# IEC 62321-3-2

Edition 2.0 2020-06
REDLINE VERSION

# INTERNATIONAL STANDARD

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inside

HORIZONTAL STANDARD

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

IEC 62321-3-2:2020-06 RLV(en)

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

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# DETERMINATION OF CERTAIN SUBSTANCES IN ELECTROTECHNICAL PRODUCTS –

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

## FOREWORD

1) The International Electrotechnical Commission (IEC) is a worldwide organization for standardization comprising all national electrotechnical committees (IEC National Committees). The object of IEC is to promote international co-operation on all questions concerning standardization in the electrical and electronic fields. To this end and in addition to other activities, IEC publishes International Standards, Technical Specifications, Technical Reports, Publicly Available Specifications (PAS) and Guides (hereafter referred to as “IEC Publication(s)”). Their preparation is entrusted to technical committees; any IEC National Committee interested in the subject dealt with may participate in this preparatory work. International, governmental and non-governmental organizations liaising with the IEC also participate in this preparation. IEC collaborates closely with the International Organization for Standardization (ISO) in accordance with conditions determined by agreement between the two organizations.

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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.

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# 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 ~~of concern~~ 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 ~~total~~ bromine in polymers and electronics by combustion-ion chromatography (C-IC)

## 1 Scope

~~Part 3-2 of IEC 62321 specifies the screening analysis of the total bromine (Br) in homogeneous materials found in polymers and electronics by using the analytical technique of combustion ion chromatography (C-IC).~~

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** mg/kg | PC |
| Concentration or concentration range tested | | 575 |

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

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

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

| **Substance/element** | **Bromine** | | | |
|---|---|---|---|---|
| ~~**Parameter**~~ | **Unit of measure** mg/kg | ~~Medium/material tested~~ | | |
| Polymer | | ABS | EMC | PE |
| Concentration or concentration range tested | | 124 to 890 | 195 to 976 | 96 |

~~This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.~~

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 60754-1:2011, *Test on gases evolved during combustion of materials from cables – Part 1: Determination of the halogen acid gas content*~~

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

IEC 62321-2, *Determination of certain substances in electrotechnical products – Part 2: Disassembly,* ~~*disjointment*~~ *disjunction and mechanical sample preparation*~~[1]~~

~~IEC 62321-3-1, *Determination of certain substances in electrotechnical products – Part 3-1: Screening –Lead, mercury, cadmium, total chromium and total bromine in electrotechnical products using X-ray fluorescence spectrometry*[2]~~

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~~/DIS~~ 10304-1:~~2006~~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 terms and definitions given in IEC 62321-1 as well as~~ 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

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~~[1] To be published.~~

~~[2] To be published.~~

### 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:~~1995~~1994, 3.6]~~ [1]~~

### ~~3.1.2~~

~~**laboratory control sample**~~

~~a known matrix spiked with compound(s) representative of the target analytes, used to document laboratory performance~~

~~[Based on US EPA SW-846] [2]~~

### 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 %

~~Note 1 to entry: The symbol used is $r$.~~

[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 %

~~Note 1 to entry: The symbol used is $R$.~~

[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 ~~sample~~ and from which test portions will be taken

[SOURCE: ISO 6206:1979, 3.2.13] ~~[3]~~

### 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 |
| ~~PBBs~~ | ~~Polybrominated biphenyls~~ |
| ~~PBDEs~~ | ~~Polybrominated diphenyl ethers~~ |
| PC | polycarbonate |
| PE | polyethylene |
| PP | polypropylene |
| ~~XRF~~ | ~~X-Ray fluorescence spectroscopy~~ |
| SOP | standard operation procedure |
| US EPA | United States Environmental Protection Agency |

## 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 bromine (Br) in polymers and electronics in electrotechnical products. C-IC provides information on the total quantity of bromine present in the sample, but does not identify compounds or valence states of the bromine. Therefore, special attention shall be paid when screening for bromine, where the result will reflect only the total bromine present. The presence of brominated flame retardants PBB or PBDE shall be confirmed by a verification test procedure. When applying this method to electronics "as received", which, by the nature of their design, are not uniform, care shall be taken in interpreting the results.~~

### ~~4.2 Principle of test~~

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 ~~bromide~~ halide (HF, HCl, HBr) formed during the combustion dissociates into its ~~respective ion~~ 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 ~~the bromine~~ 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 ~~very~~ caustic; thus the operator shall wear goggles and gloves and ~~shall~~ work under a fume hood when handling this reagent. As this method uses a gas (oxygen) at high temperature under ~~high~~ 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 ~~are recommended~~).

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

f) Burning aids, tungsten oxide ($WO_3$) or iron oxide ($Fe_3O_4$) ~~etc. Minimum particle size of burning aids should be less than 50 µm~~ 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~~, e.g.~~ 5 to 10 calibration solutions with concentrations distributed ~~as~~ evenly ~~as possible~~ over the expected working range.

   NOTE ~~1~~ The solution is either prepared from a primary standard ~~or calibrated by some other means~~ solution or calibration solution.

   ~~NOTE 2 Many standard reference solutions which can be used to prepare standard solutions are commercially available.~~

i) Eluents

   ~~Eluents are used as a solvent in separating materials in elution.~~ 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:~~2006:~~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 ~~should~~ shall not contain any of the sample components, and ~~should~~ is to be selected based on the condition of column and mobile phase (e.g. phosphate, citric acid, oxalic acid, methane sulfonic acid~~, etc.~~). 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 ~~quantifying bromine~~ 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 ~~is added to the scale~~ 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 ~~bromine~~ 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 ~~bromine compounds. It can be made by mixing certain amounts of bromine~~ 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. ~~The auto sampler may be used as long as the accuracy and performance of the method are not degraded;~~

   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 ~~1 100~~ 1 000 °C and has a quartz or ceramic tube installed inside ~~of the device~~ 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 ~~must~~ 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 ~~bromine of~~ halogen at high concentration (e.g. samples containing more than one percent concentration of halogen), a trap column ~~should~~ 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 – ~~a glass pipe size is capable of maintaining about one-half of the total volume by putting 10 ml to 20 ml of the absorption solution. This has the configuration that the discharge gas pipe of the heating furnace is submerged in the absorption solution to absorb the discharged gas. Further, it has the configuration that the absorption solution of ion chromatograph can be injected through the connecting device. For preventing contamination from other samples, the absorption tube should be washed after sample analysis.~~ 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 – ~~in general,~~ 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

~~For sampling of liquid sample, sampling should be performed after rinsing the inside of the pipette a few times with the sample liquid.~~

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

## 8 Procedure

### 8.1 Combustion

~~General combustion procedures by using electric furnace are described in Clause 7 (Test procedure) of IEC 60754-1:2011.~~

a) ~~After a sample boat is heated sufficiently in the electric furnace to remove the contaminants, 1 mg to 100 mg of samples are weighed with precision of 0,1 mg and loaded into the sample boat. If samples are difficult to combust (e.g. flux, solder paste), burning aids (e.g. $WO_3$) have to be used. Generally a 5 to 1 ratio of burning aids to sample is sufficient. If any burning aid is being used apply approximately 100 mg of it in a thin layer over the surface of the sample boat, evenly spread the weighed sample on it, and then cover the sample with approximately 300 mg of the burning aid.~~

After a sample boat is heated sufficiently in the electric furnace to remove the contaminants, remove the sample boat from the furnace with clean tongs, let it cool to room temperature, then weigh (typically 10 mg to 100 mg) the sample to the nearest 0,1 mg and load into the sample boat. If samples are difficult to combust (e.g. flux, solder paste), a burning aid (e.g. WO3) shall be used. Generally, a 5 to 1 ratio of burning aids to sample is sufficient. If any burning aid is being used, apply approximately 1/4 of its total mass in a thin layer over the surface of the sample boat, place the weighed sample on it and then cover the sample with approximately ¾ of the total burning aid mass. Detailed analysis conditions are described in Annex G (Table G.1, Table G.2, Table G.3)

b) ~~It is then~~ The sample and boat are heated in the combustion furnace for 10 min to 20 min together with argon, oxygen and water by using the sample injection device located at the centre of the quartz tube of the combustion furnace. ~~An example of~~ Suitable combustion conditions are described in Table G.1. If the combustion boat shows evidence of soot generation or unburned sample particles, the combustion shall be judged to be insufficient and the procedure shall be repeated. The contaminated area shall be cleaned thoroughly before repeating the procedure.

NOTE 1 If insufficient combustion is suspected (e.g. visible soot in the combustion boat), the combustion and chromatography on the residue can be repeated until no further halides are detected. Any halides detected can be summed. Alternatively, the analysis can be repeated with a fresh sample altering the conditions (e.g. reduce sample size, increase furnace temperature or time) to achieve complete combustion.

c) Upon completion of combustion operations, wash the tubing at the combustion gas discharge outlet, and pour all washing solutions into the absorbing bottle for measuring.

d) For the blank test, perform a similar operation without inserting the sample or ~~the combustion~~ a blank boat, and use this absorption solution obtained as the blank solution. Follow the procedure described in 8.3.

NOTE 2 If the combustion furnace and IC are connected and operated automatically, the absorption solution ~~absorbing~~ adsorbing the combustibles can be injected into the IC.

### 8.2 IC analysis

The general ~~rules on ion chromatographic analysis as set out~~ procedures for ion chromatography described in ISO 10304-1 shall be followed:

a) Set up the IC according to the instrument manufacturer's instructions or laboratory standard operation procedure (SOP). ~~Typical~~ Suitable operating conditions for IC are shown in Table G.1;

b) Run the eluent and wait for a stable baseline;

c) Perform the calibration as described in 8.5. Measure the samples, ~~calibration~~ calibrants (Clause 5 h)) and at least two blank solutions ~~(5 g))~~ as described in ~~8.5~~ 8.3.

Operating conditions ~~should~~ shall be selected and stabilized according to the device manufacturer or to the standard operation procedure (SOP).

### 8.3 Blank test

~~blank test is performed by quantifying the blank solution (5 g)) which is prepared by following exactly the same procedure described above but without actual sample. A blank solution (5 g)) which does not contain bromine (lower than 0,05 mg/l) can be used as a method blank sample.~~

A method blank test is performed by quantifying at least two blank solutions which are prepared by following exactly the same procedure described above (Clause 5 h)) without the actual sample. A blank solution (Clause 5 g)) which does not contain halides (lower than MDL, or normally 0,1 mg/l) shall be used for preparing the method blank.

### 8.4 Cleaning and recalibration

Clean any coke or soot from the combustion tube and sample boats as per the manufacturer's instructions. After ~~any~~ cleaning ~~or adjustment~~, assemble the apparatus and check for leaks. Run a check ~~standard~~ laboratory control sample or reference material to determine if the instrument needs to be recalibrated or cleaned again.

### 8.5 Calibration

A calibration curve shall be developed for quantitative analysis. The calibration curve is prepared by using a standard solution of fluoride, chloride and bromide.

~~When the analytical system is first evaluated and at intervals afterwards, establish a calibration function (e.g. as specified in ISO 8466-1) for the measurement. An example is shown in Table G.2.~~

~~The following calibration solutions are prepared from the stock solution of the bromine (1 000 mg/l). The volumes indicated in Table G.2 are placed in a 1 000 ml volumetric flask with a pipette and filled with water (5 a)) up to the mark and 0,5 ml to 8 ml of 1 000 mg/l bromine standard solution are added to the mark and mixed. This solution contains 0,5 mg/l to 8,0 mg/l of bromine:~~

When the analytical system is first evaluated and at intervals afterwards, establish a calibration function (e.g. as specified in ISO 8466-1) bracketing the range of expected halide concentrations for the measurement. Example calibration solutions and their concentrations for fluorine, chlorine and bromine are shown Annex H (see Table H.2, Table H.3 and Table H.4).

For example, fluorine, chlorine and bromine calibration standards indicated in Table H.2, Table H.3 and Table H.4 can be prepared by adding 0,5, 1,0, 2,0, 4,0 and 8,0 ml of a 1 000 mg/l stock solution for each halide in a 1 000 ml volumetric flask with a pipette and filled with water (Clause 5 a)) up to the mark.

a) Prepare the calibration standard solutions (Clause 5 h)).

b) Inject the calibration standard solutions (Clause 5 h)) directly to the IC.

c) Identify the peaks for particular anions by comparing the retention times with those of the calibration standard solutions (Clause 5 h)). Deviation of retention times shall not exceed ~~± 10~~ ±5 % within a batch.

d) 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 or heights. ~~For example, proceed as follows for the range of 0,5 mg/l to 8,0 mg/l.~~ The calibration curve is generally used at a concentration of 0,5 mg/l to 8,0 mg/l. However, the concentration can be adjusted if the detection limit is lowered or raised.

### 8.6 Measurement of the sample

After development of the calibration curve, the ~~laboratory reagent~~ method blank and the sample solution are measured. If the sample concentration is above the range of the ~~concentration~~ calibration curve, the solution shall be diluted with water (Clause 5 a)) to the range of the calibration curve, if possible, to the middle range, and measured again. ~~Measurement precision is checked with standard calibration solutions at regular intervals (such as once every 10 samples). If necessary, a calibration curve is developed again.~~

~~The obtained chromatogram should exhibit the same separation of the halide ions, including the bromide ion, as shown in Figure G.1 which gives an example of a chromatogram of a standard solution (4 mg/l) by IC.~~

After every tenth sample run and at the end of each sample set, analyse a continuing calibration verification (CCV) standard. The percent recovery for ~~bromine~~ halogen shall be between 90 % and 110 %. If the percent recovery for ~~bromine~~ F, Cl and Br in the CCV standard falls outside of this range, the CCV standard should be re-analysed within 12 h. If the recovery is still out of range after re-analysis of the CCV standard, the analysis is stopped and maintenance shall be performed on the system to return it to optimal operating conditions. All samples loaded before the last successful CCV standard may be reported, but all samples after the last successful CCV standard shall be re-analysed with a new calibration. A suitable separation for each of the halide ions is shown in Figure H.1 which gives an example of a chromatogram of a standard solution (4 mg/l) by IC.

### 8.7 Interference

Substances that co-elute with the anions of interest ~~will interfere~~ are filled in the laboratory library and/or database. An anion of high concentration can interfere with other constituents if their retention times are close enough to affect the resolution of their peaks. Additional information on checked inferences is specified in ISO~~/DIS~~ 10304-1:~~2006~~2007, Annex B.

## 9 Calculation

~~Concentration of bromine contained in the samples (peak area or peak height of bromine ion) is calculated from the following equation:~~

~~Br (mg/l) = [(A-Y) × Va ] / (S × Vi × D)~~

~~where~~

~~A is the peak area or peak height of bromine anion standard component;~~

~~Va is the volume of the absorption solution, ml;~~

~~D is the dilution factor of the volume method, mass of the sample specimen/volume of the test specimen having the dilution medium added thereto, g/ml;~~

~~S is the slope of the calibration curve;~~

~~slope of the standard curve with (area or height of the anion standard component; y axis) and (concentration of the standard sample; × axis, mg/l);~~

~~Vi is the volume of the sample injected into the sample boat, ml;~~

~~Y is the y intercept of the calibration curve;~~

~~y the intercept of the standard curve with (area or height of the anion standard component; y axis) and (concentration of the standard sample; × axis, mg/l).~~

Concentration of halogen contained in the samples (peak area or peak height of halides (fluoride, chloride and bromide) ion) is calculated from the following formula:

$$\text{F, Cl and Br (mg/kg)} = [(A - Y) \times V_a] / (S \times M \times D_g) \tag{1}$$

or

$$\text{F, Cl and Br (mg/kg)} = [(A - Y) \times V_a] / (S \times V \times D_v) \tag{2}$$

where

$A$ is the peak area or peak height of halides anion standard component;

$D_g$ is the dilution factor of the mass method, mass of the sample specimen/mass of the test specimen having the dilution medium added thereto, in g/g;

$D_v$ is the dilution factor of the volume method, mass of the sample specimen/volume of the test specimen having the dilution medium added thereto, in g/ml;

$M$ is the mass of the sample injected into the sample boat, in g;

$S$ is the slope of the calibration curve;

slope of the standard curve with area or height of the anion standard component (y axis) and concentration of the standard sample (x axis, in mg/l);

$V$ is the volume of the sample injected into the sample boat, M/ρ (density), in ml;

$V_a$ is the volume of the absorption solution, in ml;

$Y$ is the y intercept of the calibration curve;

y intercept of the standard curve with area or height of the anion standard component (y axis, µS/cm x min) and concentration of the standard sample (x axis, in mg/l).

## 10 Precision

When the values of two 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 below, the absolute difference between the two test results obtained will not exceed the repeatability limit $r$ deduced by statistical analysis on the international inter-laboratory study (IIS 4A) and (IIS 3-2) results in more than 5 % of cases. See Table 4, Table 5 and Table 6.

~~Mean bromine value (mg/l): 94,8 896,2~~

~~r (mg/l): 18,97 137,49~~

~~See Annex D for supporting data.~~

**Table 4 – Fluorine results of international inter-laboratory study (IIS 4A)**

| | |
|---|---|
| Mean fluorine value (mg/l): | 575 |
| *r* (mg/l): | 40,62 |

**Table 5 – Chlorine results of international inter-laboratory study (IIS 4A)**

| | |
|---|---|
| Mean chlorine value (mg/l): | 102,2 |
| *r* (mg/l): | 9,43 |

**Table 6 – Bromine results of international inter-laboratory study (IIS4A and IIS 3-2)**

| | | |
|---|---|---|
| Mean bromine value (mg/l): | 94,8 | 896,2 |
| *r* (mg/l): | 18,97 | 137,49 |

See Annex E "Results of international inter-laboratory study (IIS4A and IIS 3-2)" for supporting data.

## 11 Quality assurance and control

### 11.1 General

The following parameters in Table 7 are taken for quality control:

**Table 7 – Acceptance criteria of items for quality control**

| Parameters | Concentration of mg/kg in test sample | Acceptance criteria |
|---|---|---|
| Calibration curve | | $R^2$ ~~>~~ ≥ 0,995 |
| Initial calibration verification (ICV) | e.g. 1 mg/l for F, Cl, Br | Recovery: 90 % to 110 % |
| Continuing calibration verification (CCV) | e.g. 1 mg/l for F, Cl, Br | Recovery: 90 % to 110 % |
| Method blank | | < MDL |
| Laboratory control sample (LCS) | Middle of calibration range solution or reference material | Recovery: 80 % to 120 % |
| Laboratory control sample duplicate (LCSD) | Middle of calibration range solution or reference material | Relative deviation < 20 % |

NOTE ~~1~~ Initial calibration verification (ICV) is performed whenever a calibration curve is established, using a standard from a source different from the calibration standard.

~~One method blank should be analysed at once per batch. A blank matrix which does not contain bromine can be used as a method blank sample.~~

~~Two laboratory control samples (LCS) per batch should be analysed by spiking bromine in the blank matrix. Alternatively, a certified reference material containing bromine can be tested in duplicate.~~

~~After every tenth sample run and at the end of each sample set, analyse a continuing calibration verification (CCV) standard. The per cent recovery for bromine shall be between 90 % and 110 %. If the per cent recovery for bromine in the CCV standard falls outside of this range, the CCV standard should be re-analysed within 12 h. If the recovery is still out of range after re-analysis of the CCV standard, the analysis is stopped and maintenance shall be performed on the system to return it to optimal operating conditions. All samples loaded before the last successful CCV standard may be reported, but all samples after the last successful CCV standard shall be re-analysed with a new calibration.~~

One method blank should be analysed at least once for each batch of samples tested. A method blank which does not contain halogen can be used as a method blank sample.

One laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) per batch should be analysed by means of either using certified reference material (CRM) or spiked with a specific concentration of halides in the blank matrix. The percent recovery for halogen shall be between 80 % and 120 %. If the percent recovery for F, Cl and Br in the LCS and LCSD standard falls outside of this range, the LCS and LCSD standard should be re-analysed within 12 h. If the recovery is still out of range after re-analysis of the LCS and LCSD standard, the analysis is stopped and maintenance shall be performed on the system to return it to optimal operating conditions

## 11.2 Limits of detection (LOD) and limits of quantification (LOQ)

In its simplest form, a limit of detection (LOD) or method detection limit (MDL) is typically described as the lowest amount or concentration of analyte in a test sample that can be reliably differentiated from zero for a given measurement system.

Instrument detection limits represent an instrument’s ability to differentiate low concentrations of analytes from "zero" in a blank or standard solution, and are commonly used by manufacturers to demonstrate the measurement capability of a system ~~(e.g. atomic absorption spectrometer)~~. Whilst instrument detection limits are useful, they are often considerably lower than a limit of detection representing a complete analytical method measurement process.

Complete analytical method detection limits are most appropriately determined experimentally by performing replicate, independent measurements on low-level or fortified sample matrices (e.g. plastic) carried out through the entire test procedure, including sample digestion or extraction. A minimum of six replicates and analyte concentrations of 3 to 5 times the estimated method detection limit have been suggested as suitable for this analysis. The complete method detection limit for an entire test procedure is determined by multiplying the standard deviation of the replicates by an appropriate factor. The International Union of Pure and Applied Chemistry (IUPAC) recommends a factor of 3 for a minimum of six replicates, while US 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). See Table 8.

All analyses used to calculate an MDL should be consecutive.

**Table 8 – Student's *t* values used for calculation of method detection limit (MDL = $t \times s_{n-1}$)**

| **Number of samples** | **Student's *t*-statistic**<br>(99 % confidence) |
|---|---|
| 6 | 3,36 |
| 7 | 3,14 |
| 8 | 3,00 |
| 9 | 2,90 |
| 10 | 2,82 |

The limit of quantification (LOQ) or estimated quantitation limit for a given measurement system is typically described as the lowest concentration that can be reliably determined within specified or acceptable limits of precision during routine laboratory operating conditions. The acceptable precision limit is often defined as 10 % relative standard deviation or simply expressed as a fixed multiple (2 to 10) of the method detection limit.

## 12 Test report

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

- the sample;
- the International Standard used (including its year of publication);
- the method used (if the standard includes several);
- the result(s), including a reference to Clause 9;
- any deviations from the procedure;
- any unusual features observed;
- the date of the test.

# Annex A
(informative)

# Screening for fluorine, chlorine, bromine and iodine in polymers and electronics by oxygen bomb combustion-ion chromatography

## A.1 General

Annex A specifies a combustion method for the screening of halogen (fluorine, chlorine, bromine and iodine) contents in polymers and electronics by oxygen bomb combustion with ion chromatography. This method is applicable to solid, pasty and liquid samples containing more than 0,025 g/kg of ~~bromine~~ halogen contents.

