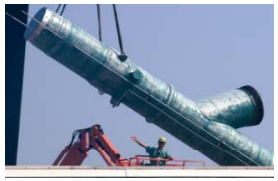
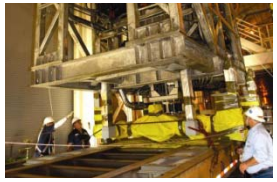
Recent Improvements in Column Extraction Methods at SRS



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Washington Savannah River Co.
53rd Radiobioassay and Radiochemical Measurements Conference
Eichrom Workshop

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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 $(NO_3)_2$ and 5 mL $(NH_4)_2 HPO_4$
  - Ca added so water blanks will precipitate (not really needed for milk)
- Add phenolphthalein indicator
- Add NH_4OH to dark pink
- Centrifuge
- What happens?

Calcium Phosphate Precipitation

- What could we do?
- Add 25 mL of 3M HNO_3 into each tube
- What happens?
- $Ca_3(PO_4)_2$ dissolves
- Fat coagulates

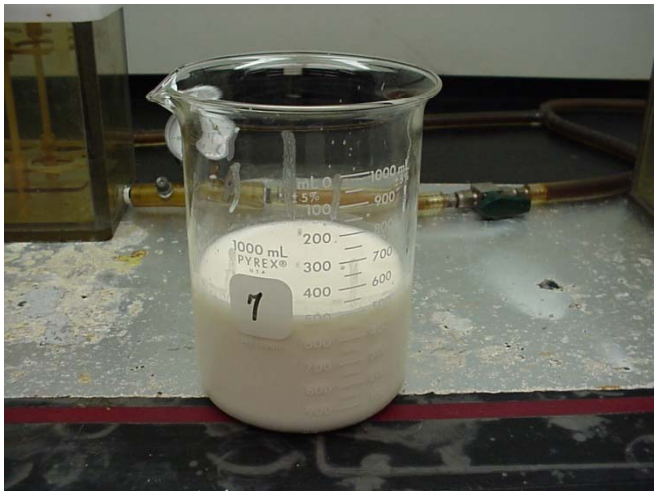
Calcium Phosphate Precipitation

- Centrifuge
- Transfer supernate to beaker
- Rinse solids with 10-15 ml 3M HNO_3
- Transfer supernate to beaker
- Evaporate beaker to dryness

Calcium Phosphate Precipitation

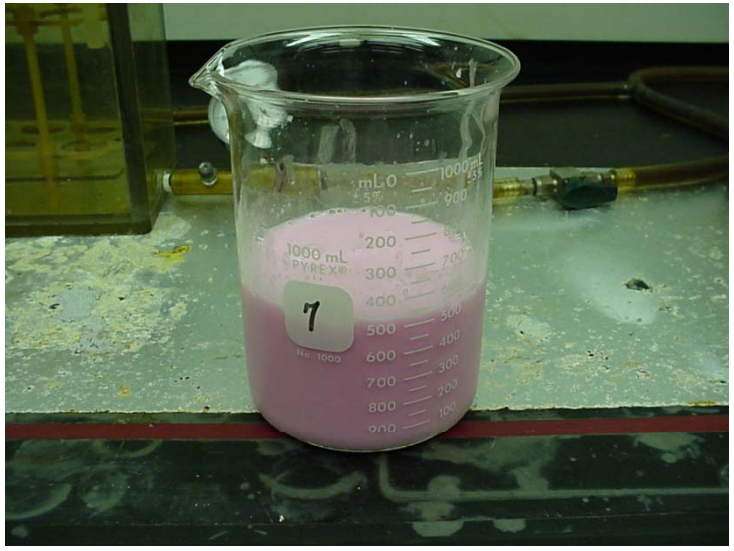
- Wet ash
  - 15 ml concentrated HNO_3 and 5 ml 30 wt% H_2O_2
- Heat beakers in a furnace
  - at 550C for 30-60 minutes to turn the solids white
- Wet ash
  - 15 ml concentrated HNO_3 and 5 ml 30 wt% H_2O_2

