Rapid methods for the determination of actinides, radiostrontium and radium in environmental and bioassay samples

Scope

- Actinides and Sr in soil, food, fecal, concrete and brick samples
- Determination of radiostrontium in sea water samples
- Determination of Ra-226 in environmental samples

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.

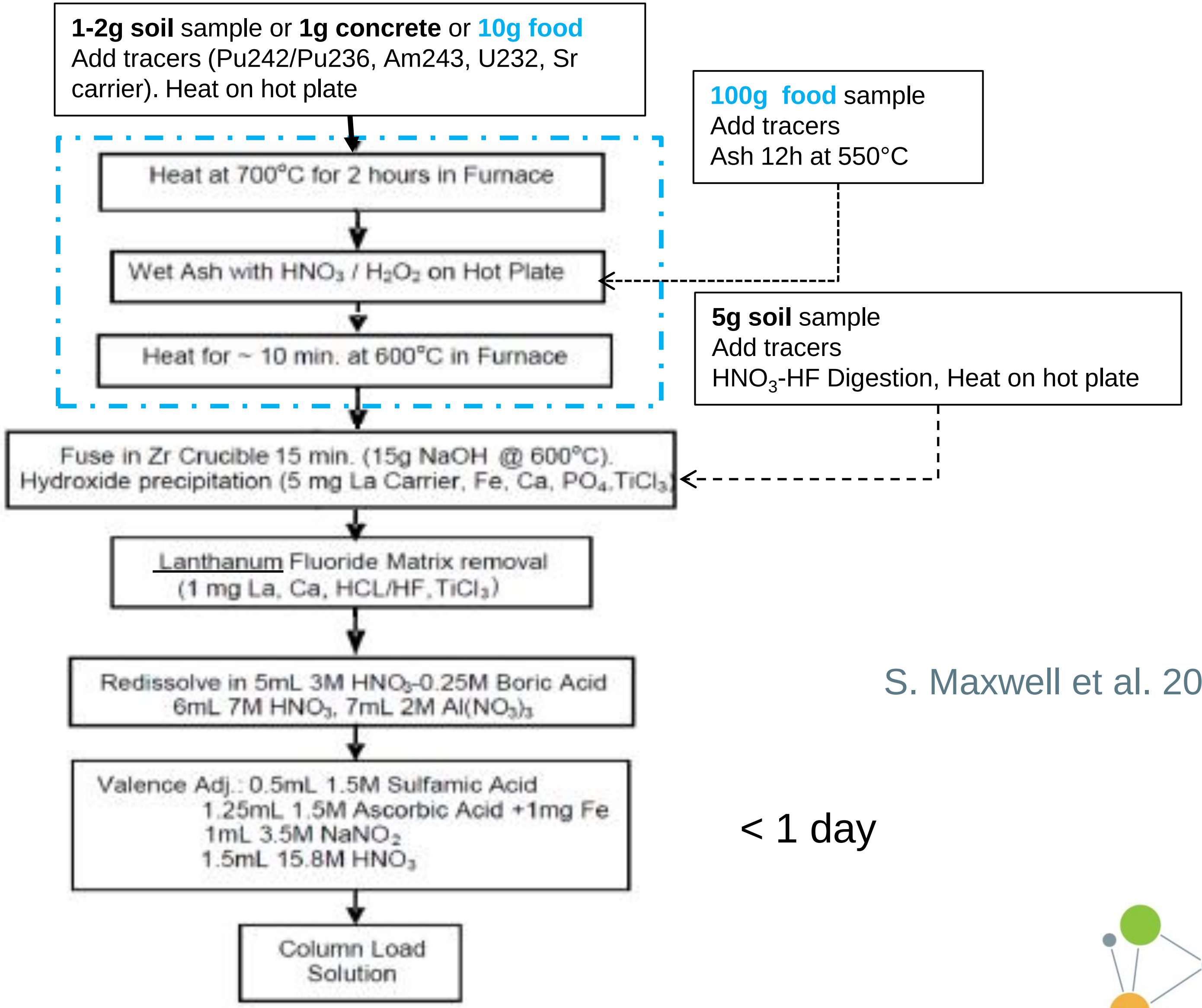
SL Maxwell, BK Culligan, A Kelsey-Wall, PJ Shaw: Rapid determination of actinides in emergency food samples, J. Radioanal. Nucl. Chem., 292(1), 2011, 339-347

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

- 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) / $NaNO_2$

- 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)

Sample preparation



1-2g soil sample or **1g concrete** or **10g food**
Add tracers (Pu242/Pu236, Am243, U232, Sr carrier). Heat on hot plate

Heat at 700°C for 2 hours in Furnace

Wet Ash with HNO_3 / H_2O_2 on Hot Plate

Heat for ~ 10 min. at 600°C in Furnace

100g food sample
Add tracers
Ash 12h at 550°C

5g soil sample
Add tracers
HNO_3-HF Digestion, Heat on hot plate

Fuse in Zr Crucible 15 min. (15g NaOH @ 600°C).
Hydroxide precipitation (5 mg La Carrier, Fe, Ca, PO_4,$TiCl_3$)

Lanthanum Fluoride Matrix removal
(1 mg La, Ca, HCL/HF,$TiCl_3$)

