Standardization of ^{55}Fe by Isothermal Microcalorimetry

(and its use for a NIST SRM calibration & in the BIPM intercomparison)

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Saclay, France
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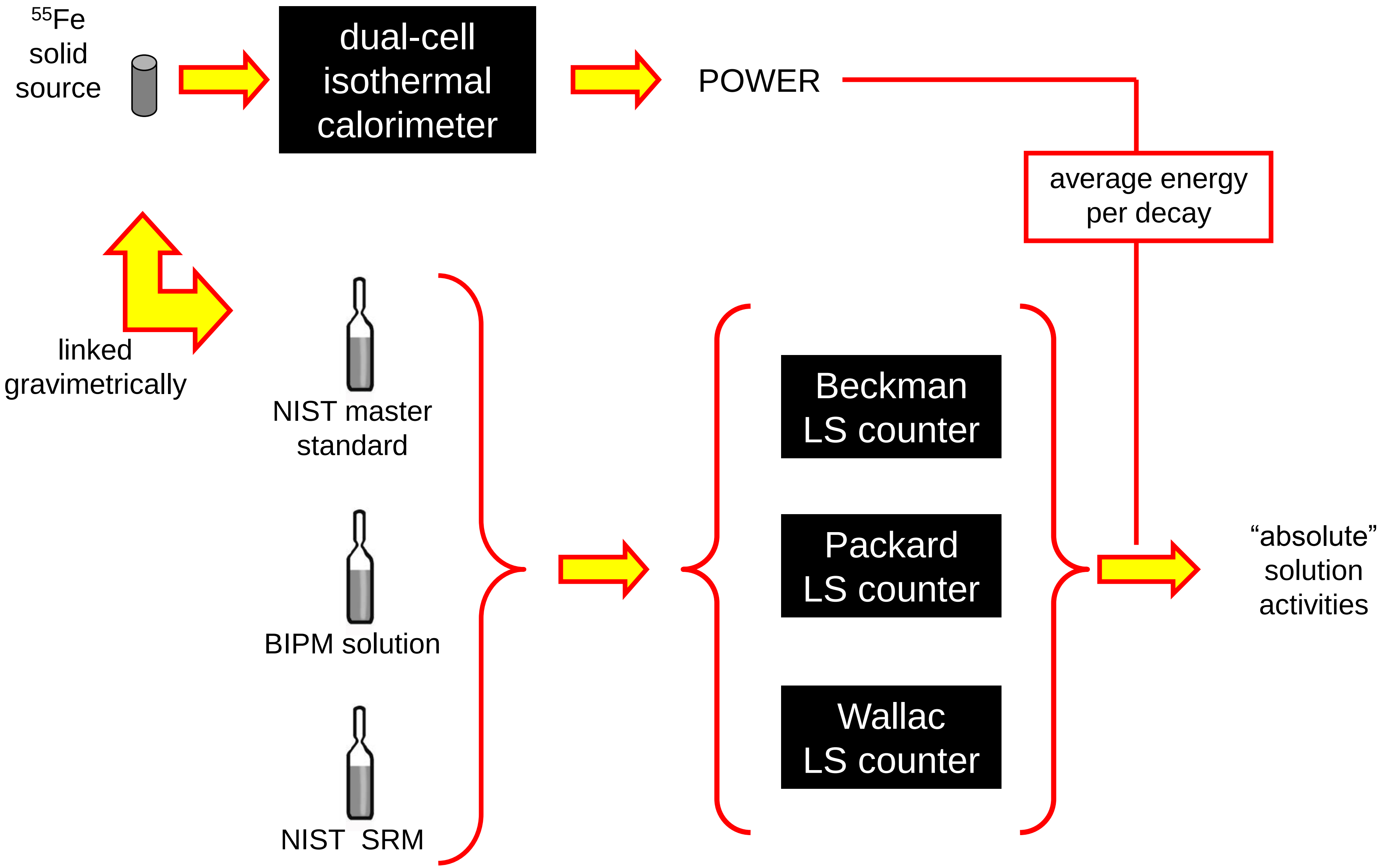
SUBTITLE:

How to do “absolute” (primary) standardizations

with BLACK BOXES .....



55Fe 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

1456 days

ago

calorimetric-based standardizations of brachytherapy sources

2000-2003

- verified extant calibration factors for (i) *Radiance* ^{32}P “hot-wall” angioplasty balloons and (ii) *Novoste* old-style, ceramic-cored, ^{90}Sr - ^{90}Y intravascular seeds

- performed primary standardization for *Novoste*, new-generation, aluminum-cored ^{90}Sr seeds to establish calibration factors

- primary standardization for 103Pd for calibration of *Theragenics* prostate seeds

This work on ^{55}Fe

is another foray by NIST

into a microcalorimetric-based,

primary (“absolute”) radionuclidic standardization ...

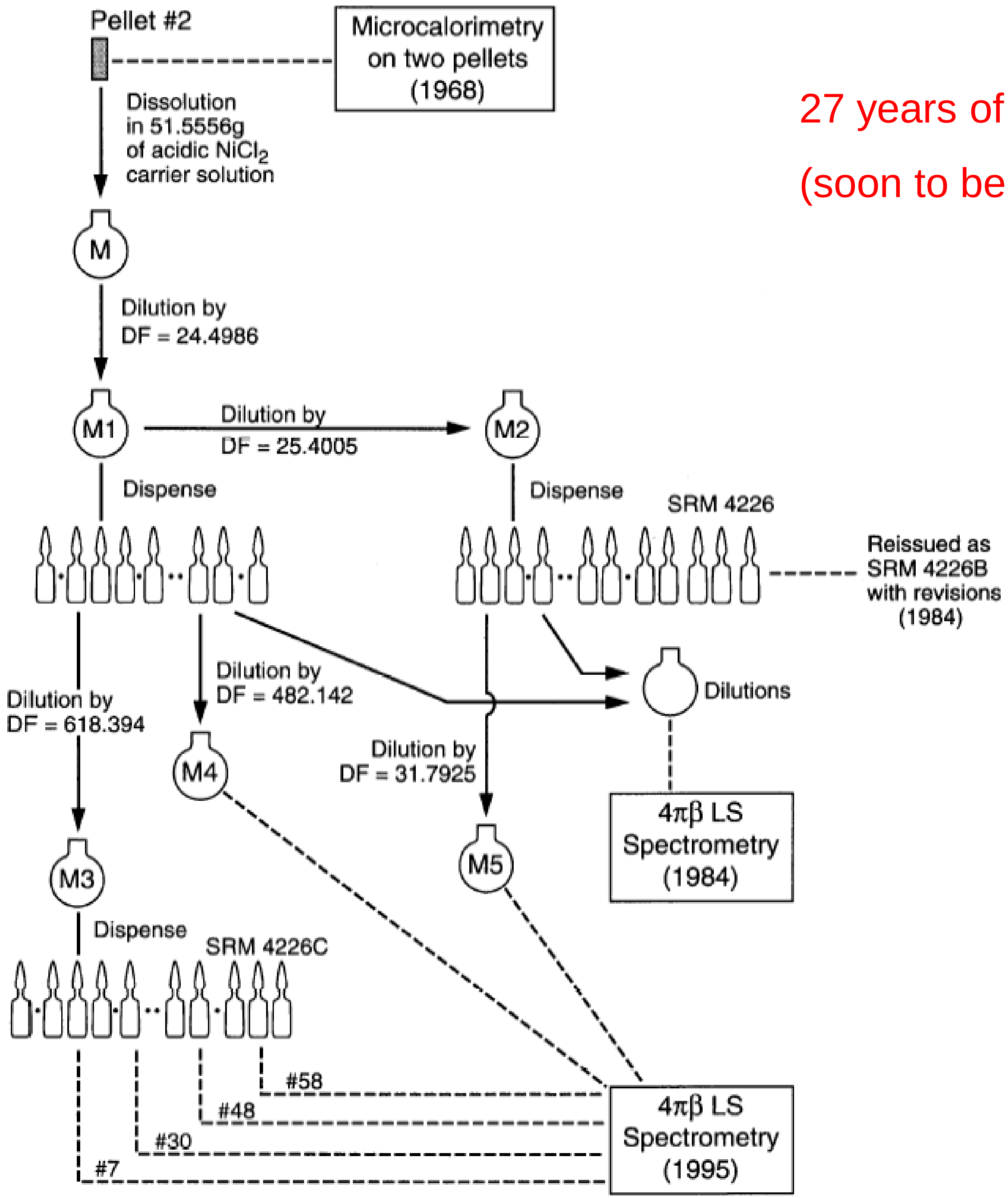
Which dates back to the seminal work

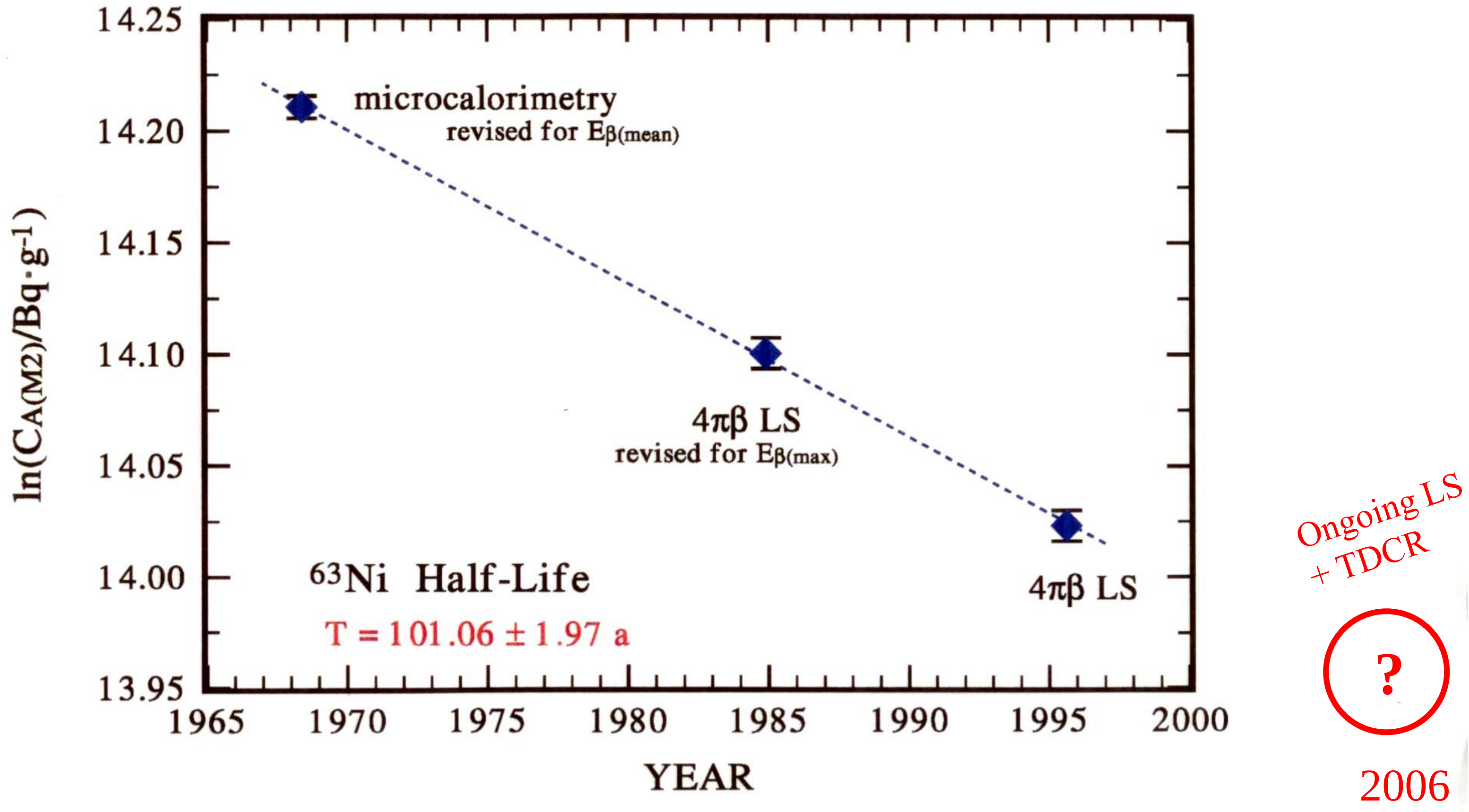
of Mann, et al. in 1968 on ^{63}Ni.....

If you recall ...

27 years of ^{63}Ni “traceability” work

(soon to be 38 years !)

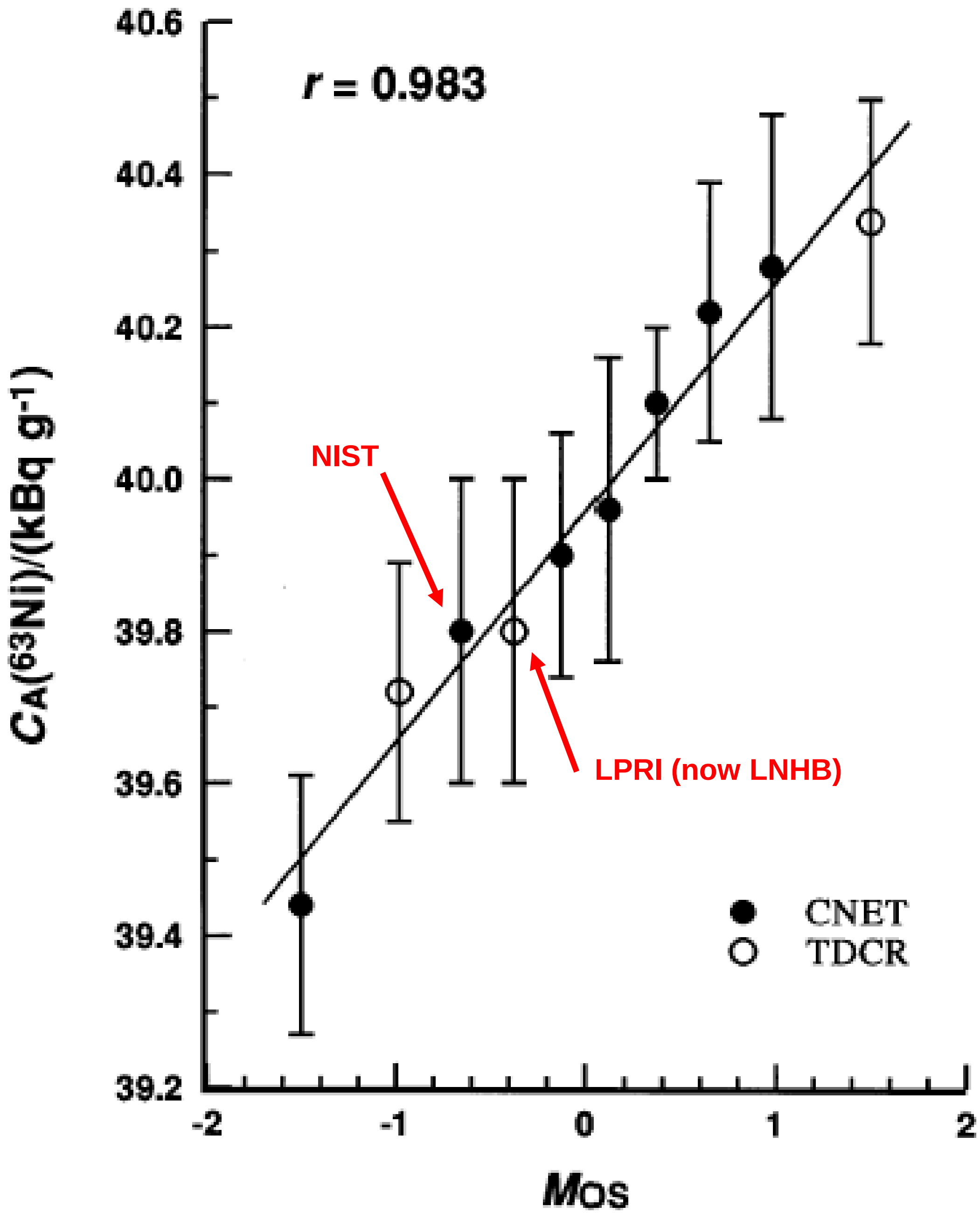




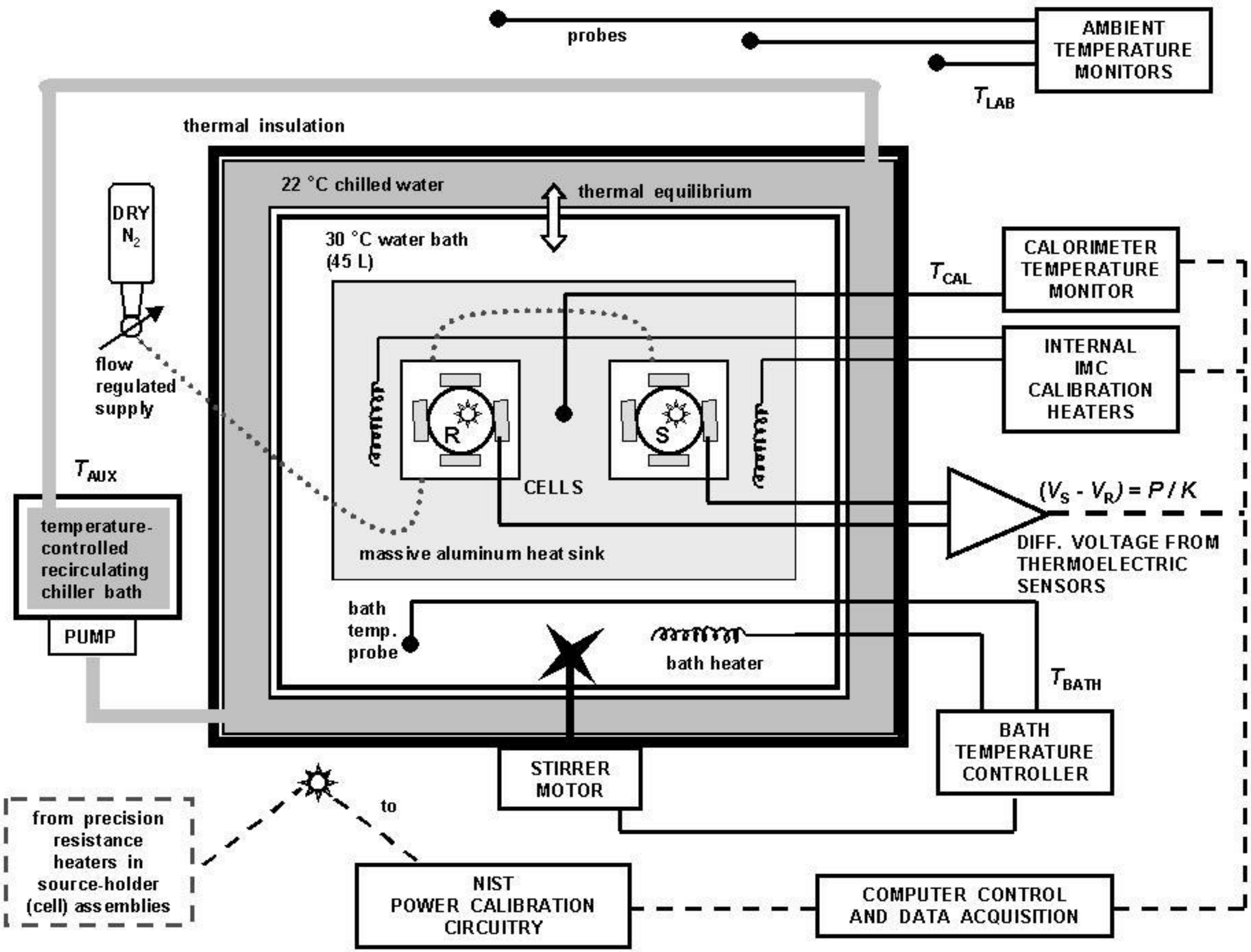
14.25
14.20
14.15
14.10
14.05
14.00
13.95
ln(CA(M2)/Bq·g-1)
microcalorimetry
revised for Eβ(mean)
4πβ LS
revised for Eβ(max)
4πβ LS
63Ni Half-Life
T = 101.06 ± 1.97 a
1965
1970
1975
1980
1985
1990
1995
2000
YEAR
Ongoing LS
+ TDCR
?
2006

And we sort of think we know what we are doing ....

