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**Controlled-potential coulometric assay of
plutonium**

iTeh STANDARD PREVIEW
Dosage de plutonium par coulométrie à potentiel imposé
(standards.iteh.ai)

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Foreword

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Controlled-potential coulometric assay of plutonium

1 Scope

This International Standard specifies an analytical method for the determination of plutonium in plutonium nitrate solutions of nuclear grade with an accuracy better than 0,1 %. The method is suitable for aqueous solutions containing more than $0,05 \text{ g}\cdot\text{l}^{-1}$ plutonium using test samples between 1 mg and 3 mg of plutonium.

2 Principle

The method consists of the following steps:

- preliminary purification by anion exchange to remove interfering substances if they are present in significant amounts (see clause 8);
- fuming with sulfuric acid;
- dissolution of the residue in nitric acid;
- reduction at a controlled potential of almost 99,9 % of the plutonium to valency III and measurement of the equilibrium potential at the end of this step;
- oxidation at a controlled potential of almost 99,9 % of the plutonium to valency IV and measurement of the equilibrium potential at the end of this step.

When calculating the result, allowance is made for the background current and the fraction of plutonium not electrolyzed.

3 Reagents

Use only reagents of recognized analytical grade.

All aqueous solutions shall be prepared with double-distilled or deionized water with a resistivity greater than $1 \text{ M}\Omega\cdot\text{cm}$.

3.1 Nitric acid solution, $c(\text{HNO}_3) = 0,9 \text{ mol/l}$.

3.2 Sulfamic acid solution,
 $c(\text{NH}_2\text{HSO}_3) = 1,5 \text{ mol/l}$.

3.3 Sulfuric acid solution,
 $c(\text{H}_2\text{SO}_4) = 3 \text{ mol/l}$.

3.4 Pure argon or nitrogen (O_2 content lower than 10 parts per million).

3.5 Pure air, (free of any organic compounds).

4 Apparatus

Usual laboratory equipment found in a medium-activity radiochemical laboratory suitable for work with plutonium.

4.1 Analytical balance, capable of weighing to an accuracy of 0,01 mg.

4.2 Equipment for sample evaporation in the coulometric cell, comprising

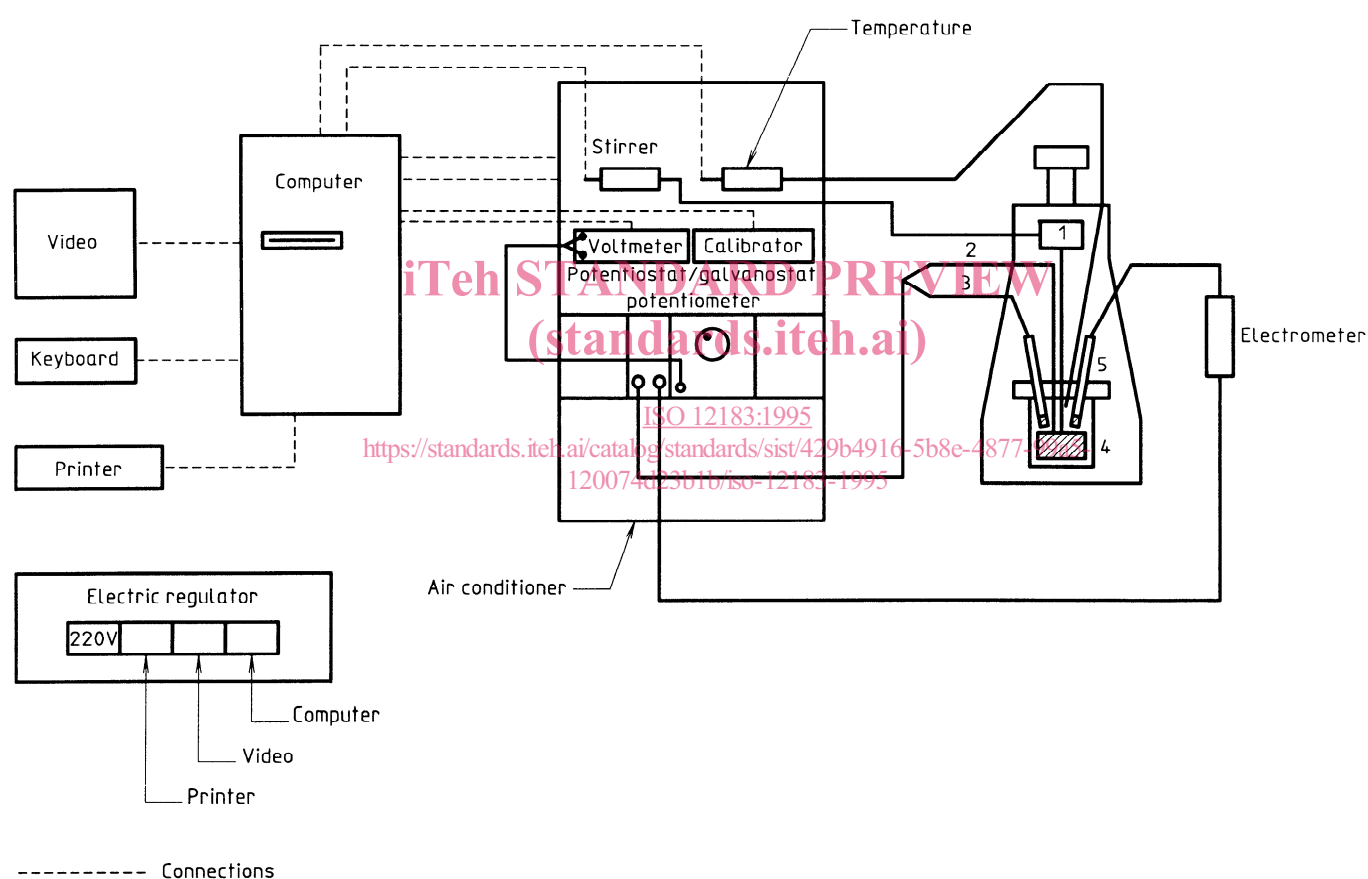
- an overhead radiant heater with means of temperature adjustment;
- an air supply with the delivery tube directed towards the surface of the liquid.

