Rapid methods for the analysis of environmental, decommissioning and bioassay samples – an update

S. Happel

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Actinides and Sr in soil, food, concrete and brick samples (decommissioning and emergency 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

S. L. Maxwell and B.K. Culligan: Rapid Method for Determination of Actinides in Fecal Samples, 31/10/12, 58th Annual RRMC, Fort Collins, CO October 29 to November 2, 2012

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Rapid Fusion Method for Concrete, Brick, Soil Validated by US EPA

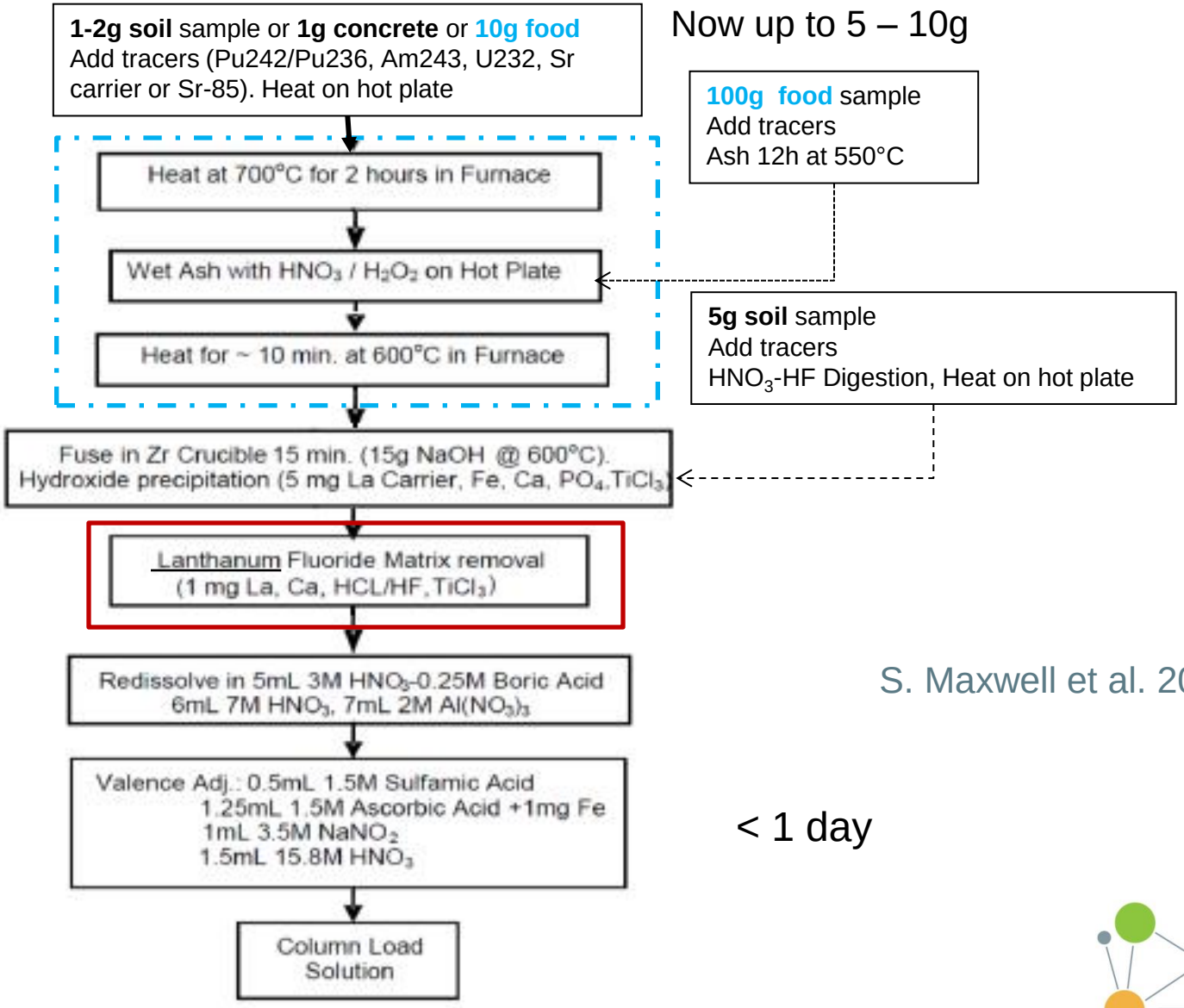
Rapid Method for Sodium Hydroxide Fusion of Concrete and Brick Matrices Prior to Americium, Plutonium, Strontium, Radium, and Uranium Analyses for Environmental Remediation Following Radiological Incidents

U.S. Environmental Protection Agency

Office of Air and Radiation
Office of Radiation and Indoor Air
National Analytical Radiation Environmental Laboratory
Montgomery, AL 36115

Office of Research and Development
National Homeland Security Research Center
Cincinnati, OH 45268

Sample preparation



S. Maxwell et al. 2011

< 1 day

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Fluoride co-precipitation

- Carrier: Lanthanides and/or Ca
- Co-precipitate actinides and Sr
- U(IV) precipitates, U(VI) does not
  - Control of oxidation state allows for U discrimination
  - Ti(III) as reducing agent, H_2O_2 as oxidizing agent
- Many matrix elements do not co-precipitate
  - Fe, Al, Ti,..

- Problematic: Use of HF
  - can be replaced by NaF/NH_4F

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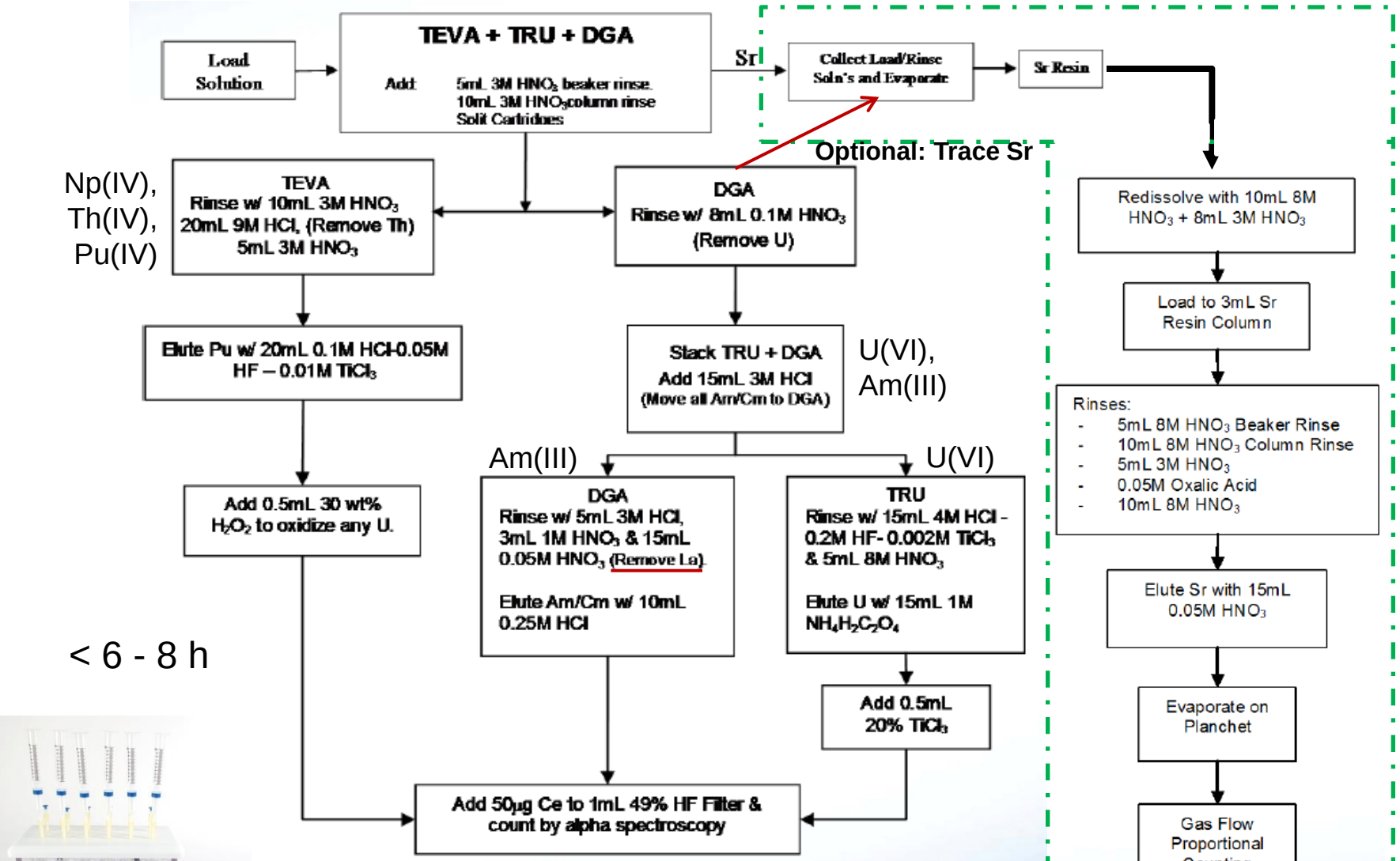
Separation scheme (Sr optional)

