Rapid methods for the determination of actinides and Sr in environmental samples

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Scope

- Actinides and Sr in aqueous samples
- Actinides and Sr in soil, food, concrete and brick samples
- Determination of radiostrontium in large soil and sea water samples

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Rapid methods

- Emergency situation
  - Rapid results, high sample throughput
  - Evaluation of situation, decision on measures to be taken
  - Usually low sample mass and short counting times
- Routine analysis
  - High sample throughput
  - Sample volume / mass and counting time depending on detection limits to be obtained

➢ SRNL (Sherrod Maxwell) very active in developing new methods)

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Determination of Sr, Pu, Am and U in water and urine samples

S.L. Maxwell: Rapid Analysis of Emergency Urine and Water Samples, Journal of Radioanalytical and Nuclear Chemistry , 275(3), 2008, 497 - 502

Eichrom method ACW17 VBS: Am, Np, Pu, Th, Cm, U and Sr in Water (with Vacuum Box System), Version 1.0, Eichrom Technologies LLC, October 2006

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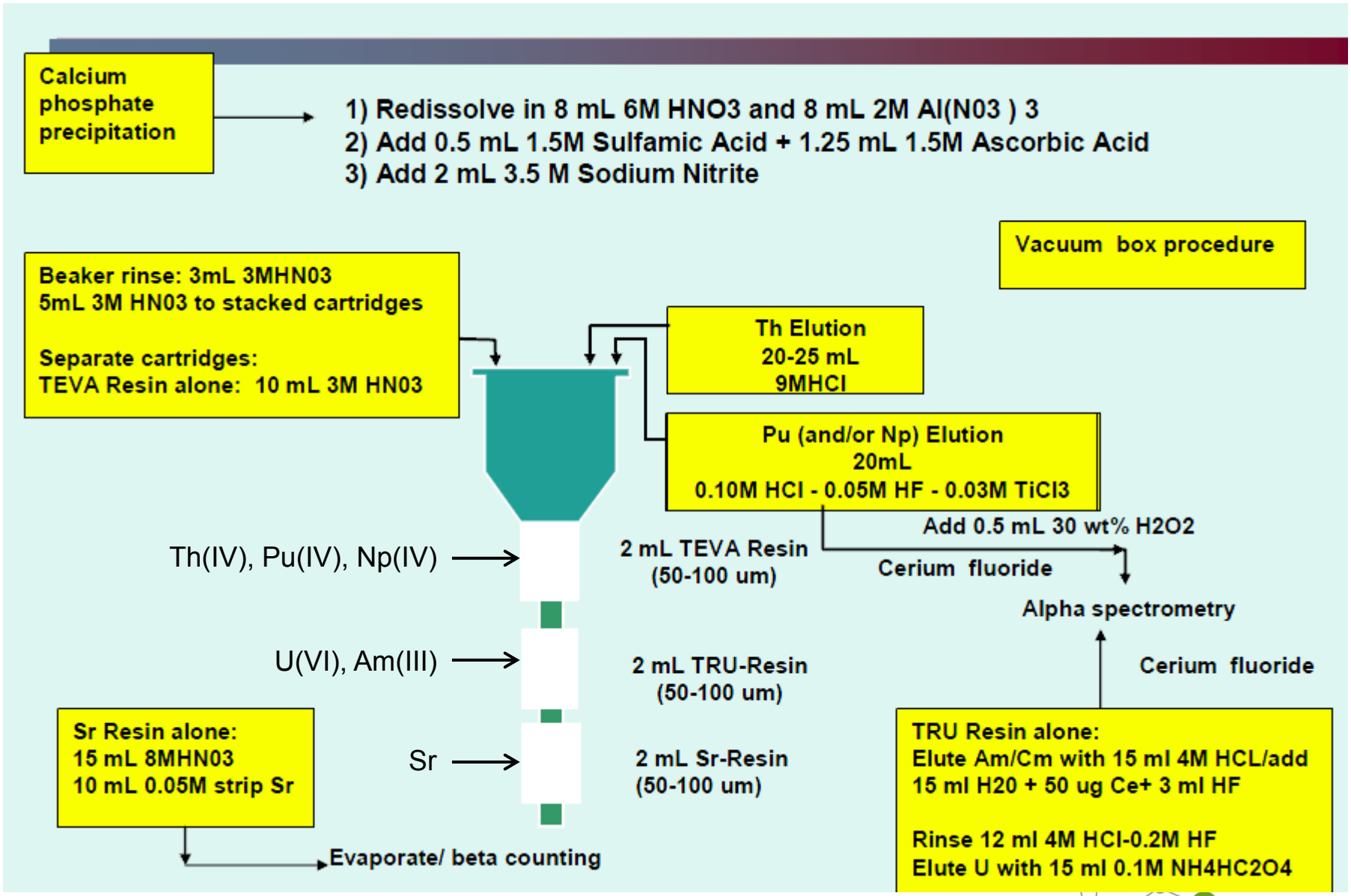
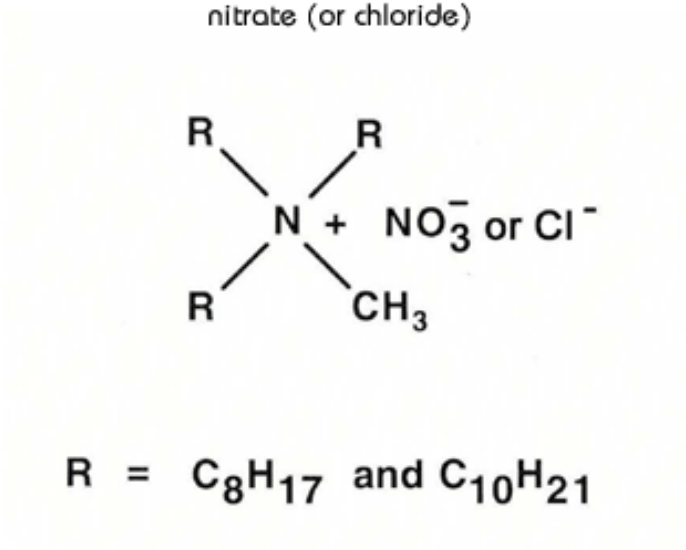
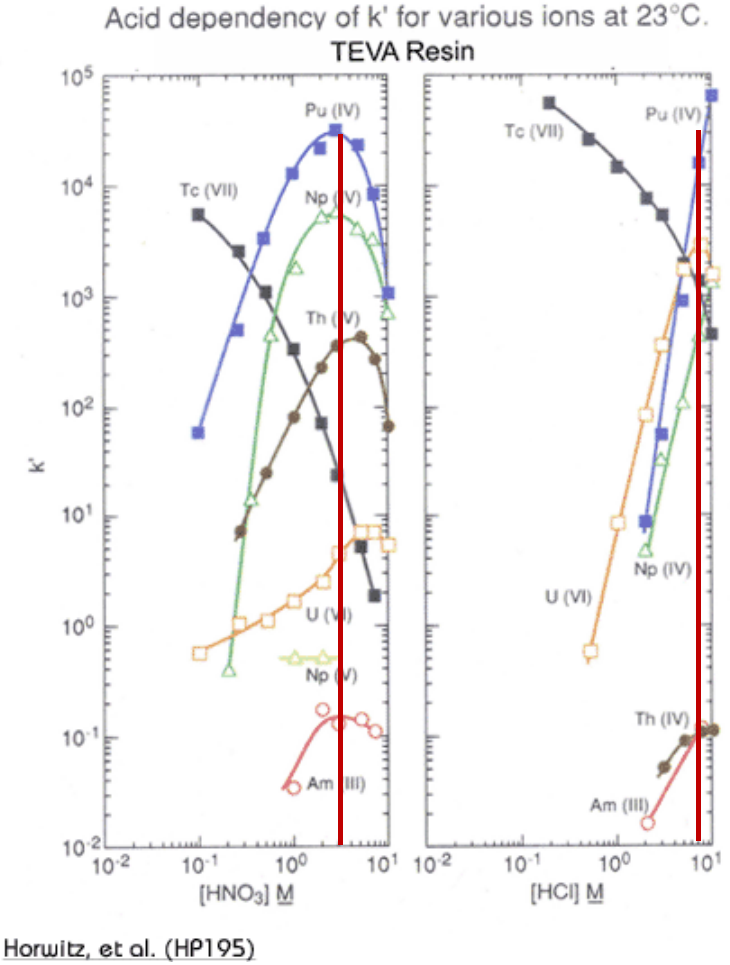
- Stacked TEVA, TRU and Sr cartridges
- Separation in < 6h (vacuumbox / cartridges)
  - Flow rates: 1 $mL.min^{-1}$ (load and elution), 3 $mL.min^{-1}$ (rinse)
- Results can be obtained in < 8h
  - incl. measurement, « emergency level » ≈ several $Bq.L^{-1}$
- 1 L water (pH 2) or mineralised urine
- Addition of internal standards and Sr-carrier (or Sr-85)
- Ca-Phosphat co-precipitation
- Dissolution in 3M HNO_3 / 1M $Al(NO_3)_3$
- Redox (Pu(IV)): Fe(II) / $NaNO_2$
- Load through all 3 cartridges
- Rinse with 3M HNO_3


