ON THE STANDARDIZATION OF ^{209}Po AND ^{210}Pb

R. Collé

(with L. Laureano-Perez)

Ionizing Radiation Division
Physics Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899   USA

LSC 2008

Advances in Liquid Scintillation Spectrometry

May 2008   Davos, Switzerland

Who are we ?

And what do we do ?

NIST (**NBS**)

1901 - 1998

> 1998

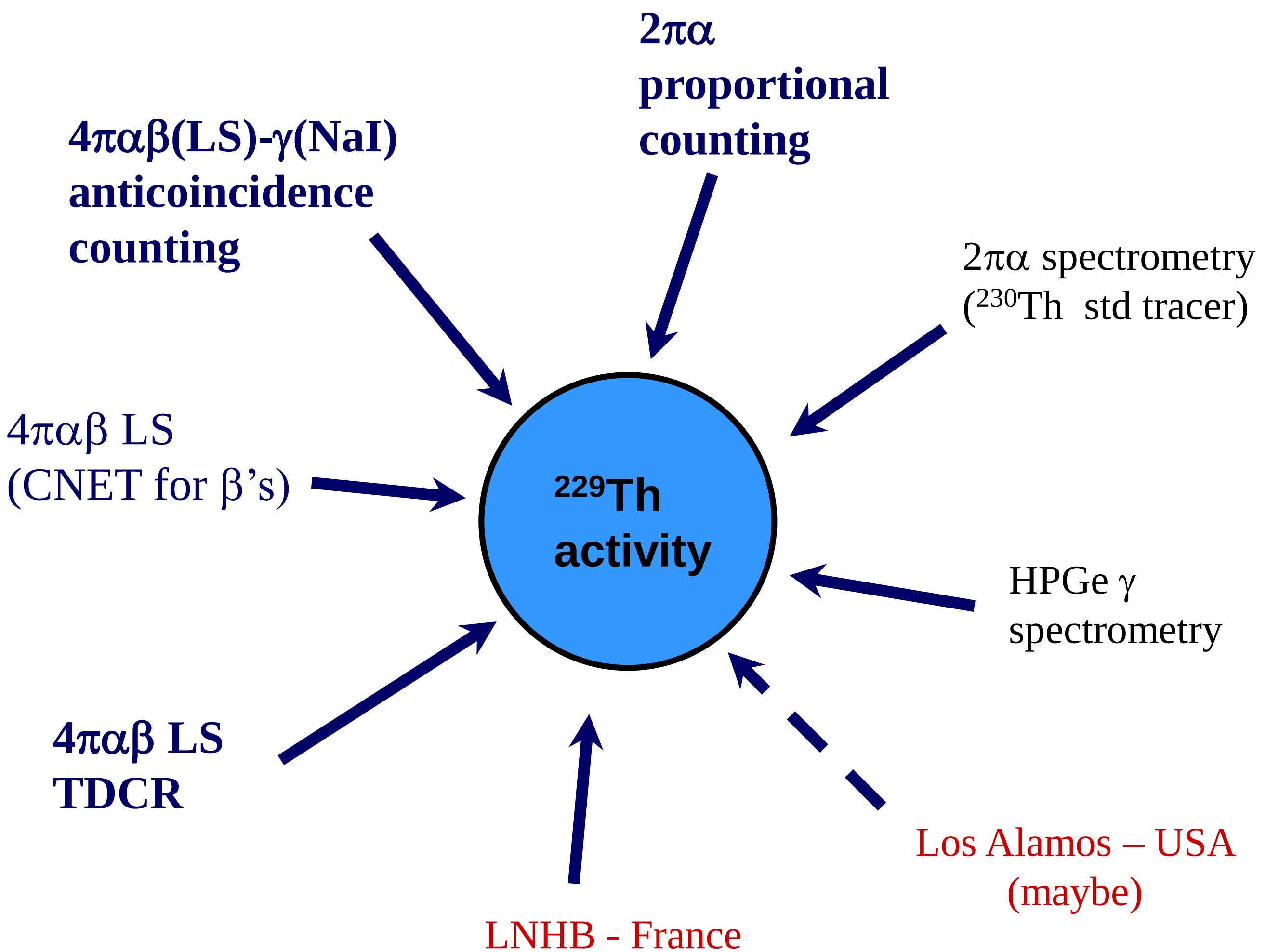
doing radioactivity
since 1910

Highest authority in USA

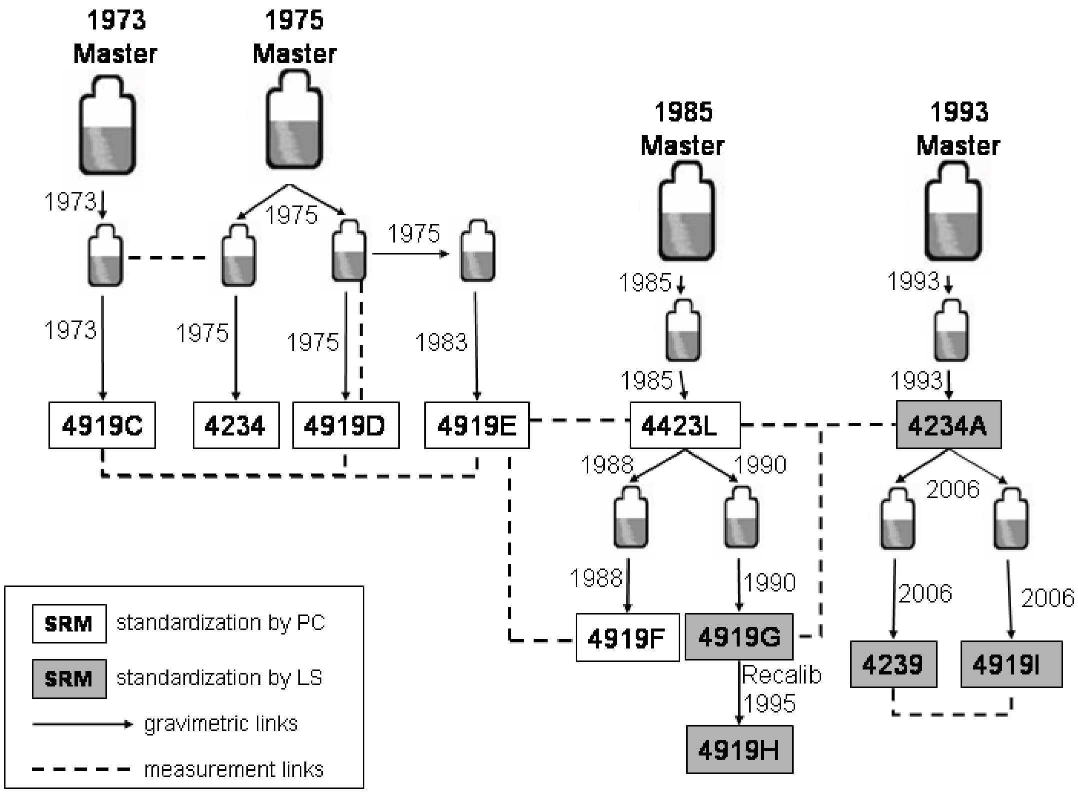
- for setting physical measurement standards
- and ensuring accurate measurements

typical features of NIST standardization work

- Standardized by **primary method** ("direct," w/o recourse to other calibrations or standards)
- Validity supported & **confirmed** by one or more <u>independent</u> confirmatory measurement methods
- Utilize **many trials**, experimental conditions, etc..
- **Linked** back to all previous standardizations (when possible) through stored solutions or through calibration factors for secondary instruments
- **Uncertainties** (k = 2) typically < 1 % **------** u (k = 1) few tenths of %
- **Comparisons** with other metrology labs / demonstrate international consistency



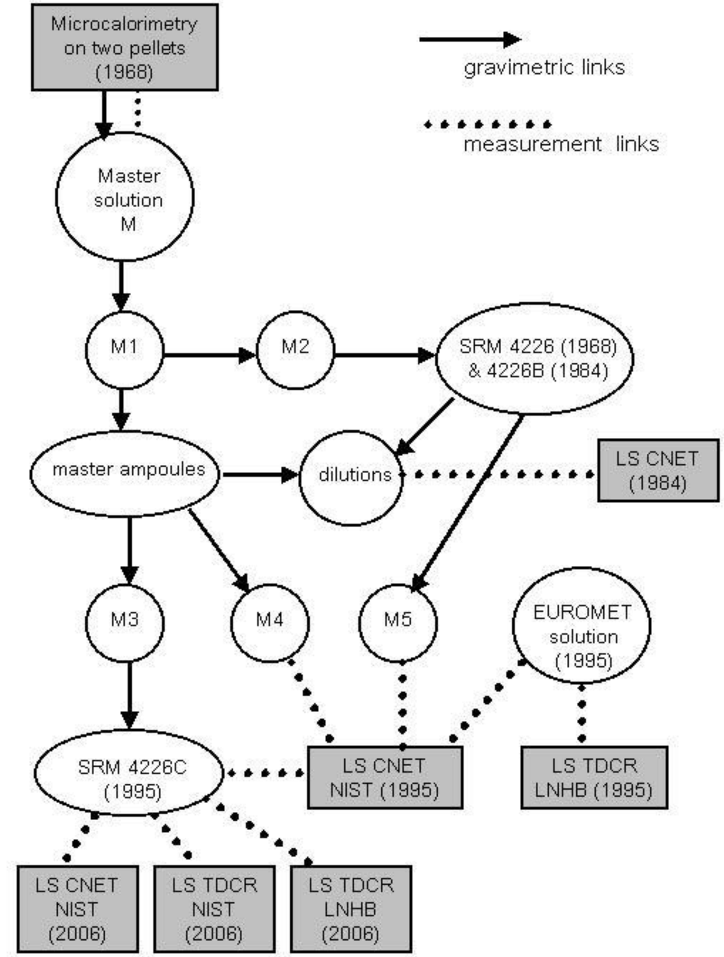
+ radionuclidic impurity analyses for ^{228}Th impurity correction



