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Radioactivity - Physics Lab
14 october 2009

NOTES ON
UNCERTAINTY ANALYSES FOR RADIOACTIVITY SRMs
&
SED INTERACTIONS

NATURAL MATRIX SRMs

Consideration of "natural matrix" radioactivity SRMs is largely excluded here. This work is done under the direction of Ken Inn as part of the low-level radiochemistry project, and is considerably separate from the production and standardization of the more routine radioactivity SRMs. Underway efforts include those for Shellfish (principal, Svetlana Nour) and Peruvian Soil (principal, Jerry LaRosa). As in the past for other natural matrix SRMs, these two projects will require considerable collaboration with Jim Filliben.

OTHER RADIOACTIVITY SRMs

The experimental design & uncertainty analyses need for the production and standardization of radioactivity SRMs are largely NOT statistical issues.

- The standards are largely homogeneous and chemically stable, pristine, inorganic solutions.
- The experimental design (basic measurement model) is largely fixed and based on efficacious procedures developed in the 1970s.
- Sampling considerations for the stable & homogeneous solutions are trivial.
- Uncertainty analyses for the type-A -method components is derived directly from the measurement data; *viz.*, statistical estimators.
- Uncertainty analyses for the type-B-method components is obtained from an understanding of the METROLOGY and the underlying science and effects. These are largely judgment based (often canonically assumed) as obtained from experience, testing, and sensitivity analyses.
- The magnitudes of both components (A & B methods) are largely driven and determined by the variables and parameters chosen for the primary standardization measurement (replications and trials varying instruments, times, counting source preparation, etc.).
- With rare exceptions, the type-B-method components are largely dominant; with statistical uncertainties making negligent to small contributions to the combined standard uncertainty.

- Uncertainty budget often consists of one component from type-A evaluation (maybe two at times) and up to a dozen or more components from type-B evaluations.
- Discrepant data in our SRM work is rarely encountered (unlike Ken's multi-lab & multi-method results)
- By a wise policy decision made many years ago, the primary standardization for any of our radioactivity SRMs is based on only ONE METHOD (the best method available to us).
- Other standardization methods (invariably inferior with larger uncertainties) performed at the same time are used only for confirmatory purposes, to ensure the validity of the primary method.
- GUM principles (as given in ISO & NIST documents) are adhered to religiously (as interpreted by one of the original GUM founders)

SED ROLE

We do not need design help or data analysis help (Ken does).

We recognize that SED has responsibility to ensure that SRM Certificates are compliant (as directed by Administrative Manual). The existing delays at SRM Office are needless and need to be obviated.

We would like SED review to be as painless as possible, and we would prefer to interact with only one assigned individual (perhaps Stephan Leigh because of some familiarity with Radioactivity Group work) so that we don't have to "reinvent the wheel" every month in our interactions.

I will be pleased to work out details with designated SED individual on how review will proceed, in terms of, what need to see, etc.

Most helpful SED contribution for us would be if they would develop easy to use and efficient analysis tools (like eFIT package) for ANOVA, simple regressions, etc. (Dataplot is way too cumbersome & painful). This request has been made previously. need graphical and tabular data output (eFIT could be improved along these lines as well).

ATTACHED

Elements of NIST Radioactivity Standardizations

Typical certificate & underlying data (^{239}Pu)

Recent SRM uncertainty contributions

Radioactivity Standardization Program Elements (R. Collé)

- Choice of nuclides / standards based on identified user needs
- Standardization based on at least one primary method
- Validity of primary method supported & confirmed by one or more independent confirmatory methods
- Standardizations typically utilize many trials, with widely varying experimental conditions,
    - minimizing type-B uncertainty assessments
- Any new standardization linked back to all previous ones (when possible)
    - through stored solutions or calibration factors for secondary instruments
- Disseminated standards from primary methods used as SRM transfer standards
    - and/or employed as sources for quality assurance, & proficiency testing programs
- Primary standardization uncertainties ($k = 2$) are typically < 1 % (few tenths at $k = 1$)
- Comparisons with others metrology labs to demonstrate & ensure international consistency

National Institute of Standards & Technology

Certificate

Standard Reference Material® 4330C

Plutonium-239 Radioactivity Standard

This Standard Reference Material (SRM) consists of a solution of a standardized and certified quantity of radioactive plutonium-239 in a suitably stable and homogeneous matrix. It is intended primarily for the calibration of instruments that are used to measure radioactivity and for the monitoring of radiochemical procedures. A unit consists of a solution, whose composition is specified in Table 1, contained in a flame-sealed 5 mL borosilicate-glass ampoule (see Note 1)*.

The certified **Plutonium-239** massic activity value, at a **Reference Time of 1200 EST, 1 May 2009**, is:

$$(38.41 \pm 0.18)\ \mathrm{Bq \cdot g^{-1}}$$

Additional physical, chemical, and radiological properties for this SRM, as well as details on the standardization method, are given in Table 1. Uncertainties for the certified quantities are expanded ($k = 2$). The uncertainties are calculated according to the ISO and NIST Guide (see Note 2). Table 2 contains a specification of the components that comprise the uncertainty analyses.

