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Rapid Determination of Radiostrontium in Large Soil Samples

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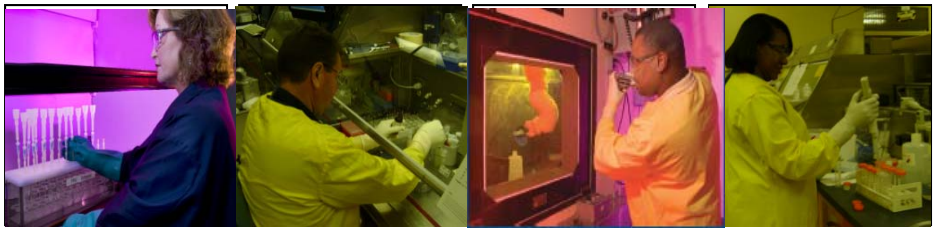
October 31, 2012



Rapid Radiostrontium analyses

- **Important assay after Fukushima Daiichi accident**
- **SRNL support**
  - 1.5g soil-fusion
  - 10g acid leach –lower MDA
- **Larger aliquots may be needed to assess low level activities/isotope ratios**
- *Could we analyze even larger soil aliquots for Sr isotopes?*

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Fukushima Soil Samples

Received samples in early April, 2011 Via DOE FRMAC

- **Was it ok to plant rice?**
  - Needed very rapid results
- **Rapid approval of USDA permit for foreign soil**
- **Gamma, Sr-89/90, actinides**
- **Higher than normal activity samples**
  - Cs-134/137 gamma measurements from Japan
  - Rad Con and facility support
  - DOE RAP (Radiological Assistance Program) team
    - Responds to US radiological emergencies

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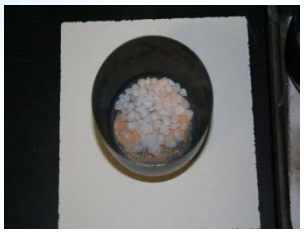
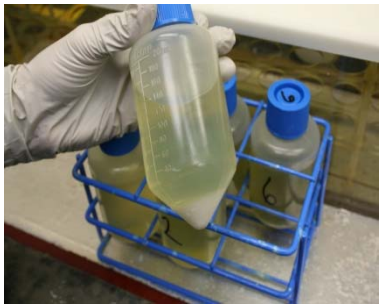
Rapid Sr-89, Sr-90 Sample Fusion Method for Soil



1-2 g Soil Sample
Add 6 mg Sr carrier

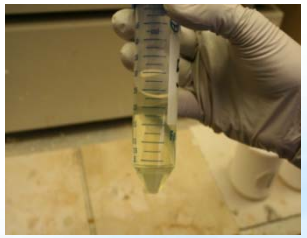
Fuse in Zr Crucible 5 -10 min. (15g NaOH 600^{o}C)
Hydroxide precipitation (Fe, Ca, PO_4)



Calcium Fluoride Matrix removal
(HCL/HF)

Redissolve in 8M HNO_3-0.5M Al $(NO_3)_3$
- 0.1M boric acid

Column Load
Solution



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Sr-89/90 Fukushima Soil Work

SOIL Batch	N	Avg. Sr Carrier % Recovery	+/- 1 sigma	% Sr-90 Recovery LCS	MS	Approximate MDC (pCi/g)
1	14	78.1	9.4	115.5	98.8	1
2	21	71.5	8.5	100.5	89.1	0.9
3	22	74.2	5.1	100.3	94.5	0.8
4	22	79.7	5.3	106.4	98.5	0.7
5	22	82.1	8.8	105.2	91.7	0.7
6	12	74.1	5.8	106.3	107.1	0.8
7	11	77.5	3.8	91.3	109.9	0.4
8	7	77.1	7.6	90.2	108.9	0.05
9	11	86.1	8.4	105.4	94.9	0.05
10	10	71.9	12.5	99.7	97.4	0.05
11	10	76.6	11.7	94.3	94.3	0.04
Avg.		77.2		101.4	98.6	

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Sr-89 and Sr-90 in soil

- What about very large soil aliquots?
- Is that even possible?
- Soil matrix interferences
- Literature?