^{90}Sr standards ---- 33 years of linkage

Primary method shift

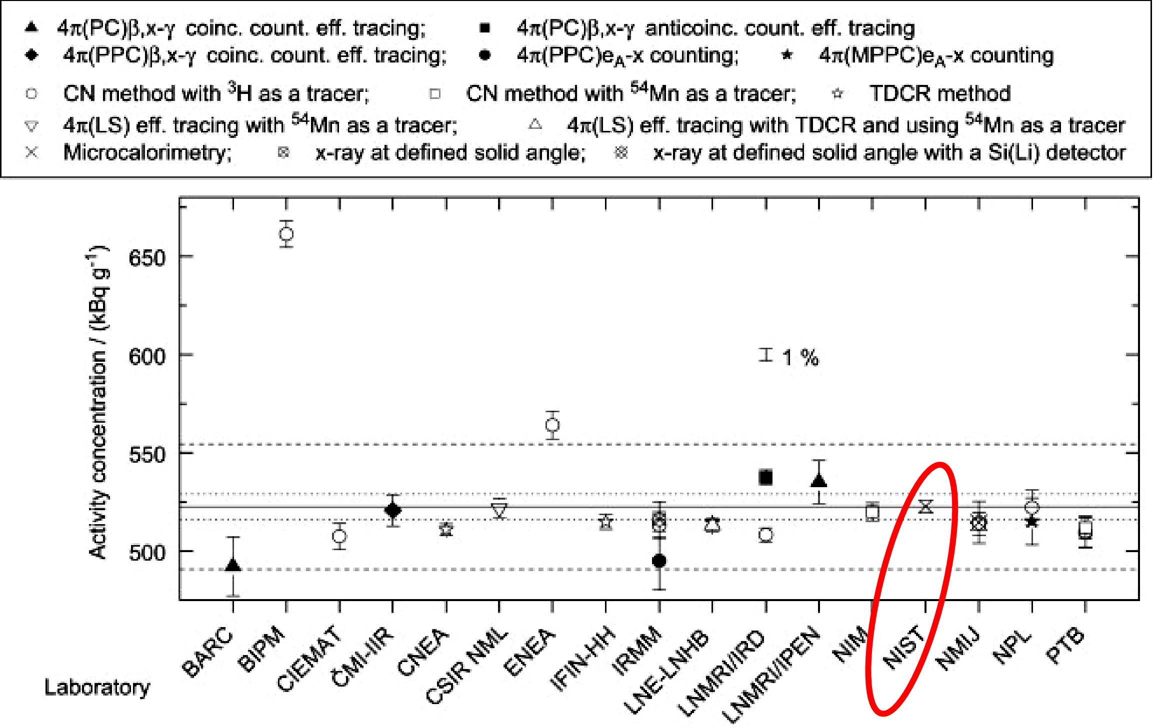
Collé, *et al*., to be publ., *J. Res.NIST* (2008).



^{63}Ni standards ---- 38 years of linkage

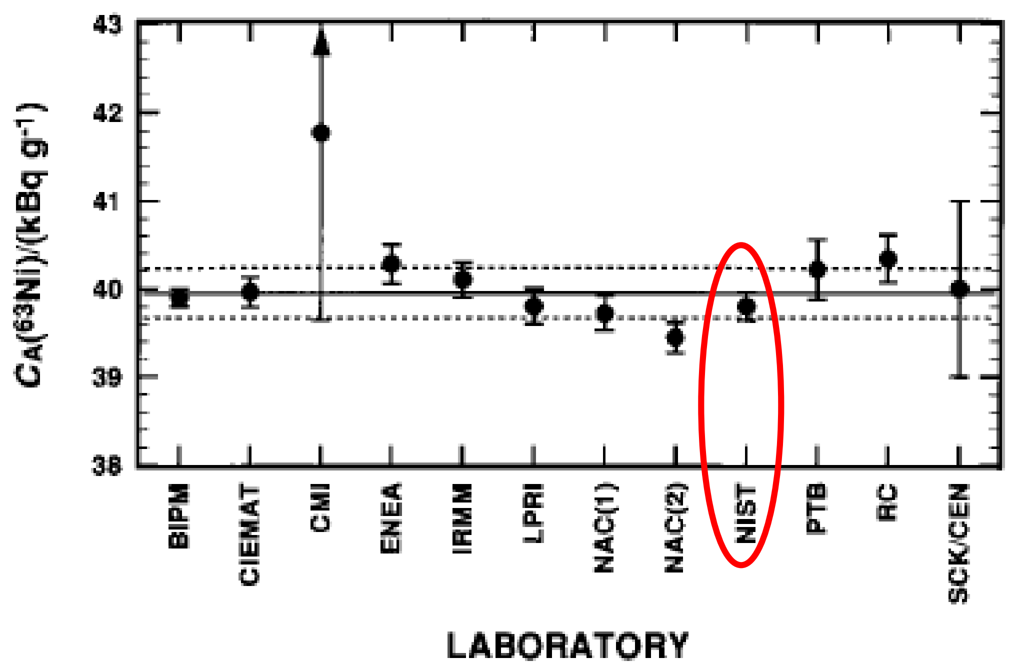
Different methods + another lab

Collé, *et al*., *Appl. Radiat. Isot.* **66**, 60 (2008).



^{55}Fe international comparison

^{63}Ni international comparison



Metrology

- **130+ nuclides**
- Many geometries
- > 30 systems

^{209}Po first 1994

^{210}Pb first 2006

Standards (SRMs)

- **60+ nuclides**
- 9 natural matrix (multi-nuclide)
- 500 – 1000 units per year // > 200 users
- 20 users buy 10 or more SRMs per year

Calibrations

- > 100 routine per year
- 20 – 30 nuclides; many geometries

MQA programs

- environment
- radiopharmaceuticals
- source suppliers
- nuclear power

^{209}Po ^{210}Pb

LINKED

In applications

– use of ^{210}Po tracer for ^{210}Pb assays

In our standardization measurements

World needs a Po tracer standard !

^{210}Po	0.4 a	5.3 MeV α
^{208}Po	2.9 a	5.1 MeV α
^{209}Po	102 a	4.9 MeV α + *junk*

at NIST

< 1980	only ^{210}Po calibration sources
1984	^{208}Po standard (SRM 4327)
1994	^{209}Po standard (SRM 4326)
> 2007	no Po tracer standard available

Po solutions & standards are stable

"Long-term stability of carrier-free polonium solution standards"

