Radioactivity Group meeting

10 May 2017

R. Collé

Natural Uranium SRM

Comparison of Two ^{229}Th Standards

SRM 4321d

Natural uranium radioactivity solution standard

200 flame-sealed ampoules

5 mL solution (ρ = 1.057 g mL^{-1})

21 mg UO_2^{+2} per gram in 1 mol L^{-1} HNO_3

^{234}U	220 Bq g^{-1}
^{235}U	10 Bq g^{-1}
^{238}U	230 Bq g^{-1}

starting point

Uranium metal isotopic standard

U. S. Department of Commerce
Peter G. Peterson
Secretary

National Bureau of Standards
Certificate of Analysis
Standard Reference Material 960
Uranium Metal

Uranium Assay . . . . 99.975 ± 0.017 Weight Percent

This metal standard of normal isotopic composition is issued as a primary assay standard for uranium determinations. The value of the atomic weight of this material is 238.0289 as determined at NBS by thermal ionization mass spectrometry.

The uranium assay is based on the constant-current coulometric reduction of uranyl ion with electrogenerated titanous ion in 7M sulfuric acid. The value of the assay has been corrected for 42 ppm of iron and 4 ppm of vanadium which are the titratable impurities present in the metal. The certified value, 99.975 weight percent, represents the mean of 21 determinations. The precision of the method, expressed in terms of the standard deviation of a single determination is 0.008 percent. The estimated value of the uncertainty of the mean assay is 0.006 percent. This figure includes the estimates of all known sources of error inherent to this determination: the random error component, 0.004 percent (the 95 percent confidence interval for the mean based on 20 degrees of freedom), and an additional 0.002 percent error term as an allowance for all known possible sources of systematic error. An overall mass balance of 99.9970 percent is obtained when the estimate of total impurities present in the material (223 ppm) is taken into account.

The uncertainty ascribed to the certified assay value is the 95 percent confidence interval for a single determination.

The metal as received will contain a significant amount of surface oxide. In assaying the material, the oxide was removed from the uranium samples just prior to weighing. The metal surface was cleaned by the procedure outlined on the back of this certificate.

This material was prepared by the United States Atomic Energy Commission. Impurities were analyzed by the AEC Paducah Laboratory, Paducah, Kentucky. Assay of the material was performed by G. Marinenko and E. S. Etz, the iron content was determined polarographically by E. J. Maienthal, and the atomic weight was determined by isotopic ratio measurements performed by E. L. Garner, all of the NBS Analytical Chemistry Division.

The overall direction and coordination of the technical measurements leading to the certification were performed under the chairmanship of W. R. Shields.

The technical and support aspects involved in the preparation, certification, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by W. P. Reed.

Washington, D.C. 20234
May 12, 1972

J. Paul Cali, Chief
Office of Standard Reference Materials

(over)

New Brunswick Laboratory
U.S. Department of Energy

Certificate of Analysis
CRM 112-A
Uranium (normal) Metal Assay and Isotopic Standard

Uranium Assay:	0.99975 g U/g metal
Uranium Assay Uncertainty:	0.00006 g U/g metal

	$^{234}U/^{238}U$	$^{235}U/^{238}U$
Atom Ratio:	0.000052841	0.0072543
Atom Ratio Uncertainty:	0.000000082	0.0000040

	^{234}U	^{235}U	^{238}U
Atom Percent:	0.0052458	0.72017	99.27458
Atom Percent Uncertainty:	0.0000081	0.00039	0.00039
Weight Percent:	0.0051579	0.71114	99.28370
Weight Percent Uncertainty:	0.0000080	0.00038	0.00038

Relative Atomic Weight:	238.028918
Relative Atomic Weight Uncertainty:	0.000012

Note: ^{233}U and ^{236}U were not detected. The limit of detection of uranium ratios for the technique used is 5×10^{-9}. The $^{238}U/^{235}U$ ratio and uncertainty may be calculated as 137.849 ± 0.076.

This Certified Reference Material (CRM) is a uranium concentration and isotopic solution standard intended for use in calibration of and/or quality control for uranium analysis methods. Each unit of CRM 112-A consists of metal piece of nominal mass as listed on the container.

NOTE: The CRM should be handled under proper radiologically-controlled conditions at all times.

The uncertainty assigned to the certified assay value is the 95% confidence limit for the mean. This limit includes components due to both random analytical error and allowances for all known and quantified sources of systematic uncertainties. The uranium assay was determined using a constant-current coulometric reduction of uranyl ions with electrogenerated titanous ions in dilute sulfuric acid. A correction was made for the iron and vanadium content of the material. The total estimated impurities in the CRM (223 µg/g) yield a calculated uranium assay value of 0.99978.

September 30, 2010
Argonne, Illinois

www.nbl.doe.gov

Jon Neuhoff, Director
New Brunswick Laboratory

(Revision of Certificate dated July 31, 2002

Calculations for activity from mass data

U	atom %	atoms / g 960	T 1/2 in a	T 1/2 in s	lambda	Bq / g 960
234	5.245800E-03	1.326857637E+17	2.45500E+05	7.747225333E+12	8.947037820E-14	1.187145E+04
235	7.201700E-01	1.821577385E+19	7.04000E+08	2.221607590E+16	3.120025263E-17	5.683367E+02
238	9.927458E+01	2.511022811E+21	4.46800E+09	1.409963454E+17	4.916064872E-18	1.234435E+04

Results verified by Dr. Fitzgerald

... and then there was chemistry to deal with

STOCHIOMETRY

at 8 $mol \cdot L^{-1}$ HNO_3 or less

$$\boxed{U + 4HNO_3 \rightarrow UO_2(NO_3)_2 + 2H_2O + 2NO}$$

at higher (concentrated) HNO_3

$$\boxed{U + 8HNO_3 \rightarrow UO_2(NO_3)_2 + 4H_2O + 6NO_2}$$

☆ 4:1 OR 8:1 ?