Redissolve in 5mL 3M HNO_3-0.25M Boric Acid
6mL 7M HNO_3, 7mL 2M $Al(NO_3)_3$

Valence Adj.: 0.5mL 1.5M Sulfamic Acid
1.25mL 1.5M Ascorbic Acid +1mg Fe
1mL 3.5M $NaNO_2$
1.5mL 15.8M HNO_3

Column Load Solution

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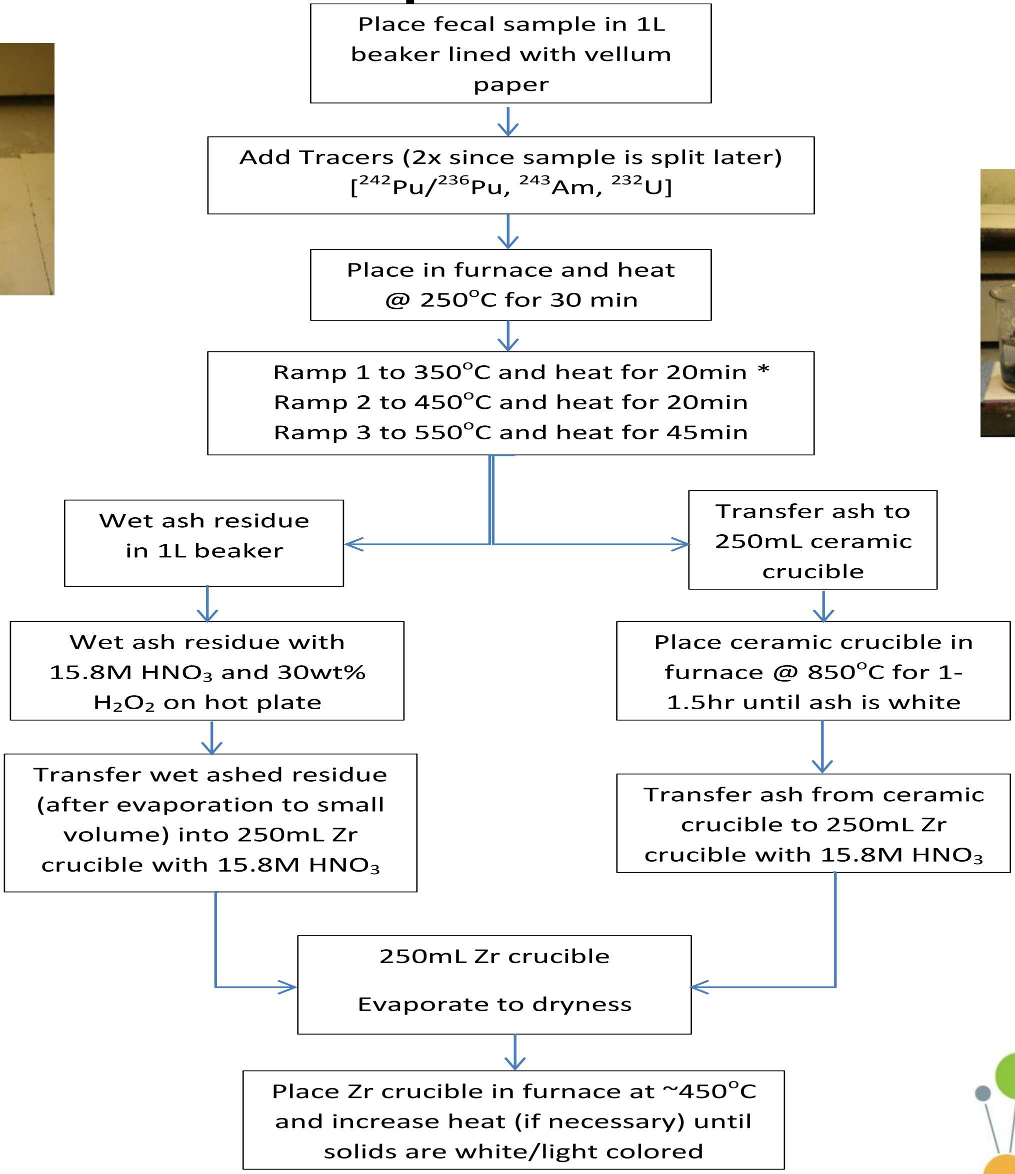
< 1 day

Rapid Fecal Sample Furnace Heating



Place fecal sample in 1L beaker lined with vellum paper

Add Tracers (2x since sample is split later) [^{242}Pu/^{236}Pu, ^{243}Am, ^{232}U]

Place in furnace and heat @ 250°C for 30 min

Ramp 1 to 350°C and heat for 20min *
Ramp 2 to 450°C and heat for 20min
Ramp 3 to 550°C and heat for 45min

Wet ash residue in 1L beaker

Wet ash residue with 15.8M HNO_3 and 30wt% H_2O_2 on hot plate

Transfer wet ashed residue (after evaporation to small volume) into 250mL Zr crucible with 15.8M HNO_3

Transfer ash to 250mL ceramic crucible

Place ceramic crucible in furnace @ 850°C for 1-1.5hr until ash is white

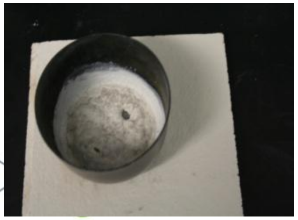
Transfer ash from ceramic crucible to 250mL Zr crucible with 15.8M HNO_3

