

Determination of certain substances in electrotechnical products

Part 3-3: Screening — Polybrominated biphenyls, polybrominated diphenyl ethers and phthalates in polymers by gas chromatography-mass spectrometry using a pyrolyser/thermal desorption accessory (Py/TD-GC-MS)

National foreword

This British Standard is the UK implementation of EN IEC 62321-3-3:2021. It is identical to IEC 62321-3-3:2021. Together with BS EN 62321-1:2013, BS EN 62321-2:2014, BS EN 62321-3-1:2014, BS EN 62321-3-2:2014, BS EN 62321-4:2014, BS EN 62321-5:2014, BS EN 62321-6:2015, BS EN 62321-7-1:2015, BS EN 62321-7-2:2017 and BS EN 62321-8:2017 it supersedes BS EN 62321:2009, which is withdrawn.

The UK participation in its preparation was entrusted to Technical Committee GEL/111, Electrotechnical environment committee.

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

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English Version

Determination of certain substances in electrotechnical products
- Part 3-3: Screening - Polybrominated biphenyls,
polybrominated diphenyl ethers and phthalates in polymers by
gas chromatography-mass spectrometry using a
pyrolyser/thermal desorption accessory (Py/TD-GC-MS)
(IEC 62321-3-3:2021)

Détermination de certaines substances dans les produits
électrotechniques - Partie 3-3: Détection - Diphényles
polybromés, diphényléthers polybromés et phthalates dans
les polymères par chromatographie en phase gazeuse-
spectrométrie de masse par pyrolyse/thermodésorption
(Py/TD-GC-MS)
(IEC 62321-3-3:2021)

Verfahren zur Bestimmung von bestimmten Substanzen in
Produkten der Elektrotechnik - Teil 3-3: Screening der
polybromierten Biphenyle, polybromierten Diphenylether
und Phthalate in Polymeren durch Pyrolyse (Py-GC-MS)
oder Thermodesorption-Gaschromatographie-
Massenspektrometrie (TD-GC-MS)
(IEC 62321-3-3:2021)

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The following dates are fixed:

- latest date by which the document has to be implemented at national (dop) 2022-07-19 level by publication of an identical national standard or by endorsement
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In the official version, for Bibliography, the following notes have to be added for the standards indicated:

IEC 62321-1:2013	NOTE Harmonized as EN 62321-1:2013 (not modified)
IEC 62321-2:2013	NOTE Harmonized as EN 62321-2:2014 (not modified)
IEC 62321-8:2017	NOTE Harmonized as EN 62321-8:2017 (not modified)
IEC 62321-3-1:2013	NOTE Harmonized as EN 62321-3-1:2014 (not modified)
IEC 62321-3-2:2020	NOTE Harmonized as EN IEC 62321-3-2:2020 ¹ (not modified)
IEC 62321:2008 ²	NOTE Harmonized as EN 62321:2009 ³ (not modified)
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² Withdrawn.

³ Withdrawn.

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS –

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FOREWORD

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The text of this International Standard is based on the following documents:

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Full information on the voting for its approval can be found in the report on voting indicated in the above table.

The language used for the development of this International Standard is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available at www.iec.ch/members_experts/refdocs. The main document types developed by IEC are described in greater detail at www.iec.ch/standardsdev/publications.

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 document will remain unchanged until the stability date indicated on the IEC website under webstore.iec.ch in the data related to the specific document. At this date, the document 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 polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs) and certain phthalates in electrotechnical products is of concern in many regions of the world.

The purpose of this document is therefore to provide a test method that will allow the electrotechnical industry to determine the levels of polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), di-isobutyl phthalate (DIBP), di-n-butyl phthalate (DBP), benzylbutyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP) in electrotechnical products on a consistent global basis.

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 3-3: Screening – Polybrominated biphenyls, polybrominated diphenyl ethers and phthalates in polymers by gas chromatography-mass spectrometry using a pyrolyser/thermal desorption accessory (Py/TD-GC-MS)

1 Scope

This part of IEC 62321 specifies the screening analysis of polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs), di-isobutyl phthalate (DIBP), di-n-butyl phthalate (DBP), benzylbutyl phthalate (BBP), di-(2-ethylhexyl) phthalate (DEHP), di-n-octyl phthalate (DNOP), di-isononyl phthalate (DINP), and di-isodecyl phthalate (DIDP) in polymers of electrotechnical products using the analytical technique of gas chromatography-mass spectrometry using a pyrolyser/thermal desorption accessory (Py/TD-GC-MS).

This test method has been evaluated through the analysis of PP (polypropylene), PS (polystyrene), and PVC (polyvinyl chloride) materials containing deca-BDE between 100 mg/kg and 1 000 mg/kg and individual phthalates between 100 mg/kg to 4 000 mg/kg as depicted in Annex J. Use of the methods described in this document for other polymer types, PBBs (mono-deca), PBDEs (mono-deca) and phthalates or concentration ranges other than those specified above has not been specifically evaluated.

