IEC 62321-6

Edition 1.0 2015-06

INTERNATIONAL STANDARD

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HORIZONTAL STANDARD

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Determination of certain substances in electrotechnical products – Part 6: Polybrominated biphenyls and polybrominated diphenyl ethers in polymers by gas chromatography–mass spectrometry (GC-MS)

Détermination de certaines substances dans les produits électrotechniques – Partie 6: Diphényles polybromés et diphényléthers polybromés dans des polymères par chromatographie en phase gazeuse–spectrométrie de masse (GC-MS)

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International Standard IEC 62321-6 has been prepared by IEC technical committee 111: Environmental standardization for electrical and electronic products and systems.

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

The first edition of IEC 62321:2008 was a 'stand-alone' standard that included an introduction, an overview of test methods, a mechanical sample preparation as well as various test method clauses.

This first edition of IEC 62321-6 is a partial replacement of IEC 62321:2008, forming a structural revision and generally replacing Annex A.

Future parts in the IEC 62321 series will gradually replace the corresponding clauses in IEC 62321:2008. Until such time as all parts are published, however, IEC 62321:2008 remains valid for those clauses not yet re-published as a separate part.

The text of this standard is based on the following documents:

FDIS	Report on voting
111/368/FDIS	111/379/RVD

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

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

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

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

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- withdrawn,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

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INTRODUCTION

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

The use of certain substances (e.g. lead (Pb), cadmium (Cd) and polybrominated diphenyl ethers (PBDE's)) 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.

WARNING – Persons using this International Standard should be familiar with normal laboratory practice. This standard 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 6: Polybrominated biphenyls and polybrominated diphenyl ethers in polymers by gas chromatography–mass spectrometry (GC-MS)

1 Scope

This Part of IEC 62321 specifies one normative and two informative techniques for the determination of polybrominated biphenyls (PBB) and diphenyl ethers (PBDE) in polymers of electrotechnical products.

The gas chromatography–mass spectrometry (GC-MS) test method is suitable for the determination of monobrominated to decabrominated biphenyls (PBB) and monobrominated to decabrominated diphenyl ethers (PBDE).

Annexes A and C contain methods using ion attachment mass spectrometry (IAMS) coupled with direct injection probe (DIP) and high-pressure liquid chromatography coupled to photo diode array ultra violet detector (HPLC-PDA/UV). These techniques have utility as fast, qualitative or semi-quantitative type methods but are subject to limitations including interferences or the number or type of PBB and PBDE compounds within their scope.

The ion attachment mass spectrometry (IAMS) technique is limited to the determination of decabromo biphenyl and technical mixtures of decabromodiphenyl ether, octabromodiphenyl ether, and pentabromo diphenyl ether flame retardant compounds. The determination of other PBBs or PBDEs by this method has not been evaluated.

The high-pressure liquid chromatography technique is limited to the determination of technical mixtures of decabromodiphenyl ether, octabromo diphenyl ether, decabromo biphenyl and octabromo biphenyl technical flame retardants. The determination of other PBBs or PBDEs by this method has not been evaluated.

These test methods have been evaluated for use with PS-HI (polystyrene, high-impact) and PC/ABS (a blend of polycarbonate and acrylonitrile butadiene styrene) containing individual PBDEs between 20 mg/kg to 2 000 mg/kg and total PBDEs between 1 300 mg/kg to 5 000 mg/kg as depicted in this standard including in Annex F. The use of these methods for other polymer types, PBBs or other PBDE compounds or concentration ranges other than those specified above has not been specifically evaluated.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

IEC 62321:2008, *Electrotechnical products – Determination of levels of six regulated substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)*

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

IEC 62321-2:2013, *Determination of certain substances in electrotechnical products – Part 2: Disassembly, disjointment and mechanical sample preparation*

3 Terms, definitions and abbreviations

3.1 Terms and definitions

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

3.1.1
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 %

3.1.2
technical mixture
commercial product (e.g. flame retardants) manufactured for industrial use whose purity is not as clearly defined as an individual high purity calibration standard