R. Collé, *Radioact. Radiochem.* **4**, no.2, 20-35 (1993).

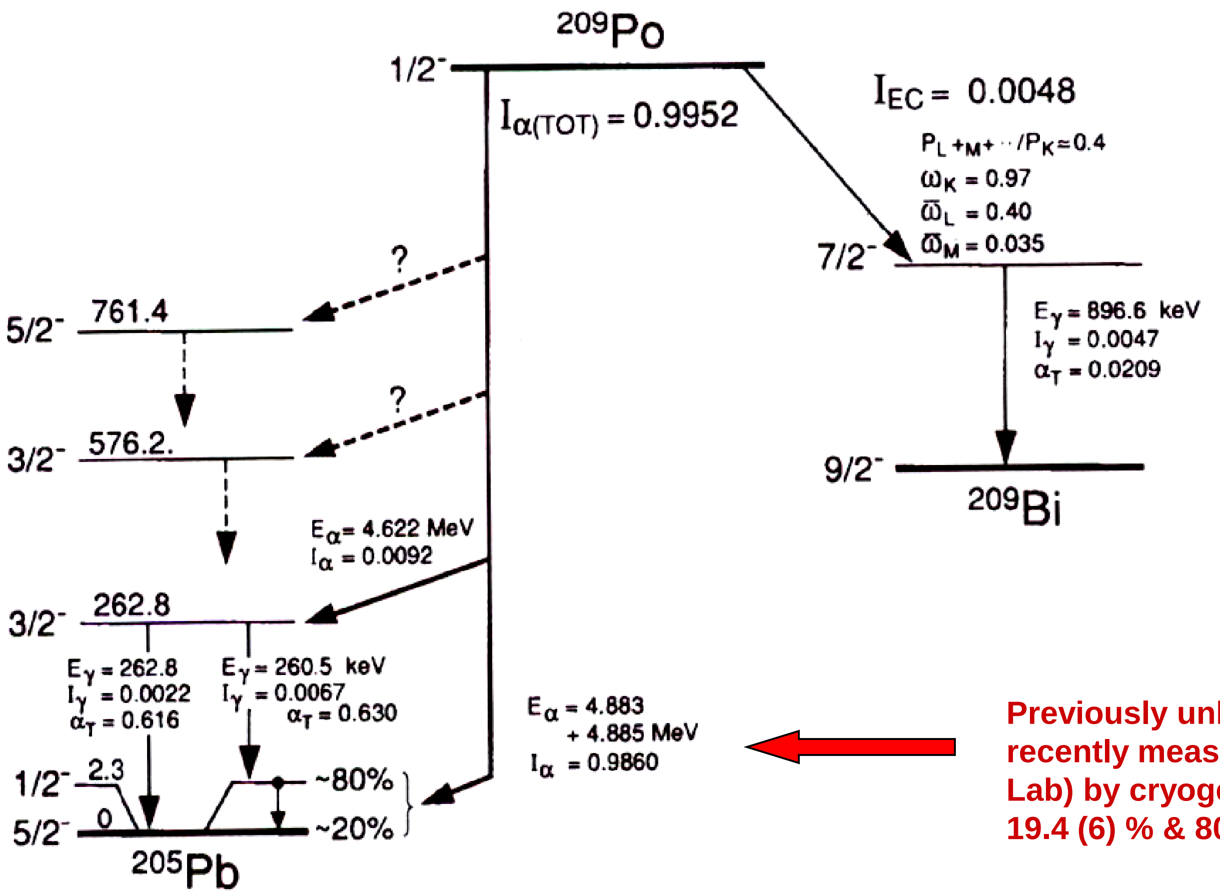


Fig. 2. Partial decay scheme for the ^{209}Po alpha and electron capture branch decays.

4

Previously unknown branching recently measured by NIST (Boulder Lab) by cryogenic calorimeter -- 19.4 (6) % & 80.6 (6) %

Collé, et al. *Appl. Radiat. Isot.* **45,** 1165 (1994);
Nucl. Instr. Meth. **A369,** 498 (1996).

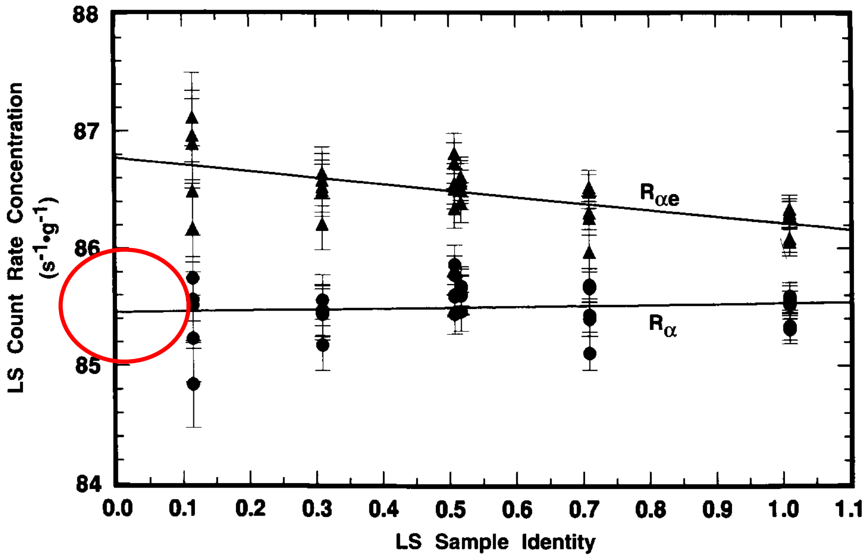


Fig. 11. LS counting rate concentrations $R_{\alpha e}$ (closed triangles) and R_{α} (closed circles) obtained with the Beckman instrument for the N series samples as a function of m_s (and sample quenching). The solid lines are linear regressions fitted to the data.

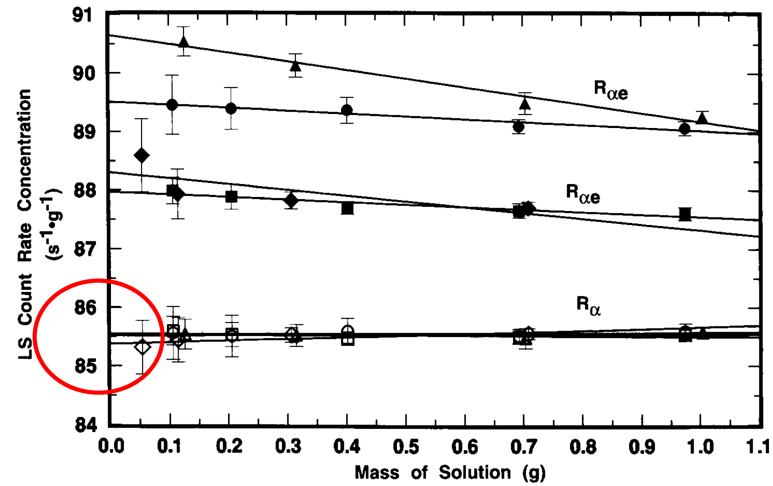


Fig. 13. LS counting rate concentrations $R_{\alpha e}$ and R_{α} obtained with the two LS systems for the P and Q series samples in 1994. Closed squares ($R_{\alpha e}$) and open squares (R_{α}) represent the mean values for samples Q5 through Q8 with the Packard; closed and open triangles represent $R_{\alpha e}$ and R_{α}, respectively, for samples P1 through P5 with the Packard; closed and open triangles ($R_{\alpha e}$ and R_{α}) are for samples Q1 through Q4 with the Beckman; and closed and open circles ($R_{\alpha e}$ and R_{α}) are for samples P1 through P5 with the Beckman. Each plotted value corresponds to the mean of 5 to 18 replicate measurements on each sample. The error bars represent standard deviation uncertainty intervals on the means. The solid lines are unweighted linear fits to the data. Although the $R_{\alpha e}$ values vary with the instrument used to perform the measurements (Packard or Beckman) and with sample compositions, all of the R_{α} values are statistically equivalent and invariant.

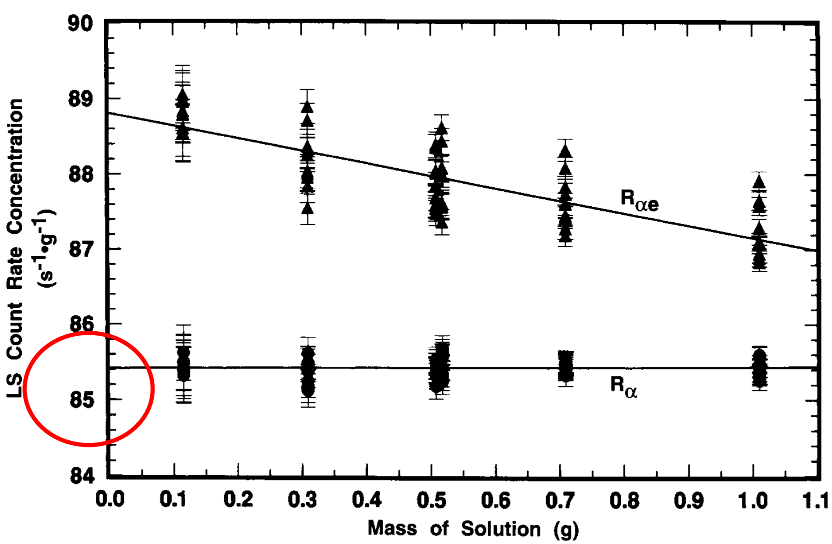


Fig. 12. LS counting rate concentrations $R_{\alpha e}$ and R_{α} as a function of m_s (analogous to that of Fig. 11) as obtained with the Packard instrument.

In 1994

LS result confirmed by $2\pi\alpha$ proportional counting

from

Collé, et al., *J. Res. Natl. Inst. Stds. Tech.* **100**, 1 (1995).

