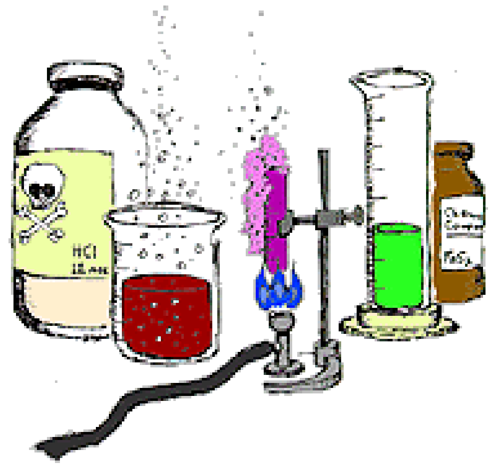
Classical Isothermal Microcalorimetry
(for radionuclidic standardizations)

R. Collé

research chemist (retired)

formerly of NIST (1974 - 2003)



VERMI

Virtual European Radionuclide Metrology Institute

Young Researchers Workshop

1-5 December 2003 – Paris

… I have not much doubt but that the two standards will be found in very good agreement, but it will be a devil of a mess if they are not.

… I think I can compare two nearly equal standards [to] an accuracy of 1 in 1000. I suppose, however, we shall not worry if the agreement of the two standards is within 1 in 300 or 400.

Ernest Rutherford (University of Manchester)

letter to Bertram Boltwood (Yale University)

18 march 1912

Some quick history

1896	radioactivity discovered
1903-4	first primary ("absolute") measurements of radioactivity (?)
	P. Curie & Labord (1903) – first calorimetry of radioactivity
	P. Curie & Dewar (1904) – cryogenic calorimetry at liquid water & liquid hydrogen temperatures
	Rutherford & Barnes (1903-4) dual cell & differential calorimetry
1914 – 45+	calorimetry was a principal tool for international intercomparison of standards (radium)
1925	Ellis & Wooster – confirmed need for neutrino
> 1950	calorimetry of "special nuclear materials" (power & bombs)
Now !	milli-K calorimetry / quantum bolometry

But you can still do old-fashioned calorimetry …..

Some references – classical calorimetry

- O.E. Meyers, *Nucleonics* **5** (11), 37 (1949) -- exhaustive review & bibliography of calorimetric measurements of radioactivity up to 1949.
- W.B. Mann, *Encyclopedic Dictionary of Physics*, Pergamon, Oxford (1962) – updates Meyer's review to 1958.
- H.L. Callandar, *Proc. Phys. Soc*. **23**, 1 (1910) – Peltier effect "radiobalance" for comparison of international standards
- W.B. Mann, *Nucl. Instr. Meth*. **112**, 273 (1973); *Appl. Radiat. Isot*. **46**, 185 (1995) – the NIST radiobalance in use from 1953 to 1980s
- H. Ramthun, *Nucl. Instr. Meth* **112**, 265 (1973) – GREAT survey of different types of "classical" calorimeters
- R. Collé, *Appl. Radiat. Isot*. **56**, 223 (2001). Classical isothermal microcalorimetry at cryogenic (8 K) temperatures
- R. Collé, …. coming soon … use of a commercial microcalorimeter

Radionuclidic Microcalorimetry

WHY ?

Need to standardize GBq sources

Non-destructive (?)

➡ ***dual-compensated cryogenic (8 K) microcalorimeter***

Appl. Radiat. Isot. **56, 223-230 (2002)**

➡ ***dual-cell near-isothermal (heat flow) microcalorimeter (303 K)***

Recent calorimetric-based standardizations 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 ^{103}Pd (and for calibration of *Theragenics* prostate seeds)

Basic relationship between

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

and

Activity A

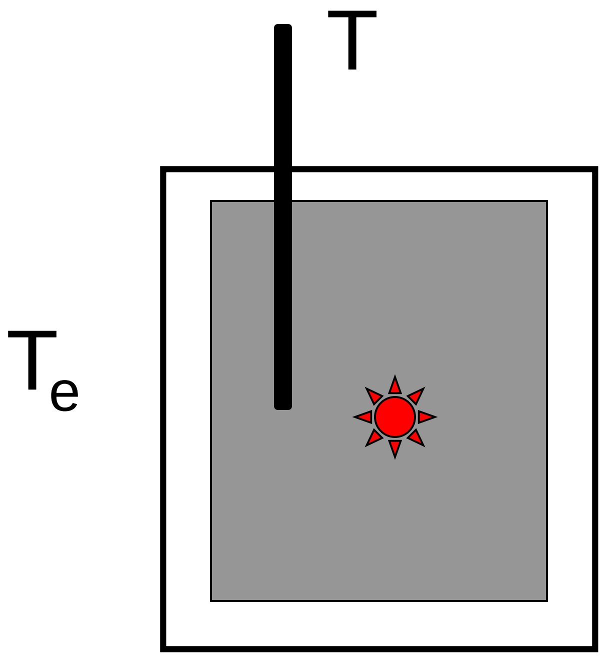
is $$\mathrm{d}H/\mathrm{d}t = P = A\,\hat{E}$$

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

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

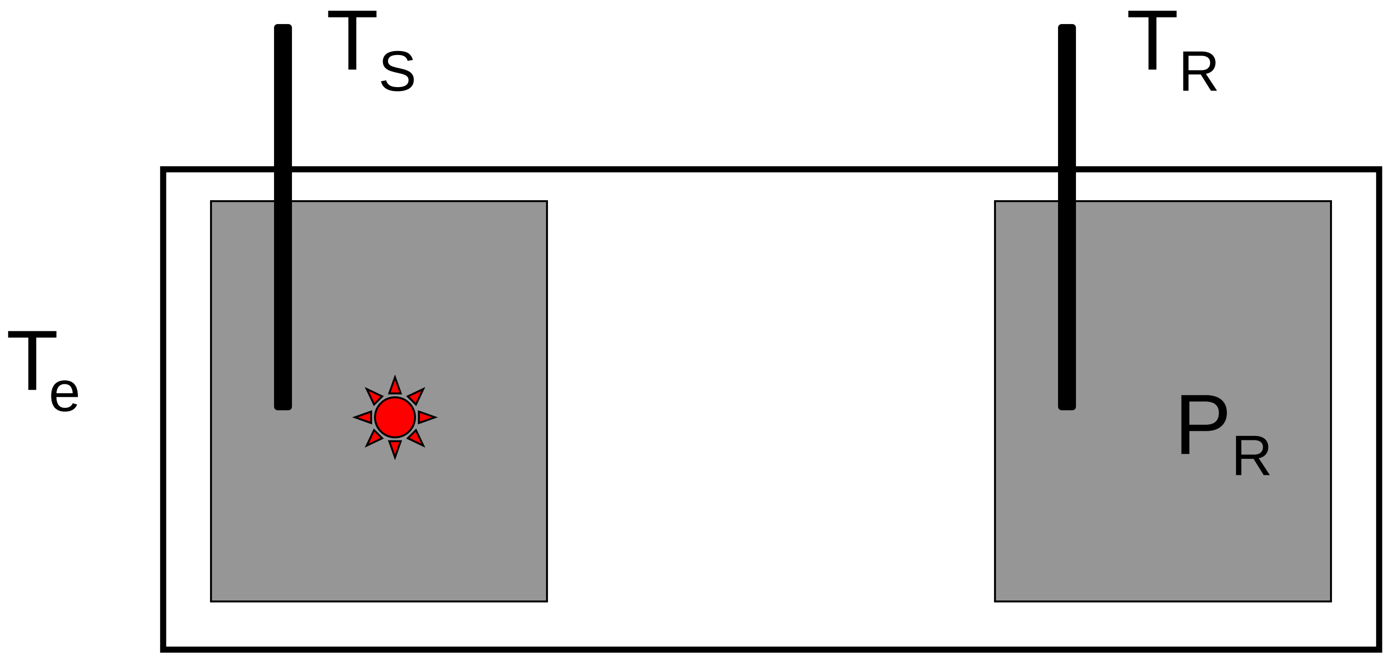
Assumes absorb & measure ALL ionizing radiation (no losses)

