



Edition 1.0 2024-08

TECHNICAL SPECIFICATION

Nanomanufacturing – Key control characteristics –
Part 6-30: Graphene-based material – Anion concentrated colour

Part 6-30: Graphene-based material – Anion concentration: Ion chromatography

Aniq Aniq Click to view the full



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Part 6-30: Graphene-based material – Anion concentration: Ion chromatography method

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CONTENTS

| Ε(| SREWC | DRD | 4 |
|----|----------|--|----|
| IN | ITRODU | JCTION | 6 |
| 1 | Scop | oe | 7 |
| 2 | Norn | native references | 7 |
| 3 | Term | ns and definitions | 7 |
| | 3.1 | General terms | 8 |
| | 3.2 | Key control characteristics measured in accordance with this document | |
| | 3.3 | Terms related to the measurement method | A |
| 4 | Gene | eral |)9 |
| | 4.1 | Measurement principle | ۵ |
| | 4.2 | Description of measurement apparatus | 9 |
| | 4.3 | Description of measurement apparatus Reagents Calibration solutions Sample preparation Ambient conditions during measurement | 10 |
| | 4.4 | Calibration solutions | 11 |
| | 4.5 | Sample preparation | 11 |
| | 4.6 | Ambient conditions during measurement | 12 |
| 5 | Meas | surement procedure | 12 |
| | 5.1 | Instrument set-up | 12 |
| | 5.2 | Calibration | 13 |
| | 5.3 | Detailed protocol of the measurement procedure | |
| | 5.3.1 | Preparation of sample solutions | 14 |
| | 5.3.2 | | 14 |
| | 5.3.3 | | |
| 6 | Data | analysis and interpretation of results | 15 |
| 7 | Mea | surement accuracy | 15 |
| 8 | Test | renort | าก |
| _ | 8.1 | Cover sheet | 16 |
| | 8.2 | Sample identification | 16 |
| | 8.3 | Measurement specific information | |
| | 8.4 | Test results. | |
| Αı | | (informative) Reference graphs | |
| | | (informative) Results of interlaboratory validation study | |
| | | (informative) Example format of the test report | |
| | | | |
| ΑI | | (Informative) Case study | |
| | D.1 | | |
| | D.2 | Preparation of calibration solution | |
| | D.3 | IC condition | |
| | D.4 | Data analysis / interpretation of results | |
| | D.4. | | |
| | D.4.2 | | |
| р: | D.5 | Measurement report | |
| ВI | piiograf | phy | 25 |
| Fi | gure 1 - | - Schematic diagram of ion chromatographic system | 10 |
| | - | Change of wettability by ball milling | |
| | - | - Change of dispersibility after shaking the sample vial sufficiently | |
| | J~, U U | and an all paralleling and an analytic via common and an annual and an annual and an | т |

| Figure A.1 – Chromatogram of the calibration solution using potassium hydroxide eluent | . 17 |
|--|------|
| Figure A.2 – Chromatogram of the calibration solution using sodium carbonate and sodium hydrogen carbonate eluent | . 17 |
| Figure D.1 – Photos and typical transmission electron microscope (TEM) images of the samples before and after ball milling | . 21 |
| Figure D.2 – Chromatogram of the sample solution by IC | .22 |
| Table 1 – Typical operation conditions I for potassium hydroxide eluent | . 13 |
| Table 2 – Typical operation conditions II for sodium carbonate and sodium hydrogen carbonate eluent | . 13 |
| Table 3 – Concentration of calibration solutions | . 14 |
| Table 4 – Limit of detection of two different eluents | . 16 |
| Table 3 – Concentration of calibration solutions | . 18 |
| Table C.1 – Product identification (in accordance with the relevant blank detail specification) | . 19 |
| Table C.2 – Measurement conditions | . 19 |
| Table C.3 – Calibration results | .20 |
| Table C.4 – Measurement results | . 20 |
| Table C.4 – Measurement results | .22 |
| Table D.2 – Data of sample solution test | . 23 |
| Table D.3 – Product identification of sample #1A | . 23 |
| Table D.4 – Measurement conditions of sample #1A | . 24 |
| Table D.5 – Measurement results of sample #1A | . 24 |
| Table D.5 – Measurement results of sample #1A | |

INTERNATIONAL ELECTROTECHNICAL COMMISSION

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-30: Graphene-based material – Anion concentration: Ion chromatography method

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The text of this Technical Specification is based on the following documents:

| Draft | Report on voting |
|-------------|------------------|
| 113/824/DTS | 113/846/RVDTS |

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

The language used for the development of this Technical Specification is English.