The limit of detection depends on the element, matrix and determination technique used. Insoluble ~~bromine present~~ halogens in the original sample or produced during the combustion step ~~is~~ are not completely determined by this method.

## A.2 Principle

The sample is oxidized by oxygen bomb combustion in a closed system under pressure. Halogenated (fluorine, chlorine, bromine and iodine) ~~containing~~ compounds are converted to ~~bromide~~ halides which are absorbed and/or dissolved in an absorption solution. In general, this method is applicable for concentrations over 0,025 g/kg depending on the element, matrix and the determination technique. It may be used for aqueous samples or samples that burn with difficulty, which involves the use of a burning aid.

## A.3 Reagents and materials

All reagents shall be at least of analytical grade and suitable for their specific purposes. Particularly, they shall ~~be free of bromine~~ not contain halogen above MDL values.

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

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

c) Hydrazine, a mass fraction of 35 % in $H_2O$, ($N_2H_4$), (hydrazine is only required for iodine testing).

WARNING – Hydrazine is an inorganic compound with the chemical formula $N_2H_4$ (also written $H_2NNH_2$). It is a colourless flammable liquid with an ammonia-like odour. Therefore, the operator shall wear goggles and gloves and shall work under a fume hood when handling this reagent. Hydrazine is highly toxic and dangerously unstable unless handled in solution.

d) Absorption solution – for the determination of ~~bromine~~ halogen, the nature and concentration of which may depend on the end-determination technique and on the expected ~~content~~ concentrations of ~~bromine~~ halogen. For example:

- water (a); or
- 0,3 mol/l potassium or sodium hydroxide solution: dissolve 16,8 g of KOH or 12,0 g of NaOH pellets in water (a) and dilute to 1 l; or
- carbonate/bicarbonate solution: dissolve 2,52 g sodium bicarbonate $NaHCO_3$ and 2,54 g sodium carbonate $Na_2CO_3$ in water (a) and dilute to 1 l.

NOTE Ascorbic acid and large amounts of nitrate ~~may~~ can interfere with early eluting halogens ~~(fluoride, chloride and bromide)~~ when detected by ion chromatography.

e) Oxygen – free of combustible material, available at a pressure of 3 MPa to 4 MPa (30 atm to 40 atm) (e.g. medical grade).

f) Burning aids (e.g. paraffin).

g) Aluminium oxide, $Al_2O_3$ – neutral, particle size is less than 200 µm, pre-heated to 600 °C.

h) Reference materials – ensure recovery rates fall between 90 % to 110 %.

i) Gelatine or aceto-butyrate capsules.

## A.4 Apparatus

~~The following apparatus shall be used:~~

a) Oxygen bomb (see Figure A.1), with a capacity of not less than 200 ml and equipped with a purging system.

   This bomb shall not leak during testing and shall permit a quantitative recovery of the liquid. Its inner surface may be made of stainless steel or any other material that will not be affected by combustion gases. Materials used for the bomb assembly, such as the head gasket and wire insulation, shall be heat and chemical action resistant and shall not undergo any reaction that will affect the results. Bombs with pitted surfaces should never be used because of their tendency to retain ~~bromine~~ halogen. After repeated use of the bomb, a film may build up on the inner surface. This dullness should be removed by periodically polishing the bomb according to the manufacturer's instructions.

   NOTE 1 The internal surface of some calorimetric bombs ~~may~~ can have a ceramic coating and/or platinum ~~buckets~~ sample cups, which have better resistance to corrosion.

b) Sample cup, platinum or stainless steel or quartz.

c) Firing wire, platinum or stainless steel.

d) Ignition circuit, capable of supplying a sufficient current to ignite the sample without melting the wire.

e) Absorption flask, (e.g. 200 ml test tube equipment with a glass frit dip-tube for bubbling the combustion gases).

f) Usual laboratory equipment such as homogenization devices (e.g. mixers, stirrers, grinders, mills), analytical balance (accurate at least to 0,1 mg~~, etc.~~).

g) Safety precautions.

The bomb shall not contain any organic residue (vapours of organic solvents, grease, etc.).

Follow the manufacturer's instructions, especially with regard to the oxygen pressure inside the bomb and the maximum allowable calorific value of the test portion.

NOTE 2 Combustion of 1 g of hydrocarbons such as lubricating oil produces about 40 kJ (the calorific powers of benzoic acid and isooctane are about 26 MJ/kg and 48 MJ/kg respectively).

## A.5 Sampling

~~The test sample is prepared according to IEC 62321-2. For solid materials the particle size should be less than 200 µm. During preparation of the test sample the use of brominated polymers should be avoided. Drying the laboratory sample may be carried out for homogenization purposes if the sample, according to the accuracy of the method, contains only negligible amounts of bromine compounds volatile at the temperature intended for the drying process. Dry matter is determined according to EN 14346 [4] on a separate sub-sample (the result will be used for calculation).~~

The test sample is prepared according to IEC 62321-2. The solid sample shall be cut into small pieces (approximately less than 1,5 mm × 1,5 mm × 1,5 mm) using scissors or shears (Clause 6 b). During preparation of the test sample the use of halogenated (F, Br, Cl) polymers should be avoided. Drying the laboratory sample can be carried out for homogenization purposes if the sample, according to the accuracy of the method, contains only negligible amounts of halogen compounds volatile at the temperature intended for the drying process.

NOTE Heterogeneous moist or paste like samples ~~may~~ can be mixed with aluminium oxide (Clause A.3.g)) until granular material is obtained and then reduced to a granular powder, preferably with a particle size less than 200 µm. In this case, the ratio of aluminium oxide to sample ~~should be~~ is incorporated into the calculation of ~~the bromine~~ halogen contents and burning aids ~~should be~~ are added if necessary.

## A.6 Procedure

### A.6.1 General

Before each series of determinations, a blank and quality check ~~have to~~ shall be carried out. The blank test is performed by quantifying the blank solution (Clause 5 g)) which is prepared by following exactly the same procedure described above (Clause 5 h)) but without the actual sample.

Alternately running samples that are high and low in ~~bromine~~ halogen content ~~should~~ is to be avoided whenever possible as it is difficult to rinse the last traces of ions from the internal surfaces of the apparatus and a tendency for residual elements to carry over from sample-to-sample has been observed. When a sample high in ~~bromine~~ halogen content ~~has~~ preceded a sample low in concentration, the test on the second sample ~~should~~ is to be repeated and one or both of the low values thus obtained ~~should~~ shall be considered suspect if they do not fall within the limits of repeatability of this method. It is good practice to insert a blank between each sample, unless the series of samples being analysed has similar expected concentrations. When the composition or homogeneity of the sample is unknown, it is better to carry out the analysis in duplicate or triplicate and report the mean result from all determinations.

In the case of significant carry over it is recommended to collect the exhaust~~ion~~ gases of the sample and the following method blank ~~sample~~ in one absorption liquid. After that, determine the degree of contamination (carry over) and take measures to reduce the concentration for cleaning.

### A.6.2 Choice of the absorption solution

The combustion gases can be collected inside and/or outside the bomb in an absorption solution. Water is generally used when low concentrations of ~~bromine~~ halogen are expected (usually, less than 10 g/kg). It is recommended to add 0,5 ml of hydrogen peroxide solution (Clause A.3 b)) to the absorption solution.

The pH control of the absorption solution is very important to control for the analysis of iodine. Therefore, it is recommended that the absorption solution is prepared at a concentration of 90 mg/kg of $H_2O_2$ and then hydrazine solution is added to adjust the pH to approximately 10. (Add a mass fraction of 35 % hydrazine solution in water to reach a pH of 10 as measured with a pH meter or pH paper).

In the case of iodine, even though it is a member of the same elemental family as F, Cl and Br; it is more likely to be oxidized to the neutral form ($I_2$) because of its lower electron affinity. The absorbing liquid (water) is neutral, but when the sample is burned, the combusted gases containing halogens are captured by the absorbing liquid and the resulting solution becomes acidic if no additional materials are added to the water used to capture the released halogens. However, hydrogen iodide in the presence of water will decompose to form elemental iodine ($I_2$) which cannot be detected by IC and should be reduced back to iodide ($I^-$). So, hydrazine (Clause A.3.c), which is a good reducing agent for iodine and is also weakly alkaline, is an excellent choice as a reagent added to the absorbing solution. So, it is recommended that the absorbent be made of alkaline.

~~Alkaline solution should be used for high contents of bromine, to ensure neutralization of the acid compounds produced. When ion chromatography is used for the determination of bromine,~~

~~the absorption may be the mobile phase, e.g. the carbonate/bicarbonate solution described in A.3 c).~~

Alkaline solution shall be used for samples with high halogen content to ensure neutralization of the acid compounds produced.

### A.6.3 Preparation of the bomb

The bomb is prepared according to the manufacturer's instructions and the free ends of the firing wire (Clause A.4 c)) attached to the electric terminals of the ignition circuit (Clause A.4 d)). If using an absorption solution inside the bomb, add 10 ml of this absorption solution (Clause A.3 d)) with or without the hydrogen peroxide (Clause A.3 b)) wetting the sides of the bomb (Clause A.4 a)).

The sample cup ~~should~~ shall not be in contact with the absorption solution. Depending on the bomb design, and/or the expected concentration range of the analytes of interest, it may be necessary to ~~add less than 10 ml of the absorption solution~~ adapt the amount of the absorption or trap the combustion gases in an external absorption flask (see Clause A.3 e)).

### A.6.4 Combustion

~~Depending on its bromine content, the amount of element present and on the end determination method, weigh 0,05 g to 1 g of the sample, (to the nearest 0,1 mg) into the sample cup (A.4 b))~~ Depending on halogen content and the calorific value in the sample (obtained by determinization method), 0,05 g to 1 g of the sample is weighed (to the nearest 0,1 mg) into the sample cup (Clause A.4 b). Samples that burn with difficulty (e.g. mineral samples or samples with high water content), may require the addition of a burning aid (Clause A.3 f)). Liquid samples may be weighed in a capsule (Clause A.3 i)). To avoid ~~swirling~~ stirring up of the sample when filling the bomb with oxygen, powdery samples may be covered with inert material (e.g. aluminium oxide (Clause A.3 g)) or soaked with burning aid (Clause A.3 f)), depending ~~of their bromine~~ on halogen content. Depending on the type of bomb, the total sample mass plus enhancer ~~should~~ shall not exceed 1 g to 1,5 g to avoid dangerous high pressure and possibly rupturing the bomb.

The combined energy from sample and ~~enhancer~~ burning aids (Clause A.3 f)) is ~~not~~ important to recover ~~bromine~~ the halogen from the sample compounds. Hence it may be necessary to optimize the enhancer/sample amount ratio. Place the sample cup in position and arrange the firing wire (Clause A.4 c)) so that it ~~will be~~ is just in contact with the sample but not touching the sample cup (Clause A.4 b)).

NOTE Some operators use a nylon thread or cotton wick and loop it around the wire so that its ends immerse directly in the liquid sample or is in contact with the solid sample.

Assemble the bomb and tighten the cover securely. Admit oxygen (Clause A.3 e)) carefully (to avoid blowing the sample from the cup) to a pressure below the safety pressure specified by the manufacturer. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Let the bomb cool to ambient temperature, for example in a water bath.

### A.6.5 Collection of ~~the bromine~~ halides

When relatively high levels of ~~bromine~~ halogen (e.g. over 20 g/kg) are expected, and/or when there is no absorption solution inside the bomb, connect the exit of the bomb to an absorption flask filled with 20 ml of the same absorption solution (Clause A.3 d)) used in Clause A.3 d) and release the pressure at a slow, uniform rate so that only small bubbles are observed in the absorption tube.

If high levels of ~~bromine~~ halogen are expected, it is highly recommended to measure a blank value between the samples.

The volume of the absorption solution depends on the type and volume of the absorption flask. In other cases, this collection of combustion gases in the absorption flask is not necessary and it is possible to release the pressure quickly. Open the bomb and examine the content: if traces of sooty deposits are found, discard the determination and repeat again with burning aid and/or with a smaller test portion.

If pink vapours are seen, discard the determination and repeat using precautions to trap all the iodine (e.g. smaller test portion and/or addition of ascorbic acid). Rinse the interior of the bomb, terminals, inner surface of the bomb cover and the sample cup thoroughly with 20 ml of absorption solution (see A.6.2).

Some oxygen bombs are connected to a demineralized water supply, which enables automatic rinsing of the bomb interior before opening. In this case, the rinsing water is pushed by weak overpressure out of the bomb and combined with the absorption solution. Transfer the solution into a volumetric flask. Dilute to the mark with water (Clause A.3 a)) or absorption solution (Clause A.3 c)). The choice of the final volume depends on the concentration of ~~the bromine~~ halogen as well as on the final method used for analysis.

### A.6.6 Cleaning procedure

~~If necessary,~~ Remove any residual fuse wire from the bomb terminals and the cup. Using hot water, rinse the interior of the bomb, sample cup, terminals and the inner surface of the bomb cover. Thoroughly rinse the bomb, cover and cup with water (Clause A.3 a)).

## A.7 Ion chromatographic analysis

See 8.2 to 8.6.

## A.8 Calculation

Calculate the ~~bromine~~ halogen content in g/kg of waste using Formula (A.1):

$$X = (C \times V) / 1\,000 \times m \qquad \text{(A.1)}$$

where

$X$ is the element (fluorine, chlorine, bromine and iodine) content in the test sample in grams per kilogram (g/kg);

$C$ is the concentration expressed in milligram per litre (mg/l) of this fluorine, chlorine, bromine ~~and~~ iodine content in the absorption solution;

$V$ is the final volume of the absorption solution, expressed in millilitres (ml);

$m$ is the mass of the test portion, expressed in grams (g).

If the sample contains inert materials, for example aluminium oxide, which have been added during sample preparation, the ratio of this addition should be incorporated into the calculation.

The element content resulting from Formula (A.1) is calculated on a dry matter basis according to Formula (A.2):

$$X_d = X \times 100 / W_{dw} \qquad \text{(A.2)}$$

where

$X_d$ is the element (fluorine, chlorine, bromine and iodine) content calculated on dry matter in grams per kilogram (g/kg);

$W_{\text{dw}}$ is the dry matter of the original sample, according to Clause A.5, as mass fraction in per cent (%).

These results may also be calculated and reported in milligram per kilogram (mg/kg) or in a mass fraction of per cent. Fluorine, chlorine and bromine content is usually determined on an undried sample but is always reported on dry matter.

## A.9 Quality assurance and control and test report

Information on control measurements and on the test report is given in Clauses 11 and 12.

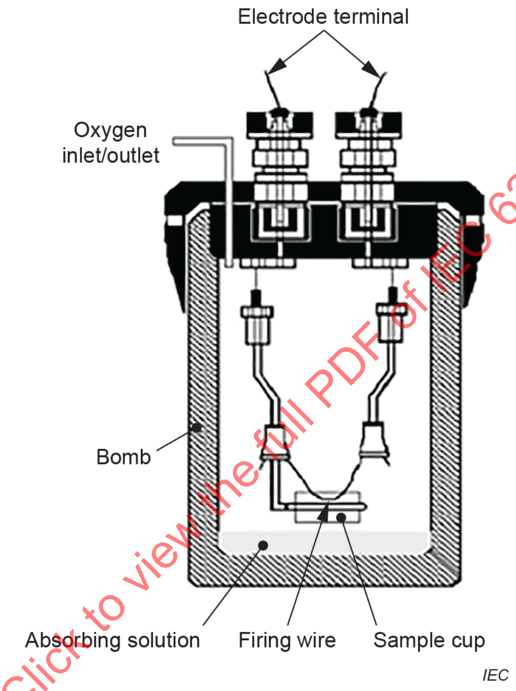

Figure A.1 – Example of oxygen bomb combustion device

# Annex B
(informative)

# Screening for fluorine, chlorine, bromine and iodine in polymers and electronics by oxygen flask combustion-ion chromatography

## B.1 General

Annex B specifies a combustion method for screening of halogen (fluorine, chlorine, bromine and iodine) contents in materials by combustion in a closed system containing oxygen (oxygen flask combustion (Schoeniger flask)), and the subsequent analysis of the combustion product using ~~different analytical techniques~~ ion chromatography.

The method is applicable to solid, pasty and liquid samples containing more than 0,25 g/kg of ~~bromine content~~ halogen. The limit of detection depends on the element, matrix and determination technique used. Insoluble ~~bromine present~~ halogen in the original sample or produced during the combustion step are not completely determined by this method.

## B.2 Principle

The sample is oxidized by combustion in a closed system (heavy walled glass flask – Schoeniger apparatus – filled with oxygen). Halogen (fluorine, chlorine, bromine and iodine) containing compounds are converted to fluorides, bromides, chlorides and iodides which are absorbed and/or dissolved in an absorption solution. ~~Several methods~~ Ion chromatography may be used for determining ~~the bromine~~ halogen concentrations in the absorption solution.

~~It uses~~ When using a smaller amount of sample ~~and therefore needs~~, more attention has to be paid on homogenization. In general, it is applicable ~~for concentrations over 250 mg/kg~~ to solid, pasty and liquid samples containing more than 0,25 g/kg of halogen, depending on the matrix and determination technique.

## B.3 Reagents and materials

The following reagents and materials apply:

a) filter paper wrappers, e.g. 3 cm × 3 cm with a 3,5 cm × 1 cm extension (see Figure B.2);

b) all other reagents and control mixtures are mentioned in Clause A.3.

## B.4 Apparatus

The following apparatus shall be used:

a) Combustion flask (see Figure B.1), chemically resistant heavy-walled, 500 ml to 1 000 ml Erlenmeyer flask equipped with a slightly enlarged neck, fitted with a standard-taper ground-glass stopper.

   The flask shall not contain any residue or vapours of organic solvents used for rinsing and drying. If these materials are present, a violent explosion ~~may~~ can take place when the burning filter paper is introduced. After inserting the flaming paper into the flask, the stopper shall be held securely. A slight pressure drop inside the flask during the initial stage of burning normally happens, while a slight vacuum is formed after complete absorption of the combustion products. Combustion shall be carried out under a fume hood and the operator ~~must~~ shall wear safety goggles and gloves.

b) Platinum gauze sample carrier sealed into another standard taper ground glass stopper (see Figure B.1).

c) Usual laboratory equipment including homogenization devices (e.g. mixers, stirrers, grinders, mills) and an analytical balance (accurate at least to 0,1 mg), etc.

~~d) safety precautions.~~

## B.5 Sampling

### B.5.1 General

The test sample is prepared according to IEC 62321-2. Between 10 mg and 50 mg of homogeneous (or homogenized) sample are weighed to the nearest 0,1 mg. The weighed sample shall not contain more than 10 mg to 20 mg of ~~bromine~~ halogen.

### B.5.2 Solid and paste-like samples

Fold the filter paper (Clause B.3 a)) used for wrapping the sample to form a boat as shown in Figure B.2. Wait several minutes before weighing to allow the filter paper to equilibrate to the conditions of humidity of the room and record the tare weight to 0,1 mg. Using a small spatula, place the estimated amount of sample on the tared paper and reweigh to 0,1 mg. Then, using the spatula, fold the filter paper as shown in Figure B.2. Squeeze the packed filter with clean tweezers.

Place the sample in the platinum sample carrier (Clause B.4 b)).

### B.5.3 Liquid samples

Placing small-size drops on the paper, introduce the estimated amount of sample into a tared capsule (Clause A.3 i)) containing a small piece of folded filter paper. Immediately reweigh the capsule to 0,1 mg. Wrap the capsule in the filter paper (Clause B.3 a)) as in the case of solid samples and insert in the platinum sample carrier (Clause B.4 b)).

## B.6 Procedure

### B.6.1 General

Before each series of determinations, a method blank and quality check (i.e. initial calibration verification and continuing calibration verification, refer to Table 7) shall be carried out. The blank test is performed by quantifying the blank solution (Clause 5 g)) which is prepared by following exactly the same procedure described above (Clause 5 h)) without the actual sample. Running samples that are alternately high and low in ~~bromine~~ halogen content ~~should~~ is to be avoided whenever possible as it is difficult to rinse the last traces of ions from the internal surfaces of the apparatus and a tendency for residual elements to carry over from a sample to the next sample has been observed. When a sample high in ~~bromine~~ halogen content ~~has preceded~~ precedes a sample low in concentration, the test on the second sample ~~should~~ shall be repeated and one or both of the low values thus obtained should be considered suspect if they do not fall within the limits of repeatability of this method. It is good practice to insert a method blank between each sample, unless the series of samples being analysed has similar expected concentrations. When the composition or homogeneity of the sample is unknown, it is better to carry out the analysis in duplicate or triplicate and report the mean result from all determinations.

In the case of significant carry-over of the analyte, it is recommended to collect the exhaustion gases of the sample and the following blank sample in one absorption liquid.

### B.6.2 Choice of the absorption solution

See A.6.2.

### B.6.3 Combustion

Add 10 ml of absorption solution (Clause 5 k)) into the combustion flask (Clause B.4 a)). Flush the flask with oxygen for 1 min, keeping the gas delivery tube near the bottom of the flask to displace the air. ~~Stopper~~ Seal the flask with ~~the regular~~ a standard stopper.

~~While observing safety precautions,~~ Ignite the filter paper packet containing the sample, remove the regular stopper, and quickly replace it by inserting the stopper (Clause B.4 b)) with the burning paper into the flask. Immediately invert the stoppered flask so that the absorbing liquid forms a tight seal around the stopper.

NOTE Systems with electrical remote ignition are also applicable.

As shown in Figure B.1, the flask shall be held so that the open part of the platinum sample carrier faces upward so that the sample cannot fall out during combustion. After the combustion is complete, allow the inverted flask to cool for 1 min, and then vigorously shake it for 3 min to absorb the combustion products. Allow to stand for 5 min in the normal position. Carefully pipette 10 ml of the absorption solution (Clause 5 k)) into the neck-well of the flask. Lift the stopper slightly to allow the liquid to be sucked into the flask. Then let the stoppered flask gently cool for 15 min. Transfer the contents of the flask into a volumetric flask, dilute to the mark with water (Clause A.3 a)) or absorption solution (Clause 5 k)). The choice of the final volume depends on the expected concentration of the solution and on the end-method of analysis.

## B.7 Ion chromatographic analysis, calculation, quality assurance and control and test report

See Clauses A.7, A.8 and A.9.