This document has the status of a horizontal standard in accordance with IEC Guide 108 [1]¹.

2 Normative references

There are no normative references in this document.

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 terminological databases for use in standardization at the following addresses:

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

¹ Numbers in square brackets refer to the bibliography.

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 with respect to analyte(s) concentration(s) or mass

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;

RF_A is the response factor of compound A;

RF_B is the response factor of compound B

3.1.6**substitute compound**

compound used to calculate RRFs of each analyte

Note 1 to entry: More than one compound can be selected as a substitute compound. The RRF of the analyte is the ratio of the RF of the analyte to this compound. In Equation (3), compound B corresponds to this. 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. From the RF of the substitute compound and the RRF of the analyte, the RF of each analyte is calculated.

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

where

RF_A is the response factor of compound A;

RF_B is the response factor of compound B; substitute compound

3.2 Abbreviated terms

BB-003	4-bromobiphenyl
BB-015	4,4'-dibromobiphenyl
BB-029	2,4,5-tribromobiphenyl
BB-049	2,2',4,5'-tetrabromobiphenyl
BB-103	2,2',4,5',6-pentabromobiphenyl
BB-153	2,2',4,4',5,5'-hexabromobiphenyl
BB-189	2,3,3',4,4',5,5'-heptabromobiphenyl
BB-194	2,2',3,3',4,4',5,5'-octabromobiphenyl
BB-206	2,2',3,3',4,4',5,5',6- nonabromobiphenyl
BB-209	decabromo biphenyl
BBP	benzyl butyl phthalate
BDE-003	4-bromodiphenyl ether
BDE-015	4,4'-dibromodiphenyl ether
BDE-028	2,4,4'-tribromodiphenyl ether
BDE-047	2,2',4,4'-tetrabromodiphenyl ether
BDE-099	2,2',4,4',5-pentabromodiphenyl ether
BDE-153	2,2',4,4',5,5'-hexabromodiphenyl ether
BDE-183	2,2',3,4,4',5',6-heptabromodiphenyl ether
BDE-203	2,2',3,4,4',5,5',6-octabromodiphenyl ether
BDE-206	2,2',3,3',4,4',5,5',6-nonabromodiphenyl ether
BDE-209	decabromodiphenyl ether
CRM	certified reference material
DBP	di-n-butyl phthalate
DEHP	di-(2-ethylhexyl) phthalate
DIBP	di-isobutyl phthalate
DIDP	di-isodecyl phthalate
DINP	di-isononyl phthalate
DNOP	di-n-octyl phthalate
EGA	evolved gas analysis
EI	electron ionization

GC	gas chromatography
LOQ	limit of quantification
MDL	method detection limit
MS	mass spectrometry
PBB	polybrominated biphenyl
PBDE	polybrominated diphenyl ether
PBMS	performance-based measurement system
PE	polyethylene
PP	polypropylene
PS	polystyrene
PVC	polyvinyl chloride
Py/TD-GC-MS	gas chromatography-mass spectrometry using a pyrolyser/thermal desorption accessory
QC	quality control
RF	response factor
RRF	relative response factor
SIM	selected ion monitoring
THF	tetrahydrofuran

4 Principle

4.1 Overview

The concept of 'screening' has been developed to reduce the amount of testing. Executed as a predecessor to any other test analysis, the main objective of screening is to quickly determine whether the screened part or section of a product:

- contains a certain substance at a concentration significantly higher than its value or values chosen as criterion, and therefore may be deemed unacceptable;
- contains a certain substance at a concentration significantly lower than its value or values chosen as criterion, and therefore may be deemed acceptable;
- contains a certain substance at a concentration so close to the value or values chosen as criterion that when all possible errors of measurement and safety factors are considered, no conclusive decision can be made about the acceptable absence or presence of a certain substance and, therefore, a follow-up action may be required, including further analysis using verification testing procedures.

This test method is designed specifically to screen for PBBs, PBDEs, DIBP, DBP, BBP, DEHP, DNOP, DINP, and DIDP in polymers in electrotechnical products by using the analytical technique of Py/TD-GC-MS. Annex A provides a flow chart as an example of how this method can be used for screening.

4.2 Principle of test

Py/TD-GC-MS uses gas chromatography-mass spectrometry coupled with a pyrolyser/thermal desorption accessory (see Annex B, Figure B.1) to screen the presence of PBBs, PBDEs, DIBP, DBP, BBP, DEHP, DNOP, DINP and DIDP in polymers in electrotechnical products. Since Py/TD-GC-MS does not require any prolonged solvent extraction process, a fast screening of PBBs, PBDEs and phthalates is available. The polymer sample is directly introduced into the pyrolyser, which thermally extracts PBBs, PBDEs and phthalates from a polymer under a specific heat zone. Thermally desorbed PBBs, PBDEs and phthalates are then transferred to the gas chromatograph. PBBs, PBDEs and phthalates are separated by a gas chromatographic capillary column and detected by a mass spectrometer. The respective PBBs, PBDEs and phthalates are identified based on the retention times, m/z (quantification and confirmation ions), and ion ratio as a result of standard specimen analysis. The selected ion monitoring (SIM) mode is used as the measuring mode of MS to improve detection limits. Calculation of the PBBs, PBDEs and phthalates concentration in the original sample is achieved by using response factors (RFs) and relative response factors (RRFs) normalized by RF of the substitute compound. 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 are determined by a different Py/TD-GC-MS system can be applied.

