भारतीय मानक

Indian Standard

IS 16197 (Part 3/Sec 4) : 2024
IEC 62321-3-4 : 2023

इलेक्ट्रोटेक्निकल उत्पादों में कुछ पदार्थों का निर्धारण

भाग 3 स्क्रीनिंग

अनुभाग 4 पराबैंगनी डिटेक्टर (एचपीएलसी-यूवी), पतली परत क्रोमैटोग्राफी (टीएलसी) और थर्मल डिसोर्प्शन मास स्पेक्ट्रोमेट्री (टीडी-एमएस) के साथ उच्च प्रदर्शन तरल क्रोमैटोग्राफी द्वारा इलेक्ट्रोटेक्निकल उत्पादों के पॉलिमर में थैलेट्स)

Determination of Certain Substances in Electrotechnical Products

Part 3 Screening

Section 4 Hthalates in Polymers of Electrotechnical Products by High Performance Liquid Chromatography with Ultraviolet Detector HPLC-UV Thin Layer Chromatography TLC and Thermal Desorption Mass Spectrometry TD-MS

ICS 01.110; 13.020.01; 29.100.01

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Standardization of Environmental Aspects for Electrical and Electronic Products, ETD 43

NATIONAL FOREWORD

This Indian Standard (Part 3/Sec 4) which is identical to IEC 62321-3-4 : 2023 'Determination of certain substances In electrotechnical products — Part 3-4: Screening — Phthalates in polymers of electrotechnical products by high performance liquid chromatography with ultraviolet detector (HPLC-UV), thin layer chromatography (TLC) and thermal desorption mass spectrometry (TD-MS)' issued by the International Electrotechnical Commission (IEC) was adopted by the Bureau of Indian Standards on the recommendation of the Standardization of Environmental Aspects of Electrical and Electronics Products Sectional Committee and approval of the Electrotechnical Division Council.

The text of IEC Standard has been approved as suitable for publication as an Indian Standard without deviations. Certain terminologies and conventions are, however, not identical to those used in Indian Standards. Attention is particularly drawn to the following:

a) Wherever the words 'International Standard' appear referring to this standard, they should be read as 'Indian Standard'; and
b) Comma (,) has been used as a decimal marker, while in Indian Standards the current practice is to use a point (.) as the decimal marker.

In this standard, reference appears to International Standards for which Indian Standards also exist. The corresponding Indian Standards, which are to be substituted, are listed below along with their degree of equivalence for the editions indicated:

International Standard	*Corresponding IndianStandard*	*Degree of Equivalence*
IEC 62321-1 : 2013 Determination of certain substances in electrotechnical products — Part 1: Introduction and overview	IS 16197 (Part 1) : 2014/ IEC 62321-1 : 2013 Determination of certain substances in electrotechnical products: Part 1 Introduction and overview	Identical
IEC 62321-2 : 2021 Determination of certain substances in electrotechnical products — Part 2: Disassembly, disjointment and mechanical sample preparation	IS 16197 (Part 2) : 2014 Determination of certain substances in electrotechnical products: Part 2 Disassembly, disjointment and mechanical sample preparation	Identical

Only the English language text has been retained while adopting it in this Indian Standard, and as such, the page numbers given here are not the same as in the IEC publication.

For the purpose of deciding whether a particular requirement of this standard is complied with the final value, observed or calculated expressing the result of a test or analysis shall be rounded off in accordance with IS 2 : 2022 'Rules for rounding of numerical values (*second revision*)'. The number of significant places retained in the rounded off value should be the same as that of the specified value in this standard.

CONTENTS

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 first edition of IEC 62321-3-4 introduces a new part in the IEC 62321 series.

Appropriate test methods are required in order to facilitate the monitoring of the contents of certain substances in affected materials. Faced with the enormous task of testing a diversity of electronic and electric equipment, the industry adopted the concept of 'screening' in order to reduce the amount of testing. As defined in IEC 62321-1:2013, 3.1.10, *"...screening is an 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"*. Executed as a predecessor to any other test analysis of the product, the main objective of screening is to quickly, expediently, inexpensively and preferably in a non-destructive manner, determine whether the screened product:

- contains a certain substance at a concentration significantly higher than its value accepted as criterion, and therefore can be rejected as being above the threshold;
- contains a certain substance at a concentration significantly lower than its value accepted as criterion, and therefore can be considered below the threshold;
- contains a certain substance at a concentration so close to the value accepted as criterion that when all possible errors of measurement and safety factors and measurement uncertainty are considered, no conclusive decision can be made about the absence or presence of substance and, therefore, a follow-up action can be required, such as another, more specific or more precise and accurate analysis.

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.

Indian Standard

DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS

PART 3 SCREENING

SECTION 4 HTHALATES IN POLYMERS OF ELECTROTECHNICAL PRODUCTS BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY WITH ULTRAVIOLET DETECTOR HPLC-UV THIN LAYER CHROMATOGRAPHY TLC AND THERMAL DESORPTION MASS SPECTROMETRY TD-MS

1 Scope

This part of IEC 62321 specifies procedures for the screening of di-isobutyl phthalate (DIBP), di-n-butyl phthalate (DBP), benzyl butyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP) in polymers of electrotechnical products by using high performance liquid chromatography with ultraviolet detector (HPLC-UV), thin layer chromatography (TLC) and thermal desorption mass spectrometry (TD-MS).

High performance liquid chromatography with ultraviolet detector (HPLC-UV), thin layer chromatography (TLC) and thermal desorption mass spectrometry (TD-MS) techniques are described in the normative part of this document. Fourier transform infrared spectroscopy (FT-IR) is described in the informative annexes of this document.

The HPLC-UV and TLC techniques are suitable for screening and semi-quantitative analysis of DIBP, DBP, BBP and DEHP in polymers that are used as parts in electrotechnical products above 300 mg/kg.

Theu TD-MS technique is suitable for screening and semi-quantitative analysis of DIBP, DBP, BBP and DEHP in polymers that are used as parts in electrotechnical products above 300 mg/kg.

The FT-IR technique is suitable for preliminary screening of total phthalates (DIBP, DBP, BBP, DEHP and so forth) in polymers that are used as parts in electrotechnical products above 50 000 mg/kg.

These test methods have been evaluated by testing polyethylene (PE), polyvinyl chloride (PVC) materials containing individual phthalates between 500 mg/kg to 3 000 mg/kg as depicted in this document. The use of the methods described in this document for other polymer types, phthalate compounds or concentration ranges other than those specified above has not been specifically evaluated.

A flow chart is given as an example of how each method included in this document can be used for screening. The test methods in this document differ from those given in IEC 62321-8 [1][1] in that not all phthalates in this scope are separated from each other. Detectable combinations are DIBP + DBP + BBP and DEHP for the HPLC-UV technique, DIBP + DBP, BBP and DEHP for the TLC technique and TD-MS technique, total phthalates for the FT-IR technique. FT-IR is a suitable analytical technique for preliminary screening in the first step of phthalates screening. These test methods are characterized by a shorter measuring time compared with IEC 62321-8 because all phthalates in this scope are not separated from each other.

NOTE See Annex F for commonly used phthalates in products.

This document has the status of a horizontal publication in accordance with IEC Guide 108 [2].

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[1] Numbers in square brackets refer to the Bibliography.

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.

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

IEC 62321-2:2021, *Determination of certain substances in electrotechnical products – Part 2: Disassembly, disjointment and mechanical sample preparation*

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

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

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

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

3.1.1
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]

3.1.2
semi-quantitative
level of accuracy in a measurement amount where the relative uncertainty of the result is typically 30 % or better at a defined level of confidence of 68 %

[SOURCE: IEC 62321-6:2015, 3.1.1 [3]]

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)

3.2 Abbreviated terms

ACN	acetonitrile
APCI	atmospheric pressure chemical ionization
APCI-MS	atmospheric pressure chemical ionization mass spectrometry
BBP	benzyl butyl phthalate
CRM	certified reference material
DBP	di-n-butyl phthalate
DEHP	di-(2-ethylhexyl) phthalate
DIBP	di-isobutyl phthalate
DIP	direct injection probe
DNOP	di-n-octyl phthalate
FT-IR	Fourier Transform infrared spectroscopy
HPLC-UV	high performance liquid chromatography with ultraviolet detector
IA-MS	ion attachment mass spectrometry
TLC	thin layer chromatography
IS	internal standard
LOD	limit of detection
LOQ	limit of quantification
MDL	method detection limit
MS	mass spectrometry
PVC	polyvinyl chloride
QC	quality control
SIM	selected ion monitoring
TD-MS	thermal desorption mass spectrometry
THF	tetrahydrofuran

4 Principle

In the HPLC-UV method, DIBP, DBP, BBP and DEHP are determined using ultrasonic extraction followed by high-pressure, liquid chromatography separation and ultraviolet detection. Owing to the peak overlapping of DIBP, DBP and BBP, occurrence of the peak indicates only qualitative information of possible presence of DIBP, DBP and BBP or a combination of one or two of either of these phthalates.

The TLC method, as well as the HPLC method, is one of the liquid chromatography methods and can be performed with simple instruments. In the TLC method, DIBP, DBP, BBP and DEHP in the polymer are separated by TLC after ultrasonic extraction and detected by image analysis after photography under UV light. DIBP and DBP are detected as sum peaks because it is difficult to separate them by TLC.

TD-MS techniques use a thermal desorption system directly connected to mass spectrometry with ionization systems such as an atmospheric pressure chemical ionization or ion attachment to screen for the presence of DIBP, DBP, BBP and DEHP in polymers. This method allows for the direct analysis of a polymer sample without pre-treatment process. For example:

- The APCI-MS method has an ion source that attaches H^+ to target molecules by a corona discharge under atmospheric pressure and is coupled with a furnace stabilized at 330 °C and a sample heater. The sample heater is programmed to heat up to 230 °C to thermally desorb sample molecules. The thermally desorbed sample molecules (M) form adducts ($M + H^+$) with H^+ in the reaction and are analysed by a mass spectrometer via select ion monitoring.
- The IA-MS method includes a Li^+ attachment reaction chamber with a Li^+ emitter and is coupled with a direct injection probe (DIP). The DIP is programmed to heat up to 350 °C to thermally desorb sample molecules. The thermally desorbed sample molecules (M) form adducts ($M + Li^+$) with Li^+ in the reaction chamber and those adducts are analysed by a mass spectrometer via select ion monitoring.

Therefore, target molecules with the same molecular weight such as DBP and DIBP, DEHP and Di-n-octyl phthalate (DNOP) are detected as sum peaks by TD-MS techniques.

The principle of phthalate detection by FT-IR can be referenced in Annex A.

These test methods are based on the concept of performance. Apparatus, sampling and calibration are specified in this document in relatively general terms. It is the responsibility of the user to document all procedures developed in the laboratory that uses the test methods described in this document. The user shall establish a written procedure for all cases denoted in the test methods described in this document by the term ″work instructions″. A flowchart is provided in Annex E as an example of how these methods can be used for screening.

5 HPLC-UV and TLC method

5.1 Reagents and materials

5.1.1 Reagents and materials of HPLC-UV method

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

a) methanol (HPLC grade, purity greater than a volume fraction of 99,7 %);
b) THF (HPLC grade, purity greater than a volume fraction of 99,7 %);
c) ethanol (HPLC grade, purity greater than a volume fraction of 99,7 %);
d) ultrapure water (HPLC grade);
e) standard mixture solution or reference polymer materials as calibrants:
one contains approximately 1 000 mg/kg of phthalates.

NOTE Commercially available reference materials are listed in Annex D.

5.1.2 Reagents and materials of TLC method

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

a) acetonitrile;
b) methanol;
c) standard mixture solution or reference polymer materials as calibrants:
one contains approximately 1 000 mg/kg of phthalates;

NOTE Commercially available reference materials are listed in Annex D.

5.2 Equipment, apparatus and tools

5.2.1 Equipment, apparatus and tools for HPLC-UV method

The following equipment shall be used for the analysis:

a) high-performance liquid chromatography (HPLC) system equipped with a UV or PDA/UV detector, auto sampler, pump and column oven;
b) analytical balance capable of measuring accurately to 0,000 1 g (0,1 mg);
c) ultrasonic bath (capable of heating above 50 °C);

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

d) cryogenic grinding or milling with liquid N_2 cooling.

The following items shall be used for the analysis:

e) column;
f) glass vials for HPLC-UV;
g) glass vials for extraction (40 ml volume is recommended);
h) volumetric flask;
i) adjustable pipettes;
j) paper filters, medium-fast filtration, general laboratory use.