250mL Zr crucible

Evaporate to dryness

Place Zr crucible in furnace at ~450°C and increase heat (if necessary) until solids are white/light colored

* Routine analysis heating option to 550 °C in 1 liter overnight without ceramic crucible



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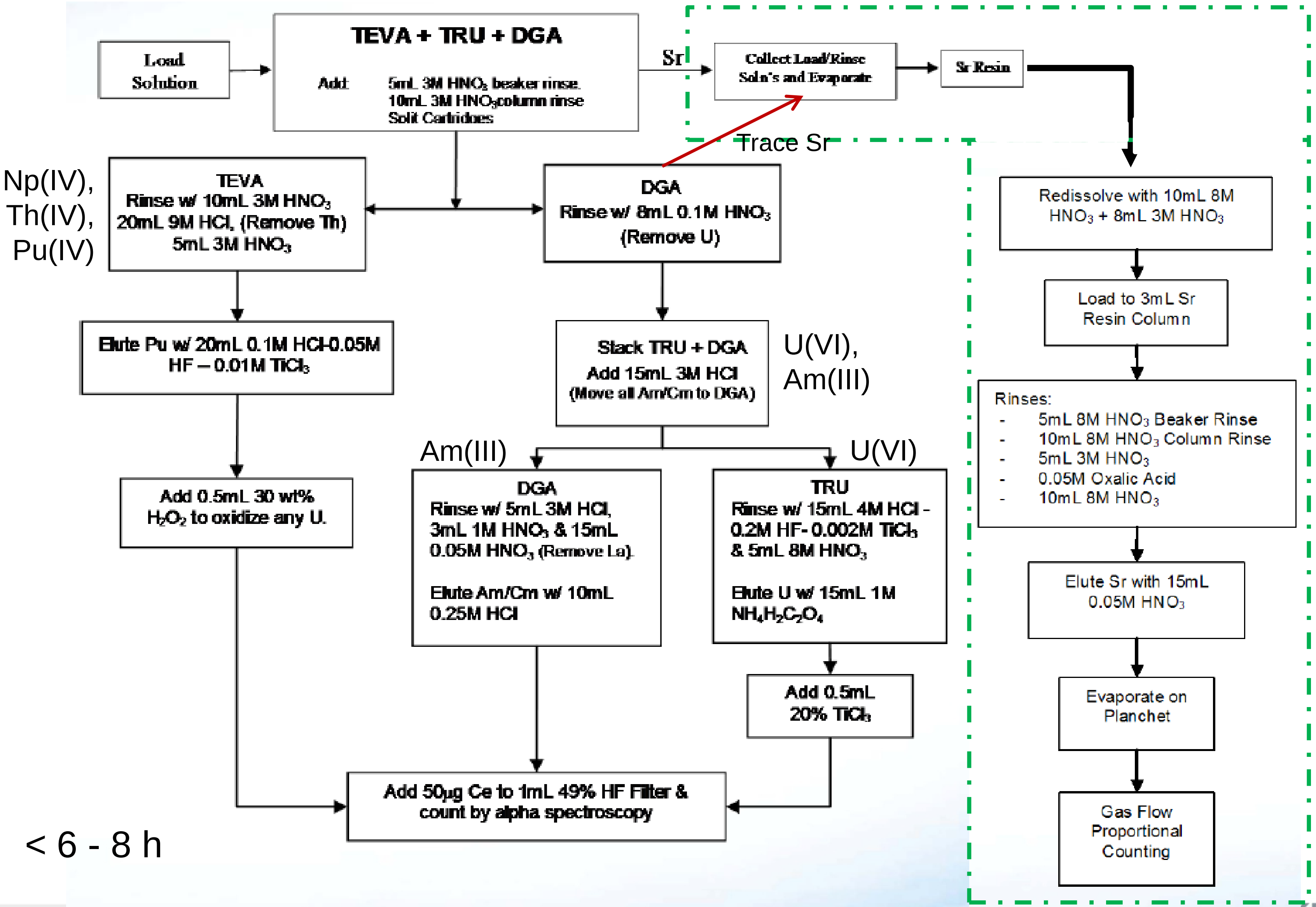
Separation scheme (Sr optional)



Load Solution

TEVA + TRU + DGA

Add 5mL 3M HNO_3 beaker rinse
10mL 3M HNO_3 column rinse
Split Cartridges

Sr

Collect Load/Rinse Soln's and Evaporate

Sr Resin

Trace Sr

Np(IV), Th(IV), Pu(IV)

TEVA
Rinse w/ 10mL 3M HNO_3
20mL 9M HCl, (Remove Th)
5mL 3M HNO_3

Elute Pu w/ 20mL 0.1M HCl-0.05M HF – 0.01M $TiCl_3$

Add 0.5mL 30 wt% H_2O_2 to oxidize any U.

DGA
Rinse w/ 8mL 0.1M HNO_3
(Remove U)

U(VI), Am(III)

Stack TRU + DGA
Add 15mL 3M HCl
(Move all Am/Cm to DGA)

Am(III)

DGA
Rinse w/ 5mL 3M HCl, 3mL 1M HNO_3 & 15mL 0.05M HNO_3 (Remove La).

