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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

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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 12183 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

This second edition cancels and replaces the first edition (ISO 12183:1995), which has been technically revised.

Nuclear fuel technology — Controlled-potential coulometric assay of plutonium

1 Scope

This International Standard specifies an analytical method for the electrochemical assay of pure plutonium nitrate solutions of nuclear grade, with a total uncertainty of 0,1 % to 0,2 % at the confidence level of 0,95 for a single determination. 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, must be demonstrated by the user as having adequate reliability for their specific application.

Preliminary purification by anion exchange is required to remove interfering substances when present in significant amounts. Purification is also appropriate in situations where the purity of the sample is unknown or when it may unpredictably fluctuate in the manufacturing process. Refer to Clause 9 for a discussion of interferences and iron corrections.

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

2 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 10980:1995, *Validation of the strength of reference solutions used for measuring concentrations*

3 Principle

The method consists of the following steps:

— test samples are prepared by weight and fumed with sulfuric acid to achieve a consistent and stable chemical form that is free from chloride, fluoride, nitrate, nitrite, hydroxylamine, and volatile organic compounds;

— when appropriate, preliminary purification by anion exchange with fuming in sulfuric acid to restore the dry plutonium sulfate chemical form in preparation for measurement;

— measuring a blank of the nitric-acid supporting electrolyte and performing an appropriate calculation to determine the background current correction applicable to the electrolysis of the test sample from charging, faradic, and residual current; [1]

— dissolution of the residue in the previously measured supporting electrolyte (the blank);

— reduction at a controlled potential that electrolyses the plutonium to greater than 99,8 % Pu^{3+} and measurement of the equilibrium solution potential at the end of this electrolysis by control-potential adjustment; [2]

— oxidation at a controlled potential that electrolyses the plutonium to greater than 99,8 % Pu^{4+} and measurement of the equilibrium solution potential at the end of this electrolysis by control-potential adjustment;

— periodically, the formal potential of the plutonium couple, $E_{0,}$ is measured for the specific supporting electrolyte, cell components, and design;

— the result is corrected for the background current and the fraction of plutonium not electrolysed;

— coulometer calibration, traceable to electrical standards through Ohm's law and Faraday's constant, is used to convert the coulombs of integrated current from the electrolyses to equivalents of plutonium;

— quality-control plutonium standards are used to independently demonstrate measurement performance.

4 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 10 MΩ·cm.

4.1 Nitric acid solution, $c(HNO_3)$ = 0,9 mol/L.

4.2 Amidosulfuric acid solution, $c(NH_2HSO_3)$ = 1,5 mol/L.

4.3 Sulfuric acid solution, $c(H_2SO_4)$ = 3 mol/L.

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

4.5 Pure air, free of any organic compounds.

5 Apparatus

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

5.1 Analytical balance, capable of weighing after installation in radiological containment with an accuracy of 0,1 mg, or less. (The test sample size must be correspondingly greater than the minimum 1 g size, if the accuracy, as installed, does not meet this 0,1 mg criteria.)

5.2 Weighing burette, glass or plastic; the material selection is not critical provided it maintains a stable tare weight and is not susceptible to static charge.

5.3 Equipment for sample evaporation in the coulometric cell, comprising the following:

— an overhead radiant heater or hotplate with a means of temperature adjustment;

— for optimum evaporation rate and to minimize the concentration of acid fumes, an air supply with the delivery tube directed towards the surface of the liquid may be used;

— additional design feature to control acid fumes, including vapour capture and local neutralization may be appropriate depending upon facility design and requirements.

The evaporation/fuming apparatus shall be adjusted to provide both rapid and well-controlled evaporation, followed by fuming to dryness of the plutonium sulfate test sample. The apparatus shall prevent mechanical loss of the test-sample solution from boiling and spattering during the process and from contamination by chemicals, which may be used to neutralize acid vapours.

The equipment in Figure 1 is suitable.

Dimensions in centimetres

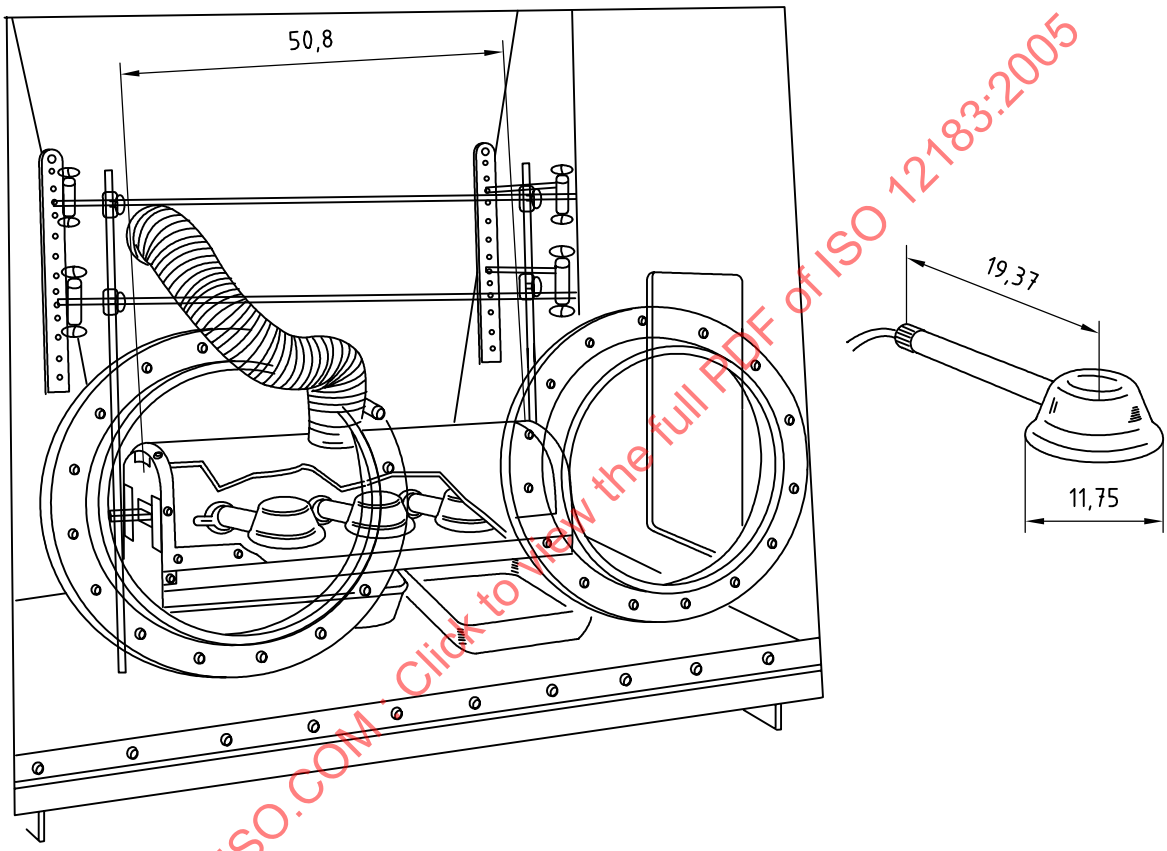


Figure 1 — Sample evaporation system

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 1 000 min^{-1};

NOTE Adjustable-speed motors allow optimizing for individual cell designs. Stirring motors powered by isolated direct-current supplies have the advantage of reducing electrical noise that is superimposed on the blank and test-sample electrolysis current signal sent to the integrator.