NOTE The size of the required glass vial for HPLC depends on the instrument.

5.2.2 Equipment, apparatus and tools for TLC method

The following equipment shall be used for the analysis:

a) ultrasonic bath (capable of heating above 60 °C);
b) analytical balance (capable of measuring accurately to 0,000 1 g (0,1 mg));
c) TLC plate (stationary phase C18, size 20 cm × 20 cm, cut in half to 20 cm × 10 cm);
d) TLC developing chamber;
e) UV lamp (λ = 254 nm, 2 units required);
f) digital camera (with UV lens filter for ultraviolet adsorption as optional);
g) clamp (for fixing UV lamps and a camera);
h) desktop darkroom.

The following items shall be used for the analysis:

a) glass vials for extraction (4 ml volume is recommended);
d) capillary (capacity 1 µl);
c) volumetric flask;
d) adjustable pipettes or micro syringes;
e) scissors or cutter knife.

5.3 Sampling

Unless otherwise specified in this document, the sampling procedure described in IEC 62321-2 shall be referred to.

All items used in the samples preparation for measurements shall be shown to be free of contamination, specific for the analytes of this TLC method. This means that all grinding materials, solvents, fluxes, etc. shall not contain detectable quantities of phthalates (DIBP, DBP, BBP, and DEHP).

Tools used in the handling of samples shall be chosen to minimize contamination by the analytes of this TLC test method as well as by any other elements or species. The procedures which will be used for cleaning different tools shall not introduce any contaminants.

5.4 Procedure

5.4.1 Procedure of HPLC-UV method

5.4.1.1 Sample preparation

5.4.1.1.1 General

Sample preparation requires clean glassware (e.g. single use items) to avoid cross contamination.

5.4.1.1.2 Polymer sample

a) Cryogenic grinding with liquid N_2 cooling is recommended to achieve a particle size under 1 mm.
b) Weigh 150 mg ± 20 mg of the sample and transfer it into a glass vial for extraction. Record the mass to the nearest 0,1 mg.
c) Transfer 5 ml of THF to the vial.
d) Tightly cap the sample vial. Place it in an ultrasonic bath (50 °C) and sonicate for 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.
e) After the sample is dissolved, allow the vial to cool to ambient temperature.
f) Accurately add 10 ml of ethanol dropwise into the vial to precipitate the sample matrix.
g) Allow the polymer to settle or filter the mixture through a paper filter made of hydrophilic polytetrafluoroethylene.

5.4.1.1.3 Standard solution

Whenever possible, the solvent used for the HPLC sample and standard solutions shall be the same to avoid any potential solvent effects.

The standard mixture solutions of phthalates given in Table 1 are used for calibration. A reference polymer material which concentration is approximately 1 000 mg/kg can be used for preparing the standard stock solution. When using reference polymer materials, the standard mixture solution shall be prepared in accordance with 5.4.1.1.2.

Table 1 – Standard mixture solution concentrations

No.	DIBP	DBP	BBP	DEHP
1	10 µg/ml (equivalent to 1 000 mg/kg)	10 µg/ml (equivalent to 1 000 mg/kg)	10 µg/ml (equivalent to 1 000 mg/kg)	10 µg/ml (equivalent to 1 000 mg/kg)

5.4.1.2 Instrumental parameters

Different conditions can be necessary to optimize a specific HPLC-UV system to achieve effective determination of phthalates and meet the requirements of 5.7.1 (Quality assurance and control).

The following parameters given in Table 2 have been found suitable and are provided as an example. For every measurement the peaks for each phthalate shall be identified by the retention times with the standard stock solution. Deviation of retention times shall not exceed ±5 % within a batch.

NOTE See Annex C for examples of chromatogram at suggested conditions.

Table 2 – Measurement conditions of HPLC-UV

Liquid (mobile) phase	95 % methanol / 5 % water (volume fraction)
Stationary (column) phase	C18 stationary phase, 150 mm in length and 4,6 mm in diameter, 5 µm particle size or equivalent
Measurement conditions	
Run time	15 min
Flow rate	1,0 ml/min
Wavelength	254 nm
Injection volume	10 µl
Column temperature	40 °C ± 2 °C
NOTE In the measurement conditions described in this Table 2, examples of retention time of each phthalate are for DIBP/DBP/BBP: 2,5 min to 3,5 min, for DEHP: 5,5 min to 6,0 min.	

5.4.1.3 Calibration

The HPLC-UV method shall be calibrated taking into account interference effects and any other effects that influence the determination of the peak area.

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

A slope of a one-point calibration curve is calculated by using Equation (1).

$$a = A / m \tag{1}$$

where

a is the slope of the calibration curve;

A is the peak area of each phthalate in the standard mixture solution or the extract of reference polymer material;

m is the absolute amount of each phthalate in the standard mixture solution or the extract of referenced polymer material (ng).

The calibration curve is specified by using Equation (2):

$$y = ax \tag{2}$$

where

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

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

a is the slope of the calibration curve calculated by Equation (1).

5.4.2 Procedure of TLC method

5.4.2.1 Sample preparation

5.4.2.1.1 General

Sample preparation requires clean glassware (e.g. single use items) to avoid cross contamination. See Annex B for details of analysis by the TLC method.

5.4.2.1.2 Polymer sample

a) Cut samples into 2 mm to 4 mm by scissors or a cutter knife.

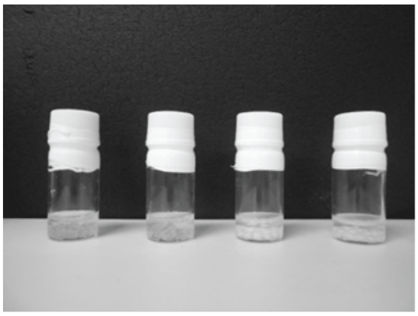
b) Weigh 250 mg ± 10 mg of the sample and transfer it into a glass vial for extraction. Record the mass to the nearest 0,1 mg.

c) Transfer 0,5 ml of acetonitrile to the vial.

d) Tightly cap the sample vial. Place it in an ultrasonic bath (60 °C ± 5 °C, setting beforehand) and sonicate for 60 min. A small piece of sealing tape may be used to prevent the cap from loosening due to vibration (Figure 1).

NOTE 1 If the amount of sample is limited, the weight of the sample can be reduced to 100 mg and the amount of solvent is reduced to 0,2 ml.

NOTE 2 If there is too much suspended solids and the supernatant liquid cannot be collected, the liquid is centrifuged to precipitate the suspended solids.



IEC

Figure 1 – Polymer samples in glass vials with acetonitrile (tightened with sealing tape)

5.4.2.1.3 Standard solution

The standard mixture solutions of phthalates given in Table 3 are used for calibration.

A reference polymer material which concentration is approximately 1 000 mg/kg can be used for preparing the standard stock solution. When using reference polymer materials, the standard stock solution shall be prepared in accordance with 5.4.2.1.2.

Table 3 – Standard mixture solution concentrations

No.	DIBP	DBP	BBP	DEHP
1	2,5 mg/ml (equivalent to 1 000 mg/kg)	2,5 mg/ml (equivalent to 1 000 mg/kg)	2,5 mg/ml (equivalent to 1 000 mg/kg)	2,5 mg/ml (equivalent to 1 000 mg/kg)

5.4.2.2 Analysis procedure of TLC method

Different conditions can be necessary to optimize a specific TLC system to achieve effective determination of phthalates and meet the requirements of 5.7.2 (Quality assurance and control).

The following parameters given in Table 4 have been found suitable and are provided as an example. For every measurement, the peaks for each phthalate shall be identified by the retention factor values (Rf values) with the standard mixture solutions which should be spotted on each TLC plate. As DBP and DIBP cannot be separated, they are detected as one spot. Deviation of Rf values shall not be out of the range from −0,02 to +0,05 for DEHP, ±0,02 for BBP and the combination DBP + DIBP within a batch.

NOTE 1 The separation method by TLC, detection by image analysis, and re-measurement method when affected by coexisting substances are shown in Annex B as reference information.

NOTE 2 All or part of 5.4.2.2 can also be performed automatically by commercially available equipment.

NOTE 3 See Annex C for examples of chromatogram at suggested conditions.

Table 4 – Measurement conditions of TLC

TLC plate	Stationary phase; silica gel 60 RP-18F254s, Plate length: 10 cm
Liquid (mobile) phase	Acetonitrile
Apply amount of sample solution	1 µl × 5 times
Apply amount of standard solution	1 µl × 1 time
UV wavelength for detection	254 nm

5.4.2.3 Calibration

Calibration for TLC should be the same as for HPLC-UV (5.4.1.3).

The TLC method shall be calibrated taking into account interference effects and any other effects that influence the determination of the peak area.

To produce calibration straight lines, the peak area is plotted against the concentration (mg/kg) of each phthalate.

A slope of a one-point calibration curve is calculated by using Equation (3).

$$a = A/m \tag{3}$$

where

a is the slope of the calibration curve;

A is the peak area of each phthalate in the standard mixture solution or the extract of reference polymer material;

m is the absolute amount of each phthalate in the standard mixture solution or the extract of referenced polymer material (ng).

The calibration curve is specified by using Equation (4):

$$y = ax \tag{4}$$

where

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

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

a is the slope of the calibration curve calculated by Equation (3).

5.5 Calculation of phthalates concentration

The concentration of each phthalate in the extracted sample can be calculated by using Equation (5):

$$c = y \times (1/a) \tag{5}$$

where

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

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

a is the slope of the calibration curve calculated by Equation (1);

The final concentration of each phthalate in the sample can be calculated by using Equation (6):

$$c_{\text{final}} = c \times v \times (1/M) \times 10^3 \tag{6}$$

where

c_{final} is the concentration of each phthalate in the sample (mg/kg);

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

v is the volume of extracted solvent (ml);

M is the weight of the sample (mg).

When the reference polymer material is used for preparing the standard stock solution, the final concentration of each phthalate in the sample is corrected by weight of the reference polymer material:

$$c'_{\text{final}} = c_{\text{final}} \times (M_{\text{cal}} / M) \tag{7}$$

where

c'_{final} is the corrected concentration of each phthalate in the sample (mg/kg);

c_{final} is the concentration of each phthalate in the sample (mg/kg);

M_{cal} is the weight of the reference polymer material (mg);

M is the weight of the sample (mg).

5.6 Precision

5.6.1 Precision of HPLC-UV method

When the values of three independent single test results, obtained using the same method on an identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, lie within the range of the mean values cited in Table 5 below, the absolute difference between the mean value of three test results and the test result obtained will not exceed the repeatability limit r deduced by statistical analysis of the international inter-laboratory study 3-4 (IIS 3-4) results in more than 5 % of cases.

When the values of three single test results, obtained using the same method on an identical test material in different laboratories by different operators using different equipment, lie within the range of the values cited in Table 5 below, the absolute difference between the mean value of three test results and the test result will not be greater than the reproducibility limit *R* deduced by statistical analysis of the international inter-laboratory study 3-4 (IIS 3-4) results in more than 5 % of cases.

Table 5 – IIS 3-4 Repeatability and reproducibility of HPLC-UV

Sample	**Component**	**Mean value** $\bar{x}$ mg/kg	**Repeatability** r mg/kg	**Reproducibility** R mg/kg
IIS3-4-A01	DIBP/DBP/BBP	Below detection limit	Not applicable	Not applicable
	DEHP	Below detection limit	Not applicable	Not applicable
IIS3-4-B02	DIBP/DBP/BBP	1 137	85	1 224
	DEHP	396	53	476
IIS3-4-C03	DIBP/DBP/BBP	2 326	169	1 873
	DEHP	869	50	836
IIS3-4-D04	DIBP/DBP/BBP	3 791	223	5 649
	DEHP	2 604	178	706
IIS3-4-E05	DIBP/DBP/BBP	Below detection limit	Not applicable	Not applicable
	DEHP	262 470	10 190	81 717

See Annex G for supporting data.

5.6.2 Precision of TLC method

When the values of three independent single test results, obtained using the same method on an identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, lie within the range of the mean values cited in Table 6 below, the absolute difference between the mean value of three test results and the test result obtained will not exceed the repeatability limit *r* deduced by statistical analysis of the international inter-laboratory study 3-4 (IIS 3-4) results in more than 5 % of cases.

When the values of three single test results, obtained using the same method on an identical test material in different laboratories by different operators using different equipment, lie within the range of the values cited in Table 6 below, the absolute difference between the mean value of three test results and the test result will not be greater than the reproducibility limit *R* deduced by statistical analysis of the international inter-laboratory study 3-4 (IIS 3-4) results in more than 5 % of cases.