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



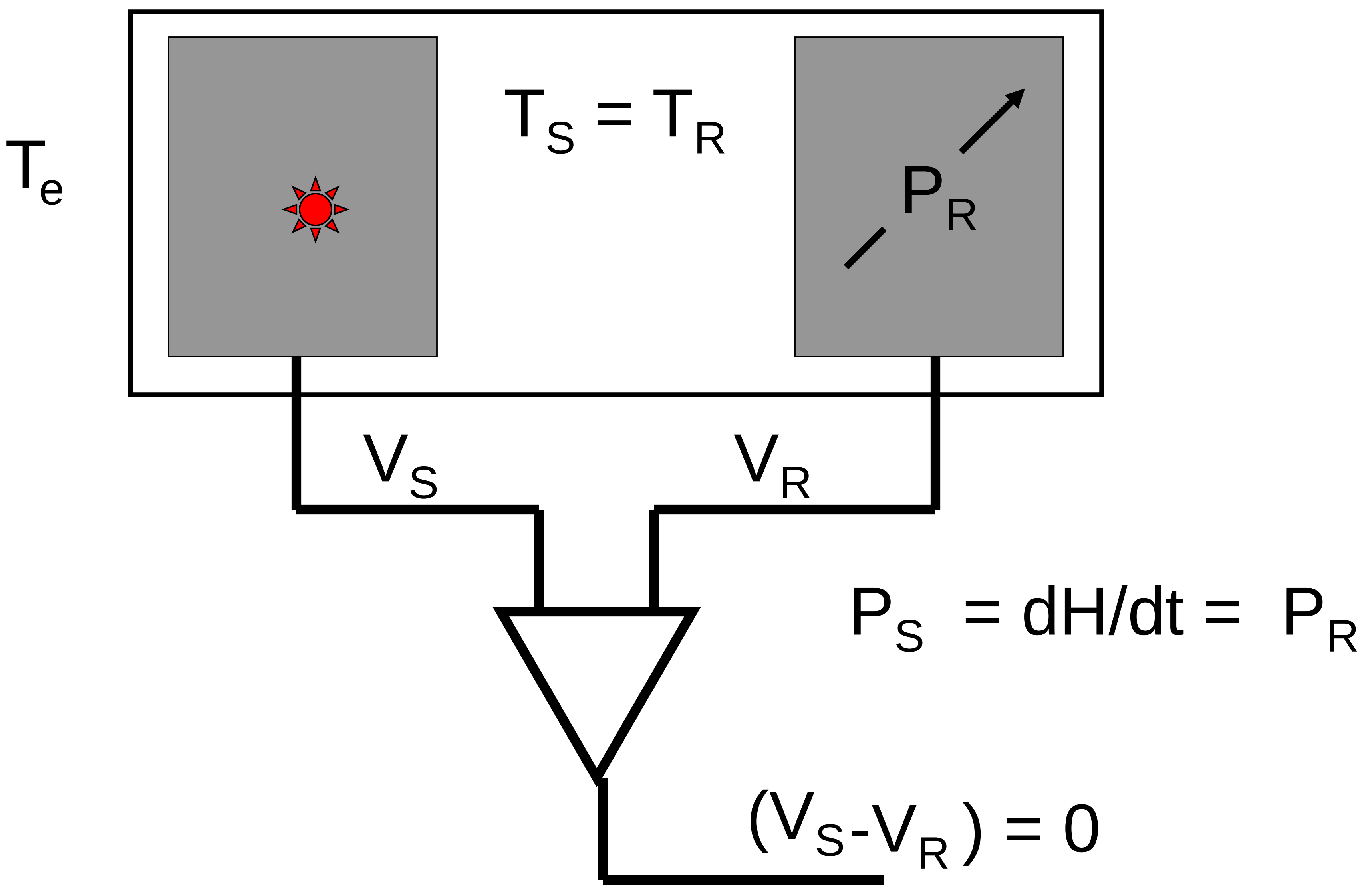
$$P = dH/dt = -k\,(T - T_e)$$

constant



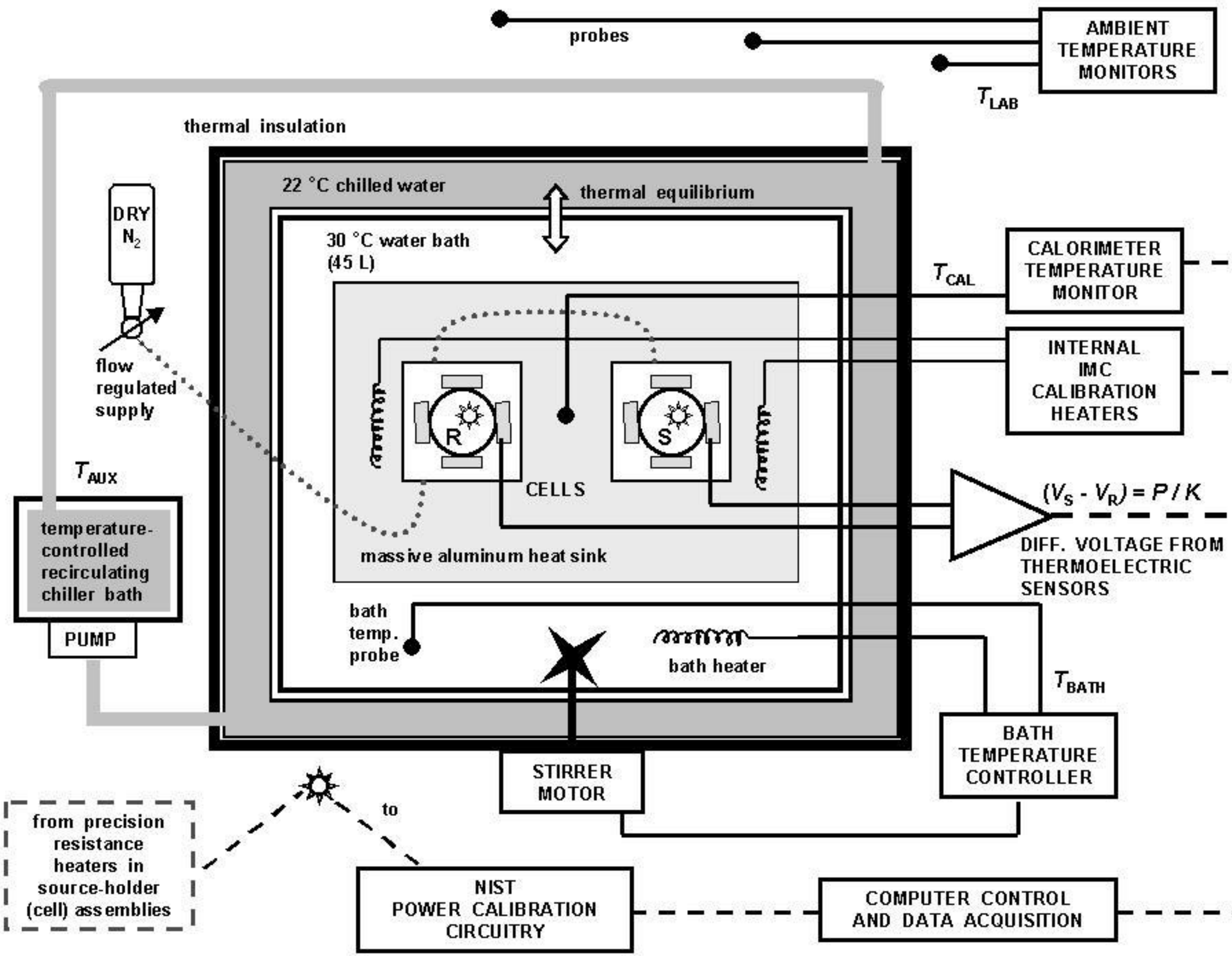
$$T_S = T_R$$

$$P_S = dH/dt = P_R$$

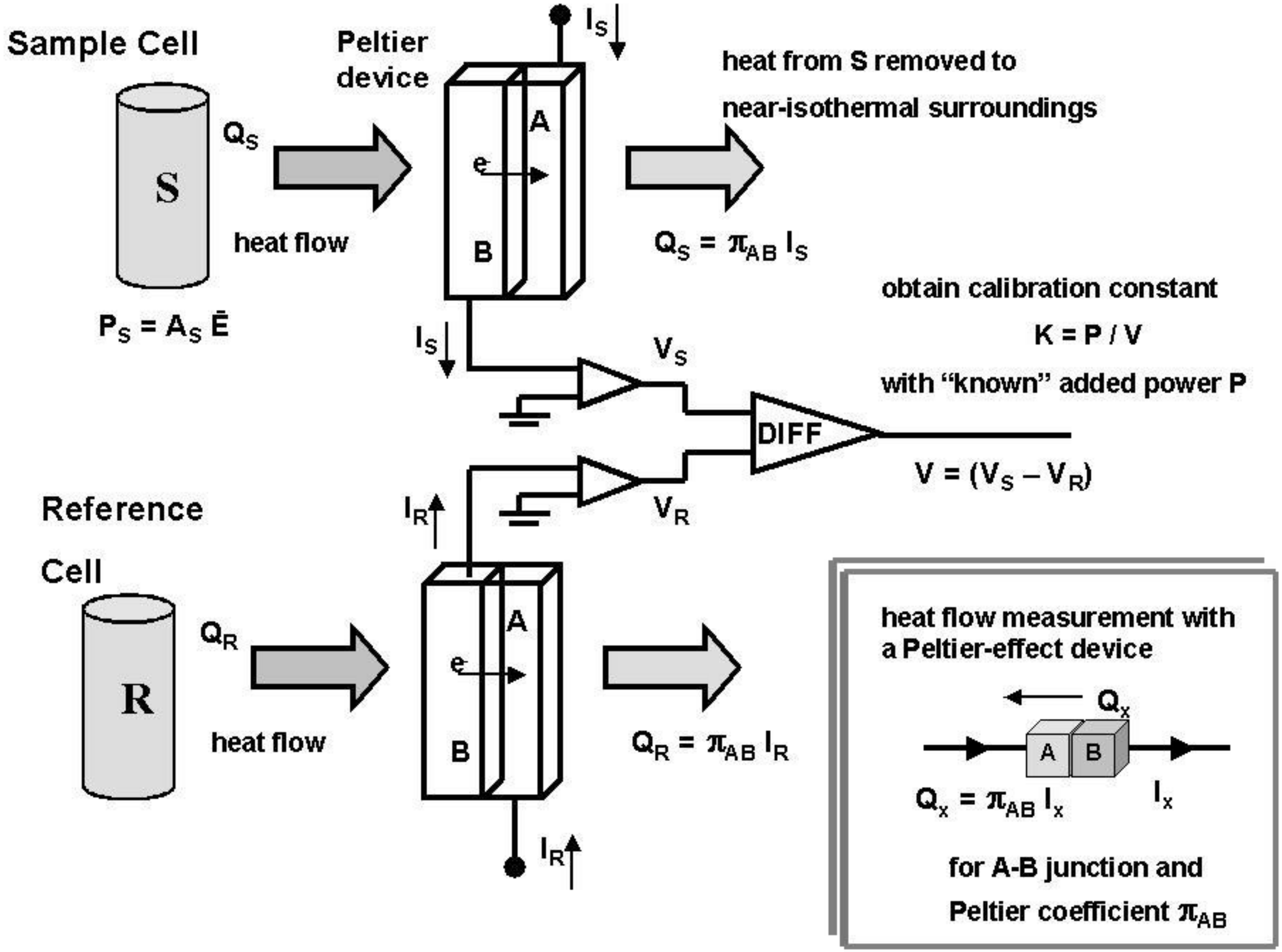


T_e
$T_S = T_R$
P_R
V_S
V_R
$P_S = dH/dt = P_R$
$(V_S - V_R) = 0$

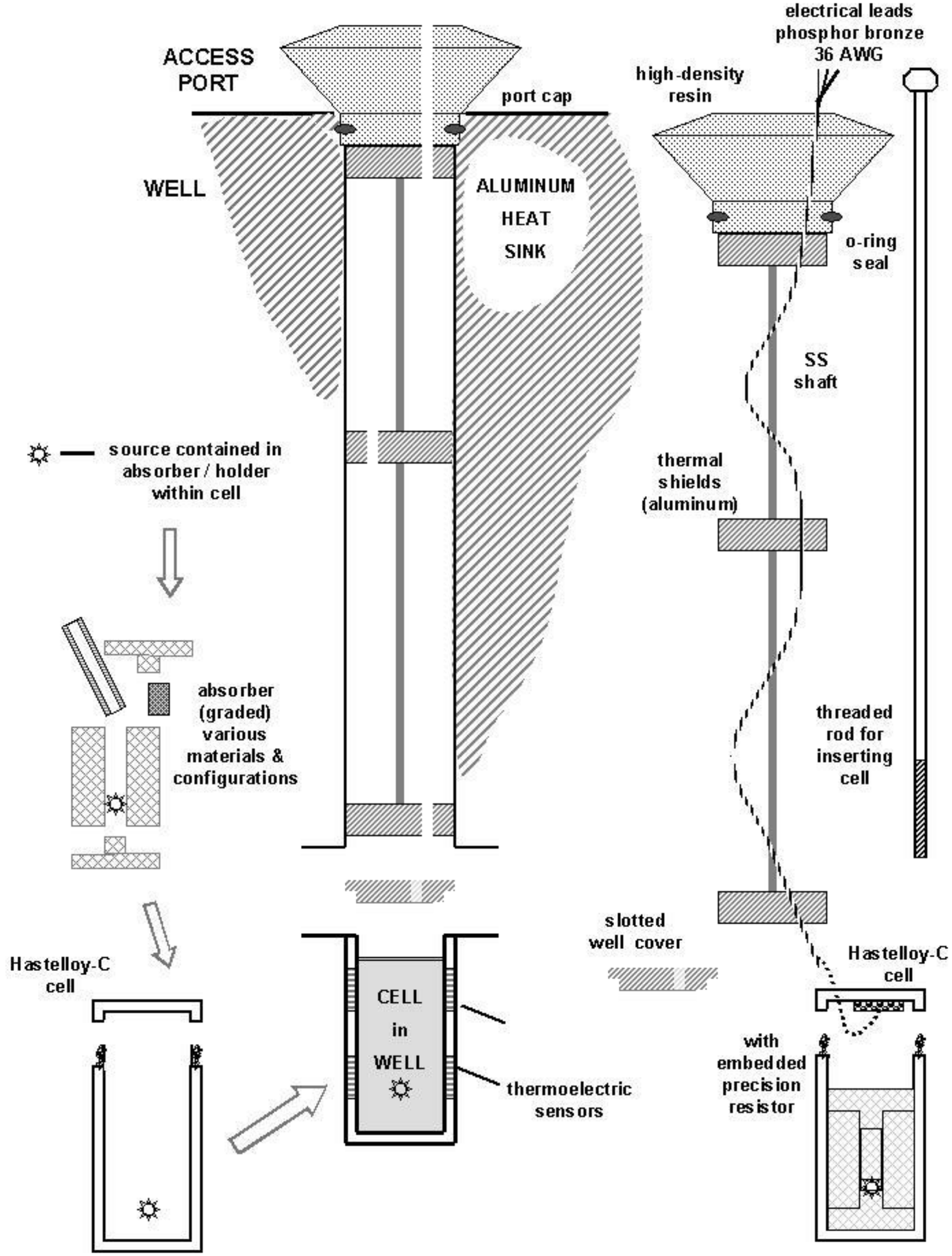
CSC "Isothermal Microcalorimeter (IMC)"



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
T_{AUX}
$(V_S - V_R) = P / K$
temperature-controlled recirculating chiller bath