Elute Am/Cm w/ 10mL 0.25M HCl

U(VI)

TRU
Rinse w/ 15mL 4M HCl - 0.2M HF- 0.002M $TiCl_3$ & 5mL 8M HNO_3

Elute U w/ 15mL 1M $NH_4H_2C_2O_4$

Add 0.5mL 20% $TiCl_3$

Add 50µg Ce to 1mL 49% HF Filter & count by alpha spectroscopy

Redissolve with 10mL 8M HNO_3 + 8mL 3M HNO_3

Load to 3mL Sr Resin Column

Rinses:
- 5mL 8M HNO_3 Beaker Rinse
- 10mL 8M HNO_3 Column Rinse
- 5mL 3M HNO_3
- 0.05M Oxalic Acid
- 10mL 8M HNO_3

Elute Sr with 15mL 0.05M HNO_3

Evaporate on Planchet

Gas Flow Proportional Counting

< 6 - 8 h

S. Maxwell et al. 2011

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

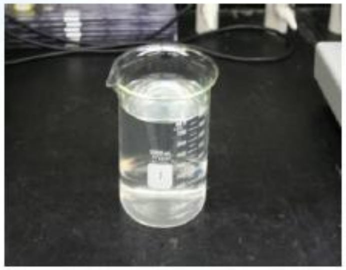
Sr in sea water samples

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

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)

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

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

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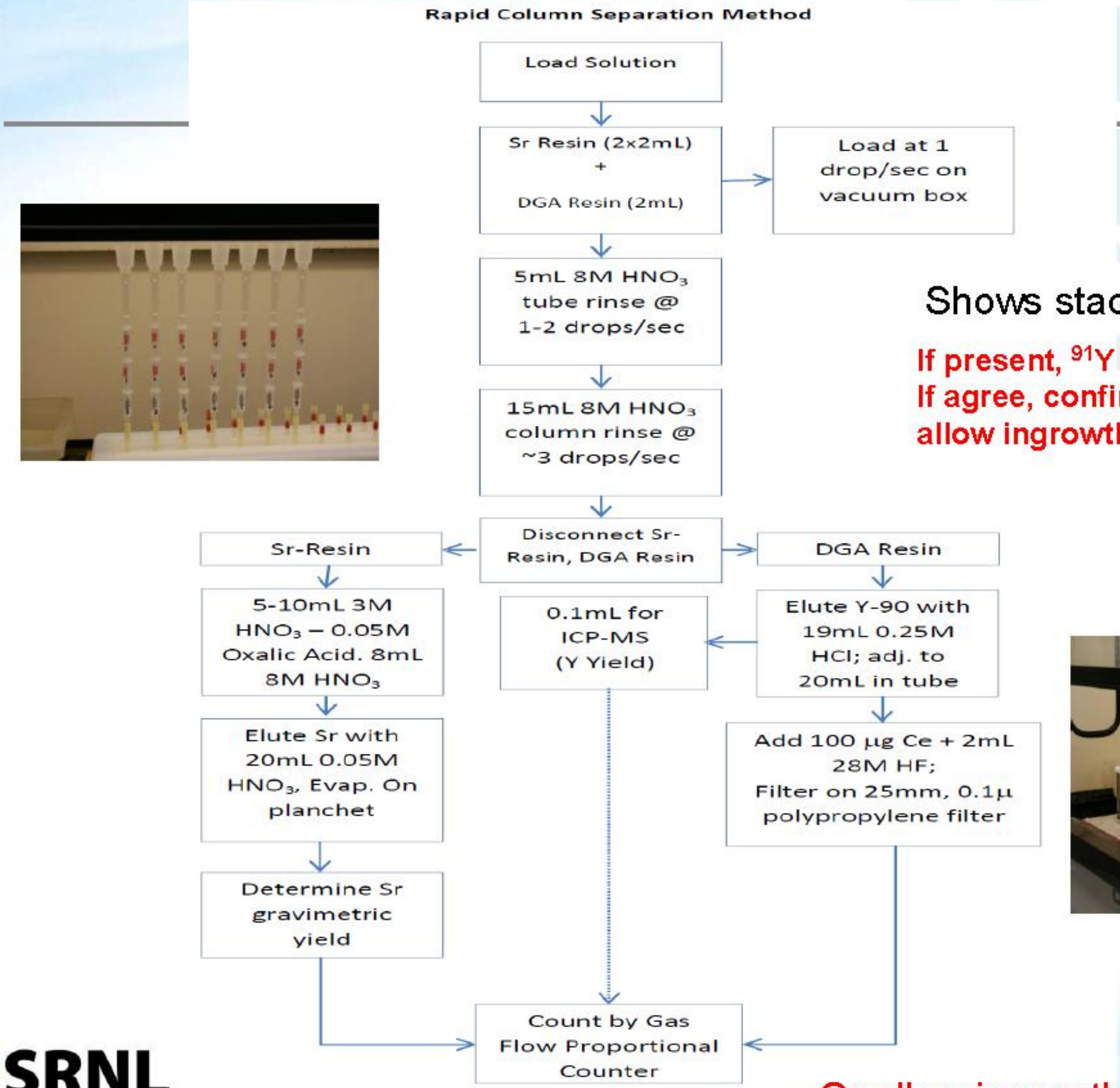
<4 hours!



