at 110 °C for at least 15 min. Once dry it is ready for use.

NOTE 2 To achieve the required data quality for each phthalate GC peak, 3 to 4 scans of the quantification ions selected are acquired per second. This will give the appropriate dwell time for each ion (m/z) to be monitored. The scan rate will result in a dwell time in the range of 50 ms per ion. By default, some software sets the dwell time as a function of the scan rate. The analysis of each phthalate is carried out in SIM mode with the mass traces given in Table 2. These have been found suitable and are provided as examples.

NOTE 3 DIDP, DINP, DIHP and DHP have multiple chromatogram peaks. The total areas of these peaks above the baseline is integrated.

Table 3 – Reference masses for the quantification of each phthalate

Substance	Ions (m/z) monitored in the extract		
	Quantification ion	Confirmation ion-1	Confirmation ion-2
DBP-3,4,5,6-d ₄	153	227	-
DEHP-3,4,5,6-d ₄	153	171	-
Anthracene-d ₁₀	188	94	160
Benzyl benzoate	105	194	212
DIBP	223	205	149
DBP	223	205	149
DMEP	207	194	149
DIPP	237	219	149
PIPP	237	219	149
DnPP	237	219	149
BBP	206	91	149
DnHP	251	233	149
DIHP	265	167	149
DCHP	249	122	231
DEHP	279	167	149
DNOP	279	167 261	149
DINP	293	167	149
DIDP	307	167	149
DPP ^a	-	-	-
DHP ^a	-	-	-
1,2-benzenedicarboxylic acid, di-C6-10-alkyl esters; 1,2-benzenedicarboxylic acid, mixed decyl and hexyl and octyl diesters with ≥ 0,3 % of dihexyl phthalate ^a	-	-	-
DHNUP ^a	-	-	-

DDP ^b	307	167	149
DIHxP ^b	251	167	149
DeHP ^b	307	289	149
DOP ^b	279	307	149
HOP ^b	251	279	149
DHP ^b	265	247	149
HNP ^b	265	293	149
DNP ^b	293	275	149
HUP ^b	321	265	149
NUP ^b	321	275	293
DUP ^b	321	167	149
^a These substances are UVCB (Unknown or Variable Composition, Complex Reaction Products, or Biological Materials)			
^b These substances are monitoring phthalates for qualitative and quantitative analysis of UVCB.			

755

756 8.3.2 Py/TD-GC-MS method

757 Different conditions may be necessary to optimize a specific Py/TD-GC-MS system to achieve
758 effective separation of each phthalate and meet the QC and MDL requirements. The following
759 parameters have been found suitable and are provided as an example (see Table 4). The total
760 ion current chromatogram and the extracted ion chromatogram are shown in Annex C (see
761 from Figure C.12).

762

Table 4 – Measurement condition of Py/TD-GC-MS

Pyrolyser	
Furnace temperature	200 °C → 20 °C/min → 300 °C → 5 °C/min → 340 °C (1 min)
Interface temperature	300 °C (interface temperature control mode: manual)
GC	
Column	100% Dimethyl polysiloxane, length 15 m, inner diameter 0,25 mm, film thickness 0,1 µm with 2 m guard column (See Annex J)
Injection port temperature	300 °C
Column oven temperature	80 °C → (20 °C /min) → 320 °C (4 min)
Injection mode	Split (split ratio: 1/50)
Carrier gas	Helium, 52,1 cm/s, constant linear velocity
MS	
Ion source temperature	230 °C
Ionization method	Electron ionization (EI), 70 eV.
Monitoring mass ion (m/z)	See the table 3
Scan range	50 m/z to 1 000 m/z
NOTE 1 Additionally, scan measurement of MS is available to check matrix interference from other additives in the polymer. Matrix interference causes ion suppression which provides a wrong quantitation result. Simultaneous scan and SIM measurement are also acceptable. NOTE 2 Scan measuring of MS is available for the detection of other additives. NOTE 3 See Annex F for an optimization of furnace temperature.	

763

764 **8.4 Calibration**765 **8.4.1 GC-MS method**766 **8.4.1.1 General**

767 A calibration curve shall be developed for quantitative analysis. At least five calibration
768 solutions shall be prepared in equidistant concentration steps. Quantification is made on the
769 basis of the measurement of the peak areas. The linear regression fit of each calibration
770 curve is required to have a relative standard deviation (RSD) of less than or equal to 15 % of
771 the linear calibration function.