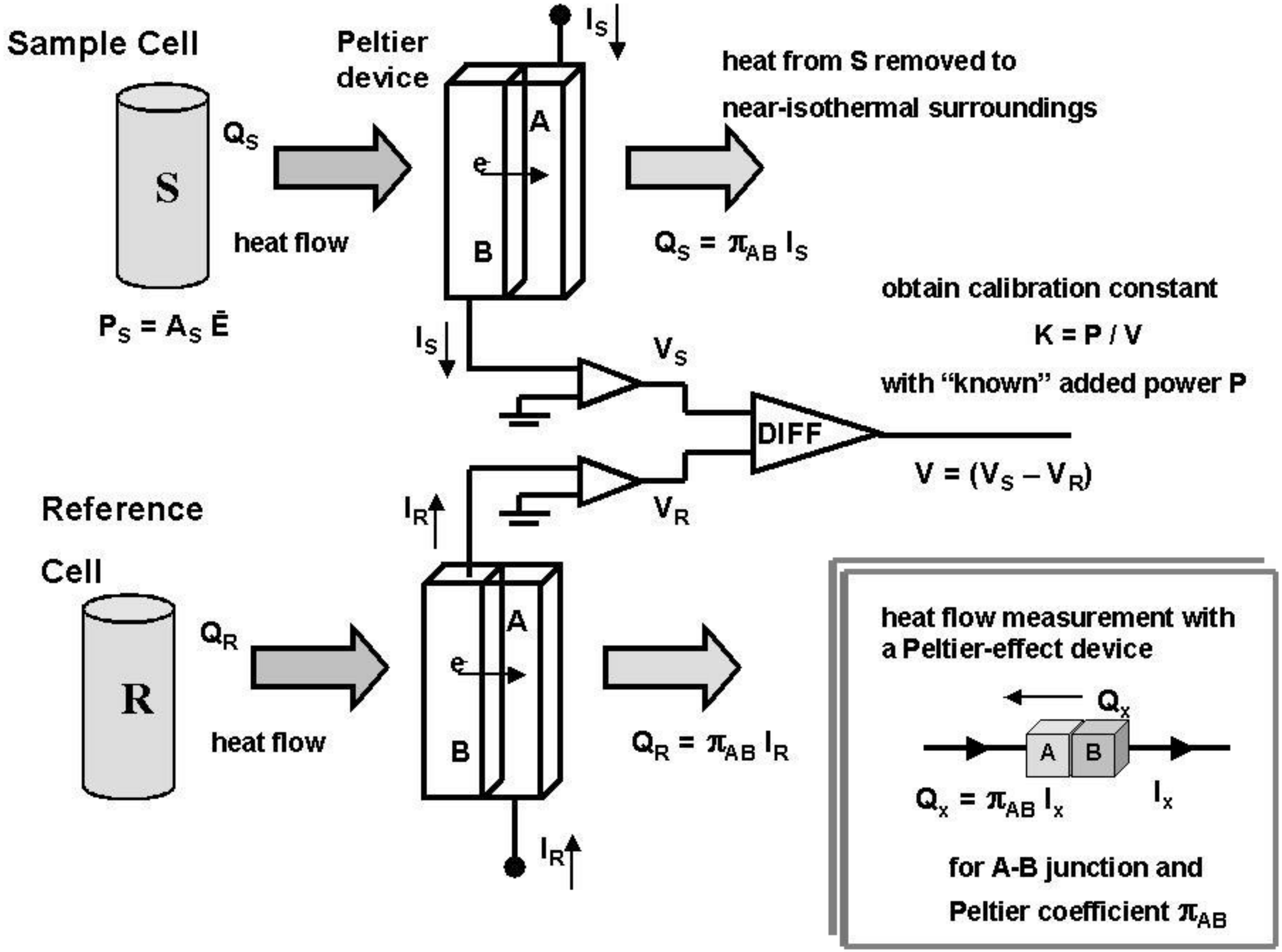
at least with respect to you !



CSC “Isothermal Microcalorimeter (IMC)”



probes
AMBIENT TEMPERATURE MONITORS
T_{LAB}
thermal insulation
22 °C chilled water
thermal equilibrium
DRY N_2
30 °C water bath (45 L)
T_{CAL}
CALORIMETER TEMPERATURE MONITOR
INTERNAL IMC CALIBRATION HEATERS
flow regulated supply
R
S
CELLS
$(V_S - V_R) = P / K$
DIFF. VOLTAGE FROM THERMOELECTRIC SENSORS
T_{AUX}
temperature-controlled recirculating chiller bath
PUMP
massive aluminum heat sink
bath temp. probe
bath heater
T_{BATH}
BATH TEMPERATURE CONTROLLER
STIRRER MOTOR
to
from precision resistance heaters in source-holder (cell) assemblies
NIST POWER CALIBRATION CIRCUITRY
COMPUTER CONTROL AND DATA ACQUISITION



Sample Cell
S
Q_S
heat flow
$P_S = A_S \bar{E}$
Peltier device
I_S
A
e
B
heat from S removed to
near-isothermal surroundings
$Q_S = \pi_{AB} I_S$
obtain calibration constant
$K = P / V$
with “known” added power P
V_S
DIFF
$V = (V_S - V_R)$
V_R
Reference Cell
R
Q_R
heat flow
I_R
A
e
B
$Q_R = \pi_{AB} I_R$
heat flow measurement with a Peltier-effect device
Q_x
A
B
$Q_x = \pi_{AB} I_x$
I_x
for A-B junction and
Peltier coefficient π_{AB}

Basic relationship between

Rate of energy (heat) input , or power *P*,

and

Activity *A*

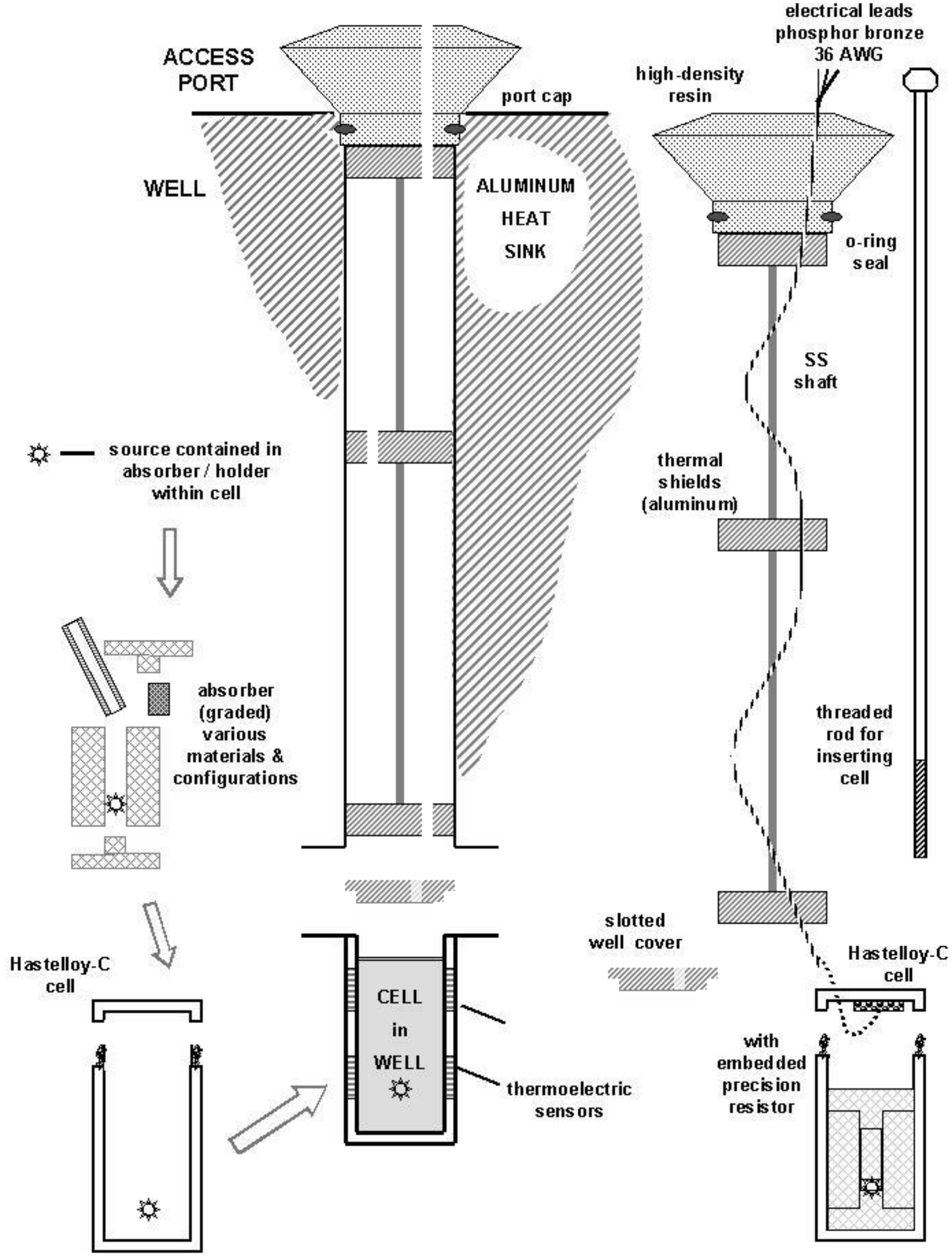
is $$\mathrm{d}H/\mathrm{d}t = P = A\,\hat{E}$$

$\hat{E}$ **= average energy per decay**

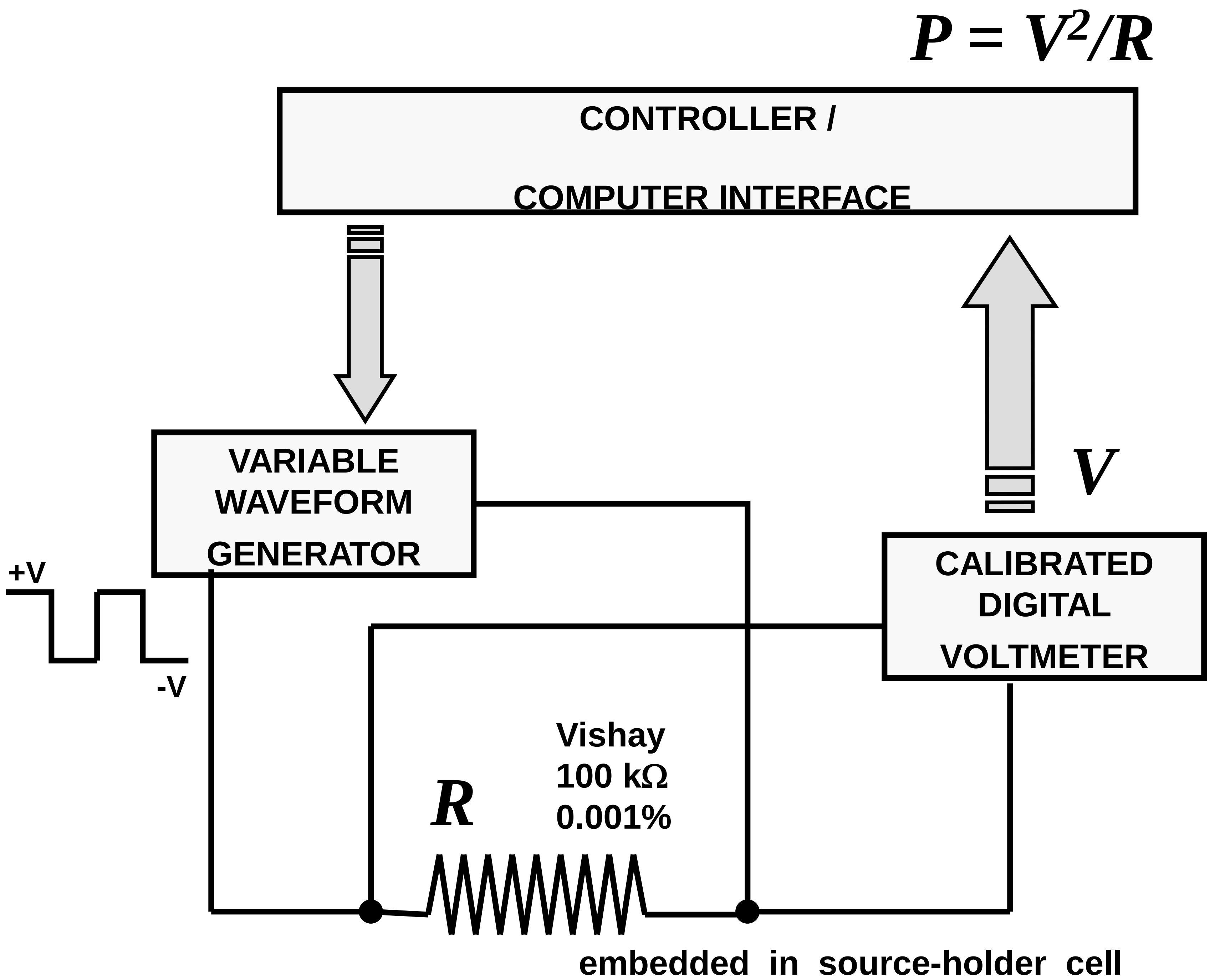
^{3}H / ^{55}Fe	0.9	$\mu W \cdot GBq^{-1}$
^{103}Pd / ^{125}I	9.	
^{32}P	111.	
^{90}Sr-^{90}Y	181.	
^{226}Ra	4338.	