Rapid Column Separation Method

Load Solution

Sr Resin (2x2mL)
+
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 column rinse @ ~3 drops/sec

Disconnect Sr-Resin, DGA Resin

Sr-Resin

5-10mL 3M HNO_3 – 0.05M Oxalic Acid. 8mL 8M HNO_3

Elute Sr with 20mL 0.05M HNO_3, Evap. On planchet

Determine Sr gravimetric yield

DGA Resin

Elute Y-90 with 19mL 0.25M HCl; adj. to 20mL in tube

0.1mL for ICP-MS (Y Yield)

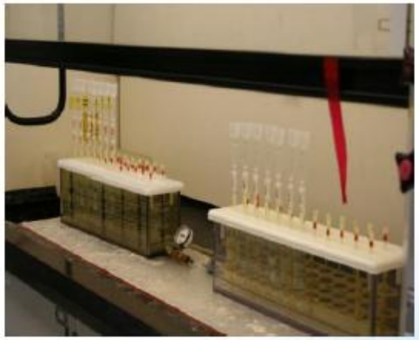
Add 100 µg Ce + 2mL 28M HF;
Filter on 25mm, 0.1µ polypropylene filter

Count by Gas Flow Proportional Counter

Alternative:
Cerenkov counting

Shows stacked option

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



Or allow ingrowth and separate ^{90}Y

SRNL

Results Sr-89/90 option

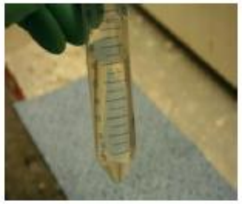
- 1L spiked sea water sample (7,66 mg $Sr.L^{-1}$), 4 mL Sr resin:
  - 2h counting time
  - Measurement via Sr-90: Yield: 88,8% (+/- 5,9%, N = 11), Bias: 1,2%
  - Measurement via Y-90: Yield: 95,0% (+/- 1,6%, N = 11), Bias: 3,1%
  - Good correspondance
- 2L sea water sample (7,70 mg $Sr.L^{-1}$), 6 mL 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)

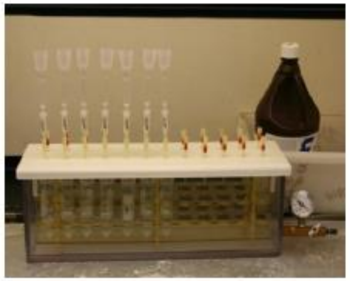
Sr-89/90 option

- 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

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

Avoids stable Sr limitation





Column Load Solution

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)

Wait 7-10 Days for ^{90}Y ingrowth.

Separate using DGA Resin again.

Column Rinses:

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

@ 1-2 drops/sec

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

0.1mL for ICP-MS

(Yield)

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

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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*

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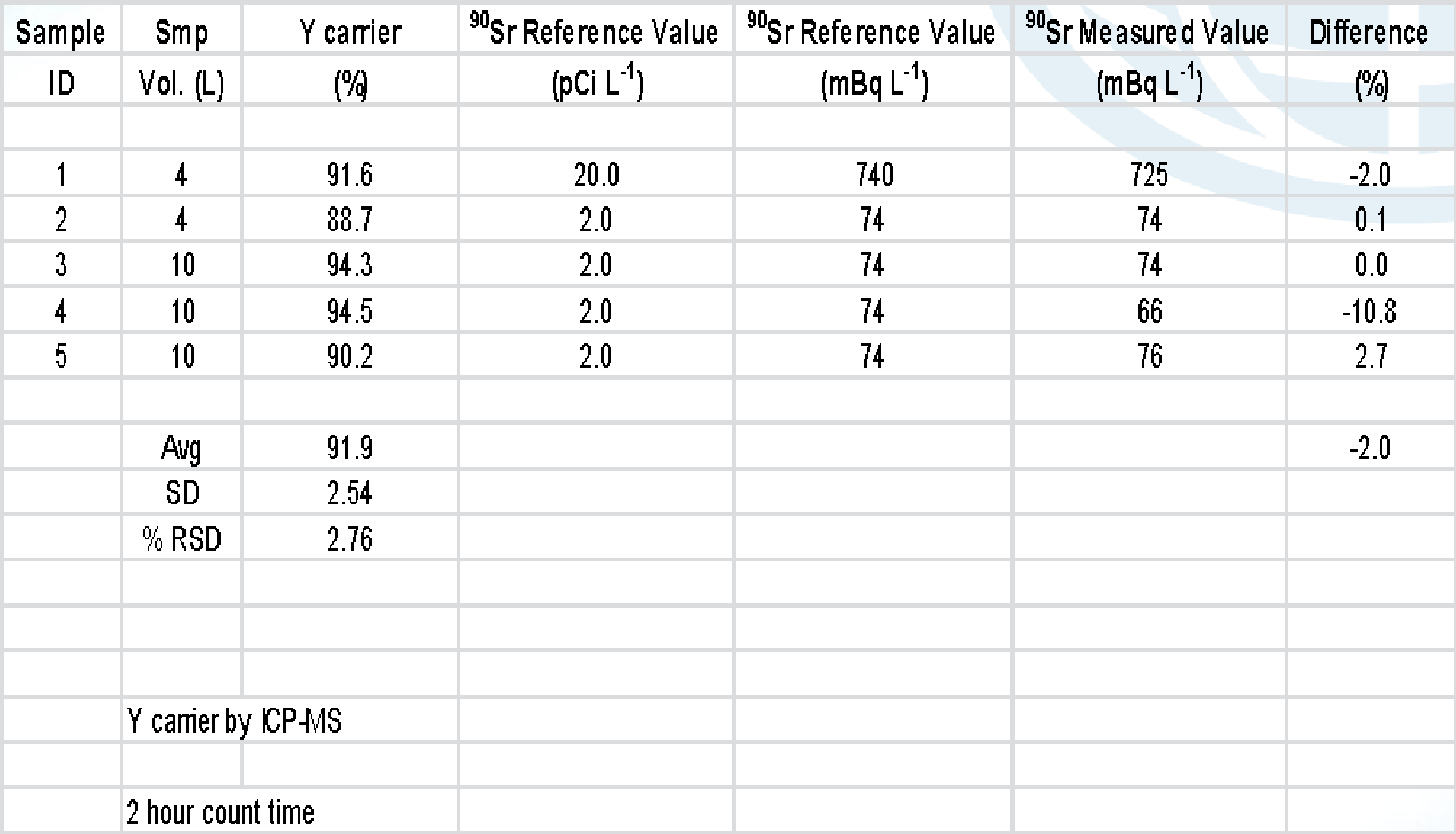
Rapid Method for Sr-90 in Seawater – DGA Resin only