— a cylindrical or tapered glass coulometric cell of capacity 50 mL, or less, with an O-ring seal and a lid suitable for the following internal equipment:

  — an inlet tube for inert gas, to exclude atmospheric oxygen;

— a chemically inert stirrer, designed to prevent splashing, centrally located, and connected to a stirrer motor;

— a working electrode made of gold (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 may be of several layers (e.g, four layers);

— a glass tube plugged at the bottom end with a 2,5 mm thick sintered-glass disc (pore size $< 0{,}01$ µm), filled with nitric acid (4.1) and the tip positioned within the ring of the working electrode;

— a reference electrode, saturated calomel electrode (SCE), or other reference electrodes as described in 10.3, housed in the glass tube;

— another glass tube, similar to the first one, also filled with nitric acid (4.1), and mounted within the ring of the working electrode;

— an auxiliary electrode consisting of a platinum wire, 0,5 mm to 3,0 mm in diameter, housed in the glass tube;

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

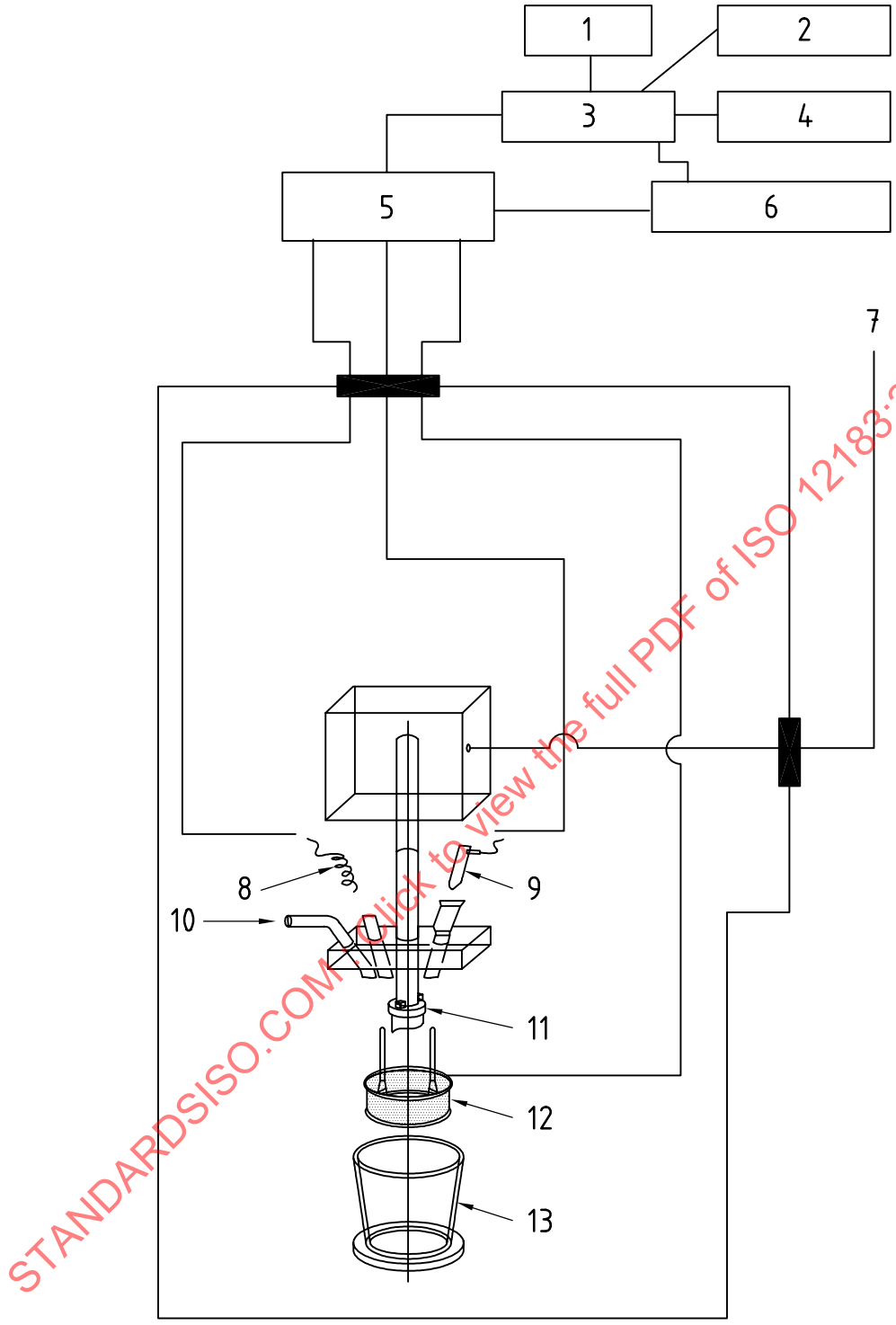
a) A thermocouple for measuring the temperature of the test-sample solution is an optional feature. If it is not possible to measure the solution temperature either during or immediately following the analysis, then a thermometer inside the containment unit may be used to estimate the solution temperature from the ambient air temperature. An accuracy of $\pm$ 0,1 °C is recommended.

b) For optimum potential control, design the cell assembly to position the sintered-glass discs of the glass tubes to meet the following requirements:

— the reference electrode connection is 1 mm to 2 mm from the working electrode;

— the distance between auxiliary and reference electrode discs is less than or equal to the distance between the auxiliary electrode disc and the nearest point on the working electrode.

c) The hole for the stirrer shaft provides a gas vent. Except for the stirrer passage, all openings in the lid shall be relatively gastight such that the inert-gas flow rate selected is sufficient to quickly degas oxygen from the supporting electrolyte and the test-sample solution and to prevent in-leakage of atmospheric oxygen. For ease of operation and consistent performance, the gas-flow inlet tube may be designed to direct all or part of the inert gas toward the test-sample solution, such that a 2 mm to 4 mm dimple is produced on the sample solution without causing the solution to splash. For cell assemblies with an optimized design and fit, degassing is accomplished in 5 min or less.