Table 6 – IIS 3-4 Repeatability and reproducibility of TLC

Sample	Component	Mean value $\bar{x}$ mg/kg	Repeatability r mg/kg	Reproducibility R mg/kg
IIS3-4-A01	DIBP/DBP	Below detection limit	Not applicable	Not applicable
	BBP	Below detection limit	Not applicable	Not applicable
	DEHP	Below detection limit	Not applicable	Not applicable
IIS3-4-B02	DIBP/DBP	797	267	659
	BBP	337	194	488
	DEHP	347	188	310
IIS3-4-C03	DIBP/DBP	1 372	487	1 070
	BBP	821	133	215
	DEHP	774	157	696
IIS3-4-D04	DIBP/DBP	2 191	604	1 582
	BBP	2 074	392	1 476
	DEHP	2 490	361	3 331
IIS3-4-E05	DIBP/DBP	Below detection limit	Not applicable	Not applicable
	BBP	Below detection limit	Not applicable	Not applicable
	DEHP	32 537	4 548	63 838

See Annex E for a flowchart of DIBP, DBP, BBP and DEHP with the respective thresholds set at 1 000 mg/kg and Annex G for supporting data.

5.7 Quality assurance and control

5.7.1 Quality assurance and control of HPLC-UV method

5.7.1.1 Recalibration period and stability test

Frequent measurements of internal control samples and blank values ensure that the instrument is running properly.

The quality of the measurement is ensured by limiting the validity of the liquid standard solutions to six months.

A full recalibration is required at least each month of operation. Independent quality control standards are used to maintain the peak areas of each phthalate standard as quality control checks. Acceptable recovery rates for the independent quality control standards are 70 % to 130 % for qualitative samples.

5.7.1.2 Sensitivity

Instrumental sensitivity shall be confirmed by the S/N ratio of 1 µg/ml of phthalates. The confirmed S/N ratio should be greater than 10 for DEHP.

NOTE DEHP is not detected as a sum peak.

The reference solution is recommended as the sensitivity check sample.

A reference polymer material which concentration is approximately 100 mg/kg can be used for the sensitivity check. When using reference polymer materials, the sensitivity check solution shall be prepared in accordance with 5.4.1.1.2.

5.7.1.3 Blank test

5.7.1.3.1 Contamination from apparatus and tools

In the extraction process, unintended contamination of analytes from the apparatus (cap and septum of the vial) can occur. To ensure there is no contamination from the apparatus, a blank test which includes the whole extraction process shall be executed in advance. When the blank sample is analysed after extraction, the detected concentration of the analytes shall be equal to or lower than the MDL or LOD.

5.7.1.3.2 Carryover or cross-contamination from samples

Check of carryover or cross-contamination is particularly important when samples containing high levels of phthalates are analysed. If the instrument is contaminated by analytes, this will result in falsely elevated results.

The concentration producing carryover not less than the MDL (or LOD) in a sample sequence shall be confirmed in advance. When the concentration confirmed above is detected, blank samples should be analysed until the background level of each phthalate is decreased to a value less than the MDL (or LOD). Samples after the carryover should be re-analysed as necessary.

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

5.7.1.4 Limit of detection (LOD) or method detection limit (MDL) and limit of quantification (LOQ)

A limit of detection (LOD) or method detection limit (MDL) study shall be completed before conducting this HPLC-UV testing and each time there is a significant change in the method or instrument type. The LOD or MDL is most appropriately determined experimentally by performing replicate, independent measurements on low-level or fortified sample matrices (e.g. plastic) carried out through the entire test procedure, including extraction. A minimum of six replicates and analyte concentrations of 3 to 5 times the estimated LOD or MDL shall be performed for this analysis. The complete LOD or MDL for an entire test procedure is determined by multiplying the standard deviation of the replicates by an appropriate factor. IUPAC recommends a factor of 3 for a minimum of six replicates, whilst EPA utilizes a one-sided confidence interval with the multiplier equal to Student's t value chosen for the number of replicates and the level of confidence (e.g. t = 3,36 for six replicates for 99 % confidence). All analyses used to calculate an LOD or MDL shall be consecutive.

Weigh 150 mg ± 10 mg of the finely cut or powdered reference polymer material (approximately 1 000 mg/kg is recommended) and transfer it into a glass vial for extraction. Record the mass to the nearest 0,1 mg. Repeat this step six times.

Use the procedure (according to 5.4.1.1.2) to extract each of the samples and carry out the analysis accordingly.

Each phthalate shall have a calculated MDL of less than or equal to 300 mg/kg. If the calculated MDL for any of the phthalates is above these limits, the procedure, extraction and analysis shall be repeated for that phthalate.

The limit of quantification (LOQ) for each phthalate shall be, at a minimum, three times the respective MDL. Unlike the MDL, which relates to detection only, the limit of quantification (LOQ) is a concentration that can be accurately quantified for a given compound.

5.7.2 Quality assurance and control of TLC method

5.7.2.1 Recalibration period and stability test

Frequent measurements of internal control samples and blank values ensure that the instrument is running properly.

The quality of the measurement is ensured by limiting the validity of the liquid standard solutions to six months.

A full recalibration is required at least each month of operation. Independent quality control standards are used to maintain the peak areas of each phthalate standard as quality control checks. Acceptable recovery rates for the independent quality control standards are 50 % to 150 % for qualitative samples.

5.7.2.2 Sensitivity

Instrumental sensitivity shall be confirmed by the S/N ratio of 1,25 mg/ml of phthalates. The confirmed S/N ratio should be greater than 3 for DEHP.

The reference solution is recommended as the sensitivity check sample.

NOTE DEHP is not detected as a sum peak.

5.7.2.3 Blank test

In the extraction process, unintended contamination of analytes from the apparatus (caps and septums of the vial) can occur. To ensure there is no contamination from the apparatus, a blank test which includes the whole extraction process shall be executed in advance. When the blank sample is analysed after extraction, the detected concentration of the analytes shall be equal to or lower than the MDL or LOD.

5.7.2.4 Limit of detection (LOD) or method detection limit (MDL) and limit of quantification (LOQ)

A limit of detection (LOD) or method detection limit (MDL) study shall be completed before conducting this HPLC-UV testing and each time there is a significant change in the method or instrument type. The LOD or MDL is most appropriately determined experimentally by performing replicate, independent measurements on low-level or fortified sample matrices (e.g. plastic) carried out through the entire test procedure, including extraction. A minimum of six replicates and analyte concentrations of 3 to 5 times the estimated LOD or MDL shall be performed for this analysis. The complete LOD or MDL for an entire test procedure is determined by multiplying the standard deviation of the replicates by an appropriate factor. IUPAC recommends a factor of 3 for a minimum of six replicates, whilst EPA utilizes a one-sided confidence interval with the multiplier equal to Student's t value chosen for the number of replicates and the level of confidence (e.g. t = 3,36 for six replicates for 99 % confidence). All analyses used to calculate an LOD or MDL shall be consecutive.

Weigh 250 mg ± 10 mg of the finely cut or powdered reference polymer material (approximately 1 000 mg/kg is recommended) and transfer it into a glass vial for extraction. Record the mass to the nearest 0,1 mg. Repeat this step six times.

Use the procedure (according to 5.4.2.1.2) to extract each of the samples. Analyse accordingly.

Each phthalate shall have a calculated MDL of less than or equal to 300 mg/kg. If the calculated MDL for any of the phthalates is above these limits, the procedure, extraction and analysis shall be repeated for that phthalate.

The limit of quantification (LOQ) for each phthalate shall be, at a minimum, three times the respective MDL. Unlike the MDL, which relates to detection only, the limit of quantification (LOQ) is a concentration that can be accurately quantified for a given compound.

5.8 Test report

For the purposes of this document, IEC 62321-1:2013, 4.8 (Test report) applies.

6 TD-MS method

6.1 Reagents and materials

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

a) dry N_2 or dry air;

NOTE 1 The required air depends on the instrument.

b) reference polymer materials as calibrants:
one contains approximately 1 000 mg/kg of phthalates;

c) blank polymer material (no phthalates shall be included).

NOTE 2 Commercially available reference materials are listed in Annex D.

6.2 Equipment, apparatus and tools

6.2.1 Equipment

The following equipment shall be used for the analysis:

a) TD-MS:
   1) mass spectrometer equipped with an atmospheric pressure chemical ionization ion source (APCI-MS); or
   2) mass spectrometer capable of performing select ion monitoring and equipped with an ion attachment ion source (IA-MS).

b) analytical balance capable of measuring accurately to 0,000 01 g (0,01 mg);

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

c) cryogenic grinding or milling with liquid N_2 cooling.

6.2.2 Apparatus and tools

The following item shall be used for the analysis:

a) sample pan.

NOTE The required sample pan size depends on the instrument.

6.3 Sampling

Unless otherwise specified in this document, the sampling procedure described in IEC 62321-2 shall be referred to.

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

All items used in the sample preparation for TD-MS measurements shall be free of contamination, specifically by the analytes of this TD-MS method. This means that all grinding materials, solvents, fluxes, etc. shall not contain detectable quantities of phthalates (DIBP, DBP, BBP, and DEHP).

Tools used in the handling of samples shall be chosen to minimize contamination by the analytes of this test method as well as by any other elements. The procedures which will be used for cleaning different tools shall not introduce any contaminants.

6.4 Procedure

6.4.1 Procedure of APCI-MS method

6.4.1.1 Sample preparation

6.4.1.1.1 Polymer sample

a) Place approximately 0,2 mg of the cut or powdered sample into a pre-weighed sample pan using a micro spatula or tweezers.

NOTE The required sample amount depends on the instrument.

b) Record the total weight of the pan with the sample in it to the nearest 0,01 mg and record the sample weight by subtracting the weight of the sample pan from the total weight.

c) Place the sample pan into the instrument.

When the powdered sample is tested, ensure that the sample does not scatter and spill out e.g. by using a static eliminator.

6.4.1.1.2 Reference polymer materials

A reference polymer material (1 000 mg/kg) is recommended for the calibration and sensitivity check. A thinly stretched reference polymer sheet or film would be particularly convenient.

a) Place approximately 0,2 mg of the reference polymer material into a pre-weighed sample pan using a micro spatula or tweezers.

NOTE 1 The required reference material amount depends on the instrument.

b) Record the total weight of the pan with the sample in it to the nearest 0,01 mg and record the sample weight by subtracting the weight of the sample pan from the total weight.

c) Place the sample pan into the instrument.

NOTE 2 When reference materials are not available, the following stock solutions are prepared.

a) PVC solution: a PVC polymer using a suitable solvent such as THF is dissolved to a concentration of 50 mg/ml.

b) Standard mixture solution: a standard mixture solution containing DIBP, DBP, BBP and DEHP at a concentration of 100 µg/ml is prepared.

6.4.1.2 Instrumental parameters

Different conditions can be necessary to optimize a specific APCI-MS system to achieve effective separation of each phthalate and meet the requirements of 6.7 (Quality assurance and control).

The following parameters have been found suitable and are provided as an example (see Table 7).

NOTE See Annex C for examples of mass spectrum at suggested conditions.

Table 7 – Measurement conditions of APCI-MS

Furnace temperature	330 °C	
Interface temperature	300 °C	
Sample heater temperature	Sample temperature. → (Max 153 °C /min) 230 °C (5 min 30 s hold)	
Ion source temperature	150 °C	
Ionization method	Ion attachment (H^+)	
Ionization voltage	3 000 V	
Pressure	0,3 MPa with dry N_2	
Scan range	20 m/z to 1 000 m/z	
Monitoring mass ion (m/z)	DIBP	205
	DBP	205
	BBP	313
	DEHP	391
Dwell time	100 ms	
Measurement time	7 min	

6.4.1.3 Calibration

The APCI-MS method shall be calibrated taking into account interference effects and any other effects that influence the determination of the peak area of the target ion.

To produce calibration straight lines, the peak area divided by the weight of the reference polymer material is plotted against the concentration (mg/kg) of each phthalate.

A slope of a one-point calibration curve is calculated by using Equation (8).

$$a = A / \left(M_{\text{cal}} \times C\right) \tag{8}$$

where

a is the slope of the calibration curve;

A is the peak area of each phthalate in the reference polymer material;

M_{cal} is the weight of the reference polymer material (mg);

C is the concentration of each phthalate in the reference polymer material (mg/kg).

