An Intercomparison Study on Gamma Spectrometry Methods Used by FDA Food Emergency Response Radiological Laboratory Network

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OUTLINE

- Background
- Exercise Design and Objectives
- Sample Preparation and Verification
- Observations
- Results and Discussions
- Recommendations
- Participant’s Questions and Comments

Background

The Issue: Various gamma spectrometry methods will be used for detecting gamma-emitting radionuclides in foods by the members of FERN radiological laboratory network. The suitability and equivalency of these methods for food analysis are not well understood..

The Need: To assess the current network methods and capability to ensure data quality and comparability

The Objective: Improve and harmonize network methodologies and capability

The Approach: Use a wide range of food-based proficiency test samples to identify method deficiencies and address performance and methodological issues via course training and collaborative study

Exercise Design and Objectives

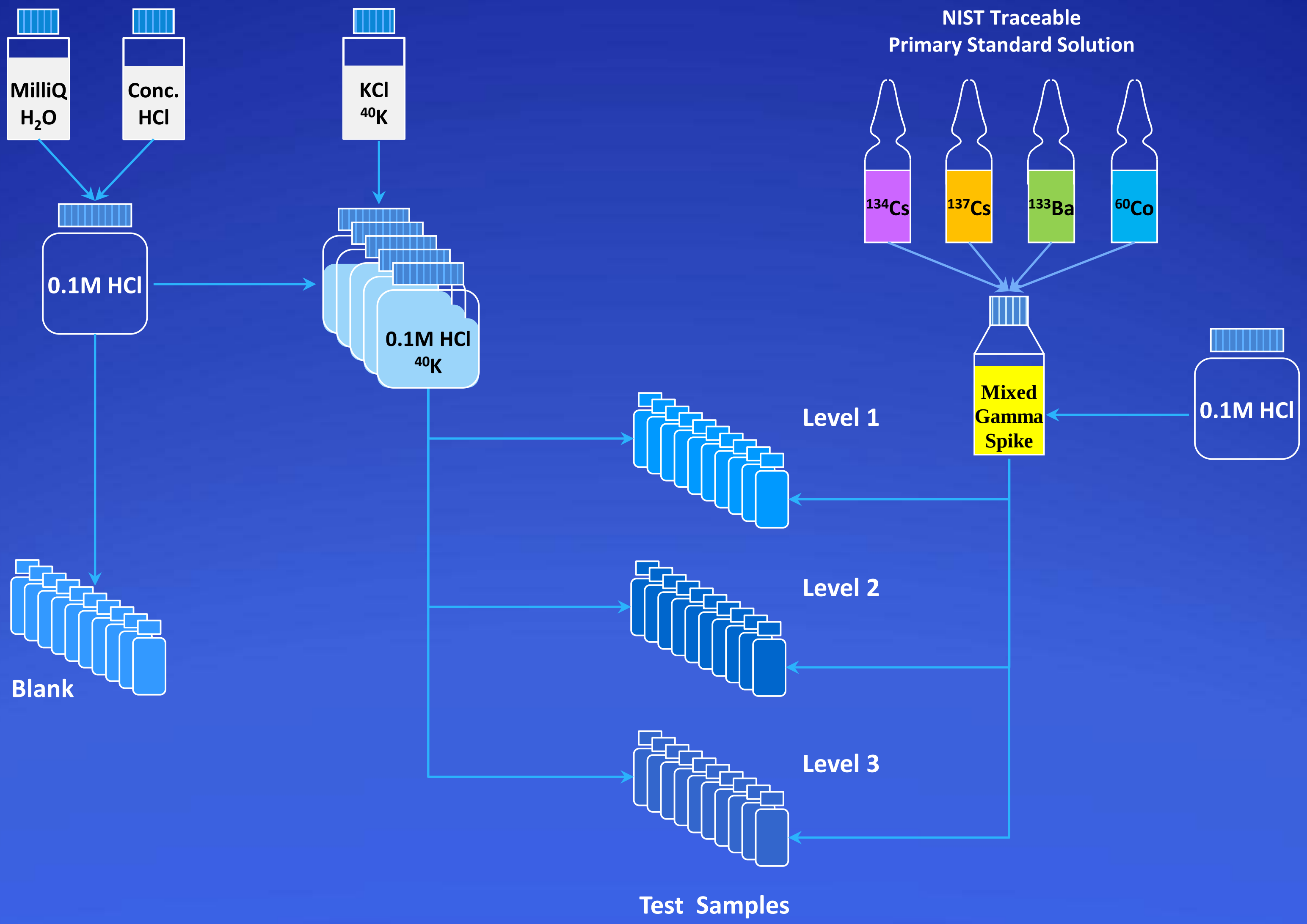
Questions to be answered:

- What does FERN network’s data quality as a whole look like in high-throughput gamma screening?
- Can the network’s methods reliably detect gamma-emitting radionuclides at the radioactivity levels that have regulatory significance?
- Are individual laboratories’ counting efficiency curves established correctly over the energy range of interest?
- How significant is the coincidence-summing effect on the measured activity for the sample geometries used in the FERN laboratories?
- Do laboratories realistically estimate their measurement uncertainty?
- How to best develop food-based PT samples to suit FERN gamma methodological needs?

This exercise is intended to assess the followings:

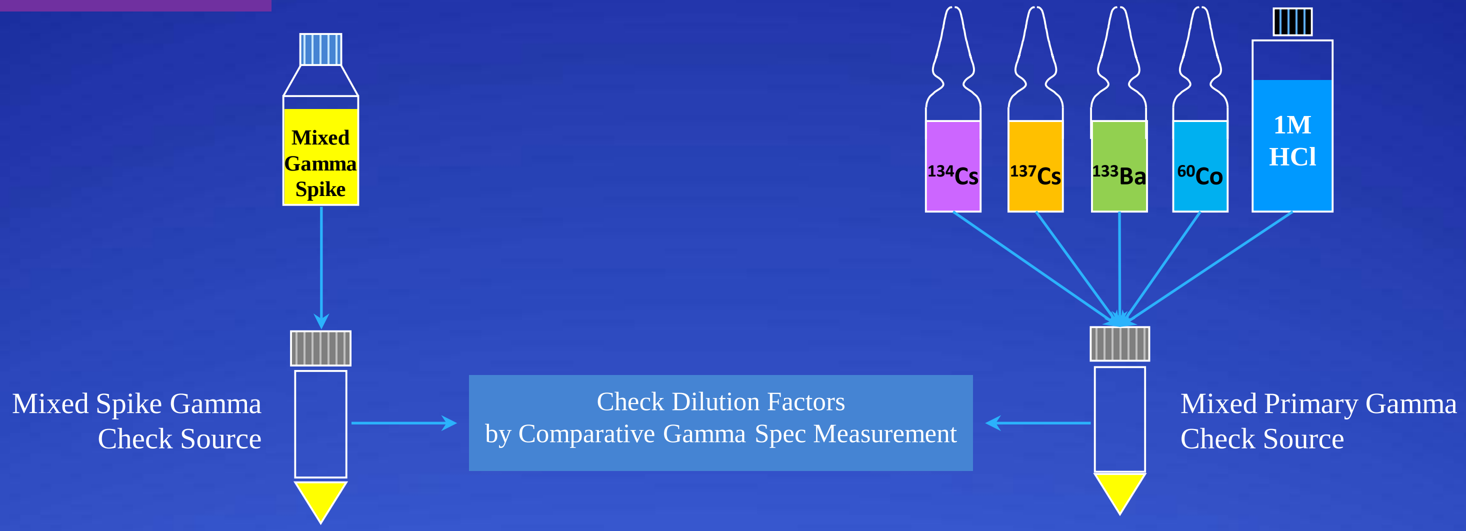
- Network’s ability to make quick turnaround sample analysis
- Network’s methods for identifying the radionuclides presented in the test samples
- Network’s methods for quantifying each radionuclide at different levels of concentration
- Network’s methods’ minimum detectable concentration for each radionuclide
- Network’s methods’ limit of quantification for each radionuclide
- Level of coincidence summing effect associated with laboratories’ default counting geometries
- Network data reporting mechanism

