IEC 62321-11

Edition 1.0 2023-12

INTERNATIONAL STANDARD

NORME INTERNATIONALE

Determination of certain substances in electrotechnical products – Part 11: Tris(2-chloroethyl) phosphate (TCEP) in plastics by gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS)

Détermination de certaines substances dans les produits électrotechniques – Partie 11: Phosphate de tris(2-chloroéthyle) (TCEP) dans les plastiques par chromatographie en phase gazeuse-spectrométrie de masse (GC-MS) et chromatographie en phase liquide-spectrométrie de masse (LC-MS)

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IEC 62321-11 has been prepared by IEC technical committee 111: Environmental standardization for electrical and electronic products and systems, in collaboration with ISO subcommittee SC 5: Physical-chemical properties of ISO technical committee 61: Plastics. It is an International Standard.

It is published as a double logo standard.

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

Draft	Report on voting
111/723/FDIS	111/735A/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/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- withdrawn, or
- revised.

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 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 62321-11 introduces a new subject covering tris(2-chloroethyl) phosphate (TCEP) in the IEC 62321 series.

TCEP is a halogenated phosphorus-based flame retardant that is disclosable as a substance of very high concern (SVHC) as it is classified as toxic to reproduction category 2 (R60) and was included in the candidate list for authorization on 13 January 2010, following ECHA's decision ED/68/2009 [1][1] and in regulation (EC) No 1907/2006 ANNEX XVI [2].

TCEP is used as a flame retardant in plastics such as polyester and polyurethane foam and as a plasticizer in polyvinyl chloride. Additionally, TCEP is used as an alternative for brominated flame retardants that have been restricted. No applicable testing standard exists for TCEP analysis in plastics.

As a result, analysis criteria have been established by an IEC TC 111 and ISO/TC 61/SC 5 joint working group for the joint development of an IEC and ISO double logo International Standard, to provide a test method that will allow the industry to determine the concentrations of TCEP in plastics.

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.

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

DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS –

Part 11: Tris(2-chloroethyl) phosphate (TCEP) in plastics by gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS)

1 Scope

This part of IEC 62321 specifies two different techniques for the determination of tris(2-chloroethyl) phosphate (TCEP) in plastics, the GC-MS or LC-MS method, both of which are applicable to quantitative analysis.

These two techniques are applicable to use with polyurethane, polyvinylchloride, and polyethylene materials containing TCEP between 200 mg/kg to 2 000 mg/kg.

These test methods do not apply to plastic materials having a processing temperature higher than 230 °C.

GC-MS using a pyrolyser/thermal desorption accessory (Py/TD-GC-MS) technique is described in Annex A and can be used for the screening of TCEP in plastics.

NOTE TCEP starts thermal decomposition at approximately 230 °C. Polymer types that have a processing temperature into shapes of plastics (e.g. pellets, moulded parts or sheets) not exceeding the decomposition temperature can contain TCEP.

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 can be necessary to make a final presence or absence decision.

3.1.2
plastic
material that contains as an essential ingredient a high polymer and which, at some stage in its processing into finished products, can be shaped by flow

Note 1 to entry: Elastomeric materials, which are also shaped by flow, are not considered to be plastics.

Note 2 to entry: In some countries, particularly the United Kingdom, the term "plastics" is used as the singular form as well as the plural form.

[SOURCE: ISO 472:2013 [3], 2.702]

3.1.3
polymer
substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional units) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few of the constitutional units

[SOURCE: ISO 1382:2020 [4], 3.369]

3.1.4
blank
test that follows the same procedures and conditions as the sample test without a sample, which enables quantification of the contamination in the test

3.2 Abbreviated terms

ACN	acetonitrile
API-ES	atmospheric pressure ionization-electrostatic
BSA	N,O-bis(trimethylsilyl)acetamide
BSTFA	N,O-bis(trimethylsilyl)trifluoroacetamide
CCC	continuing calibration check standard
D	dilution factor
DEHP	di-(2-ethylhexyl) phthalate
DMDCS	dimethyldichlorosilane
EI	electron ionization
GC-MS	gas chromatography-mass spectrometry
HPLC	high-performance liquid chromatography
ID	internal diameter
IIS	international interlaboratory study
IS	internal standard
LC-MS	liquid chromatography-mass spectrometry
LOD	limit of detection
MDL	method detection limit

