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Title: Factors Affecting the Quality of Plutonium Deposits by Electrodeposition

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Factors Affecting the Quality of Plutonium Deposits by Electrodeposition

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ABSTRACT

Ultra-high resolution alpha spectrometry by microcalorimetry has demonstrated a dramatic improvement in alpha energy resolution over silicon based detectors. To characterize the optimal resolution obtained by the microcalorimeter alpha spectrometers, high quality deposits that are virtually massless are required; electrodeposition is the preferred method for the preparation of high quality deposits. In order to better understand the factors that contribute to lower alpha energy resolution and deposit yield, we have conducted a study to determine the effect of some of the parameters that are used for preparing electrodeposits. We have compared four different electrodeposition methods and four different substrate materials to determine the effect on the deposit yield and alpha energy resolution of plutonium as measured by full width at half maximum (FWHM) using silicon based detectors. Furthermore, we wanted to understand the effect of sample contaminants from environmental samples on electrodeposits. Therefore, the effect on deposit yield and alpha energy resolution with several common soil constituents (Al^{3+} , Eu^{3+} , Fe^{3+} , K^+ , Lu^{3+} , Mg^{2+} , Na^+ , Zn^{2+}) have been studied.

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Outline

- **Ultra High Resolution Alpha Spectrometry**
 - Microcalorimeter
 - Sample Preparation Requirements
- **Experimental**
 - Electrodeposition Methods
 - Alpha Spectrometry
- **Results**
 - Substrates and Deposition Methods
 - Contamination effects
- **Conclusions**
- **Collaborators**



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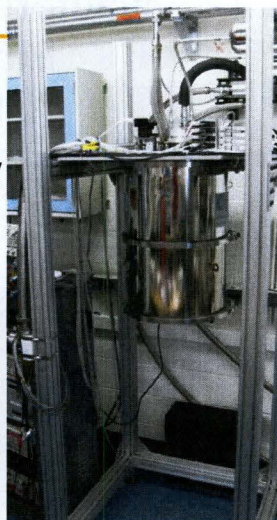
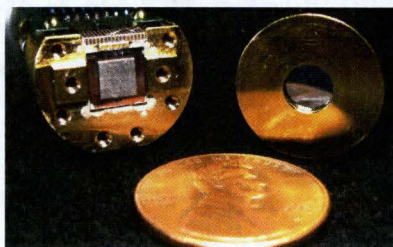
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Microcalorimeters

Measures the temperature change caused by the energy deposited when a particle interacts with a thermally isolated absorber.

- Alpha Particle resolution 1.06 keV @ 5.3 MeV
- LANL system in operation since 2008
- New LANL system online in 2011



Croce, M. P. et al. IEEE Trans. Appl. Supercond. 21 (2011) 207.

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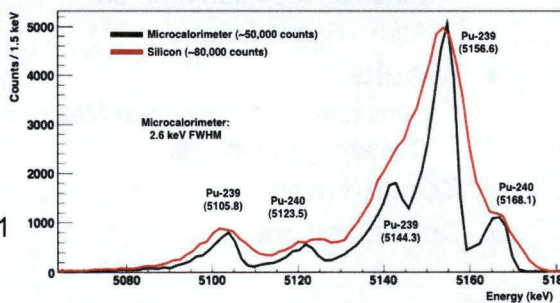
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Ultra High Resolution Alpha Spectrometry

- Greater resolution is possible with microcalorimeters
- Measure isotopes with overlapping alpha peaks without chemical separation
 - ²⁴¹Am and ²³⁸Pu
 - No need to separate actinides
- Measure isotopes of same element with overlapping alpha peaks
 - For example, mixtures of U isotopes
 - Current methods require mass spec

Croce, M. P. et al. IEEE Trans. Appl. Supercond. 21 (2011) 207.