NOTE 1 Additionally, scan measurement of MS is suitable to check negative matrix interference from other additives in the polymer. Negative matrix interference causes ion suppression which provides lower concentration results. Scan/SIM measurement (simultaneous measurements) is also applicable.

NOTE 2 Annex C provides the potential alternative test methods for the screening.

NOTE 3 Since IEC 62321 (all parts) employs PBMS, test methods that provide equivalent performance criteria required in this document do not prevent its use.

5 Reagents and materials

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

When measuring PBBs and/or PBDEs, low degradable materials (such as PP and PS) shall be used as a standard sample for the determination of response factors, refer to Annex D:

NOTE 1 Deca-BB and deca-BDE are known to become highly degradable in some types of polymers.

- a) blank polymer material from a pure source which does not contain the specific analytes and other compounds that may interfere with the analysis by peak overlapping or ion suppression: refer to Annex D;
- b) helium (purity greater than a volume fraction of 99,999 %);

NOTE 2 The nitrogen gas can be used if it is confirmed that the required performance is satisfied.

- c) calibrants: refer to Annex D;
- d) polymer reference materials: One contains approximately 100 mg/kg of analytes (PBBs, PBDEs and/or phthalates) and the other 1 000 mg/kg;

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

- e) toluene for preparing the PBBs, PBDEs and phthalates standard solution, GC grade or higher;
- f) THF for preparing the polymer solution, GC grade or higher.

6 Apparatus

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) deactivated glass wool;
- c) deactivated sample cup; if a sample cup is re-used, analyte carry-over shall be confirmed by analysing without a sample;

NOTE 1 Before a sample cup is re-used, it is baked out to prevent cross contamination. However, if a re-used sample cup causes certain PBDE and PBB decomposition, the sample cup is not re-used.

- d) gas chromatograph – mass spectrometer equipped with a 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 monitoring ("full scan");

NOTE 2 An auto-sampler is used to ensure repeatability.

- e) pyrolyser/thermal desorption accessory;
- f) capillary column;

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

- g) cryogenic grinding mill with liquid nitrogen cooling;
- h) polymer sample preparation tools to cut or file polymer such as nipper, micro spatula, tweezers, cutter, file, and micro puncher;
- i) micro syringe or automated pipettes;
- j) glass equipment; made from brown or amber glass for long-term storage of PBDEs.

NOTE 3 To avoid decomposition and/or debromination of PBDEs by UV light during long-term sample storage, glass equipment made from brown or amber glass is used.

7 Sampling

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

8 Procedure

8.1 General instructions for the analysis

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.

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 PBBs, PBDEs and phthalates is decreased to a value equivalent to 100 mg/kg or even lower.

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 the sample preparation.

8.2 Sample preparation

8.2.1 General

The sample preparation requires clean labware (e.g. cutter, tweezers) to avoid cross contamination.

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 [3].

8.2.2 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 Refer to Annex E.

8.2.3 Stock solution or polymer reference material

The PS solution and standard mixture solution are available for the calibration and sensitivity check. When polymer reference materials are available, they shall be used for the calibration and sensitivity check. A thinly stretched polymer reference sheet or film would also be available (see Annex D).

NOTE 1 The following solution concentrations and solvent types are examples and can be changed.

- a) PS solution: 50 mg/ml in THF solvent;

NOTE 2 The other type of base polymer is available if it is dissolved completely by a suitable solvent.

NOTE 3 When measuring PBBs and/or PBDEs, deca-BDE is known to become highly degradable in some types of polymers and a PS solution is used as a standard sample for the determination of response factors; refer Annex D.

- b) PBB solution: 50 µg/ml mono to deca-BB in toluene;
- c) PBDE solution: 50 µg/ml mono to deca-BDE in toluene;
- d) phthalate solution: 100 µg/ml in organic solvent such as hexane or toluene; the phthalate solution should contain all phthalates necessary for analysis of DIBP, DBP, BBP, DEHP, DNOP, DINP and DIDP;
- e) stock solution of substitute compound such as DEHP: 100 µg/ml in organics solvent such as hexane or toluene.

NOTE 4 When more than one compound is used as a substitute compound, each stock solution or mixture solution is prepared.

8.3 Instrumental parameters

Different conditions may be necessary to optimize a specific Py/TD-GC-MS system to achieve effective separation of each substance and meet the quality control (QC) and method detection limits (MDL) requirements. The following parameters have been found suitable and are provided as an example (see Table 1). The total ion current chromatogram and mass chromatogram is shown in Annex G (see Figure G.1).

