Recent Improvements in Column Extraction Methods at SRS

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New Developments

• **New Sr-89/90 in milk method**
  - Is there an alternative to drying/furnacing or cation exchange collection?

• **Developing new actinides and Sr-90 in fecal method**
  - Can our soil matrix removal method help with fecal samples?
Sr-89/90 in Milk

- Routinely measured in environmental monitoring samples from locations near SRS
- Sr-90 from fallout consumed by cows and gets into human diet
  - Classical method-dry, furnace, slow
  - Newer-cation resin affinity, pH adjustment, long contact times, elute Sr from resin with large volume of acid
    - Complex precipitations or Sr Resin to separate Sr
- Important for emergency response
  - Chernobyl accident
Need for Faster Method

• **Previous SRS method**
  - Cation exchange collection of Sr-89/90 from milk
  - Requires large volume of 8M HNO3 (350 ml) to elute Sr from resin (30 grams) and long processing/evaporation times

• **Long, tedious method**
  - 4 days before column work begun

• **Could we use calcium phosphate precipitation instead?**
Calcium Phosphate Precipitation

- 500 ml aliquot
- Add 2 mL 1.25M Ca(NO₃)₂ and 5 mL (NH₄)₂ HPO₄
  - Ca added so water blanks will precipitate (not really needed for milk)
- Add phenolphthalein indicator
- Add NH₄OH to dark pink
- Centrifuge
- What happens?
Calcium Phosphate Precipitation

- What could we do?
- Add 25 mL of 3M HNO₃ into each tube
- What happens?
- Ca₃(PO₄)₂ dissolves
- Fat coagulates
Calcium Phosphate Precipitation

- Centrifuge
- Transfer supernate to beaker
- Rinse solids with 10-15 ml 3M HNO₃
- Transfer supernate to beaker
- Evaporate beaker to dryness
Calcium Phosphate Precipitation

- **Wet ash**
  - 15 ml concentrated HNO₃ and 5 ml 30 wt% H₂O₂
- **Heat beakers in a furnace**
  - at 550°C for 30-60 minutes to turn the solids white
- **Wet ash**
  - 15 ml concentrated HNO₃ and 5 ml 30 wt% H₂O₂
Sample Preparation

500 ml milk

Add Ca, PO4, NH₄OH
Sample Preparation

Ca$_3$(PO$_4$)$_2$ and fat

Add 3M HNO$_3$
Sample Preparation

Centrifuge

Most fat is removed
Sample Preparation

Heat on hot plate
Sample Preparation

Heat to dryness
Sample Preparation

Heated at 550°C for 30 min.
Column Load Solution
Sr-89/90 in Milk Column Extraction

- Redissolve in 10 ml 8M HNO₃-1M Al(NO₃)₃
  - Or for actinides also, 3M HNO₃
  - HNO₃-1M Al(NO₃)₃

- Perform typical Sr Resin Separation using 3 ml Sr resin (2 ml +1 ml cartridges)
<table>
<thead>
<tr>
<th>Sr-90 Added (pCi)</th>
<th>Carrier Recovery (%)</th>
<th>Sr-90 Measured (pCi)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>76.28</td>
<td>67.3%</td>
<td>74.23</td>
<td>97.3%</td>
</tr>
<tr>
<td>76.28</td>
<td>78.4%</td>
<td>80.86</td>
<td>106%</td>
</tr>
<tr>
<td>76.28</td>
<td>87.4%</td>
<td>71.56</td>
<td>93.8%</td>
</tr>
<tr>
<td>Avg</td>
<td>77.7%</td>
<td>75.55</td>
<td>99.0%</td>
</tr>
</tbody>
</table>
SRS Fecal Method

- Current method - drying, furnacing, wet ashing, dissolution in HCL-HF and HCL-boric acid
- Load to Diphonix Resin
- Strip actinides with HEDPA
- Destroy HEDPA with Fenton’s reagent (Fe + H$_2$O$_2$)
- Use TEVA+TRU Resin
- Long method, plus Np-237 has to track well with Pu-236 tracer across two resins: Diphonix Resin and TEVA Resin
New SRS Fecal method

