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(U, Pu)O2 Powders and sintered pellets — Determination of chlorine and fluorine

Poudres et pastilles frittées (U,Pu)O2 — Détermination du chlore et du fluor

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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).

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT) see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection*, Subcommittee SC 5, *Nuclear fuel cycle*.

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(U, Pu)O2 Powders and sintered pellets — Determination of chlorine and fluorine

1 Scope

This International Standard describes a method for determining chlorine and fluorine in mixed (U,Pu) O_2 powders and sintered pellets. It is applicable for the analysis of samples containing 5 µg.g⁻¹ to 50 µg. g⁻¹ of chlorine and 2 µg.g⁻¹ to 50 µg.g⁻¹ of fluorine.

For UO₂ powder and sintered pellets, refer to ISO 22875.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. 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 22875, Nuclear energy Betermination of chlorine and fluorine in uranium dioxide powder and sintered pellets

ISO 9892, 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 Principle

The samples are pyrohydrolyzed at 850 °C – 1 000 °C in a tubular furnace with steam or moist oxygen. Chlorine and fluorine are trapped as halogenated acids and entrained in an aqueous solution. Chloride and fluoride ions are measured using selective electrodes or another appropriate method, for instance, ionic chromatography.

4 Reagents

Use only reagents of recognized analytical grade.

4.1 Demineralised water, complying with at least grade 1 in accordance with ISO 3696 is recommended.

- 4.2 Anhydrous sodium chloride (NaCl), analytical grade.
- **4.3** Anhydrous sodium fluoride (NaF), analytical grade.

4.4 Concentrated sodium hydroxide solution, w(NaOH) = 32 %, relative density approximately 1,35 g.ml⁻¹.

Concentrated sodium hydroxide solution (4.4) is used to prepare sodium hydroxide solutions (4.4.1, 4.4.2, and 4.4.3). Concentrations of solutions (4.4.1, 4.4.2, and 4.4.3) are examples of reference solutions that are acceptable for use.

4.4.1 Sodium hydroxide solution, $c(NaOH) = 5 mol.l^{-1}$.

This reagent can also be prepared by using solid sodium hydroxide in various ways.

For example, the procedure can be as follows.

Pour 460 ml of concentrated sodium hydroxide solution (4.4) into 1 000 ml volumetric flask, dilute to the mark using demineralised water (4.1), and mix.

This reagent can also be prepared by dissolving solid sodium hydroxide (4.5) in solution using demineralised water (4.1).

4.4.2 Sodium hydroxide solution, $c(NaOH) = 0.5 \text{ mol.}l^{-1}$.

Pour 46 ml of concentrated sodium hydroxide solution (4.4) into 1 000 ml volumetric flask, dilute to the mark using demineralised water (4.1), and mix.

4.4.3 Sodium hydroxide solution, $c(NaOH) = 0.05 \text{ mol.}l^{-1}$.

Pour 100 ml of 0,5 mol/l⁻¹ sodium hydroxide (4.4.2) into 1 000 ml volumetric flask, dilute to the mark using demineralised water (4.1), and mix.

4.4.4 Sodium hydroxide solution, $c(\text{NaOH}) = 10^{-4} \text{ mol.}l^{-1}$ (or pH 10).

The concentration of solution (4.4.4) is an example of a receiver solution that can be used for a measurement by chromatography.

4.5 Anhydrous sodium hydroxide (NaOH), granules.

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- **4.6** Glacial acetic acid, (CH₃COOH), relative density approximately 1,06 g.ml⁻¹.
- **4.7 Sodium acetate**, (CH₃COONa) analytical grade.

4.8 Buffer solution. ISO 21613:2015 https://standards.iteh.ai/catalog/standards/sist/b30b4afe-744c-41ef-8254-0897251f8af5/iso-21613-2015

Using the following buffer solution is recommended in order to ensure that the absorbing solution remains alkaline. An example of the procedure to prepare the buffer solution is as follows.

Pour 15 ml of acetic acid (4.6) into 1 000 ml polyethylene volumetric flask and dissolve 50 g of sodium acetate (4.7). Adjust the solution volume to about 900 ml with demineralised water (4.1). Adjust the pH to 5,3 with the 5 mol.l⁻¹ sodium hydroxide solution (4.4.1), for example, then dilute to the mark using demineralised water (4.1) and mix.

pH adjustment can be performed with a different sodium hydroxide solution concentration.

Another reagent such as NaOH solution with phenolphthalein can also be used.