Table 1 – Measurement conditions 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; internal diameter 0,25 mm; film thickness 0,05 µm			
Injection port temperature	320 °C			
Column oven temperature	80 °C → (20 °C /min) → 300 °C (5 min)			
Injection mode	Split (split ratio: 1/50)			
Carrier gas	Helium, 1,5 ml/min, constant linear velocity			
MS				
Ion source temperature	230 °C			
Ionization method	Electron ionization (EI), 70 eV.			
Monitoring mass ion (m/z)	Compound name	Quantification ion	Confirmation ion-1	Confirmation ion-2
	BB-003	231,9	233,9	-
	BB-015	311,8	309,8	313,8
	BB-029	389,8	387,8	391,8
	BB-049	309,8	307,8	467,7
	BB-103	387,7	385,7	545,6
	BB-153	467,6	465,6	627,5
	BB-189	545,6	543,6	705,4
	BB-194	625,5	623,5	627,5
	BB-206	703,4	701,4	705,4 (863,4)
	BB-209	783,3	781,3	785,3 (943,1; 215,8; 382,6; 384,5)
	BDE-003	247,9	249,9	
	BDE-015	327,8	325,8	329,8
	BDE-028	405,8	403,8	407,8
	BDE-047	325,8	323,8	483,7
	BDE-099	403,7	401,7	561,6
	BDE-153	483,6	481,6	643,5
	BDE-183	561,6	559,6	721,4
	BDE-203	641,5	639,5	643,5 (801,3)
	BDE-206	719,4	717,4	721,4 (879,2)
	BDE-209	799,3	797,3	959,1
	DIBP	223	205	149
	DBP	223	205	149
	BBP	206	91	149
	DEHP	279	167	149
	DNOP	279	167	149
	DINP	293	167	149
	DIDP	307	167	149
Scan range	m/z 50 to 1 000			

NOTE 1 Additionally, scan measurement of MS is available to check negative matrix interference from other additives in the polymer. Negative 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 DIDP and DINP have multiple chromatogram peaks. The areas of these peaks above the baseline are integrated.

NOTE 4 See Annex F for an optimization of furnace temperature.

NOTE 5 To prevent decomposition of PBDEs and PBBs, an inert or a thermally treated ion source box is available.

8.4 Calibration

8.4.1 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. Substitute compounds can be selected for each group of analytes such as PBDEs, PBBs and phthalates, which have close physical and chemical properties. The following describes the case where DEHP is used as the substitute compound.

8.4.2 Determination of RRFs

RRFs are determined for six phthalates (DIBP, DBP, BBP, DNOP, DINP, DIDP), mono- to decabrominated biphenyl (PBB) and mono- to decabrominated diphenyl ether (PBDE). For PBBs and PBDEs, the RRFs are determined for each congener. If DEHP is used as a substitute compound, the RRF of DEHP becomes one.

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 are 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 analytes at a concentration of 1 000 mg/kg.
 - Inject 10 µl of PS solution (50 mg/ml) into the sample cup.
 - Inject 10 µl of PBB solution (50 µg/ml), 10 µl of PBDE solution (50 µg/ml) and 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 these analytes at a concentration of 1 000 mg/kg, can be used as well as DEHP at the concentration of 1 000 mg/kg as a substitute compound sample.

- f) Analyse polymer reference materials (8.2.1).
- g) Record peak area.
- h) Calculate the RF of DEHP and that of each analyte using Equations (4) and (5).
- 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 response factors of DEHP and 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 available, use approximately 0,5 mg of the cut or powdered polymer reference material, replace the mass of DEHP and that of analyte in Equations (4) and (5) 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);

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

where

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

RF_A is the response factor of the analyte (mg^{-1});

RF_{DEHP} is the response factor of DEHP (mg^{-1}).

NOTE 2 Both the polymer solution and the standard solution can be injected to avoid the risk of volatilization of low boiling compounds (e.g. mono-BB, mono-BDE) when only the standard solution is injected.

NOTE 3 DIDP and DINP have multiple chromatogram peaks, the total areas of these peaks above the baseline can be integrated.

NOTE 4 See Annex H for examples of RRFs.

9 Calculation of PBBs, PBDEs and phthalates concentration

9.1 General

When DEHP is used as the substitute compound, it shall not be added to a test sample like an internal standard because it is one of the analytes. It is therefore analysed before test sample analysis. The RF of each analyte is calculated from the RF of substitute compound and the RRF of the analyte. The mass of the analyte is calculated from the peak area and the RF of the analyte.

The final concentration of each phthalate shall be determined.

Only detected PBB and PBDE compounds which are above the limit of detection shall be included in a total summation. If any of the PBDEs (or PBB, from mono- to deca-) were to be detected above the limit of detection, they should be reported with each quantification result.

9.2 Determination of RF of DEHP

A substitute compound sample is prepared and analysed before test sample analysis to calculate the RF of each analyte.

