Emergency Method for Radiochemical Separations in Bioassay and Environmental Samples

2015-RRMC, Iowa City, IA
Corey White, Steven N. Bakhtiar, Mansour Akbarzadeh

WIPP LABORATORIES
Carlsbad, NM
WIPP LABORATORIES

MATRICES:
• URINE
• FECES
• AIR FILTERS
• WATERS
• SOILS/SEDIMENTS
• ANIMAL TISSUE
• VEGETATION
• ROCK SALT
• BRINE
• OTHERS, AS REQUESTED

CAPABILITIES:
• ALPHA SPECTROSCOPY
• GAS PROPORTIONAL COUNTING
• GAMMA SPECTROSCOPY
• LIQUID SCINTILLATION COUNTING
• ICP-MASS SPECTROSCOPY

PERFORMANCE EVALUATION:
• DOELAP
• NRIP ROUTINE/EMERGENCY
• MAPEP
• EPA
### History of NRIP Emergency Samples at WIPP Labs

<table>
<thead>
<tr>
<th>Year</th>
<th>Matrix</th>
<th>Measured Analyses</th>
<th>TAT (Destructive)</th>
<th>TAT (Non-Destructive)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2004</td>
<td>Water/Filters</td>
<td>Co-60, Ba-133, Cs-137, Eu-152</td>
<td>NA</td>
<td>&lt;8 hours</td>
</tr>
<tr>
<td>2005</td>
<td>Filters</td>
<td>Mn-54, Zn-65, Cs-137, Gross Alpha &amp; Beta</td>
<td>NA</td>
<td>&lt;8 hours</td>
</tr>
<tr>
<td>2007</td>
<td>Synthetic Urine</td>
<td>Th-230, Sr-90, Co-60, Ba-133, Cs-237, Eu-152</td>
<td>9.8 hours</td>
<td>4 hours</td>
</tr>
<tr>
<td>2007</td>
<td>Synthetic Urine/ Synthetic Feces</td>
<td>Am-241, Cm-243, Pu-238, Pu-240, U-238, U-234, Sr-90, Co-60, Co-57, Cs-137</td>
<td>8.7 hours (urine)</td>
<td>10.5 hours (Feces)</td>
</tr>
<tr>
<td>2009</td>
<td>Synthetic Urine/ Synthetic Feces</td>
<td>Am-241, Pu-238, Pu-240, Sr-90, Co-60, Co-57, Cs-137</td>
<td>11.9 hours (urine)</td>
<td>7.5 hours (Feces)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>3.7 hours (Feces)</td>
<td></td>
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</tbody>
</table>
### History of Emergency Samples at WIPP Labs

#### Continued

<table>
<thead>
<tr>
<th>Year</th>
<th>Matrix</th>
<th>Measured Analyses</th>
<th>TAT (Destructive)</th>
<th>TAT (Non-Destructive)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2010</td>
<td>Synthetic Urine/ Synthetic Feces</td>
<td>Cm-243, Am-241, Pu-238, Pu-240, U-238, U-235, U-234, Sr-90, Co-60, Co-57, Cs-237</td>
<td>7.9 hours (urine)</td>
<td>4.9 hours</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>9.8 hours (feces)</td>
<td></td>
</tr>
<tr>
<td>2011</td>
<td>Synthetic Feces</td>
<td>Am-241, Pu-238, Pu-240, U-238, U-235, U-234, Sr-90, Mn-54, Co-60, Cs-134</td>
<td>8 hours</td>
<td>8 hours</td>
</tr>
<tr>
<td>2012</td>
<td>Synthetic Feces</td>
<td>Cm-243, Am-241, Pu-238, Pu-240, U-238, U-235, U-234, Sr-90, Co-60, Cs-137</td>
<td>8 hours</td>
<td>3.8 hours</td>
</tr>
<tr>
<td>2013</td>
<td>Synthetic Feces</td>
<td>Am-241, Pu-240, Pu-238, U-238, U-234, Sr-90, Cs-134, Co-60</td>
<td>7.7 hours</td>
<td>6.0 hours</td>
</tr>
<tr>
<td>2014</td>
<td>Synthetic Feces</td>
<td>Am-241, Pu-240, Pu-238, U-238, U-234, Sr-90, Cs-137, Co-60</td>
<td>8.1 hours</td>
<td>5.1 hours</td>
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<tr>
<td>2015</td>
<td>Synthetic Feces/ Synthetic Urine</td>
<td>Am-241, Pu-240, Pu-238, U-238, U-234, Sr-90, Cs-137, Co-60</td>
<td>7.8 hours (urine)</td>
<td>4.0 hours (Feces)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.9 hours (feces)</td>
<td></td>
</tr>
</tbody>
</table>
History of Emergency Samples at WIPP Labs