Sample Preparation



Spike Verification

Experimental Design



Mixed Spike Gamma
Check Source

Check Dilution Factors
by Comparative Gamma Spec Measurement

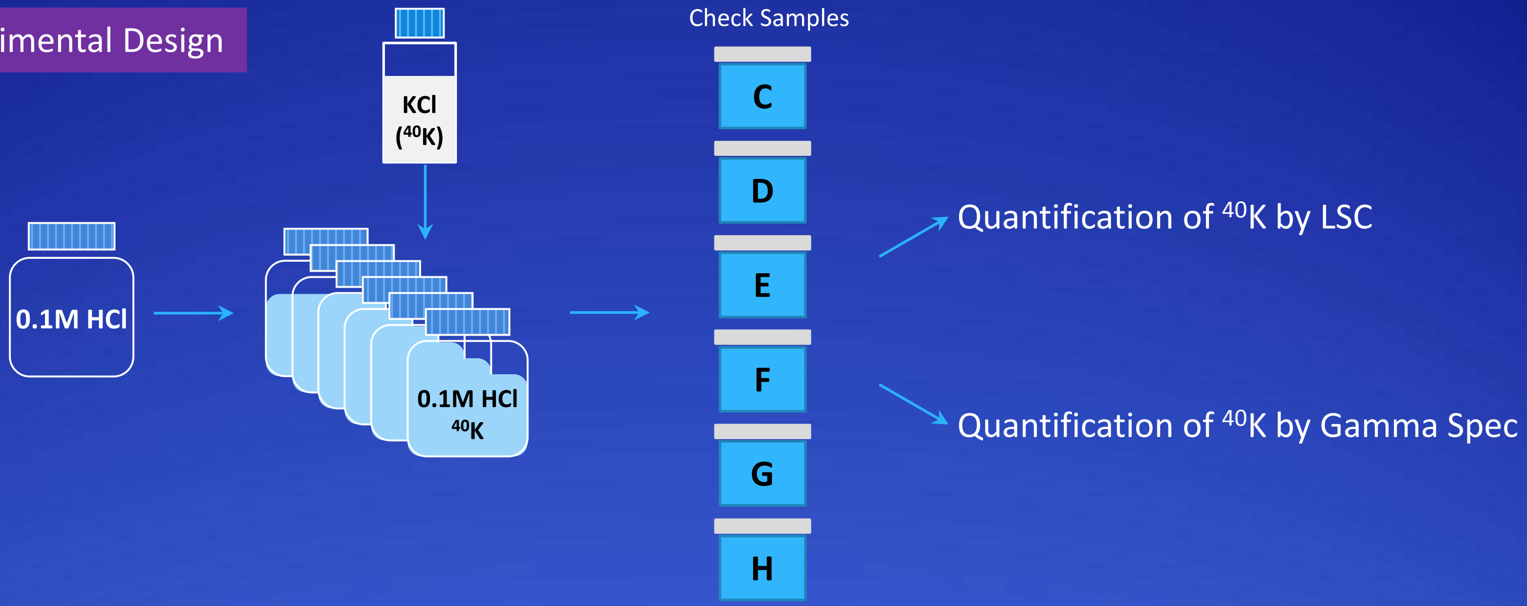
Mixed Primary Gamma
Check Source

Verification Results

Radionuclide	Gravimetric Dilution Factor	Measured Dilution Factors	Difference, %
^{60}Co	0.93 ± 0.02	0.93 ± 0.03	0.27
^{134}Cs	0.99 ± 0.01	0.98 ± 0.02	-0.62
^{137}Cs	1.58 ± 0.02	1.59 ± 0.02	0.59
^{133}Ba	1.00 ± 0.01	1.00 ± 0.01	0.32

Verification of ^{40}K Concentration

Experimental Design



KCl (^{40}K)

0.1M HCl

0.1M HCl ^{40}K

Check Samples

C

D

E

F

G

H

Quantification of ^{40}K by LSC

Quantification of ^{40}K by Gamma Spec

Verification Results

Assigned Value*:	999.99 ± 90.64	Bq/kg
Measured by LSC:	1012.56 ± 8.80	Bq/kg
Measured by γ–Spec:	1001.57 ± 26.48	Bq/kg
Difference:	0.71	%

