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

National foreword

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ISO copyright office
Ch. de Blandonnet 8 • CP 401
CH-1214 Vernier, Geneva, Switzerland
Tel. +41 22 749 01 11
Fax +41 22 749 09 47
copyright@iso.org
www.iso.org

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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*.

(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 $\mu g.g^{-1}$ to 50 $\mu g.g^{-1}$ of chlorine and 2 $\mu g.g^{-1}$ to 50 $\mu g.g^{-1}$of fluorine.

For UO_2 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 — Determination 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*

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 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 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(NaOH) = 10^{-4} 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.

4.6 **Glacial acetic acid**, (CH_3COOH), relative density approximately 1,06 g.ml^{-1}.

4.7 **Sodium acetate**, (CH_3COONa) analytical grade.

4.8 Buffer solution.

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 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 mol.l^{-1} sodium hydroxide solution (4.4.3) and mix.

4.9.3 **Chloride reference solution**, $c(Cl^-)$ = 8 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 mol.l^{-1} sodium hydroxide solution (4.4.3) and mix.

4.9.4 **Chloride reference solution**, $c(Cl^-)$ = 2,5 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 mol.l^{-1} sodium hydroxide solution (4.4.3) and mix.

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

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 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 4.9.1 with the 0,05 mol.l^{-1} sodium hydroxide solution (4.4.3) to obtain the reference solution (4.9.6).

4.10 **Fluoride reference solution**.

4.10.1 **Primary fluoride reference solution**, $c(F^-)$ = 0,5 g.l^{-1}.

Dissolve 221 mg of dry anhydrous sodium fluoride (4.3) 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, 4.10.4, 4.10.5, and 4.10.6). Concentrations of solutions (4.10.2, 4.10.3, 4.10.4, and 4.10.5) 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.

4.10.2 **Fluoride reference solution**, $c(F^-)$ = 5 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 mol.l^{-1} sodium hydroxide solution (4.4.3) and mix.

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

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 U_3O_8 or anhydrous tungsten acid.

Application of halogen free U_3O_8 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 $c(HOC_6H_4COOH) = 10\ mmol.l^{-1}$ and N,N-Diethylethanolamine, $c((C_2H_5)_2NCH_2CH_2CH_2OH) = 11\ mmol.l^{-1}$.

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 $NaHC0_3/Na_2CO_3$ can also be used.

4.13 Standard eluent solutions for chromatography.

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-hydroxybenzoic acid, $c(HOC_6H_4COOH) = 1,0\ mmol.l^{-1}$ and N,N-Diethylethanolamine, $c((C_2H_5)_2NCH_2CH_2CH_2OH)) = 1,1\ mmol.l^{-1}$ (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 $NaHC0_3/Na_2CO_3$ 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 (4.1) 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.

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

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

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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.

6 Operating procedure

6.1 Sample pyrohydrolysis

6.1.1 Blank test

Blank tests can be carried out before and after each series of analyses according to the procedure describe in 6.1.4 (for the blank test, the empty combustion boat is introduced into the furnace).

Before the series of analyses, a blank test is performed to establish the initial background (blank B_0) for the series of determinations.

After completing the series of determinations, another blank test (final blank test B_F) is performed to confirm if the background did not change significantly during the analysis.

If negligible F or Cl were found in the blank measurements, only the initial blank result is used for the calculation of the blank value (6.3.1).

6.1.2 (U,Pu)O_2 powder sample

Weigh powder to obtain a sample with a mass, *M*. Frequently, sample mass, *M,* is 10 g (±0,001 g), but sample mass could be less down to 1 g according to the chloride or fluoride concentration in the sample or according to the required analytical performance.

Pour the sample into the combustion boat at room temperature.

Carry out the pyrohydrolysis according to the procedure described in 6.1.4 (same procedure as for the blank test 6.1.1, but with sample in the combustion boat).

6.1.3 (U,Pu)O_2 pellet sample

Sample one or two pellets from the analysis lot with a total mass, *M*.