Emergency Exercise Bias (Feces)

Year

% Bias

-50% -40% -30% -20% -10% 0% 10% 20% 30% 40% 50%


-20% -10% 0% 10% 20% 30% 40% 50%

-50%

241Am 239Pu 238U 60Co 137Cs
Standard Procedure for Emergency Samples at WIPP Labs

1. Aliquot tracers prior to arrival

2. Rapid digestion methods

3. Standard Eichrom Vacuum Box Methods
   A. TEVA/TRU/SR column cartridge stack
   B. Double SR resin to increase Sr recoveries

4. NdF$_3$ micro-precipitation, utilizing vacuum box to filter multiple samples simultaneously

5. Improved back end data V+V with implementation of automated LIMS
History of Emergency Samples at WIPP Labs

Sr Recoveries For Emergency Feces Samples

Year

Recovery


0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8
Assembly Line Processing
Sample Loading

• OXIDATION STATE ADJUSTMENT
  • 1.5M SULFAMIC ACID
  • 1.5M ASCORBIC ACID
  • 5mg/mL FERRIC NITRATE
  • 3.5M SODIUM NITRITE

• LOAD COLUMNS
Assembly Line Processing
Split Columns
Assembly Line Processing

\[ \text{SrCO}_3 \text{ Precipitation} \]

- Double SR resin cartridge for improved Sr recoveries
Assembly Line Processing
Rapid Micro-Filtration
## TIME BREAKDOWN

**Fecal**

<table>
<thead>
<tr>
<th>Activity</th>
<th>Pu</th>
<th>Am</th>
<th>U</th>
<th>Sr</th>
<th>Gamma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Prep</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>Separations</td>
<td>120</td>
<td>100</td>
<td>115</td>
<td>100</td>
<td>NA</td>
</tr>
<tr>
<td>Post Columnning</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>60</td>
<td>NA</td>
</tr>
<tr>
<td>Mounting</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>30</td>
<td>NA</td>
</tr>
<tr>
<td>Count Time</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Processing</td>
<td>60</td>
<td>60</td>
<td>60</td>
<td>40</td>
<td>20</td>
</tr>
<tr>
<td>V+V / Reporting</td>
<td>46</td>
<td>55</td>
<td>45</td>
<td>45</td>
<td>38</td>
</tr>
<tr>
<td><strong>Total (min)</strong></td>
<td>466</td>
<td>455</td>
<td>455</td>
<td>455</td>
<td>238</td>
</tr>
<tr>
<td><strong>Total (Hours)</strong></td>
<td>7.92</td>
<td>7.58</td>
<td>7.58</td>
<td>7.58</td>
<td>3.98</td>
</tr>
<tr>
<td><strong>NIST Reporting Time (hrs)</strong></td>
<td>7.92</td>
<td>7.58</td>
<td>7.58</td>
<td>7.58</td>
<td>3.98</td>
</tr>
</tbody>
</table>
AMERICIUM SPECTRUM
PLUTONIUM SPECTRUM
Normal TAT Urine
CURRENT & FUTURE IMPROVEMENTS

