A Coulometric Measurement System for Plutonium Assay

Michael K. Holland, SRNS Analytical Laboratory and
Joseph V. Cordaro, Savannah River National Laboratory

The Coming Nuclear Renaissance for the Next Generation Safeguards Expert
Maximizing Benefits While Minimizing Proliferation Risks
Oak Ridge National Laboratory – Bldg. 5100
December 16, 2008

SRNL-STI-2008-00489

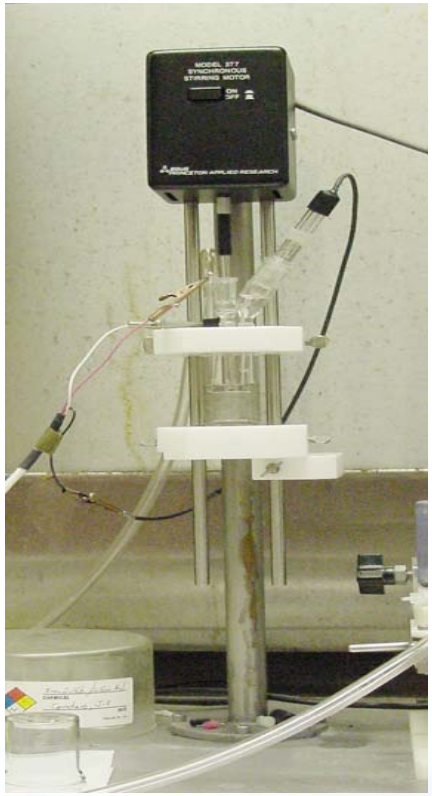
Savannah River
Nuclear Solutions, LLC
A Fluor Daniel Partnership

Presentation Outline

- SRNL Controlled-Potential Coulometer
  - Instrumentation
  - Cell design
- Pedigree of SRNL Coulometer
- Coulometry overview
- Electronics
- Cell hardware
- Software
- Electrical calibration
- Uncertainty of electrical calibration

SRNL Coulometer

Cell Designs



SRNL Coulometer Customers

- Savannah River Site (SRNS) – 2 systems
  – Pu Analytical Laboratory & SRNL Equipment Mock-up
- DOE's New Brunswick Laboratory – 2 systems
- International Atomic Energy Agency - Safeguards Analytical Laboratory (sponsor: Department of State) – 1 system
- Russia - Mayak Laboratory – 1 system
- Japan Atomic Energy Agency - Tokai – 2 systems
- Rokkasho Reprocessing Plant – 3 systems

CPC Applications, Programs, Methodology

Applications

- Destructive Pu & Np assay (and concentration)
  - Solution samples
  - Dissolved solid samples

Programs

- Product samples (MC&A & assay specifications)
- Nuclear safety & process control
- Material characterization
- Standard certification (primary, secondary, calibration)
- Safeguards & referee samples