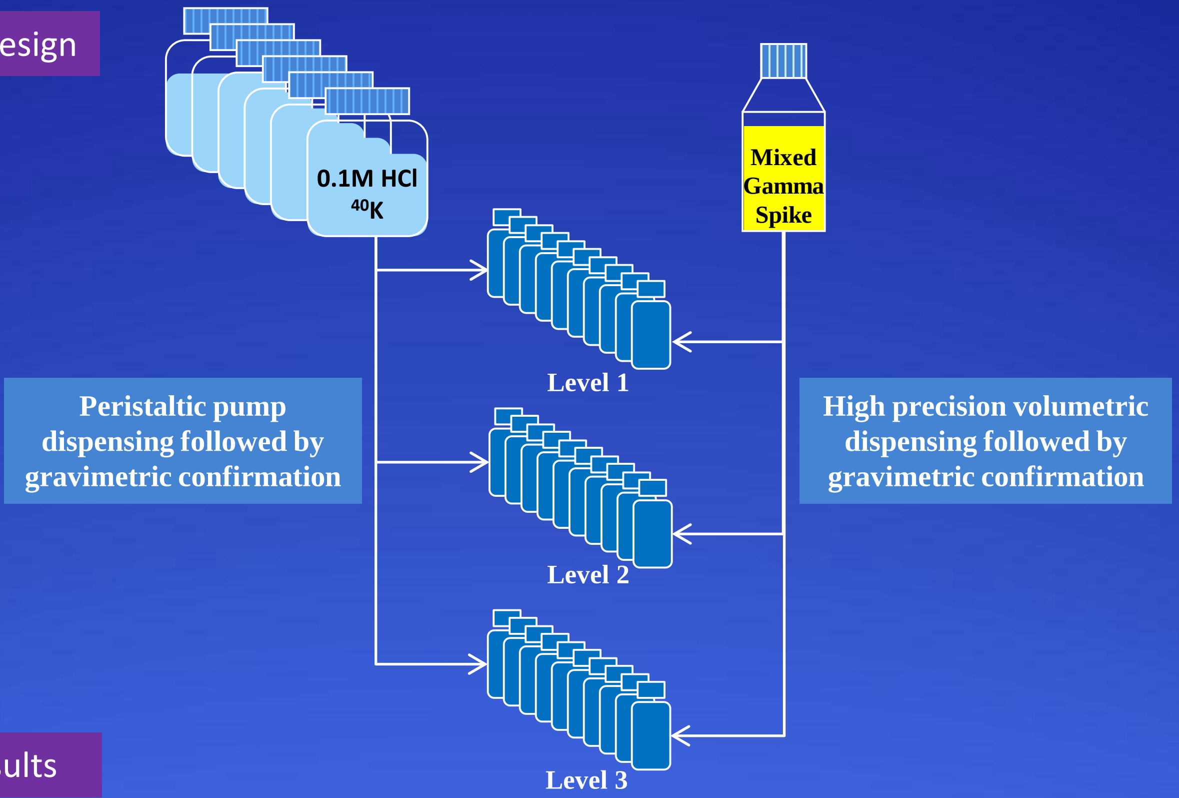
Published Natural K to ^{40}K Conversion Factor, Bq/g

30.93	Burkinshaw (1967)
31.19	Ross and Morris (1968)
27.33	Havlik (1970)
31.31	Young *et al* (1975)
30.02	Manocha and Mohindra (1976)
29.07	Holtzman (1977)
30.30	Graham (1983)
27.4	HMSO (1985–6)
30.47	Lykken *et al* (1987)
28.22	Lan and Weng (1989)
31.18	Fenwick *et al* (1991)
30.18	S.B. Samat *et al* (1997, experimental value)
30.45	S.B. Samat *et al* (1997, calculated value $T_{1/2}$=1.3E9 year, Amersham 1966)
31.67	S.B. Samat *et al* (1997, calculated value $T_{1/2}$=1.25E9 year, Adams and Dams 1970)
31:00	S.B. Samat *et al* (1997, calculated value $T_{1/2}$=1.277E9 year, IAEA 1989)
31.41	S.B. Samat *et al* (1997, calculated value $T_{1/2}$=1.26E9 year, Lide 1994–5)
30.92	S.B. Samat *et al* (1997, calculated value $T_{1/2}$=1.28E9 year, Lide 1994–5)

Mean ± 2s
30.18 ± 2.74

Verification of Radionuclide Concentrations

Experimental Design



Peristaltic pump dispensing followed by gravimetric confirmation

High precision volumetric dispensing followed by gravimetric confirmation

Verification Results

Radionuclide	%Difference @ Level-1	%Difference @ Level-2	%Difference @Level-3
^{60}Co	1.47	-3.60	-3.56
^{134}Cs	-1.69	-0.90	-3.75
^{137}Cs	1.14	-0.96	-6.51
^{133}Ba	4.03	-3.32	-2.44
^{40}K	1.19	6.02	0.85

Observations

Methods Cited	No. of Labs
EPA 901.1	12
EPA 901.1 Modified	2
EML-95-140-Rev. 2	1
HASL-300 Ga-01-R	1
DOE Method	1
In-House Developed Method	5

Sample Geometry Used	No. of Labs
400-mL Straight Wall Cylindrical Container	1
400-mL Cottage Cheese Container	2
500-mL Marinelli Beaker	3
1-L Marinelli Beaker	13
2-L Marinelli Beaker (Half Full)	2
3-L Marinelli Beaker	1

Observations

Efficiency Calibrations	No. of Labs
Source-Based	21
Computational-Based (LabSOCS)	1

Radionuclides Used for Calibrations	No. of Labs
EZ Mixed Gamma (^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{137}Cs, ^{88}Y, ^{60}Co)	11
^{109}Cd, ^{57}Co, ^{123m}Te, ^{51}Cr, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{88}Y, ^{60}Co	1
^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{88}Y, ^{60}Co	1
^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{210}Pb, ^{137}Cs, ^{88}Y, ^{60}Co	1
^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{137}Cs, ^{54}Mn, ^{88}Y, ^{65}Zn, ^{60}Co	1
^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{137}Cs, ^{54}Mn, ^{88}Y, ^{65}Zn	1
^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{51}Cr, ^{113}Sn, ^{85}Sr, ^{137}Cs, ^{54}Mn, ^{88}Y, ^{65}Zn, ^{60}Co	1
^{109}Cd, ^{57}Co, ^{123m}Te, ^{51}Cr, ^{113}Sn, ^{137}Cs, ^{88}Y, ^{60}Co	1
^{109}Cd, ^{57}Co, ^{123m}Te, ^{51}Cr, ^{113}Sn, ^{85}Sr, ^{88}Y, ^{60}Co	1
LabSOCS (^{241}Am, ^{109}Cd, ^{57}Co, ^{139}Ce, ^{203}Hg, ^{113}Sn, ^{137}Cs, ^{88}Y, ^{40}K, ^{60}Co)	1

Corrections Applied in Sample Activity Calculation

Sample Density Correction	Yes (2)	No(20)
Coincidence-Summing Correction	Yes (12)	No (10)