4.3 Controlled-potential coulometer. The following equipment is suitable (see figure 1).

4.3.1 Cylindrical glass coulometric cell, of capacity 50 ml, with an O-ring seal and a lid suitable for the following internal equipment:

- a chemically inert stirrer, designed to prevent splashing, centrally located, with a constant rotation speed of about 1 500 r/min;

- a glass tube plugged at the bottom end with a 2,5 mm thick sintered glass disc (pore size < 5 µm) and filled with nitric acid (3.1);
 - a saturated calomel reference electrode (SCE) housed in the glass tube;
 - another glass tube, identical to the first one and mounted diametrically opposite, also filled with nitric acid (3.1);
 - an auxiliary electrode consisting of a spiral of platinum wire, 0,5 mm in diameter, housed in the glass tube;
 - a working electrode made of gold (99,99 %) and consisting of a gold wire welded to a cylindrical gold wire frame, 15 mm high and 20 mm in diameter, around which are welded several layers (for example four layers) of very fine gold mesh. The stirrer passes through the centre of the working electrode;
 - an inlet tube for inert gas to exclude atmospheric oxygen;
 - a thermocouple for temperature measurement.
- Except for the stirrer passage, all openings in the lid shall be gas-tight.

**Key**

- 1 Stirrer
- 2 Working electrode
- 3 Auxiliary electrode
- 4 Cell
- 5 Reference electrode

Figure 1 — Coulometric cell connections

The flowrate of the solution through the glass disc shall be less than 0,05 ml/min. The flowrate of the liquid through the sintered glass discs depends on gas pressure over the sample and thus has to be checked and adjusted, for example, by changing the gas flowrate. The hole for the stirrer shaft provides a gas vent.

4.3.2 Measuring unit, located in a temperature-controlled cabinet (± 1 °C) to prevent electronic drift, comprising

- a high power quick response controlled potential coulometric system with two accurate potentiometers for selecting and reading the oxidation and reduction potentials;
- a coulometric integrator capable of being read to 10 μ C and able to integrate currents varying from 1 μ A to 100 mA (temperature coefficient of output less than 4 ppm of programmed level or 0,4 ppm of range per degree Celsius);
- accurate electronic clock (accuracy within the selected range better than 0,01 %);
- a calibrated current source delivering a current with an accuracy better than 2×10^{-5} % of current range.