Assumes absorb & measure ALL ionizing radiation (no losses)

And no “heat defect” effects (I.e., no chemistry)


ACCESS PORT
WELL
port cap
ALUMINUM HEAT SINK
electrical leads phosphor bronze 36 AWG
high-density resin
o-ring seal
SS shaft
thermal shields (aluminum)
threaded rod for inserting cell
source contained in absorber / holder within cell
absorber (graded) various materials & configurations
slotted well cover
Hastelloy-C cell
CELL in WELL
thermoelectric sensors
Hastelloy-C cell
with embedded precision resistor

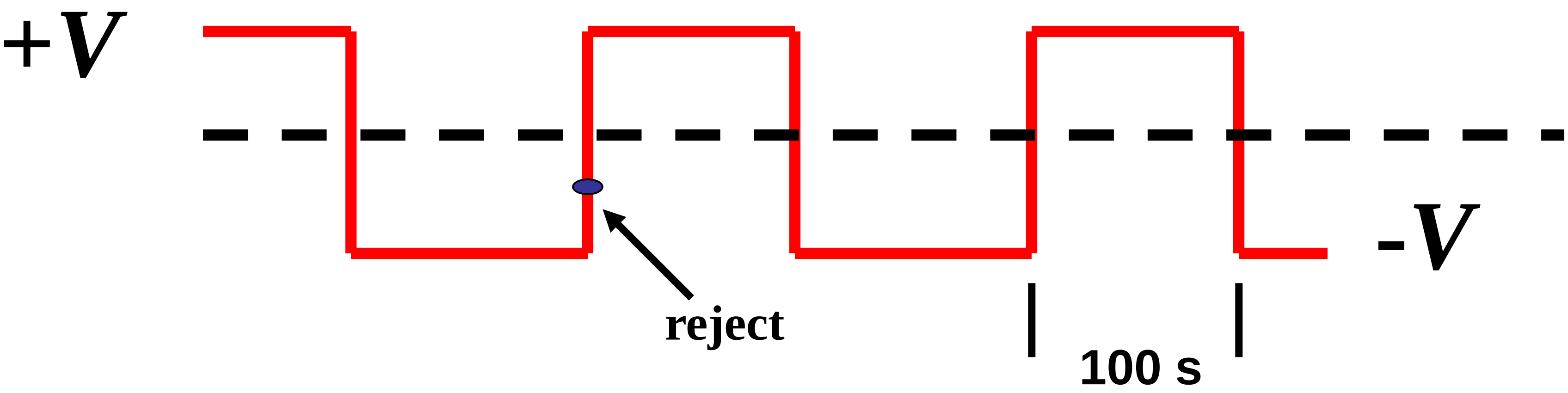
port assemblies -- source (absorbers) holders & cells



$P = V^2/R$
CONTROLLER /
COMPUTER INTERFACE
VARIABLE
WAVEFORM
GENERATOR
+V
-V
CALIBRATED
DIGITAL
VOLTMETER
V
R
Vishay
100 kΩ
0.001%
embedded in source-holder cell

$|+V| = |-V|$

$f = 0.005\ s^{-1}$



$$P = V^2 / R$$

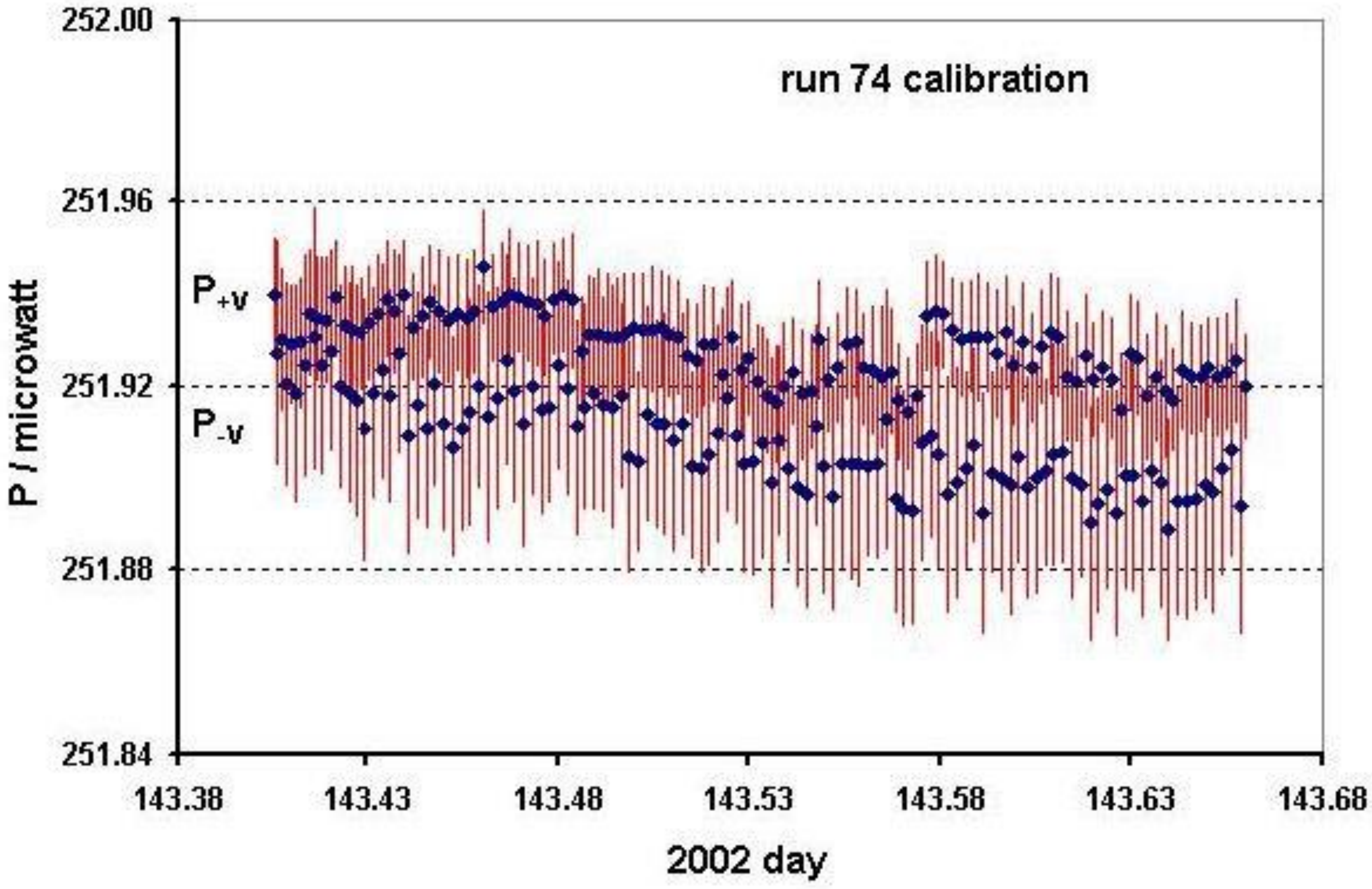
Average 100 points ($1\ s^{-1}$) $\Rightarrow$ P_{+V} or P_{-V}

mean (P) = 1/2 mean (P_{+V}) + 1/2 mean (P_{-V})

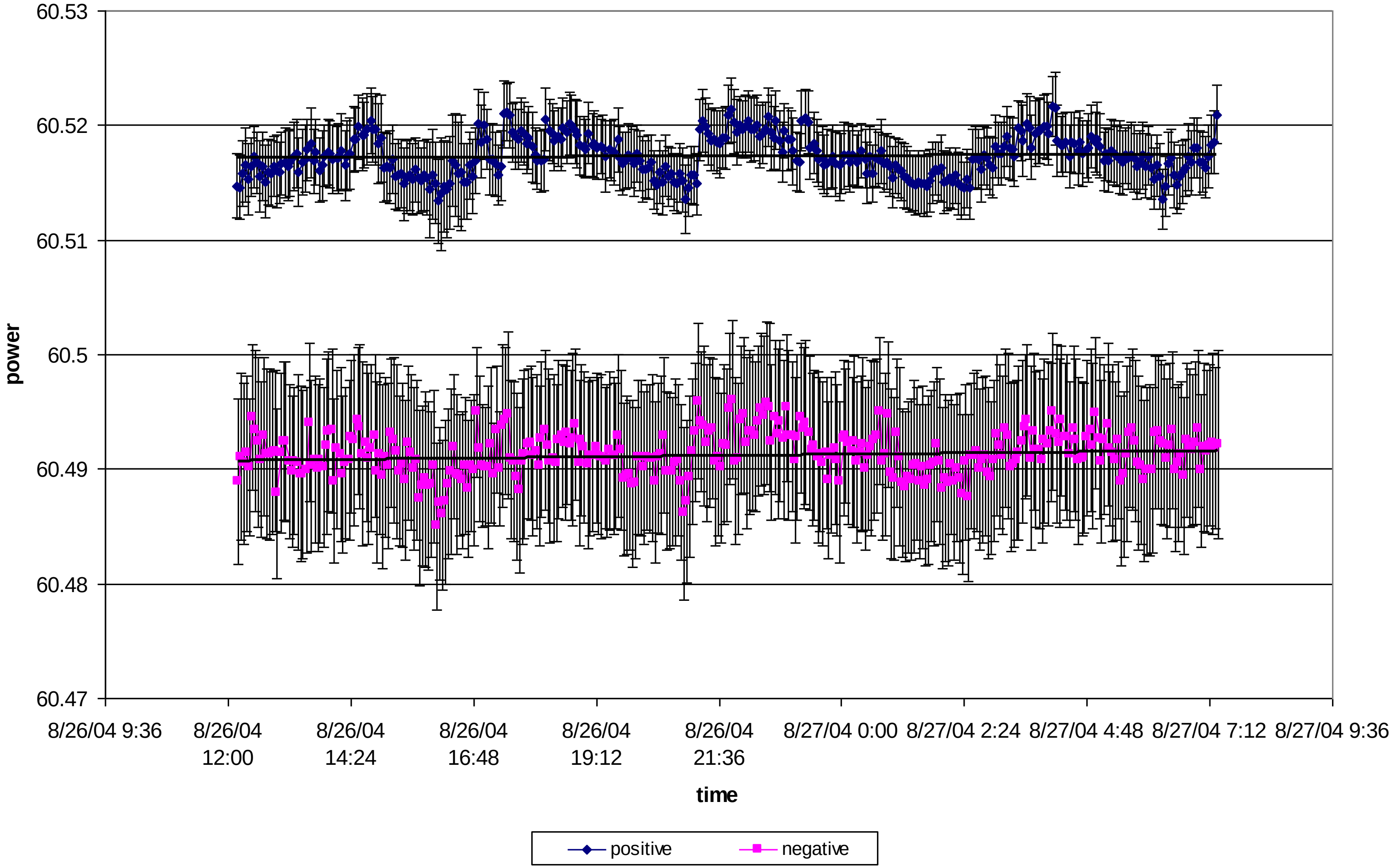
var (P) = 1/2 var (P_{+V}) + 1/2 var (P_{-V}) + covar (P_{+V}, P_{-V})

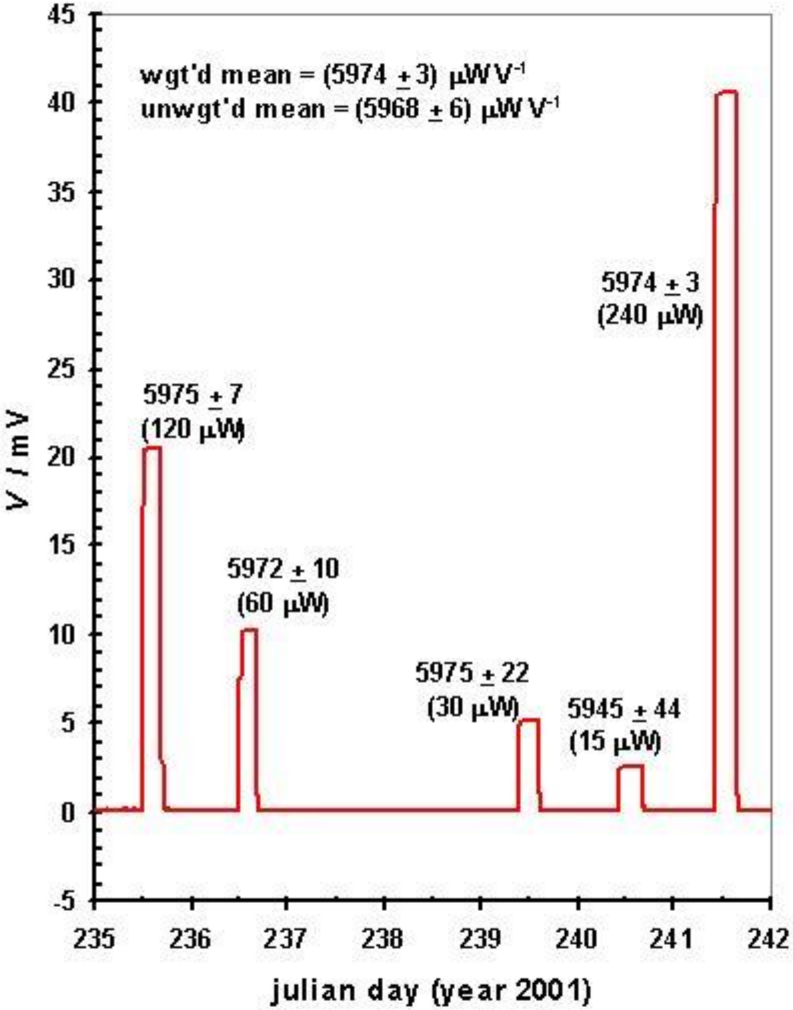
+ autocorr(P_{+V}) + autocorr(P_{-V})

So, the calibration data kind of looks like this ...

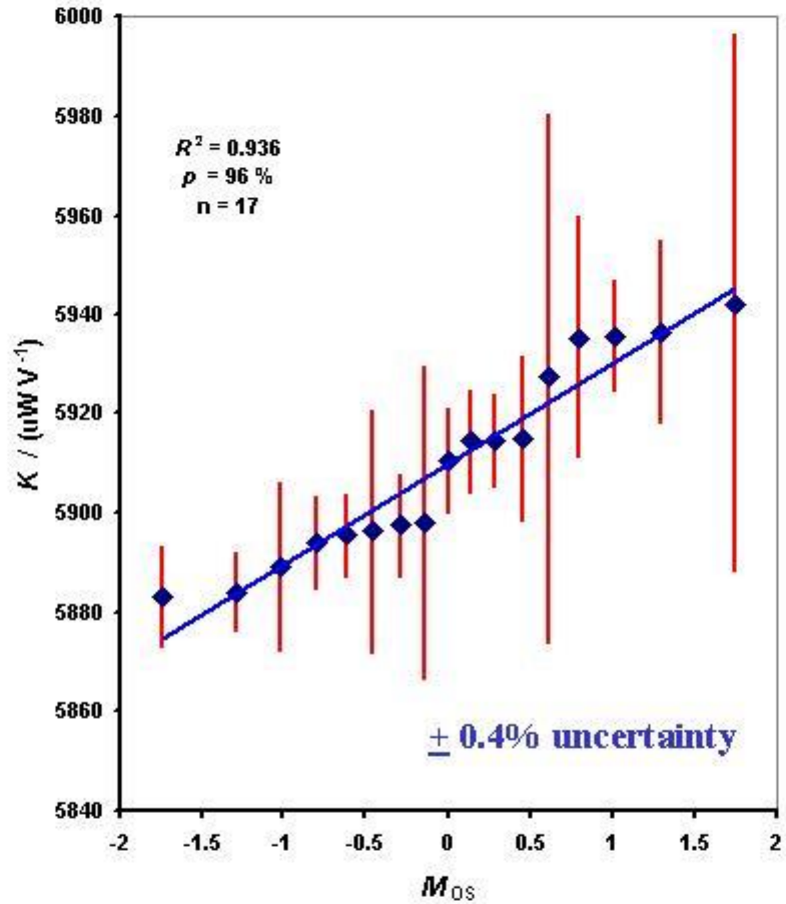


Run 132 (^{55}Fe) –calibration 4





typical calibration data set



Filliben normality test for calibration data (Novoste seeds)

Two cases

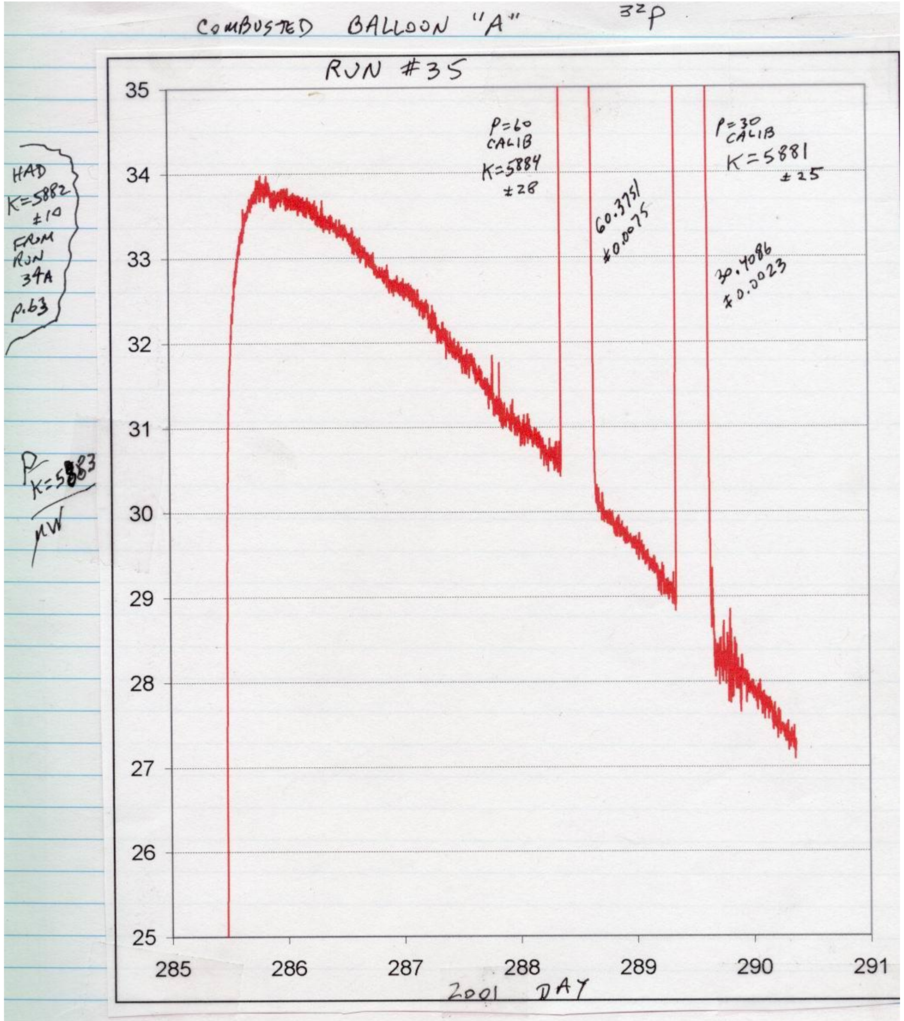
(with different measurement requirements)