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Literature

- **Number of methods reported in literature that use ion exchange/extraction chromatography to determine radiostrontium in soil**
  - Not so rapid…
- **R. Bojanowski and D. Knapinska- Skiba, Determination of low-level ^{90}Sr in environmental samples: a novel approach to the classical method, J. Radioanal. Nucl.Chem, VoL 138, No. 2 (1990), 207**
  - Fuming nitric acid presents handling difficulties and can be very tedious and time-consuming

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Literature, continued

- **J. Wang, I. Chen, and J. Chiu, Sequential isotopic determination of plutonium, thorium, americium, strontium and uranium in environmental and bioassay samples, Applied Radiation and Isotopes, 61 (2004.), 299**
  - A large anion resin column (Dowex 1x8) was used to collect and separate Pu and Th. Rinse fractions from the anion resin were treated further and processed individually for Am, U and Sr
  - Several sequential precipitations were carried out. An oxalate precipitation was performed at pH 4.2 on the anion resin rinse solution followed by a Sr Resin separation.
  - Strontium was counted using Čerenkov counting, while all actinide fractions were electrodeposited for counting by alpha spectrometry.
  - Chemical recoveries using this method on NRIP (National Institute of Standards and Technology [NIST] Radiochemistry Intercomparison Program) soil for strontium were 63-77%.

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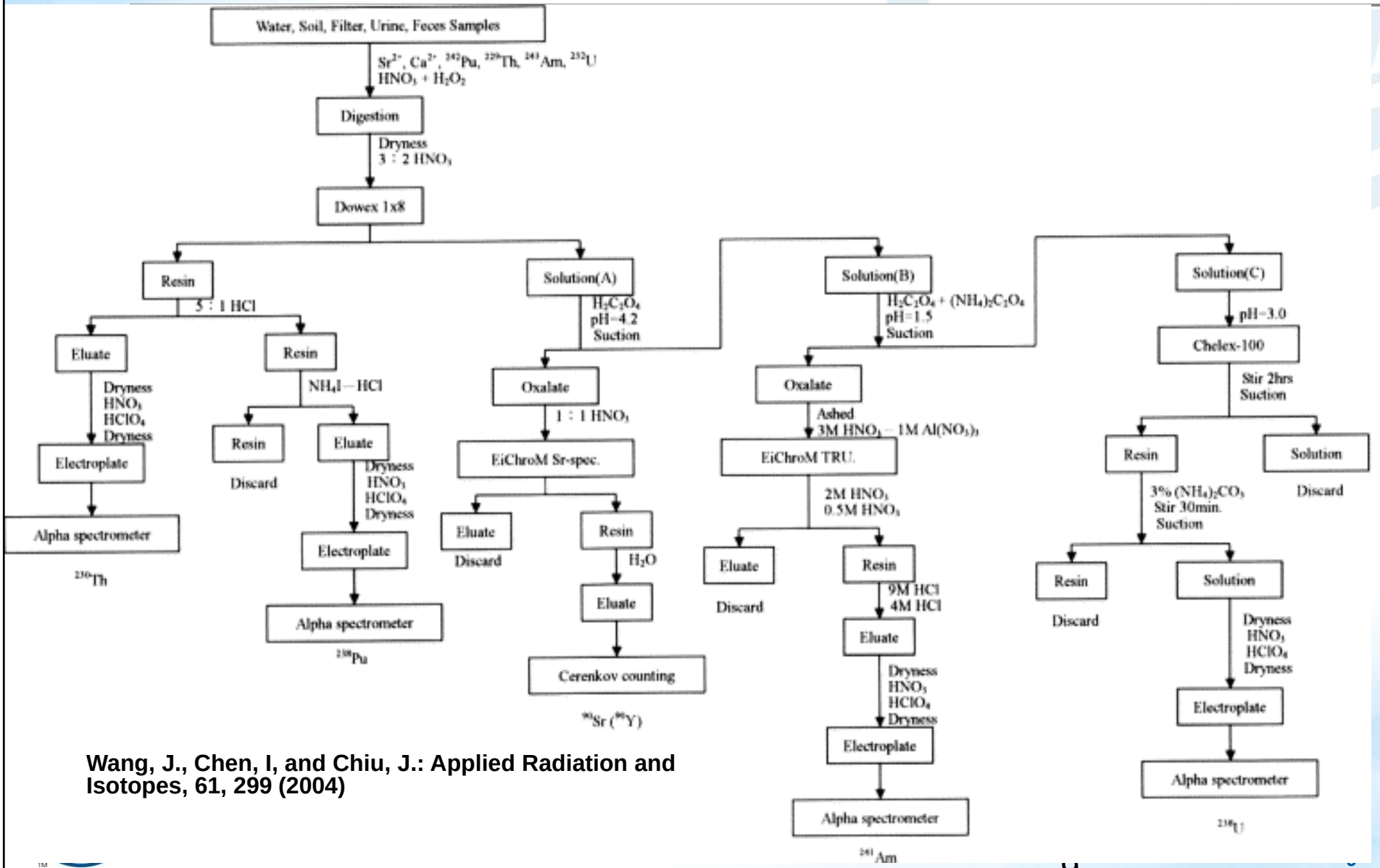
Wang, et al Flow Chart



