Radioactivity Group Meeting

29 March 2007

The State of the SRM Program

(and what we've been doing)

Featuring:

Ron Collé

Lizbeth Laureano-Perez

We are COORDINATORS of program – not sole workers !

LiZBETH

Handles all administrative functions

Performs most labwork / data analyses

Learning design

Me

train / teach

make decisions / deal with bosses

enlist help / encourage others

think great thoughts / devil’s advocacy

do some labwork / data analyses

Ron

Overview of SRM Program

Group (worker-bee) participation

Activities

- ^{55}Fe SRM + BIPM intercomparison (link to calorimetry)
- ^{209}Po / ^{210}Pb problems
- ^{209}Po half-life (Poland, France, NIST ?)
- ^{63}Ni standardization & half-life --38 years (LNHB)
- calorimetry / ^{14}C half-life / (Columbia Univ.)
- Si(Li) x-ray detection

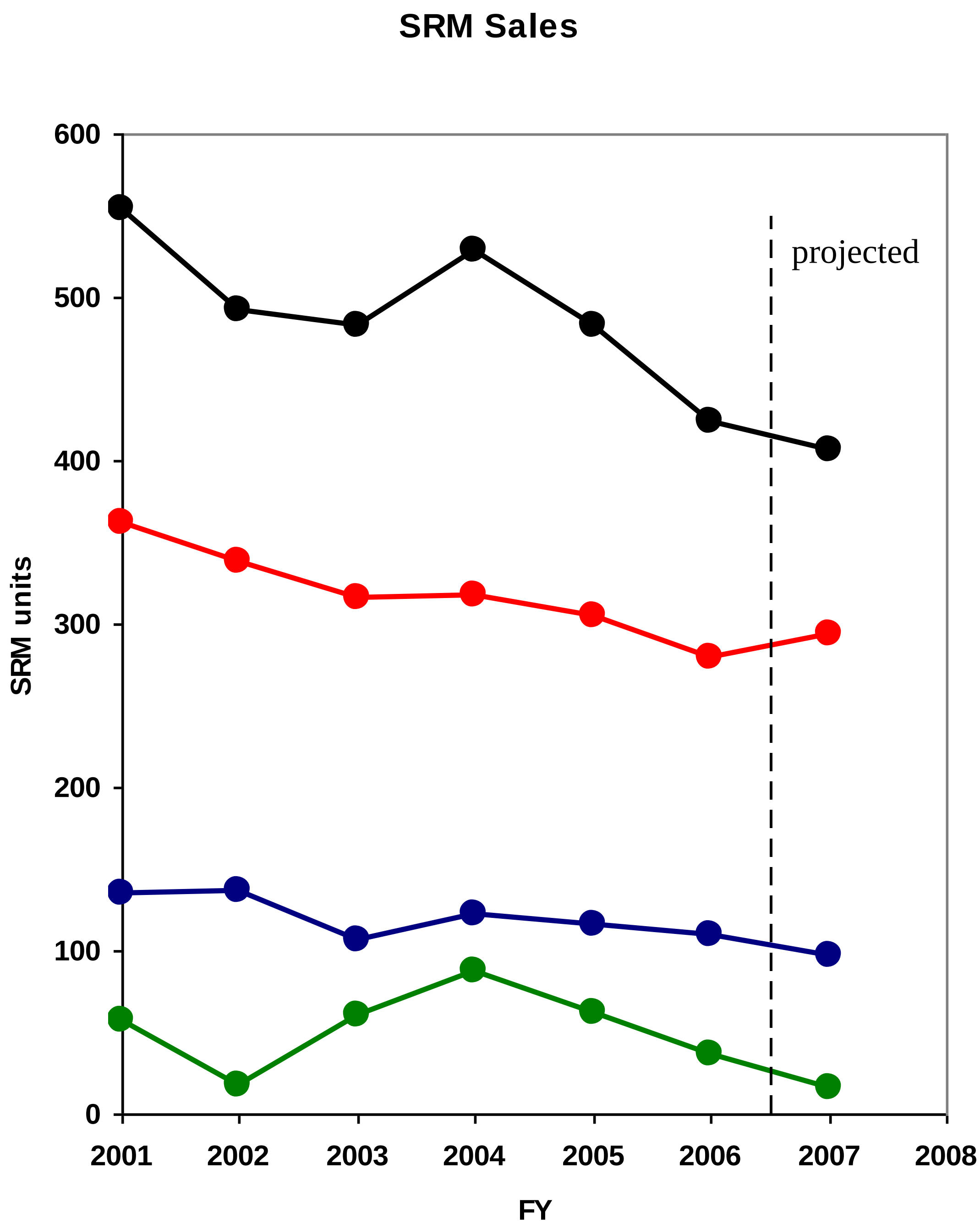
Liz

Status of SRM Program

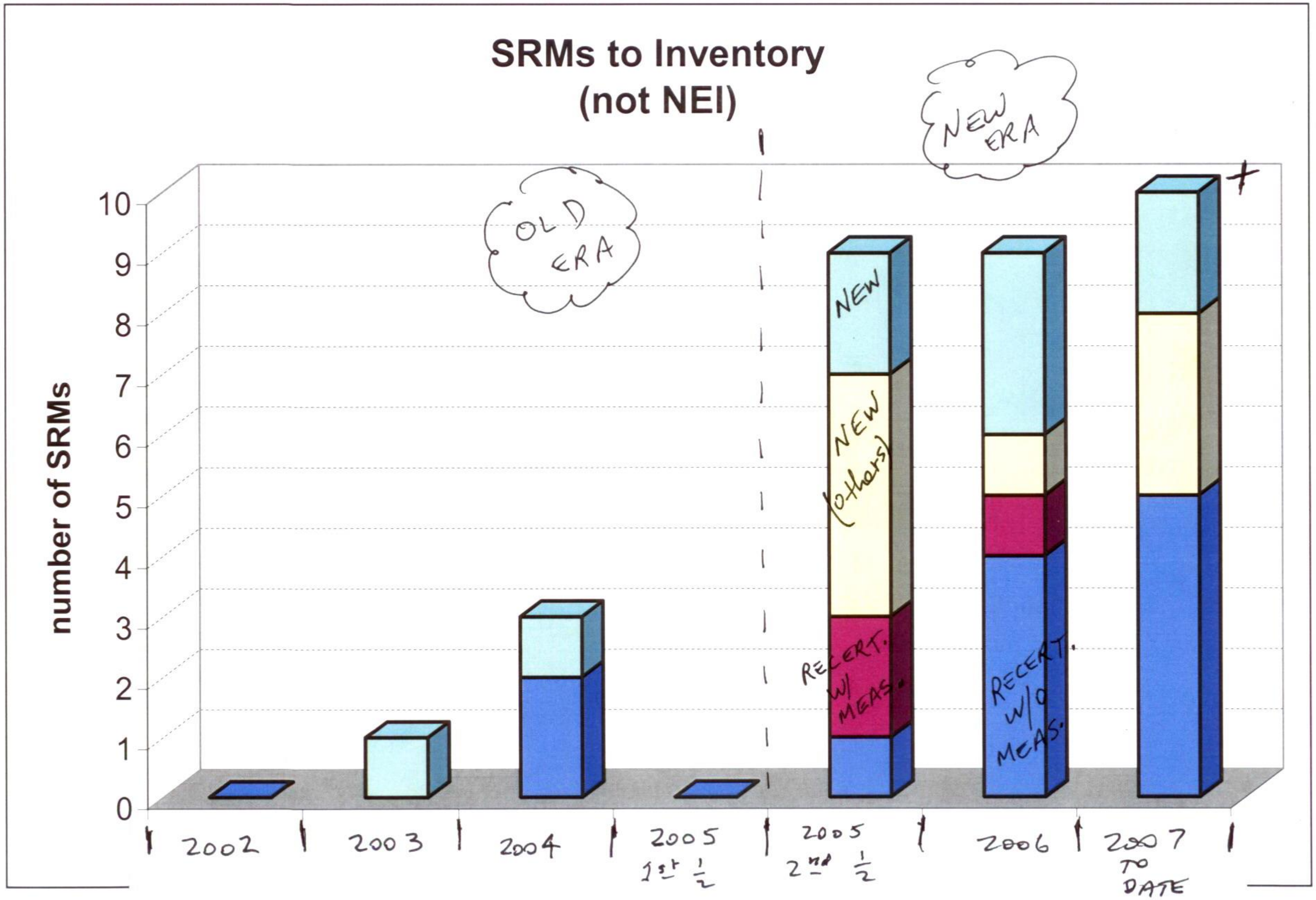
paperwork + technical

Activities

- re-certifications (w & w/o meas.)
- new SRMS of others [nat'l matrix (2); ^{226}Ra-Rn (6)]
- new SRMs
  - ^{60}Co & ^{137}Cs
  - ^{55}Fe & ^{210}Pb
  - ^{166m}Ho
  - ^{90}Sr (2)
- ongoing & future SRMs
- measurement comparison compilations



	average decrease per year
Total	21
SRM	12
NEI	6
Nat'l Matrix	3


SRMs to Inventory
(not NEI)
number of SRMs
0
1
2
3
4
5
6
7
8
9
10
OLD ERA
NEW ERA
NEW
NEW (others)
RECERT. W/ MEAS.
RECERT. W/O MEAS.
2002
2003
2004
2005 1st 1/2
2005 2nd 1/2
2006
2007 TO DATE

The State of the SRM Program

Vastly improved – Now Good – slowly getting Great

NEI & Nat’l Matrix programs work - DFWI

Improved relations with SRM office

Paperwork moves fast now

More cooperation in Group (members now involved)

Vast productivity increases

Revised certificate

Increasing scientific / metrology rigor

worker bees who have helped

Dan & Ophelia (NEI program + production help)

Brian (TDCR +.........

Ryan ....

Ken’s empire

- Iisa (LS + Po)
- Svetlana (LS)
- Jerry (228Ra soooooooooooon)

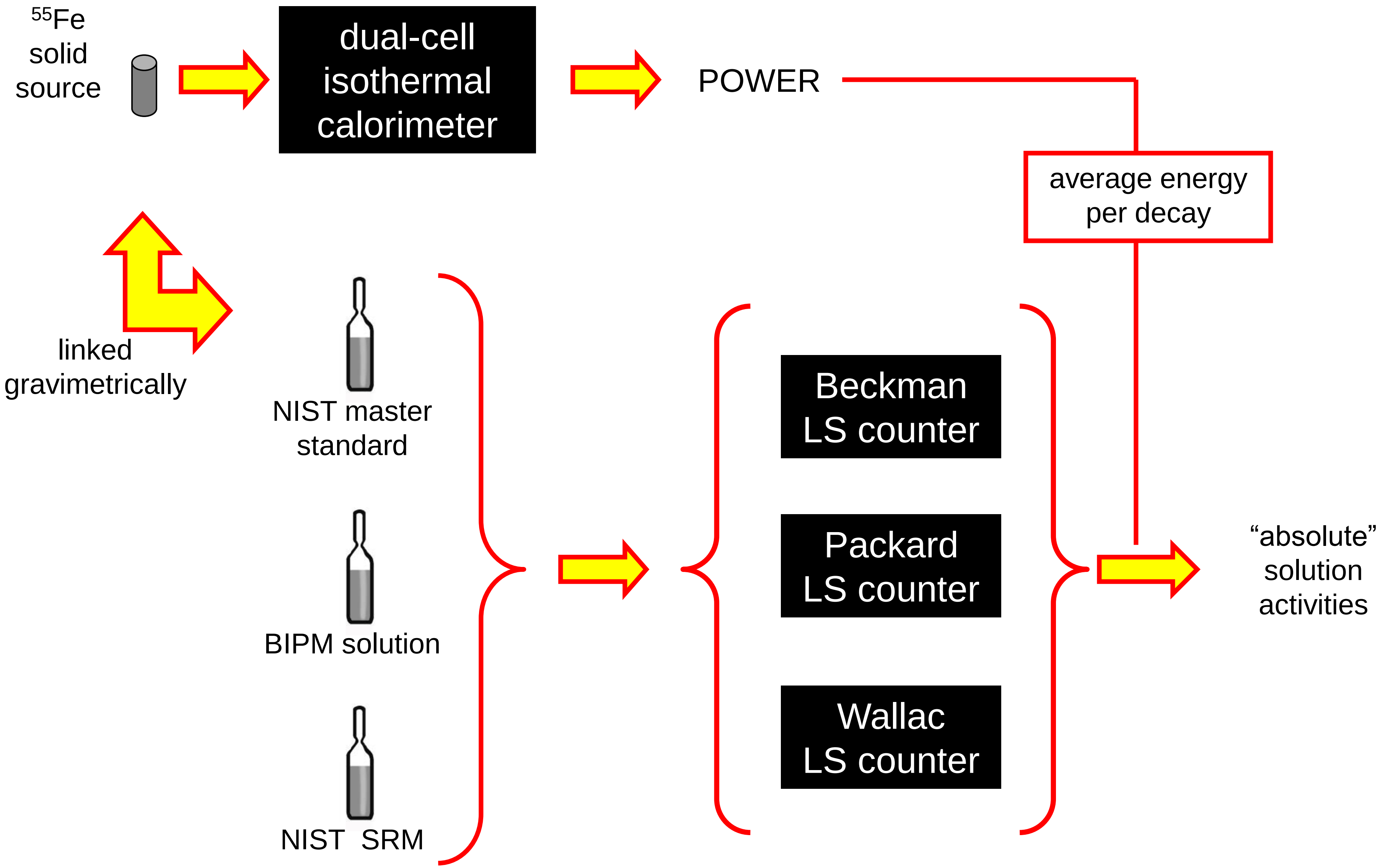
Peter (Ra & Rn)