Results and Discussions

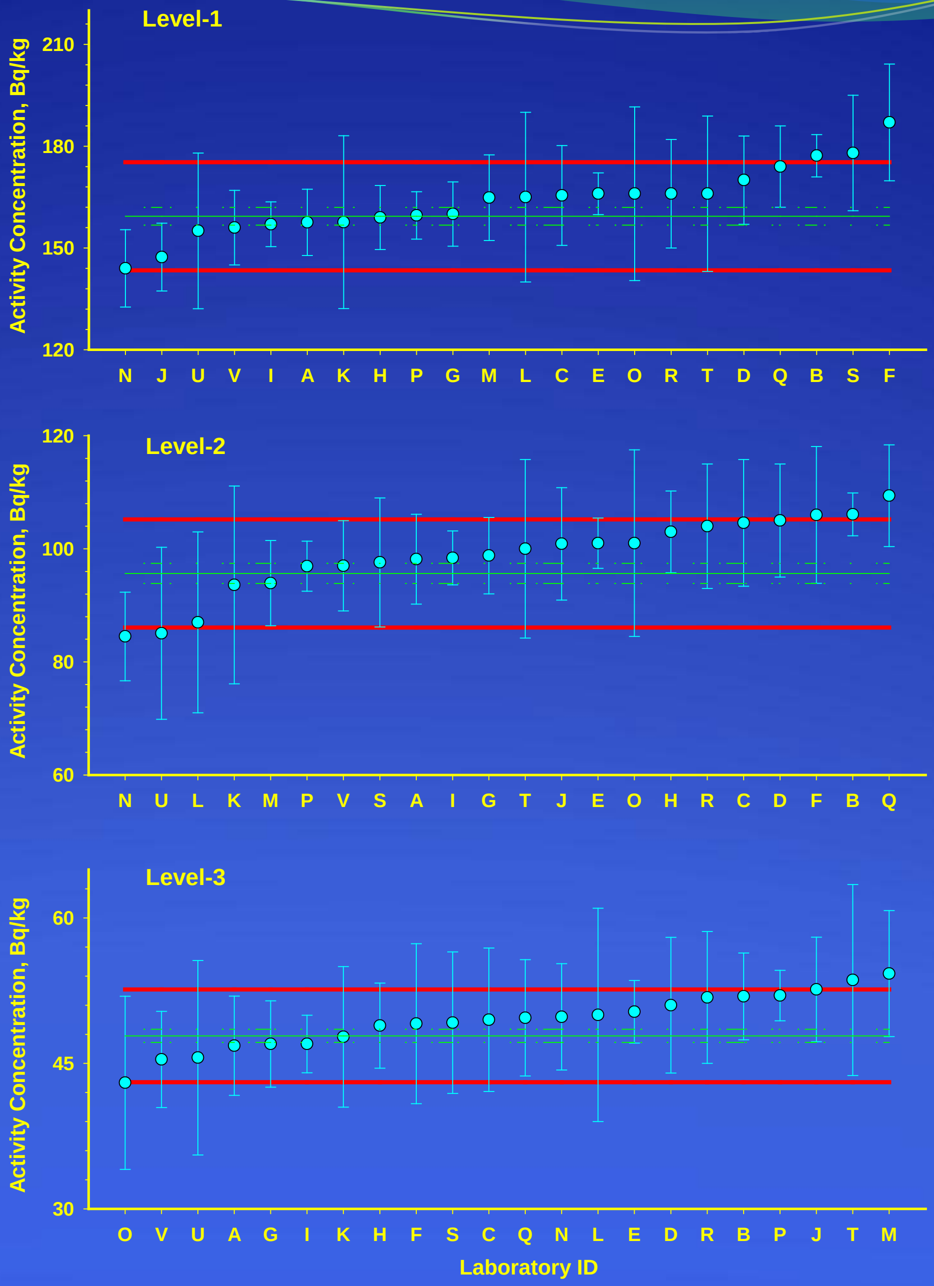
Identification of Radionuclides

Near 1/3 FDA’s DILs			Near 1/5 FDA’s DILs			Near 1/10 FDA’s DILs		
☑	^{134}Cs	100%	☑	^{134}Cs	100%	☑	^{134}Cs	100%
☑	^{137}Cs	100%	☑	^{137}Cs	100%	☑	^{137}Cs	100%
☑	^{133}Ba	100%	☑	^{133}Ba	100%	☑	^{133}Ba	100%
☑	^{60}Co	100%	☑	^{60}Co	100%	☑	^{60}Co	100%
☑	^{40}K	100%	☑	^{40}K	100%	☑	^{40}K	100%

