Rapid Preconcentration of Ra-226 in Hydraulic Fracturing Wastewater Samples for Gamma Spectrometry Assay

Sherrod L. Maxwell
Senior Fellow Scientist

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Co-authors:
Dr. Dan McAlister, PG Research
Dr. Richard Warren, SRNS
Brian Culligan, SRNS
Background

- Need for rapid method to preconcentrate Ra-226 in hydraulic fracturing samples
  - Lower MDA
  - Rapid processing

- Challenges
  - Hard to collect Ra-226
  - High levels of dissolved solids: Ca, Ba, Sr, Mg, Na, K, etc.
  - Interference of U-235 on Ra-226 186 keV gamma ray
  - Waiting on Ra-226 progeny hurts turnaround times

- Wanted to use modification of SRNS methods for seawater to help solve the analytical issues
Literature


  – very low chemical yields using a wide array of analytical approaches
  – sample processing problems associated with high levels of dissolved solids

  – 20g/L Ca, 10 g/L Ba, 10 g/L Sr
    • “alkaline earth nightmare”

  – Direct gamma spectrometry (precipitation problems)
    • using agar/heating to prevent precipitation of ultrafine particulate matter
    • ~80 pCi/L MDA
    • reliance on assumption U-235 is not present

- Need to remove isobaric interferences Ba + Sr using small amount of Sr Resin
- Sr Resin ability to remove Ba can be easily exceeded with these samples
- Some residual Ba noted in high Ba samples
- Goal: 100 pCi/L MDA
- No tracer noted!

<table>
<thead>
<tr>
<th>sample</th>
<th>Na (mg/L)</th>
<th>Ca (mg/L)</th>
<th>Ba (mg/L)</th>
<th>Sr (mg/L)</th>
<th>TDS (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>11,500</td>
<td>3,440</td>
<td>1,060</td>
<td>808</td>
<td>28,500</td>
</tr>
<tr>
<td>S2</td>
<td>23,000</td>
<td>6,880</td>
<td>2,120</td>
<td>1,620</td>
<td>57,000</td>
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<tr>
<td>S3</td>
<td>46,000</td>
<td>13,760</td>
<td>4,230</td>
<td>3,230</td>
<td>114,000</td>
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<tr>
<td>S4</td>
<td>69,000</td>
<td>20,640</td>
<td>6,360</td>
<td>4,850</td>
<td>171,000</td>
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<td>S5</td>
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<td>3,440</td>
<td>1,060</td>
<td>808</td>
<td>28,500</td>
</tr>
<tr>
<td>S6</td>
<td>46,000</td>
<td>13,760</td>
<td>4,240</td>
<td>3,230</td>
<td>114,000</td>
</tr>
<tr>
<td>S7</td>
<td>69,000</td>
<td>20,640</td>
<td>6,360</td>
<td>4,850</td>
<td>171,000</td>
</tr>
</tbody>
</table>
What did not work for Ra-226...

- Calcium phosphate precipitation
  - 100 ml simulant might results in 80 ml ppt
- Direct barium sulfate precipitation
  - Nelson et al called “intractable”
- MnO$_2$ ppt (high Ba...)
- Iron hydroxide

- Nelson et al covered all this and more....
Got an idea....

- High Ca level is a major component in the "nightmare"
- Difficult to separate large amounts of alkaline earth metals
- Tried everything but there was one option left...

- Contacted Dan McAlister, PG Research, and told him what I was thinking.....
Breakthrough!

- Calcium fluoride $\text{CaF}_2$ $5.3 \times 10^{-9}$
- Strontium fluoride $\text{SrF}_2$ $2.5 \times 10^{-9}$
- Magnesium fluoride $\text{MgF}_2$ $3.7 \times 10^{-8}$
- Barium fluoride $\text{BaF}_2$ $1.0 \times 10^{-6}$

- Let’s acidify to 1.5M HCl, add HF to try to remove Ca and test...
- Then precipitate Ra/Ba sulfate with ammonium sulfate/10% ethanol

- Ca/some of Sr/Mg removed and 80-90% Ba/Ra chemical yield
Final Geometry

• Initially 500 ml polyethylene bottle, BaSO₄ suspension
  – Hard to control/settled

• 250 ml Nalgene bottle with centrifuging (Dan McAlister)
  – Reproducible, even layer with varying thicknesses

• Used 356 keV gamma ray for Ba-133 tracer recovery

• **Used Ba-133 81 keV gamma ray correlation with 186 keV Ra-226 gamma ray to correct for geometry/mass attenuation**
  – Plot of 81keV efficiency vs. 186 keV gamma ray efficiency
  – Minor correction also in 356 keV Ba-133 from 81 keV as well (if needed)
    • low abundance gamma rays (~0.2%) Ra-226, Ra-224, Ra-223 near 81 keV so we use enough Ba-133 to minimize any impact

• **What about U-235??**
U-235 Gone...