Sample Preparation

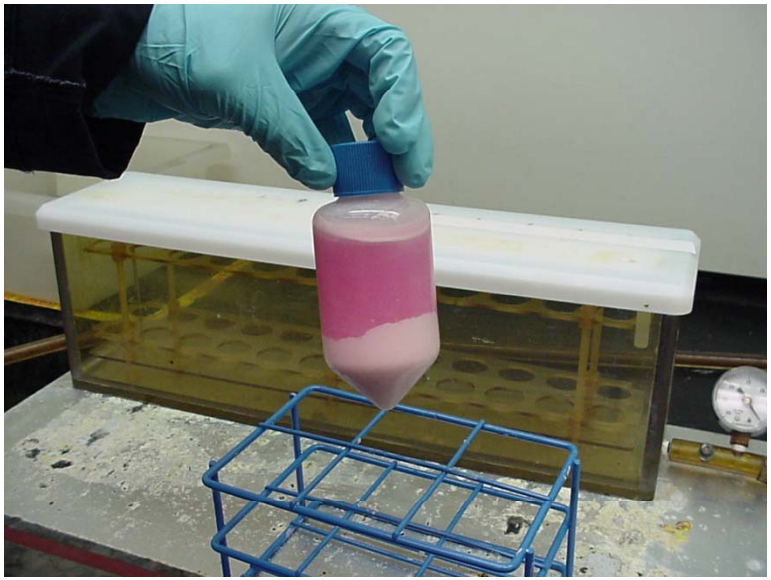


500 ml milk

Add Ca, PO4, NH_4OH



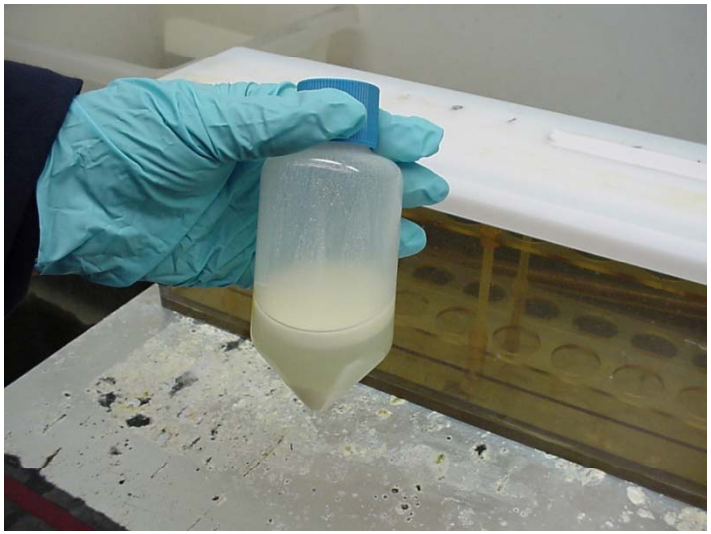
Sample Preparation



$Ca_3(PO_4)_2$ and fat

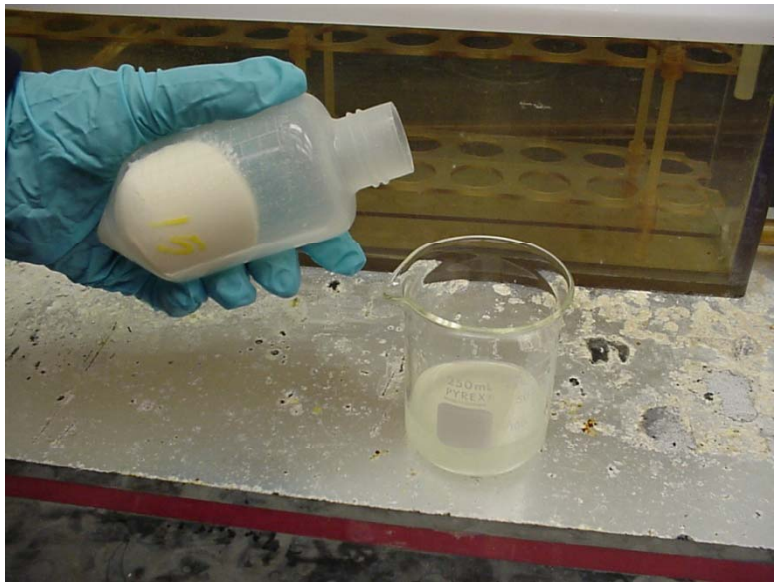
Add 3M HNO3

Sample Preparation

