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Plutonium Isotopic Analysis: Alternative Sample Loading for Thermal Ionization MS

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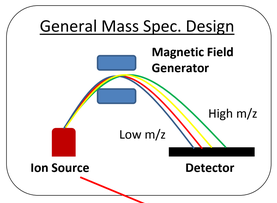
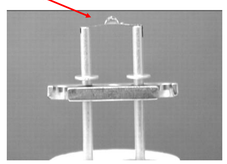
Project Relevance

- Thermal Ionization Mass Spectrometry (TIMS) analysis is known as the "gold standard" in isotopic ratio measurements for plutonium.
- Isotopic distribution of plutonium indicates the "grade" of material and can be used to determine the source ; a common measurement being the $^{239}Pu/^{240}Pu$ ratio.
- TIMS is used widely for nuclear forensics and nuclear safeguards analyses of long-lived isotopes; due partly to ultra-low detection limits offered by TIMS (on order of ~femtograms for Pu) and unparalleled accuracy.

What is Thermal Ionization Mass Spec.?

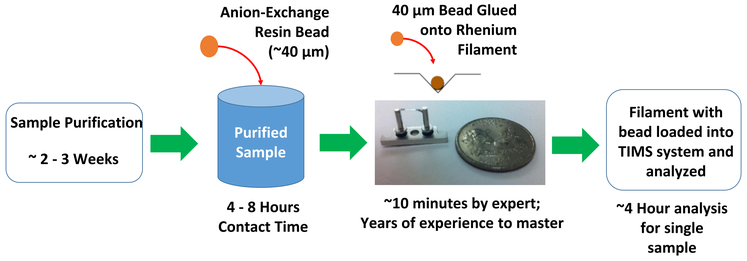


Thermo Scientific Triton Plus™ Multicollector TIMS



Ionization occurs at or near the surface of a hot (~2000 °C) rhenium filament.

Current Sample Loading Process: Bead Loading



Bead loading offers the lowest detection limit of any current TIMS sample loading method by:

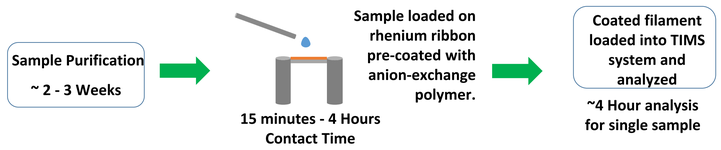
- Maintaining a reducing atmosphere within the TIMS
- Producing plutonium –carbide species
- Providing an ion point source

Cons of Bead Loading:

- Bead loading is difficult, time-consuming, and expensive.
- SRNL reports that approximately 20% sample loss occurs from bead-loading.
- It is estimated that approximately 95% of the sample could remain in the graphitic skeleton left by the bead.

Alternative Sample Loading Method: Thin-Film Loading

Goal: Simplify sample loading by pre-coating the rhenium filaments with anion-exchange material, eliminate/reduce sample loss, and improve overall efficiency.



Production of a Thin-Film Ion Point Source

Bead loading provides an "ion-point source" greatly improving ion transportation into the mass spec region of the instrument relative to more dispersed ion sources.

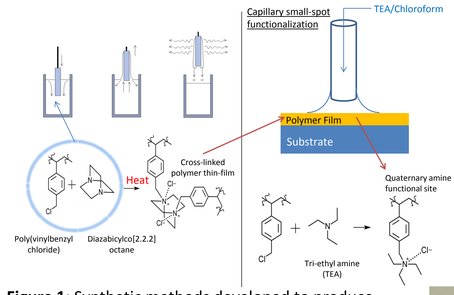


Figure 1: Synthetic methods developed to produce chemically stable films with small functionalized spots.

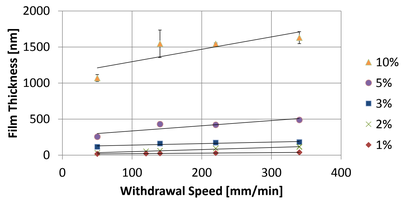


Figure 2: A wide range of film thicknesses are attainable through modification of dip-coating conditions.

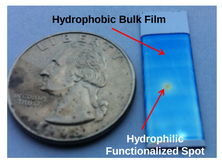


Figure 3: Small spots modified with tri-ethyl amine produce "hydrophilic wells" aiding in sample loading and concentration.