- a) A polymer reference material containing the substitute compound (DEHP) at a concentration of approximately 1 000 mg/kg is available. Place approximately 0,5 mg of the cut or powdered polymer reference material into a sample cup for Py/TD-GC-MS (see Annex D).
- b) Calculate the response factor RF_{DEHP-2} using Equation (4):

NOTE If the polymer reference material is not available, the following procedure is also used to prepare alternative substitute compound samples.

10 µl of PS solution (50 mg/ml) and 5 µl of standard solution of DEHP (100 µg/ml) is injected into the sample cup. The solution is dried at room temperature.

9.3 Calculation

9.3.1 Calculation of RF

When the substitute compound sample (DEHP) contains other analytes, the RFs of those analytes are determined using Equation (5) without using the RRF of DEHP.

NOTE This procedure is the same as the screening procedure of IEC 62321-8 [4].

When the polymer reference material does not contain the analytes, the RF of those analytes are determined using Equation (9):

$$RF_{A-2} = RRF_{A/DEHP} / RF_{DEHP-2} \quad (9)$$

where

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

RF_{A-2} is the response factor of the analyte (mg^{-1});

RF_{DEHP-2} is the response factor of DEHP (mg^{-1}).

9.3.2 Calculation of concentration

The final concentration of each phthalate and each congener of PBB and PBDE in the sample can be calculated by using Equation (10):

$$C_{final} = A_{A-2} \times \left(\frac{1}{RF_{A-2}} \right) \times \left(\frac{1}{M_S} \right) \quad (10)$$

where

C_{final} is the concentration of each analyte in the sample in mg/kg;

A_{A-2} is the peak area of each analyte;

RF_{A-2} is the response factor of each analyte (mg^{-1});

M_S is the mass of the sample (kg).

NOTE The RRF is determined for each congener of PBB and PBDE, therefore C_{final} is determined for each congener of PBB and PBDE.

$$C_{\text{total PBB}} = \Sigma (C_{\text{MonoBB}} + C_{\text{DiBB}} + \dots + C_{\text{DecaBB}}) \quad (11)$$

$$C_{\text{total PBDE}} = \Sigma (C_{\text{MonoBDE}} + C_{\text{DiBDE}} + \dots + C_{\text{DecaBDE}}) \quad (12)$$

where

$C_{\text{total PBB}}$ is the concentration of total PBBs in the sample in mg/kg;
 $C_{\text{total PBDE}}$ is the concentration of total PBDEs in the sample in mg/kg;
 $C_{\text{MonoBB}}, C_{\text{DiBB}}, \dots$ are the concentrations of each PBB in the sample in mg/kg;
 $C_{\text{MonoBDE}}, C_{\text{DiBDE}}, \dots$ are the concentrations of each PBDE in the sample in mg/kg.

10 Precision

10.1 Screening judgement

The overall screening judgement from the international inter-laboratory study 3-3 (IIS3-3) results are shown in Table 2.

The screening judgement has been made in accordance with the flow chart in Annex A as an example of how the Py/TD-GC-MS method can be used for screening when the acceptability threshold for individual DIBP, DBP, BBP, DEHP, DNOP, DINP, DIDP, total PBBs and total PBDEs concentrations are set at 1 000 mg/kg, respectively. Expected screening results are shown as "BL" for "below limit" or passing, "OL" for "over limit" or failing and "INC" for "inconclusive" requiring GC-MS referee testing.

All of the laboratories (from six to eleven laboratories) except one laboratory submitted threshold judgement results as shown in Table 2. The laboratory detected DNOP in the sample IIS3-3_5 due to misidentification.

Table 2 – IIS3-3 Screening and threshold judgement

Sample ID	Target compound	Mean value	Expected value	Expected screening results	Number of laboratories submitting screening judgement results			Number of laboratories submitted incorrect threshold judgement results
					Phthalate mg/kg			
					≤ 500	500 to 1 500	≥ 1 500	
					PBB/ PBDE mg/kg			
					≤ 300	300 to 1 700	≥ 1 700	
IIS3-3_1	DIBP	88,1	88	BL	11	0	0	0
IIS3-3_1	DBP	86,5 (94,9)	84	BL	10 (11)	0	0	0
IIS3-3_1	BBP	68,7	77	BL	11	0	0	0
IIS3-3_1	DEHP	78,9 (103,9)	87	BL	9 (11)	0	0	0
IIS3-3_1	DNOP	74,1	92	BL	11	0	0	0
IIS3-3_1	DINP	64,2 (60,2)	93	BL	10 (11)	0	0	0
IIS3-3_1	DIDP	84,8	96	BL	11	0	0	0
IIS3-3_1	PBB	0,0	0	BL	11	0	0	0
IIS3-3_1	PBDE	45,7 (25,1)	83	BL	6 (11)	0	0	0
IIS3-3_2	DIBP	910,9	849	INC	0	11	0	0