massive aluminum heat sink
DIFF. VOLTAGE FROM THERMOELECTRIC SENSORS
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

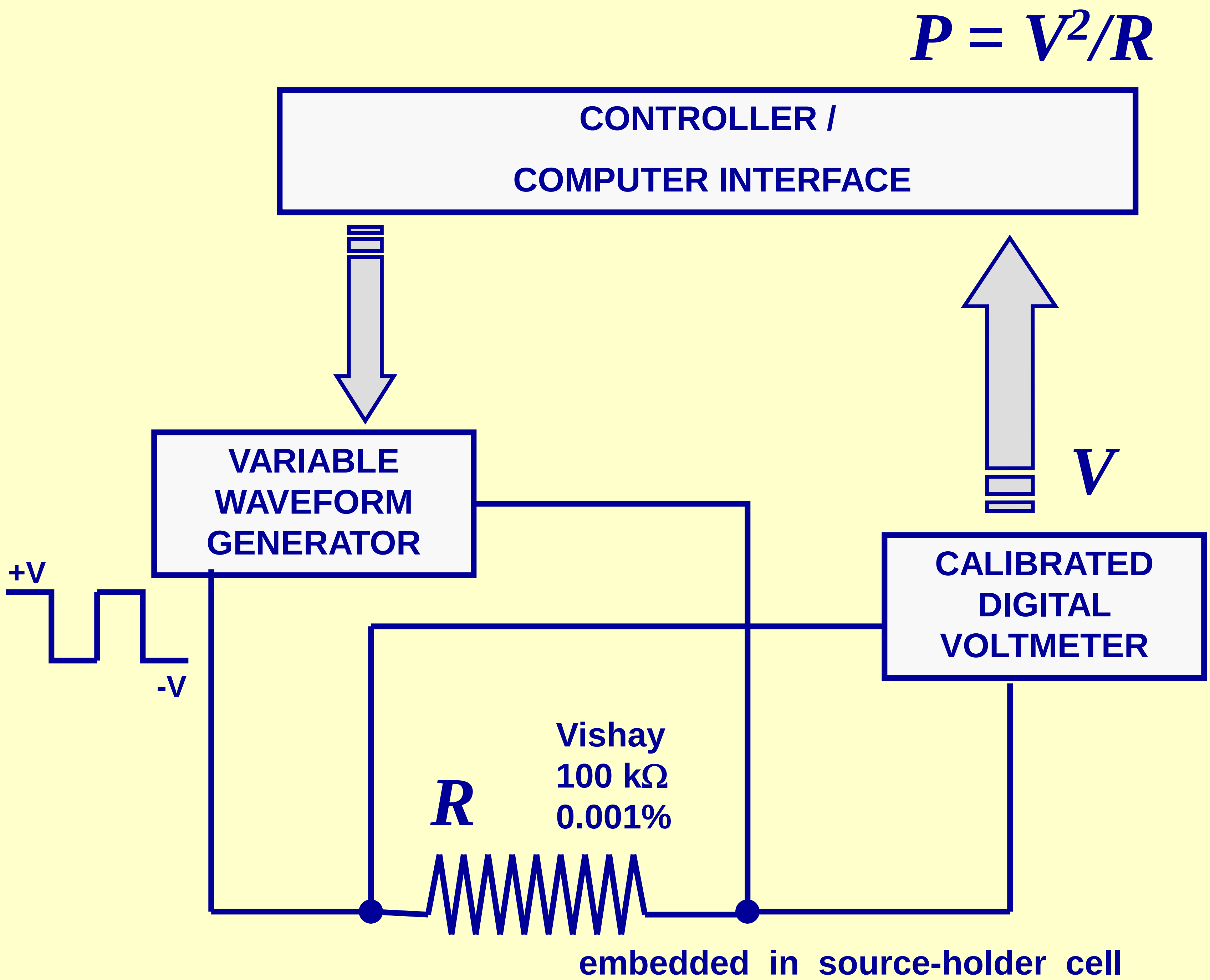


Sample Cell
S
Q_S
heat flow
$P_S = A_S \bar{E}$
Peltier device
A
e
B
I_S
heat from S removed to
near-isothermal surroundings
$Q_S = \pi_{AB} I_S$
obtain calibration constant
K = P / V
with "known" added power P
V_S
DIFF
$V = (V_S - V_R)$
V_R
I_R
Reference
Cell
R
Q_R
heat flow
$Q_R = \pi_{AB} I_R$
heat 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}