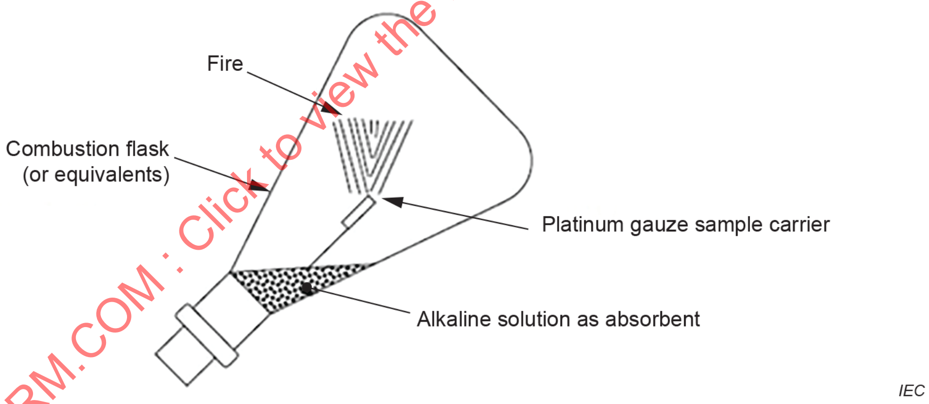

Figure B.1 – Example of oxygen flask combustion device

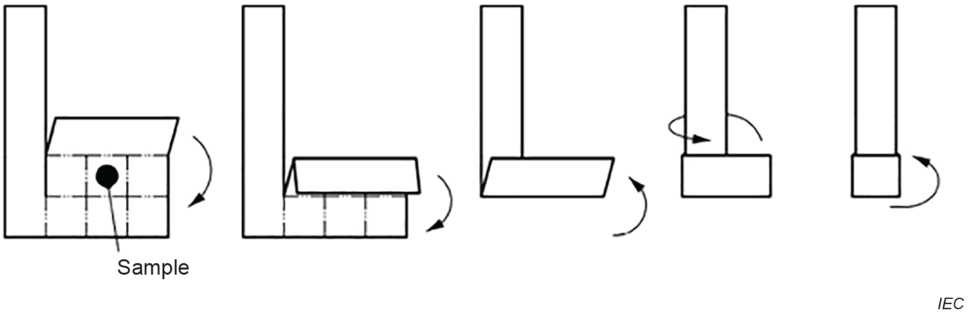

Figure B.2 – Example of wrapping of sample

# Annex C
(informative)

## Example of a combustion device and IC system

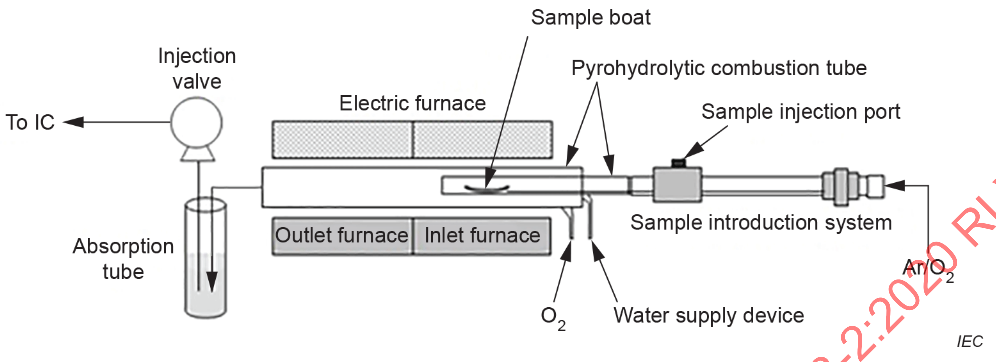

Figure C.1 – Example of a combustion device connected to an ion chromatograph (IC)

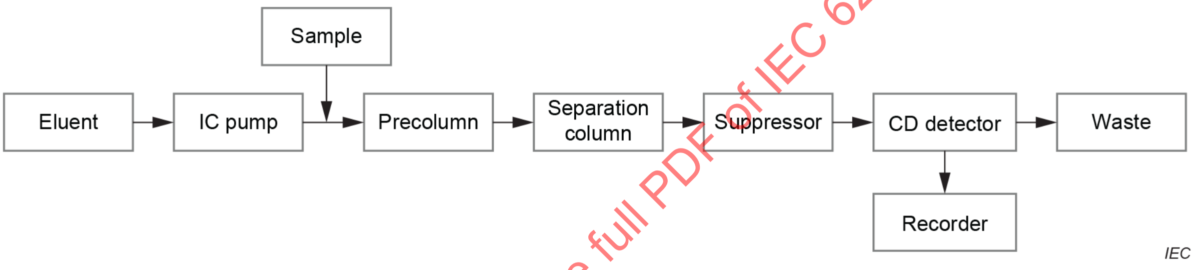

Figure C.2 – Example of ion chromatographic system

# Annex D
(informative)

# Screening for iodine in polymers and electronics by combustion-ion chromatography (C-IC)

## D.1 General

Annex D specifies a combustion method for the screening of iodine in polymers and electronics by combustion-ion chromatography.

## D.2 Principle

Generally, the iodine analysis method in polymers and electronics is the same as that described in the normative section of this document. However, in the case of iodine, recovery is ensured only when alkaline pH conditions (8 to 10) in the absorbent solution are used. Therefore, in this informative annex, iodine analysis is carried out specifically using this principle.

## D.3 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. All reagents used shall not contain observable amount of halides.

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

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

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

c) Hydrazine, a mass fraction of 35 % in $H_2O$, ($N_2H_4$).

WARNING – Hydrazine is an inorganic compound with the chemical formula $N_2H_4$ (also written $H_2NNH_2$). It is a colourless flammable liquid with an ammonia-like odour. Therefore, the operator shall wear goggles and gloves and shall work under a fume hood when handling this reagent. Hydrazine is highly toxic and dangerously unstable unless handled in solution.

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

e) Argon, carrier gas minimum of 99,9 % purity.

NOTE 1 Purification scrubbers such as moisture (molecular sieve) and hydrocarbon trap filters (activated charcoal or equivalent) can be used to ensure the removal of contamination.

f) Oxygen, combustion gas of minimum of 99,6 % purity.

g) Burning aids, tungsten oxide ($WO_3$) or iron oxide ($Fe_3O_4$), etc. Minimum particle size of burning aids shall be less than 50 µm. $WO_3$ and $Fe_3O_4$ purity of more than 90 % is required. And also, before using burning aids, it is necessary to check if the halogens contained or not are below the MDL level by using a method blank.

h) Blank solution, fill a volumetric flask (e.g. 100 ml flask) with water (Clause D.3 a)).

i) 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, for example 5 to 10 calibration solutions distributed as evenly as possible over the expected working range.

NOTE 2 The solution is either prepared from a primary standard or calibrated.

j) Eluents

Eluents are used as a solvent in separating materials in elution. The choice of eluent depends on the chosen column and detector (seek advice from 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.

k) Internal standard (IS) solution (optional)

An internal standard can be used to correct analytical errors.

The internal standard used in the absorption solution should not contain any of the sample components, and should be selected based on the condition of column and mobile phase (e.g. phosphate, citric acid, oxalic acid, methane sulfonic acid).

l) Absorption solution, used for trapping halogen – 3 ml of $H_2O_2$ (Clause D.3 b)), is poured into a 1 000 ml volumetric flask and water is added to the scale and mixed. This solution contains 900 mg/kg of $H_2O_2$ depending on testing target samples. Especially, the pH control of the absorption solution is very important to analyse iodine. Therefore, it is recommended that the absorption solution is prepared at a concentration of 90 mg/kg of $H_2O_2$ and then hydrazine solution is added to adjust the pH to approximately 10. (Add a mass fraction of 35 % hydrazine solution in water to reach a pH of 10 with a pH meter or pH paper.)

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, use a minimum amount of hydrogen peroxide to diminish IC peak identification issues.

In the case of iodine, even though it is a member of the same elemental family as F, Cl and Br, it is more likely to be oxidized to the neutral form ($I_2$) because of its lower electron affinity. The absorbing liquid (water) is neutral, but when the sample is burned, the combusted gases containing halogens are captured by the absorbing liquid and the resulting solution becomes acidic if no additional materials are added to the water used to capture the released halogens. However, hydrogen iodide in the presence of water will decompose to form elemental iodine ($I_2$) which cannot be detected by IC and shall be reduced back to iodide ($I^-$). So, hydrazine (Clause D.3.c), which is a good reducing agent for iodine and is also weakly alkaline, is an excellent choice for a reagent added to the absorbing solution. Reference materials – A reference material can be used to ensure recovery rates of the halogen fall within 90 % to 110 %. A certified reference material is the best choice for that purpose. If a certified reference material is not available, a reference material can be prepared by mixing certain amounts of the iodine compounds, diluting with cellulose or aluminium oxides to obtain a suitable concentration, and then pulverizing the mixture to homogenize.

## D.4 Apparatus

The following apparatuses shall be used.

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

b) Scissors.

c) Combustion system – in general, it 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. The auto sampler may be used as long as the accuracy and performance of the method are not degraded.
   2) Sample boat – the boat is generally made of quartz, nickel, ceramics, platinum or stainless steel.
   3) Sample introduction system – the system provides a sampling port for the 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 have the quartz or ceramic tube installed inside of the device 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 of high concentration, a trap column should be installed between the absorption tube and the combustion tube.
   6) Water supply device – this device is capable of delivering grade 1 water (Clause D.3 a)) to the combustion tube at a controlled rate sufficient to provide a pyrohydrolytic environment.
   7) Absorption tube – a size of glass pipe capable of maintaining about one-half of the total volume by putting 10 ml to 20 ml of the absorption solution. This has the configuration that the discharge gas pipe of the heating furnace is submerged in the absorption solution to absorb the discharged gas. Further, it has the configuration that the absorption solution of the ion chromatograph can be injected through the connecting device. For preventing contamination from other samples, the absorption tube should be washed after sample analysis.

d) Ion chromatographic system – in general, it consists of the following components (see Figure C.2):

## D.5 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 (Clause D.4 b)).

b) Liquid sample

   For sampling of liquid sample, sampling should be performed after rinsing the inside of the pipette a few times with the sample liquid.

## D.6 Procedure

### D.6.1 Combustion

General combustion procedures by using an electric furnace are described in IEC 60754-3:2018, Clause 7 (Test procedure).

a) After a sample boat is heated sufficiently in the electric furnace to remove the contaminants, remove the sample boat from the furnace with clean tongs, let it cool to room temperature, then normally 10 mg to 100 mg of samples are weighed with a precision of 0,1 mg and loaded into the sample boat. If samples are difficult to combust (e.g. flux, solder paste), a burning aid (e.g. $WO_3$) has to be used. Generally, a 5 to 1 ratio of burning aids to sample is sufficient. If any burning aid is being used, apply approximately 100 mg of it in a thin layer over the surface of the sample boat, evenly spread the weighed sample on it, and then cover the sample with approximately 300 mg of the burning aid.

b) It is then heated in the combustion furnace for 10 min to 20 min together with argon, oxygen and water by using the sample injection device located at the centre of the quartz tube of the combustion furnace. An example of combustion conditions is described in Table F.1. If the combustion boat shows evidence of soot generation or unburned sample particles, the combustion shall be judged to be insufficient and the procedure shall be repeated. The contaminated area shall be cleaned thoroughly before repeating the procedure.

c) Upon completion of combustion operations, wash the tubing at the combustion gas discharge outlet, and pour all washing solutions into the absorbing bottle for measuring.

d) For the blank test, perform a similar operation without inserting the sample or a blank boat, and use this absorption solution obtained as the blank solution. Follow the procedure described in D.5.3.

NOTE If the combustion furnace and IC are connected and operated automatically, the absorption solution absorbing the combustibles can be injected into the IC.

### D.6.2 IC analysis

The general rules on ion chromatographic analysis as set out in ISO 10304-1 shall be followed:

a) Set up the IC according to the instrument manufacturer's instructions or laboratory standard operation procedure (SOP). Typical operating conditions for IC are shown in Table H.1.

b) Run the eluent and wait for a stable baseline.

c) Perform the calibration as described in D.6.5. Measure the samples, calibration (Clause D.6.5)) and at least two blank solutions as described in D.6.5.

Operating conditions should be selected and stabilized according to the device manufacturer's instructions or to the standard operation procedure (SOP).

### D.6.3 Blank test

A blank test is performed by quantifying and with at least two blank solutions which are prepared by following exactly the same procedure described in Clause 5 h) but without the actual sample. A blank solution (Clause D.3 h)) which does not contain halides (lower than MDL, or normally 0,1 mg/l) can be used as a method blank sample.

### D.6.4 Cleaning and recalibration

Clean any coke or soot as per the manufacturer's instructions. After cleaning, assemble the apparatus and check for leaks. Run a check standard to determine if the instrument needs to be recalibrated.

### D.6.5 Calibration

A calibration curve shall be developed for quantitative analysis. The calibration curve is prepared by using a standard solution of iodide.

When the analytical system is first evaluated and at intervals afterwards, establish a calibration function (e.g. as specified in ISO 8466-1) bracketing the range of expected iodine concentrations for the measurement.

For example, iodine calibration standards can be prepared by adding 0,5, 1,0, 2,0, 4,0 and 8,0 ml of a 1 000 mg/l stock solution in a 1 000 ml volumetric flask with a pipette and filled with water (Clause 5 a)) up to the mark.

a) Prepare the calibration standard solutions (Clause D.3 i)).
b) Inject the calibration standard solutions (Clause D.3 i)) directly to the IC.
c) Identify the peaks for particular anions by comparing the retention times with those of the calibration standard solutions (Clause D.3 i)). Deviation of retention times shall not exceed ±5 % within a batch.
d) 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 or heights. For example, proceed as follows for the range of 0,5 mg/l to 8,0 mg/l.

## D.7 Measurement of the sample

After development of the calibration curve, the laboratory reagent blank and the sample solution are measured. If the sample concentration is above the range of the concentration curve, the solution shall be diluted with water (Clause D.3 a)) to the range of the calibration curve, if possible to the middle range, and measured again. Measurement precision is checked with standard calibration solutions at regular intervals (such as once every 10 samples). If necessary, a calibration curve is developed again.

The obtained chromatogram should exhibit the same separation for each of the halide ions as shown in Figure H.1 which gives an example of a chromatogram of a standard solution (4 mg/l) by IC. Additional IIS results (Difference in recovery rate of iodine according to adsorbents ($H_2O_2$, Hydrazine)) are shown in Table G.4.

## D.8 Interference

Substances that co-elute with the anions of interest are filled in the specific laboratory library. An anion of high concentration can interfere with other constituents if their retention times are close enough to affect the resolution of their peaks. Additional information on checked inferences is specified in ISO 10304-1:2007, Annex B.

## D.9 Calculation

Concentration of iodine contained in the samples (peak area or peak height iodide ion) is calculated from the following formula:

$$\text{I (mg/kg)} = [(A - Y) \times V_a] / (S \times M \times Dg) \tag{D.1}$$

or

$$\text{I (mg/kg)} = [(A - Y) \times V_a] / (S \times V \times D_v) \tag{D.2}$$

where

$A$ is the peak area or peak height of the iodide anion standard component;

$D_g$ is the dilution factor of the mass method, mass of the sample specimen/mass of the test specimen having the dilution medium added thereto, in g/g;

$D_v$ is the dilution factor of the volume method, mass of the sample specimen/volume of the test specimen having the dilution medium added thereto, in g/ml;

$M$ is the mass of the sample injected into the sample boat, in g;

$S$ is the slope of the calibration curve,

slope of the standard curve with area or height of the anion standard component (y axis) and concentration of the standard sample (x axis, in mg/l);

$V$ is the volume of the sample injected into the sample boat, $M/\rho$ (density), in ml;

$V_a$ is the volume of the absorption solution, in ml;

$Y$ is the y intercept of the calibration curve,

y intercept of the standard curve with area or height of the anion standard component (y axis, µS/cm × min) and concentration of the standard sample (x axis, in mg/l).

# Annex E
(informative)

## Results of international interlaboratory study ~~#4A (IIS 4A)~~ (IIS 4A and IIS 3-2)

### Table E.1 – Mean results and recovery rates for ~~total~~ bromine obtained in the IIS4A study using C-IC

| **Sample number** | **Sample description** | **Certified value of Br** mg/kg | **Mean result of Br** mg/kg | **Standard deviation** mg/kg | **Recovery rate**[a] % | **Range of recovery rate** % | **Total number of data sets**[b] | **Number of data sets used** |
|---|---|---|---|---|---|---|---|---|
| IIS4A-04 | KRISS CRM<br>113-01-015 (acrylonitrile butadiene styrene) | 890 | 896 | 47,2 | 101 | 90 to 111 | 10 | 9 |
| IIS4A-07 | ERM CRM<br>680k<br>(poly ethylene) | 96 | 95 | 6,9 | 99 | 84 to 112 | 10 | 10 |

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

### Table E.2 – Statistical ~~total~~ bromine data for IIS 4A results using C-IC

| **Sample** | **Parameter** | $m$ mg/kg | $v$ mg/kg | $N$ | s($r$) mg/kg | $r$ mg/kg | s($R$) mg/kg | $R$ mg/kg |
|---|---|---|---|---|---|---|---|---|
| IIS4A-04 | Br | 896,2 | 890 | 25 | 12,14 | 34,00 | 49,10 | 137,49 |
| IIS4A-07 | Br | 94,8 | 96 | 27 | 2,14 | 6,01 | 6,78 | 18,97 |

**Key**

$m$ = arithmetic mean of test results

$v$ = expected value

$N$ = number of accepted results

s($r$) = repeatability standard deviation

$r$ = repeatability limit

s($R$) = reproducibility standard deviation

$R$ = reproducibility limit

### Table E.3 – Mean results and recovery rates for fluorine obtained in the IIS 3-2 study using C-IC

| Sample number | Sample description | Estimated value of F mg/kg | Mean result of F mg/kg | Standard deviation mg/kg | Recovery rate[a] % | Range of recovery rate % | Total number of data sets[b] | Number of data sets used |
|---|---|---|---|---|---|---|---|---|
| IIS3-B02 | Custom made sample (polycarbonate) | 575 | 535,2 | 82,5 | 93 | 76 to 121 | 18 | 18 |

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

### Table E.4 – Statistical fluorine data for IIS 3-2 results using C-IC

| Sample | Parameter | $m$ mg/kg | $v$ mg/kg | $N$ | s($r$) mg/kg | $r$ mg/kg | s($R$) mg/kg | $R$ mg/kg |
|---|---|---|---|---|---|---|---|---|
| IIS3-B02 | F | 535,2 | 575 | 18 | 14,5 | 40,62 | 87,67 | 245,48 |

**Key**

$m$ = arithmetic mean of test results

$v$ = expected value

$N$ = number of accepted results

s($r$) = repeatability standard deviation

$r$ = repeatability limit

s($R$) = reproducibility standard deviation

$R$ = reproducibility limit

### Table E.5 – Mean results and recovery rates for chlorine obtained in the IIS 3-2 study using C-IC

| Sample number | Sample description | Certified value of Cl mg/kg | Mean result of Cl mg/kg | Standard deviation mg/kg | Recovery rate[a] % | Range of recovery rate % | Total number of data sets[b] | Number of data sets used |
|---|---|---|---|---|---|---|---|---|
| IIS3-A01 | ERM®-EC680k[c]<br>(polyethylene) | 102,2 | 103,5 | 8,68 | 101 | 92 to 116 | 18 | 18 |

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

[c] ERM® (European Reference Materials) is a registered trademark of the European Commission.

### Table E.6 – Statistical for chlorine data for IIS 3-2 results using C-IC

| Sample | Parameter | $m$<br>mg/kg | $v$<br>mg/kg | $N$ | s($r$)<br>mg/kg | $r$<br>mg/kg | s($R$)<br>mg/kg | $R$<br>mg/kg |
|---|---|---|---|---|---|---|---|---|
| IIS3-A01 | Cl | 103,5 | 102,2 | 18 | 3,4 | 9,43 | 9,16 | 25,64 |

**Key**

$m$ = arithmetic mean of test results

$v$ = expected value

$N$ = number of accepted results

s($r$) = repeatability standard deviation

$r$ = repeatability limit

s($R$) = reproducibility standard deviation

$R$ = reproducibility limit

# Annex F
(informative)

## Additional results of TG 3-2 test

**Table F.1 – Mean results and recovery rates for ~~total~~ bromine obtained in the TG 3-2 internal test study by using C-IC**

| Sample number | Sample description | Certified value of Br<br>mg/kg | Mean result of Br<br>mg/kg | Standard deviation<br>mg/kg | Recovery rate [a]<br>% | Range of recovery rate<br>% | Total number of data sets [b] | Number of data sets used |
|---|---|---|---|---|---|---|---|---|
| TG 3-2-01 | KRISS CRM<br>113-01-013 (acrylonitrile butadiene styrene) | 124,4 | 120 | 8,0 | 97 | 80 to104 | 10 | 10 |
| TG 3-2-02 | KRISS CRM<br>113-01-015 (acrylonitrile butadiene styrene) | 890 | 872 | 55,3 | 98 | 89 to 107 | 10 | 10 |
| TG 3-2-03 | EMC<br>(epoxy moulding compound) | 195 | 178 | 13,0 | 91 | 82 to 99 | 9 | 9 |
| TG 3-2-04 | EMC<br>(epoxy moulding compound) | 976 | 902 | 82,4 | 92 | 79 to 102 | 9 | 9 |

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

### Table F.2 – Mean results and recovery rates for ~~total~~ bromine obtained in the TG 3-2 internal test study by using oxygen bomb-IC

| **Sample number** | **Sample description** | **Certified value of Br**<br>mg/kg | **Mean result of Br**<br>mg/kg | **Standard deviation**<br>mg/kg | **Recovery rate** [a]<br>% | **Range of recovery rate**<br>% | **Total number of data sets** [b] | **Number of data sets used** |
|---|---|---|---|---|---|---|---|---|
| TG 3-2-01 | KRISS CRM<br>113-01-013 (acrylonitrile butadiene styrene) | 124,4 | 113 | 10,7 | 91 | 80 to107 | 8 | 8 |
| TG 3-2-02 | KRISS CRM<br>113-01-015 (acrylonitrile butadiene styrene) | 890 | 788 | 73,8 | 89 | 81 to 101 | 10 | 8 |
| TG 3-2-03 | EMC<br>(epoxy moulding compound) | 195 | 146 | 18,7 | 75 | 58 to 85 | 8 | 8 |
| TG 3-2-04 | EMC<br>(epoxy moulding compound) | 976 | 736 | 60,9 | 75 | 64 to 83 | 8 | 8 |

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

# Annex G
(informative)

# Additional validation data

### Table G.1 – General conditions for the combustion furnace and the absorption solution

| Parameters | Conditions |
|---|---|
| Temperature of combustion furnace | 900 °C to ~~1 100~~ 1 000 °C |
| Flow rate of oxygen | 400 ml/min |
| Flow rate of argon | 200 ml/min |
| Flow rate of water | 0,01 ml/min to 0,04 ml/min |
| Amount of absorption solution | 10 ml to 20 ml |

