INTERNATIONAL STANDARD

ISO 22875

First edition
2008-01-15

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

Reference number
ISO 22875:2008(E)

PDF disclaimer

This PDF file may contain embedded typefaces. In accordance with Adobe's licensing policy, this file may be printed or viewed but shall not be edited unless the typefaces which are embedded are licensed to and installed on the computer performing the editing. In downloading this file, parties accept therein the responsibility of not infringing Adobe's licensing policy. The ISO Central Secretariat accepts no liability in this area.

Adobe is a trademark of Adobe Systems Incorporated.

Details of the software products used to create this PDF file can be found in the General Info relative to the file; the PDF-creation parameters were optimized for printing. Every care has been taken to ensure that the file is suitable for use by ISO member bodies. In the unlikely event that a problem relating to it is found, please inform the Central Secretariat at the address given below.

COPYRIGHT PROTECTED DOCUMENT

© ISO 2008

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from either ISO at the address below or ISO's member body in the country of the requester.

ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

Published in Switzerland

Contents

Page

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

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.

ISO 22875 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

Introduction

This International Standard 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-exchange chromatography systems and ion-selective electrode measurement systems are available; the equipment and operating procedure are, therefore, not described in detail.

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

1 Scope

This International Standard describes a method for determining chlorine and fluorine in uranium dioxide powder and sintered pellets. It is applicable for the analysis 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

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*

3 Principle

The samples are pyrohydrolysed at 900 °C to 1 000 °C in a tubular furnace with wet air or steam 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-exchange chromatography;

b) selective electrode measurement.

4 Reagents

Use reagents of recognized analytical grade.

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

4.2 Anhydrous sodium chloride (NaCl).

4.3 Anhydrous sodium fluoride (NaF).

4.4 Sodium carbonate (Na_2CO_3).

4.5 Anhydrous sodium bicarbonate ($NaHCO_3$).

4.6 Glacial acetic acid (CH_3COOH), $\rho(CH_3COOH) = 1{,}06$ g/ml.

4.7 Potassium acetate (CH_3COOK).

4.8 Concentrated eluant solution, $c(Na_2CO_3) = 0{,}018$ mol/l and $c(NaHCO_3) = 0{,}017$ mol/l.

Dissolve 1,908 g of Na_2CO_3 (4.4) and 1,428 g of $NaHCO_3$ (4.5) in water (4.1). Pour into a 1 l volumetric flask. Dilute to 1 l with water (4.1). Homogenize.

4.9 Standard eluant solution, Add 100 ml of concentrated eluant solution (4.8) to a 1 l volumetric flask. Dilute to 1 l with water (4.1). Homogenize.

4.10 Make-up eluant solution, $c(Na_2CO_3) = 0{,}09$ mol/l and $c(NaHCO_3) = 0{,}085$ mol/l.

Dissolve 9,540 g of Na_2CO_3 (4.4) and 7,140 g of $NaHCO_3$ (4.5) in water (4.1) Pour into a 1 l volumetric flask. Dilute to 1 l with water (4.1). Homogenize.

4.11 Buffer solution, $c(CH_3COOH) = 0{,}005$ mol/l and $c(CH_3COOK) = 0{,}005$ mol/l.

Pour 250 µl of acetic acid (4.6) and 0,50 g of potassium acetate (4.7) into a 1 l polyethylene volumetric flask. Dilute to 1 l with water (4.1). Homogenize.

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

4.12 Chloride reference solution, $\rho(Cl) = 1$ g/l. Dissolve 1,648 g of dry anhydrous sodium chloride (4.2) in water (4.1). Pour into a 1 l volumetric flask. Dilute to 1 l with water (4.1). Homogenize.

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

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

Pipette 10 ml reference solution (4.12) into a 100 ml volumetric flask. Dilute to 100 ml with water (4.1). Homogenize.

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

Pipette 10 ml reference solution (4.13) into a 100 ml volumetric flask. Dilute to 100 ml with water (4.1) Homogenize.

Solutions may be stored for two months.