-- for decaying short-lived nuclides

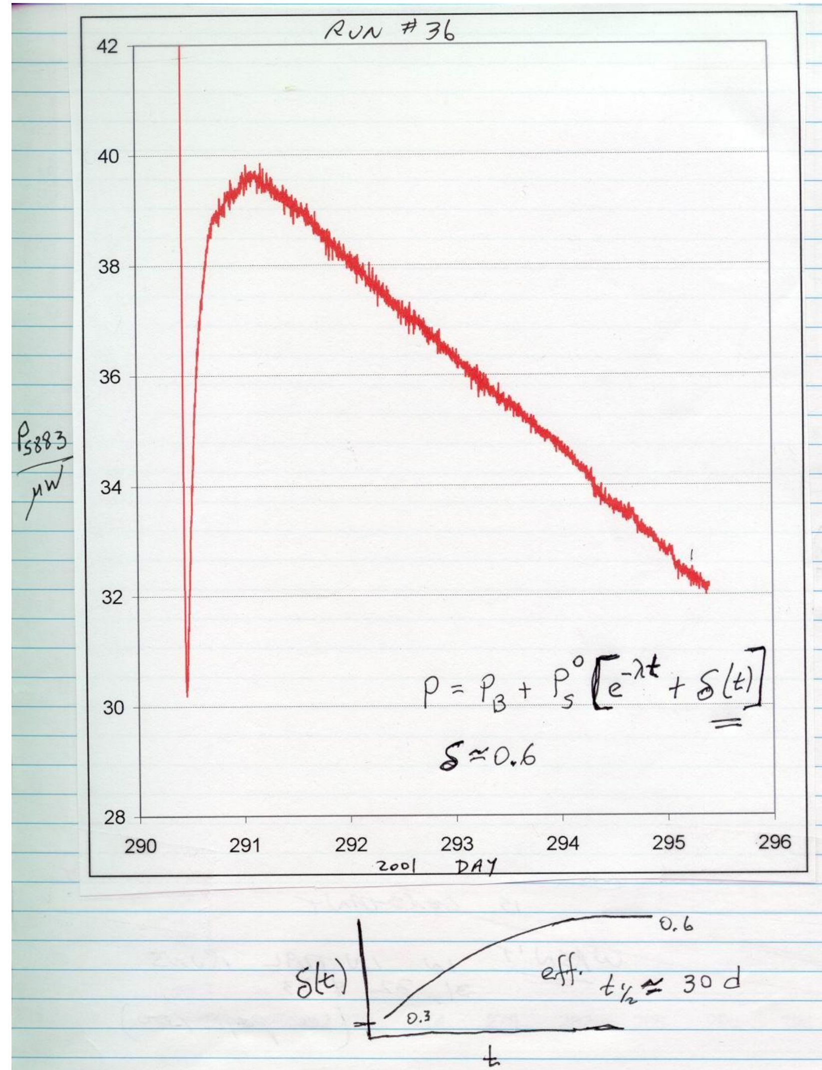
-- for long-lived nuclides (need baseline determinations)

...and source “heat defect / heat excess” precautions

Historic measurement & calibration data illustrate these



IMC Lab Book II, p.79



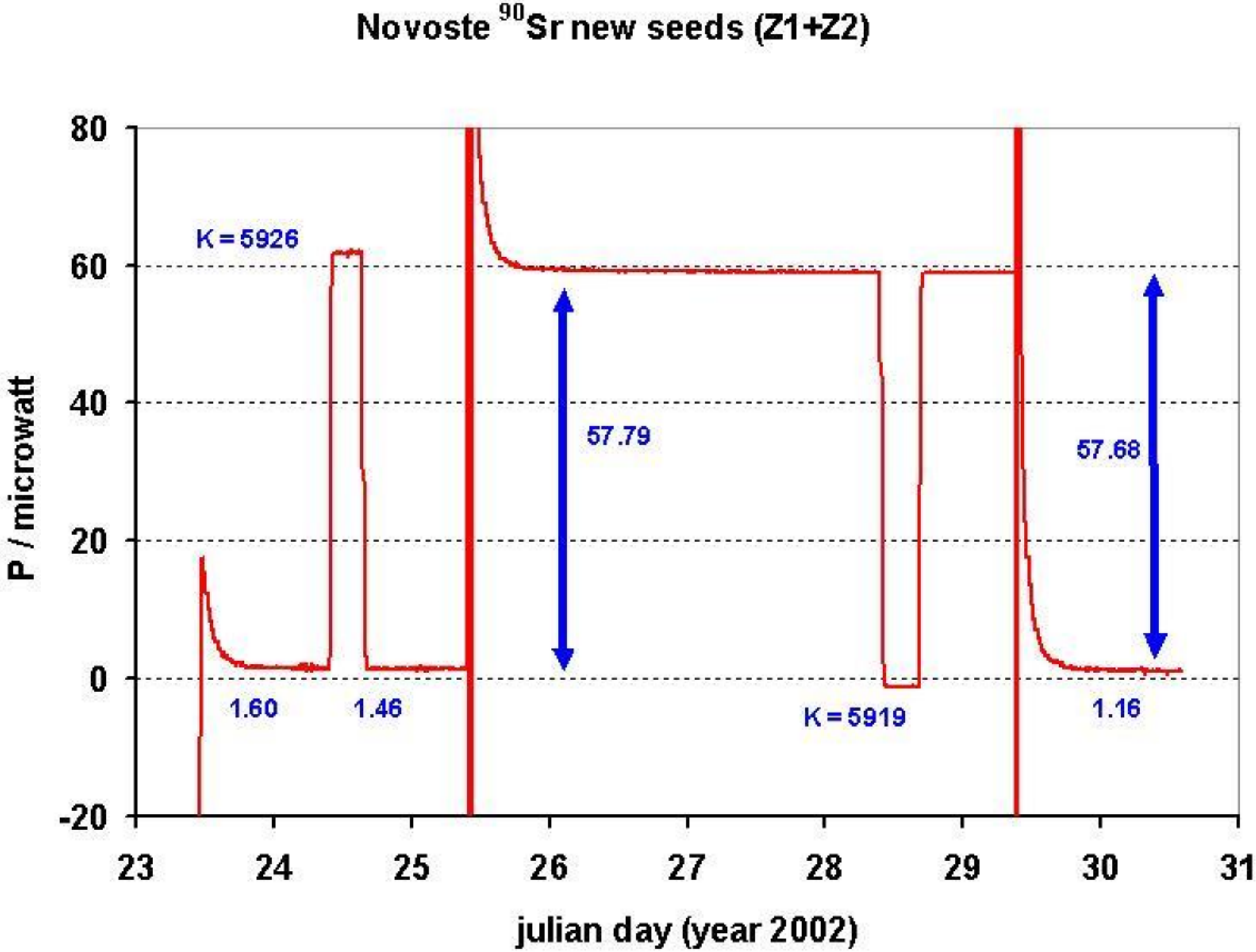
IMC Lab Book II, p.97

combusted ^{32}P balloon "A"

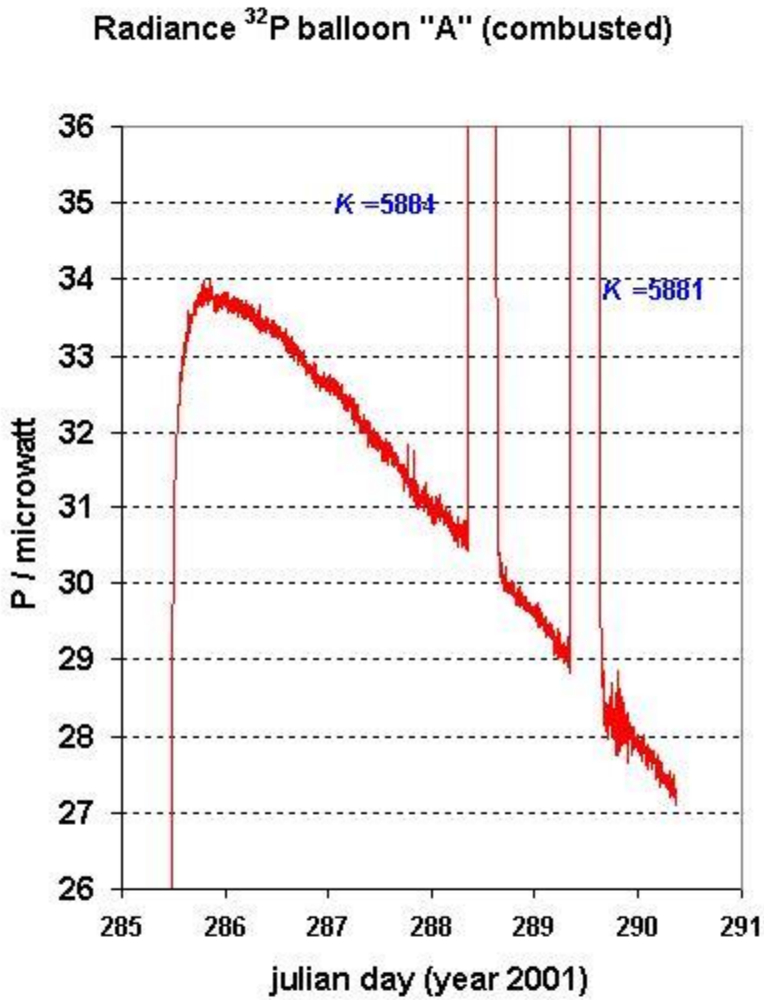
uncombusted ^{32}P balloon "C"

Run59

Bk3p173



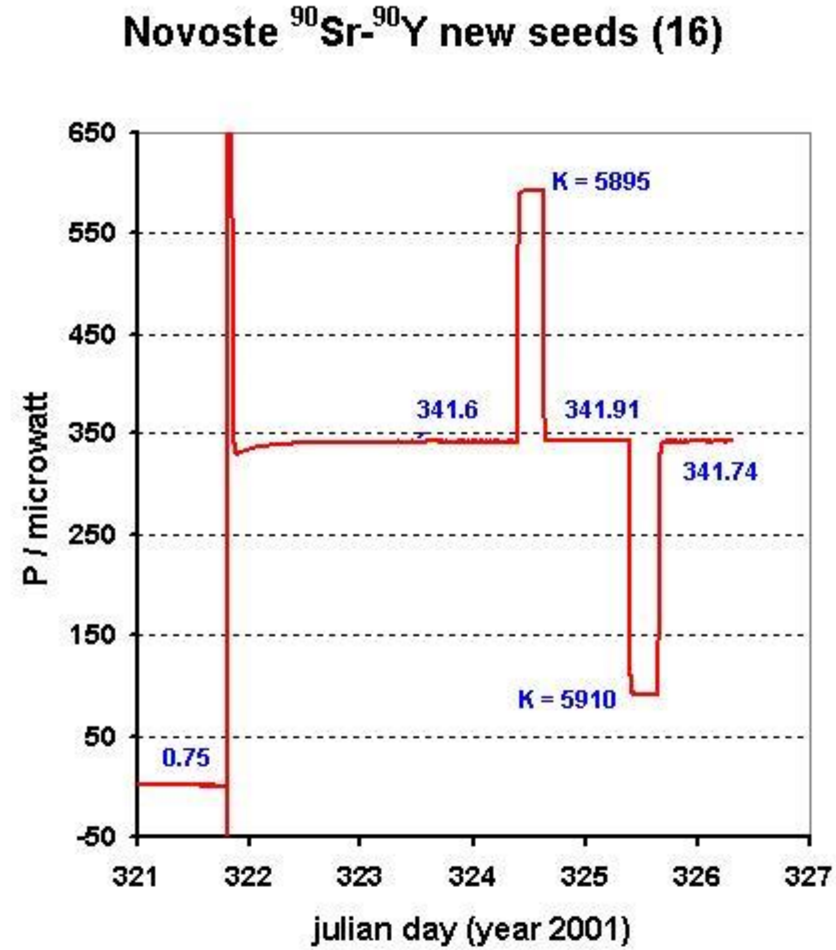
Run35
Bk2,p79



Get P_B and P_0 from "fit"

$$P = P_B + P_0 \exp(-\lambda t)$$

Run43
Bk2,p167

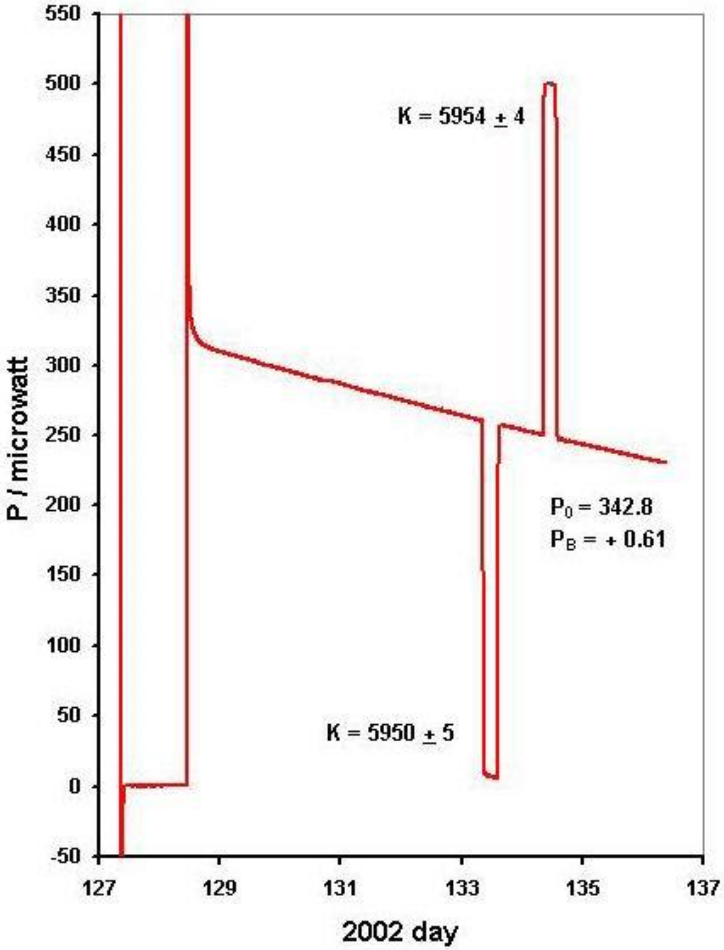


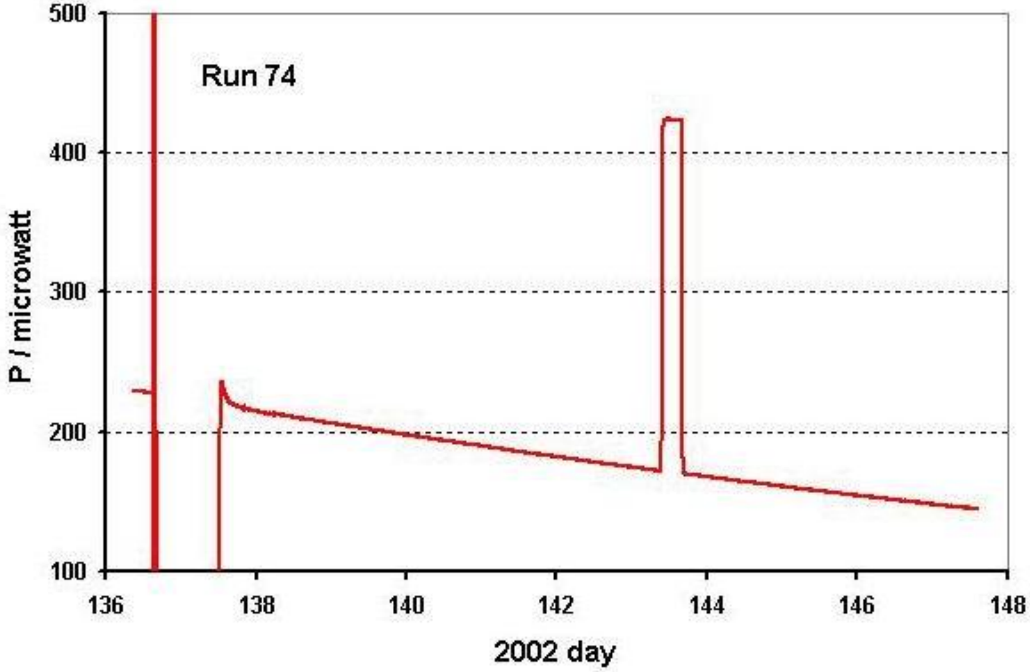
requires baseline P_B measurement

^{103}Pd data

1st & 2nd insertions (brass)

Runs 73 & 74





So... How good is calorimetry ?

