International Standard

ISO 12183

Fourth edition
2024-05

Nuclear fuel technology — Controlled-potential coulometric measurement of plutonium

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

Reference number
ISO 12183:2024(en)

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO document should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

ISO draws attention to the possibility that the implementation of this document may involve the use of (a) patent(s). ISO takes no position concerning the evidence, validity or applicability of any claimed patent rights in respect thereof. As of the date of publication of this document, ISO had not received notice of (a) patent(s) which may be required to implement this document. However, implementers are cautioned that this may not represent the latest information, which may be obtained from the patent database available at www.iso.org/patents. ISO shall not be held responsible for identifying any or all such patent rights.

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection,* Subcommittee SC 5, *Nuclear fuel cycle,* in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 430, *Nuclear energy,* in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This fourth edition cancels and replaces the third edition (ISO 12183:2016), which has been technically revised.

The main changes are as follows:

— Figures 1 and 2 have been revised to resolve errors introduced in the third edition of this document;

— quantity values and uncertainties values have been reformatted to comply with requirements for properly stating these values with SI units;

— editorial changes were made throughout the document to ensure clarity of the instructions;

— words with optional spellings were corrected to match ISO/IEC guidance;

— an additional key step was added to Clause 4 to indicated that the moles of plutonium obtained by controlled-potential coulometry is multiplied by the molar mass of plutonium obtained by other means, such as mass spectrometry or process knowledge;

— a formula has been added to 8.4 to calculate the amount of substance of plutonium in millimoles in addition to the mass of plutonium in milligrams;

— Clause 12 has been added to discuss traceability to SI units.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Nuclear fuel technology — Controlled-potential coulometric measurement of plutonium

1 Scope

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

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminology databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

The key steps and their purposes are outlined below:

— test samples are prepared from homogenous solutions by weighing and then fuming to dryness with sulfuric acid to achieve a stable anhydrous plutonium sulfate 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 sulfuric acid to obtain the anhydrous plutonium sulfate salt;

— measure the supporting electrolyte blank and calculate the background current correction applicable to the electrolysis of the test sample from charging, faradaic, and residual currents[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 a Pu^{3+} amount of substance fraction greater than 99,8 % and measure the equilibrium solution potential at the end of this step by control-potential adjustment[2];

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

— correct the integrated current (integrator output from the test sample) for the background current, including the residual current corrections, and for the amount fraction of plutonium not electrolysed;

— calibrate the coulometer using traceable electrical standards and Ohm's law;

— use the measured value of the electrical calibration factor and the Faraday constant to convert the integrator output to coulombs and then to moles of plutonium measured by the coulometer;

— calculate the mass of plutonium by multiplying the moles of plutonium determined by controlled-potential coulometry times a molar mass of plutonium determined by other means, such as thermal ionization mass spectrometry, magnetic sector inductively coupled plasma mass spectrometry, or process knowledge.

— use quality-control standards with traceable plutonium quantity values 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, acid-type and molarity of the supporting electrolyte, and the presence of any complexing agents in the electrolyte.

These steps ensure that test samples are taken from reproducible and stable sample solutions and prepared for measurement. The test samples are measured using a protocol based upon first principles and a traceable, electrical calibration of the coulometer. Further details are provided in Clauses 10 and 11.

5 Reagents

Use only analytical grade reagents.

All aqueous solutions shall be prepared with double-distilled or distilled, demineralized water with a resistivity greater than 10 MΩ·cm, i.e. ISO 3696[3] Grade 1 purified water.

5.1 Nitric acid solution, $c(HNO_3)$ = 0,9 mol/l.

NOTE Refer to 11.4 for alternative electrolyte options.

5.2 Amidosulfuric acid solution, $c(NH_2HSO_3)$ = 1,5 mol/l.

5.3 Sulfuric acid solution, $c(H_2SO_4)$ = 3 mol/l.

NOTE The concentration of the sulfuric acid solution used to fume the plutonium test samples is not a critical parameter, provided the sulfate ion concentration remains in large excess (above 50) compared to the plutonium ion in order to avoid the formation of colloidal Pu complexes.

5.4 Pure argon or nitrogen, (O_2 amount of substance fraction less than 10 µmol/mol).

5.5 Pure air (optional reagent), free of organic contaminants.

6 Apparatus

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

6.1 Analytical balance, installed in radiological containment unit and shall be capable of weighing a mass of 1 g, with a standard uncertainty of ±0,1 mg, k = 1. This represents a relative standard 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 criterion of ±0,1 mg, then test samples greater than 1 g should be used.

6.2 Weighing bottle, glass or plastic, the material selection is not critical provided it is chemically inert, maintains a stable mass (tare weight), and static charge is controlled as described in 7.1.1.

6.3 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:

— providing settings that allow both a rapid and well-controlled rate of initial evaporation, followed by fuming the remaining sulfuric acid solution to dryness at a higher temperature;

— preventing mechanical loss of the test sample solution from boiling and/or spattering;

— preventing contamination by extraneous chemicals, such as those which may be used to neutralize acid vapours;

— heating of the coulometer cell wall to optimize fuming and minimize refluxing of sulfuric acid by placing the cell inside an optional aluminium tube (inner diameter 1 mm to 3 mm larger than the outer diameter of the cell, tube height 1 mm to 5 mm shorter than the cell) placed around the cell during the fuming step;

NOTE An aluminium block with holes bored to a similar specification for inserting the coulometer cell can be used instead of the aluminium tubes.

— addition of an optional air supply with the delivery tube directed towards the surface of the liquid to optimize the evaporation rate and disperse the acid fumes, with appropriate controls and feature that will depend upon facility design and ventilation system requirements;

— addition of an optional vapour capture and local neutralization to control acid fumes, with appropriate controls and features that will depend upon facility design and ventilation system requirements.

See Figure 1.

Dimensions in millimetres

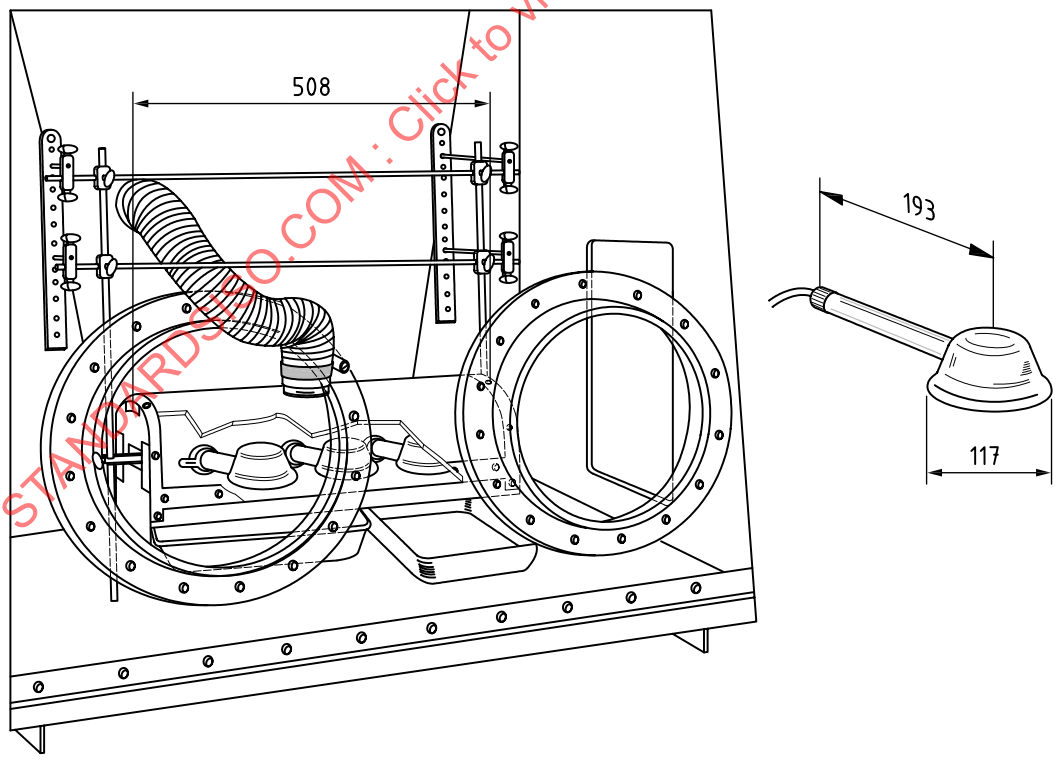


Figure 1 — Sample evaporation system

6.4 Controlled-potential coulometer.

See Figure 2.

