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Chemical Analysis of Plutonium-238 for Space Applications

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Los Alamos National Laboratory (LANL) has produced general-purpose heat sources (GPHS) from plutonium-238 oxides for space and terrestrial uses in the past two decades. Power Source Technologies Group (NMT-9) has full capabilities to recover and purify $^{238}PuO_2$ from scraps and aged fuels and fabricate oxides into fuel pellets for heat sources.

Analytical chemistry supports process control and product certification for ^{238}Pu operations. The ^{238}Pu oxides are dissolved and distributed for plutonium assay (% Pu), actinide impurity (^{236}Pu, ^{237}Np, ^{234}U), plutonium isotopic composition, and non-actinide cationic and anionic impurities analyses. The data obtained from these measurements provide base line parameters for processing, waste disposal, and product certifications.

Due to source term and material-at-risk issues at the aging CMR Facility (Chemistry Metallurgy Research building), we have begun the process of relocating ^{238}Pu analytical capabilities to the Plutonium Facility in 1999. In addition, we are installing several in-line process controls capabilities in the full-scale aqueous scrap recovery operation.

In this paper, an overview of chemical analysis capabilities that support ^{238}Pu programs and the progress of establishing these capabilities at Plutonium Facility will be discussed. These chemical and in-line analysis capabilities include UV-visible spectrometry, gamma-ray spectrometry, alpha spectrometry, direct-current arc (DC Arc), inductively coupled plasma mass (ICP-MS) spectrometry, plutonium process monitoring (PPM) system for ion exchange operation, and solution in-line alpha counter (SILAC) for gross alpha determination of aqueous solutions.

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Introduction

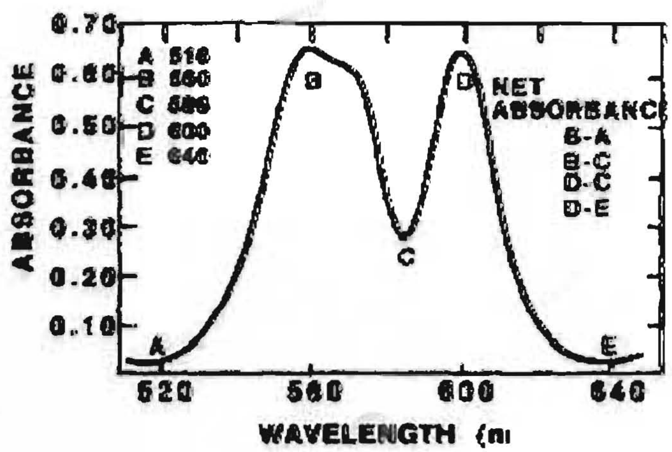
- Between 1994 to 1997, LANL produced and delivered 235 GPHS capsules and 180 LWRHUs for the Cassini Mission.
- Analytical chemistry supports process monitoring and product certification for ^{238}Pu aqueous scrap recovery and fuel fabrication.
- To ensure the quality of the product oxides and fuel pellets, the chemical requirements of GPHS specifications must be met.

GPHS = General Purpose Heat Source

LWRHU = Lightweight Radioisotope Heater Unit

Plutonium Assay - % Pu in oxide

- PuO_2 is dissolved with concentrated HCl, HNO_3, and few drops of HF in a sealed reflux tube.
- The purity of plutonium is determined by Pu (III) chloride spectrophotometric method. Five peaks at 516, 560, 586, 600, and 640 nm are measured by uv-visible spectrometer.



Plutonium Isotopic Composition

- The isotopic composition (^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu) is determined by thermal ionization mass spectrometry (TIMS). It is a time consuming and expensive process.
- Alternative method: Use nondestructive analysis (NDA) technique based on gamma-ray spectroscopy.
  - Proven for weapon grade ^{239}Pu and enriched uranium analysis using PC/FRAM (LANL) and MGA (LLNL) methods.
  - Difficulties for ^{238}Pu: lack of strong gamma-ray signature for ^{240}Pu due to low abundance in $^{238}PuO_2$.
  - Proposed option: develop ^{238}Pu-specific analysis parameters based on historical isotopic data.