This document was drafted in accordance with ISO/IEC Directives, Part 2, and developed in accordance with ISO/IEC Directives, Part 1 and ISO/IEC Directives, IEC Supplement, available at www.iec.ch/members_experts/refdocs. The main document types developed by IEC are described in greater detail at www.iec.ch/publications.

A list of all parts of the IEC TS 62607 series, published under the general title Nanomanufacturing - Key control characteristics, can be found on the IEC website.

The committee has decided that the contents of this document will remain unchanged until the iatec at the second sec stability date indicated on the IEC website under webstore.iec.ch in the data related to the specific document. At this date, the document will be

- reconfirmed,
- withdrawn, or
- revised.

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INTRODUCTION

In recent years, graphene-based materials have drawn increasing attention from academia and industry due to their unique physical and chemical properties. Powders consisting of graphene-based material are now mass produced and widely used in fields such as battery, capacitor, coating, heat conducting, etc.

Anions are common and significant non-metallic impurities in graphene-based materials, originating from raw materials or chemicals used during the production process. These anions play a crucial role in influencing the applications of graphene-based materials. For instance, anions can lead to changes in reversible capacity and coulombic efficiency when graphene-based materials are employed in batteries and capacitors. Therefore, anion concentration stands as a key characteristic of graphene-based materials. Fluoride, nitrite, bromide, nitrate, sulphate, and phosphate are among the prevalent anions detected in numerous graphene-based materials gathered from the market.

Various methods have been utilized for determination of anions. The most common techniques for quantifying anions include titration, colorimetric determination, and ion chromatography (IC). IC offers several advantages – such as unique selectivity, fast analysis speed, high sensitivity, good accuracy, and easy operation – over alternative techniques in the analysis of anions. Moreover, one of its significant advantages is the capability to simultaneously determine multiple types of anions.

Sample preparation is a critical step in the analytical process, particularly when dealing with powders characterized by very low density and strong hydrophobic properties. It is essential to obtain a sample extraction solution to effectively isolate the analytes from the matrix before conducting IC instrumental determinations. Consequently, the accuracy, precision, and quantification limits of the analysis are significantly influenced by the sample preparation process. This document furnishes specific sample preparation details tailored for powders composed of graphene-based materials. Importantly, the described method is not confined solely to graphene-based materials but is also applicable to other carbonaceous materials such as graphite and graphite oxide.

The purpose of this document is to describe a test method to determine contents of anions in graphene-based material. A case study illustrating the application of this document can be found in Annex D.

NANOMANUFACTURING – KEY CONTROL CHARACTERISTICS –

Part 6-30: Graphene-based material – Anion concentration: Ion chromatography method

1 Scope

This part of IEC TS 62607 establishes a standardized method to determine the chemical key control characteristic

- anion concentration for powder of graphene-based material by
- ion chromatography.

In this document, the measured anions are fluoride, chloride, nitrite, bromide, nitrate, sulphate, and phosphate. These anions, present in the extraction solution of graphene-based materials, are separated into distinct elution bands on the ion chromatographic separation column and subsequently measured using a conductivity detector. Quantification of these anions is accomplished by establishing a proportional relationship between the measured signal (peak area or peak height) and the concentration of each anion. This is achieved by calibrating the system using a series of standards containing known amounts of each anion. Subsequently, unknown samples are analysed under the same conditions as the standards to determine their anion concentrations.

- Powder of graphene-based material addressed by this document includes graphene oxide, reduced graphene oxide and functionalized graphene, graphene, bilayer graphene, trilayer graphene and few-layer graphene.
 - NOTE This document can also be used for other carbonaceous material such as graphite and graphite oxide.
- This document targets graphene-based material manufacturers and downstream users to guide their material design, production and quality control.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

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

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

- IEC Electropedia: available at https://www.electropedia.org/
- ISO Online browsing platform: available at https://www.iso.org/obp

3.1.1

two-dimensional material

2D material

material, consisting of one or several layers with the atoms in each layer strongly bonded to neighbouring atoms in the same layer, which has one dimension, its thickness, in the nanoscale or smaller and the other two dimensions generally at larger scales

- 8 -

Note 1 to entry: The number of layers when a two-dimensional material becomes a bulk material varies depending on both the material being measured and its properties. In the case of graphene layer, it is a two-dimensional material up to 10 layers thick for electrical measurements, beyond which the electrical properties of the material are not ECTS 62601.6.30:201 distinct from those for the bulk (also known as graphite).