6.4.1 Coulometer cell assembly, comprising the following:

a) A stirrer motor with a rotation frequency of at least 16,7 s^{-1} (1 000 min^{-1}).

NOTE 1 Adjustable-speed motors allow users to optimize the rate of rotation to the individual cell designs. Stirrer motors powered by isolated DC power supplies are recommended as they prevent electrical noise from being superimposed on the blank and test sample electrolysis current signals sent to the integrator.

b) A cylindrical or tapered glass coulometric cell of capacity 50 ml, or less.

c) A tight-fitting lid made from chemically and electrochemically inert material [e.g. polytetrafluoroethylene (PTFE)], that includes an O-ring seal, and 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 and electrochemically inert materials [e.g. polytetrafluoroethylene (PTFE)], 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 [mass fraction (purity) 9999 g/kg or greater] and consisting of a gold wire welded or machined to a cylindrical gold wire frame, a nominal height of 15 mm and a diameter of 20 mm, around which is welded or machined a very fine gold mesh, which is typically several layers (e.g. four layers);

NOTE 2 Refer to 11.4 for other working electrode options.

— a glass salt bridge tube plugged at the bottom end with a sintered-glass disc (typical thickness of 2,5 mm and pore size of <0,01 µm), the tube is filled with nitric acid (5.1) and the tip of the sintered-glass end is positioned within the ring of the working electrode;

NOTE 3 The diameter of the glass salt bridge tube and sintered-glass disc containing the auxiliary (counter) electrode can be larger than that of the glass salt bridge tube and sintered-glass disc containing the reference electrode. The desired flow rate of the solution through both glass discs is 0,05 ml/h, or less.

— a reference electrode, saturated calomel electrode (SCE), or other reference electrodes as described in 11.3, is inserted into the glass salt bridge tube;

— another glass salt bridge tube, similar to the first one, also filled with nitric acid (5.1), and the tip of the sintered-glass end positioned within the ring of the working electrode;

— an auxiliary (counter) electrode consisting of a platinum wire [mass fraction (purity) 999,5 g/kg or greater] with a diameter of 0,5 mm to 3,0 mm, is inserted into the second glass salt bridge tube;

NOTE 4 Coiling the platinum wire increases the surface area submerged in the supporting electrolyte, as illustrated in Figure 2.

d) A gas washer bottle, filled with reagent water as described in Clause 5, to humidify the inert gas before it is introduced into the coulometer cell assembly.

e) 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. A goal for the standard uncertainty of the temperature measurement is ±0,2 °C, $k = 1$.

NOTE 5 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.

NOTE 6 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 the solution temperature can be estimated from the ambient air temperature or the reagent temperature. The measured air or reagent temperature value is then corrected for this cooling effect and a higher standard uncertainty of ±1 °C, k = 1, is expected in the calculated solution temperature.

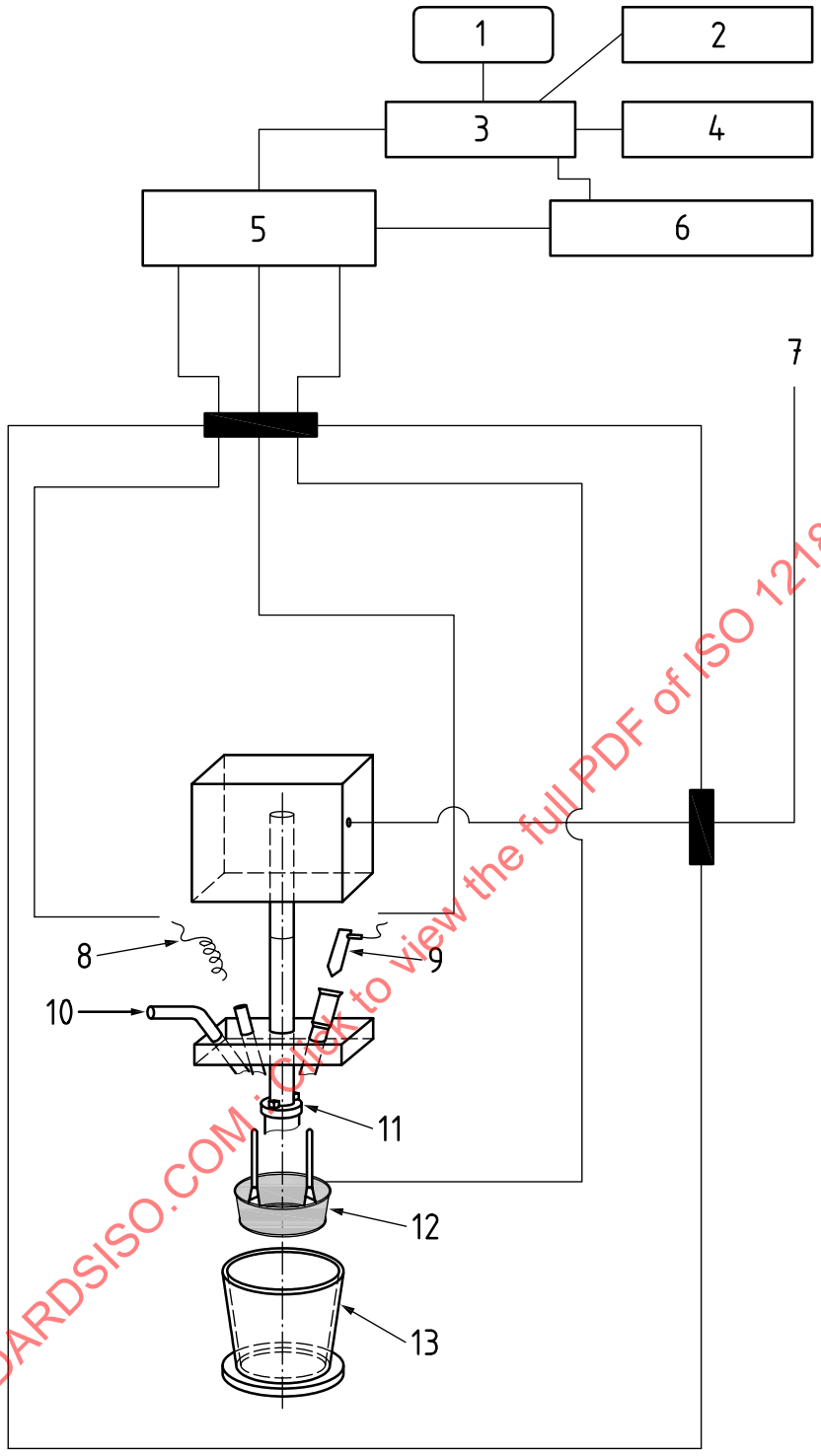
f) For optimum potential control, position the sintered-glass discs of the reference and auxiliary electrodes' glass tubes in order to meet the following requirements:

— 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.

g) 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 shall be sufficiently high such that it removes oxygen quickly from the supporting electrolyte and the test sample solution. Furthermore, it shall 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 dimple is formed on the surface with a depth of 2 mm to 4 mm without causing the solution to splash. An inert gas flow rate of 0,000 1 $m^3\ s^{-1}$ is sufficient for the coulometer cell assembly illustrated in Figure 2.