Expiration of Certification: The certification of **SRM 4330C** is valid indefinitely provided the SRM is handled and stored properly and no evaporation or change in composition has occurred. The solution matrix, in an unopened ampoule, is indefinitely homogeneous and stable within its half-life-dependent useful lifetime provided the SRM is handled in accordance with instructions given in this certificate (see "Instructions for Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

This SRM may represent a radiological hazard and a chemical hazard. Consult the Material Safety Data Sheet (MSDS), enclosed with the SRM shipment, for details (see Note 1).

This Standard Reference Material was prepared in the Physics Laboratory, Ionizing Radiation Division, Radioactivity Group, M.P. Unterweger, Group Leader. The overall technical direction and physical measurement leading to certification were provided by R. Collé and L. Laureano-Pérez of the NIST Radioactivity Group, with production assistance by D.B. Golas, Research Associate of the NRMAP, Inc., and photon-emitting impurity analyses by L. Pibida

Support aspects involved in the issuance of this SRM were coordinated through the NIST Measurement Services Division.

INSTRUCTIONS FOR USE

Storage: SRM 4330C should be stored and used at a temperature between 5 °C and 65 °C. The ampoule (or any subsequent container) should always be clearly marked as containing radioactive material.

Handling: If the ampoule is transported, it should be packed, marked, labeled, and shipped in accordance with the applicable national, international, and carrier regulations. The solution in the ampoule is a dangerous good (hazardous material) because of both the radioactivity and the strong acid. The ampoule should be opened only by persons qualified to handle both radioactive material and alkaline and/or acidic solutions. Appropriate shielding and/or distance should be used to minimize personnel exposure. Refer to MSDS for further information.

Lisa R. Karam, Chief
Ionizing Radiation Division

Gaithersburg, Maryland 20899
Certificate Issue Date: 17 July 2009
See Certificate Revision History on Last Page

Robert L. Watters, Jr., Chief
Measurement Services Division

* Notes and references may be found on page 4.

Table 1. Properties of SRM 4330C

Certified values

Radionuclide	**Plutonium-239**
Reference time	**1200 EST, 1 May 2009**
Massic activity of the solution	**38.41 Bq•g^{-1}**
Relative expanded uncertainty ($k = 2$)	**0.46 %** (see Note 2)*

Uncertified information

Source description	Liquid in a flame-sealed 5 mL borosilicate-glass ampoule (see Note 1)
Solution composition	3.4 mol•L^{-1} HNO_3
Solution density	(1.1082 ± 0.002) g•mL^{-1} at 23.9 °C (see Note 3)
Solution mass	(2.7707 ± 0.0003) g (see Note 3)
Photon-emitting impurities	None detected (see Note 4)
Half-lifes used	^{239}Pu: (24100 ± 11) a (see Note 5) [1]
Calibration methods (and instruments)	The certified massic activity for ^{239}Pu was obtained by 4πα liquid scintillation (LS) spectrometry with three commercial LS counters.

* Notes and references may be found on page 4.

Table 2. Uncertainty evaluation for the massic activity of SRM 4330C

	Uncertainty component	Assessment Type †	Relative standard uncertainty contribution to massic activity of ^{239}Pu (%)
1	LS measurement precision; standard deviation for $n = 9$ mean determinations as obtained with 3 different cocktail compositions (5 sources of each composition) measured 3 times in 3 different LS counters (135 determinations in all). See Note 6*. Data passes normality test at 95 % and 99 %. The typical internal relative standard deviation of the mean (n =15 for the 5 sources measured 3 times) for each of the 9 determinations ranged from 0.06 % to 0.10%.	A	0.17
2	Background LS measurement variability; wholly embodied in component 1	A	---
3	Gravimetric (mass) determinations for LS sources; estimated from calibration data and tests.	B	0.07
4	Decay correction due to the decay time interval and 0.046 % uncertainty in half-life.	B	5×10^{-8}
5	Live time determinations for LS counting time intervals, includes uncorrected dead time effects; assumed from specified tolerance limits of counters' gated oscillators	B	0.1
6	LS detection efficiency, including wall effects loss and extrapolation to zero energy; estimated from nuclear data and tests.	B	0.07
7	Alpha decay probability; assumed from nuclear decay data based on % of spontaneous fission	B	3×10^{-10}
8	LS non-detection of 26 min $^{235}U^{m}$; estimated from nuclear data and tests of LS counter detection threshold	B	< 0.001
9	Correction for ingrowth of ^{235}U; estimated from nuclear data	B	3×10^{-8}
10	Alpha-particle emitting impurities; based on nuclear data and mass spectrometric measurements of supplier. (See Note 7)	B	0.06
11	Photon-emitting impurities (non-detected). See Note 4.	B	---
Relative combined standard uncertainty			**0.23**
Relative expanded uncertainty ($k = 2$)			**0.46**

† = (A) denotes evaluation by statistical methods; (B) denotes evaluation by other methods.

* Notes and references may be found on page 4.