Note 2 to entry: Interlayer bonding is distinct from and weaker than intralayer bonding.

Note 3 to entry: Each layer may contain more than one element.

Note 4 to entry: A two-dimensional material can be a nanoplate

[SOURCE: ISO/TS 80004-13:2017, 3.1.1.1]

3.1.2

graphene graphene layer single-layer graphene monolayer graphene

single layer of carbon atoms with each atom bound to three neighbours in a honeycomb structure

Note 1 to entry: It is an important building block of many carbon nano-objects.

Note 2 to entry: As graphene is a single layer, it is also sometimes called monolayer graphene or single-layer graphene and abbreviated as 1LG to distinguish it from bilayer graphene (2LG) and few-layer graphene (FLG).

Note 3 to entry: Graphene has edges and can have defects and grain boundaries where the bonding is disrupted.

ISOURCE: ISO/TS 80004-13:2017

graphene-based material

GBM

graphene material-

grouping of carbon-based 2D materials that include one or more of graphene, bilayer graphene, few-layer graphene, graphene nanoplate, and functionalized variations thereof as well as graphene oxide and reduced graphene oxide

Note 1 to entry: "Graphene material" is a short name for graphene-based material.

[SOURCE: IEC TS 62607-6-3:2020, 3.2.4]

3.2 Key control characteristics measured in accordance with this document

3.2.1

anion concentration

amount of negatively charged ions divided by the mass of graphene-based material

Note 1 to entry: The term is presumed to mean mass concentration. The unit "milligram per kilogram" is recommended.

Note 2 to entry: Anions (fluoride, chloride, nitrite, bromide, nitrate, sulphate and phosphate) present in graphene-based material can be non-intentionally added substances that come from raw materials or chemicals used during production process or intentionally added substances to improve the performance.

3.3 Terms related to the measurement method

3.3.1

ion chromatography

IC

chromatography technique that separates ions based on their affinity for the immobilized ion exchange sites on the ion exchanger followed by quantification of ions through conductivity measurement

[SOURCE: IEC TR 62697-2:2018, 3.1]

3.3.2

eluent

liquid phase used to achieve separation and transport of analytes

[SOURCE: ISO/TS 21362:2018, 3.12, modified - The Notes to entry have been deleted.

4 General

4.1 Measurement principle

Anions are extracted by distilled or deionized water from the powder consisting of graphene-based material. After filtering the extract with a 0,22 µm polyethersulphone membrane filter, the filtrate is analysed by IC to determine anions. Anions are separated into individual elution bands on the separation column of the ion chromatograph. 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 anions in the powder sample is achieved by calibrating the system with a series of standards containing known amounts of anions and then analysing unknown samples under the same conditions as the standards.

4.2 Description of measurement apparatus

The measurement system consists of the following components:

- Analytical balance, with sensitivity not worse than 0,000 1 g or even finer.
- Ball mill.
- Ultrasonic cleaners with maximum input power no less than 250 W and working frequency no less than 40 kHz.
- Glass sample vials, with volume of 25 ml and rinsed thoroughly with water before use.
- Polyether sulfone membrane filter, 0,22 µm.
- Ion chromatographic system, as shown in Figure 1.

Pump: IC systems have a high-pressure pump that delivers the mobile phase (usually an aqueous solution) at a constant flow rate through the system.

Sample injector: This is where the sample is introduced into the system. It is typically an autosampler that precisely injects a known volume of the sample into the chromatographic column.

Chromatographic column: This is a critical component where the separation of ions occurs. It is typically packed with a stationary phase that interacts with the ions in the sample. The type of stationary phase can vary depending on the analysis.

Detector: The eluent (the mobile phase carrying the sample) that exits the chromatographic column flows through a detector. Common detectors in IC include conductivity detectors, UV detectors, and amperometric detectors. The choice of detector depends on the type of ions being analysed.

Suppressor: In some IC applications, especially for measuring anions, a suppressor is used to convert ions into their corresponding acids, improving sensitivity.

- 10 -

Data system: Modern ion chromatographic systems are controlled by a computer-based data system that records and processes the detector's output, creating chromatograms that represent the concentration of ions as a function of time.

Gradient controller: In some cases, a gradient controller is used to vary the composition of the eluent over time, which can improve separation efficiency. It consists of eluent reservoir, pump, injection valve, sample loop, separator column, suppressor and conductivity detector (CD).

