Rapid Radiochemical Analyses

In Support of Fukushima

Sherrod L. Maxwell and Brian K. Culligan

Savannah River National Laboratory
Aiken, SC
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57th Radiobioassay and Radiochemical Measurements Conference
Destin, FL
Background

- Need for rapid radiochemical methods
  - Emergency response
    - IND, RDD, nuclear accident
    - Large numbers of samples
      - Environmental and bioassay analyses
    - Rapid turnaround times
  - Routine sample analyses
    - Lowers costs
    - Allows more with less
- Rapid analysis support for Fukushima
  - Air filters and soil samples
# Analytical Laboratories: Environmental Bioassay Laboratory

**Our Mission:** To provide quality driven, cost competitive Environmental, Bioassay and Industrial Hygiene analytical services in a timely manner while meeting the needs of current and future Savannah River Site missions and for other customers. The Environmental Bioassay Laboratory (EBL) specializes in high volume sample loads (average of 42,000 samples/100,000 determinations per year) and rapid Turn Around Times (TAT) for analyses.

### Accreditations and Certifications

<table>
<thead>
<tr>
<th>Radiological Processing (Environmental Levels)</th>
<th>Tritium</th>
<th>Gross AB</th>
<th>Gamma Spec</th>
<th>Sr-89/Sr (Sr-Sr)</th>
<th>Alpha Suites (Am, Na, Pu, U, Th, Cm Series)</th>
<th>Tc-99</th>
<th>I-129</th>
<th>C-14</th>
<th>Ni-63</th>
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<tbody>
<tr>
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<td>Water, air filter, rain ion column, vegetation, foodstuff, sediment, soil, concrete</td>
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<table>
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<tr>
<th>DOELAP Certified</th>
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<th>TSS</th>
<th>pH</th>
<th>Residual Chlorine Temperature</th>
<th>ICP-ES Metals</th>
<th>ICP-MS Metals</th>
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<th>Bulk Asbestos</th>
<th>Air Asbestos</th>
<th>Gravimetrics</th>
<th>Hexavalent Chromium by ICP</th>
<th>Metals by ICP-ES</th>
<th>Deryllium by Optical Fluorescence</th>
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<tr>
<td>Various</td>
<td>Filters</td>
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<td>Filters</td>
<td>Filters, Wipes, Various</td>
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</tr>
</tbody>
</table>

**SCDHEC:** South Carolina Department of Health and Environmental Control  | **AIHA:** American Industrial Hygiene Association  | Foodstuff includes: fuit, gree, bee, fish, mif, deer, hog, and crows.

For all your EBL analytical laboratory needs, please contact:

- **Jim Collins**  
  Operations Lab Support Manager  
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  jim.collins@srns.gov

- **Ken Cheeks**  
  Environmental Bioassay Lab Manager  
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  ken.cheeks@srns.gov

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80,000 sq ft facility (35,000 sq ft lab space)
Approach

- **Rapid Radiochemical Methods**
  - Combine innovative sample preparation methods with rapid column extraction techniques
    - Soil, vegetation, air filters, water, food, milk, urine
  - Rugged, rapid preparation steps
  - Stacked cartridge technology
    - Sequential separation (5X faster than gravity flow)
    - Rapid flow rates

- **Time is money**
SRS – Rapid Extraction Chromatography

- Vacuum box technology
  - 1980’s with ion exchange
- SRS Bioassay lab-switch to TEVA and TRU Resin -1998
  - higher chemical yields
  - better alpha peak resolution
  - lowers costs significantly
Gravity Flow vs. Vacuum
EBL Cost Effectiveness Timeline

Cost Ratio


"World Class"

Cost Reduction vs Private Commercial Labs
Fukushima Air Filters

- **Cellulose nitrate filters**
  - $\text{HNO}_3$, $\text{H}_2\text{O}_2$, HF digestion
    - Repeat $\text{HNO}_3/\text{H}_2\text{O}_2$ to dryness several times, then with 3ml 3M $\text{HNO}_3$-boric acid
  - Redissolve in 20 ml 8M $\text{HNO}_3$
  - Took 10 ml aliquot/held back 10 ml in reserve
  - Added 2 ml 2M $\text{Al(NO}_3\text{)}_3$
  - **Separate using 2 ml Sr Resin**
    - twice for very high total beta samples (>1000 pCi/filter)
    - Important to ensure all beta interferences were removed
  - **High, consistent Sr gravimetric yields (85-95%)**
  - **Gas flow proportional counting**
    - Simultaneous drawer counting system
  - **Results within hours!**
Approach