Typically, better than 1 % agreement w/ LS-based standardizations of ^{32}P and $^{90}Sr/^{90}Y$ (ion chamber transfer)

Power calibrations (for n>20 determinations) has typical s.d.m. < 0.1 %

Replicate measurement uncertainty (s.d.) is about 1 % (s.d.m = s.d./$\sqrt{n}$) if can get P_B by fit with decay
or if one has sufficient replications to get ΔP (with little decay)

^{55}Fe pure EC decay

For calorimetry, we only need 2 pieces of nuclear/atomic data

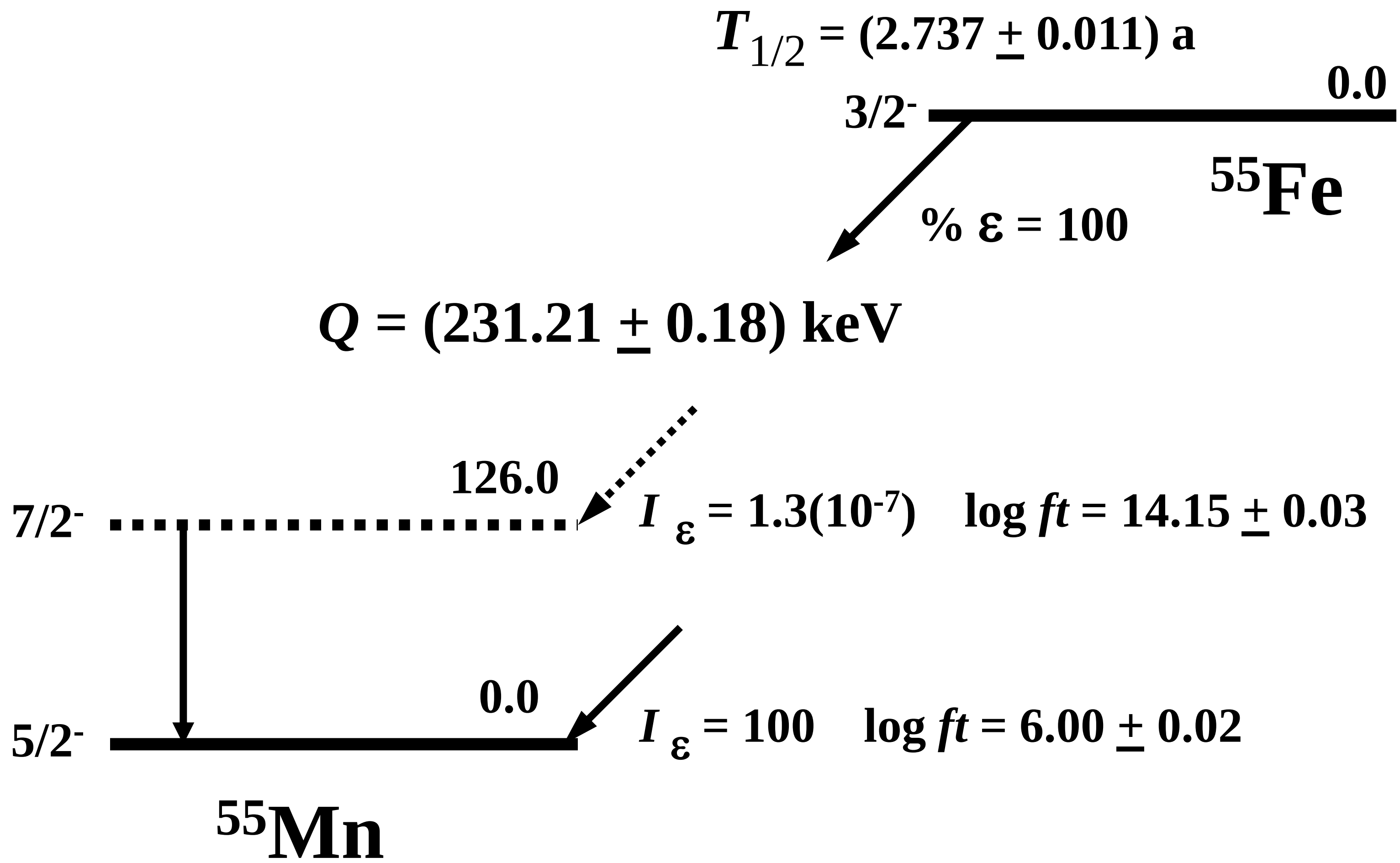
Half-life:

(1001.1 + 2.2) d -- CEA (BIPM)

(999.7 + 4.0) d -- ENSDF

Average energy per decay:

(5.87 + 0.02) keV -- M.M. Bé (sept. 2004)



ENSDF (2001)
Audi (2003)

$\hat{E}$ = (5.87 ± 0.02) keV /decay
Bé (2004)

THE PLAN:

Get a 1 Ci (37 GBq) supply of activity ...

Make a solid source for the calorimetry ....

Use part of the supply to make solutions that would be gravimetrically linked to the calorimetry source ...

USEFUL ADVICE:

Don’t change your **plan** just before starting your work .. !

$Fe^{+3} + OH^{-} \rightarrow Fe(OH)_3 \rightarrow Fe_2O_3$ messy & quantifiability (?)

$Fe^{+3} + H_2S^{-} \rightarrow Fe_2S_3$ smelly

$Fe^{+3} + 3Cl^{-} \rightarrow FeCl_3$

$$FeCl_3 \rightarrow FeCl_3 \bullet nH_2O + \Delta H_{hydr} \rightarrow Fe^{+3} + 3Cl^{-} + \Delta H_{soln}$$

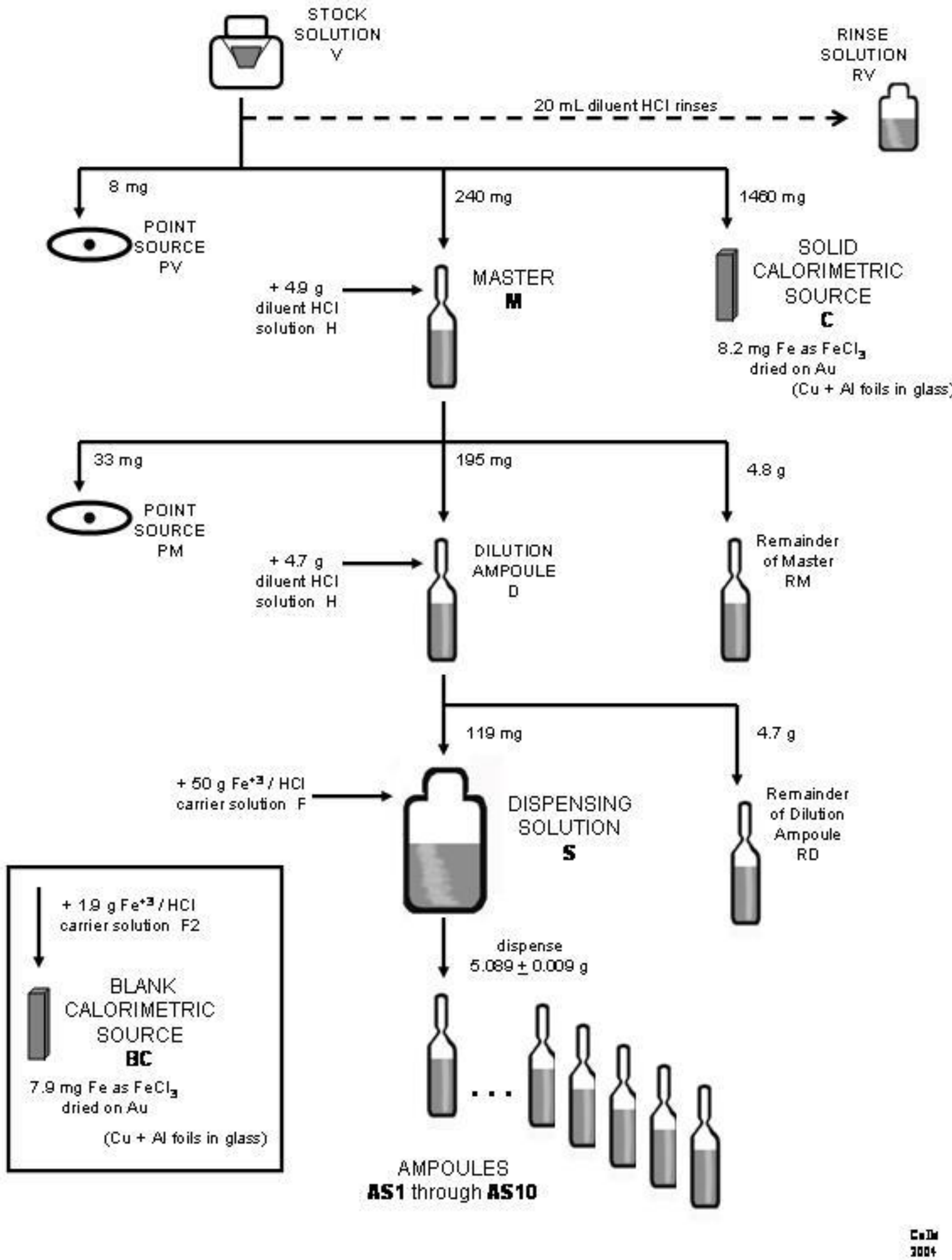
endothermic

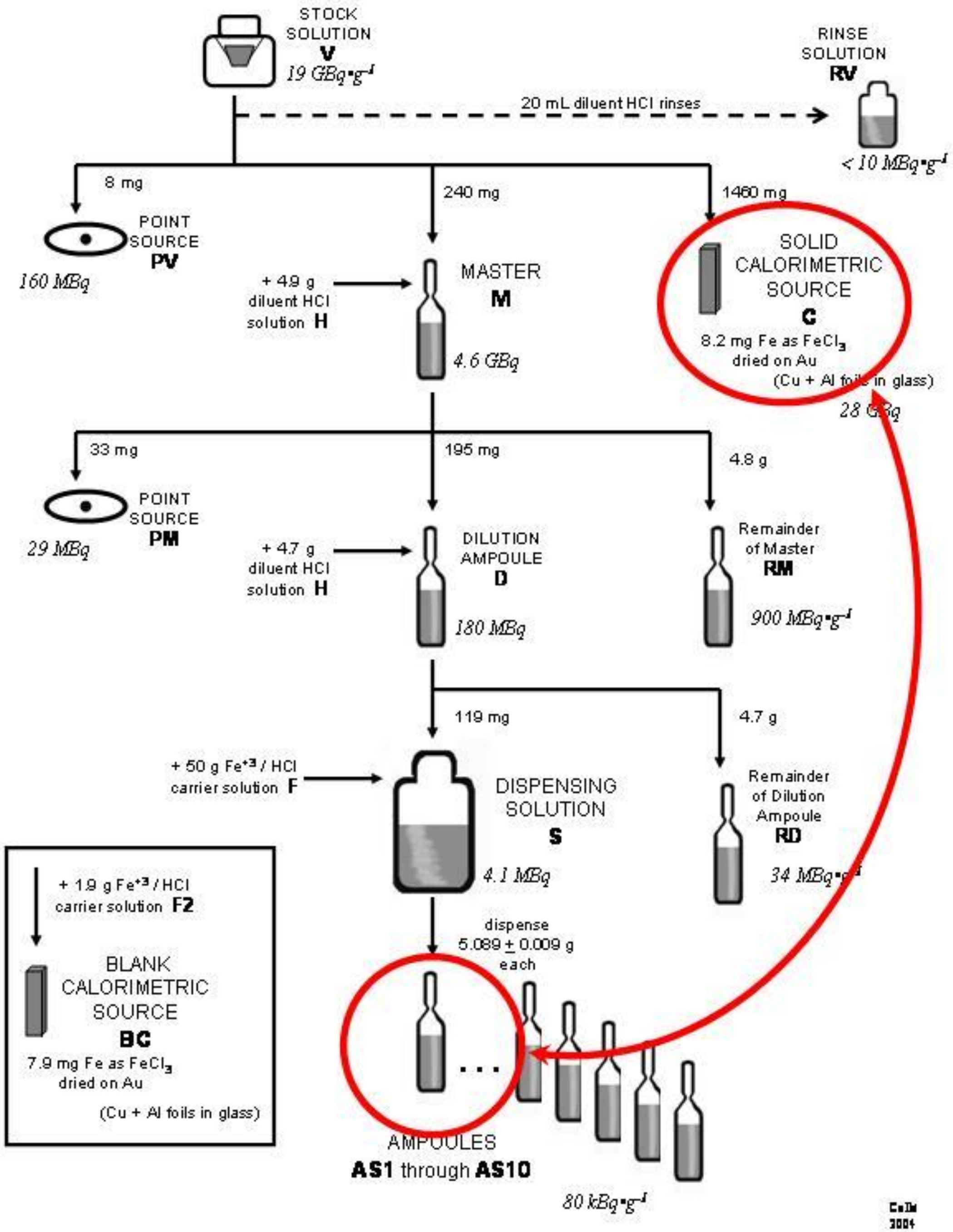
exothermic

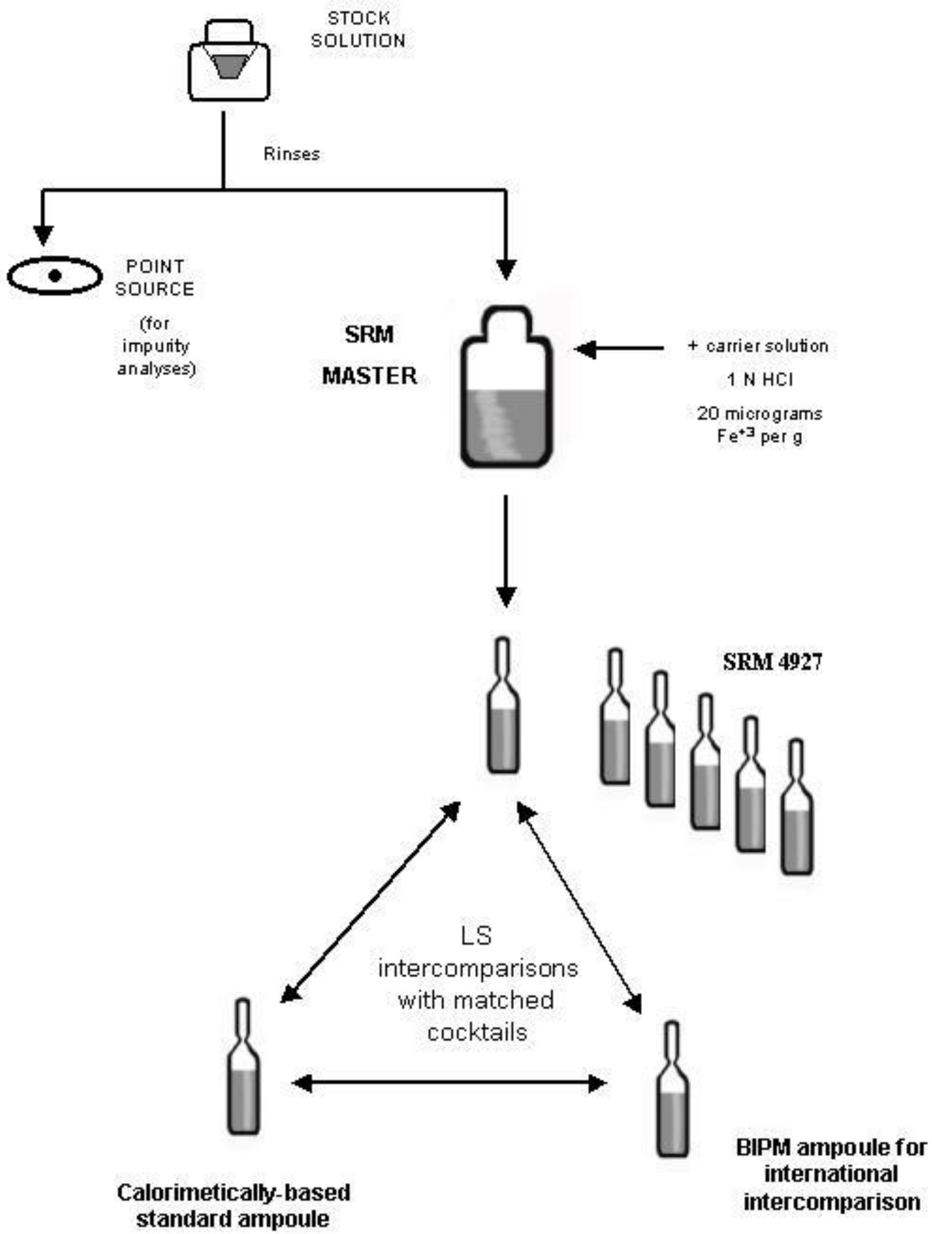
(0.8 kJ/g)

$$\Delta H_{soln} = -U + \Delta H_{hydr}$$

Lattice energy


STOCK SOLUTION V
RINSE SOLUTION RV
20 mL diluent HCl rinses
8 mg
240 mg
1460 mg
POINT SOURCE PV
+ 4.9 g diluent HCl solution H
MASTER M
SOLID CALORIMETRIC SOURCE C
8.2 mg Fe as $FeCl_3$ dried on Au
(Cu + Al foils in glass)
33 mg
195 mg
4.8 g
POINT SOURCE PM
+ 4.7 g diluent HCl solution H
DILUTION AMPOULE D
Remainder of Master RM
119 mg
4.7 g
+ 50 g Fe^{+3} / HCl carrier solution F
DISPENSING SOLUTION S
Remainder of Dilution Ampoule RD
+ 1.9 g Fe^{+3} / HCl carrier solution F2
BLANK CALORIMETRIC SOURCE BC
7.9 mg Fe as $FeCl_3$ dried on Au
(Cu + Al foils in glass)
dispense
5.089 ± 0.009 g
AMPOULES
AS1 through AS10
CeIk
2004


STOCK SOLUTION
V
19 GBq•g-1
20 mL diluent HCl rinses
RINSE SOLUTION
RV
< 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
CoIn 2004