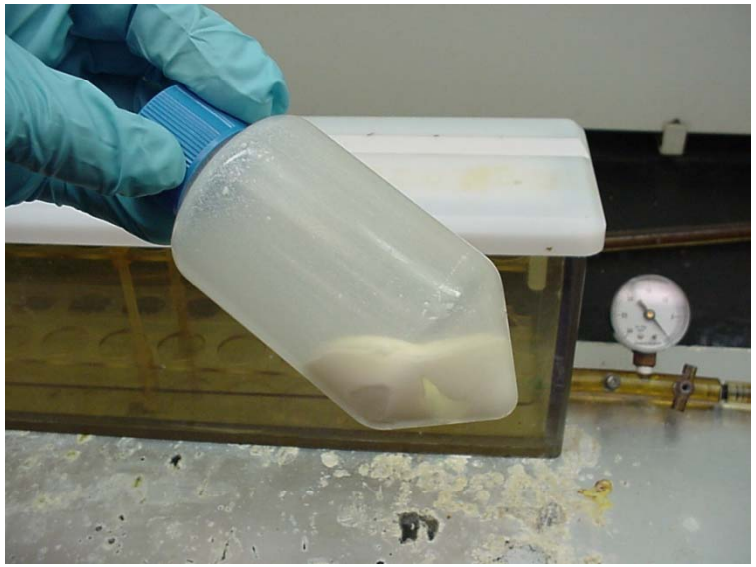


Centrifuge

Most fat is removed



Sample Preparation

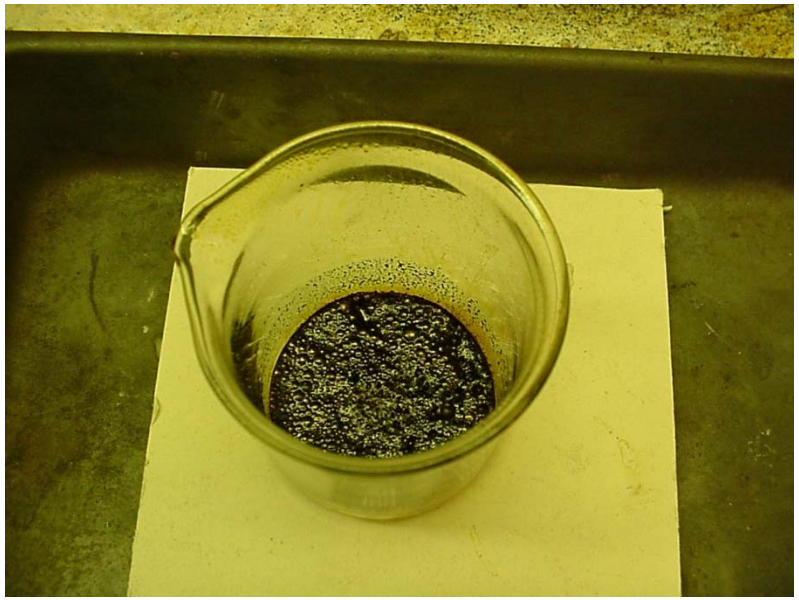


Heat on hot plate

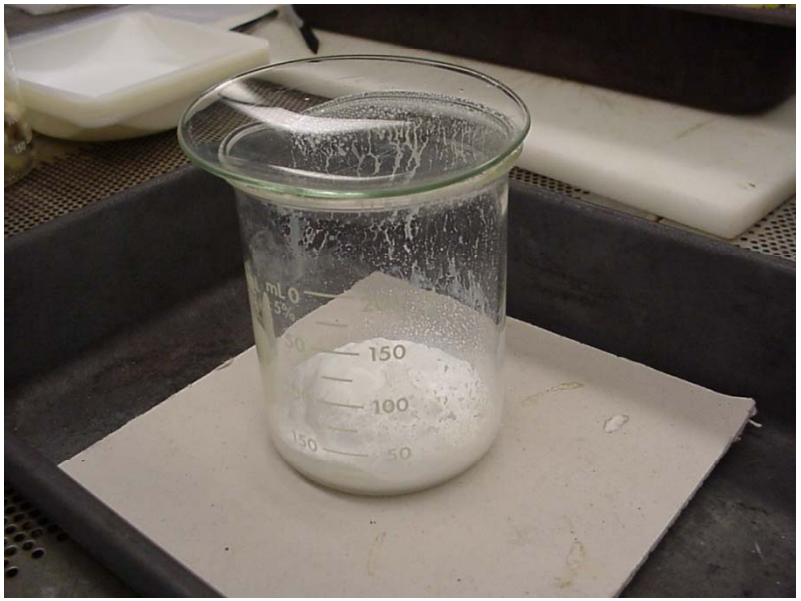
Sample Preparation

Heat to dryness

Sample Preparation



Heated at 550C 30 min.