Leticia (166mHo)

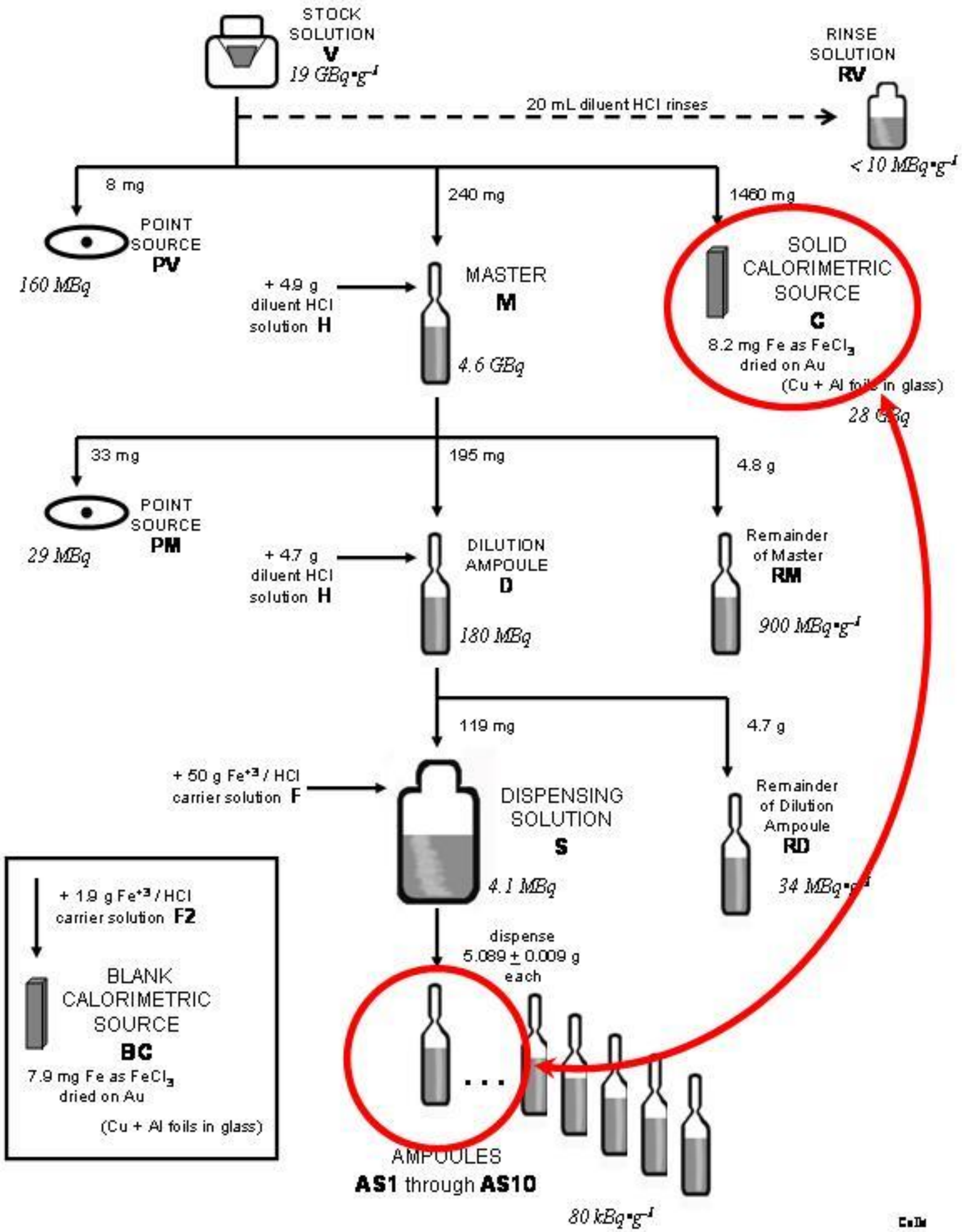
Michelle (LS + impurities)

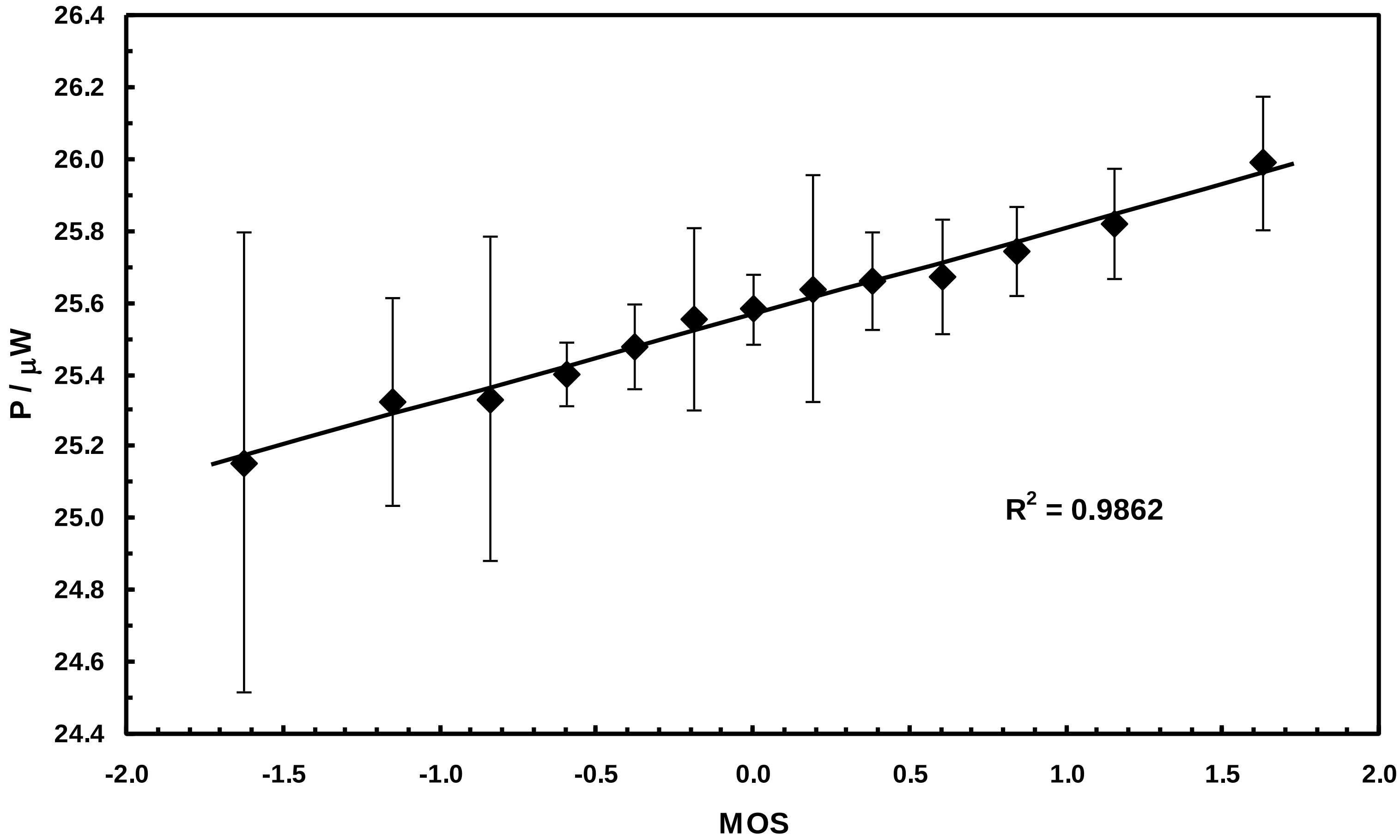
Bruce ....

^{55}Fe

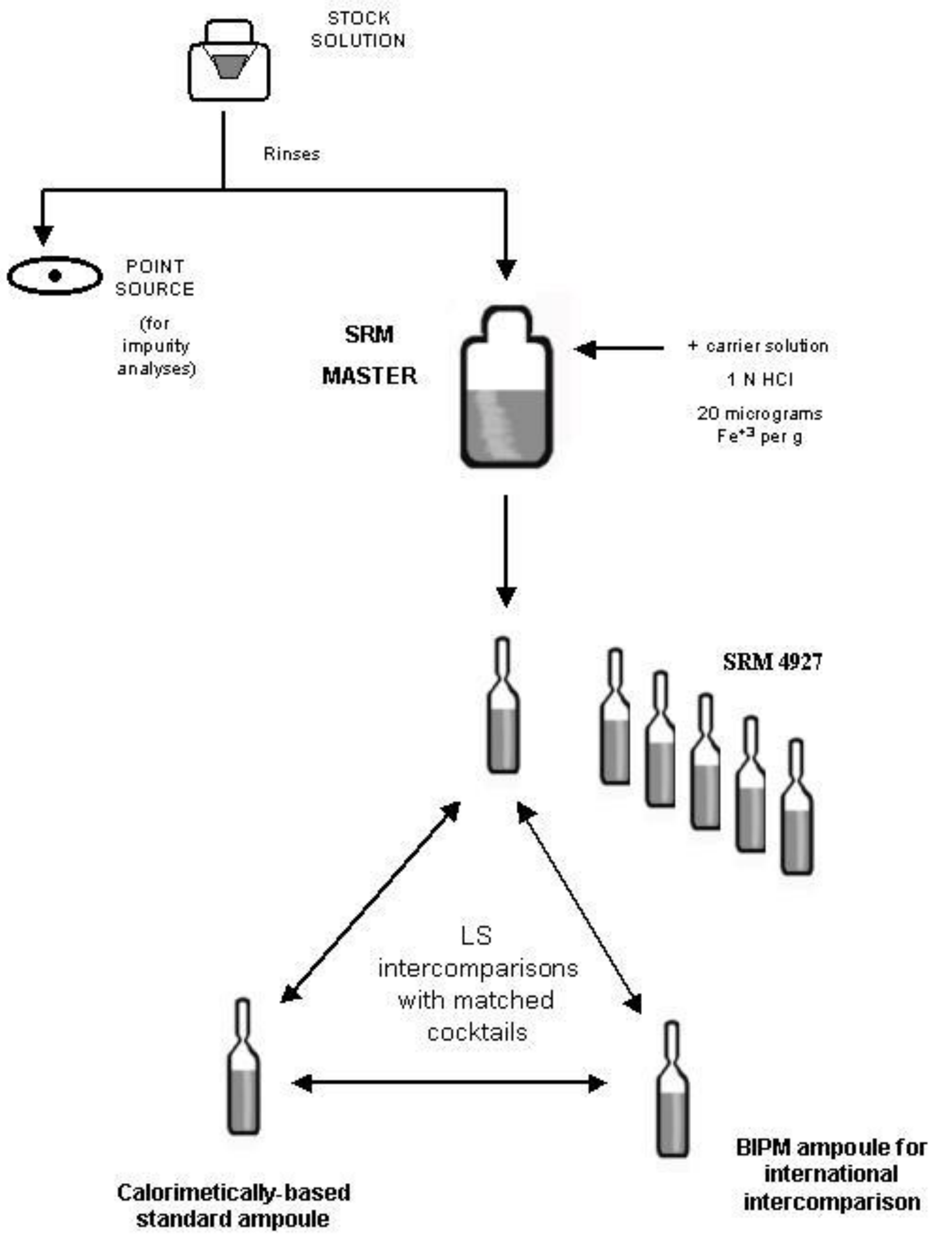


^{55}Fe solid source
dual-cell isothermal calorimeter
POWER
average energy per decay
linked gravimetrically
NIST master standard
BIPM solution
NIST SRM
Beckman LS counter
Packard LS counter
Wallac LS counter
"absolute" solution activities