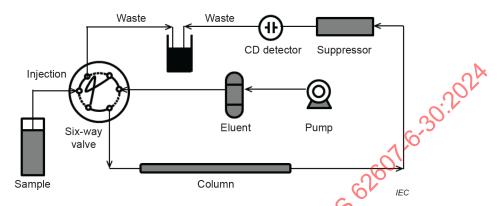


Figure 1 - Schematic diagram of ion chromatographic system

4.3 Reagents

Use only reagents of recognized analytical grade.

- 4.3.1 Water, complying with grade 1 as defined in ISO 3696.
- 4.3.2 Potassium hydroxide, KOH.
- 4.3.3 Sodium carbonate, Na₂CO₃
- 4.3.4 Sodium hydrogen carbonate, NaHCO₃.
- **4.3.5 Eluents**, the choice of which (e.g. potassium hydroxide, sodium hydrogen carbonate, sodium carbonate, sodium hydroxide solutions; mixed with organic modifiers if needed) depends on the chosen column and detector (seek advice from IC manufacturer or column supplier). Apply eluents that were prepared manually, automatically or in situ electrochemically prepared. The chosen combination of separator column and eluent should conform to the resolution requirements that the peak resolution R between the anion of interest and its nearest peak shall not fall below 1,3.

One example of an appropriate eluent prepared using a generating device is given in a). Additionally, another example for an appropriate manually prepared eluent is given in b).

- a) Potassium hydroxide eluent
 - If the ion chromatographic system has a generating device for KOH eluent, generate appropriate concentration of KOH eluent for resolution requirements. Typical operation conditions are given in Table 1.
- b) Sodium carbonate and sodium hydrogen carbonate eluent
 - Concentration of sodium carbonate and sodium hydrogen carbonate depends on the column requirements. For the eluent concentration as shown in Table 2, place 0,339 2 g of sodium carbonate (4.3.3) and 0,084 g of sodium hydrogen carbonate (4.3.4) into a 1 000 ml volumetric flask, dissolve in water and dilute to volume with water. The solution contains 3,2 mmol/l sodium carbonate and 1,0 mmol/l sodium hydrogen carbonate.

CAUTION: Take the necessary safety precautions when handling these materials.

4.4 Calibration solutions

Calibration solutions of seven anions (fluoride, chloride, nitrite, bromide, nitrate, sulphate and phosphate) can be prepared from certified standard solutions, or the stock standard solutions of analytical reagents containing the analytes of interest. Depending on the concentrations expected in the sample, five levels of concentration should be prepared over the expected working ranges as evenly as possible.

4.5 Sample preparation

All the test specimens shall be ground below room temperature before testing to improve water wettability of powder, preventing it from accumulating massively above water and enabling the powder to cross easily the air—water interface when it is added to a water container (Figure 2). The procedure is as follows.

- a) A sample weighing no less than 300 mg is taken and is placed in the glinding tank of the ball mill. The tank is sealed and immersed in liquid nitrogen for 3 min to 5 min or stored at -20 °C or below for more than 30 min to ensure that the sample is always below room temperature during the grinding process.
- b) The tank is installed back into ball mill and the grinding time is set in the range 30 s to 1 min.
- c) The as-prepared sample is obtained from the tank when the grinding tank returns to room temperature after grinding and is stored in a desiccator for use.



Figure 2 – Change of wettability by ball milling

4.6 Ambient conditions during measurement

The measurements can be performed under regular laboratory conditions without precise temperature and humidity control.

5 Measurement procedure

5.1 Instrument set-up

The IC instrument is set up in accordance with the instrument manufacturer's instructions. Typical operating conditions for IC are shown in Table 1 and Table 2.

Table 1 - Typical operation conditions I for potassium hydroxide eluent

| Analytical column | Column packing ethylvinylbenzene crosslinked with 55 % divinylbenzene resin with quaternary ammonium groups |
|---------------------------|---|
| Column temperature | 30 °C |
| Gradient eluent programme | 0 min to 12 min 8 mmol/l KOH; 12 min to 20 min 8 mmol/l to 15 mmol/l KOH; 20 min to 25 min 15 mmol/l to 40 mmol/l KOH; 25 min to 30 min 40 mmol/l KOH; 30 min to 31 min 40 mmol/l to 8 mmol/l KOH; 31 min to 36 min 8 mmol/l KOH |
| Eluent flow rate | 1,5 ml/min |
| Suppressor mode | Auto suppression recycle mode |
| Injection volume | 25 μΙ |