5 Procedure

5.1 Plutonium determination

5.1.1 Weighing the test sample

- a) Fill a polyethylene weighing burette with the solution to be analysed.
- b) Weigh the burette to 0,1 mg.
- c) Deliver the test sample, drop by drop, into a coulometric cell.
- d) Weigh the burette again to 0,1 mg.
- e) The mass difference gives the mass of the sample in the cell.

NOTE 1 To achieve an accuracy better than 0,1 %, the mass of the test sample containing 1 mg to 3 mg of plutonium must be greater than 1 g. Care is needed to avoid any loss of microdrops. During weighing of the polyethylene weight burette, the problem of static electricity is eliminated by contact between the dropping tube and a copper plate connected to the ground.

5.1.2 Preparation of the test sample

- a) Add 1 ml of sulfuric acid solution (3.3) to the coulometric cell containing the test sample.
- b) Place the cell containing the test sample under the radiant heater, adjusted to red heat, and open the air inlet to deliver air with sufficient force to form a shallow conical depression in the liquid surface.
- c) Evaporate until SO₃ fumes disappear and a residue of plutonium sulfate (orange coloured precipitate) is formed.

NOTE 2 The colour of the plutonium sulfate is dependent on the type of lighting used in the laboratory. Under fluorescent lighting the dried sulfate is coral pink. Degradation of plutonium sulfate to plutonium oxide should not be expected even after baking the residue unless extreme temperatures are employed. Failure to use high purity reagents, anion exchange resins washed free of resin fines, and heating equipment that is not well maintained and clean can produce visible black residue in combination with the dried sulfate powder. These residues could be mistaken for plutonium oxide, and depending on their composition might interfere in subsequent measurements.

- d) Continue heating until the residue is completely dry but do not bake the dry residue.
- e) Allow to cool to room temperature.

5.1.3 Electrode pretreatment

The electrodes shall be pretreated if they are not used for more than one day. The platinum tip of the auxiliary electrode is heated in a flame until the platinum becomes white. The working electrode is cleaned with concentrated sulfuric acid with 10 % hydrofluoric acid. The tip is dried using a radiant heater. These electrodes are preserved in 8 mol/l nitric acid.

- a) Assemble the cell lid complete with the electrodes and other internal equipment (see 4.3.1).
- b) Take a clean dry coulometric cell and add a sufficient amount of nitric acid solution (3.1) to immerse the working electrode, and the sintered glass tips of the reference and auxiliary electrode tubes.
- c) Add one drop of sulfamic acid solution (3.2).
- d) Firmly fit the cell under the lid.
- e) Start the stirrer at about 1 500 r/min (avoid forming a vortex).

- f) Open the gas inlet and maintain a flow of inert gas throughout the electrolysis period.
- g) Preselect the oxidation potential at + 1 V (SCE) and the reduction potential at + 0,3 V (SCE).
- h) After degassing for 5 min, start the oxidation and oxidize at + 1 V (SCE) until a residual current of 10 μA is obtained.
- i) Start the reduction and reduce at + 0,3 V (SCE) until a residual current lower than 5 μA is obtained.
- j) Oxidize at +1 V (SCE).
- k) Stop the electrolysis when the current is lower than 10 μA .
- l) Rinse the electrolysis cell and the outside wall of the fritted glass tubes with double distilled or deionized water. Allow to dry.

5.1.4 Coulometric blank determination

- a) Rinse the outside wall of the fritted glass tubes and, if necessary, fill them up with 0,9 mol/l nitric acid solution (3.1).
- b) Repeat steps 5.1.3 b) to f).
- c) Preselect the oxidation potential at + 0,91 V (SCE) and the reduction potential at + 0,4 V (SCE).
- d) After degassing for 5 min, start the oxidation and oxidize at + 0,91 V (SCE) until a residual current of 5 μA is obtained.
- e) Start the reduction and reduce at + 0,4 V (SCE) until a residual current ranging between 60 μA and 100 μA is obtained.
- f) Slowly raise the potential until the residual current is lower than 1 μA .
- g) Read the equilibrium reduction potential E_1 from the potentiostat potentiometer. E_1 shall be less than 0,5 V (SCE).
- h) Reset the integrator. The starting of the integrator and timer shall coincide with the beginning of the oxidation.
- i) Start the oxidation and oxidize at + 0,91 V (SCE) for 200 s and then slowly lower the potential until the residual current I_{r1} is lower than 1 μA . Read

the equilibrium oxidation potential E_2 from the potentiostat potentiometer. E_2 shall be less than 0,85 V (SCE).