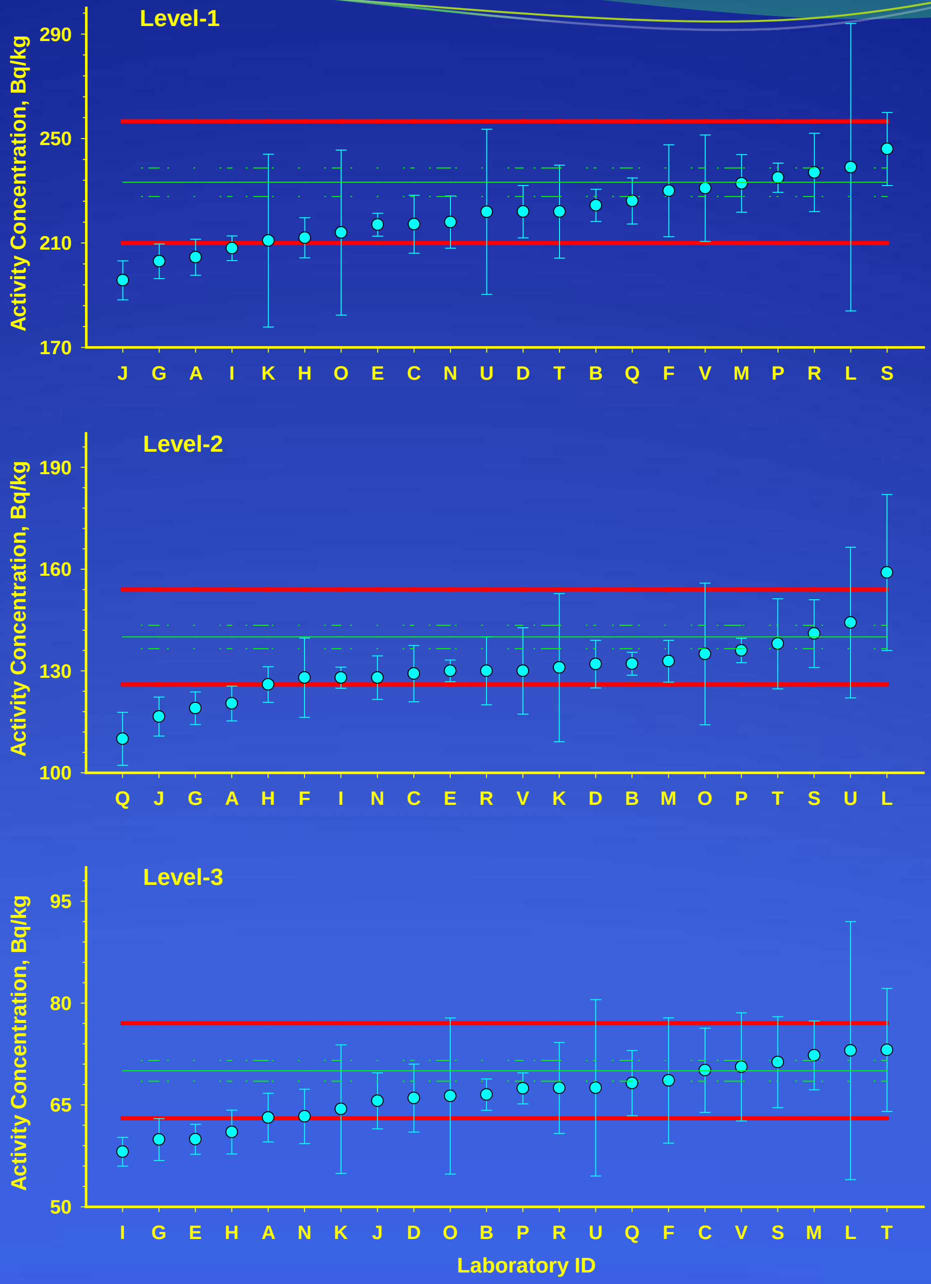
Quantification of Radionuclides

- Nearly all of the results are within the limits of +/-10% of true value
- Bias exists for some radionuclides due to coincidence-summing effect
- Measurement uncertainties are not estimated uniformly throughout network
- Detection and quantification limits for all methods are far below the level of regulatory significance

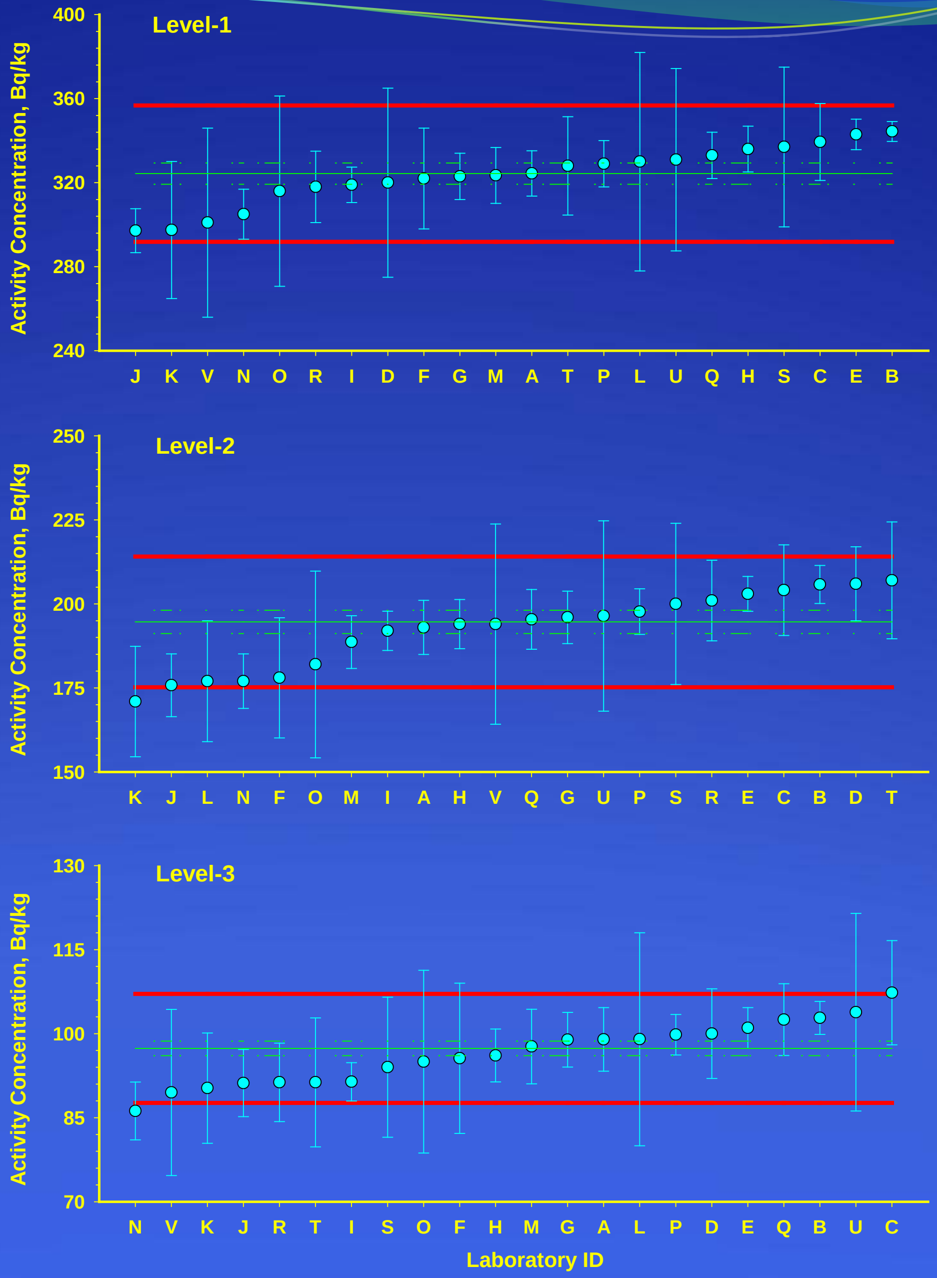
Cs-137


Level-1
Activity Concentration, Bq/kg
210
180
150
120
N J U V I A K H P G M L C E O R T D Q B S F
Level-2
Activity Concentration, Bq/kg
120
100
80
60
N U L K M P V S A I G T J E O H R C D F B Q
Level-3
Activity Concentration, Bq/kg
60
45
30
O V U A G I K H F S C Q N L E D R B P J T M
Laboratory ID