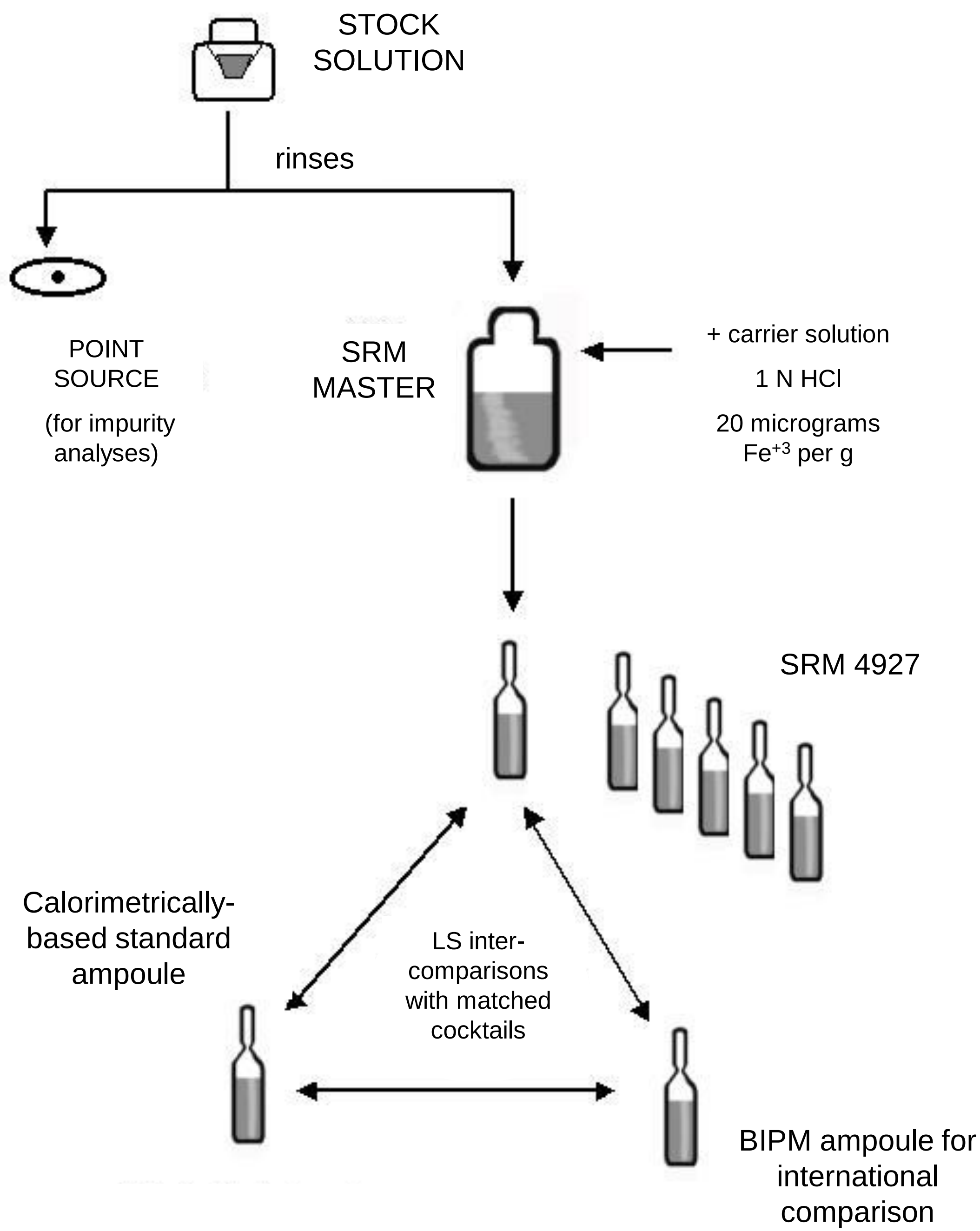
Calorimetry

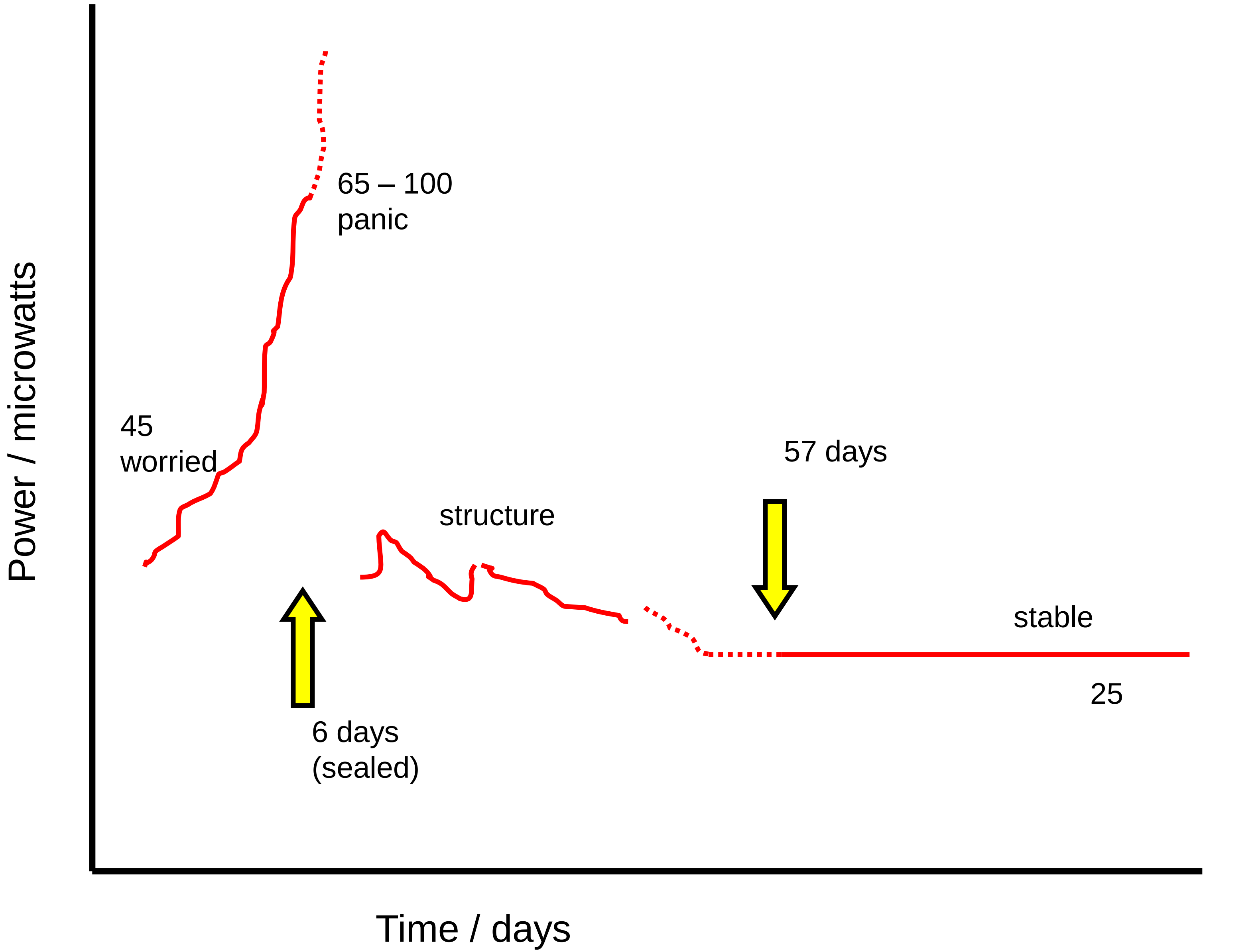
13 independent determinations

LS intercomparisons

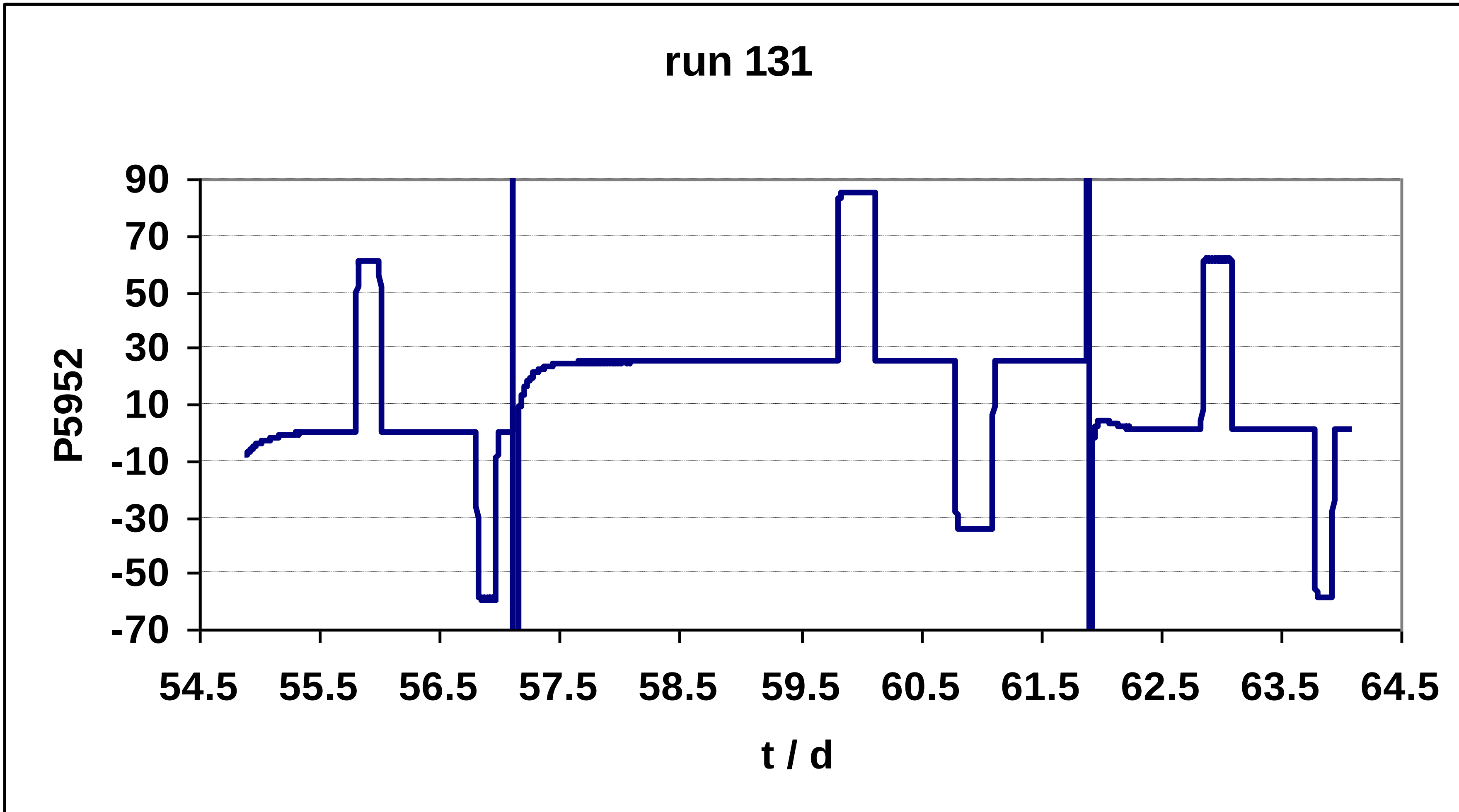
776 activity ratios; variables include:

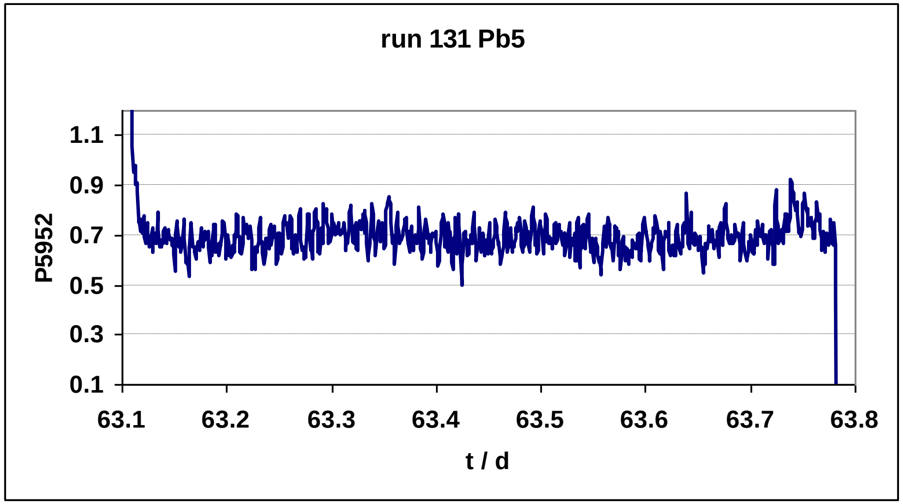
- 3 counters
- 3 scintillators
- 44 matched cocktails
- 4 distinct aq. fraction (+Fe) compositions
- 2 NIST solution dilutions
- 97 days of aging

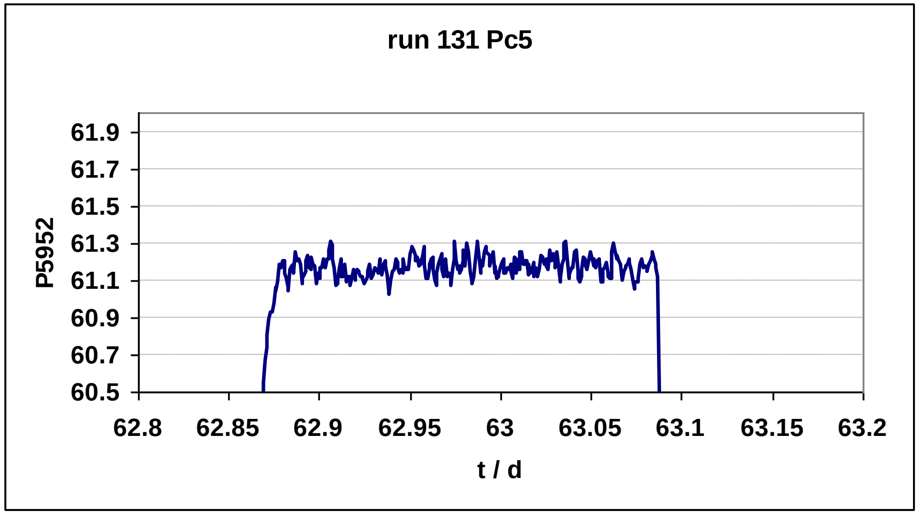

STOCK SOLUTION
rinses
POINT SOURCE
(for impurity analyses)
SRM MASTER
+ carrier solution
1 N HCl
20 micrograms Fe^{+3} per g
SRM 4927
Calorimetrically-based standard ampoule
LS inter-comparisons with matched cocktails
BIPM ampoule for international comparison

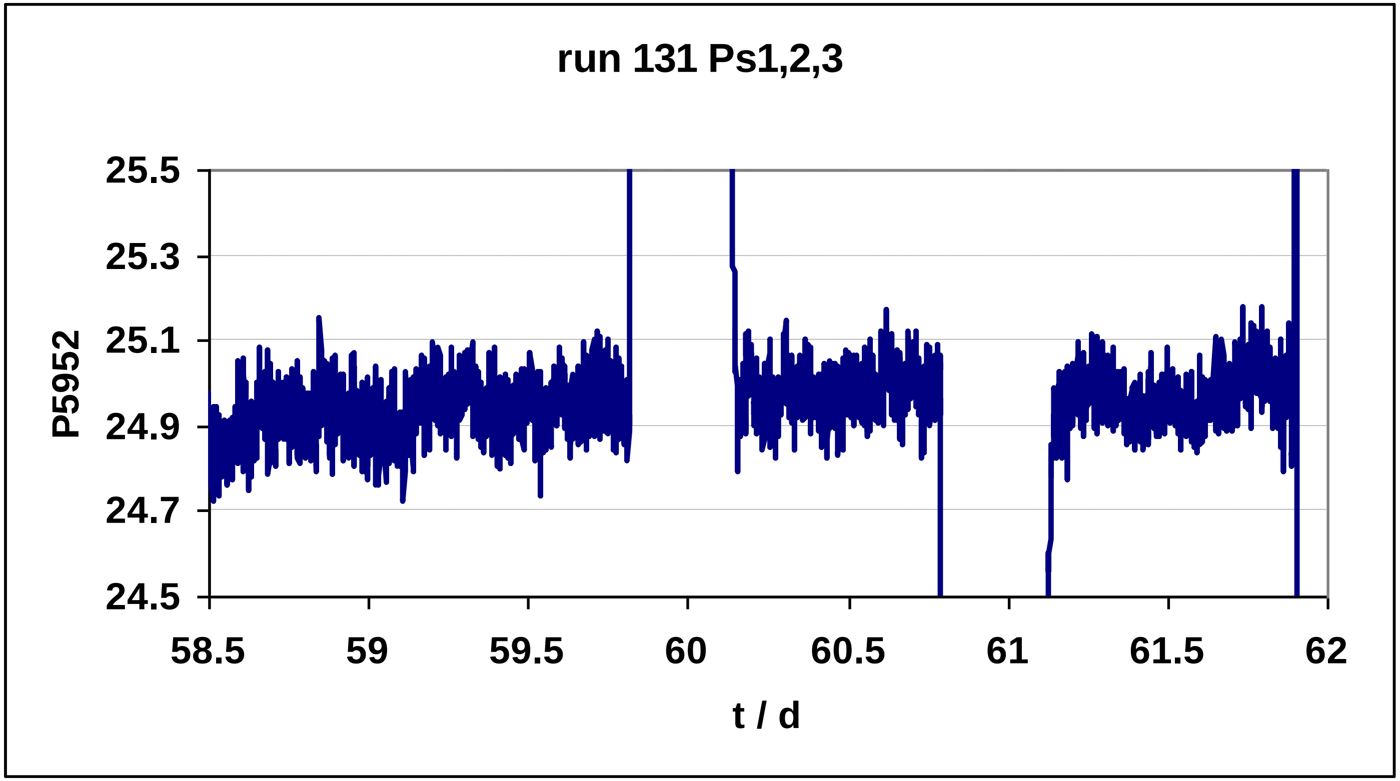


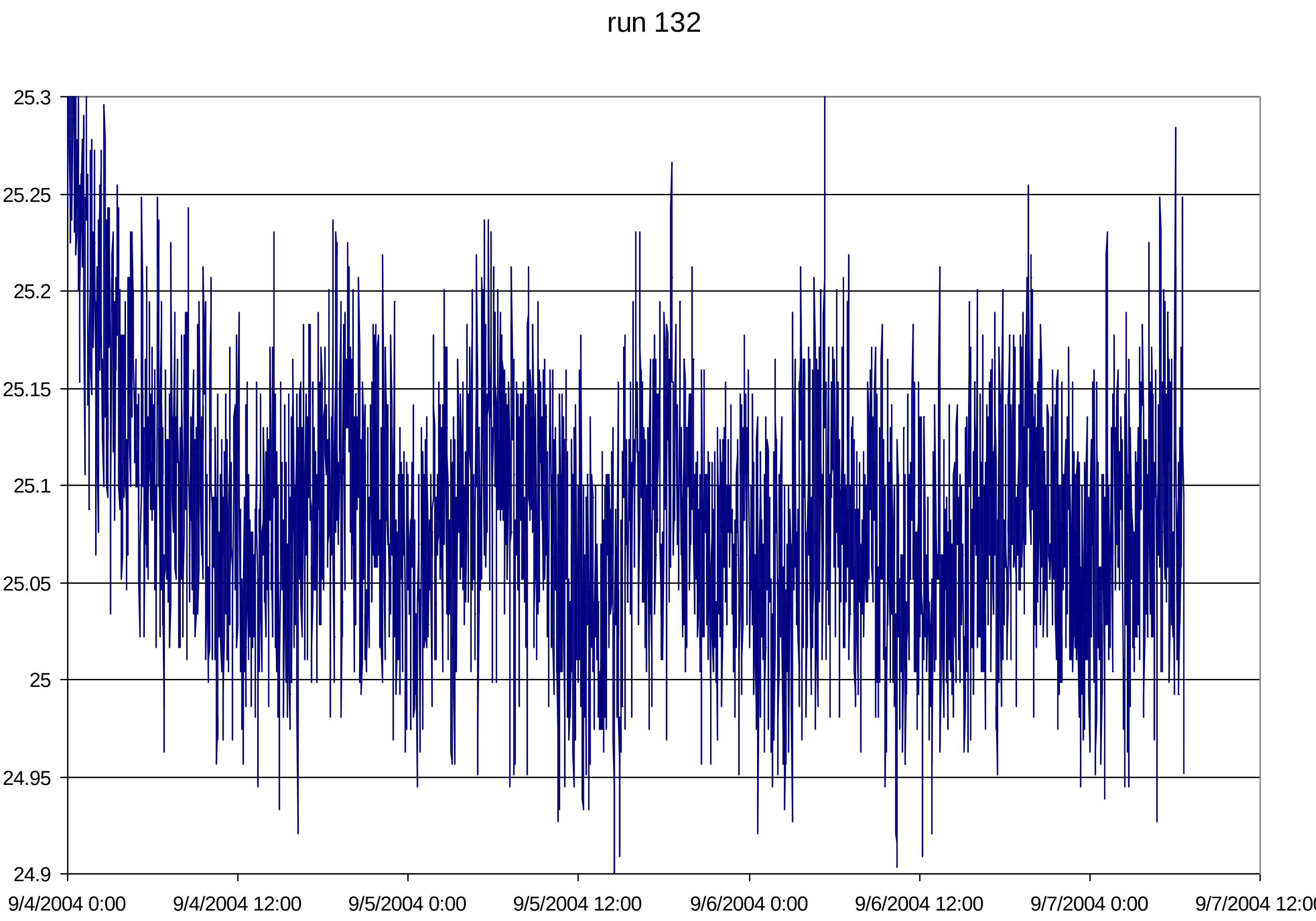
Power / microwatts
65 – 100
panic
45
worried
57 days
structure
stable
25
6 days
(sealed)
Time / days