SAME IN 2005

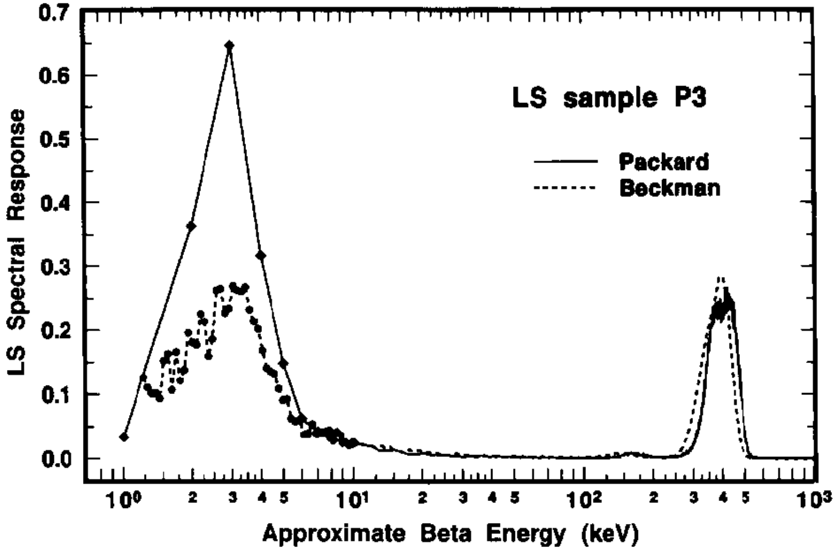


Fig. 6. Comparison of the ^{209}Po LS spectra obtained with the Beckman and Packard instruments.

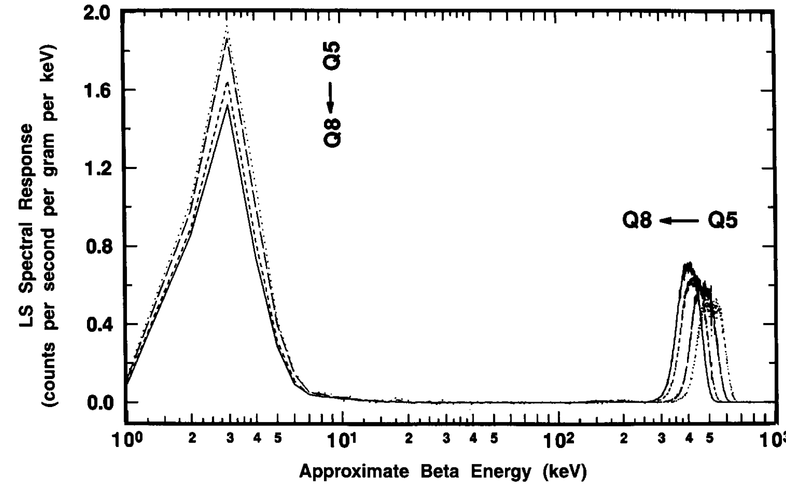


Fig. 14. LS spectra of increasingly quenched samples Q5 through Q8 obtained with the Packard counting system.

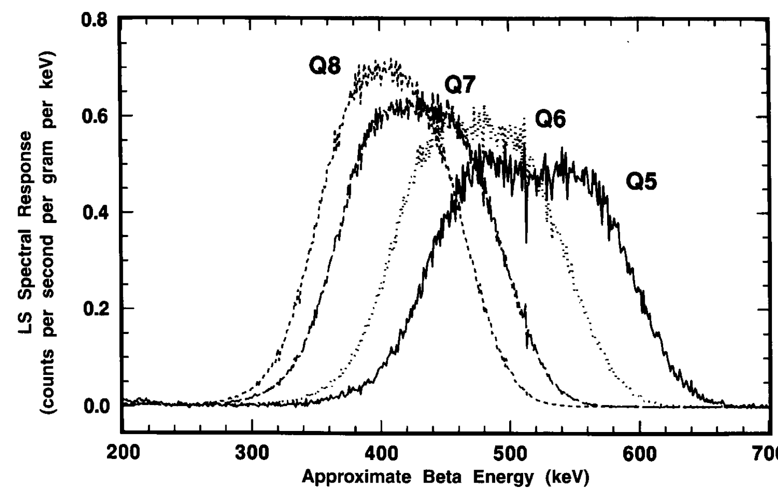


Fig. 15. Details of the broad alpha peaks shown in the full spectra of Fig. 14. The peak widths (FWHM) on a relative basis and peak areas are approximately equal in all four samples Q5 through Q8.

15 march 1994

$R_\alpha = (85.42 \pm 0.18)\ s^{-1}g^{-1}$

15 November 2005

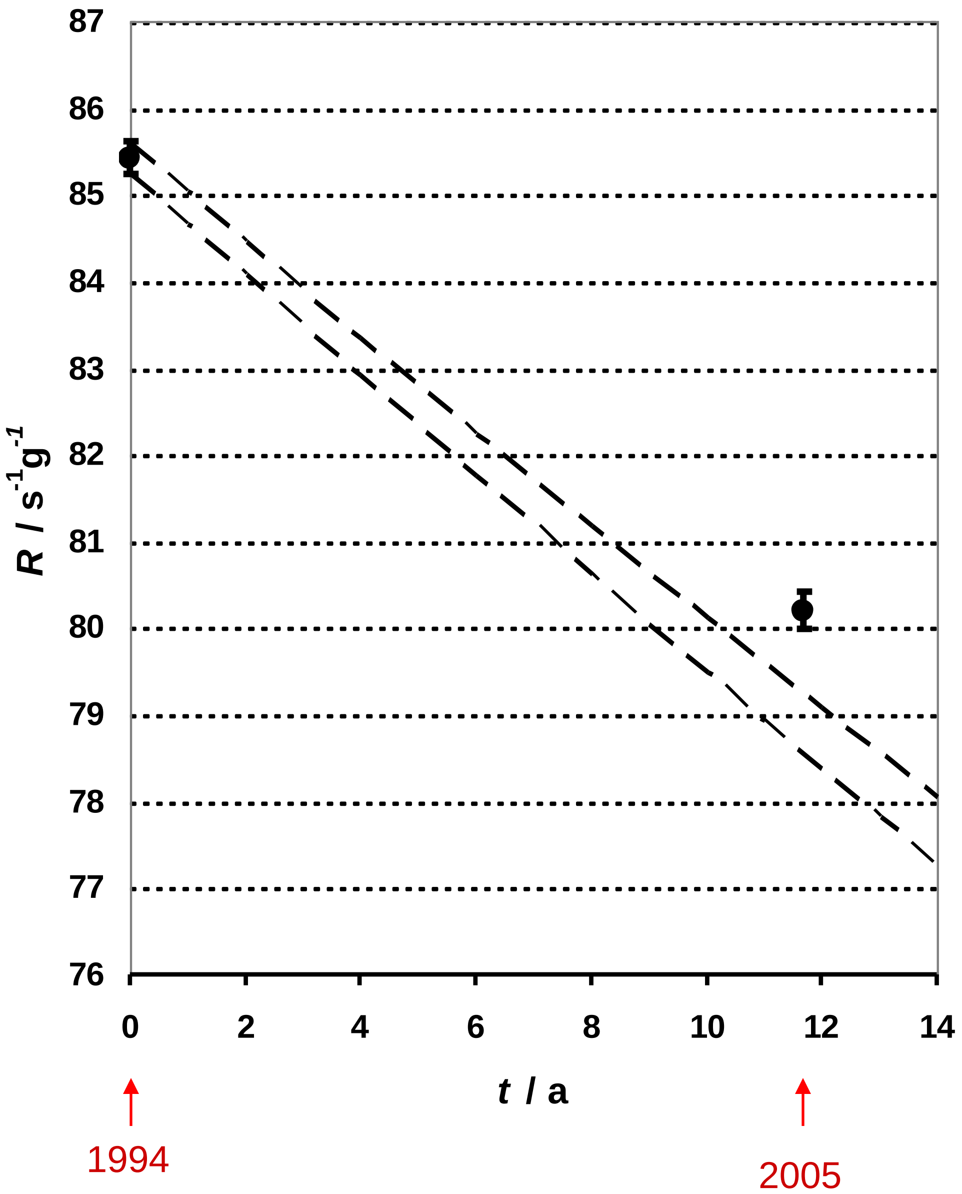
R_α = (80.20 ± 0.22) s-1g-1

2 point fit gives

$T_{1/2}$ = 128 a

U = 5.5 % (7 a)

<u>Not</u> considered a new determination



Collé, et al., *Appl. Radiat. Isot.* **65**, 728 (2007)

HOW COULD IT BE SO WRONG ?

Andre, Huizenga, et al. 1956 *Phys Rev.* 101, 645-651

^{208}Po/^{209}Po mass ratio 1.14 %

^{208}Po/^{209}Po activity ratios 5 %

"private communication"

with $T_{1/2}(^{208}\text{Po}) = (2.93 \pm 0.03)$ a,

got $T_{1/2}(^{208}\text{Po}) = 103$ a

$$\underline{A / N} = \lambda$$

$$T_{209} = T_{208}\left(\frac{N_{209}}{N_{208}}\right)\left(\frac{A_{208}}{A_{209}}\right)$$

Compiler M. Martin,1991

must be wrong

with $T_{1/2}(^{208}\text{Po}) = 2.898 \pm 0.002$ a,

got $T_{1/2}(^{208}\text{Po}) = (102 \pm 5)$ a 4.9 %

^{209}Po half-life in error by 25 % !!

