Natural Uranium SRM

Radiation Physics Division Seminar

4 October 2017

R. Collé

NIST

SRM 4321d

Natural uranium radioactivity solution standard

SRM ampoules

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
Page 1 of 2

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

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

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

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

at higher (concentrated) HNO_3

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

4 : 1 or 8 : 1 ?

Makes big difference in needed acid to dissolve metal and to maintain acidity of solution

Clean metal bar

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

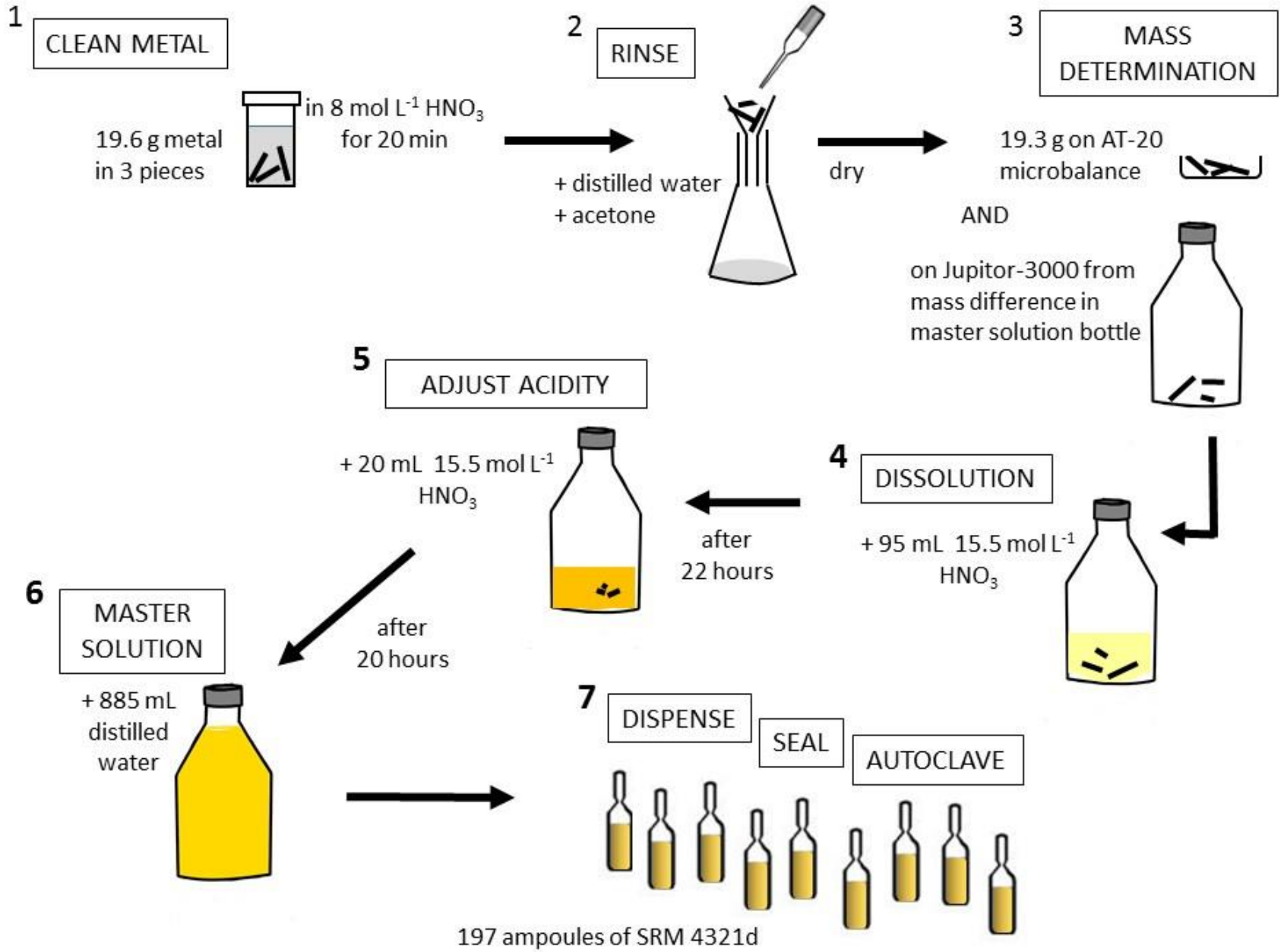
2 Rinse with distilled water

3 Remove excess water

4 Rinse with pure acetone

5 Allow evaporation 60 seconds

6 Weigh metal – observe mass as function of time


1
CLEAN METAL
19.6 g metal
in 3 pieces
in 8 mol L-1 HNO3
for 20 min
2
RINSE
+ distilled water
+ acetone
3
MASS
DETERMINATION
dry
19.3 g on AT-20
microbalance
AND
on Jupitor-3000 from
mass difference in
master solution bottle
4
DISSOLUTION
+ 95 mL 15.5 mol L-1
HNO3
after
22 hours
5
ADJUST ACIDITY
+ 20 mL 15.5 mol L-1
HNO3
after
20 hours
6
MASTER
SOLUTION
+ 885 mL
distilled
water
7
DISPENSE
SEAL
AUTOCLAVE
197 ampoules of SRM 4321d

PRODUCTION

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

From calculations of certified values in CRM 112-A

Uranium isotope	Atom percent of isotope (%)	Half-life (a)	Activity per unit mass of CRM 112-A (Bg g^{-1})
^{234}U	0.0052458 (81)	2.455 (6) 10^5	1.1871 (30) 10^4
^{235}U	0.72017 (39)	7.04 (1) 10^8	5.6834 (82) 10^2
^{238}U	99.24748 (39)	4.468 (5) 10^9	1.2344 (14) 10^4

And mass of U metal = (19.3180 $\pm$ 0.01) g
total solution mass = 1041.67 $\pm$ 0.05) g

Get massic activity of each isotope in SRM 4321d

Uranium isotope	Massic activity of isotope in SRM 4321d	Relative expanded uncertainty *U* (*k* = 2)
^{234}U	220.16 Bq g^{-1}	0.52 %
^{235}U	10.540 Bq g^{-1}	0.31 %
^{238}U	228.93 Bq g^{-1}	0.25 %