### Table G.2 – Additional information – Difference in sample sizes and measured bromine values in solder paste with burning aid ($WO_3$ powder)

| Amount of sample mg | IC results of bromine mg/kg |
|---|---|
| 7,9 | 1 670 |
| 18,3 | 1 672 |
| 36,1 | 1 794 |
| 55,6 | 1 788 |
| 72,8 | 1 824 |
| 93,5 | 1 833 |

### Table G.3 – Additional information – Difference in combustion temperatures and measured bromine values in solder paste with burning aid ($WO_3$ powder)

| Combustion temperature Inlet (°C)/Outlet (°C) | Amount of sample mg | IC results of bromine mg/kg |
|---|---|---|
| 500 / 500 | 38,5 | 880 |
| 600 / 600 | 36,9 | 1 461 |
| 700 / 700 | 40,3 | 1 573 |
| 800 / 800 | 36,8 | 1 708 |
| 900 / 900 | 38,0 | 1 728 |
| 1 000 / 1 000 | 37,9 | 1 760 |
| ~~1 000/1 100~~ | ~~36,1~~ | ~~1 794~~ |

## Table G.4 – Additional information – Difference in recovery rate of iodine according to adsorbents ($H_2O_2$, hydrazine)

| Sample | Adsorbent | Mean result of iodine mg/kg | Expected value of iodine mg/kg | Range mg/kg | Standard deviation mg/kg | Relative standard deviation % | Recovery rate mg/kg | Total number of data sets |
|---|---|---|---|---|---|---|---|---|
| IIS3-C03<br>(Nylon 66) | $H_2O_2$ | 1 263 | 1 775 | 951 | 255,2 | 20,2 | 71,2 | 12 |
| IIS3-D04<br>(Nylon 66) | $H_2O_2$ | 2 416 | 3 320 | 3079 | 1 100,3 | 45,5 | 72,8 | 12 |
| IIS3-C03<br>(Nylon 66) | Hydrazine | 1 462 | 1 775 | 178 | 34,00 | 3,8 | 82,4 | 12 |
| IIS3-D04<br>(Nylon 66) | Hydrazine | 3 505 | 3 320 | 801 | 6,01 | 6,9 | 105,6 | 12 |

# Annex H
(informative)

## Additional IC data

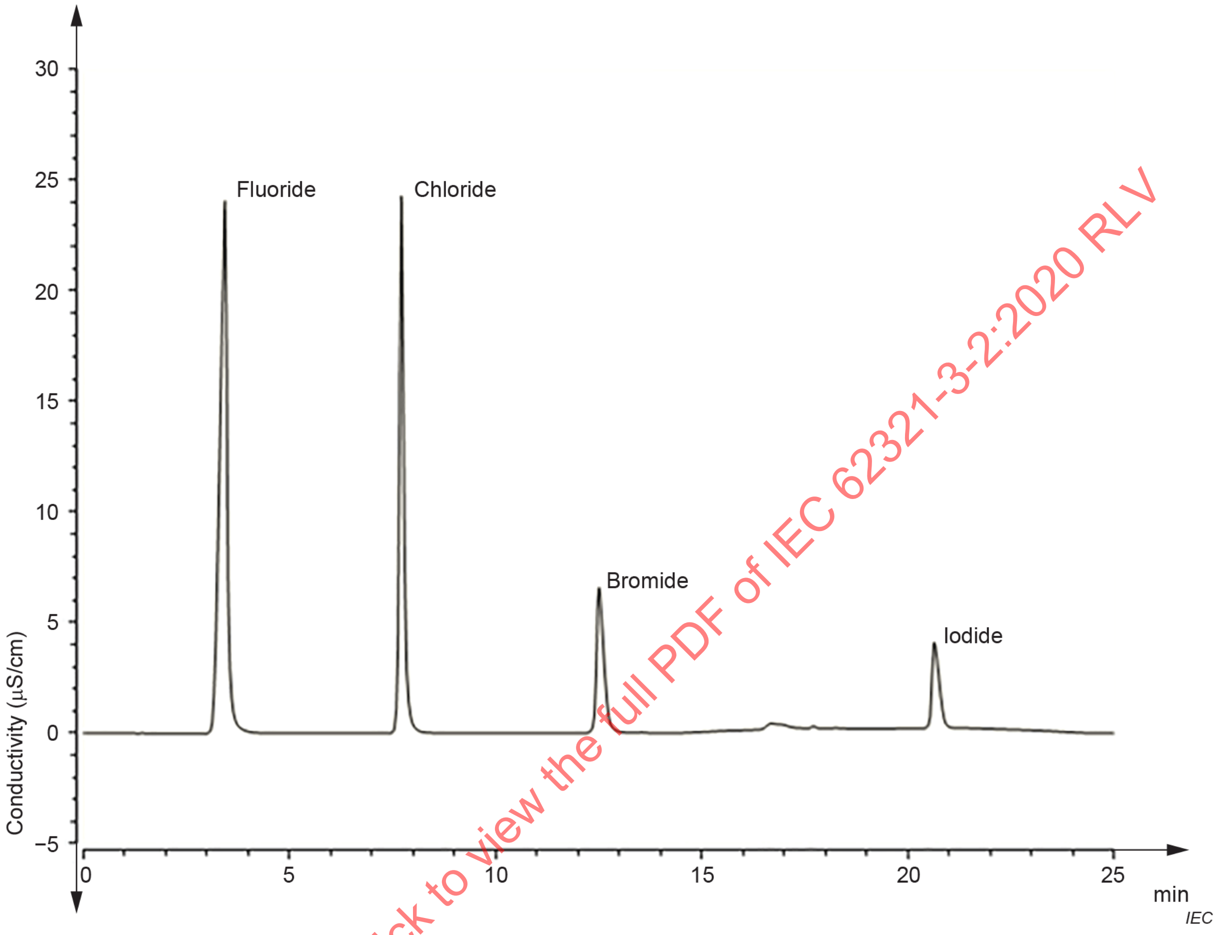

**Figure H.1 – Example of a chromatogram of the standard solution (4 mg/~~kg~~l of each standard) by IC**

**Table H.1 – Typical operating conditions for IC**

| Parameters | Conditions |
|---|---|
| Analytical column | Anion exchange column (4 mm × 250 mm) |
| Eluent | 1,8 mmol/l $Na_2CO_3$ / 1,7 mmol/l $NaHCO_3$ |
| Flow rate | 1,0 ml/min |
| Injection volume | 100 µl |
| Detection | Conductivity (with suppressor) |

### Table H.2 – Example of fluorine calibration solutions for IC

| ~~No.~~ | ~~Concentration of calibration standard solutions (Br)~~ ~~mg/l~~ | ~~Peak area of calibration standard solutions (Br)~~ ~~ìS*min~~ | ~~Peak height of calibration standard solutions (Br)~~ ~~ìS~~ |
|---|---|---|---|
| ~~1~~ | ~~0,5~~ | ~~0,129~~ | ~~0,722~~ |
| ~~2~~ | ~~1,0~~ | ~~0,296~~ | ~~1,640~~ |
| ~~3~~ | ~~2,0~~ | ~~0,608~~ | ~~3,347~~ |
| ~~4~~ | ~~4,0~~ | ~~1,283~~ | ~~6,800~~ |
| ~~5~~ | ~~8.0~~ | ~~2,646~~ | ~~13,164~~ |

| No. | Concentration of calibration standard solutions (F) mg/l | Peak area of calibration standard solutions (F) µS × min | Peak height of calibration standard solutions (F) µS |
|---|---|---|---|
| 1 | 0,5 | 0,658 | 6,91 |
| 2 | 1,0 | 1,264 | 11,65 |
| 3 | 2,0 | 2,438 | 18,41 |
| 4 | 4,0 | 4,762 | 27,48 |
| 5 | 8.0 | 9,294 | 39,60 |

### Table H.3 – Example of chlorine calibration solutions for IC

| No. | Concentration of calibration standard solutions (Cl) mg/l | Peak area of calibration standard solutions (Cl) µS × min | Peak height of calibration standard solutions (Cl) µS |
|---|---|---|---|
| 1 | 0,5 | 0,373 | 4,36 |
| 2 | 1,0 | 0,753 | 8,73 |
| 3 | 2,0 | 1,485 | 17,09 |
| 4 | 4,0 | 3,007 | 34,21 |
| 5 | 8.0 | 6,112 | 66,48 |

### Table H.4 – Example of bromine calibration solutions for IC

| No. | Concentration of calibration standard solutions (Br) mg/l | Peak area of calibration standard solutions (Br) µS × min | Peak height of calibration standard solutions (Br) µS |
|---|---|---|---|
| 1 | 0,5 | 0,157 | 1,53 |
| 2 | 1,0 | 0,322 | 3,09 |
| 3 | 2,0 | 0,653 | 6,05 |
| 4 | 4,0 | 1,306 | 11,30 |
| 5 | 8.0 | 2,663 | 20,03 |

# Bibliography

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~~ASTM D 808, *Standard test method for chlorine in new and used petroleum products (bomb method)*~~

~~EN 14346, *Characterization of waste – Calculation of dry matter by determination of dry residue or water content*~~

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[2] IEC PAS 62596:2009, *Electrotechnical products – Determination of restricted substances – Sampling procedure – Guidelines*

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# IEC 62321-3-2

Edition 2.0 2020-06

# INTERNATIONAL STANDARD

# NORME INTERNATIONALE

HORIZONTAL STANDARD
NORME HORIZONTALE

## 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)

IEC 62321-3-2:2020-06(en-fr)

## CONTENTS

INTERNATIONAL ELECTROTECHNICAL COMMISSION

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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)

## 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** mg/kg | PC |
| Concentration or concentration range tested | | 575 |

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

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

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

| **Substance/element** | **Bromine** | | | |
|---|---|---|---|---|
| **Polymer** | **Unit of measure** mg/kg | ABS | EMC | PE |
| Concentration or concentration range tested | | 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.

# 8 Procedure

## 8.1 Combustion

a) After a sample boat is heated sufficiently in the electric furnace to remove the contaminants, remove the sample boat from the furnace with clean tongs, let it cool to room temperature, then weigh (typically 10 mg to 100 mg) the sample to the nearest 0,1 mg and load into the sample boat. If samples are difficult to combust (e.g. flux, solder paste), a burning aid (e.g. $WO_3$) shall be used. Generally, a 5 to 1 ratio of burning aids to sample is sufficient. If any burning aid is being used, apply approximately 1/4 of its total mass in a thin layer over the surface of the sample boat, place the weighed sample on it and then cover the sample with approximately ¾ of the total burning aid mass. Detailed analysis conditions are described in Annex G (Table G.1, Table G.2, Table G.3)

b) The sample and boat are heated in the combustion furnace for 10 min to 20 min together with argon, oxygen and water by using the sample injection device located at the centre of the quartz tube of the combustion furnace. Suitable combustion conditions are described in Table G.1. If the combustion boat shows evidence of soot generation or unburned sample particles, the combustion shall be judged to be insufficient and the procedure shall be repeated. The contaminated area shall be cleaned thoroughly before repeating the procedure.

NOTE 1 If insufficient combustion is suspected (e.g. visible soot in the combustion boat), the combustion and chromatography on the residue can be repeated until no further halides are detected. Any halides detected can be summed. Alternatively, the analysis can be repeated with a fresh sample altering the conditions (e.g. reduce sample size, increase furnace temperature or time) to achieve complete combustion.

c) Upon completion of combustion operations, wash the tubing at the combustion gas discharge outlet, and pour all washing solutions into the absorbing bottle for measuring.

d) For the blank test, perform a similar operation without inserting the sample or a blank boat, and use this absorption solution obtained as the blank solution. Follow the procedure described in 8.3.

NOTE 2 If the combustion furnace and IC are connected and operated automatically, the absorption solution adsorbing the combustibles can be injected into the IC.

## 8.2 IC analysis

The general procedures for ion chromatography described in ISO 10304-1 shall be followed:

a) Set up the IC according to the instrument manufacturer’s instructions or laboratory standard operation procedure (SOP). Suitable operating conditions for IC are shown in Table G.1;

b) Run the eluent and wait for a stable baseline;

c) Perform the calibration as described in 8.5. Measure the samples, calibrants (Clause 5 h)) and at least two blank solutions as described in 8.3.

Operating conditions shall be selected and stabilized according to the device manufacturer or to the standard operation procedure (SOP).

## 8.3 Blank test

A method blank test is performed by quantifying at least two blank solutions which are prepared by following exactly the same procedure described above (Clause 5 h)) without the actual sample. A blank solution (Clause 5 g)) which does not contain halides (lower than MDL, or normally 0,1 mg/l) shall be used for preparing the method blank.

## 8.4 Cleaning and recalibration

Clean any coke or soot from the combustion tube and sample boats as per the manufacturer’s instructions. After cleaning, assemble the apparatus and check for leaks. Run a check laboratory control sample or reference material to determine if the instrument needs to be recalibrated or cleaned again.

### 8.5 Calibration

A calibration curve shall be developed for quantitative analysis. The calibration curve is prepared by using a standard solution of fluoride, chloride and bromide.

When the analytical system is first evaluated and at intervals afterwards, establish a calibration function (e.g. as specified in ISO 8466-1) bracketing the range of expected halide concentrations for the measurement. Example calibration solutions and their concentrations for fluorine, chlorine and bromine are shown Annex H (see Table H.2, Table H.3 and Table H.4).

For example, fluorine, chlorine and bromine calibration standards indicated in Table H.2, Table H.3 and Table H.4 can be prepared by adding 0,5, 1,0, 2,0, 4,0 and 8,0 ml of a 1 000 mg/l stock solution for each halide in a 1 000 ml volumetric flask with a pipette and filled with water (Clause 5 a)) up to the mark.

a) Prepare the calibration standard solutions (Clause 5 h)).

b) Inject the calibration standard solutions (Clause 5 h)) directly to the IC.

c) Identify the peaks for particular anions by comparing the retention times with those of the calibration standard solutions (Clause 5 h)). Deviation of retention times shall not exceed ±5 % within a batch.

d) 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 or heights. The calibration curve is generally used at a concentration of 0,5 mg/l to 8,0 mg/l. However, the concentration can be adjusted if the detection limit is lowered or raised.

### 8.6 Measurement of the sample

After development of the calibration curve, the method blank and the sample solution are measured. If the sample concentration is above the range of the calibration curve, the solution shall be diluted with water (Clause 5 a)) to the range of the calibration curve, if possible, to the middle range, and measured again. After every tenth sample run and at the end of each sample set, analyse a continuing calibration verification (CCV) standard. The percent recovery for halogen shall be between 90 % and 110 %. If the percent recovery for F, Cl and Br in the CCV standard falls outside of this range, the CCV standard should be re-analysed within 12 h. If the recovery is still out of range after re-analysis of the CCV standard, the analysis is stopped and maintenance shall be performed on the system to return it to optimal operating conditions. All samples loaded before the last successful CCV standard may be reported, but all samples after the last successful CCV standard shall be re-analysed with a new calibration. A suitable separation for each of the halide ions is shown in Figure H.1 which gives an example of a chromatogram of a standard solution (4 mg/l) by IC.

### 8.7 Interference

Substances that co-elute with the anions of interest are filled in the laboratory library and/or database. An anion of high concentration can interfere with other constituents if their retention times are close enough to affect the resolution of their peaks. Additional information on checked inferences is specified in ISO 10304-1:2007, Annex B.

## 9 Calculation

Concentration of halogen contained in the samples (peak area or peak height of halides (fluoride, chloride and bromide) ion) is calculated from the following formula:

$$\text{F, Cl and Br (mg/kg)} = [(A - Y) \times V_\text{a}] / (S \times M \times D_\text{g}) \quad (1)$$

or

$$\text{F, Cl and Br (mg/kg)} = [(A - Y) \times V_a] / (S \times V \times D_v) \qquad (2)$$

where

$A$ is the peak area or peak height of halides anion standard component;

$D_g$ is the dilution factor of the mass method, mass of the sample specimen/mass of the test specimen having the dilution medium added thereto, in g/g;

$D_v$ is the dilution factor of the volume method, mass of the sample specimen/volume of the test specimen having the dilution medium added thereto, in g/ml;

$M$ is the mass of the sample injected into the sample boat, in g;

$S$ is the slope of the calibration curve;

slope of the standard curve with area or height of the anion standard component (y axis) and concentration of the standard sample (x axis, in mg/l);

$V$ is the volume of the sample injected into the sample boat, M/ρ (density), in ml;

$V_a$ is the volume of the absorption solution, in ml;

$Y$ is the y intercept of the calibration curve;

y intercept of the standard curve with area or height of the anion standard component (y axis, µS/cm x min) and concentration of the standard sample (x axis, in mg/l).

## 10 Precision

When the values of two 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 below, the absolute difference between the two test results obtained will not exceed the repeatability limit *r* deduced by statistical analysis on the international inter-laboratory study (IIS 4A) and (IIS 3-2) results in more than 5 % of cases. See Table 4, Table 5 and Table 6.

**Table 4 – Fluorine results of international inter-laboratory study (IIS 4A)**

| | |
|---|---|
| Mean fluorine value (mg/l): | 575 |
| *r* (mg/l): | 40,62 |

**Table 5 – Chlorine results of international inter-laboratory study (IIS 4A)**

| | |
|---|---|
| Mean chlorine value (mg/l): | 102,2 |
| *r* (mg/l): | 9,43 |

**Table 6 – Bromine results of international inter-laboratory study (IIS4A and IIS 3-2)**

| | | |
|---|---|---|
| Mean bromine value (mg/l): | 94,8 | 896,2 |
| *r* (mg/l): | 18,97 | 137,49 |

See Annex E "Results of international inter-laboratory study (IIS4A and IIS 3-2)" for supporting data.

## 11 Quality assurance and control

### 11.1 General

The following parameters in Table 7 are taken for quality control:

**Table 7 – Acceptance criteria of items for quality control**

| Parameters | Concentration of mg/kg in test sample | Acceptance criteria |
|---|---|---|
| Calibration curve | | $R^2 \geq 0{,}995$ |
| Initial calibration verification (ICV) | e.g. 1 mg/l for F, Cl, Br | Recovery: 90 % to 110 % |
| Continuing calibration verification (CCV) | e.g. 1 mg/l for F, Cl, Br | Recovery: 90 % to 110 % |
| Method blank | | < MDL |
| Laboratory control sample (LCS) | Middle of calibration range solution or reference material | Recovery: 80 % to 120 % |
| Laboratory control sample duplicate (LCSD) | Middle of calibration range solution or reference material | Relative deviation < 20 % |

NOTE Initial calibration verification (ICV) is performed whenever a calibration curve is established, using a standard from a source different from the calibration standard.

One method blank should be analysed at least once for each batch of samples tested. A method blank which does not contain halogen can be used as a method blank sample.

One laboratory control sample (LCS) and laboratory control sample duplicate (LCSD) per batch should be analysed by means of either using certified reference material (CRM) or spiked with a specific concentration of halides in the blank matrix. The percent recovery for halogen shall be between 80 % and 120 %. If the percent recovery for F, Cl and Br in the LCS and LCSD standard falls outside of this range, the LCS and LCSD standard should be re-analysed within 12 h. If the recovery is still out of range after re-analysis of the LCS and LCSD standard, the analysis is stopped and maintenance shall be performed on the system to return it to optimal operating conditions

### 11.2 Limits of detection (LOD) and limits of quantification (LOQ)

In its simplest form, a limit of detection (LOD) or method detection limit (MDL) is typically described as the lowest amount or concentration of analyte in a test sample that can be reliably differentiated from zero for a given measurement system.

Instrument detection limits represent an instrument’s ability to differentiate low concentrations of analytes from "zero" in a blank or standard solution, and are commonly used by manufacturers to demonstrate the measurement capability of a system. Whilst instrument detection limits are useful, they are often considerably lower than a limit of detection representing a complete analytical method measurement process.

Complete analytical method detection limits are most appropriately determined experimentally by performing replicate, independent measurements on low-level or fortified sample matrices (e.g. plastic) carried out through the entire test procedure, including sample digestion or extraction. A minimum of six replicates and analyte concentrations of 3 to 5 times the estimated method detection limit have been suggested as suitable for this analysis. The complete method detection limit for an entire test procedure is determined by multiplying the standard deviation of the replicates by an appropriate factor. The International Union of Pure and Applied Chemistry (IUPAC) recommends a factor of 3 for a minimum of six replicates, while US 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). See Table 8.

All analyses used to calculate an MDL should be consecutive.

**Table 8 – Student's $t$ values used for calculation of method detection limit ($\mathrm{MDL} = t \times s_{n-1}$)**

| **Number of samples** | **Student's $t$-statistic** (99 % confidence) |
|---|---|
| 6 | 3,36 |
| 7 | 3,14 |
| 8 | 3,00 |
| 9 | 2,90 |
| 10 | 2,82 |

The limit of quantification (LOQ) or estimated quantitation limit for a given measurement system is typically described as the lowest concentration that can be reliably determined within specified or acceptable limits of precision during routine laboratory operating conditions. The acceptable precision limit is often defined as 10 % relative standard deviation or simply expressed as a fixed multiple (2 to 10) of the method detection limit.

## 12 Test report

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

- the sample;
- the International Standard used (including its year of publication);
- the method used (if the standard includes several);
- the result(s), including a reference to Clause 9;
- any deviations from the procedure;
- any unusual features observed;
- the date of the test.

# Annex A
(informative)

# Screening for fluorine, chlorine, bromine and iodine in polymers and electronics by oxygen bomb combustion-ion chromatography

## A.1 General

Annex A specifies a combustion method for the screening of halogen (fluorine, chlorine, bromine and iodine) contents in polymers and electronics by oxygen bomb combustion with ion chromatography. This method is applicable to solid, pasty and liquid samples containing more than 0,025 g/kg of halogen contents.

The limit of detection depends on the element, matrix and determination technique used. Insoluble halogens in the original sample or produced during the combustion step are not completely determined by this method.

## A.2 Principle

The sample is oxidized by oxygen bomb combustion in a closed system under pressure. Halogenated (fluorine, chlorine, bromine and iodine) compounds are converted to halides which are absorbed and/or dissolved in an absorption solution. In general, this method is applicable for concentrations over 0,025 g/kg depending on the element, matrix and the determination technique. It may be used for aqueous samples or samples that burn with difficulty, which involves the use of a burning aid.

## A.3 Reagents and materials

All reagents shall be at least of analytical grade and suitable for their specific purposes. Particularly, they shall not contain halogen above MDL values.

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

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

c) Hydrazine, a mass fraction of 35 % in $H_2O$, ($N_2H_4$), (hydrazine is only required for iodine testing).

