A Primary Standardization of ^{55}Fe

by Isothermal Microcalorimetry

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

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Comparisons and Uncertainties Workshop
Bureau International des Poids et Mesures
Pavillon de Breteuil Sèvres, FRANCE
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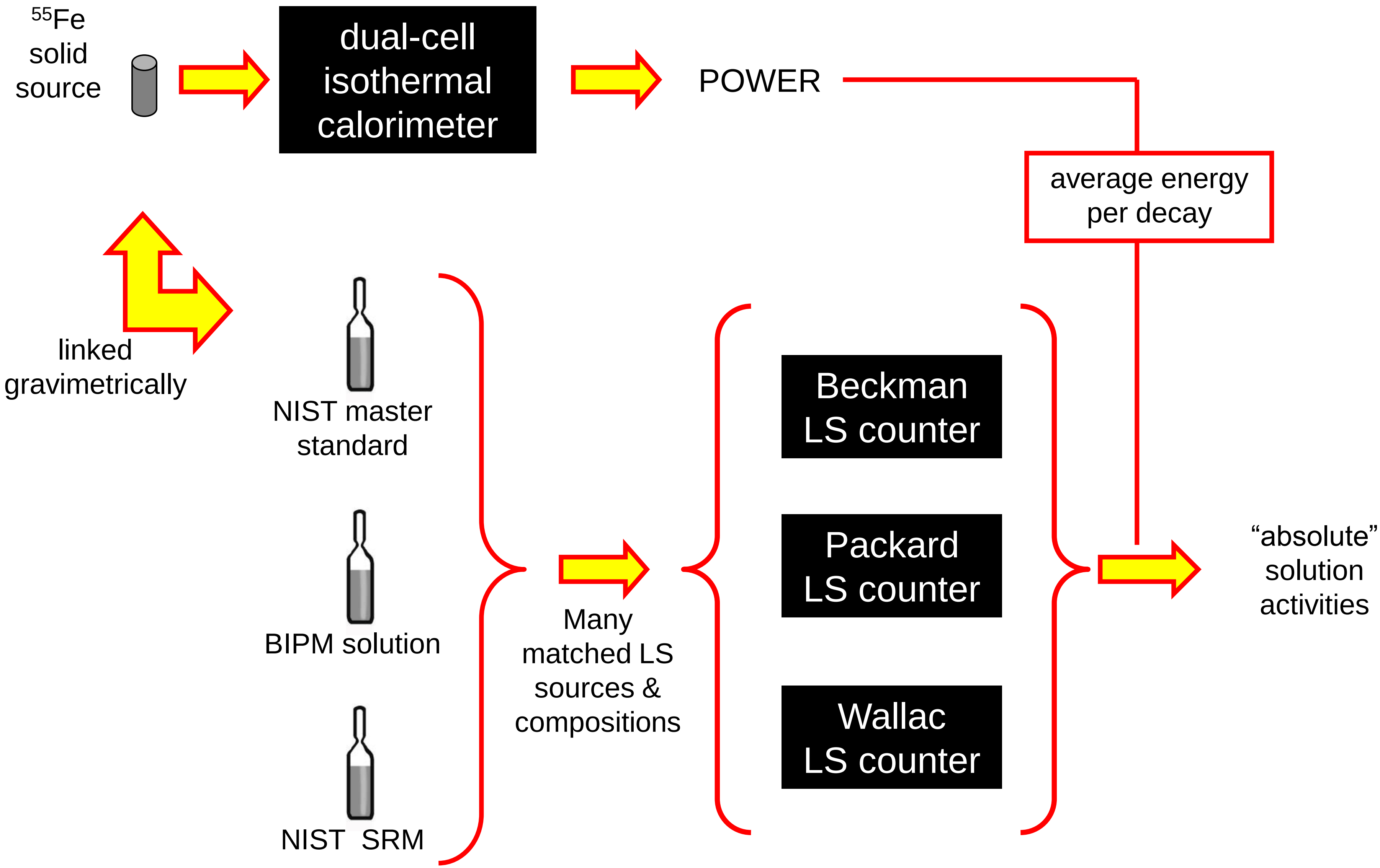


BLACK BOX METROLOGY

Basic relationship between

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

and

Activity A

is $$dH/dt = P = A\,\hat{E}$$

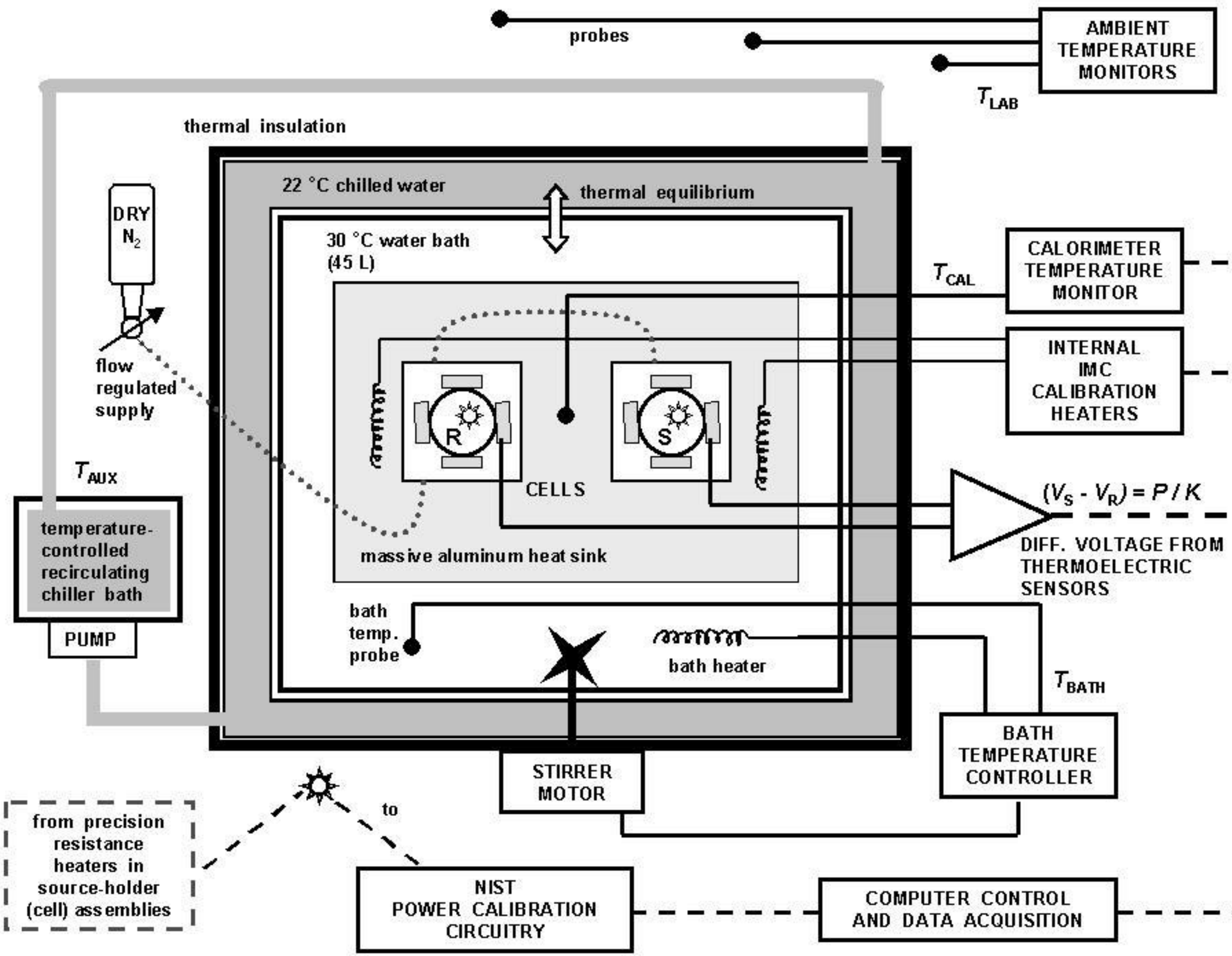
$\hat{E}$ = average energy per decay

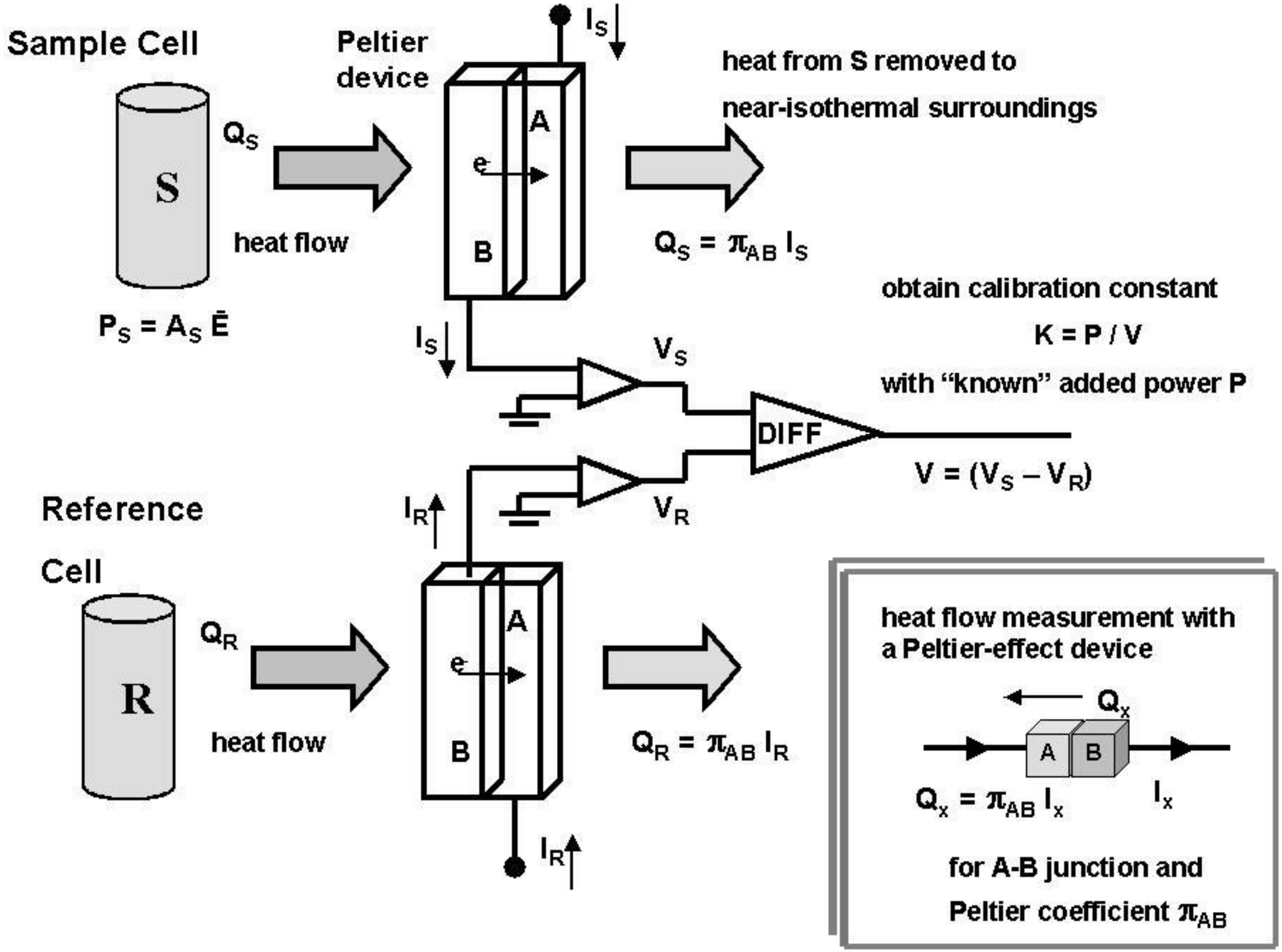
^{3}H / ^{55}Fe	0.9 $\mu W \cdot GBq^{-1}$
^{103}Pd / ^{125}I	9.
^{32}P	111.
^{90}Sr-^{90}Y	181.
^{226}Ra	4338.

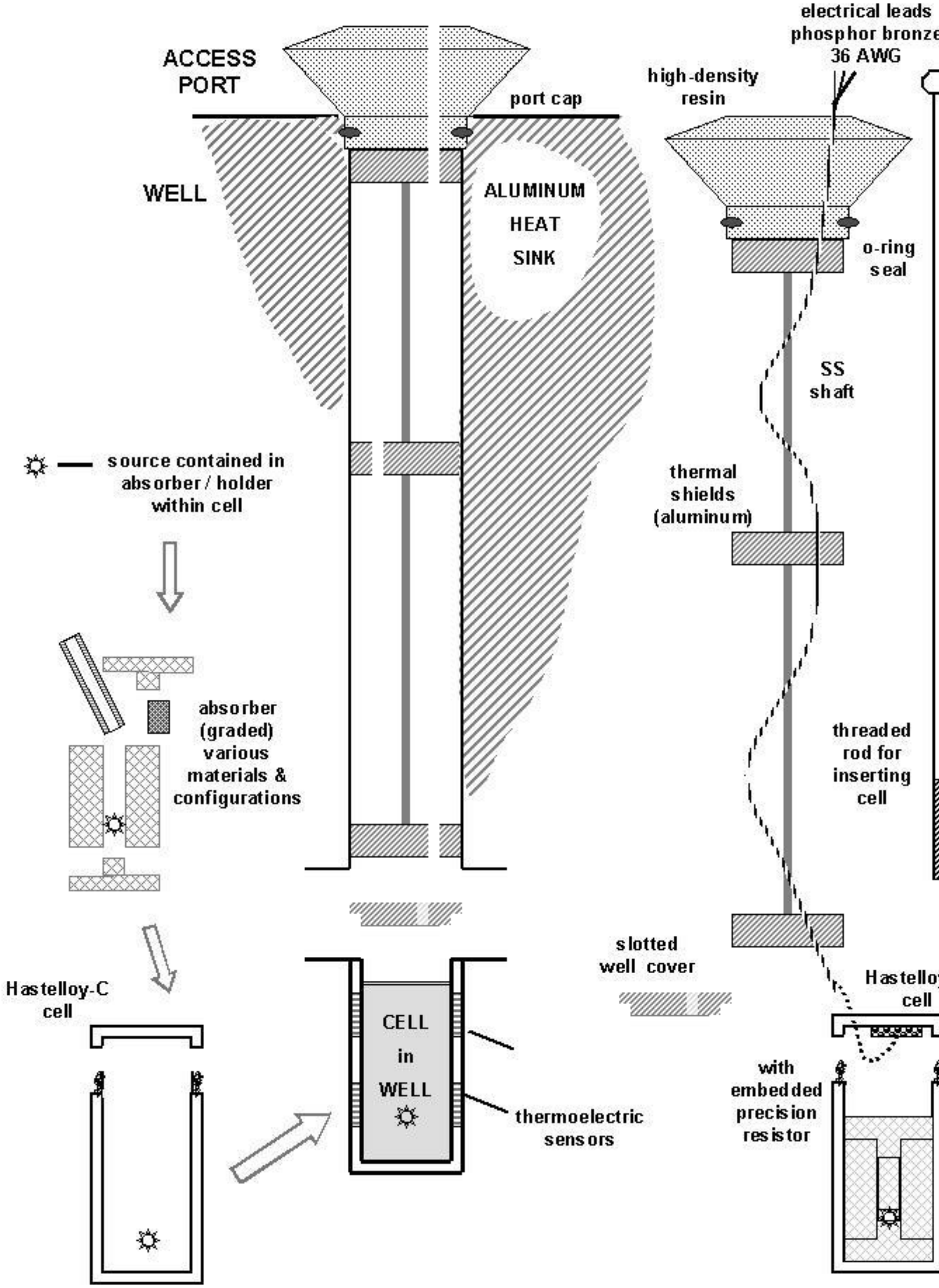
Assumes absorb & measure ALL ionizing radiation (no losses)

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

CSC "Isothermal Microcalorimeter (IMC)"