STOCK SOLUTION
V
19 GBq•g⁻¹
RINSE SOLUTION
RV
20 mL diluent HCl rinses
< 10 MBq•g⁻¹
8 mg
240 mg
1460 mg
POINT SOURCE
PV
160 MBq
+ 4.9 g diluent HCl solution H
MASTER
M
4.6 GBq
SOLID CALORIMETRIC SOURCE
C
8.2 mg Fe as FeCl3 dried on Au
(Cu + Al foils in glass)
28 GBq
33 mg
195 mg
4.8 g
POINT SOURCE
PM
29 MBq
+ 4.7 g diluent HCl solution H
DILUTION AMPOULE
D
180 MBq
Remainder of Master
RM
900 MBq•g⁻¹
119 mg
4.7 g
+ 50 g Fe+3 / HCl carrier solution F
DISPENSING SOLUTION
S
4.1 MBq
Remainder of Dilution Ampoule
RD
34 MBq•g⁻¹
+ 1.9 g Fe+3 / HCl carrier solution F2
BLANK CALORIMETRIC SOURCE
BC
7.9 mg Fe as FeCl3 dried on Au
(Cu + Al foils in glass)
dispense 5.089 ± 0.009 g each
AMPOULES
AS1 through AS10
80 kBq•g⁻¹



26.4
26.2
26.0
25.8
25.6
25.4
25.2
25.0
24.8
24.6
24.4
P / μW
R² = 0.9862
-2.0
-1.5
-1.0
-0.5
0.0
0.5
1.0
1.5
2.0
MOS



Calorimetry

13 independent determinations

LS intercomparisons

776 activity ratios; variables include:

- 3 counters
- 3 scintillators
- 44 matched cocktails
- 4 distinct aq. fraction (+Fe) compositions
- 2 NIST solution dilutions
- 97 days of aging

cal soln S

T_0 = 1 july 2004

78.78 kBq/g

U (k=1) = 0.39 %

BIPM

T_0 = 30 november 2005

522.6 kBq/g

U (k=1) = 0.66 %

SRM 4929F

T_0 = 30 november 2005

58.43 kBq/g

U (k=2) = 1.7 %

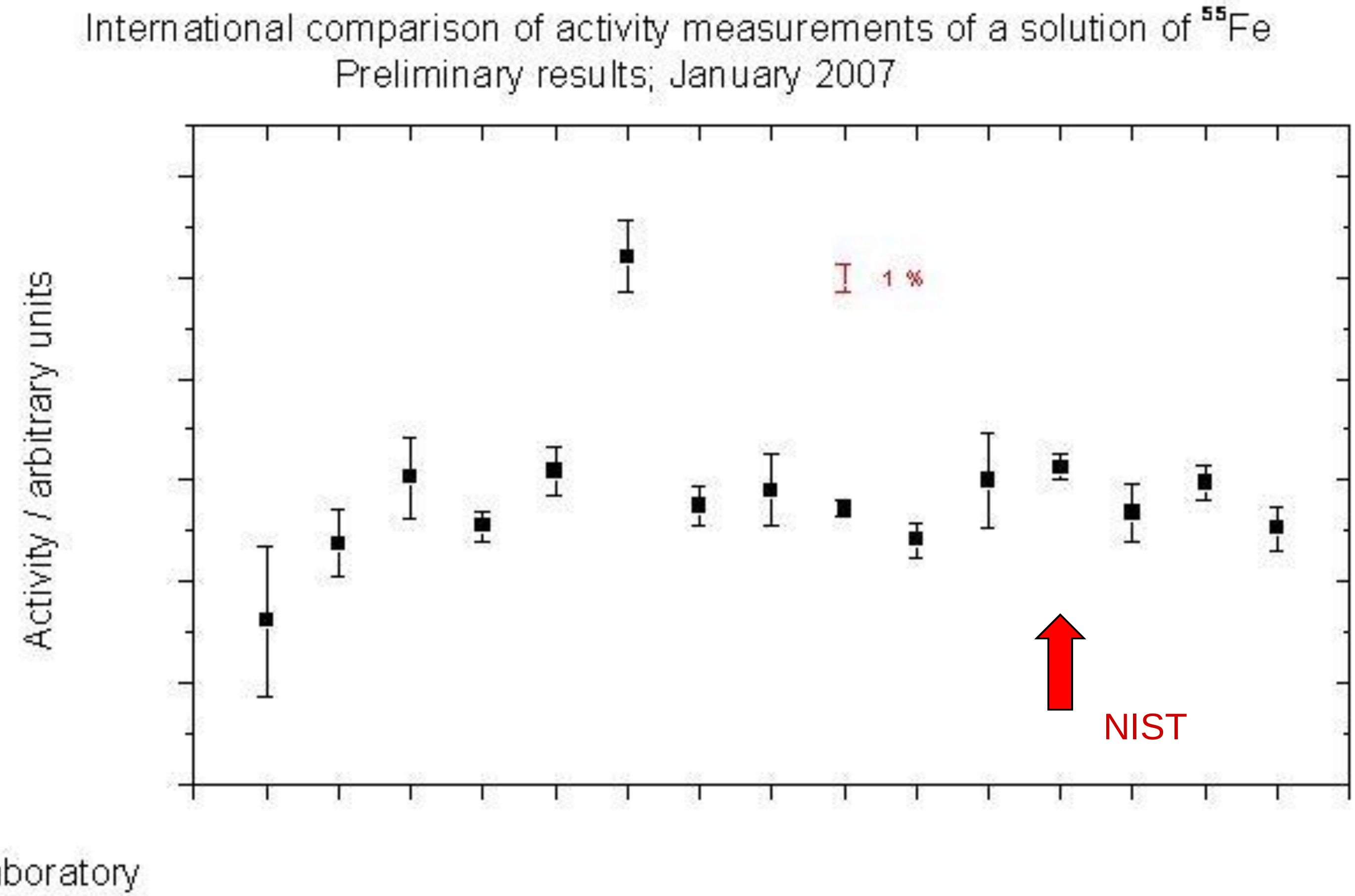
Item	Uncertainty component	Assessment Type	Relative standard uncertainty contribution on massic activity of ^{55}Fe (%)
1	LS measurement precision; reproducibility in activity ratio w/ 44+ sets of cocktails of matched composition; std. dev mean for ν =765 degrees freedom (passes Normal test)	A	0.26
2	LS cocktail stability and composition mismatch effects ; std dev mean for ν_{eff}=11 effective degrees freedom (3 scintillants; 4 aqueous fractions; 2 dilutions); passes Normal test	A	0.47
3	Background LS measurement variability; wholly embodied in items 1 & 2	A	---
4	LS counter (energy threshold) dependencies	A	0.06
5	Scintillator dependencies; wholly embodied in items 1 & 2	A	---
6	Gravimetric (mass) measurements for LS sources	B	0.05
7	Gravimetric (mass) measurements for dilutions	B	0.07
8	Livetime determinations for LS counting time intervals; includes uncorrected deadtime effects	B	0.06
9	Decay corrections for ^{55}Fe (assumed half-life unc.)	B	0.012
10	Limit for photon-emitting impurities	B	0.11
11	Calorimetric primary standardization of NIST 55Fe solutiuons (see ATTACHMENT # 6)	B	0.39
	COMBINED STANDARD UNCERTAINTY		**0.68**

NIST Uncertainty Analysis for ^{55}Fe Massic Activity for the BIPM International Intercomarison

Uncertainty for the ^{55}Fe SRM is comparable;

U (k=2) = 1.7 %

Results (without the outlier value)



^{209}Po and ^{210}Pb problems

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*

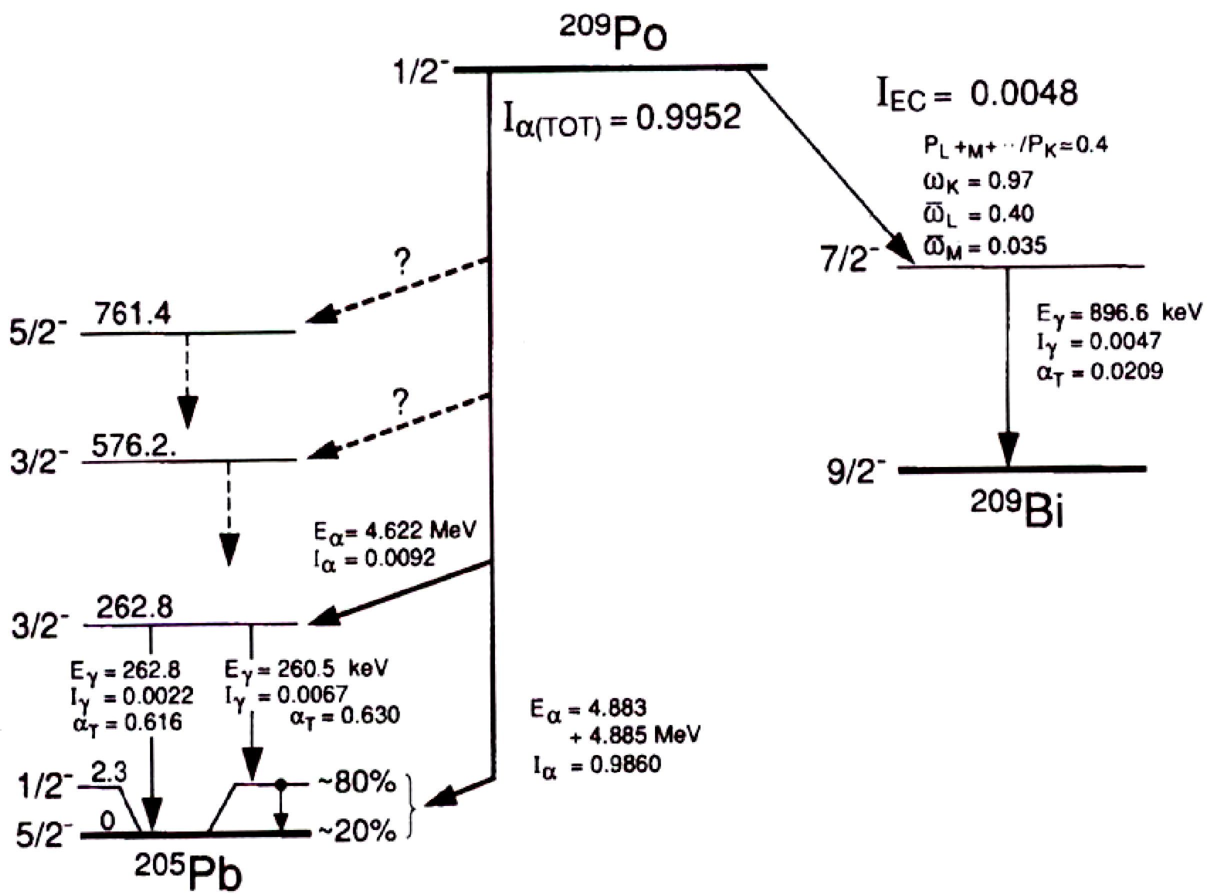


Fig. 2. Partial decay scheme for the ^{209}Po alpha and electron capture branch decays.

