NRIP: NIST Radiochemistry Intercomparison Program

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NIST Physical Measurement Laboratory Radioactivity Group
NRIP inception year 1997

Exercise types (2):  **Routine** (60 day turnaround)  
**Emergency** (8 hour turnaround)

Objectives (Wu et al., Applied Rad. Isotopes 56 [2002], 379)

1. Assess **measurement traceability** for radiochem analysis of environmental and radiobioassay samples

2. Evaluate capability of radiochemical methods to handle **matrix effects** and **RN interferences**

3. Validate **new radiochemical methods** to improve quality of low level measurements
Measurement Traceability in NRIP

NIST: must prepare and verify high-quality samples with accurately known RN content and uncertainties

Participating Labs (Clients): measure RN amounts in real samples, report activities or activity concentrations ± uncertainties (k=2)

Evaluation of traceability: according to ANSI N42.22 and/or ANSI N13.30 acceptance criteria

(more detailed explanation of traceability coming later --- stay tuned!)
NRIP matrices (5):

Current

1. Air filters (glass fiber and paper)
2. Acidified water (1 Liter, 5% HNO3)
3. Soil (1 g)
4. Synthetic urine (100 mL or 1 Liter, acidified)
5. Synthetic fecal (~ 100 g)

Future (?)

- Vegetation
- Food (e.g., applesauce, milk)
- Drinking water
Radionuclides and Levels (NRIP 2012 SOW)

Activity levels:

Low enough to minimize lab contamination

High enough to reliably test accuracy & precision
<table>
<thead>
<tr>
<th>Category</th>
<th>Radionuclides (potentially present)</th>
<th>Maximum Activity (Bq/Sample)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Routine</td>
</tr>
<tr>
<td>Gamma-emitters</td>
<td>$^{54}$Mn, $^{57,58,60}$Co, $^{65}$Zn, $^{133}$Ba, $^{134,137}$Cs, $^{134,137}$Cs, $^{152}$Eu, $^{192}$Ir</td>
<td>250</td>
</tr>
<tr>
<td>Beta-emitters</td>
<td>$^{89}$Sr, $^{210}$Pb, $^{228}$Ra</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$^{90}$Sr</td>
<td>4</td>
</tr>
<tr>
<td>Alpha-emitters</td>
<td>$^{210}$Po, $^{226}$Ra, $^{234,235,238}$U, $^{237}$Np, $^{238,239,240}$Pu, $^{241}$Am, $^{244}$Cm</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$^{228,230,232}$Th</td>
<td>2</td>
</tr>
<tr>
<td>Gross Alpha</td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>Gross Beta</td>
<td></td>
<td>3000</td>
</tr>
</tbody>
</table>
Sample preparation: (1) Master Spiking Solution

Gravimetric additions

SRMs (\(^{60}\)Co, \(^{90}\)Sr, \(^{137}\)Cs, \(^{210}\)Pb, \(^{226}\)Ra, \(^{230}\)Th, natU, \(^{238}\)Pu, \(^{240}\)Pu, \(^{241}\)Am)

NIST-calibrated RNs (\(^{54}\)Mn, \(^{57}\)Co, \(^{65}\)Zn, \(^{134}\)Cs)

HNO\(_3\) (1 – 3 M)

Carriers (Co, Zn, Cs)

Sealed ampoules (5 – 20 mL)
(2) Verification of RN concentrations in Master Spiking Solution

<table>
<thead>
<tr>
<th>Gamma-emitters ($^{54}\text{Mn}, , ^{57,60}\text{Co}, , ^{65}\text{Zn}, , ^{134,137}\text{Cs}$): 2 mL RN mix against 2 mL pure RN source on HPGe (matched geometries), compare net photopeak rates (gamma spectrometry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beta-emitters (e.g., $^{90}\text{Sr}$): radiochemical separation from aliquant of RN mix after carrier addition &amp; chemical equilibration; gravimetric chemical recovery (e.g., SrCO$_3$), beta counting on calibrated gas-flow proportional counter</td>
</tr>
<tr>
<td>Alpha-emitters (e.g., $^{238}\text{Pu}$): radiochemical separation from aliquant of RN mix after tracer (e.g., $^{236}\text{Pu}$ or $^{242}\text{Pu}$) addition &amp; chemical equilibration; source preparation and alpha spectrometry</td>
</tr>
</tbody>
</table>
How good are NIST’s verification capabilities?