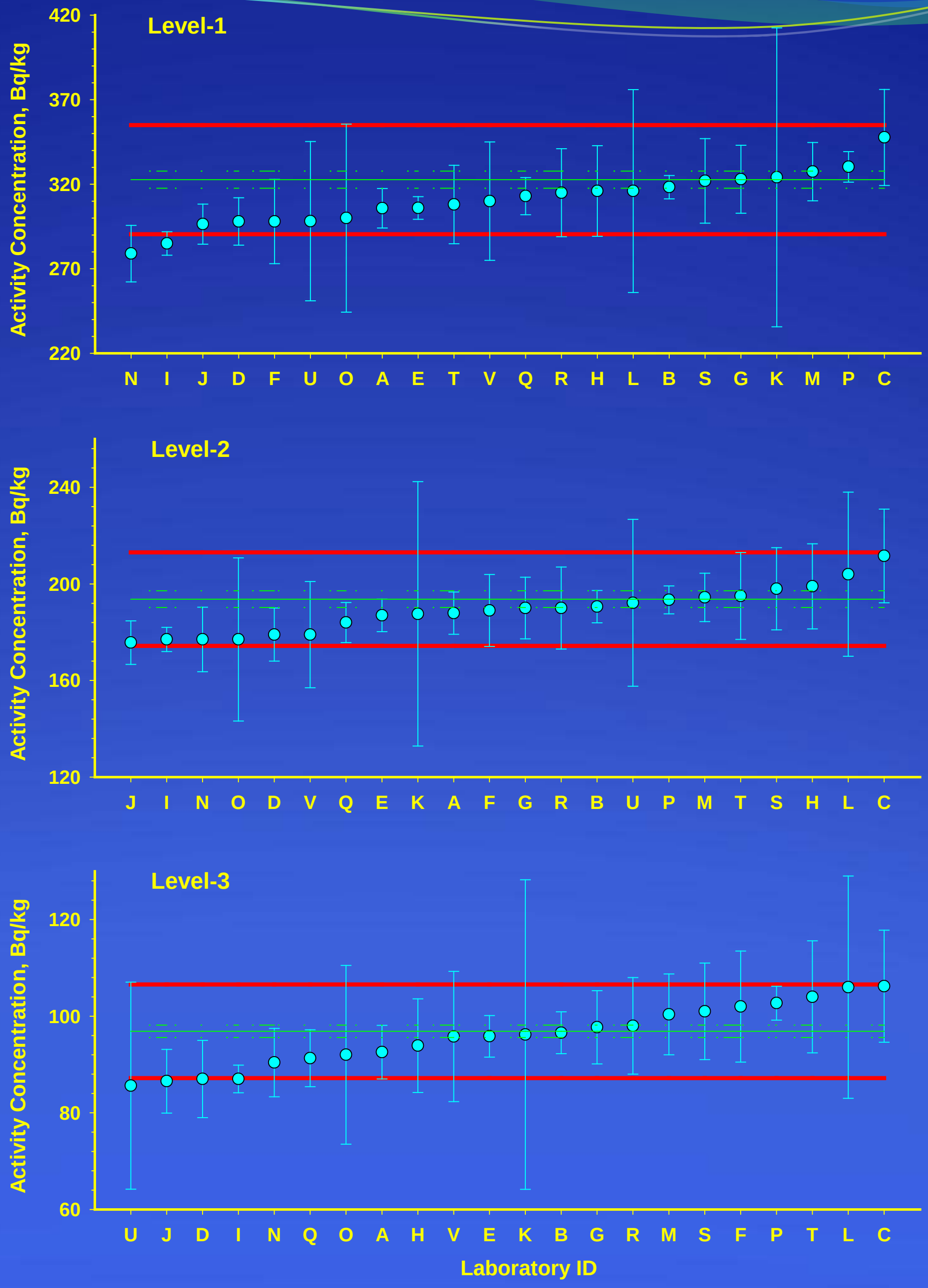
Cs-134


Level-1
Activity Concentration, Bq/kg
290
250
210
170
J G A I K H O E C N U D T B Q F V M P R L S
Level-2
Activity Concentration, Bq/kg
190
160
130
100
Q J G A H F I N C E R V K D B M O P T S U L
Level-3
Activity Concentration, Bq/kg
95
80
65
50
I G E H A N K J D O B P R U Q F C V S M L T
Laboratory ID

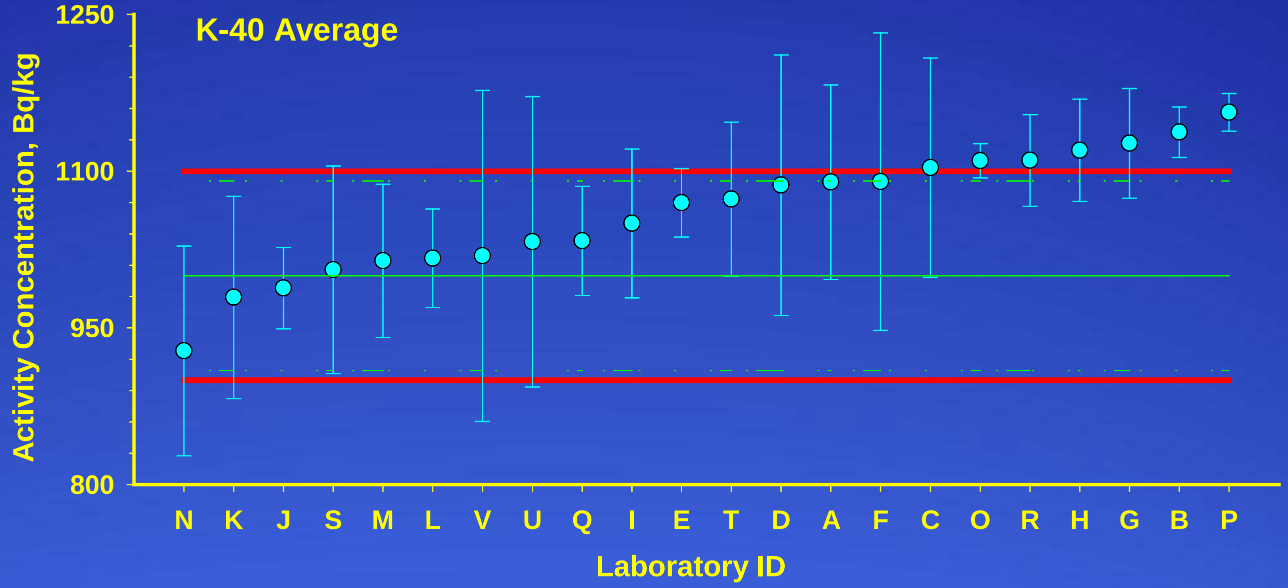
Co-60


Level-1
Activity Concentration, Bq/kg
400
360
320
280
240
J K V N O R I D F G M A T P L U Q H S C E B
Level-2
Activity Concentration, Bq/kg
250
225
200
175
150
K J L N F O M I A H V Q G U P S R E C B D T
Level-3
Activity Concentration, Bq/kg
130
115
100
85
70
N V K J R T I S O F H M G A L P D E Q B U C
Laboratory ID

Ba-133


Level-1
Activity Concentration, Bq/kg
420
370
320
270
220
N I J D F U O A E T V Q R H L B S G K M P C
Level-2
Activity Concentration, Bq/kg
240
200
160
120
J I N O D V Q E K A F G R B U P M T S H L C
Level-3
Activity Concentration, Bq/kg
120
100
80
60
U J D I N Q O A H V E K B G R M S F P T L C
Laboratory ID

K-40


K-40 Average
Activity Concentration, Bq/kg
1250
1100
950
800
N
K
J
S
M
L
V
U
Q
I
E
T
D
A
F
C
O
R
H
G
B
P
Laboratory ID