CONFIRMATIONS

Homogeneity

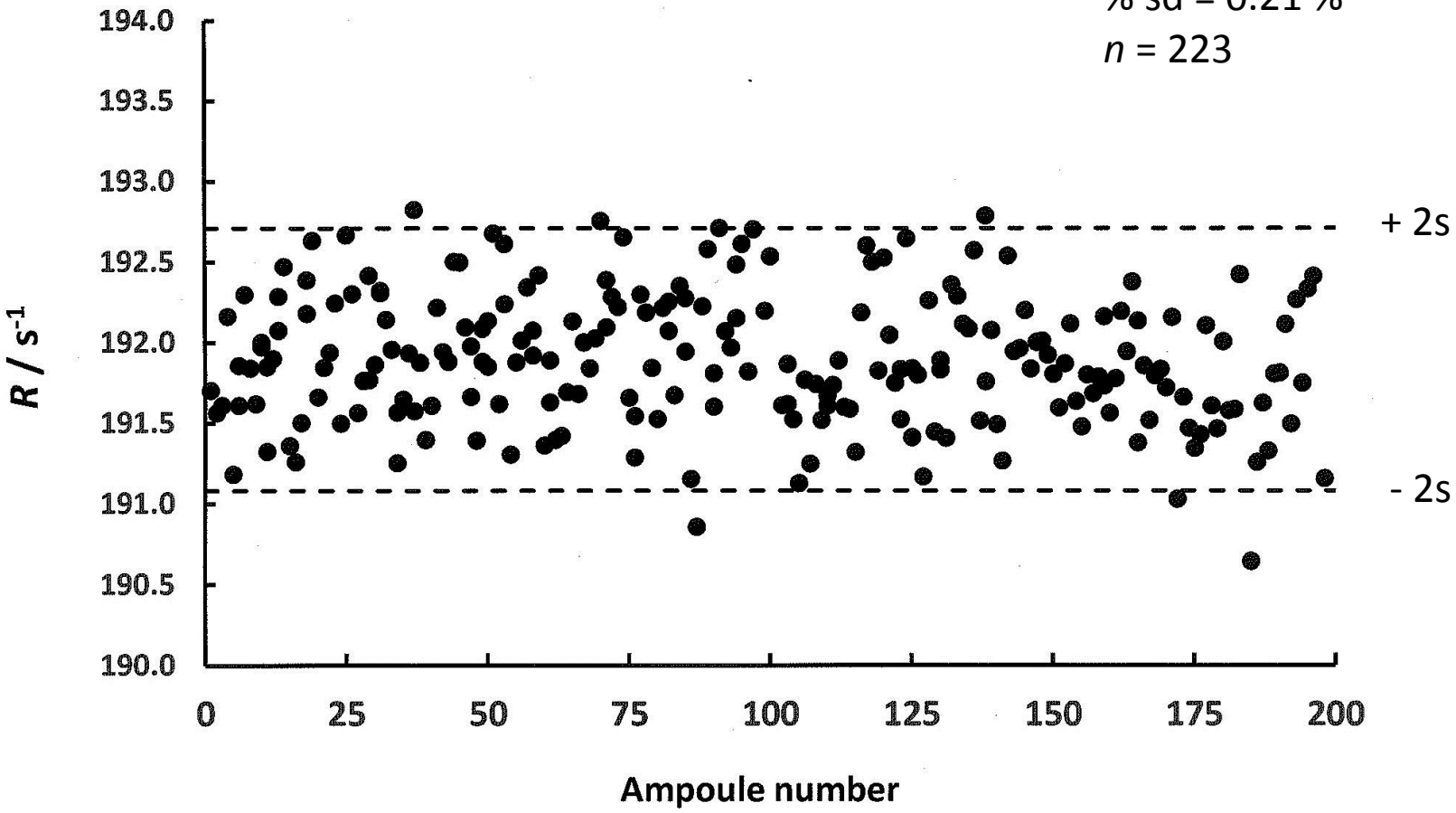
Radionuclidic impurity analysis

LS measurements

IDAS

Homogeneity Data

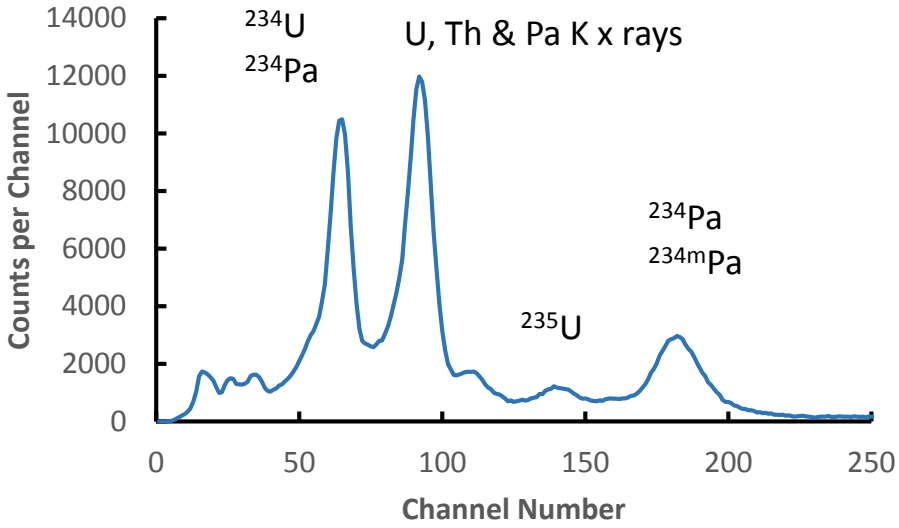
mean = 191.89 s^{-1}
% sd = 0.21 %
n = 223

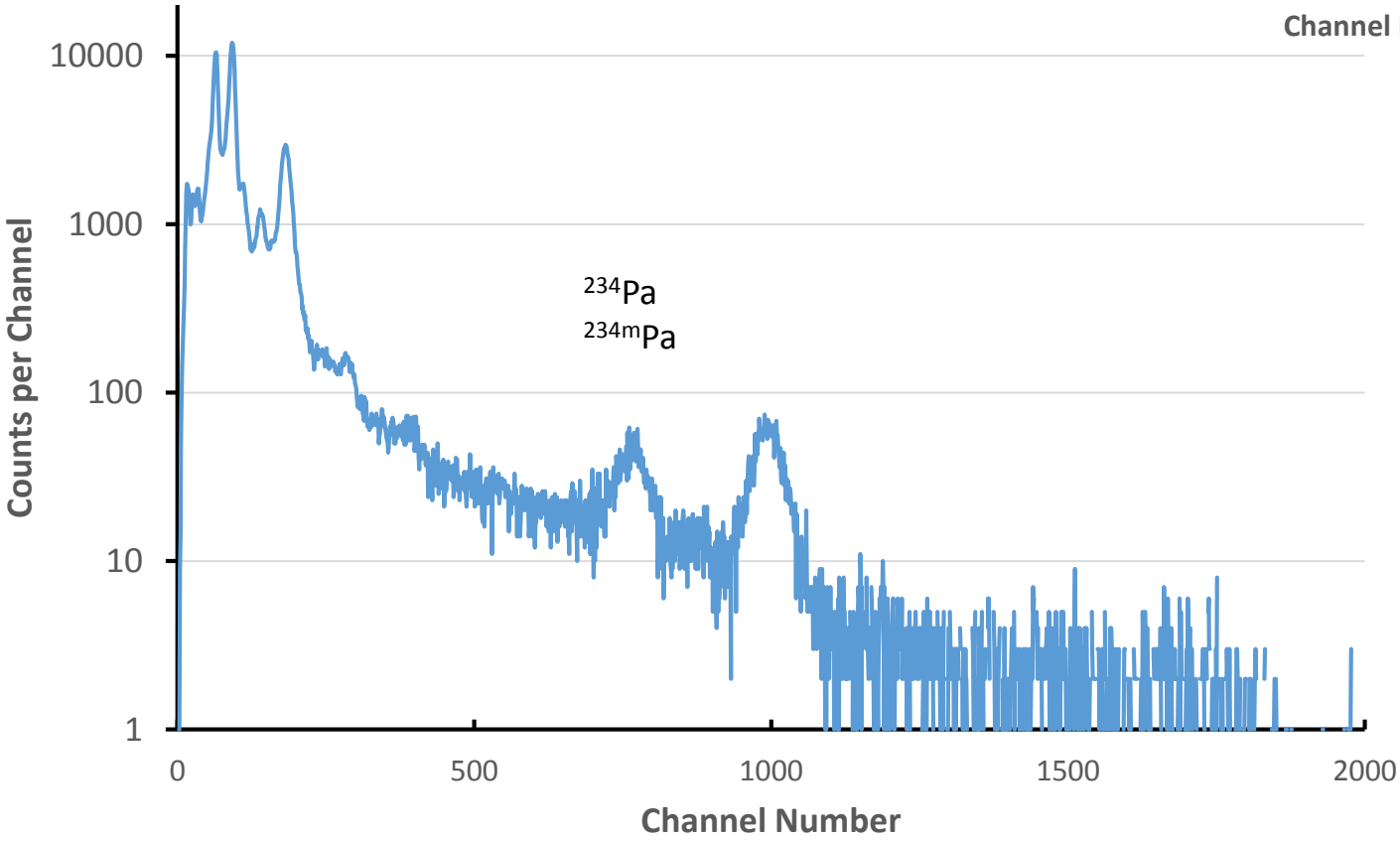


Poisson counting statistics on each value = 0.15 %
28 duplicate measurements; average difference = 0.16 %

N.B.
(223-8) / 223
≈ 96 %
Statistics works !