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Actinide Impurities in $^{238}PuO_2$

(Total actinide impurities must be < 1 % of total Pu)

^{237}Np: $^{237}Np + {}^{1}n \rightarrow {}^{238}Np \rightarrow {}^{238}Pu$; target for ^{238}Pu production

^{236}Pu: $^{237}Np + {}^{1}n \rightarrow {}^{236}Np + 2\ {}^{1}n \rightarrow {}^{236}Pu + \beta$

- *The daughter products of ^{236}Pu ($t_{1/2}$ = 2.85 years) emit high energy gammas (^{208}Tl: 2.614 MeV)*

^{241}Am: in-growth from ^{241}Pu ($t_{1/2}$ = 14.35 years) at ~ 10 µg/g/month

$^{238}Pu + {}^{1}n \rightarrow {}^{239}Pu + {}^{1}n \rightarrow {}^{240}Pu + {}^{1}n \rightarrow {}^{241}Pu + {}^{1}n \rightarrow {}^{242}Pu$

$^{241}Pu \rightarrow {}^{241}Am + \beta$

^{234}U: in-growth from ^{238}Pu ($t_{1/2}$ = 87.5 years) at ~500 mg/g/month

$^{238}Pu \rightarrow {}^{234}U + \alpha$

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Radiochemical Analysis Methods

^{236}Pu:

- GPHS specification: < 2 μg/g
- Use alpha spectroscopy, ratio ^{236}Pu (5.721 and 5.728 MeV) and ^{238}Pu (Pu-238: 5.457 and 5.499 MeV) peaks.

^{241}Am:

- GPHS specification: < 0.5 %
- Use high-resolution gamma-ray spectroscopy, measure ^{241}Am peak at 59.5 keV

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Radiochemical Analysis Methods

^{237}Np: GPHS specification: < 0.5 %

- Current method: sequential use of cation exchange, followed by a thenoylrifluoroacetone (TTA) extraction. ^{239}Np tracer (daughter of ^{243}Am, t1/2 = 2.3 days) is used to determined extraction efficiency.
- Improved method: developed by Savannah River Site, uses TEVA® resins

^{234}U: GPHS specification: < 0.5 %

- Current method: sequential use of cation exchange
- Possible alternative method: in conjunction with TEVA® and UTEVA® resins.

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Trace Elements Analysis

- Direct-current arc (DC Arc) spectroscopy:
  - Non-cationic impurities: Al, B, Be, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, Pb, Si, Sn, and Zn
  - Direct-solid analysis technique
- Inductively coupled plasma mass spectrometry (ICP-MS):
  - Phosphorus and thorium
  - Use dissolved oxide solution

Relocating ^{238}Pu Analytical Capabilities

- Current analytical chemistry capabilities are located in the CMR building at LANL. CMR was built in 1952– an aging facility.
- An effort has begun in 1999 to consolidate ^{238}Pu source terms to the TA-55 Plutonium Facility and reduce material-at-risk limit at CMR building .
- Benefits of relocating analytical chemistry capabilities:
  - Minimize shipping delays issues
  - Improve turn around time for sample results
  - Instrumentation systems are for Pu-238 programs only.
  - Have unified QA/QC Plan for process production and product certification

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Analysis Needs	Applications			Current Status	
Analysis Needs Analytical Chemistry Capabilities	Product Certification	Process Monitoring	Waste Disposal	Current Location	TA-55 PF-4 Implementation Schedule
Analytical Sample Dissolution	x		x	CMR Wing-5	FY02
Pu Assay (oxide samples)					
UV-Visible Spectrometer	x	x		CMR Wing-5	FY02
Pu Isotopic Determination					
Thermal Ionization Mass Spectrometry	x			CMR Wing-5	No plan for relocation
Non-Destructive Analysis by High Resolution Gamma-Ray Spectrometry Method	x	x		No capability available	Will begin method development in summer 2001
^{241}Am, ^{237}Np, ^{234}U, ^{236}Pu Determinations by Radiochemical Methods					
Sample Preparation	x	x	x	Relocate to CMR Wing-5; end of FY01	FY02
Radiation Detection Systems (alpha and gamma spectrometry; gross alpha; gross gamma)	x	x	x	Relocate to CMR Wing-7; end of FY01	FY02
^{241}Am, ^{234}U, ^{238}Pu Determination-Semi-quantitative/qualitative analysis for Aqueous Recovery Process					
Plutonium Process Monitoring System		x		PF-3 cold-process lab; setup and testing	FY02
Non-Actinide Cationic Trace Impurities					
Direct-Current Arc Spectrometer	x	x		CMR Wing-7	Cannot be relocated.
Direct-Current Arc Spectrometer-New and improved unit	x	x		Cold testing in PF-3, FY01/02	FY03
Other Trace Impurities- P, Th					
Inductively-Coupled Plasma Mass Spectrometry	x	x	x	CMR Wing-7	No plan for relocation
2nd trace element analysis capability-TBD	x	x	x	TBD	TBD

Plutonium Process Monitoring System

- Provide real-time analysis during the ion-exchange steps for aqueous scrap recovery process.
- Monitor ^{241}Am, ^{237}U, and ^{238}Pu gamma rays
- Allow for optimal collection of Pu-238 in eluate (product) stream, while minimizing total collected eluate volume.
- Use as a process monitoring tool to minimize solution waste volumes.