MAKES BIG DIFFERENCE IN NEEDED ACID TO DISSOLVE & TO MAINTAIN ACIDITY OF SOLUTION

LUCAS DATA SHOWS 4:1 w/ CONC. HNO_3

assumed 3:1

R.P. LARSEN
Dissolution of U metal and its alloys
Anal. Chem 31, 545 (1959).

Clean metal bar

1 Soak in 8 mol L^{-1} HNO_3 for 20 minutes
(removes black dusty UO_2)

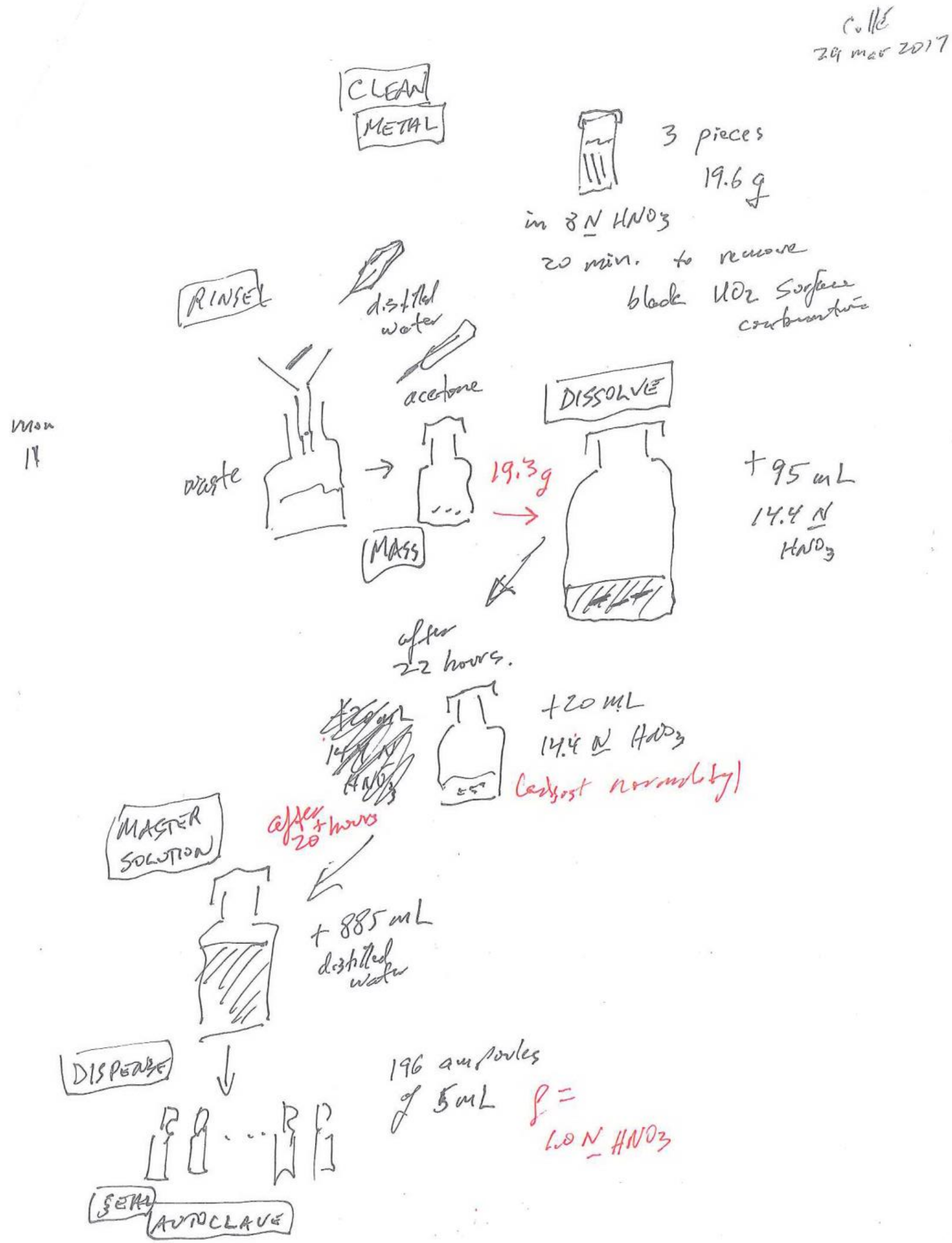
2 Rinse with distilled water

3 Remove excess water

4 Rinse with pure acetone

5 Allow evaporation 60 seconds

6 Weigh metal – observe mass as function of time



Clean metal

Rinse

Weigh

Dissolve

Adjust acidity

Take master to volume

Dispense

Seal

Autoclave

Mass of U metal

AT-20	**19.318045 g**	Δ = 0.042 %
Jupiter	19.31159 g	

Mass master solution

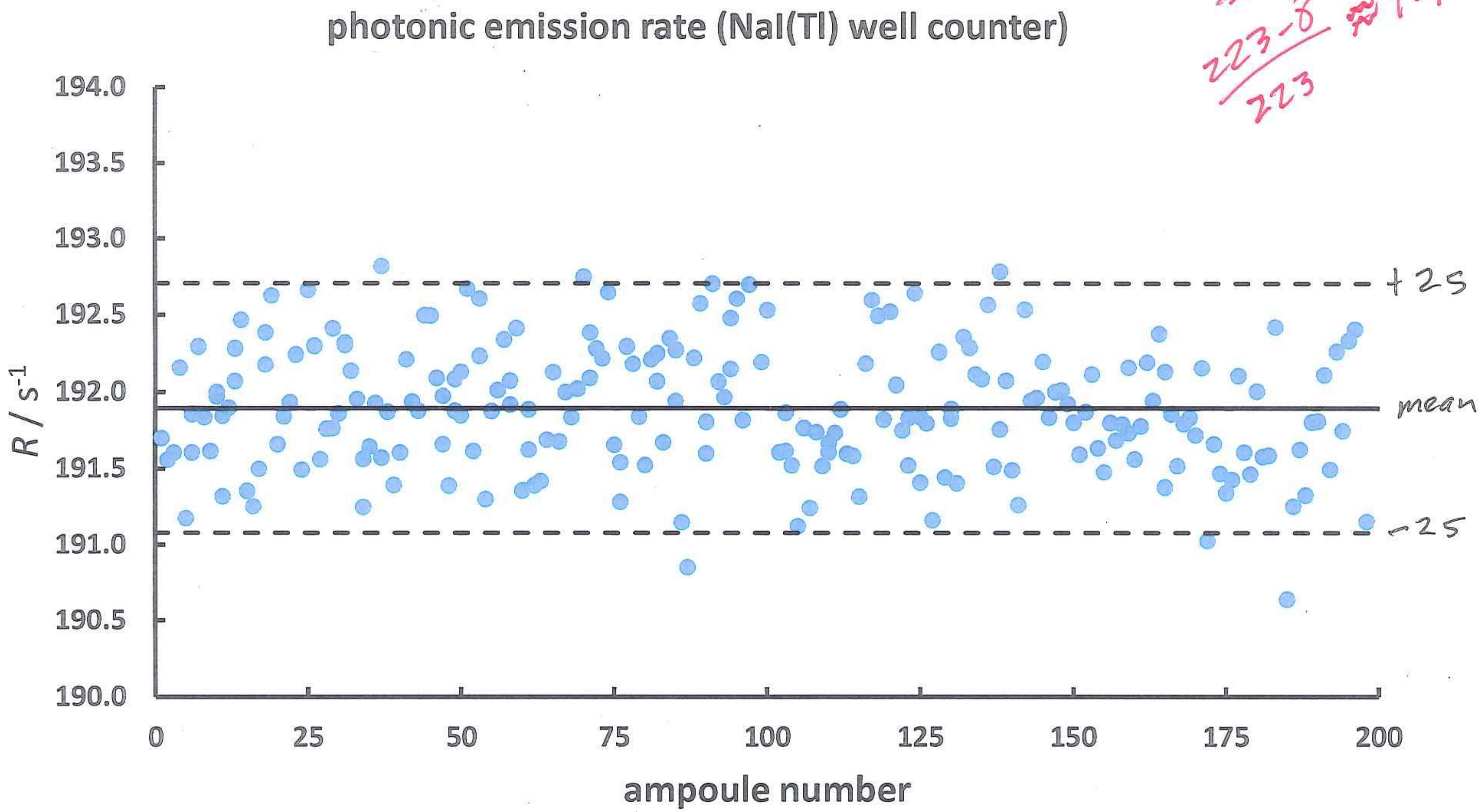
standard weights	observed mass (ts_m)	% difference
607.8 + δ	607.80089 (25)	+ 1.5 (10^{-4}) %
	607.83444 (32)	
607.9 + δ	607.90158 (87)	+ 2.6 (10^{-4}) %
1648.4 + δ	1648.39948 (94)	- 3.2 (10^{-5}) %
	1648.49083 (147)	
1648.5 + δ	1648.49997 (50)	- 1.8 (10^{-6}) %
	1040.65639 (173)	
	x 1.000974836	= **1041.67 g**

δ = standard weight corrections

NATURAL
U
SOL'N

mean = 191.89
% sd = 0.21%
n = 223

N.B.
$\frac{223-8}{223} \approx 96\%$



28 duplicate
measurements

average
difference = 0.16%

Counting
statistics
on each
value
(Poisson)
0.15%

19 APRIL
2017