Calcium phosphate precipitation
1) Redissolve in 8 mL 6M HNO3 and 8 mL 2M Al(N03) 3
2) Add 0.5 mL 1.5M Sulfamic Acid + 1.25 mL 1.5M Ascorbic Acid
3) Add 2 mL 3.5 M Sodium Nitrite
Vacuum box procedure
Beaker rinse: 3mL 3MHN03
5mL 3M HN03 to stacked cartridges
Separate cartridges:
TEVA Resin alone: 10 mL 3M HN03
Th Elution
20-25 mL
9MHCl
Pu (and/or Np) Elution
20mL
0.10M HCl - 0.05M HF - 0.03M TiCl3
Add 0.5 mL 30 wt% H2O2
Cerium fluoride
Alpha spectrometry
Th(IV), Pu(IV), Np(IV)
2 mL TEVA Resin
(50-100 um)
U(VI), Am(III)
2 mL TRU-Resin
(50-100 um)
Cerium fluoride
Sr Resin alone:
15 mL 8MHN03
10 mL 0.05M strip Sr
Sr
2 mL Sr-Resin
(50-100 um)
TRU Resin alone:
Elute Am/Cm with 15 ml 4M HCL/add
15 ml H20 + 50 ug Ce+ 3 ml HF
Rinse 12 ml 4M HCl-0.2M HF
Elute U with 15 ml 0.1M NH4HC2O4
Evaporate/ beta counting

TEVA Resin

Trialkyl, methylammonium nitrate (or chloride)





Horwitz, et al. (HP195)

- **Extractant**: Aliquat 336®
- TEVA: **TE**tra**V**alent **A**ctinides
- Retention of Pu(IV), Th(IV), Np(IV)
- Sr, Am(III) and U(VI) not retained
- Th elution with 9M HCl
- Np/Pu co-elution with 0.1M HCl / 0.05M HF / 0.03M $TiCl_3$ or rongalite

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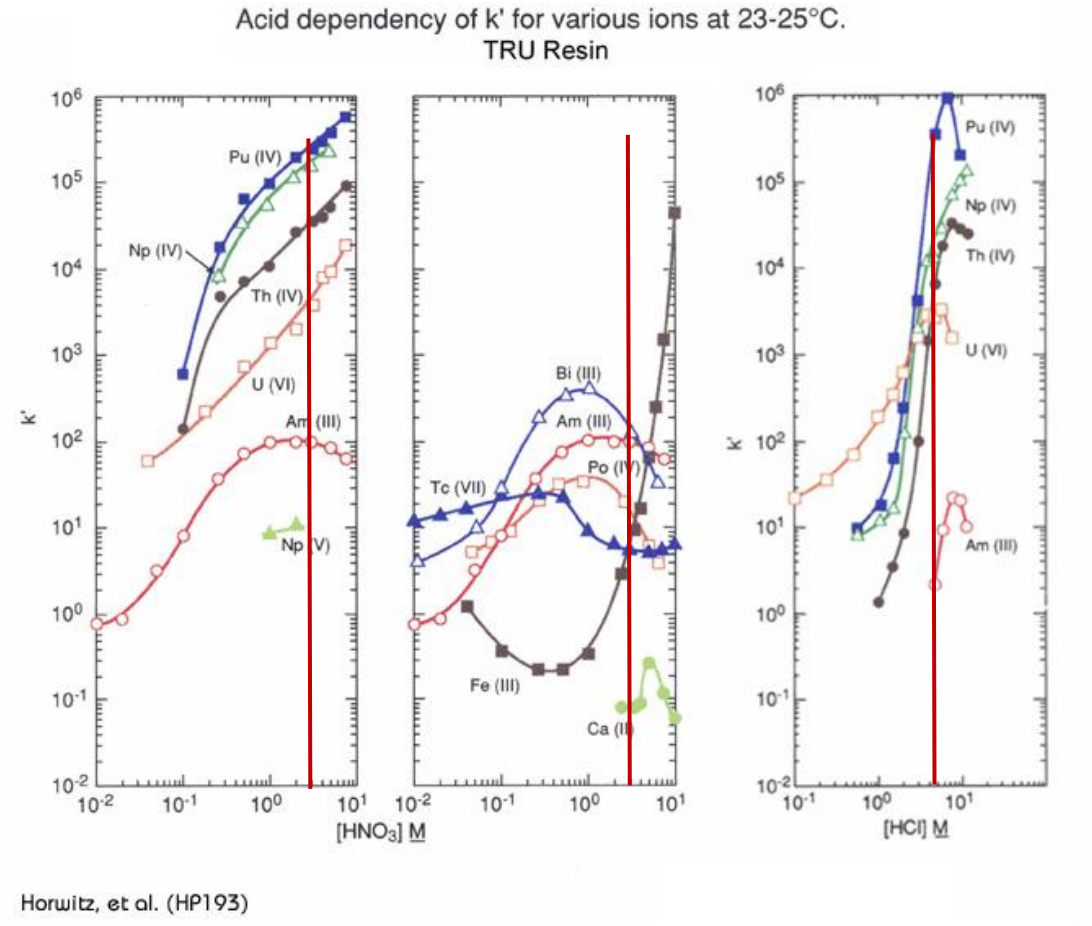
TRU Resin