NOTE 7 Cell assemblies with an optimized design, an adequate inert-gas flow rate, and a tight fit, will remove oxygen from nitric acid supporting electrolyte in 150 s or less. Due to the variabilities of factors involved (e.g. cell geometry, volume of electrolyte), the time required to remove oxygen from the solution can be established by users based on testing of their cell assembly under routine conditions.



Key

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

Figure 2 — Coulometric cell assembly connections

6.4.2 Instrumentation, comprising the following[4][5]:

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 a maximum rise-time of 1 ms from zero volts to the desired control potential, with a 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} Ω;
- capability to monitor the electrolysis current, including charging current from -500 mA to +500 mA, with a detection capability of ±0,5 µA, or less.

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 µA, or less, with a readability of ±10 µC (refer to 7.1.4 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 with temperature controls sufficient to limit electronic drift within these specifications.
- An electronic clock, with a standard uncertainty of ±0,002 %, k = 1, for determining the duration of electrical calibrations and electrolyses.
- 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 7.1.4.
- 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 shall 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.

6.5 Digital voltmeter (DVM), with an input impedance of 10^{10} Ω or greater and having a standard uncertainty within ±0,001 %, k = 1, for voltages in the range 0,5 V to 10 V, and within ±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 7.1.4.

6.6 Regulated power, instrumentation should be protected with an uninterruptable power supply that provides a regulated voltage within ±1 % of the standard for the country in which the analysis is performed, and provides appropriate surge protection.

7 Procedure

7.1 Plutonium determination

7.1.1 **Weighing the test sample,** with a standard uncertainty of ±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 Formula (1) or Formula (2), as described below.

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

NOTE 1 For test samples at high plutonium concentrations (e.g. 15 g/l or more), it is recommended that the solution be diluted to achieve a standard uncertainty of ±0,01 %, k = 1 for the overall mass measurement process.

NOTE 2 If a weight bottle made of polyethylene, or other material susceptible to static electricity, is used, then the problem of static electricity is eliminated by contact between the weighing bottle and a copper plate connected to the ground, or a similar arrangement.

a) Fill a weighing bottle with the solution to be analysed.

b) Weigh the bottle to ±0,1 mg.

c) Deliver a test sample of at least 1 ml, drop by drop, into a coulometric cell, ensuring that at least 4 mg of plutonium has been delivered.

d) Weigh the bottle again to ±0,1 mg.

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

f) The real mass of the test sample, M_{real}, is obtained by correcting the apparent mass of the test sample for the air buoyancy effect using Formula (1):

$$M_{real} = M_a \cdot (1 - D_a / D_b) \cdot (1 - D_a / D_s)^{-1} \quad (1)$$

where

D_a is the density of air, which is a function of room temperature, atmospheric pressure, and relative humidity. When the room temperature is 22 °C ± 5 °C, the atmospheric pressure is 1 000 kPa ± 40 kPa, and the relative humidity is 45 % ± 15 %, D_a is 1,18 kg m^{-3} ± 0,07 kg m^{-3}

D_b is the density of the stainless-steel weights used in modern analytical balances, 8 000 kg m^{-3}

D_s is the density of the test sample, in kilograms per cubic metre

NOTE 3 Equations for calculating the density of air from the room temperature, atmospheric pressure, and the relative humidity are available from several sources including the International Organization of Legal Metrology[6], which is based on guidance from the International Committee for Weights and Measures (CIPM).

In addition to applying an air buoyancy correction to the apparent 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 approach 0,1 % for solutions. The correction is less for a solid test sample, but can still be significant.

For plutonium metal and alloy test samples, an additional buoyancy correction term for self-heating from radioactive decay, as detailed in Formula (2) is also appropriate for the apparent mass of metal or alloy[7].

$$M_{real} = M_a \cdot (1 - D_a / D_b) \cdot (1 - D_a / D_s)^{-1} \cdot [1 - (\Delta m)' \cdot \left(M_a^{-2/3}\right) \cdot (P_{u,heat})]^{-1} \quad (2)$$

where

M_a is the apparent mass of the metal or alloy, in grams

$\Delta m'$ is the mass coefficient for the heat buoyancy term, with a value of 0,000 03 $g^{1/3}$ mW^{-1} ± 0,000 01 $g^{1/3}$ mW^{-1} (1σ) for test samples ranging from 1 g to 15 g

$P_{u,heat}$ is the specific heat of the plutonium, in milliwatts per gram, calculated from the plutonium isotopic abundance and the isotope mass fraction of ^{241}Am. [This value is nominally 2 mW g^{-1} to 3 mW g^{-1} for plutonium metal whose origin is a spent nuclear fuel with a burn up ranging from 2 MW·d·kg^{-1} to 8 MW·d·kg^{-1}. The specific heat increases with higher reactor burn up and increased isotope mass fractions of ^{238}Pu and ^{241}Am.]

7.1.2 Preparation of the test sample

a) Add 1 ml of sulfuric acid solution (5.3) to the coulometric cell containing the test sample.

b) Place the cell containing the test sample into the sample evaporation system and carefully evaporate the liquid in the test sample so as to avoid splashing.

c) Evaporate the remaining liquid in the test sample at a temperature sufficient to evolve fumes of nitrous oxide (N_2O) and sulfur trioxide (SO_3), and continue until SO_3 fumes are no longer observed and a residue of anhydrous plutonium sulfate salt (pink/orange-coloured precipitate) is formed. Do not allow the solution to boil or splash as this will cause mechanical loss of the sample.

NOTE 1 The colour of the anhydrous plutonium sulfate salt is dependent on the type of lighting used in the laboratory. Under fluorescent lighting the dried sulfate appears coral pink.

NOTE 2 Degradation of anhydrous plutonium sulfate salt to plutonium oxide is not expected even after baking the residue unless subjected to extremely high temperatures.

NOTE 3 Failure to use 1) high purity reagents, 2) anion-exchange resins washed free of resin fines, and 3) heating equipment that is well maintained and clean will impact the fuming operation adversely. Any or all of these failures can produce a 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 the coulometric measurement.

d) Allow the test sample to cool to room temperature.

e) If Pu^{6+} (PuO_2^{2+}) is known to be present, reduction to lower oxidation states (Pu^{3+} and/or Pu^{4+}) is required prior to coulometric measurement by the addition of either hydrogen peroxide, nitrite ion, or ferrous ion. The excess reducing agent shall be removed by purification or destroyed prior to coulometric measurement, and the test sample again fume to dryness in sulfuric acid as detailed in steps a) through d), above. Refer to Clause 10 for details.

NOTE 4 If the presence of Pu^{6+} (PuO_2^{2+}) is suspected, the test sample can be treated with one of the reducing agent and processed appropriately. Alternatively, the test sample electrolysis can be monitored and the result rejected if the reduction step is slow, indicating the presence of Pu^{6+} (PuO_2^{2+}).

NOTE 5 When Pu^{6+} (PuO_2^{2+}) is reduced using hydrogen peroxide in 8 mol/l nitric acid, then step e) can be performed promptly after weighing the test samples, prior to fuming the test sample in sulfuric acid, as described in steps a) through d).

f) If the presence of significant amounts of impurities is suspected, dissolve and purify the dried test sample to eliminate the interfering elements. Repeat the sulfuric acid fuming step as detailed in 7.1.2. Anion-exchange is an effective purification process; it is outlined in Annex A.