• New approach being tested
• Use cerium fluoride matrix removal we use with soil
• Benefits
  – simpler, faster, better Np-237 results
• Instead of adding HCL-HF to Diphonix, add 5 mg Ce, TiCl₃ and HF, ice 5 min.
• Centrifuge
New Approach

- Redisolve precipitate in 3M nitric acid-1M aluminum nitrate
- Use TEVA+TRU+DGA Resins
- Perform TEVA-SCN separation to remove Ce as we do in SRS soil method
- What about Sr-90?
  - one lab performs calcium phosphate precipitation of the supernate after a LaF$_3$ matrix removal step
- Can we get the Sr-90 to follow the actinides?
Can we add anything to make the Sr precipitate?

- What would precipitate with Ce as a fluoride and maybe enhance Sr precipitation?
- Calcium!
Fecal Sample Preparation

- After drying, fumacing, wet-ashing, fecal samples are dissolved in two fractions
  - HCL-HF fraction and a HCL-boric acid fraction
  - Typically~100 ml HC-HF and 25 ml HCl-boric acid fractions
  - Aliquots taken/reserve held
- Transfer the aliquot from the HCL-boric acid fraction into a glass 100 ml beaker
  - heat to dryness on a hot plate.
- Remove the beakers from the hot plate and add 7 ml of 6M HNO3
  - Warm to dissolve on the hotplate and set aside for use later.
- Transfer the aliquot of the HCL-HF sample fraction into a 50 ml centrifuge tube for CeF3
Cerium Fluoride Matrix Removal

- Pipet 1 mL of 5 mg Ce/mL to each HCL-HF tube.
- Pipet 1 mL of 1.25 M calcium nitrate (50 mg Ca) to each HCL-HF tube.
- Pipet 2 mL of 20 wt% TiCl₃ into each tube.
- Pipet 5 mL of concentrated HF into each tube.
- Cap and mix.
- Place tubes to sit in an ice bath for 5 to 10 minutes.
- Centrifuge for 10 minutes at 3500 rpm or as needed.
Cerium Fluoride Matrix Removal

- Discard supernate liquid to waste.
- Transfer the dissolved boric acid fraction into each tube containing the cerium fluoride precipitate.
- Pipet 7 ml of 2M aluminum nitrate into each beaker.
- Transfer this beaker rinse to the tube containing the dissolved precipitate.
- Now we have 14 ml 3M HNO₃-1M AL(NO₃)₃ load solution
Actinide Column Separation

1) Redissolve in 7 mL warm 6M HN0₃ and 7mL 2M Al(NO₃)₃
2) Add 0.5 mL 1.5M Sulfamic Acid + 1.25 mL 1.5M Ascorbic Acid/ 1 mg Fe
   (if Np-237 analyzed)
3) Add 1 mL 3.5 M Sodium Nitrite

Rinse
Beaker rinse: 3mL 6MHN0₃
Separate cartridges:
TEVA:10 mL 5M HN0₃
10 mL 3M HN0₃

Th Elution
20mL 9MHC1

Pu (and/or Np) Elution
20mL
0.10MHC1 - 0.05MHF - 0.03M TiCl3*

Add 0.5 mL 30 wt% H2O2
Cerium fluoride
Alpha spectrometry

*Use rongalite instead of TiCl3 for electrodeposition

DGA resin not affected by Fe3+

Sr passes through/collection/evaporated
Rinse DGA Resin to remove any Sr

- Work with DGA only
- Pipet 6 mL of 0.1M HNO₃ directly into each DGA column
- Pipet 5 mL of concentrated nitric acid into each tube.
- Cap, mix, and set tubes aside for addition to TRU Resin (if any U present on DGA).
Stack TRU + DGA Resin

- Place TRU cartridges above each DGA cartridge.
- Pipet 15 mL of 4M HCl into each column to strip any Am from the TRU Resin onto the DGA resin.
- Set aside TRU cartridges to process later for U.
- Add 10 mL of 0.25M HCl directly into each DGA column to elute Am/Cm.
Am/RE Removal on TEVA

1) Evaporate 0.25M HCl with 5mL con. HNO₃, 50 uL of 1.8M H₂SO₄, then ash with nitric acid and hydrogen peroxide.