1 video
2 printer
3 control computer
4 keyboard
5 potentiostat and integrator
6 voltmeter digital
7 AC or DC power for stirring motor
8 auxiliary (or counter) electrode in bridge tube filled with supporting electrolyte
9 reference electrode in bridge tube filled with supporting electrolyte
10 inert gas
11 stirrer
12 working electrode
13 cell

Figure 2 — Coulometric-cell assembly connections

5.4.2 Measuring unit, comprising the following [3,4].

a) **A potentiostat** with the desired range of electrolysis potentials for plutonium measurement and the following capabilities:

- a high power, minimum current output capability of 250 mA;
- a quick-response control-potential circuit, maximum rise-time from zero volts to the desired control potential of 1 ms, with maximum voltage overshoot of 1 mV;
- a control amplifier with a common-mode rejection of 90 dB or greater;
- automatic control-potential adjustment, with an output stepping capability resolution of 0,001 V, or less;
- a voltage-follower amplifier used to isolate the reference electrode (electrometer), with a minimum input impedance of 10^{11} Ω;
- detection capability for monitoring the full range of the electrolysis currents, including a sensitivity of 0,5 µA at zero current.

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

b) **A coulometric integrator** capable of being read to ± 10 µC and able to integrate currents varying from 1 µA to 150 mA. (Refer to 6.1.4 for integrator capabilities and calibration requirements.)

- The control-potential system should not drift more than ± 1 mV and the 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. The system should be located in a cabinet having adequate temperature control to limit electronic drift within the specified accuracy, if the room temperature varies excessively.
- An electronic clock, accurate within the selected range to better than 0,002 %.
- A system for generating a known constant current, stable to 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 connectors at the cell are recommended to avoid contact problems from corrosion.

5.5 Digital voltmeter (DVM), having an accuracy of ± 0,001 % of the voltage reading in the range 0,5 V to 10 V, and 0,01 % of the voltage reading in the range 100 mV to 500 mV, with an input impedance of 10^{10} Ω or greater. This accuracy is required for electrical calibration, as described in 6.1.4.

5.6 Regulated power: equipment should be protected with an uninterruptable power supply that provides a regulated voltage of ± 1 % of the national standard, and provides appropriate surge-protection features.

6 Procedure

6.1 Plutonium determination

6.1.1 **Weighing the test sample**, with an accuracy of 0,01 %.

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

Alternatively, the test sample may be delivered by weighing into the coulometer cell, as follows:

NOTE Care is needed to avoid any loss of microdrops. During weighing of the polyethylene weighing burette, the problem of static electricity is eliminated by contact between the dropping tube and a copper plate connected to the ground or a similar arrangement.

For test samples with concentrations greater than 15 g/L of plutonium, the solution should be diluted by weight so that all weights are greater than 1 g and the overall weighing uncertainty remains acceptably small.

a) Fill a polyethylene weighing burette with the solution to be analysed.

b) Weigh the burette to 0,1 mg.

c) Deliver a test sample of at least 1 mL, drop by drop, into a coulometric cell.

d) Weigh the burette again to 0,1 mg.

e) The mass difference gives the apparent mass, m_a, of the test sample in the cell.

f) Correct the apparent mass of the test sample for the air buoyancy affect using Equation (1):

$$m_{\text{Real}} = m_a \times \frac{1-(D_a/D_b)}{1-(D_a/D_s)} \qquad (1)$$

where

D_a is the density of air, which is a function of temperature, pressure, and humidity, but typically is 0,001 16 g/cm^3 to 0,001 2 g/cm^3;

D_b is the density of the stainless steel weights used in modern analytical balances, 8,0 g/cm^3;

D_s is the density of the test sample.

In addition to applying an air buoyancy correction to the mass of the test sample, air buoyancy corrections should be applied to all mass measurements (including any bulk-material mass measurements). This correction is required to eliminate systematic errors that can exceed 0,1 % for solutions. The correction is less for solids, but can still be significant.

6.1.2 Preparation of the test sample

a) Add 1 mL of sulfuric acid solution (4.3) to the coulometric cell containing the test sample.

b) Place the cell containing the test sample into the sample evaporation system and evaporate the liquid in the test sample.

c) Evaporate at a temperature sufficient to evolve SO_3 fumes, and continue until SO_3 fumes are no longer observed and a residue of plutonium sulfate (orange-coloured precipitate) is formed. Do not allow the solution to boil or splash as this will cause mechanical loss.

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) Allow the test sample to cool to room temperature.

e) If the presence of significant amounts of impurities is suspected, purify the plutonium in the test sample by a suitable purification process, then repeating the sulfuric acid fuming step as detailed in 6.1.2. Anion-exchange separation as outlined in Annex A is an effective purification process.

6.1.3 Electrode pretreatment

Electrode conditioning is critical and shall be repeated periodically. The laboratory shall therefore have the capability to perform aggressive electrode treatments. The following techniques may be used individually, or in combination with each other, to treat the working and auxiliary electrodes:

— storing in 8 mol/L nitric acid (recommended as the general overnight practice);

— soaking in concentrated sulfuric acid containing 10 % hydrofluoric acid, followed by 8 mol/L nitric acid;

— boiling in nitric acid;

— soaking in aqua regia (limited to several minutes to prevent damage to the working electrode);

— flaming the platinum auxiliary electrode to white or red heat.

Electrode treatment may be performed on a preventative basis, at the beginning and/or the end of the day that the electrode is used. Alternatively, treatment may be on an “as needed” basis, particularly in the case of failure to obtain optimum electrode performance when measuring either the blank or the test sample. The typical background current levels should be relatively constant for a given installation and are normally used as indicators of the desired performance.

Each day, or more often as desired, before performing the actual blank determination, further conditioning of the electrodes is achieved by performing the following sequence of electrolyses.

a) Assemble the cell lid complete with the electrodes and other internal equipment (see 5.4.1).

b) Take a clean dry coulometric cell and add sufficient nitric acid solution (4.1) to immerse the working electrode, and the sintered-glass tips of the reference and auxiliary electrode tubes.

c) Add one drop of amidosulfuric acid solution (4.2).

d) Firmly fit the cell under the lid.

e) Start the stirrer at the desired speed. (Using the maximum speed, while avoiding splashing or forming any excessive vortex that would interrupt electrical connections, is recommended.)

f) Open the gas inlet and maintain a sufficient flow of inert gas throughout the electrolysis period. (Inadequate purging to remove oxygen can be mistaken for an electrode-conditioning problem.)

g) Preselect the oxidation potential at E_0 + 0,32 V and the reduction potential at E_0 − 0,36 V.

h) After degassing for 5 min, start the oxidation and oxidize at E_0 + 0,32 V until a residual current of 10 µA is obtained.

i) Start the reduction and reduce at E_0 – 0,36 V until a residual current lower than 10 µA is obtained.

j) Oxidize at E_0 + 0,32 V.

k) Stop the electrolysis when the current is lower than 10 µA.

l) Based upon electrode performance:

— proceed with the blank determination, see 6.1.6.c); or

— rinse the electrolysis cell and the outside wall of the fritted-glass tubes with fresh supporting electrolyte to prepare it for further conditioning, see 6.1.3; or

— rinse the electrolysis cell and the outside wall of the fritted-glass tubes with fresh supporting electrolyte to prepare it for blank determination, see 6.1.6.