Sample ID	Target compound	Mean value	Expected value	Expected screening results	Number of laboratories submitting screening judgement results			Number of laboratories submitted incorrect threshold judgement results
					Phthalate mg/kg			
					≤ 500	500 to 1 500	≥ 1 500	
					PBB/ PBDE mg/kg			
					≤ 300	300 to 1 700	≥ 1 700	
IIS3-3_2	DBP	935,8	810	INC	0	11	0	0
IIS3-3_2	BBP	820,0	787	INC	0	11	0	0
IIS3-3_2	DEHP	892,8	849	INC	0	11	0	0
IIS3-3_2	DNOP	898,4	834	INC	0	11	0	0
IIS3-3_2	DINP	697,3	1 001	INC	0	11	0	0
IIS3-3_2	DIDP	1 044,3	1 086	INC	0	11	0	0
IIS3-3_2	PBB	0,0	0	BL	11	0	0	0
IIS3-3_2	PBDE	929,2 (895,1)	884	INC	0	10 (11)	0	0
IIS3-3_4	DIBP	2,3	0	BL	8	0	0	0
IIS3-3_4	DBP	3,1 (15,1)	0	BL	7 (8)	0	0	0
IIS3-3_4	BBP	0,5	0	BL	8	0	0	0
IIS3-3_4	DEHP	6,9 (52,3)	0	BL	6 (8)	0	0	0
IIS3-3_4	DNOP	2,0	0	BL	8	0	0	0
IIS3-3_4	DINP	1,0	0	BL	8	0	0	0
IIS3-3_4	DIDP	0,4	0	BL	8	0	0	0
IIS3-3_4	PBB	0,5	0	BL	8	0	0	0
IIS3-3_4	PBDE	744,5 (635,1)	886	INC	0	6 (8)	0	0
IIS3-3_5	DIBP	9,9	0	BL	10	0	0	0
IIS3-3_5	DBP	129,9 (117,0)	0	BL	9 (10)	0	0	0
IIS3-3_5	BBP	29,7	0	BL	10	0	0	0
IIS3-3_5	DEHP	4 700,9	3 923	OL	0	0	10	0
IIS3-3_5	DNOP	0,0 (5 314,7)	0	BL	9	0	(1)	(1)
IIS3-3_5	DINP	78,7	0	BL	10	0	0	0
IIS3-3_5	DIDP	11,0	0	BL	10	0	0	0
IIS3-3_5	PBB	0,0	0	BL	10	0	0	0
IIS3-3_5	PBDB	0,0 (9,0)	0	BL	9 (10)	0	0	0
Key								
BL Below limit								
INC Inconclusive expected value								
OL Over limit								
() Including outline data								

See Annex J for supporting data.

10.2 Repeatability and reproducibility

When the values of three independent single test results, obtained using the same method on 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 3, Table 4 and 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 (IIS) results in more than 5 % of cases.

When the values of three single test results, obtained using the same method on identical test material in different laboratories by different operators using different equipment, lie within the range of the values cited in Table 3, Table 4 and 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 by statistical analysis of the international inter-laboratory study (IIS) results in more than 5 % of cases.

Table 3 – IIS3-3 Repeatability and reproducibility (phthalate)

Phthalate	Sample	Mean value μ mg/kg	Repeatability r mg/kg	Reproducibility R mg/kg
DIBP	IIS3-3_1	88,1	16,9	56,6
	IIS3-3_2	910,9	116,2	490,7
	IIS3-3_4	2,3	1,8	18,4
	IIS3-3_5	9,9	11,6	21,3
DBP	IIS3-3_1	86,5	22,3	66,0
	IIS3-3_2	935,8	120,4	325,3
	IIS3-3_4	3,1	4,1	12,2
	IIS3-3_5	129,9	87,4	152,3
BBP	IIS3-3_1	68,7	23,1	59,7
	IIS3-3_2	820,0	143,7	303,8
	IIS3-3_4	0,5	1,1	4,1
	IIS3-3_5	29,7	13,9	38,5
DEHP	IIS3-3_1	78,9	21,4	45,8
	IIS3-3_2	892,8	135,9	282,6
	IIS3-3_4	6,9	17,4	33,7
	IIS3-3_5	4 700,9	2 093,4	3 964,0
DNOP	IIS3-3_1	74,1	26,3	56,6
	IIS3-3_2	898,4	143,9	263,4
	IIS3-3_4	2,0	6,2	11,9
	IIS3-3_5	0,0	0	0
DINP	IIS3-3_1	64,2	27,8	51,4
	IIS3-3_2	697,3	110,7	279,2
	IIS3-3_4	1,0	6,3	9,4
	IIS3-3_5	78,7	46,3	269,4
DIDP	IIS3-3_1	84,8	37,6	67,7
	IIS3-3_2	1 044,3	241,8	391,2
	IIS3-3_4	0,0	2,9	4,1
	IIS3-3_5	11,0	11,2	37,2

Table 4 – IIS3-3 Repeatability and reproducibility (PBB)