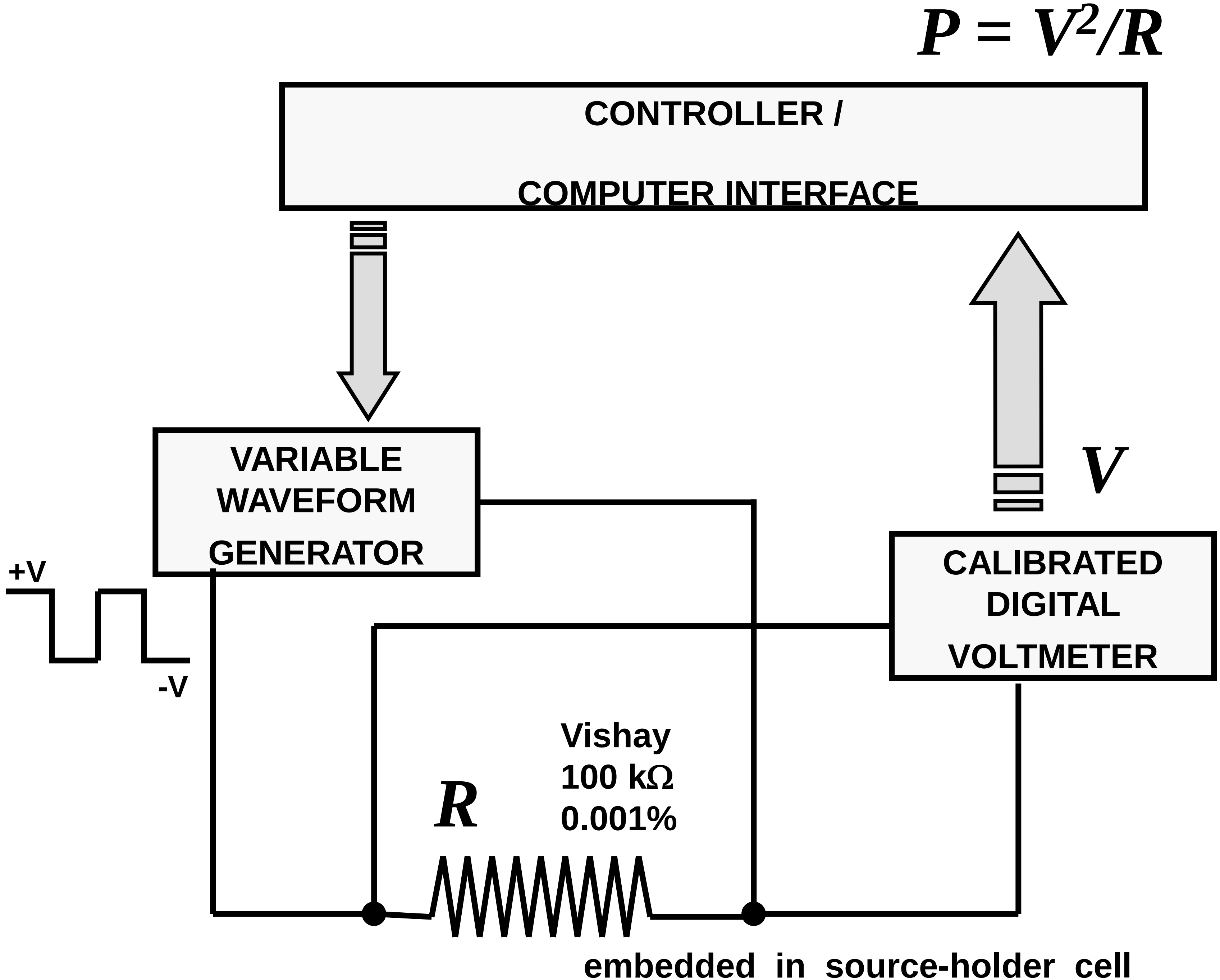

probes
AMBIENT TEMPERATURE MONITORS
T_{LAB}
thermal insulation
22 °C chilled water
thermal equilibrium
DRY N_2
30 °C water bath (45 L)
T_{CAL}
CALORIMETER TEMPERATURE MONITOR
INTERNAL IMC CALIBRATION HEATERS
flow regulated supply
R
S
CELLS
$(V_S - V_R) = P / K$
DIFF. VOLTAGE FROM THERMOELECTRIC SENSORS
T_{AUX}
temperature-controlled recirculating chiller bath
massive aluminum heat sink
PUMP
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
Peltier device
I_S
heat from S removed to
near-isothermal surroundings
Q_S
S
A
e
B
heat flow
$Q_S = \pi_{AB} I_S$
obtain calibration constant
$K = P / V$
with "known" added power P
$P_S = A_S \bar{E}$
I_S
V_S
DIFF
$V = (V_S - V_R)$
Reference
Cell
I_R
V_R
Q_R
R
A
e
B
heat flow
$Q_R = \pi_{AB} I_R$
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}

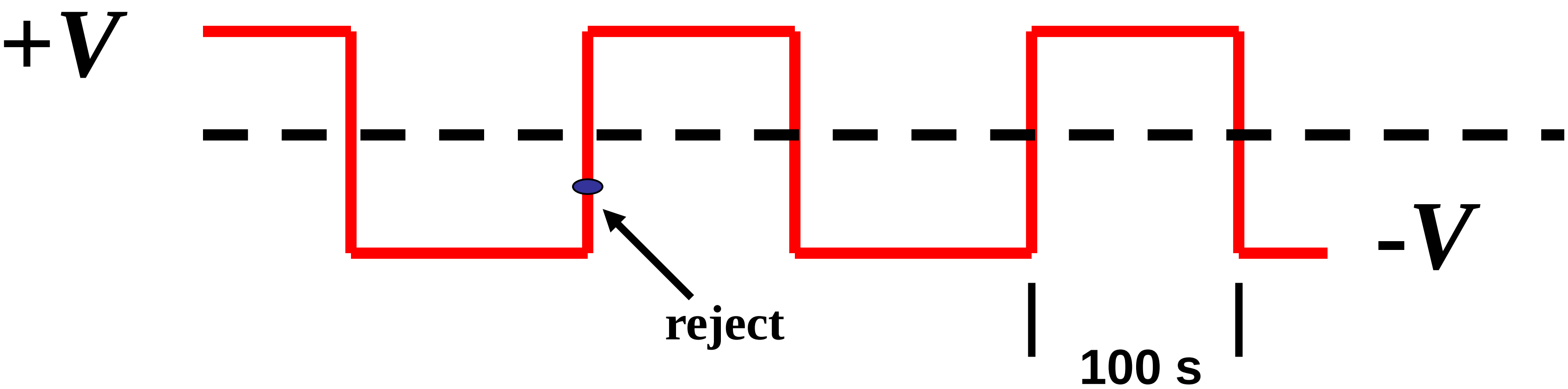


ACCESS PORT
port cap
WELL
ALUMINUM HEAT SINK
electrical leads phosphor bronze 36 AWG
high-density resin
o-ring seal
SS shaft
source contained in absorber / holder within cell
thermal shields (aluminum)
absorber (graded) various materials & configurations
threaded rod for inserting cell
slotted well cover
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
V
CALIBRATED
DIGITAL
VOLTMETER
Vishay
100 kΩ
0.001%
R
embedded in source-holder cell

$f = 0.005\ s^{-1}$ $\qquad |+V| = |-V|$



$$P = V^2 / R$$

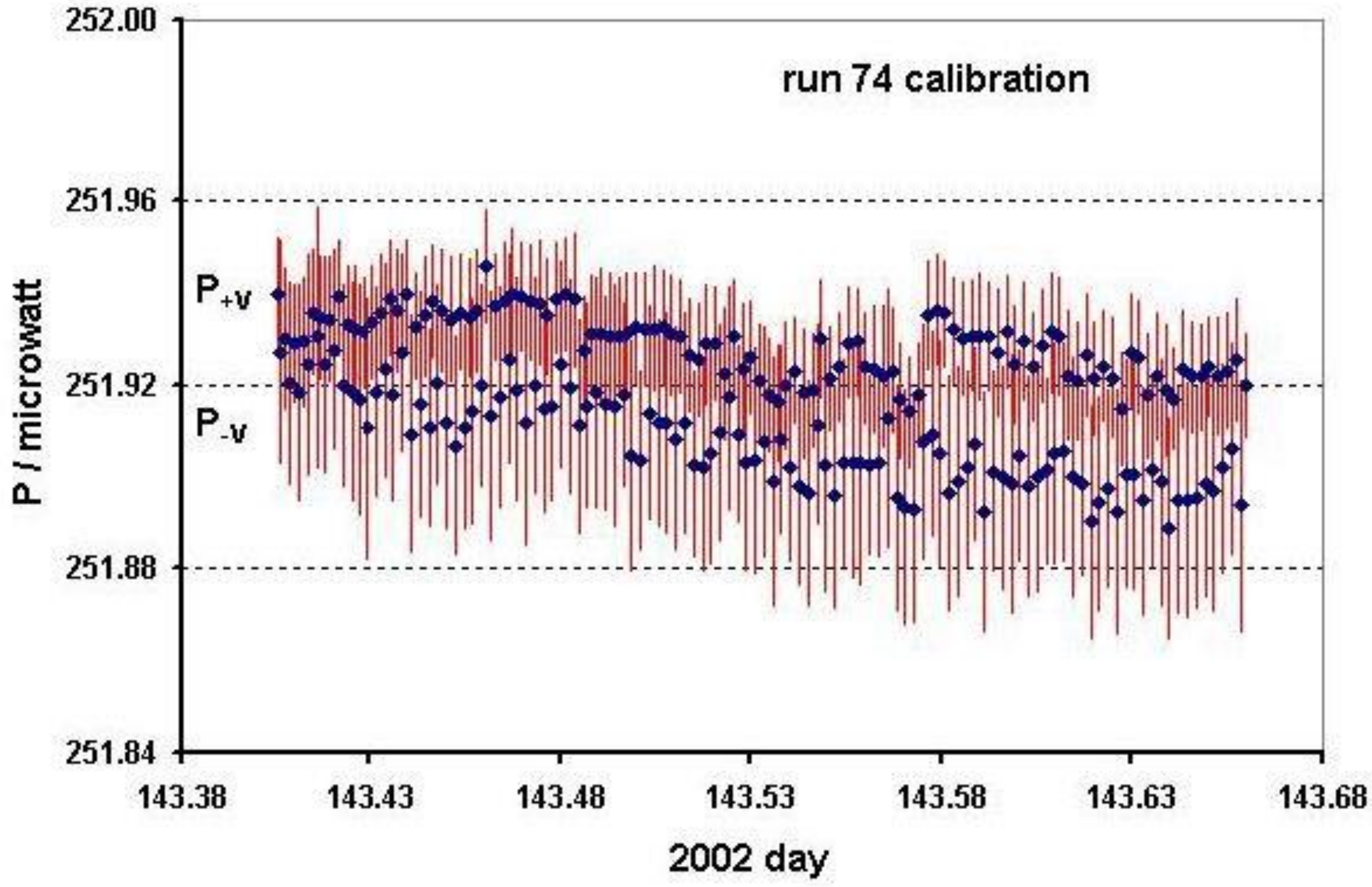
Average 100 points ($1\ s^{-1}$) $\Rightarrow$ P_{+V} or P_{-V}

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

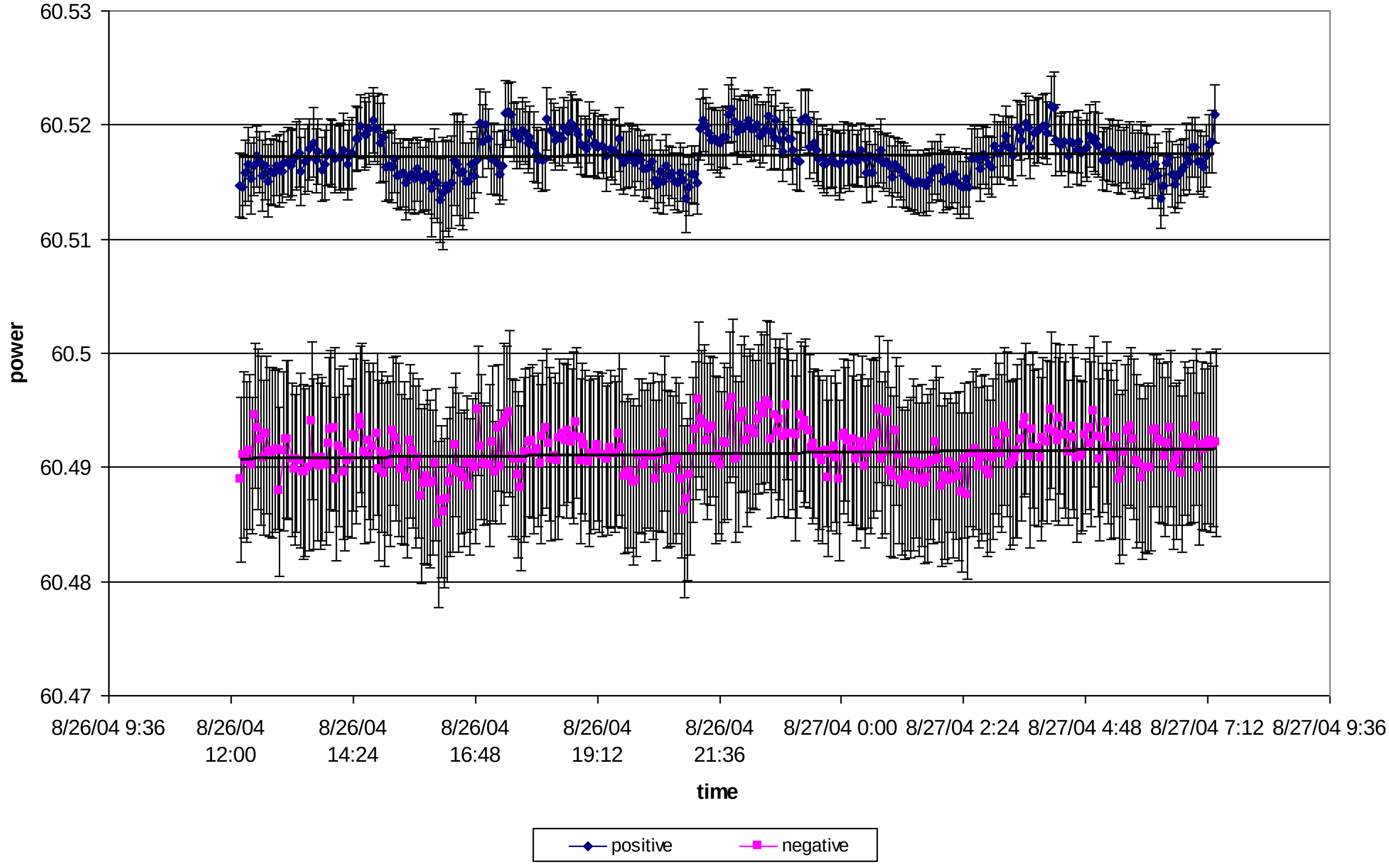
$$\text{var}(P) = 1/2\ \text{var}(P_{+V}) + 1/2\ \text{var}(P_{-V}) + \text{covar}(P_{+V}, P_{-V})$$

$$+\ \text{autocorr}(P_{+V}) \quad +\ \text{autocorr}(P_{-V})$$

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



Run 132 (^{55}Fe) –calibration 4



Two cases

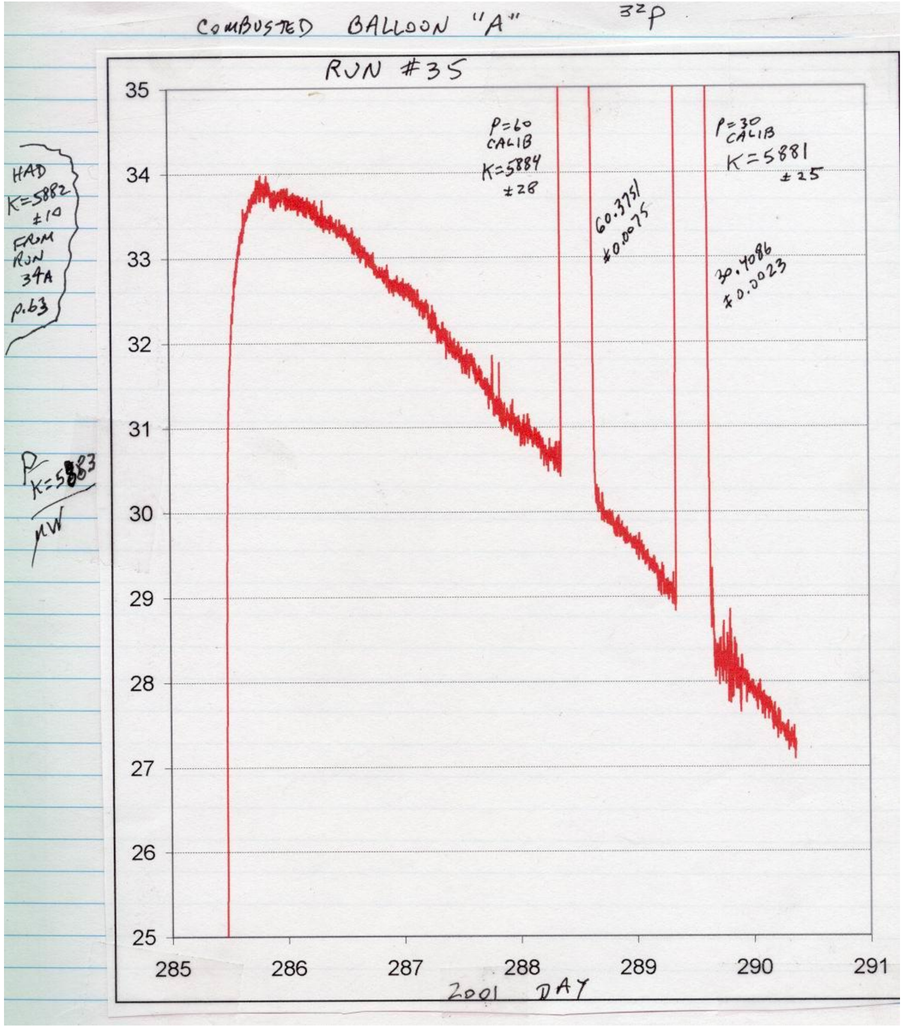
(with different measurement requirements)