Wang, J., Chen, I, and Chiu, J.: Applied Radiation and Isotopes, 61, 299 (2004)

Literature, continued

- **P. Tavčar, R. Jakopič, and L. Benedik,. Sequential Determination of ^{241}Am, ^{237}Np, Pu Radioisotopes and ^{90}Sr in Soil and Sediment Samples, Acta. Chim.Slov. 52 (2005), 60**
  - Reported a method to determine actinides in soil. Soil and sediment samples up to 10g were leached using strong nitric acid, filtration, evaporation, and the residue was redissolved in 1M HNO_3.
  - The acid concentration was increased to 8M HNO_3 and the samples were loaded onto Dowex 1x8 resin.
  - Sr was collected from the anion exchange eluent solution using calcium oxalate and the Sr was then separated using Sr Resin. Very large elution volumes were used in this method, including 100 ml of water to elute Sr from Sr Resin.
  - The Sr was precipitated as an oxalate, redissolved and measured using liquid scintillation counting. The average chemical yield for Sr was 67%.

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P. Tavčar et al

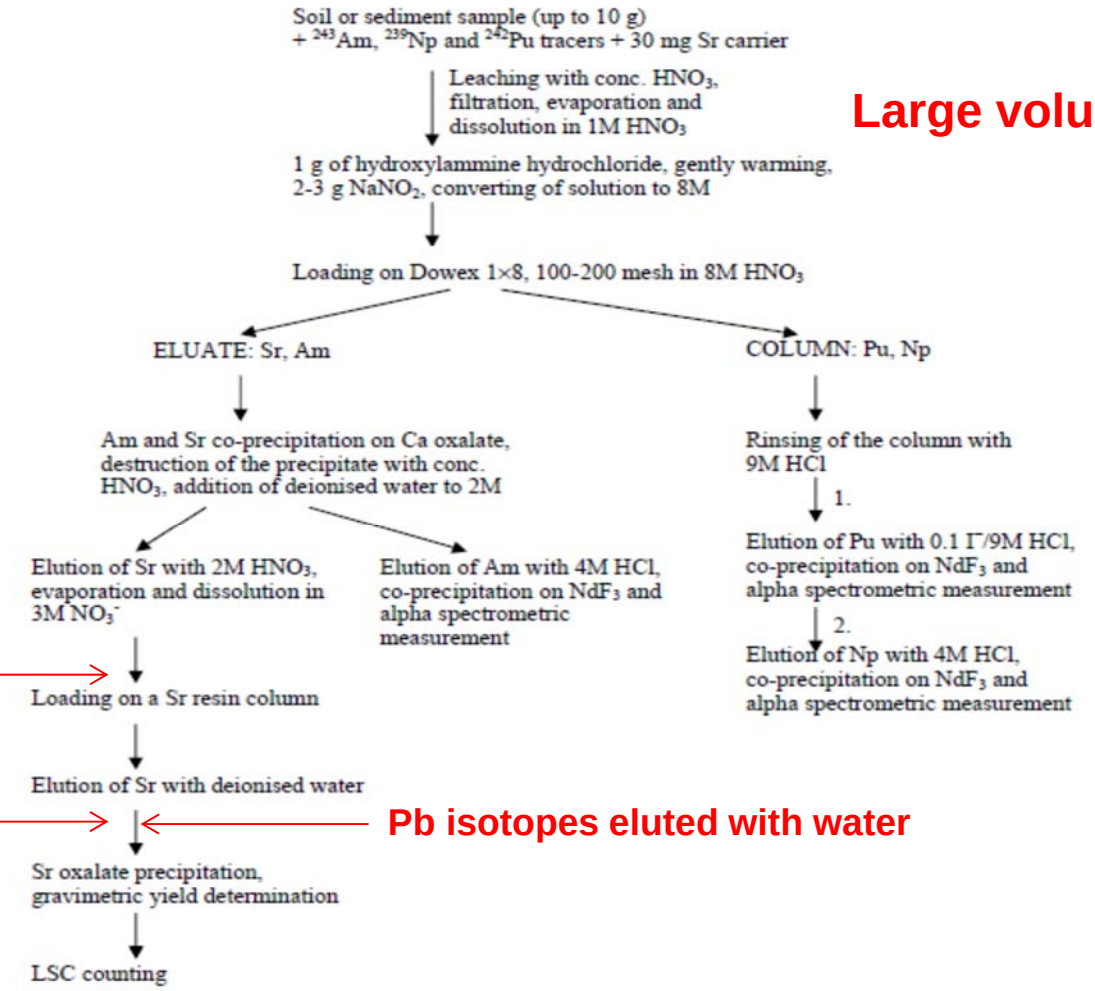

Figure 1. Analytical procedure for the simultaneous determination of plutonium, neptunium, americium, and strontium in soil and sediment samples.

Large volume rinses

100 ml 3M HNO_3 rinse

100 ml water elution

Pb isotopes eluted with water