Result supported by work on ^{210}Pb – next story

Collé, Laureano, Outola, *Appl. Radiat. Isot.* 65, 728 (2007)

$$T_{209} = T_{208}\left(\frac{N_{209}}{N_{208}}\right)\left(\frac{A_{208}}{A_{209}}\right)$$

New determination urgently needed

<u>Attempts</u> at collaboration with other labs ... not going well

- Institute of Nuclear Physics (Krakow) / Institute of Geological Sciences (Warsaw) -- Polish Academy of Sciences labs
- Laboratoire National Henri Bequerel (France)
- Los Alamos Natl. Lab (USA)

Need supply of ^{208}Po

^{210}Pb

Difficult case

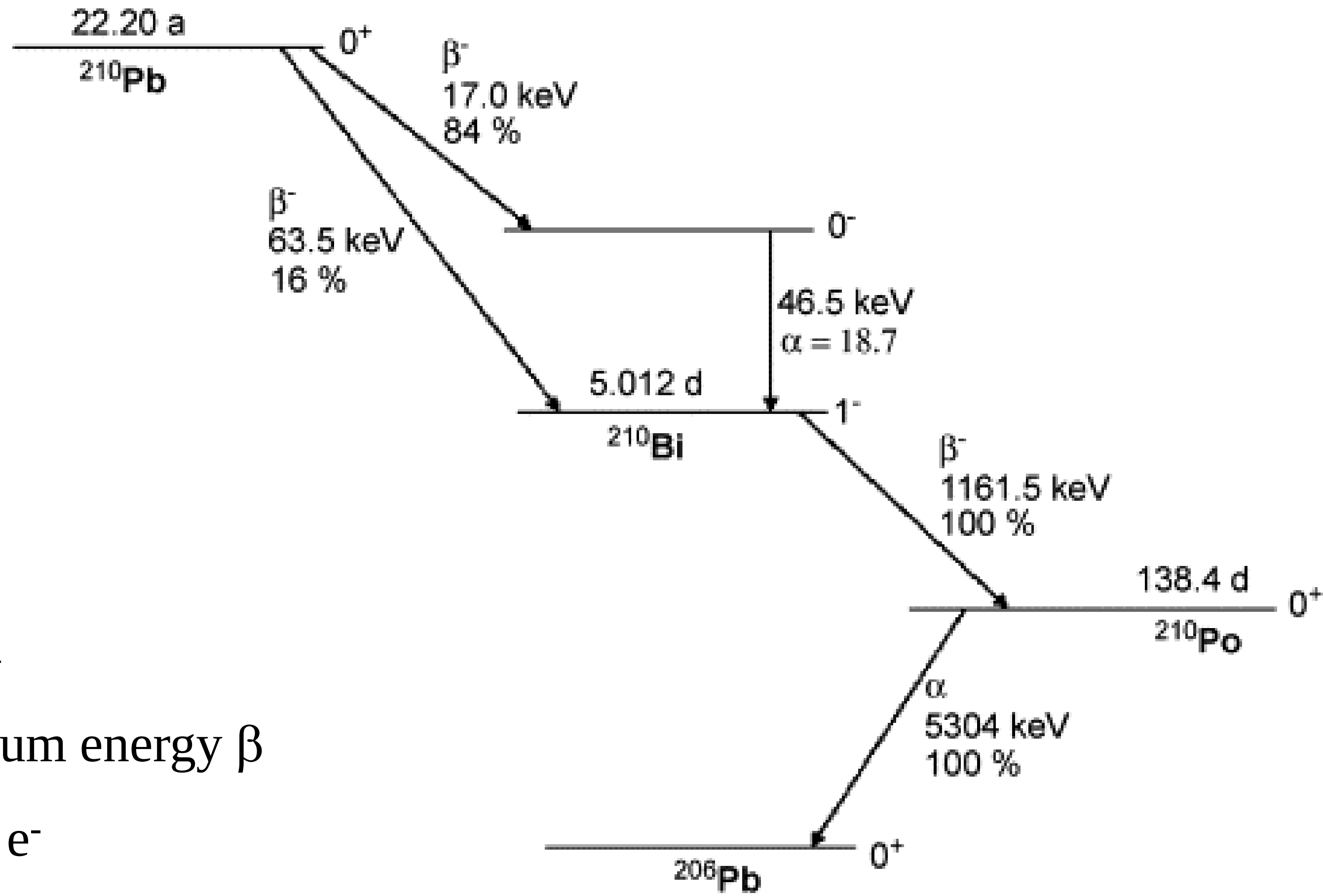
rarely done by metrology labs

different methods used

Compare with NPL standard

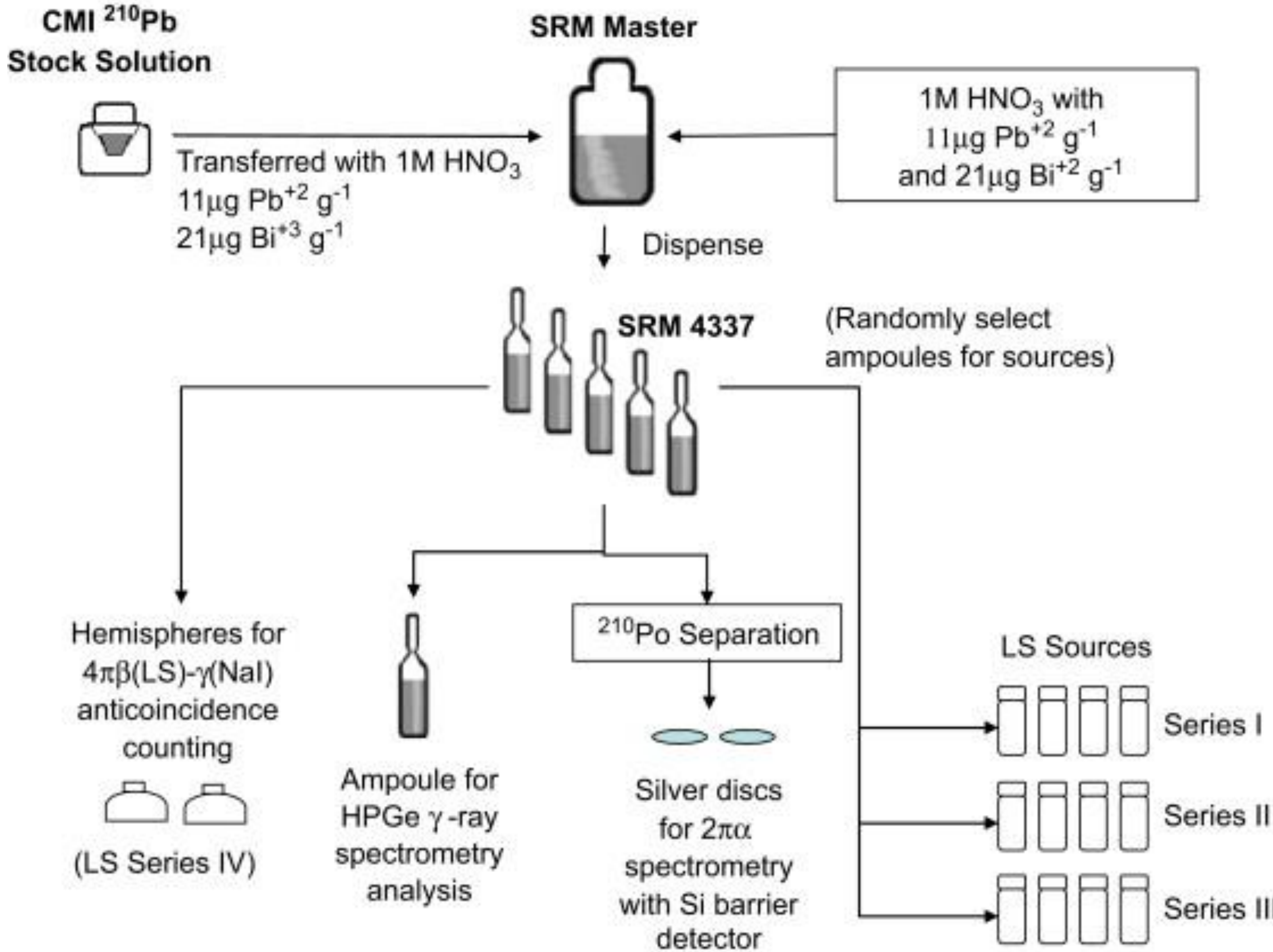
NIST standardization

Laureano-Perez, et al. *Appl. Radiat. Isot.* **65**, *1368 (2007)*



Need to detect

- low – medium energy β
- conversion e$^-$
- high energy β
- α



CMI ^{210}Pb
Stock Solution
SRM Master
1M HNO_3 with
11µg Pb^{+2} g^{-1}
and 21µg Bi^{+2} g^{-1}
Transferred with 1M HNO_3
11µg Pb^{+2} g^{-1}
21µg Bi^{+3} g^{-1}
Dispense
SRM 4337
(Randomly select
ampoules for sources)
Hemispheres for
4πβ(LS)-γ(NaI)
anticoincidence
counting
(LS Series IV)
Ampoule for
HPGe γ -ray
spectrometry
analysis
^{210}Po Separation
Silver discs
for 2πα
spectrometry
with Si barrier
detector
LS Sources
Series I
Series II
Series III