Note 1. Refer to http://physics.nist.gov/Divisions/Div846/srm.html for assistance and instructions on how to properly open an ampoule. Information on additional storage and handling requirements is also included on the website. This SRM is contained in a generic borosilicate-glass ampoule and not in the standard NIST ampoule.

Note 2. The uncertainties on certified values are expanded uncertainties, $U = ku_c$. The quantity u_c is the combined standard uncertainty calculated according to the ISO and NIST Guides [2-3]. The combined standard uncertainty is multiplied by a coverage factor of $k = 2$ and was chosen to obtain an approximate 95 % level of confidence.

Note 3. The stated uncertainty is two times the standard uncertainty. See reference [3].

Note 4. The estimated lower limit of detection for photon-emitting impurities, expressed as massic photon emission rate, on 1 May 2009 is:

$0.64\ s^{-1} \cdot g^{-1}$ for energies between 40 keV and 50 keV,
$0.17\ s^{-1} \cdot g^{-1}$ for energies between 50 keV and 250 keV, and
$0.13\ s^{-1} \cdot g^{-1}$ for energies between 250 keV and 2600 keV.

provided that the photons are separated in energy by 4 keV or more from photons emitted in the decay of ^{239}Pu or progeny.

Note 5. The stated uncertainty is the standard uncertainty. See reference [3].

Note 6. The mean was found to be invariant of: (i) cocktail composition based on scintillation fluid used and the aqueous fraction, (ii) aliquant mass in cocktails, (iii) sample quenching; and (iv) instrument (with different detection thresholds).

Note 7. From mass spectrometric measurements performed by the supplier, the non-certified massic activities of other detected radionuclides (in $Bq \cdot g^{-1}$ as of 1200 EST, 15 November 1999) are: $^{240}Pu = 0.002$, $^{241}Pu = 0.02$, $^{241}Am = 0.001$. Solution was purified 10 December 1979.

REFERENCES

[1] E. Browne, *Nuclear Data Sheets* 98, 665 (2003), Evaluated Nuclear Structure Data File (ENSDF), online database, National Nuclear Center, Brookhaven National Laboratory (Upton, NY), accessed May 2009. Refer to http://www.nndc.bnl.gov/ensdf/.

[2] International Organization for Standardization (ISO), *Guide to the Expression of Uncertainty in Measurement*; 1993 (corrected and reprinted, 1995). Ordering and purchasing information available at http://physics.nist.gov/cuu/Uncertainty/isoorder.html.

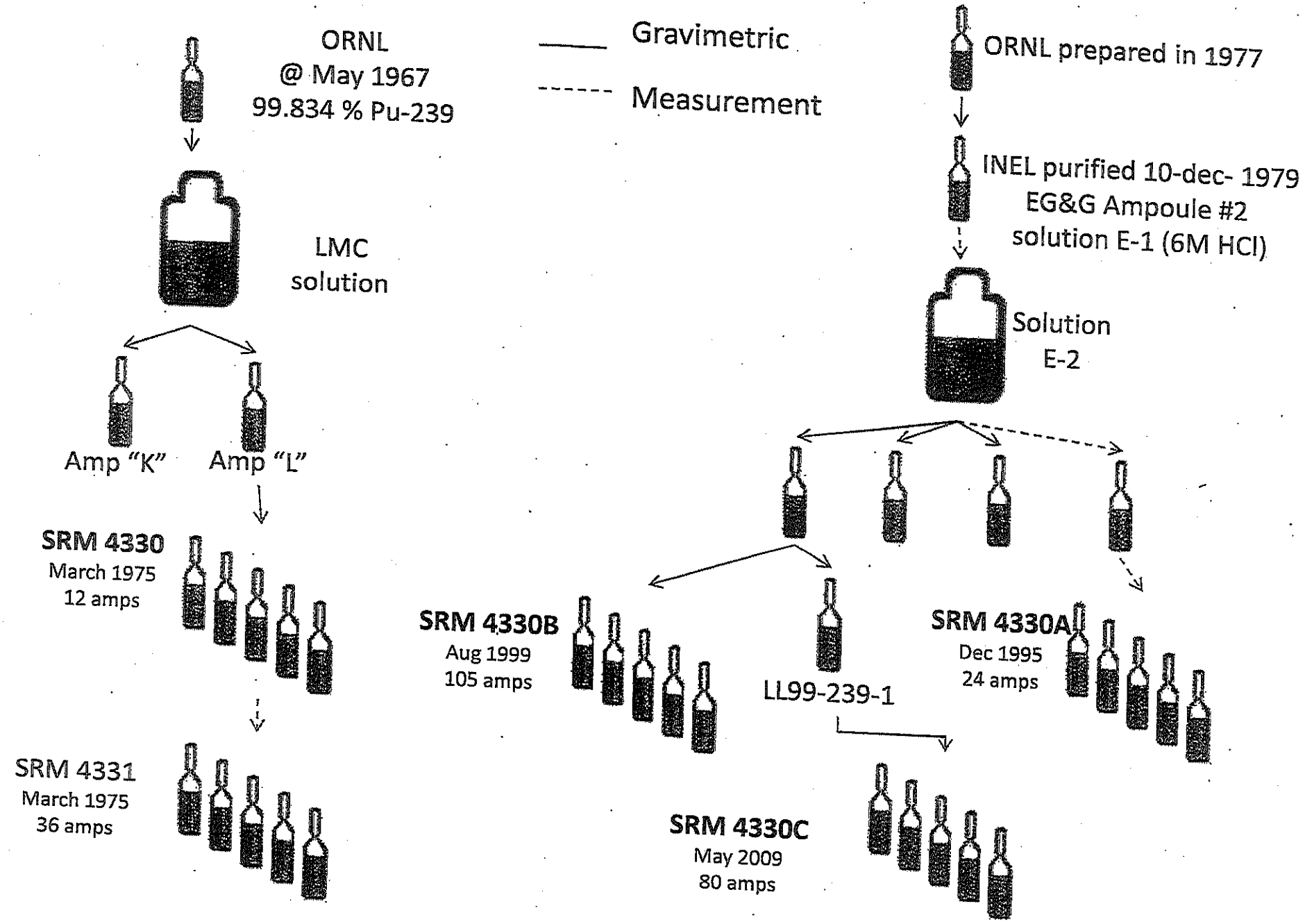
[3] B.N. Taylor and C.E. Kuyatt; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results,* NIST Technical Note 1297, 1994. Available at http://physics.nist.gov/Pubs/guidelines/contents.html.