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SRNL Approach

- **Can we improve sample preparation chemistry for Sr-89/90 assay in larger soil samples?**
  - Improve matrix removal steps
  - Minimize column rinse/elution volumes
  - increase chemical yields
  - Lower MDA

S. Maxwell et al, Rapid Determination of Radiostrontium in Large Soil Samples, Journal of Radioanalytical and Nuclear Chemistry, online June 2012, 10.1007/s10967-012-1863-2

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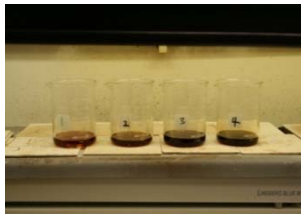
Rapid Sr-89, Sr-90 Acid Leach Method for Larger Soil Aliquots

50 g samples

Add Sr carrier to large soil sample



Acid leach with 15.8M HNO_3; centrifuge, decant and evaporate leachate

Redissolve with 15-20mL 1M HCl

Transfer to 225mL tube and dilute to 180mL with water

Fe hydroxide matrix removal (25mL con. NH_4OH, 50mg Ca, PO_4) Mix and centrifuge

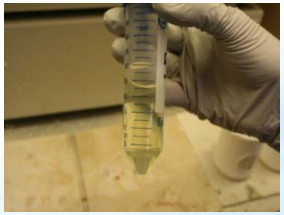
Discard Supernatant

Add 40mL 1.5M HCl. Dilute to 170mL with 0.01M HCl

Ca Fluoride matrix removal Add 25mL 28M HF. Mix and centrifuge

Discard supernatant

Redissolve in 7mL 15.8M HNO3+7mL 3MHNO_3-0.25M H_3BO_3, 7mL $Al(NO_3)_3$



Column Load Solution

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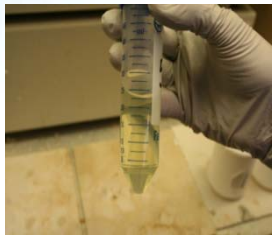
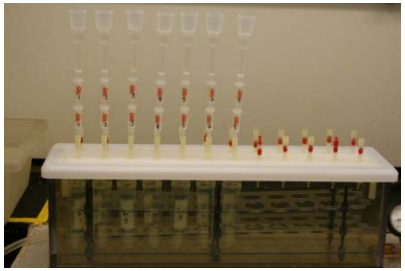
Rapid Sr-89, Sr-90 Column Separation Method for Soil