- Actinides (Pu, Np, Am, Cm, U) and Sr-89/90
  - Air Filters
    - HNO$_3$ + HF digestion
    - Rapid and quantitative
    - TEVA Resin + TRU Resin + Sr Resin
    - CeF$_3$ microprecipitation-alpha spectrometry
    - Sr-89/90- gas proportional counting
      - Gravimetric recovery-Sr carrier (4mg)

Actinides and Sr-90 in Air Filters

**Acid Digestion**

1. Redissolve in 6 mL 6M HNO₃ and 6 mL 2M Al(NO₃)₃
2. Add 0.5 mL 1.5M Sulfamic Acid + 1.25 mL 1.5M Ascorbic Acid
3. Add 1.25 mL 3.5 M Sodium Nitrite

**Beaker rinse:** 3mL 3M HNO₃
10mL 3M HNO₃ to stacked cartridges

**Separate cartridges:**
- TEVA Resin alone: 10 mL 3M HNO₃

**Th Elution**
20mL 9M HCl

**Pu Elution**
20mL
0.10M HCl - 0.05M HF - 0.01M TiCl₃

2 mL TEVA Resin (50-100 um)

2 mL TRU-Resin (50-100 um)

2 mL Sr-Resin (50-100 um)

**Evaporate/ beta counting**

Optional enhanced Po-210 removal

**Vacuum box procedure**

**Sr Resin alone:**
- 15 mL 8M HNO₃
- 10 mL 0.05M HNO₃
- Sr strip

Add 0.5 mL 30 wt% H₂O₂

TRU Resin alone:
Elute Am/Cm with 15 ml 4M HCL/add
15 ml H₂O + 50 ug Ce+ 3 ml HF
12 ml 4M HCl-0.2M HF -0.002M TiCl₃
Elute U with 15 ml 0.1M NH₄HC₂O₄

Add 0.5 mL 30 wt% H₂O₂

Cerium fluoride

Alpha spectrometry
<table>
<thead>
<tr>
<th>Nuclide</th>
<th>Turnaround Time (Hrs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$Pu</td>
<td>3.9</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>3.9</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>3.6</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>3.7</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>3.7</td>
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<tr>
<td>$^{90}$Sr</td>
<td>3.3</td>
</tr>
<tr>
<td>Nuclide</td>
<td>Avg. Difference (%)</td>
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<tr>
<td>----------</td>
<td>---------------------</td>
</tr>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>3.3</td>
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<tr>
<td>$^{240}\text{Pu}$</td>
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<td>$^{238}\text{U}$</td>
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<td>$^{234}\text{U}$</td>
<td>-3.4</td>
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<tr>
<td>$^{90}\text{Sr}$</td>
<td>-9.9</td>
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</table>
## Routine Performance Test Results (air filters)

**MAPEP 24**

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Result</th>
<th>Ref Value</th>
<th>Flag</th>
<th>Notes</th>
<th>Bias (%)</th>
<th>Acceptance Range</th>
<th>Unc Value</th>
<th>Unc Flag</th>
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<tbody>
<tr>
<td>Americium-241</td>
<td>0.00036</td>
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<td></td>
<td>3.2</td>
<td>False Positive Test</td>
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<tr>
<td>Cesium-134</td>
<td>3.60</td>
<td>3.49</td>
<td>A</td>
<td></td>
<td>3.2</td>
<td>2.44 - 4.54</td>
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<tr>
<td>Cesium-137</td>
<td>2.32</td>
<td>2.28</td>
<td>A</td>
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<td>1.60 - 2.96</td>
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<td>Cobalt-57</td>
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<td>3.33</td>
<td>A</td>
<td></td>
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<td>2.33 - 4.33</td>
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<td>Cobalt-60</td>
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<td>False Positive Test</td>
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<tr>
<td>Manganese-54</td>
<td>2.71</td>
<td>2.64</td>
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<td>2.7</td>
<td>1.85 - 3.43</td>
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<tr>
<td>Plutonium-238</td>
<td>0.102</td>
<td>0.096</td>
<td>A</td>
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<td>6.3</td>
<td>0.067 - 0.125</td>
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<td>Plutonium-239/240</td>
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<td>0.0765</td>
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<tr>
<td>Strontium-90</td>
<td>1.43</td>
<td>1.36</td>
<td>A</td>
<td></td>
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<td>0.95 - 1.77</td>
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<td>Uranium-234/233</td>
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<td>2.23 - 4.13</td>
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</tr>
</tbody>
</table>