Table 2 – Typical operation conditions II for sodium carbonate and sodium hydrogen carbonate eluent

| Analytical column | Column packing polyvinyl alcohol resin with quaternary ammonium groups | | | | |
|--------------------|---|--|--|--|--|
| Column temperature | Room temperature | | | | |
| Eluent | 3,2 mmol/L Na ₂ CO ₃ -1,0 mmol/L NaHCO ₃ | | | | |
| Eluent flow rate | 0,7 ml/min | | | | |
| Suppressor | Chemical suppressor | | | | |
| Injection volume | 20 µl | | | | |

5.2 Calibration

Prepare the calibration solutions at five different concentration levels (Table 3) and inject. The measured signal (peak area or peak height) is proportional to the concentration of anions. Typical chromatograms of seven anions in calibration solution are provided in Annex A (see Figure A.1 and Figure A.2). Calibration curves are produced as the following Formula (1) by linear fitting. Linear correlation coefficient (R^2) of every curve should not be less than 0,995.

$$A = a \times C + b \tag{1}$$

where

- A is the peak area of anion;
- C is the concentration of anion, in mg/l;
- a is the slope of the calibration curve;
- b is the intercept of the calibration curve.

| No | Fluoride | Chloride | Nitrite | Bromide | Nitrate | Sulphate | Phosphate |
|-----|----------|----------|---------|---------|---------|----------|-----------|
| No. | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l | mg/l |
| 1 | 0,02 | 0,04 | 0,10 | 0,20 | 0,20 | 0,20 | 0,10 |
| 2 | 0,40 | 0,80 | 2,00 | 4,00 | 4,00 | 4,00 | 2,00 |
| 3 | 0,80 | 1,60 | 4,00 | 8,00 | 8,00 | 8,00 | 4,00 |
| 4 | 1,40 | 2,80 | 7,00 | 14,00 | 14,00 | 14,00 | 7,00 |
| 5 | 2,00 | 4,00 | 10,00 | 20,00 | 20,00 | 20,00 | 10,00 |

Table 3 - Concentration of calibration solutions

_ 14 _

5.3 Detailed protocol of the measurement procedure

5.3.1 Preparation of sample solutions

- a) 50 mg of ball milled sample is weighed with precision of 0,1 mg and loaded into the sample vial (4.2).
- b) 10 ml water is infused into the sample vial as the extraction solvent,
- c) The sample vial is sealed with cap and shaken to make sure that the sample is finely dispersed in water (Figure 3), which means there is no obvious aggregation of sample floating on the water.



Figure 3 - Change of dispersibility after shaking the sample vial sufficiently

- d) The sample vial is put into ultrasonic cleaners and processed for 30 min.
- e) Manually mix sample and water in the vial uniformly and then cool to room temperature.
- f) The extraction solution obtained by standing for some time or centrifugal separation shall be filtered through polyether sulfone membrane filter before being injected into the IC instrument.

5.3.2 Blank test

Blank test is performed by quantifying the blank solution which is prepared by exactly following the procedure described in 5.3.1 but without actual sample.

5.3.3 Measurement of sample extraction solution

Measure the sample extraction solution by ion chromatograph set up as described in 5.1.

Identify the peaks for particular anions by comparing the retention times with those of the calibration standard solutions. Deviation of retention time should not exceed 5 % within a batch.

If the anion concentration in sample solution is above the range of the calibration curve, the solution shall be diluted with water to the range of the calibration curve and measured again. The concentration is less than the limit of detection if it is below the least value of the range.

Data analysis and interpretation of results

Concentration of each anion in the sample (X) is calculated from Formula (2).

imit of detection if it is below the least value of the range.

Eation of results

sample (
$$X$$
) is calculated from Formula (2).

$$X = \frac{A - A_0 - b}{a} \times V \times \frac{1}{m}$$

(2)

tion, in mg/kg;
extraction liquid;
blank solution;

where

is the value of anion concentration, in mg/kg; X

is the peak area of anion in the extraction liquid; A

is the peak area of anion in the blank solution A_0

is the slope of the calibration curve; а

b is the intercept of the calibration curve;

Vis the volume of the sample extraction solution, in ml;

is the mass of sample in g.

Perform two individual measurements for the same sample. If the relative error does not exceed 10 % of the arithmetical average value, take the arithmetical average value as the results, precise to 0,1 mg/kg. If the telative error in two parallel measurements exceeds 10 %, a repetition test is needed.