Column
Load Solution

↓

Sr Resin* (3mL)
cartridge

↓

Rinse column;
15mL 8M HNO_3;
*5mL 3M HNO_3-
0.05M Oxalic Acid;
15mL 8M HNO_3

← Sample matrix and ^{90}Y removal; start time for ^{90}Y ingrowth after final 8M HNO_3 rinse

↓

Elute Sr
*15mL 0.05M HNO_3

↓

Evaporate on planchet; weigh for gravimetric yield

↓

Count $^{89,90}Sr$ by Gas Flow Proportional Counter

↓

Recount after ^{90}Y ingrowth 10 days later to determine ^{89}Sr and ^{90}Sr

For large soil aliquots:

*4 ml Sr Resin

*10mL 3M HNO_3-0.05M Oxalic Acid

*18 mL 0.05M HNO_3

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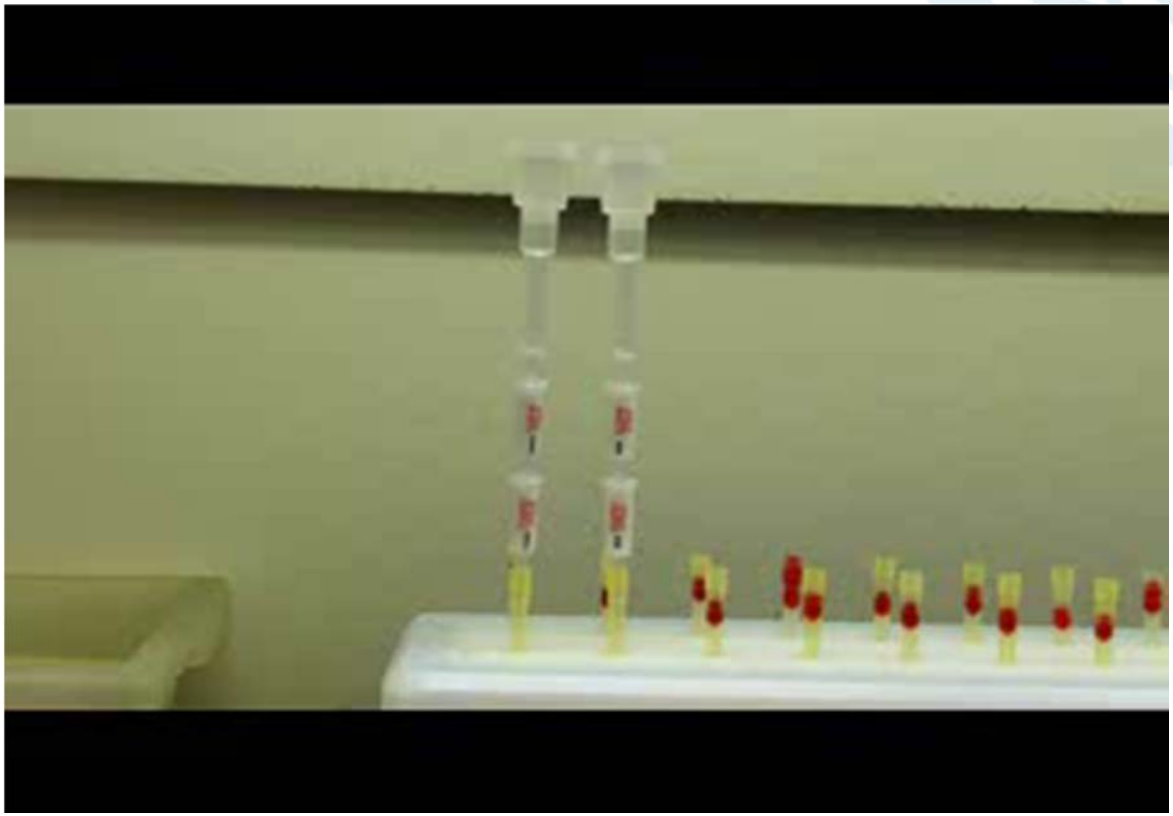
Sr Resin Separation