The calibration curve is specified by using Equation (9):

$$y = ax \tag{9}$$

where

y is the peak area of each phthalate in the sample divided by the weight of the sample;

x is the concentration of each phthalate in the sample (mg/kg);

a is the slope of the calibration curve calculated by Equation (8).

6.4.2 Procedure of IA-MS method

6.4.2.1 Sample preparation

6.4.2.1.1 Polymer sample

a) Place approximately 0,5 mg of the cut or powdered sample into a pre-weighed sample pan using a micro spatula or tweezers.

NOTE The required sample amount depends on the instrument.

b) Record the total weight of the pan with the sample in it to the nearest 0,01 mg and record the sample weight by subtracting the weight of the sample pan from the total weight.

c) Place the sample pan into the DIP and insert it into the instrument.

When a powdered sample is tested, ensure that the sample does not scatter and spill out e.g. by using a static eliminator.

6.4.2.1.2 Reference polymer materials

A reference polymer material (1 000 mg/kg) is recommended for the calibration and sensitivity check. A thinly stretched reference polymer sheet or film would be particularly convenient.

a) Place approximately 0,5 mg of the reference polymer material into a pre-weighed sample pan using a micro spatula or tweezers.

NOTE 1 The required reference material amount depends on the instrument.

b) Record the total weight of the pan with the sample in it to the nearest 0,01 mg and record the sample weight by subtracting the weight of the sample pan from the total weight.

c) Place the sample pan into the DIP and insert it onto the instrument.

NOTE 2 When reference materials are not available, the following stock solutions are prepared.

a) PVC solution: a PVC polymer using a suitable solvent such as THF is dissolved to a concentration of 50 mg/ml.

b) Standard mixture solution: a standard mixture solution containing DIBP, DBP, BBP and DEHP at a concentration of 100 µg/ml is prepared.

6.4.2.2 Instrumental parameters

Different conditions can be necessary to optimize a specific IA-MS system to achieve effective separation of each phthalate and meet the requirements of 6.7 (Quality assurance and control).

The following parameters have been found suitable and are provided as an example (see Table 8).

NOTE See Annex C for examples of mass spectrum at suggested conditions.

Table 8 – Measurement conditions of IA-MS

<table>
<tr><td>Ion source temperature</td><td colspan="2">220 °C</td></tr>
<tr><td>DIP temperature</td><td colspan="2">50 °C → (128 °C /min) 170 °C → (64 °C /min) → 300 °C (3 min hold)</td></tr>
<tr><td>Ionization method</td><td colspan="2">Ion attachment (Li^+)</td></tr>
<tr><td>Pressure</td><td colspan="2">25 Pa to 80 Pa with dry air or dry N_2 (recommend pressure: 80 Pa)</td></tr>
<tr><td>Scan condition</td><td colspan="2">Mass range: 200 m/z to 600 m/z   Cycle time: 3 s/scan</td></tr>
<tr><td rowspan="8">SIM condition</td><td colspan="2">Monitored ion (m/z)</td></tr>
<tr><td>DIBP</td><td>285</td></tr>
<tr><td>DBP</td><td>285</td></tr>
<tr><td>BBP</td><td>319</td></tr>
<tr><td>DEHP</td><td>397</td></tr>
<tr><td>DNOP</td><td>397</td></tr>
<tr><td>DINP</td><td>425</td></tr>
<tr><td>DIDP</td><td>452</td></tr>
<tr><td>Dwell time</td><td colspan="2">200 ms</td></tr>
<tr><td>Measurement time</td><td colspan="2">6 min</td></tr>
</table>

6.4.2.3 Calibration

A reference polymer material (1 000 mg/kg) is recommended as the calibrant for the IA-MS method. Put approximately 0,5 mg of the powdered, cut or punched-out reference polymer material into a pan for the IA-MS.

NOTE The following procedure is also used to prepare the calibrants:

a) 5 µl of standard mixture solution (100 µg/ml) is injected into the sample pan;

b) the solution is dried at room temperature.

The IA-MS method shall be calibrated taking into account interference effects and any other effects that influence the determination of the peak area of target ions.

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

A slope of a one-point calibration curve is calculated by using Equation (10).

$$a = A / m = A / \left(M_{\text{cal}} \times C\right) \tag{10}$$

where

a is the slope of the calibration curve;

A is the peak area of each phthalate in the reference polymer material;

m is the absolute amount of each phthalate in the reference polymer material (ng);

M_{cal} is the weight of the reference polymer material (mg);

C is the concentration of each phthalate in the reference polymer material (mg/kg).

The calibration curve is specified by using Equation (11):

$$y = ax \tag{11}$$

where

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

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

a is the slope of the calibration curve calculated by Equation (10).

6.5 Calculation of phthalates concentration

The final concentration of each phthalate in the sample can be calculated by using Equation (12):

$$C_{\text{final}} = y \times (1/a) \times (1/M) \tag{12}$$

where

C_{final}	is the concentration of each phthalate in the sample (mg/kg);
y	is the peak area of each phthalate in the sample;
a	is the slope of the calibration curve calculated by Equation (8);
M	is the mass of the sample (mg).

NOTE Peak areas with the same molecular weight such as DIBP and DBP, DEHP and DNOP are detected as sum peaks. Therefore, C_{final} is calculated as the sum concentration of these phthalates.

6.6 Precision

When the values of three independent single test results, obtained using the same method on an identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, lie within the range of the mean values cited in Table 9 below, the absolute difference between the mean value of three test results and the test result obtained will not exceed the repeatability limit r deduced by statistical analysis of the international inter-laboratory study 3-4 (IIS 3-4) results in more than 5 % of cases.

When the values of three single test results, obtained using the same method on an identical test material in different laboratories by different operators using different equipment, lie within the range of the values cited in Table 9 below, the absolute difference between the mean value of three test results and the test result will not be greater than the reproducibility limit R deduced by statistical analysis of the international inter-laboratory study 3-4 (IIS 3-4) results in more than 5 % of cases.

Table 9 – IIS 3-4 Repeatability and reproducibility of TD-MS

Sample	Component	Mean value $\bar{x}$ mg/kg	Repeatability r mg/kg	Reproducibility R mg/kg
IIS3-4-A01	DIBP/DBP	Below detection limit	Not applicable	Not applicable
	BBP	Below detection limit	Not applicable	Not applicable
	DEHP	Below detection limit	Not applicable	Not applicable
IIS3-4-B02	DIBP/DBP	886	133	576
	BBP	428	91	286
	DEHP	384	63	302
IIS3-4-C03	DIBP/DBP	1 688	649	1 895
	BBP	614	135	638
	DEHP	1 654	527	2 339
IIS3-4-D04	DIBP/DBP	2 639	803	2 206
	BBP	2 468	976	2 404
	DEHP	4 969	1 503	4 470
IIS3-4-E05	DIBP/DBP	717	424	3 423
	BBP	Below detection limit	Not applicable	Not applicable
	DEHP	140 635	34 168	297 933

See Annex E for a flowchart of DIBP, DBP, BBP and DEHP with respective threshold set at 1 000 mg/kg and Annex G for supporting data.

6.7 Quality assurance and control

6.7.1 Sensitivity

Instrumental sensitivity shall be confirmed by the S/N ratio of 50 ng phthalates. The confirmed S/N ratio should be greater than 10 for BBP.

NOTE 1 BBP is not detected as a sum peak.

A reference polymer material is recommended as the sensitivity check sample.

NOTE 2 When the required sample amount is 0,5 mg, approximately 0,5 mg of the cut or powdered reference polymer material (100 mg/kg) is put into the sample pan.

NOTE 3 The following procedure is also used to prepare the sensitivity check sample:

a) 0,2 µl of standard mixture solution (100 µg/ml) is injected into the sample pan using a microlitre syringe;

b) the solution is dried at room temperature.

6.7.2 Stability test

The timing of a system stability test in a sample sequence shall be determined in advance. Following the determined timing in a sample sequence, a reference polymer material (1 000 mg/kg) shall be analysed. The percent recovery of each phthalate shall be between 50 % and 150 %. If the percent recovery for any phthalate in the reference polymer material falls outside of this range, the analysis is stopped. All samples tested before the last successful stability test may be reported, but samples after the failing stability test shall be re-analysed after a corrective action (e.g. re-calibration).

NOTE 1 When the stability test is performed every 20 samples, the number of samples that ensure the stability in sequence does not need to be determined in advance.

NOTE 2 If the stability test fails repeatedly, a system maintenance can be necessary to return it to optimal operating conditions.

6.7.3 Blank test

Check of carryover or cross-contamination is particularly important when samples containing high levels of phthalates are analysed. If the instrument is contaminated by analytes, this will result in falsely elevated results.

The concentration producing carryover not less than the MDL (or LOD) in a sample sequence shall be confirmed in advance. When the concentration confirmed above is detected, blank samples should be analysed until the background level of each phthalate is decreased to a value less than the MDL (or LOD). Samples after the carryover should be re-analysed as necessary.

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

6.7.4 Limit of detection (LOD) or method detection limit (MDL) and limit of quantification (LOQ)

A limit of detection (LOD) or method detection limit (MDL) study shall be completed before conducting this TD-MS testing and each time there is a significant change in the method or instrument type. The LOD or MDL is most appropriately determined experimentally by performing replicate, independent measurements on low-level or fortified sample matrices (e.g. plastic) carried out through the entire test procedure, including extraction. A minimum of six replicates and analyte concentrations of 3 to 5 times the estimated LOD or MDL shall be performed for this analysis. The complete LOD or MDL for an entire test procedure is determined by multiplying the standard deviation of the replicates by an appropriate factor. IUPAC recommends a factor of 3 for a minimum of six replicates, whilst EPA utilizes a one-sided confidence interval with the multiplier equal to Student's t value chosen for the number of replicates and the level of confidence (e.g. t = 3,36 for six replicates for 99 % confidence). All analyses used to calculate an LOD or MDL shall be consecutive.

A reference polymer material (1 000 mg/kg) is recommended for the determination of the LOD or MDL. Place approximately 0,2 mg of the cut or powdered reference polymer material into the sample pan.

NOTE The following procedure is also used to prepare the method detection check sample:

a) 0,2 µl of standard mixture solution (100 µg/ml) is injected into the sample pan using a microlitre syringe;

b) the solvent is dried at room temperature;

c) the replicate samples are analysed.

Each phthalate shall have a calculated MDL of less than or equal to 300 mg/kg. If the calculated MDL for any of the phthalates is above these limits, the procedure and analysis shall be repeated.

The limit of quantification (LOQ) for each phthalate shall be, at a minimum, three times the respective MDL. Unlike the MDL, which relates to detection only, the limit of quantification (LOQ) is a concentration that can be accurately quantified for a given compound.

6.8 Test report

For the purposes of this document, IEC 62321-1:2013, 4.8 (Test report) applies.

Annex A
(informative)

FT-IR method

A.1 Principle

The principle of phthalate detection by FT-IR relies on the presence of a limited number of specific bands in the infrared spectrum. The two most remarkable ones, which are present in most phthalates used as plasticisers are positioned at 1 580 cm^{-1} and 1 600 cm^{-1}. These phthalates consist of an ortho-substituted aromatic ring.

FT-IR measurements can be performed in many different measurement modes:

- attenuated total reflection (ATR):
  - single bounce;
  - multi-bounce;
- transmission;
- reflection;
- transmission/reflection (via transmission measured via a reflecting surface);
- grazing incidence reflection (not applicable for quantification).

The direct detection of phthalates is often performed via the ATR method. In this method the sample under study is brought into contact with an infrared transmissive crystal. For solid samples this is realized by pressing the material onto the crystal. The method offers a clear advantage compared to other screening methods such as HPLC: It is fast (a spectrum is obtained within a minute), and there is no need for sample preparation.

However, the method is not 100 % conclusive for identification of a specific phthalate type and further data processing is necessary if quantification is desired. The matrix plays a dominant role in the determination of phthalates. In general, if the matrix is comprised of a large quantity of aromatic moieties, identification, let alone quantification, becomes challenging via the ATR method.

The ATR method discussed above is based on single bounce reflection, and is the most widely used method, given its applicability in many areas. Other ATR methods exist that offer increased sensitivity. They consist of a multi-bounce ATR crystal (long crystal) causing a plurality of passages, note that "passage" here means the number of times the evanescent wave extends from the crystal.

Next to ATR, transmission measurements can also be performed. In transmission, the Lambert-Beers' law directly applies. Then it is important that the layer thickness through which the transmission is recorded is known. For any given phthalate the amount of phthalate can be calculated based on the extinction coefficient of the bands at 1 580 cm^{-1} and 1 600 cm^{-1}, assuming little to no interference from other compounds. Otherwise spectral contributions from the matrix can be minimized by subtraction. Advanced multivariate data analysis techniques such as PCR (principle component regression) can be applied.