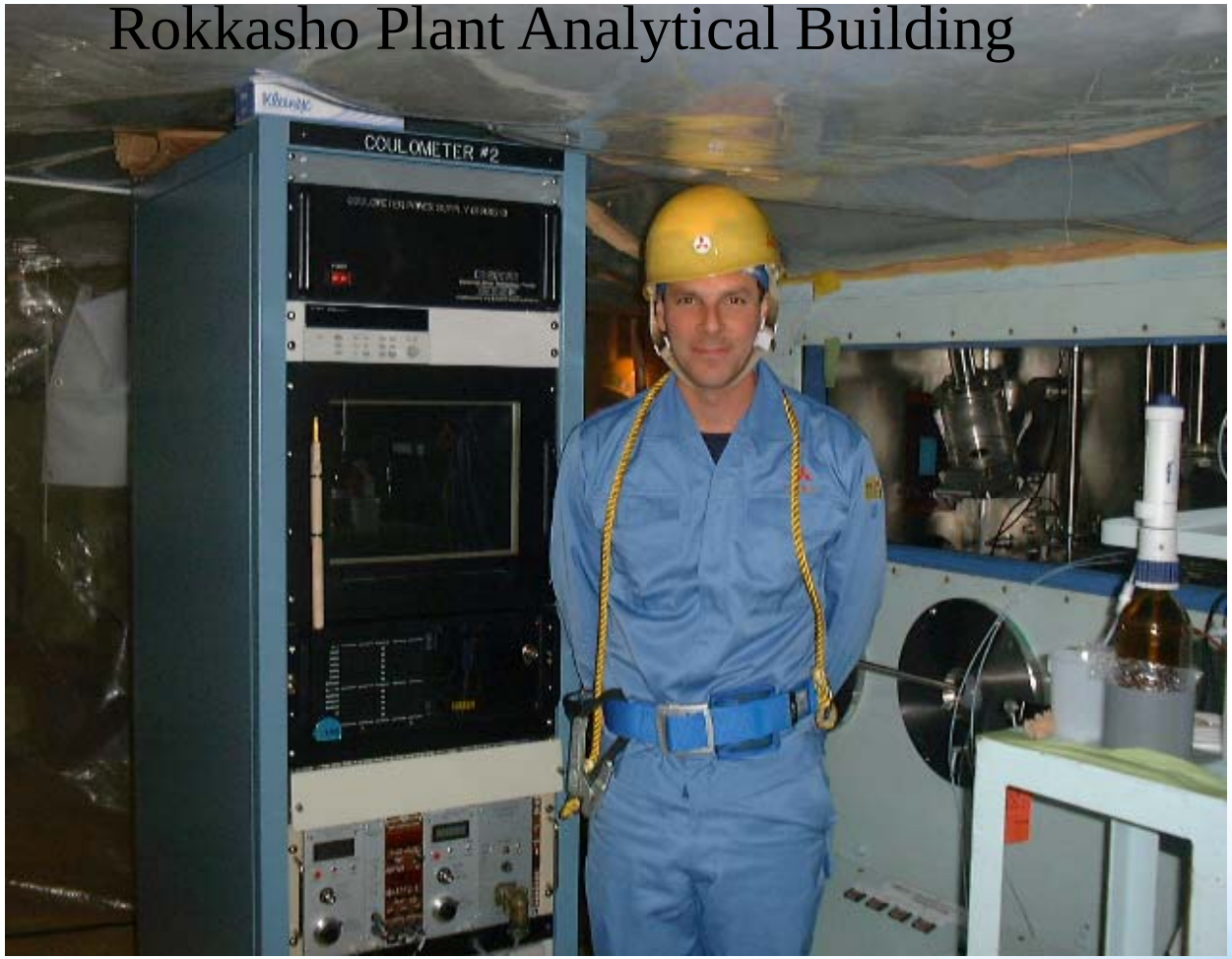
Methodology

- First principles – [CPC is definitive method per NIST]
- Electrical calibration
- ISO 12183:2005 procedural standard for CPC assay of Pu

Coulometer Applications

- Accountability for PUREX product stream (past) – SRS
- Pu metal assay (standards & exchange program mat'l) – SRS
- Acct. & spec. for Np product streams & Np oxide – SRS
- Select material characterization (Pu/MOX) – SRS
- 'Certify' internal Pu QC and Calibration Standards – SRS
- Pu MC&A, safeguards, and dispute samples – DOE-NBL
- Certify primary reference materials (Pu CRM) – DOE-NBL
- International safeguards & std. confirmation – IAEA-SAL
- Large size dry (LSD) spike characterization – JAEA
- TBD safeguards measurements – RRP

Installation Rokkasho Reprocessing Plant



Coulometry Overview

Pu in sample is reduced to Pu^{3+}

$Pu^{3+} \rightarrow Pu^{4+} + e^{-}$ (oxidation)

$$q \text{ (columbs)} = \int_0^t i \text{ (current) } dt$$

$$\text{Grams Pu in sample} = \frac{\text{(Coulombs sample) (Grams / Equivalent of Pu)}}{\text{(96,485.34 Coulombs / Equivalent)}}$$

Pedigree of SRNL Coulometry

Definitive Method – Traceable to SI basic units & derived constants:

- Mass, grams
- Current, mA
- Temperature, Kelvin
- Faraday Constant, 96485.3399 C mol^{-1} ± 0.0024 C mol^{-1} (1-σ)
- Molar Gas Constant 8.314472 J mol^{-1} K^{-1} ± 0.000015 J mol^{-1} K^{-1} (1-σ)
- Pu relative atomic mass calculated from TIMS isotopic abundance & isotope masses

Methodology:

- Based on First Principles
  - -- Constant current electrical calibration (Ohms Law)
  - -- Background current measured / subtracted
  - -- Control-Potentials selected for Pu^{4+}/Pu^{3+} electrolysis
  - -- Pu fraction electrolyzed calculated using Nernst Equation

Performance Characteristics:

- Independent of Certified Reference Material
- Negligible Systematic Error, <0.02% achievable
- Minimal Random Error, <0.05% 1-σ achievable