COLLÉ

4/17/2017

Photonic emission spectrometry

impurity check

assay ?

Uranium source #4321d-101

Average of T-detector, B-detector and X-detector measurements

Reference time 4/12/2017

$m = 5.2437\ g$

Radionuclide	Activity (Bq)	Std dev (Bq)	std dev %
U-235	55.3	8.6	15.5
U-238	1288.7	194.9	15.1
U-234	1484.4	499.6	33.7

Runs were between 1 and 2 days in difference geometries

Detection limits X-detector

15 < E < 20 keV	7.5 gammas/s
25 < E < 105 keV	1.9 gammas/s
110 < E < 490 keV	1.3 gammas/s
500 < E < 2000 keV	1.7 gammas/s

$^{234}U \quad \frac{1484.4}{5.2437} = 283.08 \pm 34\% \qquad 220.16 \qquad \Delta = 29\%$

$^{235}U \quad \frac{55.3}{5.2437} = 10.546 \pm 16\% \qquad 10.54 \qquad \Delta = 0.05\%$

$^{238}U \quad \frac{1288.7}{5.2437} \approx 245.76 \pm 15\% \qquad 228.93 \qquad \Delta = 7.4\%$

$\frac{^{238}U}{^{234}U} = \frac{228.93}{220.16} \qquad \frac{245.76}{283.08} = 0.868$

std.

1.0398

$\Delta = 17\%$

didn't expect much

^{234}U $2.455(10^5)\,a$ $\xrightarrow{\alpha}$ ^{230}Th $7.538(10^4)\,a$

^{235}U $7.04(10^8)\,a$ $\xrightarrow{\alpha}$ ^{231}Th $25.52\,hr$ $\xrightarrow{\beta}$ ^{231}Pa $3.267(10^4)\,a$

^{238}U $4.468(10^9)\,a$ $\xrightarrow{\alpha}$ ^{234}Th $24.10\,d$ $\xrightarrow{\beta}$ ^{234m}Pa $1.159\,min$ $\xrightarrow{\beta}$ ^{234}U $2.455(10^5)\,a$