The flow diagram for analysis of phthalates in polymers is shown in Figure A.1 and Figure A.2.

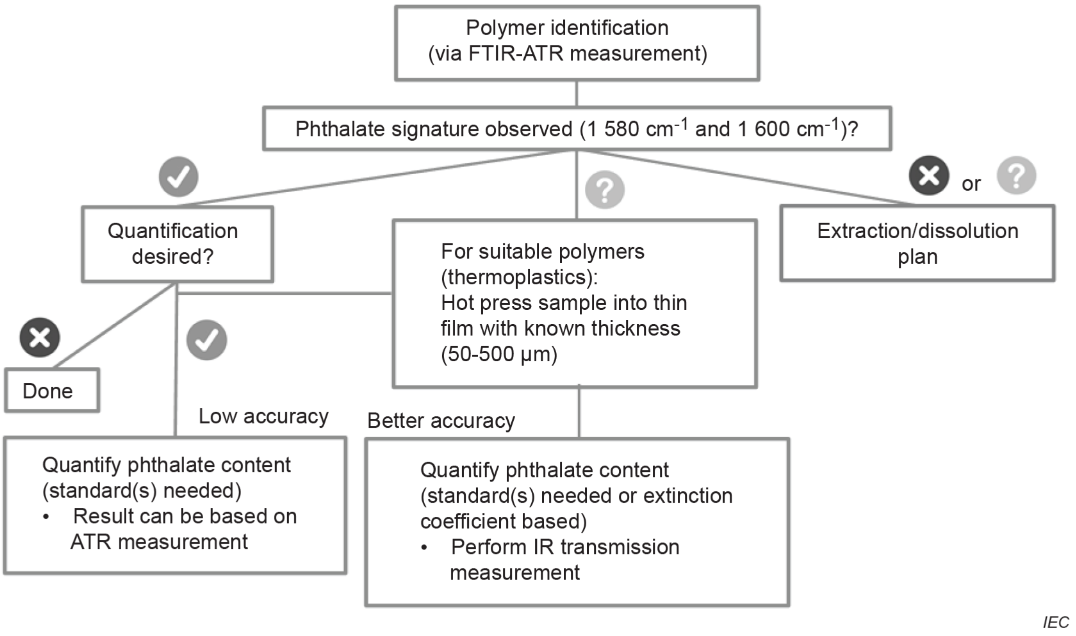


Figure A.1 – Phthalate analysis in polymers (check)

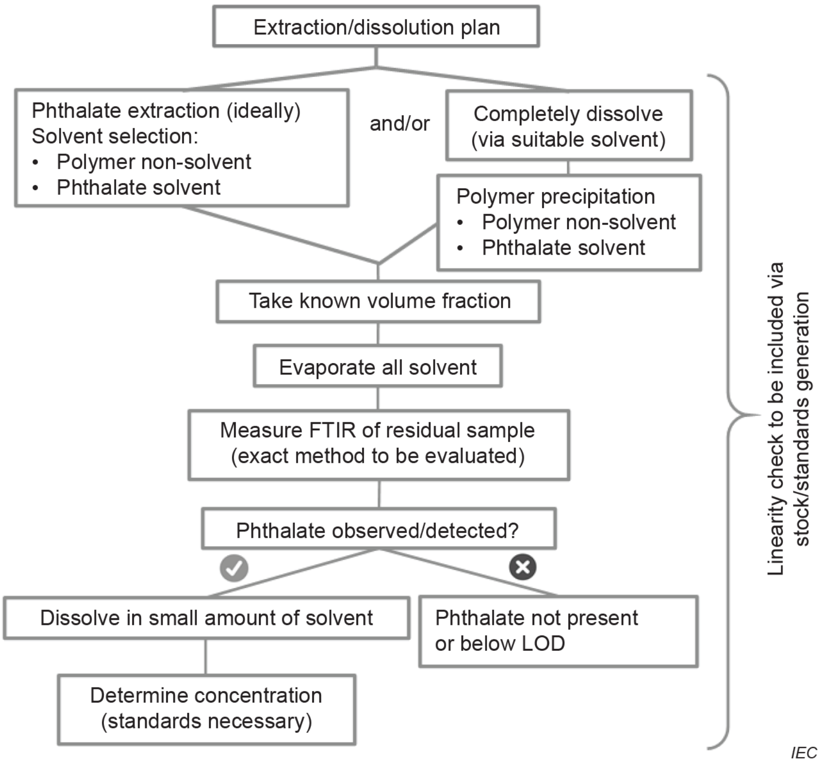


Figure A.2 – Phthalate analysis in polymers with pre-treatment

As shown in the flowchart (Figure A.1) the step towards quantification or qualification of phthalates starts with the identification of the polymer, which is performed via an ATR measurement. Sometimes the presence of phthalates is evident from the presence of the 1 580/1 600 cm^{-1} doublet. For aromatic polymers the typical doublet can be interfered with the aromatic bands of the polymer. Spectra from the pure polymer can help the interpretation or support the hypothesis for the presence or absence of phthalates. If no signal of a phthalate is observed, it can mean that either the ATR method sensitivity is insufficient or that no phthalate is present.

A quick check (not shown in the flowchart) can be performed by putting a droplet of solvent suitable for phthalates (such as ethanol or isopropanol) over the plastic part. The contents in the droplet can be analysed via evaporation of the solvent on an ATR crystal and subsequent FT-IR analysis.

For rather high concentrations (single bounce) ATR can also be used for direct quantification (standard necessary). To increase the sensitivity for small concentrations of additives, but not to start with wet chemicals for extraction, the hot press method can be applied. The plastic part is then spread by heat into a film of material with a given thickness. Also a wedge or a step structure can be pressed in order to achieve a range of different thicknesses. Next an FT-IR measurement can be conducted in transmission. The thickness of the film should be selected or adjusted such as to transmit only a limited amount of radiation (but not too much to avoid saturation) in the wave number range suited for phthalates. Note that this method can only be used for thermoplastics. Examples of thermoplastics are: acrylic resin such as polymethyl methacrylate (PMMA), acrylonitrile butadiene styrene (ABS), polyester (PE), polyethylene (PE), polypropylene (PP), polystyrene (PS), cellulose acetate, polytetrafluoroethylene (PTFE), nylon (polyamides), polylactic acid (PLA), polybenzimidazole (PBI), polycarbonate (PC), polyether sulfone (PES), polyoxymethylene (POM), polyether ether ketone (PEEK), polyetherimide (PEI), polyphenylene oxide (PPO), polyphenylene sulphide (PPS), polyvinyl chloride (PVC) and polyvinylidene fluoride (PVDF).

If the concentration of phthalates is limited or it is unclear if a phthalate is present the extraction or dissolution plan comes into play. The plan consists of two possible routes: extraction of the plastic part or complete dissolution of the plastic followed by polymer precipitation. Both routes require the mass of the plastic part to be known (or weighed).

A linearity check should be applied as solubility of short and longer phthalates will show huge differences. Also, the detection limit (LOD) in solvent should be determined for the different phthalates as longer phthalates will show a worse LOD. The linearity and the LOD can be checked using a calibration curve with stock or standard solutions of each phthalate. A calibration curve (or single point calibration) with stock or standard solutions of each phthalate will be used for phthalate quantification.

The FT-IR and ATR test methods follow a concept that is performance-based. Apparatus, sampling and calibration are specified in this document in relatively general terms. It is the responsibility of the user to document all procedures developed in the laboratory that uses the test method. The user shall establish a written procedure for all cases denoted in The FT-IR and ATR methods by the term ″work instructions″.

A.2 Reagents and materials

Chemicals which were used in carrying out the FT-IR analysis are:

a) dichloromethane (DCM), for analysis, purity greater than 99,8 %;

b) isopropyl alcohol (IPA), electronic MOS grade, purity greater than 99,8 %;

c) tetrahydrofuran (THF), for HPLC, unstabilized, purity 99,8 %.

A.3 Apparatus

The following equipment was used for the analysis:

a) vacuum concentrator;

b) FT-IR for transmission/reflection measurements;

c) FT-IR with ATR accessory;

d) headspace vials with screw top and rounded bottom (volume 10 ml);

e) microtubes (volume 1,5 ml).

A.4 Sampling

Small pieces of material were cut out from the samples.

A.5 Procedure

A.5.1 Sample preparation

A.5.1.1 Dissolution

This approach has the advantage that the complete phthalate package resides in the solvent, whereas when the part is extracted, there is a possibility that some regions of the plastic will not be accessed, even after milling, and therefore will not be extracted by the solvent. Dissolution requires a good solvent for the polymer (solvents and non-solvents for polymers can for example be found in the Polymer Handbook [4]). The dissolution process can take quite some time (especially if the part is not milled).

After dissolution, the polymer in the plastic shall be precipitated using a polymer non-solvent, and a phthalate solvent (such as a lower alcohol). From here the strategy will be similar to the extraction plan.

A.5.1.2 Extraction

The solvent used in the polymer precipitation process for the dissolution plan can also be used for the extraction.

After extraction a known volume fraction is retrieved, and from this fraction the solvent is completely evaporated.

Residual extraction may be used in combination with a horizontal ATR for the identification of additives or for quantification (which requires the amount of solvent to be known).

After complete evaporation the residuals are dissolved again in a known, small amount of solvent that hardly shows any evaporation (e.g. propylene carbonate). Now a measurement can be performed either in transmission or via the horizontal ATR module, which is referenced against one or more standards.

A.5.2 Instrumental parameters

Every FT-IR spectrum is recorded with 128 scans from 4 000 cm^{-1} to 650 cm^{-1} and with a resolution of 4 cm^{-1}.

NOTE See Annex C for examples of spectrum at suggested conditions.

A.5.3 Calibration

The strength of the phthalate signal depends on the type of phthalate analysed.

To prevent under-estimation of a specific phthalate concentration it can be advantageous to base the amount of phthalate observed in a material on a calibration line generated from the largest molecular weight phthalate known to be commonly used, DIDP (MW = 446,66). If the type of phthalate present is unknown or cannot be resolved one can state that the concentration is ″at most″ the concentration linked to the calibration line. Supposing that only DMP (MW = 194,18) is present, the shortest phthalate available, the maximum degree of overestimation would be 2,3.

Standards which have been used for the investigation until now are:

dimethyl phthalate (DMP), 99 %;
diethyl phthalate (DEP), 99 %;
diisobutyl phthalate (DIBP), 99 %.

A.6 Calculation of phthalates concentration

$$C(\text{sample}) = \frac{C(\text{standard}) \times PA(\text{sample})}{PA(\text{standard})} \tag{A.1}$$

$$Wt\ \% = \frac{C(\text{sample}) \times V}{M} \times 100\% \tag{A.2}$$

where

C is the concentration of phthalates (mg/ml);
PA is the peak area (FT-IR spectra);
Wt % is the weight percentage of phthalates;
V is the volume (ml);
M is the mass of the weighted sample (mg).

A.7 Precision

When the values of three independent single test results, obtained using the same method on an identical test material in the same laboratory by the same operator using the same equipment within a short interval of time, lie within the range of the mean values cited in Table A.1 below, the absolute difference between the mean value of three test results and the test result obtained will not exceed the repeatability limit r deduced by statistical analysis of the international inter-laboratory study 3-4 (IIS 3-4) results in more than 5 % of cases.

When the values of three single test results, obtained using the same method on an identical test material in different laboratories by different operators using different equipment, lie within the range of the values cited in Table A.1 below, the absolute difference between the mean value of three test results and the test result will not be greater than the reproducibility limit R deduced by statistical analysis of the international inter-laboratory study 3-4 (IIS 3-4) results in more than 5 % of cases.

Table A.1 – IIS 3-4 Repeatability and reproducibility of FT-IR

Sample	Component	Mean value $\bar{x}$ mg/kg	Repeatability r mg/kg	Reproducibility R mg/kg
IIS3-4-A01	Phthalates	Below detection limit	Not applicable	Not applicable
IIS3-4-B02	Phthalates	Below detection limit	Not applicable	Not applicable
IIS3-4-C03	Phthalates	39 588	37 550	165 174
IIS3-4-D04	Phthalates	75 412	15 768	77 935
IIS3-4-E05	Phthalates	333 152	93 334	317 895

See Annex G for supporting data.

A.8 Quality assurance and control

The quality of the analysis can be ensured by analysing a reference polymer with a known amount of phthalates as a quality control (QC) sample with each analysis performed.