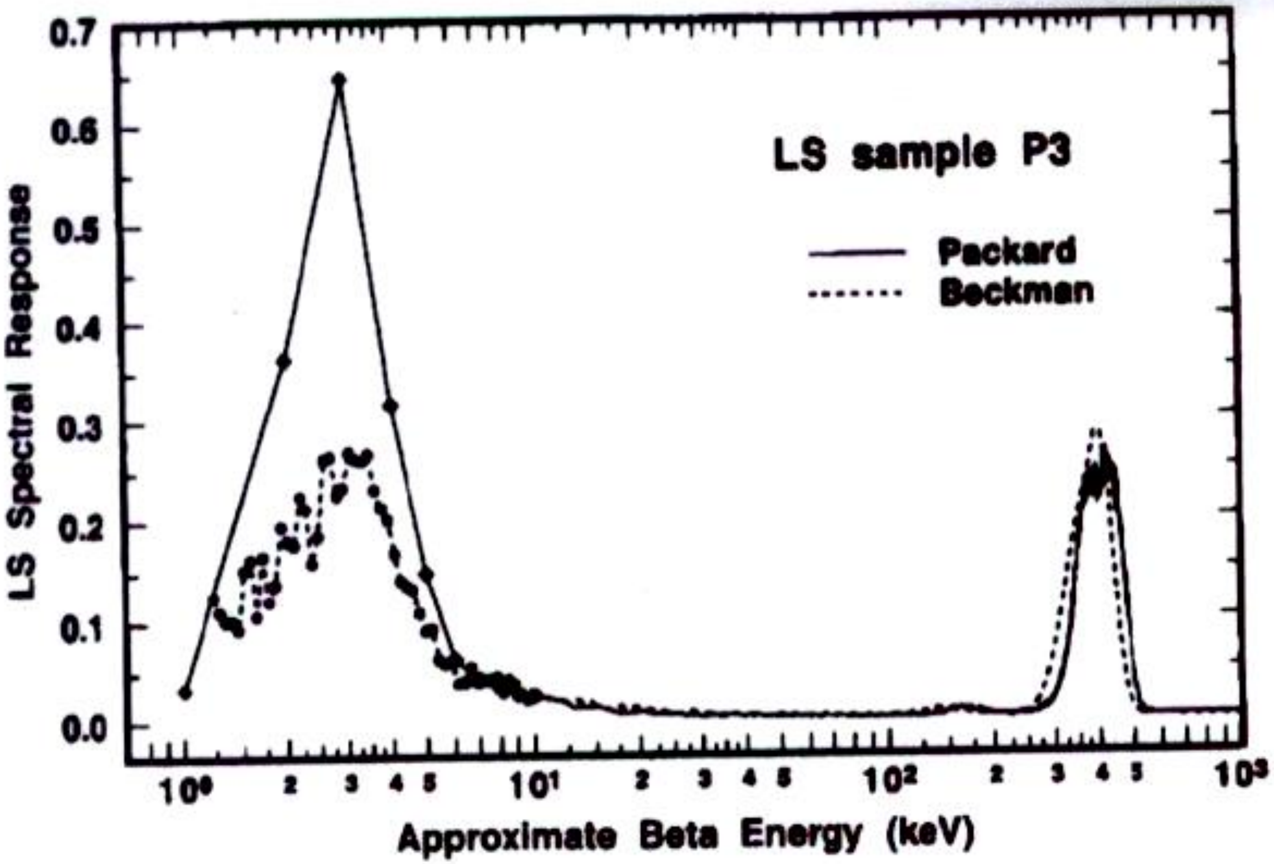


Fig. 6. Comparison of the ^{209}Po LS spectra obtained with the Beckman and Packard instruments.

1995

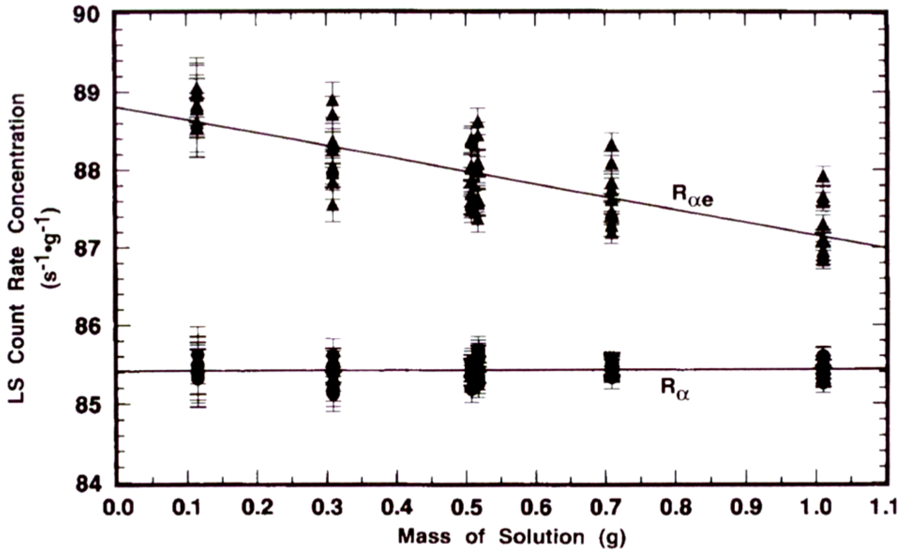


Fig. 12. LS counting rate concentrations $R_{\alpha e}$ and R_{α} as a function of m_s (analogous to that of Fig. 11) as obtained with the Packard instrument.

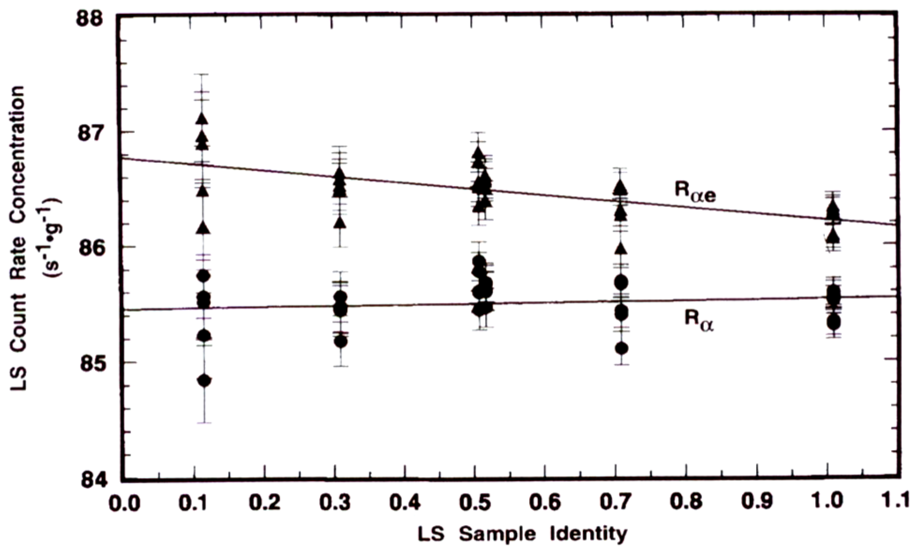


Fig. 11. LS counting rate concentrations $R_{\alpha e}$ (closed triangles) and R_{α} (closed circles) obtained with the Beckman instrument for the N series samples as a function of m_s (and sample quenching). The solid lines are linear regressions fitted to the data.

Same
in 2005

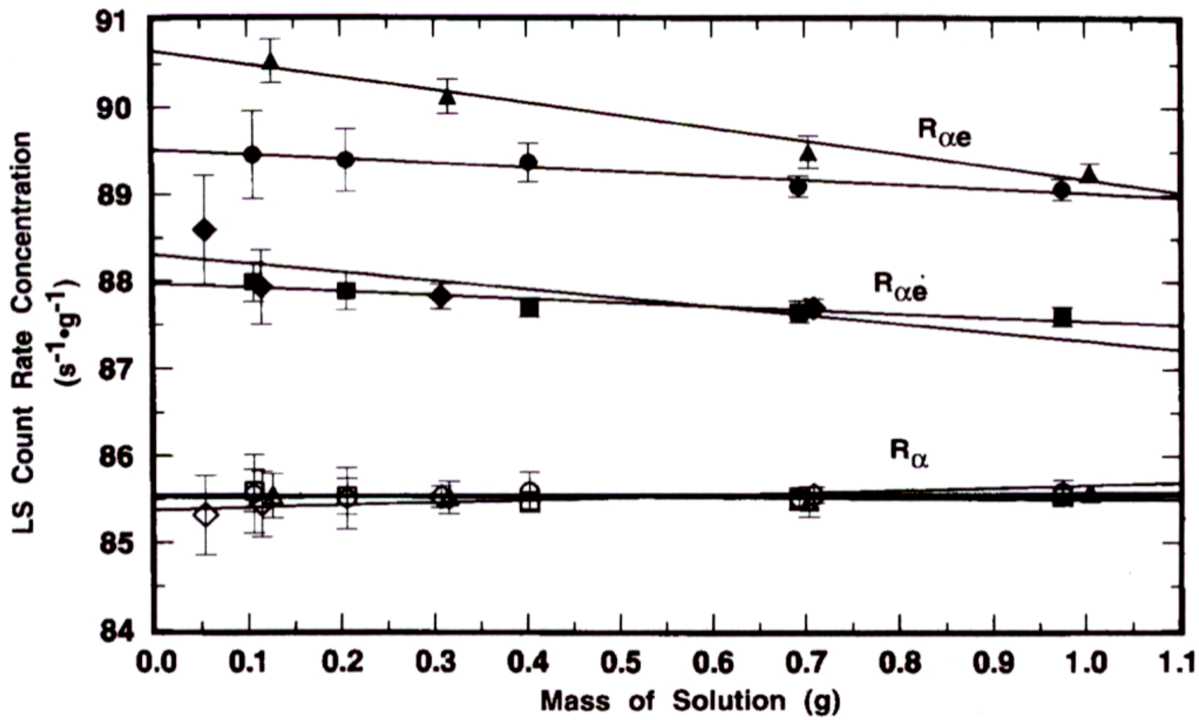


Fig. 13. LS counting rate concentrations $R_{\alpha e}$ and R_{α} obtained with the two LS systems for the P and Q series samples in 1994. Closed squares ($R_{\alpha e}$) and open squares (R_{α}) represent the mean values for samples Q5 through Q8 with the Packard; closed and open triangles represent $R_{\alpha e}$ 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.