- U removed with CaF$_2$ (at high levels) regardless for U$^{+4}$ and U$^{+6}$
- H$_2$O$_2$ added initially and all water rinses to ensure U$^{+6}$
  - Additional U removal as U$^{+6}$

- U removed 99.9%++
  - 185.715 keV  57.0 %  abundance

- Ra-226
  - 186.211 keV  3.64 %  abundance

- Ba-133
  - 80.9979 keV  32.9 %  abundance
  - 356.013 keV  62.05 %  abundance
Higher Ca/Ba ratio results in greater initial U removal.
% Removal by CaF$_2$.ppt

25mL conc HCl, 15mL conc. HF per 250mL Sample

Ca/Ba ratio = ~2
% U in CaF$_2$ and CeF$_3$ ppt

U added as $^{233}$U(VI)

Not in simulant; Ce or Ca only
Rapid Preconcentration Method for Ra-226

1. Add Ba-133 tracer and 1ml 30 wt% H$_2$O$_2$ to sample aliquot in 250 ml or 500 ml tubes*. Add 50 ml 12M HCl per 400 ml sample aliquot. Mix well.

2. Add 20 ml 28M HF per 400 ml aliquot to each tube. Cap and mix well. Centrifuge 10-20 minutes at 3000 rpm or more as needed until supernate is clear.

3. Transfer supernate to 250 ml or 500 ml centrifuge tube. Add 0.5 ml 30 wt% H$_2$O$_2$ and mix well. Add 20 g ammonium sulfate to each tube. Add ~40 ml ethanol to each tube per 400 ml aliquot. Mix well and wait 10 to 15 minutes. Centrifuge 5 to 10 minutes.

4. Discard supernate. Add 50-100 ml water, 0.2 ml 30 wt% H$_2$O$_2$, mix well and centrifuge 5 minutes.

5. Transfer precipitate to 50 ml tube (or 250 ml tube if large) using 10-20 ml aliquots of water. Add 0.05 ml 30 wt% H$_2$O$_2$, mix well and centrifuge 5 minutes.

6. Transfer to 250 ml wide mouth plastic bottle using 10-20 ml aliquots of water. Centrifuge at 1600-2000 rpm in flat bottom centrifuge bucket.

* Some sample may need to be diluted with water 50% or more if silicates that cause cloudiness are high. Aliquots and tracer may be split between multiple tubes to increase total sample aliquot.

** If samples were split between tubes, combine the respective barium sulfate precipitates in a single tube then rinse the combined precipitate with water and proceed.

Count by gamma spectrometry

<2 hours!
Calcium + U/Th Removal

Discard CaF$_2$

Transfer supernate (Ra/Ba) to new tube
Precipitate Ra/Ba

Ammonium sulfate + ~10% ethanol
\( \text{H}_2\text{O}_2 \) and water rinses – ensure no U-235
Transfer to 250 ml Bottle and Centrifuge

Flat BaSO$_4$ layer from 450 ml simulant
Efficiency Plot of Ra-226 vs Ba-133 (81 keV)

Also plotted as $y = 0.0327\ln(x) + 0.2156$
# Ra-226 in Simulant Measurements

<table>
<thead>
<tr>
<th>Simulant Aliquot (ml)</th>
<th>U-235 Added (1388 pCi)</th>
<th>Count Time (min)</th>
<th>Ba-133 Yield (%)</th>
<th>Ra-226 Added (pCi)</th>
<th>Ra-226 Measured (pCi)</th>
<th>Ra-226 Measured (pCi/L)</th>
<th>Bias (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 200</td>
<td>Yes</td>
<td>960</td>
<td>83.5</td>
<td>25.4</td>
<td>25.8</td>
<td>129.0</td>
<td>1.6</td>
</tr>
<tr>
<td>2 400</td>
<td>No</td>
<td>720</td>
<td>90.3</td>
<td>634.5</td>
<td>622.0</td>
<td><strong>1555.0</strong></td>
<td>-2.0</td>
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<tr>
<td>3 450</td>
<td>No</td>
<td>720</td>
<td>89.1</td>
<td>634.5</td>
<td>620.2</td>
<td>1378.2</td>
<td>-2.3</td>
</tr>
<tr>
<td>4 450</td>
<td>No</td>
<td>720</td>
<td>87.3</td>
<td>31.7</td>
<td>42.5</td>
<td>94.4</td>
<td>34.1</td>
</tr>
<tr>
<td>5 450</td>
<td>No</td>
<td>720</td>
<td>86.3</td>
<td>20.0</td>
<td>20.4</td>
<td><strong>45.3</strong></td>
<td>2.0</td>
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<tr>
<td>6 200</td>
<td>No</td>
<td>960</td>
<td>83.9</td>
<td>25.4</td>
<td>27.9</td>
<td>139.5</td>
<td>9.8</td>
</tr>
<tr>
<td>8 450</td>
<td>No</td>
<td>960</td>
<td>80.6</td>
<td>126.9</td>
<td>117.9</td>
<td>262.0</td>
<td>-7.1</td>
</tr>
<tr>
<td>9 900</td>
<td>No</td>
<td>960</td>
<td>82.0</td>
<td>126.9</td>
<td>118.2</td>
<td>131.3</td>
<td>-6.9</td>
</tr>
<tr>
<td>10 1800</td>
<td>Yes</td>
<td>960</td>
<td>71.2</td>
<td>126.9</td>
<td>138.8</td>
<td>77.1</td>
<td>9.4</td>
</tr>
</tbody>
</table>

