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Nuclear fuel technology — Controlled-potential coulometric assay of plutonium

Technologie du combustible nucléaire — Dosage du plutonium par coulométrie à potentiel imposé

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Foreword

ISO (the International Organisation for Standardisation) 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 organisations, 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 standardisation.

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ISO 12813 was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection*, Subcommittee SC 5, *Nuclear fuel cycle*.

This third edition cancels and replaces the second edition (ISO 12183:2005), which has been technically revised.

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Nuclear Energy — Fuel Technology — Controlled-potential coulometric assay of plutonium

1 Scope

This International Standard describes an analytical method for the electrochemical assay of pure plutonium nitrate solutions of nuclear grade, with a total uncertainty not exceeding $\pm 0,2\%$ at the confidence level of 0,95 for a single determination (coverage factor, $K = 2$). The method is suitable for aqueous solutions containing more than 0,5 g/L plutonium and test samples containing between 4 mg and 15 mg of plutonium. Application of this technique to solutions containing less than 0,5 g/L and test samples containing less than 4 mg of plutonium requires experimental demonstration by the user that applicable data quality objectives will be met.

For some applications, purification of test samples by anion exchange is required before measurement to remove interfering substances when present in significant amounts. Refer to Clause 9 for a discussion of interferences and corrective actions. Purification is also appropriate in situations where the purity of the test sample is unknown or when it may fluctuate unpredictably in a manufacturing process.

Clause 10 discusses the changes in application of the method and methodology that can be applied and important considerations when selecting measurement parameters, whilst still remaining within the intended scope of this standard.

2 Normative references

The following document is an indispensable reference for the application of the analysis procedure described in this document.

ISO 10980, "Validation of the strength of reference solutions used for measuring concentrations."

Note that for dated references, only the edition cited applies. For undated references, the latest edition is the appropriate reference.

3 Principle

The key steps and their purposes are outlined below:

- test samples are prepared by weighing and then fuming to dryness with sulphuric acid to achieve a consistent and stable anhydrous plutonium sulphate salt that is free from chloride, fluoride, nitrate, nitrite, hydroxylamine, and volatile organic compounds;
- if needed to remove interferences, dissolve test samples and purify by anion exchange, then fume the eluted plutonium solution in the presence of sulphuric acid to obtain the dry plutonium sulphate chemical form;
- measure a blank of the nitric acid supporting electrolyte and calculate the background current correction applicable to the electrolysis of the test sample from charging, faradaic, and residual current; ^[1]
- dissolve the dried test sample in the previously measured supporting electrolyte (the blank);
- reduce the test sample at a controlled potential that electrolyses the plutonium to greater than 99,8 % Pu^{3+} and measure the equilibrium solution potential at the end of this step by control-potential adjustment; ^[2]

- oxidise the test sample at a controlled potential that electrolyses the plutonium to greater than 99,8 % Pu⁴⁺ and measure the equilibrium solution potential at the end of this electrolysis by control-potential adjustment;
- correct the result for the background current and the fraction of plutonium not electrolysed;
- calibrate the coulometer using traceable electrical standards and Ohm's Law;
- use the measured value of the coulometer calibration factor and the Faraday constant to convert the coulombs of integrated current from the electrolyses to moles of plutonium;
- use traceable quality-control plutonium standards to demonstrate independently the performance of the measurement system;
- periodically measure the formal potential of the plutonium couple, E_0 , which is user-specific based on the cell design, connections, reference electrode type, and the acid-type and molarity of the supporting electrolyte.

These steps ensure that representative, reproducible, and stable test samples are prepared for measurement. The test samples are measured using a protocol that is based upon first principles and is consistent with a traceable, electrical calibration of the coulometer. Additional details are provided in Clauses 9 and 10.

4 Reagents

Use only analytical grade reagents.

All aqueous solutions shall be prepared with double-distilled or distilled, demineralised water with a resistivity greater than 10 M Ω -cm, i.e., ISO 3696 Grade 1 purified water.

4.1 Nitric acid solution, c (HNO₃) = 0,9 mol/L.

NOTE Refer to 10.4 for other electrolyte options.

