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

Métal d'uranium, poudre et pastilles frittées de dioxyde d'uranium, et solutions de nitrate d'uranyle — Détermination de la teneur en fluor — Méthode de l'électrode sélective des ions fluorure

Reference number
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Foreword

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Annex A forms an integral part of this International Standard.

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

1 Scope

1.1 This International Standard specifies an analytical method for determining the fluorine content in uranium metal, uranium dioxide powder and pellets and solutions of uranyl nitrate.

1.2 The method can be used within the concentration range of 1 µg to 0,01 g of fluorine per gram of the sample. Impurity levels of up to 300 µg of boron and 3 000 µg of silicon, aluminium and iron in the final measured solution can be tolerated. Zirconium interferes seriously and should be absent. The applicability of the method to samples containing significant impurity levels can be confirmed by modifying the basic procedure.

2 General requirements

2.1 Principle

A weighed portion of the laboratory sample of uranium metal or uranium dioxide is dissolved in nitric acid in a closed polyethylene bottle to prevent loss of hydrogen fluoride. The nitric acid used is dosed with a known amount of fluoride to give a blank concentration which is higher than the lowest concentration of linear response of the fluoride electrode, thus ensuring that all subsequent measurements will take place within the linear response range of the electrode.

The determination is performed by a known addition procedure in which a small volume of a relatively concentrated fluoride standard solution is added to the initial solution. The result is then calculated using the basic standard addition equation, which is readily deduced from the Nernst equation (see 2.2) as follows:

$$m_i = \frac{m_a}{10^{|E_2 - E_1|/S} - 1}$$

where

m_i is the total mass, in micrograms, of fluorine in the inital solution;

m_a is the total mass, in micrograms, of fluorine in the known addition of fluoride standard solution;

$|E_2 - E_1|$ is the absolute value of the change in potential, in millivolts, which occurs on making the standard addition;

S is the electrode slope at the temperature of the determination.

Potentials are measured using a fluoride ion-selective electrode, reference electrode and digital millivoltmeter.

2.2 Use of Nernst equation

In solutions of constant ionic strength, the fluoride-ion-selective electrode responds to the fluoride ion concentration $[F^-]$ of a solution according to the Nernst equation:

$$E = E'_o - S \lg [F^-]$$

where

E is the measured potential, in millivolts;

E'_o is the standard cell potential, in millivolts;

S is the theoretical value of the Nernst slope (58,2 mV at 20 °C).

In nitric acid solutions of uranium (VI), fluoride ion is complexed by H^+ and UO_2^{2+} ions mainly as HF and UO_2F^+. Both these complexes dissociate to give a very small fraction of free fluoride ions, to which the electrode responds.

The function ϕ is defined as

$$\phi = [F_T]/[F^-]$$

where $[F_T]$ is the total fluorine concentration of the solution. Provided that ϕ remains constant, therefore, the Nernst equation can be written in the form

$$E = E''_o - S \lg [F_T]$$

where $E''_o = E'_o + S \lg \phi$

Under the experimental conditions, ϕ and the ionic strength of the solution remain constant and this equation thus indicates that the total fluorine concentration of the initial solution can be determined.

3 Reagents

Use only reagents of recognized analytical grade and distilled or deionized water.

3.1 Fluoride standard solution, $\rho = 5{,}00$ g/l.

Dry about 2 g of sodium fluoride by heating for 4 h at 120 °C. Allow to cool in a desiccator. Weigh 1,105 g of the dried product, dissolve it in water and dilute to 100 ml in a volumetric flask. Mix and transfer the solution immediately to a 100 ml polyethylene bottle for storage.

3.2 Nitric acid pretreated with fluoride (PWF), diluted 1 + 3.

Carefully mix together 375 ml of water and 125 ml of nitric acid (ρ 1,42 g/ml) and transfer to a 500 ml bottle which is fitted with a 10 ml automatic tilt pipette. When not in use, protect the solution from atmospheric or dust contamination by placing an inverted plastic bag over the pipette and fastening it with a rubber band around the neck of the bottle.

Dilute a 10 ml portion of this reagent with 15 ml of water and proceed as described in 6.2, 6.3 and 7.1.1. Depending on the mass m_2 of fluorine in the blank solution proceed to step a), b) or c).

a) $m_2 < 1{,}25$ µg

Add 60 µg of fluorine [i.e. 0,012 ml of fluoride standard solution (3.1)] to the remaining 490 ml of the mix.

b) $1{,}25$ µg $< m_2 < 2{,}50$ µg

The reagent is satisfactory and does not require treatment.

c) $m_2 > 2{,}50$ µg

Reject the reagent and re-prepare it using a different batch of nitric acid (ρ 1,42 g/ml).