7 Measurement accuracy

- a) The maldistribution of anions is common in some kinds of powder consisting of graphenebased material. This situation will be improved by grinding of specimens before testing.
- b) Some kinds of powder consisting of graphene-based material have moisture absorption. It can affect the measurement results. Thus, these powders are recommended to dry to remove residual moisture before the measurement.
- c) An interlaboratory test was used to evaluate validity and comparability of the measurement method. Details are given in Annex B. Under the conditions specified in this document, limit of detection values listed in Table 4 can be achieved.

Table 4 - Limit of detection of two different eluents

- 16 -

| | Concentration | | | | | | | |
|---|---------------|----------|---------|---------|---------|----------|-----------|--|
| Item | | | | (mg/kg) | | | | |
| | Fluoride | Chloride | Nitrite | Bromide | Nitrate | Sulphate | Phosphate | |
| Potassium hydroxide eluent | 0,2 | 0,4 | 2,0 | 2,0 | 4,0 | 2,0 | 6,0 | |
| Sodium carbonate and sodium hydrogen carbonate eluent | 1,0 | 1,6 | 4,0 | 16,0 | 4,0 | 2,0 | 12,0 | |

8 Test report

8.1 Cover sheet

The results of the measurement shall be documented in a measurement report providing

- introduction with background of the test,
- date and time of the measurement,
- name of the person in charge to perform the measurements, and
- name and signature of the person responsible for the accuracy of the report.

8.2 Sample identification

The report shall contain all information to identify the test sample and trace back the history of the sample. Guidelines are given in Annex C.

- General procurement information, in accordance with the relevant blank detail specification.
- General material description in accordance with the relevant blank detail specification, including a technical drawing.

NOTE A blank detail specification for graphene is under development (IEC 62565-3-1).

8.3 Measurement specific information

- The method parameters with the laboratory equipment.
- Raw data and calibration curve.

8.4 Test results

Results of anion concentration measured in accordance with this document.

Annex A (informative)

Reference graphs

Chromatograms of the calibration solution under two different eluents are shown in Figure A.1 and Figure A.2.

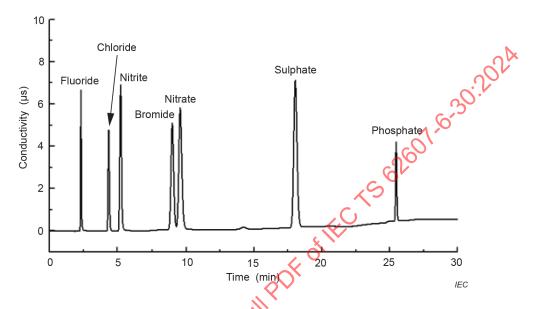


Figure A.1 – Chromatogram of the calibration solution using potassium hydroxide eluent

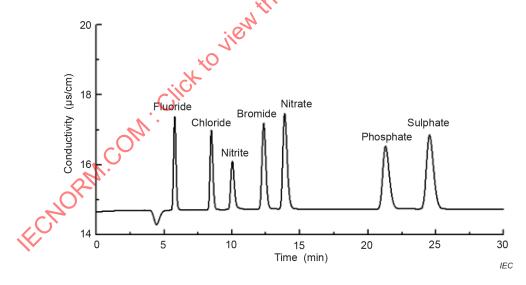


Figure A.2 – Chromatogram of the calibration solution using sodium carbonate and sodium hydrogen carbonate eluent

Annex B

(informative)

Results of interlaboratory validation study

An interlaboratory test was conducted on two different materials by nine laboratories. The details of test results can be seen in Table B.1.