4.2 Amidosulphuric acid solution, c (NH₂HSO₃) = 1,5 mol/L.

4.3 Sulphuric acid solution, c (H₂SO₄) = 3 mol/L.

NOTE Molarity is not a critical parameter for sulphuric acid used to fume plutonium test samples, provided the concentration of the reagent is well above the level where colloidal plutonium complexes form.

4.4 Pure argon or nitrogen, (O₂ content lower than 10 parts per million).

4.5 Pure air, (free of organic contaminants).

5 Apparatus

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

5.1 Analytical balance, installed in radiological containment unit must be capable of weighing 1 g mass with an uncertainty of $\pm 0,1$ mg (coverage factor, $K = 1$). This represents a relative uncertainty of 0,01 %.

- weighing less than 1 g will increase the relative uncertainty to $>0,01$ %, in an inversely proportional manner;

- If the uncertainty of the balance, as installed, does not meet the $\pm 0,01$ mg criterion, then correspondingly larger test samples are required.

5.2 Weighing burette, glass or plastic, the material selection is not critical provided it maintains a stable mass (tare weight) and static charge is controlled as described in 6.1.1.

5.3 Equipment for test sample evaporation in the coulometric cell, comprising of an overhead radiant heater or hot-plate with controls to adjust temperature. Design requirements and optional features for effective evaporation and fuming include:

- provide settings that allow both rapid and well-controlled rate of initial evaporation, followed by fuming the remaining sulphuric acid solution to dryness at a higher temperature.
- prevent mechanical loss of the test sample solution from boiling and/or spattering.
- prevent contamination by extraneous chemicals, such as those which may be used to neutralise acid vapours.
- the coulometer cell wall may be heated to optimise fuming and minimise refluxing of sulphuric acid by placing the cell inside an aluminium tube with an inner diameter that is 1 mm to 3 mm larger than the outer diameter of the cell and a height that is 1 mm to 5 mm shorter than the cell may be placed around the cell during the fuming step to heat the walls of the cell. An aluminium block with holes bored to a similar specification for inserting the cell may be used instead of the aluminium tubes.
- an air supply with the delivery tube directed towards the surface of the liquid may be added to the apparatus to optimum the evaporation rate and disperse the acid fumes.
- vapour capture and local neutralisation may be appropriate to control acid fumes depending upon facility design and ventilation system requirements.

The equipment in figure 1 is suitable.

Dimensions in centimetres

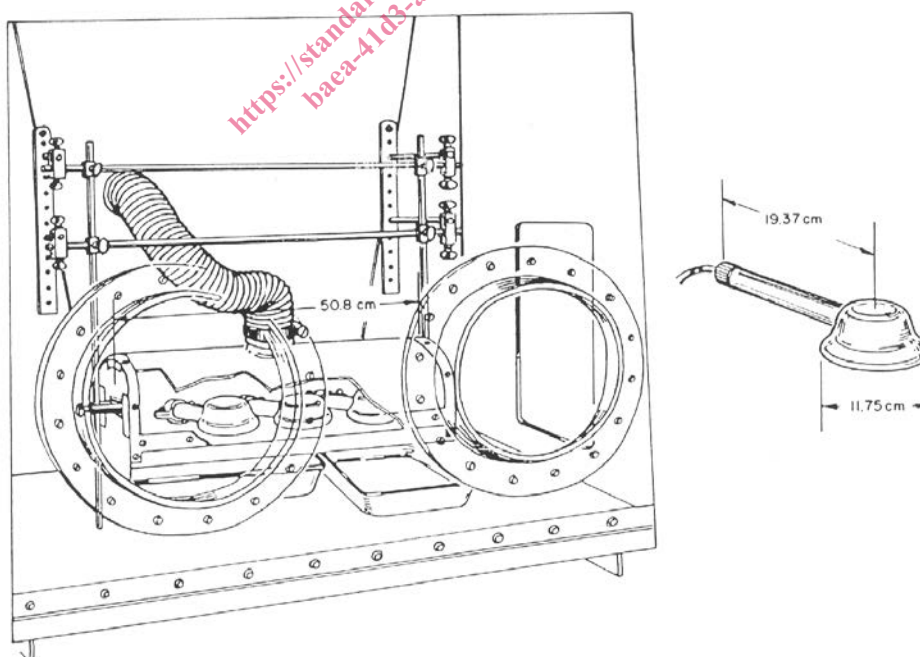


Figure 1 Sample evaporation system

5.4 Controlled-potential coulometer

The following equipment is suitable (see figure 2).