15 march 1994

R_α = (85.42 ± 0.18) $s^{-1}g^{-1}$

15 November 2005

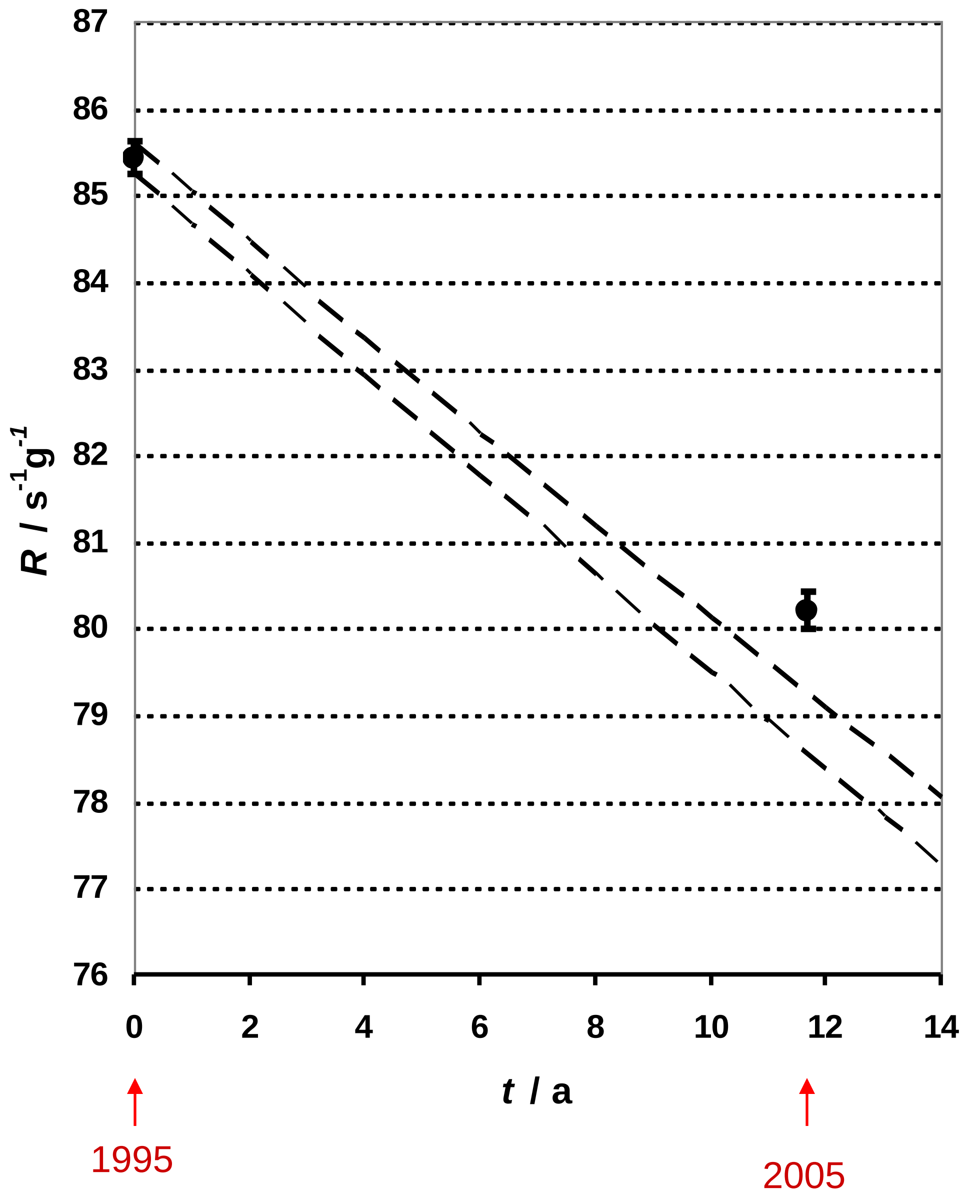
R_α = (80.20 ± 0.22) s-1g-1

2 point fit gives

$T_{1/2}$ = 128 a

U = 5.5 % (7 a)

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



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

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

Collé, Laureano, Outola, *Appl. Radiat. Isot.* In press

$$A / N = \lambda$$

(link)

New determination urgently needed

Collaboration with Polish Academy of Sciences labs

Institute of Nuclear Physics (Krakow)

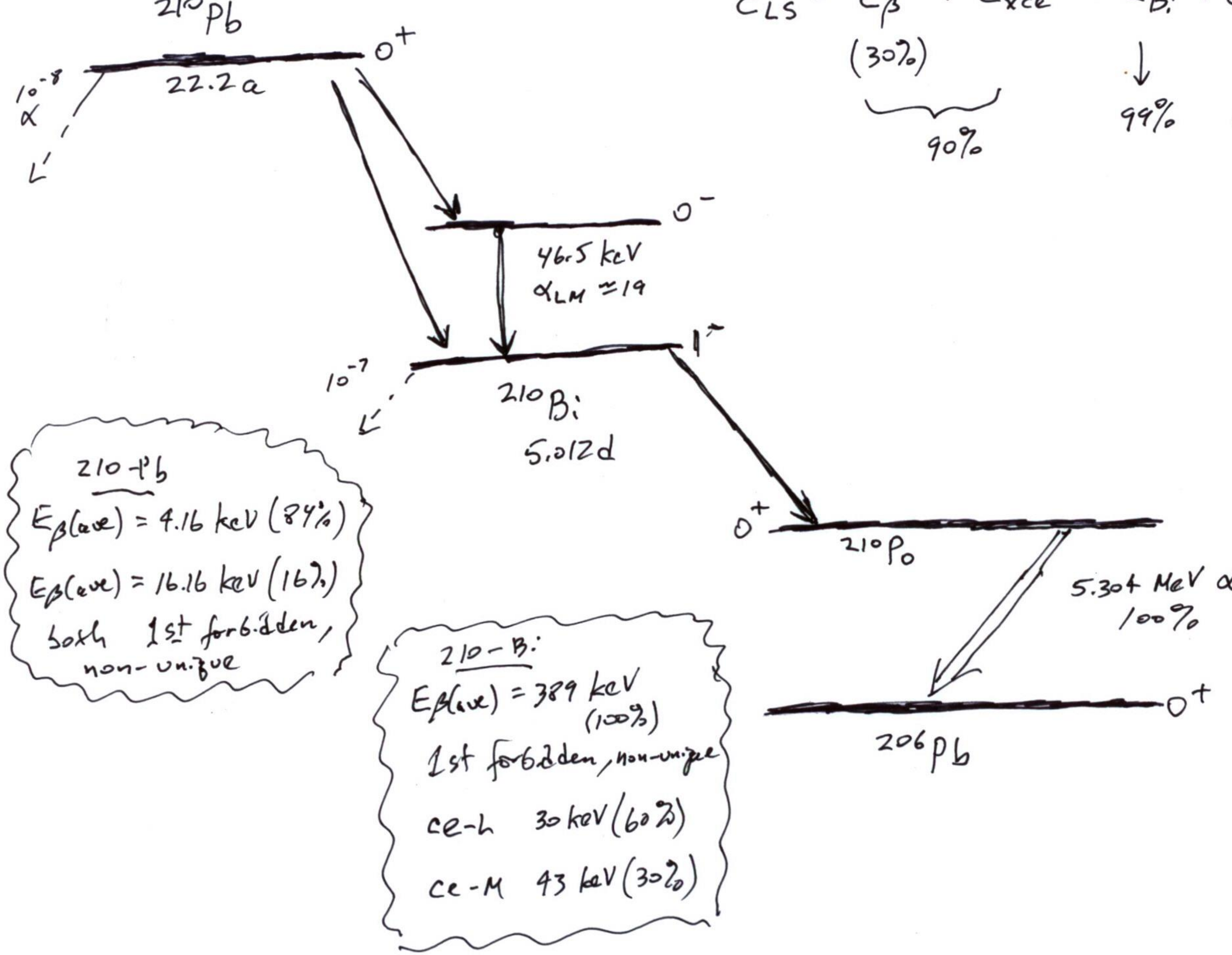
Institute of Geological Sciences (Warsaw)

not going well ...

^{210}Pb

^{210}Pb

$$\varepsilon_{LS} = \underbrace{\underset{(30\%)}{\varepsilon_\beta} + \varepsilon_{xce}}_{90\%} + \underset{\downarrow\,99\%}{\varepsilon_{Bi}} + \underset{\downarrow\,100\%}{\varepsilon_{Po}}$$



LS results (CN2003 code)

Pb-210

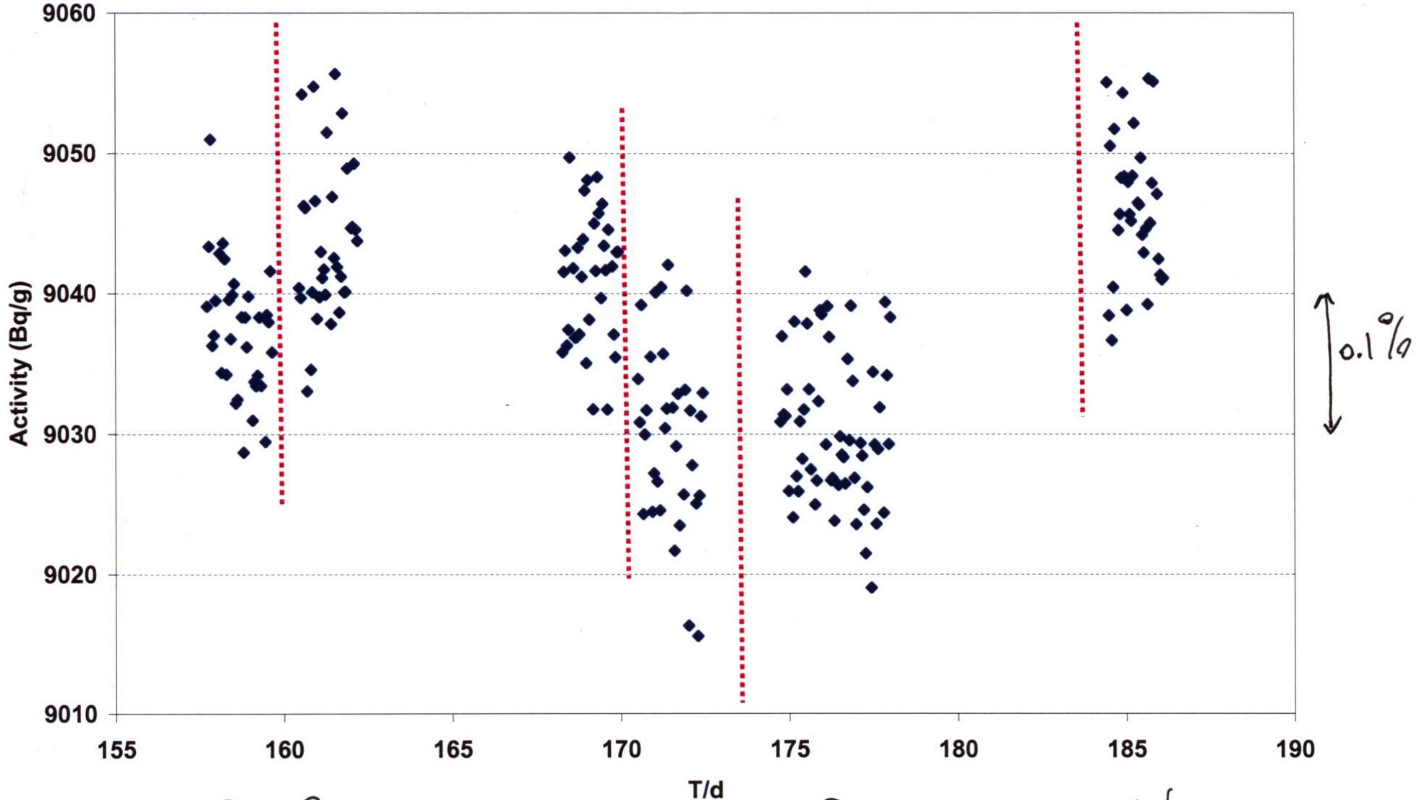
Series	Average	sd (%)	Normal	nc	ns	Counter	Scint	Age start	Age end	f_{H2O}	ε_{H-3}
	9037.397	0.029	Y	3	11	Packard	HS	0.21	2.12		
	9043.779	0.008	Y	3	11	Beckman	HS	2.95	4.65		
	9041.030	0.014	Y	3	11	Wallac	HS	10.76	12.4	0.1	0.36-0.30
1	9030.169	0.021	Y*	3	11	Packard	HS	13	14.9		
	9030.377	0.017	Y*	5	11	Packard	HS	17.22	20.46		
	9046.129	0.007	Y*	3	11	Wallac	HS	26.93	28.57		
	9034.269	0.031	N	5	7	Packard	PCS	0.11	4.06	0.01	
	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	
2	9044.048	0.014	Y	3	7	Wallac	PCS	4.78	6.91	0.04	0.40-0.22
	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

