
**Nuclear energy — Determination
of chlorine and fluorine in uranium
dioxide powder and sintered pellets**

*Énergie nucléaire — Détermination du chlore et du fluor dans les
poudres de dioxyde d'uranium et les pastilles frittées*

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html. (standards.iteh.ai)

This document was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies and radiological protection*, Subcommittee SC 5, *Nuclear installations, processes and technologies*.

This second edition cancels and replaces the first edition (ISO 22875:2008), which has been technically revised with the following changes:

- pyrohydrolysis temperature is lowered;
- information has been added concerning decomposition of species including fluoride and chloride (see footnote 2);
- calculation of the result takes into account pyrohydrolysis yield if needed.

Introduction

This document describes a method for determining the chlorine and fluorine concentrations in uranium dioxide and in sintered fuel pellets by pyrohydrolysis of samples, followed either by liquid ion-exchange chromatography or by selective electrode measurement of chlorine and fluorine ions.

Many ion chromatography systems and ion-selective electrode measurement systems are available. The equipment and operating procedure are, therefore, not described in detail.

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Nuclear energy — Determination of chlorine and fluorine in uranium dioxide powder and sintered pellets

1 Scope

This document describes a method for determining chlorine and fluorine in uranium dioxide powder and sintered pellets. It is applicable for the measurement of samples with a mass fraction of chlorine from 5 µg/g to 500 µg/g and with a mass fraction of fluorine from 2 µg/g to 500 µg/g.

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.

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

ISO 9892:1992, *Uranium metal, uranium dioxide powder and pellets, and uranyl nitrate solutions — Determination of fluorine content — Fluoride ion selective electrode method*

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3 Terms and definitions (standards.iteh.ai)

No terms and definitions are listed in this document.

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>

4 Principle

The samples are pyrohydrolysed at 850 °C to 1 000 °C in a tubular furnace with steam or moist air or moist oxygen heated to the same temperature. Chlorine and fluorine are trapped as halogenated acids and entrained in an aqueous solution.

Two measurement methods may be used to measure the chlorine and fluorine ions:

- a) liquid ion chromatography;
- b) ion-selective electrode.

5 Reagents

Use reagents of recognized analytical grade.

5.1 Water, complying with at least grade 1 in accordance with ISO 3696.

5.2 Anhydrous sodium chloride (NaCl).

5.3 Anhydrous sodium fluoride (NaF).

5.4 Sodium carbonate (Na_2CO_3).

5.5 Anhydrous sodium bicarbonate (NaHCO_3).

5.6 Glacial acetic acid (CH_3COOH), $\rho(\text{CH}_3\text{COOH}) = 1,06 \text{ g/ml}$.

5.7 Potassium acetate (CH_3COOK).

5.8 Concentrated eluent solution, $c(\text{Na}_2\text{CO}_3) = 0,018 \text{ mol/l}$ and $c(\text{NaHCO}_3) = 0,017 \text{ mol/l}$.

Dissolve 1,908 g of Na_2CO_3 (5.4) and 1,428 g of NaHCO_3 (5.5) in water (5.1). Pour into a 1 l volumetric flask. Dilute to 1 l with water (5.1). Homogenize.

Instead of Na_2CO_3 , the eluent solution can also be NaOH solution for instance, $c(\text{NaOH}) = 0,2 \text{ mol/l}$. This solution can be prepared by dilution in water (5.1) of concentrated sodium hydroxide solution (5.22).

Depending of the sample to be measured and the column used, Na_2CO_3 or NaOH is used.

5.9 Standard eluent solution, add 100 ml of concentrated eluent solution (5.8) to a 1 l volumetric flask.

Dilute to 1 l with water (5.1). Homogenize.

5.10 Make-up eluent solution, $c(\text{Na}_2\text{CO}_3) = 0,09 \text{ mol/l}$ and $c(\text{NaHCO}_3) = 0,085 \text{ mol/l}$.

Dissolve 9,540 g of Na_2CO_3 (5.4) and 7,140 g of NaHCO_3 (5.5) in water (5.1). Pour into a 1 l volumetric flask. Dilute to 1 l with water (5.1). Homogenize.

5.11 Buffer solution, $c(\text{CH}_3\text{COOH}) = 0,005 \text{ mol/l}$ and $c(\text{CH}_3\text{COOK}) = 0,005 \text{ mol/l}$.

Pour 250 μl of acetic acid (5.6) and 0,50 g of potassium acetate (5.7) into a 1 l polyethylene volumetric flask. Dilute to 1 l with water (5.1). Homogenize.

The concentration of the buffer solution can alternatively be chosen between 0,001 mol/l and 0,1 mol/l.