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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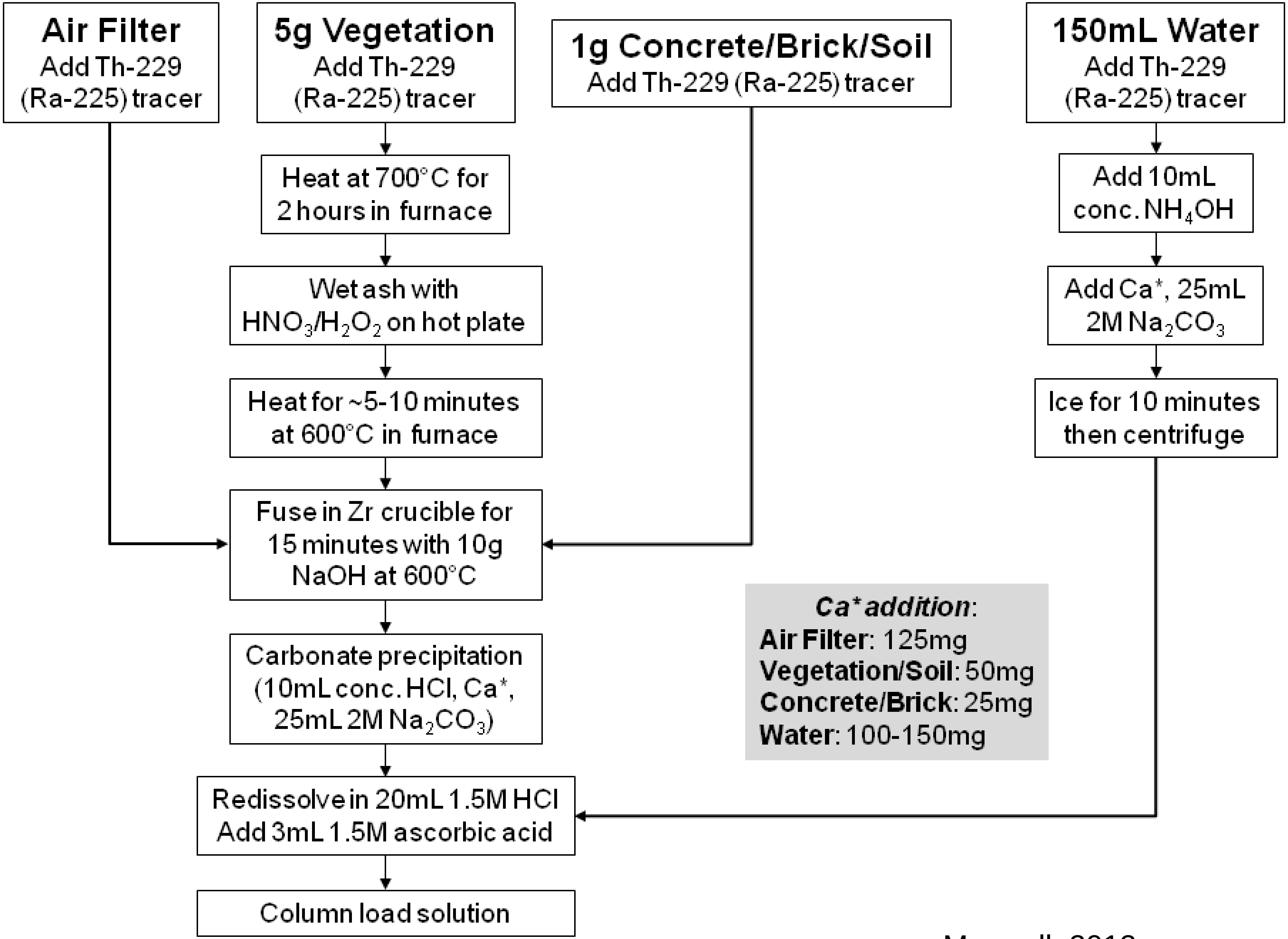
Rapid determination of Ra-226 in environmental samples