NOTE 6 The interfering elements gold, iridium, palladium, and platinum, along with the elements that do not interfere: cerium, lanthanum, niobium, silver, tantalum, thallium, and thorium are not separated from plutonium using the anion exchange purification in Annex A. Refer to Clause 10 for additional information on interferences.

7.1.3 Electrode pre-treatment

Electrode conditioning is critical to ensuring reproducibility. The following storage and treatment techniques may be used individually or in combination to condition the working and auxiliary electrodes:

— storing in 8 mol/l nitric acid when the electrodes are not in use (this storage technique is recommended as the general practice);

— soaking in concentrated nitric acid;

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

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

— boiling in nitric acid;

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

Electrode treatment may be performed on a preventative basis, at the beginning and/or at the end of the day of electrode use. Alternatively, treatment may be on an "as needed" basis, particularly needed in case of failure to obtain optimum electrode performance in either the blank or the test sample measurements. The background current values (total mC, charging current mA maximum, and residual current µA) should be reproducible for a given coulometer cell assembly and are normally used as indicators of satisfactory performance.

Each day, or more frequently if desired, before performing the actual blank determination, a further conditioning of the electrodes is performed through the following sequence of electrolyses:

a) Assemble the cell lid, complete with the electrodes and other internal equipment (6.4.1).

b) Take a clean dry coulometric cell and add nitric acid solution (5.1) in sufficient quantities to immerse the working electrode, and the sintered-glass discs at the bottom of the salt bridge tubes for the reference and auxiliary electrodes.

c) Add one drop of amidosulfuric acid solution (5.2).

d) Firmly fit the cell under the lid.

e) Start the stirrer at the desired speed. This speed should be selected in order to maximize the stirring rate, while avoiding splashing or the formation of an excessive vortex that would interrupt electrical connections.

f) Open the gas inlet and maintain a sufficient flow of inert gas throughout the electrolysis period, as described in 6.4.1 g). 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 150 s, 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) Rinse the electrolysis cell and the outside wall of the salt bridge tubes with fresh supporting electrolyte.

m) Based upon electrode performance,

— perform further electrode conditioning according to 7.1.3, until the desired performance is observed, or

— measure the supporting electrode blank determination according to 7.1.6, in preparation for the subsequent measurement of plutonium test samples.

7.1.4 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 general principles and specifications apply toward determining the calibration factor within a standard uncertainty not exceeding ±0,01 %, k = 1.

— Generate a constant current (stable and known to within ±0,002 %, k = 1) in a manner that is electronically equivalent to the process by which the electrolysis current from the test sample and the blank are integrated.

NOTE Typically, the potentiostat is converted into a constant current source with the current flowing through a standard resistor, instead of the cell assembly. The voltage drop across the standard resistor is measured to determine accurately the actual calibration current. Alternatively, if a constant current source is used instead of the potentiostat, then this external source requires periodic calibration to ensure consistency and traceability.

— Determine the duration of calibration (i.e. current flow) within ~0,002 %, k = 1.

The linearity of the integrator response shall be demonstrated for the range of currents observed during plutonium measurement from the maximum current at time equals 0 seconds to the current when the control-potential adjustment begins (e.g. 100 mA to 50 µA). Ensure that the impact of the integrator nonlinearity on the plutonium measurement is 0,005 %, or less, k = 1.

A typical sequence for performing an electrical calibration is:

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 signal from the integrator, Q_C (in the units 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 8.1 for further details.

7.1.5 Formal potential determination

The formal potential, E_0, of the Pu^{4+}/Pu^{3+} couple should be measured at regular intervals (as described in Annex B), especially when electrodes have been replaced, if the electrodes have been out of use for a considerable time, or if the studied solution is liable to contain a different amount of Pu-complexing agents than that of solutions previously studied. Before performing this measurement, ensure that the working and auxiliary electrodes have been properly pre-treated and conditioned. Also ensure that the SCE is filled with saturated potassium chloride solution and contains a few free-flowing salt crystals, but is not clogged by excessive amounts of salt crystals.

When the control potentials for reduction, E_3, and oxidation, E_4, are measured during the analysis of the test sample, as described in 7.1.7, these potentials are approximately equal to E_0-0,17 V and E_0+0,17 V, respectively. Thus, the average of E_3 and E_4 is highly correlated with E_0. The average of E_3 and E_4 may be plotted on a control chart and used as an indicator of the stability of the electrolysis cell and the reference electrode between periodic E_0 determinations.

The formal potential is close to +0,668 V vs SCE when 0,9 mol/l nitric acid is used as the supporting electrolyte but small variations can be expected because different calomel electrodes exhibit slightly different potentials. The formal potential is also moderately dependent on the concentration of the nitric acid supporting electrolyte and any Pu-complexing agents that may be present in the solution. 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 fume test samples completely to a dry (anhydrous) plutonium sulfate salt before dissolving in nitric acid supporting electrolyte will result in an inconsistent shift of the formal potential due to the varying amount of excess sulfuric acid. In the analysis of U/Pu mixed oxides, additional sulfate ions from dried uranium sulfate will also shift the formal potential as a function of the U:Pu ratio[8].

The appropriate formal potential value should be used in Formula (6) when mixed oxide materials are measured for plutonium. Use the appropriate formal potential value in Formula (6) whenever the formal potential is shifted by any complexing agent.

7.1.6 Coulometric blank determination

Blank measurement parameters are set to correspond with the electrolysis conditions of the test sample. Optimum reliability in the blank value is obtained when the initial and final oxidation potentials during the blank and the test samples, as well as the duration of the blank and the test sample are matched. Matching the current level at which the control potential is adjusted for both the blank and test sample is not appropriate. Refer to 8.2 for additional details.

a) Rinse the outside wall of the salt bridge tubes and, if necessary, fill them with 0,9 mol/l nitric acid solution (5.1).

b) Repeat the steps b) through f) as detailed in 7.1.3.

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

d) Degas the supporting electrolyte, as described in 6.4.1 g), until all the dissolved oxygen is removed. Oxygen removal should be accomplished within 150 s or less.

e) Start the oxidation at E_0+0,24 V 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 about 120 s to 180 s when 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 between 1 µA and 3 µA.

h) Measure the control potential E_1 supplied by the potentiostat at the end of the reduction step, using the DVM (6.5).

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 for 200 s, or a period of time that matches the typical duration for the plutonium test sample to be oxidized to 1/750 of the initial current, or less.

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 between 1 µA and 3 µA.

l) Measure the control potential E_2 supplied by the potentiostat at the end of the oxidation step, using the DVM (6.5).

m) Record

- the final reduction and oxidation potentials, E_1 and E_2 (V),
- the residual current, I_{r1} (mA),
- the integrated current, Q_1, in the units of the output signal from the integrator (ideally, this quantity equates to 5 mC, or less), and
- the electrolysis time, t_b (s).

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

7.1.7 Plutonium measurement

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

b) Inspect the test sample solution to determine if the anhydrous plutonium sulfate salt has dissolved completely. Even if the solids have not dissolved completely, continue with steps c) to g) below, 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 6.4.1 g).

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

g) Degas the solution, as described in 6.4.1 g), until all the dissolved oxygen is removed. Oxygen removal should be accomplished within 150 s or less.

h) Start the reduction at E_0−0,26 V and reduce until an electrolysis current is obtained that is 1/750 of the initial reduction current, or less, typically in the range of 50 µA to 150 µA depending upon the quantity of plutonium in the test sample. Reduction should not take more than about 600 s, if the stirring and degassing are adequate.

i) 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 between 1 µA and 5 µA.

j) Measure the control potential E_3 supplied by the potentiostat at the end of the reduction, using the DVM (6.5). E_3 should be approximately E_0−0,17 V.

k) Reset the integrator and timer.

l) Start the oxidation at E_0+0,24 V and oxidize until an electrolysis current is obtained that is 1/750 of the initial oxidation current, or less, typically in the range of 50 µA to 150 µA depending upon the quantity of plutonium in the test sample. This should not take more than 600 s, if the stirring is adequate.