The buffer solution can also be NaOH solution for instance, $c(\text{NaOH}) = 0,1 \text{ mol/l}$. Instead of Na_2CO_3 , the eluent solution can also be NaOH solution for instance, $c(\text{NaOH}) = 0,2 \text{ mol/l}$. This solution can be prepared by dilution in water (5.1) of concentrated sodium hydroxide solution (5.22).

If NaOH is used for the concentrated eluent solution (5.8), NaOH is also used for the buffer solution.

5.12 Chloride reference solution, $\rho(\text{Cl}) = 1 \text{ g/l}$.

Dissolve 1,648 g of dry anhydrous sodium chloride (5.2) in water (5.1). Pour into a 1 l volumetric flask. Dilute to 1 l with water (5.1). Homogenize.

To achieve dry sodium salt, heat at 120 °C for 4 h just before use and keep in desiccators.

5.13 Chloride reference solution, $\rho(\text{Cl}) = 0,1 \text{ g/l}$.

Pipette 10 ml reference solution (5.12) into a 100 ml volumetric flask. Dilute to 100 ml with water (5.1). Homogenize.

5.14 Chloride reference solution, $\rho(\text{Cl}) = 0,01 \text{ g/l}$.

Pipette 10 ml reference solution (5.13) into a 100 ml volumetric flask. Dilute to 100 ml with water (5.1). Homogenize.

Solutions may be stored for two months.

5.15 Fluoride reference solution, $\rho(\text{F}) = 1 \text{ g/l}$.

Dissolve $2,210 \pm 0,001 \text{ g}$ of dry anhydrous sodium fluoride (5.3) in water (5.1). Pour into a 1 l volumetric flask. Dilute to 1 l with water (5.1). Homogenize.

To achieve dry sodium salt, heat at $120 \text{ }^\circ\text{C}$ for 4 h just before use and keep in a desiccator.

5.16 Fluoride reference solution, $\rho(\text{F}) = 0,1 \text{ g/l}$.

Pipette 10 ml reference solution (5.15) into a 100 ml volumetric flask. Dilute to 100 ml with water (5.1). Homogenize.

5.17 Fluoride reference solution, $\rho(\text{F}) = 0,01 \text{ g/l}$.

Pipette 10 ml reference solution (5.16) into a 100 ml flask. Dilute to 100 ml with water (5.1). Homogenize.

Solutions may be stored for two months.

5.18 Chloride and fluoride calibration standard solutions for ion chromatography, $\rho(\text{Cl}) = 0,2 \text{ mg/l}$; $\rho(\text{Cl}) = 0,5 \text{ mg/l}$; $\rho(\text{Cl}) = 1,0 \text{ mg/l}$; $\rho(\text{F}) = 0,2 \text{ mg/l}$; $\rho(\text{F}) = 0,5 \text{ mg/l}$; $\rho(\text{F}) = 1,0 \text{ mg/l}$.

Into three 100 ml volumetric flasks, pipette quantities (2 ml, 5 ml and 10 ml, respectively) of the 0,01 g/l chloride reference solution (5.14) and the 0,01 g/l fluoride reference solution (5.17). Add 2 ml of concentrated eluent solution (5.8) to each flask. Dilute to 100 ml with water (5.1). Homogenize.

These solutions now contain 0,2 mg/l, 0,5 mg/l and 1,0 mg/l, respectively, of chloride and fluoride ions.

Prepare the calibration solutions fresh on the day of use.

5.19 Chloride calibration standard solutions for ion-selective electrode measurement, $\rho(\text{Cl}) = 0,5 \text{ mg/l}$; $\rho(\text{Cl}) = 1,0 \text{ mg/l}$; $\rho(\text{Cl}) = 2,0 \text{ mg/l}$.

Into three 100 ml volumetric flasks, pipette quantities (5 ml, 10 ml and 20 ml) of the 0,01 g/l chloride reference solution (5.14). Add 20 ml of buffer solution (5.11). Dilute to 100 ml with water (5.1). Homogenize.

These solutions now contain 0,5 mg/l, 1,0 mg/l and 2,0 mg/l, respectively, of chloride ions.

Prepare the calibration solutions fresh on the day of use.

5.20 Fluoride calibration standard solutions for ion-selective electrode measurement, $\rho(\text{F}) = 0,5 \text{ mg/l}$; $\rho(\text{F}) = 1,0 \text{ mg/l}$; $\rho(\text{F}) = 2,0 \text{ mg/l}$.

Pipette 5 ml, 10 ml and 20 ml of the 0,01 g/l fluoride reference solution (5.17) into three 100 ml volumetric flasks. Add 20 ml of buffer solution (5.11). Dilute to 100 ml with water (5.1). Homogenize.

These solutions now contain 0,5 mg/l, 1,0 mg/l and 2,0 mg/l, respectively, of fluoride ions.