4.15 Fluoride reference solution, $\rho(F) = 1$ g/l.

Dissolve 2,210 ± 0,001 g of dry anhydrous sodium fluoride (4.3) in water (4.1). Pour into a 1 l volumetric flask. Dilute to 1 l with water (4.1). Homogenize.

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

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

Pipette 10 ml reference solution (4.15) into a 100 ml volumetric flask. Dilute to 100 ml with water (4.1). Homogenize.

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

Pipette 10 ml reference solution (4.16) into a 100 ml flask. Dilute to 100 ml with water (4.1). Homogenize.

Solutions may be stored for two months.

4.18 Chloride and fluoride calibration standard solutions for chromatography, $\rho(Cl) = 0{,}2$ mg/l; $\rho(Cl) = 0{,}5$ mg/l; $\rho(Cl) = 1{,}0$ mg/l; $\rho(F) = 0{,}2$ mg/l; $\rho(F) = 0{,}5$ mg/l; $\rho(F) = 1{,}0$ 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 (4.14) and the 0,01 g/l fluoride reference solution (4.17). Add 2 ml of concentrated eluant solution (4.8) to each flask. Dilute to 100 ml with water (4.1). 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.

4.19 Chloride calibration standard solutions for ion analysis, $\rho(\mathrm{Cl}) = 0{,}5$ mg/l; $\rho(\mathrm{Cl}) = 1{,}0$ mg/l; $\rho(\mathrm{Cl}) = 2{,}0$ 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 (4.14). Add 20 ml of buffer solution (4.11). Dilute to 100 ml with water (4.1). 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.

4.20 Fluoride calibration standard solutions for ion analysis, $\rho(\mathrm{F}) = 0{,}5$ mg/l; $\rho(\mathrm{F}) = 1{,}0$ mg/l; $\rho(\mathrm{F}) = 2{,}0$ mg/l.

Pipette 5 ml, 10 ml and 20 ml of the 0,01 g/l fluoride reference solution (4.17) into three 100 ml volumetric flasks. Add 20 ml of buffer solution (4.11). Dilute to 100 ml with water (4.1). 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 Apparatus

5.1 Standard laboratory equipment.

5.2 Pyrohydrolysis apparatus.

5.2.1 Tubular furnace, equipped with a calibrated temperature regulator.

5.2.2 Tube with steam heater and condenser.

The tube (Inconel[1], platinum or quartz) in the furnace is 400 mm long and 20 mm in diameter.

The diameter of the junction tube is 5 mm.

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.

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

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

5.3 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.

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

---

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.

5.5 Ion-exchange chromatography system.

5.5.1 Injection loop, 100 µl capacity, able to achieve the reproducibility reported.

5.5.2 Pump.

5.5.3 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.

5.5.4 Neutralization column.

5.5.5 Conductivity measurement sensor.

5.5.6 Sample changer.

5.5.7 PC and software.

5.5.8 Printer.

5.6 Ion analysis measuring equipment.

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

5.6.2 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.

5.6.3 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.

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

5.7 Mortar.

6 Procedure

Make-up eluant solution (4.10) is added to the flasks for calibration solutions and for the solution used to recover the pyrohydrolysis condensates.

6.1 Calibration

6.1.1 Ion-exchange chromatography calibration

Successively perform chromatography analysis on the standard eluant solution (4.9) as a blank sample, and on the three calibration standards (4.18).

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.

6.1.2 Millivoltmeter calibration

Pour about 60 ml of each chloride calibration standard solution (4.12, 4.13 and 4.14) into a separate beaker. Stir each beaker slowly and regularly. Insert the chloride ion-selective electrode (5.6.2). Record the potential value after the equilibrium is reached, then remove and carefully rinse the electrode in water (4.1). 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 (4.15, 4.16 and 4.17) and the fluorine ion-selective electrode (5.6.3).

