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**Determination of certain substances in electrotechnical products –
Part 9: Hexabromocyclododecane in polymers by gas chromatography-mass spectrometry (GC-MS)**

**Détermination de certaines substances dans les produits électrotechniques –
Partie 9: Hexabromocyclododécane dans les polymères par chromatographie en phase gazeuse-spectrométrie de masse (GC-MS)**

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FDIS	Report on voting
111/620/FDIS	111/631/RVD

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

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- 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- withdrawn,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 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 (PBDEs) in electrotechnical products is a source of concern in current and proposed regional legislation.

The purpose of this document 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 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 9: Hexabromocyclododecane in polymers by gas chromatography-mass spectrometry (GC-MS)

1 Scope

This part of IEC 62321 specifies two techniques for the determination of hexabromocyclododecane (HBCDD) in polymers of electrotechnical products.

The gas chromatography-mass spectrometry (GC-MS) test method is described in the normative part of this document. The GC-MS method is suitable for the determination of hexabromocyclododecane (HBCDD).

A method using high-pressure liquid chromatography-mass spectrometry (HPLC-MS) is given in informative Annex A.

These test methods have been evaluated for use with EPS (expanded polystyrene foam), XPS (extruded polystyrene foam) and ABS (acrylonitrile butadiene styrene) within the concentration ranges as specified in Table 1. The use of this method for other types of materials or concentration ranges outside those specified below has not been evaluated.

Table 1 – Tested concentration ranges for HBCDD by GC-MS in various materials

Substance or element	HBCDD		
Parameter	Unit of measurement mg/kg	Medium or material tested	
		EPS/XPS	ABS
Concentration range tested		6 080 to 11 940	1 000 to 10 000

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

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*

3 Terms, definitions and abbreviated terms

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in IEC 62321-1 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

3.2 Abbreviated terms

ABS	acrylonitrile butadiene styrene
API-ES	atmospheric pressure-electrospray
BFR	brominated flame retardant
BSA	N,O-Bis(trimethylsilyl)acetamide
BSTFA	N,O-Bis(trimethylsilyl)trifluoroacetamide
CCC	continuing calibration check
C-IC	combustion-ion chromatography
EI	electron ionization
EPS	expanded polystyrene foam
HBCDD	hexabromocyclododecane
HPLC-MS	high-pressure liquid chromatography-mass spectrometry
ID	internal diameter
IS	internal standard
GC-MS	gas chromatography-mass spectrometry
LOD	limit of detection
LOQ	limit of quantification
MDL	method detection limit
PTFE	polytetrafluoroethylene
QC	quality control
RSD	relative standard deviation
SIM	single (or "selected") ion monitoring
THF	tetrahydrofuran
TIF	tentatively identified compound
XPS	extruded polystyrene foam
XRF	X-ray fluorescence
UV	ultraviolet

4 Principle

HBCDD is determined using ultrasonic or Soxhlet extraction followed by gas chromatography separation and mass spectrometry determination. This technique is suitable to determinate total HBCDD instead of separated HBCDD isomers.

NOTE The thermal stability of HBCDD is poor. The results can be influenced by the temperature testing conditions.

5 Reagents and materials

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

a) toluene (guaranteed reagent, purity of greater than a volume fraction of 99 %);
b) tetrahydrofuran (THF) (guaranteed reagent, purity of greater than a volume fraction of 99 %);
c) acetonitrile (guaranteed reagent, purity of greater than a volume fraction of 99 %);
d) methanol (guaranteed reagent, purity of greater than a volume fraction of 99 %);

e) mixed solvent solution (tetrahydrofuran and acetonitrile or methanol),
   – add 500 ml tetrahydrofuran and 1 000 ml acetonitrile or methanol to a 2 000 ml beaker and mix;
f) calibrants hexabromocyclododecane (guaranteed reagent, purity of greater than a volume fraction of 99 %): see 8.4;
g) helium (purity of greater than a volume fraction of 99,999 %);
h) internal standard used to correct for injection errors (e.g. CB 209 (2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl)).