CMPO



- **Extractant**: CMPO / TBP
- **TR**ans**U**ranium elements
- Retention of Am(III) and U(VI)
- Am elution with 4M HCl
- Rinse with 4M HCl / 0.2M HF for Th removal
- U elution with 0.1M ammonium oxalate

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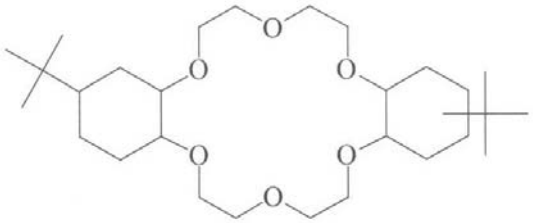
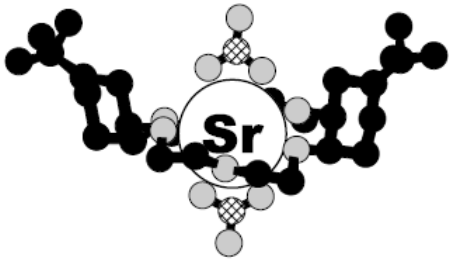
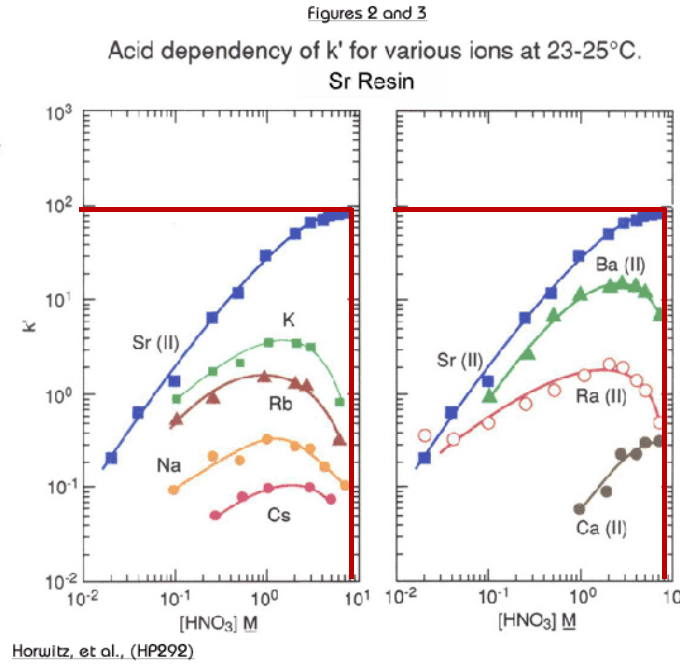
Sr Resin

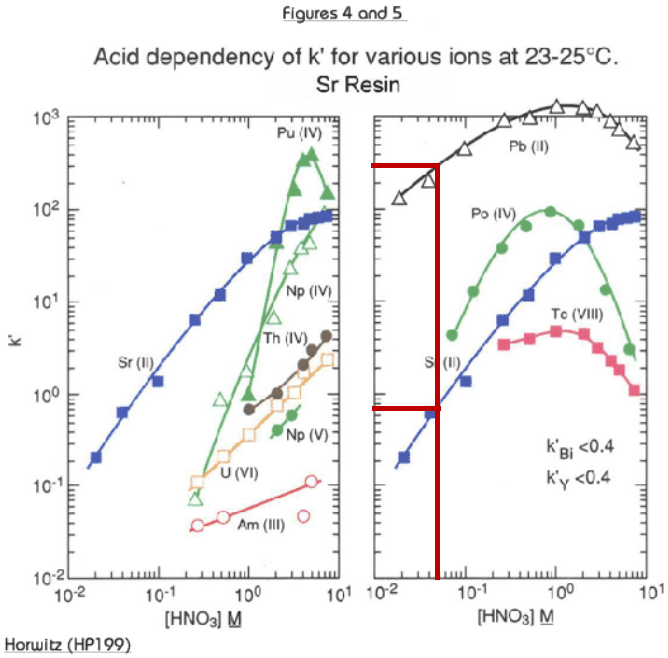


Diluent: 1-octanol



Dietz et al. 2004





- Extractant: 1.0M 4,4'(5')-di-t-butylcyclohexano 18-crown-6 in 1-octanol.
- Retention of Sr (and Pb)
- Rinse with 10 mL 8M HNO_3 , 5 mL 3M HNO_3 / 0.05M oxalic acid (in case of presence of tetravalent actinides) and 5 mL 8M HNO_3
- Sr elution with 10 mL 0.05M HNO_3 (Pb remains retained)
- Counting via GPC (alternatively LSC)

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NRIP-2008 Water Analysis Results

Nuclide	Avg. Difference Reported vs NIST	Avg. Difference Longer Recounts
Pu-238	13 %	6.3%
Pu-240	- 2.3%	-4.5%
Am-241	9.6%	1%
U-238	-0.5%	-5.4%
U-234	9.0%	-6.7%
Sr-90	-14 %	N/A

Actinides: 45 minute count time / Recounts: 2 hour count time

Separation time 3 – 4h

S. Maxwell at 2007

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Actinides and Sr in soil, food, concrete and brick samples

SL Maxwell, BK Culligan, A Kelsey-Wall, PJ Shaw:Rapid radiochemical method for determination of actinides in emergency concrete and brick samples. Anal Chim Acta., 701(1):2011;112-118.