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

6.2 Sample pyrohydrolysis

6.2.1 Blank test

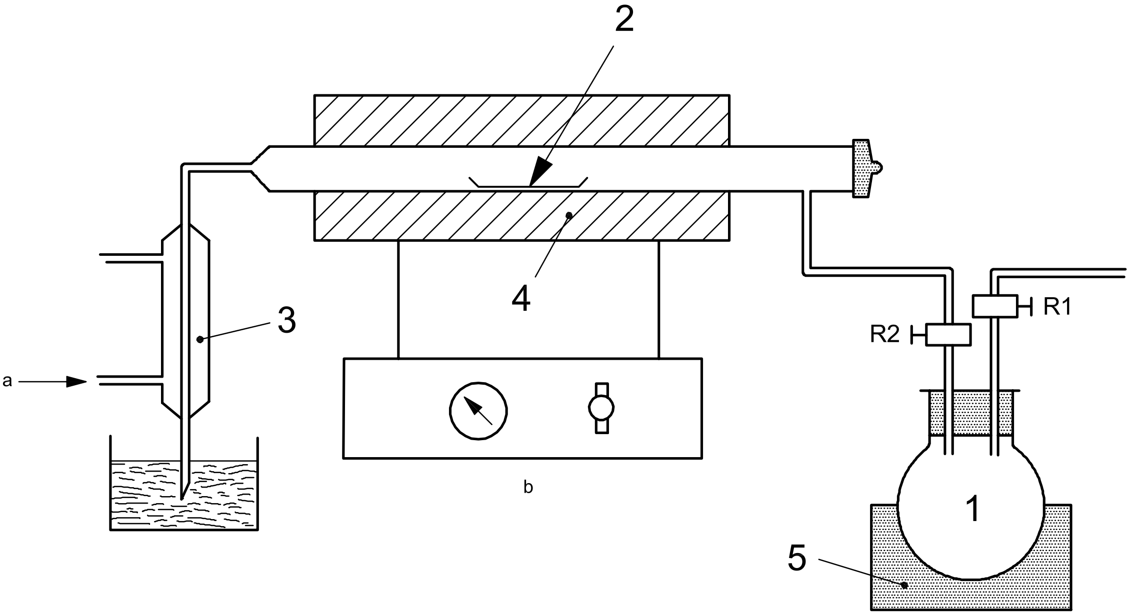
Blank tests shall be carried out before and after each series of analyses, as described below.

a) Assemble the pyrohydrolysis apparatus (5.2; c.f. example in Figure 1).

b) Adjust the temperature of the furnace (5.2.1) to between 900 °C and 1 000 °C and check the validity of the furnace temperature-regulating system.

c) Adjust the distillate flow rate to 80 ml per 15 min. Purge the device with steam for 30 min.

d) Shut off the steam flow by opening stopcock R1 to atmosphere and closing stopcock R2 leading to the tube (5.2.2). Open the tube.



Key

1 water

2 combustion boat

3 condenser

4 furnace

5 regulated steam generator

[a] water.

[b] regulated heating.

Figure 1 — Schematic diagram of a pyrohydrolysis apparatus

e) For a measurement, carry out one of the two following operations:

- For a chromatographic measurement, add 4 ml of eluant solution (4.9) and about 30 ml of water (4.1) to a 250 ml flask (5.3) and insert the flask so that the outlet of the condenser is immersed in the solution.

- For a measurement with an ion-selective electrode, add 50 ml of buffer solution (4.11) and water (4.1) to a 200 ml flask (5.3) and insert the flask so that the outlet of the condenser is immersed in the solution.

f) Place the empty combustion boat (5.2.4) in the tube (5.2.2) and close the tube.

g) Restore the steam flow by closing stopcock R1 and opening stopcock R2.

h) Collect about 150 ml of distillate, then shut off the steam flow by opening stopcock R1 and closing stopcock R2.

i) Rinse the outlet tube with demineralized water, allowing the water to drain into the flask. Adjust to the gauge mark (250 ml for a chromatographic measurement, 200 ml for an ion-analysis measurement) with demineralized water and homogenize.

j) This blank test constitutes the initial blank, $c_{\text{bl,in}}$, for the series of determinations.

k) After completing the series of determinations, proceed with a final blank test, $c_{\text{bl,fi}}$.