Alpha spectrometry, gas-flow proportional counting (beta), and gamma spectrometry (geometry-matched) capabilities:

Bias < 1% with respect to NIST SRMs
(experimentally confirmed)

Typical precision for comparative activity measurements (gamma, beta) from spiked matrix sources:

Precision ≤ 2% (1s, n = 5)
(experimental results)
(3) Spiking individual samples – gravimetric addition

Master Spiking Solution

- Spiked air filter
- Air filter
- Soil (1g)
- Acidified Water
- Synthetic Urine
- Synthetic Feces
Traceability of samples: to establish a link from the actual sample to the master spiking solution

How? Select randomly 5 samples for quantitative radiochemical analysis focusing on alpha-emitters and $^{90}$Sr

results of analyses: $^{90}$Sr, $^{230}$Th, $^{234,238}$U, $^{238,240}$Pu, $^{241}$Am

average $C \pm u_C (k=2)$ (Bq/g of spike)

Check agreement: Differences typically $\leq 1\%$ actinides, $\leq 2\%$ $^{90}$Sr

Well-known activity concentrations, $C_{MSS}$

Master Spiking Solution
(4) Confirmation of relative activity of sample series

Counts/channel

Channel no. (gamma-ray energy)

Normal distribution check (outlier search)

Count rate/g of spike
Traceability Chain for NRIP Samples

- Primary NIST SRMs
- Verification
- Gravimetric dilution
- Master Spiking Solution
- Gravimetric addition
- Verification
- Selected Samples
- Confirmation of relative activity of set
- Sample Set
Participating labs:

- **Choose 4 sets** of samples from 5 matrices and 2 exercise types
- Receive samples & instruction sheets, reporting forms
- **Select which RNs** to analyze and report
- Submit results ± unc (k=2) to NIST for evaluation

NIST

- Evaluates lab’s reported RN results against NIST values *(differences)*
- Determines **traceability limits** based on lab unc and NIST unc according to ANSI N42.22 and N13.30 criteria
- Issues **Report of Traceability** with traceability limits and pass/fail determination for each reported RN
ANSI N42.22 defines the acceptance criteria for verification testing by NIST as:

$$|V_R - V_N| < 3 \times [(U_{CR})^2 + (U_{CN})^2]^{1/2}$$

$V_N$ = NIST Value;
$V_R$ = Reported Value
$U_{CN}$ = Standard combined uncertainty of the NIST value, $V_N$
$U_{CR}$ = Standard combined uncertainty of the Laboratory value, $V_R$

$3 \times [(U_{CR})^2 + (U_{CN})^2]^{1/2} = \text{Traceability Limit}$ (limit to which measurement traceability may be claimed with 99% confidence)

Reference: ANSI N42.22-1995, “Traceability of Radioactive Sources to the National Institute of Standards and Technology (NIST) and Associated Instrument Quality Control.”
ANSI N13.30 defines the radiobioassay acceptance criteria as -25% to +50% for relative bias and as -40% to +40% for relative precision (one sigma total propagated uncertainty):

\[ B_{ri} = \frac{(C_i - C_{si})}{C_{si}} \]

is the relative bias of measurement for sample i,

\[ C_i \]

is the lab’s measured activity concentration,

\[ C_{si} \]

is the NIST spike activity concentration

\[ B_r = \sum_{i=1}^{N} \frac{(B_{ri})}{N} \]

is the relative bias of the lab’s measurement for the complete sample set of N samples

\[ S_B^2 = \sum_{i=1}^{N} (B_{ri} - B_r)^2 \]

where \( S_B \) is the relative precision of the lab’s set of measurements

(N – 1)