-- for decaying short-lived nuclides

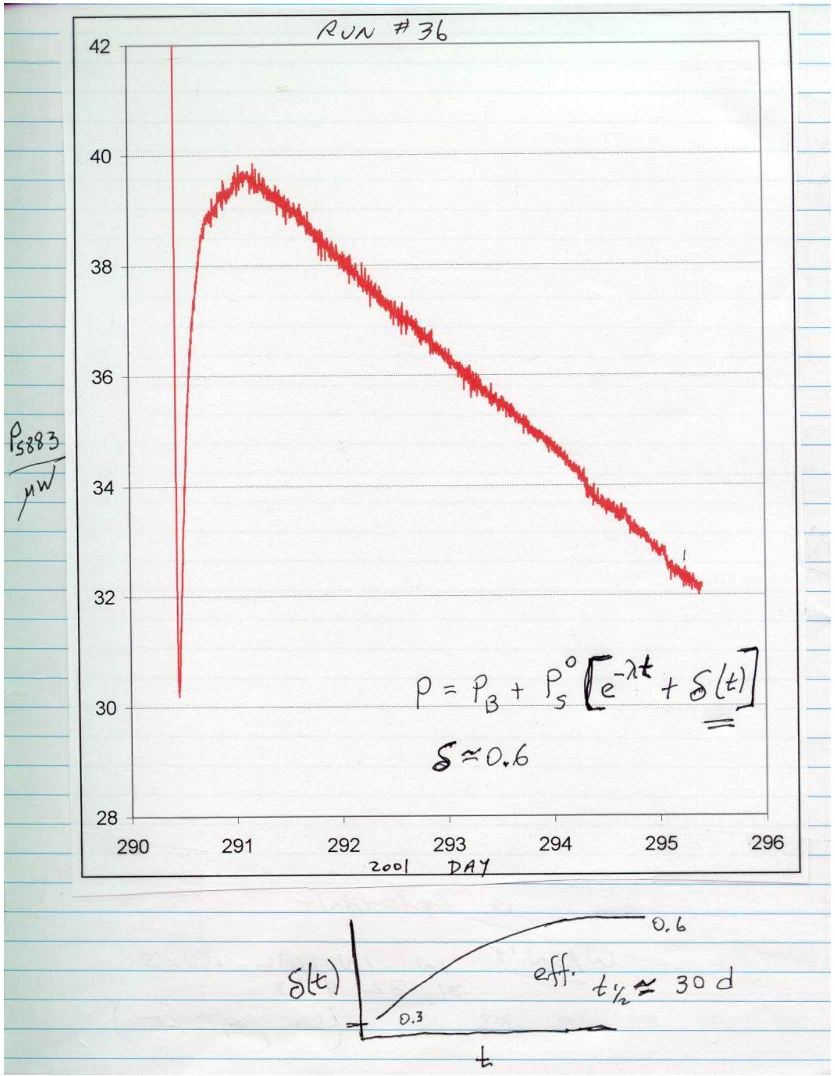
-- for long-lived nuclides (need baseline determinations)

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

Historic measurement & calibration data illustrate these



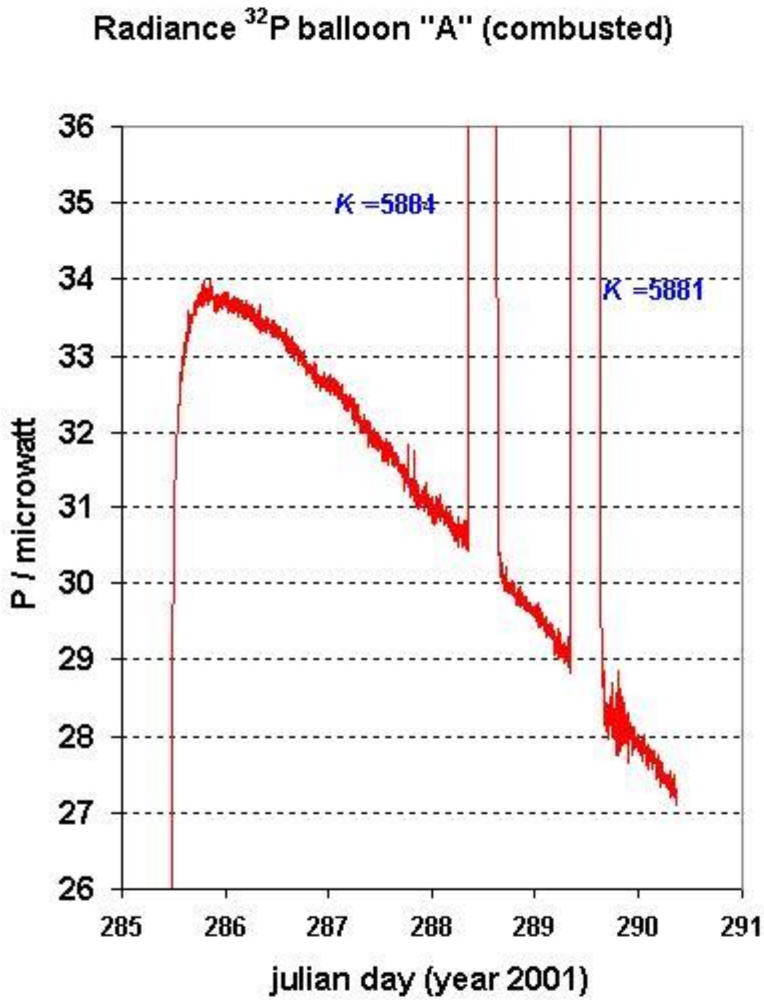
IMC Lab Book II, p.79



IMC Lab Book II, p.97

combusted ^{32}P balloon "A" **uncombusted ^{32}P balloon "C"**

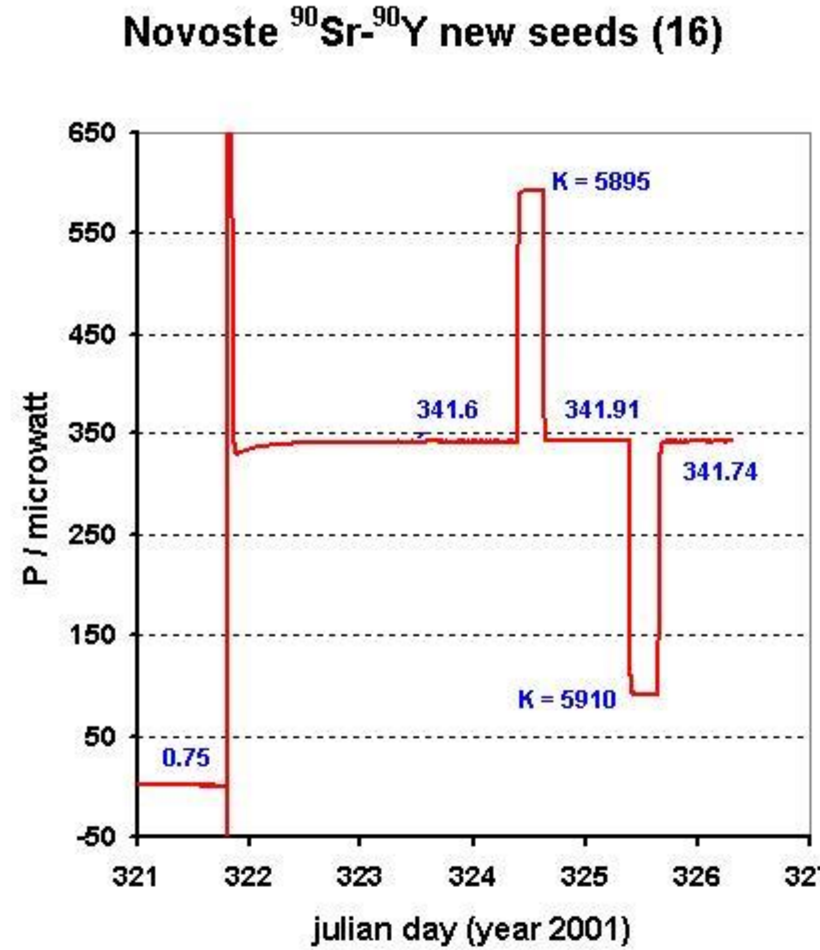
Run35
Bk2,p79



Get P_B and P_0 from "fit"

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

Run43
Bk2,p167



requires baseline P_B measurement

^{55}Fe pure EC decay

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

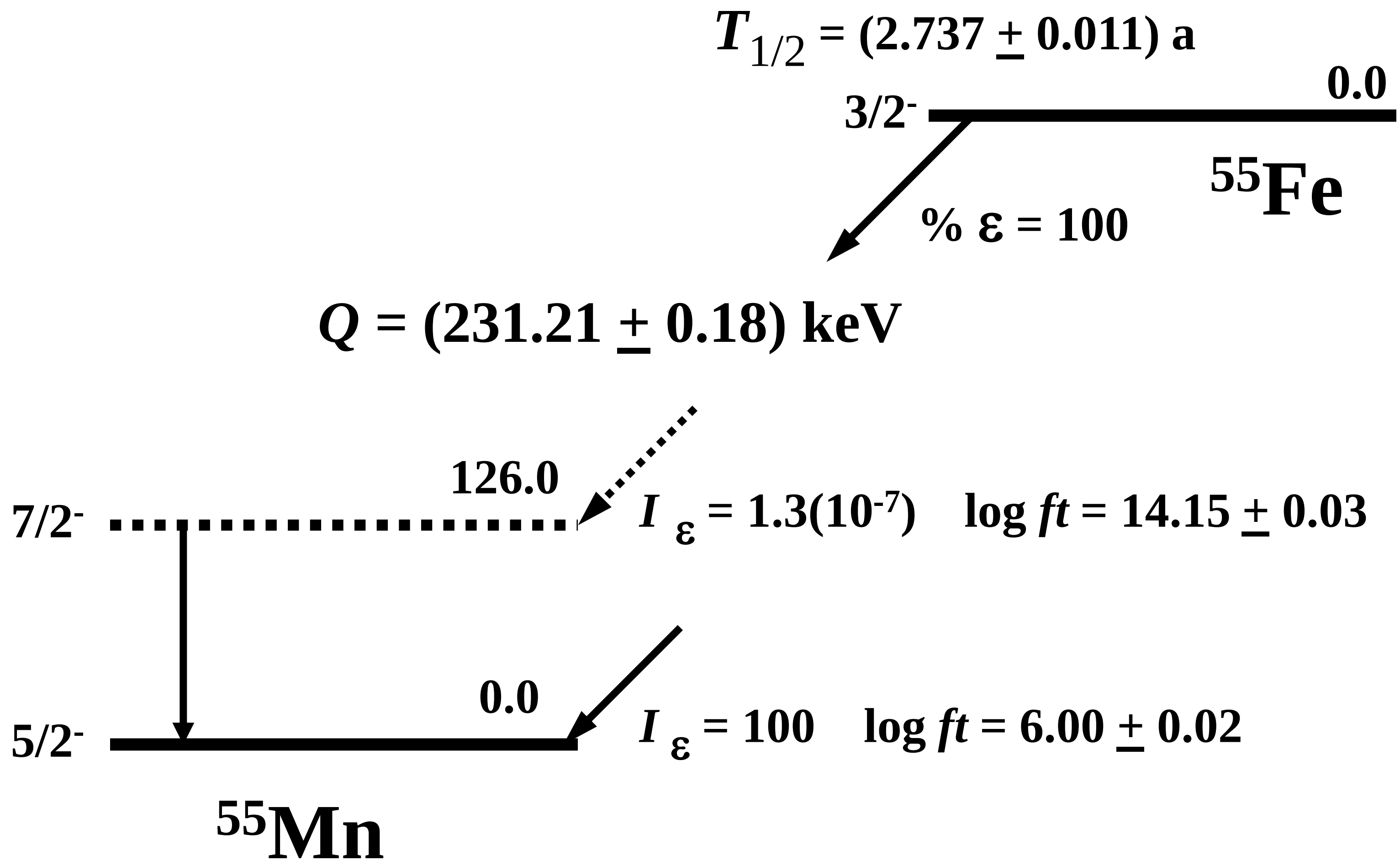
Half-life:

(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, toxic (& wasn't arranged in my absence)*

