Rapid Method for $^{226}$Ra in Urine Samples

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RRMC
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**Background**

- **Need for rapid radiochemical methods**
  - *Emergency response*
    - Radiological event
    - Rapid turnaround times
    - High capacity

- **Ra-226**
  - *in hospitals, laboratories*
  - alpha emitter, 4.78 MeV (94.5%), 4.61 MeV (5.55%)
  - 1600 year half-life (alpha spectrometry and ICP-MS)
  - radiotoxic, follows calcium in food chain into bones

- **Urine**
  - Rapid assay needed
  - Simple, fast and reliable
Risk from Ra-226

- More dangerous “dirty bomb” than Uranium RDD
  - Delivers much higher dose

- Besides RDD...
  - Risk of addition at post-treatment water supply

- Ra-226 has been trafficked repeatedly in different countries
  - Po-210 has already been used successfully for a criminal act

- Risk Due to Radiological Terror Attacks With Natural Radionuclides
  - Steinhäusler Friedrich, Rydell Stan, and Zaitseva Lyudmila
  - Citation: AIP Conference Proceedings 1034, 3 (2008); doi: 10.1063/1.2991254
Passive Radiological Attack

- May 2002, a nuclear expert working in a hospital in China's Guangdong Province tried to kill his colleague by installing an iridium-192 source in the ceiling of his office.
  - The radioactive material sickened the man and 73 other staff members in the hospital, before it was eventually discovered and removed.

- September 1998, a graduate student in Providence, Rhode Island tried to poison his ex-girlfriend by tainting her food with iodine-125 he had stolen from Brown University's molecular pharmacology laboratory.

- 1995, 26 employees of the National Institutes of Health in Bethesda, Maryland, were exposed to radioactive phosphorus, which someone had used to contaminate a water cooler.
  - The FBI and other investigating agencies were never able to identify the culprit.
Need for Rapid Methods

• 1998: Chechen authorities foiled a possible terrorist act when they found and defused a mine attached to a container "full of radioactive substances" near Grozny, (terrorists stole radioactive waste from Russian RADON storage facility)

• “Mexico Finds Stolen Radioactive Material Amid Dirty Bomb Fears”
  “A dirty bomb detonated in a major city could cause mass panic, as well as serious economic and environmental consequences”

• Are we ready??
  – Environmental and bioassay
## Primary Laboratory Target CDG Levels (For Child or Pregnant Female)

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Class</th>
<th>Day 1</th>
<th>Bq/L</th>
<th>Day 2</th>
<th>Bq/L</th>
<th>Day 3</th>
<th>Bq/L</th>
<th>Day 5</th>
<th>Bq/L</th>
<th>Day 7</th>
<th>Bq/L</th>
<th>Day 10</th>
<th>Bq/L</th>
<th>Day 15</th>
<th>Bq/L</th>
<th>Day 20</th>
<th>Bq/L</th>
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<tbody>
<tr>
<td>Ra-226</td>
<td>M</td>
<td>2.44E+01</td>
<td>6.68E-04</td>
<td>4.74E+00</td>
<td>1.30E-04</td>
<td>3.21E+00</td>
<td>8.77E-05</td>
<td>1.68E+00</td>
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<td>8.71E-01</td>
<td>2.38E-05</td>
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<td>2.14E-01</td>
<td>5.85E-06</td>
<td>1.68E-01</td>
<td>4.60E-06</td>
</tr>
</tbody>
</table>

4.54 pCi/L

**Calculations by David Saunders, CDC based on NCRP 161**
• K. Kehagia, C. Potiriadis, S. Bratakos, V. Koukouliou and G. Drikos, Determination of 226Ra in Urine Samples by Alpha Spectrometry, Radiation Protection Dosimetry (2007), pp. 1–4
  – Evaporation, wet-ash, **overnight** in furnace, redissolution, lead sulfate ppt.
  – Anion resin, cation resin, EDTA, electrodeposition
  – 2 days to prep 4 samples, wait 4 days to begin count
  – 7200 minute count time, **50-70% yields**, Ra-225 (At-217)
  – Radium is separated from urine matrix using cation and anion exchange
  – $^{224}$Ra tracer is added, together with its parent $^{228}$Th, for chemical recovery correction
  – After separation, hydrous titanium oxide precipitation and BaSO(4) micro-precipitation
  – MDA 0.22 Bq/L with 4 h of counting for 20 ml of urine sample.
  – Ra-224 has 3.66 day half-life
    • Is Ra-224 present in sample?
    • What if Ra-224 assay is needed?
Rapid Ra-226 Aqueous Sample Preparation