6.1.4 Electrical calibration of the current integration system

The electrical calibration factor of the coulometer is measured by using a high-accuracy, highly stable constant current in place of the electrolysis cell. Detailed instructions for the calibration of a current integration system are highly dependent upon the design of the specific integration circuit. However, the following principles and specifications apply to achieve an accuracy of ~ 0,01 % for this aspect of the overall measurement process:

Generate a constant current (stable and accurately known to within ~ 0,002 %) in a manner that is electronically equivalent to the process by which the electrolysis current from the test sample and the blank are integrated. (Typically, the potentiostat is converted into a constant current source by replacing the cell assembly with a standard resistor. The voltage drop across the standard resistor is accurately measured to accurately determine the actual calibration current. Alternatively, voltage and resistance measurements are used to periodically calibrate an external constant current source.)

Time the duration of calibration within ~ 0,002 %.

The linearity of the integrator response shall be demonstrated for the range of currents observed during plutonium measurement (~ 50 µA – 100 mA). The impact on plutonium measurements from integrator nonlinearity shall be less than 0,005 %, to avoid introducing excessive uncertainty in the electrical calibration process.

A typical sequence for performing an electrical calibration is the following:

a) configure the instrumentation for electrical calibration and set to the desired constant current, for example 10,000 mA;

b) set the integration time to an appropriate duration, for example 300 s;

c) reset the integrator;

d) allow time for the electronics to stabilize;

e) initiate the calibration and record the constant current used, $I_{c,}$, mA;

f) at the completion of the calibration, record the output for the integrator, Q_C (in the unit appropriate for the specific measurement system) and the actual calibration time, t_C, in seconds;

Electrical calibration should be performed at least daily, and in the same laboratory where the plutonium measurements are performed. An automated coulometer should perform the electrical calibration without the user needing to reconfigure the instrumentation. Refer to 7.1.

6.1.5 Formal potential determination

The formal potential, E_0, should be measured regularly (as described in Annex B). It is particularly important to remeasure the formal potential when electrodes have been replaced, or if the electrodes have been out of use for a considerable time. Before performing this measurement, ensure that the working and auxiliary electrodes have been properly pretreated and conditioned and that the SCE is functioning properly, filled with saturated potassium chloride solution, and not clogged by excessive crystals of salt.

The formal potential is close to + 0,668 V vs. SCE using nitric acid as the supporting electrolyte but small variations can be expected. This is because different calomel electrodes exhibit slightly different potentials. The formal potential is moderately dependent on the concentration of the nitric acid supporting electrolyte. The selection of a different supporting electrolyte such as 0,5 mol/L sulfuric acid would significantly shift the formal potential into the range of + 0,492 V vs. SCE. Failure to completely fume test samples to a dry plutonium residue before dissolving in nitric acid supporting electrolyte will result in an inconsistent shift of the formal potential from the varying amount of excess sulfuric acid.

6.1.6 Coulometric blank determination

The objective when measuring the blank is to match the electrolysis conditions of the test sample. Optimum reliability is obtained when matching the initial and final oxidation potentials used for both the blank and test samples, as well as the times that the blank and test sample are electrolysed at these potentials. (Matching the current level at which the control potential is adjusted for both the blank and test sample is less accurate.) Refer to 7.2.

a) Rinse the outside wall of the fritted-glass tubes and, if necessary, fill them up with 0,9 mol/L nitric acid solution (4.1).

b) Repeat steps 6.1.3 b) to f).

c) Preselect the oxidation potential at E_0 + 0,24 V (SCE) and the reduction potential at E_0 – 0,26 V (SCE).

d) Degas the supporting electrolyte for 5 min., as described in 5.4.1.c).

e) Start the oxidation at E_0 + 0,24 V (SCE) until a residual current of approximately 5 µA is obtained.

f) Start the reduction at E_0 – 0,26 V until the electrolysis current decreases to approximately 10 µA, or less. (This should not take more than 2 min to 3 min if degassing is adequate.)

g) Slowly raise the control potential to the typical final reduction potential of test samples (nominally E_0 – 0,17 V), then allow the electrolysis current to equilibrate as needed (typically 30 s to 60 s) to a residual current in the range 1 µA to 10 µA. (Ideally, this residual current is 1 µA to 3 µA.)

h) Measure the control potential E_1 supplied by the potentiostat at the end of the reduction step, using the DVM (5.5).

i) Reset the integrator. The starting of the integrator and timer shall coincide with the beginning of the oxidation.

j) Start the oxidation at E_0 + 0,24 V and wait 200 s, or wait a period of time that matches the typical duration for the plutonium test sample to be oxidized to 1/750 or less of the initial current.

k) Slowly lower the control potential to the typical final oxidation potential of the plutonium test samples (nominally E_0 + 0,17 V), then allow the electrolysis current to equilibrate as needed (typically 30 s to 60 s) to a residual current I_{r1} in the range 1 µA to 10 µA. (Ideally, this residual current is 1 µA to 3 µA.)

l) Measure the control potential E_2 supplied by the potentiostat at the end of the oxidation step, using the DVM (5.4).

m) Record

— the final reduction and oxidation potentials E_1 and E_2, in volts,

— the residual current I_{r1}, in milliamperes,

— the integrated current Q_1, expressed in the units of the output by the integrator (ideally, this quantity is less than 5 mC), and

— the electrolysis time, t_b, in seconds.

n) Stop the stirrer (and, if desired, the gas supply).