772 NOTE If the limiting value of the RSD of 15 % is exceeded, from the point of view of quality assurance, second
773 order curve fitting does not guarantee any significantly better adjustment. Only statistical tests such as the F-test
774 fulfil these requirements by comparing linear/second order. That means that although the RSD value is exceeded,
775 the calibration is linear.

776 **8.4.1.2 Stock solutions for each phthalate (100 µg/ml) and surrogate standard**
777 **(100 µg/ml)**

778 Transfer 0,1 ml of each phthalate (8.2.1.1 c)) stock solution (10 000 µg/ml) and 1,0 ml of the
779 surrogate (8.2.1.1 a)) stock solution (1 000 µg/ml) into a 10 ml volumetric flask and fill with
780 solvent up to the mark.

8.4.1.3 Internal standard solution (100 µg/ml of anthracene-d₁₀ or benzyl benzoate)

Transfer 1,0 ml of internal standard (8.2.1.1 b)) solution (1 000 µg/ml) into a 10 ml volumetric flask and fill with solvent up to the mark.

8.4.1.4 Standard solutions

The following calibration standard solutions are prepared from the stock solution of each phthalate (100 µg/ml) and surrogate standard (100 µg/ml) (8.5.1.2). The volumes indicated in Table 5 are pipetted in 10 ml volumetric flasks with a pipette. Add 100 µl of 100 µg/ml internal standard solution (8.5.1.3) into the respective flasks, and then fill with solvent up to the mark.

Table 5 – Calibration standard solution of phthalates

No.	Volume phthalate + surrogate µl	Volume internal standard µl	<i>c</i> (each phthalate) µg/ml	<i>c</i> (surrogate) µg/ml
1	50	100	0,5	0,5
2	100	100	1,0	1,0
3	250	100	2,5	2,5
4	500	100	5,0	5,0
5	1 000	100	10	10

The internal standard is used for the correction of the injection error. The evaluation of the response factor or ratio is therefore carried out by A/A_{IS} .

To produce the calibration straight lines the response A/A_{IS} is plotted against the concentration ratio c/c_{IS} .

A linear regression is carried out using Equation (1):

$$\frac{A}{A_{IS}} = a \times \frac{c}{c_{IS}} + b \quad (1)$$

where

A is the peak area of the phthalate or the surrogate in the sample;

A_{IS} is the peak area of the internal standard in the sample;

c is the concentration of each phthalate or the surrogate in the sample (µg/ml);

c_{IS} is the concentration of the internal standard in the sample (µg/ml).

NOTE 1 It is a common practice to set the internal standard concentration to 1,0 µg/ml for internal standard methods when the amount and concentration of internal standard added to the sample and calibrants prior to injection are the same.

NOTE 2 DIDP, DINP, DIHP and DHP have multiple chromatogram peaks. The total areas of these peaks above the baseline is integrated.

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

A polynomial (e.g. second-order) regression shall be utilized in the event that the relative standard deviation curve requirements cannot be achieved using linear regression. All quality control requirements are still in effect when using polynomial regression.

8.4.2 Py/TD-GC-MS method

8.4.2.1 One-point calibration

Polymer reference material (1 000 mg/kg) is recommended for Py/TD-GC-MS method calibrants. Place approximately 0,5 mg of the cut or powdered polymer reference material into a sample cup for Py/TD-GC-MS (see Annex I).

NOTE 1 The following procedure is also used to prepare the calibrants.

Inject 10 µl of polymer solution (50 mg/ml) and 5 µl of standard mixture solution (100 µg/ml) into the sample cup.

Dry the solution at room temperature.

To produce calibration straight lines, the signal area of each phthalate is plotted against the absolute amount (ng).

A one-point calibration is carried out using Equation (2):

$$y = ax \quad (2)$$

where

y is the peak area of the phthalates in the sample;

x is the absolute amount of the phthalates in the sample (ng);

a is the slope of the calibration curve.

NOTE 2 DIDP, DINP, DIHP and DHP have multiple chromatogram peaks. The total areas of these peaks above the baseline are integrated.

8.4.2.2 RRF database calibration

8.4.2.2.1 General

The RRF for each analyte shall be calculated from the RF of each analyte and that of the substitute compound. Selection of the substitute compound is critical in this method. DEHP is a preferred compound because it is thermally and chemically stable especially in the process of Py/TD-GC-MS analysis. More than one compound can be selected as a substitute compound. The following describes the case where DEHP is used as the substitute compound.