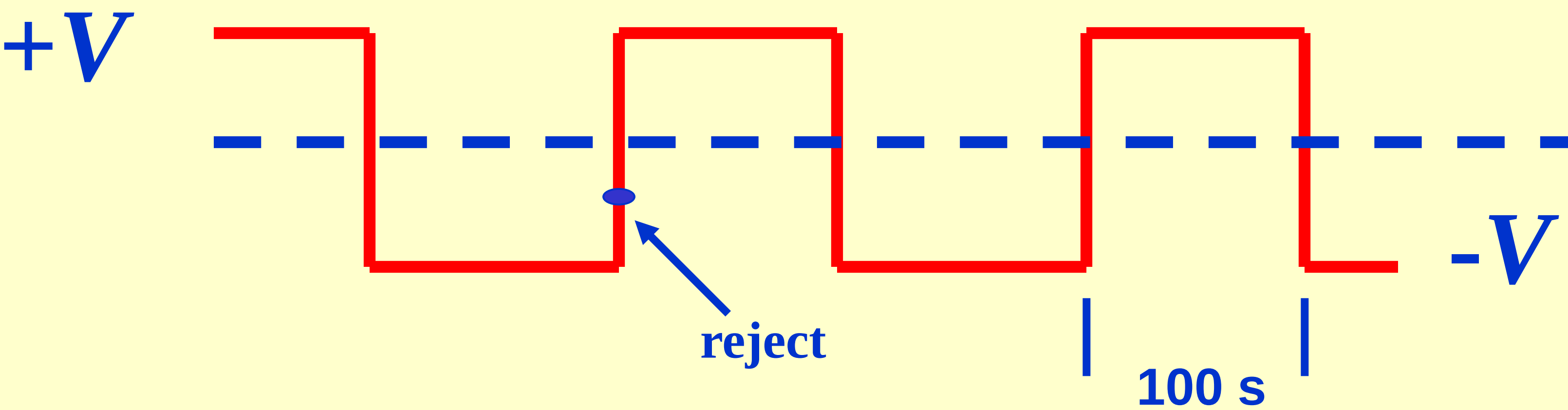
ACCESS PORT
port cap
WELL
ALUMINUM HEAT SINK
electrical leads phosphor bronze 36 AWG
high-density resin
o-ring seal
SS shaft
thermal shields (aluminum)
threaded rod for inserting cell
source contained in absorber / holder within cell
absorber (graded) various materials & configurations
Hastelloy-C cell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

port assemblies -- source (absorbers) holders & cells

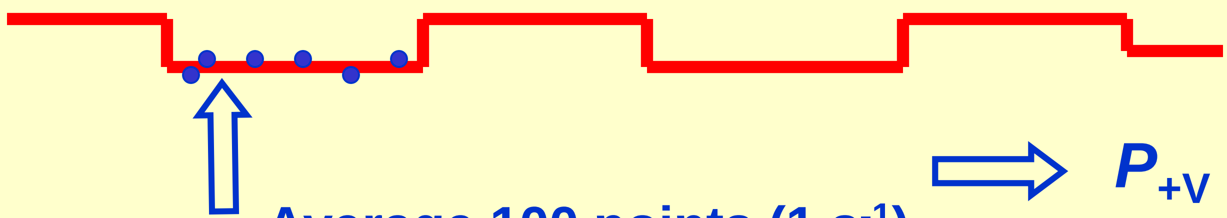

P = V2/R
CONTROLLER /
COMPUTER INTERFACE
VARIABLE
WAVEFORM
GENERATOR
+V
-V
V
CALIBRATED
DIGITAL
VOLTMETER
R
Vishay
100 kΩ
0.001%
embedded in source-holder cell

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

$|+V| = |-V|$



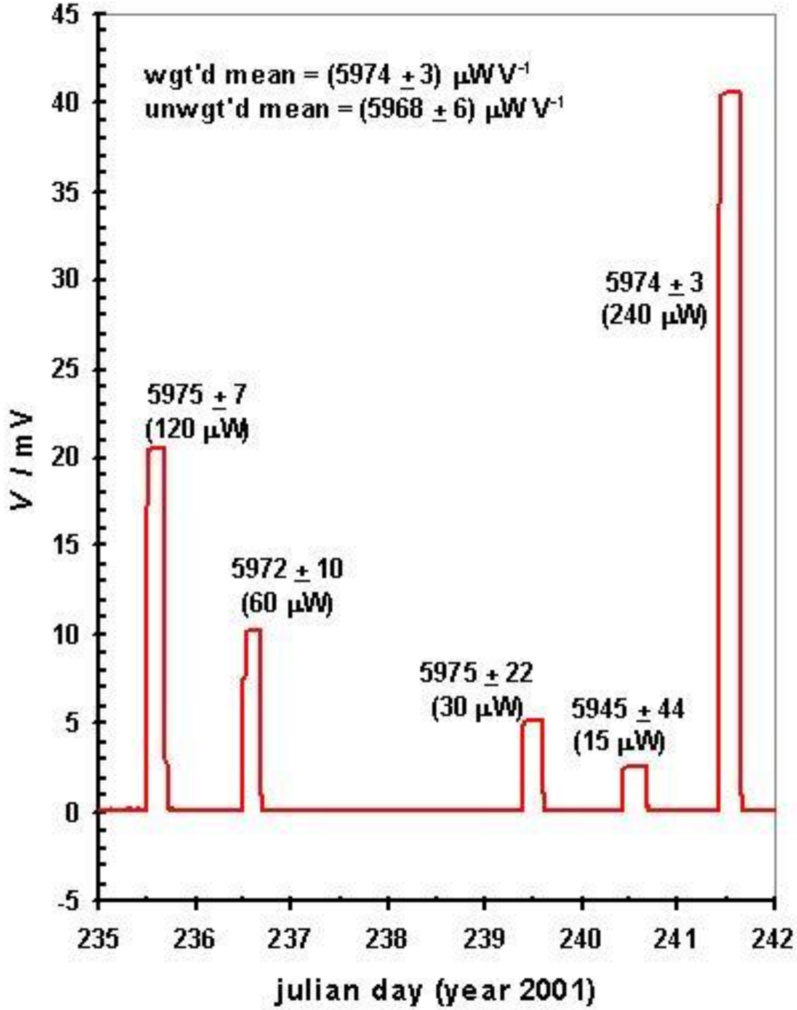
$P = V^2/R$



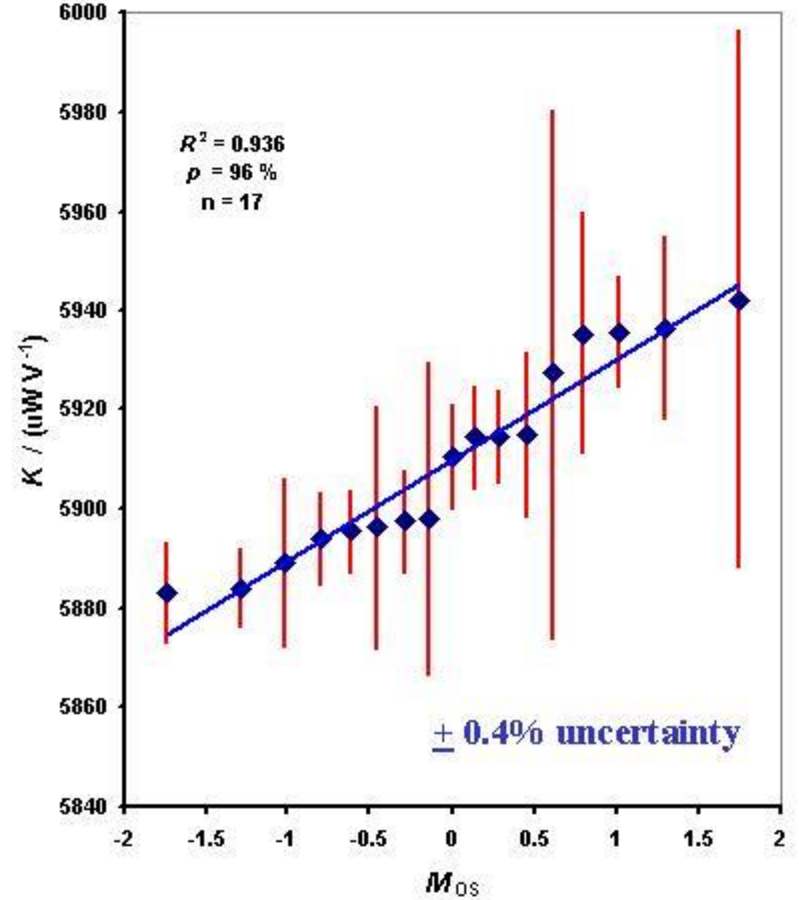
Average 100 points (1 s^{-1}) $\Rightarrow$ P_{+V} or P_{-V}