A.9 Test report

For the purposes of this document, IEC 62321-1:2013, 4.8 (Test report) applies.

Annex B
(informative)

Details of analysis by TLC method

B.1 Separation by TLC

The separation procedure is as follows.

a) Put solvent (acetonitrile) into the development chamber to a depth of approximately 1 cm and close the cover, then leave for more than 30 min for the solvent vapour to fill in the chamber.

b) Prepare each TLC plate as follows: draw the start line at 2 cm from the lower side and the end line at 0,5 cm from the upper side. Draw the spot points at intervals of 1,5 cm and space 2,5 cm from the sides. Make the cut edge as the upper side of the TLC plate (Figure B.1).

c) Apply 1 ml of the extracts at once by means of a capillary tube. Apply one point of the standard solution per one TLC plate. After drying the solvent of the applied extracts, apply 1 ml more of the extracts again on the same points. Repeat the application of the extracts 5 times (1 time for the standard solution).

d) After confirmation that the extracts on the TLC plates have dried, put the TLC plates in the development chamber smoothly and close the cover quickly.

e) Take out the TLC plates from the development chamber when the development solvent reaches the end line of the TLC plates.

NOTE The caps of the vials are kept closed to prevent volatilization of solvent in the vials, when the vials are not in use.

Dimensions in centimetres

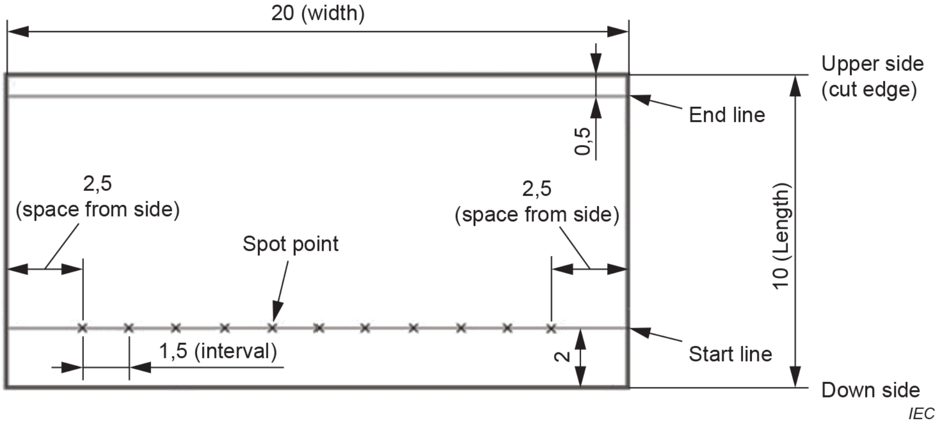


Figure B.1 – Usage of TLC plate (20 cm × 10 cm)

B.2 Detection by image analysis

The detection procedure by image analysis is as follows.

a) After drying the solvent on the TLC plate, put the TLC plate in a dark place, such as a darkroom, and expose the TLC plate under UV light (λ = 254 nm) from the top. Set the UV lamp in order to expose light uniformly on the whole TLC plate. It is desirable to set the UV lamp about 5 cm above the plate and to set the camera about 15 cm above the plate. Further, it is desirable to set two UV lamps above both sides of the plate. An example of the photography set-up and conditions are shown in Figure B.2 and Table B.1.

Table B.1 – Conditions of photography

Distance from camera to TLC plate	Approx. 15 cm
Distance from UV lamps to TLC plate	Approx. 5 cm
Photographing mode	Manual
Flash	Not used
Aperture (Focus)	f/5,6
Exposure time	1/800 s
ISO speed	6 400
Filter	Used

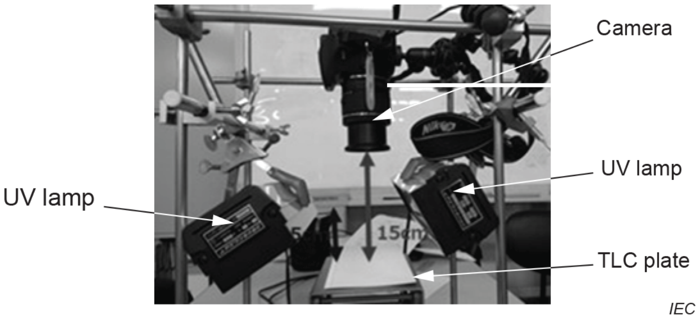


Figure B.2 – Set-up of camera-equipment for TLC (inside of darkroom)

b) Transfer the image data of the TLC plate to a PC. Convert the development patterns of samples and the standard on the image data to chromatograms by image analysis.

c) Calculate the Rf value (reference factor value) by using Equation (B.1).

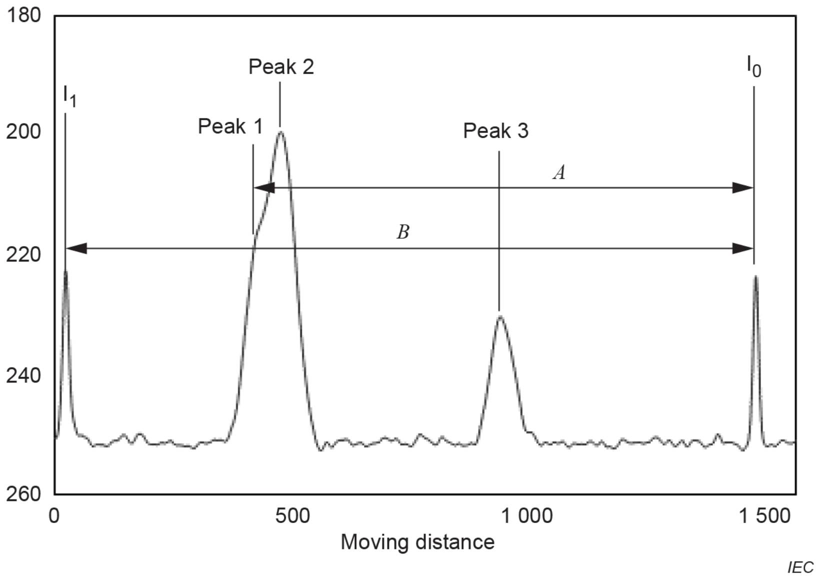
$$Rf = A / B \tag{B.1}$$

where

A is the distance from the start point where the spot was applied to the centre of the separated spot;

B is the distance from the start point where the spot was applied to the end line of the development solvent;

Rf is the RF value.



Key

I_0 start point where the spot was applied

I_1 end line of the development solvent

A distance from I_0 to the peak top

B distance from I_0 to I_1

Figure B.3 – TLC chromatogram

d) In the case of detection spots within the limits of Rf values as shown in Table B.2, identify that the target phthalate is included in the sample (Take 0 for the Rf values of the target phthalates in the standard solution.). In the case where a broad peak outside the limit of DEHP's Rf overlaps with the range of DEHP's Rf or a peak is detected between the Rf values 0,40 and 0,62, DEHP can be included. When the inclusion of DEHP is confirmed, re-measurement is required in accordance with Clause B.3.

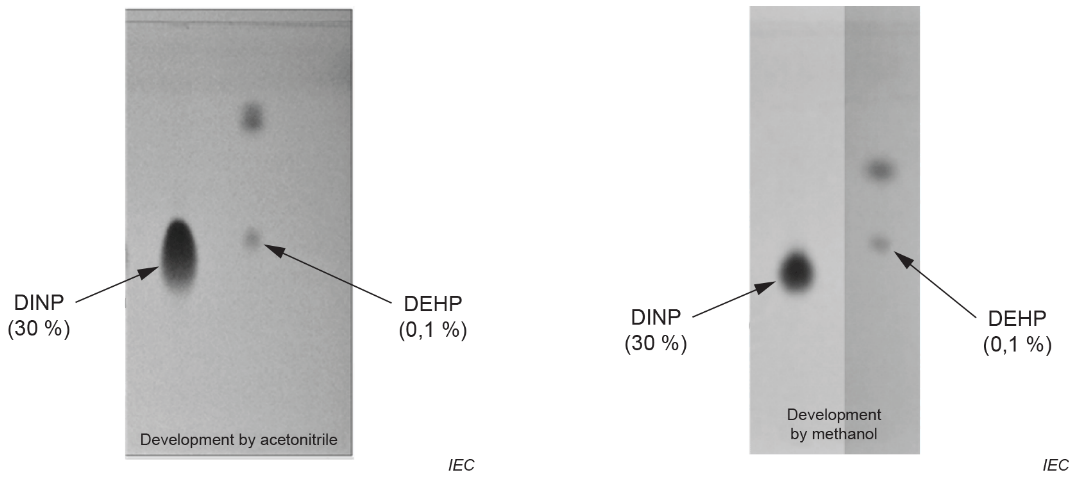
Table B.2 – Range of Rf values of target phthalates

Target phthalates	Rf values (reference values)	Range of Rf values (the Rf values of the phthalates in the standard solution = 0)
BBP	0,77	±0,02
DBP + DIBP	0,74	±0,02
DEHP	0,41	−0,02 to +0,05

B.3 Re-measurement

The re-measurement procedure is as follows.

a) In the case of a broad peak (e.g. large amount of DINP) overlapping with DEHP, methanol is used for the development solution (an example of re-measurement is shown in Figure B.4). Before re-measurement, acetonitrile in the development chamber should be removed completely. Apply the extracts on the TLC plate 3 times. As an alternative, a 20 cm long TLC plate is also used for re-measurement with acetonitrile as a development solution.



Normal measurement condition **Re-measurement condition (a)**

Figure B.4 – Separation by re-measurement conditions (in case of pattern a))

b) In the case of a peak detection between the Rf values 0,40 and 0,62 (e.g. containing a large amount of DEHA: di(2-ethylhexyl) adipate, see Figure B.5), re-measurement should be performed by a standard addition method as follows. Apply the extract on two or more positions on a new TLC plate (e.g. positions A and B). Apply again the standard solution (x g/L DEHP concentration) on positions other than A. Then put the TLC plate in the development chamber with the acetonitrile solution. If Rf values of positions A and B match, it is judged that DEHP is detected. The concentration (y) of DEHP is calculated by using the formula shown in Figure B.6.

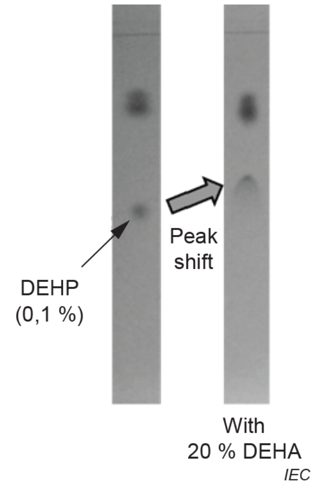


Figure B.5 – Peak shift affected by large amount of DEHA

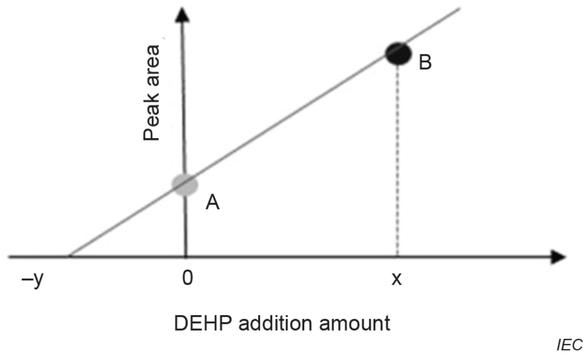


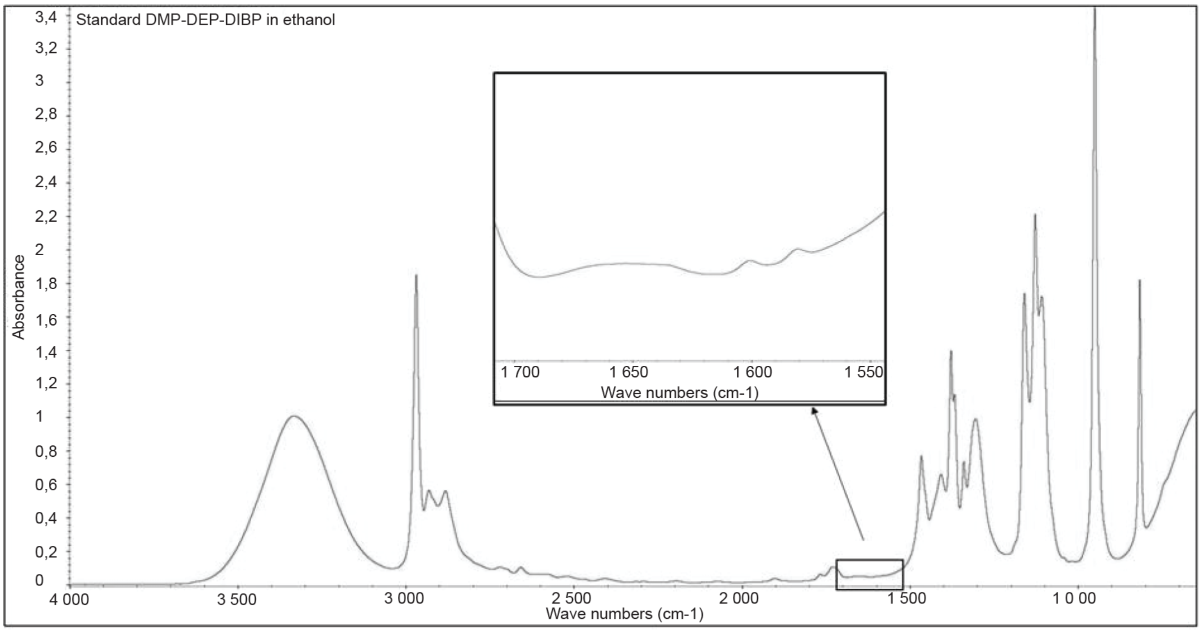
Figure B.6 – TLC re-measurement by standard addition method (in case of pattern b))

Annex C
(informative)

Examples of spectrums and chromatograms at suggested conditions

C.1 FT-IR spectrum

The following spectrum was obtained by FT-IR analysis using the parameters described in Annex A. See Figure C.1.