### Lab “A” Acidified Water NRIP’12 Measurement Results

Reported value = mean of 5 sample analyses

<table>
<thead>
<tr>
<th>Nuclide</th>
<th>NIST Value $^{2,3}$</th>
<th>Reported Value $^4$</th>
<th>Difference $^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Massic Activity Bq$\cdot$g$^{-1}$</td>
<td>Relative Expanded Uncertainty (%), $k=2$</td>
<td>Massic Activity Bq$\cdot$g$^{-1}$</td>
</tr>
<tr>
<td>$^{60}$Co</td>
<td>504</td>
<td>0.59</td>
<td>491</td>
</tr>
<tr>
<td>$^{137}$Cs</td>
<td>682</td>
<td>0.76</td>
<td>687</td>
</tr>
<tr>
<td>$^{234}$U</td>
<td>4.23</td>
<td>1.00</td>
<td>3.92</td>
</tr>
<tr>
<td>$^{235}$U</td>
<td>0.202</td>
<td>0.65</td>
<td>0.189</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>4.39</td>
<td>0.63</td>
<td>4.24</td>
</tr>
<tr>
<td>$^{238}$Pu</td>
<td>1.29</td>
<td>0.71</td>
<td>1.25</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>1.65</td>
<td>0.79</td>
<td>1.60</td>
</tr>
<tr>
<td>$^{241}$Am</td>
<td>3.86</td>
<td>0.82</td>
<td>3.89</td>
</tr>
</tbody>
</table>

### Methods

<table>
<thead>
<tr>
<th>Activity Measurements</th>
<th>NIST$^6$</th>
<th>Reporting Laboratory$^7$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alpha-, Beta-, Gamma-Spectrometry Mass Spectrometry</td>
<td>Alpha-, Gamma-Spectrometry</td>
</tr>
</tbody>
</table>

Differences range from -7.3% to 0.7%
<table>
<thead>
<tr>
<th>Nuclide</th>
<th>ANSI N42.22 Traceable</th>
<th>Traceability Limit (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{60}\text{Co}$</td>
<td>Yes</td>
<td>6.2</td>
</tr>
<tr>
<td>$^{137}\text{Cs}$</td>
<td>Yes</td>
<td>6.1</td>
</tr>
<tr>
<td>$^{234}\text{U}$</td>
<td>Yes</td>
<td>12.4</td>
</tr>
<tr>
<td>$^{235}\text{U}$</td>
<td>Yes</td>
<td>39</td>
</tr>
<tr>
<td>$^{238}\text{U}$</td>
<td>Yes</td>
<td>12.9</td>
</tr>
<tr>
<td>$^{238}\text{Pu}$</td>
<td>Yes</td>
<td>15.4</td>
</tr>
<tr>
<td>$^{240}\text{Pu}$</td>
<td>Yes</td>
<td>14.2</td>
</tr>
<tr>
<td>$^{241}\text{Am}$</td>
<td>Yes</td>
<td>19.0</td>
</tr>
</tbody>
</table>

Traceability limits from 6.1% ($^{137}\text{Cs}$) to 39% ($^{235}\text{U}$).
Possible Future Directions

- Extended radionuclide selection ($^3$H, $^{254}$Cf, . . .)?
- Additional/modified matrices (drinking water, vegetation, foodstuff [applesauce, milk], concrete, . . .)
- Labs send/specify their own special matrices for spiking (!)
- Mass spec certified RNs?
- Short-lived RNs ($t_{1/2} < 30$ days?) for emergency exercise?

“Impediments”
- Lawyer-approved contract/agreement requirements
- Variable cost depending on type & number of samples?
- Shipping (e.g., acid solutions)
Concluding Remarks

• NRIP now has 15 years of positive experience

• Participants receive benefits of careful attention to preparation of performance evaluation materials, evaluation of results, traceability assessment & official report, assistance in solving problems

• NRIP strives to maintain quality (and hold down expense)

• Feedback from participating labs helps to strengthen NRIP and focus its efforts

• Emergency exercise (unique!) offers valuable opportunities for labs to sharpen skills, prepare for real emergencies