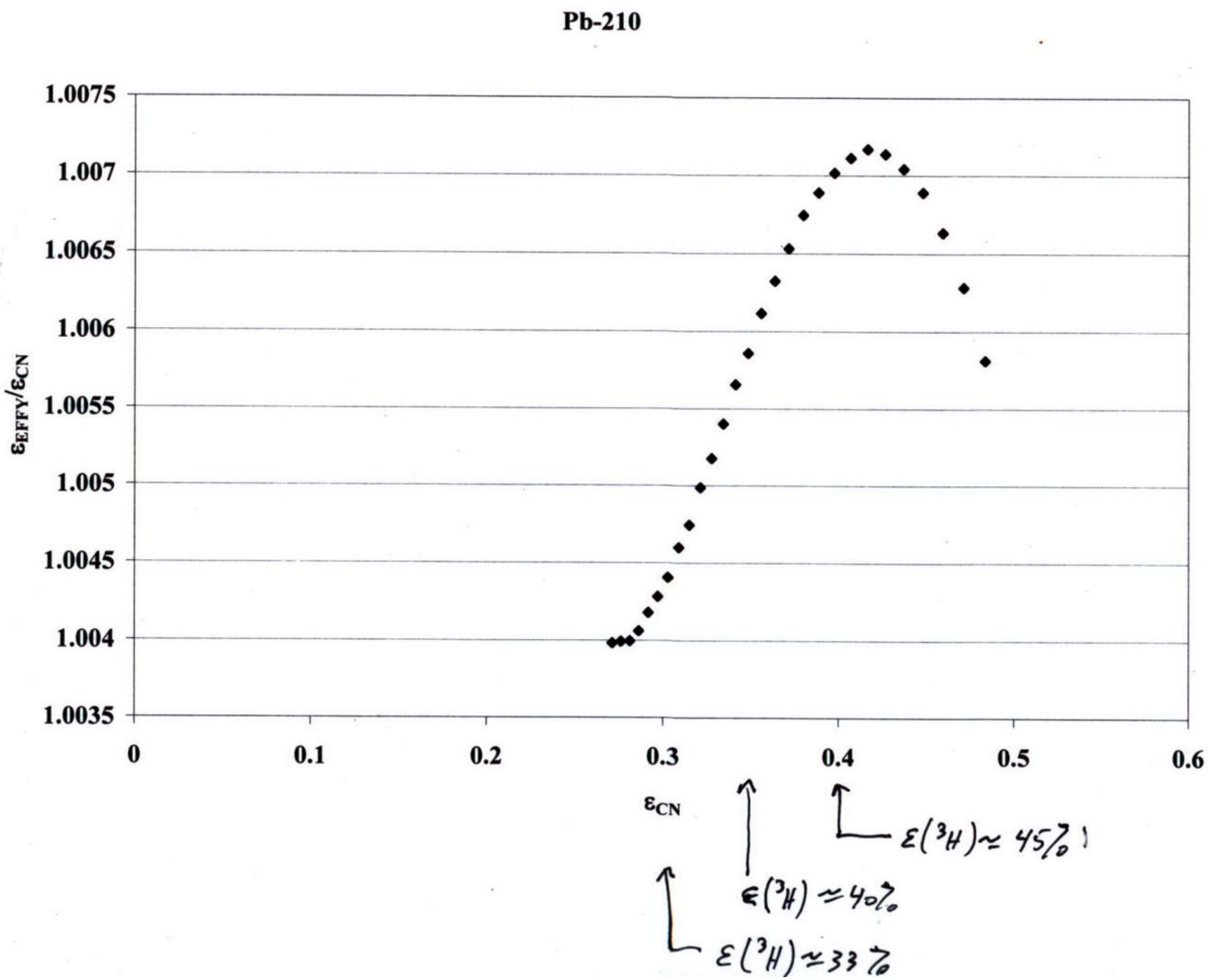


	P	B	W	P	P	W
cycles	3	3	3	3	5	3
×12 samples.	36	36	36	36	60	36

CN2003 vs EFFY4 code differences

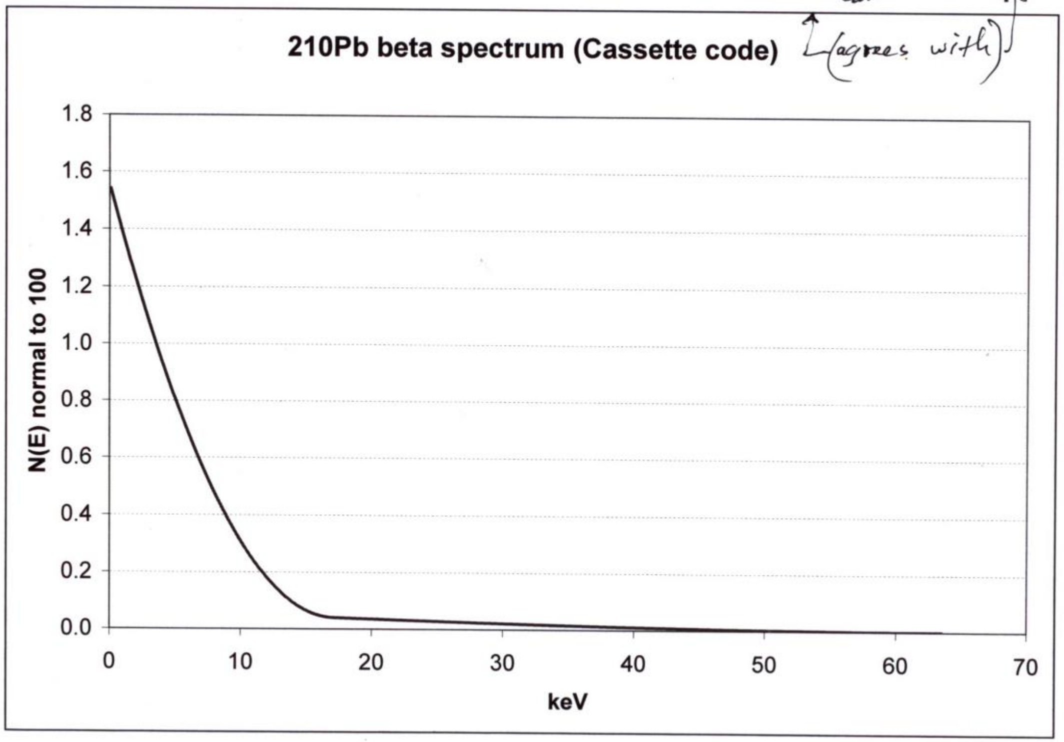
(just Beta efficiency part)

EFFY 4
CN 2003

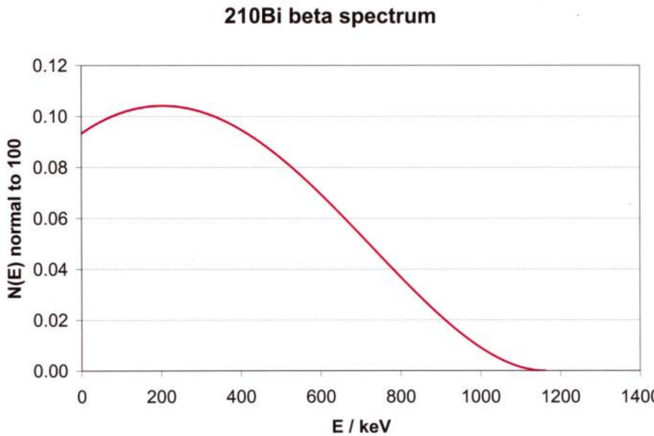


EFFY 4
CN2003 ← low E cutoff
Carine

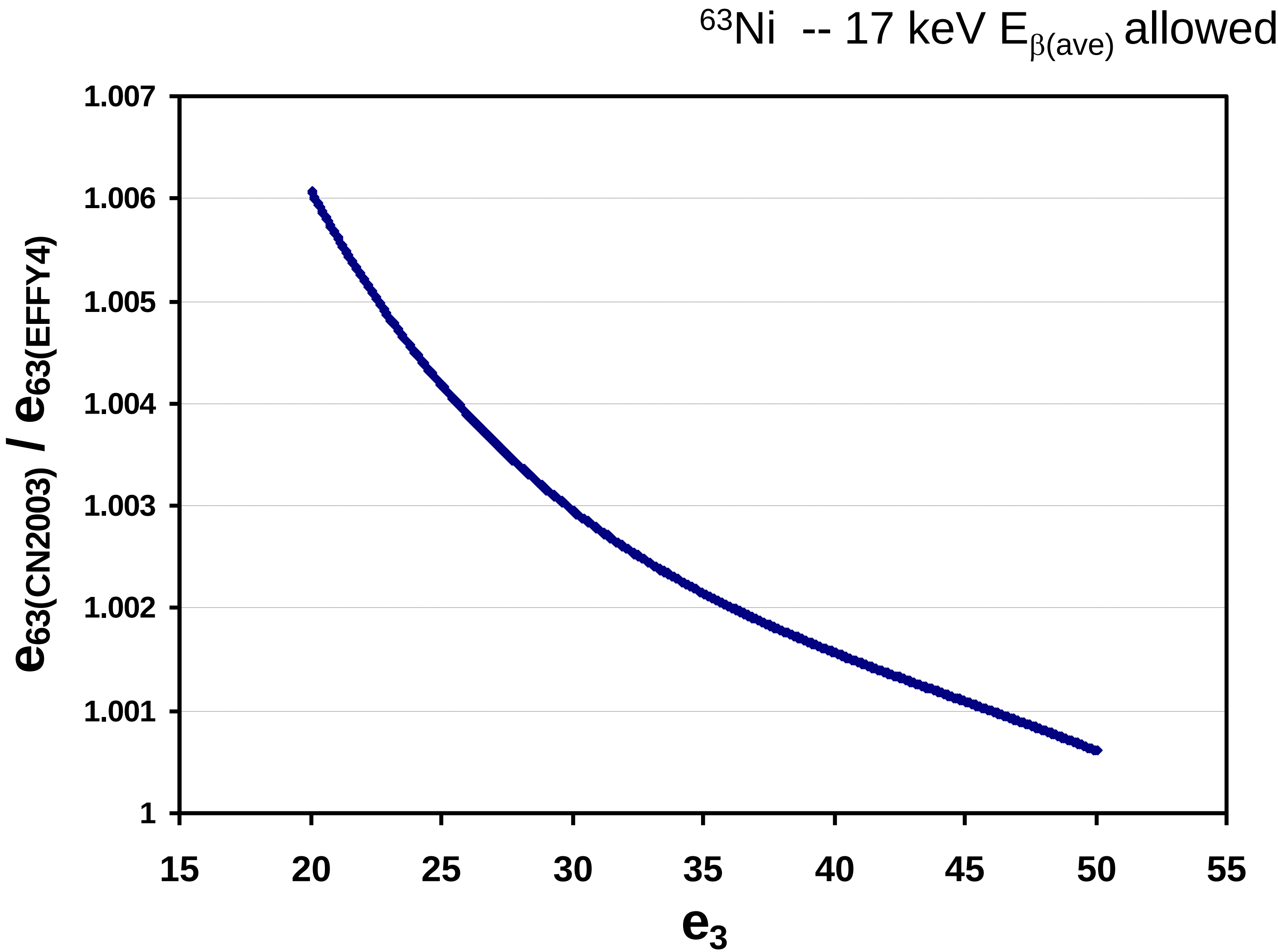
(agrees with)



differences not due to spectra



CN2003 vs EFFY4 code differences – due to assumed Quench function



^{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 %	might be wishful thinking
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