Certificate Revision History: 17 July 2009 (Original certificate date).

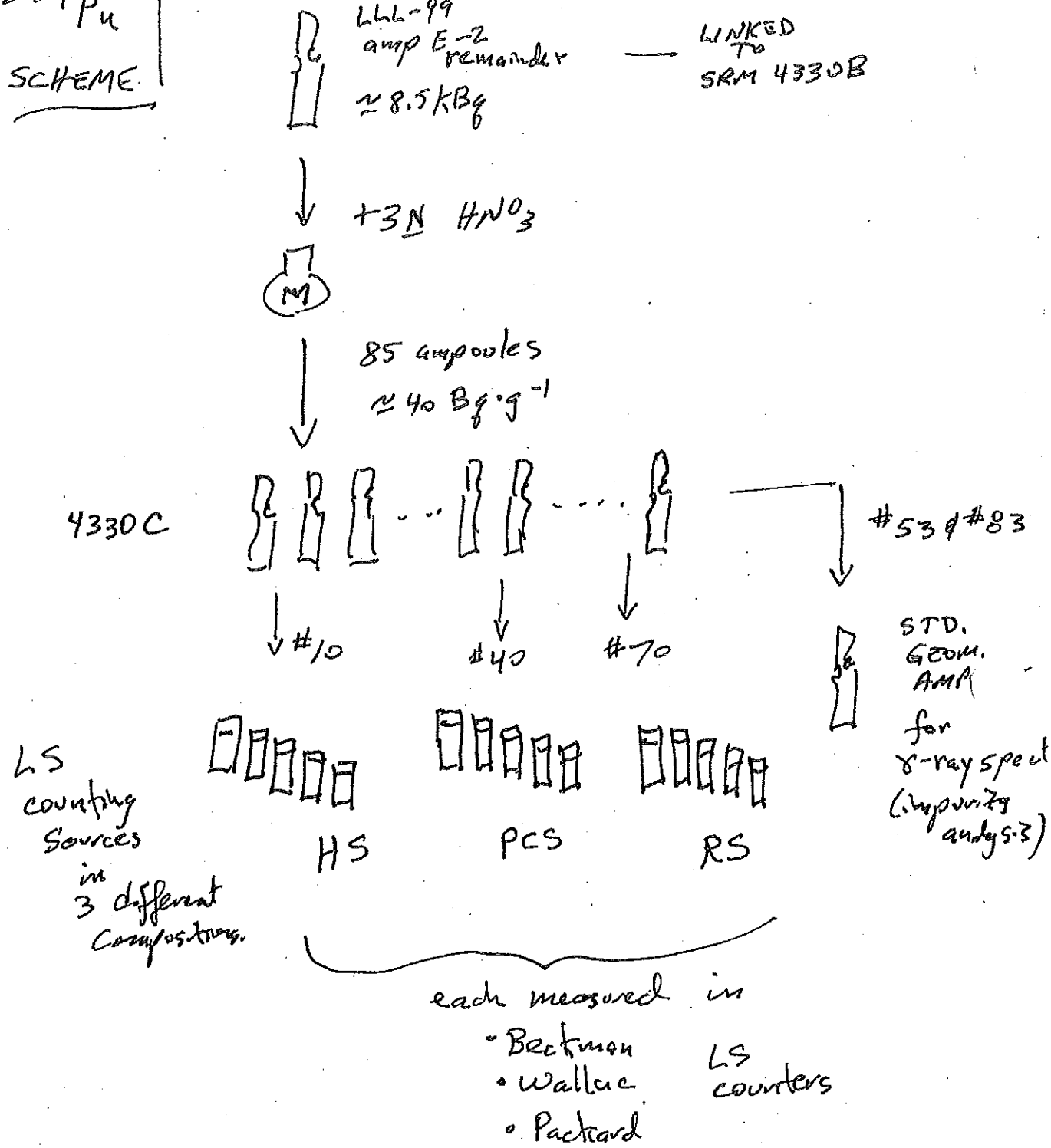
Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: telephone (301) 975-2200; fax (301) 926-4751; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