Spectra NaI(Tl) well





4/17/2017

Uranium source #4321d-101

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

Reference time 4/12/2017

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

$m = 5.2437$ g

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 $\frac{1484.4}{5.2437} = 283.08$ ±34% 220.16 Δ = 29%

^{235}U $\frac{55.3}{5.2437} = 10.546$ ±16% 10.54 Δ = 0.05%

^{238}U $\frac{1288.7}{5.2437} = 245.76$ ±15% 228.93 Δ = 7.4%

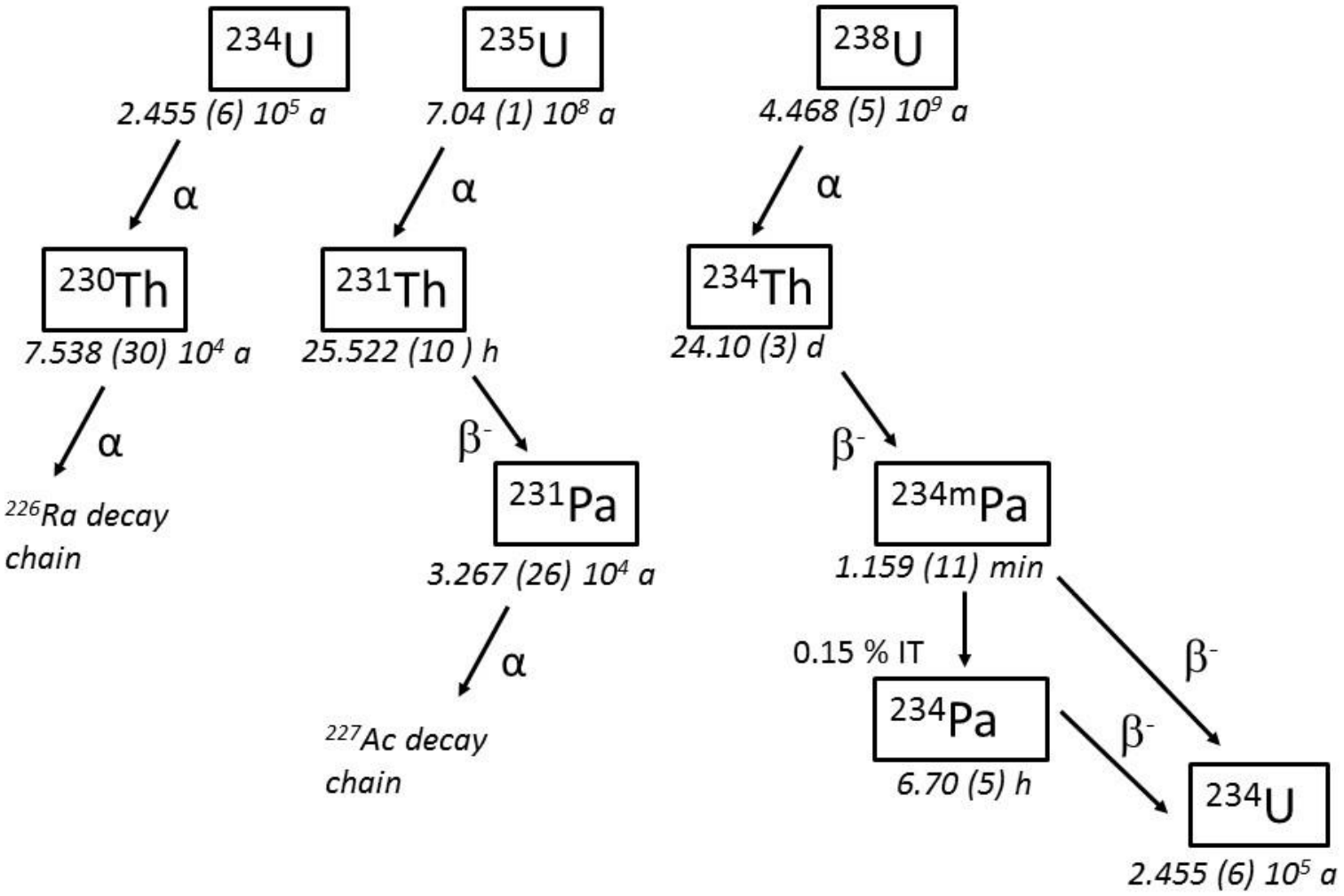
$\frac{^{238}U}{^{234}U} = \frac{228.93}{220.16}$ std. 1.0398 $\frac{245.76}{283.08} = 0.868$ Δ = 17%

Photonic emission spectrometry

impurity check

assay ?

didn't expect much


234U
2.455 (6) 10^5 a
α
230Th
7.538 (30) 10^4 a
α
226Ra decay chain
235U
7.04 (1) 10^8 a
α
231Th
25.522 (10) h
β-
231Pa
3.267 (26) 10^4 a
α
227Ac decay chain
238U
4.468 (5) 10^9 a
α
234Th
24.10 (3) d
β-
234mPa
1.159 (11) min
0.15 % IT
234Pa
6.70 (5) h
β-
β-
234U
2.455 (6) 10^5 a

LS rate

to confirm agreement compare calculated rate to measured rate

$$R = m_U [\, A_{234U}\varepsilon_{234U} + A_{235U}(\varepsilon_{235U} + \varepsilon_{234mPa}) + A_{238U}(\varepsilon_{238U} + \varepsilon_{234Th} + \varepsilon_{234mPa})]$$

$\alpha = 1$ $\quad \alpha = 1 \quad \beta \quad \alpha = 1 \quad \beta \quad \beta$

aliquot mass

calculated massic activities for SRM

my initial efficiency guesses

$^{234}U \quad \varepsilon = 1$

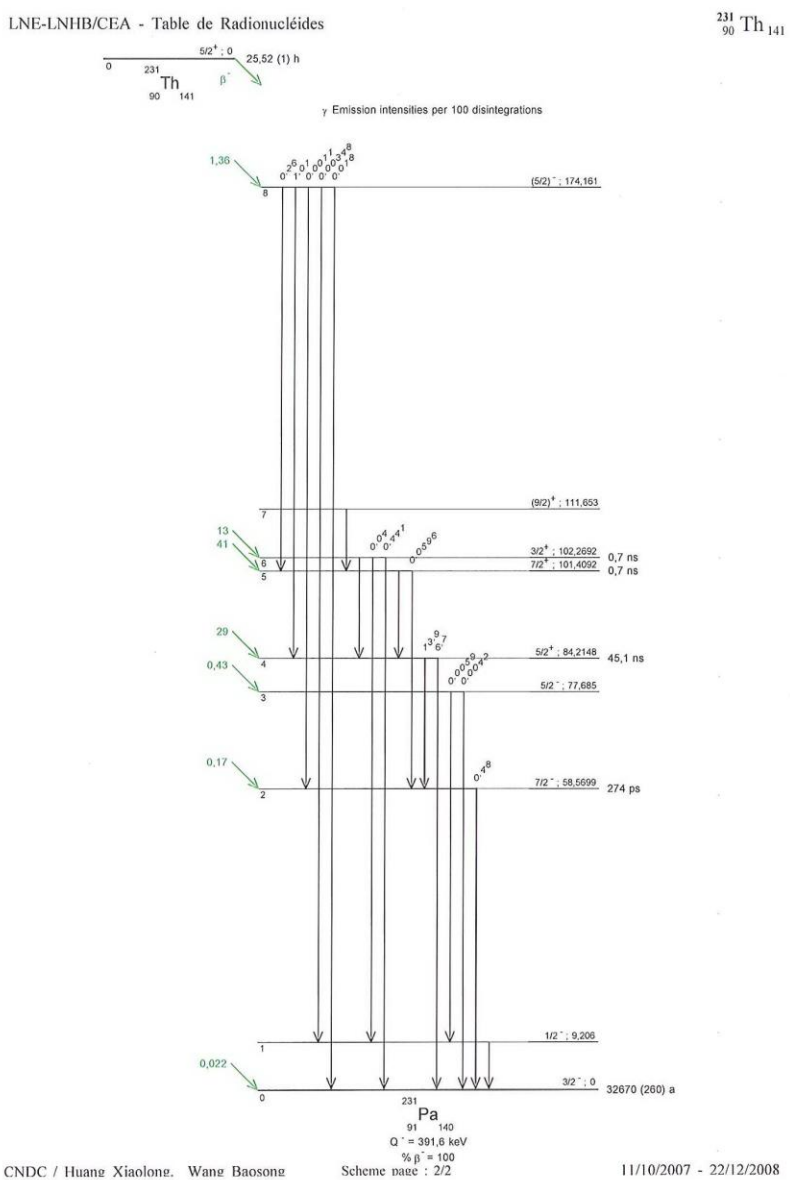
$^{235}U \quad \varepsilon = 1 + 0.95 = 1.95$