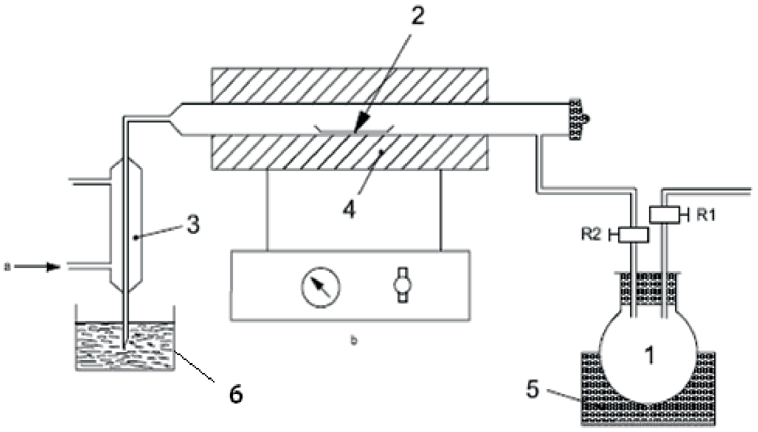
Place the pellets in the sample vessel at room temperature.

Carry out the pyrohydrolysis according to the procedure described in 6.1.4 (same procedure as for the blank test 6.1.1, but with sample in the combustion boat).

Another way to proceed is to place the pellets in a mortar (5.7) and crush them to a fine powder and homogenize. For pellets crushed into powder, refer to 6.1.2.

6.1.4 Pyrohydrolysis

For the example of assembly of the pyrohydrolysis device, see Figure 1.



Key

1	water
2	combustion boat
3	condenser
4	fumace
5	regulated steam generator
6	receiver solution (NaOH)
a	Water.
b	Regulated heating.

Figure 1 — Schematic diagram of a pyrohydrolysis device using superheated steam

a) Adjust the furnace temperature to 850 °C - 1 000 °C.

NOTE Pyrohydrolysis consists of decomposing by heating species containing fluoride and chloride. Then, chloride and fluoride are released. In the presence of water vapour, these elements are recovered either to chlorhydric or fluorhydric acid which is trapped in sodium hydroxide solution.

Species containing chloride can be organic chloride compounds (decomposition between 450 °C and 550 °C) or mineral salts (decomposition starting at 850 °C).

Species containing fluoride can be mainly mineral salts, for instance, smectite (decomposition between 550 °C and 700 °C), illite (decomposition starting at 750 °C), apatite (decomposition between 600 °C and 700 °C), and fluorine, CaF_2 (decomposition at 900 °C).

For both species containing chloride or fluoride listed above, kinetic decomposition increases with temperature so that the pyrohydrolysis yield tends to increase when the temperature increases.

To ensure the highest fluoride salts decomposition yield, it is recommended to use temperature above 900 °C. However, depending on the application, a temperature above 850 °C can be sufficient (for example, if there is no fluorite in the sample).

b) Check the calibration of the furnace temperature regulating system.

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

d) Shut off the steam flow to the furnace by opening stopcock, R1, to atmosphere and closing stopcock, R2, leading to the furnace .

e) Open the furnace.

f) Place the combustion boat (5.2.4), either empty (blank test, 6.1.1) or containing $(U,Pu)O_2$ powder sample (6.1.2) or $(U,Pu)O_2$ pellet sample (6.1.3) in the furnace, and close the furnace.

g) For the measurement of chloride and fluoride, carry out of one of the following operations:

   1) for measurements with a selective electrode, place 100 ml flask containing at least a volume of about 5 ml of 0,5 $mol.l^{-1}$ sodium hydroxide solution (4.4.2) under the condenser so that the outlet end of the condenser is immersed in the solution;

   2) for measurements by chromatography, add at least 4 ml of sodium hydroxide solution (4.4.4) to a volumetric flask or test tube and place the flask/test tube under the condenser so that the outlet end of the condenser is immersed in the solution.

h) Restore the steam flow by closing stopcock, R1, to atmosphere and opening stopcock, R2, leading to the furnace.

i) Collect about 45 ml or during a period of about 10 min (at a gas flow rate of 0,4 l.min-1) of distillate, then shut off the steam flow to the furnace by opening stopcock, R1, to atmosphere and closing stopcock, R2, leading to the furnace.

j) Rinse the outlet tube with demineralised water (4.1) allowing the water to drain into the flask. Adjust the solution in the flask/test tube to the required volume with demineralised water (4.1) and mix.