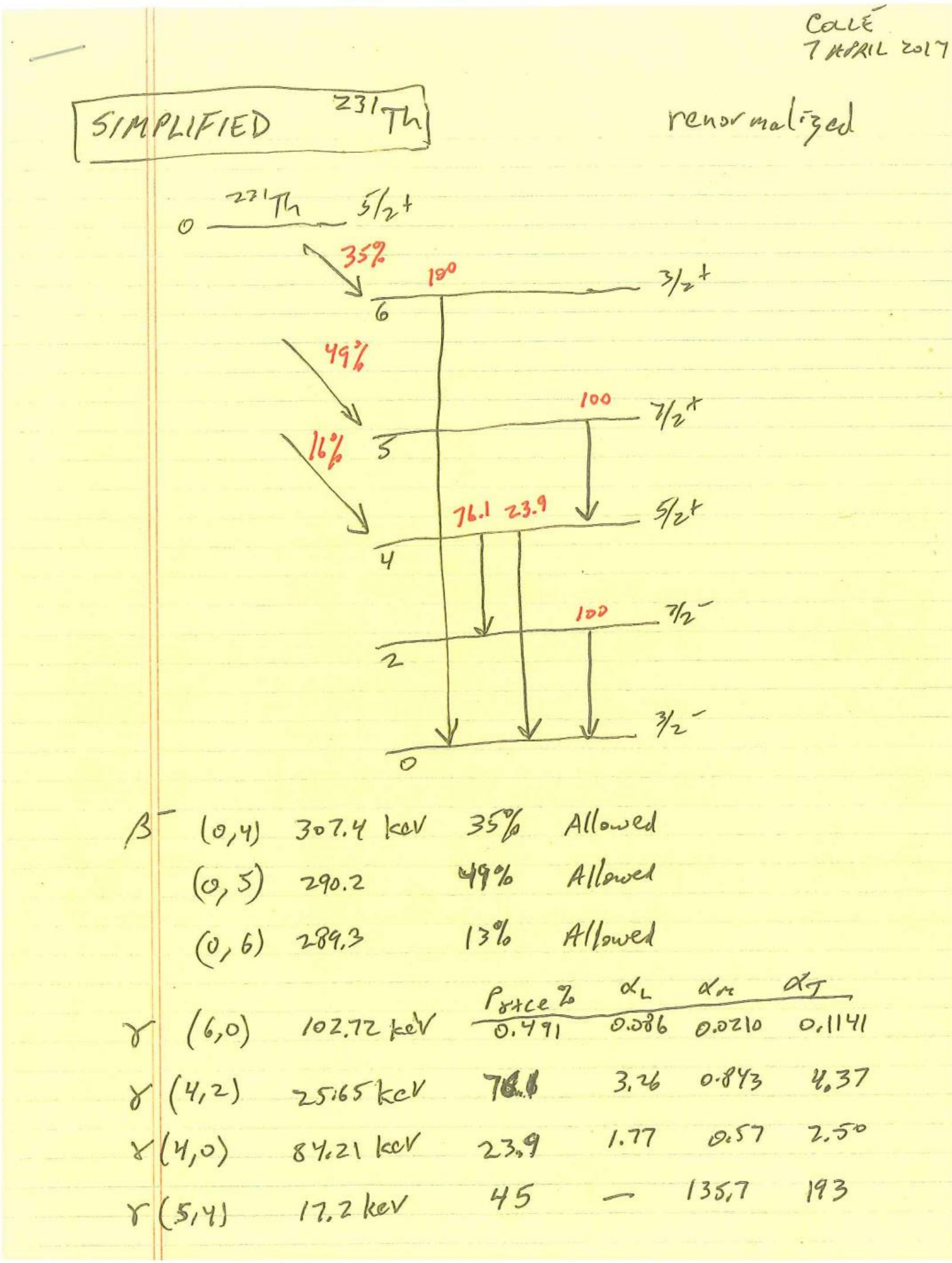
guesses

LS efficiency

234 $\varepsilon = \boxed{1}$

235 $\varepsilon = 1 + 0.95 = \boxed{1.95}$

238 $\varepsilon = 1 + 0.9 + 0.95 = \boxed{2.85}$



Calé
7 April 2017

SIMPLIFIED ^{231}Th — renormalized

β^-	(0,4)	307.4 keV	35%	Allowed
	(0,5)	290.2	49%	Allowed
	(0,6)	289.3	13%	Allowed

			$P_{\gamma+ce}$ %	α_L	α_M	α_T
γ	(6,0)	102.72 keV	0.491	0.086	0.0210	0.1141
γ	(4,2)	25.65 keV	76.1	3.26	0.843	4.37
γ	(4,0)	84.21 keV	23.9	1.77	0.57	2.50
γ	(5,4)	17.2 keV	45	—	135.7	193