MS	mass spectrometry
PBB	polybrominated biphenyl
PBDE	polybrominated diphenyl ether
PE	polyethylene
PS	polystyrene
PTFE	polytetrafluoroethylene
PUR	polyurethane
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
RSD	relative standard deviation
SIM	single (or "selected") ion monitoring
TCEP	tris(2-chloroethyl) phosphate
TD	thermal desorption
THF	tetrahydrofuran
TICS	tentatively identified compounds

4 Principle

The samples are dissolved in THF and the matrix polymer is separated by precipitation with methanol, TCEP is determined qualitatively and quantitatively using GC-MS or LC-MS.

5 Reagents and materials

Use chemicals of analytical grade, unless otherwise indicated.

a) TCEP (tris(2-chloroethyl) phosphate): CAS No. 115-96-8 (purity of greater than a mass fraction of 98 %);

b) THF (GC grade or higher, higher than 99,9 %);

c) n-Hexane (GC grade or higher, higher than 98,5 %);

d) methanol (GC grade or higher, higher than 99,9 %);

e) mixed solvent (THF mixed with methanol, the volume ratio of THF/methanol is 1/4);

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

g) calibrants; reference materials of TCEP (purity of greater than a mass fraction of 98 %);

h) surrogate and internal standards:

   – surrogate standard is used to monitor analytes recovery according to 8.2.2.1 and 8.2.3.1, for example TCEP-d_{12};

   – internal standard is used to correct injection errors, according to 8.2.2.1 and 8.2.3.1, for example anthracene-d_{10}.

The standards are acceptable when using a quadruple-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.

6 Apparatus

6.1 GC-MS method

The following items shall be used for the analysis:

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

b) cryogenic grinding mill with liquid N_2 cooling;

c) ultrasonic bath;

d) 1 ml, 5 ml, 10 ml, 50 ml, and 100 ml volumetric flasks;

e) Soxhlet extractors:
   - 30 ml Soxhlet extractors;
   - 250 ml round-bottomed flask;
   - ground-in stopper NS 29/32;
   - Dimroth condenser NS 29/32;
   - boiling stones (e.g. glass pearls or Raschig rings);

f) 30 ml cellulose extraction thimble with ID 22 mm, height 80 mm;

g) glass wool for extraction thimble;

h) heating jackets for 250 ml round-bottomed flask;

i) glass funnels;

j) aluminium foil;

k) cork rings;

l) 0,45 µm PTFE syringe filter;

m) microlitre syringe or automatic pipettes;

n) Pasteur pipettes;

o) 2 ml sample vials and a screw cap with a PTFE gasket or, depending on the analytical system, a comparable sample receptacle;

p) mini-shaker known as vortexer or vortex mixer;

q) deactivated injector liner for GC-MS;

r) gas chromatograph-mass spectrometer, split/splitless inlet, and a programmable temperature-controlled oven. The mass spectrometer shall be able to perform selected ion monitoring (SIM) and total ion current ("full scan"). The ionization box shall be treated for chemical stability and controlled at 230 °C. The kinetic energy of 70 eV shall be applied in electron ionization (EI) mode;

s) capillary column;

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

t) 50 ml amber vial;

u) vacuum rotary evaporator;

v) auto-sampler.

   The use of an auto-sampler is recommended to ensure repeatability.

6.2 LC-MS method

Items a) to p) in 6.1 and the following items shall be used for the analysis:

a) high-performance liquid chromatography (HPLC) system equipped with a mass spectrometer detector;

   The use of an auto-sampler is recommended to ensure repeatability.

b) pump;

c) column oven;

d) stationary phase: C_{18}, 150 mm × 2,1 mm, 5 µm or equivalent film thickness.

7 Sampling

Manual cutting or cryogenic grinding or milling with liquid nitrogen cooling is recommended to be performed in accordance with IEC 62321-2:2021.

The sample shall be ground as small as 500 µm in diameter. Cryogenic grinding with liquid N_2 cooling is strongly recommended. Reference polymer materials shall also be ground in the same way.

If the grinder cannot be used, the sample shall be cut to around 2 mm × 2 mm.

NOTE For a composite plastic that is made from more than one material, but cannot be separated mechanically, the concentration of TCEP can be determined for the composite material, as it cannot be confirmed which of the constituent plastics is the source of the TCEP.