8.4.2.2.2 Determination of RRFs

RRFs can be continuously used by verifying the accuracy. Moreover, when the accuracy satisfies the recovery rate between 70 % and 130 % by the test in 11.2.5, the RRFs which were determined by a different Py/TD-GC-MS system can be applied.

NOTE 1 The accuracy required for RRFs is described in 11.2.3 and 11.2.4.

The procedure for the determination of RRF using a solution is as follows:

a) Prepare 0,5 mg of sample (e.g. PS polymer) containing DEHP and analytes at a concentration of 1 000 mg/kg.

– Inject 10 µl of PS solution (50 mg/ml) into the sample cup.

– Inject 5 µl of phthalate stock solution (100 µg/ml) into the same sample cup.

– Dry the solution at room temperature.

b) Analyse the samples.

c) Record the peak area.

d) Calculate the RF of DEHP and that of each analyte using Equations (4) and (5), respectively.

e) Calculate the RRFs of each analyte using Equation (8).

Polymer reference materials, such as those containing DEHP and analytes at a concentration of 1 000 mg/kg, can be used.

f) Analyse polymer reference materials (8.2.1).

g) Record the peak area.

h) Calculate the RF of DEHP and that of each analyte using Equations (4) and (5) respectively.

i) Calculate the RRFs of each analyte using Equation (8).

$$RF_{DEHP} = A_{DEHP} / m_{DEHP} \quad (4)$$

$$RF_A = A_A / m_A \quad (5)$$

where

RF_{DEHP} and RF_A are the RF of DEHP and that of the analyte, respectively (mg^{-1});

A_{DEHP} and A_A are the peak areas of DEHP and of the analyte, respectively;

m_{DEHP} and m_A are the masses of DEHP and of the analyte, respectively (mg).

When the polymer reference materials are used, the m_{DEHP} and m_A can be calculated with the following Equations (6) and (7).

$$m_{DEHP} = M_R \times C_{DEHP} \times 10^{-6} \quad (6)$$

$$m_A = M_R \times C_A \times 10^{-6} \quad (7)$$

where

M_R is the mass of polymer reference material including DEHP and analyte (mg);

C_{DEHP} and C_A are the concentration of DEHP and that of the analyte, respectively (mg/kg);

m_{DEHP} and m_A are the masses of DEHP and of the analyte, respectively (mg).

$$RRF_{A/DEHP} = RF_A / RF_{DEHP} \quad (8)$$

where

$RRF_{A/DEHP}$ is the relative response factor of the analyte to DEHP;

RF_A and RF_{DEHP} are the RF of the analyte and that of DEHP, respectively (mg^{-1});

NOTE 2 DIDP, DINP, DIHP and DHP have multiple chromatogram peaks. The total areas of these peaks above the baseline are integrated.

NOTE 3 See Annex H for examples of RRFs.

8.4.2.3 Multi-point calibration

8.4.2.3.1 General

A calibration curve shall be developed for quantitative analysis. At least five calibrants shall be prepared in equidistant concentration steps. Quantification is made on the basis of the measurement of the peak areas. The linear regression fit of each calibration curve is required to have a relative standard deviation (RSD) of less than or equal to 15 % of the linear calibration function.

NOTE If the limiting value of the RSD of 15 % is exceeded, from the point of view of quality assurance, second order curve fitting does not guarantee any significantly better adjustment. Only statistical tests such as the F-test fulfil these requirements by comparing linear/second order. That means that although the RSD value is exceeded, the calibration is linear.

8.4.2.3.2 Calibrants

The calibrants are prepared from the stock solution of each phthalate (100 µg/ml) and polymer solution (50 mg/ml).

- Inject 10 µl of polymer solution (50 mg/ml) into a sample cup.
- Inject the phthalate stock solution (100 µg/ml) into the same sample cup; the injected volume is indicated in Table 5.
- Dry the solution at room temperature.

Table 6 – Calibrants of phthalates

No.	<i>c</i> (each phthalate) in polymer mg/kg	Volume polymer solution (50 mg/ml) µl	Volume phthalate stock solution (100 µg/ml) µl
1	100	10	0.5
2	500	10	2.5
3	1 000	10	5
4	1 500	10	7.5
5	2 000	10	10

To produce the calibration straight lines the peak area is plotted against the concentration. A linear regression is carried out using Equation (1):

$$y = ax + b \quad (1)$$

where

y is the peak area of the phthalate in the sample;

x is the absolute amount of the phthalates in the sample (ng);

NOTE DIDP, DINP, DIHP and DHP have multiple chromatogram peaks. The total areas of these peaks above the baseline is integrated.