SL Maxwell, BK Culligan, A Kelsey-Wall, PJ Shaw: Rapid determination of actinides in emergency food samples, J. Radioanal. Nucl. Chem., 292(1), 2011, 339-347

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- Methods can be adjusted for larger sample masses
- Addition of internal standards and Sr carrier (or Sr-85)
- Mineralisation in furnace at 700°C
- NaOH fusion
- Two co-precipitations for matrix removal
  - $Fe(OH)_3$ / Ca-Phosphate
  - LaF_3 under reducing conditions ($TiCl_3$ -> U(IV))
- Dissolution in 3M HNO_3 / 1M $Al(NO_3)_3$ / 0.25M boric acid
- Redox (Pu(IV)): Fe(II) / $NaNO_2$

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- Vacuumbox system
- Stacked TEVA, TRU and DGA Kartuschen -> actinide retention
- Rinse with 3M HNO_3
- Separation of the cartridges (TEVA and TRU/DGA)
  - Th, Pu (Np) purification via TEVA
  - Am/U purification via TRU/DGA
- Microprecipitation
- Eluates from sample load and first rinse (all cartridges) united and evaporated to dryness
- Sr purification on 3 mL Sr Resin column or cartridges (2 mL + 1 mL)

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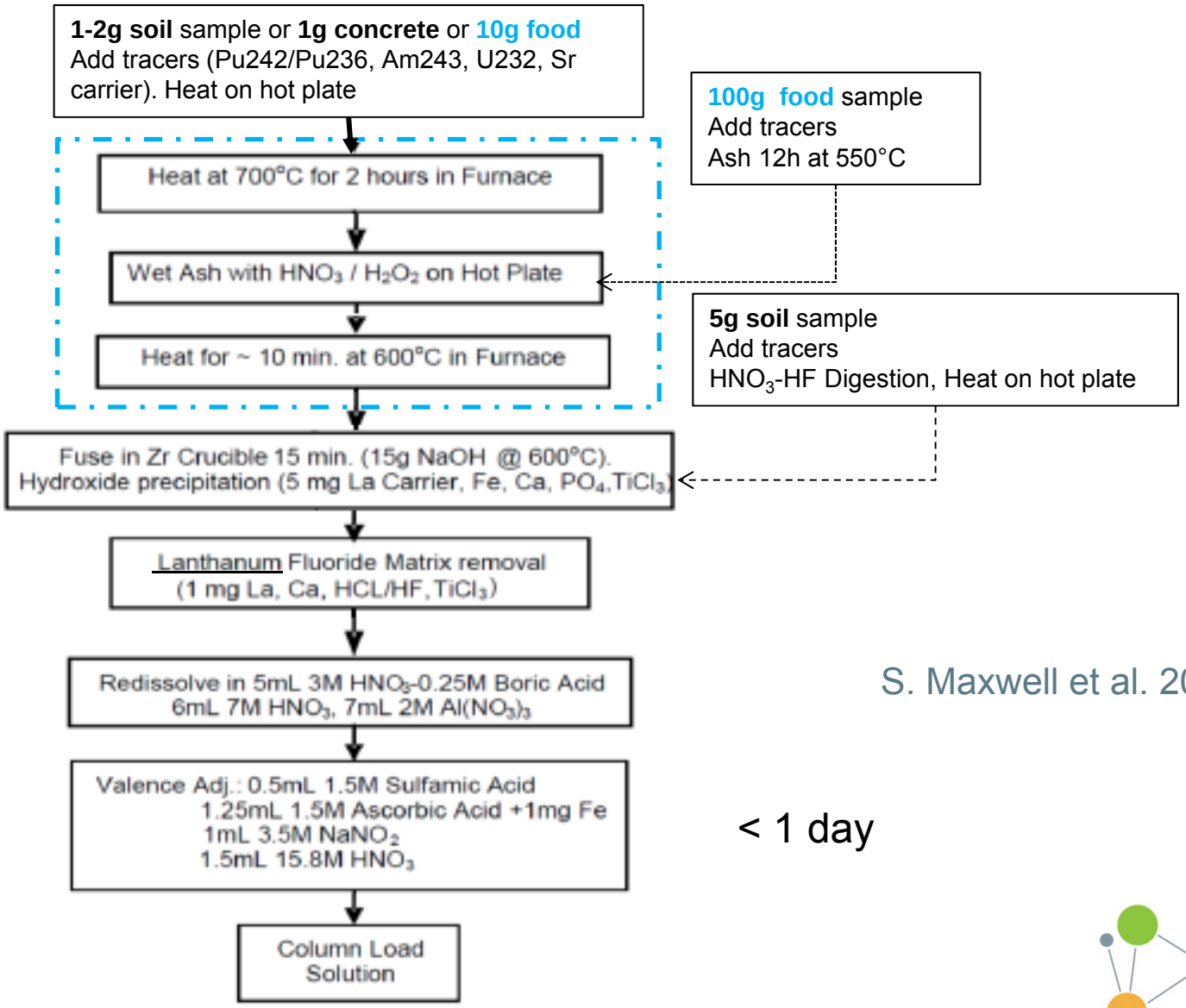
Sample preparation