6.1.7 Plutonium measurement

a) Transfer the nitric acid solution from the blank determination to the coulometric cell containing the dried test sample, taking care to thoroughly rinse the cell wall.

b) Inspect the test-sample solution to determine if the solid plutonium sulfate has dissolved completely. If the solids have not dissolved completely, continue with procedure steps c) to g), but increase the degassing time in step g), as needed, to ensure complete dissolution.

c) Firmly fit the cell under the lid.

d) Start the stirrer.

e) Ensure that the gas inlet is open and leave it open throughout the electrolysis period, as described in 5.4.1.c).

f) Preselect the oxidation potential at E_0 + 0,24 V (SCE) and the reduction potential at E_0 – 0,26 V (SCE).

g) After degassing for 5 min, start the reduction at E_0 – 0,26 V (SCE) and reduce until an electrolysis current is obtained that is 1/750 of the initial reduction current, or less, typically 50 µA to 150 µA depending upon the quantity of plutonium in the test sample. (This should not take more than 10 min, if the stirring and degassing are adequate.)

h) Slowly raise the potential so as to obtain an electrolysis current lower than 1 µA, then allow the test solution to equilibrate (10 s to 60 s) to a stable residual current, typically 1 µA to 5 µA.

i) Measure the control potential E_3 supplied by the potentiostat at the end of the reduction, using the DVM (5.5). E_3 should be approximately E_0 – 0,17 V.

j) Reset the integrator and timer.

k) Start the oxidation at E_0 + 0,24 V (SCE) and oxidize until an electrolysis current is obtained that is 1/750 of the initial oxidation current, or less, typically 50 µA to 150 µA depending upon the quantity of plutonium in the test sample. (This should not take more than 10 min, if the stirring and degassing are adequate.)

l) Slowly lower the potential so as to obtain an electrolysis current lower than 1 µA, then allow the test solution to equilibrate (10 s to 60 s) to a stable residual current I_{r2}, typically 1 µA to 5 µA.

m) Measure the control potential E_4 supplied by the potentiostat at the end of the oxidation, using the DVM (5.4). E_4 should be approximately E_0 + 0,17 V.

n) Record

— the final reduction and oxidation potentials, E_3 and E_4, in volts,

— the residual oxidation current, I_{r2}, in milliamperes,

— the integrated electrolysis current Q_S, expressed in the units of the output by the integrator,

— the electrolysis time, t_S, in seconds, and

— the temperature of the solution during electrolysis, T, in degrees Kelvin.

6.2 Analysis of subsequent samples

Subsequent test samples, that were weighed and prepared as described in 6.1.1 and 6.1.2, are measured as described in 6.1.6 and 6.1.7.

If no subsequent analysis will be performed:

— rinse the cell and components with supporting electrolyte or double-distilled water;

— store the reference electrode in a saturated solution of potassium chloride;

— store the working and the auxiliary electrodes in 8 mol/L nitric acid, or of greater concentration.

NOTE The user may elect to implement other storage protocols, which have been demonstrated to be effective for the desired electrode conditioning.

7 Expression of results

7.1 Calculation of the electrical calibration factor

Calculate the electrical calibration factor, C, in millicoulombs per unit output of the integrator, using Equation (2); (The unit output of the integrator may be in counts, volts, or directly in millicoulombs. In the latter case, the electrical calibration factor is effectively a correction factor.)

$$C = \frac{I_c t_c}{Q_c} \tag{2}$$

The calibration factor should equal the theoretical value, C_{th}, based upon circuit design and the measurement of key components in the circuit. However, the design and component layout of some coulometry systems may not lend themselves to the *in situ*, direct and independent measurement of load resistance, L_R and the response of the integrator to the input signal, R_S:

$$C_{th} = \frac{1}{L_R R_s} \tag{3}$$

For example, if the electrolysis current signal supplied to the integrator is actually a voltage drop across a high precision 100,00 Ω load resistor and the integrator utilizes a voltage-to-frequency converter with a response of 10 000,0 Hertz per volt, then the theoretical calibration factor is calculated as follows:

$C_{theoretical}$ = 1/(100,00 Ω × 10 000,0 Hz/V) = 10^{-6} Ω^{-1} V Hz^{-1} = 10^{-6} A Hz^{-1}

= 1,000 0 × 10^{-6} coulombs/count = 1,000 0 microcoulomb/count

7.2 Calculation of the blank

The integrated current Q_1, obtained during the coulometric blank determination (6.1.6) 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:

$$Q_b = \frac{(Q_1 - I_{r1}t_1)(E_4 - E_3)}{(E_2 - E_1) + I_{r2}\, t_2} \quad (4)$$

where

E_4 is the control potential measured at the completion of the plutonium oxidation, expressed in volts;

E_3 is the control potential measured at the completion of the plutonium reduction, expressed in volts;

E_2 is the control potential measured at the completion of the blank oxidation, expressed in volts;

E_1 is the control potential measured at the completion of the blank reduction, expressed in volts;

Q_1 is the integrated current for the blank determination, expressed in the units of the output by the integration system (measured during the oxidation between 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.

The parameters of the blank measurement are fully optimized when $E_1 = E_3$, $E_2 = E_4$, and $t_2 = t_1$. Under these ideal conditions, the term $(E_4 - E_3)/(E_2 - E_1)$ in Equation (4) is equal to unity; the correction for constant background current is minimized when using Equation (4) and the value of Q_b is approximately that of Q_1.

7.3 Fraction of electrolysed plutonium

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

$$f = \frac{e^{\frac{nF(E_4 - E_0)}{RT}}}{1 + e^{\frac{nF(E_4 - E_0)}{RT}}} - \frac{e^{\frac{nF(E_3 - E_0)}{RT}}}{1 + e^{\frac{nF(E_3 - E_0)}{RT}}} \quad (5)$$

where

E_0 is the formal 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 B);

R is the molar gas constant; R = 8,314 5 J mol^{-1} K^{-1} [5,6];

T is the absolute temperature, in kelvins, of the solution during electrolysis ($T = T_C$ + 273,15);

F is the Faraday constant; F = 96 485,34 C equivalent^{-1} [5,6];

n is the number of exchanged electron equivalents per mole of plutonium (n = 1 equivalent/mol for the Pu(III)/Pu(IV) couple).

NOTE For integration data collected from current cut-off measurements made before reaching a residual current without using the control-potential adjustment technique detailed in this International Standard, the correction f based on the control potentials applied during reduction and oxidation would be incomplete. Refer to Clause 10 for details.

7.4 Plutonium content

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

$$m_{Pu} = \frac{(Q_s - Q_b)\, C\, A_r}{F_f} \quad (6)$$

where

Q_s is the integrated electrolysis current, expressed in the units of the output by the integration system, during plutonium oxidation between the equilibrium potentials E_3 and E_4;

Q_b is the calculated blank from Equation (4), expressed in the units of the output by the integrator;

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

C is the electrical calibration factor of the integrator, in millicoulombs per unit output, from Equation (2);

F is the Faraday constant;

f is the fraction of electrolysed plutonium from Equation (5).