6.2.2 Uranium dioxide powder sample

a) Weigh 1 g to 10 g of powder to the nearest 1 mg, depending on the expected concentrations, to obtain a sample with a mass, m.

b) Pour the sample into the combustion boat (5.2.4) at room temperature.

c) Insert the combustion boat (5.2.4) into the tube (5.2.2) and carry out the pyrohydrolysis as described in 6.2.1.

6.2.3 Uranium dioxide pellet sample

a) Place the pellets in a mortar (5.7) and crush to a fine powder for 3 min.

b) Homogenize the powder.

c) Weigh 1 g to 10 g of powder to the nearest 1 mg, depending on the expected concentrations, to obtain a sample with a mass, m.

d) Pour the sample into the combustion boat (5.2.4) at room temperature.

e) Insert the combustion boat (5.2.4) into the tube (5.2.2) and carry out the pyrohydrolysis as described in 6.2.1.

6.3 Measurement of pyrohydrolysis solutions

6.3.1 Chromatographic measurement

a) Place the solutions in the sample changer (5.5.6) in the following order: initial blank, samples, final blank. It is advisable to insert calibration standards at regular intervals to check the calibration validity.

b) Proceed with chromatographic analysis of the solutions.

c) From the stored linear regressions, calculate the chlorine mass concentration, in milligrams per litre, and the fluorine mass concentration, in milligrams per litre, of the solution.

NOTE Bromide, iodide, sulfide and cyanide, if present in the condensate, interfere with the measurement of chloride, but have very little effect on measurement of fluoride.

6.3.2 Measurement with an ion-selective electrode

a) Sample about 60 ml of the pyrohydrolysis solution in a polyethylene beaker.

b) Perform the measurement as for the calibration solutions (4.19 and 4.20).

c) From the calibration curves, calculate the chlorine mass concentration, in milligrams per litre, and the fluorine mass concentration, in milligrams per litre, of the solution.

NOTE Bromide, iodide, sulfide and cyanide, if present in the condensate, interfere with the measurement of chloride, but have very little effect upon the measurement of fluoride.

6.4 Expression of results

6.4.1 Results of chromatographic analysis

6.4.1.1 Calculation

Calculate the mass fraction of fluorine, w_{F}, expressed in micrograms of F per gram of sample, and the mass fraction of chlorine, w_{Cl}, expressed in micrograms of Cl per gram of sample, from Equations (1) and (2), respectively:

$$w_{\text{F}} = \frac{\left[\rho_{\text{F}} - 0{,}5\left(\rho_{\text{bl,in}} + \rho_{\text{bl,f}i}\right)\right] \times 250}{m} \tag{1}$$

$$w_{\text{Cl}} = \frac{\left[\rho_{\text{Cl}} - 0{,}5\left(\rho_{\text{bl,in}} + \rho_{\text{bl,fi}}\right)\right] \times 250}{m} \tag{2}$$

where

ρ_{Cl} is the chloride ion mass concentration, expressed in milligrams per litre, of pyrohydrolysis sample measured by ion chromatography;

ρ_{F} is the fluoride ion mass concentration, expressed in milligrams per litre, of pyrohydrolysis sample measured by ion chromatography;

$\rho_{\text{bl,in}}$ is the chloride or fluoride ion mass concentration, expressed in milligrams per litre, in initial blank test measured by ion chromatography;

$\rho_{\text{bl,fi}}$ is the chloride or fluoride ion mass concentration, expressed in milligrams per litre, in final blank test measured by ion chromatography;

m is the test sample mass, expressed in grams;

250 is the pyrohydrolysis solution volume, expressed in millilitres.

6.4.1.2 Determination limits

The determination limit is the upper concentration of an analyte that can be determined with an acceptable level of repeatability, precision and trueness. The determination limit is an indicative value and should not normally be used in decision-making.