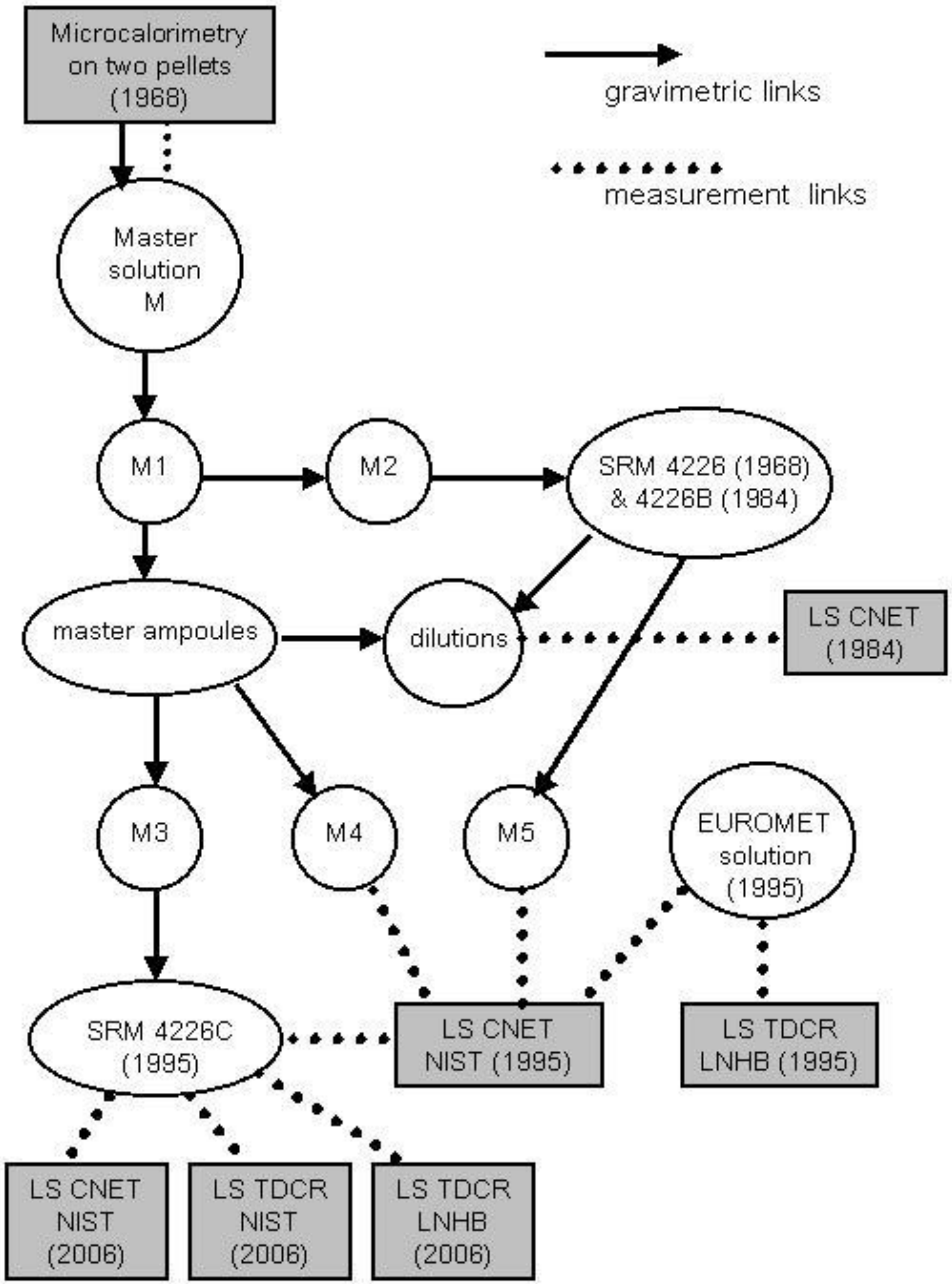
(1) LS cocktail composition effects

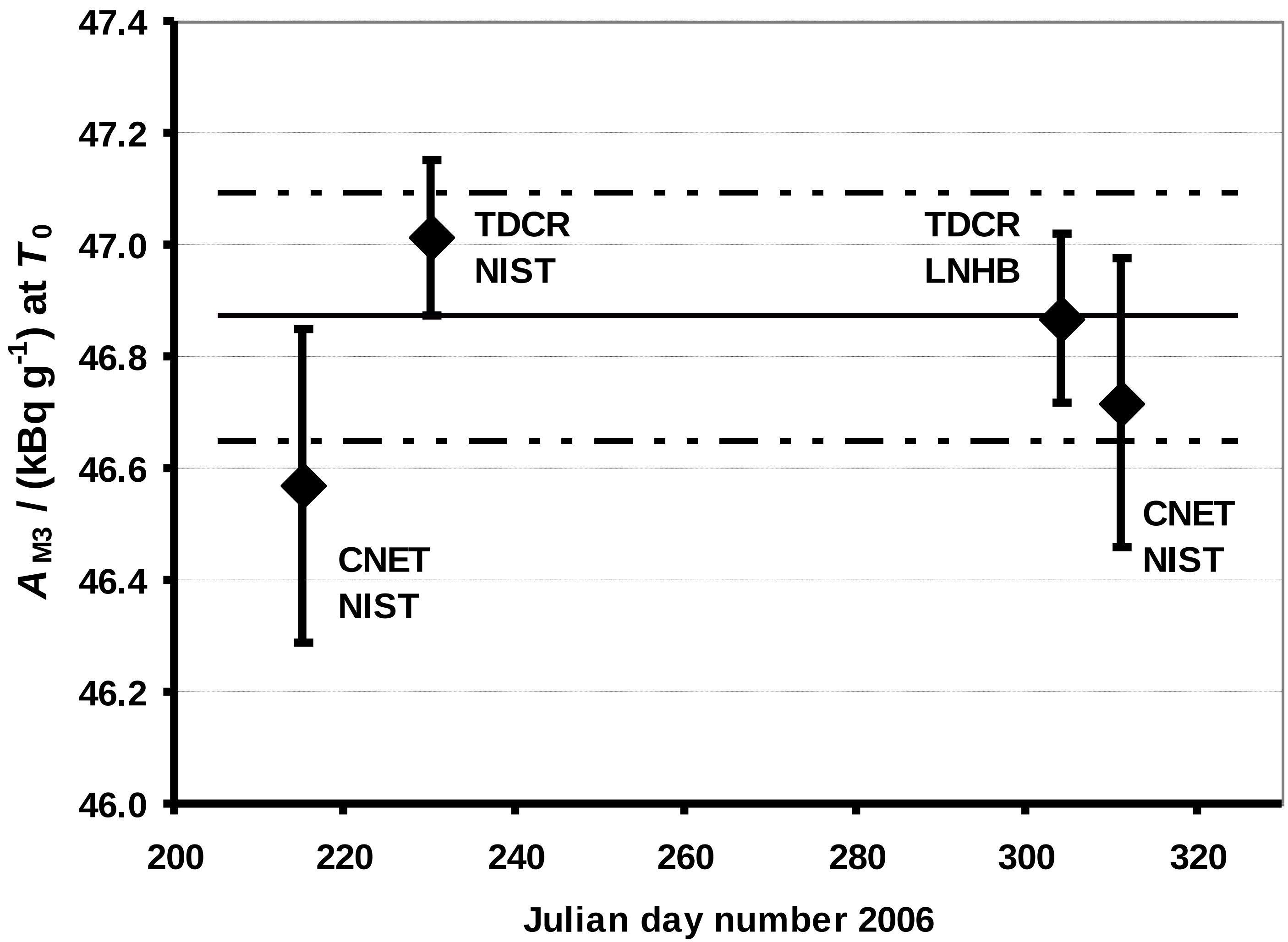
(2) tracing code differences & assumptions,

(3) lack of good confirmatory measurements,

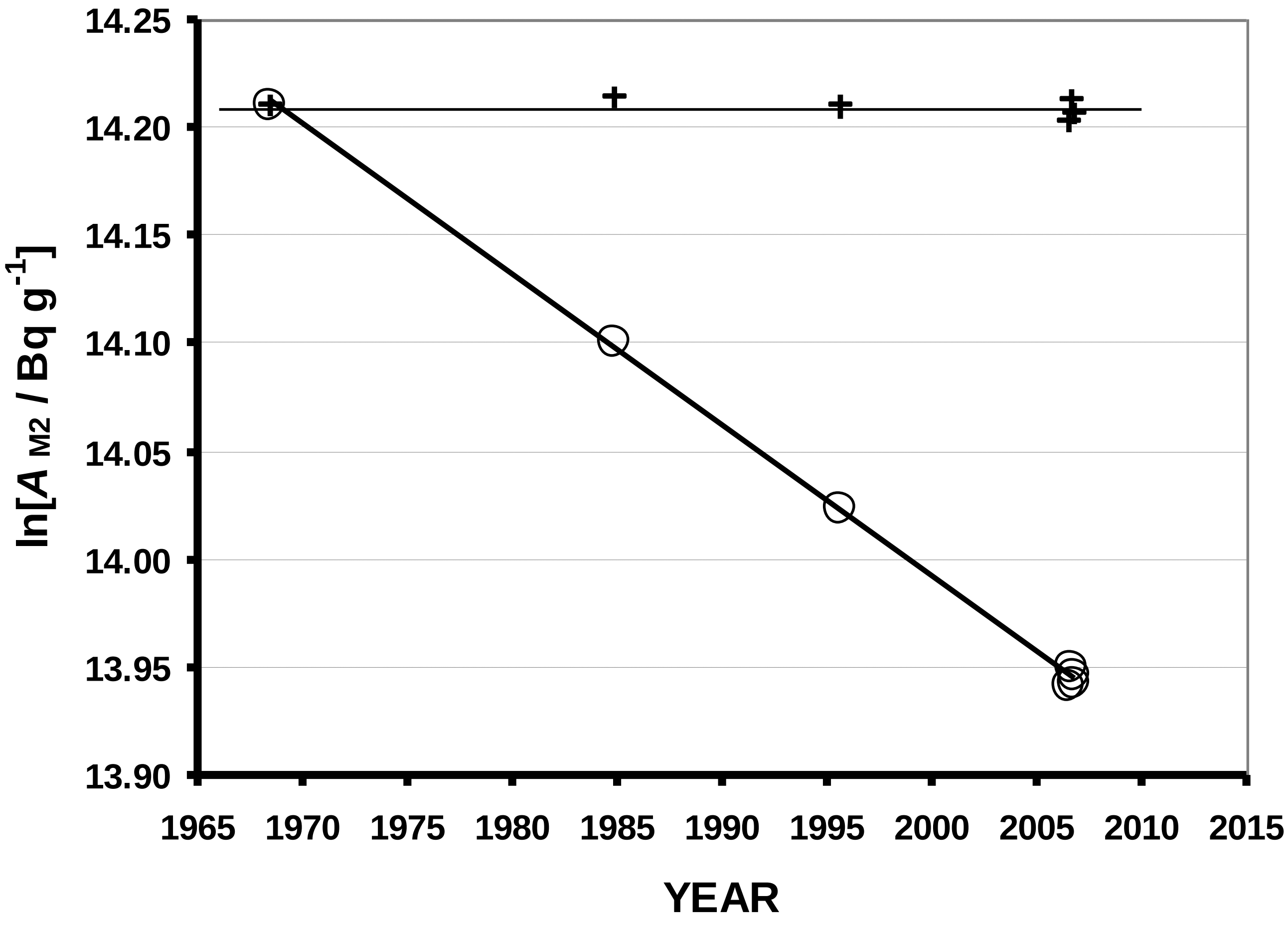
^{63}Ni

38 years of ^{63}Ni results





47.4
47.2
47.0
46.8
46.6
46.4
46.2
46.0
200
220
240
260
280
300
320
Julian day number 2006
A M3 / (kBq g-1) at T0
TDCR
NIST
TDCR
LNHB
CNET
NIST
CNET
NIST



14.25
14.20
14.15
14.10
14.05
14.00
13.95
13.90
ln[A M2 / Bq g-1]
1965
1970
1975
1980
1985
1990
1995
2000
2005
2010
2015
YEAR

Specific activity determination (Barnes, et al. 1971) = (101.2 ± 2.0) a.