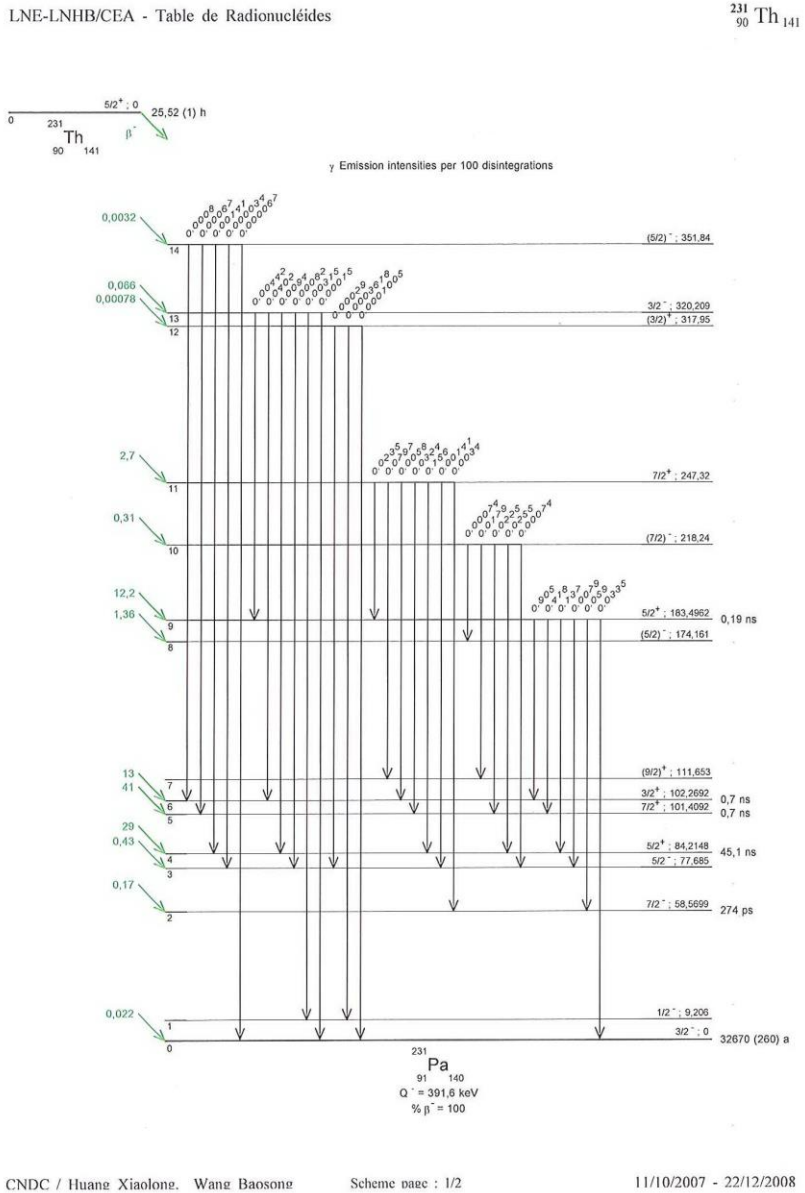
$^{238}U \quad \varepsilon = 1 + 0.90 + 0.98 = 2.88$