2) Redissolve in 5 mL of 4M NH₄SCN, warm gently.

- Rinse
  - Beaker rinse: 3mL 4M NH₄SCN, warm
  - 10 mL 1.5 M NH₄SCN to column

- Am Elution
  - 20 mL 1M HCl (warm and rinse original beaker)

- 2mL TEVA Resin (50-100 um)

- Cerium fluoride

- Alpha spectrometry
TRU Resin-U Removal

- Add 0.1M HNO3 + concentrated HNO3 rinse from DGA (for possible U)
  - Remove tube with possible Sr / add to evaporated load solution
  - If no U, could add 0.1M HNO3 rinse directly to evaporated load like we do in animal tissue method (still being tested for fecal samples)
- Rinse TRU with 12 ml 4M HCL-0.2M HF
  - Any residual Th removal
- Elute U from TRU with 15 ml 0.1M ammonium bioxalate
  - Cerium fluoride precipitation/alpha spectrometry
## Initial Fecal Test Data—Actinides

<table>
<thead>
<tr>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>% Rec.</td>
<td>% Rec.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-ORNL</td>
<td>97.60</td>
<td>110.16</td>
<td>95.96</td>
<td>102.5</td>
<td>89.7</td>
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<tr>
<td>2-ORNL</td>
<td>103.5</td>
<td>115.77</td>
<td>101.57</td>
<td>81.05</td>
<td>68.25</td>
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<tr>
<td>3-ORNL</td>
<td>108</td>
<td>121.69</td>
<td>107.49</td>
<td>111.1</td>
<td>98.3</td>
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<tr>
<td>4-ORNL</td>
<td>110.1</td>
<td>124.72</td>
<td>110.52</td>
<td>108.9</td>
<td>96.1</td>
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<td>5-HCL-HF</td>
<td>116.8</td>
<td>104.63</td>
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<td>108</td>
<td>95.2</td>
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<td>avg.</td>
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<td>115.39</td>
<td>103.89</td>
<td>102.26</td>
<td>89.46</td>
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<tr>
<td>% rsd</td>
<td>6.7</td>
<td>7.1</td>
<td>6.2</td>
<td>12.0</td>
<td>13.7</td>
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</tbody>
</table>

*Samples were tested that had already been analyzed using reserve aliquots ORNL samples already spiked with lower level U-232 and Am 243- subtracted
## Initial Fecal Test Data-Sr

<table>
<thead>
<tr>
<th></th>
<th>Sr Carrier % Rec</th>
<th>Sr-90 Added (pCi)</th>
<th>Sr-90 Meas (pCi)</th>
<th>Sr-90 % Rec</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-HCL-HF + Ce</td>
<td>16</td>
<td>80</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>2-HCL-HF + Ca</td>
<td>63.3</td>
<td>80</td>
<td>81.8</td>
<td>102.25</td>
</tr>
<tr>
<td>3-SMP + Ca + Ce</td>
<td>74.4</td>
<td>80</td>
<td>76.3</td>
<td>95.38</td>
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<tr>
<td>4-HCL-HF + Ca + Ce</td>
<td>89.4</td>
<td>80</td>
<td>80.4</td>
<td>100.50</td>
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</tbody>
</table>
Alpha Spectra: Pu-236 and Np-237
Summary

- **New rapid method for Sr in milk developed at SRS**
  - Faster
  - Utilizes calcium phosphate precipitation

- **New actinides and Sr in fecal method being developed**
  - Faster, simpler than Diphonix Method
  - Higher tracer recoveries
  - More consistent Np-237 behavior
  - Recovers Sr with actinides