LS results (CN2003 code)

Pb-210

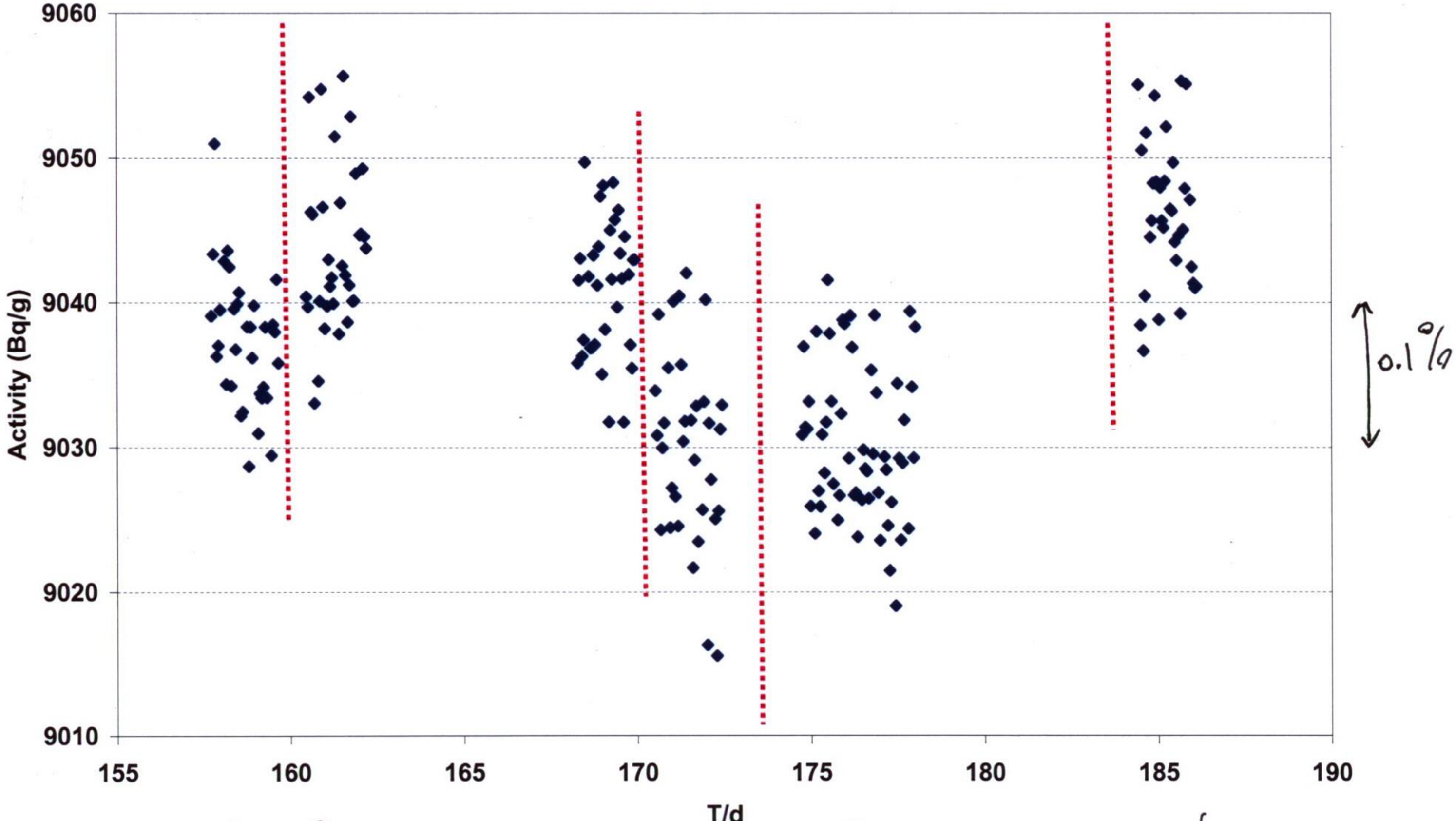
Series	Average	sd (%)	Normal	nc	ns	Counter	Scint	Age start	Age end	f_{H2O}	ε_{H-3}
1	9037.397	0.029	Y	3	11	Packard	HS	0.21	2.12	0.1	0.36-0.30
	9043.779	0.008	Y	3	11	Beckman	HS	2.95	4.65		
	9041.030	0.014	Y	3	11	Wallac	HS	10.76	12.4		
	9030.169	0.021	Y*	3	11	Packard	HS	13	14.9		
	9030.377	0.017	Y*	5	11	Packard	HS	17.22	20.46		
	9046.129	0.007	Y*	3	11	Wallac	HS	26.93	28.57		
2	9034.269	0.031	N	5	7	Packard	PCS	0.11	4.06	0.01	0.40-0.22
	9035.597	0.035	Y	5	7	Packard	PCS	0.11	4.06	0.04	
	9039.466	0.027	N	3	7	Wallac	PCS	4.78	6.91	0.01	
	9044.048	0.014	Y	3	7	Wallac	PCS	4.78	6.91	0.04	
	9040.539	0.026	no	3	7	Beckman	PCS	10.74	12.83	0.01	
	9041.935	0.026	yes	3	7	Beckman	PCS	10.74	12.83	0.04	
	9032.072	0.056	no	5	7	Packard	PCS	14.17	18.6	0.01	
	9026.263	0.034	yes	5	7	Packard	PCS	14.17	18.6	0.04	

* Data normal after removing sample with unstable cocktail

436 determinations

Series	Average	SD	SD (%)	Normal
1	9038.147	6.7577	0.07477	Yes
2	9036.774	5.8702	0.06496	Yes
Total	9037.362	6.0511	0.06696	Yes

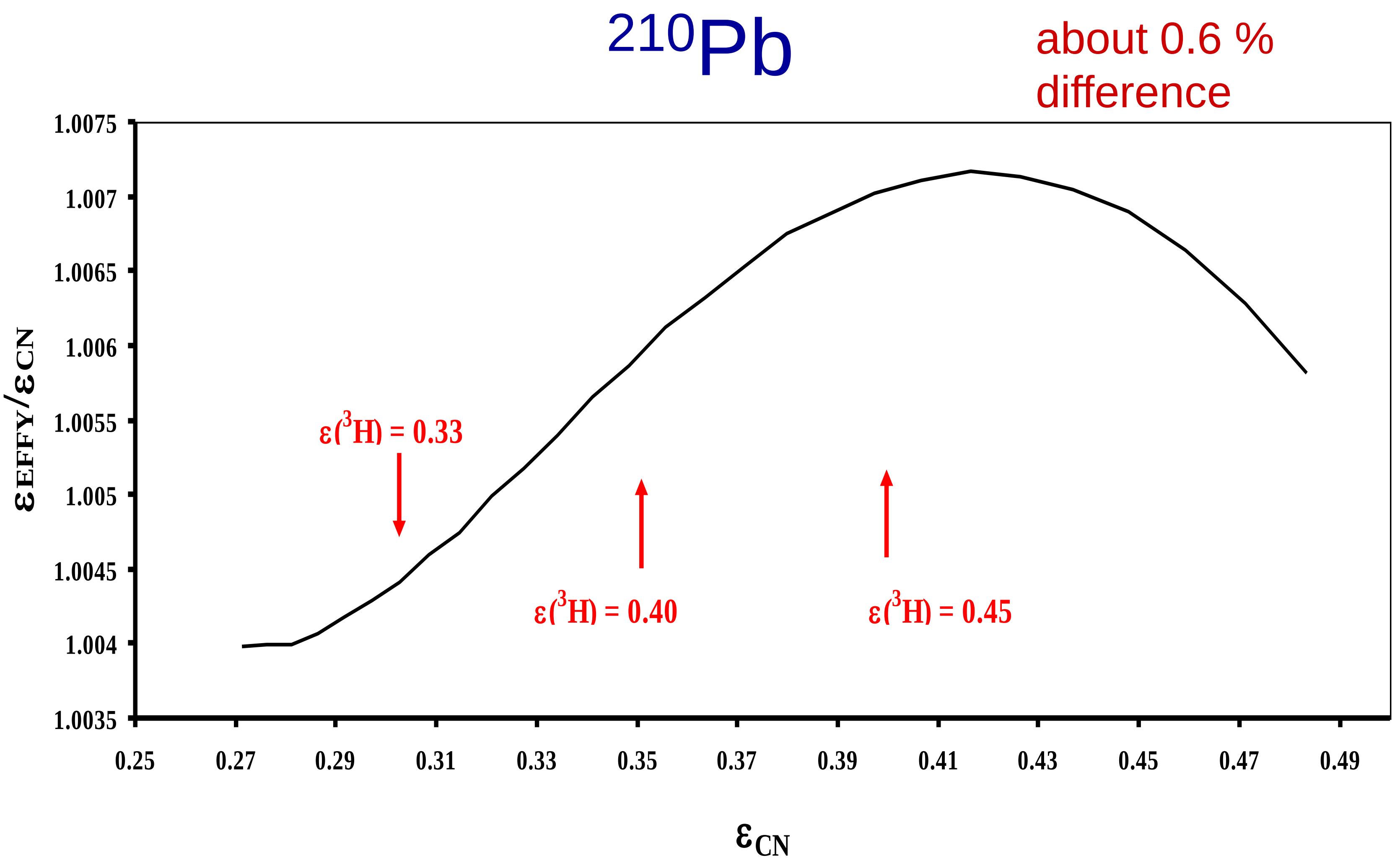
Pb-210: all counters; Composition 1 of 3