Record

- the equilibrium potentials E_1 and E_2 , in volts, from the potentiostat potentiometer;
- the residual current I_{r1} , in milliamperes;
- the integrated current Q_1 , in millicoulombs;
- the electrolysis time, t_1 , in seconds.

- j) Stop the stirrer and the gas input.

5.1.5 Plutonium measurement

- a) Transfer the nitric acid solution for the blank test to the coulometric cell containing the dried test sample (take care to thoroughly rinse the cell wall, and ensure that the solid is completely dissolved).
- b) Firmly fit the cell under the lid.
- c) Start the stirrer.
- d) Open the gas inlet and leave open throughout the electrolysis period.
- e) Preselect the oxidation potential at + 0,91 V (SCE) and the reduction potential at + 0,4 V (SCE).
- f) After degassing for 5 min, start the reduction at + 0,4 V (SCE) and reduce until a residual current between 50 μA and 100 μA is obtained.
- g) Slowly raise the potential so as to obtain a residual current lower than 1 μA .
- h) Read the reduction equilibrium potential E_3 from the potentiostat potentiometer. E_3 shall be less than + 0,5 V (SCE).
- i) Reset the integrator and timer.
- j) Start the oxidation and oxidize at + 0,91 V (SCE) until a residual current between 40 μA and 60 μA is obtained.
- k) Slowly lower the potential until a current I_{r2} lower than 1 μA is obtained. Read the equilibrium oxidation potential E_4 from the potentiostat potentiometer. E_4 shall be greater than + 0,85 V (SCE).

- l) Record
- the equilibrium potentials, E_3 and E_4 , in volts, from the potentiostat potentiometer;
 - the residual oxidation current, I_{r2} , in milliamperes;
 - the integrated electrolysis current, Q_2 , in millicoulombs;
 - the electrolysis time, t_2 , in seconds;
 - the temperature of the solution during electrolysis, T , in kelvins.

- Q_1 is the integrated current for the blank determination, expressed in millicoulombs, (measured during the oxidation between the equilibrium potentials E_1 and E_2);
- t_1 is the electrolysis time for oxidation of the blank, expressed in seconds;
- t_2 is the electrolysis time for oxidation of the plutonium, expressed in seconds;
- I_{r1} is the residual current after oxidation of the blank, expressed in milliamperes;
- I_{r2} is the residual current after oxidation of plutonium, expressed in milliamperes.

5.2 Analysis of subsequent samples

Test subsequent samples as described in 5.1.

If no subsequent analysis has to be done:

- rinse with double-distilled water and leave the fritted glass tubes and the cell to dry;
- store the reference and the auxiliary electrodes in double-distilled water;
- store the working electrode in concentrated nitric acid.

With the assumption that $I_{r1} = I_{r2} = I_r$, the equation can be simplified into

$$Q_b = Q_1 \frac{E_4 - E_3}{E_2 - E_1} + I_r \left(t_2 - t_1 \frac{E_4 - E_3}{E_2 - E_1} \right) \quad \dots (2)$$

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6.2 Fraction of electrolysed plutonium

The fraction of electrolysed plutonium, f , is given by the following equation

$$f = \frac{\exp\left(\frac{E_4 - E_0}{\frac{RT}{nF}}\right) \exp\left(\frac{E_3 - E_0}{\frac{RT}{nF}}\right)}{1 + \exp\left(\frac{E_4 - E_0}{\frac{RT}{nF}}\right) + \exp\left(\frac{E_3 - E_0}{\frac{RT}{nF}}\right)} \quad \dots (3)$$

6 Expression of results

6.1 Calculation of the blank

The integrated current Q_1 obtained during the coulometric blank determination (5.1.4) is used to calculate the blank under the conditions used for plutonium determination.