Column Load Solution

Sr-89/90 in Milk Column Extraction

- Redissolve in 10 ml 8M HNO_3-1M $Al(NO_3)_3$
  - Or for actinides also, 3M HNO3 HNO_3-1M $Al(NO_3)_3$
- Perform typical Sr Resin Separation using 3 ml Sr resin (2 ml +1 ml cartridges)

New SRS Method for Milk

Sr-90 Added (pCi)	Carrier Recovery (%)	Sr-90 Measured (pCi)	Recovery (%)
76.28	67.3%	74.23	97.3 %
76.28	78.4%	80.86	106 %
76.28	87.4%	71.56	93.8 %
Avg	77.7%	75.55	99.0 %

SRS Fecal Method

- Current method - drying, furnacing, wet ashing, dissolution in HCL-HFand HCL-boric acid
- Load to Diphonix Resin
- Strip actinides with HEDPA
- Destroy HEDPA with Fenton's reagent (Fe + H_2O_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, $TiCl_3$ and HF, ice 5 min.
- Centrifuge

New Approach

- Redissolve 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, furnacing, 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% $TiCl_3$ 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 to10 minutes.
- Centrifuge for 10 minutes at 3500 rpm or as needed.

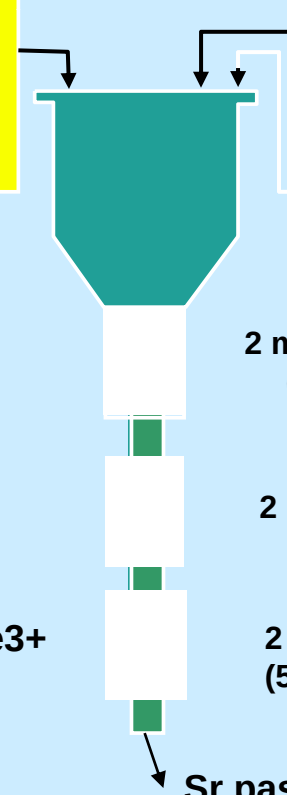
Cerium Fluoride Matrix Removal

- 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 $HN0_3$ and 7mL 2M $Al(N0_3)_3$
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 6M$HN0_3$
Separate cartridges:
TEVA:10 mL 5M HNO_3
10 mL 3M $HN0_3$



Th Elution
20mL 9MHCl

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

Add 0.5 mL 30 wt% H2O2

2 mL TEVA Resin
(50-100 um)

Cerium fluoride

Alpha spectrometry

2 mL TRU-Resin
(50-100 um)

2 mL DGA-Resin
(50-100 um)