Example

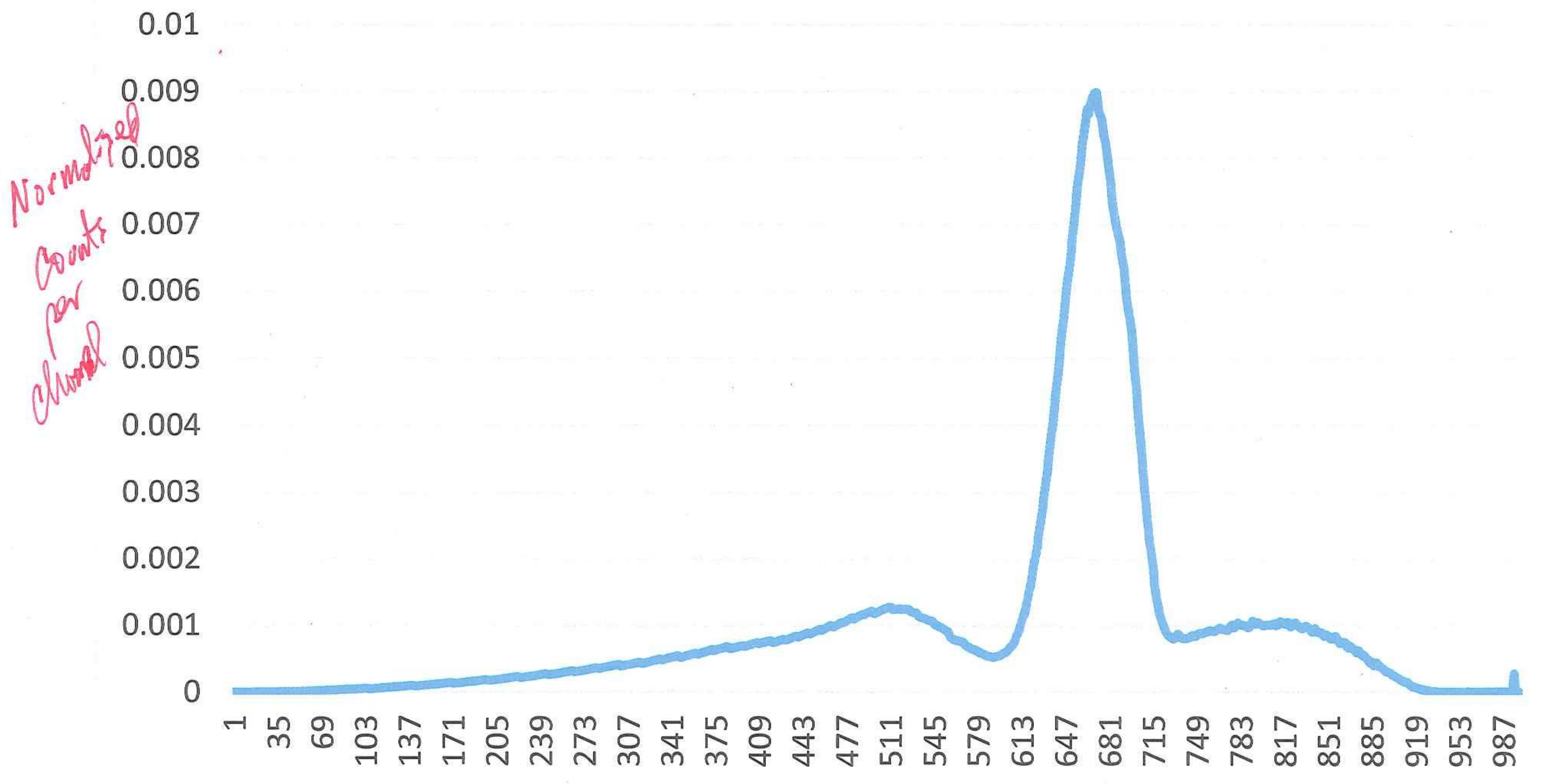
The good Doctor Zimmerman will help with LS detection efficiencies vs. ^3H

29 march 2017

NAT'L U

Al

LS log spectrum



log E

collé
31 march 2017

LS confirmation measurements

	series (n = 3)	R (s^{-1} g^{-1})	S (%)	average H#	average mass (g)	average f_W (%)
Beckman	A	905.35	0.173	102.5	0.221	7.86
29-Mar-17	B	905.45	0.093	117.7	0.424	8.42
	C	905.11	0.057	121.5	0.419	8.76
Beckman	A	905.51	0.171	104.8	0.221	7.86
30-Mar-17	B	904.22	0.095	120.8	0.424	8.42
	C	903.54	0.105	123.4	0.419	8.76

	series (n = 3)	R (s^{-1} g^{-1})	S (%)	average ESCR	averagem ass (g)	average f_W (%)
Hitachi	A	906.9	0.566	?	0.221	7.86
5-Apr-17	B	905.04	0.14	?	0.424	8.42
	C	905.03	0.62	?	0.419	8.76

1st rough cut with crude estimates of β efficiencies

efficiency guesses

U-234	e = 1	1
U-235	e = 1 + 0.95	1.95
U-238	e = 1 + 0.9 + 0.98	2.88

activity from mass spec

U-234	220.2	Bq g^{-1}
u-235	10.5	
U-238	228.9	

$\mathbf{R_{LS}}$ **=** 220.1(1) + 10.5(1.95) + 228.9(2.88)

900

alpha spectrometry confirmatory measurements

electrodeposited sources
with ^{232}U spikes

U-238	4.147 - 4.196	MeV
U-234	4.776	
U-232	5.264 - 5.320	
Th-228	5.341 - 5.423	

LaRosa 4 sources

U-234		U-238	
Bq g^{-1}	sd	Bq g^{-1}	sd
221.2	0.50%	230.9	0.39%

Nour 5 sources

U-234		U-238	
Bq g^{-1}	2U	Bq g^{-1}	2U
219.3	1.40%	228.8	1.80%

Δ -0.42% -0.05%

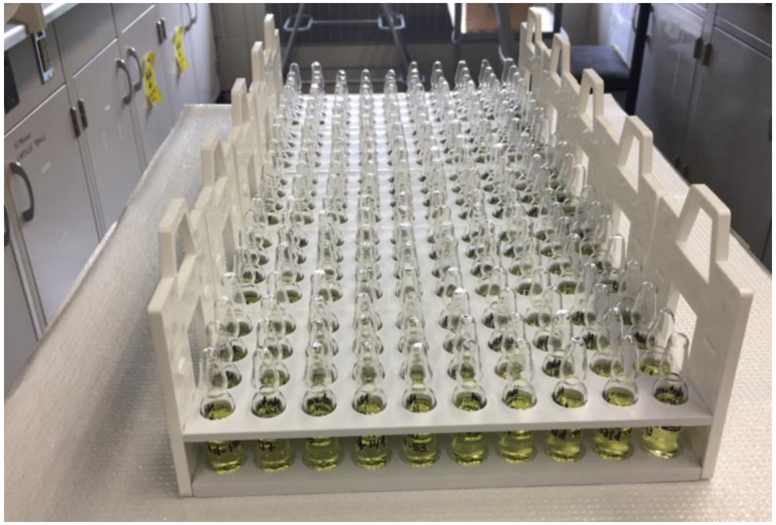
mass spec

U-234		U-238	
Bq g^{-1}	2U	Bq g^{-1}	2U
220.2	? (1 %)	228.9	? (0.7 %)