6.2 Measurement of pyrohydrolysis solutions

Measurement procedure by selective electrode and ionic chromatography is shown below for example.

6.2.1 Measurement by selective electrode

6.2.1.1 Calibration curve

a) Connect the chloride-specific electrode (5.5.2) to the millivoltmeter (5.5.1).

b) Pour 10 ml of each chloride reference solution (4.9.1, 4.9.2, 4.9.3, 4.9.4, 4.9.5, and 4.9.6) into a separate polyethylene beaker.

c) Add 10 ml of buffer solution (4.8) to each beaker. Stir each beaker slowly and regularly. Insert the electrode. Record the potential value after the equilibrium is reached. Plot the calibration curve of the measured potentials versus the decimal logarithm of the chloride concentrations ($mg.l^{-1}$) in the standard solutions.

d) Repeat the same procedure with the fluoride-specific electrode (5.5.3) and fluoride standard solutions (4.10.1, 4.10.2, 4.10.3, 4.10.4, 4.10.5, and 4.10.6).

The temperature of the standard solutions should be constant for selective electrode measurements to avoid the need for applying correction factors.

6.2.1.2 Measurement

The hydrolysis solutions for the initial and final blank tests and the sample hydrolysis solutions are measured in the same way.

a) Sample 10 ml of the pyrohydrolysis solution in a polyethylene beaker. Add 10 ml of buffer solution (4.8). Stir slowly and regularly. Insert the electrode. Record the potential value after equilibrium is reached.

b) From the calibration curves (refer to 6.2.1.1), calculate the chlorine concentration, $[Cl^-]$ (mg.l^{-1}), and the fluorine concentration, $[F^-]$ (mg.l^{-1}), of the measured solution.

6.2.2 Measurement by ionic chromatography

a) Load the solutions from the injector (5.6.1) in the order of initial blank and samples and final blank. It is advisable to insert calibration standards at regular intervals to check the calibration of the equipment.

b) Proceed with chromatographic analysis of the solutions using the standard eluent solution (4.13).

c) From the stored linear regressions, calculate the chlorine concentration, $[\text{Cl}^-]$, in milligrams per litre and the fluorine concentration, [F-], in milligrams per litre.

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

6.3 Expression of results

6.3.1 Calculation

Calculate the chlorine and fluorine content (mg.kg^{-1}or $\mu\text{g. g}^{-1}$) of the sample from the following formulas:

$$W_{Cl} = \frac{\left[\left[Cl^-\right] - \left(\frac{B_O^{Cl} + B_F^{Cl}}{2}\right)\right] \times V_p}{M}$$

$$W_F = \frac{\left[\left[F^-\right] - \left(\frac{B_O^{F} + B_F^{F}}{2}\right)\right] \times V_p}{M} \qquad (1)$$

where

W_F	is the fluorine content, in mg per kg or µg per g of sample;
W_Cl	is the chlorine content, in mg per kg or µg per g of sample;
$[Cl^-]$	is the measured chloride ion concentration, (mg.l^{-1}), of pyrohydrolysis sample;
$[F^-]$	is the measured fluoride ion concentration, (mg.l^{-1}), of pyrohydrolysis sample;
$B_O^{Cl\text{ or }F}$	measured chloride or fluoride ion concentration in initial blank test;
$B_F^{Cl\text{ or }F}$	measured chloride or fluoride ion concentration in final blank test;
M	test sample mass, (g);
V_p	pyrohydrolysis solution volume, (ml), as example 100 ml (selective electrodes detection) or 100 ml (HPLC detection).

NOTE In the formula, it is assumed that the pyrohydrolysis yield is 100 %. Pyrohydrolysis yield of 100 % is achieved if furnace sizing is in accordance with Reference [3].

If furnace sizing is not in accordance with Reference [3]:

— in the case the analysis is to check the absence of chloride or fluoride in the sample, there is no need to determine pyrohydrolysis yields;

- in the case where chloride or fluoride are detected, depending on the analysis requirement, pyrohydrolysis yields can be taken into account. Pyrohydrolysis yields are different for chloride and fluoride and depend on pyrohydrolysis temperature and chloride and fluoride concentration in the sample.

They can be determined during the equipment set up validation test, for instance, by a pyrohydrolysis of a sample with addition of known quantities of chloride and fluoride (refer to Reference [1]).