Pu, Np, Th: TEVA
Pu, Np, U, Th :TEVA+TRU
Pu, Np, Am, Cm :TEVA+DGA



< 6 - 8 h

S. Maxwell et al. 2011

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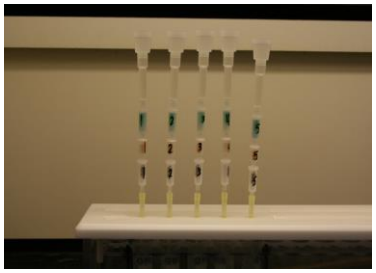
Rapid Purification of Pu for ICP-MS



Column Load Solution

TEVA Column → 3mL 3M HNO_3 30mL3M HNO_3 15mL 9M HCl Discard Rinses

Add UTEVA + DGA Cartridge

TEVA + UTEVA (1mL) + DGA → 20mL 2.7M HNO_3 – 0.1M Ascorbic Acid – 0.02M Fe^{+2} Discard Rinse (Pu^{+3} to DGA)

Split Cartridges Discard UTEVA

DGA (Pu) → 5mL 8M HNO_3 20mL 0.1M HNO_3 Discard Rinse

Elute Pu 5mL 0.02M HCL- 0.005M HF- (+0.02M HH)

Pu by ICP-MS

>10^6 removal of U-238 from Pu-239

Health Physics Journal, August 2011 – Vol 101 - Issue 2 - pp 180-186

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 spiked concrete	85.3±6.5	89.6±7.9	76.9±4.4	na
MAPEP-18 spiked brick	93.7±2.9	94.7±9.0	88.1±5.4	na
NRIP fecal	82.7±3.9	96.4±8.2	62.5±7.2	na

S. Maxwell, 2010/11

- Results in < 1d – 2d
- Method can be adapted to ICP-MS

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Actinides in seawater

J Radioanal Nucl Chem (2014) 300:1175–1189
DOI 10.1007/s10967-014-3079-0

Rapid determination of actinides in seawater samples

Sherrod L. Maxwell · Brian K. Culligan ·
Jay B. Hutchison · Robin C. Utsey ·
Daniel R. McAlister

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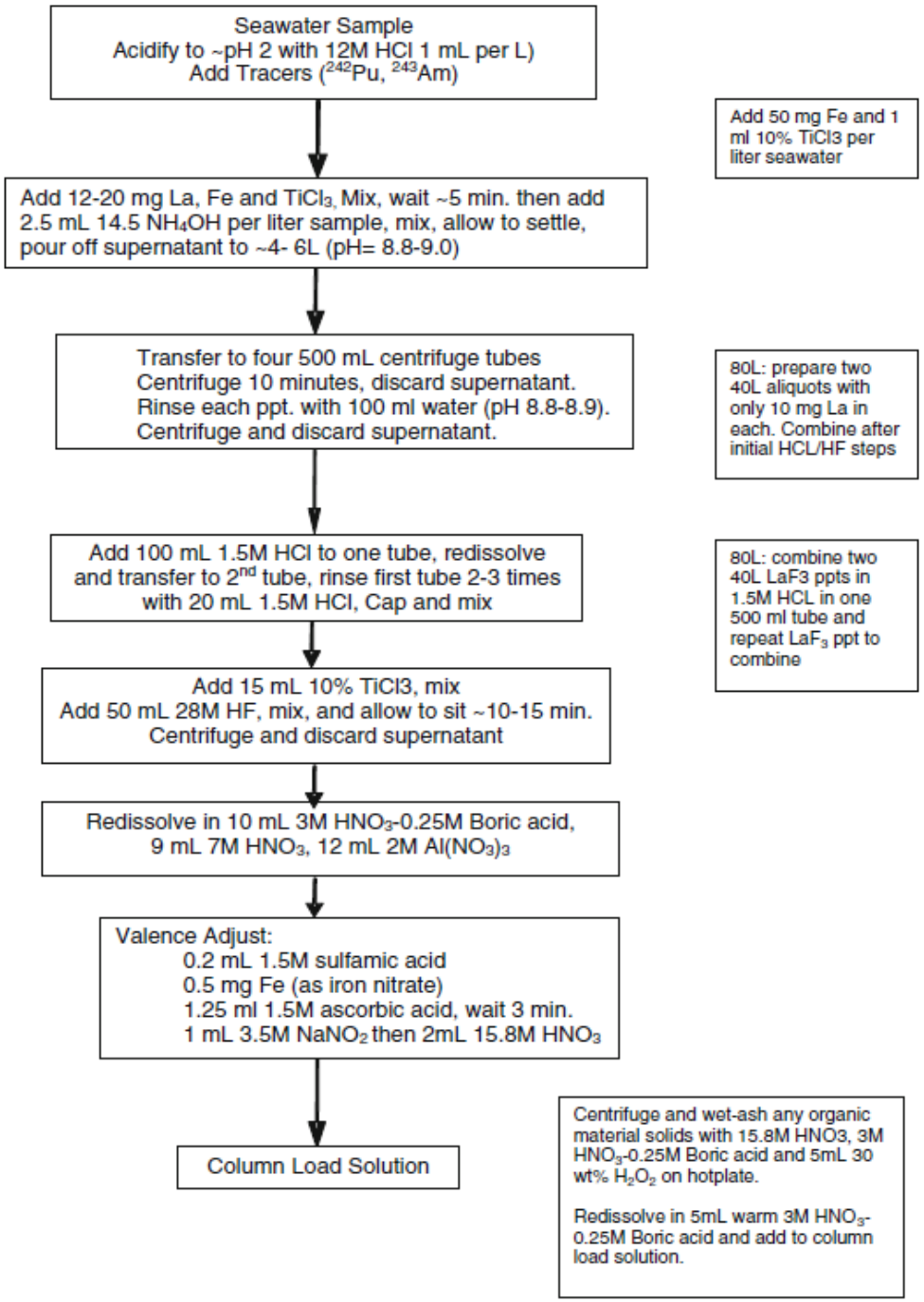
Sample preparation



- Applicable to 40 – 80L samples
  - can be simplified for 8L samples
  - Less La -> less DGA necessary
- Sample preparation in 4 – 8h
- Tracer yields between 85% and 95%