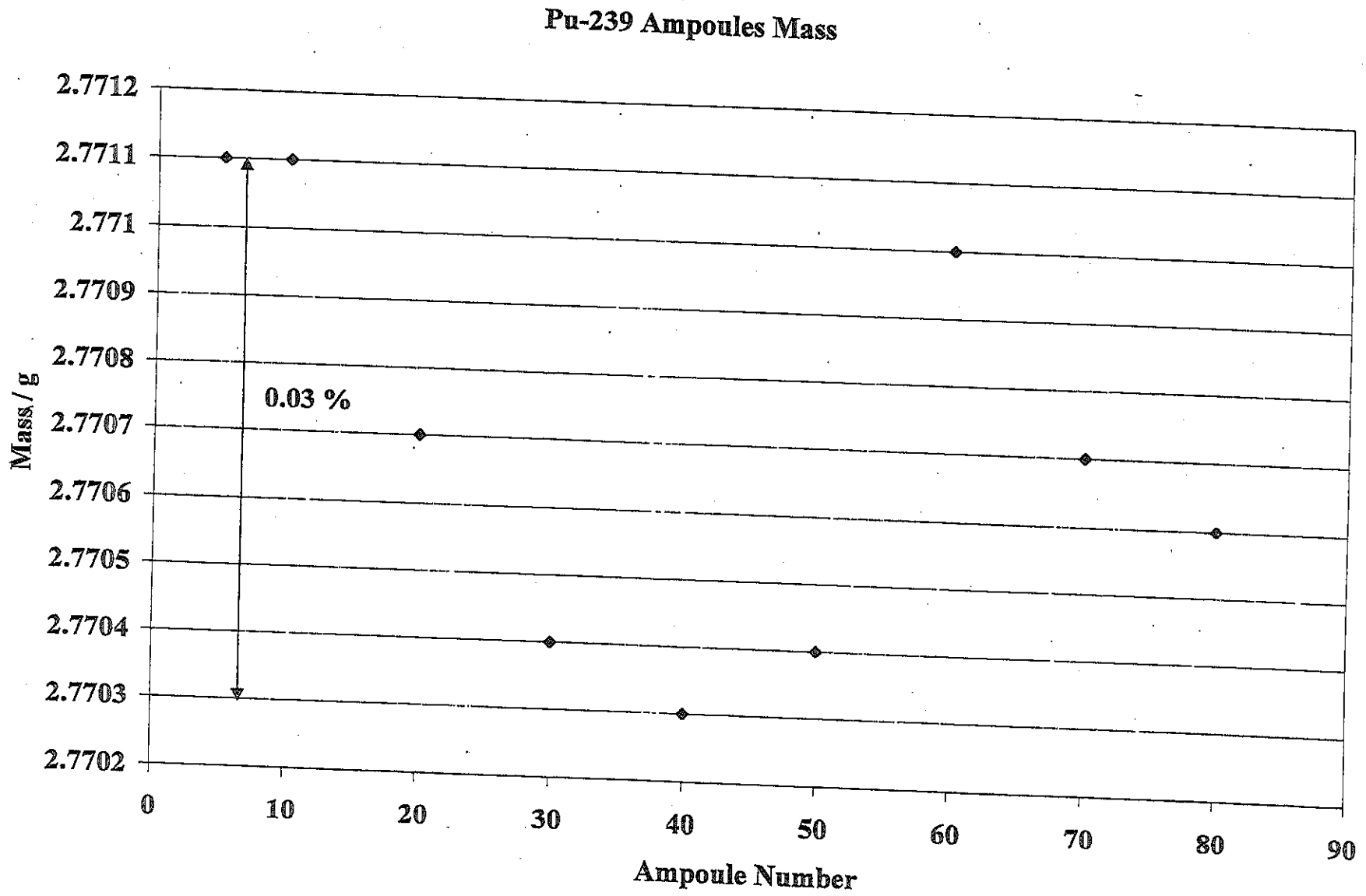
^{239}Pu

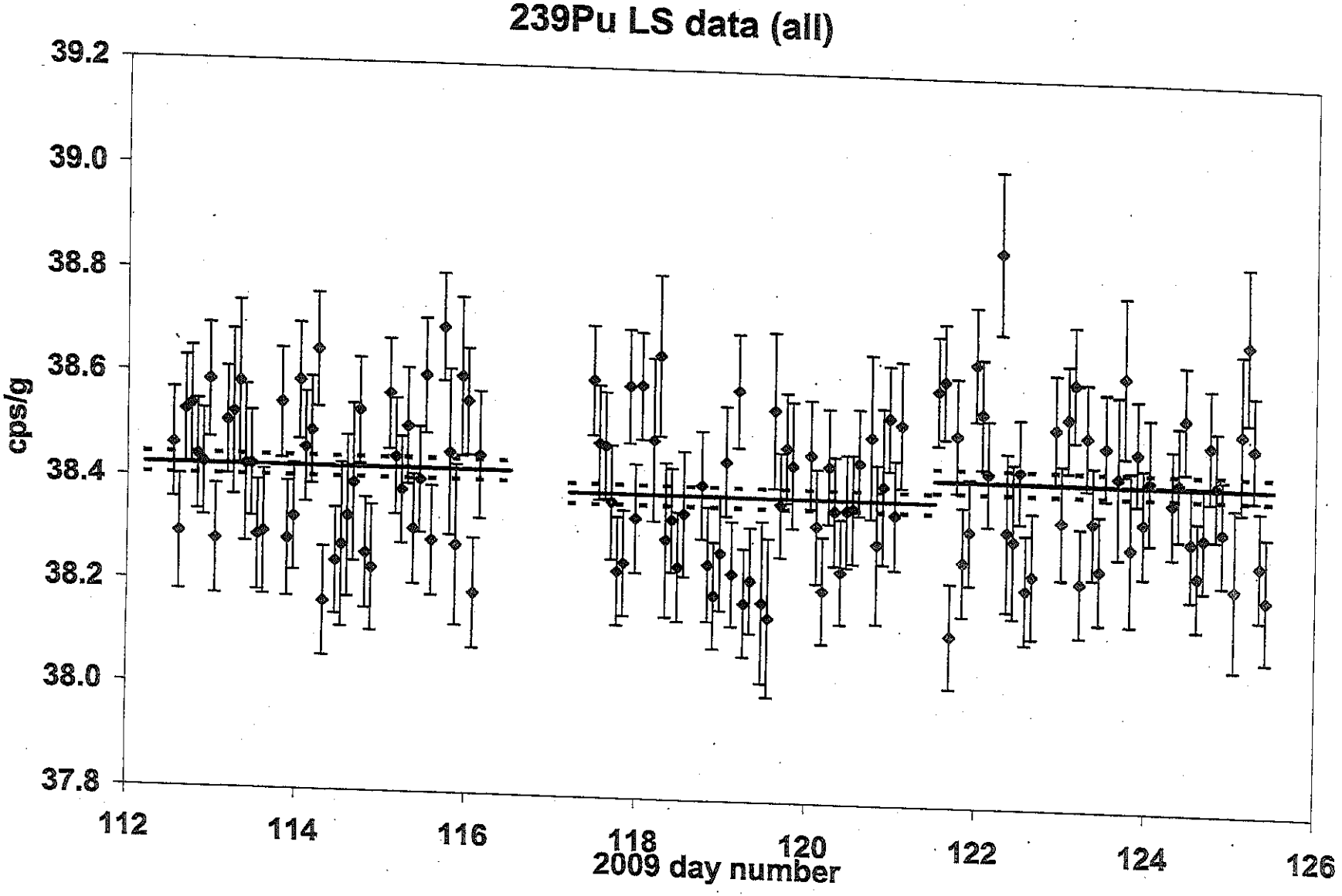
1. links to previous ^{239}Pu SRMs
2. scheme for 2009 prep. & standardization (4330C)
3. dispensing precision
4. all LS data (n=135) -- for 3 compositions on 3 instruments
5. summary of LS data averages
6. the 9 LS means
7. normal probability plot


ORNL
@ May 1967
99.834 % Pu-239
LMC
solution
Amp "K"
Amp "L"
SRM 4330
March 1975
12 amps
SRM 4331
March 1975
36 amps
Gravimetric
Measurement
ORNL prepared in 1977
INEL purified 10-dec- 1979
EG&G Ampoule #2
solution E-1 (6M HCl)
Solution
E-2
SRM 4330B
Aug 1999
105 amps
LL99-239-1
SRM 4330A
Dec 1995
24 amps
SRM 4330C
May 2009
80 amps

^{239}Pu SCHEME




Pu-239 Ampoules Mass
2.7712
2.7711
2.771
2.7709
2.7708
2.7707
2.7706
2.7705
2.7704
2.7703
2.7702
Mass / g
0.03 %
0
10
20
30
40
50
60
70
80
90
Ampoule Number


239Pu LS data (all)
39.2
39.0
38.8
38.6
38.4
38.2
38.0
37.8
cps/g
112
114
116
118
120
122
124
126
2009 day number