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

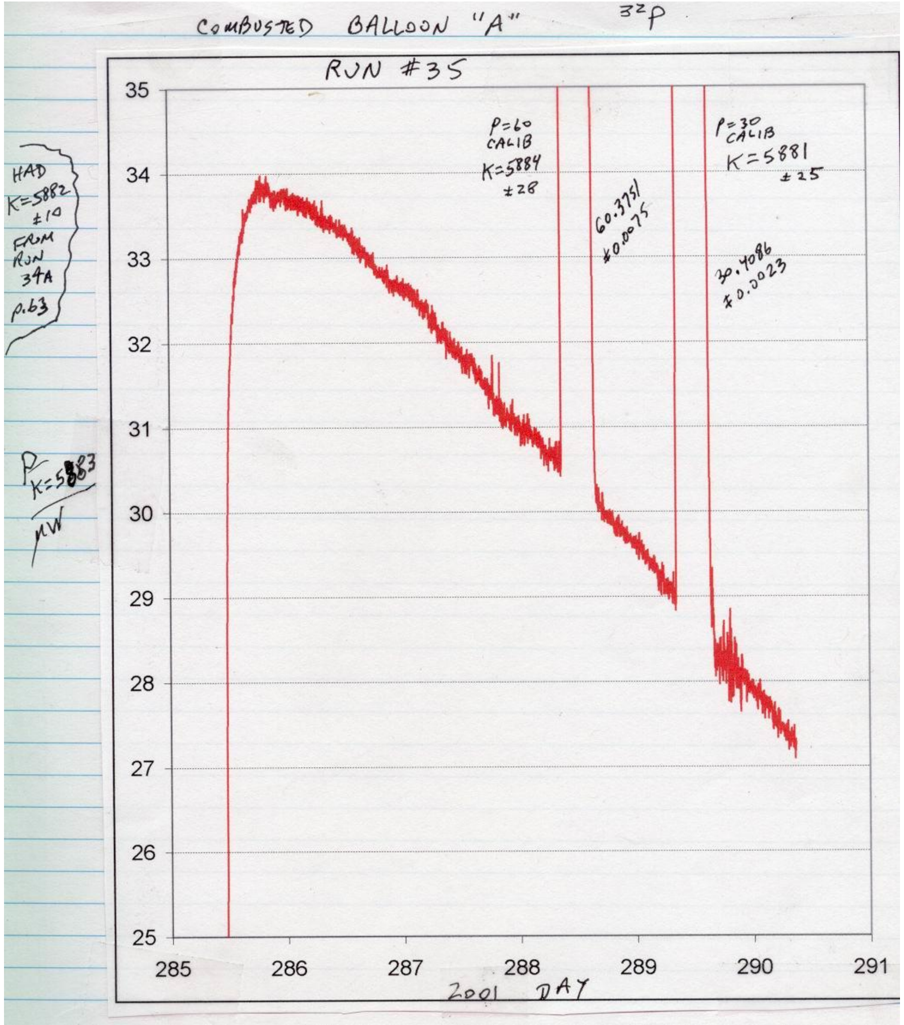
var (P) = 1/2 var (P_{+V}) + 1/2 var (P_{-V}) + covar (P_{+V}, P_{-V}) + autocorr(P_{+V}) + autocorr(P_{-V})



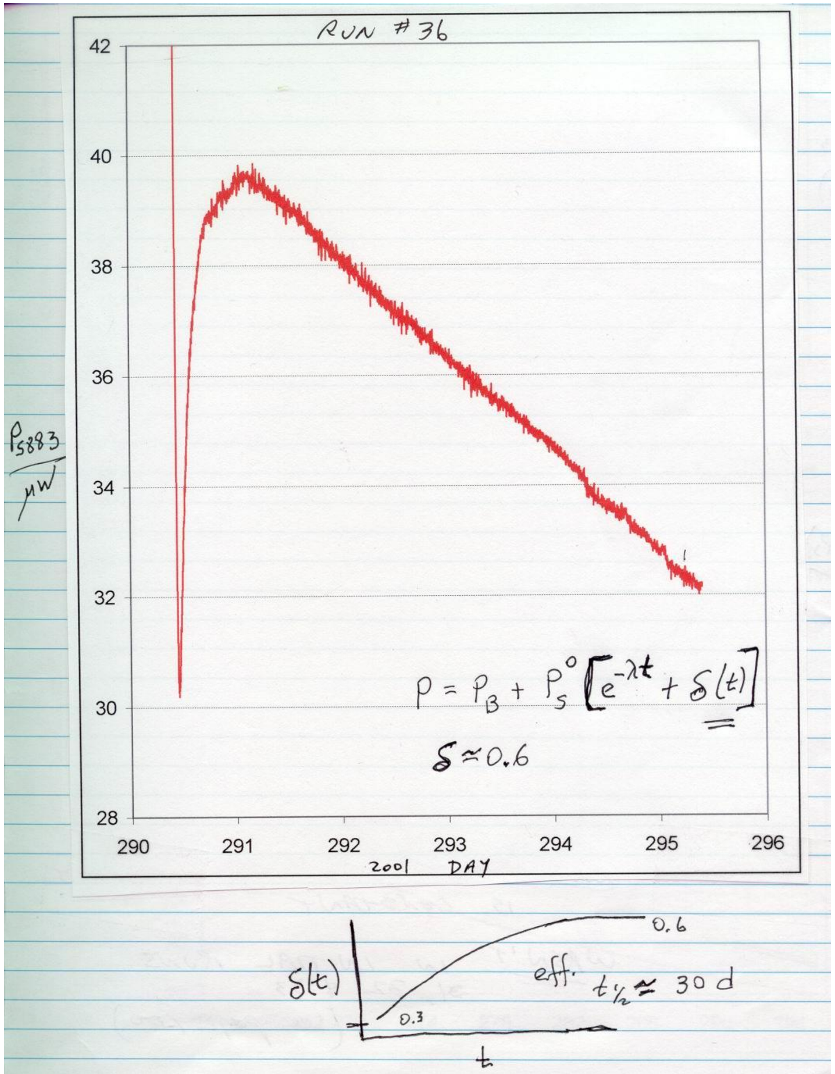
typical calibration data set



Filliben normality test for calibration data (Novoste seeds)



IMC Lab Book II, p.79

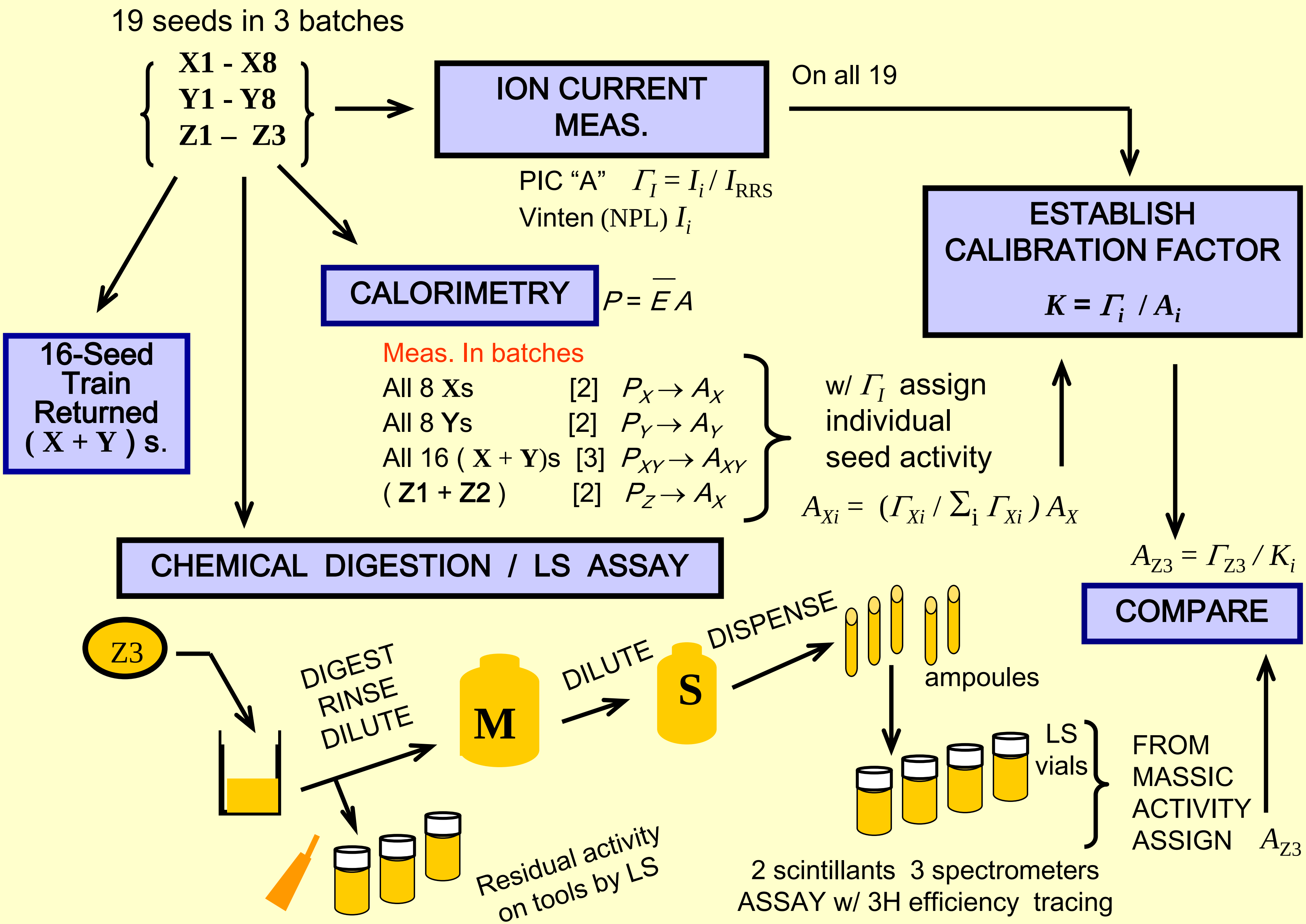


IMC Lab Book II, p.97

combusted ^{32}P balloon "A"