4 Apparatus

4.1 Polyethylene bottles, of capacity 250 ml and 500 ml, with narrow necks and screw-caps.

4.2 Micrometer syringe pipette, of capacity 500 µl, capable of delivering increments of 0,2 µl.

4.3 Fluoride-ion-selective electrode, constructed to be resistant to solutions containing nitric acid at a concentration of 2 mol/l. The sensing portion of the electrode should be immersed in water or a dilute fluoride solution of similar strength to the samples measured for storage between measurements.

4.4 Reference electrode.

4.5 Digital millivoltmeter, capable of discriminating to 0,1 mV, with an input impedance of 10^{12} Ω to 10^{13} Ω.

4.6 Polypropylene beakers, of capacity 50 ml.

5 Sampling

5.1 Preparation of the test sample

5.1.1 Uranium metal and uranyl nitrate solutions

No sample preparation is required.

5.1.2 Uranium dioxide powder

Grind impure uranium dioxide samples finely to give a homogeneous powder and to increase the dissolution rate of any fluorine present as UF_4.

5.1.3 Uranium dioxide pellets

Crush the laboratory sample in a percussion mortar.

6 Procedure

6.1 Preparation of the test solution

6.1.1 Uranium metal and uranium dioxide

Weigh a mass (m_o) of the test sample to the nearest 0,01 g as specified in table 1, and transfer it to a 250 ml polyethylene bottle (4.1) in the case of uranium dioxide, or a 500 ml polyethylene bottle (4.1) for uranium metal.

Add 10 ml of nitric acid (PWF) (3.2), squeeze the bottle to collapse the walls and screw the cap on firmly to ensure that dissolution takes place in a closed system.

Place the bottle in a boiling water bath. When dissolution of the test portion appears to be complete, shake the bottle to remove any particles which may be adhering to the upper walls and neck. Complete the dissolution, if necessary, by reheating.

Allow the solution to cool to room temperature, and dilute to volume (V_o) with water as specified in table 1.

Table 1

Range of fluorine content in laboratory sample	Test portion mass (m_o) g	Dilute to volume (V_o) ml
1 µg/g to 1 000 µg/g	3,00	50
0,1 % (*m*/*m*) to 1,0 % (*m*/*m*)	1,00	100

6.1.2 Uranyl nitrate solutions

Take a volume (V_1) of the laboratory sample as specified in table 2.

Transfer it to a volumetric flask and dilute to volume V_2 with water as specified in table 2.

Table 2

Range of fluorine content in laboratory sample	Test portion volume (V_1) ml	Dilute to volume (V_2) ml
1 µg/ml to 1 000 µg/ml	5 ± 0,01	50
0,1 g/100 ml to 1,0 g/100 ml	1 ± 0,01	100

Take 5,0 ml ± 0,05 ml of the diluted solution and transfer it to a 50 ml polypropylene beaker (4.6). Add 10 ml of nitric acid (PWF) (3.2) and 10 ml of water. Add a stirring rod.

6.2 Known addition procedure

Place the fluoride and reference electrodes in the solution (6.1) and measure the potential whilst stirring at a constant rate. Record the reading E_1, in millivolts, when it is stable, to the nearest 0,1 mV.

NOTE 1 Stirring with a magnetic stirrer should be carried out continuously and at a steady rate throughout the series of measurements. The millivolt reading is considered to be stable when it does not change by more than 0,5 mV/min.

Using the micrometer syringe, add the fluoride standard solution (3.1) until the change in millivolts is greater than 17 mV.

Record the mass m_3, in micrograms, of fluoride added.

NOTE 2 The volume of fluoride standard solution added should not be less than 0,01 ml.

Measure the potential and record the reading E_2, in millivolts, when it is stable, to the nearest 0,1 mV.

Record the temperature (t) of the solution to the nearest 0,5 °C.

6.3 Blank test

Determine the blank level of the reagents (recorded as mass m_2) (see 7.1.1) by carrying out the procedure of 6.1.1, 6.1.2 and 6.2 (as appropriate), but omit the test portion.

7 Expression of results

7.1 Method of calculation

7.1.1 Calculate the total mass of fluorine, in micrograms, in the sample solution (m_1) or blank solution (m_2) using equation (1) which is derived from the Nernst equation (see 2.1):

$$m_1 \text{ or } m_2 = \frac{m_3}{10^{|E_2 - E_1|/S} - 1} \qquad \ldots (1)$$

where

m_3 is the mass, in micrograms, of fluoride in the known standard addition (see 6.2);

$|E_2 - E_1|$ is the absolute value of the change in potential, in millivolts, produced on making the known standard addition (see 6.2);

S is the electrode slope at the temperature t, in degrees Celsius, of the determination, where $S = 54,2 + 0,2t$ (see annex A).

NOTE 3 The electrode slope is the change in millivolts for a decade change in concentration.

7.1.2 Calculate the total fluorine content (w_F) of the test sample, expressed in micrograms of fluorine per gram of sample, using equation (2) or (3).