5.4.1 Coulometer cell assembly, comprising the following:

- a stirrer motor with a rotation frequency of at least 1000 min^{-1} ;

NOTE Adjustable-speed motors allow optimising rotation rates for individual cell designs. Stirrer motors powered by isolated direct-current supplies are desirable to prevent electrical noise from being superimposed on the blank and test sample electrolysis current signals sent to the integrator.

- a cylindrical or tapered glass coulometric cell of capacity 50 mL, or less, with an O-ring seal and a tight-fitting lid with openings to insert the following internal equipment:
- an inlet tube for humidified, inert gas to displace dissolved and atmospheric oxygen from the solution and the electrolysis cell, respectively;
- a stirrer with blade and shaft made from chemically inert materials (e.g., Teflon™), and designed to prevent splashing; the shaft of the stirrer is typically located in the centre of the cell and connected directly to the stirrer motor;
- a working electrode made of gold (e.g., 99,99 %) and consisting of a gold wire welded or machined to a cylindrical gold wire frame, nominally 15 mm high and 20 mm in diameter, around which is welded or machined a very fine gold mesh. The gold mesh is typically several layers (e.g., four layers);

NOTE Refer to 10.4 for other working electrode options.

- a glass tube plugged at the bottom end with a sintered-glass disc (typical dimensions of 2,5-mm thick and pore size $<0,01 \mu\text{m}$), the tube filled with nitric acid (4.1) and the tip of the sintered-glass end positioned within the ring of the working electrode;
- a reference electrode, saturated calomel electrode (SCE), or other reference electrodes as described in 10.3, is inserted into the glass tube;
- another glass tube, similar to the first one, also filled with nitric acid (4.1), and the tip of the sintered-glass end positioned within the ring of the working electrode;
- an auxiliary electrode consisting of a platinum wire, 0,5 mm to 3,0 mm in diameter, is inserted into the second glass tube. The platinum wire may be coiled to increase the surface area submerged in the supporting electrolyte, as illustrated in Figure 2;
- a gas washer bottle, filled with reagent water as described in section 4.0, to humidify the inert gas before it is introduced into the coulometer cell assembly.