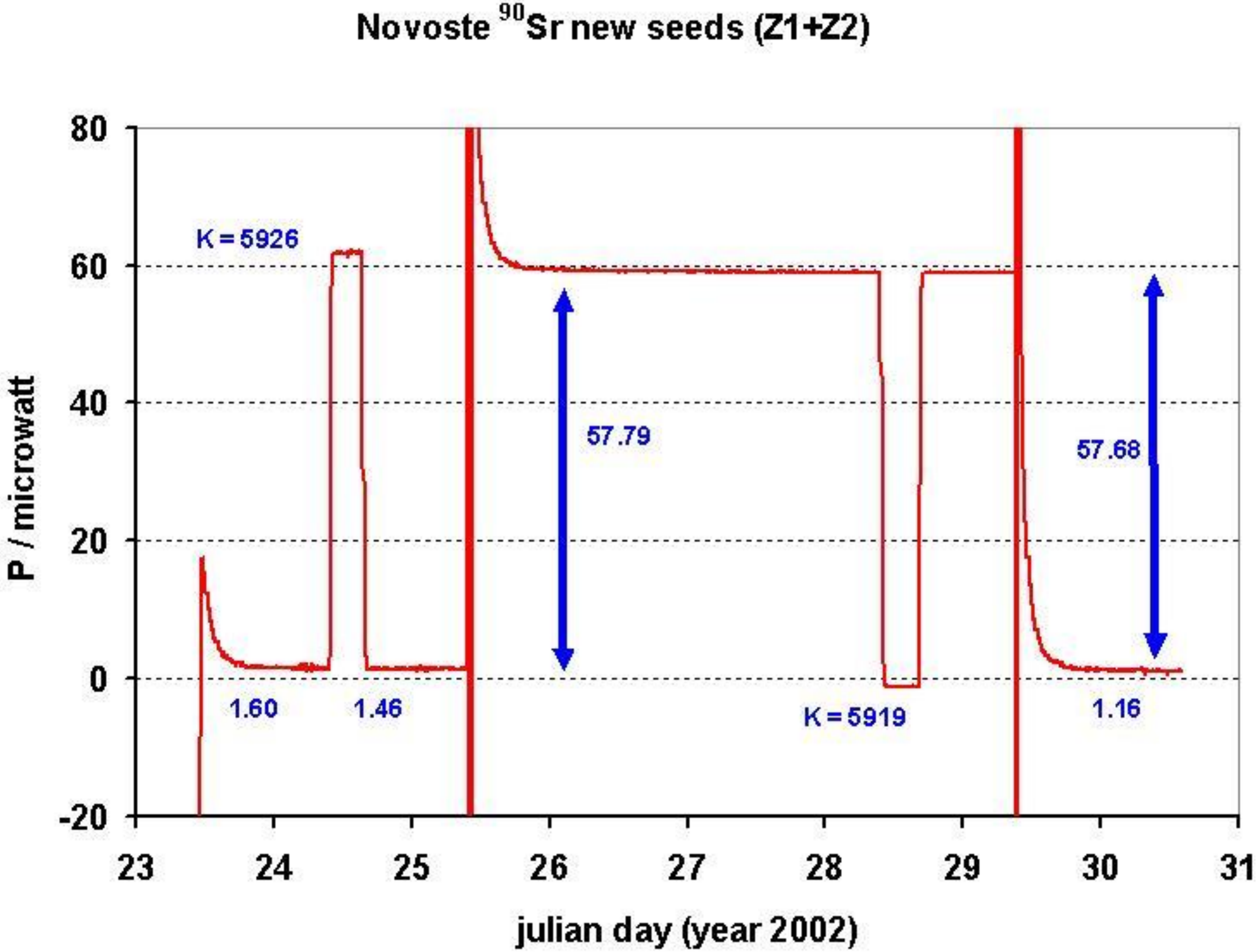
uncombusted ^{32}P balloon "C"

Standardization scheme for Novoste ^{90}Sr new-style seed

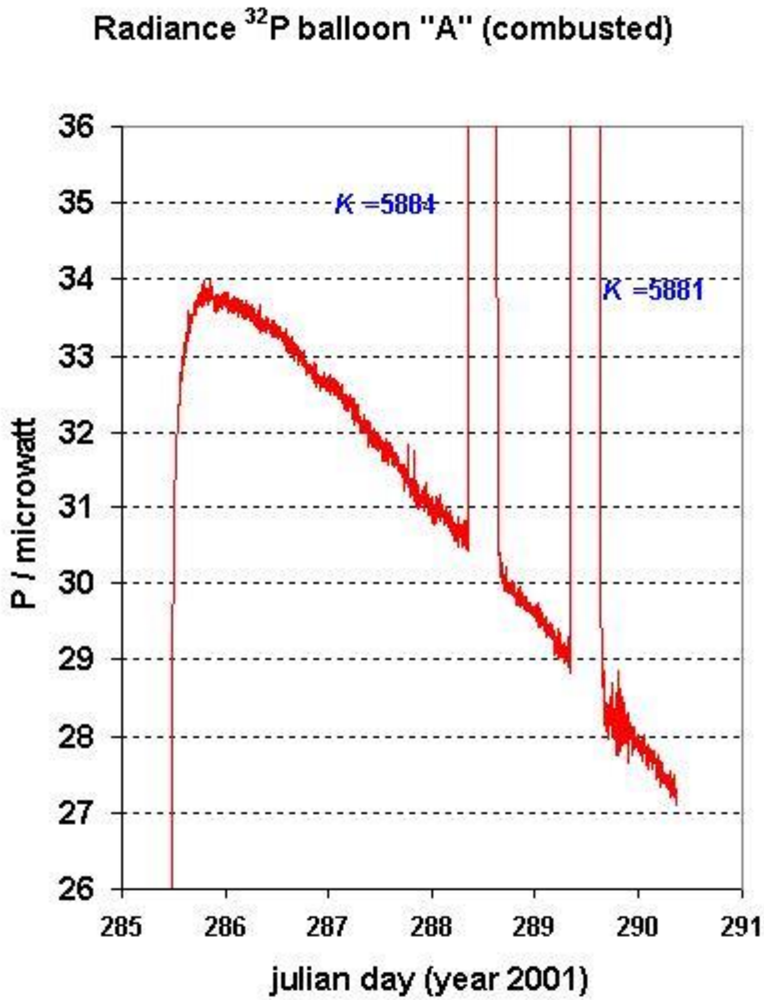


Run59

Bk3p173



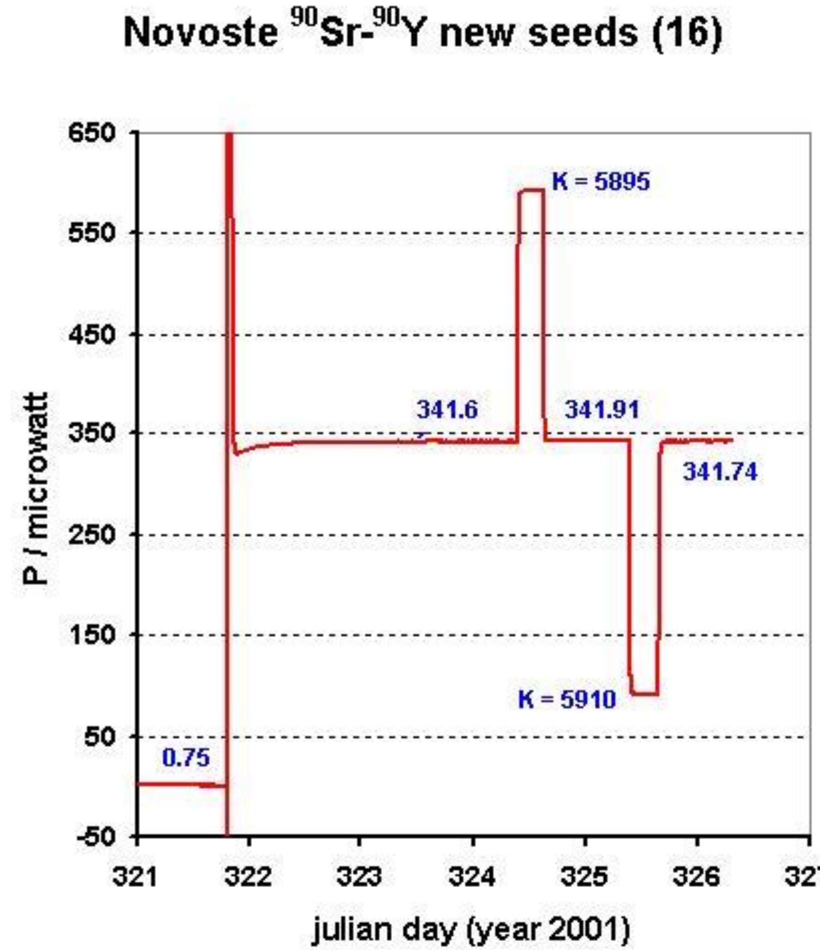
Run35
Bk2,p79



Get P_B and P_0 from "fit"