Decay value from data up to 1995 = (101.1 ± 2.0) a.

Fitted values for the ^{63}Ni half-life as obtained from weighted nonlinear regressions

Data set used for fit	ν	$T_{1/2}$ / a	goodness of fit
All six values	4	100.7 ± 1.3	0.65
excludes 1984 CNET value	3	100.9 ± 1.4	0.70
excludes both 1984 & 1995 CNET values	2	100.9 ± 1.8	0.85
Excludes all three CNET values	1	101.2 ± 1.5	0.70

*T*1/2 (present determination) = (101.2 ± 1.5) a,

***T*1/2 (recommended) = (101.2 ± 1.2) a.**

55Fe SRM + BIPM intercomparison (link to calorimetry)

209Po / 210Pb problems

209Po half-life (Poland, France, NIST ?)

63Ni standardization & half-life --38 years (LNHB)

calorimetry / 14C half-life / (Columbia Univ.)

Si(Li) x-ray detection

LIZBETH

SRMs to Stock

	Year	**NEI**	**Rewritten (w/o meas)**	**Recertified (w/meas)**	**New (others)**	**New (SRM)**
Old Era	2002	9	0	0	0	0
	2003	9	0	0	0	^{232}U
	2004	9	^{3}H (2)	0	0	^{226}Ra
	2005	9	0	0	0	0
New Era	2005	9	^{63}Ni	^{243}Am, ^{209}Po	^{226}Ra/^{222}Rn (4)	^{60}Co ^{137}Cs
	2006	9	^{240}Pu , ^{244}Cm, ^{133}Ba, ^{129}I	(^{63}Ni)	Seaweed	^{55}Fe, ^{166m}Ho, ^{210}Pb
	2007 to date	2	^{3}H (3), ^{226}Ra Natural Uranium	0	Rocky Flats #2 ^{226}Ra (2)	^{90}Sr (2)

^{60}Co

- 48 ampoules prepared in 2003
- Ion Chamber “A” measurements in 2004

- Ion Chamber “A” measurements in 2005
  - Two occasions
- Data reconciliation
- Certified

^{137}Cs

- 100 ampoules prepared in 2000
- Ion Chamber “A” measurements in 2001
  - 4 occasions

- Data reconciliation for 2001 measurements in 2005
- Re-measurement in Ion Chamber “A” in 2005
- Data Reconciliation
- Certified

^{55}Fe and ^{210}Pb

^{55}Fe

- Master and ampoules prepared in 2005
- LS measurements
- Intercomparison
- Certified

^{210}Pb

- Ampoules prepared in 1999

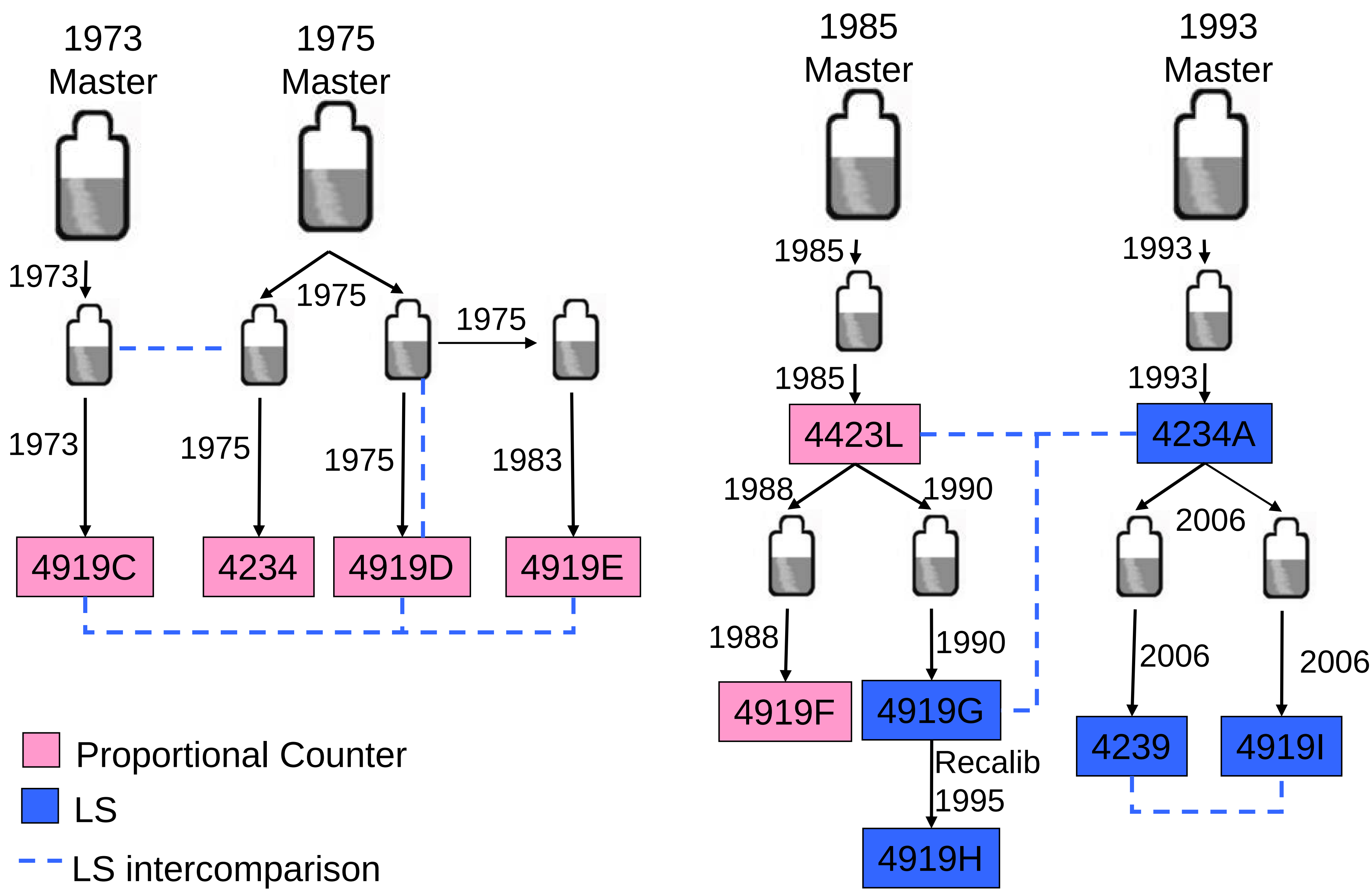
- LS measurements in 2006
- Certified

^{166m}Ho

- 226 ampoules prepared in 1997
- IC measurements in 1997

- High resolution gamma-ray spectrometry
  - gamma-ray emission rates
- IC Measurements in 2006 for confirmation
  - (based on K-value from Lucas with NaI total γ)
- Data reconciliation
- Certified

Sr-90 History



^{90}Sr

Two activity levels

- High- LS CNET
  - 294 activity determinations, variables include
    - 7 samples
    - 3 counters (one to two occasions)
    - 3 to 5 cycles
    - 3 cocktails composition
    - 15 day aging
- Low
  - 6 activity ratios for dilution confirmation

Recent Comparison of Primary Methods

Nuclide	Methods	% Difference
^{63}Ni	TDCR (LNHB) TDCR (BEZ) CNET	-0.31% 1 -0.77%*
^{90}Sr	TDCR (BEZ) CNET	1 +0.09%
^{210}Pb	CNET Anticoincidence β(LS)-γ(NaI)	1 +0.7%
^{241}Pu	TDCR (BEZ) CNET	Coming
^{241}Am	CNET Anticoincidence β(LS)-γ(NaI)	Coming

* was +0.16% from certificate

Working on…

^{230}Th (ampoules prepared)
^{241}Pu (material at hand)
^{241}Am (material at hand)
^{242}Pu (buy back & dilute)
^{228}Ra -Jerry

Next

^{209}Po
^{63}Ni
^{99}Tc

Later

^{244}Cm
^{229}Th

Projected Out of Stock

SRM	Name	Status
4353	Rocky Flats Soil #2	Out of Stock
4342	Thorium-230	Out of Stock
4340A	Plutonium-241	Out of Stock
4322B	Americium-241	Out of Stock
4326	Polonium-209	Out of Stock
4339A	Radium-228	Out of Stock
4320A	Curium-244	Out of Stock
4328B	Thorium-229	Out of Stock
4355	Peruvian Soil Powder	Out of Stock
4332D	Americium-243	Jun-07
4966	Radium-226	Sep-07
4357	Ocean Sediment	Jan-08
4218F	Europium-152 PS	Mar-08
4341	Neptunium-237	May-08
4927F	Hydrogen-3	Jul-08
4973	Radon-222 Emanation std	Aug-08
4354	Lake Sediment	Nov-08
4325	Beryllium-10/9	Jan-09
4334H	Plutonium-242	Mar-09
4926E	Hydrogen-3	Apr-09
4226C	Nickel-63	Jun-09
4974	Radon-222 Emanation std	Jun-09
4990C	Oxalic Acid	Jan-10
4350B	River Sediment	May-10
4943	Chlorine-36	May-10
4361C	Hydrogen-3	Jun-10
4949C	Iodine-129	Sep-10

Projected Out of Stock

4222C	Carbon-14 (as hexadecane)	Jan-11
4965	Radium-226	Mar-11
4947C	Hydrogen-3 (Toluene)	Jul-11
4321C	Natural Uranium	Aug-11
4929F	Iron-55	Nov-11
4324B	Uranium-232	Dec-11
4967A	Radium-226	Feb-12
4251C	Barium-133	Mar-12
4323B	Plutonium-238	Jun-12
4338A	Plutonium-240	Nov-12
4972	Radon-222 Emanation std	Jan-14
4241C	Barium-133 PS	Mar-14
4329	Curium-243	Mar-14
4330B	Plutonium-239	Mar-14
4351	Human Lung	Nov-14
4233E	Cesium-137	Dec-18
4971	Radon-222	Sep-19
4370C	Europium-152	Apr-23
4356	Ashed Bone	Jan-24
4352	Human Liver	Dec-24
4969	Radium-226	Feb-27
4201B	Niobium-94	Apr-51
4274	Holmium-166m	N/A
4337	Lead-210	N/A
4359	Seaweed	N/A

SRMs Sale History

March 9

	FY01	FY02	FY03	FY04	FY05	FY06	YTD
Total	554	492	483	528	482	424	177
NEI	135	136	107	123	116	109	42
Natural Matrix	57	18	60	88	62	36	7
SRM Program	362	338	316	317	304	279	128

Must think about NOW

^{3}H

SRM Number	Out of Stock	Activity Level	Volume/ Container
4927F	July 2008	600 $kBq \cdot g^{-1}$	5-mL ampoule
4926E	April 2009	5 $kBq \cdot g^{-1}$	20-mL septum vial
4361C	June 2010	2 $Bq \cdot g^{-1}$	500-mL bottle

Who? When? What plan?

3H plans !

Ampoules

Jupitor balance

Chemicals in attic (who responsible)

Prep. Help – 242Pu re-do (dispense & sealing)
241Pu (ophelia + dan prep)
241Am (ophelia + dan prep)
228Ra (jerry chem)
229Th (ken....)

Calib. Help – 241Pu (brian)
241Am (ryan)