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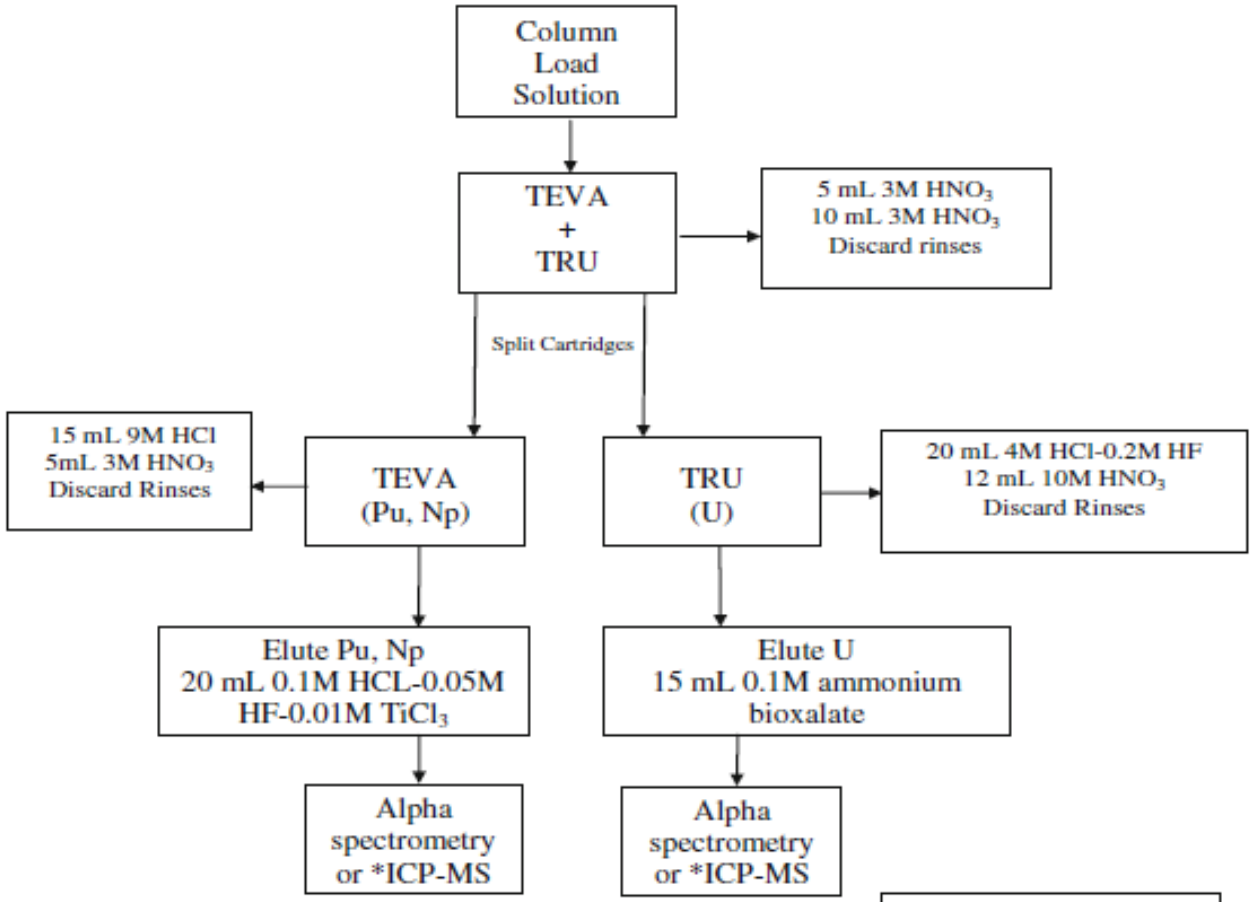
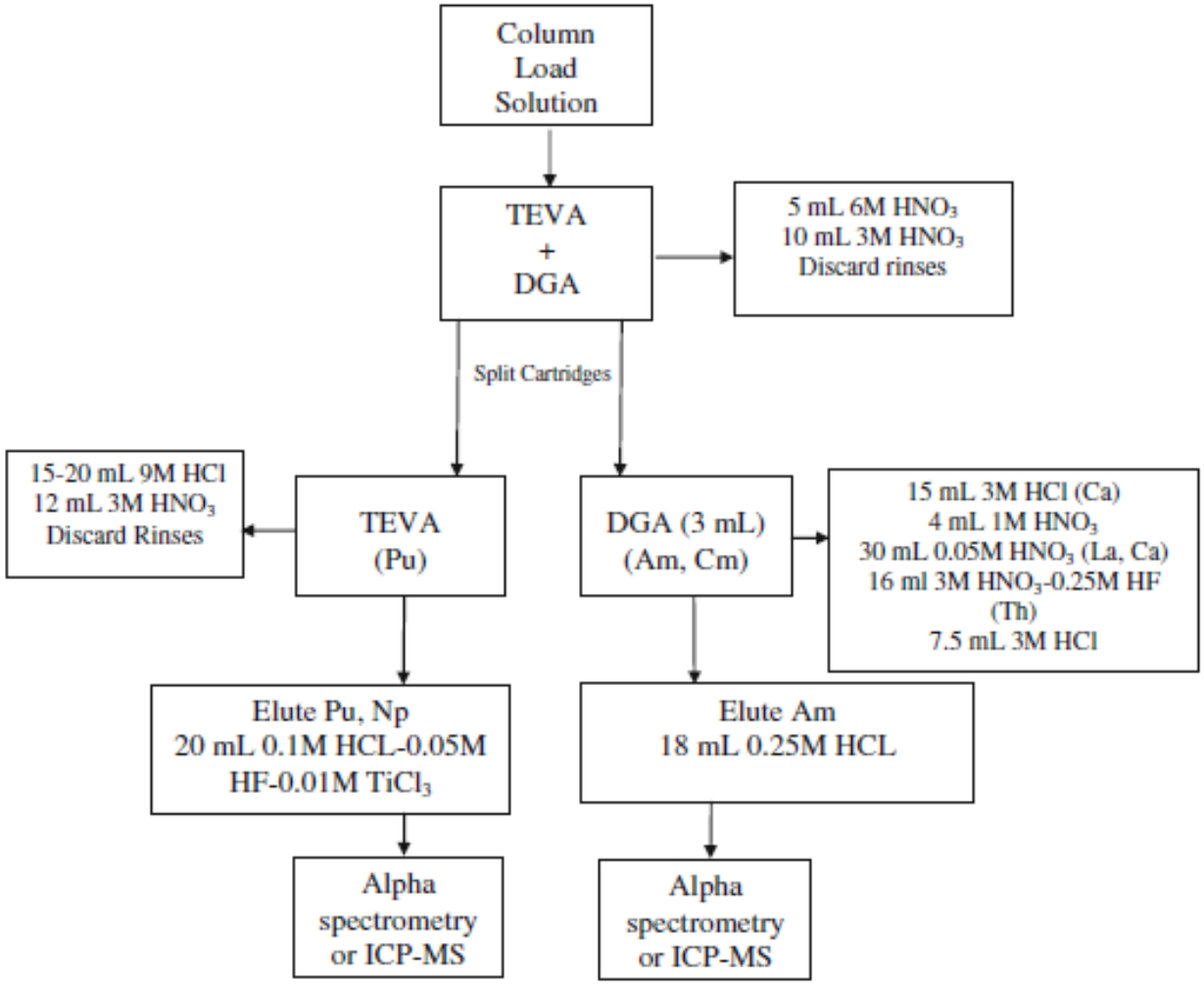
U, Pu/Np in 8L samples



Pu/Np, Am/Cm in 40 - 80L samples



When 40L seawater aliquots are combined to get 80L, 4mL DGA Resin is needed to handle the amount of La added. DGA rinse volumes and final eluent are increased proportionally.