Interferences

- Iron (common)
- Gold, iridium, palladium, platinum (rare) – not removed by I.E.
- Neptunium (in nitric acid supporting electrolyte)
- Organic materials – elevates constant & faradic background
  – fouls/poisons the electrodes
- Hydrazine – a plutonium dissolution catalyst
  – typically a serious interference
- Hydrogen peroxide -- reacts/bubbles, especially during heating
- Pu^{6+} i.e., PuO_2^{2+}
  – incomplete or very slow reduction to Pu^{3+} in nitric acid
  – slow reduction in sulfuric acid

Interferences, continued

Anion removed by fuming to dryness in sulfuric acid:

- Common: Cl^-, F^-, NO_2^-, NO_3^-, excess SO_4^{2-}
- Uncommon: CO_3^{2-} (alkaline; other Pu assay issues)
- Note: fuming also removes hydroxylamine sulfate and nitrate. $NH_2OH{\bullet}H_2SO_4$ $NH_2OH{\bullet}HNO_3$
- Note: percholorate salts, ClO_4^- should not be fumed, unless the hood is designed for the hazard.

Anions and impurities not removed by fuming to dryness:

- MnO_4^-, PO_4^{3-}, also TBP, DBP, MBP, and hydrazine.

Electrical Calibration Factor
System-Level vs. Component-Level

Component Level (Design) – Measure Load Resistance and Integrator Gain:

$$C_{design} = 1/(\mathrm{R_{Load}})(\mathrm{I_{NTEGRATOR}}\ \mathrm{R_{ESPONSE}})$$

$$C_{design} = \frac{1}{(50\Omega)\times 20{,}000\,Hz/V} = (10^{-6})(\Omega^{-1})(V)(Hz^{-1}) = 10^{-6}\,Amps \times Hz^{-1} = \frac{1\mu C}{pulse}$$

System Level – Integrate a constant current for measured time:

$$C_{measured} = \frac{V \times t_c}{(R_{Cal})(Pulses_{Total})}$$

❖SRNL Coulometer Performance (stable laboratory environment):

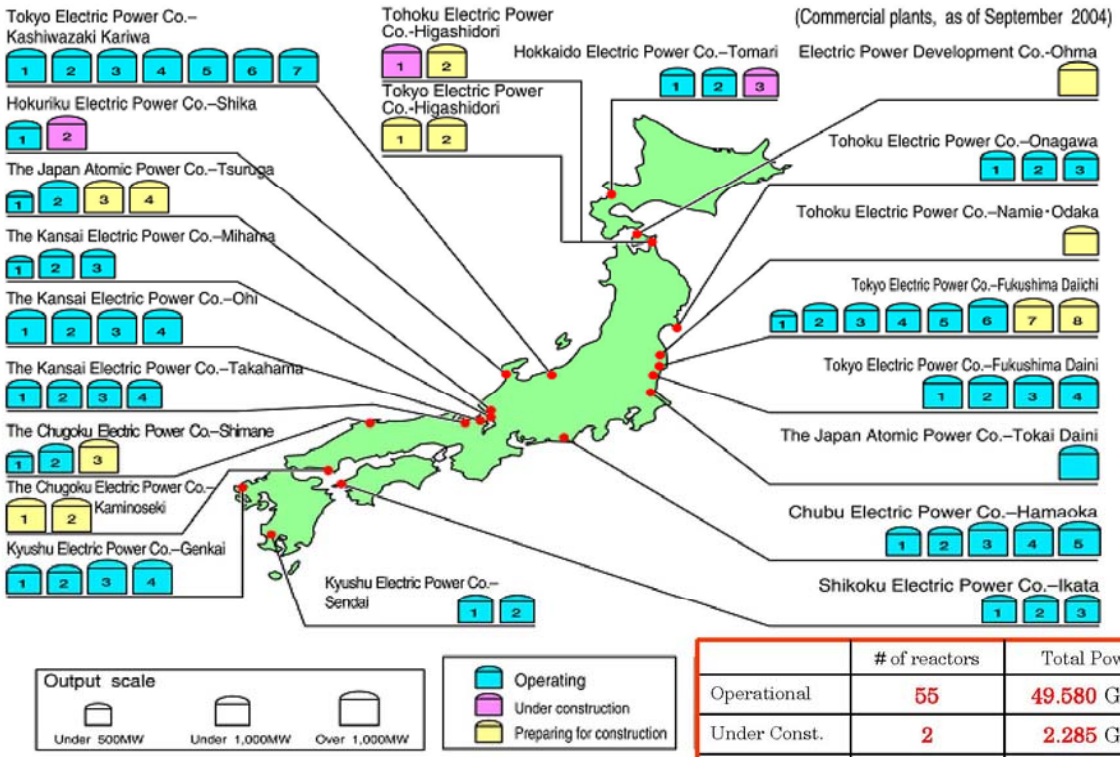
- Design-Basis, Ideal Case: 1.00000 *u*C per pulse
- Component-level calibration: 1.00003 *u*C per pulse
- System-level calibration: 1.00004 *u*C per pulse
- 0.001% agreement