Example

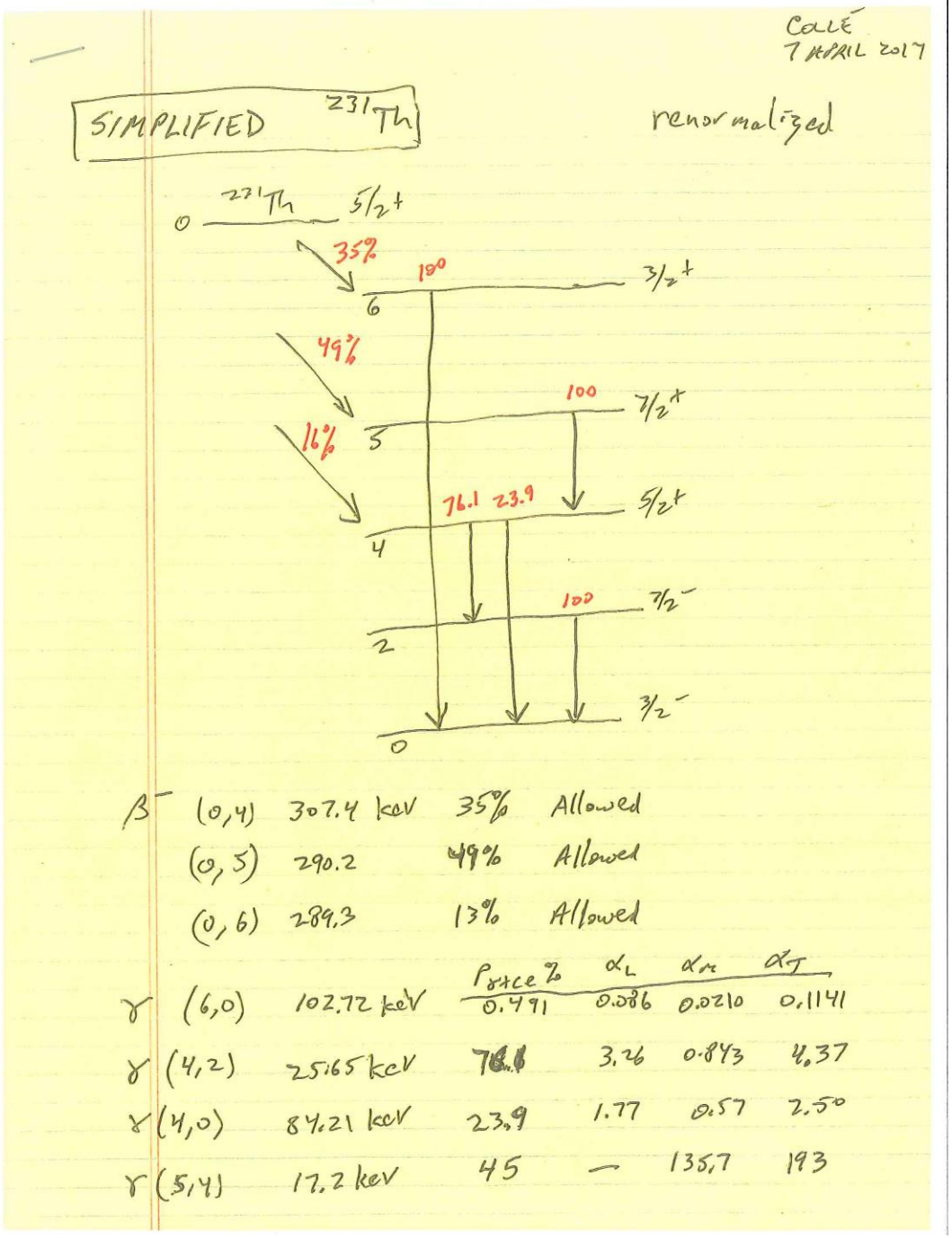
^{231}Th decay

13 β branches
49 γ transitions

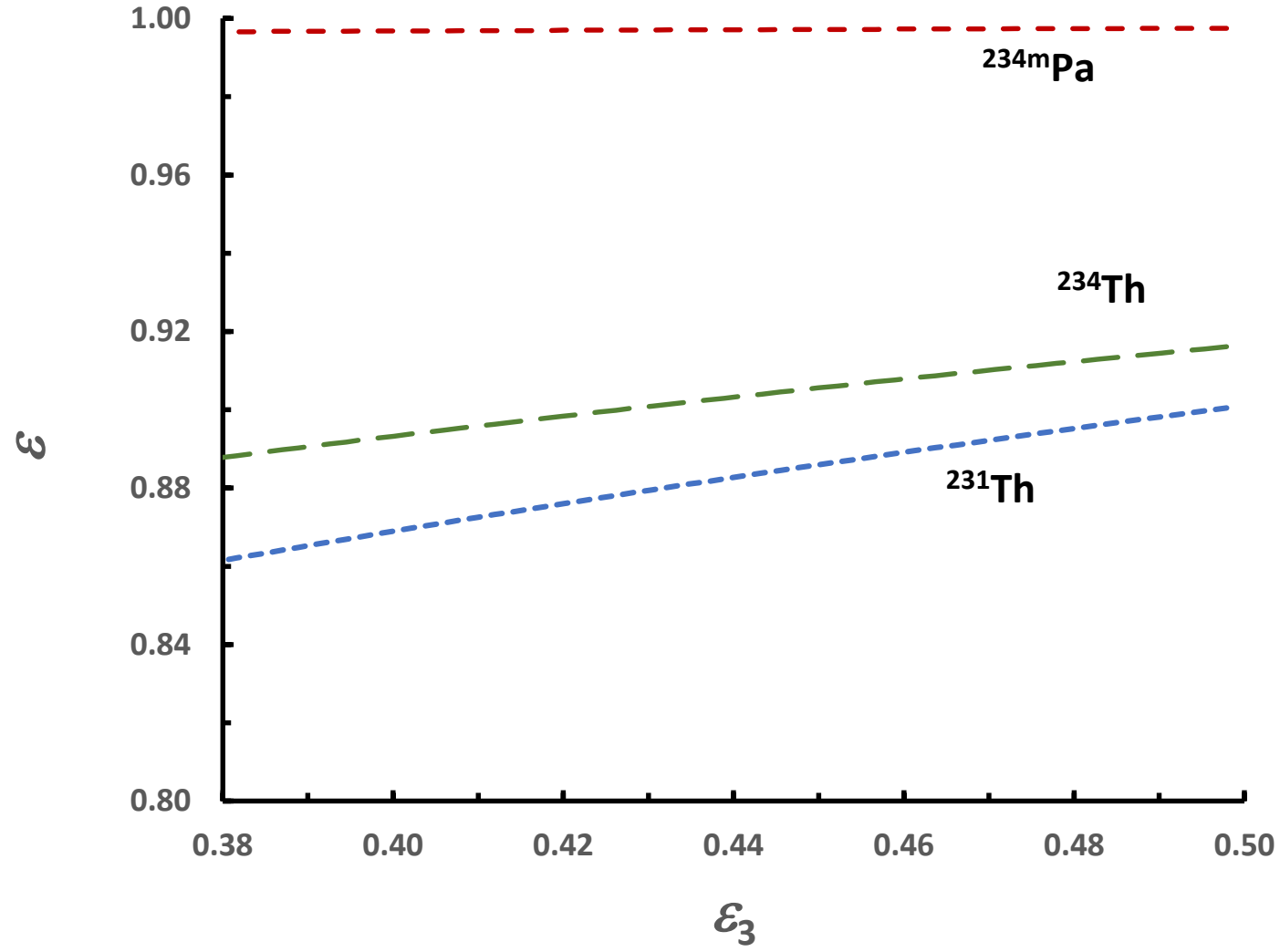




Example



The good Doctor Zimmerman calculated the LS detection efficiencies vs. ^3H using MICELLE2 code



Zimmerman calculations with MICELLE2 code

1st LS trials

LS SOURCES

3 replicates for each series

series	mass of UGAB (g)	mass of blank HNO3 (g)	aliquot mass of SRM solution (g)	total cocktail mass (g)	f_{aq} (%)
A	9.804	0.620	0.221	10.70	7.86
B	9.804	0.483	0.424	10.77	8.43
C	9.629	0.619	0.419	10.72	9.67

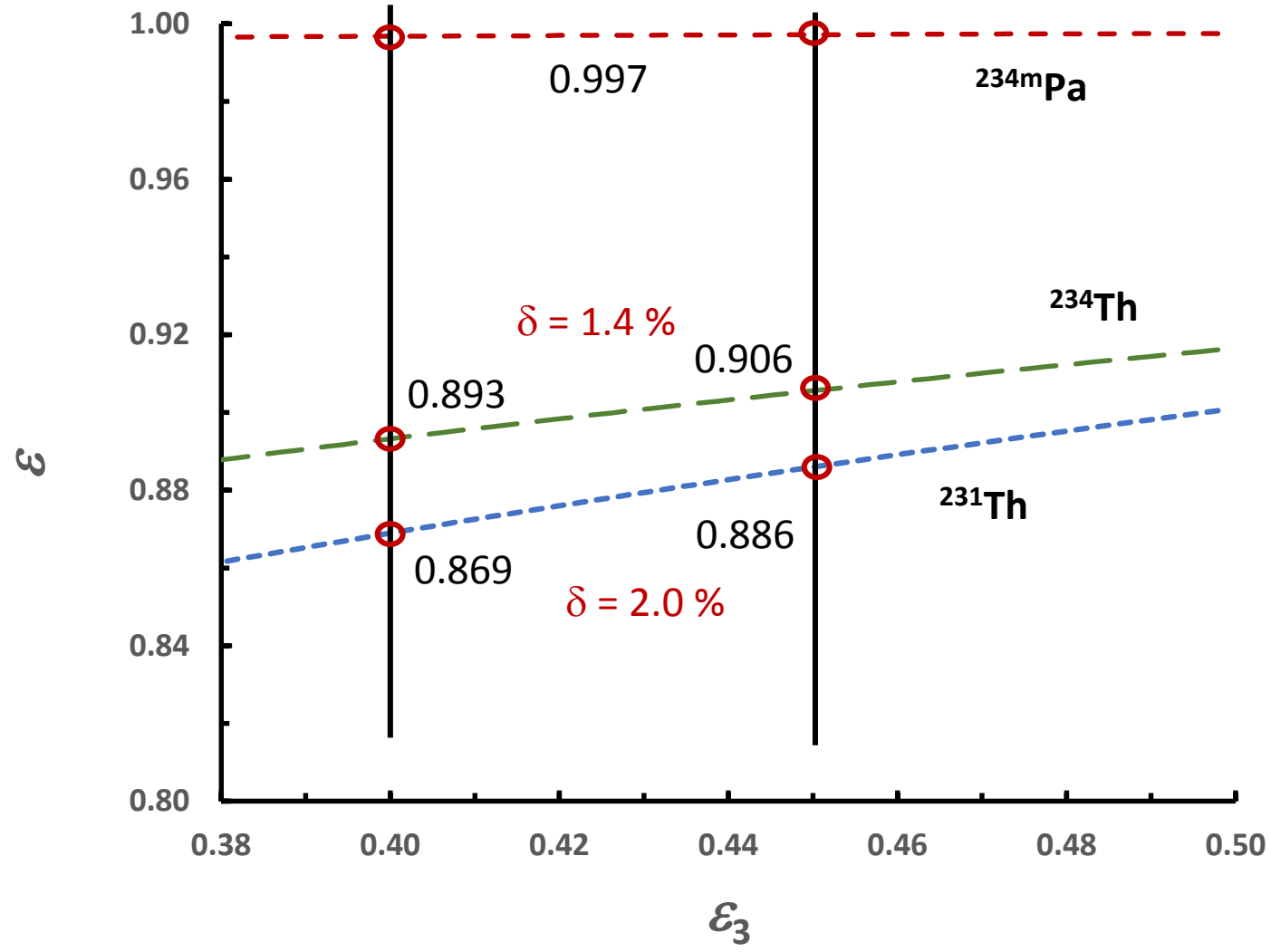
COUNTING RESULTS

n = 4 for "B" & n = 3 for "H"

Series	Average H#	"B" counter		"H" counter	
		R_U/m ($s^{-1}g^{-1}$)	S (%)	R_U/m ($s^{-1}g^{-1}$)	S (%)
A	104.2	905.5	0.17	906.9	0.56
B	120.0	904.5	0.10	905.0	0.14
C	122.9	903.9	0.11	905.0	0.62

S is precision estimator considering within-source and between-source components of variance

don't know equivalent ^{3}H efficiency for these cocktails (colored & uranyl ions), but guessed in range of 40 % to 45 %