4.9 Chloride reference solution.

4.9.1 Primary chloride reference solution, $c(Cl^{-}) = 0.5$ g.l⁻¹.

Dissolve 166 mg of dry anhydrous sodium chloride (4.2) in demineralised water (4.1). Pour into a 200 ml volumetric flask, then dilute to the mark using demineralised water (4.1) and mix.

Primary chloride reference solution (4.9.1) is used to prepare chloride reference solutions (4.9.2, 4.9.3, 4.9.4, 4.9.5, and 4.9.6). Concentrations of solutions (4.9.2, 4.9.3, 4.9.4, and 4.9.5) are examples of reference solutions that can be used for calibration of selective electrodes. Exact concentrations of calibration solutions should be determined by the user based upon the expected concentration of analyte in the NaOH buffer solution.

4.9.2 Chloride reference solution, $c(Cl^{-}) = 35 \text{ mg.}l^{-1}$.

Pipette 70 ml of the primary reference solution (4.9.1) into 1 000 ml flask. Dilute to the mark with the $0,05 \text{ mol.}l^{-1}$ sodium hydroxide solution (4.4.3) and mix.

4.9.3 Chloride reference solution, $c(Cl^{-}) = 8 \text{ mg.}l^{-1}$.

Pipette 16 ml of the primary reference solution (4.9.1) into 1 000 ml flask. Dilute to the mark with the $0.05 \text{ mol.}l^{-1}$ sodium hydroxide solution (4.4.3) and mix.

4.9.4 Chloride reference solution, $c(Cl^{-}) = 2,5 \text{ mg.}l^{-1}$.

Pipette 5 ml of the primary reference solution (4.9.1) into 1 000 ml flask. Dilute to the mark with the $0,05 \text{ mol.}l^{-1}$ sodium hydroxide solution (4.4.3) and mix.

Chloride reference solution, $c(Cl^{-}) = 2 \text{ mg.}l^{-1}$. 4.9.5

Pipette 25 ml of the reference solution (4.9.3) into a 100 ml flask. Dilute to the mark with the 0,05 mol. l^{-1} sodium hydroxide solution (4.4.3) and mix.

4.9.6 Chloride reference solution, $c(Cl^{-}) = X \text{ mg.}l^{-1}$.

Other chloride reference solution concentrations may be used. For example, a reference solution can be prepared by diluting the reference solution of <u>4.9.1</u> with the 0,05 mol.l⁻¹ sodium hydroxide solution (4.4.3) to obtain the reference solution (4.9.6) A RD PREVIEW

4.10 Fluoride reference solution tandards.iteh.ai)

4.10.1 Primary fluoride reference solution, *c*(**P**) = 0,5 g.l-1.

Dissolve 221 mg of dry anhydrous sodium fluoride 1433 in demineralised water (4.1). Pour into a 200 ml volumetric flask, dilute to the mark using demineralised water (4.1), and mix.

Primary fluoride reference solution (4.10.1) is used to prepare fluoride reference solutions (4.10.2, 4.10.3, <u>4.10.4</u>, <u>4.10.5</u>, and <u>4.10.6</u>). Concentrations of solutions (<u>4.10.2</u>, <u>4.10.3</u>, <u>4.10.4</u>, and <u>4.10.5</u>) are examples of reference solutions that can be used for calibration of selective electrodes. Exact concentrations of calibration solutions should be determined by the user based upon the expected concentration of analyte in the NaOH buffer solution.

4.10.2 Fluoride reference solution, $c(F^{-}) = 5 \text{ mg.}l^{-1}$.

Pipette 10 ml of the primary reference solution (4.10.1) into 1 000 ml flask. Dilute to the mark with the $0.05 \text{ mol.}l^{-1}$ sodium hydroxide solution (4.4.3) and mix.

4.10.3 Fluoride reference solution, $c(F) = 2,5 \text{ mg.}l^{-1}$.

Pipette 25 ml of the reference solution (4.10.2) into a 50 ml flask. Dilute to the mark with the 0,05 mol. l^{-1} sodium hydroxide solution (4.4.3) and mix.

4.10.4 Fluoride reference solution, $c(F^-) = 1 \text{ mg.}l^{-1}$.

Pipette 10 ml of the reference solution (4.10.2) into a 50 ml flask. Dilute to the mark with the 0,05 mol. l^{-1} sodium hydroxide solution (4.4.3) and mix.