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

A polynomial (e.g. second-order) regression shall be utilized in the event that the relative standard deviation curve requirements cannot be achieved using linear regression. All quality control requirements are still in effect when using polynomial regression.

9 Calculation of phthalate concentration

9.1 GC-MS method

Typically the calibration level of the internal standard for all five calibration levels are set to 1,0 in the instrument method, but it can also be done manually using the equation of the fit from the calibration.

For a linear fit, the equation takes the form of:

$$y = ax + b \quad (3)$$

where

y is the response factor or ratio (A/A_{IS}) for each phthalate in the sample;

a is the slope of the calibration curve;

x is the instrumental result in $\mu\text{g/ml}$ (the concentration of each phthalate in the extract);

b is the intercept on the y-axis of the calibration curve.

For a quadratic fit the equation takes the form of:

$$y_q = ax_q^2 + bx_q + c_q \quad (4)$$

where

y_q is the response factor or ratio (A/A_{IS}) for each phthalate in the sample;

a_q and b_q are constants that correspond to the curve that best fits the calibration;

x_q is the instrumental result in $\mu\text{g/ml}$ (the concentration of each phthalate in the extract);

c_q is the intercept on the y-axis of the calibration curve.

Equation (3), which is in the form of a linear equation, can be rewritten in the form of Equation (5):

$$c = \left(\frac{A}{A_{IS}} - b \right) \left(\frac{c_{IS}}{a} \right) \quad (5)$$

where

A is the peak area of each phthalate or the surrogate;

A_{IS} is the peak area of the internal standard;

c is the concentration of each phthalate or the surrogate in $\mu\text{g/ml}$;

c_{IS} is the concentration of the internal standard in $\mu\text{g/ml}$.

NOTE It is a common practice to set the internal standard concentration to 1,0 $\mu\text{g/ml}$ for the internal standard methods when the amount and concentration of internal standard added to the sample and calibrants prior to injection are the same.

a is the slope of the calibration curve;

b is the intercept on the y-axis of the calibration curve.

A polynomial (e.g. second-order) regression shall be utilized in the event that the relative standard deviation curve requirements cannot be achieved using linear regression. All quality control requirements are still in effect when using polynomial regression.

If the concentration of each phthalate in a sample does not fall within the range of its respective calibrants, a serial sample dilution shall be prepared that will bring the concentration of the phthalates to the midpoint of the calibration. Analyse the dilution and use the dilution factor to quantify the concentration of those phthalates that were not within the calibration range in the original analysis. The dilution factor (D) can be calculated by dividing the final volume of the dilution by the volume of the aliquot:

$$D = \frac{V_f}{V_a} \quad (6)$$

where

D is the dilution factor;

V_f is the final volume in ml;

V_a is the volume of the aliquot in ml.

Equation (5) does not give the final concentration as the volume of the organic solvent, the mass of the sample and the volume of the extract and any dilution factor needs to be taken into account. The final concentration of phthalates or the surrogate in the sample can be calculated by using Equation (7):

$$c_{\text{final}} = \left(\frac{A}{A_{\text{IS}}} - b \right) \times \frac{c_{\text{IS}}}{a} \times \frac{V}{m} \times D \quad (7)$$

where

c_{final} is the concentration of each phthalate or the surrogate in the sample in $\mu\text{g/g}$;

V is the final extraction volume (30 ml or 50 ml);

m is the mass of the sample in grams.

The calculation shown above is for linear regression calibration only. If necessary, a separate calculation for polynomial regression calibration shall be utilized.

The phthalates isolated from the sample extraction described in 8.2.1.3 or 8.2.1.4 are quantified by adding the internal standard (anthracene- d_{10} or benzyl benzoate) (8.2.1.1.e)) to an extract aliquot, injecting the solution into the GC-MS, measuring the area of the analyte peak(s) and the area of the anthracene- d_{10} or benzyl benzoate peak, and calculating the concentration of the analyte according to the formula given in Equation (11). Data on the surrogate standard (8.2.1.1 a)) are not used in the formula and are not used in any way to calculate the analyte concentration(s).

9.2 Py/TD-GC-MS method

9.2.1 One-point calibration

The final concentration of each phthalate in the sample can be calculated by using Equation (8):

$$c_{\text{final}} = y \times \left(\frac{1}{a} \right) \times \left(\frac{1}{m} \right) \quad (8)$$

where