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Title: PuF4 Dissolution and Analysis: Pre-detonation Nuclear Forensics Perspective

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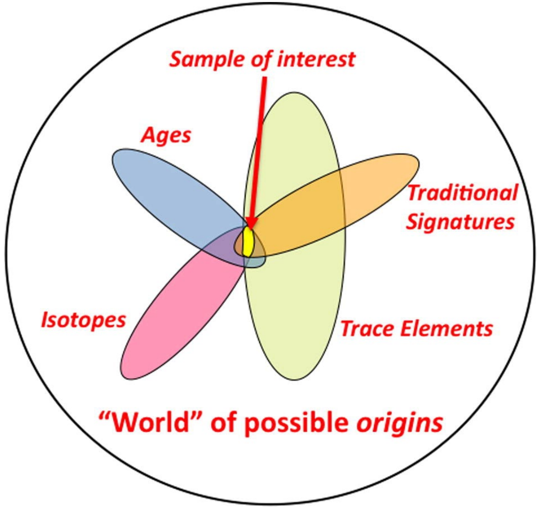
MARC XIII Meeting

Introduction



- Nuclear Forensics
  - "…is the application of laboratory analysis and interpretation to provide technical conclusions (provenance, design, etc.) about a nuclear device or interdicted nuclear material."
- Pre-detonation nuclear forensics focuses on interdicted nuclear material(s)
- Accomplished by application of multiple signatures, which are determined via technical nuclear forensic analysis
- Requires extensive knowledge and expertise in shipping, handling, processing, analyzing, and disposal of special nuclear materials
- Case studies allow analytical groups to practice these processes and determine areas for growth and R&D

Kristo, M.J.; Tumey, S.J. The state of nuclear forensics. *Nucl. Instrum. Meth. B,* **2013,** *294*, 656-661.

Operational Full Forensic Analysis

- To achieve the goals of pre-detonation nuclear forensics, analytical groups practice and perform operational full forensic analyses
- This suite of analyses often encompasses (but is not limited to):
  - Physical characterization
  - Chemical (molecular) form
  - Matrix element isotopic composition
  - Matrix element assay
  - Trace actinide concentration and isotopic composition
  - Minor and trace element concentration
  - Morphology
  - Radiochronometry
- *A good case study will challenge analytical groups to determine if this suite of analyses may be performed on various material types of interest*

Bulk Pu Matrices

- Pu metal
- Pu alloys
- Pu oxide

Well-known processing procedures for analysis

- Pu Compounds
  - Chlorides
  - **Fluorides**
  - Phosphates
  - Nitrates
  - Peroxides
  - Small organic compounds used in processing (e.g., oxalate)
  - Not an exhaustive list!

Focus of case-study in this presentation!

Compounds can present challenges, can have diverse chemistry

Acid Matrix: Does HCl or HNO_3 Matter?

- Often, HF is added to assist in Pu dissolution, not useful for Pu Fluoride materials
- HNO_3 preferred for ICP-based instruments
- HCl preferred for spectrophotometric methods (Fe, Si, Pu^{3+}) and some chromatography-based separations needed for mass spectrometry and radiometric measurements
- HCl easily removed from solutions when a change to another matrix is required (coulometry for Assay)
- ***Need to use the acid matrix that is best for the intended analytical method***

Analytical Technique	Typical Acid Matrix
Spectrophotometric Methods	Dil. HCl
Coulometry	Dil. H_2SO_4
Mass Spectrometry (incl. separations)	Dil. HCl
Radiometric Measurements (incl. separations)	Dil. HCl
Trace Analysis (incl. separations)	HNO_3
XRF (DA preparation)	HNO_3

Historical approaches at LANL:
Option 1 – Combustion

- Process:
  1. Fire 700 mg (ensures 500 mg of Pu in a dissolution) at 600°C for 4 hours in air
  2. Fully cool, weigh out
  3. Dissolve resulting PuO_2 using existing oxide dissolution method (12M HCl + HF)
- Pros:
  - Gives the most accurate Pu assay, as it will drive off any adsorbed water
  - Converts the PuF_4 to Pu Oxide that has a straightforward dissolution approach
  - Dissolution of the Oxide can be done in either HCL or HNO_3
  - Most commonly used approach in the past
- Cons:
  - Trace element analyses will lose any Si via SiF_4 formation

Historical approaches at LANL:
Option 2 – F^- Getter/Capture

- Process:
  1. Weigh out 0.3-1 g Pu fluoride sample into a Savillex container
  2. Add an appropriate amount of Al, B, or Si source material as a fluorine getter, amount will depend on what material is desired as the getter and how much of the bulk Pu fluoride is being dissolved
  3. Dissolve using 5-7 mL concentrated HCl or HNO_3
  4. If precipitate is observed or solid material from the getter remains, filter from solutions