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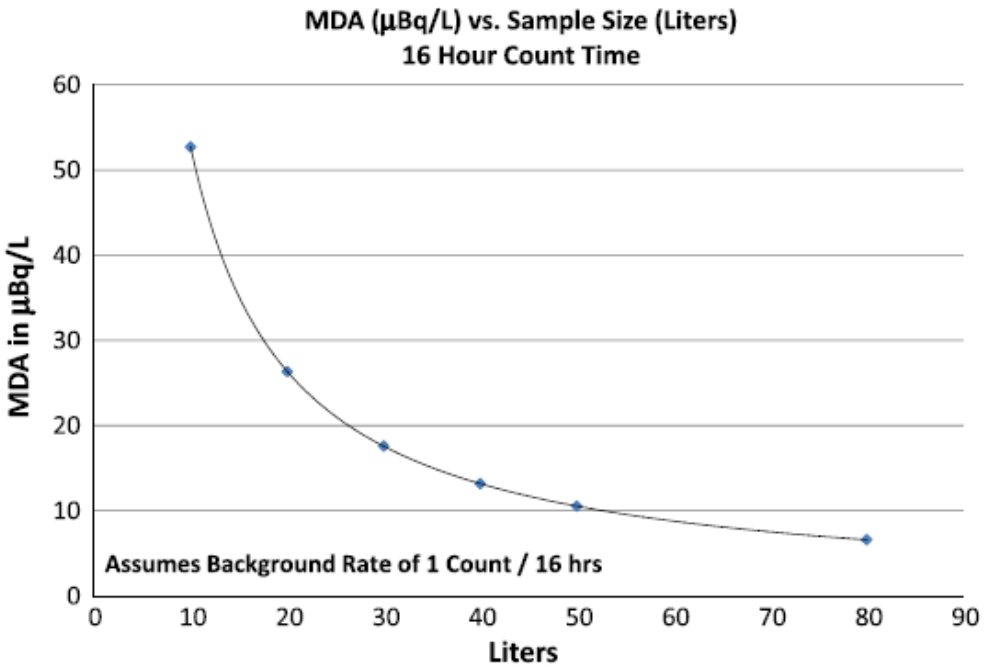
- Methods tested up to 80L
- Resin combination in function of radionuclides to be determined
- Tests on spiked reral samples (various volumes and activity levels)

➢ TEVA/TRU method (1 – 8L)
  – Pu-239: R_C = 89.3 ± 9.7%, Bias: -3.5 ± 3.7%
  – Np-237: R_C = 89.8 ± 9.4%, Bias: 1.8 ± 11.2%
  – U-238: R_C = 94.7 ± 6.3%, Bias: -4.4 ± 2.6%

➢ TEVA/DGA method (16 – 80L)
  – Pu-239: R_C = 86.4 ± 4.6%, Bias: -0.3 ± 8.0%
  – Am-241: R_C = 94.0 ± 3.6%, Bias: -
  – Cm-244: R_C = 94.0 ± 6.3%, Bias: -

➢ TEVA method (10 – 20L)
  – Pu-239: R_C = 91.1 ± 5.9%, Bias: -
  – Np-237: R_C = 91.1 ± 5.9%, Bias: -

- Detection limit in function of sample volume for 16h count



Sr-90 in seawater samples

J Radioanal Nucl Chem
DOI 10.1007/s10967-014-3391-8

Rapid determination of ^{90}Sr in seawater samples

Sherrod L. Maxwell · Brian K. Culligan ·
Jay B. Hutchison · Robin C. Utsey ·
Daniel R. McAlister

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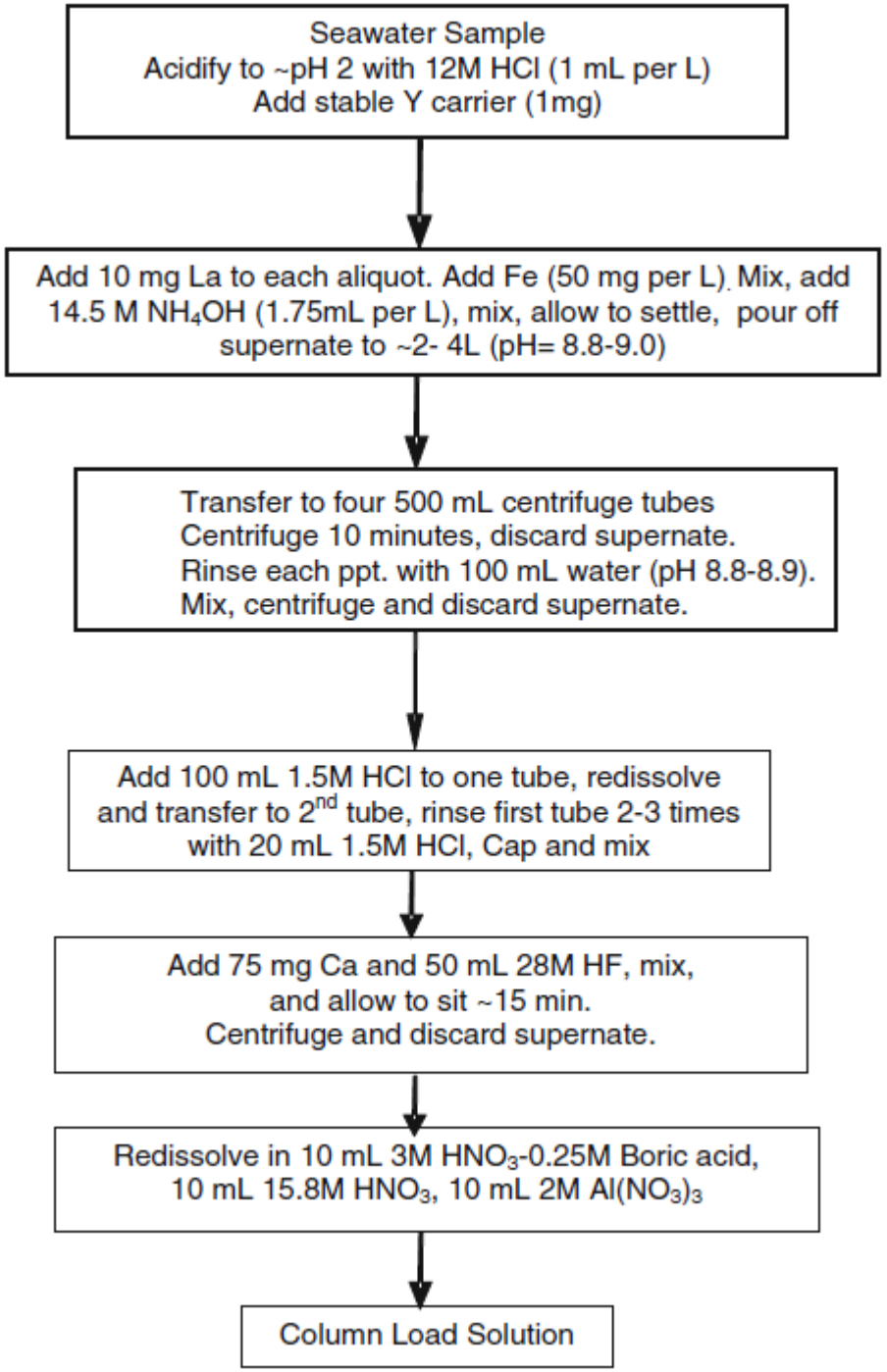
Sample preparation



- Challenge: seawater contains high amounts of Sr and Ca
  - Sample volume for use of Sr resin limited
- Applicable to 40L samples
  - Sr-90 via Y-90
  - Separation on DGA
  - No Sr-89!
- Sample preparation in <8h

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Column Load Solution

DGA Resin

(2mL)

Load at 1 drop/sec on Vacuum Box

5mL 8M HNO_3

tube rinse @

1-2 drops/sec

15mL 8M HNO_3

(removes Ca, Sr, Pb)

Column rinse @ ~2 drops/sec

Column Rinses:

1. 20 mL 0.05M HNO_3 (removes La, Ca, Sr, U)
2. 15mL 3M HNO_3-0.25M HF (removes U, Th)
2. 10mL 3M HCl (removes Ca, La, Pb)