WARNING – Hydrazine is an inorganic compound with the chemical formula $N_2H_4$ (also written $H_2NNH_2$). It is a colourless flammable liquid with an ammonia-like odour. Therefore, the operator shall wear goggles and gloves and shall work under a fume hood when handling this reagent. Hydrazine is highly toxic and dangerously unstable unless handled in solution.

d) Absorption solution – for the determination of halogen, the nature and concentration of which may depend on the end-determination technique and on the expected concentrations of halogen. For example:

- water (a); or
- 0,3 mol/l potassium or sodium hydroxide solution: dissolve 16,8 g of KOH or 12,0 g of NaOH pellets in water (a) and dilute to 1 l; or
- carbonate/bicarbonate solution: dissolve 2,52 g sodium bicarbonate $NaHCO_3$ and 2,54 g sodium carbonate $Na_2CO_3$ in water (a) and dilute to 1 l.

NOTE Ascorbic acid and large amounts of nitrate can interfere with early eluting halogen when detected by ion chromatography.

e) Oxygen – free of combustible material, available at a pressure of 3 MPa to 4 MPa (30 atm to 40 atm) (e.g. medical grade).

f) Burning aids (e.g. paraffin).

g) Aluminium oxide, $Al_2O_3$ – neutral, particle size is less than 200 µm, pre-heated to 600 °C.

h) Reference materials – ensure recovery rates fall between 90 % to 110 %.

i) Gelatine or aceto-butyrate capsules.

## A.4 Apparatus

a) Oxygen bomb (see Figure A.1), with a capacity of not less than 200 ml and equipped with a purging system.

   This bomb shall not leak during testing and shall permit a quantitative recovery of the liquid. Its inner surface may be made of stainless steel or any other material that will not be affected by combustion gases. Materials used for the bomb assembly, such as the head gasket and wire insulation, shall be heat and chemical action resistant and shall not undergo any reaction that will affect the results. Bombs with pitted surfaces should never be used because of their tendency to retain halogen. After repeated use of the bomb, a film may build up on the inner surface. This dullness should be removed by periodically polishing the bomb according to the manufacturer's instructions.

   NOTE 1 The internal surface of some calorimetric bombs can have a ceramic coating and/or platinum sample cups, which have better resistance to corrosion.

b) Sample cup, platinum or stainless steel or quartz.

c) Firing wire, platinum or stainless steel.

d) Ignition circuit, capable of supplying a sufficient current to ignite the sample without melting the wire.

e) Absorption flask, (e.g. 200 ml test tube equipment with a glass frit dip-tube for bubbling the combustion gases).

f) Usual laboratory equipment such as homogenization devices (e.g. mixers, stirrers, grinders, mills), analytical balance (accurate at least to 0,1 mg).

g) Safety precautions.

The bomb shall not contain any organic residue (vapours of organic solvents, grease, etc.).

Follow the manufacturer's instructions, especially with regard to the oxygen pressure inside the bomb and the maximum allowable calorific value of the test portion.

NOTE 2 Combustion of 1 g of hydrocarbons such as lubricating oil produces about 40 kJ (the calorific powers of benzoic acid and isooctane are about 26 MJ/kg and 48 MJ/kg respectively).

## A.5 Sampling

The test sample is prepared according to IEC 62321-2. The solid sample shall be cut into small pieces (approximately less than 1,5 mm × 1,5 mm × 1,5 mm) using scissors or shears (Clause 6 b). During preparation of the test sample the use of halogenated (F, Br, Cl) polymers should be avoided. Drying the laboratory sample can be carried out for homogenization purposes if the sample, according to the accuracy of the method, contains only negligible amounts of halogen compounds volatile at the temperature intended for the drying process.

NOTE Heterogeneous moist or paste like samples can be mixed with aluminium oxide (Clause A.3.g)) until granular material is obtained and then reduced to a granular powder, preferably with a particle size less than 200 µm. In this case, the ratio of aluminium oxide to sample is incorporated into the calculation of halogen contents and burning aids are added if necessary.

## A.6 Procedure

### A.6.1 General

Before each series of determinations, a blank and quality check shall be carried out. The blank test is performed by quantifying the blank solution (Clause 5 g)) which is prepared by following exactly the same procedure described above (Clause 5 h)) but without the actual sample.

Alternately running samples that are high and low in halogen content is to be avoided whenever possible as it is difficult to rinse the last traces of ions from the internal surfaces of the apparatus and a tendency for residual elements to carry over from sample-to-sample has been observed. When a sample high in halogen content preceded a sample low in concentration, the test on the second sample is to be repeated and one or both of the low values thus obtained shall be considered suspect if they do not fall within the limits of repeatability of this method. It is good practice to insert a blank between each sample, unless the series of samples being analysed has similar expected concentrations. When the composition or homogeneity of the sample is unknown, it is better to carry out the analysis in duplicate or triplicate and report the mean result from all determinations.

In the case of significant carry over it is recommended to collect the exhaust gases of the sample and the following method blank in one absorption liquid. After that, determine the degree of contamination (carry over) and take measures to reduce the concentration for cleaning.

### A.6.2 Choice of the absorption solution

The combustion gases can be collected inside and/or outside the bomb in an absorption solution. Water is generally used when low concentrations of halogen are expected (usually, less than 10 g/kg). It is recommended to add 0,5 ml of hydrogen peroxide solution (Clause A.3 b)) to the absorption solution.

The pH control of the absorption solution is very important to control for the analysis of iodine. Therefore, it is recommended that the absorption solution is prepared at a concentration of 90 mg/kg of $H_2O_2$ and then hydrazine solution is added to adjust the pH to approximately 10. (Add a mass fraction of 35 % hydrazine solution in water to reach a pH of 10 as measured with a pH meter or pH paper).

In the case of iodine, even though it is a member of the same elemental family as F, Cl and Br; it is more likely to be oxidized to the neutral form ($I_2$) because of its lower electron affinity. The absorbing liquid (water) is neutral, but when the sample is burned, the combusted gases containing halogens are captured by the absorbing liquid and the resulting solution becomes acidic if no additional materials are added to the water used to capture the released halogens. However, hydrogen iodide in the presence of water will decompose to form elemental iodine ($I_2$) which cannot be detected by IC and should be reduced back to iodide ($I^-$). So, hydrazine (Clause A.3.c), which is a good reducing agent for iodine and is also weakly alkaline, is an excellent choice as a reagent added to the absorbing solution. So, it is recommended that the absorbent be made of alkaline.

Alkaline solution shall be used for samples with high halogen content to ensure neutralization of the acid compounds produced.

### A.6.3 Preparation of the bomb

The bomb is prepared according to the manufacturer's instructions and the free ends of the firing wire (Clause A.4 c)) attached to the electric terminals of the ignition circuit (Clause A.4 d)). If using an absorption solution inside the bomb, add 10 ml of this absorption solution (Clause A.3 d)) with or without the hydrogen peroxide (Clause A.3 b)) wetting the sides of the bomb (Clause A.4 a)).

The sample cup shall not be in contact with the absorption solution. Depending on the bomb design, and/or the expected concentration range of the analytes of interest, it may be necessary to adapt the amount of the absorption or trap the combustion gases in an external absorption flask (see Clause A.3 e)).

### A.6.4 Combustion

Depending on halogen content and the calorific value in the sample (obtained by determinization method), 0,05 g to 1 g of the sample is weighed (to the nearest 0,1 mg) into the sample cup (Clause A.4 b). Samples that burn with difficulty (e.g. mineral samples or samples with high water content), may require the addition of a burning aid (Clause A.3 f)). Liquid samples may be weighed in a capsule (Clause A.3 i)). To avoid stirring up of the sample when filling the bomb with oxygen, powdery samples may be covered with inert material (e.g. aluminium oxide (Clause A.3 g)) or soaked with burning aid (Clause A.3 f)), depending on halogen content. Depending on the type of bomb, the total sample mass plus enhancer shall not exceed 1 g to 1,5 g to avoid dangerous high pressure and possibly rupturing the bomb.

The combined energy from sample and burning aids (Clause A.3 f)) is important to recover the halogen from the sample compounds. Hence it may be necessary to optimize the enhancer/sample amount ratio. Place the sample cup in position and arrange the firing wire (Clause A.4 c)) so that it is just in contact with the sample but not touching the sample cup (Clause A.4 b)).

NOTE Some operators use a nylon thread or cotton wick and loop it around the wire so that its ends immerse directly in the liquid sample or is in contact with the solid sample.

Assemble the bomb and tighten the cover securely. Admit oxygen (Clause A.3 e)) carefully (to avoid blowing the sample from the cup) to a pressure below the safety pressure specified by the manufacturer. Connect the terminals to the open electrical circuit. Close the circuit to ignite the sample. Let the bomb cool to ambient temperature, for example in a water bath.

### A.6.5 Collection of halides

When relatively high levels of halogen (e.g. over 20 g/kg) are expected, and/or when there is no absorption solution inside the bomb, connect the exit of the bomb to an absorption flask filled with 20 ml of the same absorption solution (Clause A.3 d)) used in Clause A.3 d) and release the pressure at a slow, uniform rate so that only small bubbles are observed in the absorption tube.

If high levels of halogen are expected, it is highly recommended to measure a blank value between the samples.

The volume of the absorption solution depends on the type and volume of the absorption flask. In other cases, this collection of combustion gases in the absorption flask is not necessary and it is possible to release the pressure quickly. Open the bomb and examine the content: if traces of sooty deposits are found, discard the determination and repeat again with burning aid and/or with a smaller test portion.

If pink vapours are seen, discard the determination and repeat using precautions to trap all the iodine (e.g. smaller test portion and/or addition of ascorbic acid). Rinse the interior of the bomb, terminals, inner surface of the bomb cover and the sample cup thoroughly with 20 ml of absorption solution (see A.6.2).

Some oxygen bombs are connected to a demineralized water supply, which enables automatic rinsing of the bomb interior before opening. In this case, the rinsing water is pushed by weak overpressure out of the bomb and combined with the absorption solution. Transfer the solution into a volumetric flask. Dilute to the mark with water (Clause A.3 a)) or absorption solution (Clause A.3 c)). The choice of the final volume depends on the concentration of halogen as well as on the final method used for analysis.

### A.6.6 Cleaning procedure

Remove any residual fuse wire from the bomb terminals and the cup. Using hot water, rinse the interior of the bomb, sample cup, terminals and the inner surface of the bomb cover. Thoroughly rinse the bomb, cover and cup with water (Clause A.3 a)).

## A.7 Ion chromatographic analysis

See 8.2 to 8.6.

## A.8 Calculation

Calculate the halogen content in g/kg of waste using Formula (A.1):

$$X = (C \times V) / 1\,000 \times m \tag{A.1}$$

where

$X$ is the element (fluorine, chlorine, bromine and iodine) content in the test sample in grams per kilogram (g/kg);

$C$ is the concentration expressed in milligram per litre (mg/l) of this fluorine, chlorine, bromine and iodine content in the absorption solution;

$V$ is the final volume of the absorption solution, expressed in millilitres (ml);

$m$ is the mass of the test portion, expressed in grams (g).

If the sample contains inert materials, for example aluminium oxide, which have been added during sample preparation, the ratio of this addition should be incorporated into the calculation.

The element content resulting from Formula (A.1) is calculated on a dry matter basis according to Formula (A.2):

$$X_\mathrm{d} = X \times 100 / W_\mathrm{dw} \tag{A.2}$$

where

$X_\mathrm{d}$ is the element (fluorine, chlorine, bromine and iodine) content calculated on dry matter in grams per kilogram (g/kg);

$W_\mathrm{dw}$ is the dry matter of the original sample, according to Clause A.5, as mass fraction in per cent (%).

These results may also be calculated and reported in milligram per kilogram (mg/kg) or in a mass fraction of per cent. Fluorine, chlorine and bromine content is usually determined on an undried sample but is always reported on dry matter.

## A.9 Quality assurance and control and test report

Information on control measurements and on the test report is given in Clauses 11 and 12.

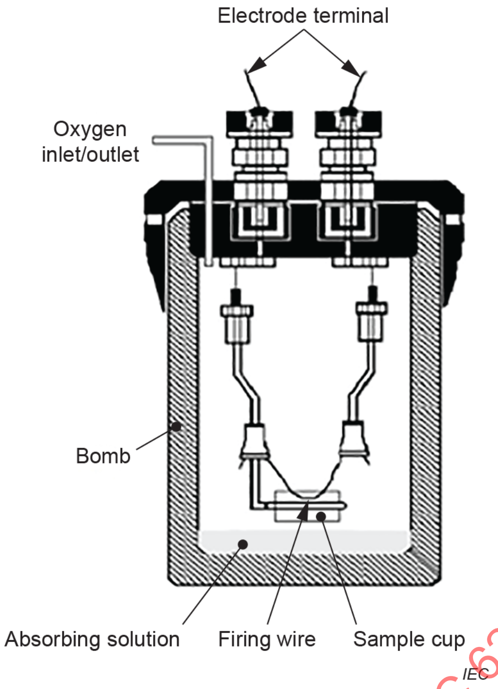

Figure A.1 – Example of oxygen bomb combustion device

# Annex B
(informative)

# Screening for fluorine, chlorine, bromine and iodine in polymers and electronics by oxygen flask combustion-ion chromatography

## B.1 General

Annex B specifies a combustion method for screening of halogen (fluorine, chlorine, bromine and iodine) contents in materials by combustion in a closed system containing oxygen (oxygen flask combustion (Schoeniger flask)), and the subsequent analysis of the combustion product using ion chromatography.

The method is applicable to solid, pasty and liquid samples containing more than 0,25 g/kg of halogen. The limit of detection depends on the element, matrix and determination technique used. Insoluble halogen in the original sample or produced during the combustion step are not completely determined by this method.

## B.2 Principle

The sample is oxidized by combustion in a closed system (heavy walled glass flask – Schoeniger apparatus – filled with oxygen). Halogen (fluorine, chlorine, bromine and iodine) containing compounds are converted to fluorides, bromides, chlorides and iodides which are absorbed and/or dissolved in an absorption solution. Ion chromatography may be used for determining halogen concentrations in the absorption solution.

When using a smaller amount of sample, more attention has to be paid on homogenization. In general, it is applicable to solid, pasty and liquid samples containing more than 0,25 g/kg of halogen, depending on the matrix and determination technique.

## B.3 Reagents and materials

The following reagents and materials apply:

a) filter paper wrappers, e.g. 3 cm × 3 cm with a 3,5 cm × 1 cm extension (see Figure B.2);

b) all other reagents and control mixtures are mentioned in Clause A.3.

## B.4 Apparatus

The following apparatus shall be used:

a) Combustion flask (see Figure B.1), chemically resistant heavy-walled, 500 ml to 1 000 ml Erlenmeyer flask equipped with a slightly enlarged neck, fitted with a standard-taper ground-glass stopper.

   The flask shall not contain any residue or vapours of organic solvents used for rinsing and drying. If these materials are present, a violent explosion can take place when the burning filter paper is introduced. After inserting the flaming paper into the flask, the stopper shall be held securely. A slight pressure drop inside the flask during the initial stage of burning normally happens, while a slight vacuum is formed after complete absorption of the combustion products. Combustion shall be carried out under a fume hood and the operator shall wear safety goggles and gloves.

b) Platinum gauze sample carrier sealed into another standard taper ground glass stopper (see Figure B.1).

c) Usual laboratory equipment including homogenization devices (e.g. mixers, stirrers, grinders, mills) and an analytical balance (accurate at least to 0,1 mg), etc.

## B.5 Sampling

### B.5.1 General

The test sample is prepared according to IEC 62321-2. Between 10 mg and 50 mg of homogeneous (or homogenized) sample are weighed to the nearest 0,1 mg. The weighed sample shall not contain more than 10 mg to 20 mg of halogen.

### B.5.2 Solid and paste-like samples

Fold the filter paper (Clause B.3 a)) used for wrapping the sample to form a boat as shown in Figure B.2. Wait several minutes before weighing to allow the filter paper to equilibrate to the conditions of humidity of the room and record the tare weight to 0,1 mg. Using a small spatula, place the estimated amount of sample on the tared paper and reweigh to 0,1 mg. Then, using the spatula, fold the filter paper as shown in Figure B.2. Squeeze the packed filter with clean tweezers.

Place the sample in the platinum sample carrier (Clause B.4 b)).

### B.5.3 Liquid samples

Placing small-size drops on the paper, introduce the estimated amount of sample into a tared capsule (Clause A.3 i)) containing a small piece of folded filter paper. Immediately reweigh the capsule to 0,1 mg. Wrap the capsule in the filter paper (Clause B.3 a)) as in the case of solid samples and insert in the platinum sample carrier (Clause B.4 b)).

## B.6 Procedure

### B.6.1 General

Before each series of determinations, a method blank and quality check (i.e. initial calibration verification and continuing calibration verification, refer to Table 7) shall be carried out. The blank test is performed by quantifying the blank solution (Clause 5 g)) which is prepared by following exactly the same procedure described above (Clause 5 h)) without the actual sample. Running samples that are alternately high and low in halogen content is to be avoided whenever possible as it is difficult to rinse the last traces of ions from the internal surfaces of the apparatus and a tendency for residual elements to carry over from a sample to the next sample has been observed. When a sample high in halogen content precedes a sample low in concentration, the test on the second sample shall be repeated and one or both of the low values thus obtained should be considered suspect if they do not fall within the limits of repeatability of this method. It is good practice to insert a method blank between each sample, unless the series of samples being analysed has similar expected concentrations. When the composition or homogeneity of the sample is unknown, it is better to carry out the analysis in duplicate or triplicate and report the mean result from all determinations.

In the case of significant carry-over of the analyte, it is recommended to collect the exhaustion gases of the sample and the following blank sample in one absorption liquid.

### B.6.2 Choice of the absorption solution

See A.6.2.

### B.6.3 Combustion

Add 10 ml of absorption solution (Clause 5 k)) into the combustion flask (Clause B.4 a)). Flush the flask with oxygen for 1 min, keeping the gas delivery tube near the bottom of the flask to displace the air. Seal the flask with a standard stopper.

Ignite the filter paper packet containing the sample, remove the regular stopper, and quickly replace it by inserting the stopper (Clause B.4 b)) with the burning paper into the flask. Immediately invert the stoppered flask so that the absorbing liquid forms a tight seal around the stopper.

NOTE Systems with electrical remote ignition are also applicable.

As shown in Figure B.1, the flask shall be held so that the open part of the platinum sample carrier faces upward so that the sample cannot fall out during combustion. After the combustion is complete, allow the inverted flask to cool for 1 min, and then vigorously shake it for 3 min to absorb the combustion products. Allow to stand for 5 min in the normal position. Carefully pipette 10 ml of the absorption solution (Clause 5 k)) into the neck-well of the flask. Lift the stopper slightly to allow the liquid to be sucked into the flask. Then let the stoppered flask gently cool for 15 min. Transfer the contents of the flask into a volumetric flask, dilute to the mark with water (Clause A.3 a)) or absorption solution (Clause 5 k)). The choice of the final volume depends on the expected concentration of the solution and on the end-method of analysis.

## B.7 Ion chromatographic analysis, calculation, quality assurance and control and test report

See Clauses A.7, A.8 and A.9.

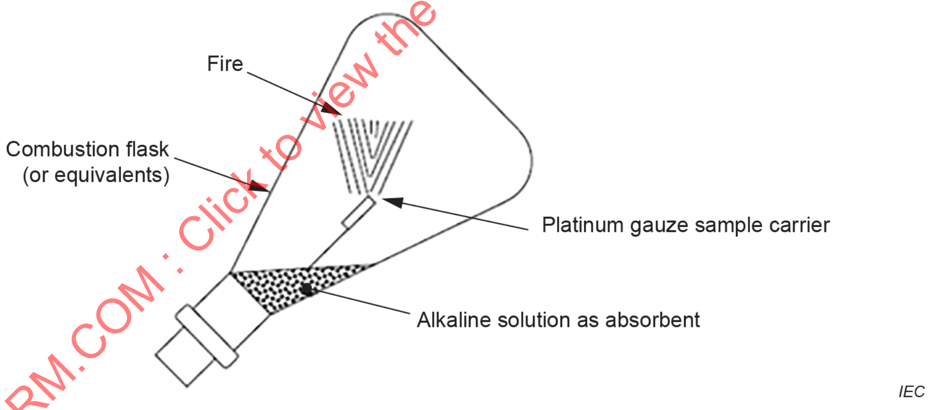

Figure B.1 – Example of oxygen flask combustion device

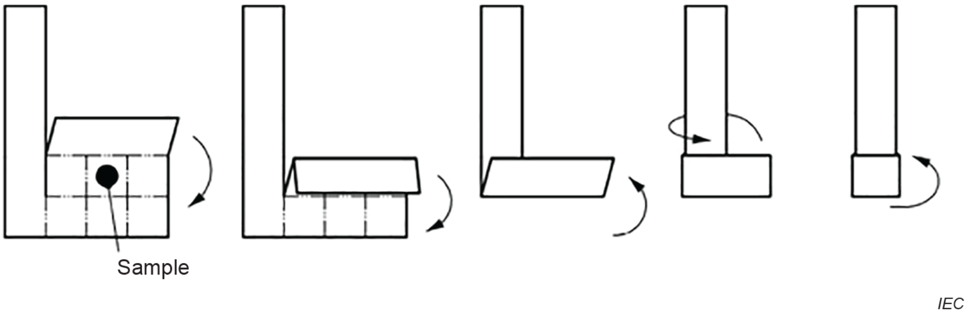

Figure B.2 – Example of wrapping of sample

# Annex C
(informative)

## Example of a combustion device and IC system

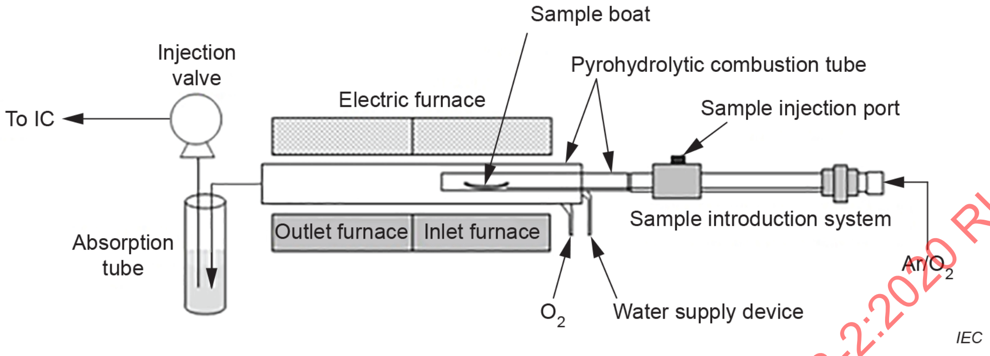

Figure C.1 – Example of a combustion device connected to an ion chromatograph (IC)

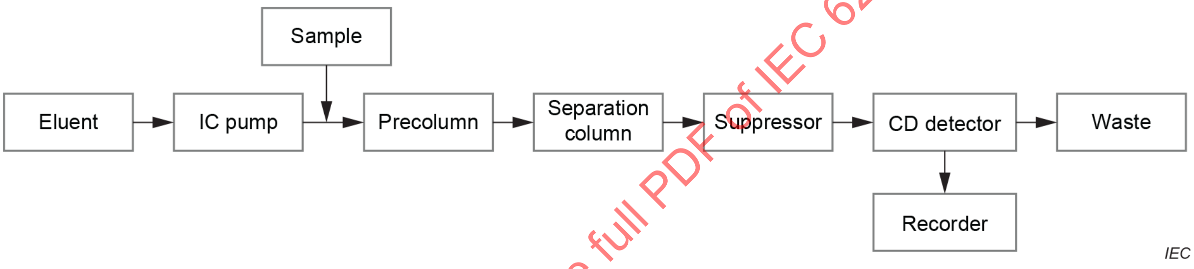

Figure C.2 – Example of ion chromatographic system

# Annex D
(informative)

# Screening for iodine in polymers and electronics by combustion-ion chromatography (C-IC)

## D.1 General

Annex D specifies a combustion method for the screening of iodine in polymers and electronics by combustion-ion chromatography.