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

Run43
Bk2,p167



requires baseline P_B measurement

Standardization results

source batch	number in batch	power (micowatt)	equivalent activity (MBq)
all (Xs + Ys)	16	342.70 342.30 344.41	1893.2 1891.0 1902.6
all Xs	8	172,45 172.76	952.7 954.4
all Ys	8	169.84 170.75	938.3 943.3
(Z1 + Z2)	2	57.81 58.27 58.09	319.4 321.9 320.9

From ion current measurements on individual seeds

X1 -X2 ranged from 114.4 MBq to 121.7 MBq

Y1 -Y2 ranged from 113.9 MBq to 119.9 MBq

$\}$ $\pm$ 1.6 % (k = 2)

Z1 -Z3 ranged from 156.3 MBq to 164.3 MBq $\pm$ 3 % (k = 2)

Destructive assay (by LS) on Z3 agreed with calorimetry *initially* by - 1.1 % (*now* with n = 5 determinations to 0.4 %)

Novoste new-style (Z batch) ^{90}Sr seeds

at power = 60 microwatt

number of determinations	agreement with LS-based destructive assay
1	1.8 % *
3	0.7 %
7	0.4 %

* typical 1-2 % accuracy for a single determination at this power level

FINDINGS

Got 1 to 2 % agreement w/ extant IC calibrations for both

Radiance ^{32}P balloons

Novoste ^{90}Sr-^{90}Y seeds (old)

Calibration factors (15 determinations) for Novoste seeds (new)

has s.d.m < 0.1% and 1/2range = 0.5 %

Better than 0.5 % agreement between LS-based digestive assay

for new-style Novoste ^{90}Sr-^{90}Y seeds

Replicate measurement uncertainty is about 0.5 % to 1 % or so

if can get P_B by fit with decay

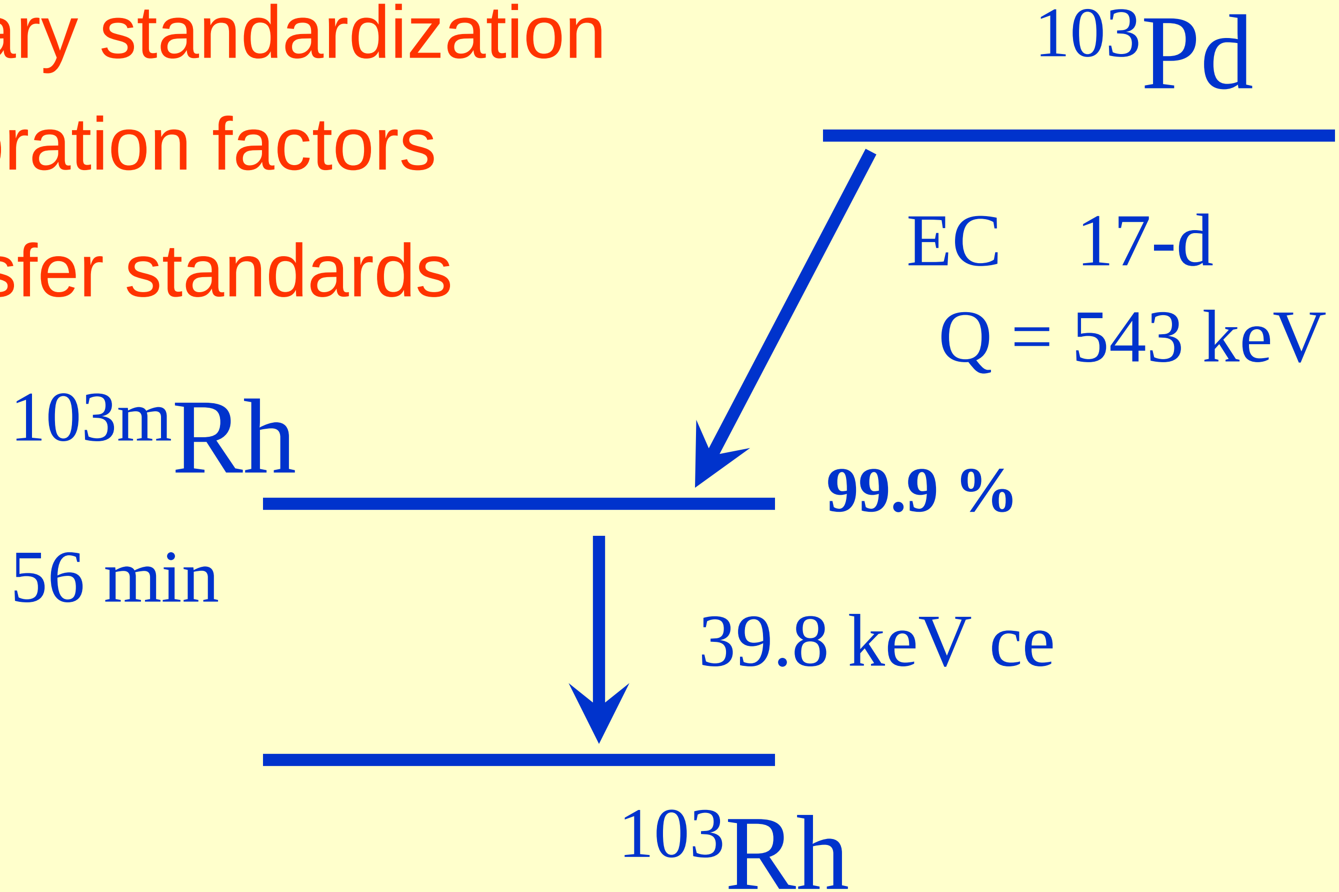
or if one has sufficient replications to get ΔP

(with little decay)

