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INTERNATIONAL STANDARD

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Determination of certain substances in electrotechnical products – Part 3-2: Screening – Fluorine, chlorine and bromine in polymers and electronics by combustion-ion chromatography (C-IC)

Détermination de certaines substances dans les produits électrotechniques – Partie 3-2: Détection – Fluor, chlore et brome dans les polymères et les produits électroniques par combustion-chromatographie ionique (C-CI)

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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INTERNATIONAL ELECTROTECHNICAL COMMISSION

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FOREWORD

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International Standard IEC 62321-3-2 has been prepared by IEC technical committee 111: Environmental standardization for electrical and electronic products and systems.

This second edition cancels and replaces the first edition published in 2013. This edition constitutes a technical revision.

This edition includes the following significant technical changes with respect to the previous edition:

a) In the previous edition, a screening test method for bromine (Br) content only was provided. In this edition, a screening test method by C-IC for fluorine (F), chlorine (Cl) and bromine (Br) has been added to the normative part of the document.
b) A screening test method by C-IC for iodine (I) has been added in Annex D (informative).

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

FDIS	Report on voting
111/573/FDIS	111/577/RVD

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

This document 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 document will remain unchanged until the stability date indicated on the IEC website under "http://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- withdrawn,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 certain substances (e.g. lead (Pb), cadmium (Cd), polybrominated diphenyl ethers (PBDEs) and phthalates) in electrotechnical products is a source of concern in current and proposed regional legislation.

The purpose of the IEC 62321 series is therefore to provide test methods that will allow the electrotechnical industry to determine the levels of certain substances in electrotechnical products on a consistent global basis.

The first edition of IEC 62321-3-2 (2013) was published to address screening for total bromine.

This document (revised edition of IEC 62321-3-2) describes the test methods to quantify halogen (fluorine, chlorine and bromine) in polymers and electronics by C-IC in the normative section and to quantify iodine (I) in an informative Annex D.

In addition, information on oxygen bomb combustion-ion chromatography and oxygen flask-ion chromatography is provided in Annex A (informative) and Annex B (informative).

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 3-2: Screening – Fluorine, chlorine and bromine in polymers and electronics by combustion-ion chromatography (C-IC)

1 Scope

This part of IEC 62321 specifies the screening analysis of fluorine, chlorine and bromine in polymers and electronics using combustion-ion chromatography (C-IC). A C-IC screening analysis procedure for iodine can be found in Annex D.

This test method has been evaluated for ABS (acrylonitrile butadiene styrene), EMC (epoxy moulding compound), PE (polyethylene) and PC (polycarbonate) within the concentration ranges as specified in Table 1, Table 2 and Table 3. (Detailed results are shown in Table E.1 to Table E.6, and in Annex F (Table F.1 and Table F.2).

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 fluorine by C-IC in PC

Substance/element	Fluorine	
Polymer	Unit of measure	PC
Concentration or concentration range tested	mg/kg	575

Table 2 – Tested concentration ranges for chlorine by C-IC in PE

Substance/element	Chlorine	
Polymer	Unit of measure	PE
Concentration or concentration range tested	mg/kg	102,2

Table 3 – Tested concentration ranges for bromine by C-IC in various materials

Substance/element	Bromine			
Polymer	Unit of measure	ABS	EMC	PE
Concentration or concentration range tested	mg/kg	124 to 890	195 to 976	96

This horizontal standard is primarily intended for use by technical committees in the preparation of standards in accordance with the principles laid down in IEC Guide 108.

One of the responsibilities of a technical committee is, wherever applicable, to make use of horizontal standards in the preparation of its publications. The contents of this horizontal standard will not apply unless specifically referred to or included in the relevant publications.

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

ISO 3696, *Water for analytical laboratory use – Specification and test methods*

ISO 8466-1, *Water quality – Calibration and evaluation of analytical methods and estimation of performance characteristics – Part 1: Statistical evaluation of the linear calibration function*

ISO 10304-1:2007, *Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate*

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

3.1.1
accuracy
closeness of agreement between a test result and an accepted reference value

Note 1 to entry: The term accuracy, when applied to a set of test results, involves a combination of random components and a common systematic error or bias component.

[SOURCE: ISO 5725-1:1994, 3.6]

3.1.2
precision
closeness of agreement between independent test results obtained under stipulated conditions

[SOURCE: ISO 5725-1:1994, 3.12, modified – The notes have been deleted.]