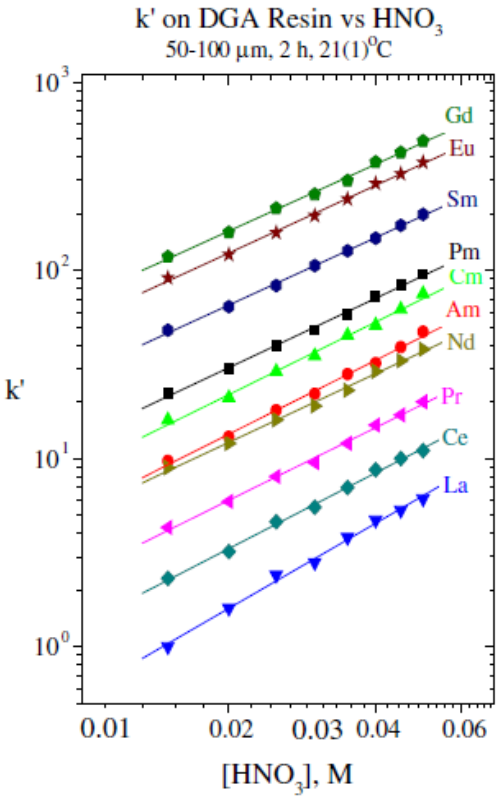
@ 1.5-2 drops/sec

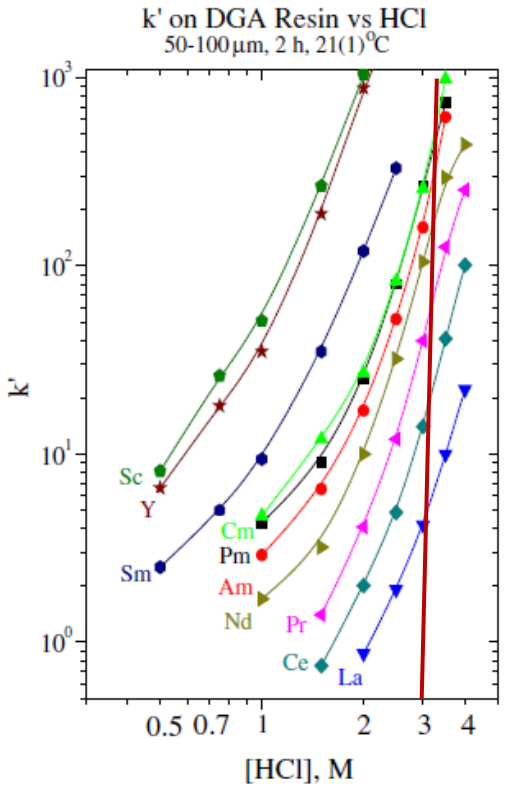
0.1mL for ICP-MS in 50 ml tube

(Yield)

Elute ^{90}Y @ 1 drop/sec with 19mL 0.25M HCl; Adjust to 20mL in tube

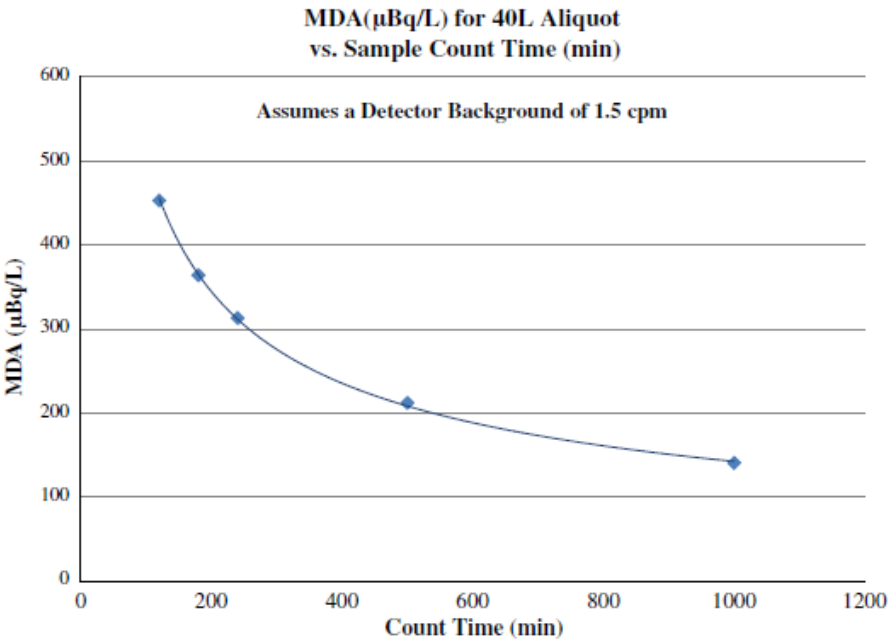
Add 100µg Ce + 2mL 28M HF; Filter on 25mm, 0.1µ polypropylene filter

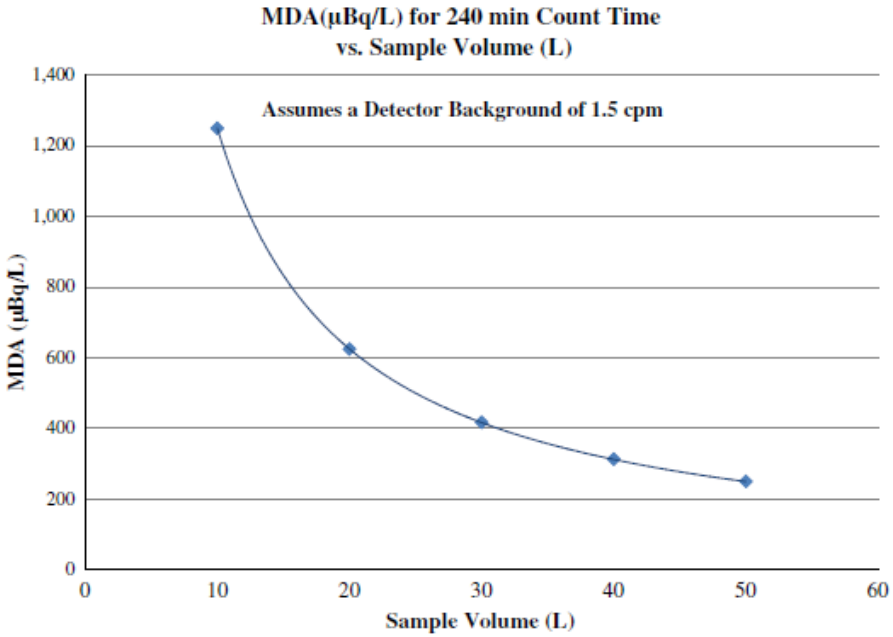




Optional: LSC or Cerenkov counting

- Sample preparation: $Fe(OH)_3$ and CaF_2 co-precipitation
- Y separation on DGA, yield via ICP-MS
- Method applicable up to 40L
  - 80L when two 40L aliquots are combined
- Tested on spiked real samples
  - Varying volumes (10 – 40L) and activity levels (14.1 – 296 mBq/L)
  - RC(Y) = 84.2 ± 8.1%, Bias: -1.4 ± 2.9%
- Detection limits depend on counting time and sample volume
  - For GPC e.g.:





Sr-89/90 via SR/DGA

- Publications of Vajda et al and Maxwell et al.
- Stacked SR/DGA cartridges
- Load from 8M HNO_3
- Sr retained and purified on SR resin
- Y retained and purified on DGA resin
- Both fraction analysed by Cerenkov counting
  - Sr fraction: Sr-89
  - Y fraction: Y-90 -> Sr-90
- Advantageous in case of high Sr-89/Sr-90 activity ratios
  -> Y-91

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Rapid Method for ^{226}Ra in Urine Samples

Sherrod L. Maxwell
Senior Fellow Scientist

Radiobioassay and Radiochemical Measurements Conference 2013 – Rohnert Park, Ca
10/25/13