Table B.1 - Statistical anion concentration results of two materials

| | ı | 1 | | 1 | 1 | | |
|----------|-------------------------------|-----------------|--------|-------|-----|-------|------------------------|
| Sample | Parameter | M | N | s(r) | r | s(R) | \sim $^{R_{\times}}$ |
| - Cumpic | - urumotor | mg/kg | | mg/kg | | mg/kg | 00r |
| G-a | F- | 205,8 | 9 | 5,7 | 2,8 | 14,9 | 7,2 |
| G-b | F- | 83,2 | 9 | 2,4 | 2,9 | 6,50 | 7,8 |
| G-a | CI ⁻ | 177,9 | 9 | 9,8 | 5,5 | 77,0 | 9,6 |
| G-b | CI ⁻ | 231,1 | 9 | 7,9 | 3,4 | 10,1 | 4,4 |
| G-a | NO ₂ - | 950,0 | 9 | 35,6 | 3,7 | 80,3 | 8,4 |
| G-b | NO ₂ - | Not detected | 9 | 31,9 | 2)2 | 67,2 | 4,5 |
| G-a | Br ⁻ | 1 477,6 | 9 | 11,2 | 3,7 | 27,0 | 8,8 |
| G-b | Br ⁻ | 306,9 | 9 | 34,6 | 2,4 | 94,2 | 6,5 |
| G-a | NO ₃ - | 1 443,3 | 9 | 38,0 | 3,5 | 40,9 | 3,8 |
| Go-b | NO ₃ - | 1 090,1 | 9 | 45,2 | 1,9 | 81,0 | 3,4 |
| G-a | SO ₄ ²⁻ | 2 347,4 | 9 // e | 134,7 | 3,0 | 272,2 | 6,0 |
| G-b | SO ₄ ²⁻ | 4 509,5 | | 20,1 | 3,6 | 33,4 | 6,0 |
| G-a | PO ₄ ³⁻ | 558,6 | 9 | 4,5 | 3,3 | 12,5 | 9,1 |
| G-b | PO ₄ ³⁻ | 138,5 | 9 | 5,7 | 2,8 | 14,9 | 7,2 |

Key

- M arithmetic mean of test results
- N number of accepted results
- s(r) repeatability standard deviation
- r repeatability limit
- s(R) reproducibility standard deviation
- R reproducibility limit

Annex C

(informative)

Example format of the test report

Table C.1 to Table C.4 are guidelines to write the test report.

Table C.1 – Product identification (in accordance with the relevant blank detail specification)

| Ito | em | Information |
|-------------------------|--------------------|---------------|
| Supplier | | |
| Trade name | | 2 |
| ID number | | 6,3 |
| Physical form | | |
| Typical batch quantity | □ Mass [kg] | 200 |
| | ☐ Batch number | |
| Traceability | ☐ Serial number | |
| requirements | ☐ Others, specify | V.C |
| | Manufacturing date | |
| | Number | 40 |
| Specification | Revision level | > , |
| | Date of issue | |
| Packaging requirements | Q ₁ | |
| Factory name and locati | on W | _ |

Table 62 - Measurement conditions

| Citem | Information |
|---------------------------|-------------|
| Instrument type | |
| Analytical column | |
| Column temperature | |
| Gradient eluent programme | |
| Eluent flow rate | |
| Suppressor mode | |
| Injection volume | |

Table C.3 – Calibration results

| Item | | 1 | 2 | 3 | 4 | 5 | Calibration curve | R ² | |
|-----------|---------------|---|-----|-----|----------|-----|-------------------|----------------|------------|
| | Concentration | | | | | | | | |
| Fluoride | (mg/l) | | | | | | | | |
| | Peak area | | | | | | | | |
| | Concentration | | | | | | | | |
| Chloride | (mg/l) | | | | | | | | |
| | Peak area | | | | | | | | |
| | Concentration | | | | | | | | 2 |
| Nitrite | (mg/l) | | | | | | | | 2 |
| | Peak area | | | | | | | 3 |) . |
| | Concentration | | | | | | | 1,0 | |
| Bromide | (mg/l) | | | | | | S |) | |
| | Peak area | | | | | | 5 | | |
| | Concentration | | | | | | 15 | | |
| Nitrate | (mg/l) | | | | | | | | |
| | Peak area | | | | | . (| | | |
| | Concentration | | | | | 0, | | | |
| Sulphate | (mg/l) | | | | X | | | | |
| | Peak area | | | . < | Y | | | | |
| | Concentration | | | 110 | | | | | |
| Phosphate | (mg/l) | | 0 | | | | | | |
| | Peak area | 7 | 111 | | | | | | |

Table C.4 - Measurement results

| | .V- | | | | | | |
|--------------------------|-----|-----------------|-------------------|-----------------|-------------------|-------------------------------|-------------------------------|
| Item (| F⁻ | CI ⁻ | NO ₂ - | Br ⁻ | NO ₃ - | SO ₄ ²⁻ | PO ₄ ³⁻ |
| Concentration (mg/kg) | | | | | | | |
| Average (mg/kg) | | | | | | | |

Annex D (informative)

Case study

D.1 Sample preparation

A sample weighing 400 mg (Figure D.1 a) is taken and is placed in the grinding tank of the ball mill. The tank is sealed and immersed in liquid nitrogen for 3 min. The tank is then installed back into the ball mill and the grinding time is set to 1 min. The as-prepared sample (Figure D.1 b) is obtained from the tank when the grinding tank returns to room temperature after grinding.