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

Add 10ml conc.
NH₄OH

Add Ca⁺⁺, 25mL 2M
Na₂CO₃

Ice for 10 minutes
then Centrifuge

Redissolve in 20mL
1.5M HCl
Add 3mL 1.5M
Ascorbic Acid

Column Load
Solution

*Ca addition:
Water: 100-150mg
Urine: 100mg

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Wet-ash urine ppt
## Ra-226 in Urine

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(^{217})At Yield (%)</th>
<th>(^{226})Ra Reference Value (mBq smp(^{-1}))</th>
<th>(^{226})Ra Measured Value * (mBq smp(^{-1}))</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>91.2</td>
<td>73.8</td>
<td>75.5</td>
<td>2.4</td>
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<tr>
<td>2</td>
<td>88.3</td>
<td>73.8</td>
<td>88.4</td>
<td>19.9</td>
</tr>
<tr>
<td>3</td>
<td>84.7</td>
<td>73.8</td>
<td>82.7</td>
<td>12.1</td>
</tr>
<tr>
<td>4</td>
<td>85.0</td>
<td>73.8</td>
<td>76.8</td>
<td>4.1</td>
</tr>
<tr>
<td>5</td>
<td>94.1</td>
<td>73.8</td>
<td>78.3</td>
<td>6.1</td>
</tr>
<tr>
<td>6</td>
<td>87.7</td>
<td>73.8</td>
<td>78.7</td>
<td>6.6</td>
</tr>
<tr>
<td>7</td>
<td>99.2</td>
<td>73.8</td>
<td>70.8</td>
<td>-4.0</td>
</tr>
<tr>
<td>8</td>
<td>92.3</td>
<td>73.8</td>
<td>64.8</td>
<td>-12.1</td>
</tr>
</tbody>
</table>

Avg 90.3  
SD 4.9  
% RSD 3.4

8hr count time  
At -217 ingrowth to mid-point-17.75 hrs.  
*corrected for 5.0 mBq Ra-226 in blank urine

Cation Resin + Ln Resin

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Ra-225 Tracer Decay

$^{225}\text{Ra (Including Parent) Decay Scheme}$

The short half-lives of $^{217}\text{At}$ and $^{217}\text{Fr}$ allow the $^{217}\text{At}$ activity to be calculated from $^{225}\text{Ac}$ activity based on secular equilibrium with $^{225}\text{Ac}$.

Secular Equilibrium between $^{229}\text{Th}$ and $^{225}\text{Ra}$ is achieved after about 70 days.
Which tracer option to use?

- **It depends...**
  - Ba-133 allows for immediate counting (and Ra-224 assay)
    - But for more difficult matrices... Ba/Ra deviation may be seen
    - Ba-133 is counted by gamma spectrometry
      - so alpha spectrometry and gamma spectrometry measurement bias must be well-known and accounted for
    - For soils: use of Ba-133 means no stable Ba removal (Sr Resin) and small aliquot size
      - Ra-225 may have advantage in soil methods
  - Ra-225 behaves identically to Ra-226... but ingrowth time is needed
    - Tracking separation times accurately very important
      - recounts may have large tracer peaks
    - Ra-225 can be added with Th-229 parent or added after “milking”
      - Ra-225 milking from Th-229 can be done but it requires re-validation time and effort each month or so
      - method has to be able to handle Th-229 effectively if added with Ra-225
    - Ac-225 interferes with Ra-224
Emergency urine samples

• Ba-133 tracer may be very useful
  – No waiting for ingrowth
  – No need to remove stable Ba (as with soil)
  – Allows for Ra-224 assay
  – Assurance Ba/Ra are in sync can be managed (no divergence)

• But
  – 2 counts are needed (gamma count can be very short)
  – Gamma and alpha measurement must not have significant bias vs. each other
SRNL Approach

- **Use calcium phosphate instead of calcium carbonate**
  - Slight Ra-226 contamination in sodium carbonate
  - Need low urine blanks
  - Lower solubility of calcium phosphate – lower Ca needed
    - Less Ca ➔ less cation resin ➔ less volume ➔ less time

- **Test DGA Resin vs Ln Resin**
  - Evaporation steps after cation resin just prior to redissolution in 0.02M HCl
    - have to be “babied” to avoid lower yields (presumably from oxides) which do not redissolve in the low acid
  - Ln Resin sometimes shows inconsistent flow issues at low acid levels
  - DGA Resin removes interferences and can be used with much higher acid
Rapid Sample Preparation for Ra-226 in urine

100 mL urine
Add $^{228}$Ba as Tracer

Add 50mg Ca, 3mL 3.2M (NH$_4$)$_2$HPO$_4$, 14.5M NH$_3$OH until ~pH 10

Mix well, wait 5 min. and centrifuge @~3500 rpm for 6 min.