^{239}Pu averages

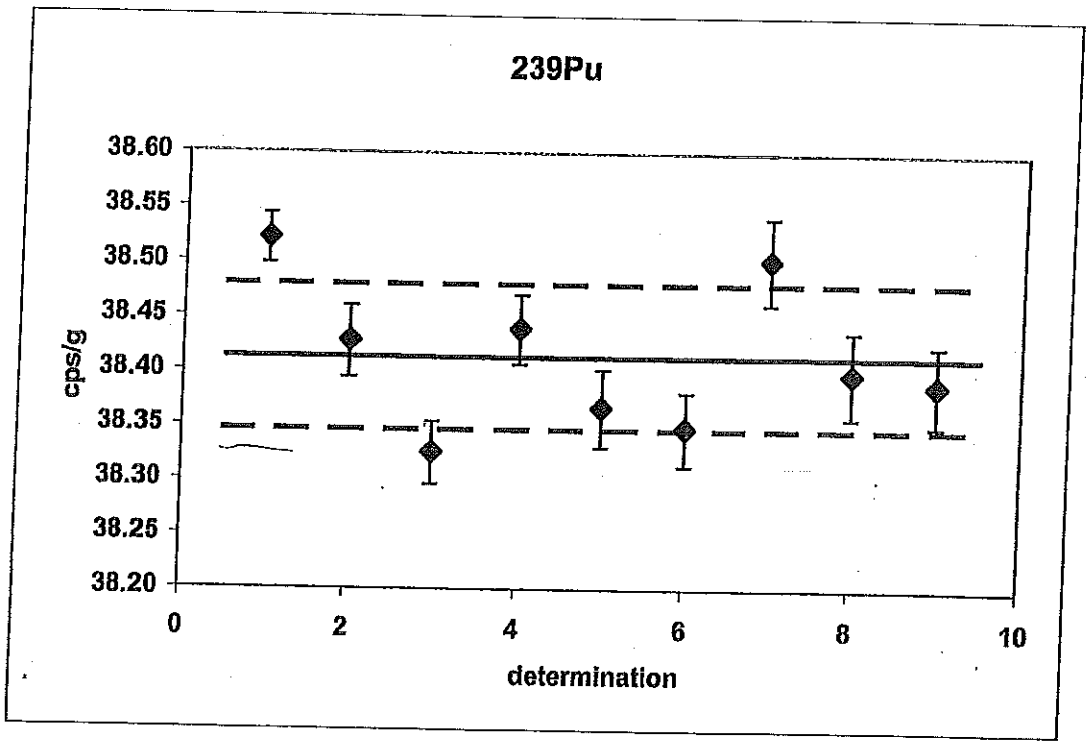
	BECKMAN	WALLAC	PACKARD	(all)
HS	38.521 0.23% n=15	38.438 0.32% n=15	38.501 0.40% n=15	38.486 0.33% n=45
PCS	38.427 0.33% n=15	38.366 0.36% n=15	38.397 0.40% n=15	38.397 0.36% n=45
RS	38.325 0.29% n=15	38.347 0.34% n=15	38.387 0.37% n=15	38.353 0.34% n=45
(all)	38.424 0.35% n=45	38.384 0.35% n=45	38.428 0.40% n=45	38.412 0.37% sd n=135
				0.032% sdm

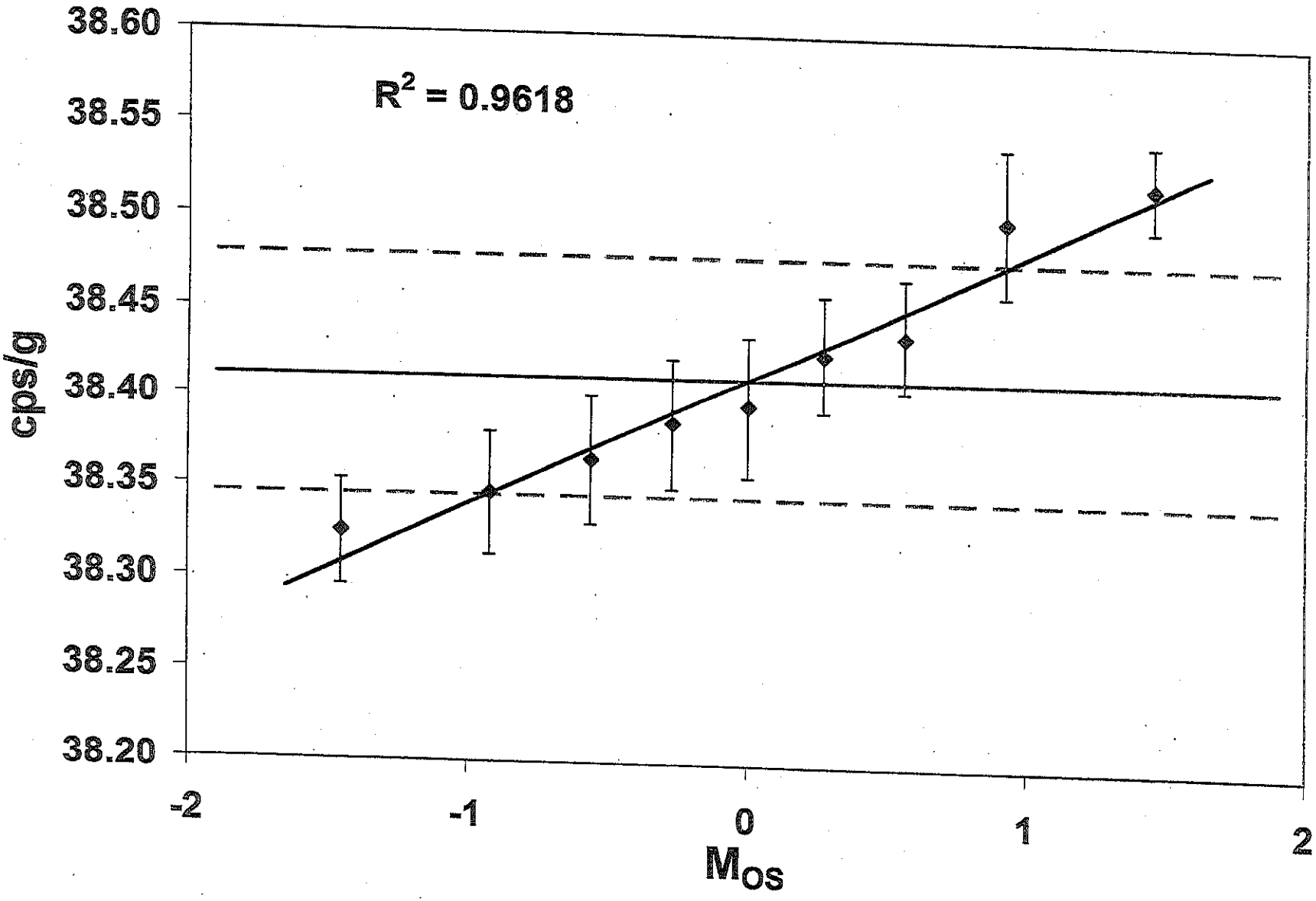
Mean was invariant of
- cocktail composition (scintillant used)
- instrument (with different detection thresholds, deadtime, etc.
- aliquant mass in cocktail
- sample quenching
- stability (time)