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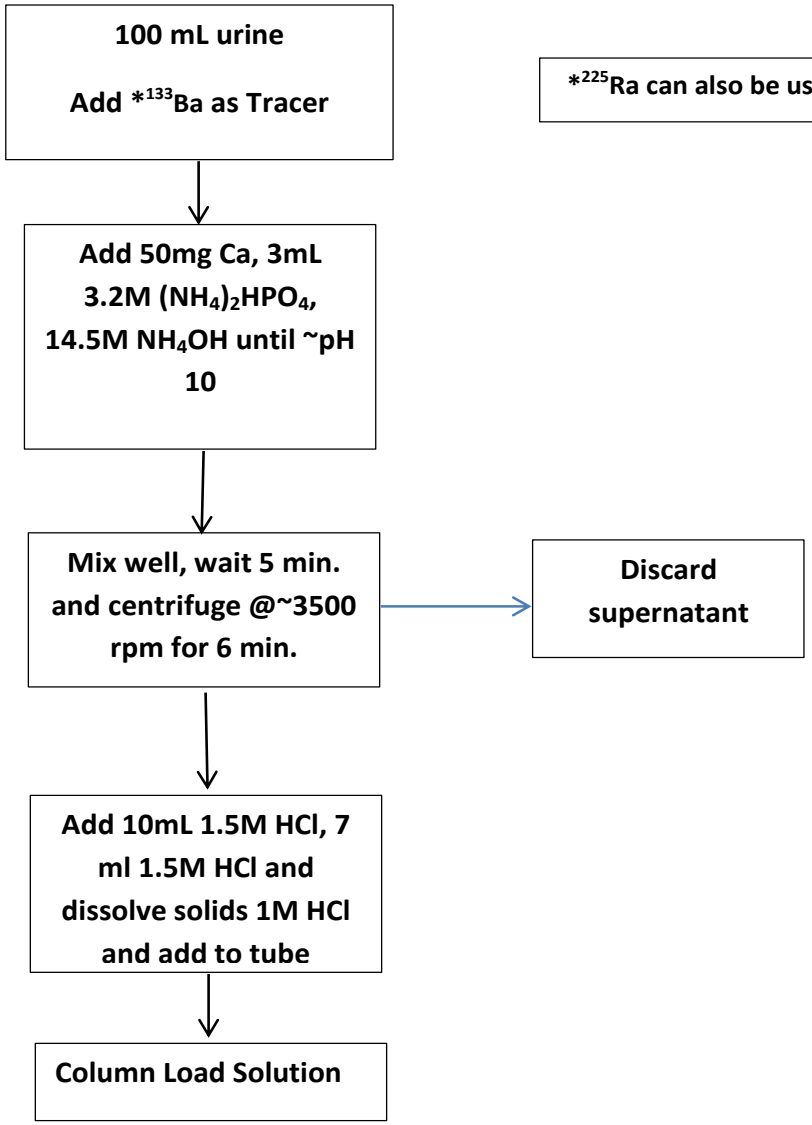
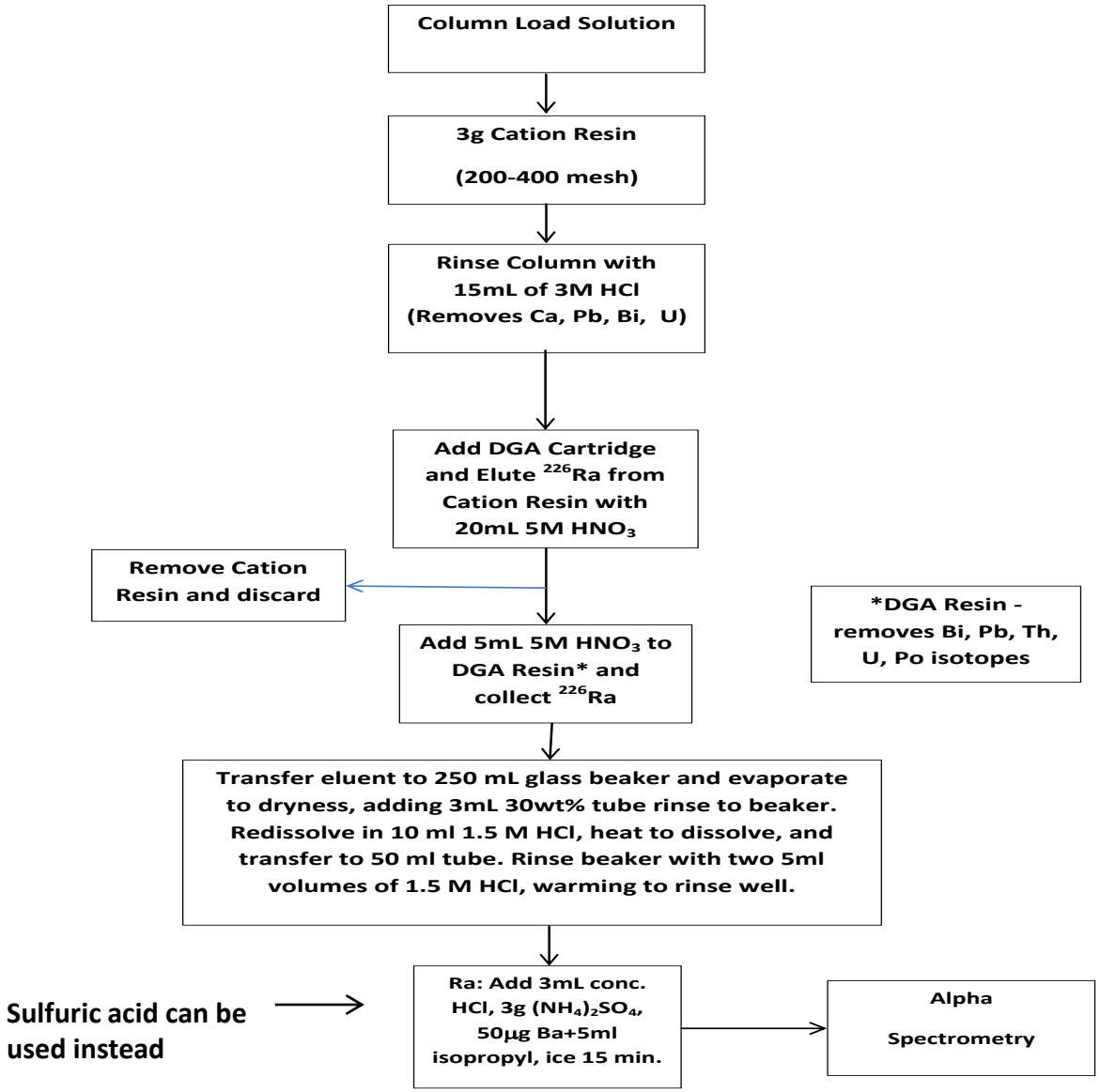
Rapid Sample Preparation for Ra-226 in urine

Less Ca, PO_4 instead of carbonate



Rapid Column Separation for Ra-226 in urine



- Improvement of existing method (Maxwell et al. 2011) for Ra-226 in urine
  - Use calcium phosphate to lower blank levels and reduce Ca (less cation resin)
  - Use DGA Resin to make method more rugged regarding evaporation steps
  - Combine cation resin elution with DGA Resin final purification of Ra-226
    - Stacked elution means only one evaporation step
    - Effective removal of U, Th, Po isotopes
  - High chemical yields
    - Spiked 100 mL urine samples (N = 6), two activity levels
    - c_A(Ra-226) =75.5 mBq/L^{-1} ± 6.1% , bias = 3.9%, R_C = 92.8% ± 3.2%
    - c_A(Ra-226) =17.9 mBq/L^{-1} ± 4.5% , bias = -2.7%, R_C = 98.0% ± 2.6%
    - U + Po decontamination > 500
  - < 3 hours with simultaneous sample preparation -> Ra-224
- Ba-133: No waiting for in-growth (but Ra-225 can be used if preferred)
- Can be adapted to smaller or larger urine aliquots as needed
  - Smaller aliquot if less urine available (spot urine sample)
  - Large aliquot if lower MDA needed

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Rapid Determination of ^{210}Po in Water Samples