Prepare the calibration solutions fresh on the day of use.

5.21 Anhydrous sodium hydroxide (NaOH), granules.**5.22 Concentrated sodium hydroxide solution**, $c(\text{NaOH}) = 20 \text{ mol/l}$.**6 Apparatus****6.1 Standard laboratory equipment.**

6.2 Pyrohydrolysis apparatus, see [Figure 1](#).

6.2.1 Tubular furnace, equipped with a calibrated temperature regulator, capable of heating up to 1 000 °C.

6.2.2 Tube with steam heater and condenser.

The dimension of the tube made in Inconel¹⁾, platinum or quartz in the furnace need to be such that the “hot zone” of the furnace allows for the entire sample to be at the recommended temperature during the heating step.

As an example, tube dimension can be 400 mm long and 20 mm in diameter with a diameter of the junction tube of 5 mm. But there are other dimensions of the hot zone which allow for the entire sample to be at the recommended temperature during the heating step.

In the case of a pyrohydrolysis device with steam heating, the junction tube is wound around the tube inside the furnace and is connected to this tube before the closing system.

In this case, the steam at the exit of the steam generator is heated to the temperature of the furnace. The extractions of chlorine and fluorine ions are more effective.

6.2.3 Steam generator, consisting of a reservoir for water ([5.1](#)) and provisions for heating and temperature regulation to adjust the flow rate of the steam.

6.2.4 Combustion boats, of Inconel, platinum, ceramic or quartz.

6.3 Flasks, 50 ml, 100 ml, 200 ml, 250 ml and 1 000 ml, of any material that can be verified not to create Cl and F contamination.

6.4 Balance, capable of reading to the nearest 0,1 mg.

6.5 Ion chromatography system, not required when using an ion-selective electrode.

6.5.1 Injection loop, able to achieve the reproducibility reported.

Injection loop volume is determined according to the need. For example, suitable results are achievable with a 100 µl or 50 µl volume.

6.5.2 Pump.

6.5.3 Separation column, with a separating power sufficient to ensure effective separation of the fluoride and chloride anion peaks all the way to the baseline under the specified operating conditions.

6.5.4 Suppressor, placed before the conductivity measurement sensor to remove cations from eluent, in order to reduce background to more clearly separate the Cl/F peaks.

Depending on the equipment used, both cation exchange resin or electrolysis type suppressor can be used. Main part of electrolysis type suppressor, are permeable membrane in the cation, a cathode for water hydrolysis and an anode for cation transfer.

6.5.5 Conductivity measurement sensor, not required when using an ion chromatography system.

6.5.6 Sample changer.

1) Inconel is an example of a suitable product available commercially. This information is given for the convenience of users of ISO 22875 and does not constitute an endorsement by ISO of this product.

6.5.7 PC and software.

6.5.8 Printer.

6.6 Ion-selective electrode system.

6.6.1 Millivoltmeter, capable of reading to the nearest 0,1 mV.

6.6.2 Chlorine ion-selective electrode, compatible with the millivoltmeter.

Test the electrode for satisfactory operation by determining the response curve according to the procedure described in ISO 9892:1992, Annex A, and in accordance with the manufacturer's manual.

6.6.3 Fluorine ion-selective electrode.

Use an electrode compatible with the millivoltmeter.

Test the electrode for satisfactory operation by determining the response curve according to the procedure described in ISO 9892:1992, Annex A, and in accordance with the manufacturer's manual.

6.6.4 Double-junction reference electrode, compatible with the millivoltmeter.

6.7 Mortar.

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7 Procedure

Make-up eluent solution (5.10) is added to the flasks for calibration solutions and for the solution used to recover the pyrohydrolysis condensates.

7.1 Calibration

7.1.1 Ion chromatography calibration

Successively perform chromatography measurement on the standard eluent solution (5.9) as a blank sample, and on the three calibration standards (5.18).

For each anion, measure the peak area for each standard solution and subtract the area of the blank solution peak. Calculate the calibration curves for the net peak area (less the blank solution area) versus the concentration of the standard solutions.

7.1.2 Millivoltmeter calibration

Pour about 60 ml of each chloride calibration standard solution (5.12, 5.13 and 5.14) into a separate beaker. Stir each beaker slowly and regularly. Insert the chloride ion-selective electrode (6.6.2). Record the potential value after the equilibrium is reached, then remove and carefully rinse the electrode in water (5.1). Plot the calibration curve of the measured potentials versus the decimal logarithm of the chloride concentration in the standard solutions.

Repeat the same procedure with fluoride calibration standard solutions (5.15, 5.16 and 5.17) and the fluorine ion-selective electrode (6.6.3).

The temperature of the standard solutions shall be constant for the ion-selective electrode measurements to avoid the requirement for applying correction factors.