Economic value (in USD)

$ 360 000

(September 2017)



197 ampoules of Natural Uranium radioactivity solution standard (5 mL)

$373 500

(21 September 2017, 10:00 NY)

9 kilobars of Gold (1000 g each)

PART TWO

Comparison of two ^{229}Th standards

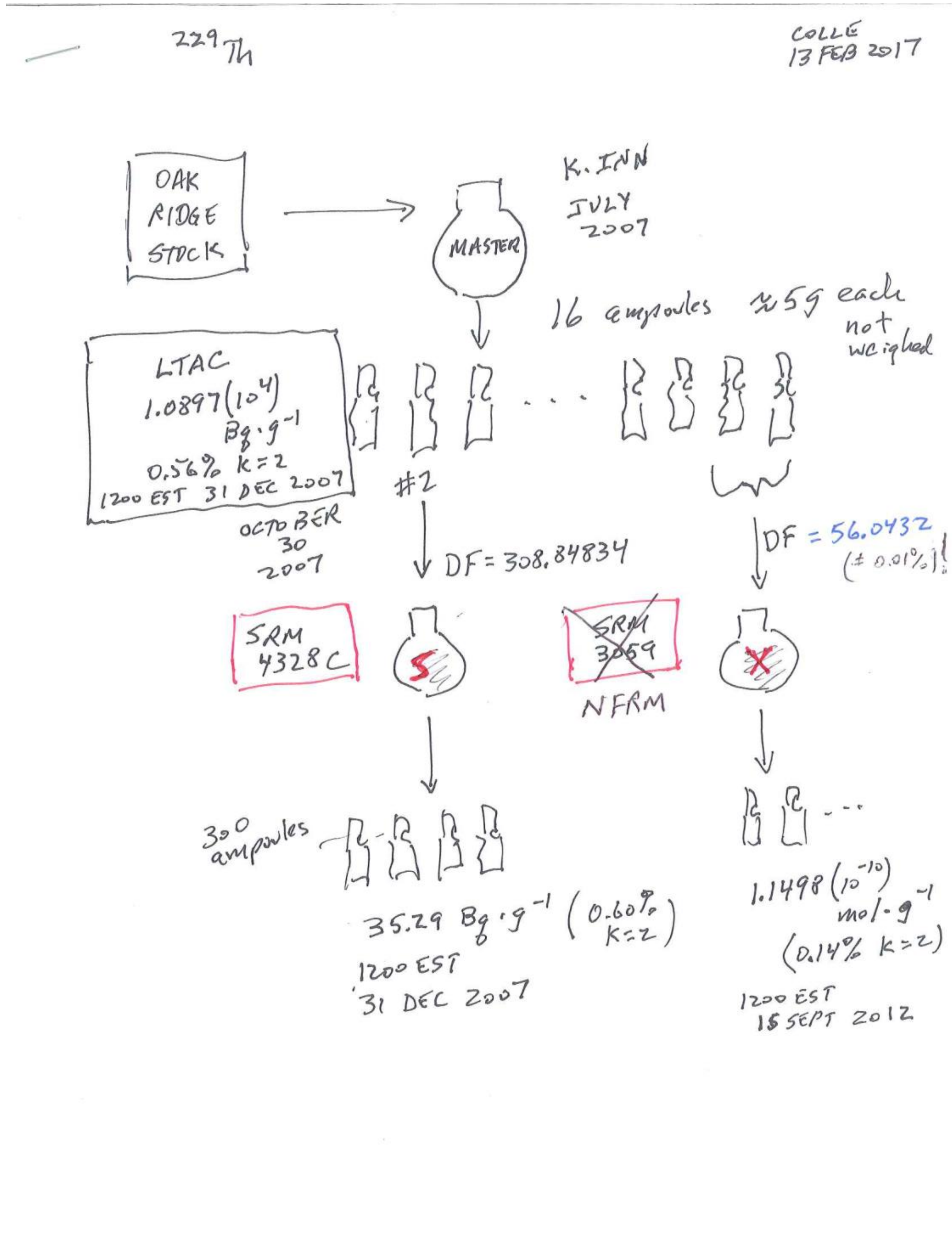
S = SRM 4328c (2007)

4παβ(LS)-γ(NaI) live-timed anti-coincidence counting. Confirmatory measurements were performed by five other methods: (i) 4παβ liquid scintillation (LS) spectrometry (with ^{3}H standard efficiency tracing for β efficiencies); (ii) an LS-based 4παβ triple-to-double coincidence ratio (TDCR) method; (iii) 2πα proportional counting; (iv) 2πα spectrometry using Si detectors, following chemical separation, with a ^{230}Th standard tracer; and (v) HPGe γ ray spectrometry.