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

n) Measure the control potential E_4 supplied by the potentiostat at the end of the oxidation, using the DVM (6.5). E_4 should be approximately E_0+0,17 V.

o) Record

- the final reduction and oxidation potentials, E_3 and E_4 (V),
- the residual oxidation current, I_{r2} (mA),
- the integrated electrolysis current Q_2, in the units of the output signal from the integrator,

— the electrolysis time, t_S (s), and

— the temperature of the solution during electrolysis, T (K).

7.2 Analysis of subsequent test samples

Subsequent test samples that were weighed and prepared as described in 7.1.1 and 7.1.2, are measured as described in 7.1.6 and 7.1.7.

If no subsequent analysis will be performed:

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

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

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

NOTE The user can implement other storage protocols, which have been demonstrated as effective for maintaining the desired electrode condition.

8 Expression of quantity values

8.1 Calculation of the electrical calibration factor

Calculate the electrical calibration factor, C, using Formula (3). This factor is used to convert the integrator output signal to millicoulombs. The integrator output signal may be in pulses, volts, or directly in millicoulombs. In the last case, the electrical calibration factor is a quantity of dimension one.

$$C = I_C \cdot t_C \cdot Q_C^{-1} \tag{3}$$

where

I_C is the constant current generated during the electrical calibration, in milliamperes

t_C is the time of the electrical calibration, in seconds

Q_C is the integral of the calibration current, expressed in the units of the output signal from the integration system

The electrical calibration factor calculated above should equal the theoretical value, $C_{theoretical}$, based upon circuit design and the measurement of key components in the circuit. However, the design and component layout 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:

$$C_{theoretical} = L_R^{-1} \cdot R_S^{-1} \tag{4}$$

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 Hz per volt, then the theoretical calibration factor is calculated as follows:

$$C_{theoretical} = (100{,}00\ \Omega \times 10\ 000{,}0\ \text{Hz/V})^{-1} = 10^{-6}\ \Omega^{-1}\ \text{V Hz}^{-1} = 10^{-6}\ \text{A Hz}^{-1} = 10^{-6}\ \text{A s pulse}^{-1}$$

$$= 1{,}000\ 0 \times 10^{-6}\ \text{C pulse}^{-1} = 1{,}000\ 0\ \mu\text{C pulse}^{-1}$$

8.2 Calculation of the blank

The integrated current Q_1, obtained during the coulometric blank determination (7.1.6) is used to calculate the blank correction that is appropriate for the conditions observed during the plutonium determination.

The value of the blank correction, B_{mC}, expressed in millicoulombs, is given by the following formula:

$$B_{mC} = (Q_1 \cdot C - I_{r1} \cdot t_1) \cdot (E_4 - E_3) \cdot (E_2 - E_1)^{-1} \quad (5)$$

where

C is the electrical calibration factor, calculated using Formula (3)

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

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

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

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

Q_1 is the integral of the current from the blank determination, expressed in the units of the output signal from the integration system, (measured during the oxidation between potentials E_1 and E_2)

I_{r1} is the residual current after oxidation of the blank, in milliamperes

t_1 is the electrolysis time for oxidation of the blank, in seconds

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 Formula (5) is equal to unity and the corrections for constant background current are minimized when using Formula (5) and Formula (7).

8.3 Fraction of electrolysed plutonium

The amount fraction of electrolysed plutonium, f, is given by Formula (6):

$$f = \frac{e^{\frac{nF(E_4 - E_0)}{RT}}}{1 + e^{\frac{nF(E_4 - E_0)}{RT}}} - \frac{e^{\frac{nF(E_3 - E_0)}{RT}}}{1 + e^{\frac{nF(E_3 - E_0)}{RT}}} \quad (6)$$

where

E_0 is the formal potential of the Pu^{4+}/Pu^{3+} couple in the supporting electrolyte, in volts

NOTE 1 This potential is determined with chemically pure plutonium analysed in the same manner as the test sample (see Annex B).

R is the molar gas constant; R = 8,314 462 618… J mol^{-1} K^{-1} (exactly; expressed to 10 significant figures)[9]

T is the absolute temperature, in Kelvin, of the solution during electrolysis ($T = T_C$ + 273,15 °C) where T_C is the temperature in degrees Celsius

F is the Faraday constant; F = 96 485,332 12… C mol^{-1} (exactly; expressed to 10 significant figures) [9]

n is the number of moles of electrons exchanged per mole of plutonium electrolysed, n = 1 (a dimensionless quantity; i.e. a quantity of dimension one)

NOTE 2 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 document, the correction f based on the control potentials applied during reduction and oxidation would be inaccurate. Refer to Clause 11 for details.

NOTE 3 The CODATA values for the Faraday constant and the molar gas constant are available at https://physics.nist.gov/cuu/Constants/index.html. Future changes to these quantity values are not expected.

8.4 Plutonium, amount of substance and mass

The amount of substance of plutonium in the test sample, n_{Pu}, expressed in millimoles, is given by Formula (7):

$$n_{Pu} = (Q_2 \cdot C - B_{mC} - I_{r2} \cdot t_2) F^{-1} \cdot f^{-1} \quad (7)$$

where

Q_2 is the integral of the electrolysis current, expressed in the units of the output signal from the integration system, during plutonium oxidation between the equilibrium potentials E_3 and E_4;

B_{mC} is the calculated blank from Formula (5), in millicoulombs;

C is the electrical calibration factor from Formula (3);

F is the Faraday constant, 96 485,332 12... C mol^{-1};

f is the amount fraction of plutonium electrolysed from Formula (6), in moles per mole;

I_{r2} Is the residual current after oxidation of plutonium, in milliamperes;

t_2 is the electrolysis time for oxidation of the plutonium, in seconds.

The mass of plutonium in the test sample, m_{Pu}, expressed in milligrams, is given by Formula (8):

$$m_{Pu} = n_{Pu} \cdot M_{Pu} \quad (8)$$

where M_{Pu} is the molar mass of plutonium calculated from its isotopic composition, typically obtained by mass spectrometry, in grams per mole (or in milligrams per millimole).

8.5 Quality control

Electrical calibration of the instrumentation provides an accurate and reliable conversion of the integrator output signal into millicoulombs, from which the amount of plutonium is calculated. Electrical calibration does not independently test all of the parameters involved in measuring plutonium. A reliable quality-control programme[10][11] based upon analysis of reference materials with traceable plutonium quantity values (see ISO 10980[12]) is needed to verify reliability of mass measurements and proper fuming of the test samples with sulfuric acid; quantitative recovery of plutonium, if anion-exchange purification is used; satisfactory electrode treatment and conditioning practices (verified through consistently low background currents during the blank and test sample measurements); reliability in instrument operations; and the overall performance of the analyst. Control charting is recommended for

a) quality-control standards measured utilising electrical calibration,

b) electrical calibration data,

c) periodic formal potential, E_0, measurements, and

d) the average of the E_3 and E_4 potentials measurements.

A distinct advantage of combining electrical calibration and quality-control standards with traceable plutonium quantity values 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. Accreditation of the user's coulometric measurement capabilities in accordance with ISO/IEC 17025[13] and participation in external sample exchange programmes and/or performance evaluation test programmes will enhance measurement quality assurance and continuous improvement efforts.