Sherrod L. Maxwell
Senior Fellow Scientist

Radiobioassay and Radiochemical Measurements Conference 2013 – Rohnert Park, Ca
10/24/13

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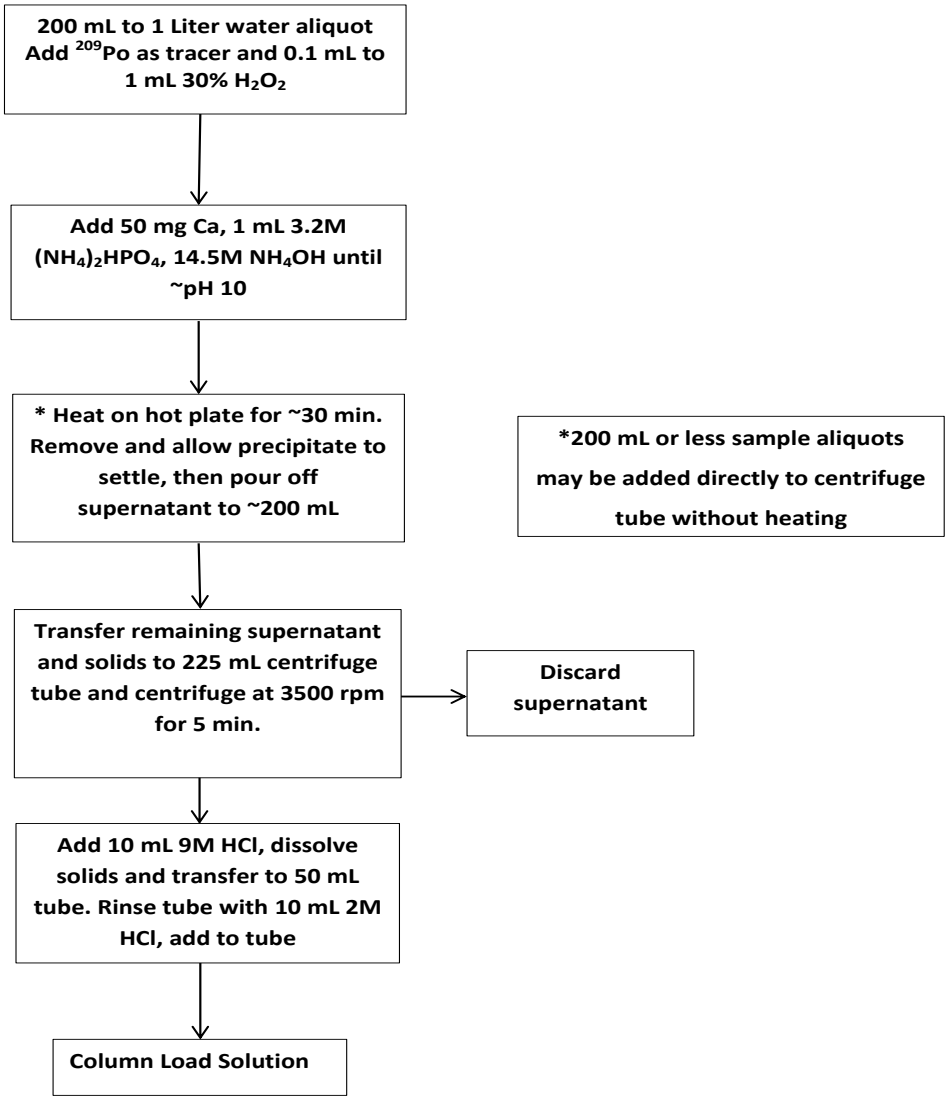
Rapid Sample Preparation Method for Po-210 in Water