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

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

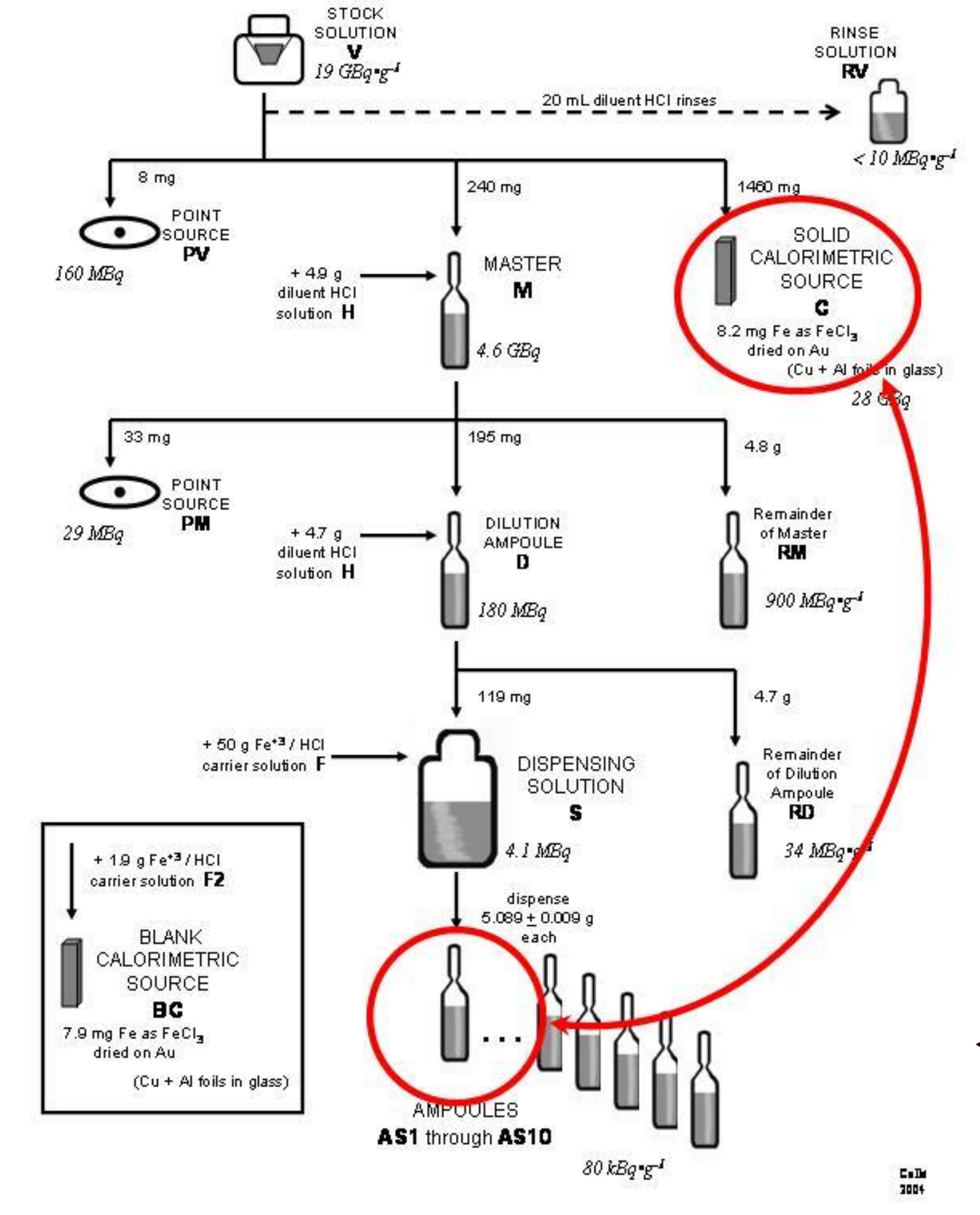
endothermic

exothermic

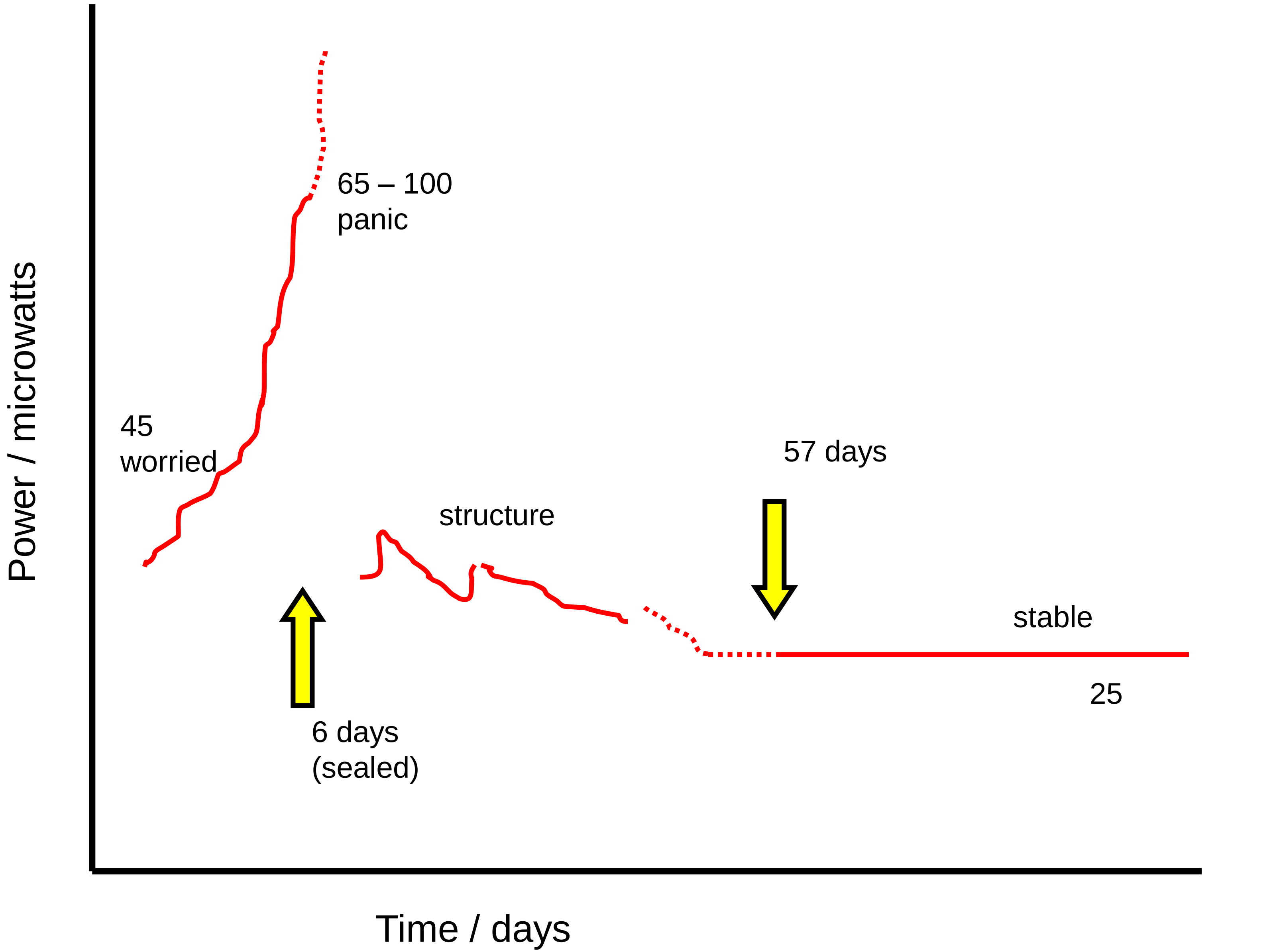
(0.8 kJ/g)

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

Lattice energy

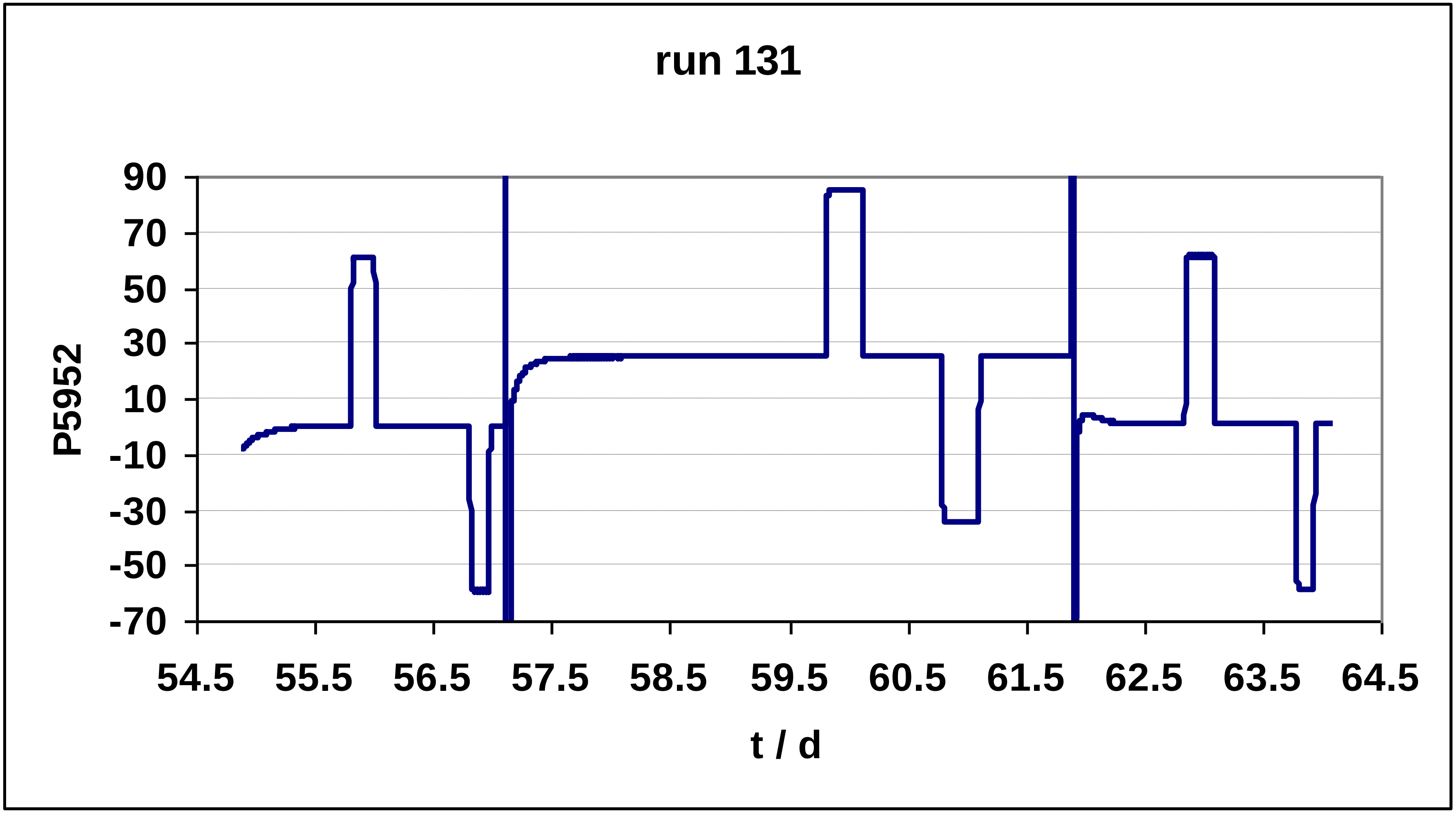


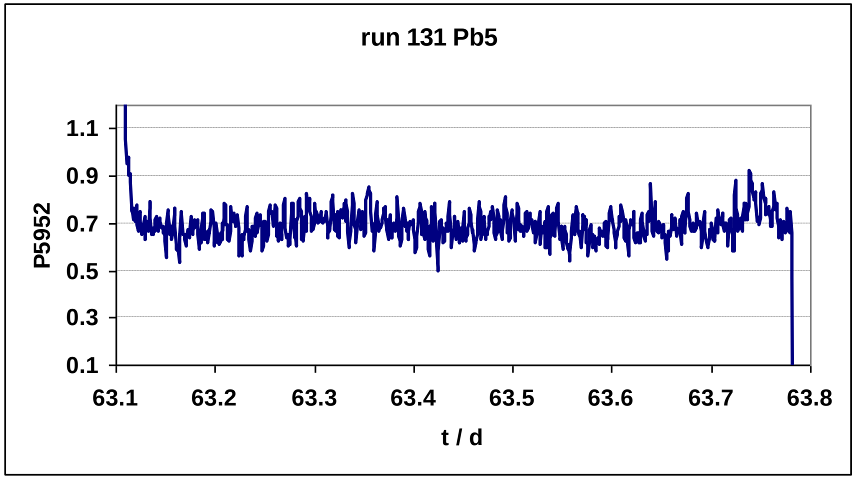
LNHB &
Polatom LS
TDCR
comparisons

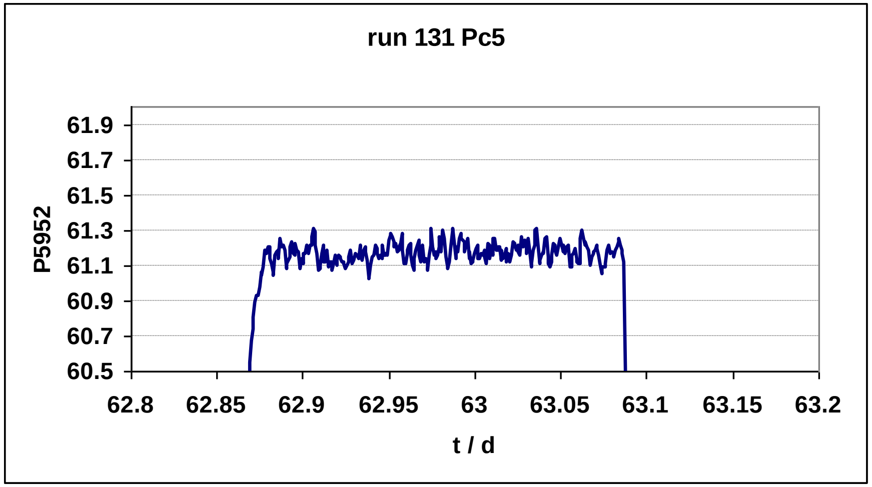


Power / microwatts
65 – 100
panic
45
worried
structure
57 days
stable
25
6 days
(sealed)
Time / days

Typical run data

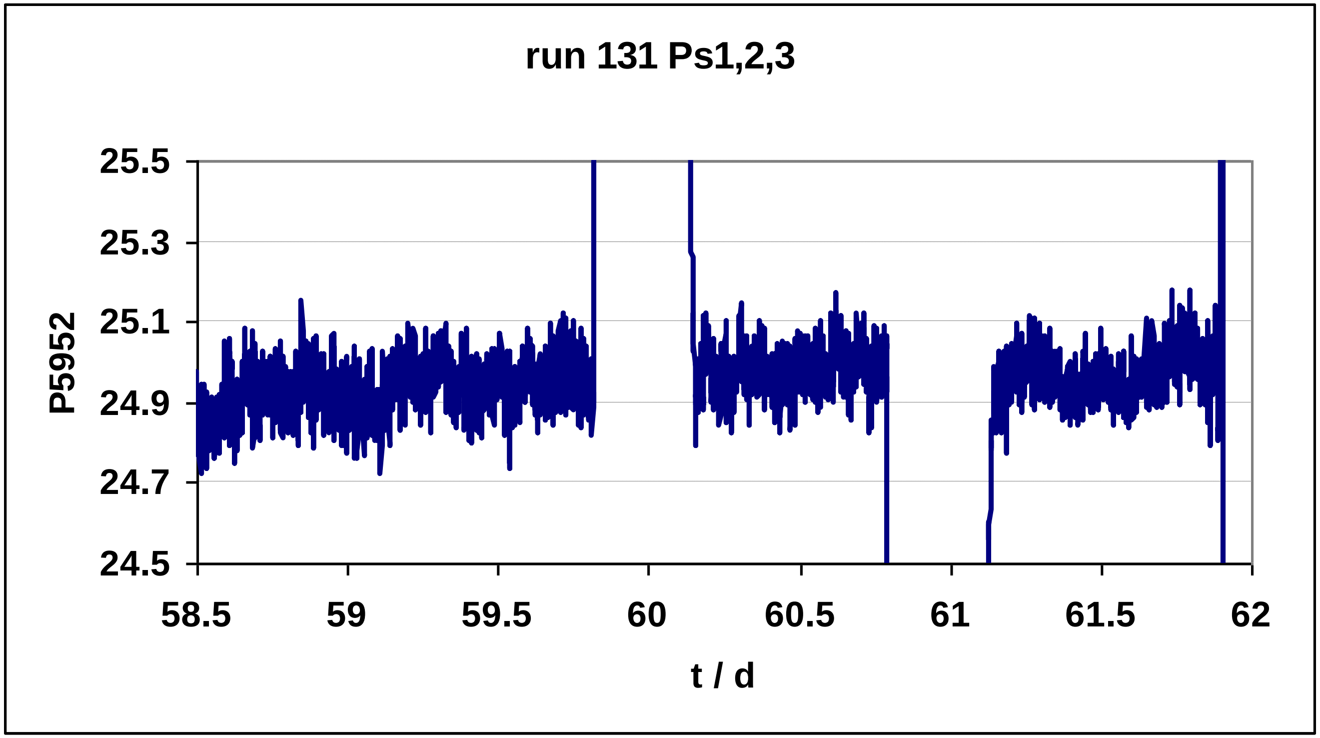






Typical

(in)stability



baseline & calibration reproduction -- in support slides

Results of 13 insertion trials

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...