6 Apparatus

The following items shall be used for the analysis:

a) analytical balance capable of measuring accurately to 0,000 1 g;
b) 10 ml, 20 ml, 500 ml, 1 000 ml volumetric flasks;
c) Soxhlet device, Soxhlet extractor of 200 ml or suitable volume;
d) extraction thimble;
e) heating jackets;
f) funnel (non plastic);
g) aluminium foil;
h) ultrasonic bath;
i) Pasteur pipette;
j) glass wool;
k) 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;
l) a gas chromatograph with a capillary column coupled to a mass spectrometric detector (electron ionization, EI). The mass spectrometric detector shall be able to perform selective ion monitoring. The use of an autosampler is strongly recommended to ensure repeatability. A column length of approximately 30 m is suitable for sufficient separation efficiency for HBCDD;
m) rotary evaporator with water bath;
n) milling equipment;
o) 0,45 µm PTFE filter membrane.
p) No. 5A filter paper.

7 Sampling

As described in IEC 62321-2, unless indicated otherwise, the following procedure a) is recommended.

a) Cut samples approximately to a size of 2 mm × 2 mm, and mix them well.

   NOTE 1 When using the alternative ultrasonic dissolution procedure for polymers that are difficult to dissolve, cryogenic grinding with liquid nitrogen cooling is necessary. The samples are ground to pass through a 500 µm sieve.

   NOTE 2 Contact with polymer material are avoided during sampling.

8 Procedure

8.1 General instructions for the analysis

The following general instructions shall be followed:

In order to reduce blank values, ensure the cleanliness of all glass equipment (excluding volumetric flasks) and deactivate the glass wool by subjecting it to 450 °C for at least 30 min. To avoid decomposition and/or debromination of HBCDD 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.

If the amount of Br in the sample (determined by XRF, C-IC 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

a) Standard mixture solution: Prepare a standard mixture solution containing α, β, γ-HBCDD in an organic solvent at a concentration of 10 µg/ml made from each 100 µg/ml standard solution.

b) Internal standard (to correct for injection error): 50 µg/ml in toluene or an organic solvent (e.g. CB 209).

8.2.2 Pre-extraction of the Soxhlet extractors

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

8.2.3 Soxhlet extraction

The following steps shall be followed for sample extraction:

a) Weigh 0,5 g of the crushed sample to the nearest 0,000 1 g. The sample is transferred through a funnel into the extraction thimble. Put the extraction thimble into the Soxhlet extractor. Toluene shall be used as the extraction solvent.

b) In order to ensure a quantitative transfer, the funnel is rinsed with approximately 10 ml of extraction solvent.

c) In order to prevent the sample from floating, the extraction thimble is closed with glass wool (Clause 6, j)). Approximately 80 ml of solvent is placed in the 200 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.

NOTE Sample amount and volume of extraction can be reduced in the same ratio to keep the same cycle rate.

d) After Soxhlet extraction, allow it to cool down at room temperature.

e) Evaporate the extracted solution in the round-bottomed flask on a rotary evaporator until approximately 10 ml remains.

f) Transfer the contents into a 20 ml volumetric flask and then bring to volume using solvent.

g) Filter the sample solution through a 0,45 µm syringe filter (Clause 6, o)) and transfer into a vial for GC-MS analysis.

8.2.4 Alternative extraction procedure for soluble polymers

As an alternative to Soxhlet extraction, an ultrasonic dissolution procedure is applicable for polymers soluble in tetrahydrofuran as described in the following steps:

a) Weigh 0,5 g of the sample to the nearest 0,000 1 g into a suitable glass vessel.

b) Quantitatively add 30 ml of tetrahydrofuran, and put the sample in an ultrasonic bath at 40 °C for approximately one hour or until dissolved.

c) Slowly add 70 ml of methanol dropwise to precipitate the polymer resin portion of the polymer from the solution.

d) Allow the solution and sample mixture to stand for 30 min at room temperature (the precipitated polymer resin will settle in the solution). Filter with No. 5A filter paper.

e) Evaporate the extracted solution in the round-bottomed flask on a rotary evaporator until approximately 10 ml remains.

f) Transfer the contents into a 20 ml volumetric flask and then bring to volume using solvent.

g) Filter the sample solution through a 0,45 µm syringe filter (Clause 6, o)) and transfer into a vial for GC-MS analysis.

8.2.5 Addition of the internal standard (IS)

Prepare a 1 ml aliquot of each sample and standard to be analysed and place it in an appropriate sample vial. Add 20 µl of internal standard solution (8.2.1, b)) to the vial and cap the vial. Invert the vial twice to mix.