- For solid samples use of MnO_2 resin not possible
  - High matrix load after sample dissolution, precipitation at pH 7
- Solid samples frequently contain elevated amounts of Ba
  - Problematic for preparation of source for α-spectrometry
  - Polyatomic Interferences at ICP-MS measurements
- Ba removal necessary
  - Ba/Ra separation (e.g.SR Resin)
  - Ba-133 can not be used as internal standard
  - Alternative: Ra-225/At-217 (from Th-229), advantage: α-Spectrometry

Rapid determination of Ra-226 in environmental samples

- Rapid method Sherrod Maxwell (SRS)
  - Filter, 5g vegetation, 1g soil, brick or concrete, 150 mL water samples
  - Ashing (2h 700°C, wet ashing, 5 – 10 min 600°C)
  - NaOH fusion in Zr crucible
  - Carbonate precipitation
  - Cation exchange (Ca removal)
  - Optional: SR Resin (for Ba-rich samples)
  - LN Resin (Ac, Ca,… removal)
  - Microprecipitation and α-Spectrometry



Air Filter
Add Th-229 (Ra-225) tracer

5g Vegetation
Add Th-229 (Ra-225) tracer

Heat at 700°C for 2 hours in furnace

Wet ash with HNO_3/H_2O_2 on hot plate

Heat for ~5-10 minutes at 600°C in furnace

1g Concrete/Brick/Soil
Add Th-229 (Ra-225) tracer

Fuse in Zr crucible for 15 minutes with 10g NaOH at 600°C

Carbonate precipitation (10mL conc. HCl, Ca*, 25mL 2M Na_2CO_3)

150mL Water
Add Th-229 (Ra-225) tracer

Add 10mL conc. NH_4OH

Add Ca*, 25mL 2M Na_2CO_3

Ice for 10 minutes then centrifuge

Redissolve in 20mL 1.5M HCl
Add 3mL 1.5M ascorbic acid

Column load solution

Ca* addition:
Air Filter: 125mg
Vegetation/Soil: 50mg
Concrete/Brick: 25mg
Water: 100-150mg

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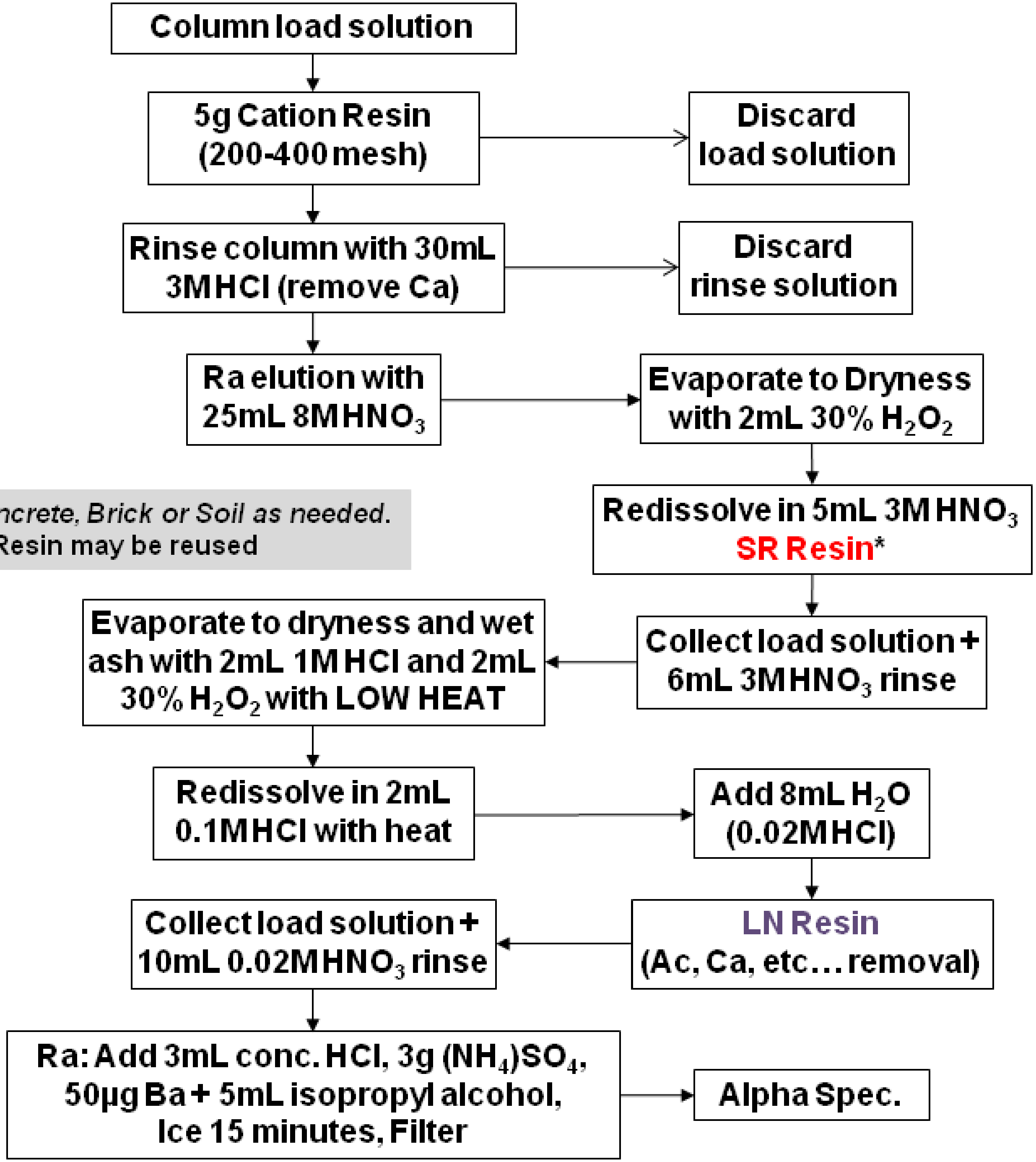