	P	B	W	P	P	W
cycles	3	3	3	3	5	3
x12 samples.	36	36	36	36	60	36

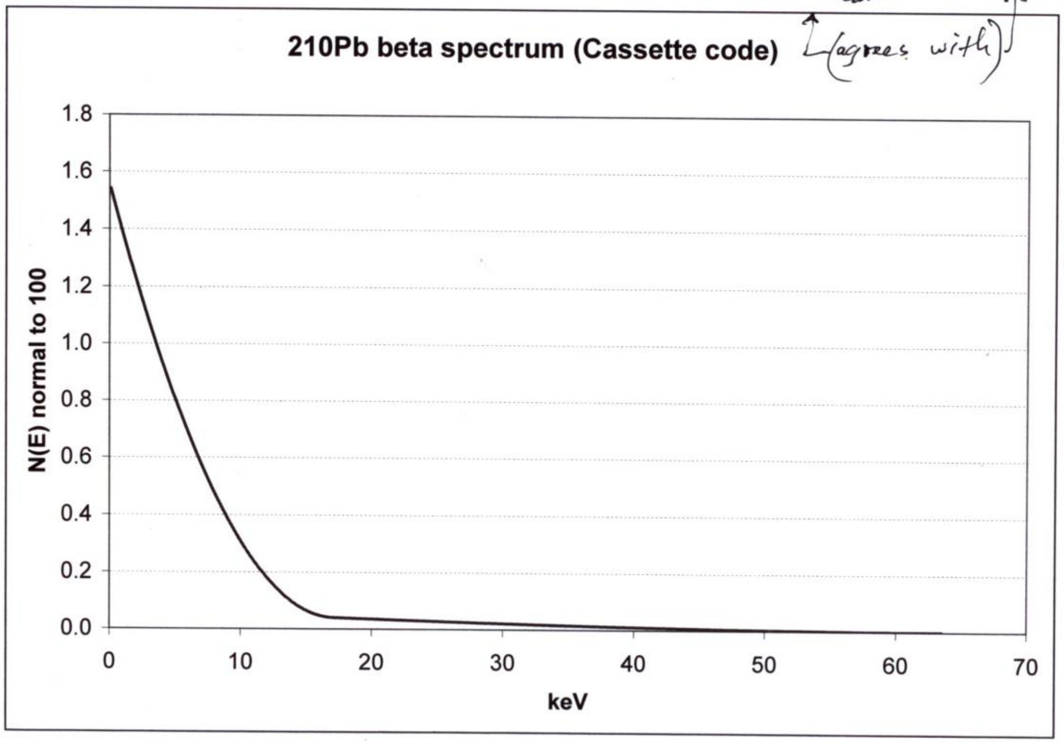
CN2003 vs EFFY4 code differences

(just Beta efficiency part)

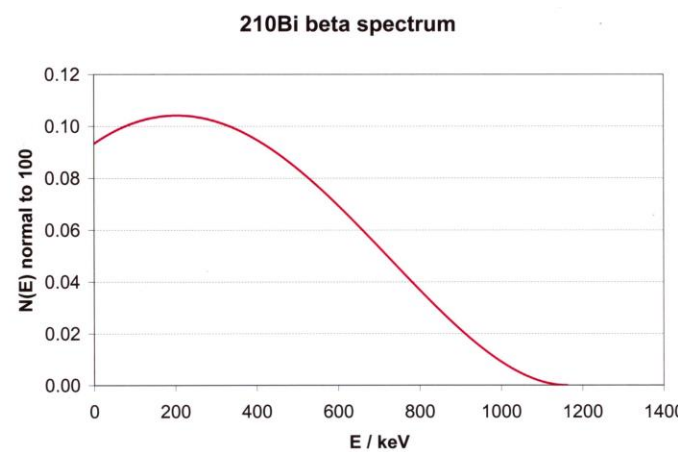


EFFY 4
CN2003 ← low E cutoff
Carine

(agrees with)



differences not due to spectra

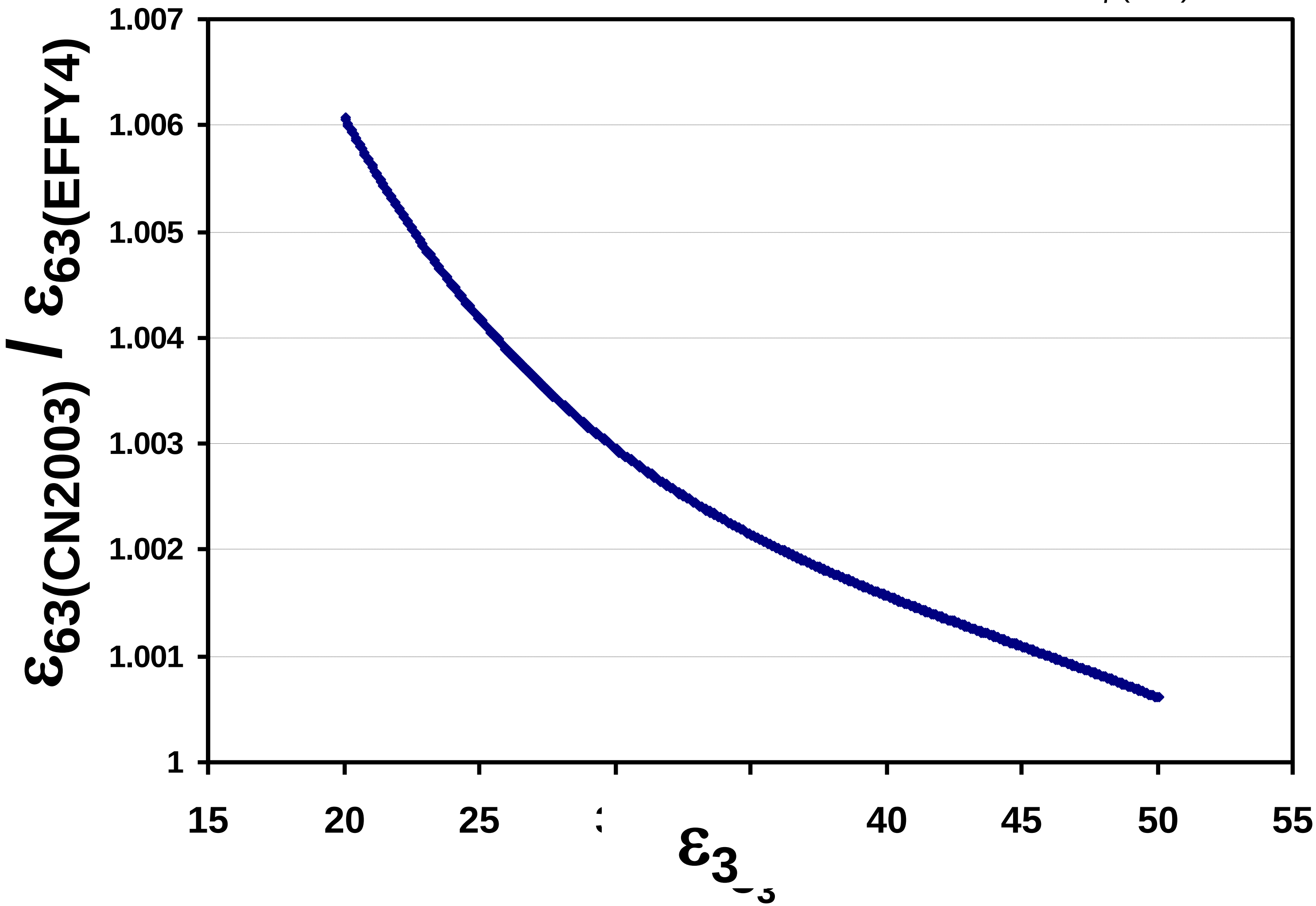


CN2003 vs EFFY4 code differences – due to assumed Quench function

EFFY4 – for toluene cocktails
CN2003 – for DIN (like HS3 used)
but also used xylene based (PCS)

Effect seen for other nuclides, like

^{63}Ni -- 17 keV $E_{\beta(ave)}$ allowed



^{210}Pb massic activity results

	kBq/g (*k* = 2)	diff from LS	
LS (CN2003)	9.037 ± 2.4 %	----	
γ-spect (HPGe)	9.46 ± 8.3 %	+ 4.7 %	big unc. if don't use ^{210}Pb γ std
$4\pi\beta$(LS)-γ(NaI) anticoincidence *(attempt)*	9.10 ± 3.3 %	+ 0.7 %	lots of assumptions, big extrapolation
α-spect (Po tracer)	8.77 ± 1 % 8.92	- 3.0 % - 1.3 %	$T_{1/2}$ = 102 a $T_{1/2}$ = 128 a

