NRIP: NIST Radiochemistry Intercomparison Program

CIRMS 2012 Meeting at the National Institute of Standards and Technology, Gaithersburg, MD

October 22 – 25, 2012

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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% HNO_3)**
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)

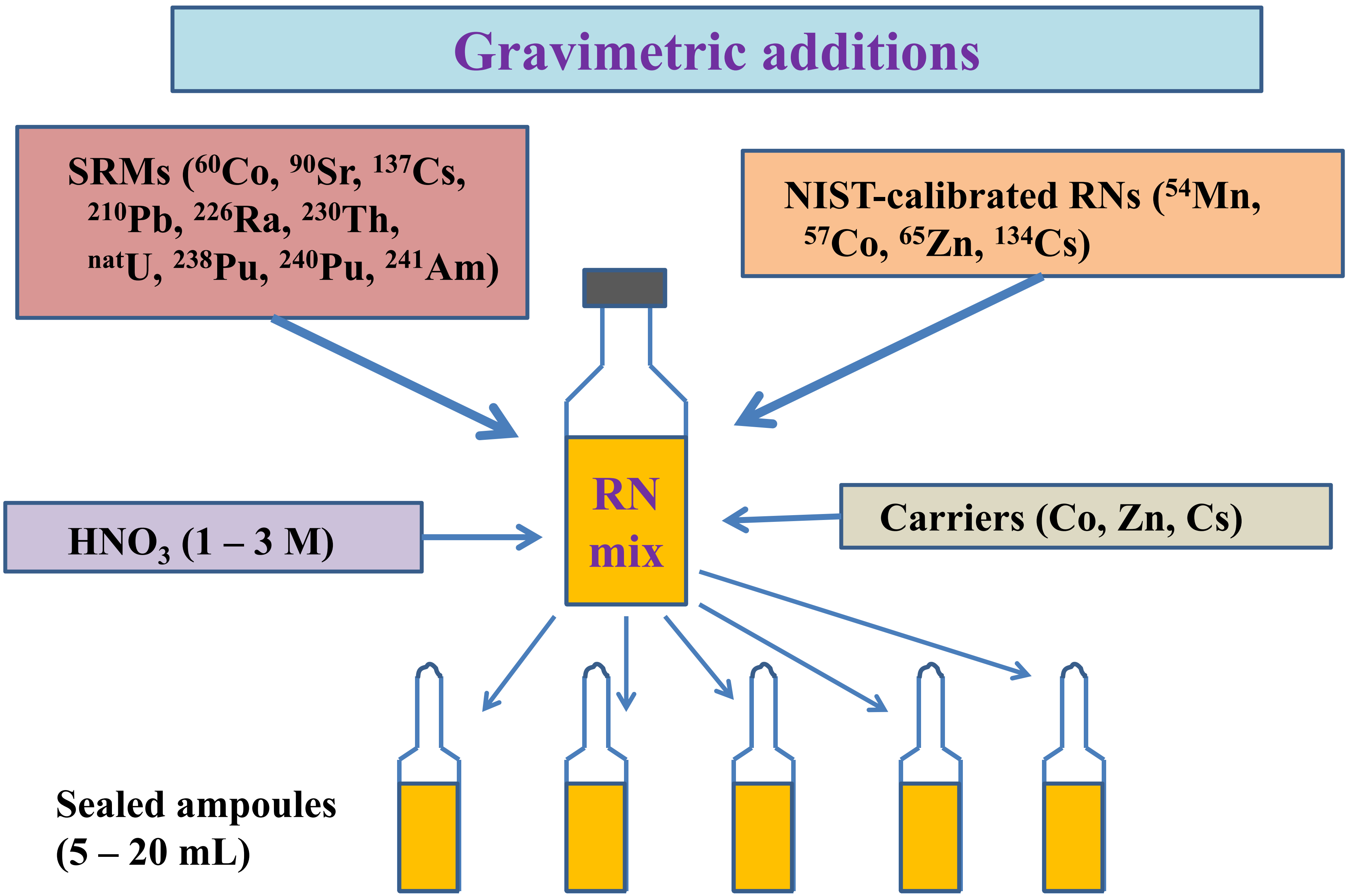
Activity levels:

Low enough to minimize lab contamination

High enough to reliably test accuracy & precision

Category	Radionuclides (potentially present)	Maximum Activity (Bq/Sample)	
		Routine	Emergency
Gamma-emitters	^{54}Mn, ^{57,58,60}Co, ^{65}Zn, ^{133}Ba, ^{134,137}Cs, ^{134,137}Cs, ^{152}Eu, ^{192}Ir	250	250
Beta-emitters	^{89}Sr, ^{210}Pb, ^{228}Ra	1	10
	^{90}Sr	4	10
Alpha-emitters	^{210}Po, ^{226}Ra, ^{234,235,238}U, ^{237}Np, ^{238,239,240}Pu, ^{241}Am, ^{244}Cm	1	10
	^{228,230,232}Th	2	20
Gross Alpha		60	550
Gross Beta		3000	3000

Sample preparation: (1) Master Spiking Solution



(2) Verification of RN concentrations in Master Spiking Solution

Gamma-emitters (^{54}Mn, ^{57,60}Co, ^{65}Zn, ^{134,137}Cs): 2 mL RN mix against 2 mL pure RN source on HPGe (matched geometries), compare net photopeak rates (gamma spectrometry)

Beta-emitters (e.g., ^{90}Sr): radiochemical separation from aliquant of RN mix after carrier addition & chemical equilibration; gravimetric chemical recovery (e.g., $SrCO_3$), beta counting on calibrated gas-flow proportional counter

Alpha-emitters (e.g., ^{238}Pu): radiochemical separation from aliquant of RN mix after tracer (e.g., ^{236}Pu or ^{242}Pu) addition & chemical equilibration; source preparation and alpha spectrometry

How good are NIST's verification capabilities?

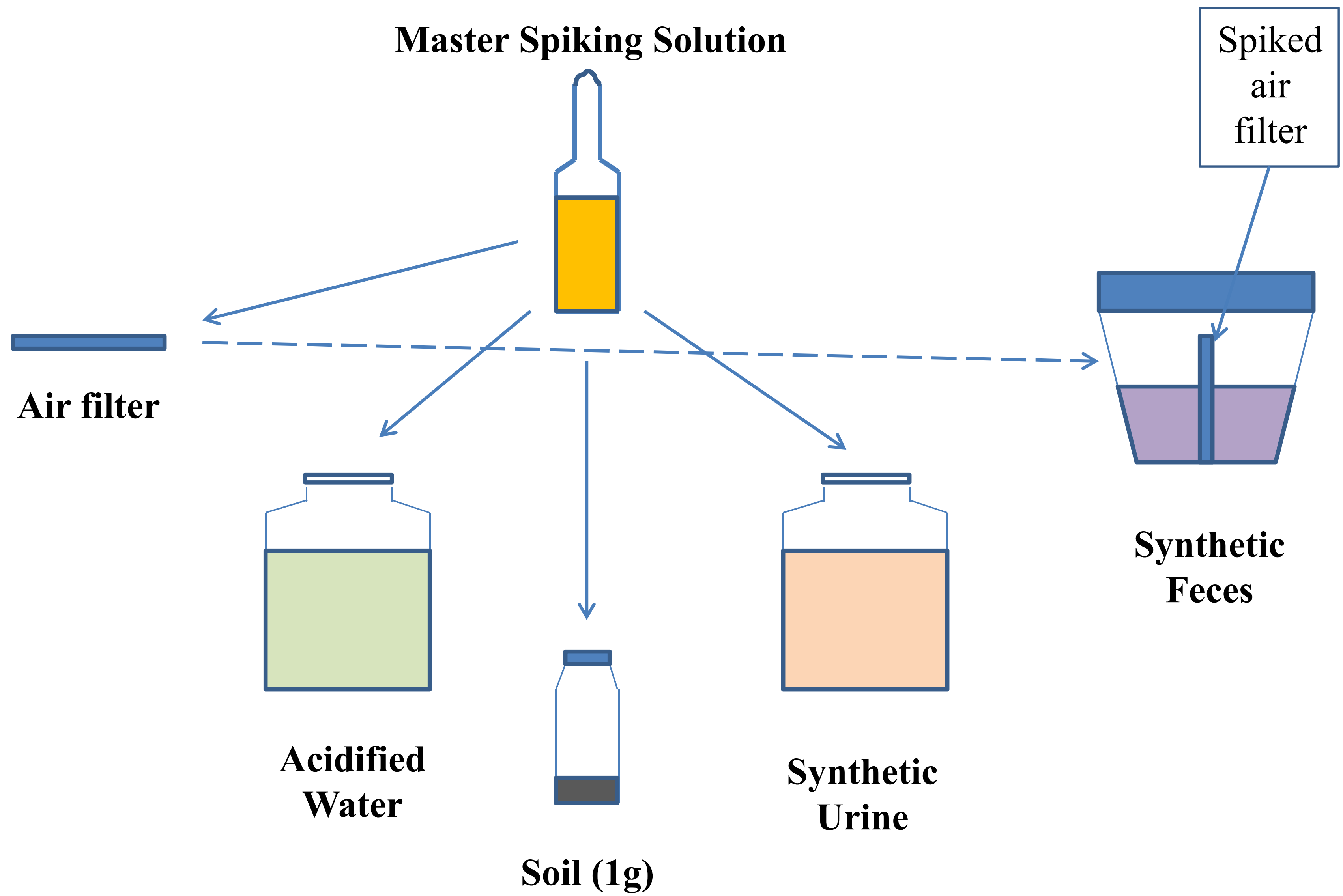
Alpha spectrometry, gas-flow proportional counting (**beta**), and **gamma** spectrometry (geometry-matched) capabilities:

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

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

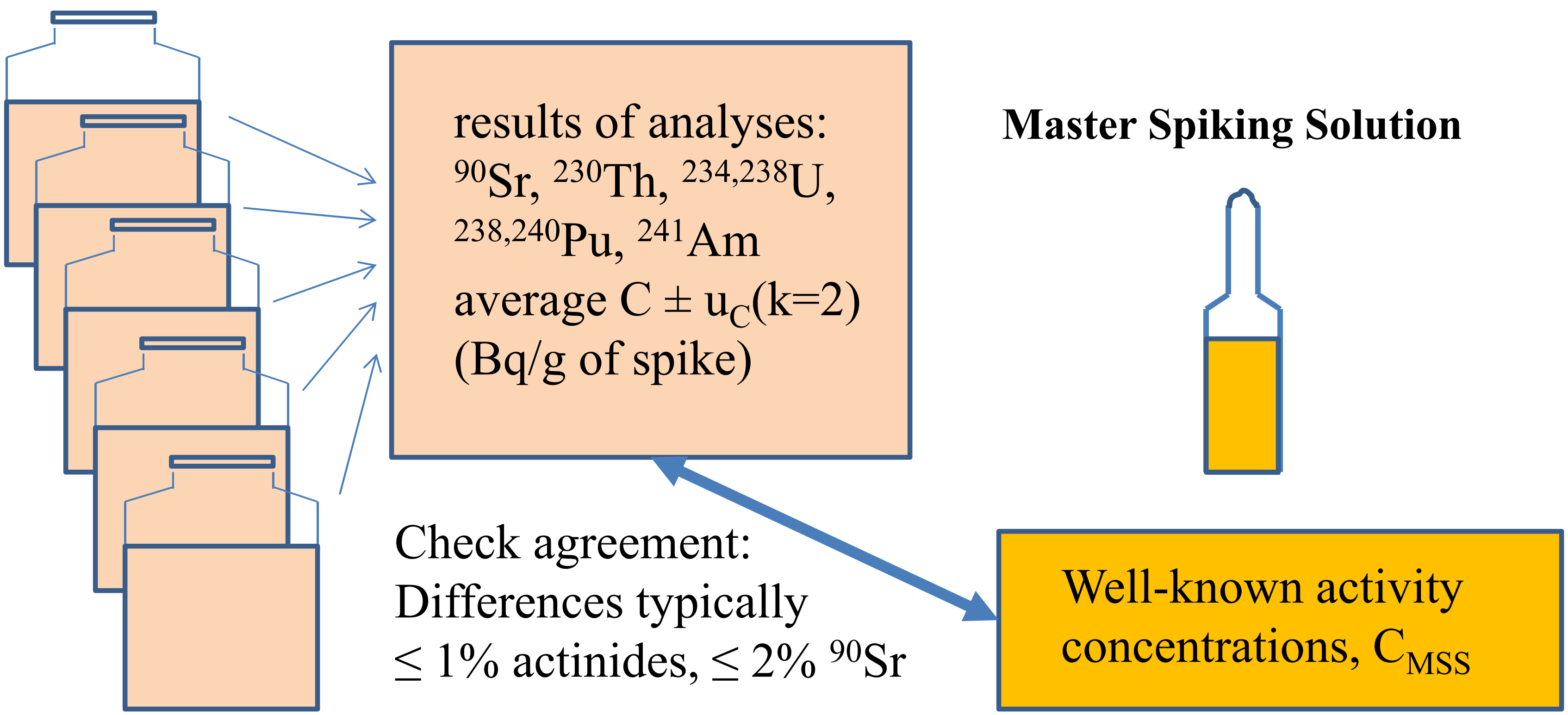
Precision ≤ 2% (1s, n = 5)
(experimental results)