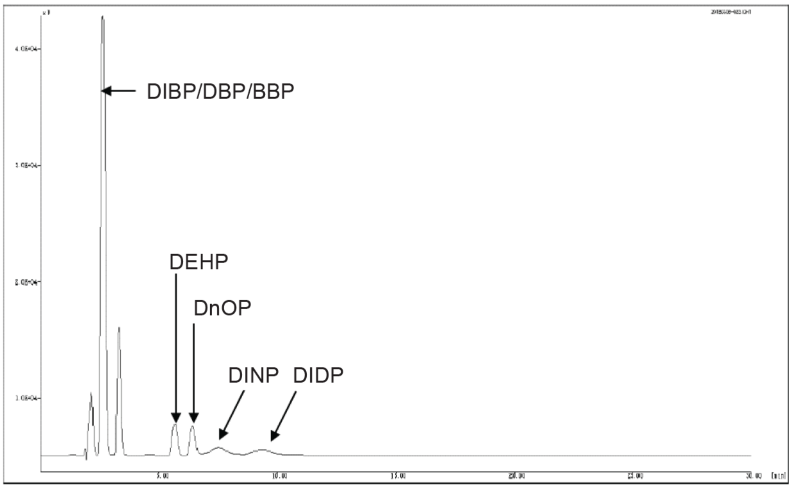


IEC

Figure C.1 – Spectrum of FT-IR

C.2 HPLC-UV chromatogram

The following chromatogram was obtained by HPLC analysis using the parameters described in 5.4.1. See Figure C.2.



IEC

Figure C.2 – Chromatogram of HPLC-UV

C.3 TLC chromatogram

The following Figure C.3 and Figure C.4 were obtained by TLC analysis using the parameters described in 5.4.2.

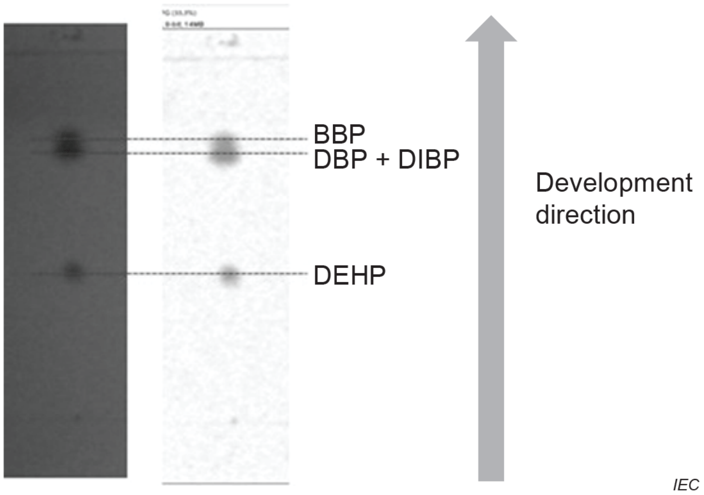
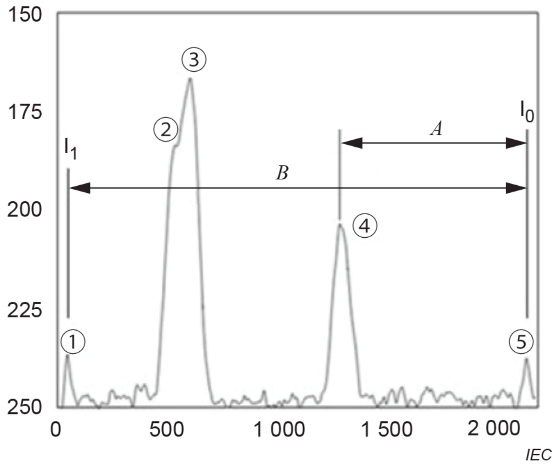


Figure C.3 – Developed TLC plate exposed to UV light of 254 nm



Key

I_1(①)	end line of the development solvent
②	peak of BBP
③	peak of DBP + DIBP
④	peak of DEHP
I_0 (⑤)	start point where the spot was applied
A	distance from I_0 to the peak top
B	distance from I_0 to I_1

Figure C.4 – Image processed TLC chromatogram of Figure C.3

C.4 APCI-MS mass spectrum

The following mass spectrums were obtained by APCI-MS analysis using the parameters described in 6.4.1. See Figure C.5.

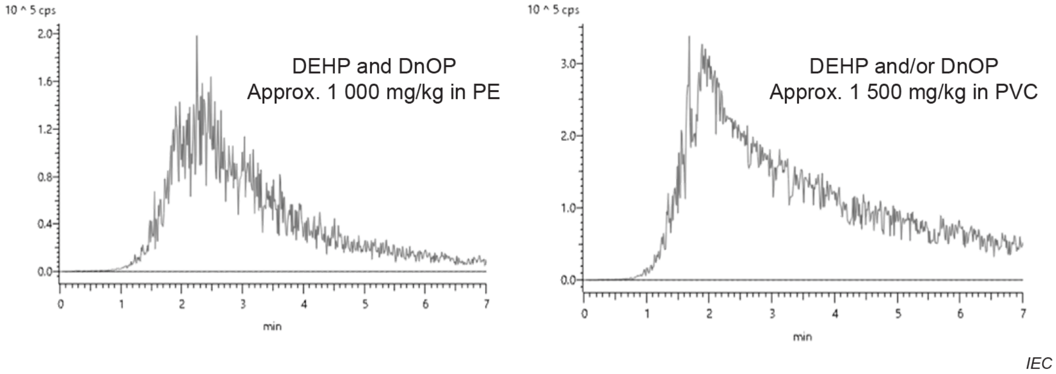


Figure C.5 – Mass spectrums of APCI-MS

C.5 IA-MS mass spectrum

The following mass spectrums were obtained by IA-MS analysis using the parameters described in 6.4.2. See Figure C.6.

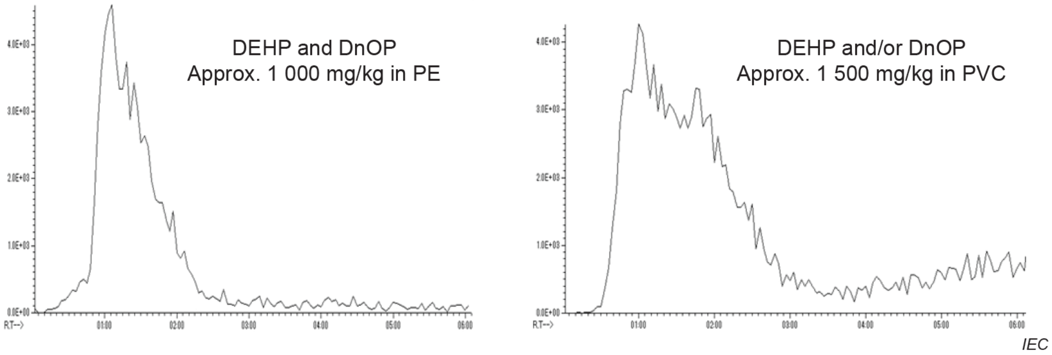


Figure C.6 – Mass spectrums of IA-MS

Annex D
(informative)

Commercially available reference materials and solutions considered suitable for the suggested methods

Table D.1 shows reference materials considered suitable for the suggested methods.

Table D.1 – Example list of commercially available reference materials[2]

Product name	Specification	Manufacturer	Suitable method
NMIJ® CRM 8152-b	Pellet of PVC containing DBP, BBP, DEHP, DEP (diethyl phthalates) and DCHP (dicyclohexyl phthalate) with certified values. DIBP, DnOP, DIDP and DEHA (di-(2-ethylhexhyl adipate) are also contained with the informational values.	National Metrology Institute of Japan	FT-IR, HPLC-UV, TLC, TD-MS
KTR® CRM 113-02-PT-002	Pellet of PS containing DBP, BBP, DEHP, DnOP, DMP (dimethyl phthalates) and DEP (diethyl phthalates).	Korea Testing & Research Institute	FT-IR, HPLC-UV, TLC, TD-MS
CRM SVO-STC-146 CRM SVO-STC-147 CRM SVO-STC-167 CRM SVO-STC-163-5 CRM SVO-STC-148	Sheet of PVC containing DIBP, DBP, BBP and DEHP at 0 mg/kg (SVO-STC-146), 100 mg/kg (SVO-STC-147), 300 mg/kg (SVO-STC-167), 500 mg/kg (SVO-STC-163-5) and 1 000 mg/kg (SVO-STC-148).	SPEX CertiPrep®, US	FT-IR, HPLC-UV, TLC, TD-MS
CRM SVO-STC-149 CRM SVO-STC-150 CRM SVO-STC-151	Sheet of PVC containing DIBP, DBP, BBP, DEHP, DnOP, DIDP and DINP at 0 mg/kg (SVO-STC-149), 100 mg/kg (SVO-STC-150) and 1 000 mg/kg (SVO-STC-151).	SPEX CertiPrep®, US	FT-IR, HPLC-UV, TLC, TD-MS
CRM PE-001	Powder of polyethylene containing DBP, BBP, DEHP, DnOP, DINP and DIDP, DMP (dimethyl phthalates) and DEP (diethyl phthalates).	SPEX CertiPrep®, US	FT-IR, HPLC-UV, TLC, TD-MS
CRM-PVC BLK	PVC purity 99 %.	SPEX CertiPrep®, US	FT-IR, HPLC-UV, TLC, TD-MS
S225-31003-91	Sheet of polyethylene containing DIBP, DBP, BBP, DEHP, DnOP, DINP and DIDP at 0 mg/kg, 100 mg/kg and 1 000 mg/kg.	Shimadzu Corp.	FT-IR, HPLC-UV, TLC, TD-MS
43540-100MG	Reference solution of DIBP (CAS No. 84-69-5).	SIGMA-ALDRICH	HPLC-UV, TLC
48559	Reference solution of DBP (CAS No. 84-74-2).	SIGMA-ALDRICH	HPLC-UV, TLC
442503	Reference solution of BBP (CAS No. 85-68-7).	SIGMA-ALDRICH	HPLC-UV, TLC
D201154-5ML	Reference solution of DEHP (CAS No. 117-81-7).	SIGMA-ALDRICH	HPLC-UV, TLC
Phthalate standard solution III (Product No. 34109-43)	Technical calibration mixture containing DBP, BBP, DEHP, DnOP, DINP and DIDP 100 µg/ml each in acetone.	KANTO CHEMICAL CO., INC.	HPLC-UV, TLC

