Rapid Fusion Method for Plutonium in Large Rice Samples

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October 31, 2012
Background

- If a radiological dispersive device (RDD), Improvised Nuclear Device (IND) or nuclear accident (Fukushima Daiichi) occurs...
  - there will be a urgent need for rapid analyses of environmental, food and bioassay matrices

- Developed rapid methods for actinides in food (up to 100g)
  - Submitted as US FDA Food Emergency Response Network (FERN) method

- Large aliquots may be needed to assess low level activities/isotope ratios

- Could we analyze much larger aliquots of rice for Pu isotopes?
Rice Sample Furnace Heating

1. Place 1-1.25 kg Rice Sample in 2L Beaker
2. Add $^{244}$Pu Tracer
3. Place in furnace and ramp to 350°C for 300 min
4. Ramp to 525°C and heat for 1000 min
5. Wet ash residue in 2L Beaker
6. Wet ash residue with 15.8M HNO$_3$ and 30wt% H$_2$O$_2$ on hot plate
7. Transfer wet ashed residue (after evaporation to small volume) into 250mL Zr Crucible with 15.8M HNO$_3$
8. 250mL Zr Crucible Evaporate to dryness on hot plate
9. Place Zr crucible in furnace at ~450°C and increase heat (if necessary) until solids are white/light colored then wet ash with 15.8M HNO$_3$ and 30wt% H$_2$O$_2$ until purple/light color, heating again in furnace as needed
10. Rapid Sodium Hydroxide Fusion
Rapid Rice Sample Fusion

Fuse combined sample and residue in Zr crucible ~15min with 15g NaOH @600°C

Hydroxide precipitation using 10mg La carrier, Fe, Ca, TiCl₃

Redissolve in ~100mL 1.5M HCl into 225mL tube

Lanthanum Fluoride Matrix removal. Adjust volume to 170mL with 0.01M HCl, TiCl₃ and HF; centrifuge

Redissolve in 5mL 3M HNO₃-0.25M Boric Acid, 6mL 7M HNO₃, 7mL 2M Al(NO₃)₂

*Ascorbic acid converts Fe³⁺ to Fe²⁺

Valence adjust: 0.5mL 1.5M Sulfamic Acid 2mg Fe (as iron nitrate) 1.25mL 1.5M Ascorbic Acid 1mL 3.5M NaNO₂

Column Load Solution
Anion Resin such as Dowex 1- HNO_3

Fig. 1. Removal of Elements from Nitric Acid Solution with Strong-Base Anion Exchange Resin.
Pu and Np retained
Th and Am/Cm not retained
Why TEVA Resin for Pu/Np?

- 2 ml resin cartridge
- Minimal U tailing
- Lower HNO₃
- Good alpha resolution
- Stack cartridges
- Vacuum flow rates
- Acid volumes small
- Less time and waste

High $k'$ at 3M HNO₃

Aliquat 336 extractant

Horwitz, et al. (HP195)
Rapid Pu Column Separation

Load Solution

TEVA Resin
Add 3mL 3M HNO₃
Beaker Rinse

Rinse column with:
- 15mL 3M HNO₃
- 20mL 9M HCl (Remove Th),
- 5mL 3M HNO₃

Elute Pu with 20mL
0.1M HCl-0.05M HF
- 0.01M TiCl₃

Add 0.5mL 30wt% H₂O₂
to oxidize any U

Add 50µg Ce to 1mL 49% HF. Filter
and Count by Alpha Spectroscopy

Soratite reductant can be used
instead of TiCl₃ for electrodeposition

Less HF (0.01M) and TiCl₃
(0.0001M) if ICP-MS assay

Multiple 1 kg purified sample solutions
may be combined as CeF₃ or evaporated
to analyze 5 kg samples

2mL TEVA cartridge

SRNL
Load solution: ~1 drop/second
Rinse solution: ~2-3 drops/second
Pu Elution: 1 drop/second
Spiked $^{238}\text{Pu}$ in Rice Results - 1 kg samples

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$^{242}\text{Pu}$ Yield (%)</th>
<th>$^{238}\text{Pu}$ Reference Value (pCi kg$^{-1}$)</th>
<th>$^{238}\text{Pu}$ Reference Value (mBq kg$^{-1}$)</th>
<th>Measured Value (mBq kg$^{-1}$)</th>
<th>Difference (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>88.9</td>
<td>0.287</td>
<td>10.6</td>
<td>11.8</td>
<td>11.0</td>
<td>3.7 E-4</td>
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<td>2</td>
<td>91.5</td>
<td>0.287</td>
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<td>Avg</td>
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<td></td>
<td>-0.7</td>
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<tr>
<td>% RSD</td>
<td>4.7</td>
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Pu-239 is refractory in MAPEP 12
Spiked $^{239}\text{Pu}$ in Rice Results - 5 kg samples