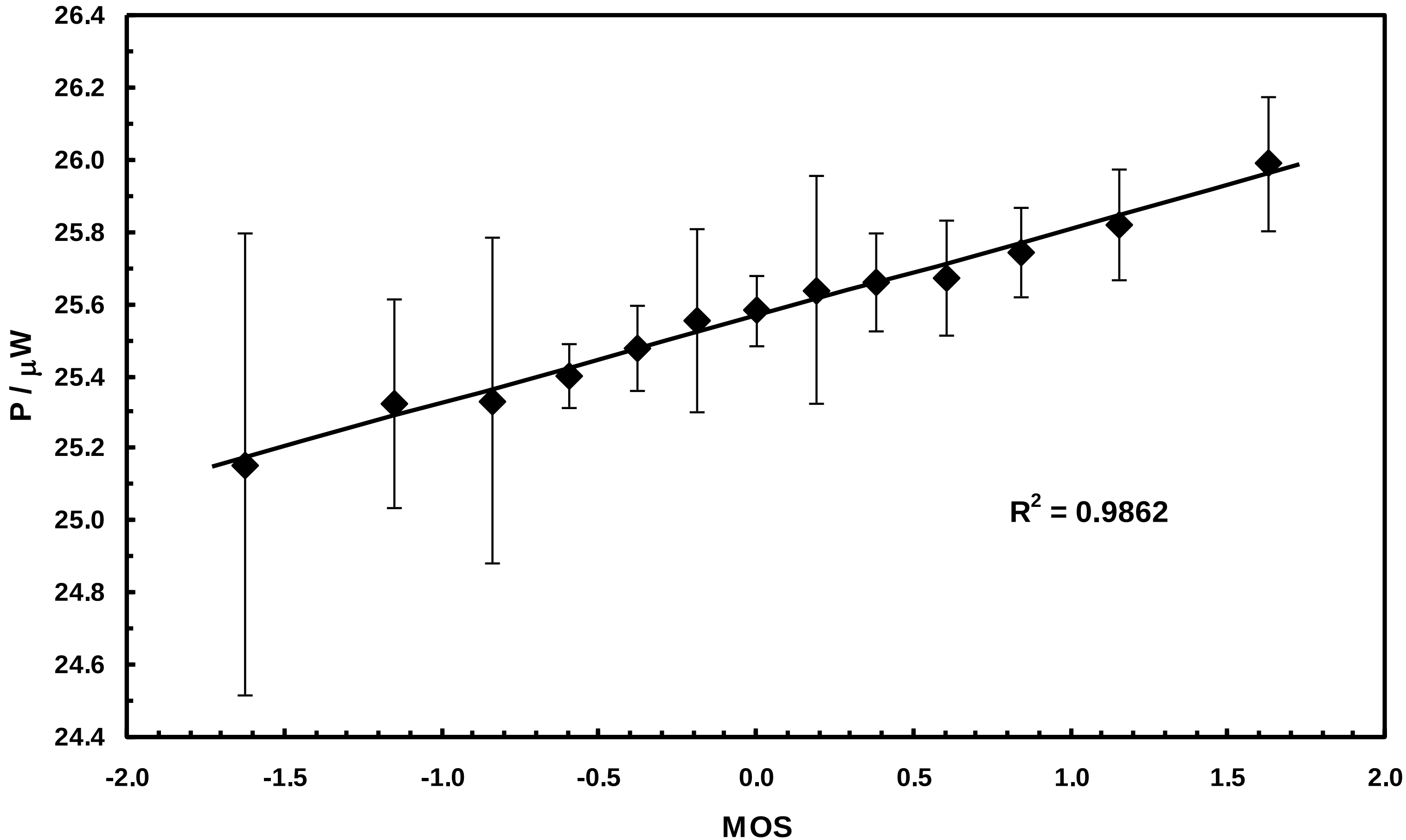
additional runs mar-apr 2006

T_0 = 1200 EST **1 July 2004**

Mean P = 25.567 μW(w/ 998.9 d)

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

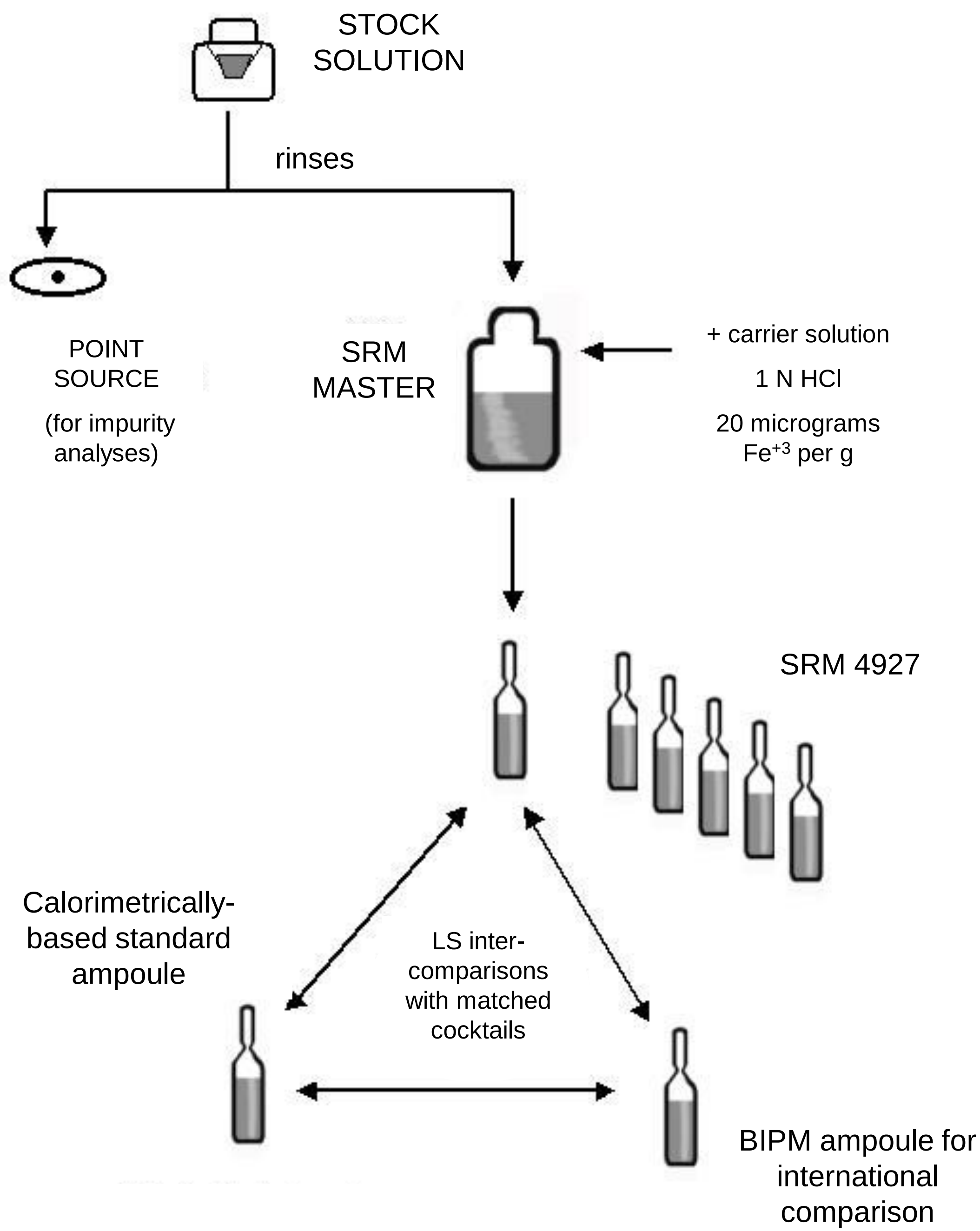
% sdm = 0.25 %


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

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

Nuclide	**Method**	**relative standard uncertainty**	**Confirmatory Measurement**	**Difference (%)**
^{55}Fe (NIST solution)	**4π calorimetry**	**0.39 %**	**4π LS TDCR (Polatom)** **4π LS TDCR (LNHB)**	**-0.87** **-0.43**
^{55}Fe (BIPM solution)	4π calorimetry (linked by LS)	0.68 %	weighted mean value of 15 NMI labs unweighted mean of 15 NMI labs (all methods *n* = 24)	-0.37 -0.02


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

3 LS counters

LS Counters

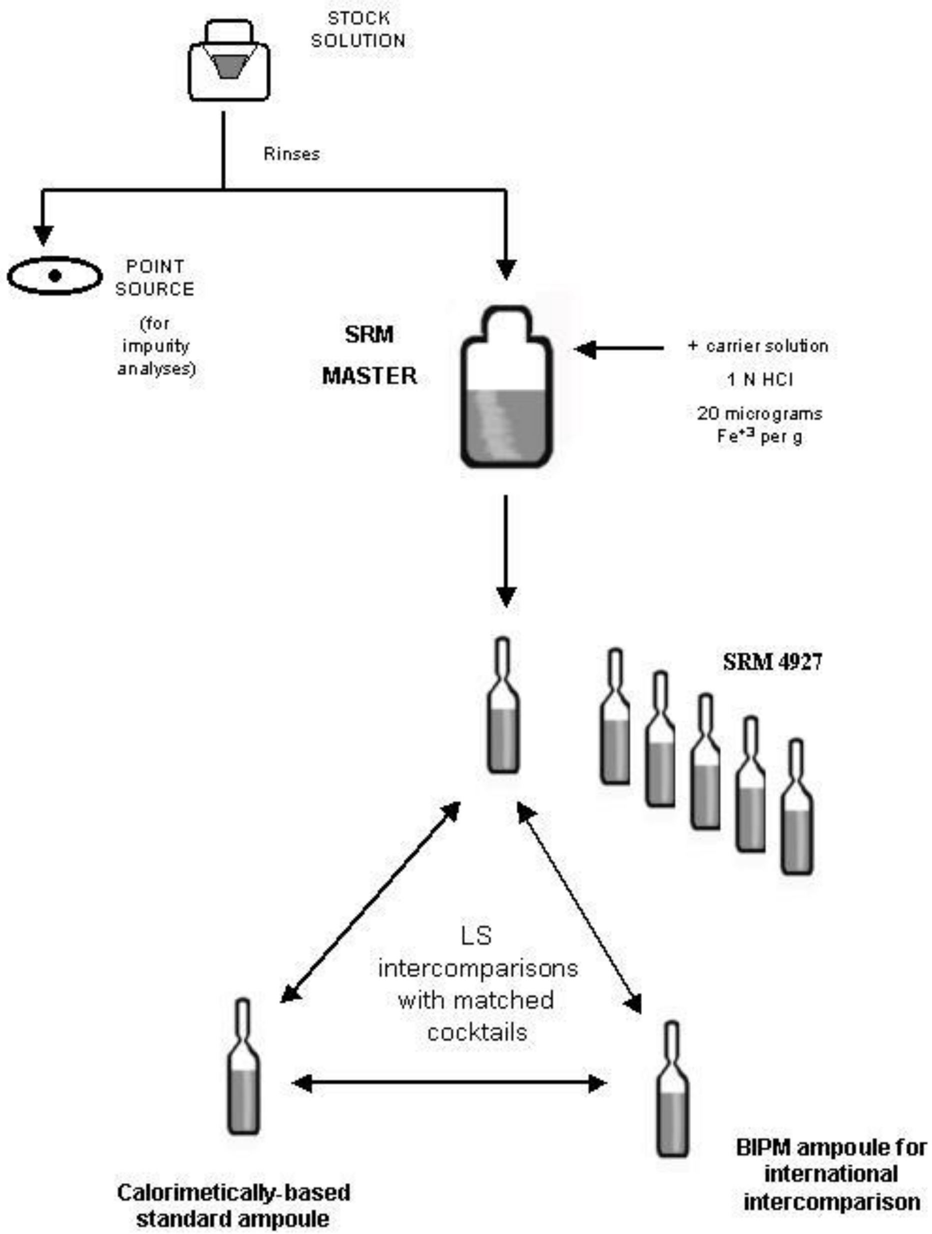
	LS spectrometer model	Sum-coincidence pulse spectrum & ADC	Other stuff
system B2	Beckman LS 6500	**Logarithmic** ? 32K analyzer / variable (0.06 keV per channel)	H # with ^{137}Cs unknown resolving time 5.6% - 2.5 keV - ^{209}Po ce(γ) about 50% - ^{55}Fe
system P	Packard Tri-carb A2500TR	**Linear** 2048 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



Calorimetry

13 independent determinations

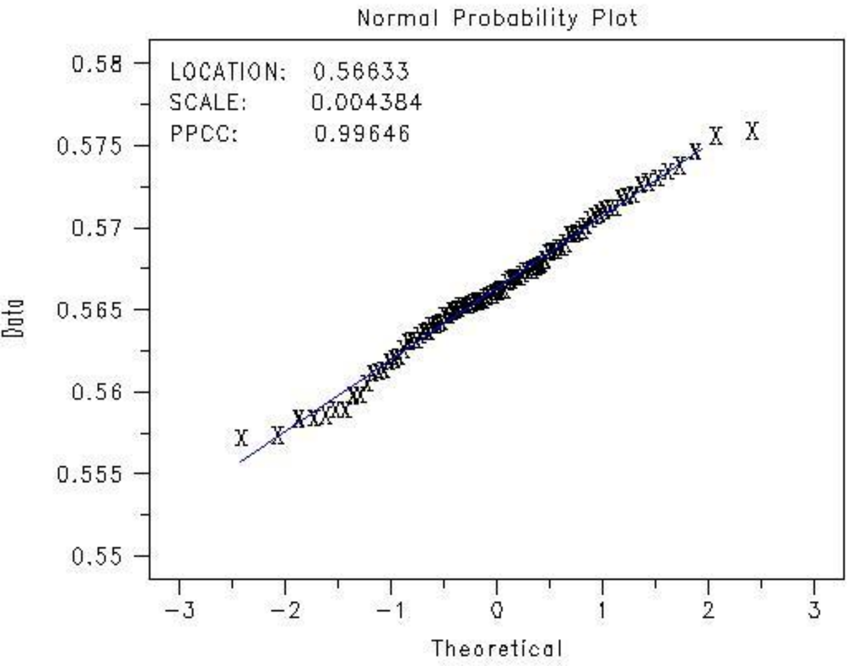
LS intercomparisons

776 activity ratios; variables include:

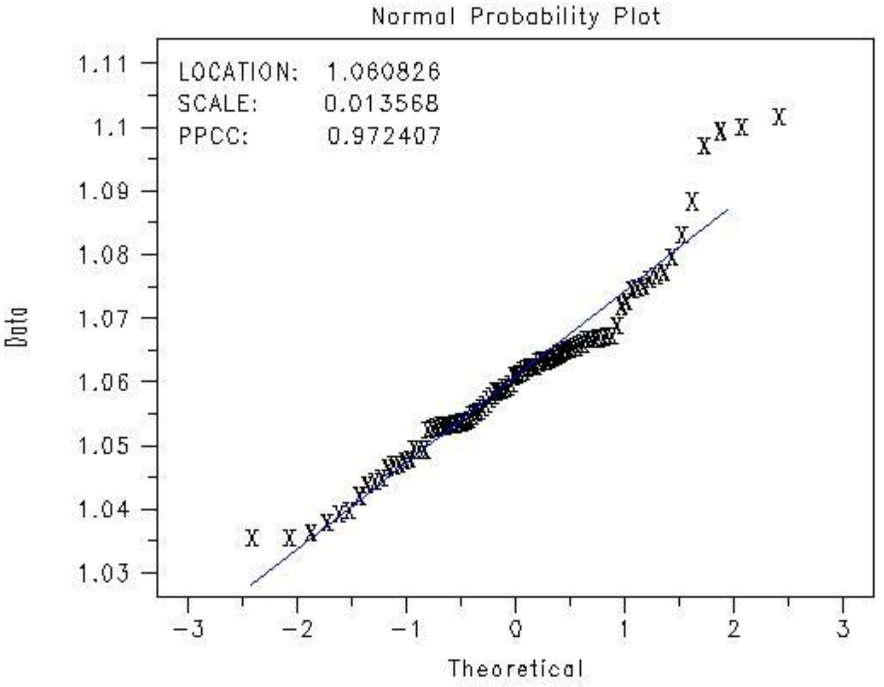
- 3 counters
- 3 scintillators
- 44 matched cocktails
- 4 distinct aq. fraction (+Fe) compositions
- 2 NIST solution dilutions
- 97 days of aging