7.5 Quality control

Electrical calibration of the instrumentation provides an accurate and reliable conversion of the integrator output signal into coulombs and ultimately into equivalents electrolysed. However, this methodology does not independently test all of the parameters involved in measuring plutonium. A reliable quality-control program [7,8] based upon traceable standard reference materials, in accordance with ISO 10980, is needed to verify: reliable weighing and fuming of the test sample; quantitative recovery, if anion-exchange purification is used; satisfactory electrode treatment and conditioning (which is also evidenced by consistently low background currents observed during the blank and sample measurements); and the overall performance of the analyst and the instrumentation. Plotting and trending quality-control standards, that have been measured based upon electrical calibration, also provides significantly more information on system performance and reliability than can be obtained from tracking only the electrical calibration data. Another distinct advantage of combining electrical calibration and traceable quality-control standards is the increased confidence from independently ensuring system performance, demonstration of measurement uncertainty, and the ability to monitor all aspects of the measurement process including the preparation and control of plutonium reference materials.

8 Characteristics of the method

8.1 Repeatability

The short-term repeatability has been demonstrated by several laboratories measuring certified reference materials to be 0,02 % to 0,03 % relative standard deviation (1-sigma). The long-term repeatability has been demonstrated by these laboratories to be 0,04 % to 0,08 % (1-sigma). The long-term precision estimate is based on routine measurements, both quality-control standards and replicate measurements of test samples that meet the requirements of Clause 1.

8.2 Confidence interval

A control of both short-term and long-term systematic errors demonstrated these errors to be 0,03 % or less. Combining systematic and random errors yields a confidence interval of 0,1 % to 0,2 % at the confidence level of 0,95 for a single determination.

8.3 Analysis time

The time needed for a plutonium determination is 30 min to 60 min depending upon the cell design, electrode conditioning, and the selection of measurement parameters. Analysis times can be longer if conditions are not optimized.

9 Interferences

Iron present at 500 parts per millionincreases the result by about 0,1 % in nitric acid. If the iron content is both known and 1 000 parts per million or less, and the formal potential of pure iron has been measured for the system, then a mathematical correction for the iron is possible, using Equation (5) with the formal potential for iron replacing that of plutonium. Table 1 gives the calculation, for a reversible couple such as the Fe^{3+}/Fe^{2+} couple, the fraction of the atoms of the impurity element that would be electrolysed by the final reduction and oxidation potentials used for plutonium measurement.

Table 1 — Fraction electrolysed for impurity elements

Given E_o(Pu) = 0,668 V vs. SCE.

Given Pu control-potential adjustment at 1/750 of the initial electrolysis currents.

Assuming final Pu solution potentials: reduction, E_3, at 0,500 V vs. SCE; and oxidation, E_4, at 0,836 V vs. SCE.

E_o(Impurity) vs. SCE	Fraction of impurity reduced during plutonium reduction	Fraction of impurity oxidized during plutonium oxidation	Total fraction of impurity electrolysed during Pu measurement, $f_{impurity}$
	0,002 9	1,000 0	0,002 9
0,350	0,007 6	1,000 0	0,007 6
0,375	0,020 0	1,000 0	0,020 0
0,400	0,051 2	1,000 0	0,051 2
0,425	0,125 0	1,000 0	0,125 0
0,450	0,274 3	1,000 0	0,274 3
0,475	0,500 0	1,000 0	0,500 0
0,500	0,725 7	1,000 0	0,725 7
0,525	0,875 0	1,000 0	0,875 0
0,550	0,948 8	1,000 0	0,948 8
0,575	0,980 0	0,999 9	0,979 9
0,600	0,992 4	0,999 7	0,992 1
0,625	0,997 1	0,999 3	0,996 4
0,650	0,998 9	0,998 1	0,997 0
0,675	0,999 6	0,995 0	0,994 6
0,700	0,999 8	0,986 9	0,986 7
0,725	0,999 9	0,966 0	0,966 0
0,750	1,000 0	0,914 9	0,914 8
0,775	1,000 0	0,802 4	0,802 4
0,800	1,000 0	0,605 4	0,605 4
0,825	1,000 0	0,367 0	0,367 0
0,850	1,000 0	0,179 7	0,179 7
0,875	1,000 0	0,076 5	0,076 5
0,900	1,000 0	0,030 3	0,030 3
0,925	1,000 0	0,011 7	0,011 7
0,950	1,000 0	0,004 4	0,004 4
0,975	1,000 0	0,001 7	0,001 7

These fraction-electrolysed corrections are only applicable for a reversible couple, such as iron.

The mass, in milligrams, of plutonium corrected for iron impurity, $m_{\text{Pu Co}}$, is calculated as follows:

$$m_{\text{Pu Co}} = m_{\text{Pu}} - \frac{m_{\text{Fe}}\, f_{\text{Fe}}\, A_{\text{rPu}}}{A_{\text{rFe}}} \tag{7}$$

where

m_{Pu} is the mass, in milligrams, of plutonium, from Equation (6);

m_{Fe} is the mass, in milligrams, of iron in the aliquot, based upon the measurement of the iron impurity content by an appropriate measurement technique, such as inductively coupled plasma optical-emission spectrometry;

f_{Fe} is the fraction of iron electrolysed, calculated as in Equation (5), with E_0 assigned the value of the formal potential of iron;

A_{rPu} is the relative atomic mass of plutonium, calculated from its isotopic composition.

A_{rFe} is the relative atomic mass of iron, 55,847 g/mol.

The accuracy of the correction factor for the fraction of iron electrolysed is dependent upon the potential difference between the plutonium reduction potential and the formal potential of the iron. The closer they are, the greater the uncertainty. This is illustrated in Table 1 by the rapid change in the fraction electrolysed when the formal potential of an impurity is close to either the final plutonium reduction or oxidation potentials. A 25 mV difference in potentials will shift the fraction of the impurity electrolysed from 0,50 to either 0,27 or 0,73, depending upon the direction of the shift. When the E_0 of the impurity is within 70 mV of the E_0 of Pu, the fraction electrolysed approaches unity. In this case and because of the typical uncertainties associated with the concentration measurement of the trace impurity, the interference can be assumed to be quantitative. Refer to Clause 10 for additional details.

Neptunium interferes for plutonium measurement in nitric acid. (Np^{4+} is especially problematic since it does not react electrochemically at the same rate as the reversible Np^{6+}/Np^{5+} couple. The percent of neptunium in the Np^{4+} oxidation state is dependent on the sample source and sample pretreatment, increasing the uncertainty of corrections based upon neptunium impurity measurements and background current measurements.)

Interference from uranium has been reported, but its mechanism is not well defined.