S. Maxwell et al. 2011

< 1 day

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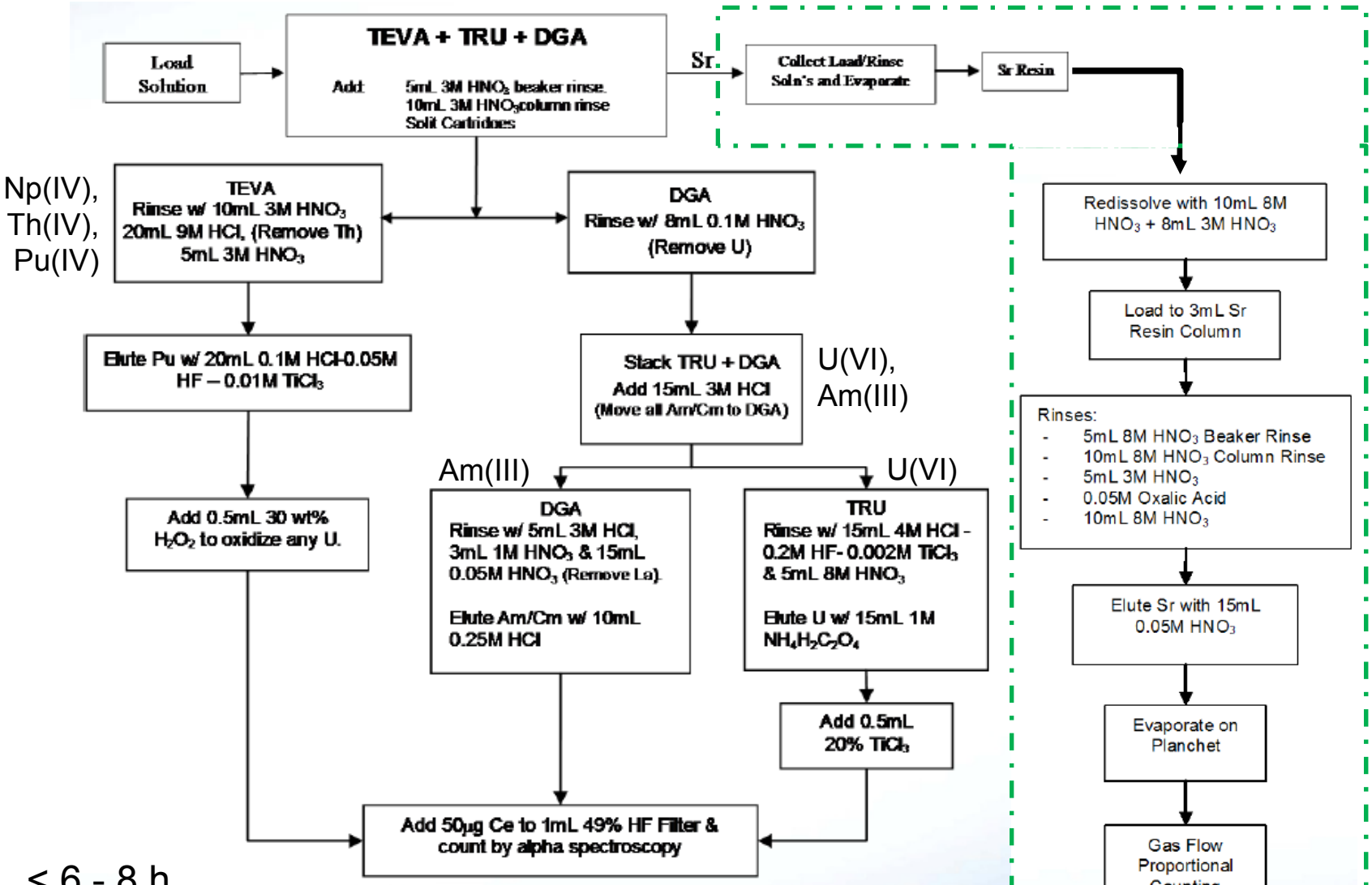
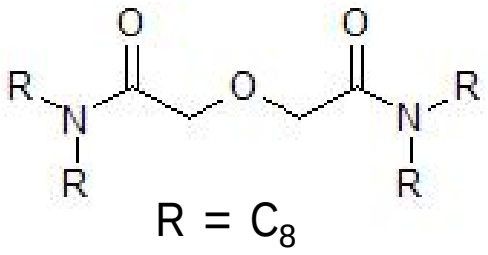
Separation scheme (Sr optional)

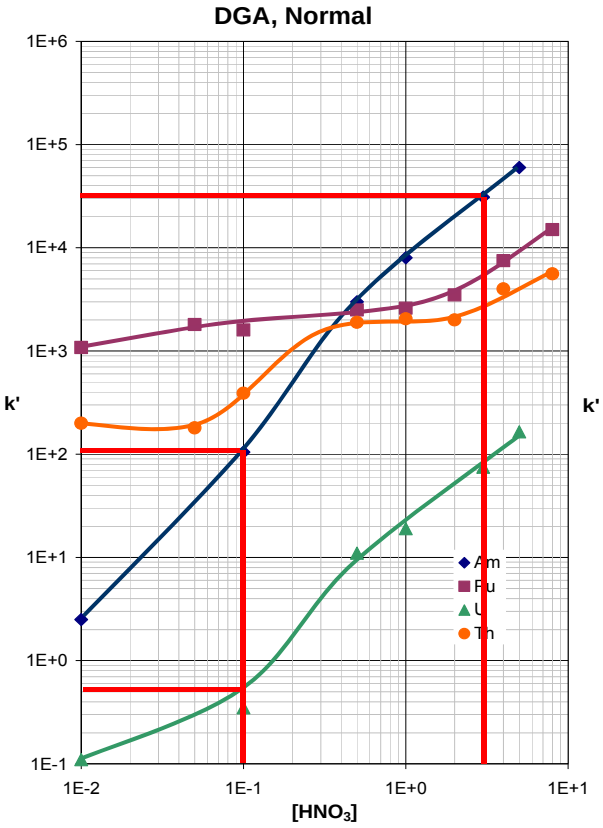


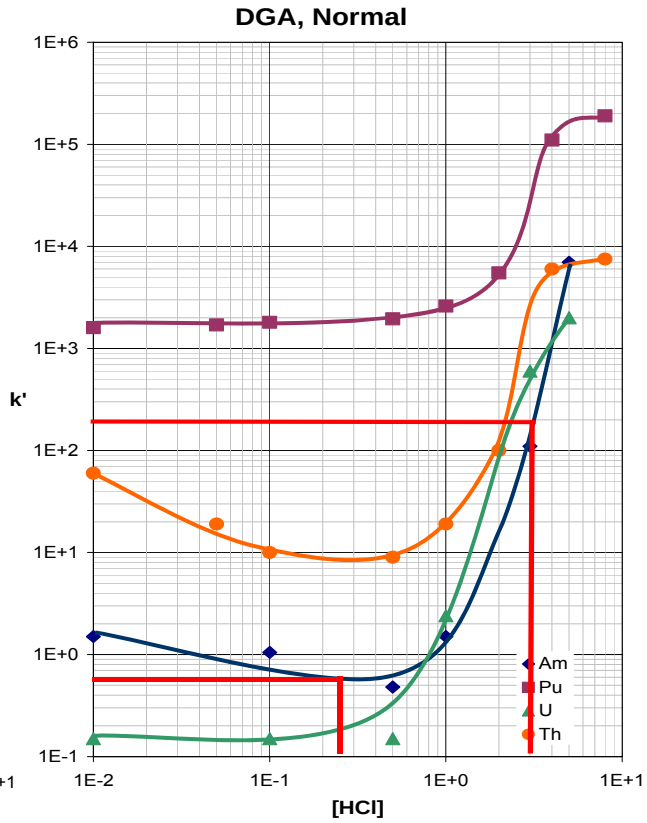
DGA Resin

Extractant



R = C_8





- DGA, Normal (*N,N,N',N'*-tetra-n-octyldiglycolamide), TODGA = DN
- High uptake of Actinides from 3M HNO_3
- Am / U separation with 0.1M HNO_3
- Am retained from 3M HCl
- Fe removal with 1M HNO_3 and La removal with 0.05M HNO_3
- Am elution with 0.25M HCl