3.1.3
repeatability
precision under repeatability conditions

[SOURCE: ISO 5725-1:1994, 3.13]

3.1.4
repeatability limit
r
value less than or equal to which the absolute difference between two test results obtained under repeatability conditions may be expected to be with a probability of 95 %

[SOURCE: ISO 5725-1:1994, 3.16]

3.1.5
reproducibility
precision under reproducibility conditions

[SOURCE: ISO 5725-1:1994, 3.17]

3.1.6
reproducibility limit
R
value less than or equal to which the absolute difference between two test results obtained under reproducibility conditions may be expected to be with a probability of 95 %

[SOURCE: ISO 5725-1:1994, 3.20]

3.1.7
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]

3.1.8
test sample
sample prepared from the laboratory and from which test portions will be taken

[SOURCE: ISO 6206:1979, 3.2.13]

3.1.9
test portion
quantity of material drawn from the test sample (or from the laboratory sample if both are the same) and on which the test or observation is actually carried out

[SOURCE: ISO 6206:1979, 3.2.14]

3.2 Abbreviated terms

ABS	acrylonitrile butadiene styrene
CCV	continuing calibration verification
CD	conductivity detector
C-IC	combustion-ion chromatography
CRM	certified reference material
EMC	epoxy moulding compound
IC	ion chromatography
ICV	initial calibration verification
IS	internal standard
IUPAC	International Union of Pure and Applied Chemistry
KRISS	Korea Research Institute of Standards and Science
LCS	laboratory control sample

LCSD	laboratory control sample duplicate
LOD	limit of detection
LOQ	Limit of quantification
MDL	method detection limit
PC	polycarbonate
PE	polyethylene
PP	polypropylene
SOP	standard operation procedure
US EPA	United States Environmental Protection Agency

4 Principle

A sample of known weight or volume is placed into a sample boat and introduced at a controlled rate into a high-temperature combustion tube. There the sample is combusted in an oxygen-rich pyrohydrolytic environment. The gaseous by-products of the combusted sample are trapped in an absorption medium where the hydrogen halide (HF, HCl, HBr) formed during the combustion dissociates into its specific anion (F^-, Cl^-, and Br^-) and cation (H_30^+). An aliquot of known volume of the absorbing solution is then manually or automatically injected into an ion chromatograph (IC) by means of a sample injection valve. The halide anions, including fluoride, chloride and bromide are separated into individual elution bands on the separation column of the IC. The conductivity of the eluent is reduced with an anion suppression device prior to the ion chromatograph's conductivity detector, where the anions of interest are measured. Quantification of halogen in the original combusted sample is achieved by calibrating the system with a series of standards containing known amounts of fluoride, bromide and chloride and then analysing unknown samples under the same conditions as the standards. The combined system of pyrohydrolytic combustion followed by ion chromatographic detection is referred to as combustion-ion chromatography (C-IC).

5 Reagents and materials

WARNING – All recognized health and safety precautions shall be in effect when carrying out the operations specified in this document. Failure to heed the directions contained in this document, or those of the manufacturer of the devices used, may result in injury or equipment damage.

Use only reagents of recognized analytical grade. Weigh the reagents with an accuracy of ±1 % of the nominal mass, unless stated otherwise. The reagents listed in Clause 5 b) and g) to k) may be considered representative examples for the preparation of eluents (Clause 5 i)). All reagents used shall not contain an amount of halides above the limit of detection (LOD).

a) Water, complying with grade 1 as defined in ISO 3696.

b) Hydrogen peroxide, a mass fraction of 30 % (H_2O_2)

   Hydrogen peroxide is caustic; thus the operator shall wear goggles and gloves and work under a fume hood when handling this reagent. As this method uses a gas (oxygen) at high temperature under pressure, precautions shall be taken by the operator.

c) Quartz wool, fine grade or other suitable medium.

d) Argon, carrier gas minimum of 99,9 % purity

   Purification scrubbers to ensure the removal of contaminants are recommended such as moisture (molecular sieve) and hydrocarbon trap filters (activated charcoal or equivalent).

e) Oxygen, combustion gas, minimum 99,6 % purity.

f) Burning aids, tungsten oxide (WO_3) or iron oxide (Fe_3O_4) with < 50 μm particle size and purity > 90 %. Before using burning aids, it is necessary to check that the halogen content is below the MDL level and in addition always use a method blank.

g) Blank solution, fill a volumetric flask (e.g. 100 ml flask) with water (Clause 5 a)).

h) Calibration standard solutions

Certified calibration standards from commercial sources, or calibration standards prepared in the laboratory, containing the elements of interest at the concentrations of interest are used. Depending on the concentrations expected in the sample, use the standard solution to prepare 5 to 10 calibration solutions with concentrations distributed evenly over the expected working range.

NOTE The solution is either prepared from a primary standard solution or calibration solution.

i) Eluents

The choice of eluent depends on the chosen column and detector (seek advice from IC manufacturer or column supplier). Eluent preparation is carried out as specified in ISO 10304-1:2007, 5.10.