If present, Pu^{6+} shall be reduced to Pu^{4+} prior to coulometric assay. The oxidation state adjustment in preparation for anion-exchange purification is effective at reducing Pu^{6+}. Alternatively, the addition of NO_2^- preceding the fuming step could be used to reduce Pu^{6+} to Pu^{4+} in pure plutonium solutions.

In principle, anion-exchange purification can be effective at removing the interferences listed above and achieving quantitative plutonium recovery. [9,10] Quantitative recovery of plutonium using the methodology outlined in Annex A is dependent upon achieving the plutonium (IV) hexanitrate divalent anion complex in a narrow acid range around 7,8 M nitric acid, and this particular purification sequence does not effectively remove neptunium. However, the addition of an excess of NO_2^- to the 7,8 M HNO_3 anion-exchange load solution, and heating at 70 °C to 80 °C for 10 min, selectively oxidizes a significant fraction of the neptunium to Np^{5+}, which is not absorbed on the resin with plutonium. Fuming to dryness in sulfuric acid, and oxidation state adjustment before anion purification, are normally required to obtain the plutonium complex and achieve quantitative plutonium recovery (and impurity removal). Attention to reagent purity, resin selection, and analyst technique are also critical parameters. [10]

Gold, iridium, palladium and platinum interfere quantitatively and are not easily removed by anion-exchange purification. However, these elements are rarely ever present at concentrations of interest in nuclear-grade materials.

Fuming is essential in the overall process of the plutonium measurement. It minimizes matrix effects from organic materials and anions. Independent of the dilute mineral acid selected for the supporting electrolyte, eliminating the fuming step before measurement is not consistent with the methodology detailed in this International Standard. It is likely to result in the generation of significant induced background current during plutonium measurements that is not included in the background current from the blank measurement. In addition, electrode performance typically degrades from introducing test samples that have not been fumed.

Organic compounds can cause both electrochemical and physical problems by reacting at or with the working electrode. Volatile organic compounds can be removed by fuming to dryness in sulfuric acid. Sulfuric acid can also degrade some organic material to inert ash.

The anions chloride, fluoride, nitrate and nitrite, and the inorganic reducing agent hydroxylamine are removed by fuming to dryness in sulfuric acid.

Nitrite anions in the nitric acid supporting electrolyte are destroyed by adding amidosulfuric acid.

The periodic table illustrated in Figure 3 details the elements that are not quantitatively removed by the anion-exchange purification described in Annex A. In addition, the table indicates which elements interfere in the quantitative electrochemical oxidation of the plutonium(III)/plutonium(IV) couple.

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	**Fe**	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	*Nb*	Mo	Tc	Ru	Rh	*Pd*	*Ag*	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	*La*	Hf	*Ta*	W	Re	Os	*Ir*	*Pt*	*Au*	Hg	*Tl*	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Lanthanides	*Ce*	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Actinides	*Th*	Pa	U	*Np*	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

The boxes for the elements Fe, Pd, Ir, Pt, Au and Np are marked with diagonal lines in the periodic table to indicate that these elements interfere during plutonium measurement, as described in this International Standard. Fe is removed by the anion-exchange purification described in this International Standard. The symbols for the elements Pd, Ir, Pt, Au and Np, along with the elements that do not interfere, Nb, Ag, La, Ta, Tl, Ce et Th, are shown in italics to indicate that these elements remain with the plutonium after anion-exchange purification.

Figure 3 — Periodic table

10 Procedure variations and optimization

10.1 Accountability measurements

The application of controlled-potential coulometry for plutonium safeguards and accountability measurements, as well as the characterization or verification of plutonium reference materials are well-established practices. Controlling uncertainties associated with the sampling of product materials is recognized to be an integral component for these applications. The impacts from sampling and measurement uncertainties are understood

for safeguards and the accountability applications, and do not require further discussion within this International Standard. Refer to applicable International Standards and guidelines.

10.2 Process control measurements

The application of controlled-potential coulometry to process control measurements, especially if the plutonium measurement is used to make process decisions that are important for nuclear safety, requires the same rigor, although some considerations are different. The point where the process is sampled shall have a qualified sampling procedure, as well as a plutonium matrix that has been demonstrated to be free from significant interferences (or be appropriately purified). The ability to independently detect a process-upset condition, especially one that can be anticipated to introduce interferences that are not normally present, shall be a part of the overall measurement process for the sample point. The consequence of sampling and analytical errors shall be well defined. The replication processes should be well understood and arranged to eliminate common mode failures from the sampling and measurement process, or from the individuals providing these services. Sample validation measurements, such as solution density, sample inspection, and independent verification of the sampling process can be effective tools for identifying sample errors and process upsets. For applications involving nuclear safety, a second plutonium measurement method may be appropriate to adequately reduce the probability of an undetected measurement error.

10.3 Measurement cell design

The basic cell design presented in this International Standard has been shown to be effective. However, other cell designs may be more efficient or reduce the background current by: minimizing electrolyte volume; decreasing the working electrode size, increasing ratio of the area of the working electrode to the volume of electrolyte, and/or positioning of the auxiliary electrode more symmetrically with respect to the working electrode. [11,12] The smaller the quantity of plutonium taken for the test sample, the more significant the uncertainty associated with background current measurement and the more desirable it may become to optimize the cell parameters. Any new cell design must be qualified for plutonium measurement with appropriate testing.

The basic cell design illustrated in this International Standard uses a SCE that is separated from the test solution by an additional electrolysis bridge that is filled with supporting electrolyte. This configuration should minimize or eliminate any leakage of chloride ion from the saturated KCl solution. Alternatively, a mercury(I) sulfate reference electrode may be employed to eliminate the source of chloride ions. For laboratories wishing to eliminate mercury for regulatory purposes, the silver/silver chloride reference electrode may be used. The formal potential of the plutonium couple shall be measured using the reference electrode that is selected and this E_0 value used when selecting control potentials for blank and sample electrolyses.

10.4 Electrolyte and electrode options

Other options that are considered within the existing scope of this International Standard are

— using dilute nitric acid at a concentration other than 0,9 molar,

— using dilute sulfuric acid as the supporting electrolyte, and

— substituting platinum or platinum alloy for gold as the working electrode.

Platinum and platinum alloy electrodes may require flaming to achieve optimum electrode condition, if boiling in nitric acid is not effective.

Using sulfuric acid presents the challenge of a much greater dependence on adequate oxygen removal prior to blank and test sample measurement. The significance of total oxygen removal (i.e. degassing with an inert gas) in sulfuric acid supporting electrolyte cannot be underestimated. The cell shall be sufficiently sealed to the cell head, and flushed with an adequate flow rate of the inert gas to eliminate oxygen from the solution and to blanket the atmosphere in the cell. High and erratic background currents will be obtained if the purging time before beginning any electrolyses is not adequate and the flow rate is not sufficient to prevent oxygen in-leakage. Oxygen in-leakage during measurements will increase the measurement time, significantly increase

background currents, prevent accurate control-potential adjustments, and produce serious measurement biases for both the blank and the test sample. However, when oxygen is properly removed, sulfuric acid can be an excellent choice for a supporting electrolyte. Sulfuric acid also has the advantage that neptunium does not interfere in the plutonium measurement.