LSD Spike Story

Nuclear Reactors In Japan

Nuclear Power Plants in Japan

FEPC, JAPAN



	# of reactors	Total Power
Operational	55	49.580 GWe
Under Const.	2	2.285 GWe
Planned	11	14.945 GWe
Total	68	66.810 GWe

All NPPs are located on the seacoast.

4

Savannah River Nuclear Solutions, LLC
A Fluor Daniel Partnership

Reprocessing In Japan – JAEA TRP

Reprocessing In Japan – JNFL RRP

Reprocessing In Japan – JNFL JMOX

Japan Safeguards – Input Accountability

Traditional IDMS Method (before LSD Spike)

- Sample Dilution x150
- Spike 1-mL aliquot w. 10 µg ^{242}Pu & 1 mg ^{233}U
- Possible to measure isotopic abundance and assay on same TIMS measurement (except ^{242}Pu)

Japan Safeguards – Input Accountability

Original Issues & Challenges (addressed by LSD Spike)

- Accurate sample dilution in shielded analytical cells
- Sample stability for IAEA shipment before spiking
- IDMS by TRP Lab, IAEA-SAL, & Jp's NMCC
- Planning for RRP Lab and RRP OSL (IAEA NMCC)

Basis for Application of LSD Spike

Burn-up 1000 MWD/t [1]	^{238}Pu At%	^{239}Pu At%	^{240}Pu At%	^{241}Pu At%	^{242}Pu At%	$^{239}Pu/^{240}Pu$ Ratio
Low Burn-up	0.01%	93.88%	5.92%	0.16%	0.04%	15.9
8-10	0.20%	87.00%	10.00%	2.50%	0.30%	8.7
16-18	0.40%	76.00%	18.00%	4.60%	1.00%	4.2
25-27	1%	58%	25%	9%	7%	2.3
38-40	2%	44%	27%	15%	12%	1.6

[1] Megawatt day per ton;
unit for the thermal energy output for one ton of nuclear fuel during the service time in the reactor.

Japan Safeguards – Input Accountability, cont'd

LSD Spike IDMS Method

- Typical Sample is 1.3 gPu/L and 170 gU/L
- Take small sample aliquot for TIMS PuISO only
- Add 1-mL of sample by weight to LSD Spike vial

LSD Spike:

- IRMM in Geel, Belgium prepares LSD Spikes
- Pu Std: CRM-126 or EQRAIN
- LSD spike contains 2 mg Pu and 40 mg U
- Pu is Low Burnup (WG) and U is 19% ^{235}U