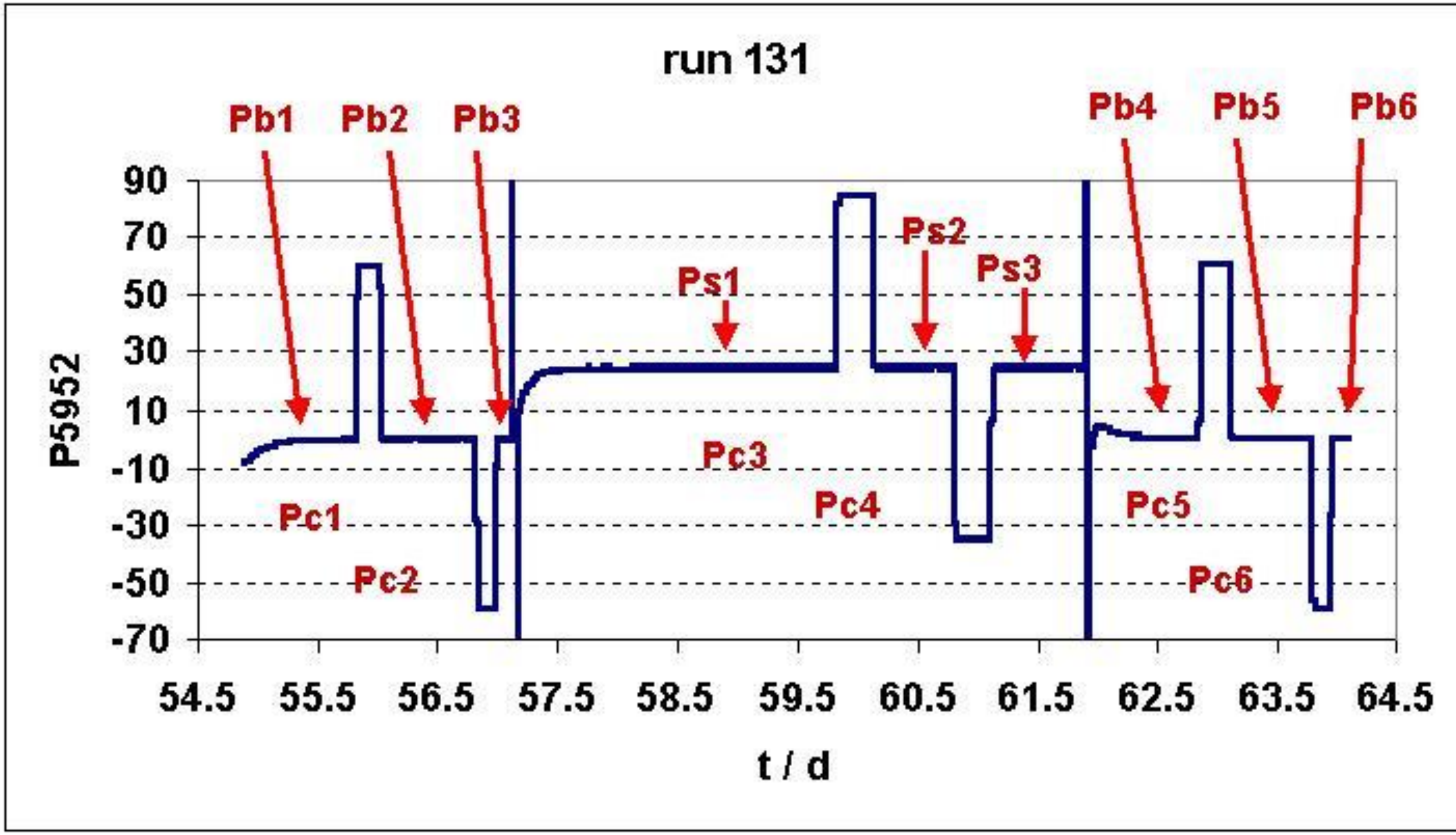

run 131
P5952
90
70
50
30
10
-10
-30
-50
-70
54.5
55.5
56.5
57.5
58.5
59.5
60.5
61.5
62.5
63.5
64.5
t / d


run 131 Pb5
P5952
1.1
0.9
0.7
0.5
0.3
0.1
63.1
63.2
63.3
63.4
63.5
63.6
63.7
63.8
t / d


run 131 Pc5
P5952
61.9
61.7
61.5
61.3
61.1
60.9
60.7
60.5
62.8
62.85
62.9
62.95
63
63.05
63.1
63.15
63.2
t / d

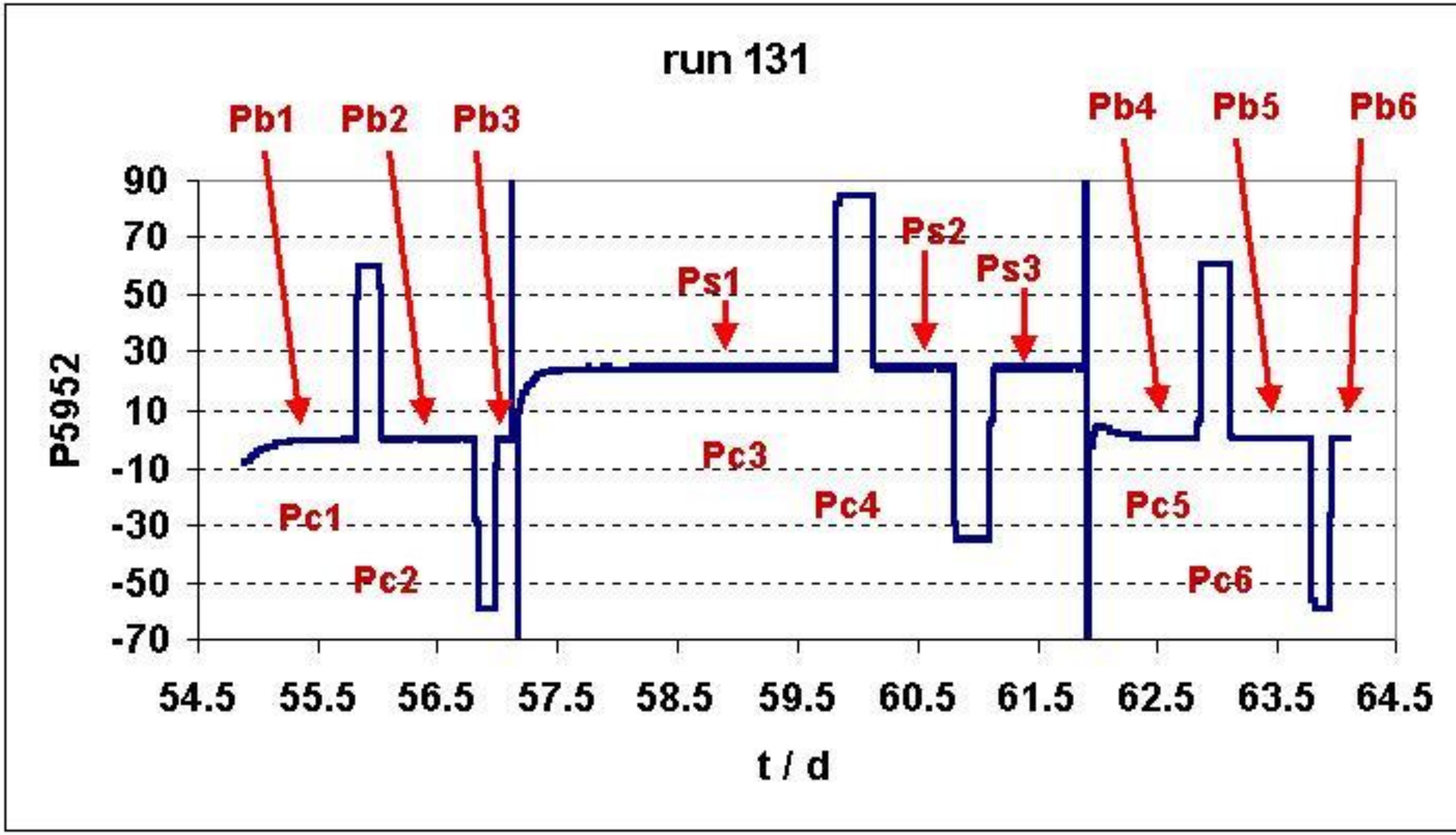

run 131 Ps1,2,3
P5952
25.5
25.3
25.1
24.9
24.7
24.5
58.5
59
59.5
60
60.5
61
61.5
62
t / d


run 132
25.3
25.25
25.2
25.15
25.1
25.05
25
24.95
24.9
9/4/2004 0:00
9/4/2004 12:00
9/5/2004 0:00
9/5/2004 12:00
9/6/2004 0:00
9/6/2004 12:00
9/7/2004 0:00
9/7/2004 12:00



Baseline reproduction

Pb1	-0.0203
Pb2	0.1359
Pb3	0.1391
Pb4	0.6878
Pb5	0.6880
Pb6	0.6359



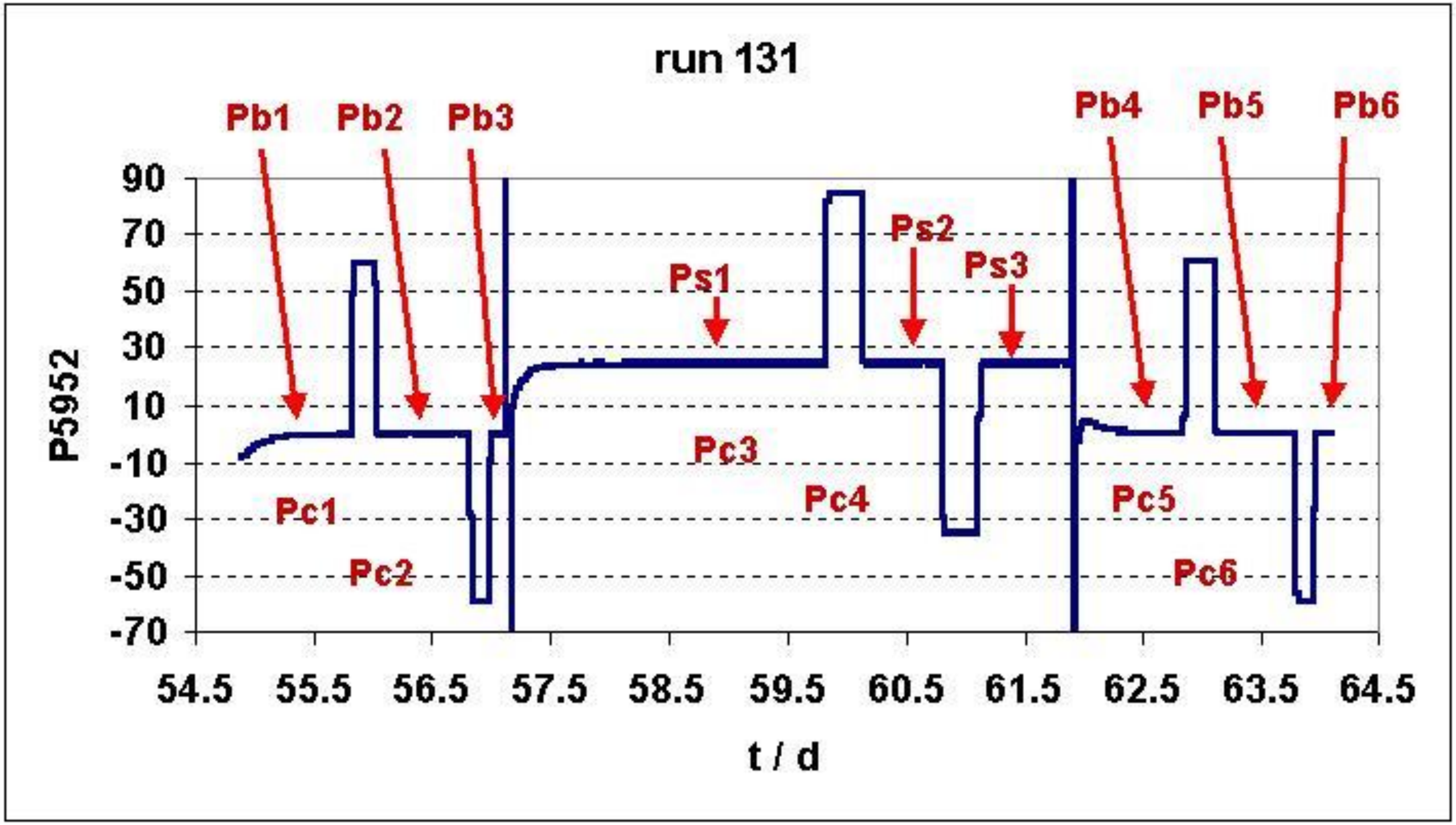
Calibration reproduction

Run 131	S cell (+)	R cell (-)
Pc1	5963	
Pc2		6051
Pc3	5979	
Pc4		6032
Pc5	5954	
Pc6		6055

Compare prior run

Run 130	S cell (+)	R cell (-)
Pc1	5979	
Pc2		6045
Pc3	5922	
Pc4		6031

S/R cell difference was new !



Power measurement reproducibility (with run)

Run 131	P(5952) at t0
Ps1	25.562
Ps2	25.629
Ps3	25.637
mean	**25.609**
sd (%)	0.16
sdm (%)	**0.093**

Compare prior run

Run 130	P(5952) at t0
Ps1	25.399
Ps2	25.200
Ps3	25.212
mean	**25.270**
sd (%)	0.440
sdm(%)	**0.250**

run	temp C	date	days	net P	unc
130	23	18-Aug-04	7	**25.156**	0.64
131	23	25-Aug-04	9	**25.641**	0.289
132	23	3-Sep-04	7	**25.990**	0.451
134	23	14-Sep-04	23	**25.584**	0.088
135	23	7-Oct-04	8	**25.555**	0.119
136	23	15-Oct-04	7	**25.746**	0.253
137	23	22-Oct-04	7	**25.334**	0.098
139	23	5-Nov-04	13	**25.326**	0.317
140	23	18-Nov-04	8	**25.478**	0.137
141	23	26-Nov-04	8	**25.661**	0.159
142	23	3-Dec-04	12	**25.402**	0.124
150	23	17-Mar-05	31	**25.822**	0.154
152	23	5-May-05	26	**25.675**	0.186

vary conditions of absorbers, calibrations, water levels, etc...