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Ultra High Resolution Alpha Spectrometry Sample Preparation Requirements

- **High resolution detectors require high quality samples.**
- **Electrodeposition is preferred method**
- **Yield and resolution affected by**
 - Substrate Material
 - Uniformity of substrate
 - Sample purity
- **Goal:**
 - Conduct a survey of substrates and electrodeposition methods for yield and resolution.
 - Conduct a study of common sample contaminants for effect on yield and resolution
 - Long term goal is to optimize electrodeposition and separations for preparation of samples for microcalorimetry



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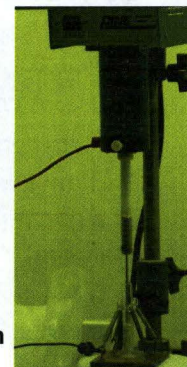
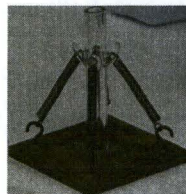
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Experimental

- **Four methods tested**
- **Four substrates tested**
 - Aluminum
 - Platinum
 - Stainless Steel
 - Titanium
- **Electrodeposition**
 - Glass cell, 0.9 cm diameter deposit
 - Pine Instruments AFCPRB rotating electrode, 200 rpm
 - Fisher Scientific FB200 DC power supply
 - 0.53 nCi weapons grade plutonium



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Experimental—Electrodeposition Methods

■ Ammonium Chloride¹

- 3 ml 1 M HCl, 2 drops methyl red, 0.15 g NH₄Cl, 0.025 mL Pu in 0.1 M HCl
- pH adjusted to ~4.4 with NH₄OH and HCl
- 2.0 Å constant current
- 15 minutes deposit time, then 0.5 mL NH₄OH; 1 minute more

■ Ammonium Sulfate²

- 4 ml 0.5 M (NH₄)₂SO₄ @ pH 2; 0.025 mL Pu in 0.1 M HCl
- 0.45 Å constant current
- 30 minutes deposit time, then 0.5 mL NH₄OH; 1 minute more

1. Kleinberg J. (Ed.) *Collected Radiochemical and Geochemical Procedures*, 5th ed., (1990) I-176

2. Talvitie NA (1972) *Anal Chem* 44: 280-283



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Experimental—Electrodeposition Methods

■ Molecular Plating³

- 4 mL isopropyl alcohol, 0.025 mL Pu in 0.1 M HCl, 0.075 mL 0.1 M HCl, 0.1 ml 0.1 M HNO₃.
- 0.03 Å constant current
- 30 minutes deposit time, then 0.5 mL NH₄OH; 1 minute more

■ Sodium Bisulfite⁴

- 0.025 mL Pu in 0.1 M HCl dried, + 1 mL 5% NaHSO₄, dried, dissolved in 4 mL 15% Na₂SO₄
- 0.5 Å constant current
- 90 minutes electrodeposition time, then 0.5 mL 25% NaOH, 1 minute more

3. FitzPatrick JR, Bond E, Slemmons A, Vieira, D J *Radioanal Nucl Chem* 279: 561-566

4. Hallstadius L (1984) *Nucl Instrum Methods* 223: 266-267



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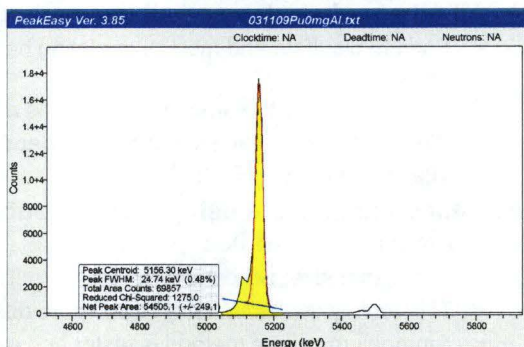
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Experimental—Alpha Spectrometry

- Ortec Octet Alpha spectrometry system
- Silicon surface barrier detector
- Alpha Vision
- 1000 minutes count time
- FWHM calculated from 5.155 MeV ²³⁹Pu peak using PeakEasy Software