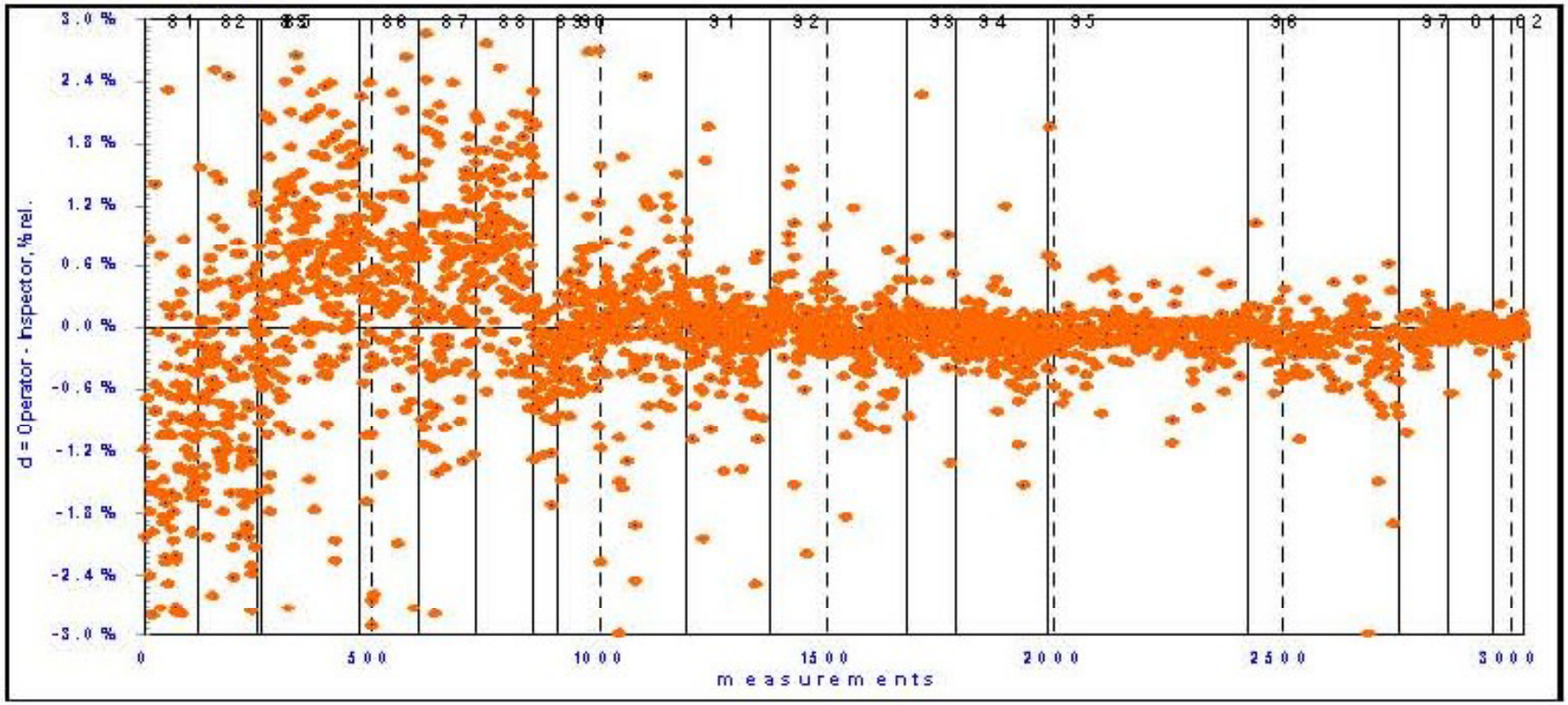
Japan Safeguards – Input Accountability, cont'd

Issues & Challenges for LSD Spike IDMS Method

- Supply of Pu reference material was always an issue
- Aliquot is optimized for typical vs. individual sample
- TRP & RRP apply LSD Spike-IDMS beyond input accountability.

The LSD Spike for Input Solutions
- Experience (1) -

Pu-concentration



Reference Material Availability in U.S.

- LANL prepares the metal for CRM Pu Assay & Isotopics
- Metal Value + Manufacturing cost: ~$10-20 M, minimum
- NBL and LANL characterize CRM for certification
- Full characterization cost (assay, Isotopics, impurities): ~ $2M
- LANL keeps 80% of the metal for PIT manufacturing
- 200 1-gram unit of CRM-126a will be available for sale
- Life-cycle: 10 yrs for a CRM batches @ 20 units/yr
- EQRAIN supply is smaller – less sharing in future?
- When U.S. builds MOX and PDCF – Need 20-30% supply
- If SRS MOX Feed is full characterization – Need CRM
- If U.S. builds Consolidate Pu Center – Needed CRM before making

TRP + RRP usage of U.S. CRM

- IRMM uses 2 units CRM per batch of LSD Spike
- Requests for LSD Spike are Quadrupling over 2008-12
- In 2012 JMOX comes on line (more LSD Spike)

<u>Issues – Path Forward</u>

- Issues were recognized in Japan 10 years ago.
- JAEA/JNFL actions did not match their knowledge
- Followed path of technical success w. LSD Spike – IDMS
- Avoided pain of implementing coulometry per ISO12183.
- U.S. cannot (will not) support Japan's Future needs
- Japan & world have significant Low-BU Pu (not certified)
- JAEA must prepare LSD Spike and characterize by CPC

LSD Spikes Characterization – Program Goals

- Develop Pu characterization protocol(s) for coulometric measurement on LSD material(s)
- Effectively implement ISO 12183 "Controlled-potential coulometric assay of plutonium" including:
  - Preparing samples and aliquots
  - Eliminating or avoiding interferences
  - Meeting ISO 12183 acceptance criteria