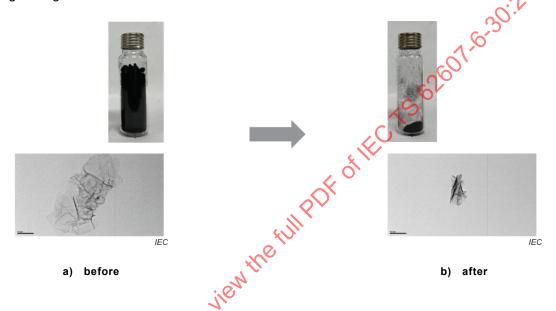


Figure D.1 – Photos and typical transmission electron microscope (TEM) images of the samples before and after ball milling

D.2 Preparation of calibration solution

- a) Mixed stock standard solution
 - 0,1 ml fluoride standard solution, 0,2 ml chloride standard solution, 0,5 ml nitrite standard solution, 1,0 ml bromide standard solution, 1,0 ml nitrate standard solution, 1,0 ml sulphate standard solution and 0,5 ml phosphate standard solution are placed in a 50 ml volumetric flask with a pipette and filled with water (4.3.1) up to the mark and mixed.
- b) Mixed midst standard solution
 - 1,0 ml mixed stock standard solution is placed in a 10 ml volumetric flask with a pipette and filled with water (4.3.1) up to the mark and mixed.
- c) Mixed working standard solution
 - 2,0 ml, 4,0 ml, 7,0 ml and 10,0 ml mixed stock standard solution are placed individually in a 10 ml volumetric flask with a pipette and filled with water (4.3.1) up to the mark and mixed. Those solutions are listed as concentration levels 2, 3, 4 and 5, respectively. 1,0 ml mixed midst standard solution is placed individually in a 10 ml volumetric flask with a pipette and filled with water (4.3.1) up to the mark and mixed. This is listed as concentration level 1.

D.3 IC condition

The operation conditions are listed in Table 1.

D.4 Data analysis / interpretation of results

D.4.1 Results of sample test of IC chromatogram

The chromatogram of sample solution is shown in Figure D.1.

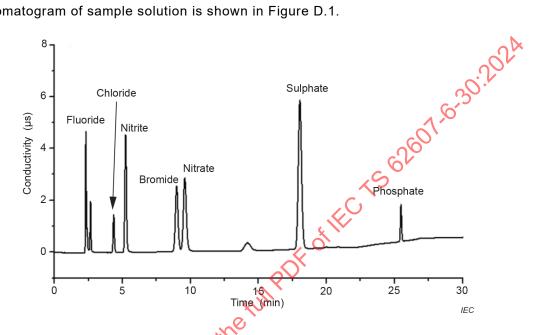


Figure D.2 - Chromatogram of the sample solution by IC

Data recorded and calculation D.4.2

Concentration and peak area of seven anions are recorded in Table D.1. Then the calibration curve can be calculated from these data. The sample amount and peak area are also recorded in Table D.2 to calculate the concentration of seven anions in accordance with Formula (2).

| Item | | 1 | 2 | 3 | 4 | 5 | Calibration curve | R ² |
|----------|-------------------------|---------|---------|---------|---------|---------|----------------------------|----------------|
| Fluoride | Concentration (mg/l) | 0,02 | 0,40 | 0,80 | 1,40 | 2,00 | y = 0,327 2 x - 0,005 6 | 0,999 9 |
| | Peak area | 0,004 5 | 0,121 7 | 0,255 5 | 0,451 5 | 0,650 3 | | |
| Chloride | Concentration (mg/l) | 0,04 | 0,80 | 1,60 | 2,80 | 4,00 | y = 0,196 8 x - 0,009 6 | 0,999 6 |
| | Peak area | 0,006 9 | 0,141 2 | 0,301 1 | 0,539 0 | 0,782 1 | | |
| Nitrite | Concentration (mg/l) | 0,10 | 2,00 | 4,00 | 7,0 | 10,00 | y = 0,415 1 x - 0,007 5 | 0,999 9 |
| | Peak area | 0,011 8 | 0,275 1 | 0,574 4 | 1,009 5 | 1,443 3 | | |
| Bromide | Concentration (mg/l) | 0,20 | 4,00 | 8,00 | 14,00 | 20,00 | y = 0,085 3 x - 0,024 1 | 0,999 6 |
| | Peak area | 0,011 8 | 0,304 2 | 0,645 7 | 1,168 3 | 1,691 4 | | |

Table D.1 - Data of calibration curve