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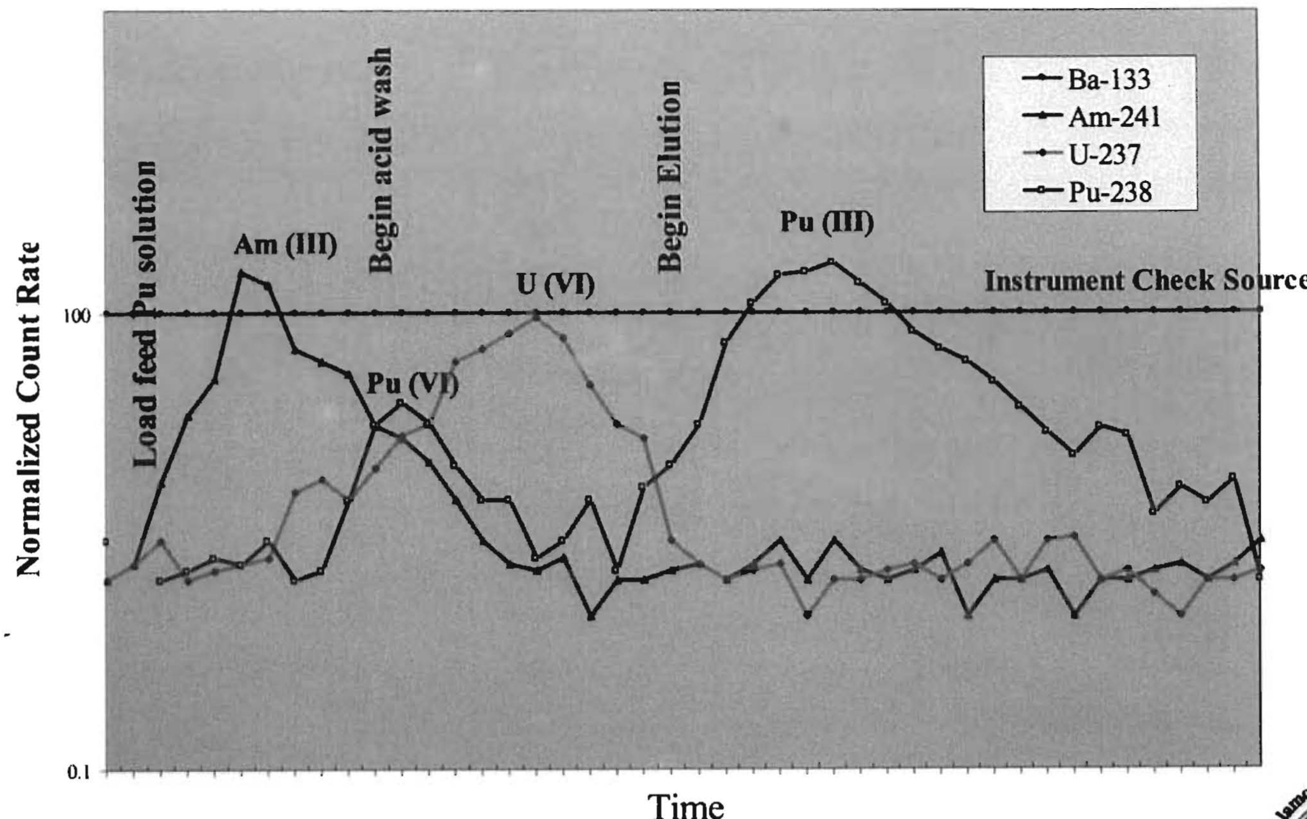
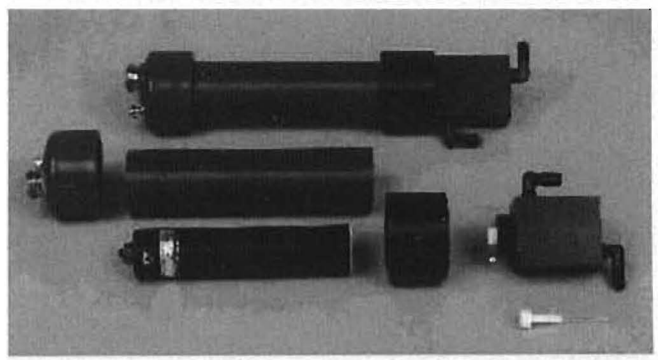
Full-Scale Aqueous Scrap Recovery Plutonium Process Monitoring System



Solution In-Line Alpha Counter (SILAC)

- Provide an estimate of alpha concentration in solution inside of gloveboxes without sampling out and submitting for analysis
- Semi-quantitative analysis
- Large dynamic range: ~ 0.1 to 6000 mCi/L (~ 6 μg/L to 300 mg/L ^{238}Pu) in aqueous solutions
- Is designed to withstand hazardous chemical and radiation environment.



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