Load solution -1 drop/sec
Rinses - 2 or 3 drops/sec

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Sr-90 Soil Method (50 gram)

Sample ID	Sr carrier (%)	^{90}Sr Reference Value (pCi g^{-1})	^{90}Sr Reference Value (mBq g^{-1})	^{90}Sr Measured Value (mBq g^{-1})	Difference (%)
1	95.9	0.160	5.92	6.05	2.20
2	98.6	0.160	5.92	6.02	1.69
3	94.6	0.160	5.92	5.82	-1.69
4	91.8	0.160	5.92	6.32	6.76
5	93.2	0.160	5.92	5.96	0.68
6	92.5	0.160	5.92	5.60	-5.41
7	91.2	0.160	5.92	5.85	-1.18
Avg	94.0			5.95	0.43
SD	2.6			0.22	
% RSD	2.8			3.77	
	Measured values corrected for 1.35 mBq ^{90}Sr/g found in unspiked soil				

MDC = 0.011 pCi/g (0.41 mBq/g)
90 minute count

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Sr-90 Soil Method (50 gram)

Sample ID	Sr carrier (%)	^{90}Sr Reference Value (pCi g^{-1})	^{90}Sr Reference Value (mBq g^{-1})	^{90}Sr Measured Value (mBq g^{-1})	Difference (%)
1	87.8	0.32	11.84	11.2	-5.41
2	88.4	0.32	11.84	11.9	0.51
3	87.1	0.32	11.84	12.2	3.04
4	93.9	0.32	11.84	12.7	7.26
5	92.5	0.32	11.84	11.2	-5.41
6	87.1	0.32	11.84	10.9	-7.94
7	90.5	0.32	11.84	10.7	-9.63
Avg	89.6			11.5	-2.51
SD	2.7			0.7	
% RSD	3.1			6.4	
	Measured values corrected for 1.35 mBq ^{90}Sr/g found in unspiked soil				

MDC = 0.0045 pCi/g (0.17 mBq/g)
if 480 minute count

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Sr-90 Soil Method (50 gram)

Sample ID	Sr carrier (%)	^{90}Sr Reference Value (pCi g^{-1})	^{90}Sr Reference Value (mBq g^{-1})	^{90}Sr Measured Value (mBq g^{-1})	Difference (%)
1	86.4	1.60	59.2	60.6	2.36
2	93.9	1.60	59.2	54.9	-7.26
3	81.0	1.60	59.2	58.3	-1.52
4	92.5	1.60	59.2	57.7	-2.53
5	87.8	1.60	59.2	57.6	-2.70
6	93.9	1.60	59.2	58.3	-1.52
7	89.8	1.60	59.2	57.2	-3.38
Avg	89.3			57.8	-2.36
SD	4.7			1.7	
% RSD	5.3			2.9	
	Measured values corrected for 1.35 mBq ^{90}Sr/g found in unspiked soil				

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Sr-89/90 Soil Method (25 gram) –with HF Digest

Sample ID	Sr carrier (%)	^{90}Sr Reference Value (pCi g^{-1})	^{90}Sr Reference Value (mBq g^{-1})	^{90}Sr Measured Value (mBq g^{-1})	Difference (%)
1	78.9	0.32	11.84	13.9	17.40
2	70.1	0.32	11.84	12.4	4.73
3	70.1	0.32	11.84	11.4	-3.72
Avg	73.0			12.6	6.14
SD	5.1			1.3	
% RSD	7.0			10.0	
	Measured values corrected for 1.35 mBq ^{90}Sr/g found in unspiked soil				