Rapid Column Separation Method for Po-210

Column Load Solution

Add 100 µL 30 wt% H_2O_2 to ensure Po^{+4}

↓

Load to 2 mL DGA Resin cartridge @1 drop/sec

↓

Rinse DGA cartridge

-5mL 2M HCl tube rinse @1-2 drops/sec

-5mL 2M HCl column rinse @1-2 drops/sec

-15 mL 0.25M HCl @~2 drops/sec

-5 mL 6M HNO3 @~2-3 drops/sec

↓

Elute Po from DGA Resin with 15mL 0.05M HNO_3 @~1 drop/sec

↓

Add 125µg Bi

+ 50 µL 30 wt % H_2O_2

+ 200 µL 14.5M NH_4OH

+ 0.75 mL 3.2M $(NH_4)_2HPO_4$

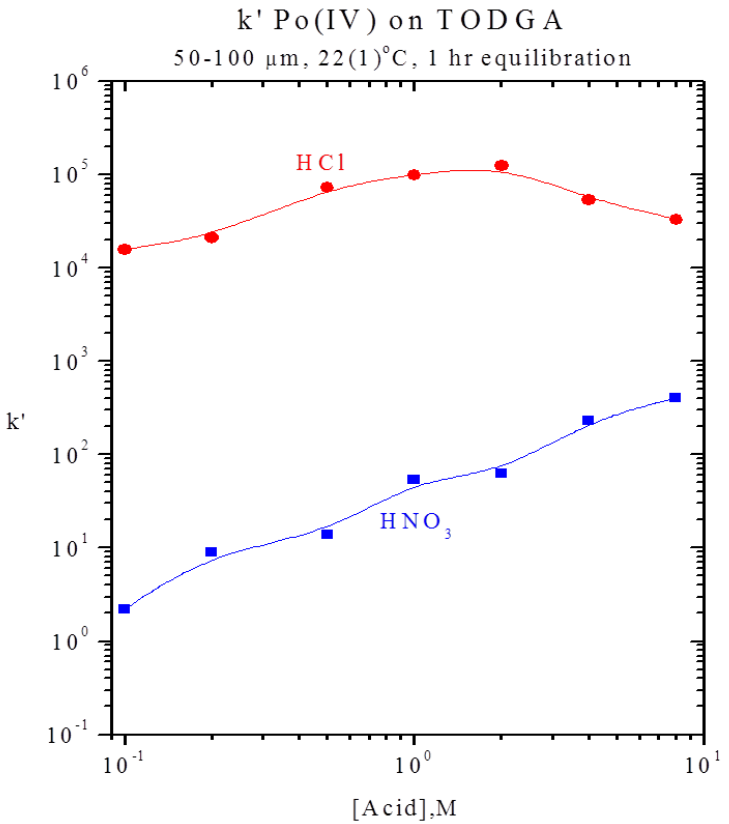
Cap and vortex, wait 15 minutes,

Collect $BiPO_4$ on 0.1 µm polypropylene filter

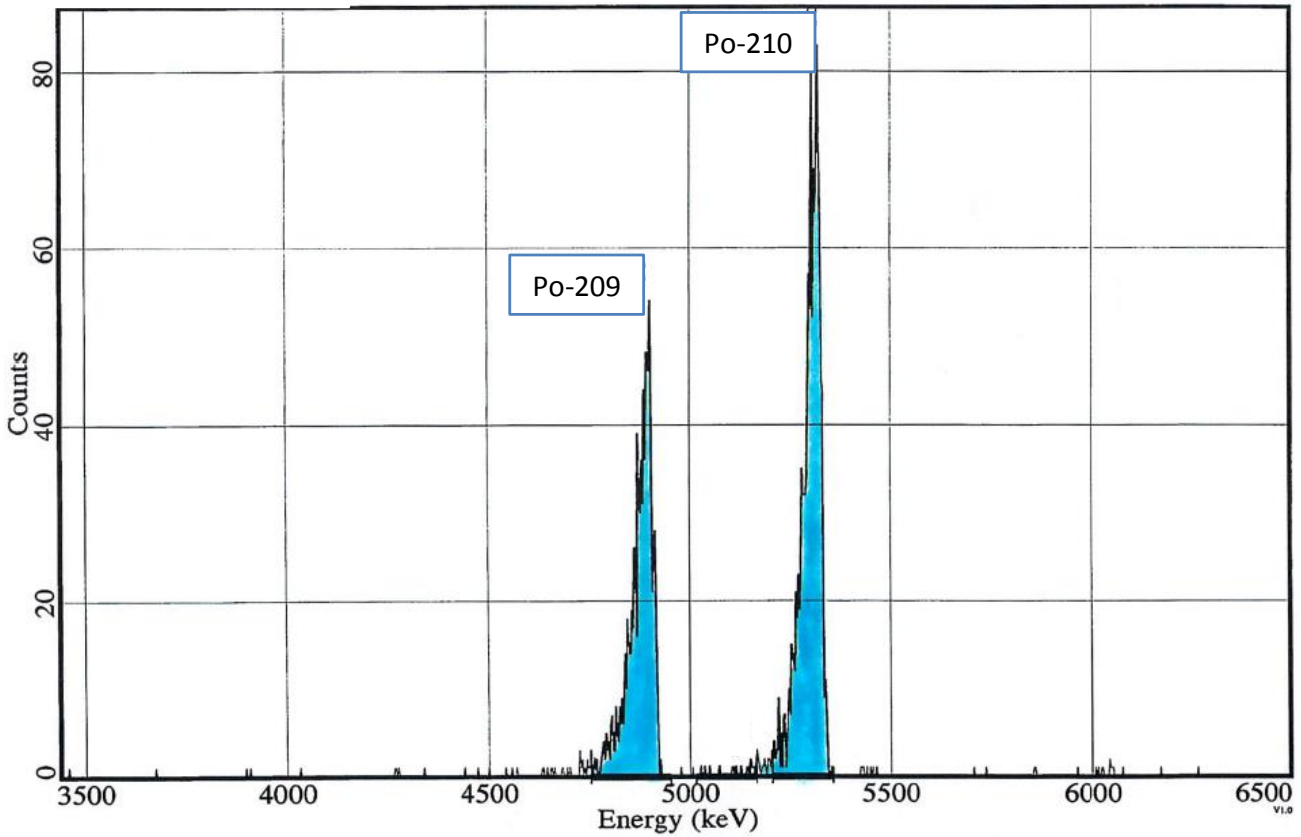
↓

Alpha spectrometry

*DGA Resin - removes Th, U, Ra, Pu, Am isotopes

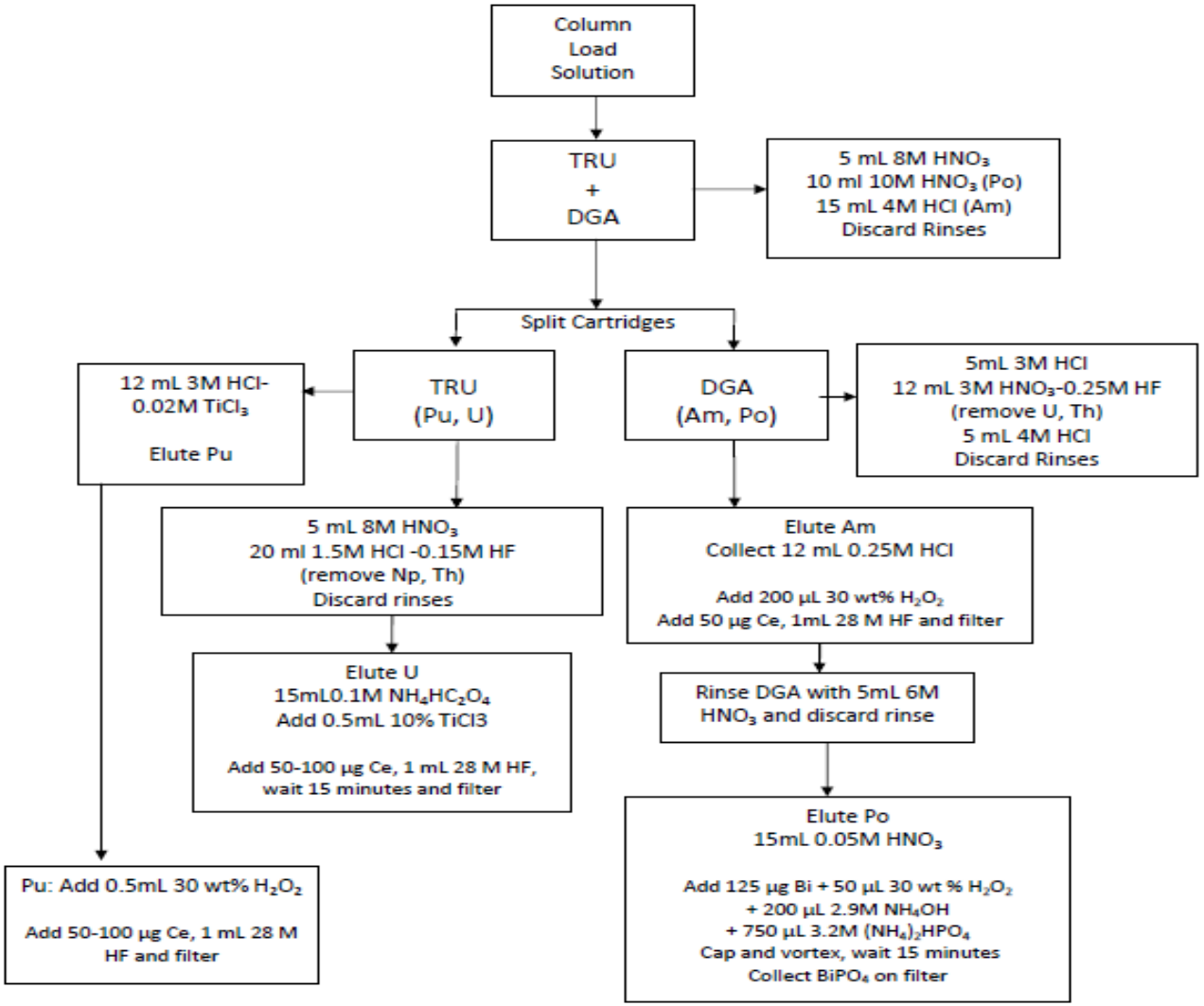


Po Isotopes - Bismuth Phosphate (125µg Bi) -1L Groundwater Sample



Yield = 87.0% **FWHM(Po-209)=46.0 keV**

Rapid Sequential Separation Method for Actinides and ^{210}Po in Water



- Rapid method:
  - Calcium phosphate precipitation *~15 min. to 1 hour (depending on sample volume)*
  - Separation on DGA Resin *~1 hour*
  - Microprecipitation using bismuth phosphate *~15 min*
  - Sample ready for counting in 1.5 – 2.5h

- Tested on 200 mL to 1000 mL samples
- Analysis of spiked groundwater samples (N = 6)
  - 200 mL: c_A(Po-210) =308.1 mBq/L^{-1} ± 4.8% , bias = -2,4%, R_C = 87.4% ± 5,8%
  - 1000 mL: c_A(Po-210) =61.5 mBq/L^{-1} ± 5.1% , bias = -2,8%, R_C = 85.0% ± 8.2%

- Sequential analysis of Po and actinides possible
- Analysis of spiked groundwater sample (N = 6)
  - c_A(Po-210) =1660.4 mBq/L^{-1} ± 2.9% , bias = 4.9%, R_C = 81.5% ± 2.6%
  - c_A(Pu-238) =381.1 mBq/L^{-1} ± 4.0% , bias = 3.0%, R_C = 93.4% ± 6.8%
  - c_A(Am-241) =380.8 mBq/L^{-1} ± 2.9% , bias = 2.9%, R_C = 100.2% ± 6.9%
  - c_A(Cm-244) =327.9 mBq/L^{-1} ± 3.7% , bias = 0.1%, R_C = 100.2% ± 6.9%
  - c_A(U-238) =628.8 mBq/L^{-1} ± 3.7% , bias = -4.3%, R_C = 96.6% ± 2.5%

Thank you for your attention!

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