(3) Spiking individual samples – gravimetric addition

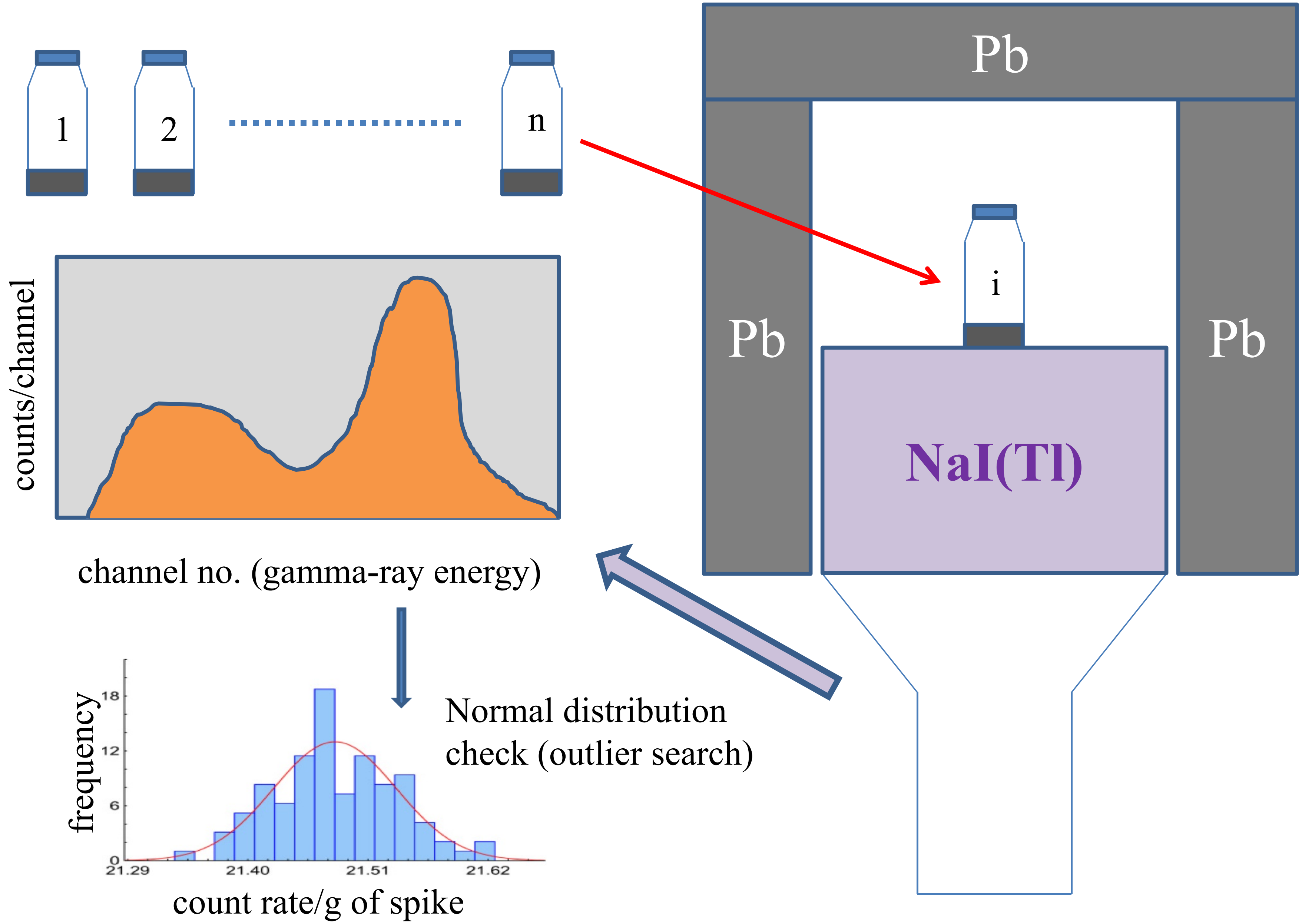


Traceability of samples: to establish a link from the actual sample to the master spiking solution