## D.2 Principle

Generally, the iodine analysis method in polymers and electronics is the same as that described in the normative section of this document. However, in the case of iodine, recovery is ensured only when alkaline pH conditions (8 to 10) in the absorbent solution are used. Therefore, in this informative annex, iodine analysis is carried out specifically using this principle.

## D.3 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. All reagents used shall not contain observable amount of halides.

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

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

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

c) Hydrazine, a mass fraction of 35 % in $H_2O$, ($N_2H_4$).

WARNING – Hydrazine is an inorganic compound with the chemical formula $N_2H_4$ (also written $H_2NNH_2$). It is a colourless flammable liquid with an ammonia-like odour. Therefore, the operator shall wear goggles and gloves and shall work under a fume hood when handling this reagent. Hydrazine is highly toxic and dangerously unstable unless handled in solution.

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

e) Argon, carrier gas minimum of 99,9 % purity.

NOTE 1 Purification scrubbers such as moisture (molecular sieve) and hydrocarbon trap filters (activated charcoal or equivalent) can be used to ensure the removal of contamination.

f) Oxygen, combustion gas of minimum of 99,6 % purity.

g) Burning aids, tungsten oxide ($WO_3$) or iron oxide ($Fe_3O_4$), etc. Minimum particle size of burning aids shall be less than 50 μm. $WO_3$ and $Fe_3O_4$ purity of more than 90 % is required. And also, before using burning aids, it is necessary to check if the halogens contained or not are below the MDL level by using a method blank.

h) Blank solution, fill a volumetric flask (e.g. 100 ml flask) with water (Clause D.3 a)).

i) 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, for example 5 to 10 calibration solutions distributed as evenly as possible over the expected working range.

NOTE 2 The solution is either prepared from a primary standard or calibrated.

j) Eluents

Eluents are used as a solvent in separating materials in elution. The choice of eluent depends on the chosen column and detector (seek advice from 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.

k) Internal standard (IS) solution (optional)

An internal standard can be used to correct analytical errors.

The internal standard used in the absorption solution should not contain any of the sample components, and should be selected based on the condition of column and mobile phase (e.g. phosphate, citric acid, oxalic acid, methane sulfonic acid).

l) Absorption solution, used for trapping halogen – 3 ml of $H_2O_2$ (Clause D.3 b)), is poured into a 1 000 ml volumetric flask and water is added to the scale and mixed. This solution contains 900 mg/kg of $H_2O_2$ depending on testing target samples. Especially, the pH control of the absorption solution is very important to analyse iodine. Therefore, it is recommended that the absorption solution is prepared at a concentration of 90 mg/kg of $H_2O_2$ and then hydrazine solution is added to adjust the pH to approximately 10. (Add a mass fraction of 35 % hydrazine solution in water to reach a pH of 10 with a pH meter or pH paper.)

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, use a minimum amount of hydrogen peroxide to diminish IC peak identification issues.

In the case of iodine, even though it is a member of the same elemental family as F, Cl and Br, it is more likely to be oxidized to the neutral form ($I_2$) because of its lower electron affinity. The absorbing liquid (water) is neutral, but when the sample is burned, the combusted gases containing halogens are captured by the absorbing liquid and the resulting solution becomes acidic if no additional materials are added to the water used to capture the released halogens. However, hydrogen iodide in the presence of water will decompose to form elemental iodine ($I_2$) which cannot be detected by IC and shall be reduced back to iodide ($I^-$). So, hydrazine (Clause D.3.c), which is a good reducing agent for iodine and is also weakly alkaline, is an excellent choice for a reagent added to the absorbing solution. Reference materials – A reference material can be used to ensure recovery rates of the halogen fall within 90 % to 110 %. A certified reference material is the best choice for that purpose. If a certified reference material is not available, a reference material can be prepared by mixing certain amounts of the iodine compounds, diluting with cellulose or aluminium oxides to obtain a suitable concentration, and then pulverizing the mixture to homogenize.

## D.4 Apparatus

The following apparatuses shall be used.

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

b) Scissors.

c) Combustion system – in general, it 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. The auto sampler may be used as long as the accuracy and performance of the method are not degraded.
   2) Sample boat – the boat is generally made of quartz, nickel, ceramics, platinum or stainless steel.
   3) Sample introduction system – the system provides a sampling port for the 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 have the quartz or ceramic tube installed inside of the device 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 of high concentration, a trap column should be installed between the absorption tube and the combustion tube.
   6) Water supply device – this device is capable of delivering grade 1 water (Clause D.3 a)) to the combustion tube at a controlled rate sufficient to provide a pyrohydrolytic environment.
   7) Absorption tube – a size of glass pipe capable of maintaining about one-half of the total volume by putting 10 ml to 20 ml of the absorption solution. This has the configuration that the discharge gas pipe of the heating furnace is submerged in the absorption solution to absorb the discharged gas. Further, it has the configuration that the absorption solution of the ion chromatograph can be injected through the connecting device. For preventing contamination from other samples, the absorption tube should be washed after sample analysis.

d) Ion chromatographic system – in general, it consists of the following components (see Figure C.2):

## D.5 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 (Clause D.4 b)).

b) Liquid sample

   For sampling of liquid sample, sampling should be performed after rinsing the inside of the pipette a few times with the sample liquid.

## D.6 Procedure

### D.6.1 Combustion

General combustion procedures by using an electric furnace are described in IEC 60754-3:2018, Clause 7 (Test procedure).

a) After a sample boat is heated sufficiently in the electric furnace to remove the contaminants, remove the sample boat from the furnace with clean tongs, let it cool to room temperature, then normally 10 mg to 100 mg of samples are weighed with a precision of 0,1 mg and loaded into the sample boat. If samples are difficult to combust (e.g. flux, solder paste), a burning aid (e.g. $WO_3$) has to be used. Generally, a 5 to 1 ratio of burning aids to sample is sufficient. If any burning aid is being used, apply approximately 100 mg of it in a thin layer over the surface of the sample boat, evenly spread the weighed sample on it, and then cover the sample with approximately 300 mg of the burning aid.

b) It is then heated in the combustion furnace for 10 min to 20 min together with argon, oxygen and water by using the sample injection device located at the centre of the quartz tube of the combustion furnace. An example of combustion conditions is described in Table F.1. If the combustion boat shows evidence of soot generation or unburned sample particles, the combustion shall be judged to be insufficient and the procedure shall be repeated. The contaminated area shall be cleaned thoroughly before repeating the procedure.

c) Upon completion of combustion operations, wash the tubing at the combustion gas discharge outlet, and pour all washing solutions into the absorbing bottle for measuring.

d) For the blank test, perform a similar operation without inserting the sample or a blank boat, and use this absorption solution obtained as the blank solution. Follow the procedure described in D.5.3.

NOTE If the combustion furnace and IC are connected and operated automatically, the absorption solution absorbing the combustibles can be injected into the IC.

### D.6.2 IC analysis

The general rules on ion chromatographic analysis as set out in ISO 10304-1 shall be followed:

a) Set up the IC according to the instrument manufacturer’s instructions or laboratory standard operation procedure (SOP). Typical operating conditions for IC are shown in Table H.1.

b) Run the eluent and wait for a stable baseline.

c) Perform the calibration as described in D.6.5. Measure the samples, calibration (Clause D.6.5)) and at least two blank solutions as described in D.6.5.

Operating conditions should be selected and stabilized according to the device manufacturer's instructions or to the standard operation procedure (SOP).

### D.6.3 Blank test

A blank test is performed by quantifying and with at least two blank solutions which are prepared by following exactly the same procedure described in Clause 5 h) but without the actual sample. A blank solution (Clause D.3 h)) which does not contain halides (lower than MDL, or normally 0,1 mg/l) can be used as a method blank sample.

### D.6.4 Cleaning and recalibration

Clean any coke or soot as per the manufacturer’s instructions. After cleaning, assemble the apparatus and check for leaks. Run a check standard to determine if the instrument needs to be recalibrated.

### D.6.5 Calibration

A calibration curve shall be developed for quantitative analysis. The calibration curve is prepared by using a standard solution of iodide.

When the analytical system is first evaluated and at intervals afterwards, establish a calibration function (e.g. as specified in ISO 8466-1) bracketing the range of expected iodine concentrations for the measurement.

For example, iodine calibration standards can be prepared by adding 0,5, 1,0, 2,0, 4,0 and 8,0 ml of a 1 000 mg/l stock solution in a 1 000 ml volumetric flask with a pipette and filled with water (Clause 5 a)) up to the mark.

a) Prepare the calibration standard solutions (Clause D.3 i)).

b) Inject the calibration standard solutions (Clause D.3 i)) directly to the IC.

c) Identify the peaks for particular anions by comparing the retention times with those of the calibration standard solutions (Clause D.3 i)). Deviation of retention times shall not exceed ±5 % within a batch.

d) 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 or heights. For example, proceed as follows for the range of 0,5 mg/l to 8,0 mg/l.

## D.7 Measurement of the sample

After development of the calibration curve, the laboratory reagent blank and the sample solution are measured. If the sample concentration is above the range of the concentration curve, the solution shall be diluted with water (Clause D.3 a)) to the range of the calibration curve, if possible to the middle range, and measured again. Measurement precision is checked with standard calibration solutions at regular intervals (such as once every 10 samples). If necessary, a calibration curve is developed again.

The obtained chromatogram should exhibit the same separation for each of the halide ions as shown in Figure H.1 which gives an example of a chromatogram of a standard solution (4 mg/l) by IC. Additional IIS results (Difference in recovery rate of iodine according to adsorbents ($H_2O_2$, Hydrazine)) are shown in Table G.4.

## D.8 Interference

Substances that co-elute with the anions of interest are filled in the specific laboratory library. An anion of high concentration can interfere with other constituents if their retention times are close enough to affect the resolution of their peaks. Additional information on checked inferences is specified in ISO 10304-1:2007, Annex B.

## D.9 Calculation

Concentration of iodine contained in the samples (peak area or peak height iodide ion) is calculated from the following formula:

$$\text{I (mg/kg)} = [(A - Y) \times V_a] / (S \times M \times Dg) \quad \text{(D.1)}$$

or

$$\text{I (mg/kg)} = [(A - Y) \times V_a] / (S \times V \times D_v) \quad \text{(D.2)}$$

where

$A$ is the peak area or peak height of the iodide anion standard component;

$D_g$ is the dilution factor of the mass method, mass of the sample specimen/mass of the test specimen having the dilution medium added thereto, in g/g;

$D_v$ is the dilution factor of the volume method, mass of the sample specimen/volume of the test specimen having the dilution medium added thereto, in g/ml;

$M$ is the mass of the sample injected into the sample boat, in g;

$S$ is the slope of the calibration curve,

slope of the standard curve with area or height of the anion standard component (y axis) and concentration of the standard sample (x axis, in mg/l);

$V$ is the volume of the sample injected into the sample boat, $M/\rho$ (density), in ml;

$V_a$ is the volume of the absorption solution, in ml;

$Y$ is the y intercept of the calibration curve,

y intercept of the standard curve with area or height of the anion standard component (y axis, μS/cm × min) and concentration of the standard sample (x axis, in mg/l).

# Annex E
(informative)

## Results of international interlaboratory study (IIS 4A and IIS 3-2)

### Table E.1 – Mean results and recovery rates for bromine obtained in the IIS4A study using C-IC

| Sample number | Sample description | Certified value of Br<br>mg/kg | Mean result of Br<br>mg/kg | Standard deviation<br>mg/kg | Recovery rate[a]<br>% | Range of recovery rate<br>% | Total number of data sets[b] | Number of data sets used |
|---|---|---|---|---|---|---|---|---|
| IIS4A-04 | KRISS CRM<br>113-01-015 (acrylonitrile butadiene styrene) | 890 | 896 | 47,2 | 101 | 90 to 111 | 10 | 9 |
| IIS4A-07 | ERM CRM<br>680k<br>(poly ethylene) | 96 | 95 | 6,9 | 99 | 84 to 112 | 10 | 10 |

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

### Table E.2 – Statistical bromine data for IIS 4A results using C-IC

| Sample | Parameter | $m$<br>mg/kg | $v$<br>mg/kg | $N$ | s($r$)<br>mg/kg | $r$<br>mg/kg | s($R$)<br>mg/kg | $R$<br>mg/kg |
|---|---|---|---|---|---|---|---|---|
| IIS4A-04 | Br | 896,2 | 890 | 25 | 12,14 | 34,00 | 49,10 | 137,49 |
| IIS4A-07 | Br | 94,8 | 96 | 27 | 2,14 | 6,01 | 6,78 | 18,97 |

**Key**

$m$ = arithmetic mean of test results

$v$ = expected value

$N$ = number of accepted results

s($r$) = repeatability standard deviation

$r$ = repeatability limit

s($R$) = reproducibility standard deviation

$R$ = reproducibility limit

### Table E.3 – Mean results and recovery rates for fluorine obtained in the IIS 3-2 study using C-IC

| Sample number | Sample description | Estimated value of F<br>mg/kg | Mean result of F<br>mg/kg | Standard deviation<br>mg/kg | Recovery rate[a]<br>% | Range of recovery rate<br>% | Total number of data sets[b] | Number of data sets used |
|---|---|---|---|---|---|---|---|---|
| IIS3-B02 | Custom made sample (polycarbonate) | 575 | 535,2 | 82,5 | 93 | 76 to 121 | 18 | 18 |

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

### Table E.4 – Statistical fluorine data for IIS 3-2 results using C-IC

| Sample | Parameter | $m$<br>mg/kg | $v$<br>mg/kg | $N$ | s($r$)<br>mg/kg | $r$<br>mg/kg | s($R$)<br>mg/kg | $R$<br>mg/kg |
|---|---|---|---|---|---|---|---|---|
| IIS3-B02 | F | 535,2 | 575 | 18 | 14,5 | 40,62 | 87,67 | 245,48 |

**Key**

$m$ = arithmetic mean of test results

$v$ = expected value

$N$ = number of accepted results

s($r$) = repeatability standard deviation

$r$ = repeatability limit

s($R$) = reproducibility standard deviation

$R$ = reproducibility limit

### Table E.5 – Mean results and recovery rates for chlorine obtained in the IIS 3-2 study using C-IC

| Sample number | Sample description | Certified value of Cl<br>mg/kg | Mean result of Cl<br>mg/kg | Standard deviation<br>mg/kg | Recovery rate[a]<br>% | Range of recovery rate<br>% | Total number of data sets[b] | Number of data sets used |
|---|---|---|---|---|---|---|---|---|
| IIS3-A01 | ERM®-EC680k[c]<br>(polyethylene) | 102,2 | 103,5 | 8,68 | 101 | 92 to 116 | 18 | 18 |

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

[c] ERM® (European Reference Materials) is a registered trademark of the European Commission.

### Table E.6 – Statistical for chlorine data for IIS 3-2 results using C-IC

| Sample | Parameter | *m*<br>mg/kg | *v*<br>mg/kg | *N* | s(*r*)<br>mg/kg | *r*<br>mg/kg | s(*R*)<br>mg/kg | *R*<br>mg/kg |
|---|---|---|---|---|---|---|---|---|
| IIS3-A01 | Cl | 103,5 | 102,2 | 18 | 3,4 | 9,43 | 9,16 | 25,64 |

**Key**

*m* = arithmetic mean of test results

*v* = expected value

*N* = number of accepted results

s(*r*) = repeatability standard deviation

*r* = repeatability limit

s(*R*) = reproducibility standard deviation

*R* = reproducibility limit

# Annex F
(informative)

## Additional results of TG 3-2 test

### Table F.1 – Mean results and recovery rates for bromine obtained in the TG 3-2 internal test study by using C-IC

| **Sample number** | **Sample description** | **Certified value of Br** mg/kg | **Mean result of Br** mg/kg | **Standard deviation** mg/kg | **Recovery rate** [a] % | **Range of recovery rate** % | **Total number of data sets** [b] | **Number of data sets used** |
|---|---|---|---|---|---|---|---|---|
| TG 3-2-01 | KRISS CRM<br>113-01-013 (acrylonitrile butadiene styrene) | 124,4 | 120 | 8,0 | 97 | 80 to104 | 10 | 10 |
| TG 3-2-02 | KRISS CRM<br>113-01-015 (acrylonitrile butadiene styrene) | 890 | 872 | 55,3 | 98 | 89 to 107 | 10 | 10 |
| TG 3-2-03 | EMC<br>(epoxy moulding compound) | 195 | 178 | 13,0 | 91 | 82 to 99 | 9 | 9 |
| TG 3-2-04 | EMC<br>(epoxy moulding compound) | 976 | 902 | 82,4 | 92 | 79 to 102 | 9 | 9 |

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

### Table F.2 – Mean results and recovery rates for bromine obtained in the TG 3-2 internal test study by using oxygen bomb-IC

| **Sample number** | **Sample description** | **Certified value of Br**<br>mg/kg | **Mean result of Br**<br>mg/kg | **Standard deviation**<br>mg/kg | **Recovery rate** [a]<br>% | **Range of recovery rate**<br>% | **Total number of data sets** [b] | **Number of data sets used** |
|---|---|---|---|---|---|---|---|---|
| TG 3-2-01 | KRISS CRM<br>113-01-013 (acrylonitrile butadiene styrene) | 124,4 | 113 | 10,7 | 91 | 80 to107 | 8 | 8 |
| TG 3-2-02 | KRISS CRM<br>113-01-015 (acrylonitrile butadiene styrene) | 890 | 788 | 73,8 | 89 | 81 to 101 | 10 | 8 |
| TG 3-2-03 | EMC<br>(epoxy moulding compound) | 195 | 146 | 18,7 | 75 | 58 to 85 | 8 | 8 |
| TG 3-2-04 | EMC<br>(epoxy moulding compound) | 976 | 736 | 60,9 | 75 | 64 to 83 | 8 | 8 |

[a] Recovery rate is defined as the ratio of the actually measured concentration of analyte to the expected one, and multiplied by 100. In other words, it illustrates inaccuracy of the results.

[b] Each data set typically represents three replicate analyses of the sample.