PBB	Sample	Mean value μ mg/kg	Repeatability r mg/kg	Reproducibility R mg/kg
Total PBB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,5	1,0	4,0
	IIS3-3_5	0,0	0,0	0,0
Mono-BB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,0	0,0
	IIS3-3_5	0,0	0,0	0,0
Di-BB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,0	0,0
	IIS3-3_5	0,0	0,0	0,0
Tri-BB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,0	0,0
	IIS3-3_5	0,0	0,0	0,0
Tetra-BB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,4	0,6	2,9
	IIS3-3_5	0,0	0,0	0,0
Penta-BB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,1	0,5	0,7
	IIS3-3_5	0,0	0,0	0,0
Hexa-BB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,1	0,6	0,8
	IIS3-3_5	0,0	0,0	0,0
Hepta-BB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,0	0,0
	IIS3-3_5	0,0	0,0	0,0
Octa-BB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,0	0,0
	IIS3-3_5	0,0	0,0	0,0
Nona-BB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,0	0,0
	IIS3-3_5	0,0	0,0	0,0

PBB	Sample	Mean value μ mg/kg	Repeatability r mg/kg	Reproducibility R mg/kg
Deca-BB	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,0	0,0
	IIS3-3_5	0,0	0,0	0,0

Table 5 – IIS3-3 Repeatability and reproducibility (PBDE)

PBDE	Sample	Mean value μ mg/kg	Repeatability r mg/kg	Reproducibility R mg/kg
Total PBDE	IIS3-3_1	45,7	26,2	46,2
	IIS3-3_2	929,2	281,6	685,6
	IIS3-3_4	744,5	243,0	484,1
	IIS3-3_5	0,0	0,0	0,0
Mono-BDE	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,0	0,0
	IIS3-3_5	0,0	0,0	0,0
Di-BDE	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,0	0,0
	IIS3-3_5	0,0	0,0	0,0
Tri-BDE	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,0	0,0
	IIS3-3_5	0,0	0,0	0,0
Tetra-BDE	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,2	1,5	2,2
	IIS3-3_5	0,0	0,0	0,0
Penta-BDE	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,6	1,2	5,2
	IIS3-3_5	0,0	0,0	0,0
Hexa-BDE	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,0	0,0
	IIS3-3_4	0,0	0,1	0,4
	IIS3-3_5	0,0	0,0	0,0
Hepta-BDE	IIS3-3_1	0,0	0,0	0,0
	IIS3-3_2	0,0	0,2	0,3
	IIS3-3_4	0,0	0,4	0,4
	IIS3-3_5	0,0	0,0	0,0

PBDE	Sample	Mean value μ mg/kg	Repeatability r mg/kg	Reproducibility R mg/kg
Octa-BDE	IIS3-3_1	0,6	2,1	4,1
	IIS3-3_2	3,2	8,8	17,8
	IIS3-3_4	4,4	27,6	32,9
	IIS3-3_5	0,0	0,0	0,0
Nona-BDE	IIS3-3_1	3,9	3,8	15,6
	IIS3-3_2	15,6	8,6	48,9
	IIS3-3_4	70,0	37,9	168,4
	IIS3-3_5	0,0	0,0	0,0
Deca-BDE	IIS3-3_1	37,8	26,3	52,9
	IIS3-3_2	879,3	352,6	713,2
	IIS3-3_4	611,4	237,0	590,4
	IIS3-3_5	0,0	0,0	0,0

11 Quality assurance and control

11.1 General

Where applicable, the quality assurance and control clauses of the test method shall include control sample requirements regarding testing frequency and acceptance criteria.

11.2 Quality control

11.2.1 Sensitivity test

Instrumental sensitivity shall be confirmed by the S/N ratio of 50 ng analyte with each sequence of samples. The confirmed S/N ratio shall be greater than 30. For this test, optimal analytes can be chosen but DEHP shall be included.

Polymer reference material (100 mg/kg) is used as the sensitivity check sample. Put approximately 0,5 mg of the punched-out, cut or powdered polymer reference material into the sample cup (Figure D.1).

NOTE 1 The following procedure is also used to prepare the sensitivity check sample. In that time, both the polymer solution and the standard solution can be injected to avoid the risk of volatilization of low boiling compounds (e.g. mono-BB, mono-BDE) when only the standard solution is injected.

- 10 μ l of PS solution (50 mg/ml) and 0,5 μ l of standard mixture solution (100 μ g/ml) is injected into the sample cup using a microlitre syringe.
- The solution is dried at room temperature.

NOTE 2 An example of a sample analysis sequence is shown in Annex I.

11.2.2 Blank test

At the beginning of each sample-set a blank run shall be executed in order to confirm that there is no analyte carryover from sample to sample. This is particularly important when samples containing high levels of PBBs, PBDEs and phthalates are analysed. If the instrument is contaminated by analytes, this will result in false positive results. After analysis of a high-concentration sample (more than 1 %), blank samples should be analysed until the background level of each of the PBBs, PBDEs and phthalates are decreased to a value equivalent to 100 mg/kg or less. Samples analysed after a high contamination shall be re-analysed if analyte carryover is recognized.

NOTE 1 Blank polymer material or a blank sample cup is used for blank-sample analysis.