9 Characteristics of the method

9.1 Repeatability

The short-term repeatability has been demonstrated by several laboratories through measurements of certified reference materials yielding quantity values with relative standard deviation of 0,02 % to 0,03 %, k = 1. The long-term repeatability has been demonstrated by these same laboratories to be 0,04 % to 0,08 %, k = 1. The long-term precision estimate is based on routine measurements of quality-control standards and replicate measurements of test samples that meet the requirements given in Clause 1.

9.2 Confidence interval

Short-term and long-term systematic uncertainties of the measurement method have been demonstrated to be ±0,03 % or less, at a confidence level of 0,95. Combining all sources of uncertainty yields a confidence interval of ±0,1 % to ±0,2 % at the confidence level of 0,95 for a single determination.

Application of the GUM methodology yields measurement uncertainty estimates for a single determination of ±0,1 % to ±0,2 % with a coverage factor of k = 2. The measurement uncertainty and associated coverage factor reported with plutonium quantity values should be computed in accordance with JCGM 100[14] and JCGM 101[15].

9.3 Analysis time

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

10 Interferences

For some applications, the purification of test samples by anion exchange is required before measurement to remove interfering substances present in significant amounts. Clause 10 provides 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 can fluctuate unpredictably in a manufacturing process.

Iron with an impurity mass fraction relative to plutonium of 500 mg/kg increases the plutonium quantity value by about 0,1 % in nitric acid supporting electrolyte. If the iron impurity mass fraction is both known and equal to 2 000 mg/kg or less, and the formal potential of pure iron has been measured for the system, then a mathematical correction for the iron is possible. The fraction of iron that would be electrolysed along with plutonium can be calculated using Formula (6) by substituting the formal potential of the Fe^{3+}/Fe^{2+} couple for E_0. See Table 1 for calculations of f for impurity elements that are reversible couples.

Table 1 — Fraction electrolysed for impurity elements

Given E_0(Pu) = 0,668 V vs SCE in 0,9 mol/l nitric acid supporting electrolyte
Given T = 298 K
Given plutonium control-potential adjustment at 1/750 of the initial electrolysis currents.
Assuming final plutonium solution potentials: reduction, E_3, at 0,500 V vs SCE and oxidation, E_4, at 0,836 V vs SCE.

E_0 (impurity) versus SCE	Fraction of impurity reduced during plutonium reduction / mol/mol	Fraction of impurity oxidized during plutonium oxidation / mol/mol	Total fraction of impurity electrolysed during Pu measurement, $f_{impurity}$ / mol/mol
0,350	0,002 9	1,000 0	0,002 9
0,375	0,007 6	1,000 0	0,007 6
0,400	0,020 0	1,000 0	0,020 0
0,425	0,051 1	1,000 0	0,051 1
0,450	0,124 9	1,000 0	0,124 9
0,475	0,274 2	1,000 0	0,274 2
0,500	0,500 0	1,000 0	0,500 0
0,525	0,725 8	1,000 0	0,725 8
0,550	0,875 1	1,000 0	0,875 1
0,575	0,948 9	1,000 0	0,948 9
0,600	0,980 0	0,999 9	0,979 9
0,625	0,992 4	0,999 7	0,992 1
0,650	0,997 1	0,999 3	0,996 4
0,675	0,998 9	0,998 1	0,997 0
0,700	0,999 6	0,995 0	0,994 6
0,725	0,999 8	0,986 9	0,986 8
0,750	0,999 9	0,966 1	0,966 0
0,775	1,000 0	0,914 9	0,914 9
0,800	1,000 0	0,802 5	0,802 5
0,825	1,000 0	0,605 5	0,605 5
0,850	1,000 0	0,367 0	0,367 0
0,875	1,000 0	0,179 7	0,179 7
0,900	1,000 0	0,076 4	0,076 4
0,925	1,000 0	0,030 3	0,030 3
0,950	1,000 0	0,011 7	0,011 7
0,975	1,000 0	0,004 4	0,004 4

The information in Table 1 is only applicable for a reversible couple, such as iron or neptunium.

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

$$m_{Pu-Fe} = m_{Pu} - m_{Fe} \cdot f_{Fe} \cdot f_{Pu}^{-1} \cdot M_{Pu} \cdot M_{Fe}^{-1} \quad (9)$$

where

m_{Pu} is the mass of plutonium, in milligrams [from Formula (8)]

m_{Fe} is the mass of iron, in milligrams, calculated from the known mass of the test sample and the iron impurity mass fraction, that is determined by an appropriate measurement technique such as spectrophotometry, inductively coupled plasma optical emission spectrometry, or inductively coupled plasma mass spectrometry

f_{Fe} is the amount fraction of iron electrolysed, calculated based on Formula (6), with E_0 assigned the value of the formal potential of iron, in moles per mole

f_{Pu} is the amount fraction of plutonium electrolysed from Formula (6), in moles per mole

M_{Pu} is the molar mass of plutonium calculated from its isotopic composition, in grams per mole

M_{Fe} is the molar mass of iron, 55,845 g mol^{-1} ± 0,002 g mol^{-1}, k = 1 (according to IUPAC 2009[16]; use most current IUPAC value)

EXAMPLE Given E°(Fe^{3+}/Fe^{2+}) = 0,475 V vs. SCE in 0,9 mol/l HNO_3, at 298 K and the same conditions of electrolysis as in Table 1, an iron mass fraction of 2 000 mg/kg (0,002 mg/mg) would lead to an overestimation of the Pu amount of substance:

$$\frac{m_{Fe}}{m_{Pu}}\frac{f_{Fe}}{f_{Pu}}\frac{M_{Pu}}{M_{Fe}} = 0{,}002 \times \frac{0{,}274}{0{,}999\,7} \times \frac{239}{55{,}8} = 0{,}23\ \%$$

Instead of correcting the mass of plutonium for the mass of iron impurity, the plutonium amount of substance may be corrected for the iron amount of substance as follows:

$$n_{Pu-Fe} = n_{Pu} - n_{Fe} \cdot f_{Fe} \cdot f_{Pu}^{-1} \quad (10)$$

where

n_{Pu} is the plutonium amount of substance, in millimoles [from Formula (7)];

n_{Fe} is the iron amount of substance, in millimoles, which is equal to $m_{Fe}/M_{Fe.}$

The uncertainty in the mass of iron in the test sample, m_{Fe}, depends upon the uncertainty and the detection limit of the method used to determine the iron impurity mass fraction. For nuclear grade materials, the uncertainty in the mass of iron in the test sample should be a minor component in the uncertainty budget for the plutonium quantity value.

The uncertainty in f_{Fe} is dependent upon the potential difference between the plutonium reduction potential and the formal potential of the iron. The closer these potentials are to each other, the greater the uncertainty. This effect is illustrated in Table 1 by the rapid change in the amount fraction electrolysed when the formal potential of an impurity is close to either the final plutonium reduction or oxidation potentials. A difference in potentials of 25 mV will thus shift the fraction of the impurity electrolysed from 0,50 mol/mol to either 0,27 mol/mol or 0,73 mol/mol, depending upon the direction of the shift.

When the E_0 of the impurity element is within 70 mV of the E_0 of Pu, the amount fraction electrolysed approaches unity and the interference can be assumed to be quantitative given the typical uncertainties associated with the concentration measurement of the trace impurity. This situation is observed for iron in sulfuric acid supporting electrolyte. Refer to Clause 11 for additional details.