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-contamination.

In order to reduce blank values, ensure the cleanliness of all glass equipment and deactivate glass wool (see 6.1 g)) by subjecting it to 450 °C for at least 30 min. To avoid the decomposition of TCEP by UV light during extraction and analysis, glass equipment made from brown or amber glass shall be used.

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

After analysis of test samples with high analyte concentration, blank samples shall be analysed, until the background level is decreased to lower than 30 mg/kg. In order to reduce blank values, ensure the cleanliness of all tools used in sample preparation.

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

8.2 Sample preparation

8.2.1 General

The sample preparation requires clean glassware (e.g. single-use items) to avoid cross-contamination. The extraction method is chosen by the solubility of the sample polymer in THF.

8.2.2 GC-MS method

8.2.2.1 Stock solution

The following stock solution shall be prepared:

a) surrogate standard to monitor analyte recovery (e.g. TCEP-d_{12}): 1 000 µg/ml in a solvent;

NOTE 1 The solvent is THF or n-hexane, which is decided by the extraction method.

b) internal standard to correct for injection error (e.g. anthracene-d_{10}): 10 µg/ml or 100 µg/ml in a solvent.

NOTE 2 The solvent is methanol or n-hexane, which is decided by the extraction method.

8.2.2.2 Extraction by sonication for soluble polymer

For a soluble polymer sample like PUR or PVC, the following procedure shall be applied:

a) Weigh 200 mg ± 10 mg of the sample and transfer it into a 50 ml vial (6.1 t)). Record the weight to the nearest 0,1 mg. Other sample amounts may be used for samples with potentially very low or very high TCEP concentrations but the maximum sample amount is 500 mg. Transfer 10 ml of THF and 10 µl of surrogate standard (8.2.2.1 a)) to the 50 ml vial (6.1 t)).

b) Tightly cap the sample 50 ml vial (6.1 t)). A small piece of adhesive tape may be used to prevent the cap from loosening due to vibration.

c) Place the 50 ml vial (6.1 t)) in an ultrasonic bath (6.1 c)) at 60 °C and sonicate for 60 min.

d) Allow the 50 ml vial (6.1 t)) to cool to ambient temperature, (20 ± 5) °C.

e) Add 40 ml of methanol (Clause 5 d)) dropwise into the 50 ml vial (6.1 t)) and mix well to precipitate the sample matrix. The resulting extracted solution should stand at room temperature for 30 min.

f) Filter the solution through a 0,45 µm PTFE membrane filter.

g) Transfer 1 ml of the filtrate into a 2 ml vial (6.1 o)) and add 10 µl of internal standard (8.2.2.1 b)) into the 2 ml vial (6.1 o)).

h) Cap the 2 ml vial (6.1 o)) with a PTFE-coated seal and stir well.

8.2.2.3 Soxhlet extraction for insoluble polymer

The following steps shall be applied for samples other than PUR and PVC:

a) To clean the Soxhlet extractors (6.1 e)), a 2 h pre-extraction is carried out with 100 ml of n-hexane (Clause 5 c)). The washing solvent is discarded after cleaning.

b) Transfer 200 mg ± 10 mg of the sample into cellulose extraction thimbles (6.1 f)) for Soxhlet extraction. Record the mass to the nearest 0,1 mg. Other sample amounts may be used for samples with potentially very low or very high TCEP concentrations but the maximum sample amount is 500 mg.

c) Allow the sample to be transferred through a funnel (6.1 i)) into the extraction thimble (6.1 f)). In order to ensure a quantitative transfer, the funnel (6.1 i)) should be rinsed with approximately 10 ml of n-hexane (Clause 5 c)).

d) 10 µl of surrogate standard (8.2.2.1 a) is added.

e) Cover the thimble (6.1 f)) with glass wool (6.1 g)) to prevent the sample from floating.

f) 100 ml of n-hexane (Clause 5 c)) is used for extraction under reflux. Allow the sample to be extracted for at least 6 h with 6 cycles/h to 8 cycles/h. Cover the flask with aluminium foil during extraction. The evaporation temperature is recommended to be controlled under 68 °C.

g) After 6 h of reflux, concentrate the extract to less than 40 ml using a vacuum rotary evaporator (6.1 u)), or a similar process.