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Results—Substrate and Method Comparison

Method	Substrate	% Yield	FWHM (keV)	Appearance	Comments
Ammonium Chloride	Al	NA	NA	Colorless or light brown	Not attempted
	Pt	74	22		
	SS	64	25		
	Ti	61	24		
Ammonium Sulfate	Al	65	40	Brown, Al surface was pitted	
	Pt	71	26		
	SS	53	22		
	Ti	100	25		
Molecular Plating	Al	86	106	Pitted	
	Pt	91	23	Colorless or light brown	
	SS	97	23		
	Ti	98	27		
Sodium Bisulfate	Al	NA	NA	Dark brown	Al destroyed
	Pt	86	25		
	SS	86	NA		28 keV by AlphaVision
	Ti	101	23		



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Results

- **Aluminum was clearly an unsuitable substrate for all the methods**
- **All other substrates and all the methods were satisfactory**
 - Sodium bisulfate and molecular plating had consistent yields for the substrates tested
 - Lower yields for the ammonium chloride method
 - Yields for ammonium sulfate method depend upon substrate
 - Titanium had best yields
- **Ammonium sulfate using titanium substrates were selected for the contamination studies**
 - Pt is expensive; SS cannot be used in microcalorimeter.
 - Ti is readily available, easy to punch to desired size.
 - Ammonium sulfate method is faster and easier to perform than ammonium chloride or sodium bisulfate methods
 - We had observed poor resolution for molecular plating with other samples



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Results: Effect contaminants on yield

- **Performed survey on effect on yield and resolution from possible contaminants**
 - 10g of Fe, Mg, and Na nitrate salts
 - 10 boric acid
 - 3.63×10^{-10} to 3.6×10^{-6} M HF

Contaminant	% Yield	FWHM (keV)
Fe	5	26
Mg	26	37
Na	91	26
Boric Acid	97	26
HF	98-107	27-29



No effect by boric acid and HF. Decided to focus on metal contaminants.

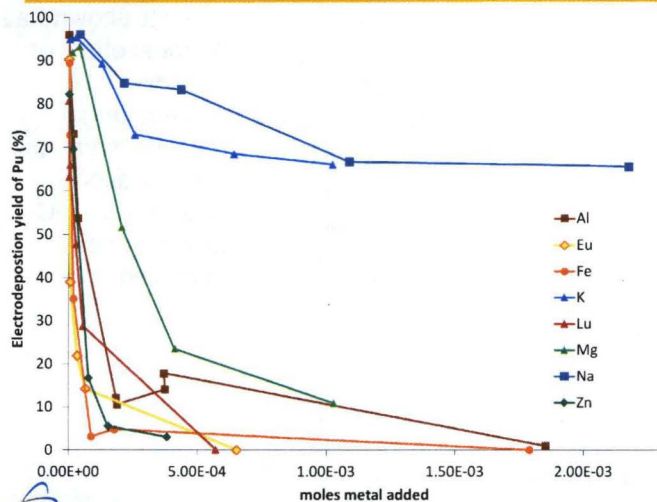
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Results: Effect of metal contaminants on yield



- K, Na--Least effect on yield
- Eu, Fe, Lu and Zn--Greatest effect on yield
- Mg--white residue

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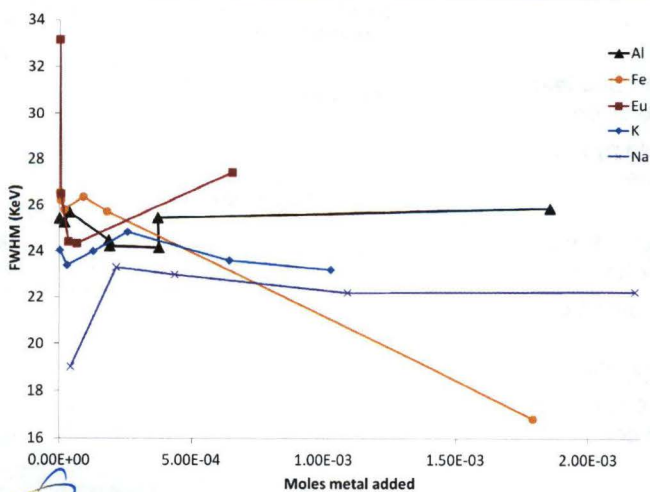
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Results: Effect of metal contaminants on FWHM