3.2 Abbreviations

BDE	brominated diphenyl ether
BFR	brominated flame retardant
Br	bromine
CIC	combustion – ion chromatography
DIP	direct injection probe
GC-MS	gas chromatography-mass spectrometry
HPLC-UV	high-performance liquid chromatography-ultra violet
IAMS	ion attachment mass spectrometry
IS	internal standard
MDL	method detection limit
LOD	limit of detection
LOQ	limit of quantification
PBB	polybrominated biphenyl
PBDE	polybrominated diphenyl ether
PDA	photodiode array (UV) detector
PS-HI (or HIPS)	high impact polystyrene
PTV	programmed temperature vaporising
QC	quality control
SIM	single (or “selected”) ion monitoring
XRF	X-ray fluorescence spectroscopy
TICS	tentatively identified compounds
RSD	relative standard deviation
CCC	continuing calibration check standard
BSA	bis(trimethylsilyl)acetamide
BSTFA	N,O-Bis(trimethylsilyl)trifluoroacetamide
BCR 681	Bureau Communautaire de Référence

NOTE BCR 681 contains 7 trace elements in a polyethylene matrix. The certified value for Br is 98 mg/kg ± 5 mg/kg

GC	gas chromatography
ABS	acrylonitrile-butadiene-styrene plastic
PDA/UV	photo diode array ultra violet detector
OFP	octafluoro pentanol
PTFE	polytetrafluoroethylene

4 Principle

PBB and PBDE compounds are quantitatively determined using Soxhlet extraction of the polymers with separation by gas chromatography – mass spectrometry (GC-MS) qualitatively and quantitatively using single (or "selected") ion monitoring (SIM).

5 Reagents and materials

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

a) toluene (GC grade or higher);

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

c) technical BDE-209 with BDE-209 ~ 96,9 % and BDE-206 ~ 1,5 % solution;

d) calibrants: refer to 8.4;

e) surrogate and internal standards

- surrogate standard used to monitor analyte recovery according to 8.2.1 a), 8.2.3 c), 8.2.4 e), 8.5.2 and 8.5.3, e.g. DBOFB (4, 4'-dibromooctafluorobiphenyl) (n),
- internal standard used to correct for injection errors, according to 8.2.1 b), 8.2.5 and 8.5.3, e.g. CB209 (2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl).

The standards are acceptable when using a quadrupole-type mass spectrometer. A high-resolution mass spectrometer will require the use of other suitable standard substances having a mass and elution time similar to that of the analyte. ^{13}C-labelled nonaBDE and ^{13}C-labelled decaBDE are recommended for the high-mass PBDEs.

NOTE The standards suggested are adequate for measuring the concentrations of mono- through octaBDE. Due to their low mass and "high" volatility, these standards can be inadequate for measuring decaBDE and nonaBDE concentrations. By far the best calibration standard for these specific analytes would be ^{13}C-labelled decaBDE or one of the ^{13}C-labelled nonaBDEs. Some laboratories, operating on the principal of high volume/low price, can find these labelled materials too expensive for their business plan. A potential low-cost substitute is decaBB (BB 209). BB 209 has a high mass (943,1 g/mol versus 959,1g/mol for decaBDE or 864,2 g/mol for nonaBDE), which elutes just before the three nonaBDEs on a typical DB-5 column. The presence of significant quantities of decaBB in the sample itself can readily be determined by monitoring the peak area of this standard, and comparing it to what is expected from the added quantity of decaBB. The use of the suggested labelled standards or decaBB can be limited to those analyses where the only analytes of interest are decaBDE and/or the nonaBDEs. With additional experimentation it can be possible to identify alternate standards that have the high mass and low volatility necessary for the quantification of the nonaBDEs and decaBDE.

6 Apparatus

The following items shall be used for the analysis:

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

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

c) Soxhlet extractors

- 30 ml Soxhlet extractors,
- 100 ml round-bottomed flask,
- ground-in stopper NS 29/32,

  - Dimroth condenser NS 29/32,
  - boiling stones (e.g. glass pearls or Raschig rings);

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

e) glass wool (for extraction thimble);

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

g) heating jackets;

h) funnel;

i) aluminium foil;

NOTE Brown or amber vessels as indicated in the text of the procedure can also be used.

j) Microlitre syringe or automatic pipettes;

k) Pasteur pipette;

l) 1,5 ml sample vials with 100 µl glass insert and a screw cap with polytetrafluoroethylene (PTFE) gasket or, depending on the analytical system, a comparable sample receptacle. Brown or amber vessels shall used as indicated in the text of the procedure.

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

n) a gas chromatograph with a capillary column coupled to a mass spectrometric detector (electron ionization, EI) is used for the analysis. The mass spectrometric detector shall be able to perform selective ion monitoring and have an upper mass range of at least 1 000 m/z. The high-range mass is required to unambiguously identify decaBDE and nonaBDE. The use of an autosampler is strongly recommended to ensure repeatability;

o) a column length of approximately 15 m has sufficient separation efficiency for PBB and PBDE compounds (see 8.3 a) for example of suitable column);

p) 0,45 µm PTFE filter membrane.