Normality

BIPM/CAL



SRM/CAL



BIPM

T_0 = 30 november 2005

522.6 kBq/g

U (k=1) = 0.66 %

cal soln S

T_0 = 1 july 2004

78.78 kBq/g

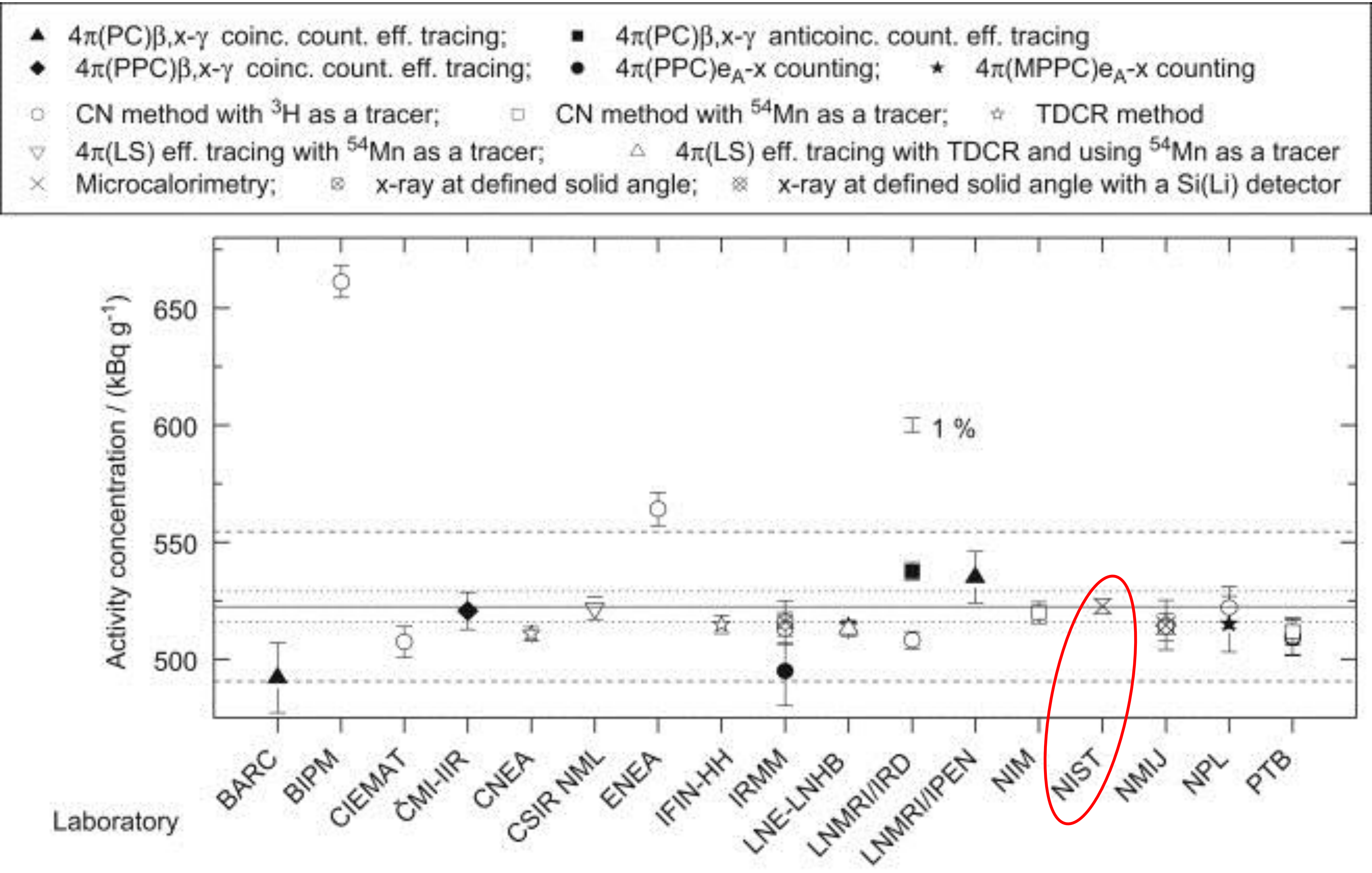
U (k=1) = 0.39 %

SRM 4929F

T_0 = 30 november 2005

58.43 kBq/g

U (k=2) = 1.7 %



4π(PC)β,x-γ coinc. count. eff. tracing;
4π(PC)β,x-γ anticoinc. count. eff. tracing
4π(PPC)β,x-γ coinc. count. eff. tracing;
4π(PPC)e_A-x counting;
4π(MPPC)e_A-x counting
CN method with 3H as a tracer;
CN method with 54Mn as a tracer;
TDCR method
4π(LS) eff. tracing with 54Mn as a tracer;
4π(LS) eff. tracing with TDCR and using 54Mn as a tracer
Microcalorimetry;
x-ray at defined solid angle;
x-ray at defined solid angle with a Si(Li) detector
Activity concentration / (kBq g-1)
650
600
550
500
1 %
Laboratory
BARC
BIPM
CIEMAT
ČMI-IIR
CNEA
CSIR NML
ENEA
IFIN-HH
IRMM
LNE-LNHB
LNMRI/IRD
LNMRI/IPEN
NIM
NIST
NMIJ
NPL
PTB

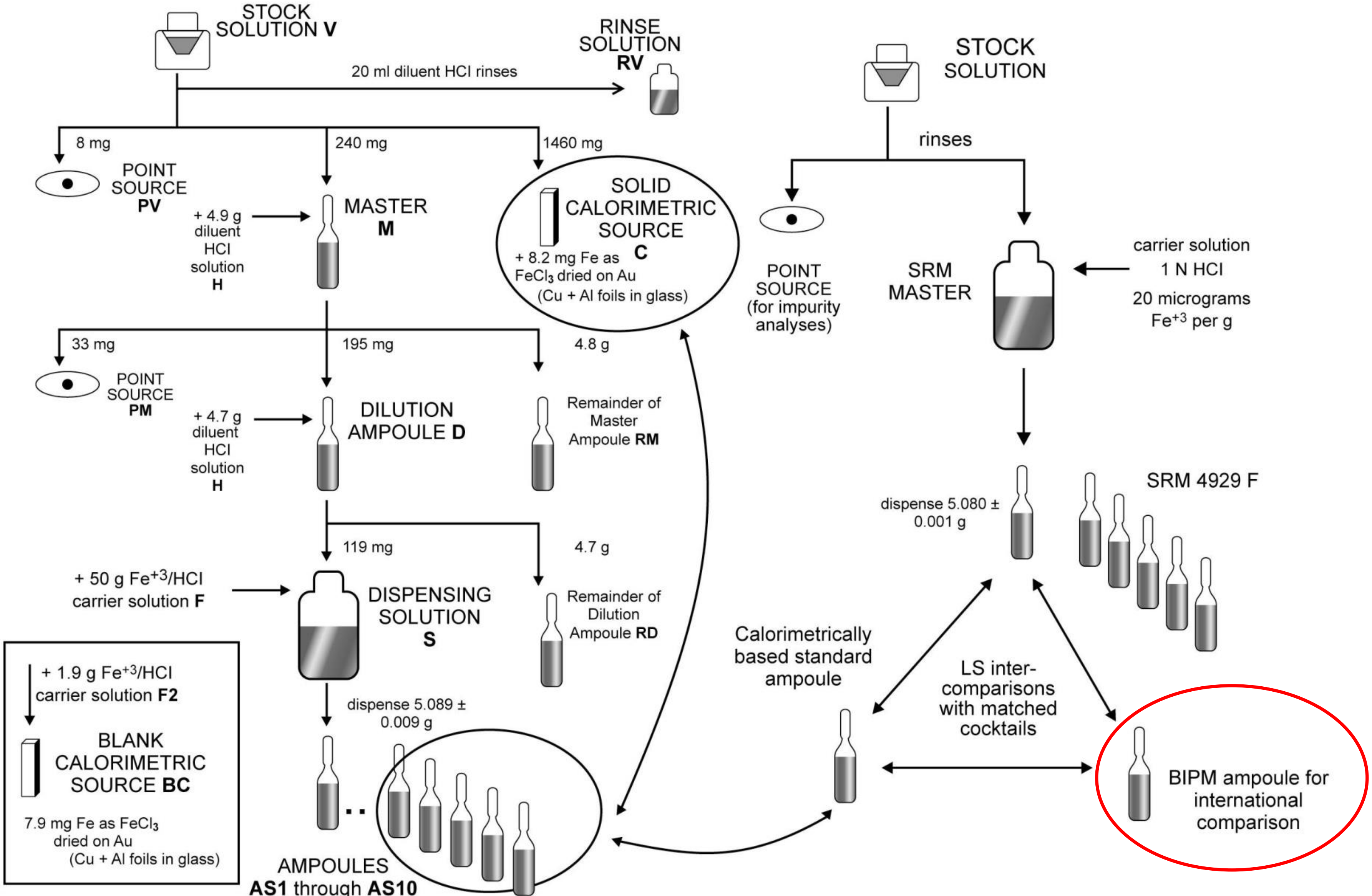
NIST Uncertainty Analysis for ^{55}Fe Massic Activity for the BIPM International Comparison

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**

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

$U\ (k=2) = 1.7\ \%$

Nuclide	Method	relative standard uncertainty	Confirmatory Measurement	Difference (%)
^{55}Fe (NIST solution)	4π calorimetry	0.39 %	4π LS TDCR (Polatom) 4π LS TDCR (LNHB)	-0.87 -0.43
^{55}Fe (BIPM solution)	**4π calorimetry (linked by LS)**	**0.68 %**	**weighted mean value of 15 NMI labs (one value per lab)** **unweighted mean of 15 NMI labs (all methods n = 24)**	**-0.37** **-0.02**



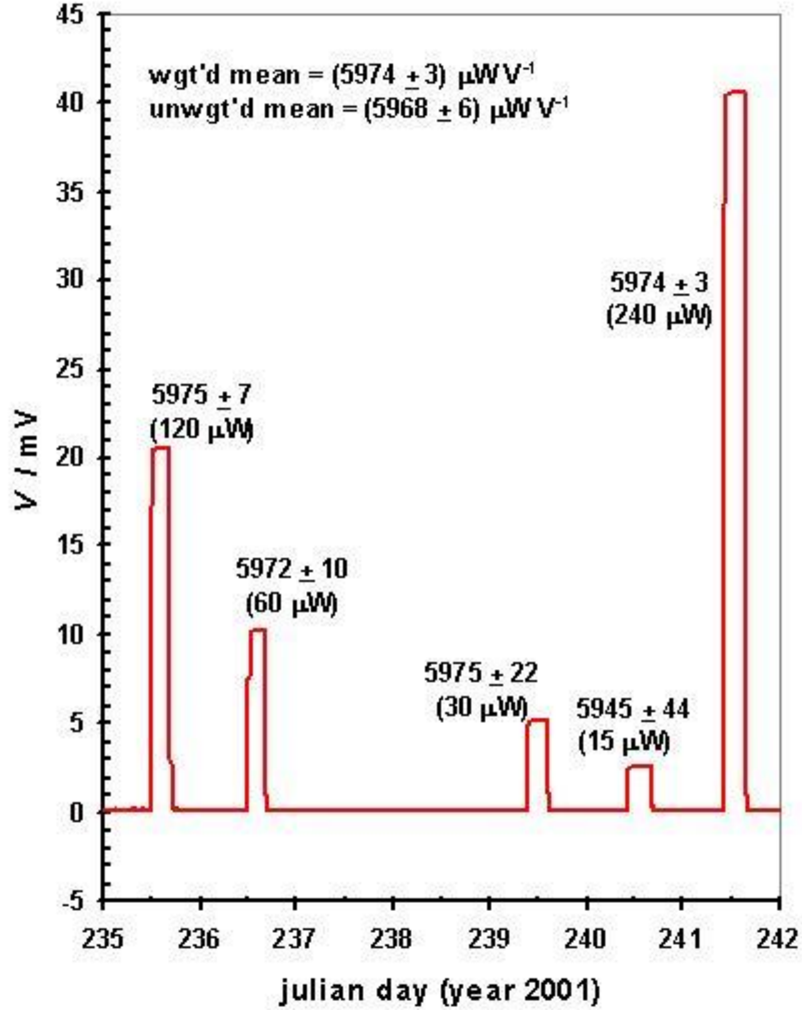
13 calorimetric determinations

(*u* = 0.39%)

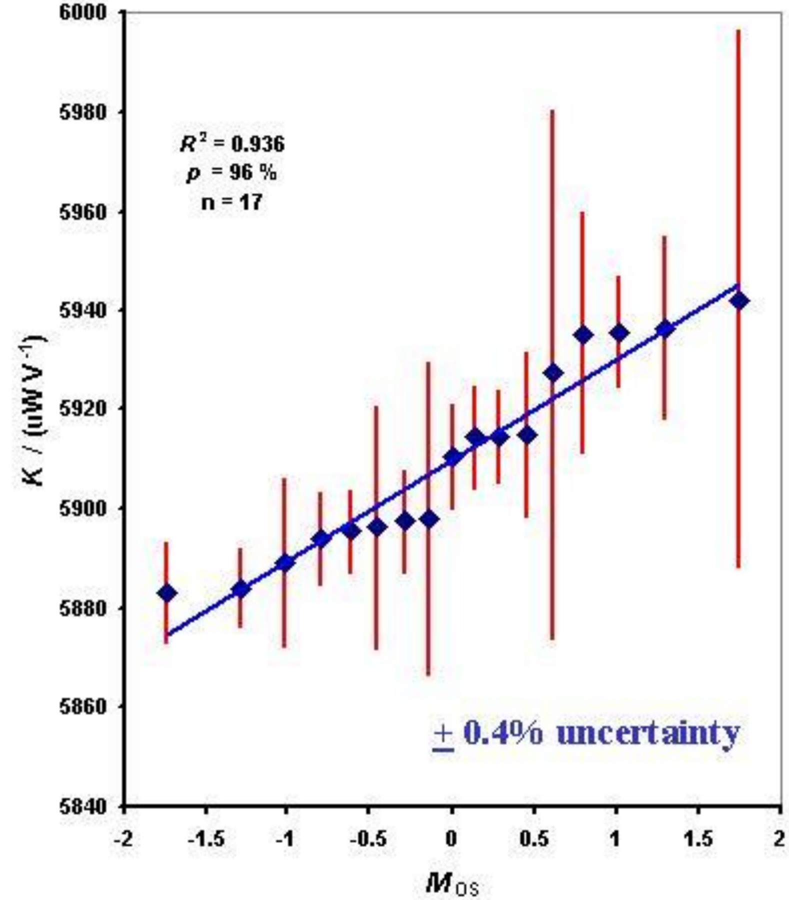
776 LS ratios

(u = 0.68 %)

Some support slides follow, if needed



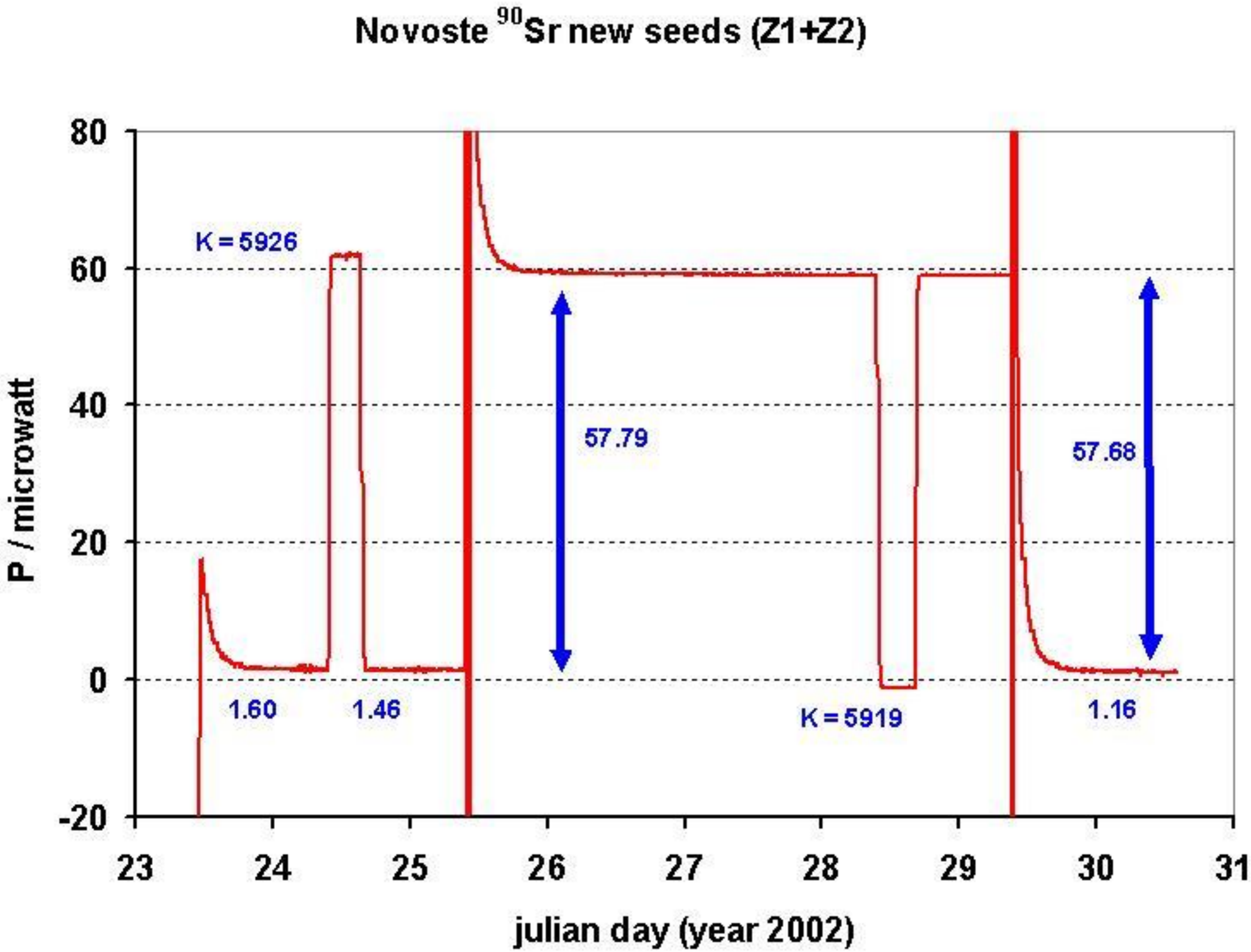
typical calibration data set



Filliben normality test for calibration data (Novoste seeds)