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#1 – 5 x 1.0 kg samples combined
#2 – 4 x 1.25 kg samples combined
#3 – 4 x 1.25 kg samples combined

Pu-239 is refractory in MAPEP 12
Plutonium Alpha Spectra - Spiked Rice

Yield = 92.8%
FWHM (Pu-242) = 30.6keV
238U interference on Pu by ICP-MS

  - concluded that uranium separation is needed
  - the 238U level in the purified solutions should be less than 100 pg mL⁻¹
  - to minimize spectral interference in the quantitative analysis of 239Pu and 237Np
Enhanced U-238 Removal for Pu-239 by ICP-MS

- Typical single column TEVA separation 1000x removal of U
- ICP-MS
  - **Option 1**
    - for more U removal — redissolve CeF₃ in warm 3M HNO₃-0.25M boric acid and separate again on TEVA Resin with much less Ti in eluent
  - **Option 2**
      (>10E6 U decontamination of Pu)
Another Enhanced Uranium Removal Option (ICP-MS)

Option 2 to achieve
U removal > 10E7
Rapid Determination of Actinides in Emergency Food Samples
S. L. Maxwell, B. K. Culligan, A. Kelsey-Wall and P. J. Shaw,

submitted as a **US FDA FERN Standard Operating Procedure** for the rapid radiochemical analysis of alpha emitting isotopes of americium, curium, plutonium, and uranium.
Rapid Method Actinides in Food

10 g Food Sample, Add Tracers 
\( ^{242}\text{Pu} / ^{236}\text{Pu}, ^{243}\text{Am}, ^{232}\text{U} \)

Heat at 700°C for 2 hours in Furnace

Wet Ash with HNO\(_3\) / H\(_2\)O\(_2\) on Hot Plate

Heat for ~ 10 min. at 600°C in Furnace

Fuse in Zr Crucible 15 min. (15g NaOH @ 600°C)
Hydroxide precipitation (5 mg La Carrier, Fe, Ca, PO\(_4\), TiCl\(_3\))

Lanthanum Fluoride Matrix removal
(1 mg La, Ca, HCl/HF, TiCl\(_3\))

Redissolve in 5mL 3M HNO\(_3\)-0.25M Boric Acid
6mL 7M HNO\(_3\), 7mL 2M Al(NO\(_3\))\(_3\)

Valence Adj.: 0.5mL 1.5M Sulfamic Acid
1.25mL 1.5M Ascorbic Acid +1mg Fe
1mL 3.5M NaNO\(_2\)
1.5mL 15.8M HNO\(_3\)

Column Load Solution
Pu and Np Alpha Spectra Spiked Food Sample

See paper for data on 10g and 100 g food samples:

Rapid Determination of Actinides in Emergency Food Samples
S. L. Maxwell, B. K. Culligan, A. Kelsey-Wall and P. J. Shaw,
MDA

• U. S. Food and Drug Administration (FDA) provided guidance for accidental contamination of foods to state and local agencies so that protective actions may be taken
  - FDA derived intervention level (DIL) for $^{238}\text{Pu} + ^{239}\text{Pu} + ^{241}\text{Am}$ is 2 Bq/kg (2 mBq/g or 0.054 pCi/g)

• SRNL method provides a typical MDA of ~0.2 mBq/g for a 10 g food sample and 2 hour count time for each of the actinide isotopes cited in the DIL.

• Method is fast and flexible
  - longer count times can be used to lower MDA levels as needed.
  - For example, for a 16 hour count time and a 10 g sample, an MDA of 0.04 mBq/g can be achieved.

• Typically, the U. S. FDA recommends MDA levels be 1/3 of the DIL
  - These MDAs are readily achievable using this rapid method
Stacked cartridges

TEVA+ DGA Resin cartridges (Pu and Am)
Summary

- New method for Pu in rice developed at SRNL Environmental Bioassay lab for up to 5 kg rice
  - MDA for Pu in 5000g rice and 30 hour count = ~7 E-5 mBq/g
- After the initial furnace and wet-ashing...
  - Rapid sodium hydroxide fusion
  - Rapid TEVA cartridge separation
    - Options to use alpha spectrometry or ICP-MS
    - Enhanced uranium removal options
      - Redissolve CeF₃ and reprocess with TEVA Resin
      - Move Pu to DGA Resin and rinse more
- Good chemical yields
- Rugged for refractory particles