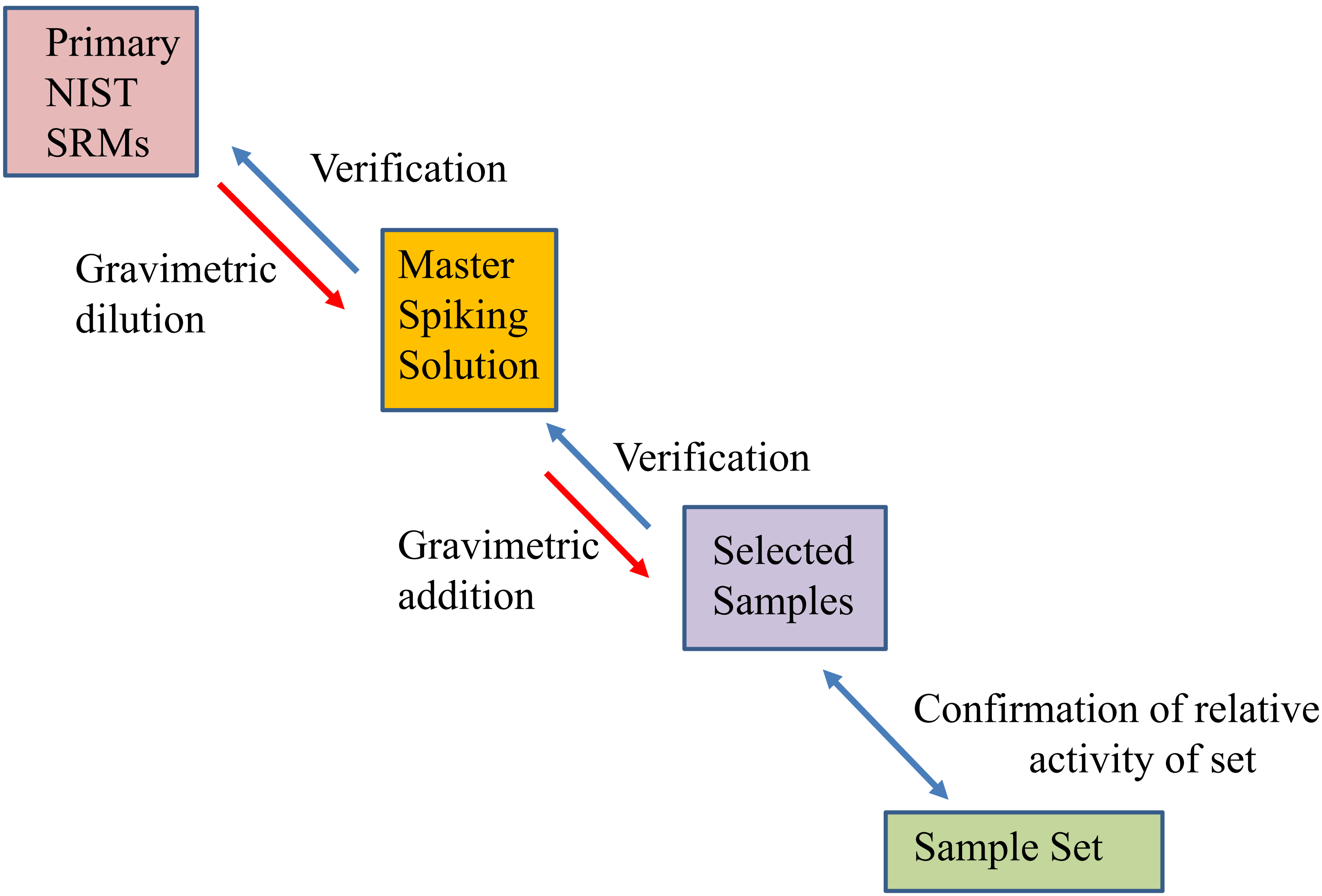
How? Select randomly 5 samples for **quantitative radiochemical analysis** focusing on alpha-emitters and ^{90}Sr