Run59

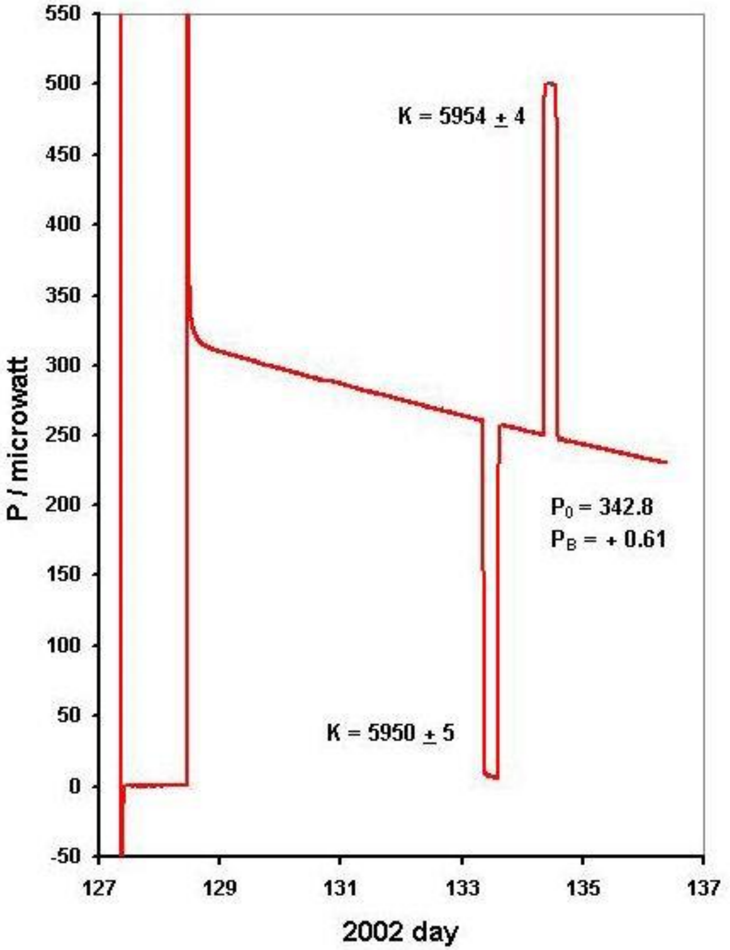
Bk3p173

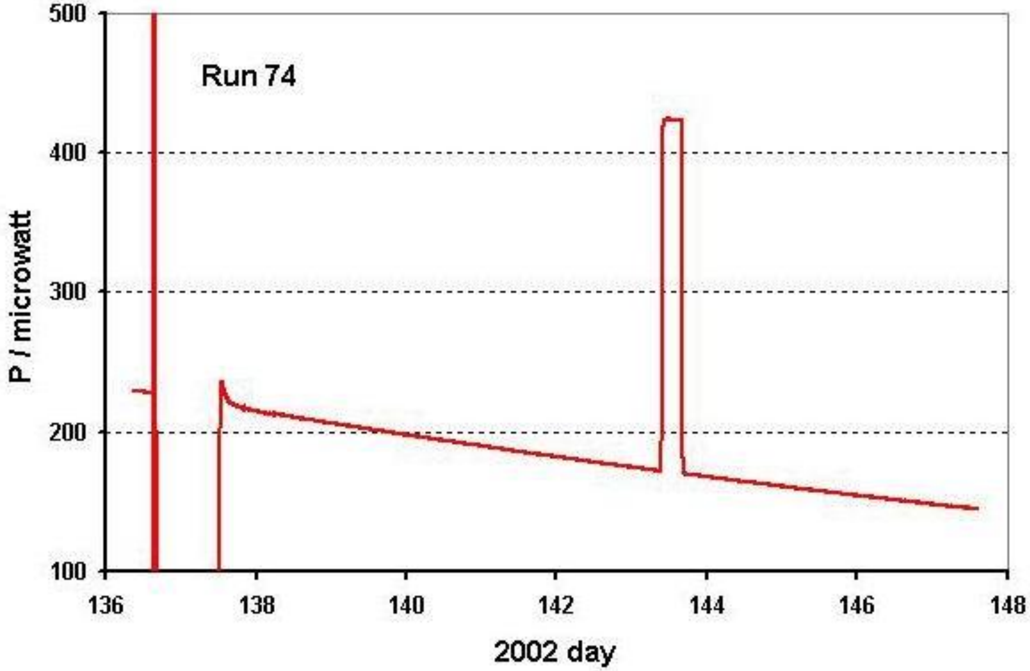


^{103}Pd data

1^{st} & 2^{nd} insertions (brass)

Runs 73 & 74



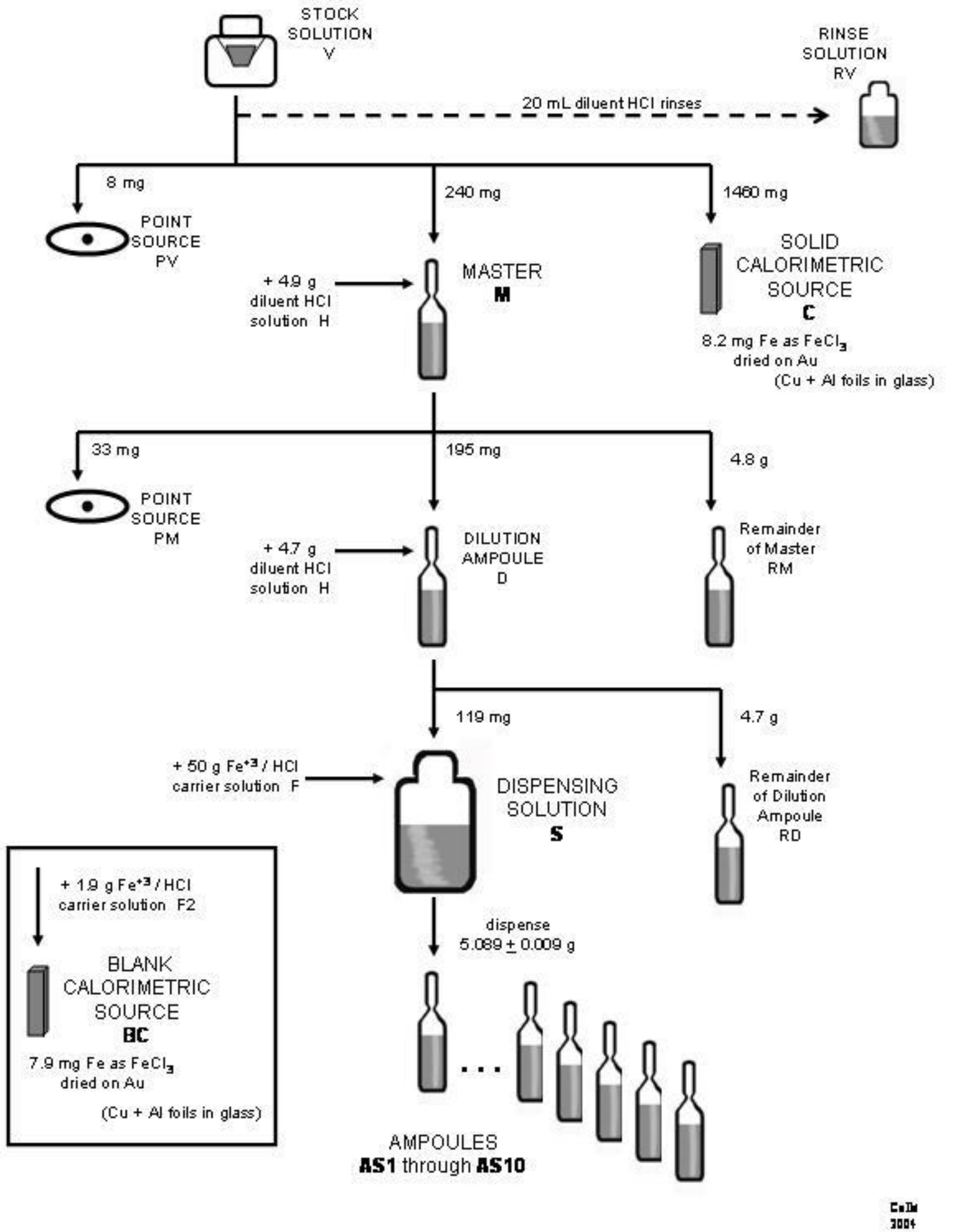


So... How good is calorimetry ?

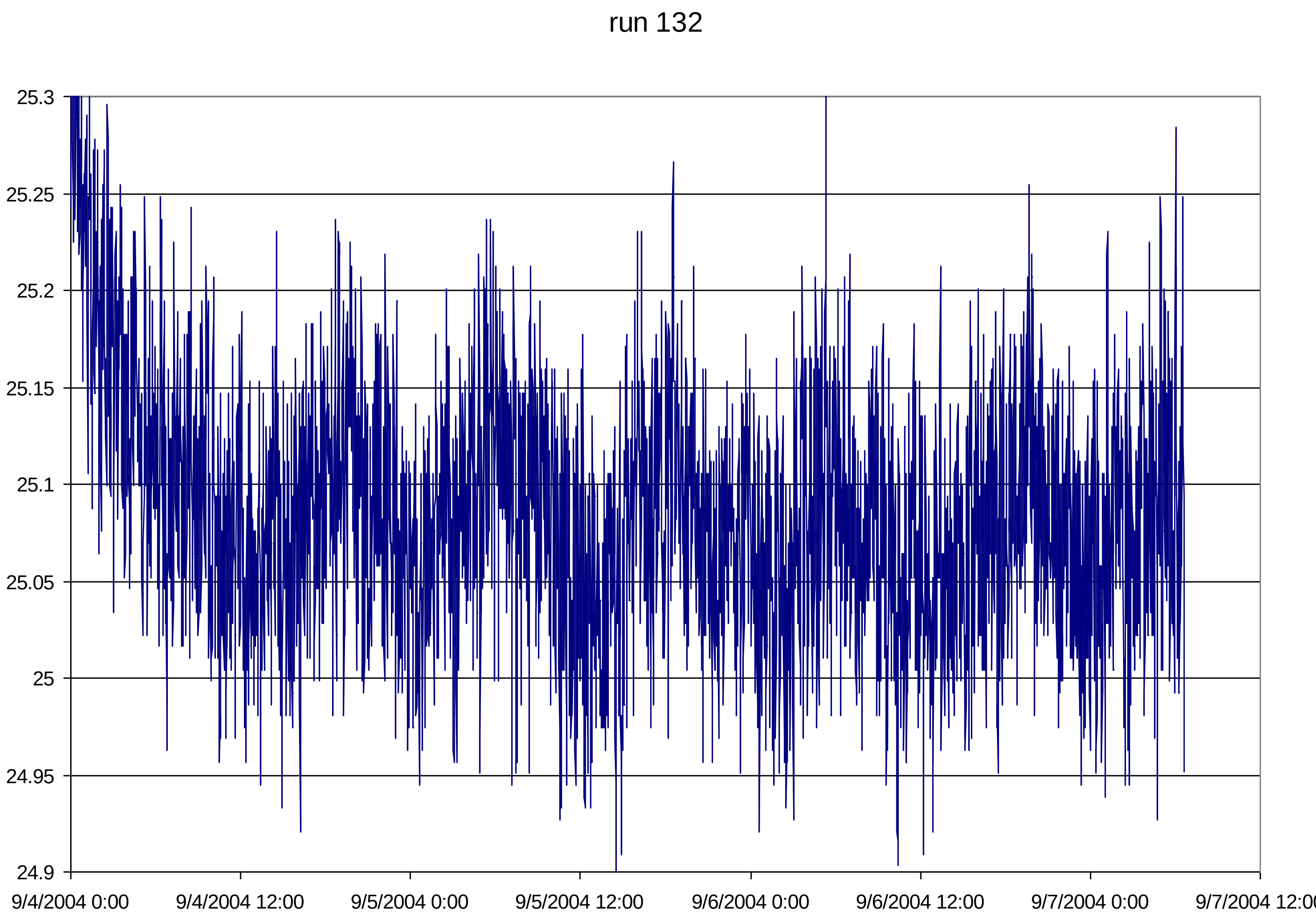
Typically, better than 1 % agreement w/ LS-based standardizations of ^{32}P and $^{90}Sr/^{90}Y$ (ion chamber transfer)

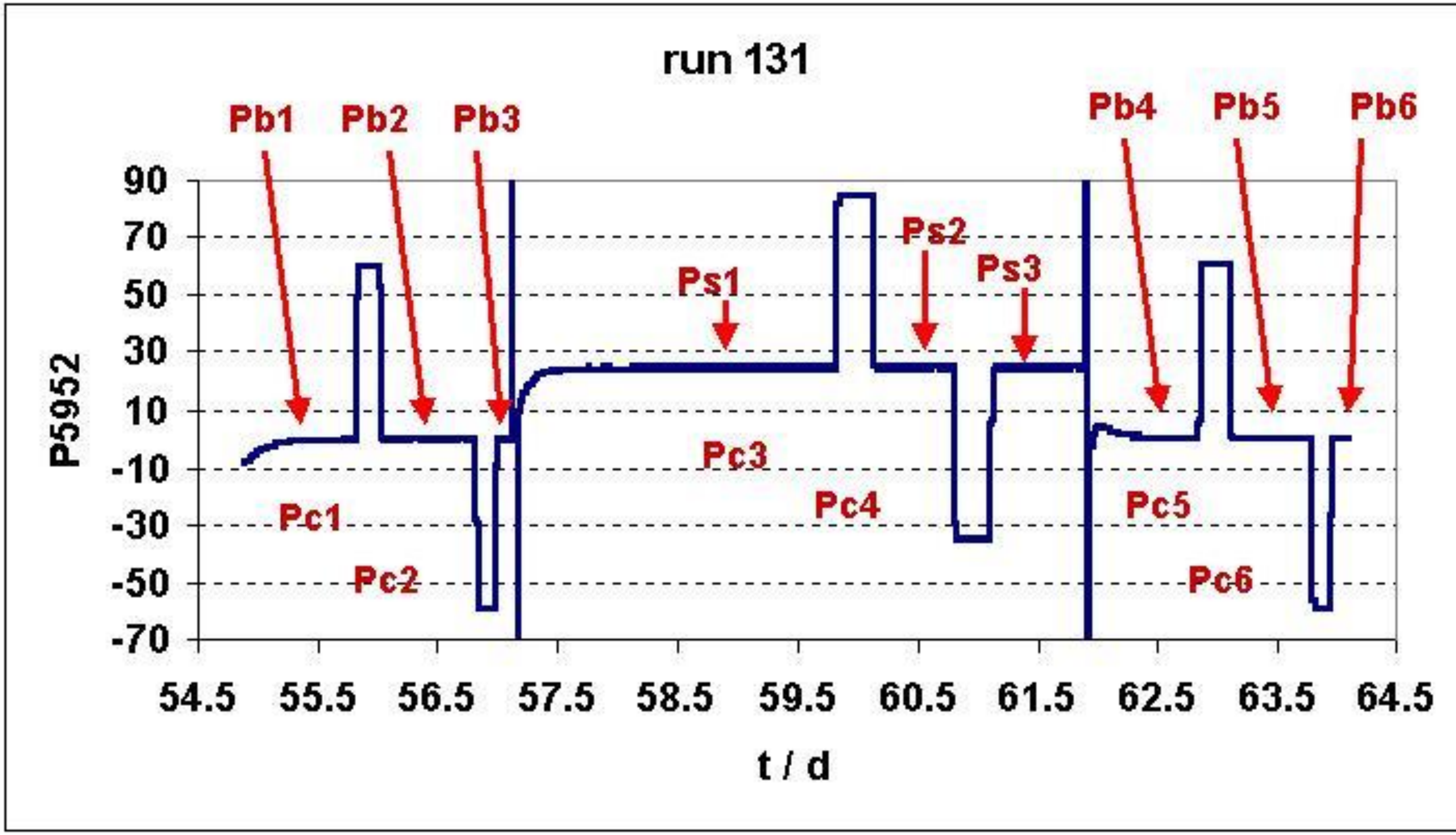
Power calibrations (for n>20 determinations) has typical s.d.m. < 0.1 %