10.5 Test sample size

Amounts of plutonium in the test sample above 15 mg are acceptable, but should not significantly improve overall measurement reliability, unless background current measurements are unusually high. In which case, correcting this deficiency should be pursued.

Test samples containing less that 4 mg of plutonium can be measured using this International Standard. However, cell design should be optimized to minimize the background currents so that their contributions to the overall measurement error are not excessive. In addition, the control-potential adjustment shall be performed in a manner that avoids even a small reversal of the electrolysis polarity, as the plutonium solution potential from smaller quantities of plutonium can be significantly shifted toward the formal potential during the adjustment process from small reversals of the electrolysis current. Note that the uncertainty in the determination of the plutonium solution potential from measuring the control potential increases for smaller sample sizes.

10.6 Background current corrections

The measurement of the background current should test the full range of the electrode/electrolyte performance for both reduction and oxidation. The criteria established for the blank measurement should be verified during each blank measurement, or at least routinely, such as at the start of the day, before beginning the measurements. Although the background criteria established for a specific cell design, electrode material and electrolyte are expected to vary, the total accumulated background current (blank) for a properly conditioned working electrode should be reproducible. The blank measured from a 5 min electrolysis should be less than 5 mC (12 µg Pu equivalent). The blank electrolysis for both reduction and oxidation should reach 30 µA in less than 1 min, and a residual current of less than 10 µA in 2 min to 3 min. If these criteria are not met, then the user should investigate the effectiveness of oxygen removal, electrode conditioning, and cell-design parameters (e.g. electrode connections, working electrode size, electrolyte volume, stirring and electrode configuration). The capability to achieve low residual current during both blank and sample measurement is equally important for reduction and oxidation. Integrated current is collected during only the oxidation of the blank and the sample. However, the control-potential adjustment technique depends upon the residual current for both reduction and oxidation being in the order of 5 µA or less, in order to determine the solution potential from the measurement of the control potential at or near 0 µA.

The accuracy of the measurement of the supporting electrolyte blank may be optimized by matching the duration of the blank oxidation to the typical test-sample electrolysis time. Simulating the control-potential adjustment for the blank measurement should be performed at approximately the same time required for the test sample to reach the desired current level where the control potential is adjusted. Do not perform this adjustment when the blank reaches the same current level. If the latter were done, the majority of the blank electrolysis would be performed at a potential that matched the end-point for the test sample electrolysis rather than at the actual control potential applied during most of the electrolysis of the test sample. Residual background currents at the different control potentials may be different and would thus reduce the accuracy of the blank measurement.

The residual background current values, I_{r1} and I_{r2}, shall be measured values, at the completion of the electrolysis, not at the initial control potential used during most of the blank and sample measurement. As such, they are estimates of the residual current actually experienced during the electrolyses. Periodically, the actual residual currents of a blank and a test sample should be measured at E_0 + 0,24 V, by performing an exhaustive electrolysis of each to ensure that the uncertainty associated with this methodology is not significant for the method, as performed by the individual laboratory.

10.7 Correction for iron

The procedure protocol is written for the measurement of pure or purified plutonium. Clause 9 provides an option for correcting the iron content in the nitric acid supporting electrolyte provided that

— iron is the only significant interfering impurity, which may be present in the test sample of nuclear-grade material

— iron is measured independently and with sufficient accuracy using an appropriate trace level measurement technique and

— the formal potential of pure iron is measured using the same protocol as provided in Annex B for plutonium, with sufficient reliability to calculate accurately the fraction of iron electrolysed during the plutonium measurement, using the same calculation methodology as provided by Equation (5).

If a dilute sulfuric acid supporting electrolyte is selected, the first two requirements remain the same. However, in dilute sulfuric acid, the formal potentials of plutonium and iron are sufficiently close that their fractions electrolysed are approximately the same. Thus, the iron impurity content can be subtracted from the total plutonium on an atom-for-atom basis. Equation (7) is simplified to:

$$m_{\mathrm{Pu\ Co}} = m_{\mathrm{Pu}} - \frac{m_{\mathrm{Fe}}\ A_{\mathrm{rPu}}}{A_{\mathrm{rFe}}} \tag{8}$$

Thus, in sulfuric acid supporting electrolyte, a mathematical correction for iron is larger per part per million of iron, but it is not dependent upon the fraction of iron electrolysed, since the formal potentials of plutonium and iron are similar in this acid.

10.8 Control-potential adjustment

The selection of the electrolysis current level of 1/750 of the initial electrolysis current at which to begin the control-potential adjustment is somewhat arbitrary. Selecting 1/500 of the initial electrolysis current to initiate this adjustment will increase the uncertainty in the determination of the fraction of plutonium electrolysed by less than 0,01 %, while decreasing slightly the total electrolysis time and thus decreasing the size of the background current correction. Alternatively, selecting 1/1 000 of the initial electrolysis current will decrease the uncertainty in the fraction electrolysed by less than 0,01 %, at the expense of efficiency and an increase in the total background current correction.

Although the following methodology and calculation is outside the scope of this International Standard, it is provided to clarify the key components in calculating the fraction electrolysed. If a current cut-off end-point greater than the residual current is chosen, without using the control-potential adjustment to locate the solution potential, then the equation for calculating the fraction electrolysed is not complete. In addition to calculating the fraction electrolysed from the control potentials applied using Equation (5), a further correction would be required, based on the ratio of the initial and final electrolysis current for both the test sample reduction and oxidation:

$$f_{\mathrm{cutoff}} = f \times [1 - I_{\mathrm{fr}}/I_{\mathrm{ir}} - I_{\mathrm{fo}}/I_{\mathrm{io}}] \tag{9}$$

where

f is the fraction electrolysed, see Equation (5);

I_{fr} is the final electrolysis current, sample reduction cut-off well before reaching residual current;

I_{fo} is the final electrolysis current, sample oxidation cut-off well before reaching residual current;

I_{ir} is the initial electrolysis current, at the start of sample reduction (t = 0 s);

I_{io} is the initial electrolysis current, at the start of sample oxidation (t = 0 s).

If the current cut-off is actually close to the residual current, the correction is significantly smaller, since the variables, I_{fr} and I_{fo}, should be reduced by the actual residual currents for reduction and oxidation, respectively, before substituting in Equation (9).