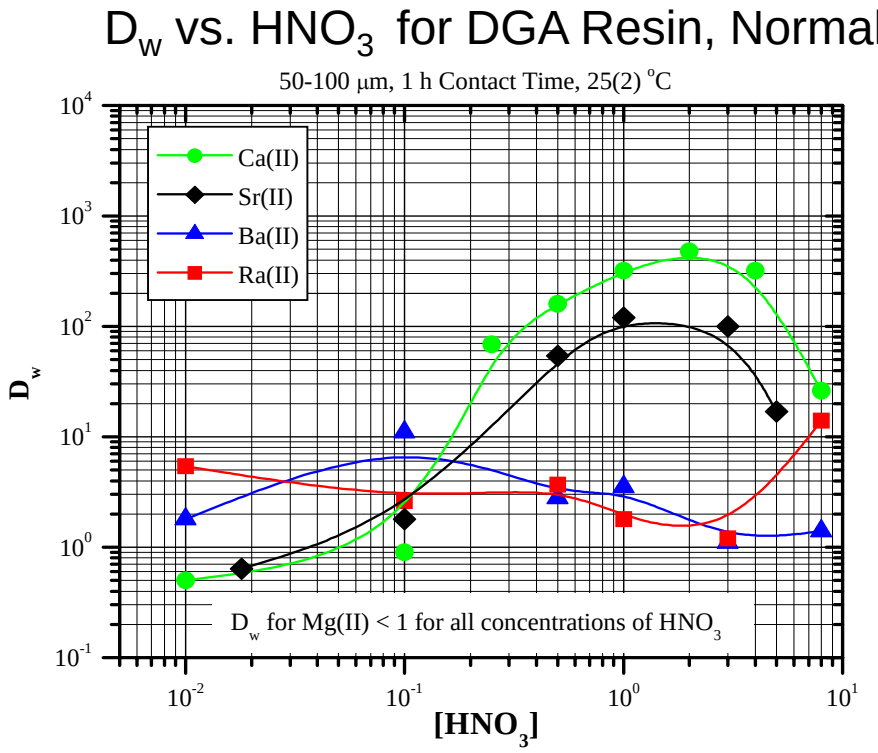
DGA resin not affected by Fe3+

***Use rongalite instead of TiCl3 for electrodeposition**

Sr passes through/collected/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).

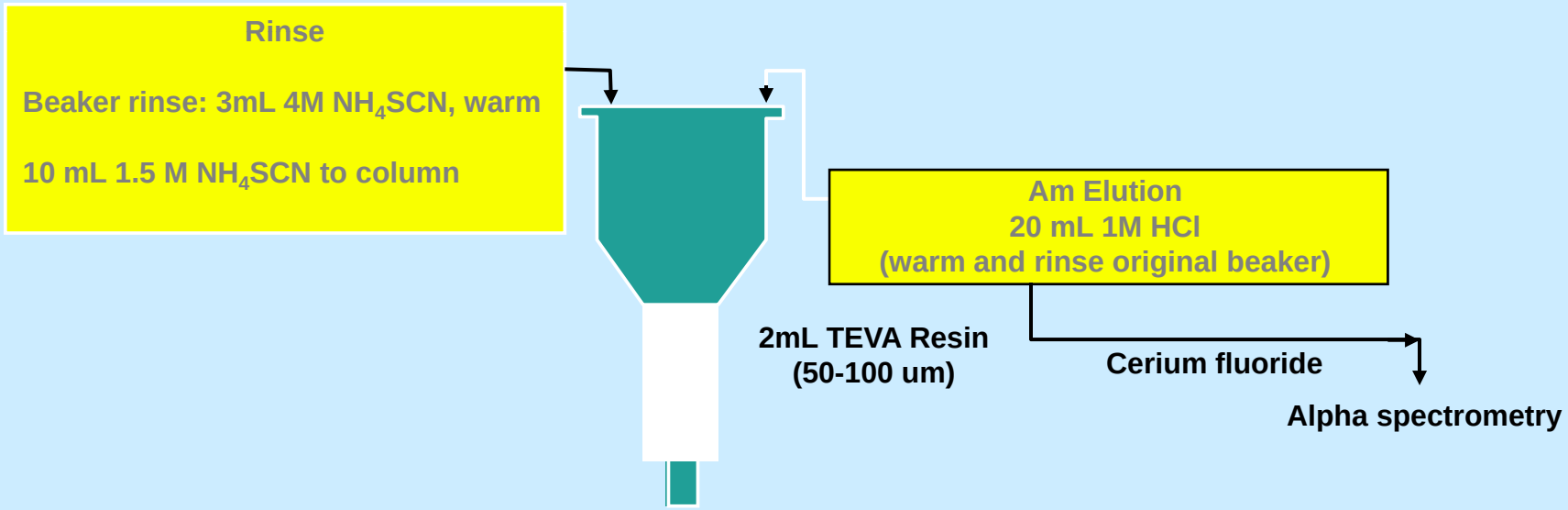


Stack TRU + DGA Resin

- 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 NH_4SCN, warm gently.