**Avg.** 83.8  | **SD** 5.71  | 4.3  | 12.7  

Germanium Detector, 40% Relative Efficiency
SRNS Approach

- **Remove Ca**
- **Remove U-235**
- **Precipitate Ra/Ba to preconcentrate Ra-226 (50-100x)**
- **Utilize Ba-133 tracer (81 keV and 356 keV)**
- **Eliminate need for mass attenuation curve**
  - Variable Ba content drives size of precipitate
- **No drying of samples**
- **No column work (Ra-226)**
- **Look at options to collect U/Th for assay**
U/Th Processing Options

- **U/Th by gamma spectrometry**
  - Th-229 tracer for both? (*U-232 has low gamma ray abundance*)
  - Fe/Ti hydroxide, water rinse, add 1 ml 12M HCl, dissolves in small volume
  - Th-229 183.93 keV (0.14%) vs. U-235 185.72 keV (57%)
  - If any resolution problems...we can separate U/Th using LaF$_3$
  - U$^{+6}$ in supernate, Th$^{+4}$ in ppt. (HNO$_3$-H$_3$BO$_3$)
  - Homogeneous liquid geometry: 200 ml simulant to 10 ml

- **U/Th by alpha spectrometry**
  - U-232/Th-229 tracers
  - Fe/Ti hydroxide, water rinse, add HCl, LaF$_3$ (removes Fe/Ti)
  - Redissolve LaF$_3$ in HNO$_3$-H$_3$BO$_3$ for separation
  - Separate using TEVA +TRU Resin
Rapid Preconcentration Method for U/Th

Add 2 ml 1M HCl to La/Th precipitate, 0.2 ml 30 wt% H$_2$O$_2$, 5 ml 28M HF. Mix well.

Redissolve LaF$_3$ precipitate with 4 ml 6M HNO$_3$, 1ml 3M HNO$_3$-0.25M H$_3$BO$_3$ and 4 ml 2M Al(NO$_3$)$_3$. Mix well. Sample may be counted by gamma spectrometry or column extraction applied for assay by alpha spectrometry.

Can process U/Th together for alpha spectrometry or separate during LaF$_3$ step for gamma assay.
## Thorium Tracer Yield

<table>
<thead>
<tr>
<th>Sample Aliquot (ml)</th>
<th>Th-229 Yield (%)</th>
<th>Matrix Ca/Ba/Sr (g/L)</th>
<th>U-238 % Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 200</td>
<td>98.8</td>
<td>12.5/6.25/6.25</td>
<td>&gt;99.5%</td>
</tr>
<tr>
<td>2 200</td>
<td>100.6</td>
<td>12.5/6.25/6.25</td>
<td>&gt;99.5%</td>
</tr>
<tr>
<td>3 200</td>
<td>99.2</td>
<td>12.5/6.25/6.25</td>
<td>&gt;99.5%</td>
</tr>
<tr>
<td>4 200</td>
<td>90.8</td>
<td>12.5/6.25/6.25</td>
<td>&gt;99.5%</td>
</tr>
<tr>
<td>5 200</td>
<td>97.7</td>
<td>12.5/6.25/6.25</td>
<td>&gt;99.5%</td>
</tr>
<tr>
<td>6 200</td>
<td>88.5</td>
<td>12.5/6.25/6.25</td>
<td>&gt;99.5%</td>
</tr>
<tr>
<td><strong>Avg.</strong></td>
<td><strong>95.9</strong></td>
<td><strong>12.5/6.25/6.25</strong></td>
<td>&gt;99.5%</td>
</tr>
<tr>
<td><strong>SD</strong></td>
<td><strong>5.0</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

TRU Resin, 16 hour count, U-238 added to test U Removal
Summary

• Rapid method to preconcentrate Ra-226 developed
  – Removal of Ca is key
  – Up to 1.8L simulant tested
  – U-235 removed
  – 2 hours or less to prepare

• Geometry attenuation correction applied using Ba-133 (81 keV)
  – To Ra-226 based on plot of Ba-133 efficiency (81 keV) vs Ra-226 efficiency (186 keV)
  – And minor yield adjustment to Ba (356 keV) via 81 keV/356 keV efficiency plot

• Difficult matrix
  – 50-100 x preconcentration
  – MDA <20 pCi/L achieved

• U/Th may be preconcentrated for alpha or gamma spectrometry