Discard supernatant

Add 10mL 1.5M HCl, 7 ml 1.5M HCl and dissolve solids 1M HCl and add to tube

Column Load Solution

$^{228}$Ra can also be used

Less Ca, PO$_4$ instead of carbonate
Rapid Column Separation for Ra-226 in urine

More cation resin would be Needed with Th-229/Ra-225 added

Combine final DGA purification with cation resin elution!
Residual Ca Removal using DGA Resin

Dw vs. HNO₃ for TN-DGA Resin
50-100 μm, 1 h Contact Time, 25(2) °C

Dw for Mg(II) < 1 for all concentrations of HNO₃
Ba and Ra Behavior on Cation Resin

Rapid Column Separation using Cation + DGA Resin: stacked elution

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$^{133}$Ba Yield (%)</th>
<th>$^{226}$Ra Reference Value (mBq smp$^{-1}$)</th>
<th>$^{226}$Ra Measured Value* (mBq smp$^{-1}$)</th>
<th>Difference (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95.4</td>
<td>73.67</td>
<td>82.9</td>
<td>12.6</td>
</tr>
<tr>
<td>2</td>
<td>96.6</td>
<td>73.67</td>
<td>70.6</td>
<td>-4.2</td>
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<td>3</td>
<td>90.1</td>
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<tr>
<td>Avg</td>
<td>92.8</td>
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<td>76.5</td>
<td>3.9</td>
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<tr>
<td>SD</td>
<td>3.0</td>
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<td>4.7</td>
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<tr>
<td>% RSD</td>
<td>3.2</td>
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<td>6.1</td>
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</table>

For 100 ml aliquot 73.67 mBq/smp = 736.7 mBq/L

16 hour count
Rapid Column Separation using Cation + DGA Resin: stacked elution

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$^{133}$Ba Yield (%)</th>
<th>$^{226}$Ra Reference Value (mBq smp$^{-1}$)</th>
<th>$^{226}$Ra Measured Value* (mBq smp$^{-1}$)</th>
<th>Difference (%)</th>
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<tbody>
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<td>18.42</td>
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<td>4</td>
<td>101.2</td>
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<td>Avg</td>
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<td>-2.7</td>
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<tr>
<td>SD</td>
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<tr>
<td>% RSD</td>
<td>2.6</td>
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For 100 ml aliquot 18.42 mBq/smp = 184.2 mBq/L

16 hour count
Blank Test using Cation + DGA Resin : Stacked elution

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>$^{133}$Ba Yield (%)</th>
<th>$^{228}$Ra Blank Value (pCi smp$^{-1}$)</th>
<th>MDC (pCi smp$^{-1}$)</th>
<th>$^{228}$Ra Blank Value (mBq smp$^{-1}$)</th>
<th>MDC (mBq smp$^{-1}$)</th>
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<tbody>
<tr>
<td>1</td>
<td>95.7</td>
<td>0.0016</td>
<td>0.017</td>
<td>0.058</td>
<td>0.629</td>
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<td>2</td>
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<td>0.0036</td>
<td>0.012</td>
<td>0.134</td>
<td>0.444</td>
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<td>3</td>
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<td>0.0026</td>
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<td>0.096</td>
<td>0.518</td>
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<td>0.301</td>
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<td>0.017</td>
<td>0.000</td>
<td>0.629</td>
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<tr>
<td>Avg</td>
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<td>0.015</td>
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<td>SD</td>
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<td>0.003</td>
<td>0.002</td>
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<tr>
<td>% RSD</td>
<td>5.1</td>
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</table>

100 ml sample aliquot

blank test with 2 pCi Po-210 and U-238 added
Summary

- Fast and reliable
  - Validated and used by US Air Force Radioanalytical Laboratory
  - Same method works well with water samples
    - DGA offers improvements over Ln Resin!
- High chemical yields
  - <4-5 hours with simultaneous sample preparation
- Ba-133: No waiting for Ra-225 in-growth
  - but Ra-225 can be used with some adjustments if preferred
  - allows Ra-224 measurement
- 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
    - German lab interested in 1.5L aliquot
    - Cation resin can be increased to 5g to handle extra Ca