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

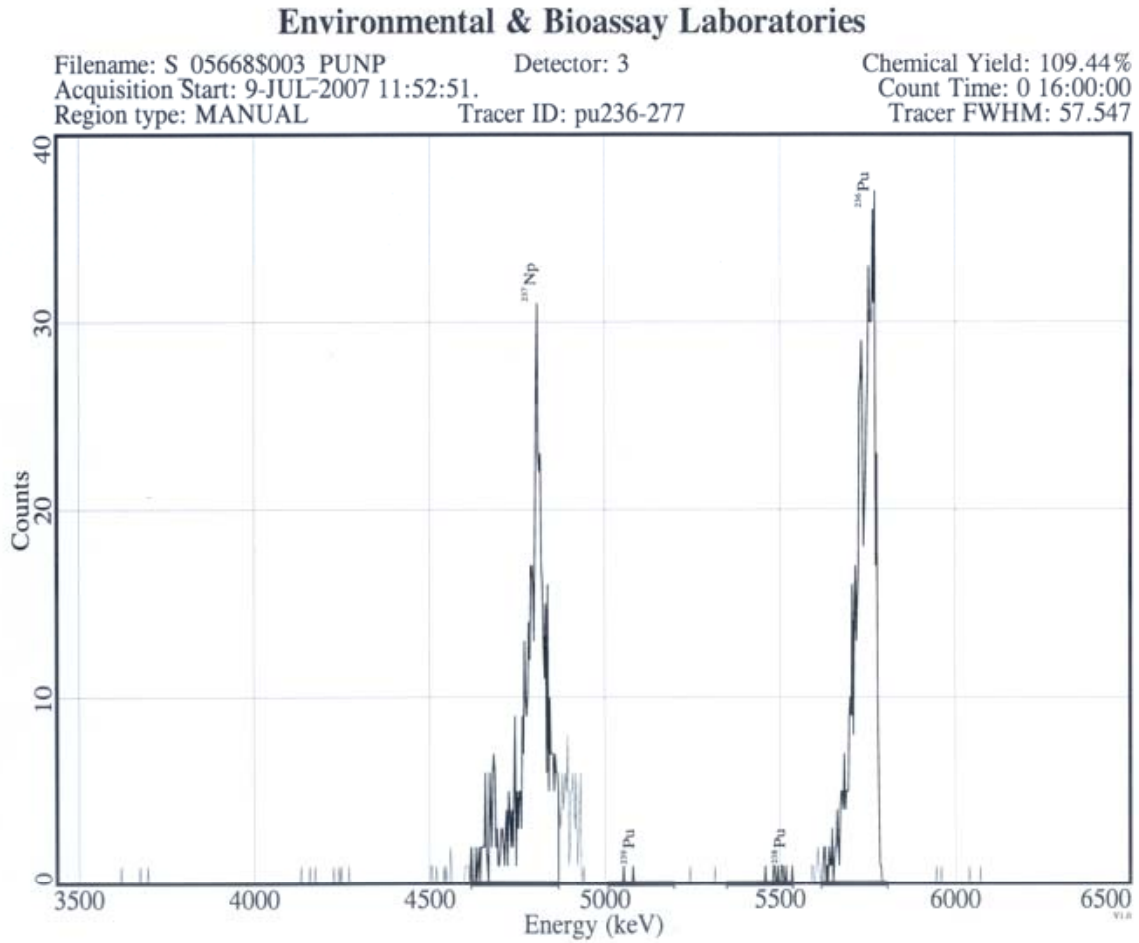
	Pu-236	U-232	U-232	Am-243	Am-243
	% Rec.	% Rec.	Corr.	% Rec.	Corr.
1-ORNL	97.60	110.16	95.96	102.5	89.7
2-ORNL	103.5	115.77	101.57	81.05	68.25
3-ORNL	108	121.69	107.49	111.1	98.3
4-ORNL	110.1	124.72	110.52	108.9	96.1
5-HCL-HF	116.8	104.63	N/A	108	95.2
avg.	107.20	115.39	103.89	102.26	89.46
% rsd	6.7	7.1	6.2	12.0	13.7

***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

	Sr Carrier % Rec	Sr-90 Added (pCi)	Sr-90 Meas (pCi)	Sr-90 % Rec
1-HCL-HF + Ce	16	80	N/A	N/A
2-HCL-HF + Ca	63.3	80	81.8	102.25
3-SMP + Ca + Ce	74.4	80	76.3	95.38
4-HCL-HF + Ca + Ce	89.4	80	80.4	100.50

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 rcoveries
  - More consistent Np-237 behavior
  - Recovers Sr with actinides