n=9 means w/ 15 per mean
38.412
0.17₃% sd

	mean	%sd	%sdm	unc	
B-H	38.521	0.23	0.059386	0.022876	-1.45
B-P	38.427	0.33	0.085206	0.032742	-0.92
B-R	38.325	0.29	0.074878	0.028697	-0.56
W-H	38.438	0.32	0.082624	0.031759	-0.27
W-P	38.366	0.36	0.092952	0.035662	0
W-R	38.347	0.34	0.087788	0.033664	+0.27
P-H	38.501	0.397	0.102505	0.039465	0.56
P-P	38.397	0.399	0.103021	0.039557	0.92
P-R	38.387	0.37	0.095534	0.036672	1.45
ave	38.41211				
sd	0.06658				

0.5	38.41211	38.47869	38.34553
9.5	38.41211	38.47869	38.34553




38.60
38.55
38.50
38.45
38.40
38.35
38.30
38.25
38.20
cps/g
R^2 = 0.9618
-2
-1
0
1
2
M_{OS}

(7)

Nuclide	$t_{1/2}$	SRM Number	Reference Time	U (k = 1)	s (k = 1)
^{239}Pu	2.4 x 10^4 a	4330C	1 May 2009	0.23	0.17
^{243}Am	7.4 x 10^3 a	4332E	1 October 2008	0.45	0.32
^{229}Th	7.3 x 10^3 a	4328C	31 December 2007	0.30	0.04
^{241}Pu*	14 a	4340B	15 June 2007	1.9	1.7
^{241}Am	4.3 x 10^2 a	4322C	16 May 2007	0.13	0.024
^{230}Th	7.5 x10^4 a	4342A	1 April 2007	0.19	0.037
^{90}Sr	28.8 a	4919I	25 December 2006	0.24	0.099
^{90}Sr	28.8 a	4239	25 December 2006	0.23	0.099
^{210}Pb	22.2 a	4337	15 June 2006	1.2	0.073
^{55}Fe	2.74 a	4929F	30 November 2005	0.84	0.73
^{60}Co	5.27 a	4915F	1 November 2005	0.25	0.066
^{137}Cs	30.1 a	4233E	30 September 2005	0.35	0.13

- Major problems: Irregular low level counting data; also discrepant with one of two confirmatory methods (issued because of importance)

These SRMs are distributed before certification because of short half-life

Nuclide	$t_{1/2}$	SRM Number	Reference Time	U (k = 1)	s (k = 1)
^{99m}Tc	6.0 h	4410H, lot 35	19 May 2009	0.44	0.004
^{67}Ga	3.3 d	4416L, lot 30	22 April 2009	0.27	0.01
^{99}Mo	2.7 d	4412L, lot 34	24 February 2009	0.38	0.01
^{131}I	8.0 d	4401L, lot 35	27 January 2009	0.34	0.01
^{125}I	59 d	4407L, lot 33	18 December 2008	0.39	0.08
^{90}Y	2.7 d	4427L, lot 12	23 October 2008	0.30	0.26
^{133}Xe	5.2 d	4415L, lot 32	23 October 2008	0.39	0.02
^{111}In	2.8 d	4417L, lot 28	20 August 2008	0.27	0.01
^{201}Tl	3.0 d	4404L, lot 31	25 June 2008	0.38	0.03