X = "Nuclear Forensic Reference Material" (2012)

Isotopic mass standard – mass spec measurements by three laboratories (LLNL, LANL. IPGP) following preparation of standards at NIST

Both standards use common master solution with known gravimetric dilution factors



LS cocktail compositions

EXPT. 1 COMPOSITION

Th-229 Comparison

UltimaGold AB

Ecoscint

comparison expt

	scintillant	HNO3	HDEHP	Th-229	Total mass	fw
ThXUG1	9.8457	0.8211	0.05459	0.202124	10.923514	0.093672
ThXUG2	9.8493	0.8207	0.06247	0.204356	10.936826	0.093725
ThXUG3	9.8547	0.7509	0.06453	0.205087	10.875217	0.087905
ThSUG1	9.8534	0	0.06412	1.002123	10.919643	0.091773
ThSUG2	9.8508	0	0.0612	0.971064	10.883064	0.089227
ThSUG3	9.8526	0	0.06183	0.999553	10.913983	0.091585
BUG1	9.8549	1	0.06621	0	10.92111	0.091566
ThXES1	8.884	0.7381	0.06087	0.20268	9.88565	0.095166
ThXES2	8.9382	0.8104	0.0641	0.203885	10.016585	0.101261
ThXES3	8.9271	0.8219	0.06439	0.191477	10.004867	0.101288
ThSES1	8.9122	0	0.06419	1.014936	9.991326	0.101582
ThSES2	8.898	0	0.06713	1.006009	9.971139	0.100892
ThSES3	8.9211	0	0.06821	1.010061	9.999371	0.101012
BES1	8.9642	1.0284	0.06226	0	10.05486	0.102279

EXPT 2 COMPOSITION

Ecoscint

standard addition expt

	Scintillant	HNO3	HDEHP	X Th-229	SRM Th-229	Total Mass	Total HNO3	fw
ThA1	13.5365	-0.0008	0.05668	0.076775	1.697757	15.366912	1.773732	0.115425
ThA2	13.5657	0.2647	0.0597	0.201698	1.30443	15.396228	1.770828	0.115017
ThA3	13.5808	0.4289	0.06299	0.348458	0.995254	15.416402	1.772612	0.114982
ThA4	13.5832	0.6948	0.05693	0.476746	0.600704	15.41238	1.77225	0.114989
ThA5	13.5711	0.8073	0.06123	0.632714	0.327851	15.400195	1.767865	0.114795
BTh	13.5824	1.7032	0.05744	0	0	15.34304	1.7032	0.111008

1

BECKMAN

19 APRIL 2017

0.2

	CPSPG	%\$	each %p	w/in %	between %
→ SE	245.0796	0.233%	0.087	0.202	0.117
SU	245.4935	0.126%	0.087	0.115	0.050
→ XE	1352.8064	0.152%	0.083	0.148	0.036
XU	1354.7772	0.178%	0.083	0.170	0.055

$\frac{XE}{SE} = 5.5199 \quad \$ = 0.279\%$

$\frac{XU}{SU} = 5.5186 \quad \$ = 0.218\%$

> 5.5192
$\$ = 0.250\%$

0.15%

DF (x) = 56.04320

DF (S) = 308.84834

$\frac{DF(S)}{DF(x)} = 5.5109$

2

HITACHI

24 April 2017

	CPSPG	\$	on each %p	w/in %	between %
SE	249.3834	0.293%	0.086	0.075	0.283
SU	250.1967	0.117%	0.086	0.059	0.101
XE	1379.109	0.0714%	0.082	0.060	0.039
XU	1381.479	0.106%	0.082	0.059	0.090

$\frac{XE}{SE} = 5.53008 \quad \$ = 0.302\%$

$\frac{XU}{SU} = 5.52157 \quad \$ = 0.158\%$

> 5.5258
$\$ = 0.241\%$

0.27%

DF (x) = 56.04320

DF (S) = 308.84834

$\frac{DF(S)}{DF(x)} = 5.5109$

Results for comparison expt

DF (S) / DF(X)	5.5109

	BECKMAN	HITACHI
XE / SE	5.5199 0.28%	5.5301 0.30 %
XU / SU	5.5186 0.22 %	5.5216 0.16 %

Δ	0.16%	0.35%
	0.14%	0.19%

mean	5.5225
between sd	0.094%
typical within sdm	0.24%
unc (k = 1)	0.26%
Δ	0.21%

0.3 % measurement (k = 1)

agrees to 0.2 %

SRM certified to 0.3 % (k = 1)

had hoped for better precision ... !