(4) Confirmation of relative activity of sample series



Traceability Chain for NRIP Samples



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

Traceability for Radiochemical Analyses

ANSI N42.22 defines the acceptance criteria for verification testing by NIST as:

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

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

$\mathbf{3 * [(U_{CR})^2 + (U_{CN})^2]^{1/2}}$ = **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."

Traceability for Radiobioassay

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):

$$\mathbf{B_{ri} = (C_i - C_{si})/C_{si}}$$

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

$$\mathbf{B_r = \sum_{i=1}^{N} (B_{ri})/N}$$

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

$$\mathbf{S_B^2 = \frac{\sum_{i=1}^{N} (B_{ri} - B_r)^2}{(N-1)}}$$

where $\mathbf{S_B}$ is the **relative precision** of the lab's set of measurements

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Reference: ANSI National Standards Institute, ANSI N13.30-1996, "Performance Criteria for Radiobioassay."

Lab "A" Acidified Water NRIP'12 Measurement Results

Reported value = mean of 5 sample analyses

Nuclide	NIST Value [2,3]		Reported Value [4]		Difference [5]
	Massic Activity Bq•g^{-1}	Relative Expanded Uncertainty (%, k=2)	Massic Activity Bq•g^{-1}	Relative Expanded Uncertainty (%, k=2)	(%)
^{60}Co	504	0.59	491	4.2	-2.6
^{137}Cs	682	0.76	687	4.0	0.7
^{234}U	4.23	1.00	3.92	8.8	-7.3
^{235}U	0.202	0.65	0.189	27.6	-6.3
^{238}U	4.39	0.63	4.24	8.9	-3.4
^{238}Pu	1.29	0.71	1.25	10.6	-3.1
^{240}Pu	1.65	0.79	1.60	9.7	-2.9
^{241}Am	3.86	0.82	3.89	12.6	0.6
Methods					
Activity Measurements		NIST [6]		Reporting Laboratory [7]	
		Alpha-, Beta-, Gamma-Spectrometry Mass Spectrometry		Alpha-, Gamma-Spectrometry	

Differences range from -7.3% to 0.7%

Lab "A" Traceability Evaluation (per ANSI N42.22)

Nuclide	ANSI N42.22 Traceable[8]	Traceability Limit (%)
^{60}Co	Yes	6.2
^{137}Cs	Yes	6.1
^{234}U	Yes	12.4
^{235}U	Yes	39
Nuclide	**ANSI N42.22 Traceable[8]**	**Traceability Limit (%)**
^{238}U	Yes	12.9
^{238}Pu	Yes	15.4
^{240}Pu	Yes	14.2
^{241}Am	Yes	19.0

Traceability limits from 6.1% (^{137}Cs) to 39% (^{235}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