4.10.5 Fluoride reference solution, $c(F) = 0.5 \text{ mg.}l^{-1}$.

Pipette 10 ml of the reference solution (4.10.2) into a 100 ml flask. Dilute to the mark with the 0,05 mol. l^{-1} sodium hydroxide solution (4.4.3) and mix.

4.10.6 Fluoride reference solution, $c(F^-) = X \text{ mg.}l^{-1}$.

Other fluoride reference solution concentrations may be used. For example, a reference solution can be prepared by diluting reference solution of 4.10.1 with the 0,05 mol.l⁻¹ sodium hydroxide solution (4.4.3) to obtain the reference solution (4.10.6).

4.11 U₃0₈ or anhydrous tungsten acid.

Application of halogen free U₃O₈ powder or anhydrous tungsten acid can be used in order to accelerate the pyrohydrolysis reaction.

4.12 Concentrated eluent solution for chromatography, 4-hydroxybenzoic acid $c(HOC_6H_4COOH) = 10 \text{ mmol.}l^{-1}$ and N,N-Diethylethanolamine, $c((C_2H_5)_2NCH_2CH_2CH_2OH) = 11 \text{ mmol.}l^{-1}$.

For example, the procedure to prepare concentrated eluent solution can be as follows.

Dissolve 1,38g of 4-hydroxybenzoic acid with 700 ml demineralised water (4.1).

Transfer 1,48 ml aliquot of N,N-Diethylethanolamine into 1 000 ml volumetric flask. Add all dissolved 4-hydroxybenzoic acid and dilute to 1 000 ml with demineralised water (4.1). Homogenize.

Prepared solution should be stored in a polyethylene bottle and kept in a refrigerator.

Other concentrated eluent solution such as KOH, NaOH, or NaHCO₃/Na₂CO₃ can also be used.

4.13 Standard eluent solutions for chromatographyRD PREVIEW

For example, the procedure to prepare standard eluent solutions can be as follows.

Transfer 50 ml aliquot of concentrated eluent solution (4.12) into a 500 ml volumetric flask and dilute to 500 ml with demineralised water (4.1) (heated to the room temperature before use). Homogenize.

The make-up of the standard eluent solution is 4^{-1} hydroxybenzoic acid, $c(HOC_6H_4COOH) = 1,0 \text{ mmol.}l^{-1}$ and N,N-Diethylethanolamine, $c((C_2H_5)_2NCH_2CH_2CH_2OH)) = 1,1 \text{ mmol.}l^{-1}$ (approximately pH 7,9).

Filtration of the solution to remove fine particles before use is recommended.

Other standard eluent solutions such as KOH, NaOH, or NaHC0 $_3$ /Na $_2$ CO $_3$ with different concentrations can also be used.

4.14 Flow gas, pure air or oxygen.

5 Equipment

5.1 Standard laboratory equipment

- 5.2 **Pyrohydrolysis equipment**, refer to Figure 1.
- **5.2.1 Tubular furnace**, equipped with a calibrated temperature regulator.

5.2.2 Tube with condenser, Inconel®¹), platinum, or quartz.

5.2.3 Steam generator, consisting of a reservoir for water (<u>4.1</u>) and provisions for heating and temperature regulation to adjust the flow rate of the steam.

5.2.4 Combustion boats, of Inconel®¹), platinum, ceramic, or quartz.

5.3 Volumetric flasks or test tube, 10, 50, 100, and 1 000 ml. Flasks of any material can be used after verification of acceptable blank levels of fluoride and chloride.

5.4 Balance, capable of reading the nearest 1 mg or less depending on the sample mass. Check the calibration validity before use.

5.5 Ion analysis measuring with selective electrode equipment

5.5.1 Millivoltmeter, required sensitivity is approx. 0,1 mV.

5.5.2 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, Annex A and in accordance with the manufacturer's manual.

5.5.3 Fluorine 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, Annex A and in accordance with the manufacturer's manual.

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5.5.4 Double-junction reference electrode, compatible4with4the4millivoltmeter. 0897251f8af5/iso-21613-2015

5.6 Ion-exchange chromatography system

High-Performance Liquid Chromatography (HPLC) or any other ionic chromatograph instrument.

5.6.1 Injector, consists of injection bulb, injection loop, and syringe or auto sampler.

5.6.2 Pump.

5.6.3 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.

5.6.4 Suppressor.

5.6.5 Conductivity measurement sensor.

5.7 Mortar

¹⁾ Inconel is an example of a suitable product available commercially. This information is given for the convenience of users of ISO 21613 and does not constitute an endorsement by ISO of this product.