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Method performance (MAPEP 18 samples)

- Good agreement (bias 15% ≤ B ≤ -15%)
- High yields for actinides, good yields for Sr

Sample Code	Am yield (%)	Pu yield (%)	U yield (%)	Sr yield (%)
MAPEP-18 soil	96.2±6.33	102.2±10.5	84.0±5.64	60.0±2.8
MAPEP-20	na	na	na	66.0 +/- 6.0
10g baby food	84.6±7.5	93.5±8.1	77.9±13.1	na
10g apple	93.4±9.1	97.5±12.1	88.9±10.9	na
10g squash	88.5±3.5	97.5±5.9	77.9±13.1	na
MAPEP-18 concrete	85.3±6.5	89.6±7.9	76.9±4.4	na
MAPEP-18 brick	93.7±2.9	94.7±9.0	88.1±5.4	na

S. Maxwell, 2010/11

- MAPEP: 15 – 30 mBq.g^{-1} level
- Results in < 1d
- Method can be adapted to ICP-MS

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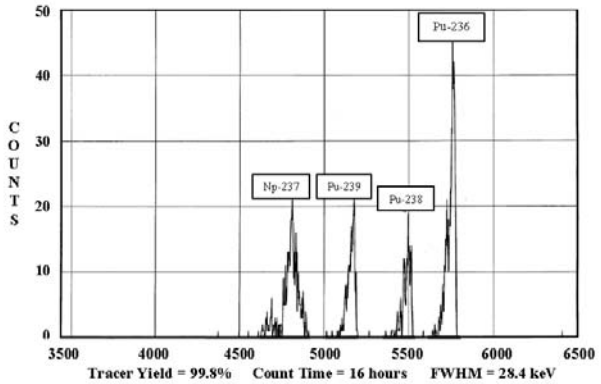
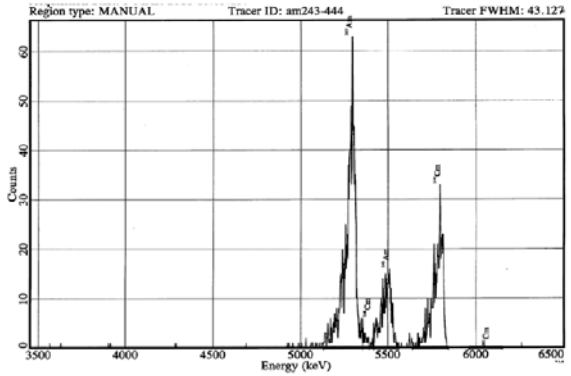
Alpha spectra

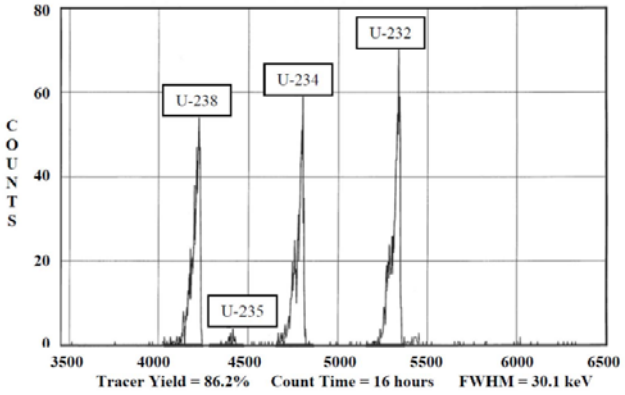
Pu and Np spectra for concrete sample



Am and Cm spectra for concrete sample



U isotope spectra for concrete sample



Alpha spectra, concrete sample
Microprecipitation

S. Maxwell, 2011

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Sr in large soil and sea water samples

Maxwell S L, Culligan B K, Shaw S J: Rapid determination of radiostrontium in large soil samples, Journal of Radioanalytical and Nuclear Chemistry (2012) DOI10.1007/s10967-012-1863-2

Maxwell S L, Culligan B K: Rapid determination of Radiostrontium in large soil samples, 31/10/12, 58th Annual RRMC, Fort Collins, CO October 29 to November 2, 2012

Maxwell S L, Culligan B K, Utsey R C: Rapid method for the determination of Radiostrontium in sea water samples, 31/10/12, 58th Annual RRMC, Fort Collins, CO October 29 to November 2, 2012

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Rapid Determination of Radiostrontium in Large Soil Samples

S. L. Maxwell and B. K. Culligan
Savannah River National Laboratory
October 31, 2012

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

50 g samples

For smaller samples (25 g) also use of HF

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

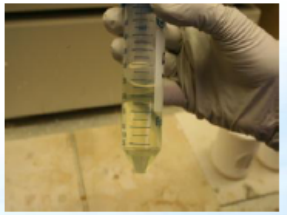
Add 40mL 1.5M HCl. Dilute to 170mL with 0.01M HCl

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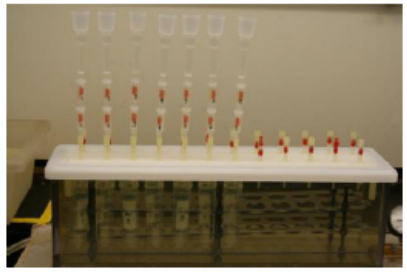
Rapid Sr-89, Sr-90 Column Separation Method for Soil



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

SRNL

Maxwell et al. 2012

Results spiked soils samples

- Leached 50g soil samples:
  - 5.92 mBq.g^{-1} level
    - Yield: 94.0% (+/- 2.6%, N=7), Bias: 0.43%,
    - MDC: 0.41 mBq.g^{-1} for 90 min count
  - 11.84 mBq.g^{-1} level
    - Yield: 89.6% (+/- 2.7%, N=7), Bias: -2.51%,
    - MDC: 0,17 mBq.g^{-1} for 8h count
  - 59.2 mBq.g^{-1} level
    - Yield: 89.3% (+/- 5,3%, N=7), bias: -2,36%
- 25g HF digest
  - 11.84 mBq.g^{-1} level
    - Yield: 73,0% (+/- 5,1%, N=7), Bias: 6,14%,
    - MDC: 0,17 mBq.g^{-1} for 8h count