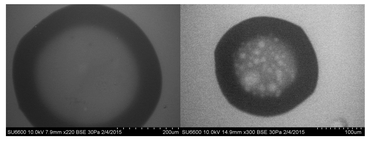
Stability and diffusion testing of extractant coated ribbons

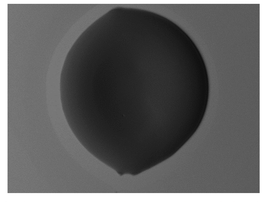
Film Description	Original film thickness	Thickness after 9 M HCl exposure	Treatment
5% CL PVBC/TEA modified	184.3 ± 3.7 nm	180.3 ± 8.0 nm	Aged for 1 month in atmosphere with no acid treatment
5% CL PVBC/TEA modified	178.1 ± 2.9 nm	174.9 ± 2.0 nm	9 M HCl – 1 h
5% CL PVBC/TEA modified	177.2 ± 4.7 nm	176.6 ± 6.7 nm	9 M HCl – 17 h
5% CL PVBC/TEA modified	183.2 ± 5.9 nm	178.4 ± 5.5 nm	9 M HCl – 3 day

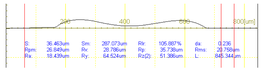
Table 1: Stability analysis of films cast on silicon. Film thicknesses measured with multi-angle ellipsometry.

High carbon loading from thick continuous films led to filament breakages; small anion-exchange polymer spots are being investigated as an alternative approach.

Figure 4: Small anion exchange spots are produced by applying a small drop of polymer solution to the substrate with a needle.







Figures 5, 6, 7: SEM and 3D SEM images of small anion-exchange polymer spots.

Rhenium Oxidation: Potential Source of Sample Loss and Unexplained Performance Variation

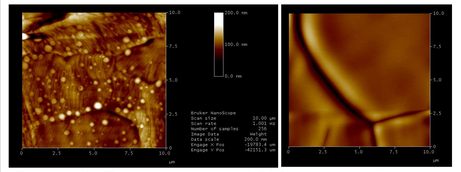


Figure 8: Tapping mode AFM images of rhenium wafer: (left) No degassing, (2nd) post-degassing.

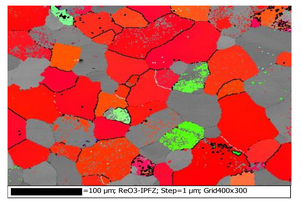
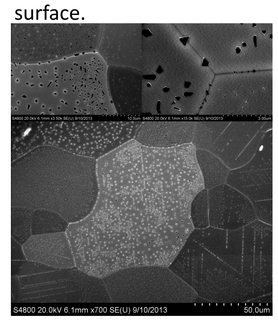


Figure 10: EBSD mapping of rhenium surface

Figure 9: SEM images of rhenium oxide crystal growth on a filament surface.



Plutonium Uptake studies and TIMS analysis

Examination of actinide extraction kinetics (batch)

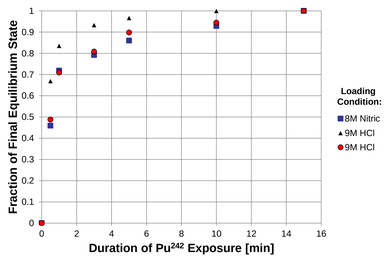


Figure 11: Batch uptake kinetics of tri-ethyl amine treated poly(vinylbenzyl chloride) films cast on silicon. Aqueous Pu^{242} concentrations were measured with ICP-MS.

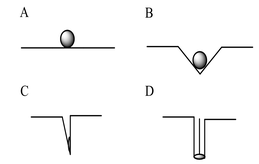
TIMS analysis of reference samples

Material loaded Pu reference (NBL CRM 128)	Filament type	Total Counts (^{242}Pu and ^{239}Pu)	Comments
11 pg	Bead loaded on carbonized filament	411884	Completed 4 hour analysis time
10 pg	Direct load on degassed filament	12524	Tuned with 500 cps on Pu and gone after 15 min
10 pg	Direct load on thin polymer film filament	276	Tuned with 400 cps on Pu and gone after 12 min
10 pg	Direct load on thin polymer film filament	1200	Tuned with 400 cps on Pu and gone after 14 min
10 pg	Direct load on thin polymer film filament	5719	Tuned with 450 cps on Pu and gone after 20 min
10 pg	Direct load on thin polymer film filament	4717	Tuned with 500 cps on Pu and gone after 19 min
10 pg	Direct load on thin polymer film filament	13027	Tuned with 300 cps on Pu and gone after 22 min
10 pg	Direct load on thin polymer film filament	11308	Tuned with 500 cps on Pu and gone after 23 min

Table 2: TIMS analysis of 180 nm films cast on flat Re ribbons performed at SRNL. Films contained low level of crosslinking and small functionalized spot.

Future Work

- Directly study effects of rhenium oxidation on TIMS performance.
- Load anion-exchange polymer with dissolved rhenium salts through anion-exchange before plutonium loading; attempt to increase Re/Pu contact.
- Study effects of rhenium filament geometry and test novel geometries such as the "extreme V" and surface holes or pitting.



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