Relatively large 2.4 % uncertainty because of

(1) LS cocktail composition effects

(2) tracing code differences & assumptions,

(3) lack of good confirmatory measurements,

NPL Standard (A050187)

nominal 10 g   1 mol·L^{-1} HNO_3 50 μg Pb^{+2} & Bi^{+3} per g

333 Bq·g^{-1} at 1200 GMT 1 January 2007

relative uncertainty (k = 2) = **1.8 %**

Certified value based on dilution of PTB standard

(4$\pi\alpha$ proportional counting of ^{210}Po ingrowth)

NPL confirmation with Cerenkov counting of ^{210}Bi ingrowth following chemical separation (^{210}Bi efficiency by LS ^{3}H std CNET)

NIST Standard (SRM 4437)

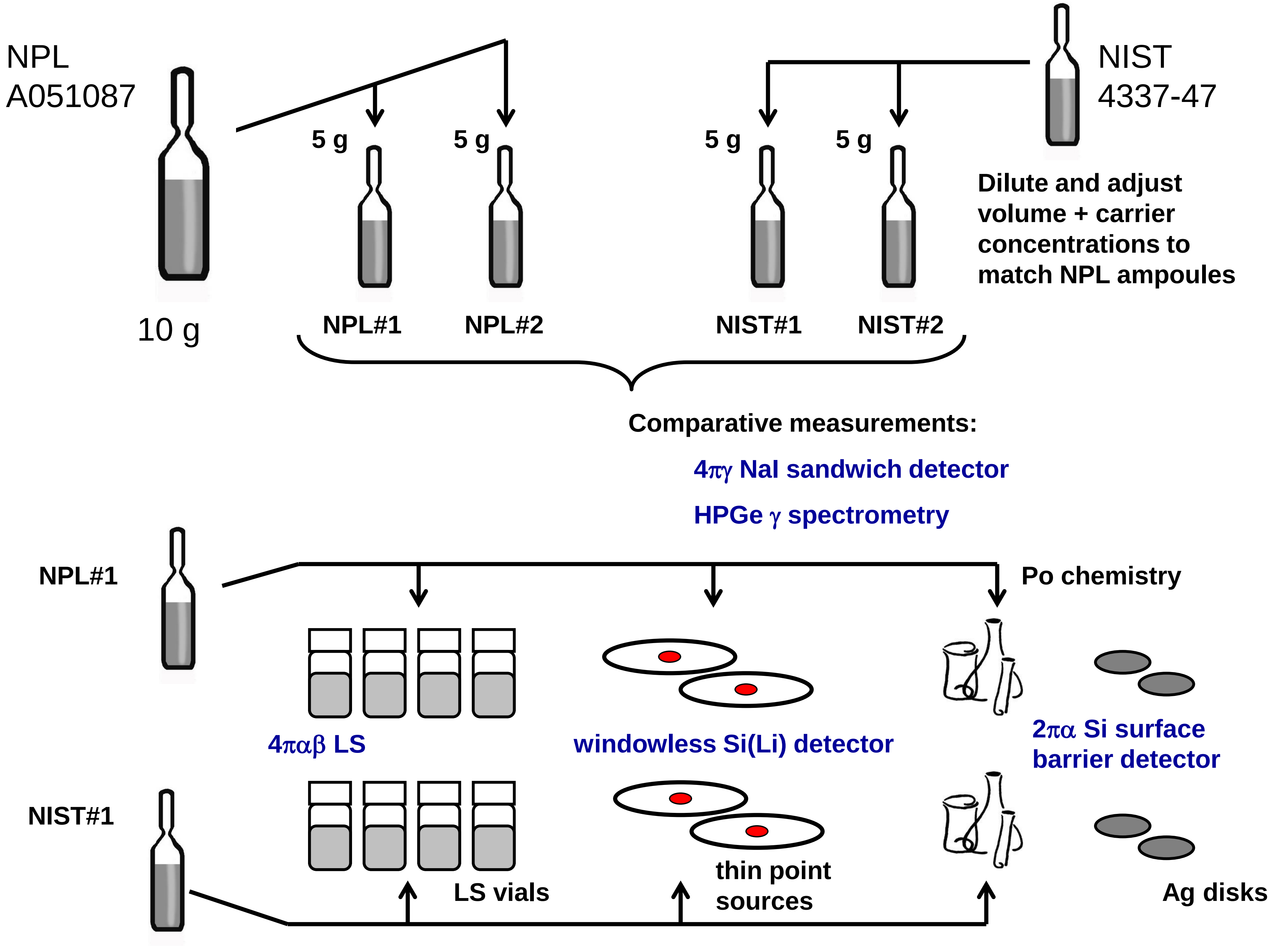
(5.133 ± 0.002) g   1 mol·L^{-1} HNO_3 11 μg Pb^{+2} per g & 21 μg Bi^{+3} per g

9.037 kBq·g^{-1} at 1200 EST 15 June 2006

relative uncertainty (k = 2) = **2.4 %**

Certified value based on 4$\pi\alpha\beta$ LS ^{3}H std CNET

Confirmatory measurements by anticoincidence counting, HPGE, and ^{210}Po assays.



NPL
A051087
10 g
5 g
5 g
NPL#1
NPL#2
5 g
5 g
NIST#1
NIST#2
NIST
4337-47
Dilute and adjust
volume + carrier
concentrations to
match NPL ampoules
Comparative measurements:
4πγ NaI sandwich detector
HPGe γ spectrometry
NPL#1
Po chemistry
4παβ LS
windowless Si(Li) detector
2πα Si surface
barrier detector
NIST#1
LS vials
thin point
sources
Ag disks

Comparison of the NIST and NPL ^{210}Pb standards by five measurement methods.

method	NPL / NIST ratio	relative standard uncertainty	difference
NPL and NIST certified values from primary standardizations	**0.037484**	**1.5 %**	----------
4πγ(NaI)	**0.037373**	**0.56 %**	- 0.30 %
HPGe spectrometry	**0.037542**	**0.71 %**	+ 0.15 %
4παβ(LS)	**0.037249**	**0.17 %**	- 0.63 %
^{210}Po assay (2πα spect.)	**0.03736**	**0.75 %**	- 0.33 %
Si(Li) low-energy spectrometry	**0.0381**	**1.9 %**	+ 1.6 %

difference in stds ***0.11 % (unwgtd)***

0.50 % (wgtd)

Suspect both NIST & NPL uncertainties are overestimated

conclude

^{209}Po

need replacement standard now !

utility limited by $T_{1/2}$ uncertainty (in doubt)
($T_{1/2}$ needs to be done)

---

^{210}Pb

stds by NIST & NPL probably have
overestimated uncertainties
(may know much better)

need to examine with another method
(TDCR ? !)

contributions & thanks to

Lizbeth Laureano-Perez (NIST)

Ryan Fitzgerald (NIST)

Iisa Outola (NIST)

Chris Gilligan (NPL)

Leticia Pibida (NIST)

Philippe Cassette (LNHB)

Brian Zimmerman (NIST)

……others (world)

fin

Summary of some recent NIST primary standardizations and comparison to confirmatory measurements.

Nuclide	Method	relative standard uncertainty	Confirmatory Measurement	Difference (%)
^{63}Ni	4π LS TDCR (NIST)	0.16 %	4πβ LS TDCR (LNHB) 4πβ LS CNET (NIST)	-0.31 -0.77
^{55}Fe (NIST)	4π calorimetry (linked by LS)	0.39 %	4π LS TDCR (Polatom) 4π LS TDCR (LNHB)	-0.87 -0.43
^{55}Fe (BIPM)	4π calorimetry (linked by LS)	0.39 %	weighted mean value of 15 NMI labs	-0.37
^{210}Pb	4παβ LS CNET	1.2 %	4παβ(LS)-γ(NaI) anticoin. counting ^{210}Po α spect. (102 a ^{209}Po tracer) ^{210}Po α spect. (128 a ^{209}Po tracer) HPGe photon spect.	+0.7 -3.0 -1.3 +4.7
^{241}Pu	4πβ LS CNET	1.9 %	LS (^{241}Am ingrowth) 4πβ LS TDCR (NIST) 4πβ LS TDCR (LNHB)	+1.2 -7.9 * -7.7 *
^{210}Pb	4παβ LS CNET	1.2 %	compare to NPL standard (5 methods) see Table2	-0.3
^{90}Sr	4πβ LS TDCR	0.51 %	4πβ LS CNET	+ 0.09
^{241}Am	4πα LS	0.22 %	4πα LS (independent) 4πα LS (independent)	-0.05 -0.01 -0.15
^{229}Th	4παβ(LS)-γ(NaI) anticoincidence counting	0.28 %	4παβ LS CNET 4παβ LS TDCR 2π α proportional counting HPGe photon spectrometry	-0.09 -1.7 -0.09 +2.1

* Values are discrepant, and not considered to have confirmed