- Metals shown had the least effect on resolution
- Literature⁵⁻⁷: No effect on resolution by Al. Fe, Ln cause lower resolutions

5. Kressin IK (1977) Anal Chem 49: 842-846
 6. Zarki R et al (2001) Appl Radia Isot 55: 167-174.
 7. Irlweck K, (1996) J Radioanal Nucl Chem Lett 214:429-437.

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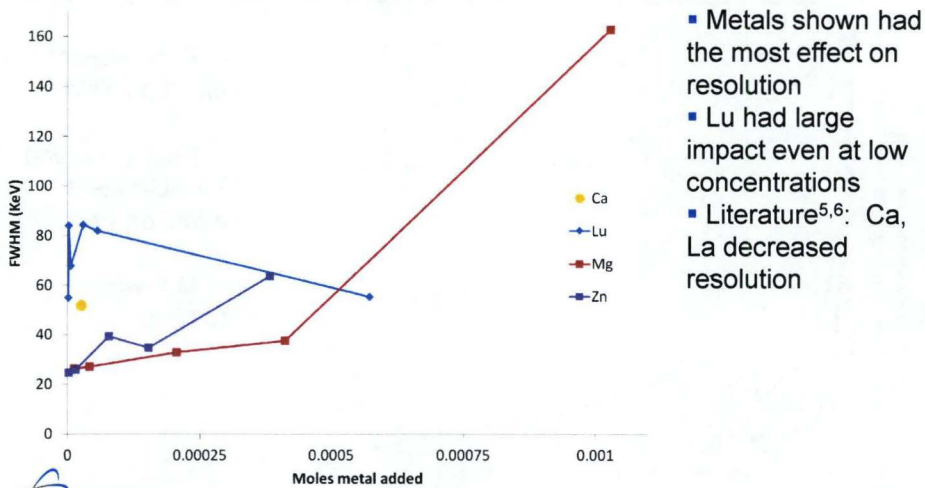
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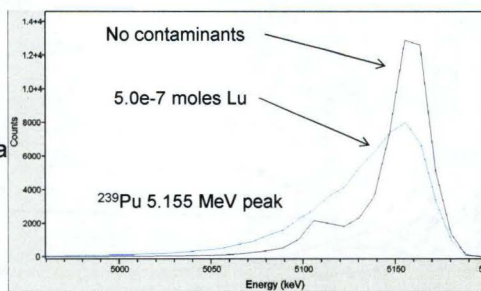
Results: Effect of metal contaminants on FWHM



- Metals shown had the most effect on resolution
- Lu had large impact even at low concentrations
- Literature^{5,6}: Ca, La decreased resolution

Contaminants Summary

- Contaminants play a significant role in yield and resolution of electrodeposited plates
- K, Na, boric acid and HF had least effect on yield and resolution
 - Possible effect on yield by K and Na by changing electrolyte concentration
- Al, Fe and Eu affected yield; no or moderate effect on resolution
- Ca, Lu, Mg, and Zn affected both yield and resolution
 - Loss of yield and resolution due to both change in electrolyte concentration and co-deposition of contaminant



Conclusions

- **Sample purity is one of the largest factors upon the yield and resolution for deposits prepared by electrodeposition**
 - Greatest impact was seen with Group II, transition metals, and lanthanides
- **All of the electrodeposition methods produced satisfactory deposits**
- **Separation efforts should focus on the elements causing greatest impact on yield and resolution**
 - Lu contamination caused loss of resolution even at low concentrations



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