# Annex G
(informative)

## Additional validation data

### Table G.1 – General conditions for the combustion furnace and the absorption solution

| **Parameters** | **Conditions** |
|---|---|
| Temperature of combustion furnace | 900 °C to 1 000 °C |
| Flow rate of oxygen | 400 ml/min |
| Flow rate of argon | 200 ml/min |
| Flow rate of water | 0,01 ml/min to 0,04 ml/min |
| Amount of absorption solution | 10 ml to 20 ml |

### Table G.2 – Additional information – Difference in sample sizes and measured bromine values in solder paste with burning aid ($WO_3$ powder)

| **Amount of sample** mg | **IC results of bromine** mg/kg |
|---|---|
| 7,9 | 1 670 |
| 18,3 | 1 672 |
| 36,1 | 1 794 |
| 55,6 | 1 788 |
| 72,8 | 1 824 |
| 93,5 | 1 833 |

### Table G.3 – Additional information – Difference in combustion temperatures and measured bromine values in solder paste with burning aid (WO3 powder)

| **Combustion temperature** Inlet (°C)/Outlet (°C) | **Amount of sample** mg | **IC results of bromine** mg/kg |
|---|---|---|
| 500 / 500 | 38,5 | 880 |
| 600 / 600 | 36,9 | 1 461 |
| 700 / 700 | 40,3 | 1 573 |
| 800 / 800 | 36,8 | 1 708 |
| 900 / 900 | 38,0 | 1 728 |
| 1 000 / 1 000 | 37,9 | 1 760 |

### Table G.4 – Additional information – Difference in recovery rate of iodine according to adsorbents ($H_2O_2$, hydrazine)

| Sample | Adsorbent | Mean result of iodine mg/kg | Expected value of iodine mg/kg | Range mg/kg | Standard deviation mg/kg | Relative standard deviation % | Recovery rate mg/kg | Total number of data sets |
|---|---|---|---|---|---|---|---|---|
| IIS3-C03<br>(Nylon 66) | $H_2O_2$ | 1 263 | 1 775 | 951 | 255,2 | 20,2 | 71,2 | 12 |
| IIS3-D04<br>(Nylon 66) | $H_2O_2$ | 2 416 | 3 320 | 3079 | 1 100,3 | 45,5 | 72,8 | 12 |
| IIS3-C03<br>(Nylon 66) | Hydrazine | 1 462 | 1 775 | 178 | 34,00 | 3,8 | 82,4 | 12 |
| IIS3-D04<br>(Nylon 66) | Hydrazine | 3 505 | 3 320 | 801 | 6,01 | 6,9 | 105,6 | 12 |

# Annex H
(informative)

# Additional IC data

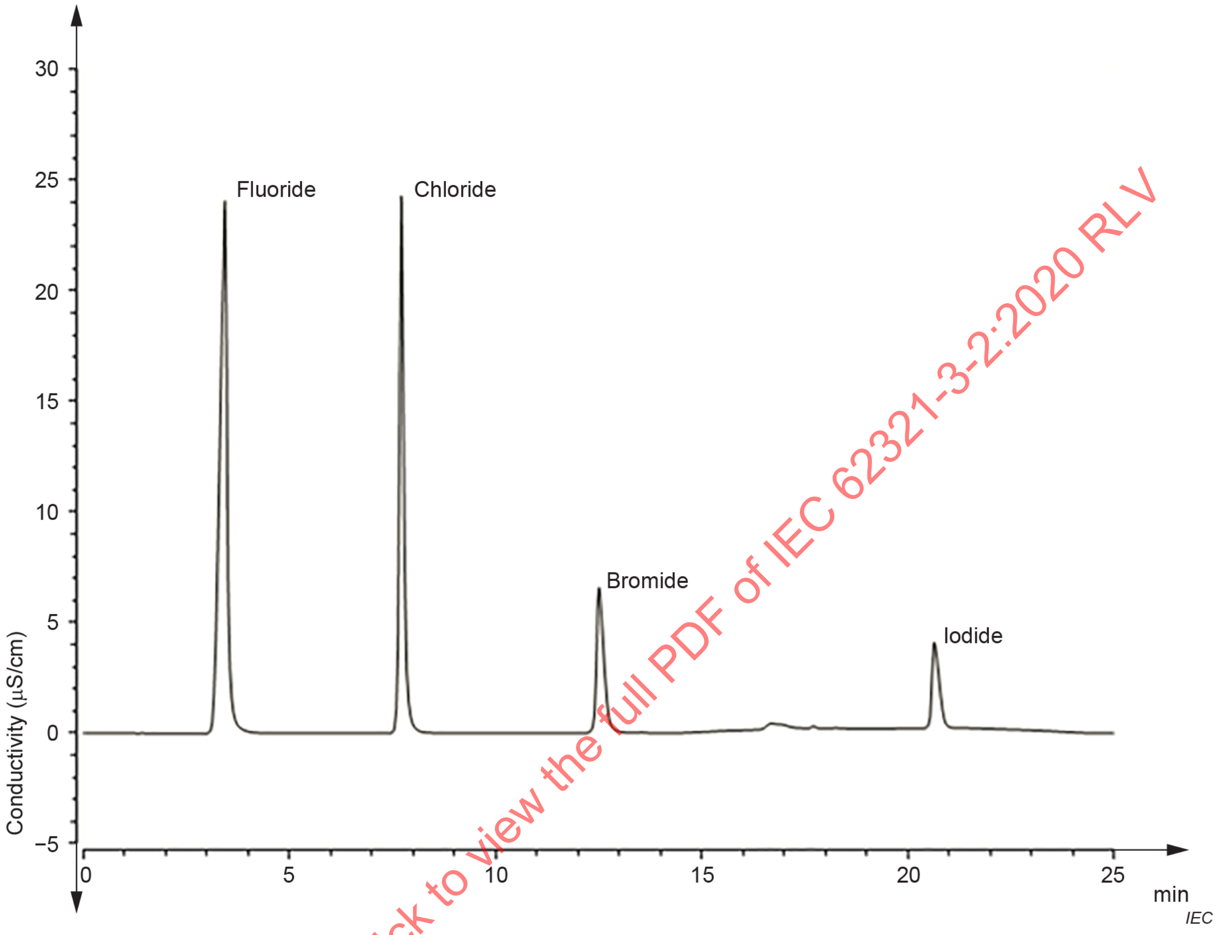

**Figure H.1 – Example of a chromatogram of the standard solution (4 mg/l of each standard) by IC**

**Table H.1 – Typical operating conditions for IC**

| Parameters | Conditions |
|---|---|
| Analytical column | Anion exchange column (4 mm × 250 mm) |
| Eluent | 1,8 mmol/l $Na_2CO_3$ / 1,7 mmol/l $NaHCO_3$ |
| Flow rate | 1,0 ml/min |
| Injection volume | 100 µl |
| Detection | Conductivity (with suppressor) |

### Table H.2 – Example of fluorine calibration solutions for IC

| No. | Concentration of calibration standard solutions (F)<br>mg/l | Peak area of calibration standard solutions (F)<br>µS × min | Peak height of calibration standard solutions (F)<br>µS |
|---|---|---|---|
| 1 | 0,5 | 0,658 | 6,91 |
| 2 | 1,0 | 1,264 | 11,65 |
| 3 | 2,0 | 2,438 | 18,41 |
| 4 | 4,0 | 4,762 | 27,48 |
| 5 | 8.0 | 9,294 | 39,60 |

### Table H.3 – Example of chlorine calibration solutions for IC

| No. | Concentration of calibration standard solutions (Cl)<br>mg/l | Peak area of calibration standard solutions (Cl)<br>µS × min | Peak height of calibration standard solutions (Cl)<br>µS |
|---|---|---|---|
| 1 | 0,5 | 0,373 | 4,36 |
| 2 | 1,0 | 0,753 | 8,73 |
| 3 | 2,0 | 1,485 | 17,09 |
| 4 | 4,0 | 3,007 | 34,21 |
| 5 | 8.0 | 6,112 | 66,48 |

### Table H.4 – Example of bromine calibration solutions for IC

| No. | Concentration of calibration standard solutions (Br)<br>mg/l | Peak area of calibration standard solutions (Br)<br>µS × min | Peak height of calibration standard solutions (Br)<br>µS |
|---|---|---|---|
| 1 | 0,5 | 0,157 | 1,53 |
| 2 | 1,0 | 0,322 | 3,09 |
| 3 | 2,0 | 0,653 | 6,05 |
| 4 | 4,0 | 1,306 | 11,30 |
| 5 | 8.0 | 2,663 | 20,03 |

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[7] ISO 5725-2, *Accuracy (trueness and precision) of measurement methods and results – Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method*

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[10] ASTM D4327, *Test Method for Anions in Water by Chemically Suppressed Ion Chromatography*

[11] ASTM D7359, *Standard Test Method for Total Fluorine, Chlorine and Sulfur in Aromatic Hydrocarbons and their Mixtures by Oxidative Pyrohydrolytic Combustion followed by Ion Chromatography Detection (Combustion Ion Chromatography-CIC)*

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[13] EN 14582*, Characterization of waste – Halogen and sulfur content – Oxygen combustion in closed systems and determination methods*

[14] JEITA ET-7304A, *Definition of Halogen-free Soldering Materials*

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[16] EN 15002, *Characterization of waste – Preparation of test portions from the laboratory sample*

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# SOMMAIRE

COMMISSION ÉLECTROTECHNIQUE INTERNATIONALE

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# 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)

## AVANT-PROPOS

1) La Commission Électrotechnique Internationale (IEC) est une organisation mondiale de normalisation composée de l'ensemble des comités électrotechniques nationaux (Comités nationaux de l'IEC). L'IEC a pour objet de favoriser la coopération internationale pour toutes les questions de normalisation dans les domaines de l'électricité et de l'électronique. À cet effet, l'IEC – entre autres activités – publie des Normes internationales, des Spécifications techniques, des Rapports techniques, des Spécifications accessibles au public (PAS) et des Guides (ci-après dénommés « Publication(s) de l'IEC »). Leur élaboration est confiée à des comités d'études, aux travaux desquels tout Comité national intéressé par le sujet traité peut participer. Les organisations internationales, gouvernementales et non gouvernementales, en liaison avec l'IEC, participent également aux travaux. L'IEC collabore étroitement avec l'Organisation Internationale de Normalisation (ISO), selon des conditions fixées par accord entre les deux organisations.
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8) L'attention est attirée sur les références normatives citées dans cette publication. L'utilisation de publications référencées est obligatoire pour une application correcte de la présente publication.
9) L'attention est attirée sur le fait que certains des éléments de la présente Publication de l'IEC peuvent faire l'objet de droits de brevet. L'IEC ne saurait être tenue pour responsable de ne pas avoir identifié de tels droits de brevets et de ne pas avoir signalé leur existence.

La Norme internationale IEC 62321-3-2 a été établie par le comité d'études 111 de l'IEC: Normalisation environnementale pour les produits et les systèmes électriques et électroniques.

Cette deuxième édition annule et remplace la première édition publiée en 2013. Cette édition constitue une révision technique.

Cette édition inclut les modifications techniques majeures suivantes par rapport à l'édition précédente.

a) La précédente édition présentait une méthode d’essai de détection pour le brome (Br) seulement. La présente édition ajoute, dans sa partie normative, une méthode d’essai de détection par C-CI pour le fluor (F), le chlore (Cl) et le brome (Br).
b) Une méthode d’essai de détection par C-CI de l’iode a été ajoutée à l’Annexe D (informative).

Le texte de cette Norme internationale est issu des documents suivants:

| FDIS | Rapport de vote |
|---|---|
| 111/573/FDIS | 111/577/RVD |

Le rapport de vote indiqué dans le tableau ci-dessus donne toute information sur le vote ayant abouti à l'approbation de cette Norme internationale.

Ce document a été rédigé selon les Directives ISO/IEC, Partie 2

Une liste de toutes les parties de la série IEC 62321, publiées sous le titre général *Détermination de certaines substances dans les produits électrotechniques*, peut être consultée sur le site web de l'IEC.

Le comité a décidé que le contenu de ce document ne sera pas modifié avant la date de stabilité indiquée sur le site web de l'IEC sous « http://webstore.iec.ch » dans les données relatives au document recherché. À cette date, le document sera

- reconduit,
- supprimé,
- remplacé par une édition révisée, ou
- amendé.

# INTRODUCTION

L'utilisation largement répandue des produits électrotechniques suscite une attention accrue concernant leur impact sur l’environnement. Dans de nombreux pays dans le monde, ceci a conduit à adapter les réglementations relatives aux déchets, aux substances et à la consommation d'énergie des produits électrotechniques.

L’utilisation de certaines substances (par exemple le plomb (Pb), le cadmium (Cd), les diphényléthers polybromés (PBDE) et les phtalates) dans les produits électrotechniques est une source d'inquiétude dans la législation régionale actuelle et en cours de préparation.

L'objet de la série IEC 62321 est par conséquent de fournir, à une échelle mondiale et de manière cohérente, des méthodes d'essai qui permettront à l'industrie électrotechnique de déterminer les niveaux de certaines substances dans les produits électrotechniques.

La première édition de l’IEC 62321-3-2 (2013) a été publiée pour permettre la détection du brome total.

Le présent document (édition révisée de l’IEC 62321-3-2) décrit dans la partie normative les méthodes d’essai permettant de quantifier le taux d’halogène (fluor, chlore et brome) dans les polymères et les produits électroniques par C-CI. Il décrit dans une Annexe D informative celles permettant de quantifier l’iode (I).

Par ailleurs, l’Annexe A (informative) et l’Annexe B (informative) fournissent des informations sur la bombe de combustion à oxygène – chromatographie ionique et la fiole purgée à l’oxygène – chromatographie ionique.

AVERTISSEMENT – Il convient que les personnes appliquant le présent document aient une bonne connaissance des pratiques normales de laboratoire. Le présent document ne prétend pas couvrir tous les problèmes de sécurité éventuels associés à son utilisation. Il incombe à l’utilisateur de mettre en place les pratiques adéquates de sécurité et de santé, mais aussi d’assurer la conformité aux conditions réglementaires nationales.

# 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)

## 1 Domaine d’application

La présente partie de l’IEC 62321 spécifie une méthode d’analyse par détection du fluor, du chlore et du brome dans les polymères et les produits électroniques en appliquant la technique de combustion-chromatographie ionique (C-CI). Une procédure d’analyse par détection C-CI de l’iode est décrite à l'Annexe D.

Cette méthode d’essai a été évaluée pour l’ABS (acrylonitrile butadiène styrène), l’EMC (composé de moulage époxy), le PE (polyéthylène) et le PC (polycarbonate) dans les plages de concentration spécifiées dans le Tableau 1, le Tableau 2 et le Tableau 3. Les résultats détaillés sont présentés du Tableau E.1 au Tableau E.6, et à l’Annexe F (Tableau F.1 et Tableau F.2)

L'utilisation de cette méthode pour d'autres types de matériaux ou plages de concentration en dehors de celles qui sont spécifiées ci-dessous n'a pas été évaluée.

**Tableau 1 – Plages de concentration de fluor soumises à l’essai par C-CI dans PC**

| **Substance/élément** | **Fluor** | |
|---|---|---|
| **Polymère** | **Unité de mesure** mg/kg | PC |
| Concentration ou plage de concentration vérifiée par essai | | 575 |

**Tableau 2 – Plages de concentration de chlore soumises à l’essai par C-CI dans PE**

| **Substance/élément** | **Chlore** | |
|---|---|---|
| **Polymère** | **Unité de mesure** mg/kg | PE |
| Concentration ou plage de concentration vérifiée par essai | | 102,2 |

**Tableau 3 – Plages de concentration de brome soumises à l’essai par C-CI dans différents matériaux**

| **Substance/élément** | **Brome** | | | |
|---|---|---|---|---|
| **Polymère** | **Unité de mesure** mg/kg | ABS | EMC | PE |
| Concentration ou plage de concentration vérifiée par essai | | 124 à 890 | 195 à 976 | 96 |

Cette norme horizontale est essentiellement destinée à l'usage des comités d'études dans la préparation des normes, conformément aux principes établis dans le Guide 108 de l'IEC.

Une des responsabilités d'un comité d'études est, partout où cela est possible, de se servir des normes horizontales lors de la préparation de ses publications. Le contenu de cette norme horizontale ne s'appliquera pas, à moins qu'il ne soit spécifiquement désigné ou inclus dans les publications concernées.

## 2 Références normatives

Les documents suivants cités dans le texte constituent, pour tout ou partie de leur contenu, des exigences du présent document. Pour les références datées, seule l'édition citée s'applique. Pour les références non datées, la dernière édition du document de référence s'applique (y compris les éventuels amendements).

IEC 62321-2, *Détermination de certaines substances dans les produits électrotechniques – Partie 2: Démontage, désassemblage et préparation mécanique de l'échantillon*

ISO 3696, *Eau pour laboratoire à usage analytique – Spécification et méthodes d'essai*

ISO 8466-1, *Qualité de l'eau – Étalonnage et évaluation des méthodes d'analyse et estimation des caractères de performance – Partie 1: Évaluation statistique de la fonction linéaire d'étalonnage*

ISO 10304-1:2007, *Qualité de l'eau – Dosage des anions dissous par chromatographie des ions en phase liquide – Partie 1: Dosage du bromure, chlorure, fluorure, nitrate, nitrite, phosphate et sulfate*

## 3 Termes, définitions et termes abrégés

### 3.1 Termes et définitions

Pour les besoins du présent document, les termes et définitions suivants s'appliquent.

L'ISO et l'IEC tiennent à jour des bases de données terminologiques destinées à être utilisées en normalisation, consultables aux adresses suivantes:

- IEC Electropedia: disponible à l'adresse http://www.electropedia.org/
- ISO Online browsing platform: disponible à l'adresse http://www.iso.org/obp

**3.1.1**
**exactitude**
étroitesse de l'accord entre le résultat d'essai et la valeur de référence acceptée

Note 1 à l'article: Le terme « exactitude », appliqué à un ensemble de résultats d'essai, implique une combinaison de composantes aléatoires et d'une erreur systématique commune ou d'une composante de biais.

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

**3.1.2**
**fidélité**
étroitesse d'accord entre des résultats d'essai indépendants obtenus sous des conditions stipulées

[SOURCE: ISO 5725-1:1994, 3.12, modifiée – Les notes ont été supprimées.]

**3.1.3**
**répétabilité**
fidélité sous des conditions de répétabilité

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

**3.1.4**
**limite de répétabilité**
*r*
valeur au-dessous de laquelle est située, avec une probabilité de 95 %, la valeur absolue de la différence entre deux résultats d'essai, obtenus sous des conditions de répétabilité

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

**3.1.5**
**reproductibilité**
fidélité sous des conditions de reproductibilité

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

**3.1.6**
**limite de reproductibilité**
*R*
valeur au-dessous de laquelle est située, avec une probabilité de 95 %, la valeur absolue de la différence entre deux résultats d'essai obtenus sous des conditions de répétabilité

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

**3.1.7**
**détection**
procédure analytique utilisée pour déterminer la présence ou l'absence de substances dans la partie ou section représentative d'un produit, eu égard à la (aux) valeur(s) choisie(s) comme critère(s) de présence, d'absence ou d'essais supplémentaires

Note 1 à l'article: Si les valeurs obtenues par la méthode de détection ne sont pas concluantes, une analyse supplémentaire ou d'autres mesures de suivi peuvent être nécessaires pour prendre la décision finale quant à la présence/absence de la substance ou du composé.

[SOURCE: IEC 62321-1:2013, 3.1.10]

**3.1.8**
**échantillon pour essai**
échantillon préparé à partir de l'échantillon du laboratoire et à partir duquel les prises d'essai seront prélevées

[SOURCE: ISO 6206:1979, 3.2.13]

**3.1.9**
**prise d'essai**
quantité de matière prélevée dans l'échantillon pour essai (ou, s'il est identique, dans l'échantillon pour laboratoire) et sur laquelle est effectivement effectué(e) l'essai ou l'observation

[SOURCE: ISO 6206:1979, 3.2.14]

## 3.2 Termes abrégés

| | |
|---|---|
| ABS | acrylonitrile butadiène styrène |
| CCV | continuing calibration verification (vérification continue de l'étalonnage) |
| CD | conductivity detector (détecteur de conductivité) |
| C-CI | combustion-chromatographie ionique |
| CRM | certified reference material (matériau de référence certifié) |
| EMC | epoxy molding compound (composé de moulage époxy) |
| CI | chromatographie ionique |
| ICV | initial calibration verification (vérification initiale de l'étalonnage) |
| IS | internal standard (étalon interne) |
| IUPAC | International Union of Pure and Applied Chemistry (Union internationale de chimie pure et appliquée) |
| KRISS | Korea Research Institute of Standards and Science (Institut coréen de recherche en sciences et en normalisation) |
| LCS | laboratory control sample (échantillon de contrôle de laboratoire) |
| LCSD | laboratory control sample duplicate (échantillon de contrôle de laboratoire – duplication) |
| LOD | limit of detection (limite de détection) |
| LOQ | limit of quantification (limite de quantification) |
| MDL | method detection limit (limite de détection de la méthode) |
| PC | polycarbonate |
| PE | polyéthylène |
| PP | polypropylène |
| SOP | standard operation procedure (procédure normalisée d’utilisation) |
| US EPA | United States Environmental Protection Agency (Agence américaine pour la protection de l'environnement) |

# 4 Principe

Un échantillon de poids ou de volume connu est disposé dans une nacelle et introduit à une vitesse contrôlée dans un tube de combustion à haute température. L'échantillon est ensuite brûlé dans un environnement pyrohydrolytique riche en oxygène. Les sous-produits gazeux de l'échantillon brûlé sont piégés dans un milieu d'absorption où l’halogénure d’hydrogène (HF, HCl, HBr) formé pendant la combustion se dissocie en son anion ($F^-$, $Cl^-$ et $Br^-$) et cation ($H_30^+$) spécifiques. Une aliquote de volume connu de la solution d'absorption est ensuite injectée manuellement ou automatiquement dans un chromatographe ionique (CI) au moyen d'un simple robinet d'injection. Les anions d'halogénure, incluant des fluorures, chlorures et bromures, sont séparés en bandes d'élution individuelles sur la colonne de séparation de la CI. La conductivité de l’éluant est réduite au moyen d'un dispositif de suppression d'anions avant le détecteur de conductivité du chromatographe ionique, où les anions concernés sont mesurés. La quantification du taux d’halogène dans l'échantillon brûlé d'origine est réalisée en étalonnant le système au moyen d'une série d'étalons contenant des quantités de fluorures, bromures, chlorures et iodures connues, puis en analysant les échantillons inconnus dans les mêmes conditions que les étalons. Le système combiné de combustion pyrohydrolytique suivi de la détection par chromatographie ionique est appelé combustion-chromatographie ionique (C-CI).

## 5 Réactifs et matériaux

AVERTISSEMENT – Toutes les précautions reconnues d'hygiène et de sécurité doivent être effectivement prises lors de l'exécution des opérations spécifiées dans le présent document. Ne pas tenir compte des directives contenues dans le présent document ou de celles du fabricant des dispositifs peut conduire à des blessures ou à des dommages matériels.

Utiliser uniquement des réactifs de qualité analytique reconnue. Peser les réactifs avec une exactitude de ±1 % de la masse nominale, sauf indication contraire. Les réactifs mentionnés à l'Article 5 b) et de g) à k) peuvent être considérés comme des exemples représentatifs pour la préparation des éluants (Article 5 i)). Aucun des réactifs utilisés ne doit contenir une quantité d'halogénure supérieure à la limite de détection.

a) Eau, conforme à la qualité 1, comme cela est défini dans l'ISO 3696.

b) Peroxyde d'hydrogène, fraction massique de 30 %, ($H_2O_2$).

   Le peroxyde d'hydrogène est caustique; l'opérateur doit donc porter une protection oculaire et des gants et doit travailler sous une hotte à fumées lorsqu'il manipule ce réactif. Cette méthode utilisant un gaz (oxygène) à une haute température et sous pression, l'opérateur doit prendre des précautions.

c) Laine de quartz, de qualité fine ou un autre milieu approprié.

d) Argon, gaz vecteur, pureté minimale 99,9 %.

   Des épurateurs, par exemple des absorbeurs d'humidité (tamis moléculaire) et à pièges d'hydrocarbures (charbon actif ou équivalent), sont recommandés, pour assurer l'élimination des contaminants.

e) Oxygène, gaz de combustion, pureté minimale 99,6 %.

f) Aides à la combustion, oxyde de tungstène ($WO_3$) ou oxyde de fer ($Fe_3O_4$), de granulométrie < 50 µm et de pureté > 90 %. Avant d'utiliser des aides à la combustion, il est nécessaire de vérifier que la teneur en halogènes est bien au-dessous du niveau de MDL. Par ailleurs, toujours utiliser un échantillon témoin.

g) Solution témoin, remplir une fiole volumétrique (par exemple une fiole de 100 ml) avec de l'eau (Article 5 a)).

h) Solutions étalons.

   Des étalons certifiés provenant de sources commerciales, ou des étalons préparés en laboratoire, contenant les éléments d'intérêt aux concentrations d'intérêt, sont utilisés. En fonction des concentrations attendues dans l'échantillon, utiliser la solution étalon pour préparer 5 à 10 solutions d'étalonnage aux concentrations distribuées régulièrement sur le domaine de travail attendu.

   NOTE La solution est préparée à partir d'une solution étalon primaire ou d'une solution d'étalonnage.

i) Éluants

   Le choix de l'éluant dépend de la colonne et du détecteur choisis (demander conseil auprès du fabricant du chromatographe ionique ou du fournisseur de colonne). La préparation de l'éluant est effectuée comme cela est spécifié dans l'ISO 10304-1:2007, 5.10.

