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


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 HNO₃
• 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 HNO₃ / H₂O₂ on Hot Plate

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

Fuse in Zr Crucible 15 min. (15g NaOH @ 600°C).
Hydroxide precipitation (5 mg La Carrier, Fe, Ca, PO₄, TiCl₃)

Lanthanum Fluoride Matrix removal
(1 mg La, Ca, HCl/ HF, TiCl₃)

Redissolve in 5mL 3M HNO₃-0.25M Boric Acid
6mL 7M HNO₃, 7mL 2M Al(NO₃)₃

Valence Adj.: 0.5mL 1.5M Sulfamic Acid
1.25mL 1.5M Ascobic Acid +1mg Fe
1mL 3.5M NaNO₂
1.5mL 15.8M HNO₃

Column Load Solution

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

5g soil sample
Add tracers
HNO₃-HF Digestion, Heat on hot plate

< 1 day

S. Maxwell et al. 2011
Place fecal sample in 1L beaker lined with vellum paper

Add Tracers (2x since sample is split later)

$[^{242}\text{Pu}/^{236}\text{Pu}, ^{243}\text{Am}, ^{232}\text{U}]$

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

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

Transfer ash to 250mL ceramic crucible

Wet ash residue in 1L beaker

Wet ash residue with 15.8M HNO$_3$ and 30 wt% H$_2$O$_2$ on hot plate

Transfer wet ashed residue (after evaporation to small volume) into 250mL Zr crucible with 15.8M HNO$_3$

Place ceramic crucible in furnace @ 850°C for 1-1.5 hr 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
Separation scheme (Sr optional)

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

TEVA + TRU + DGA
- Load Solution
- Add 5mL 3M HNO₃ beaker rinse
- 10mL 3M HNO₃ column rinse
- Split Cartridges

DGA
- Rinse w/ 8mL 0.1M HNO₃
- (Remove U)
- Slack TRU + DGA
- Add 15mL 3M HCl
- (Move all Am/Cm to DGA)

Am(III)
- Add 0.5mL 30 wt% H₂O₂ to oxidize any U.

TEVA
- Rinse w/ 10mL 3M HNO₃
- 20mL 9M HCl (Remove Th)
- 5mL 3M HNO₃

Elute Pu w/ 20mL 0.1M HCl-0.05M HF - 0.01M TiCl₃

U(VI), Am(III)

Tracer Sr

U(VI)

Add 0.5mL 20% TiCl₃

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

< 6 - 8 h

Sr Resin

Redissolve with 10mL 8M HNO₃ + 8mL 3M HNO₃

Load to 3mL Sr Resin Column

Rinses:
- 5mL 8M HNO₃ Beaker Rinse
- 10mL 8M HNO₃ Column Rinse
- 5mL 3M HNO₃
- 0.05M Oxalic Acid
- 10mL 8M HNO₃

Elute Sr with 15mL 0.05M HNO₃

Evaporate on Planchet

Gas Flow Proportional Counting

S. Maxwell et al. 2011
Method performance (MAPEP 18 samples)

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

<table>
<thead>
<tr>
<th>Sample Code</th>
<th>Am yield (%)</th>
<th>Pu yield (%)</th>
<th>U yield (%)</th>
<th>Sr yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MAPEP-18 soil</td>
<td>96.2±6.33</td>
<td>102.2±10.5</td>
<td>84.0±5.64</td>
<td>60.0±2.8</td>
</tr>
<tr>
<td>MAPEP-20</td>
<td>na</td>
<td>na</td>
<td>na</td>
<td>66.0 +/- 6.0</td>
</tr>
<tr>
<td>10g baby food</td>
<td>84.6±7.5</td>
<td>93.5±8.1</td>
<td>77.9±13.1</td>
<td>na</td>
</tr>
<tr>
<td>10g apple</td>
<td>93.4±9.1</td>
<td>97.5±12.1</td>
<td>88.9±10.9</td>
<td>na</td>
</tr>
<tr>
<td>10g squash</td>
<td>88.5±3.5</td>
<td>97.5±5.9</td>
<td>77.9±13.1</td>
<td>na</td>
</tr>
<tr>
<td>MAPEP-18 spiked concrete</td>
<td>85.3±6.5</td>
<td>89.6±7.9</td>
<td>76.9±4.4</td>
<td>na</td>
</tr>
<tr>
<td>MAPEP-18 spiked brick</td>
<td>93.7±2.9</td>
<td>94.7±9.0</td>
<td>88.1±5.4</td>
<td>na</td>
</tr>
<tr>
<td>NRIP fecal</td>
<td>82.7±3.9</td>
<td>96.4±8.2</td>
<td>62.5±7.2</td>
<td>na</td>
</tr>
</tbody>
</table>

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 Radiosrontium 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

Add 1mg stable Y
Add 200mg Fe
Add 15mL 3.2M (NH₄)₂HPO₄

Adjust pH to ~ 10,
Centrifuge in 500mL tubes

Re-dissolve
Ca₃(PO₄)₂/Fe(OH)₃
ppt. in 25mL 15.8M HNO₃

Add 8mL 2M Al(NO₃)₃ and evaporate to 25mL volume

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

Centrifuge to remove any trace solids (sand)
LOAD SOLUTION

ICP-MS Assay for Stable Strontium

*2L: higher PO₄

<4 hours!