Column load solution

5g Cation Resin (200-400 mesh)

Discard load solution

Rinse column with 30mL 3M HCl (remove Ca)

Discard rinse solution

Ra elution with 25mL 8M HNO_3

Evaporate to Dryness with 2mL 30% H_2O_2

Redissolve in 5mL 3M HNO_3 SR Resin*

Collect load solution + 6mL 3M HNO_3 rinse

Evaporate to dryness and wet ash with 2mL 1M HCl and 2mL 30% H_2O_2 with LOW HEAT

Redissolve in 2mL 0.1M HCl with heat

Add 8mL H_2O (0.02M HCl)

LN Resin (Ac, Ca, etc… removal)

Collect load solution + 10mL 0.02M HNO_3 rinse

Ra: Add 3mL conc. HCl, 3g $(NH_4)SO_4$, 50µg Ba + 5mL isopropyl alcohol, Ice 15 minutes, Filter

Alpha Spec.

Concrete, Brick or Soil as needed.
SR Resin may be reused

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Results spiked real samples

Matrix	Chemical yield / %	Obtained result / mBq per sample	Reference value / mBq per sample	Bias to ref. value / %
Vegetables	87.1 (5.7)	72.8 (5.1)	73.8	-1.2
Concrete	84.6 (6.8)	180.6 (8.0)	184.5	-2.1
Brick	86.5 (6.6)	77.8 (4.6)	73.8	5.5
Air filter	76.7 (4.2)	77.1 (6.2)	73.8	4.5
Soil	75.3 (1.9)	184.9 (6.2)	184.5	0.2
Water	91.8 (6.7)	70.9 (3.7)	73.8	-3.9

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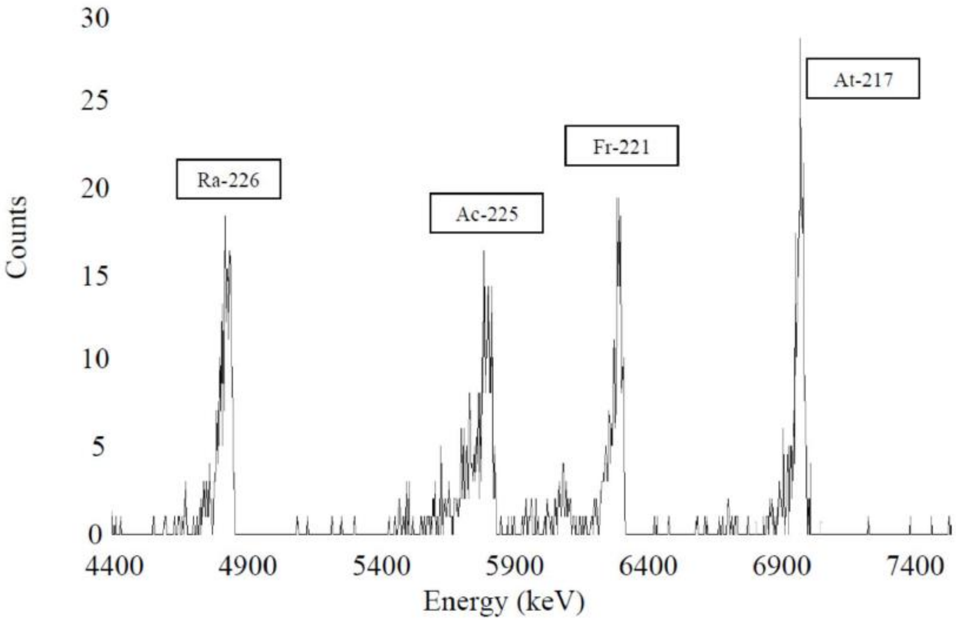
- Yields between 75 and 90%
- Good agreement with reference values
- Clean spectra



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Спасибо за внимание!

Вопросы?

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TRISKEM INTERNATIONAL
Parc de Lormandière - Bât.C - Rue Maryse Bastié - Campus de Ker Lann - 35170 BRUZ - FRANCE
Tél.+33(0)2 99 05 00 09 - Fax. +33(0)2 99 05 07 27 - www.triskem-international.fr - email : contact@triskem.fr