1.00
0.96
0.92
0.88
0.84
0.80
ε
0.38
0.40
0.42
0.44
0.46
0.48
0.50
ε_3
0.997
^{234m}Pa
^{234}Th
δ = 1.4 %
0.906
0.893
^{231}Th
0.886
0.869
δ = 2.0 %

calculated massic rates

$(R_U/m)_{calc}$ = 901.5 $s^{-1}\,g^{-1}$ at equivalent ε_3 = 0.40;

and

$(R_U/m)_{calc}$ = 904.6 $s^{-1}\,g^{-1}$ at equivalent ε_3 = 0.45,

measured massic rates

Series	Average H#	"B" counter		"H" counter	
		R_U/m ($s^{-1}g^{-1}$)	S (%)	R_U/m ($s^{-1}g^{-1}$)	S (%)
A	104.2	905.5	0.17	906.9	0.56
B	120.0	904.5	0.10	905.0	0.14
C	122.9	903.9	0.11	905.0	0.62

average across all

measured = 905.1

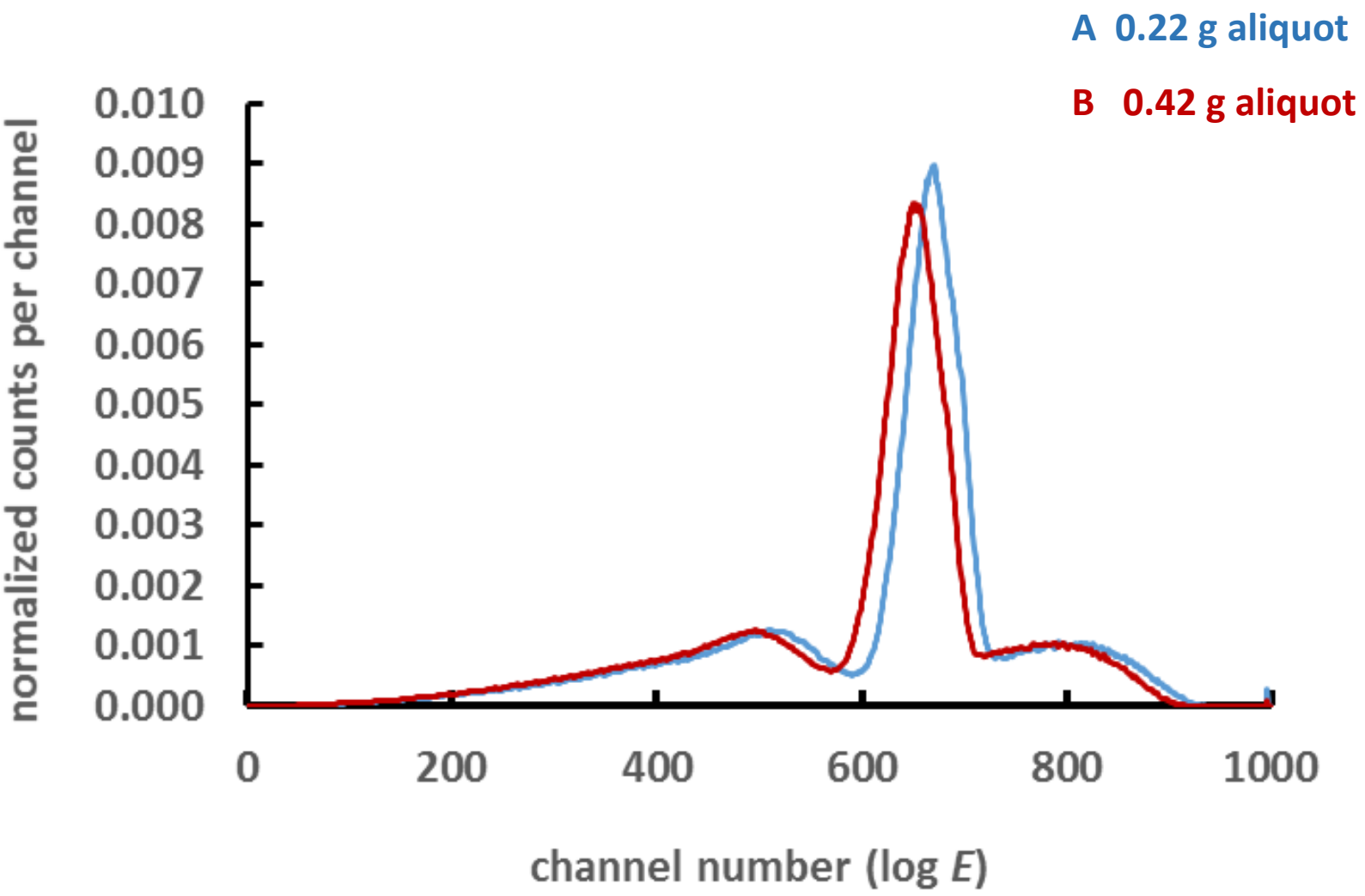
calculated = 903.1

} 0.22 %

Fortuity ?

need better efficiency evaluation

LS spectra of natural uranium solution standard



2nd LS trials

To obtain cocktail composition matched ^{3}H efficiency

using U-spiked ^{3}H cocktail matched to *n* = 3 U cocktails

Rate of spiked UT cocktail

aliquot mass of U in spiked cocktail

average U cocktail massic rate aliquot mass

^{3}H eff in equivalent U cocktail

aliquot mass of T in spiked cocktail

Massic activity of ^{3}H standard

$$R_{UT} = m_U\left(\frac{R_u}{m}\right) + \varepsilon_T m_T A_T \ ,$$

$$\varepsilon_T = \frac{R_{UT} - m_U\left(\frac{R_u}{m}\right)}{m_T A_T}$$

LS SOURCES

cocktail	mass of UGAB (g)	mass of blank HNO3 (g)	aliquot mass of SRM solution (g)	aliquot mass of ^{3}H standard (g)	total cocktail mass (g)	f_{aq} (%)
U (*n* = 3)	9.8495 (28)	0	0.2132 (12)	0	10.1758 (19)	2.638 (10)
T	9.8573	0.2251	0	0.04701	10.1377	2.684
UT	9.8458	0	0.2088	0.04705	10.1098	2.531
B	9.8583	0.2505	0	0	10.2192	2.960

2nd LS trial counting data

cocktails	H#	quantity	"B" counter	"H" counter
U (n = 3)	78.6 (8)	(R_U / m)	910.70 (34) s^{-1} g^{-1}	910.16 (29) s^{-1} g^{-1}
T	59.5	ε_3	0.4906	0.4755
UT	77.7	R_{UT}	276.61 s^{-1}	225.54 s^{-1}
UT		m_U	0.20883	0.20883
UT		$m_T A_T$	82.471 Bq	82.471 Bq
UT		ε_T	0.442	0.431
UT		ε_{231Th}	0.883	0.880
UT		ε_{234Th}	0.904	0.901
UT		ε_{234mPa}	0.997	0.997
UT		$(R_U / m)_{calc}$	904.1 s^{-1} g^{-1}	903.4 s^{-1} g^{-1}
U / UT	--	δ	0.73 %	0.75 %

measured

calculated

LS confirmation summary

Series	measured				calculated		Average ΔR (%)
	Counter "B"		Counter "H"		"B"	"H"	
	R ($s^{-1}g^{-1}$)	S (%)	R ($s^{-1}g^{-1}$)	S (%)	R ($s^{-1}g^{-1}$)	R ($s^{-1}g^{-1}$)	
A	905.5	0.17	906.9	0.56	901.5 – 904.6 est		0.22
B	904.5	0.10	905.0	0.14			
C	903.9	0.11	905.0	0.62			
U/T	910.7	0.40	910.2	0.32	904.1	903.4	0.73