1) Sodium hydrogen carbonate, $NaHCO_3$.

2) Sodium carbonate, Na_2CO_3.

3) Sodium hydroxide, NaOH.

4) Potassium hydroxide, KOH.

j) Internal standard (IS) solution (optional)

An internal standard can be used to correct analytical errors.

The internal standard used in the absorption solution shall not contain any of the sample components, and is to be selected based on the condition of column and mobile phase (e.g. phosphate, citric acid, oxalic acid, methane sulfonic acid). The internal standard solution should be prepared by selecting a middle range of concentration in the calibration curve range when preparing the calibration solution. (e.g. 1 mg/l).

k) Absorption solution, used for trapping halogen – 3 ml of H_2O_2 (Clause 5 b)), is poured into a 1 000 ml volumetric flask, brought to volume with water and mixed. This solution contains 900 mg/kg of H_2O_2.

Very careful use of H_2O_2 is required when handling especially high concentrations of fluorine-containing samples. When analysing samples containing a high concentration of fluorine, a minimum amount of hydrogen peroxide to diminish IC peak identification issues shall be used.

l) Laboratory control sample (LCS) – Reference materials can be used to ensure recovery rates of the halogen fall within 90 % to 110 %. A certified reference material is the best one for that purpose. If a certified reference material is not available, a reference material can be prepared by mixing certain amounts of the halogen (fluorine, chlorine and bromine) compounds, diluting with cellulose or aluminium oxides to obtain a suitable concentration, and then pulverizing the mixture to homogenize.

6 Apparatus

The following apparatuses shall be used. See also Annex C.

a) Balance – analytical, with sensitivity to 0,000 1 g (0,1 mg).

b) Scissors or shears.

c) Combustion system – in general, consists of the following components (see Figure C.1):

1) Auto sampler (optional) – an auto sampler is capable of accurately delivering 1 mg to 100 mg of sample into the sample boat.

2) Sample boat – made of quartz, nickel, ceramic, platinum or stainless steel.

3) Sample introduction system – the system provides a sampling port for introduction of the sample into the sample boat and is connected to the inlet of the pyrohydrolytic combustion tube. The system is swept by a humidified inert carrier gas and shall be capable of allowing the quantitative delivery of the material to be analysed into the pyrohydrolytic oxidation zone at a controlled and repeatable rate.

4) Electric furnace – it can be heated from 900 °C to 1 000 °C and has a quartz or ceramic tube installed inside and connected to the equipment for injecting the sample. Therefore, it is designed so that the combustion gas of the sample can be discharged without loss.

5) Pyrohydrolytic combustion tube – the pyrohydrolytic combustion tube is made of quartz and constructed such that when the sample is combusted in the presence of humidified oxygen, the by-products of combustion are swept into the humidified pyrohydrolytic combustion zone. The inlet end shall allow for the stepwise introduction and advancement of a sample boat into the heated zone and shall have a side arm for the introduction of the humidified carrier gas and oxygen. The pyrohydrolytic combustion tube shall be of ample volume, and have a heated zone with quartz wool or other suitable medium providing sufficient surface area so that the complete pyrohydrolytic combustion of the sample is ensured. If the sample contains halogen at high concentration (e.g. samples containing more than one percent concentration of halogen), a trap column shall be installed between the absorption tube and the combustion tube.

6) Water supply device – capable of delivering grade 1 water (Clause 5 a)) to the combustion tube at a controlled rate sufficient to provide a pyrohydrolytic environment.

7) Absorption tube – glass pipe of such a total volume that 10 ml to 20 ml of the absorption solution only occupies about half the total glass tube volume. The discharge of the gas pipe from the heating furnace is submerged in the absorption solution to absorb the discharged gas. The absorption solution can be injected into the ion chromatograph through a connecting device. The absorption tube shall be washed after sample analysis to avoid contamination from previous samples.

d) Ion chromatographic system – Consisting of the following components (see Figure C.2):

1) eluent reservoir;
2) IC pump;
3) sample injection system – incorporating a sample loop of appropriate volume (e.g. 0,02 ml) or auto sampler device;
4) precolumn or guard column;
5) separation column;
6) suppressor;
7) conductivity detector (CD);
8) recording device – e.g. computer, integrator.

7 Sampling

Sampling shall be carried out as described in IEC 62321-2. It should be done randomly and the collected segments should represent the entire sample.

a) Solid sample

The sample shall be cut into small pieces (approximately less than 3 mm × 3 mm) using scissors or shears (Clause 6 b)).

b) Liquid sample

When sampling liquids, the inside of the transfer pipette (or similar vessel) shall be rinsed several times with the sample liquid.