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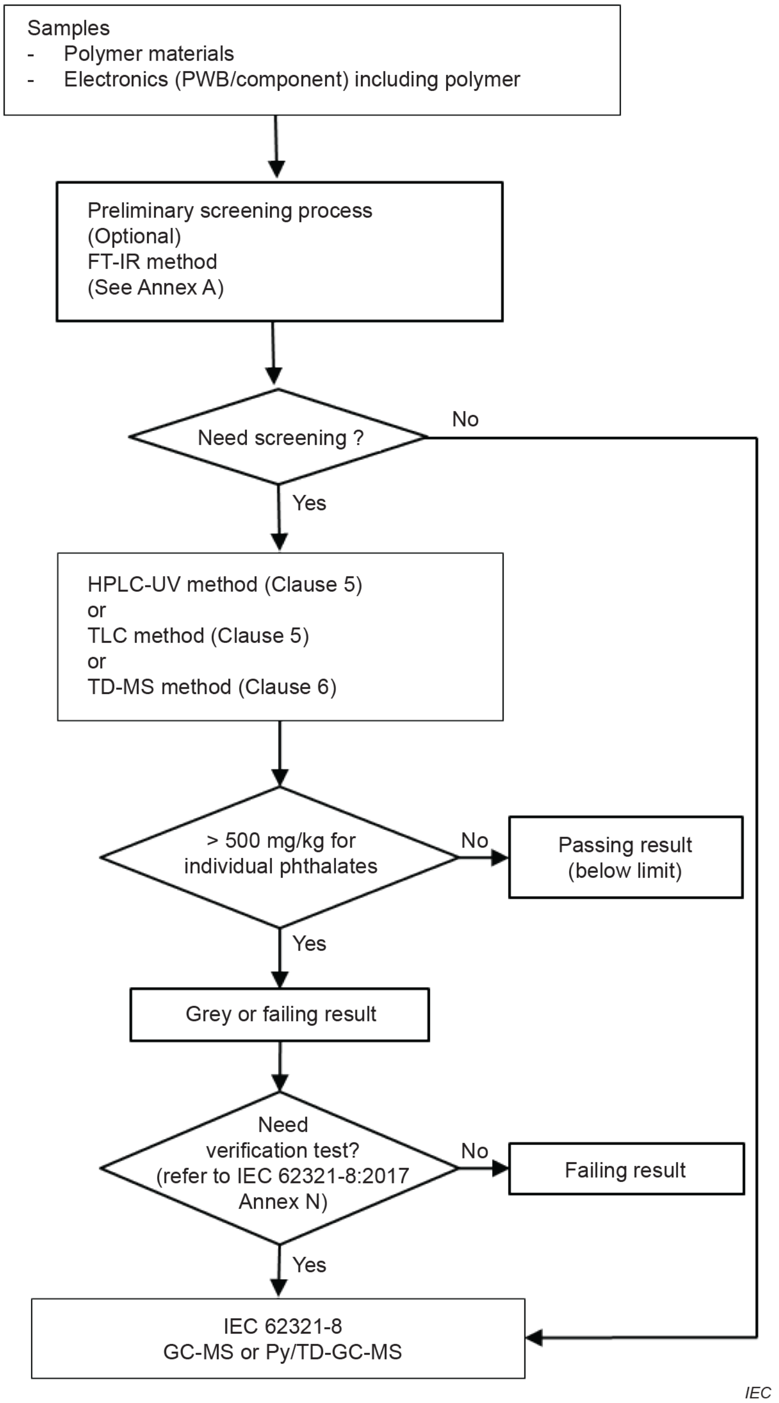
[2] These products are examples of suitable products available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by IEC of these products.

Annex E
(informative)

Flowchart of test methods

Figure E.1 provides a flowchart as an example of how each method included in this document (FT-IR, HPLC-UV, TLC, TD-MS) can be used for screening when the acceptability threshold for each DIBP, DBP, BBP and DEHP is set at 1 000 mg/kg.



Decision criteria are entity-based.

Figure E.1 – Flowchart for screening step and verification test step

Annex F
(informative)

Commonly used phthalates

Examples of commonly used phthalates in products are given in Table F.1.

Table F.1 – Example list of commonly used phthalates in products

Name	Abbreviation	Uses	Products
Dimethyl phthalate	DMP	Primarily used as a solvent	Cosmetics, perfumes, creams, candles, shampoos
Diethyl phthalate	DEP	Primarily used as a solvent and fixative in fragrances	Cosmetics, perfumes, creams, candles, shampoos, pesticides
Dibutyl phthalate	DBP	Primarily used as a solvent	Cosmetics, perfumes, creams, candles, shampoos, adhesives, paints
Benzylbutyl phthalate	BBP	Used as a plasticizer for PVC and as a solvent	Vinyl flooring, sealants, adhesives, glues, car care products, exterior paint, food conveyor belts, food wrapping material, wallpapers, shower curtains, modelling clay
Dibutyl phthalate	DBP	Used as a plasticizer for PVC and rubber. Also used as solvent and fixative in paints and cosmetics	Latex adhesives, sealants, car care products, cosmetics, inks and dyes, pesticides, food wrapping materials, home furnishing, paints, clothing, and pharmaceutical coatings
Di-n-octyl phthalate	DOP	Primarily used as a plasticizer for PVC	Floorings, bottle cap liners, conveyor belts, garden hoses, modelling clay
Di(2-ethylhexyl) phthalate	DEHP	Primarily used as a plasticizer for PVC	Toys, shoes, clothing, medical devices (plastic tubing and intravenous storage bags), furniture, automobile upholstery, electronics, plumbing, floor tiles, modelling clay
Diisononyl phthalate	DINP	Primarily used as a plasticizer for PVC	Teethers, balls, spoons, toys, gloves, drinking straws, rubber, adhesives, ink, sealant, paint and lacquers, food packaging, clothes, shoes, car and public transport interior, flooring
Diisodecyl phthalate	DIDP	Primarily used as a plasticizer for PVC	Electrical cords, leather for car interiors and PVC flooring

Annex G
(informative)

Results of international inter-laboratory study 3-4 (IIS 3-4)

The results of the international inter-laboratory study 3-4 (IIS 3-4) are given in Table G.1, Table G.2, Table G.3 and Table G.4.

Table G.1 – Formulation of samples

Phthalates	**IIS3-4-A01**	**IIS3-4-B02**	**IIS3-4-C03**	**IIS3-4-D04**	**IIS3-4-E05**
mg/kg	**RM** (Reference material)	**CRM** (Certified reference material)	**RM** (Reference material)	**CRM** (Certified reference material)	**RS** (Real sample)
DIBP	-	505	1 000	-	unknown (low)
DBP	-	502	1 000	3 001	unknown (low)
BBP	-	506	1 000	3 004	unknown (low)
DEHP	-	503	1 000	3 003	unknown (high)
DnOP	-	-	1 000	3 003	unknown (low)
DINP	-	-	1 000	30 013	unknown (low)
DIDP	-	-	1 000	30 062	unknown (low)
DEP	-	-	-	3 008	unknown (low)
DMP	-	-	-	3 010	unknown (low)
DCHP	-	-	1 000	-	unknown (low)
Material type	PVC	PVC	PVC	PE	PVC

Table G.2 – Statistical data for HPLC-UV

Sample	Component	$\bar{x}$ mg/kg	v mg/kg	n	$s(r)$ mg/kg	r mg/kg	$s(R)$ mg/kg	R mg/kg
IIS3-4-A01	DIBP/DBP/BBP	44	0	19	7	21	99	278
IIS3-4-B02	DIBP/DBP/BBP	1 137	1 513	19	30	85	437	1 224
IIS3-4-C03	DIBP/DBP/BBP	2 326	3 000	16	60	169	669	1 873
IIS3-4-D04	DIBP/DBP/BBP	3 791	6 005	16	82	223	2 108	5 649
IIS3-4-E05	DIBP/DBP/BBP	42	unknown	19	2	7	104	292
IIS3-4-A01	DEHP	33	0	19	4	12	82	229
IIS3-4-B02	DEHP	396	503	19	19	53	170	476
IIS3-4-C03	DEHP	869	1 000	16	18	50	299	836
IIS3-4-D04	DEHP	2 604	3 003	16	64	178	252	706
IIS3-4-E05	DEHP	262 470	unknown	16	3 639	10 190	29 185	81 717

Key

$\bar{x}$	arithmetic mean value of test results
v	expected value
n	number of accepted test results
$s(r)$	repeatability standard deviation
r	repeatability limit
$s(R)$	reproducibility standard deviation
R	reproducibility limit

Table G.3 – Statistical data for TLC

Sample	Component	$\bar{x}$ mg/kg	v mg/kg	n	$s(r)$ mg/kg	r mg/kg	$s(R)$ mg/kg	R mg/kg
IIS3-4-A01	DIBP/DBP	75	0	21	13	37	199	558
IIS3-4-B02	DIBP/DBP	797	1 007	21	95	267	235	659
IIS3-4-C03	DIBP/DBP	1 372	2 000	21	174	487	382	1 070
IIS3-4-D04	DIBP/DBP	2 191	3 001	21	216	604	565	1 582
IIS3-4-E05	DIBP/DBP	0	Unknown	21	0	0	0	0
IIS3-4-A01	BBP	81	0	21	42	117	143	400
IIS3-4-B02	BBP	337	506	18	69	194	174	488
IIS3-4-C03	BBP	821	1 000	18	47	133	77	215
IIS3-4-D04	BBP	2 074	3 004	18	140	392	527	1 476
IIS3-4-E05	BBP	112	Unknown	21	57	159	209	586
IIS3-4-A01	DEHP	12	0	21	15	41	34	94
IIS3-4-B02	DEHP	347	503	18	67	188	111	310
IIS3-4-C03	DEHP	774	1 000	12	56	157	248	696
IIS3-4-D04	DEHP	2 490	3 003	18	129	361	1 190	3 331
IIS3-4-E05	DEHP	32 537	unknown	21	1 624	4 548	22 799	63 838

Key

$\bar{x}$	arithmetic mean value of test results
v	expected value
n	number of accepted test results
$s(r)$	repeatability standard deviation
r	repeatability limit
$s(R)$	reproducibility standard deviation
R	reproducibility limit

Table G.4 – Statistical data for TD-MS

Sample	Component	$\bar{x}$ mg/kg	v mg/kg	n	$s(r)$ mg/kg	r mg/kg	$s(R)$ mg/kg	R mg/kg
IIS3-4-A01	DIBP/DBP	20	0	36	8	22	47	131
IIS3-4-B02	DIBP/DBP	886	1 007	32	48	133	206	576
IIS3-4-C03	DIBP/DBP	1 688	2 000	33	232	649	677	1 895
IIS3-4-D04	DIBP/DBP	2 639	3 001	36	287	803	788	2 206
IIS3-4-E05	DIBP/DBP	717	unknown	36	151	424	1 222	3 423
IIS3-4-A01	BBP	108	0	36	17	48	184	516
IIS3-4-B02	BBP	428	506	32	33	91	103	286
IIS3-4-C03	BBP	614	1 000	30	48	135	228	638
IIS3-4-D04	BBP	2 468	3 004	36	349	976	859	2 404
IIS3-4-E05	BBP	28	unknown	36	53	148	67	187
IIS3-4-A01	DEHP/DnOP	42	0	36	5	14	57	159
IIS3-4-B02	DEHP/DnOP	384	503	32	23	63	108	302
IIS3-4-C03	DEHP/DnOP	1 654	2 000	33	188	527	835	2 339
IIS3-4-D04	DEHP/DnOP	4 969	6 006	36	537	1 503	1 596	4 470
IIS3-4-E05	DEHP/DnOP	140 635	unknown	33	12 203	34 168	106 404	297 933

Key

$\bar{x}$	arithmetic mean value of test results
v	expected value
n	number of accepted test results
$s(r)$	repeatability standard deviation
r	repeatability limit
$s(R)$	reproducibility standard deviation
R	reproducibility limit

Table G.5 – Statistical data for FT-IR

Sample	Component	$\bar{x}$ mg/kg	v mg/kg	n	$s(r)$ mg/kg	r mg/kg	$s(R)$ mg/kg	R mg/kg
IIS3-4-A01	Phthalates	47 267	0	15	51 642	144 597	113 792	318 617
IIS3-4-B02	Phthalates	5 025	2 016	13	611	1 711	5 915	16 563
IIS3-4-C03	Phthalates	39 588	8 000	11	13 411	37 550	58 991	165 174
IIS3-4-D04	Phthalates	75 412	78 104	12	5 631	15 768	27 834	77 935
IIS3-4-E05	Phthalates	333 152	unknown	12	33 333	93 334	113 534	317 895

Key

$\bar{x}$	arithmetic mean value of test results
v	expected value
n	number of accepted test results
$s(r)$	repeatability standard deviation
r	repeatability limit
$s(R)$	reproducibility standard deviation
R	reproducibility limit

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