Maxwell et al. 2012
Rapid Column Separation Method

Load Solution

Sr Resin (2x2mL) +
DGA Resin (2mL)

Load at 1 drop/sec in vacuum box

5mL 8M HNO₃
tube rinse @
1-2 drops/sec

15mL 8M HNO₃
column rinse @
~3 drops/sec

Sr-Resin

Disconnect Sr-
Resin, DGA Resin

DGA Resin

0.1mL for
ICP-MS
(Y Yield)

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

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

5-10mL 3M
HNO₃ - 0.05M
Oxalic Acid, 8mL
8M HNO₃

Elute Sr with
20mL 0.05M
HNO₃, Evap. On
planchet

Determine Sr
gravimetric
yield

Count by Gas
Flow Proportional
Counter

Alternative:
Cerenkov counting

Or allow ingrowth and separate ⁹⁰⁸Y

Show stacked option

If present, ⁹¹⁸Y is a problem!
If agree, confirmatory but better to
allow ingrowth, then separate Y-90
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
  - 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

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 8M HNO$_3$
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, 0.4µm 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

- < 1 mBq/L $^{90}$Sr with 10L seawater aliquot and < 6 hour sample preparation

Maxwell et al. 2012
## Rapid Method for Sr-90 in Seawater – DGA Resin only

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Sample Vol. (L)</th>
<th>Y carrier (%)</th>
<th>(^{90}\text{Sr Reference Value} ) (pCi L(^{-1}))</th>
<th>(^{90}\text{Sr Reference Value} ) (mBq L(^{-1}))</th>
<th>(^{90}\text{Sr Measured Value} ) (mBq L(^{-1}))</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4</td>
<td>91.6</td>
<td>20.0</td>
<td>740</td>
<td>725</td>
<td>-2.0</td>
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<tr>
<td>2</td>
<td>4</td>
<td>88.7</td>
<td>2.0</td>
<td>74</td>
<td>74</td>
<td>0.1</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>94.3</td>
<td>2.0</td>
<td>74</td>
<td>74</td>
<td>0.0</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>94.5</td>
<td>2.0</td>
<td>74</td>
<td>66</td>
<td>-10.8</td>
</tr>
<tr>
<td>5</td>
<td>10</td>
<td>90.2</td>
<td>2.0</td>
<td>74</td>
<td>76</td>
<td>2.7</td>
</tr>
</tbody>
</table>

**Average:**
- Y carrier by ICP-MS: 91.9%
- SD: 2.54
- % RSD: 2.76

**Notes:**
- 2 hour count time

Maxwell et al. 2012
Rapid determination of Ra-226 in environmental samples

- For solid samples use of MnO₂ 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 HNO₃/H₂O₂ on hot plate
Heat for ~5-10 minutes at 600°C in furnace
Fuse in Zr crucible for 15 minutes with 10g NaOH at 600°C
Carbonate precipitation (10mL conc. HCl, Ca⁺, 25mL 2M Na₂CO₃)
Redissolve in 20mL 1.5M HCl
Add 3mL 1.5M ascorbic acid
Column load solution

1g Concrete/Brick/Soil
Add Th-229 (Ra-225) tracer
Heat at 700°C for 2 hours in furnace
Wet ash with HNO₃/H₂O₂ on hot plate
Heat for ~5-10 minutes at 600°C in furnace
Fuse in Zr crucible for 15 minutes with 10g NaOH at 600°C
Carbonate precipitation (10mL conc. HCl, Ca⁺, 25mL 2M Na₂CO₃)
Redissolve in 20mL 1.5M HCl
Add 3mL 1.5M ascorbic acid
Column load solution

150mL Water
Add Th-229 (Ra-225) tracer
Add 10mL conc. NH₄OH
Add Ca⁺, 25mL 2M Na₂CO₃
Ice for 10 minutes then centrifuge

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

Maxwell, 2012
Column load solution

5g Cation Resin (200-400 mesh)

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

Ra elution with 25mL 8M HNO₃

Evaporate to dryness with 2mL 30% H₂O₂

Redissolve in 5mL 3M HNO₃ SR Resin*

Evaporate to dryness and wet ash with 2mL 1M HCl and 2mL 30% H₂O₂ with LOW HEAT

Redissolve in 2mL 0.1M HCl with heat

Collect load solution + 10mL 0.02M HNO₃ rinse

Ra: Add 3mL conc. HCl, 3g (NH₄)₂SO₄, 50μg Ba + 5mL isopropyl alcohol, Ice 15 minutes, Filter

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Collect load solution + 6mL 3M HNO₃ rinse

Add 8mL H₂O (0.02M HCl)

LN Resin (Ac, Ca, etc... removal)

Discard load solution

Discard rinse solution

*Concrete, Brick or Soil as needed. SR Resin may be reused.
Results spiked real samples

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

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

Maxwell, 2012
Спасибо за внимание!
Вопросы?

www.triskem-international.com

http://www.linkedin.com/company/triskem-international?trk=hb_tab_compy_id_2897456