The determination limit for the mass fraction of chlorine is 200 µg per gram sample for a 1 g sample.

The determination limit for the mass fraction of fluorine is 200 µg per gram sample for a 1 g sample.

6.4.1.3 Determination uncertainty

Under the operating conditions defined in this International Standard, the determination uncertainty on chlorine content values ranging from 5 µg Cl per gram sample to 100 µg Cl per gram sample is ± 1,0 µg Cl per gram sample.

Under the operating conditions defined in this standard, the determination uncertainty on fluorine content values ranging from 2 µg F per gram sample to 100 µg F per gram sample is ± 0,5 µg F per gram sample.

The level of uncertainty is an estimate attached to a round-robin test organized by CETAMA. The relative standard deviation is estimated on the basis of the reference value and the statistical distribution of the results, under repeatability conditions and reproducibility conditions (with a coverage factor of 1,0).

6.4.2 Results of ion-specific electrode analysis

6.4.2.1 Calculation

Calculate the mass fraction of fluorine, w_{F}, expressed in micrograms of F per gram of sample, and the mass fraction of chlorine, w_{Cl}, expressed in micrograms of Cl per gram of sample, from Equations (3) and (4), respectively:

$$w_{\mathrm{F}} = \frac{\left[\rho_{\mathrm{F}} - 0{,}5\left(\rho_{\mathrm{bl},in} + \rho_{\mathrm{bl},f\mathrm{i}}\right)\right] \times 200}{m} \tag{3}$$

$$w_{\mathrm{Cl}} = \frac{\left[\rho_{\mathrm{Cl}} - 0{,}5\left(\rho_{\mathrm{bl},in} + \rho_{\mathrm{bl},f\mathrm{i}}\right)\right] \times 200}{m} \tag{4}$$

where

ρ_{Cl} is the chloride ion mass concentration, expressed in milligrams per litre, of pyrohydrolysis sample measured by ion chromatography;

ρ_{F} is the fluoride ion mass concentration, expressed in milligrams per litre, of pyrohydrolysis sample measured by ion chromatography;

$\rho_{\mathrm{bl,in}}$ is the chloride or fluoride ion mass concentration, expressed in milligrams per litre, in initial blank test measured by ion chromatography;

$\rho_{\mathrm{bl,fi}}$ is the chloride or fluoride ion mass concentration, expressed in milligrams per litre, in final blank test measured by ion chromatography;

m is the test sample mass, expressed in grams;

200 is the pyrohydrolysis solution volume, expressed in millilitres.

6.4.2.2 Determination limits

The determination limit, also known as “limit of quantification” (LOQ) is the upper concentration of an analyte that can be determined with an acceptable level of repeatability, precision and trueness. LOQ is an indicative value and should not normally be used in decision-making.

The upper limit for the mass fraction of chlorine is 500 µg per gram sample for a 1 g sample.

The upper limit for the mass fraction of fluorine is 500 µg per gram sample for a 1 g sample.

6.4.2.3 Determination uncertainty

Under the operating conditions defined in this International Standard, the determination uncertainty on the chlorine and fluorine content at low levels is on the order of 10 %.

The level of uncertainty (10 % relative) is an estimate attached to a round-robin test organized by CETAMA. The relative standard deviation is estimated on the basis of the reference value and the statistical distribution of the results, under repeatability conditions and reproducibility conditions (with a coverage factor of 1,0).

7 Test report

The test report shall include the following information:

a) identification of sample;

b) method used by reference to this International Standard;

c) results and the form in which they are expressed;

d) any unusual features noted during the test;

e) any operations not included in this International Standard, or regarded as optional.

Bibliography

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

[2] ASTM C696, *Standard Test Methods for Chemical, Mass Spectrometric and Spectrochemical Analysis of Nuclear-Grade Uranium Dioxide Powders and Pellets*

[3] ASTM C1502, *Standard Test Method for Determination of Total Chlorine and Fluorine in Uranium Dioxide and Gadolinium Oxide*

ICS 27.120.30

Price based on 10 pages