Neptunium interferes with plutonium measurements in a nitric acid supporting electrolyte. Np^{4+} is especially problematic since it does not react electrochemically at the same rate as the reversible Np^{6+}/Np^{5+} (NpO_2^{2+}/NpO_2^{+}) couple. The percentage of neptunium in the Np^{4+} oxidation state is dependent on the sample source and sample pre-treatment, therefore uncertainty in making the neptunium correction depends not only on the uncertainty in the neptunium impurity measurements and the amount fraction of the neptunium involved in the reversible reaction of Np^{6+}/Np^{5+} (NpO_2^{2+}/NpO_2^{+}), but also upon ensuring complete oxidation of Np^{4+} prior to the oxidation of the plutonium in a manner that does not adversely impact background current levels during the plutonium measurements.

In nitric acid supporting electrolyte the presence of U at Pu:U ratios up to 1:100 is known to cause an indirect interference by introducing sulfate ions (arising from the fuming process wherein the U present in solution, like the Pu, is converted into anhydrous sulfate salts), which complex with the Pu ions in solution during analysis and induce a shift in the formal potential of the Pu^{4+}/Pu^{3+} couple. This interference can be addressed as discussed in 7.1.5 by measuring the formal potential of the test sample being measured and calculating the amount fraction of plutonium electrolysed, *f*, using Formula (6).

If Pu^{6+} (PuO_2^{2+}) is present, it should be reduced to Pu^{4+} prior to coulometric measurement. Several options are available for reducing Pu^{6+} (PuO_2^{2+}):

— Reducing Pu^{6+} (PuO_2^{2+}) with ferrous ion is effective. However, since iron is an interference, it shall be removed or reduced significantly by anion exchange prior to coulometric measurement. Following the coulometric measurement, the mass fraction of iron in the test sample solution should be measured to calculate the mass of any trace iron after purification and to apply the appropriate correction using Formula (9).

— The Pu^{6+} (PuO_2^{2+}) can also be reduced with hydrogen peroxide preceding the fuming step by the addition of 50 µL to 100 µL of 30 % hydrogen peroxide (H_2O_2) to the test sample solution in 8 mol/l nitric acid. Cover the test sample with a watch glass to prevent loss of solution from slow effervescence caused by the hydrogen peroxide reaction. After several hours the test solution should turn blue indicating complete reduction of the Pu^{6+} (PuO_2^{2+}) to Pu^{3+}. The solution should then be gently heated on a hot plate to oxidize the plutonium to Pu^{4+}, as indicated by a colour change in the solution to green. The condensate on the watch glass should then be rinsed using sulfuric acid solution (5.3) into the test sample, then add 2 ml, or less, of sulfuric acid (5.3), and fume the solution to dryness. If the test sample is heated with overhead lamps instead of a hot plate, then sulfuric acid should be added before this heating step to prevent drying of the condensate on the watch glass as the condensate which can contain traces of the dissolved plutonium spattered from the effervescent reaction of the peroxide. If the nitric acid condensate dries on the watch glass, the resulting plutonium nitrate salt can oxidize and the resulting residue may not readily dissolve when the watch glass is rinsed.

— The addition of NO_2^- to test samples dissolved in dilute nitric acid preceding the fuming step could be used to reduce Pu^{6+} (PuO_2^{2+}) to Pu^{4+}.

Humidifying the inert gas by bubbling it through a reservoir of reagent water will (i) restore some of the heat lost by the gas from expansion prior to its introduction into the coulometer cell and (ii) minimize evaporation of the supporting electrolyte solution (typically 0,9 mol/l nitric acid) into the moist gas. Controlling temperature and humidity of the inert gas decreases the rate of evaporation of the supporting electrolyte solution and the resulting cooling during the measurement of the blank and the sample.

In principle, anion-exchange purification (see Annex A) can be effective at removing the interferences referenced above, as well as achieving quantitative plutonium recovery[17][18]. It is recommended that plutonium solutions in 7,8 mol/l nitric acid be treated with NO_2^- when neptunium is present. After NO_2^- addition, heat the solution to 70 °C to 80 °C for 600 s to obtain Np^{5+} (NpO_2^+). This step ensures separation of plutonium from neptunium in the anion exchange method, since Np^{5+} (NpO_2^+) is not adsorbed by the resin. In general, fuming to dryness in sulfuric acid and oxidation state adjustment shall be done to obtain the hexa-nitrato plutonium (iv) anion complex in the loading solution in 7,8 mol/l nitric acid for the anion exchange purification method. Attention to reagent purity, resin selection, and good experimental technique (loading the solution, washing, and elution) are other critical parameters to achieve quantitative separation and recovery of plutonium free from interfering impurity elements[18].

Gold, iridium, palladium, and platinum interfere quantitatively and are not easily removed by anion-exchange purification. However, these elements are rarely ever present in sufficient abundance in nuclear grade plutonium to be of a cause for concern. The presence of these elements at interfering concentrations can be easily detected using inductively coupled plasma mass spectrometry.

Fuming in the presence of sulfuric acid is an essential step in the plutonium measurement method described in this document, independent of the dilute mineral acid selected for the supporting electrolyte. The fuming step helps to eliminate interferences from organic materials and other anions if originally present in the test sample. Analysis of test samples that have not been fumed is likely to result in degradation of electrode

performance and may result in induced background current during the plutonium measurement that is not included in the background current from the blank measurement.

Organic compounds interfere through electrochemical reactions and through coating of the working electrode resulting in degraded performance. Volatile organic compounds are removed by fuming to dryness in sulfuric acid. Drying in sulfuric acid also facilitates conversion of some organic material to inert ash, which does not interfere in the analysis.

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 and that produced at the working electrode during the reduction step in nitric acid supporting electrolyte are destroyed by adding amidosulfuric acid.

11 Procedure variations and optimization

Clause 11 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 document.

11.1 Accountability measurements and reference material preparation

Controlled-potential coulometric determination of plutonium is an important analytical technique in accountability measurements and reference material preparation. Minimizing measurement and sampling uncertainties and providing clear traceability to the International System of Units, SI,[19] are integral components of the analytical procedure described in this document. The impacts from sampling and measurement uncertainties are understood for safeguards and the accountability applications, and do not require further discussion within this document. Users of this document are responsible for identifying requirements and implementing appropriate protocols for representative sampling of the various types of nuclear materials that they plan to measure by controlled-potential coulometry. Requirements and protocols for representative sampling of plutonium nitrate solutions are available in ISO 12083.[20] Guidance on sampling and dissolution of plutonium-bearing metal and oxide materials is available in ASTM C1168[21].

11.2 Process control measurements

Applying controlled-potential coulometry to process control measurements, especially if the plutonium measurement is used to make process decisions that are important to nuclear safety, requires the same rigor as in routine material accountability measurement, although some specifics will vary. A well developed and qualified sampling procedure and knowledge of the plutonium matrix, especially with respect to the purity of the material, are a few of those specific needed for process control measurements. The point where the process is sampled shall be demonstrated to be free from significant interferences or the test sample shall be purified appropriately. The ability to detect independently a process upset condition, especially one that can be anticipated to introduce interferences that are not normally present, shall be a part of the sampling and analysis strategy. The consequence of sampling and analytical errors shall be specified well and mitigating actions shall be taken to minimize the consequence from these error sources as well as to reduce their frequency. The replication processes should also be well understood and arranged to eliminate common mode failures from the sampling and measurement process or from the individuals providing these services. Validation measurements such as solution density on replicate test samples, physical inspection of test samples, and independent verification of the sampling process can be effective tools for identifying and controlling sampling errors as well as identifying process upsets. Certain applications, especially those demanding a high reliability such as nuclear criticality prevention, may require verification by a second plutonium measurement method for example isotope dilution mass spectrometry. Application of two different analytical techniques helps to identify hidden or unaccounted sources contributing to measurement errors in either of the techniques.