   1) Hydrocarbonate de sodium, $NaHCO_3$.
   2) Carbonate de sodium, $Na_2CO_3$.
   3) Hydroxyde de sodium, NaOH.
   4) Hydroxyde de potassium, KOH.

j) Solution étalon interne (IS) (facultative)

Un étalon interne peut être utilisé pour corriger les erreurs analytiques.

L'étalon interne utilisé dans la solution d'absorption ne doit contenir aucun des composants de l'échantillon et il doit être choisi en fonction du type de colonne et de la phase mobile (par exemple, phosphate, acide citrique, acide oxalique, acide méthane-sulfonique) Il convient de préparer la solution étalon interne en choisissant une plage de concentration moyenne incluse dans la plage de courbe d'étalonnage choisie lors de la préparation de la solution d'étalonnage. (par exemple 1 mg/l).

k) Solution d'absorption, utilisée pour piéger l'halogène – 3 ml de $H_2O_2$ (Article 5 b)) sont versés dans une fiole volumétrique de 1 000 ml et de l'eau est ajoutée pour compléter, puis mélangée. Cette solution contient 900 mg/kg de $H_2O_2$.

Une utilisation très prudente du $H_2O_2$ est exigée pour les échantillons contenant des concentrations particulièrement élevées de fluor. Lors de l'analyse d'échantillons contenant une forte concentration de fluor, une quantité minimale de peroxyde d'hydrogène doit être utilisée pour réduire les problèmes d'identification des pics de Cl.

l) Échantillon de contrôle de laboratoire (LCS) – Des matériaux de référence peuvent être utilisés pour garantir que les taux de récupération de l'halogène soient compris entre 90 % et 110 %. À cet effet, un matériau de référence certifié constitue le meilleur choix. Si aucun matériau de référence spécifié n'est disponible, un matériau de référence peut être préparé en mélangeant des quantités connues de composés halogénés (fluor, chlore et brome), diluées avec de la cellulose ou des oxydes d'aluminium pour obtenir une concentration convenable, puis en pulvérisant le mélange pour l'homogénéiser.

## 6 Appareils

Les appareils suivants doivent être utilisés: Voir également l'Annexe C.

a) Balance – analytique, avec une sensibilité de 0,000 1 g (0,1 mg).

b) Ciseaux ou pinces coupantes.

c) Système de combustion – généralement constitué des composants suivants (voir la Figure C.1):

   1) Autoéchantillonneur (facultatif) – un autoéchantillonneur est capable de placer avec exactitude 1 mg à 100 mg d'échantillon dans la nacelle.

   2) Nacelle – constituée de quartz, nickel, céramique, platine ou acier inoxydable.

   3) Système d'introduction de l'échantillon – le système comporte un accès d'échantillonnage pour introduire l'échantillon dans la nacelle et il est relié à l'entrée du tube de combustion pyrohydrolytique. Le système est parcouru par un gaz vecteur inerte humidifié et il doit être capable de permettre l'introduction quantitative du matériau à analyser dans la zone d'oxydation pyrohydrolytique à une vitesse contrôlée et répétable.

   4) Four électrique – il peut être chauffé entre 900 °C et 1 000 °C et comporte un tube en quartz ou en céramique placé à l'intérieur et relié au matériel d'injection de l'échantillon. Il est donc conçu pour que le gaz de combustion de l'échantillon puisse être récupéré sans perte.

   5) Tube de combustion pyrohydrolytique – le tube de combustion pyrohydrolytique est constitué de quartz et il est construit de telle sorte que lorsque l'échantillon est brûlé en présence d'oxygène humidifié, les sous-produits de combustion parcourent la zone de combustion pyrohydrolytique humidifiée. L'extrémité d'entrée doit permettre d'introduire et de faire avancer pas à pas une nacelle dans la zone chauffée et doit comporter un orifice latéral destiné à introduire le gaz vecteur humidifié et l'oxygène. Le tube de combustion pyrohydrolytique doit avoir un grand volume et comporter une zone chauffée avec de la laine de quartz ou un autre milieu approprié fournissant une surface suffisante pour que la combustion pyrohydrolytique complète de l'échantillon soit assurée. Lorsque l'échantillon contient de l'halogène en forte concentration (par exemple un échantillon contenant une concentration en halogène de plus de 1 %), une colonne piège doit être placée entre le tube d'absorption et le tube de combustion.

6) Dispositif d'approvisionnement en eau – capable de fournir de l'eau de qualité 1 (Article 5 a)) au sein du tube de combustion à une vitesse contrôlée, suffisante pour fournir un environnement pyrohydrolytique.
7) Tube d’absorption – tube en verre rempli à moitié de son volume lors de l’ajout de 10 ml à 20 ml de solution d’absorption. Le tuyau d'évacuation des gaz du four chauffant est immergé dans la solution d'absorption pour absorber le gaz évacué. La solution d’absorption peut être injectée dans le chromatographe ionique par le biais d’un dispositif de raccordement. Le tube d’absorption doit être lavé après analyse des échantillons pour éviter une contamination par les échantillons précédents.

d) Système de chromatographie ionique – constitué des composants suivants (voir la Figure C.2):
   1) réservoir d'éluant;
   2) pompe de CI;
   3) système d'injection d'échantillon – comportant une boucle d'échantillon de volume approprié (par exemple, 0,02 ml) ou un dispositif autoéchantillonneur;
   4) précolonne ou colonne de protection;
   5) colonne de séparation;
   6) suppresseur;
   7) détecteur de conductivité (CD);
   8) dispositif d'enregistrement – par exemple, ordinateur, intégrateur.

## 7 Échantillonnage

L'échantillonnage doit être réalisé comme cela est décrit dans l’IEC 62321-2. Il convient d'effectuer l'échantillonnage de manière aléatoire et il convient que les segments recueillis représentent tout l'échantillon.

a) Échantillon solide

   L'échantillon doit être coupé en petits morceaux (approximativement inférieurs à 3 mm × 3 mm) à l'aide de ciseaux ou pinces coupantes (Article 6 b)).

b) Échantillon liquide

   Lors de l’échantillonnage des liquides, l’intérieur de la pipette de transfert (ou récipient similaire) doit être rincé plusieurs fois avec du liquide d’échantillonnage.

## 8 Mode opératoire

### 8.1 Combustion

a) Après avoir suffisamment chauffé une nacelle dans le four électrique pour éliminer les contaminants, retirer la nacelle du four à l’aide de pinces propres, et la laisser refroidir jusqu’à la température ambiante, puis peser l’échantillon (généralement 10 mg à 100 mg d’échantillon) à 0,1 mg près et le charger dans la nacelle. Si les échantillons sont difficiles à brûler (par exemple flux, pâte de soudure), une aide à la combustion (par exemple $WO_3$) doit être utilisée. Un rapport de 5 sur 1 des aides à la combustion est généralement suffisant. Si une quelconque aide à la combustion est utilisée, appliquer approximativement 1/4 de sa masse totale en une couche mince à la surface de la nacelle, placer l'échantillon pesé sur celle-ci, puis recouvrir l'échantillon approximativement de ¾ de la masse totale de l’aide à la combustion. Les conditions d’analyse détaillées sont décrites à l’Annexe G (Tableau G.1, Tableau G.2, Tableau G.3)

b) L’échantillon et la nacelle sont chauffés dans le four de combustion pendant 10 min à 20 min avec de l'argon, de l'oxygène et de l'eau en utilisant le dispositif d'injection d'échantillon situé au centre du tube en quartz du four de combustion. Les conditions de combustion appropriées sont décrites dans le Tableau G.1. Si la nacelle de combustion présente une preuve de génération de suie ou de particules d'échantillon non brûlées, la combustion doit être considérée comme insuffisante et la procédure doit être répétée. La zone contaminée doit être soigneusement nettoyée avant de répéter la procédure.

NOTE 1 Lorsqu’une combustion insuffisante est suspectée (par exemple, suie visible dans la nacelle de combustion), il est possible de répéter la combustion et la chromatographie sur le résidu jusqu’à ce que plus aucun halogénure ne soit détecté. Les halogénures détectés peuvent être additionnés. En variante, il est possible de répéter l’analyse avec un nouvel échantillon et de modifier les conditions (par exemple, réduire la taille de l’échantillon, augmenter la température du four ou la durée de chauffage) pour obtenir une combustion complète.

c) À la fin des opérations de combustion, laver les tubes placés à la sortie d'évacuation des gaz de combustion et verser toutes les solutions de lavage dans la bouteille contenant la solution d’absorption pour effectuer un mesurage.

d) Pour l'essai témoin, exécuter une opération similaire sans insérer l'échantillon ou à l’aide d’une nacelle témoin et utiliser cette solution d'absorption obtenue comme solution témoin. Suivre la procédure décrite en 8.3.

NOTE 2 Si le four de combustion et la CI sont reliés et actionnés automatiquement, la solution d'absorption absorbant les combustibles peut être injectée dans la CI.

## 8.2 Analyse CI

Les procédures générales de chromatographie ionique décrites dans l'ISO 10304-1 doivent être suivies:

a) Mettre en marche la CI conformément aux instructions du fabricant de l’instrument ou à la procédure normalisée d’utilisation (SOP) en laboratoire. Les conditions de fonctionnement appropriées pour la CI sont indiquées dans le Tableau G.1;

b) Envoyer l'éluant et attendre une ligne de base stable;

c) Effectuer l'étalonnage comme cela est décrit en 8.5. Mesurer les échantillons, les étalons (Article 5 h)) et au moins deux solutions témoin comme cela est décrit en 8.3.

Les conditions de fonctionnement doivent être choisies et stabilisées selon les recommandations du fabricant du dispositif ou selon la SOP.

## 8.3 Essai à blanc

Un essai d’échantillon témoin est effectué en quantifiant au moins deux solutions témoin qui sont préparées en suivant exactement la même procédure que celle décrite ci-dessus (Article 5 h)), mais sans l'échantillon réel. Une solution témoin (Article 5 g)) ne contenant pas d’halogénure (moins de la limite MDL, ou généralement 0,1 mg/l) doit être utilisée pour préparer l’échantillon témoin.

## 8.4 Nettoyage et réétalonnage

Nettoyer tout le coke ou la suie du tube de combustion et des nacelles selon les instructions du fabricant. Après nettoyage, assembler l'appareil et contrôler les fuites. Effectuer une vérification de l’échantillon de contrôle de laboratoire ou du matériau de référence pour déterminer si l'instrument a besoin d'être réétalonné ou nettoyé à nouveau.

### 8.5 Étalonnage

Une courbe d'étalonnage doit être réalisée pour effectuer une analyse quantitative. La courbe d'étalonnage est préparée en utilisant une solution étalon de fluorure, de chlorure et de bromure.

Lorsque le système d’analyse est évalué pour la première fois et à intervalles réguliers par la suite, établir une fonction d'étalonnage encadrant la gamme des concentrations d'halogénures attendues lors de la mesure (par exemple, comme spécifié dans la norme ISO 8466-1). Des exemples de solutions d'étalonnage et leurs concentrations en fluor, chlore et brome sont présentés à l'annexe H (voir tableau H.2, tableau H.3 et tableau H.4).

Par exemple, les étalons pour le fluor, le chlore et le brome indiqués aux tableaux H.2, H.3 et H.4 peuvent être préparés en ajoutant à l'aide d'une pipette 0,5, 1,0, 2,0, 4,0 et 8,0 ml d'une solution mère de 1 000 mg/l de chaque halogénure dans une fiole jaugée de 1 000 ml et en complétant avec de l'eau (clause 5 a)) jusqu'au repère.

a) Préparer les solutions étalons (Article 5 h)).

b) Injecter les solutions étalons (Article 5 h)) directement dans la CI.

c) Identifier les pics d’anions particuliers en comparant leurs temps de rétention à ceux des solutions étalons (Article 5 h)). L'écart sur ces temps de rétention ne doit pas dépasser ±5 % dans un lot.

d) Au moins cinq solutions d’étalonnage doivent être préparées à des niveaux de concentration équidistants. Une quantification est effectuée en se fondant sur le mesurage des aires ou hauteurs de pics. La courbe d'étalonnage est généralement utilisée à des concentrations comprises entre 0,5 mg/l et 8,0 mg/l. Cependant la concentration peut être ajustée lorsque la limite de détection est abaissée ou relevée.

### 8.6 Mesurage de l'échantillon

Après la réalisation de la courbe d'étalonnage, l’échantillon témoin et la solution d'échantillon sont mesurés. Si la concentration en halogène de l’échantillon est au-dessus de la plage de la courbe d’étalonnage, la solution doit être diluée dans l'eau (Article 5 a) jusqu'à la plage de la courbe d’étalonnage, si possible jusqu’à la plage moyenne, et doit être à nouveau mesurée. Toutes les dix exécutions d'échantillon et à la fin de chaque ensemble d'échantillons, analyser un étalon de vérification continue de l'étalonnage (CCV). Le taux de récupération de l’halogène doit être compris entre 90 % et 110 %. Si le taux de récupération des F, Cl et Br dans l'étalon de CCV sort de cette plage, il convient d'analyser une nouvelle fois l'étalon de CCV dans les 12 h. Si la récupération est toujours en dehors de la plage après une nouvelle analyse de l'étalon de CCV, l'analyse est arrêtée et une maintenance doit être effectuée sur le système pour le ramener dans les conditions de fonctionnement optimales. Tous les échantillons chargés avant le dernier échantillon CCV réussi peuvent être consignés, mais tous les échantillons après le dernier étalon de CCV réussi doivent être à nouveau analysés avec un nouvel étalonnage. Une séparation appropriée pour chacun des ions d’halogénure est représentée à la Figure H.1 qui présente l’exemple d'un chromatogramme d’une solution étalon (4 mg/l) par CI.

### 8.7 Interférence

Les substances co-éluantes avec les anions d’intérêt sont renseignées dans la bibliothèque et/ou la base de données du laboratoire. Un anion présent en forte concentration peut interférer avec d'autres constituants si leurs temps de rétention sont suffisamment proches pour influer sur la résolution de leurs pics. Des informations supplémentaires concernant les interférences connues sont spécifiées dans l'ISO 10304-1:2007, Annexe B.

## 9 Calcul

La concentration en halogène contenue dans les échantillons (aire de pic ou hauteur de pic de l’ion d’halogénures (fluorure, chlorure et bromure) est calculée d'après la formule suivante:

$$\text{F, Cl et Br (mg/kg)} = [(A - Y) \times V_a] / (S \times M \times D_g) \quad (1)$$

ou

$$\text{F, Cl et Br (mg/kg)} = [(A - Y) \times V_a] / (S \times V \times D_v) \quad (2)$$

où

$A$ est l'aire de pic ou la hauteur de pic de l'anion d'halogénures présent dans l'étalon;

$D_g$ est le facteur de dilution de la méthode massique, masse de l'échantillon/masse totale incluant la masse de l'échantillon auquel est ajouté la masse du diluant, en g/g;

$D_v$ est le facteur de dilution de la méthode volumique, volume de l'échantillon/volume total incluant le volume de l'échantillon auquel est ajouté le volume du diluant, en g/ml;

$M$ est la masse de l'échantillon placé dans la nacelle, en g;

$S$ est la pente de la courbe d'étalonnage;

pente de la courbe d'étalonnage avec surface ou hauteur du composant anion étalon (axe y) et concentration de l'échantillon étalon (axe x, en mg/l);

$V$ est le volume de l'échantillon placé dans la nacelle, M/ρ (masse volumique), en ml;

$V_a$ est le volume de la solution d'absorption, en ml;

$Y$ est l'interception y de la courbe d'étalonnage;

Interception y de la courbe d'étalonnage avec surface ou hauteur du composant anion étalon (axe y, µS/cm x min) et concentration de l'échantillon étalon (axe x, en mg/l).

## 10 Fidélité

Lorsque les valeurs de deux résultats d'essai uniques indépendants obtenus en appliquant la même méthode sur un matériau d'essai identique dans le même laboratoire par le même opérateur utilisant le même matériel dans un court intervalle de temps, appartiennent à la plage de valeurs moyennes citée ci-dessous, la différence absolue entre les deux résultats d'essai obtenus ne dépasse pas la limite de répétabilité $r$ déduite par analyse statistique des résultats de l'étude internationale interlaboratoires (IIS 4A) et (IIS 3-2) dans plus de 5 % des cas. Voir le Tableau 4, le Tableau 5 et le Tableau 6.

**Tableau 4 – Résultats de l'étude internationale interlaboratoires (IIS 4A) pour le fluor**

| | |
|---|---|
| Teneur moyenne en fluor (mg/l): | 575 |
| $r$ (mg/l): | 40,62 |

**Tableau 5 – Résultats de l'étude internationale interlaboratoires (IIS 4A) pour le chlore**

| | |
|---|---|
| Teneur moyenne en chlore (mg/l): | 102,2 |
| $r$ (mg/l): | 9,43 |

**Tableau 6 – Résultats de l'étude internationale interlaboratoires (IIS4A et IIS 3-2) pour le brome**

| | | |
|---|---|---|
| Teneur moyenne en brome (mg/l): | 94,8 | 896,2 |

| | | |
|---|---|---|
| $r$ (mg/l): | 18,97 | 137,49 |

Voir l'Annexe E « Résultats de l'étude internationale interlaboratoires (IIS4A et IIS 3-2) » pour des données complémentaires.

# 11 Assurance qualité et contrôle de la qualité

## 11.1 Généralités

Les paramètres suivants du Tableau 7 sont pris en compte pour le contrôle de la qualité:

**Tableau 7 – Critères d'acceptation des éléments pour le contrôle de la qualité**

| Paramètres | Concentration en mg/kg dans l'échantillon pour essai | Critères d'acceptation |
|---|---|---|
| Courbe d'étalonnage | | $R^2 \geq 0{,}995$ |
| Vérification initiale de l'étalonnage (ICV) | Par exemple, 1 mg/l pour le F, Cl, Br | Récupération: 90 % à 110 % |
| Vérification continue de l'étalonnage (CCV) | Par exemple, 1 mg/l pour le F, Cl, Br | Récupération: 90 % à 110 % |
| Échantillon témoin | | < MDL |
| Échantillon de contrôle de laboratoire (LCS) | Matériau de référence ou solution du milieu de la plage d'étalonnage | Récupération: 80 % à 120 % |
| Échantillon de contrôle de laboratoire – duplication (LCSD) | Matériau de référence ou solution du milieu de la plage d'étalonnage | Écart relatif < 20 % |

NOTE Une vérification initiale de l'étalonnage (ICV) est effectuée à chaque fois qu'une courbe d'étalonnage est réalisée, en utilisant un étalon provenant d'une source différente de l'étalon.

Il convient d'analyser un échantillon témoin au moins une fois pour chaque lot d'échantillons soumis à l'essai. Un échantillon témoin ne contenant pas d'halogène peut être utilisé comme échantillon témoin.

Il convient d'analyser un échantillon de contrôle de laboratoire (LCS) et un échantillon de contrôle de laboratoire – duplication (LCSD), par lot, au moyen d'un matériau de référence certifié (CRM) ou en dopant une matrice vierge à l'aide d'une concentration spécifique d'halogénures. Le taux de récupération de l'halogène doit être compris entre 80 % et 120 %. Si le taux de récupération des F, Cl et Br dans l'étalon de LCS et de LCSD sort de cette plage, il convient d'analyser une nouvelle fois l'étalon de LCS et de LCSD dans les 12 h. Si la récupération est toujours en dehors de la plage après une nouvelle analyse de l'étalon de LCS et de LCSD, l'analyse est arrêtée et une maintenance doit être effectuée sur le système pour le ramener dans les conditions de fonctionnement optimales.

## 11.2 Limites de détection (LOD) et limites de quantification (LOQ)

Sous sa forme la plus simple, une limite de détection (LOD) ou la limite de détection de la méthode (MDL) est en général décrite comme la quantité ou la concentration la plus faible d'analyte dans un échantillon pour essai qui puisse être différenciée de zéro de manière fiable pour un système de mesure donné.

Les limites de détection d'un instrument représentent l'aptitude d'un instrument à différencier les faibles concentrations d'analytes par rapport au « zéro » dans une solution témoin ou solution étalon, et sont en général utilisées par les fabricants pour démontrer la capacité de mesure d'un système. Même si les limites de détection des instruments sont utiles, elles sont souvent bien plus basses qu'une limite de détection représentant un processus de mesure d'une méthode d'analyse complète.

Les limites de détection d'une méthode d'analyse complète sont de préférence déterminées expérimentalement en réitérant les mesurages indépendants sur des matrices d'échantillons à faible teneur ou enrichies (par exemple du plastique) effectués sur l'ensemble du mode opératoire, y compris la digestion ou l'extraction de l'échantillon. Pour cette analyse, il a été suggéré d'utiliser au minimum six répétitions et concentrations d'analytes de 3 à 5 fois la limite estimée de détection de la méthode. La limite de détection de la méthode complète pour l'ensemble d'un mode opératoire est déterminée en multipliant l'écart type des répétitions d'essais par un facteur approprié. L'Union internationale de chimie pure et appliquée (IUPAC) recommande un facteur 3 pour un minimum de six répétitions, tandis que l'US EPA utilise un intervalle de confiance unilatérale avec un multiplicateur égal à la valeur $t$ de Student, choisi en fonction du nombre de répétitions et du niveau de confiance (par exemple, $t = 3{,}36$ pour six répétitions avec un niveau de confiance de 99 %). Voir le Tableau 8.

Il convient que toutes les analyses utilisées pour calculer une MDL soient consécutives.

**Tableau 8 – Valeurs de $t$ de Student utilisées pour le calcul de la limite de détection de la méthode (MDL = $t \times s_{n-1}$)**

| **Nombre d'échantillons** | **Statistique de $t$ de Student**<br>(confiance de 99 %) |
|---|---|
| 6 | 3,36 |
| 7 | 3,14 |
| 8 | 3,00 |
| 9 | 2,90 |
| 10 | 2,82 |

La limite de quantification (LOQ) ou la limite de quantification estimée pour un système de mesure donné est en général décrite comme la concentration la plus faible qui puisse être déterminée de manière fiable dans des limites de fidélité spécifiées ou acceptables dans des conditions de fonctionnement normales de laboratoire. La limite de fidélité acceptable est souvent définie à 10 % de l'écart type relatif ou simplement exprimée comme un multiple fixe (2 à 10) de la limite de détection de la méthode.

## 12 Rapport d'essai

Les informations doivent être fournies au moins pour les aspects suivants de l'essai:

- l'échantillon;
- la Norme internationale utilisée (y compris son année de publication);
- la méthode utilisée (si la norme en comporte plusieurs);
- le ou les résultats, incluant une référence à l'Article 9;
- tout écart par rapport à la procédure;
- toutes propriétés inhabituelles observées;
- la date de l'essai.