$$R = m_s A_s + m_x A_x$$

$$\frac{R}{m_s} = A_s + \frac{m_x}{m_s} A_x$$

INTERCEPT SLOPE

IN PLOT OF

R/m_s AS FUNCTION OF m_x/m_s

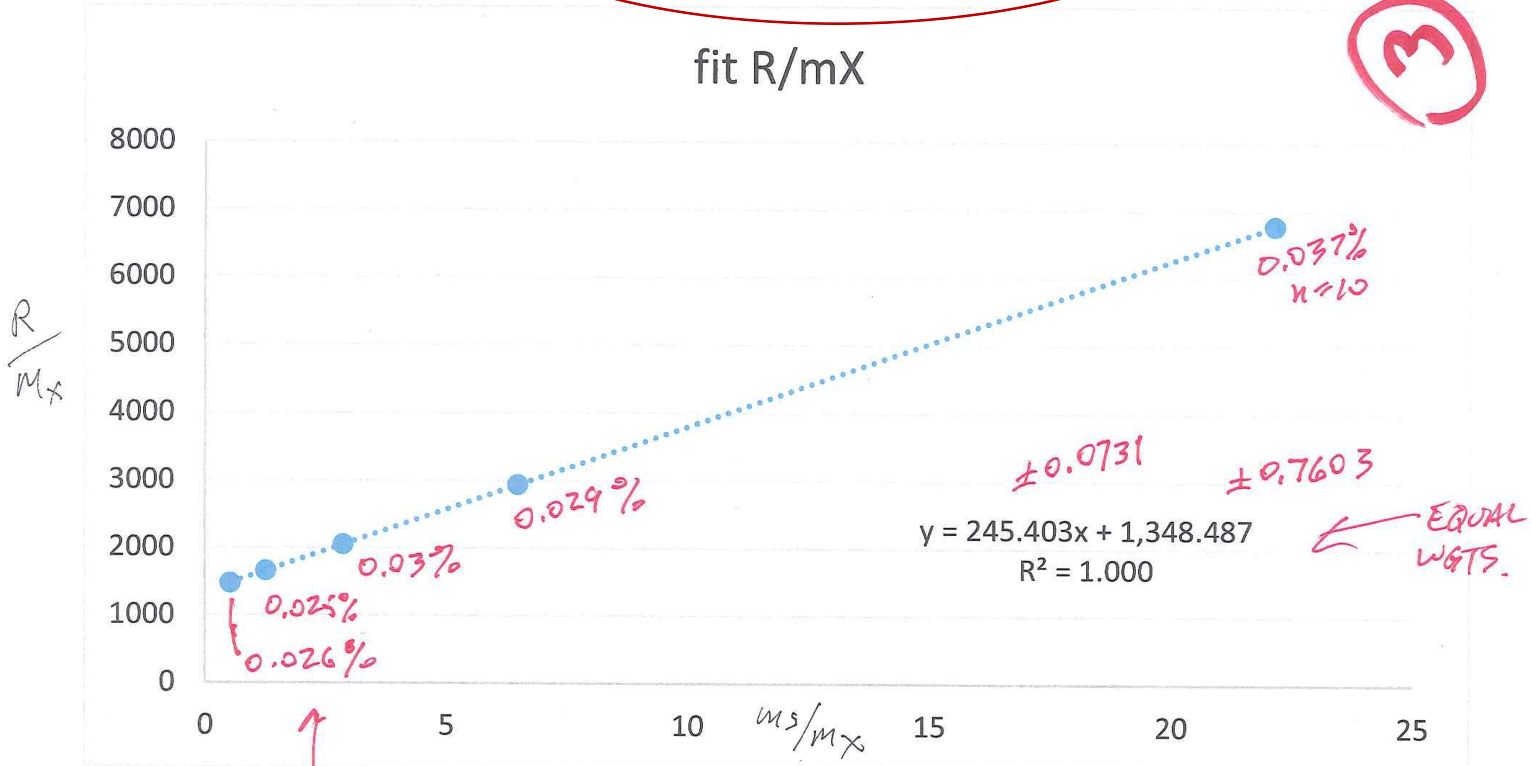
$\frac{A_x}{A_s}$ = SLOPE/INTERCEPT

EXPT 3
Beckman
Ecoscint

$A_s = 245.5730$
$A_x = 1347.863$] fit w/ wgt $\frac{1}{S^2}$
$\frac{A_x}{A_s} = 5.4886$

Collé
5/2/2017

③



% sdm
n=10

$\frac{A_x}{A_s} = \frac{1348.487}{245.403} = 5.4950$
± ~~0.0039~~ 0.0047
(0.086%)

covar = 0.63873
units.

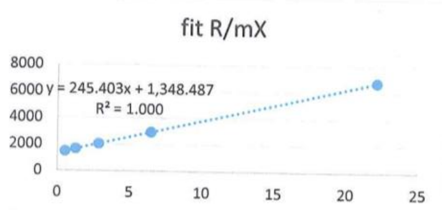
— 0.29%
from
DF's

get nice linear curves – but low compared to DFs – same result in Hitachi

5/2/201

3

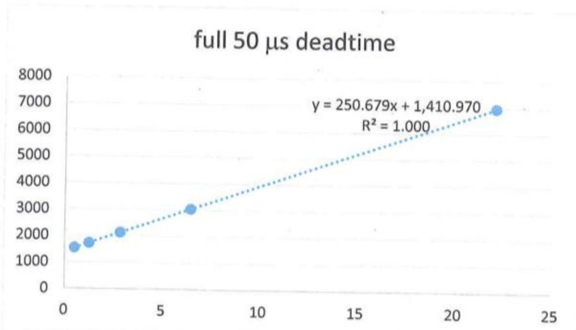
mS/mX	cpspg 2x mean	cps			full			10%
22.11341	6774.72	521	534.9351	1.026747	6955.922	0.026747	1.002675	6792.84
6.467243	2937.414	594	612.1818	1.030609	3027.326	0.030609	1.003061	2946.405
2.856166	2048.963	715	741.5089	1.037075	2124.929	0.037075	1.003708	2056.559
1.260008	1657.888	791	823.5723	1.041179	1726.158	0.041179	1.004118	1664.715
0.518166	1474.514	935	980.855	1.049043	1546.828	0.049043	1.004904	1481.745



	Ax	As	Ax/As	
none	1348.487	245.487	5.49311	-0.32282
full	1410.97	250.879	5.624106	2.054213
10%	1354.735	245.931	5.508598	-0.04177
		Df	5.5109	

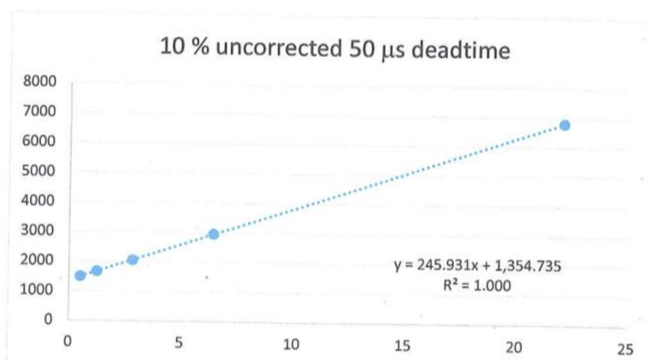
(dead time effect.)

?



slope inc by 0.46%

intercept inc by 0.22%



residuals smaller too!

wgtd by $\frac{1}{s^2}$

245.913x + 1354.936

Problem appears to be result of uncorrected deadtime

Hearty thanks to all the worker bees ...

Willie Regits
Khyra Neal
-- *amp sterilization*

Brian Zimmerman -- *β LS ε calculations*

Denis Bergeron -- *NaI homogeneity*

Leticia Pibida
Lynne King
γ

Svetlana Nour
Jerry LaRosa
α

Ryan Fitzgerald -- *think & listen*

Lizbeth Laureano-Perez – *assist wet lab work & source prep; set-up LS counting*

R. Collé -- genius expt designs; wet-lab work & source prep; data analyses