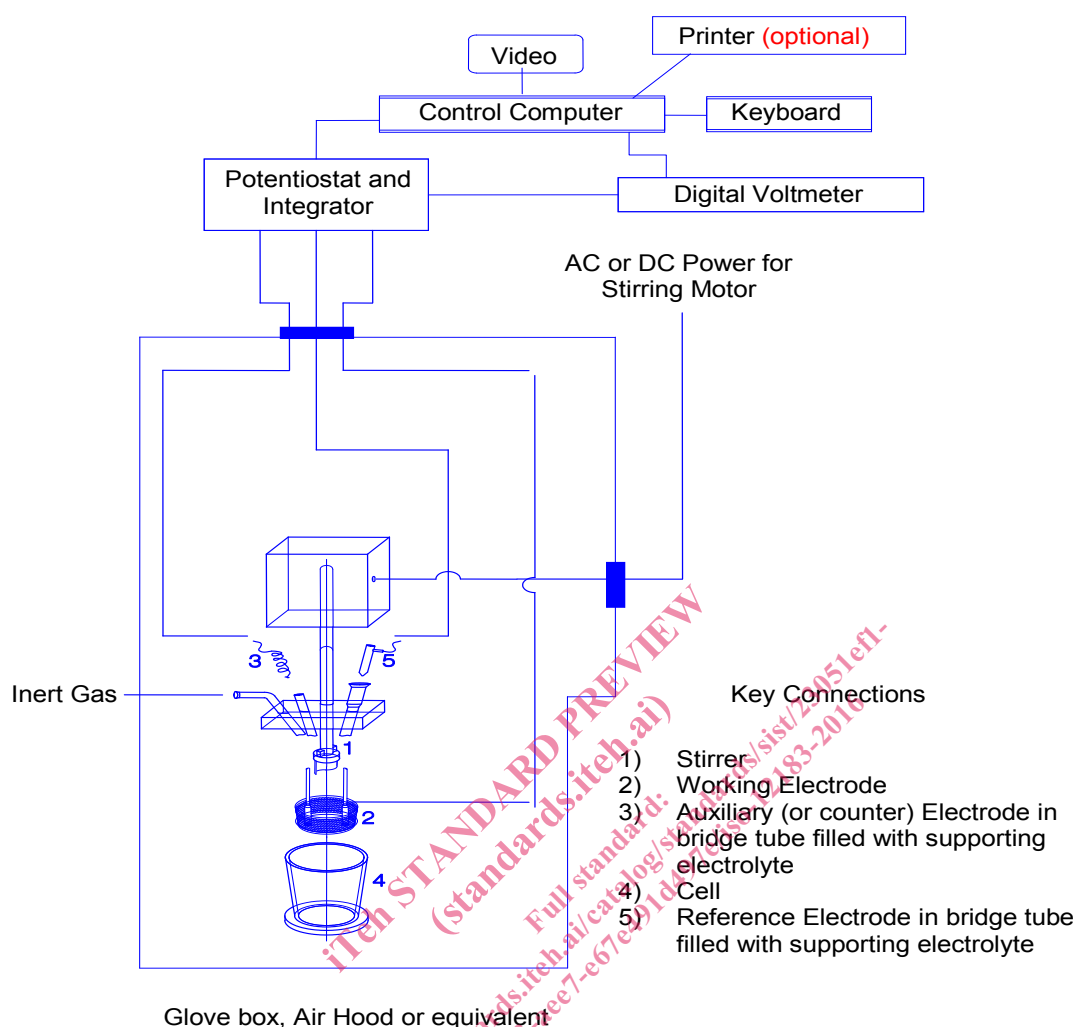
The diameter of the glass tube and sintered-glass disc containing the auxiliary electrode may be larger than that of the glass tube and sintered-glass disc containing the reference electrode. The flow rate of the solution through both glass discs shall be less than 0,05 mL/h.

- a. A thermocouple or resistance thermometer installed in the coulometer cell assembly for measuring the temperature of the test sample solution during the measurement process is an optional feature. The solution temperature should be measured either during the oxidation of the test sample or immediately following the analysis. An uncertainty goal for the temperature measurement is $\pm 0,2 \text{ }^\circ\text{C}$ ($K = 1$).
- If it is not possible to insert a temperature sensor into the electrolysis cell or not desirable to measure the temperature of the test sample solution immediately after the electrolysis is completed, then estimate the solution temperature from the ambient air temperature or the reagent temperature. Note that the purge gas is cooled by expansion causing the solution

temperature to decrease relative to the ambient temperature; the extent of this decrease is a function of the inert-gas flow rate and the cell design. The measured air or reagent temperature value must be corrected for this cooling effect. A higher uncertainty of ± 1 °C, $K = 1$, is expected in the calculated solution temperature.

- b. For optimum potential control, position the sintered-glass discs of the reference and auxiliary electrodes glass tubes to meet the following requirements:
- the closest distance from the reference electrode sintered-glass disc to the working electrode is 2 mm or less.
 - the distance between the two sintered-glass discs containing the auxiliary and reference electrodes is less than the distance between the auxiliary electrode disc and the nearest point on the working electrode.
- c. The hole through which the stirrer shaft is inserted serves as the primary escape vent for the inert gas. Except for this hole, all other insertions are tight fitting. The inert-gas flow rate must be sufficiently high to quickly remove oxygen from the supporting electrolyte and the test sample solution. Furthermore, it must prevent leakage of air into the cell assembly during the electrolysis. A practical guide for adjusting the flow rate is to direct all or part of the inert gas supply toward the solution, such that a 2 mm to 4 mm dimple is formed on the surface without causing the solution to splash.
- Cell assemblies with an optimised design, an adequate inert-gas flow rate, and a tight fit, will remove oxygen in 5 min or less. The time required to remove oxygen from the solution should be established by users based on testing of their cell assembly under routine conditions.

