1. **Objective of the Technique**

Controlled-potential coulometry is a destructive analysis method for the quantitative determination of plutonium in samples taken from nuclear-grade product materials and reference materials in oxide, metal, and alloy forms and from nuclear-grade fuel cycle streams of plutonium nitrate solution. This instrumental method may be used for nuclear material accountability and safeguards, and for material characterization and reference material certification. A measured mass of sample is dissolved and diluted; aliquots are taken by mass and chemically treated, and then subjected to electrochemical analysis. The electrochemical measurement determines the amount of plutonium in the aliquot. The assay or concentration result is calculated using the measured plutonium and the masses from the analytical sampling and dilution. For solid samples, the assay is typically reported as a percentage or mass content for solid sample, e.g. 88.04% Pu or 0.8804 g Pu/g sample. For liquid samples, the concentration is typically reported as a mass of plutonium per mass or volume of sample, e.g., 10.123 g Pu/g sample or 10.567 g Pu/mL sample. Solution density measurements are normally used to convert from a g/g-basis to a g/mL-basis.

2. **Presentation of the Technique**

2.1 **Principle of Measurement**

Sample aliquots are evaporated to dryness in sulfuric acid to remove volatile impurities and to generate a consistent and stable plutonium sulfate anhydrous salt. The dried plutonium salt is then dissolved in dilute mineral acid, typically sulfuric or nitric acid. The plutonium in solution is first reduced to Pu\(^{3+}\) at a stationary platinum or gold electrode maintained at a controlled-potential nominally 200 mV below the formal potential of plutonium. The reduction is continued for 5-10 minutes until the electrolysis current reaches a residual level, indicating completion of the sample reduction. The stationary electrode is then set to a potential that is nominally 200 mV above the formal potential of plutonium. The current that flows during the oxidation of the plutonium to Pu\(^{4+}\) is electronically integrated. The oxidation is continued for 5-10 minutes until the total coulombs of electricity generated from the reaction have been measured. The plutonium content is calculated from the coulombs of electricity using the Faraday’s Constant to convert from coulombs to moles of plutonium. The relative atomic mass of the plutonium, obtained from mass spectrometry isotopic abundance measurements, is used to convert from moles to mass. The coulometer may be calibrated using electrical standards and Ohm’s Law or using plutonium reference materials.

2.2 **Procedure outline**

- The dilute mineral acid that will be used to dissolve the dried plutonium aliquot is first subjected to the same electrochemical reduction and oxidation reaction sequence that will be used to measure the dissolved plutonium aliquot. This ‘blank’ measurement process ensures that the electrodes and the measurement cell are functioning properly. The ‘blank’ coulombs will be subtracted from the coulombs of electricity generated during the measurement of the dissolved plutonium aliquot.
- The plutonium is dissolved in the dilute mineral acid after the blank measurement is completed.
- The dissolved plutonium ions react at the polarized electrode and reduce until the Pu\(^{3+}\) ion is the dominant species and the potential of the Pu\(^{4+}/\text{Pu}^{3+}\) couple in solution matches the potential of the stationary electrode, at which time the electrolysis current is at a residual current level that is typically less than 10 µA.
- The timing circuit and the electrical integration circuit are set to zero, and the potential of the stationary electrode is then adjusted to the desired potential for plutonium oxidation.
- The plutonium reacts at the polarized electrode, oxidizing until the Pu\(^{4+}\) ion is the dominant species and the potential of the Pu\(^{4+}/\text{Pu}^{3+}\) couple in solution matches the potential of the stationary electrode, at which time the electrolysis current is at a residual current level that is typically less than 10 µA.
• The mass of plutonium measured during the oxidation of $\text{Pu}^{3+}$ to $\text{Pu}^{4+}$ is calculated from the quantity of electricity (coulombs) measured using the equation:

$\text{Pu} = (Q_s - Q_b) \times C \times A_r / F f$

Where: $Q_s$ is the integrated current measured during sample oxidation, $\int i \, dt$
$Q_b$ is the integrated current measured during blank oxidation
$C$ is the calibration factor for the integration circuit
$A_r$ is the relative atomic mass calculated from the plutonium isotopic abundance
$F$ is the Faraday constant, 96,485.3399 Coulombs per mole
$f$ is the fraction of the plutonium electrolyzed during the sample oxidation

• The assay or concentration is calculated by dividing the mass of plutonium measured by the mass of sample in the aliquot, based on the weight of sample taken and any subsequent dilutions during the preparation of the aliquot.

2.3 Chemical reactions

2.3.1 Reduction of plutonium at the stationary electrode, in preparation for measurement:

$$\text{Electrode} \quad \text{Pu}^{4+} + e^- \rightarrow \text{Pu}^{3+}$$

2.3.2 Oxidation of plutonium at the stationary electrode generates current from the flow of electrons, $e^-$, which are integrated to measure coulombs:

$$\text{Electrode} \quad \text{Pu}^{3+} \rightarrow \text{Pu}^{4+} + e^-$$

2.4 Interferences

Several metal ions interfere: gold, iridium, palladium, platinum, iron, and neptunium. The four noble metals are not typically present in the nuclear-grade plutonium product materials or process streams. The extent of the interference from iron and neptunium depends upon the selection of supporting electrolyte, and also on the oxidation state of the neptunium.