1. INCREASE $^{(D)}$COUNT TIME TO DECREASE MDA 30 MINUTES TO 60 MINUTES

2. INCREASE COLUMN FLOW RATES, CUT SEPERATION TIME. PLAN TO CONDUCT FRACTIONATION STUDIES OF ELUTION PATTERNS

3. USING $^{239}$Pu TRACER FOR $^{239}$Pu EMERGENCY SAMPLES

4. INCREASE $^{(D)}$Sr RECOVERIES FOR MORE ACCURATE MEASUREMENTS DOUBLING CARTRIDGE

5. UTILIZATION OF LSA TO REDUCE INITIAL BACKGROUND

6. INCORPORATE LIMS SYSTEM TO STREAMLINE DATA PROCESSING
Application of Emergency Methods to Routine samples

More Samples

Less Time
**APPLICATION TO WIPP LABORATORIES**

<table>
<thead>
<tr>
<th>Year</th>
<th>Destructive Analysis Samples</th>
<th>Rush Sample Analyses</th>
</tr>
</thead>
<tbody>
<tr>
<td>2011</td>
<td>832</td>
<td>9</td>
</tr>
<tr>
<td>2012</td>
<td>864</td>
<td>7</td>
</tr>
<tr>
<td>2013</td>
<td>915</td>
<td>25</td>
</tr>
<tr>
<td>2014</td>
<td>1710</td>
<td>N/A</td>
</tr>
<tr>
<td>2015</td>
<td>1170*</td>
<td>198*</td>
</tr>
</tbody>
</table>

*thru 10-1-15

- “New Normal” at WIPP Laboratories
- Apply Emergency methods to “every day” samples
New Normal

• Bioassay Monitoring Program

✓ 30 samples/quarter every year prior to February 2014

✓ 197 bioassay samples analyzed in 2014 for Pu and Am
✓ 213 samples analyzed in 2014 for Pu, Am, Sr, and Cs-137

✓ >120 samples/quarter since initial recovery requiring Pu, Am, Sr and Cs-137
New Normal

Standard Procedure for Rush Brine Samples at WIPP Labs

- Communicate with Client (midday)
- Aliquot tracers prior to arrival
- Upon arrival (3:30PM) - Sample aliquot, precipitate, spin, prep for columns
New Normal

Standard Procedure for Rush Brine Samples at WIPP Labs

Separate through TEVA/TRU Stack, NdF₃ micro-precipitation (completed by 12:00PM day after arrival)

1000 minute overnight alpha count

Data reported to client (12:00 PM 2nd day) <48 hours after receipt
Rapid Sample Processing = Quality Data Consistently!

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Average Bioassay Tracer Recovery (2015)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu</td>
<td>95%</td>
</tr>
<tr>
<td>Am</td>
<td>80%</td>
</tr>
<tr>
<td>Sr</td>
<td>70%</td>
</tr>
<tr>
<td>U</td>
<td>85%</td>
</tr>
</tbody>
</table>
Rapid Sample Processing = Quality Data Consistently!

## MAPEP Series 32 Biases

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Soil (%)</th>
<th>Water (%)</th>
<th>Vegetation (%)</th>
<th>Air Filter (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{238}$Pu</td>
<td>-0.7</td>
<td>Sensitivity (A)</td>
<td>-0.9</td>
<td>False Pos. (A)</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>-2.0</td>
<td>-4.9</td>
<td>-3.4</td>
<td>-0.7</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>-1.3</td>
<td>-10.4</td>
<td>-6.5</td>
<td>-7.5</td>
</tr>
<tr>
<td>$^{90}$Sr</td>
<td>-9.2</td>
<td>-2.2</td>
<td>0.0</td>
<td>-0.7</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>1.0</td>
<td>-3.4</td>
<td>6.0</td>
<td>-8.4</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>-5.0</td>
<td>-2.9</td>
<td>-10.2</td>
<td>-10.2</td>
</tr>
</tbody>
</table>
Conclusions

1. Trust the Data
   - Years of NRIP emergency exercise data show that the process works
   - Value in performance evaluations

2. Increased Quantity ≠ Decreased Quality

3. Adapt to the situation
ACKNOWLEDGEMENTS

Kevin Johnson, Chris Gomez, Jesse Welch, Braden Klein, Donna Guevara, Ginny Jones