Inject 1 µl of the sample solution into the GC-MS and analyse it according to the parameters described in 8.3.

8.3 Instrumental parameters

Different conditions might be necessary to optimize a specific GC-MS system to achieve effective separation of all calibration congeners and meet the QC and MDL requirements. The following parameters have been found suitable and are provided as an example:

a) GC column: non-polar (phenyl-arylene-polymer equivalent to 5 % phenyl-methyl-polysiloxane), length 30 m; internal diameter 0,25 mm; film thickness 0,25 µm;

b) injector liner: 4 mm single taper glass liner with glass wool (deactivated);

c) carrier: helium (5 g), 1,0 ml/min, constant flow;

d) oven temperature: 70 °C for 2 min, 20 °C/min to 300 °C for 5 min;

e) injection temperature: 250 °C;

f) transfer line: 300 °C;

g) injection volume: 1 µl;

h) injection mode: split (10:1);

i) ionization method: electron ionization (EI);

j) solvent delay time: 4 min;

k) ion source temperature: 250 °C;

l) scan range: m/z 50 ~ m/z 1 000 ;

m) dwell time: 80 ms.

Table 2 shows reference masses for confirmation ions and a quantification ion of HBCDD.

Table 2 – Reference masses for the quantification of HBCDD

	Confirmation ions (m/z)	Quantification ion (m/z)
HBCDD	319, 401, 561	319

NOTE 1 α-, β-, γ-HBCDD isomers are not separated by GC and therefore appear as a single peak. This is sufficient for quantification.

NOTE 2 In GC analysis, degradation of HBCDD occurs with an oven temperature above 160 °C, resulting in the formation of the degradation products, pentabromocyclododecane and tetrabromocyclododecadiene. The three isomers, α-, β-, γ-HBCDD, were detected on the same retention time. Therefore, they cannot be clearly separated in the mixed HBCDD peak.

The chromatogram in Annex B (see Figure B.1 and Figure B.2) gives an example of GC-MS analysis.

8.4 Calibrants

Reference materials are used as calibrants to make stock solutions of 100 µg/ml each in toluene. Table 3 shows recommended HBCDD reference materials suitable for GC-MS analysis.

Table 3 – Commercially available HBCDD reference materials considered suitable for GC-MS analysis

Compound name	CAS Number
α-Hexabromocyclododecane	134237-50-6
β-Hexabromocyclododecane	134237-51-7
γ-Hexabromocyclododecane	134237-52-8
Mix standards of α-, β-,γ-Hexabromocyclododecane	25637-99-4 and 3194-55-6

8.5 Calibration

8.5.1 General

Wherever possible, the solvent used for the sample and standard solutions shall be the same to avoid any potential solvent effects. A calibration curve shall be developed for quantitative analysis. At least five calibration solutions shall be prepared in equidistant concentration steps. Quantification is made on the basis of the measurement of the peak areas. The linear regression fit of each calibration curve is required to have a relative standard deviation (RSD) of less than or equal to 15 % of the linear calibration function.

NOTE If the limiting value of the RSD of 15 % is exceeded, from the point of view of quality assurance, 2nd order curve fitting does not guarantee any significantly better adjustment. Only statistical tests such as the F-test fulfil these requirements by comparing linear or 2nd order. That means that although the RSD value is exceeded, the calibration is linear.

8.5.2 Standard solutions

Stock solutions of HBCDD listed in Table 3 are used to prepare the calibration solution concentrations shown in Table 4 using the mixed solvent solution (Clause 5, e)) as a diluent.

Table 4 – Calibration solutions of HBCDD

Standard solution No.	Final concentration of HBCDD (µg/ml)	Volume of internal standard (µl)
1	0,5	20
2	1,0	20
3	2,5	20
4	5,0	20
5	10	20

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

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

where

A is the peak area of HBCDD in the calibration solution;

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

C is the concentration of HBCDD (µg/ml);

C_{IS} is the concentration of the internal standard (µg/ml);

a is the slope of the calibration curve;

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

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

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

9 Calculation of HBCDD concentration

9.1 General

In the event that there is no HBCDD compound detected in the sample, HBCDD shall be reported as a function of the compound with the highest method detection limits.

9.2 Calculation

The final concentration of HBCDD in the sample can be calculated by using Equation (2):

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

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

where

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

a is the slope of the line that best fits the calibration obtained in Equation (1);