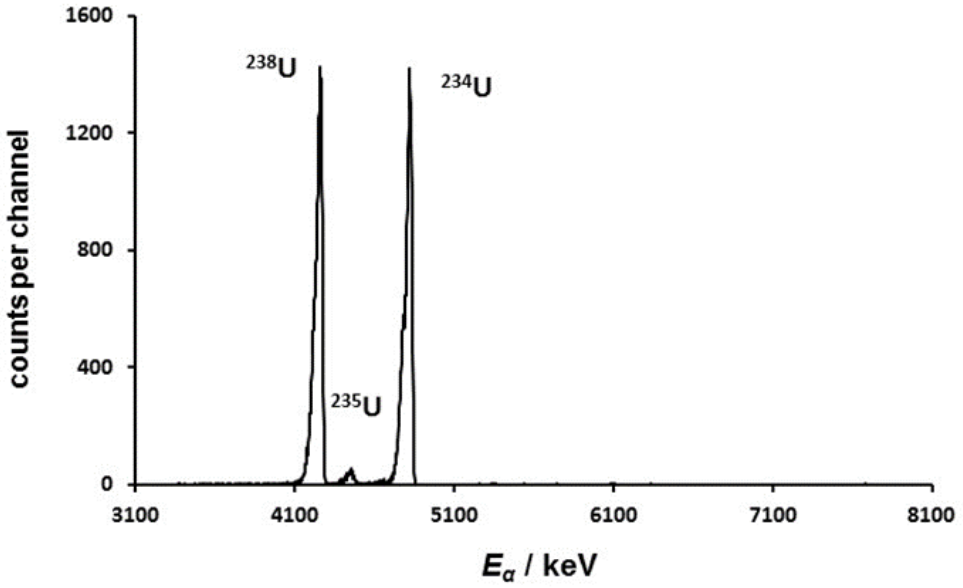
Isotope Dilution Alpha Spectrometry

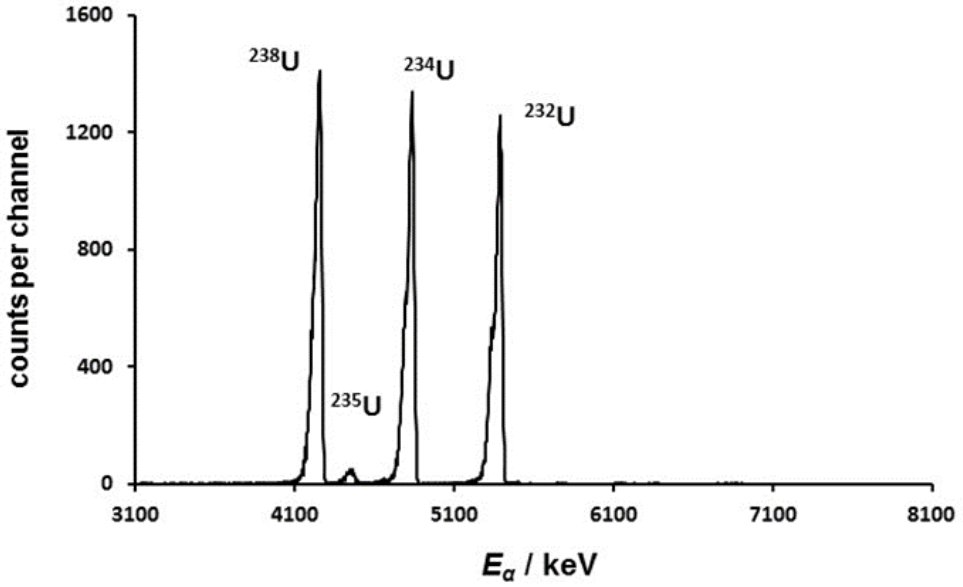
Jerry LaRosa
Svetlana Nour

- electrodeposited sources with ^{232}U spikes
- 12 determinations of ^{234}U and ^{238}U from 4 replicate counting sources in two geometries
- 4 spectra independently analyzed by two independent spectral analysis procedures
- No detected alpha impurities

	Massic activity (Bq g^{-1})	
	A_{234U}	A_{235U}
IDSA measured value	**219.9 (2.7)**	**229.5 (2.9)**
Certified value for SRM 4321d (from mass spec data)	**220.2 (1.1)**	**228.93 (57)**
Relative difference	**- 0.12 %**	**+ 0.25 %**

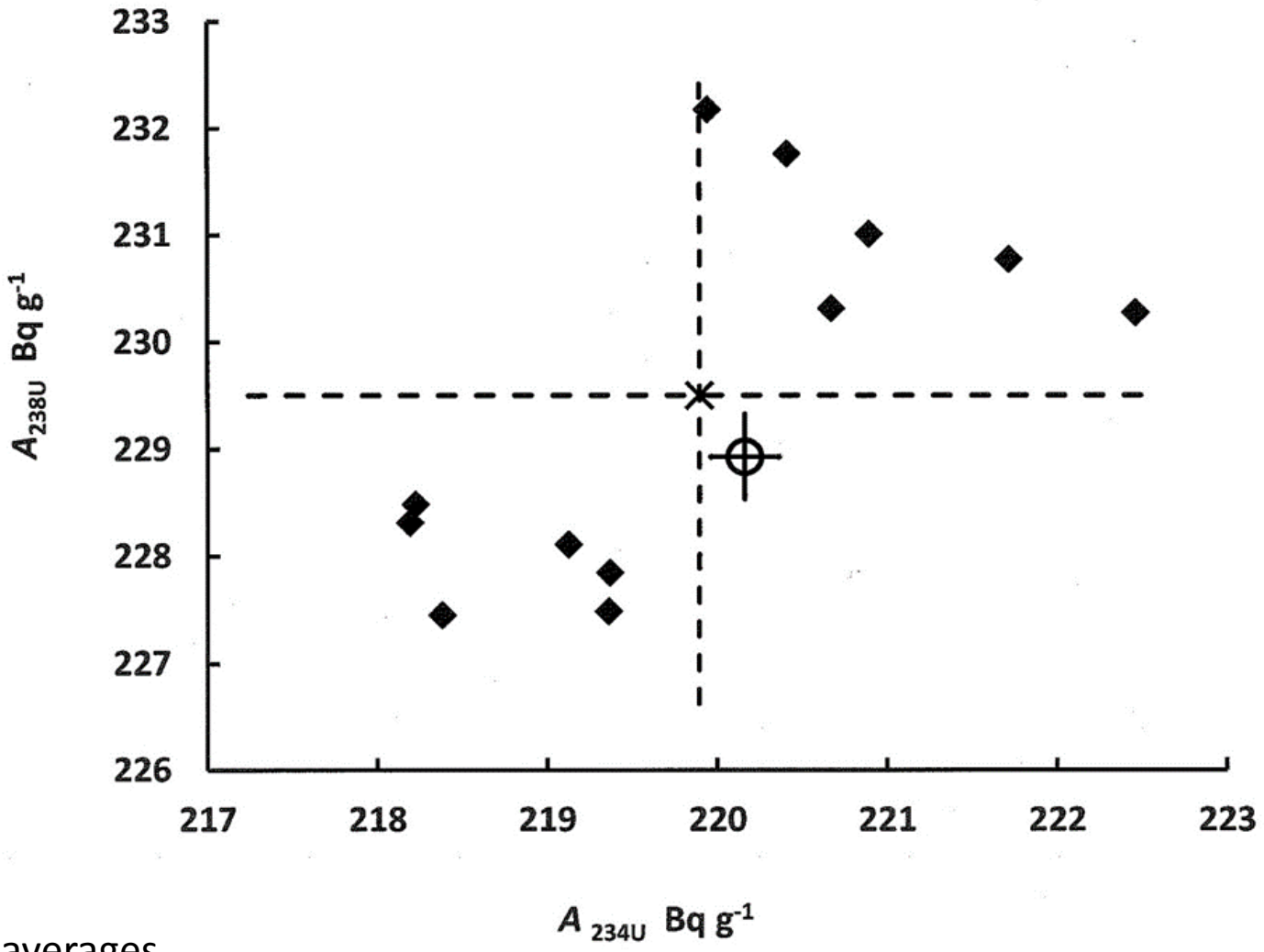
Alpha spectra





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

Paired results for the 12 determinations of 234U and 238 U by IDSA



Cross -- measured averages
Dashed line lengths are k = 2 uncertainties
Circle -- certified values