MAPEP = Mixed analyte Performance Evaluation Standards

from DOE-RESL Lab Idaho, USA

± 20 acceptance limits
## Sr-89/90 Fukushima Air Filter Work

<table>
<thead>
<tr>
<th>AF Batch</th>
<th>N</th>
<th>Avg. Sr. Carrier % Recovery</th>
<th>+/- 1 sigma</th>
<th>% Recovery LCS</th>
<th>Approximate MDC (pCi/filter)</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>14</td>
<td>60.0</td>
<td>15.0</td>
<td>82.5</td>
<td>1 - 2</td>
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<tr>
<td>B</td>
<td>14</td>
<td>92.3</td>
<td>5.3</td>
<td>100.1</td>
<td>1 - 1.5</td>
</tr>
<tr>
<td>A`</td>
<td>16</td>
<td>91.1</td>
<td>7.3</td>
<td>88.6</td>
<td>1</td>
</tr>
<tr>
<td>B`</td>
<td>16</td>
<td>91.6</td>
<td>4.3</td>
<td>94.6</td>
<td>1</td>
</tr>
<tr>
<td>C`</td>
<td>16</td>
<td>92.7</td>
<td>7.3</td>
<td>104.0</td>
<td>1</td>
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<td>ARF19</td>
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<td>79.9</td>
<td>4.7</td>
<td>92.0</td>
<td>0.7</td>
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<tr>
<td>AF/Swipes A</td>
<td>7</td>
<td>93.3</td>
<td>4.0</td>
<td>94.1</td>
<td>0.5</td>
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<tr>
<td>AF/Swipes B</td>
<td>7</td>
<td>80.2</td>
<td>10.7</td>
<td>102.7</td>
<td>0.5</td>
</tr>
</tbody>
</table>

**Avg.** 85.1 94.8

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for the air filter batches A, B, A`, B` and C` - analyzed only 10 of the 20ml dissolved aliquot

ARF19 used 15 of 20 ml

AF/Swipe batches used the entire sample
Fukushima Soil Samples

- Received samples in early April, 2011
  - Rapid approval of USDA permit
- Via DOE FRMAC (Federal Monitoring and Assessment Center)
  - Gamma, Sr-89/90, actinides
  - Higher than normal activity samples
    - Rad Con and facility support
    - DOE RAP team
Fukushima Soil Samples – Sr-89/90

- Was it ok to plant rice?
  - Required MDA 2 pCi/g (74 mBq/g)
  - Rapid turnaround needed
- Sr-89/90
  - 1.5g rapid fusion method
    - Fe and Ti OH ppt with calcium phosphate added
    - Remove silicates with La/Ca F ppt
    - 3ml Sr Resin (2ml+1ml cartridges/ 6.5 mg Sr carrier)
    - 0.8 pCi/g MDA (29.6 mBq/g)
  - Lower MDA needed later for Sr-89/90 MDA
    - used 10g leach, longer count times
    - Redissolve leachate in 1M HCl, then add NH₄OH, Fe/Ti OH ppt with calcium phosphate, plus La/Ca F ppt
    - 0.05 pCi/g MDA (1.85 mBq/g)
Rapid Sodium Hydroxide Fusion
Leach Preconcentration for Sr and Actinides

- Acid leaching with multiple rinses of solids
- Evaporate leachate and redissolve
- Iron/titanium hydroxide ppt. (+Ca\textsubscript{3}(PO\textsubscript{4})\textsubscript{2}) preconcentration
- Lanthanum fluoride ppt. matrix removal


## Sr-89/90 Fukushima Soil Work

<table>
<thead>
<tr>
<th>Soil Batch</th>
<th>N</th>
<th>Avg. Sr Carrier % Recovery</th>
<th>+/- 1 sigma</th>
<th>% Sr-90 Recovery</th>
<th>LCS</th>
<th>MS</th>
<th>MDC (pCi/g)</th>
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<tbody>
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<td>1</td>
<td>14</td>
<td>78.1</td>
<td>9.4</td>
<td>115.5</td>
<td>98.8</td>
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<td>2</td>
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<td>22</td>
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<td>4</td>
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<td>79.7</td>
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<td>94.3</td>
<td>94.3</td>
<td>0.04</td>
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**Avg.** 77.2 101.4 98.6
Fukushima Soil Samples - Actinides

- **Actinides**
  - Screening with rapid fusion method (2g)
  - Analysis of large sample aliquots to achieve lower MDAs
    - Volcanic island soil contains high levels of Fe
    - Limited sample aliquot size
  - Used multiple aliquots and loaded to TEVA+TRU+DGA
    - Recombined final purified solutions from multiple purified aliquots into a single CeF$_3$ micro-ppt
      - removes uranium with H$_2$O$_2$ present (U$^{6+}$)
  - Needed to determine actinides isotopes by alpha/ICP-MS
    - Could not split purified aliquots between alpha and ICP-MS since we needed lowest MDA possible for Pu
    - so we counted 100% of aliquot by alpha spectrometry 1st
    - And then...
Fukushima Soil Samples - Actinides