➢ All results corrected for 1.35 mBq.g^{-1} Sr-90 found in unspiked soil

➢ High Pb samples: hold before measurement or pass through 1 mL DGA cartridge for Bi removal

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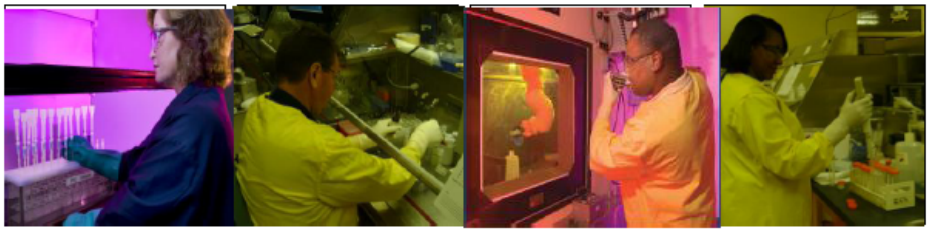
Rapid Method for Determination of Radiostrontium in Seawater Samples

S. L. Maxwell, B.K. Culligan, and Robin. C. Utsey
Savannah River National Laboratory
October 31, 2012



Radiostrontium in sea water

- Sea water: 7 – 8 mg Sr / L, 400 mg Ca / L
- ICP-MS for yield
- Preferably samples > 1L for low detection limits
- Preconcentration by coprecipitation
- 2 options for separation:
  - Sr-89/90: combined Sr/DGA resins
  - Sr-90 only: DGA resin
- Measurement via GPC (LSC or Cerenkov also possible)

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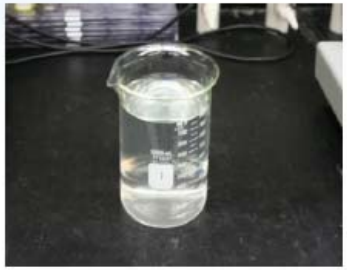
Rapid Sr-89/90 Sample Preparation Method for Seawater



Seawater Sample (1L)

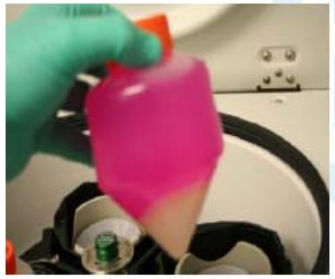
Filter

→ ICP-MS Assay for Stable Strontium

↓

Add 1mg stable Y
Add 200mg Fe
Add 15mL 3.2M $(NH_4)_2HPO_4$

*2L: higher PO_4



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Adjust pH to ~ 10, Centrifuge in 500mL tubes

↓

Re-dissolve $Ca_3(PO_4)_2/Fe(OH)_3$ ppt. in 25mL 15.8M HNO_3

↓

Add 8mL 2M $Al(NO_3)_3$ and evaporate to 25mL volume

↓

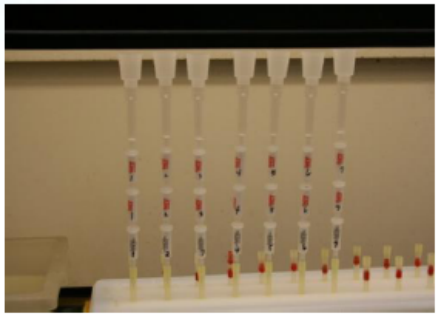
Adjust to 35ml volume using 1M HNO3 (beaker rinse)

↓

Centrifuge to remove any trace solids (sand) LOAD SOLUTION

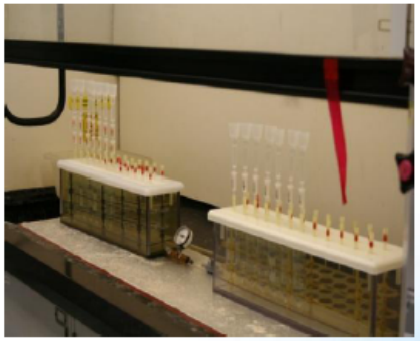
<4 hours!