IDSA Uncertainty Assessment

Uncertainty component		Assessment type	*u* (%)	
			^{234}U	^{238}U
1	Measurement precision; standard deviation of the mean for *n* = 12 determinations on four counting sources in two counting geometries (8 spectra)	A	0.26	0.31
2	Massic activity of ^{232}U tracer from SRM 4324B Certificate [24]	B	0.41	0.41
3	Poisson statistics “counting error”; partially embodied in Component 1	B	0.18	0.18
4	^{228}Th ingrowth correction in ^{232}U peak analysis; varies in range 0.1 % to 0.3 % depending on measurement time.	B	0.2	0.2
5	Gravimetric mass measurements	B	0.05	0.05
6	Spectral analysis for peak determinations	B	0.25	0.25
7	Gravimetric dilution factor	B	0.02	0.02
Relative combined standard uncertainty, u_c			**0.61**	**0.63**
Relative expanded uncertainty (*k* = 2), *U*			**1.22**	**1.26**

Certification of SRM 4321d

Radionuclides :	Natural uranium (mixture of ^{234}U, ^{235}U, and ^{238}U)
Reference time :	1200 EST, 15 March 2017
Massic activities of the solution :	^{234}U : 220.16 Bq g^{-1}
	^{235}U : 10.540 Bq g^{-1}
	^{238}U : 228.93 Bq g^{-1}
Relative expanded uncertainties :	^{234}U : 0.52 %
	^{235}U : 0.31 %
	^{238}U : 0.25 %

The solution was also characterized in terms of the following uncertified information:

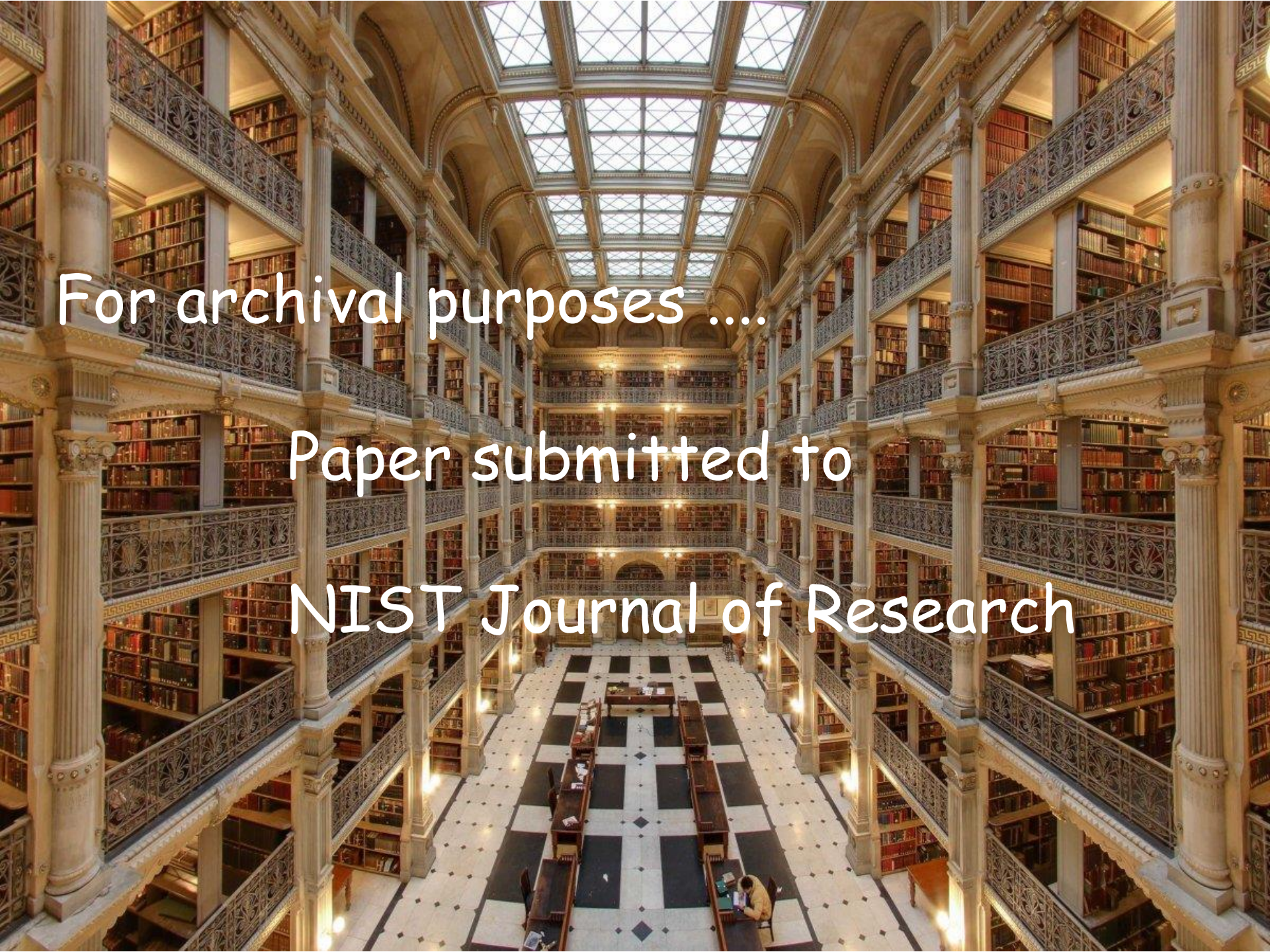
Source description :	Liquid in flame-sealed, 5 mL borosilicate glass ampoule
Solution composition :	(1.06 $\pm$ 0.06) mol L^{-1} HNO_3 with 21 mg UO_2^{+2} per gram of solution
Solution density :	(1.057 $\pm$ 0.001) g mL^{-1} at 21.6 °C
Solution mass :	(5.284 $\pm$ 0.001) g

Radionuclidic impurities, including other uranium isotopes :

None; ^{233}U and ^{236}U were not detected

Uncertainty assessment for the massic activities in SRM 4321d

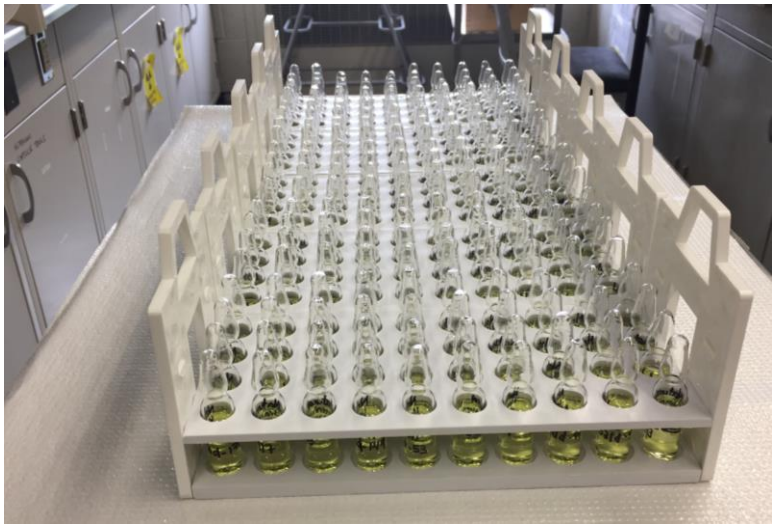
Uncertainty component		u (%)		
		^{234}U	^{235}U	^{238}U
1	Uranium mass fraction in CRM 112-A , from CRM 112-A Certificate [4]	0.003	0.003	0.003
2	Isotopic uranium atom fraction in CRM 112-A, from CRM 112-A Certificate [4]	0.077	0.0271	0.00020
3	Half-life [7] used for conversion of number of atoms to activity	0.244	0.142	0.112
4	Mass of CRM 112-A uranium metal used	0.05	0.05	0.05
5	Quantitative dissolution of metal	0.05	0.05	0.05
6	Mass of SRM 4321d master solution	0.005	0.005	0.005
Relative combined standard uncertainty, u_c		**0.261**	**0.153**	**0.123**
Relative expanded uncertainty (k = 2), U		**0.52**	**0.31**	**0.25**


For archival purposes ....
Paper submitted to
NIST Journal of Research

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)

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