Uranium metal and uranium dioxide

$$w_F = \frac{(m_1 - m_2)V_o}{5m_o} \qquad \ldots (2)$$

Uranyl nitrate solutions

$$w_F = \frac{(m_1 - m_2)V_2}{5V_1} \qquad \ldots (3)$$

where

m_1 is the mass, in micrograms, of fluorine in the sample solution;

m_2 is the mass, in micrograms, of fluorine in the blank solution;

m_o is the mass, in grams, of the test portion (see 6.2, first paragraph);

V_o is the volume, in millilitres, to which the test solution is diluted in the last paragraph of 6.1.1;

V_1 is the volume, in millilitres, of the test portion in the first paragraph of 6.1.2;

V_2 is the volume, in millilitres, to which the test solution is diluted in the first paragraph of 6.1.2.

7.2 Reproducibility

7.2.1 Uranium dioxide powder

The reproducibility (twice the standard deviation) based on 104 determinations at a fluorine content level of 200 µg/g is ± 13,3 µg/g.

7.2.2 Uranium dioxide pellets

The reproducibility (twice the standard deviation) based on 104 determinations at a fluorine content level of 2 µg/g is ± 1,7 µg/g.

8 Special case — Samples containing high levels of strong fluoride complexants

Prepare the solution of the sample as described in 6.1.1.

Determine the fluorine content of the solution as described in 6.2 and in 7.1.1.

Using the same solution, repeat the procedure described in 6.2 (except the last paragraph) twice again, recording the cumulative mass of fluoride added and the cumulative millivolt change produced.

Calculate the mass of fluorine present in the solution for each of the three known additions, as described in 7.1.1.

NOTE 4 If the volume of fluoride standard solution added exceeds 0,1 ml, correct for volume change using equation (4) instead of equation (1) in 7.1.1 and equation A.1 in A.2.2:

$$m_1 \text{ or } m_2 = \frac{m_3}{10^{|E_2 - E_1|/S} - \dfrac{25}{25 + V_3}} \qquad \ldots (4)$$

where V_3 is the volume, in millilitres, of fluoride standard solution (3.1) added.

The total mass of fluorine present in the solution shall not exceed 2 500 µg.

The three values obtained should be identical within the limits of error described in 7.2.

If the values are not identical, this is an indication that the function $\phi = [F_T]/[F^-]$ does not have a constant value and that the method cannot be applied to the sample under test.

9 Test report

The test report shall include the following information:

a) identification of sample;

b) the method used by reference to this International Standard;

c) the 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.

Annex A
(normative)

Determination of electrode slope (S)

A.1 Procedure

A.1.1 Pipette 10 ml of nitric acid (PWF) (3.2) and 15 ml of water into a 50 ml polypropylene beaker.

A.1.2 Immerse the electrodes in the nitric acid solution, stir and record the millivolt reading (E_b) when it is stable, to the nearest 0,1 mV.

A.1.3 Make cumulative additions of 10 µl, 50 µl, 200 µl, and 1 000 µl of fluoride standard solution (3.1), stirring and recording the millivolt reading (E_i) when it is stable, to the nearest 0,1 mV after each addition. Taking dilution into account, these additions correspond to resultant concentrations of fluorine (ρ_i) of 4,995 µg/ml, 24,88 µg/ml, 98,05 µg/ml and 454,6 µg/ml respectively.

Record the temperature (t) of the solution to the nearest 0,5 °C.

A.2 Expression of results

A.2.1 Determine the electrode slope, using a calculator with linear regression, taking the common logarithm ($\log_{10}$) of the four resultant concentrations ρ_i, in micrograms of fluorine per millilitre of solution as the x-values and the corresponding observed millivolt readings (E_i) as the y-values. Record the slope (S) to the nearest 0,01 mV.

A.2.2 Calculate the blank value, ρ_B, for the concentration of fluorine ρ_F, in micrograms per millilitre of solution, corresponding to each of the four resultant concentrations (ρ_i) from the equation

$$\rho_B = \frac{\rho_i}{10^{|E_i - E_b|/S} - 1} \qquad \ldots (A.1)$$

where

ρ_i is the resultant concentration, in micrograms of fluorine per millilitre of solution, after the ith standard addition;

$|E_i - E_b|$ is the absolute cumulative change, in millivolts, produced by each standard addition;

S is the determined electrode slope at temperature t, in degrees Celsius.

Determine the mean of the four blank values of the concentration of fluorine, in micrograms per millilitre of solution.

A.2.3 Correct the four resultant concentrations (see A.1.3) by adding the mean blank concentration value to each one. Redetermine the electrode slope as described in A.2.1.

A.2.4 Repeat the steps described in A.2.2 and A.2.3 until successive values of the electrode slope differ by less than 0,1 mV.

A.2.5 Record the electrode slope to the nearest 0,1 mV.

The value of S should agree to within $\pm$ 2 % with the theoretical value, at temperature t, given by the equation

$$S = 54{,}2 + 0{,}2t \qquad \ldots (A.2)$$

Results outside this range indicate malfunctions of the electrode system.

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