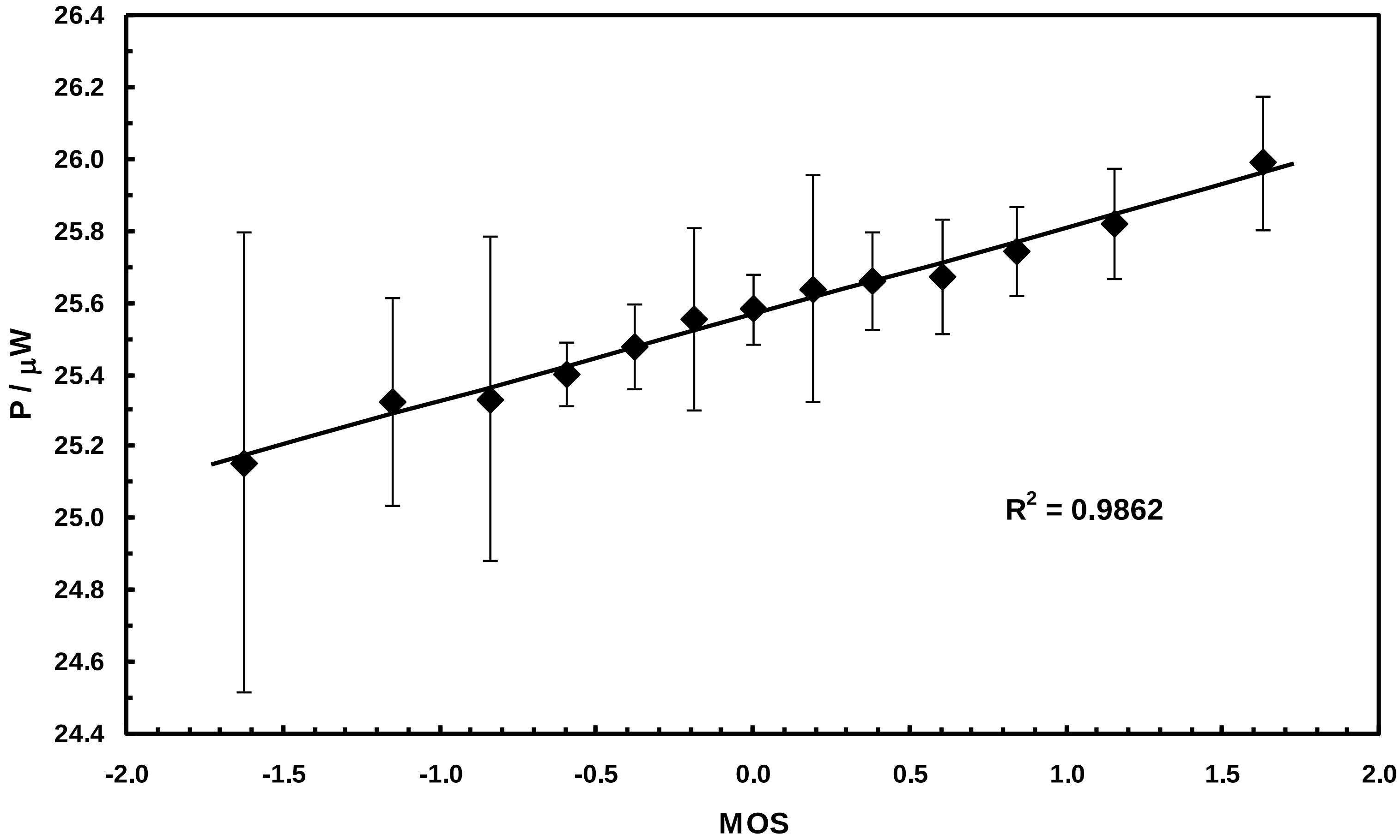
T_0 = 1200 EST **1 July 2004**

Mean P = 25.567 μW(w/ 998.9 d)

additional runs mar-apr 2006

Corrected **P = 25.562 μW** (w/ 1001.1 d)

% sdm = 0.25 %



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

NIST Uncertainty Analysis for ^{55}Fe Microcalorimetric Standardization of NIST Solution Standards

Item	Uncertainty component	Assessment Type	Relative standard uncertainty contribution on massic activity of ^{55}Fe (%)
1	Measurement precision for 13 independent calorimetric determinations of the power of solid source C; includes precision in the calibrations & baseline measurements for each determination; std. dev mean for ν=12 degrees freedom (passes Normal test)	A	0.25
2	Gravimetric (mass) linkage of source C to NIST standard solutions	B	0.07
3	Activity loss in source C preparation	B	0.15
4	Power calibration of calorimeter, includes any systemic heat losses	B	0.05
5	Possible heat defect / excess effects	B	0.1
6	^{55}Fe decay corrections during calorimetric measurements	B	0.02
7	^{55}Fe decay corrections from calorimetric reference time to BIPM reference time.	B	0.08
8	Average energy per decay for ^{55}Fe (to convert calorimetric power to activity)	B	0.17
	COMBINED STANDARD UNCERTAINTY		0.39

3 LS counters

LS Counters

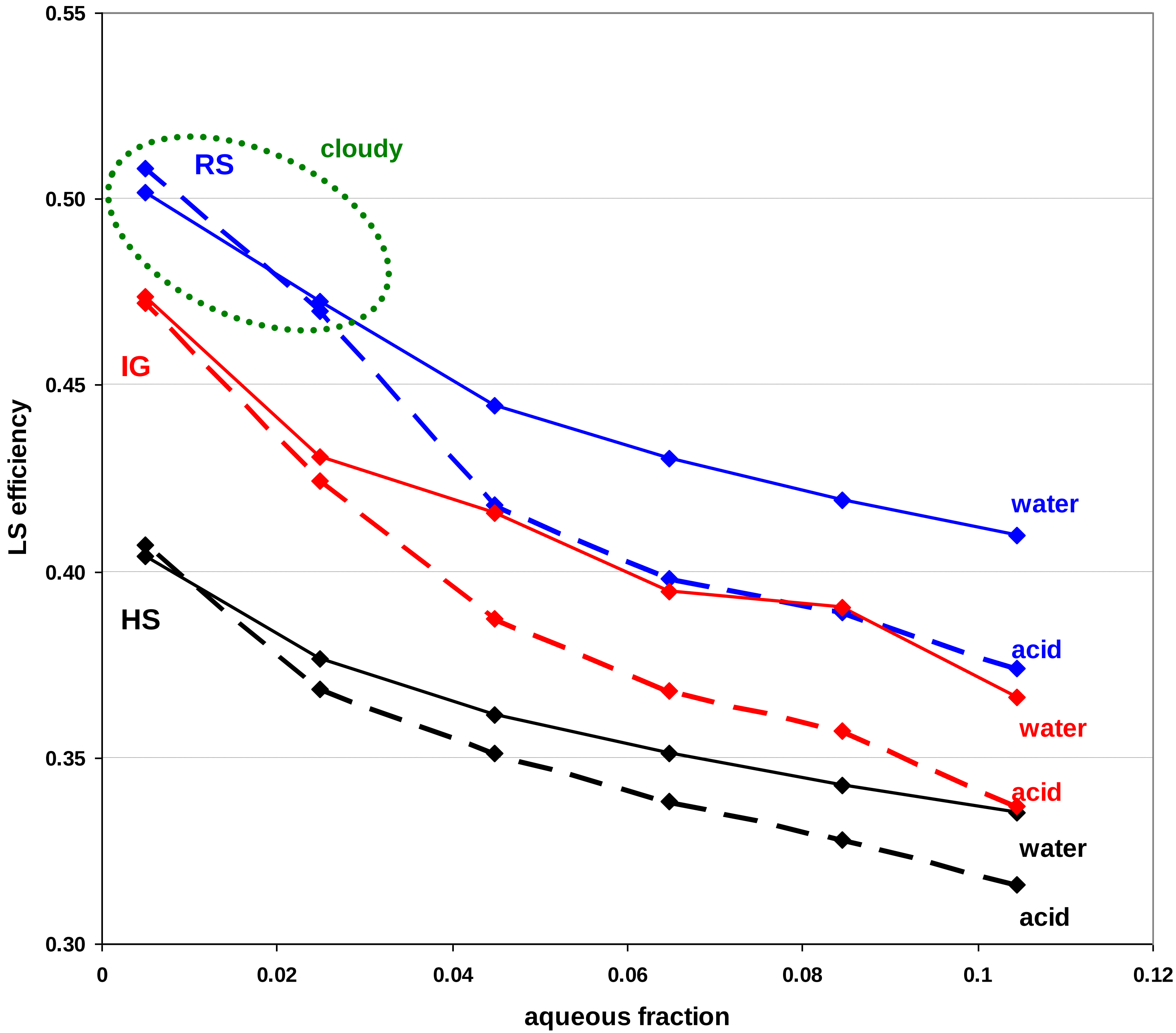
	LS spectrometer model	Sum-coincidence pulse spectrum & ADC	Other stuff
system B2	Beckman LS 6500	**Logarithmic** ? 32K analyzer / variable (0.06 keV per channel)	H # with ^{137}Cs unknown resolving time 5.6% - 2.5 keV - ^{209}Po ce(γ) about 50% - ^{55}Fe
system P	Packard Tri-carb A2500TR	**Linear** 2048 channels (linear) (1 keV per channel)	tSIE with ^{133}Ba 12 μs (fixed) ? 5.2% - 2.5 keV - ^{209}Po ce(γ) about 40% - ^{55}Fe
system W	Wallac 1414 Winspectral	**Logarithmic** (1-2000 keV)	SQP(E) with ^{152}Eu unknown resolving time 5.1% - 2.5 keV - ^{209}Po ce(γ) about 40% - ^{55}Fe

Scintillants

Commercial scintillant	Acronym descriptor	Manufacturer	Composition
Ready Safe	RS	Beckman	**Alkylated benzene** 1-Phenyl-1-Xylylethane (PXE) 50% to 80%; Alkylphenol Ethoxylate 20% to 50%
OptiPhase HiSafe 3	HS	Wallac	**DIN based** Di-isopropylnaphthalene > 60%; Poly(ethyleneglycol) mono(4-nonylphenyl)ether 25% to 30%
Insta Gel Plus	IG	Perkin Elmer	**Pseudocumine based** 1,2,4-trimethylbenzene 40% to 60%; Ethoxylated alkylphenol 40% to 60%;

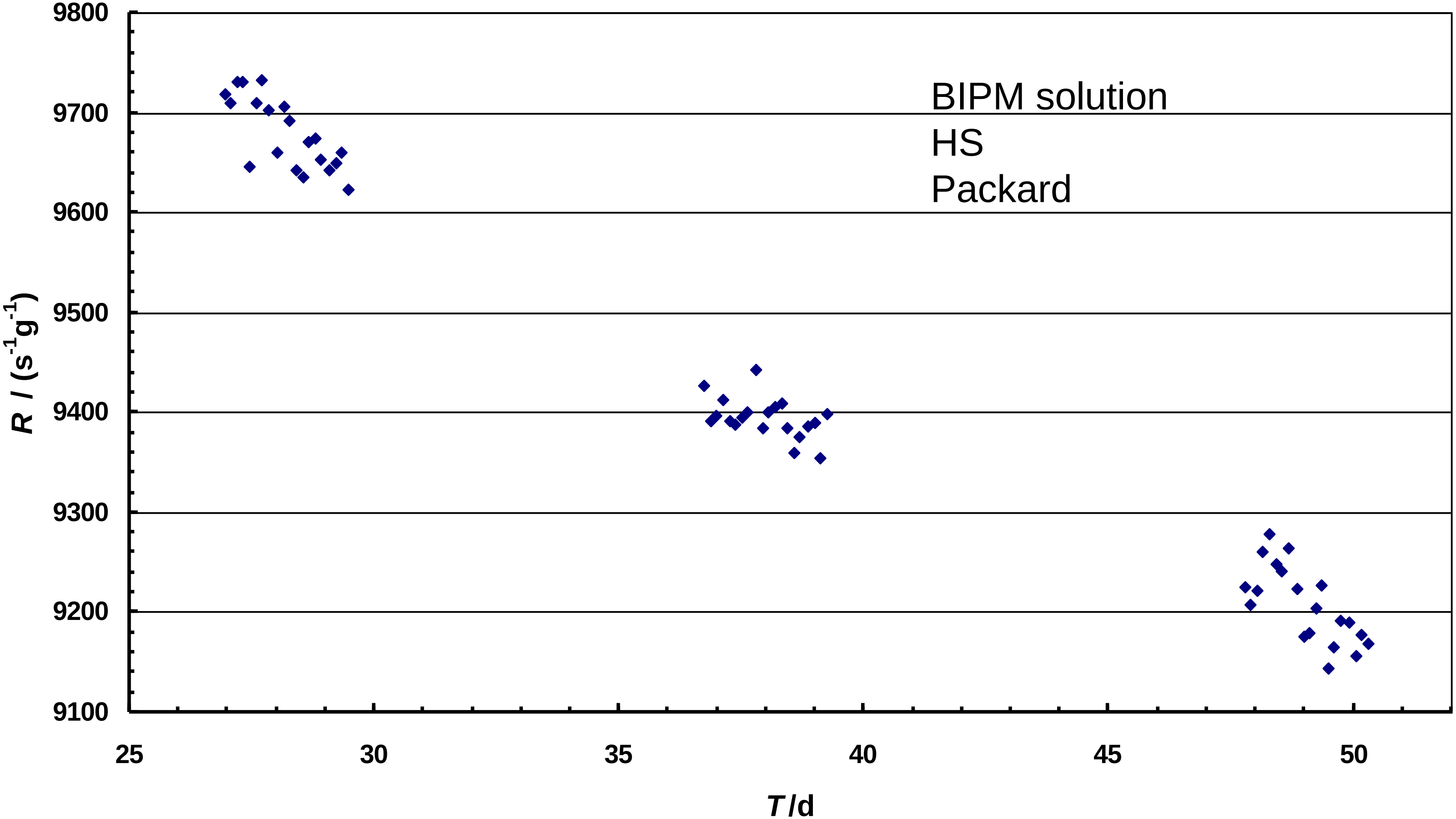
Cocktail Compositions

Series	Scintillant	Solutions	Water fraction	Aliquant (mg) / Fe mass (mg)
1	RS, HS	BIPM, SRM, Calorimetry	0.10	15 – 80 / 19 – 22
2	RS, HS, IG	BIPM, SRM, Calorimetry	0.10	11 – 47 / 0.2 – 0.8
3	RS, HS, IG	SRM	0.005 – 0.10	50 / 0.1
4	RS, HS, IG	BIPM, SRM, Calorimetry	0.04 – 0.10	44 – 70 / 8 – 20
5	IG	BIPM, SRM, Calorimetry	0.06 – 0.30	30 – 275 / 12 – 60



LS efficiency
aqueous fraction
0.55
0.50
0.45
0.40
0.35
0.30
0
0.02
0.04
0.06
0.08
0.1
0.12
cloudy
RS
IG
HS
water
acid
water
acid
water
acid

Cocktail Stability



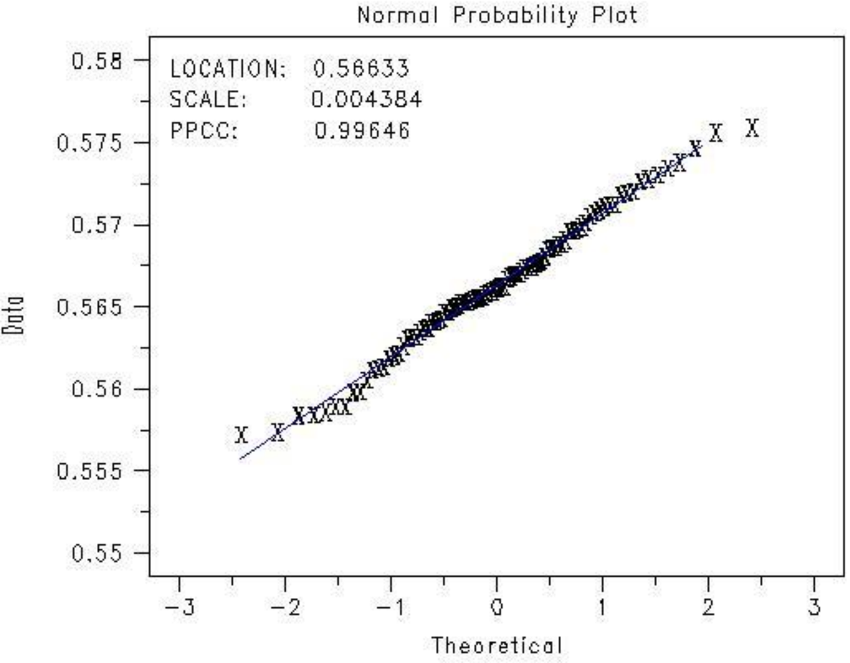
LS intercomparisons -- 776 activity ratios

variables included:

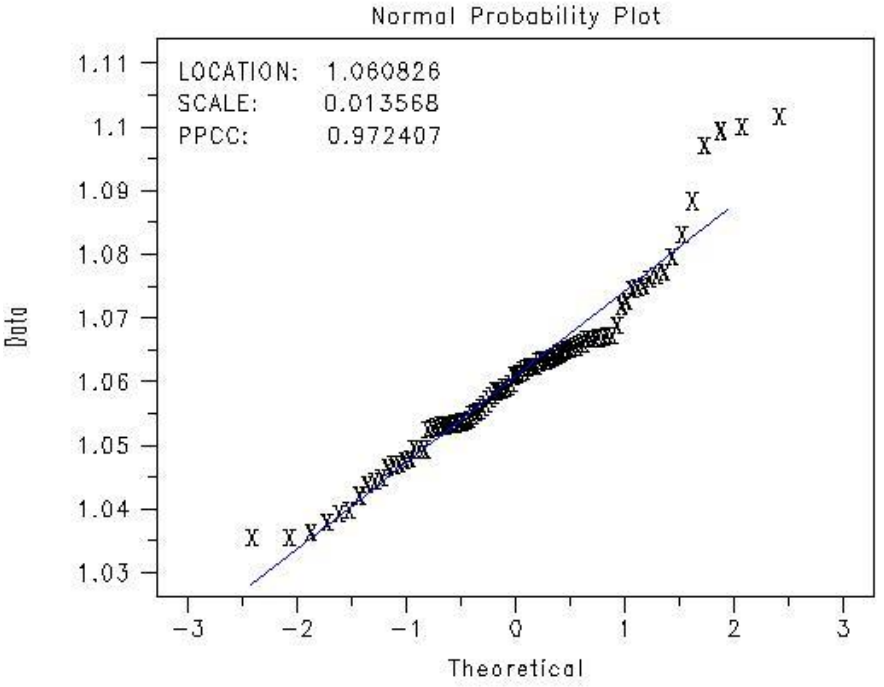
3 counters
3 scintillators
44 matched cocktails
4 distinct aq. fraction (+Fe) compositions
2 NIST solution dilutions
97 days of aging

Normality

BIPM/CAL



SRM/CAL



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 %

I guess I am supposed to have a conclusion.

So...

- **Calorimetry is SLOW**
  - **needs long time to thermally stabilize**
  - **typically need multiple determinations**
  - **different / absorbers / Monte Carlo calc. verifications**

- **Calorimetry NOT Necessarily Non-Destructive method**

- **NOW, uncertainty is in range of $\pm$ 0.5 % or so**
  - **Largely due to baseline instabilities and uncertainties in establishing baselines to get ΔP**

- **Power may be measured very accurately**
  - **But still need average energy per decay to get Activity**