Recommendations

- **Estimation of Measurement Uncertainty:**

The activity concentration, *C*, for the radionuclides of interest in the sample is calculated as:

$$C = \frac{N}{\varepsilon \times w \times \gamma \times t_s \times K_1 \times K_2 \times K_3 \times K_4 \times K_5 \times K_6}$$

The uncertainty components of the ^{137}Cs measurement in RICE007

Variable Name	Symbol	Value	Rel. Standard Uncertainty, %	Sensitivity Factor	Contribution to Combined Uncertainty, %
Sample weight, kg	w	0.1379	0.0725	1	0.06
Counting efficiency	ε	3.708E-2	0.639	1	4.3
Sample dry content, fractional	K_1	0.9075	0.055	1	0.03
Decay correction	K_2	0.9640	3.53E-4	1	0
Decay during counting correction	K_3	0.9999	9.47E-7	1	0
Attenuation correction	K_4	1.0	0.5	1	2.7
Random summing correction	K_5	1.0	1.22E-5	1	0
Coincidence summing correction	K_6	1.0	0	1	0
Net peak area	N	3057.7	2.949	1	92.3
Sample counting time, s	t_s	259200	0	1	0
Emission probability	γ	0.851	0.235	1	0.6

Activity concentration of ^{137}Cs, Bq/kg	3.10
Combined standard uncertainty, Bq/kg	0.10
Expanded uncertainty, Bq/kg	0.19

- **Derive Coincidence-Summing Correction Sample Density Factors:**

  Computational Approach

  - GESPECOR
  - ANGLE
  - LabSOCS
  - Others

  Experimental Verification

  - Food-based PT samples varying in packing density
  - Food samples spiked with cascade-decay radionuclides

- **Evaluation Method and Laboratory Performance Using Z-score**

  Estimate measurement uncertainty uniformly

  Established acceptable performance limits for food screening and confirmatory analysis

Issues Related to Efficiency Calibrations:

ANOVA: ^{40}K Activity Concentration Per Efficiency Calibration Methods

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between Eff Cal Methods	75216.5	2	37608.3	9.04	0.0004
Within Eff Cal Methods	262103.	63	4160.36		
Total (Corr.)	337319.	65			

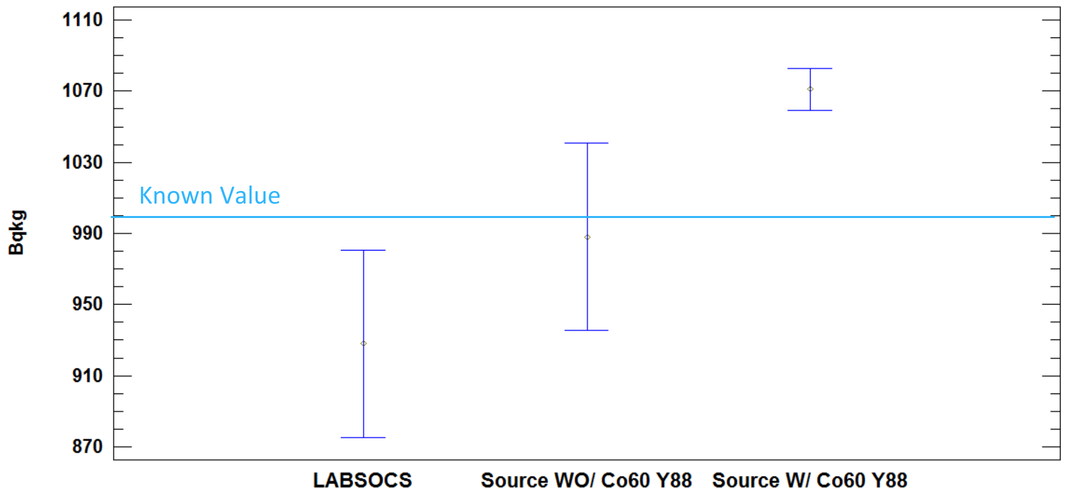
Efficiency Calibration Method – Multiple Range Tests

Level	Count	Mean	Homogeneous Groups
LABSOCS	3	928.0	X
Source WO Co60 Y88	3	988.123	X
Source With Co60 Y88	60	1071.18	X

Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the ^{40}K means from one type of efficiency calibration to another at the 95.0% confidence level. See the Multiple Range Tests and Means Plot below.

Means Plot:

^{40}K Activity Concentration Reported vs Efficiency Calibration Methods



Issues Related to Use or not Use of Coincidence Summing:

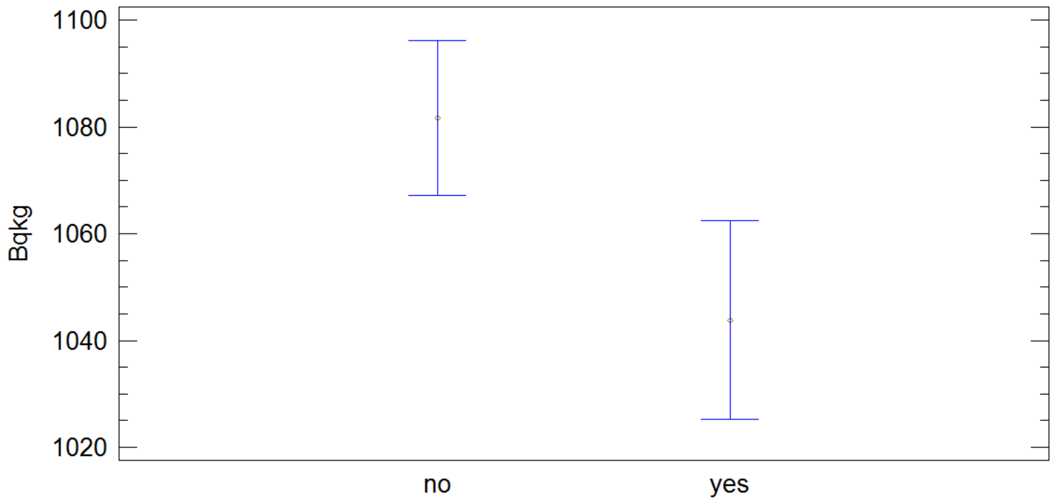
ANOVA: ^{40}K Activity Concentration w/ or wo/ Coincidence-Summing

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between Summing Groups	41080.4	1	41080.4	8.88	0.0041
Within Summing Groups	296239	64	4628.73		
Total (Corr.)	337319.	65			

Coincidence-Summing Correction – Multiple Range Tests

Level	Count	Mean	Homogeneous Groups
Without Summing Correction	27	1030.91	X
With Summing Correction	39	1081.65	X

Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the ^{40}K means from correcting or not correcting coincidence summing effect at the 95.0% confidence level. See the Multiple Range Tests and Means Plot below.