- Pros:
  - Simple, no preprocessing of sample required, minimal handling
  - Fluorine is trapped by materials that have higher affinity for F than Pu, driving the dissolution reaction to completion
  - Removes any possible PuF_4 reprecipitation

- Cons:
  - Trace element analysis will not be able to analyze for the “getter”: either Al, B, or Si
  - If glass beads or glass dissolutions vessels used, then up to 15 measured trace elements can be impacted
  - Depending on getter material, some precipitate (usually white/grey/tan in appearance) can be seen and will need to be filtered
  - Formation of precipitate or remaining solid getter material can make it difficult to visually verify that all Pu fluoride has dissolved

Are there ways to dissolve without losing elements or contaminating a sample that might be rare?

- Mass action type approaches to dissolutions can be tried.
  - This approach focuses on pushing the overall reactions toward dissolved species
    - $PuF_{4(s)} + H^+ \longrightarrow Pu^{+4} + 4HF$
    - Needs strong enough acid concentration to force the F^- to combine with H^+

- Stronger complexing agent needed to force Pu into an alternate complex, as opposed to a Pu-F complex
  - H_2SO_4 would preferentially complex Pu^{+4} in solution over F^- resulting in aqueous $Pu(SO_4)_2$

How would PuF_4 mass action dissolution work?

- Must use large enough volumes of acid to ensure F^- concentrations will not cause reprecipitation upon complete dissolution of Pu fluoride material
  - $PuF_4 \bullet 2.5H_2O$ has very low solubility and will precipitate:
    - When $0.1M > [F^-] << 0.2M$ (in HNO_3)
    - When $0.2M > [F^-] << 0.3M$ (In HCl)
- Acid matrix concentrations are critical.
  - Less than 10M of supporting acid matrix allows competition of F^- for the Pu ions.
    - PuF_3^+ is very quickly converted to PuF_4 if any HF is present, kinetics of this reaction are very nearly instantaneous
    - Complexes such as PuF_2^{2+} and PuF_3^+ are present in significant quantities when HNO_3/HCl < 10 M as these complexes are more stable at low HNO_3/HCl concentrations because of the equilibrium reaction

$$PuF_x^{(4-x)+} + HF = PuF_{x+1}^{(3-x)+} + H^+$$

  - Higher Acid matrix concentrations, ≥10M,
    - Forces HF to stay associated reducing free F^- ions

$$HF = H^+ + F^-$$

    - Prevents higher order fluorides from reforming

- Some evidence from reprocessing studies that the precipitate begins to redissolve as more Pu goes into solution, by reactions similar to:

$PuF_4 \bullet 2.5H_2O + 3Pu^{4+} = 4PuF^{3+} + 2.5\ H_2O$ Very slow though…

Historical approaches at LANL: Option 3 – Extreme oxidative ashing environment

- Process:
  1. Weigh out sample and add 2 mL of 9:1 concentrated HNO_3:H_2SO_4 acid mixture.
  2. Place on hot plate or under heat lamps, slowly evaporate until white sulfuric acid fumes appear, continue to evaporate the solution to complete dryness.
  3. Steps 1 and 2 are repeated until it PuF_4 (coral pink) appears to have been converted to $PuSO_4$ (magenta pink)
  4. Final salt is soluble in water which can also be diluted with desired low concentration HCl or HNO_3
- Pros:
  - Thought that fluorine is forced off sample during fuming due to preference for SO_4^{-2} complexing, thus reducing/removing reprecipitation issues
  - Ensures $PuSO_4$ salt is formed, which will dissolve easily in low concentration acids
  - Easiest to matrix match for multiple methods
- Cons:
  - Trace element measurements will lose any Si via SiF_4 formation
  - Requires analysts' attention the entire time it's performed, and analysts need to be familiar with the colors of both PuF_4 and $Pu(SO_4)_2$ materials

Historical approaches at LANL: Option 4 – Mass action dissolution

- Pros:
  - Simplest process of 4 options
  - Identical to how PuO_2 is typically dissolved
  - Sealed containers for most of dissolution
    - Benefit for safety, contamination control, and reducing any environmental contamination of the forensics sample
- Cons:
  - High F^-/HF concentration left in solution
  - High matrix acid concentrations
- Process:

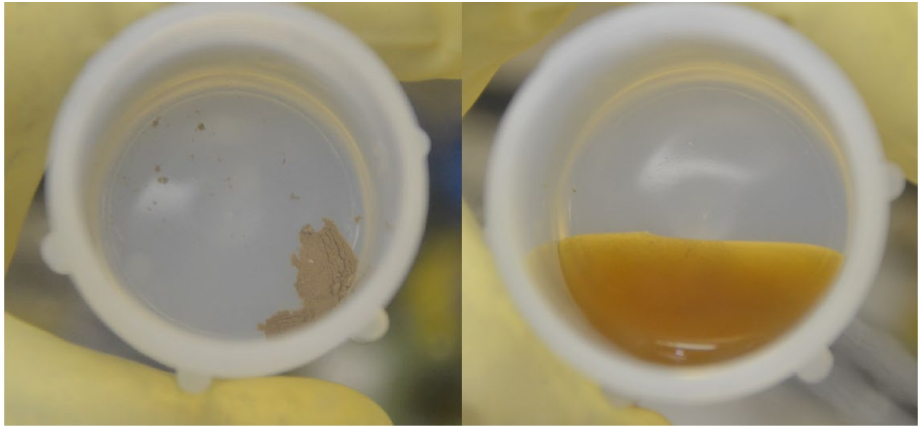
1. Weigh a 0.3-1 g sample of bulk plutonium fluoride into a Savillex container.
2. Proceed by:
   1. Omitting the HF from the acid combination.
   2. Ensure enough matrix acid is used that the HF concentrations will be <0.2M HF when using HCl or < 0.1M HF when using HNO_3

Summary of considerations for a pre-detonation nuclear forensic analysis scenario:

- **Simple approaches are not always the best approaches**
- Concentration of acid controls solution side reactions
- Better to have a sealed system to perform dissolution
- Use of getter material or glass vessels can help by capturing F^- but will add contaminants to sample solutions
- Pu fluorides can be combusted in a furnace *only* if trace analysis is not required
- Fluorides can also be dissolved in HNO_3 or HCl *as long as no HF is added*
- ***Group decided to try options 3 and 4.***

Dissolution Tests

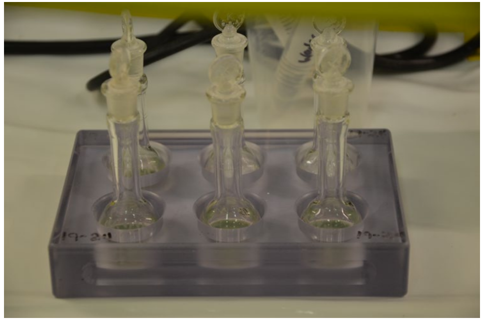
- Tested (3) and (4)
  - (3) – suspend in 9:1 HNO_3:H_2SO_4 mixture, evaporate to dryness and resuspend, repeat until dissolved then dilute in HCl or HNO_3 depending on analysis method
    - Did not dissolve fully
  - (4) – dissolve as oxide without HF addition (12M HCl in Savillex, 100-150°C)
    - Successful! (see image)



Final Dissolution Method

- Thermo Fisher ACS Plus hydrochloric acid (12M)
- Cleaned, labeled, and sealed Savillex vessels
- Pu fluoride cuts (~250 mg) were dissolved over a period of 10 days at 150°C
  - Two attempts at heating
  - Inspected partway through after removal from hot block, non-dissolved material observed, returned to hot block for continued heating
- Complications:
  - Observed different colors between sample cuts (peach vs. orange, both transparent but different vibrancy of color, potential heterogeneity)
  - Observed re-precipitation as more time passed following dissolution in cuts that were close to 2:1 F:Pu ratio
    - Cuts with lower ratios (aka dilute) weren't as impacted
    - Analysis methods need to occur within 2 weeks of dissolution, especially for solutions near 2:1 ratio
- **<u>Final Acid Matrix = 12M HCl</u>**

Complication for method- Iron by UV-VIS method



- Issues observed:
  - Samples would not reduce when hydroxylamine hydrochloride added.
    - Solution color should be blue, observed red and purple.
  - Pu precipitation with Oxalic acid resulted in a very different precipitate behavior
    - material stuck to the walls of the centrifuge tube rather than the bottom.
  - Solutions formed white crystals after separation of the precipitate.
  - Amount of ammonium hydroxide needed for final pH adjustment tripled.
  - Excess ammonium hydroxide caused heating of solutions, color to change to green (should be red orange at this step)and additional precipitation to occur.
  - Could not get an accurate Iron using UV-VIS method which is required for Pu assay by Coulometry .

Sample Analysis Summary and Future Considerations

- Although we were able to get all the desired analytes originally planned for this material, we had to think on our feet and adjust as necessary when methods didn’t work with the acid matrix
- Possible inhomogeneous sample / dissolution
  - Varying results between aliquots for some analytes, led to reporting of single aliquot with the highest confidence
- Issues with high acid concentrations and proceeding through some methods
  - Unable to perform Fe analysis (needed for controlled potential coulometry)
    - Chose to proceed with Pu-IDMS instead, less precision than coulometry
  - Leads back to choosing the right acid matrix for your analysis and how this applies to non-traditional material processing choices

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    - Pressure safety testing
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    - Historical chemistry discussions
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- C-AAC group management
- C-AAC SMEs