Taking into account pyrohydrolysis yields, the chlorine and fluorine content (mg.kg^{-1}or µg.g^{-1}) of the sample can be calculated from the following formulae:

$$W_{Cl} = \frac{\left[\left[Cl^-\right] - \left(\frac{B_O^{Cl} + B_F^{Cl}}{2}\right)\right] \times V_p}{R_{Cl} \times M}$$
$$W_F = \frac{\left[\left[F^-\right] - \left(\frac{B_O^{F} + B_F^{F}}{2}\right)\right] \times V_p}{R_F \times M} \qquad (2)$$

where

W_F	is the fluorine content, in mg per kg or µg per g of sample;
W_{Cl}	chlorine content, in mg per kg or µg per g of sample;
$[Cl^-]$	measured chloride ion concentration (mg.l^{-1}) of pyrohydrolysis sample;
$[F^-]$	measured fluoride ion concentration (mg.l^{-1}) of pyrohydrolysis sample;
$B_O^{Cl\ or\ F}$	measured chloride or fluoride ion concentration in initial blank test;
$B_F^{Cl\ or\ F}$	measured chloride or fluoride ion concentration in final blank test;
M	test sample mass (g);
V_p	pyrohydrolysis solution volume (ml);
R_F	pyrohydrolysis yield of fluoride by steam;
R_{Cl}	pyrohydrolysis yield of chloride by steam.

6.3.2 Validation limits

During validation tests, for instance, pyrohydrolysis yields have been determined within the upper and lowest mass fraction of chloride and fluoride.

In the case of fluoride and chloride measurement by selective electrode, under the operating conditions defined in this International Standard, the validation limit for chlorine can be a mass fraction of 5 mg.kg^{-1} to 50 mg.kg^{-1} and for fluoride, can be a mass fraction of 2 mg.kg^{-1} to 50 mg.kg^{-1}.

To stay within the validations limits, the sample mass has to be adjusted.

6.3.3 Determination limits

The determination limit is the lowest concentration of an analyte that can be determined with an acceptable level of repeatability, precision, and trueness. For instance, the determination limits can correspond to the lowest standard solution concentration which has been well-measured during the calibration test.

The determination limit is an indicative value and should not normally be used in decision-making.

Under the operating conditions defined in this International Standard (V_p = 100 ml), the determination limit for the mass fraction of chlorine can be 20 mg.kg^{-1} for a 10 g sample when chloride is measured by selective electrode.

Under the operating conditions defined in this International Standard (V_p = 100 ml), the determination limit for the mass fraction of fluoride can be 5 mg.kg^{-1} for a 10 g sample when fluoride is measured by selective electrode.

Under the operating conditions defined in this International Standard (V_p = 100 ml), the determination limit for the mass fraction of chlorine or fluoride is 50 mg.kg^{-1} for a 1 g sample when chloride or fluoride are measured by ionic chromatography.

6.3.4 Determination uncertainty

Under the operating conditions defined in this International Standard, the determination uncertainty on the chlorine and fluorine content is

- of the order of 20 % in the case fluoride and chloride are measured by selective electrode, and
- of the order of 5 % in the case fluoride and chloride are measured by ionic chromatography for chlorine content values ranging from 1 µg Cl per gram sample to 20 µg Cl per gram sample and for fluorine content values ranging from 1 µg F per gram sample to 20 µg F per gram sample.

7 Test report

The test report shall include the following information:

a) identification of sample;

b) method used by reference to this International Standard, i.e. ISO 21613;

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] Analytical C.H.E.M.I.S.T.R.Y. Separation of fluoride from inorganic compounds by pyrolysis. R.H. POWELL and OSCAR MENIS. Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn, 2002

[2] Analytical C.H.E.M.I.S.T.R.Y. 2002, Pyrohydrolysis in the determination of fluoride and other halides. JAMES C. WARF, W.D. CLINE and RUTH D. TEVEBAUGH. Institute for Atomic Research and Department of chemistry, Iowa State College, Ames, Iowa

[3] ASTM C698, *Standard Test Methods for Chemical, Mass Spectrometric and Spectrochemical Analysis of Nuclear-Grade Mixed Oxide (U, Pu)O2)*

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