- **Further processing for ICP-MS**
  - Redissolved actinides after alpha counting filters using HNO₃-boric acid
  - Loaded onto TEVA Resin, rinsed with 3M HNO₃, and eluted Pu with ICP-MS friendly solution (0.25M HCL-0.005M HF-0.001MTiCl₃)

- **Did not need to move Pu to DGA to remove U***
  - *since micro-CeF₃ ppt. with H₂O₂ present used to prepare counting sources removes 1000x uranium*

- **Having a range different rapid separation ‘tools’ allowed us to adapt to specific sample needs**

Actinides in Soil: Summary of SRS Approach

- 0.5 - 2 grams direct fusion (NaOH)
- 2 - 10 grams HNO₃-HF Si removal, then fusion
- 10 - 100+ grams acid leach

In all cases we use Fe/Ti OH precipitation followed by LaF₃ precipitation to preconcentrate actinides and eliminate soil matrix:
  - Silicates, Fe
  - Sr-89/90 can be collected also (Ca + PO₄)
Fukushima Emergency Soil Samples

- **Gamma**
  - important to have different size calibrated geometries for soil
  - communication on gamma library (isotopes, parent-daughter, etc)
- **Sr-89/90**
  - Capability to increase to 10g aliquot was important to allow better
determination of Cs/Sr isotopic ratios
  - Simultaneous gas proportional counters allowed longer count times
  - Samples with high total beta interferences may need 2\textsuperscript{nd} column
  - separation
- **Actinides**
  - Important to have large aliquot capability that can be used with alpha
  - spectrometry and/or ICP-MS
  - May have to adapt methods to specific needs
  - High U-238 DF critical for Pu-239/ options
    - TEVA to DGA thru UTEVA (>10E6)
    - CeF\textsubscript{3} + H\textsubscript{2}O\textsubscript{2}
Sr-89/90 in Seawater

• Received questions from Japanese scientists after Fukushima about Sr-89/90 in seawater
  – Japan still using fuming nitric method
• Asked about Eichrom Sr Resin methods
  – Seawater contains 8 mg/L Sr
  – Recommended
    • ICP-ES Sr assay, using stable Sr as yield monitor
    • Either calcium phosphate or calcium carbonate ppt
    • 8M HNO₃+Al(NO₃)₃ column load solution
    • 3ml of Sr resin (2ml resin if stable Sr 5mg or less)
    • Gas flow proportional counting
Readiness for Events Requires Continual Progress

- Actinides in
  - Concrete/Brick
  - Food
- Ra-226 using Ra-225 tracer
  - Concrete, brick, vegetation, urine, filters
Rapid Fusion Application for Concrete and Brick

Rapid radiochemical method for determination of actinides in emergency concrete and brick samples.
Maxwell SL, Culligan BK, Kelsey-Wall A, Shaw PJ.
Fukushima Impact on Food Chain

- Radiation fallout from the wrecked Fukushima nuclear plant poses a growing threat to Japan’s food chain as unsafe levels of cesium found in beef on supermarket shelves were also detected in more vegetables and the ocean.

Japan’s Food-Chain Threat Multiplies as Fukushima Radiation Spreads

By Aya Takada - JUL 25, 2011 4:59 AM ET

Rapid Determination of Actinides in Emergency Food Samples
S. L. Maxwell, B. K. Culligan, A. Kelsey-Wall and P. J. Shaw,
in press, Journal of Radioanalytical and Nuclear Chemistry
Ra-226 in Solid Samples

• Challenges
  – Difficulty separating Ca from Ra/Ba
  – Adequate tracer? (Ba-133)
  – Native barium interference on alpha spectrometry source preparation
    • Poor alpha resolution
    • Isobaric interferences using ICP-MS
    • MnO$_2$ resin can be used for waters but Ra precipitates with Fe(OH)$_3$ at high pH
• Different approach
Ra-226 Spectra using At-217 tracer
Summary

• SRS Environmental Bioassay Lab supported Japan and with fast, quality results
  – NRIP/EPA emergency preparedness testing helped prepare us
  – Rapid radiochemical methods are essential
  – Sr-89/90, gamma, actinides (alpha and ICP-MS)

• Ability to adapt / apply various analytical tools is important
  – Communication with customer
  – Data packaging/QC review was huge part of the effort

• Rapid methods for emergency response can result in cost savings for routine operations
Recent Publications

• Soil


• Concrete and Brick


• Email me at sherrod.maxwell@srs.gov for a copy
Recent Publications

• Urine and Water


Maxwell, S. and Culligan, B., (2009), Rapid separation method for emergency water and urine samples, J. Radioanal. Nucl. Chem, 279 (No.3), 901


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