11.3 Measurement cell design

The cell design presented in this document is known to be effective for plutonium coulometric analysis. 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[22][23].

The smaller the quantity of plutonium taken for the test sample, the more significant is the background correction and the higher the uncertainty contribution from it. To reduce these sources of uncertainty it may be desirable to optimize the cell parameters to reduce the background current. It is important to note that any new cell design should be qualified for plutonium measurement with appropriate testing.

The cell design shown in this document uses a SCE that is separated from the test solution by a salt bridge (sintered glass tube) that is filled with the supporting electrolyte. This design should minimize or eliminate any leakage of chloride ion from the saturated KCl solution. A few, free flowing crystals of KCl in the reference electrode indicate that the solution is saturated, however excessive crystal formation will impact the performance of the reference electrode.

An alternative to SCE is the silver/silver chloride (Ag/AgCl) reference electrode. Instead of SCE or Ag/AgCl electrodes, a mercury (I) sulfate reference electrode may be used to eliminate the source of chloride ions. The formal potential, E_0, value of the plutonium couple also depends upon the reference electrode selected and should be determined experimentally with the controlled potentials for plutonium reduction and oxidation being chosen based on this experimentally determined value.

11.4 Electrolyte and electrode options

Other options that are considered within the existing scope of this document are:

— substituting platinum, gold electroplated on platinum mesh, or platinum alloy for gold as the working electrode;

— using dilute sulfuric acid as the supporting electrolyte;

— using dilute nitric acid at a concentration other than 0,9 mol/l.

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

Dilute sulfuric acid may be used as the supporting electrolyte provided the formal potential, E_0, of the Pu^{4+}/Pu^{3+} couple is measured in the concentration of sulfuric acid selected and the dissolved oxygen in the supporting electrolyte is removed exhaustively prior to measuring the blank and the test sample. Sulfuric acid has the advantage that neptunium does not interfere in the plutonium measurement.

When oxygen is properly removed, sulfuric acid can be an excellent choice for a supporting electrolyte. However, the significance of effective oxygen removal (i.e. degassing with an inert gas) in sulfuric acid supporting electrolyte cannot be overstated. Cell assemblies with an optimized design, an adequate inert-gas flow rate and a tight fit, will remove oxygen from sulfuric acid in 600 s 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. If the purging time before beginning any electrolyses is not adequate to remove oxygen and the flow rate is not sufficient to prevent diffusion of oxygen into the cell then high and erratic background currents will be obtained, resulting in increased measurement times, inaccurate control-potential adjustments, and serious measurement biases for both the blank and the test sample.

Dilute nitric acid at a concentration other than 0,9 mol/l may be used provided the formal potential, E_0, of the Pu^{4+}/Pu^{3+} couple is measured in the chosen concentration of nitric acid.

11.5 Test sample size

Using a mass of plutonium in the test sample above 15 mg is acceptable. However, increasing the mass of plutonium may not significantly improve overall measurement reliability unless background currents are

unusually high. Achieving low background currents is an important objective and therefore large size test samples are usually not needed.

Test samples containing less than 4 mg of plutonium can be measured using this document. However, background current and plutonium solution potential measurements require more stringent controls. Cell designs should be optimized to minimize the background currents and their variability so that their contributions to the overall measurement error are not excessive. In addition, the control-potential adjustments shall be performed more slowly to avoid even small reversals in the polarity of the electrolysis current. For smaller quantities of plutonium reversals in polarity can cause significant shifts in the plutonium solution potential that move it close to the formal potential than desired. The uncertainty in determining the plutonium solution potential from measuring the control potential also increases for smaller test sample sizes.

11.6 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 measuring test samples. 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 300 s electrolysis should be less than 5 mC (equivalent to 12 µg Pu). The blank electrolysis current for both reduction and oxidation should reach 30 µA in less than 60 s and a residual current of less than 10 µA in 120 s to 180 s. 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 speed and electrode configuration). The capability to achieve low residual current during both blank and test sample measurement is equally important for reduction and oxidation. However, integrated current is measured during the oxidation only for both the blank and the sample. The control-potential adjustment technique depends upon achieving low residual current for both reduction and oxidation steps on the order of 5 µA or less. Under these conditions, the solution potential determined from measuring the control potential at or near 0 µA is reliable.

The uncertainty in the measurement of the supporting electrolyte blank may be reduced 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 (low) current level where the control potential is adjusted. Do not perform this adjustment when the blank reaches the same (low) current level. If the latter was done, the majority of the blank electrolysis would be performed at a potential that matched the endpoint 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 increase the uncertainty in the blank correction.

The residual background current values, I_{r1} and I_{r2}, are measured values, at the completion of the blank and test sample electrolysis, which only approximate the actual residual background currents at the initial control potential used during most of the blank and test sample measurements. As such, these measured values are estimates of the residual currents 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. These periodically measured values may be used in place of the measured I_{r1} and I_{r2} values when calculating the blank correction, B_{mC}, using Formula (5) and Formula (7).

11.7 Correction for iron

The procedure presented in this document is for the measurement of test samples containing pure or purified plutonium. Clause 10, Interferences, provides an option for correcting the plutonium quantity value for the interference due to iron in the test sample. The correction methodology is valid provided that

— iron is the only significant interfering impurity 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 provided in Annex B for plutonium, with sufficient reliability to calculate accurately the amount fraction of iron electrolysed during the plutonium measurement, using the same calculation methodology provided by Formula (6).

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 amount fractions electrolysed are approximately the same. Thus, iron impurity contribution can be subtracted from the total plutonium on an atom-for-atom basis. Formula (9) simplifies to:

$$m_{\mathrm{Pu-Fe}} = m_{\mathrm{Pu}} - m_{\mathrm{Fe}} \cdot M_{\mathrm{Pu}} \cdot M_{\mathrm{Fe}}^{-1} \tag{11}$$

Thus, in sulfuric acid supporting electrolyte, a mathematical correction for iron is larger per milligram of iron compared to nitric acid supporting electrolyte, but the uncertainty in this correction is not dependent upon the amount fraction of iron electrolysed since the formal potentials of plutonium and iron are similar in this acid.

11.8 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 standard uncertainty in the determination of the amount fraction of plutonium electrolysed to ±0,02 %, k = 1, 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 standard uncertainty in the amount fraction electrolysed to ±0,01 %, k = 1, or less at the expense of efficiency and an increase in the total background current correction. However, if a correction in excess of 0,05 % will be made for the interference from iron in the test sample, the electrolysis current level at which to begin the control-potential adjustment for the sample reduction should be selected to control the uncertainty in the calculation of the amount fraction of iron electrolysed, f_{Fe}. This is accomplished by ensuring that the control potential at the end of the test sample reduction, E_3, is at least 50 mV away from the formal potential of iron, E_0(Fe). Values of 1/1 000 or greater are sometimes required to accomplish this objective.

Although the following methodology and calculation is outside the scope of this document, it is provided to clarify the key components in calculating the amount fraction electrolysed. If a current cut-off endpoint greater than the residual current is chosen, without using the control-potential adjustment to locate the solution potential, then the formula for calculating the amount fraction electrolysed is not complete. In addition to calculating the amount fraction electrolysed from the control potentials applied using Formula (6), 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:

$$f_{\mathrm{cutoff}} = f \times \left(1 - I_{\mathrm{fr}} \cdot I_{\mathrm{ir}}^{-1} - I_{\mathrm{fo}} \cdot I_{\mathrm{io}}^{-1}\right) \tag{12}$$

where

f is the amount fraction electrolysed, Formula (6);

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 start of sample reduction, but after charging current (t = 0,1 s);

I_{io} is the initial electrolysis current, at start of sample oxidation, but after charging current (t = 0,1 s).