SRNL



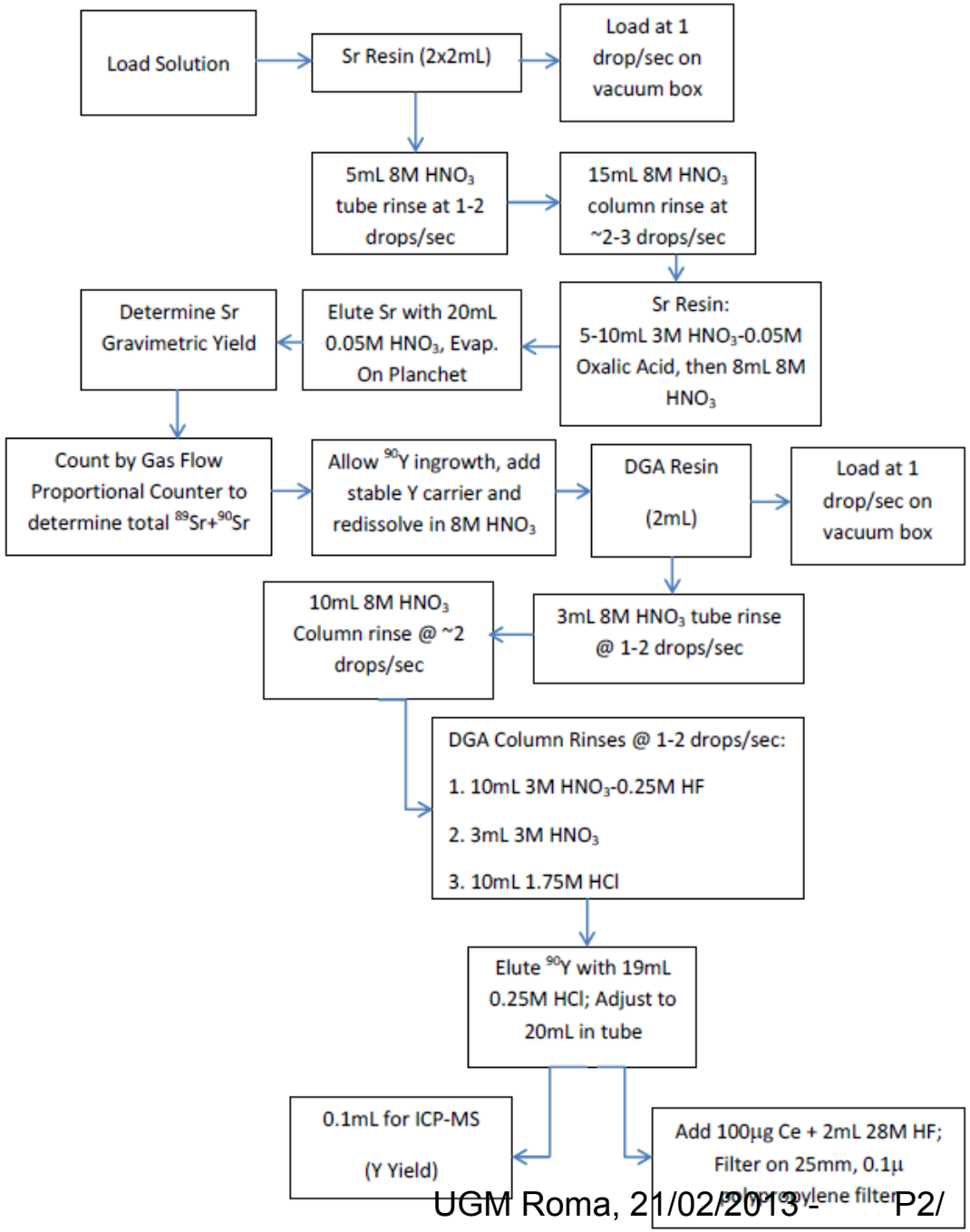
Shows stacked option

If present, ^{91}Y is a problem!
If agree, confirmatory but better to allow ingrowth, then separate Y-90



Maxwell et al. 2012

Or allow ingrowth and separate ^{90}Y



Y-90 ingrowth option

- SRNL prefered option for high Sr-89 and low Sr-90
- Y-91 no problem

Personal communication
Sherrod Maxwell, 2013

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Results Sr-89/90 option

- 1L spiked sea water sample (7,66 mg $Sr.L^{-1}$), 4 mL Sr resin:
  - 2h counting time
  - Measurement via Sr-90: Yield: 88,8% (+/- 5,9%, N = 11), Bias: 1,2%
  - Measurement via Y-90: Yield: 95,0% (+/- 1,6%, N = 11), Bias: 3,1%
  - Good correspondance
- 2L sea water sample (7,70 mg $Sr.L^{-1}$), 6 mL Sr resin:
  - 2h counting time
  - Yield: 81,9% (+/- 5,0%, N = 4), Bias: 4,2%
- Measurement via GPC
- MDAs:
  - 1L sea water (2 x 2 mL cartridges)
  - 2L sea water (3 x 2 mL cartridges)
    - MDAs: 9.1 $mBq.L^{-1}$ (2h count), 4,4 $mBq.L^{-1}$ (8h count), 3.0 $mB.L^{-1}$ (1000 min count)
  - 6L sea water (three 2L aliquots combined after purification)
    - MDAs: 1.5 $mBq.L^{-1}$ (8h count), 1.0 $mB.L^{-1}$ (1000 min count)

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Sr-89/90 option

- Similar methods suggested for environmental water samples
  - Groska J, Molnar Z, Bokori E, Vajda N: Simultaneous determination of ^{89}Sr and^{90}Sr: comparison of methods and calculation techniques, Journal of Radioanalytical and Nuclear Chemistry, March 2012, Volume 291 (3),707-715
  - T. O'Brien et al.: The rapid determination of Strontium-89 and Strontium-90 in Environmental Samples. Presented at the MARC IX conferences, Kailua-Kona, USA, 29/03/12
- Measurement by Cerenkov counting possible
  - Sr-89 and Y-90 via Cerenkov
  - Very low interference of Sr-90 on Sr-89
  - Advantageous in case of high Sr-89/90 activity ratios

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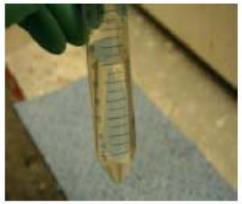
Rapid Column Separation for ^{90}Sr (^{90}Y) – DGA Only Option



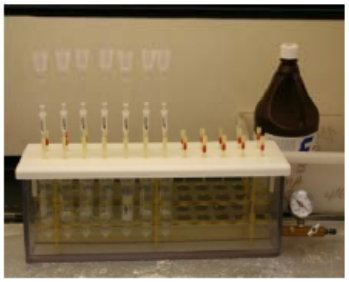
Column Load Solution

Avoids stable Sr limitation

DGA Resin (2mL)

Load at 1 drop/sec on Vacuum Box

3mL 8M HNO_3 tube rinse @ 1-2 drops/sec



10mL 8M HNO_3 Column rinse @ ~2 drops/sec

Collect load plus rinse solutions. Adjust to 50mL with 8MHNO_3

Take 0.1mL for ICP-MS (Sr Yield)

Column Rinses:

1. 15mL 3M HNO_3-0.25M HF
2. 3mL 3M HNO_3
3. 15mL 1.75M HCl

@ 1-2 drops/sec

Wait 7-10 Days for ^{90}Y ingrowth. Separate using DGA Resin again.

0.1mL for ICP-MS (Yield)

Elute ^{90}Y with 19mL 0.25M HCl; Adjust to 20mL in Tube

Add 100µg Ce + 2mL 28M HF; Filter on 25mm, 0.1µ polypropylene filter

Maxwell et al. 2012

Sr-90 (Y-90) DGA resin only option

- **1 to 10 liter method (DGA Resin only)**
  - 2 liter aliquot requires one 2 ml DGA Resin cartridge
    - *MDA with GFPC and 120 minute count = 9.1 mBq/L*
    - *MDA with GFPC and 480 minute count = 4.4 mBq/L*
    - *MDA with GFPC and 1000 minute count = 3.0 mBq/L*
  - 10 liter aliquot (5 x 2 liter aliquots combined after purification)
    - *MDA with GFPC and 480 minute count = 0.88 mBq/L*
    - *MDA with GFPC and 1000 minute count = 0.61 mBq/L*
  - *< 1mBq/L ^{90}Sr with 10L seawater aliquot and < 6 hour sample preparation*

Rapid Method for Sr-90 in Seawater – DGA Resin only

Sample ID	Smp Vol. (L)	Y carrier (%)	^{90}Sr Reference Value (pCi L^{-1})	^{90}Sr Reference Value (mBq L^{-1})	^{90}Sr Measured Value (mBq L^{-1})	Difference (%)
1	4	91.6	20.0	740	725	-2.0
2	4	88.7	2.0	74	74	0.1
3	10	94.3	2.0	74	74	0.0
4	10	94.5	2.0	74	66	-10.8
5	10	90.2	2.0	74	76	2.7
	Avg	91.9				-2.0
	SD	2.54				
	% RSD	2.76				
	Y carrier by ICP-MS					
	2 hour count time					

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