Figure 2 – Coulometric cell assembly connections



5.4.2 Instrumentation, comprising the following: ^[3,4]

- a) **Potentiostat** with the desired range of electrolysis potentials for plutonium measurement and the following capabilities:
- a power amplifier with a current output capability of 250 mA, or greater;
 - a quick-response control-potential circuit, with maximum rise-time of 1 ms from zero volts to the desired control potential, with voltage overshoot not exceeding 1 mV;
 - a control amplifier with a common-mode rejection of 90 dB, or greater;
 - automatic control-potential adjustment, with a resolution of 0,001 V, or less;
 - a voltage-follower amplifier, to isolate the reference electrode (electrometer), with a minimum input impedance of $10^{11} \Omega$;
 - Capability to monitor the electrolysis current, including charging current for zero to 500 mA, with a detection capability of 0,5 μA .

NOTE This procedure assumes that the coulometer has two accurate potentiometers one for selecting the oxidation potential and the other for the reduction potential, although this is not a system requirement.

- b) **Coulometric integrator** capable of integrating blank and test sample electrolysis currents from at least 150 mA down to 1 μ A with a readability of $\pm 10 \mu$ C; (Refer to 6.1.4 for integrator capabilities and calibration requirements.)
- The control-potential system should not drift more than ± 1 mV and the current integration system should not drift more than 0,005 % during routine measurements (between electrical calibrations), over the range of temperatures to which the control-potential circuitry will be exposed. If the room temperature varies excessively, the instrumentation should be located in a cabinet having temperature controls sufficient to limit electronic drift within these specifications.
 - An electronic clock, with an uncertainty of $\pm 0,002$ % ($K = 1$) for determining the duration of electrical calibrations and electrolyses.
 - A system for generating a known constant current, stable to $\pm 0,002$ % over the range of temperatures to which the constant-current circuitry will be exposed. This system will be used for electrical calibration of the integration circuit of the coulometer, as described in 6.1.4.
 - The cable connecting the potentiostat to the cell should be a three-wire conductor, twisted-shielded cable, preferably with the shield grounded at the potentiostat. Gold-plated connectors at the cell are recommended as these are not susceptible to corrosion.
 - The charging-current peak maximum observed during the first 25 ms to 50 ms of the blank and test sample oxidations must be within the instrument specification for the integrator circuit. The surface area of the working electrode can be decreased to reduce the charging current peak maximum. An oscilloscope or a voltmeter with high-speed data acquisition is required to measure the amplitude of this peak, which has a typical width at half the maximum of 10-ms to 20-ms.

5.5 Digital voltmeter (DVM), with an input impedance of $10^{10} \Omega$ or greater and having an uncertainty within $\pm 0,001$ % ($K = 1$) for voltages in the range 0,5 V to 10 V, and within $\pm 0,01$ % ($K = 1$) for voltages in the range 100 mV to 500 mV. These uncertainties are required for electrical calibration of the instrumentation, as described in 6.1.4.

5.6 Regulated power, instrumentation should be protected with an uninterruptable power supply that provides a regulated voltage within ± 1 % of the standard for the nation, and provides appropriate surge protection.

6 Procedure

6.1 Plutonium determination

6.1.1 Weighing the test sample, with an uncertainty of $\pm 0,01$ %, $K = 1$.

The test sample may be weighed after delivery into a tared coulometer cell, and the apparent mass corrected for the air buoyancy effect using either Equation (1) or (2), as described below.

Alternatively, a known mass of the test sample may be delivered into the coulometer cell, as described in steps a) through f).

For test samples at high plutonium concentrations (e.g., 15 g/L or more), it is recommend that the solution be diluted to achieve an overall weighing uncertainty of $\pm 0,01$ %.