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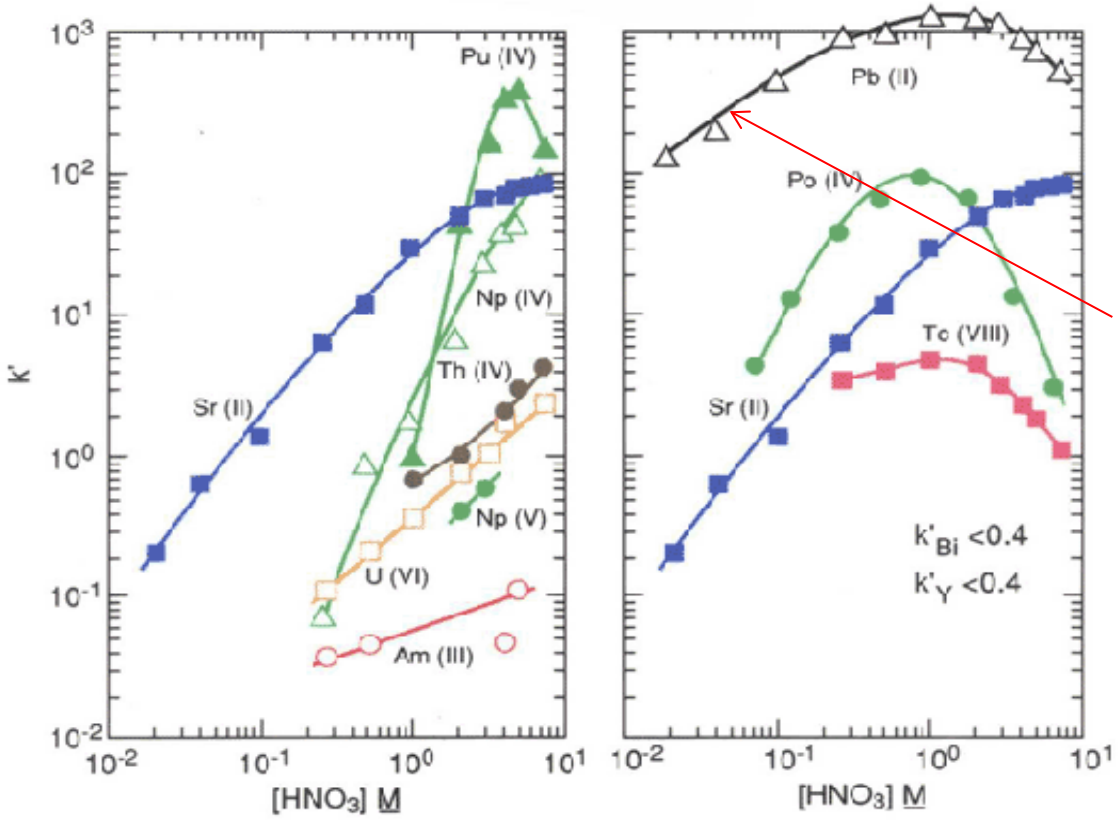
Sr Resin

Figures 4 and 5

Acid dependency of k' for various ions at 23-25°C.
Sr Resin



Horwitz (HP199)

0.05M HNO_3 Sr elution-
Pb isotopes stay on resin

3M HNO_3-0.05M oxalic acid rinse
removes any tetravalent actinides

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Sr Resin: Pb/Bi isotopes

Pb isotopes retained ***What about Bi ingrowth during elution?***

Bi isotopes removed

Isotope	Half Life	Daughter	Half Life
Pb-214	26.8m	Bi-214	19.9m
Pb-212	10.64h	Bi-212	60.55m
Pb-210	22.26y	Bi-210	5.01d

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Sr Resin

For 10 pCi Pb isotopes and 20 minute elution time:

Pb isotope	Bi ingrowth	Unsupported Bi β^- after		
10 pCi	20 min (pCi)	2 Hr	6 Hr	12 Hr
Pb-214	3.8	0.0582	1.40E-05	4.90E-11
Pb-212	2.02	0.3277	0.0211	0.00032
Pb-210	0.02	0.0197	0.0193	0.0187

Bi isotope decay from elution to count (including evaporation, mounting, weighing)

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Summary

- New method for $^{89/90}$Sr has been developed at SRNL
- High yields >90%
- Effective removal of interferences
- Preconcentration steps remove silicates, etc.
- Optimized column rinse and elution volumes
- Vacuum flow rates save time and money
- Lower MDA

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