Means Plot:
^{40}K Activity Conc. Reported vs Use of Coincidence Summing Correction

Comparison of Various Methods:

ANOVA: ^{137}Cs Activity Conc. Vs Methods

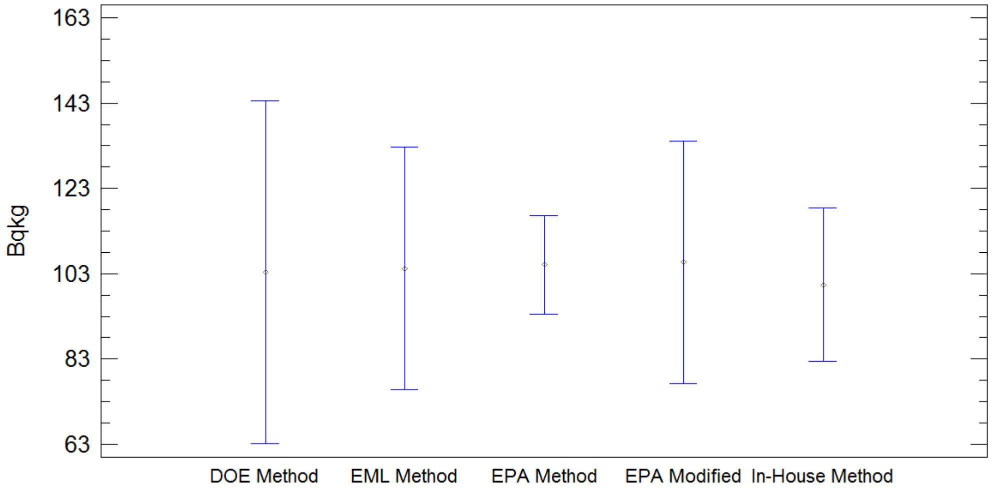
Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between groups	257.661	4	64.4152	0.03	0.9986
Within groups	147208.	61	2413.24		
Total (Corr.)	147465.	65			

Comparison of Methods - Multiple Rang Tests

Method	Count	Mean	Homogeneous Groups
In House	15	100.391	X
DOE	3	103.333	X
EML	6	104.233	X
EPA	36	105.102	X
EPA Modified	6	105.695	X

Since the P-value of the F-test is greater than 0.05, there is not a statistically significant difference between the ^{137}Cs means from one method to another at the 95.0% confidence level. See the Multiple Range Tests and Means Plot below.

Means Plot:
^{137}Cs Activity Conc. Reported vs Various Methods



Comparison of Sample Geometries:

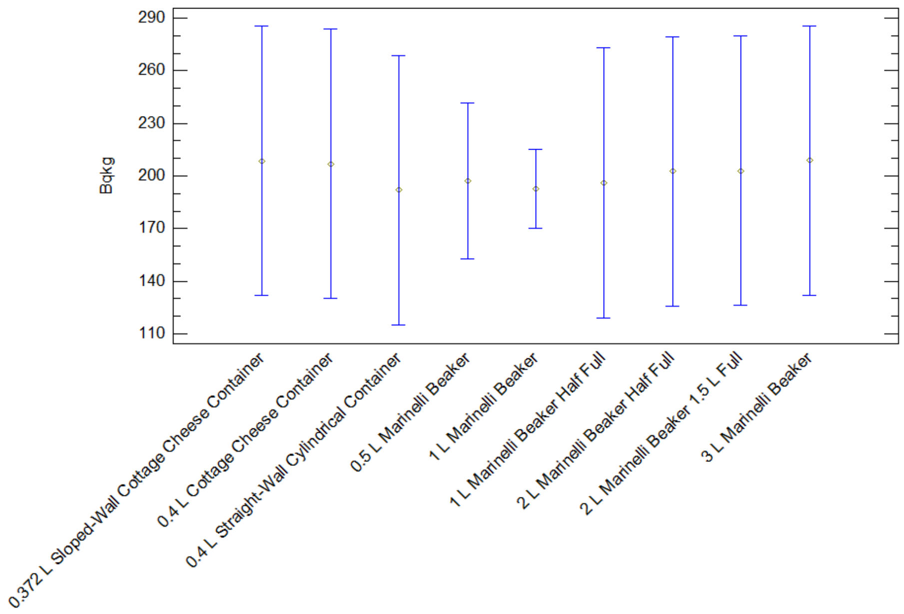
ANOVA: ^{133}Ba vs Sample Geometries

Source	Sum of Squares	Df	Mean Square	F-Ratio	P-Value
Between Geo	2069.62	8	258.703	0.03	1.0000
Within Geo	494529.	56	8830.88		
Total (Corr.)	496599.	64			

Sample Geometry – Multiple Range Tests

Sample Geometry	Count	Mean	Homogeneous Groups
0.4 L straight-wall cylindrical container	1	191.983	X
1 L marinelli beaker	7	192.592	X
1 L marinelli beaker filled to 0.5 L	1	196.1	X
0.5 L marinelli beaker	3	197.341	X
2 L marinelli beaker filled to 1 L	1	202.637	X
2 L marinelli filled to 1.5 L	1	202.967	X
0.4 L cottage cheese container	1	207.0	X
0.372 L sloped-wall cottage cheese cup	1	208.667	X
3 L marinelli beaker	1	208.8	X

Since the P-value of the F-test is greater than 0.05, there is not a statistically significant difference between the ^{133}Ba means from one sample geometry to another at the 95.0% confidence level. See the Multiple Range Tests and Means Plot.



Means Plot:
^{133}Ba Activity Conc. Reported vs Sample Geometries

Acknowledgement

1. Katherine A. Kelley Connecticut State Public Health Laboratory
2. Wisconsin State Laboratory of Hygiene - University of Wisconsin - Madison
3. Vermont Department of Health Laboratory
4. Tennessee Department of Health Nashville Laboratory Services
5. State of Washington Department of Health - Public Health Laboratory
6. South Carolina Department of Health and Environmental Control - Radiochemistry Laboratory
7. Texas Department of State Health Services - Radiochemistry Laboratory
8. Ohio Department of Health Laboratory
9. New York Wadsworth Center - Biggs Laboratory
10. New Jersey Department of Health
11. Sandia National Laboratories - Radiation Protection Sample Diagnostics
12. Minnesota Department of Health
13. Commonwealth of Massachusetts Radiation Control Program
14. State of Maine Health and Environmental Testing Laboratory
15. State of Iowa - Hygienic Laboratory at the University of Iowa
16. Maryland Department of Health and Mental Hygiene
17. Indiana State Department of Health Laboratories
18. Illinois Emergency Management Agency
19. Idaho State University Environmental Monitoring Laboratory
20. Florida Department of Health Bureau and Radiation Control
21. New Hampshire Department of Public Health
22. FDA Winchester Engineering and Analytical Center

Your Questions and Comments

Thanks!