The value of the blank, Q_b , is given by the following equation:

$$Q_b = (Q_1 - I_{r1}t_1) \frac{E_4 - E_3}{E_2 - E_1} + I_{r2}t_2 \quad \dots (1)$$

where

- E_3 is the equilibrium potential measured after plutonium reduction, expressed in volts;
- E_4 is the equilibrium potential measured after plutonium oxidation, expressed in volts;
- E_1 is the equilibrium potential measured after the blank reduction, expressed in volts;
- E_2 is the equilibrium potential measured after the blank oxidation, expressed in volts;

where

- E_0 is the standard potential of the Pu(III)/Pu(IV) couple in the 0,9 mol/l nitric acid assay medium, expressed in volts. This potential is determined with chemically pure plutonium treated in the same way as a test sample (see annex A);
- R is the gas constant ($R = 8,314 \text{ J/mol}\cdot\text{K}$);
- T is the absolute temperature, in kelvins, of the solution during electrolysis;
- F is the Faraday constant ($F = 96\,484,56 \text{ C/mol}$, see reference [1]);
- n is the number of exchanged electrons [$n = 1$ for the Pu(III)/Pu(IV) couple];

E_0 should be checked regularly and it is particularly important to remeasure it if the electrodes have been out of use for a considerable time. The potential is in the region of +0,668 V (SCE) but small variations can be expected. This is because different calomel electrodes exhibit slightly different potentials.

6.3 Integration accuracy

The integration accuracy of the coulometer is measured by using a highly stabilized current, accurate to 2×10^{-5} A, in the place of the electrolysis cell.

- connect the current supply and set to 10 000 mA;
- set the integration time to 300 s;
- reset the integrator;
- allow time for the electronics to stabilize;
- switch on the current and record the integrated current Q_i , in millicoulombs;
- use the following equation to calculate the integration error, C , in per cent:

$$C = 100 \left(\frac{Q_i}{300 \times 10,000} - 1 \right) \quad (4)$$

6.4 Plutonium content

The plutonium content in the test sample, m_{Pu} , expressed in milligrams, is given by the following equation:

$$m_{Pu} = \frac{(Q_2 - Q_b)A_r \left(\frac{100 - C}{100} \right)}{Ff} \quad \dots (5)$$

where

Q_2 is the integrated electrolysis current, expressed in millicoulombs, during plutonium oxidation between the equilibrium potentials E_3 and E_4 ;

Q_b is the calculated blank from equation (2), expressed in millicoulombs;

A_r is the relative atomic mass of plutonium calculated from its isotopic composition;

C is the integration error from equation (4);

F is the Faraday constant ($F = 96\,484,56$ C/mol);

f is the fraction of plutonium electrolysed from equation (3).

7 Characteristics of the method

7.1 Repeatability

The repeatability standard deviation is generally around 2×10^{-4} to 4×10^{-4} for pure solutions and test samples containing 1 mg to 3 mg of plutonium with less than 2 000 ppm of total metallic impurities.

7.2 Confidence interval

This interval is 0,1 % at the confidence level of 0,95.

7.3 Analysis time

The time needed for a plutonium determination is approximately 45 min.

8 Interferences

Iron and uranium interfere (1 000 ppm of Fe increases the result by about 0,2 %).

Organic compounds, chloride and fluoride anions are destroyed by fuming to dryness in sulfuric acid.

Nitrite is destroyed by sulfamic acid.

Annex A (normative)

Determination of potential E_0

The standard potential E_0 for Pu(III)/Pu(IV) in the 0,9 mol/l nitric acid can be determined immediately after a coulometric assay of pure plutonium.

- a) Carry out the procedure specified in clause 5. After completion of the steps described in 5.1.5, stop the electrolysis, keep on stirring and maintain the gas flow.
- b) Preselect the reduction potential at + 0,400 V (SCE) and the oxidation potential at + 0,460 V (SCE).
- c) Start the reduction at + 0,400 V (SCE) and reduce until a residual current lower than 1 μ A is obtained.
- d) Reset the integrator.
- e) Start the oxidation at + 0,460 V (SCE) and oxidize until a residual current lower than 1 μ A is obtained.
- f) Record the integrated current and the corresponding potential.
- g) Increase, step by step, the oxidation potential value up to + 0,840 V (SCE). For each 0,02 V step, oxidize until a residual current lower than 1 μ A is obtained. Then record the integrated current Q and the corresponding potential E_{ox} .
- h) Plot the curve $Q = f(E_{ox})$ and calculate the standard redox potential of Pu(III)/Pu(IV) in 0,9 mol/l nitric acid by the differential or the Fortuin method modified by Wolf (see references [3] and [4]).

The E_0 value obtained is valid only with the reference electrode used for the measurement.

If, between two E_0 determinations, the discrepancy is higher than 10 mV, check or change the reference electrode.