7 Sampling

As described in IEC 62321-2 unless indicated otherwise (e.g. "..using a nipper."), cryogenic grinding with liquid nitrogen cooling is recommended. The samples shall be ground to pass through a 500 µm sieve before extraction.

8 Procedure

8.1 General instructions for the analysis

The following general instructions shall be followed:

a) In order to reduce blank values, ensure the cleanliness of all glass equipment (excluding volumetric flasks) and deactivate glass wool (see Clause 6 e)) by subjecting it to 450 °C for at least 30 min. To avoid decomposition and/or debromination of PBDEs by UV light during extraction and analysis, glass equipment made from brown or amber glass shall be used.

NOTE If no brown or amber glass is available, aluminium foil can be used for protection from light.

b) If the amount of Br in the sample (determined by XRF, CIC or other means) is considerably above the 0,1 % range, it will be necessary to carry out the analysis using an adjusted sample size or by repeating the analysis using an extract that has been appropriately diluted prior to internal standard addition.

8.2 Sample preparation

8.2.1 Stock solution

The following stock solutions shall be prepared:

a) surrogate standard (to monitor analyte recovery): 50 μg/ml in toluene (e.g. DBOFB);

b) internal standard (to correct for injection error): 10 μg/ml in toluene (e.g. CB209);

c) polybrominated biphenyl (PBB) solution: 50 μg/ml in an organic solvent;

d) polybrominated diphenyl ether (PBDE) solution: 50 μg/ml in an organic solvent; all brominated species from mono- to decabrominated biphenyl (PBB) and mono- to decabrominated diphenyl ether (PBDE) shall be included in the PBB and PBDE stock solutions (see 8.4). Other stock solution concentrations can be utilized providing the standard solution concentrations given in 8.5.3 can be achieved.

e) matrix spiking solution; containing a total of four calibration congener standards in toluene as indicated in Table 1. The addition of 1 ml of a matrix spiking solution containing each of the four congeners in a concentration of 10 μg/ml is suitable for delivery of the required 10 μg (see 11.2 b)) in the matrix spike sample.

Table 1 – Matrix spiking solution

Level of bromination	Number of PBDE congeners	Number of PBB congeners
Mono to penta	1	1
Hexa- to deca-	1	1

8.2.2 Pre-extraction of the Soxhlet extractors

To clean the Soxhlet extractors (see Clause 6 c)), a 2 h pre-extraction is carried out with 70 ml of toluene. The washing solvent is discarded.

8.2.3 Extraction

The following steps shall be followed for sample extraction:

a) Quantitatively transfer 100 mg ± 10 mg of the sample into the extraction thimble (see Clause 6 d)) through a funnel (see Clause 6 h)). In order to ensure a quantitative transfer, the funnel is rinsed with approximately 10 ml of toluene extraction solvent. Record the sample mass to the nearest 0,1 mg.

b) 200 μl of the surrogate standard (see 8.2.1 a)) (50 μg/ml) is added (in accordance with 8.2.1).

c) In order to prevent the sample from floating, the extraction thimble is closed with glass wool (see Clause 6 e)). Approximately 60 ml of solvent is placed in the 100 ml round-bottomed flask, the equipment is covered with aluminium foil to exclude light and the sample is extracted for at least 2 h with each cycle being approximately 2 min to 3 min. Shorter extraction times may result in lower recoveries of the analytes, particularly for the higher molecular mass PBDEs.

d) The extract is placed in a 100 ml volumetric flask and the round-bottomed flask is rinsed with approximately 5 ml of solvent.

NOTE If the solution exhibits turbidity due to the matrix, this can be reduced by adding 1 ml of methanol. The difference between the density of methanol and toluene can be disregarded in this case in the calculation.

e) The volumetric flask is filled with 100 ml of solvent. For a soluble polymer sample, the alternative extraction procedure may be applied as described in 8.2.4.

8.2.4 Alternative extraction procedures for soluble polymers

For a soluble polymer sample, especially PS-HI (or HIPS), the following alternative extraction procedure may be applied:

a) Weigh 100 mg of sample to the nearest 0,1 mg in a brown or amber vial (see Clause 6 l)) (at least 20 ml in volume).

NOTE 1 Other sample amounts can be used for samples with potentially very low or very high PBB or PBDE concentrations.