Polymeric plutonium, if present, is not electro-active and will not be detected as plutonium. If present, $\text{Pu}^{6+}$, i.e., $\text{PuO}_2^{2+}$, may not be reduced during sample reduction, depending upon the selection of mineral acid used as the supporting electrolyte and the coulometric experimental parameters.

Organic contaminants that are not volatized during aliquot fuming can interfere by reacting at the electrode or by affecting the performance of the electrode. Hydrazine interferes and is not easily removed during routine sample pretreatment. Hydroxylamine is sometime present in process solution, but is removed when the aliquots are fumed to dryness several times in sulfuric acid.

The anions nitrate, nitrite, chloride and fluoride interfere, but are also removed during fuming in sulfuric acid. Nitrite anions in nitric acid supporting electrolyte are destroyed by adding sulfamic acid prior to measuring the blank.

Atmospheric oxygen interferes, especially in sulfuric acid, and must be removed prior to the blank and sample measurement by purging the supporting electrolyte and the atmosphere in the measurement cell above the solution with an inert gas.

The interference from iron can be eliminated by a mathematical correction when the iron content is known from another measurement, such as spectrophotometry or inductively coupled plasma mass spectrometry.
2.5 Sample size

The analytical sample must be representative of the bulk material from which it is taken. For plutonium oxide, metal, or alloy samples that are homogenous and stable, an analytical sample of 300-1000 mg that is taken with an uncertainty of ±0.05 mg, 1-sigma is typical and satisfactory. Following dissolution and dilution to obtain 3-5 mg Pu per gram of solution, aliquots containing 5-20 mg Pu are taken by mass, and fumed to dryness.

2.6 Apparatus

Instrumentation and equipment required for performing coulometric measurements:

- Analytical balances with a readability of 0.01 mg, in appropriate radiological containment.
- A potentiostat circuit that supplies the control-potential to the stationary (working) electrode.
- An integrator circuit that measures the coulombs of electricity produced from oxidizing the blank and sample.
- A digital voltmeter for measuring the control-potential supplied by the potentiostat and for electrical calibration.
- An instrument controller (computer), if automated operations is desired.
- A measurement cell composed of a glass container for the sample solution, a platinum or gold working electrode, a platinum counter electrode, a saturated calomel reference electrode, a stirrer, and an inert gas inlet, in appropriate radiological containment.
- A gas bubbler to saturate the compressed gas with water before introduction in the measurement cell, in appropriate radiological containment.
- Compressed gas cylinder and regulator system, high purity argon or nitrogen.
- Beakers, pipettes, and volumetric glassware for preparing reagents, typical laboratory equipment.
- Microwave over or hot block for sample dissolution, in glovebox containment.
- Heat lamps or hot plate for aliquot fuming, in appropriate radiological containment.
- Conditioned power and uninterruptible power supply (UPS) are recommended.

2.7 Accuracy and precision

Normal level: Results are accurate to 0.1% or better and the relative standard deviation is 0.1% or better. Measurement of aliquots containing less than 5 mg of plutonium will have greater uncertainty corresponding to the quantity of plutonium present. Alternative measurement methods such as isotope dilution mass spectrometry are recommended in preference to coulometric measurement below 5 mg of plutonium per aliquot.

2.8 International Target Values (ITV)

In nuclear safeguards measurements, the 2010 ITV for systematic (u(s)) and random (u(r)) variations for controlled potential coulometry are 0.1%. The 2010 ITV also specifics a target for the total uncertainty of 0.15% with coverage factor of 1.

2.9 Comparison with IDMS

Controlled-potential coulometry and isotope dilution mass spectrometry methods have similar levels of accuracy and precision for the determination of plutonium.

The setup cost for controlled-potential coulometry is less than IDMS; the latter is more expensive because a thermal ionization mass spectrometer (TIMS) is required for isotope ratio determinations. However, the capabilities and applicability of IDMS and the TIMS instrument are more extensive than that of a controlled-potential coulometer.

The cost for purchasing a coulometer station will range from $120,000-$200,000, (€80,000-€130,000) depending upon the instrument selected and the delivery requirements.
3.0 References

1. ISO 12183:2005, Controlled-potential coulometric assay of plutonium
2. ISO 12803:1997, Representative sampling of plutonium nitrate solutions for determination of plutonium concentration
7. HARRAR, J. E., U.S. Atomic Energy Commission Publication UCRL-50417, Platinum Working Electrode Cell for Controlled-Potential Coulometry, (March 27, 1968) University of California, Lawrence Livermore National Laboratory, Livermore, California, USA

3.1 Figures

Fig 1: Coulometer Instrumentation, Savannah River National Laboratory (SRNL) Coulometer
Fig 2: Cell Assembly, SRNL design, with modified PAR stirring motor