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)



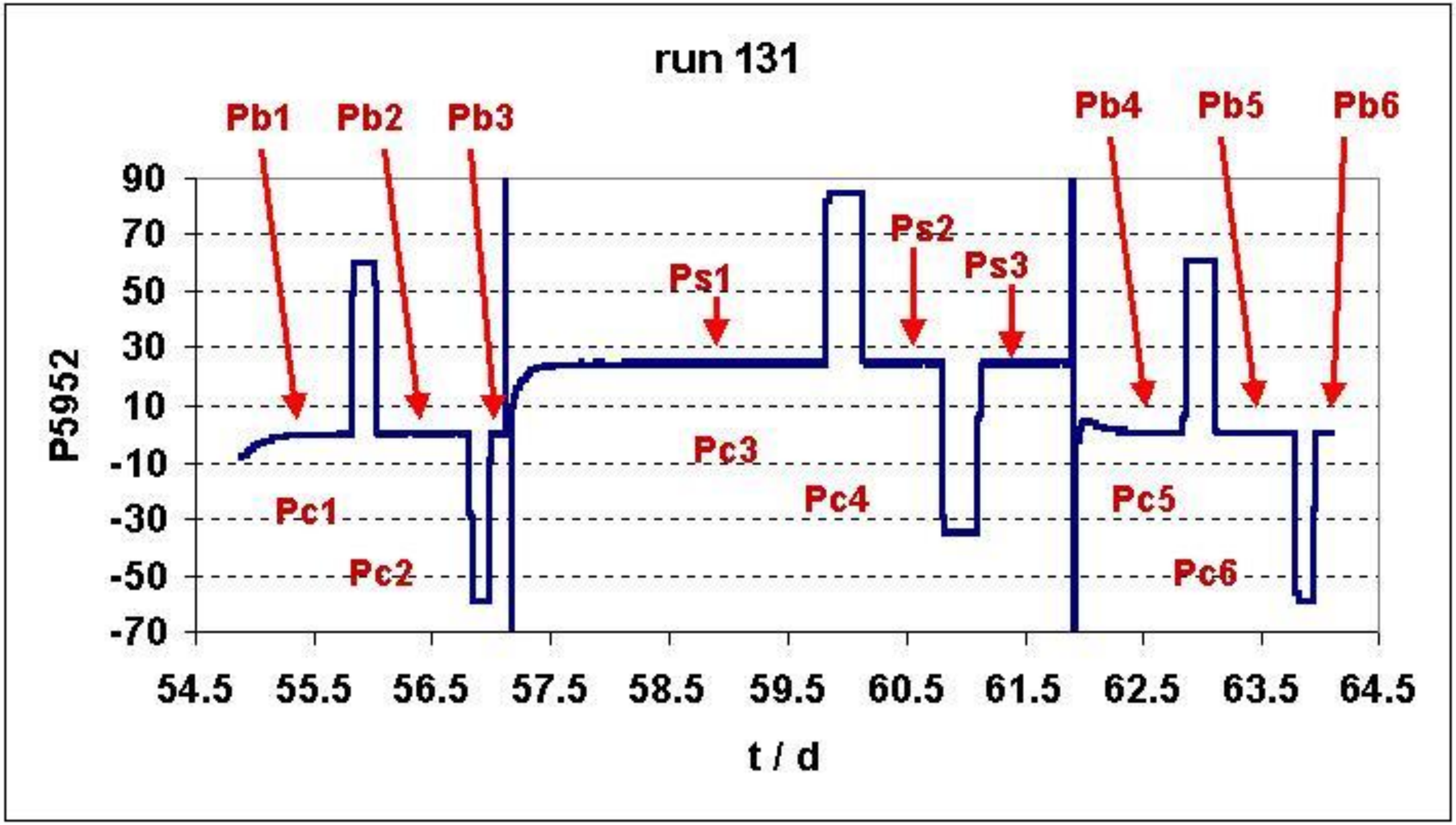
STOCK SOLUTION V
RINSE SOLUTION RV
20 mL diluent HCl rinses
8 mg
240 mg
1460 mg
POINT SOURCE PV
MASTER M
+ 4.9 g diluent HCl solution H
SOLID CALORIMETRIC SOURCE C
8.2 mg Fe as $FeCl_3$ dried on Au
(Cu + Al foils in glass)
33 mg
195 mg
4.8 g
POINT SOURCE PM
+ 4.7 g diluent HCl solution H
DILUTION AMPOULE 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
CoIn 2004


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



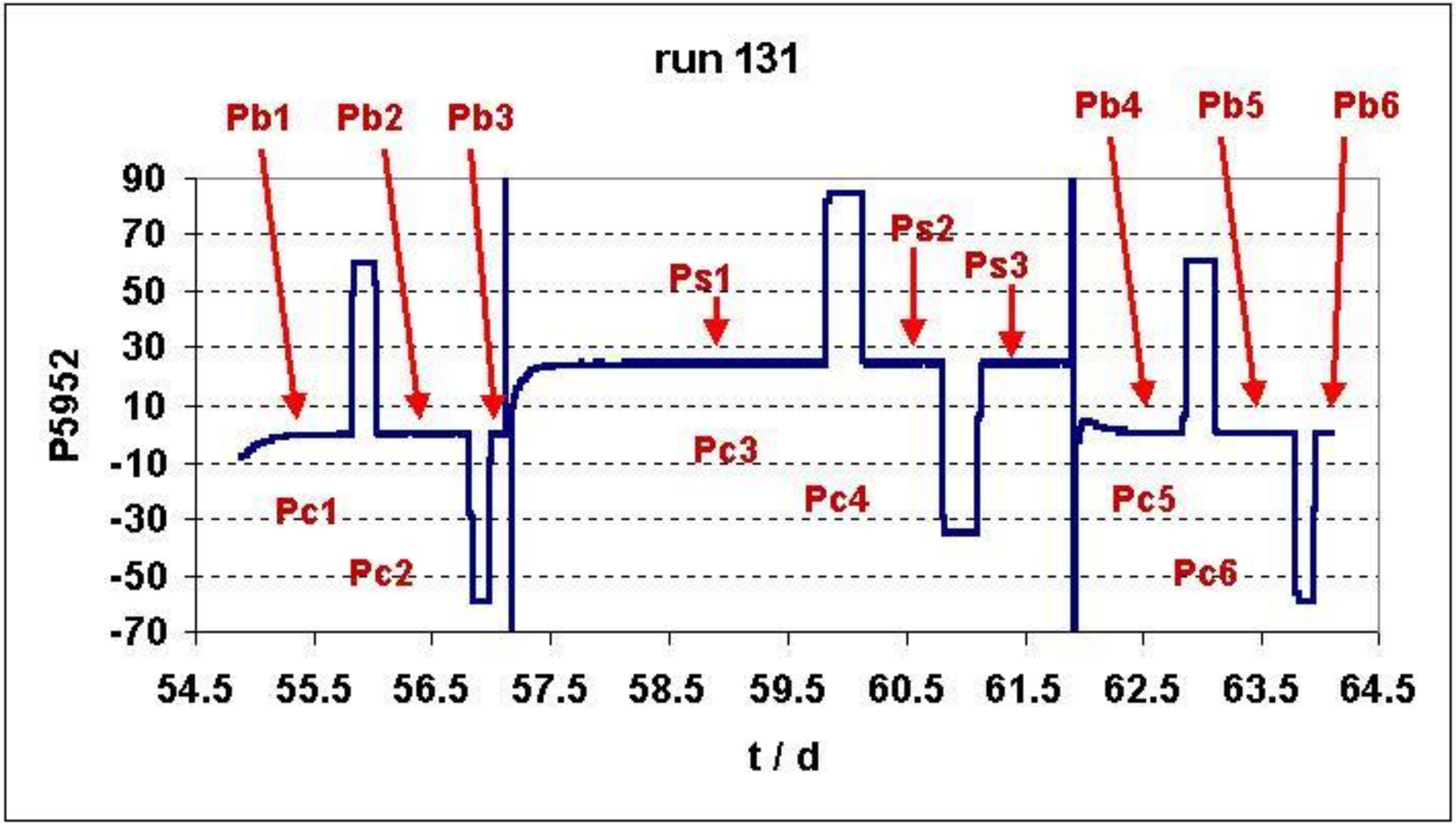
Calibration reproduction

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 !

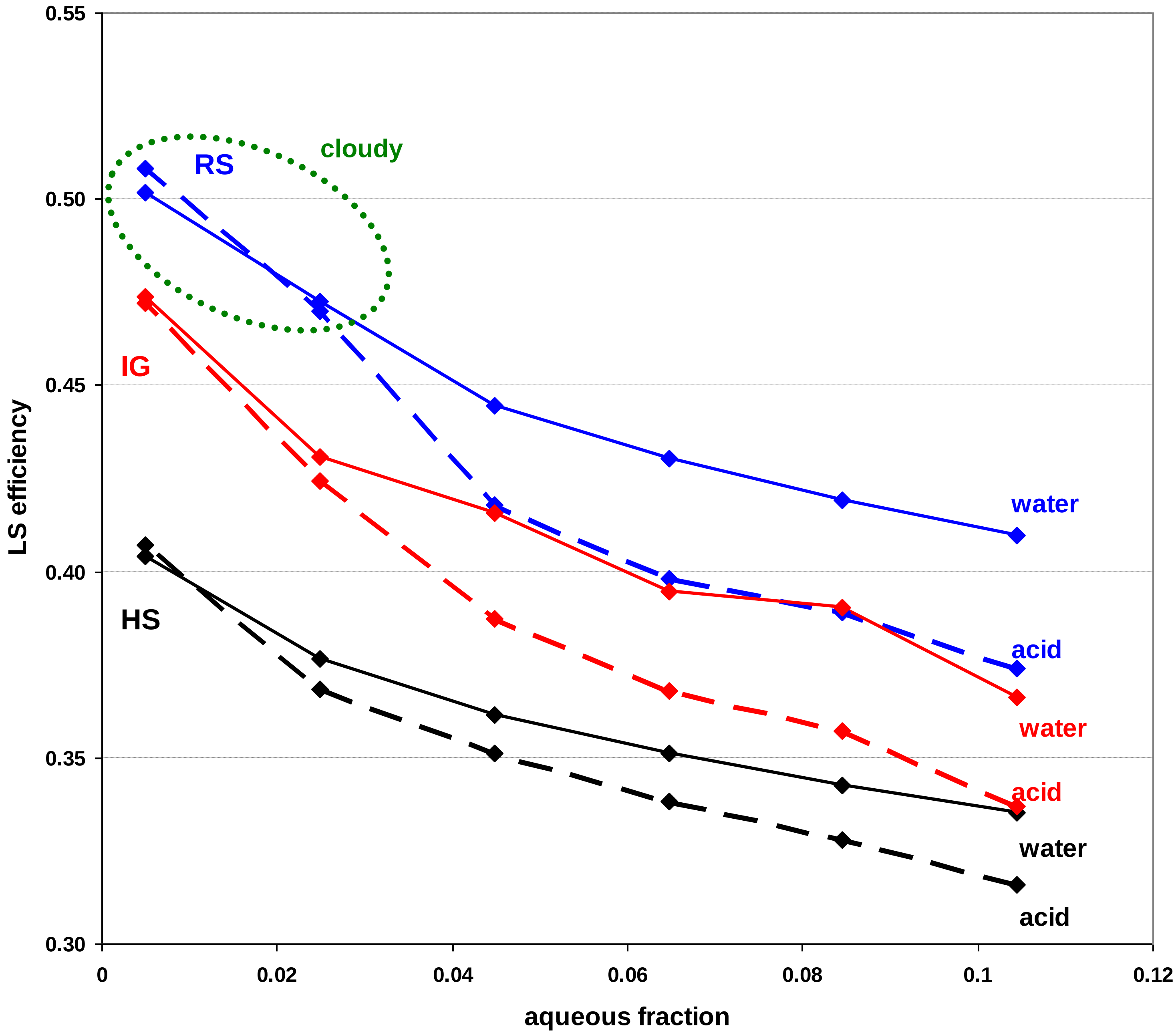


Power measurement reproducibility (with run)

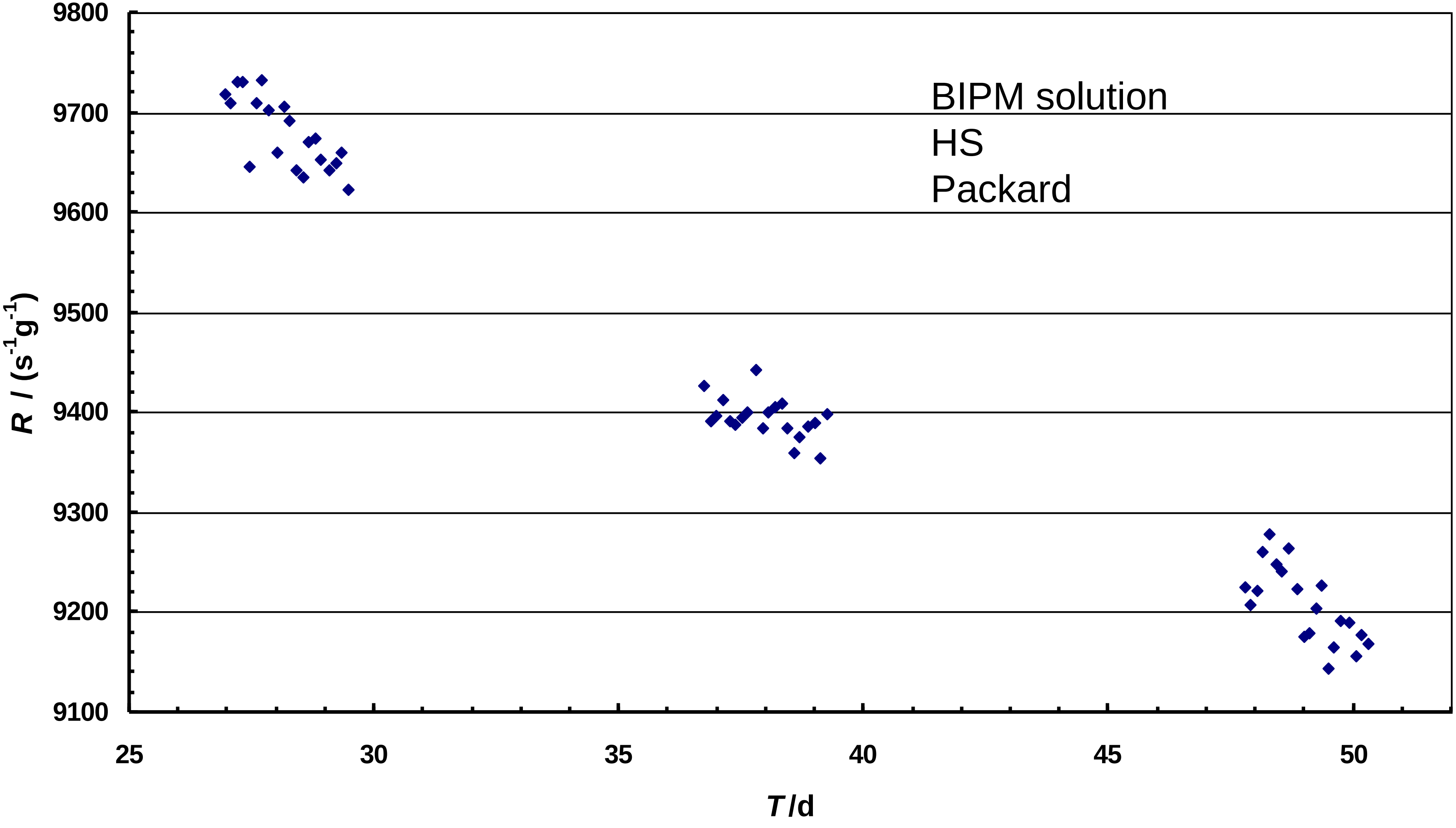
Run 131	P(5952) at t0
Ps1	25.562
Ps2	25.629
Ps3	25.637
mean	**25.609**
sd (%)	0.16
sdm (%)	**0.093**

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**


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
LS efficiency
aqueous fraction
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

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**