NOTE 2 An example of a sample analysis sequence is shown in Annex I.

11.2.3 System stability test

The timing of the system stability test in a sample sequence shall be determined in advance. Following the determined timing in a sample sequence, a polymer reference material of DEHP at 1 000 mg/kg shall be analysed. The percent recovery for DEHP shall be between 70 % and 130 %. If the percent recovery falls outside this range, the analysis is stopped. All samples injected before the last successful stability test may be reported, but samples after the failing stability test shall be re-analysed with a blank test, sensitivity test and calibration.

NOTE 1 When the stability check is performed every twenty 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, system maintenance is performed to return it to optimal operating conditions.

NOTE 3 If the polymer reference material is not available, the following procedure is also used to prepare alternative substitute compound samples.

- a) 10 µl of PS solution (50 mg/ml) and 5 µl of standard solution of DEHP (100 µg/ml) is injected into the sample cup.
- b) The solution is dried at room temperature.

11.2.4 Degradation test

The degradation test shall be performed before the RRF test (11.2.5) to confirm the inertness of the Py/TD-GC-MS system. Contamination and deterioration of the capillary column and sample path of the pyrolyser might stimulate degradation of deca-BDE which is a relatively thermally-labile compound. A polymer reference material which contains deca-BDE (for example at 1 000 mg/kg) and does not contain nona-BDE is analysed. From the concentrations of deca-BDE and the decomposed product (nona-BDE) (9.3.2), the decomposition percentage is determined using Equation (11):

$$D = \frac{C_{\text{nona-BDE}}}{(C_{\text{deca-BDE}} + C_{\text{nona-BDE}})} \times 100 \quad (11)$$

where

$C_{\text{deca-BDE}}$ is the concentration of deca-BDE (mg/kg);

$C_{\text{nona-BDE}}$ is the concentration of nona-BDE (mg/kg);

D is the degradation ratio (%).

Confirm that the degradation ratio is 30 % or less. If the degradation ratio exceeds 30 %, the system shall be maintained to reduce the degradation ratio down to 30 %.

NOTE 1 Deca-BDE is known to become highly degradable in some types of polymers such as PE. PP and PS are suitable matrix polymers as standard samples for the thermal degradable test.

NOTE 2 A thermal degradable test is performed after 500 sample analysis.

11.2.5 RRF test

The RRF test shall be completed prior to sample testing, after Py/TD-GC-MS maintenance or when a significant change is made to the method or instrument type. The RRF test shall be performed after the degradation test (11.2.4). To assess the stability of the RRF, select the specific analyte and the appropriate substitute compound, analyse these polymer reference materials (for example at 1 000 mg/kg respectively), and calculate the concentration (See 9.3). The final concentration is determined (9.3) and the deviation of the quantitative results for each analyte is confirmed at less than 30 %. If more than 30 %, RRFs shall be re-determined.

NOTE Deca-BDE is known to become highly degradable in some types of polymers. When measuring PBBs and/or PBDEs, the RRF test performed by deca-BDE is sufficient to confirm the Py/TD-GC-MS system.

11.3 Method detection limit (MDL) and limit of quantification (LOQ)

A method detection limit (MDL) study shall be completed before conducting sample testing and each time there is a significant change in the method or instrument type. The MDL is determined experimentally by performing replicate measurements on samples with the target substance present at a low-level concentration in the matrix, for example plastic. The MDL of deca-BDE is determined as a representative MDL of each congener of PBDEs and PBBs since deca-BDE shows the highest detection limit in PBDEs and PBBs. The MDL of each phthalate shall be determined, including DEHP. A minimum of six replicate measurements shall be performed to determine the calculable MDL. The complete MDL is determined by multiplying the standard deviation of the replicates by an appropriate coverage factor. The International Union of Pure and Applied Chemistry (IUPAC) recommends a factor of 3 for a minimum of six replicates, whilst the Environmental Protection Agency (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 shall be consecutively performed to calculate the MDL.

Polymer reference material (100 mg/kg) is available for MDL determination. Put approximately 0,5 mg of the punched-out, cut or powdered reference into the sample cup (Figure D.1).

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

- a) Inject 10 µl of PS solution (50 mg/ml) and 0,5 µl of standard mixture solution (100 µg/ml) into the sample cup using a microlitre syringe.
- b) Dry the solvent at room temperature and then analyse the replicate samples.

NOTE Both the polymer solution and the standard solution can be injected to avoid the risk of volatilization of low boiling compounds (e.g. mono-BB, mono-BDE) when only the standard solution is injected.

Each substance shall have a calculated MDL of less than or equal to 100 mg/kg. If the calculated MDL for any of the substances is above these limits, the procedure and analysis shall be repeated.

The limit of quantification (LOQ) of each substance shall be at least threefold 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.

12 Test report

Information shall be given on the following aspects of the test:

- the sample;
- the international standard used (including its year of publication);
- the result(s);
- any deviations from the procedure;
- any unusual features observed;
- the date of the test.