need primary standardization

+ calibration factors

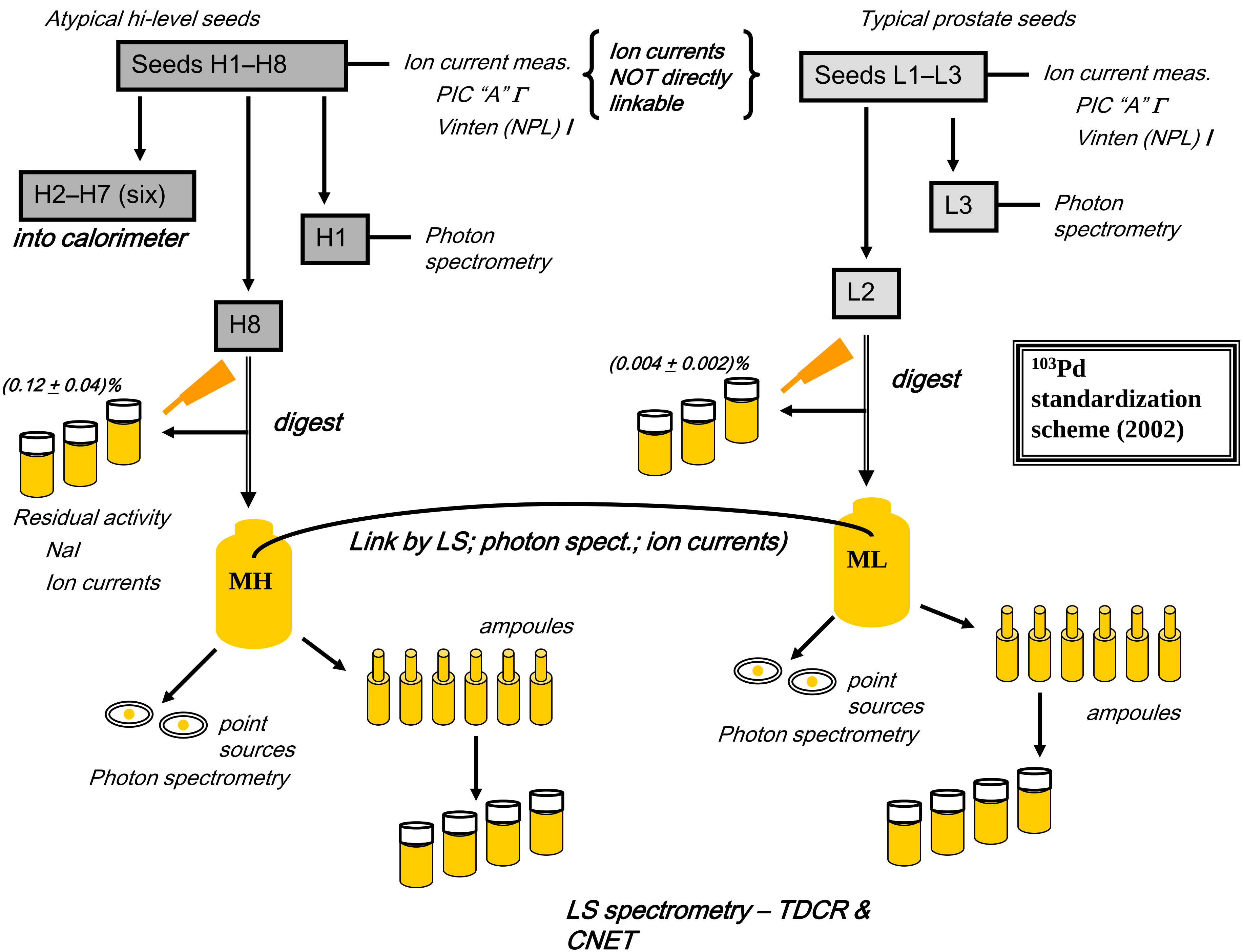
+ transfer standards



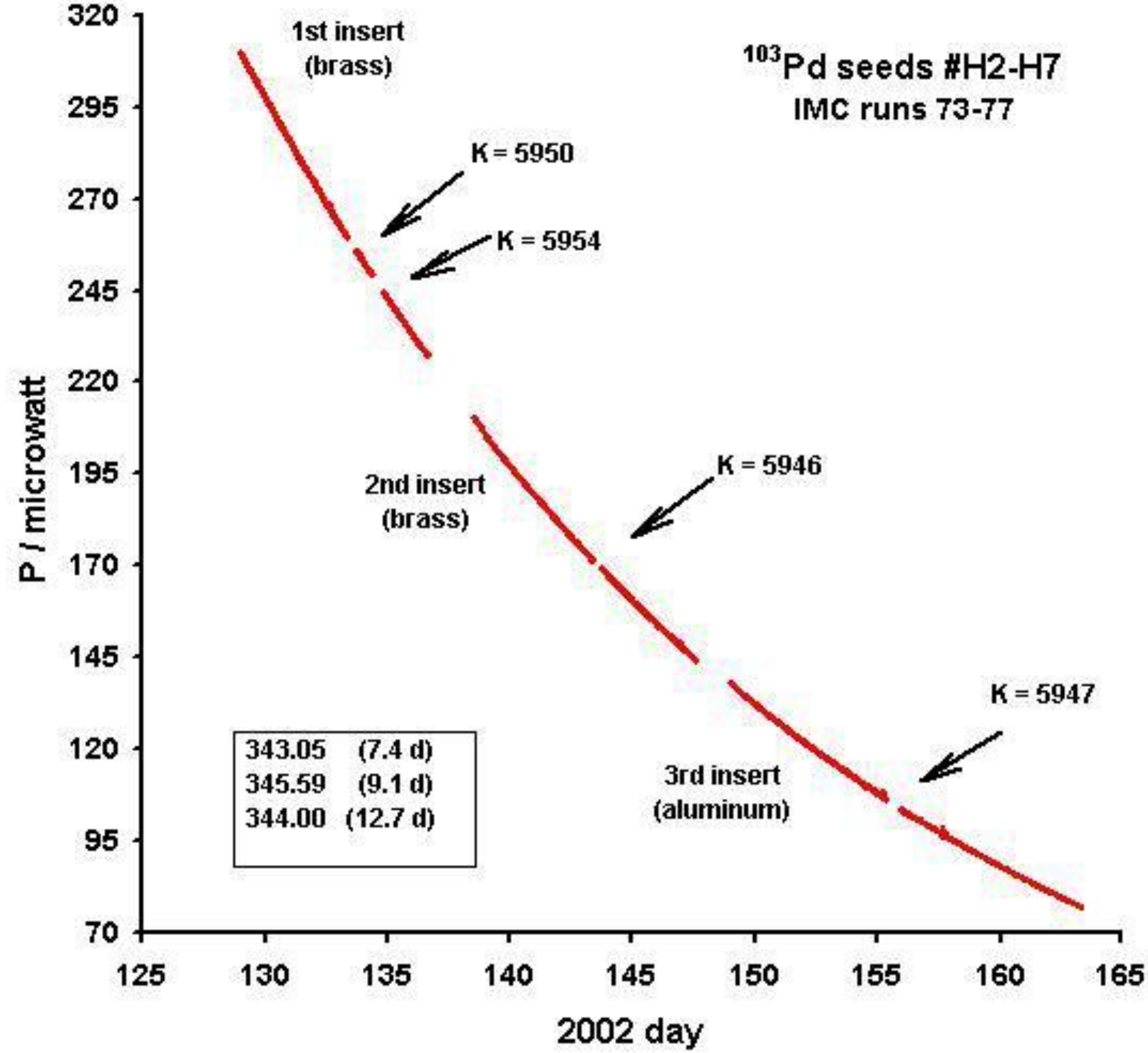
Brachytherapy source

used to treat prostate cancer

candidate for intravascular use



Atypical hi-level seeds
Seeds H1–H8
Ion current meas.
PIC "A" Γ
Vinten (NPL) I
Ion currents NOT directly linkable
Typical prostate seeds
Seeds L1–L3
Ion current meas.
PIC "A" Γ
Vinten (NPL) I
H2–H7 (six)
into calorimeter
H1
Photon spectrometry
L3
Photon spectrometry
L2
H8
(0.12 ± 0.04)%
digest
(0.004 ± 0.002)%
digest
103Pd standardization scheme (2002)
Residual activity
NaI
Ion currents
MH
Link by LS; photon spect.; ion currents)
ML
ampoules
point sources
Photon spectrometry
point sources
Photon spectrometry
ampoules
LS spectrometry – TDCR & CNET

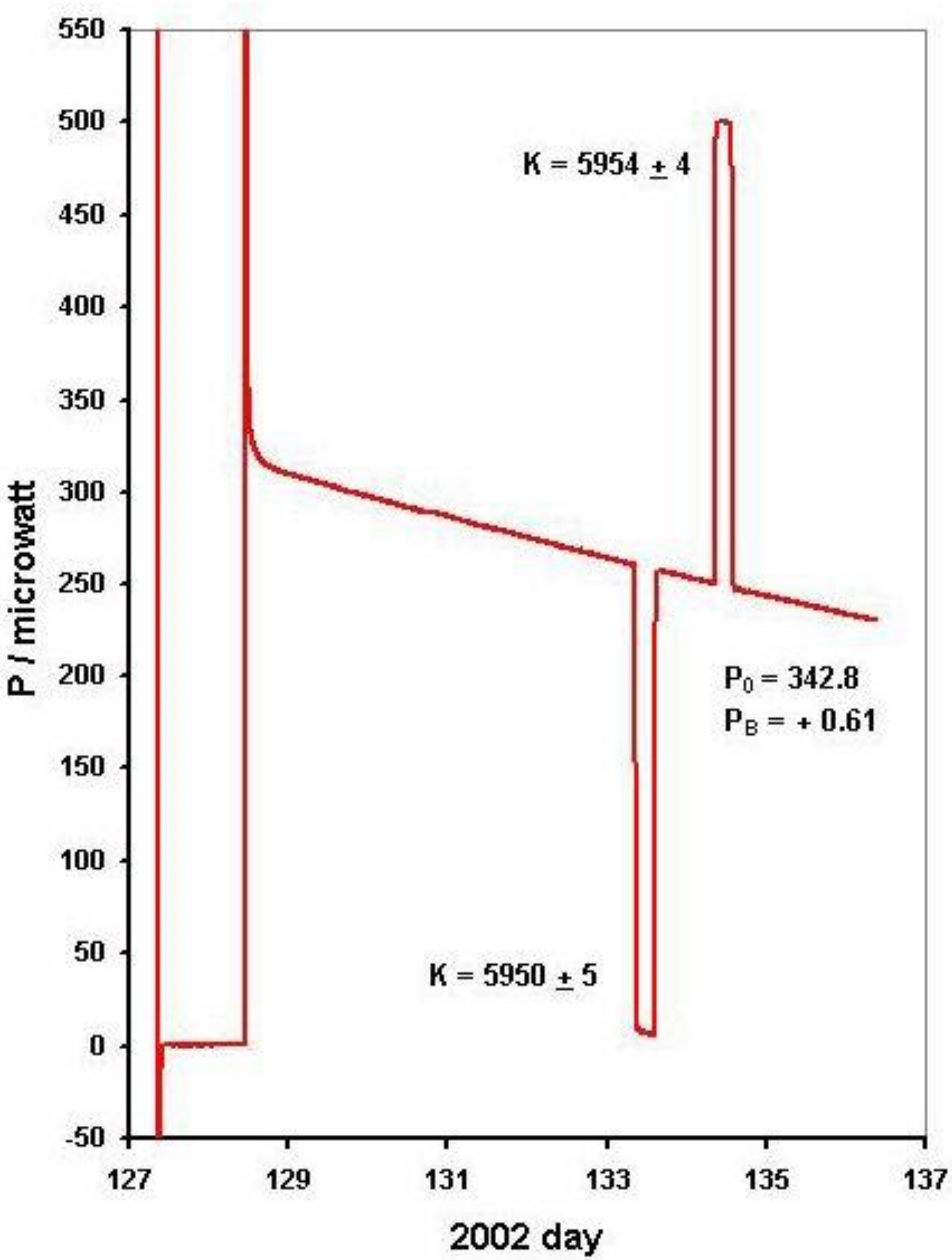


^{103}Pd seeds #H2-H7
IMC runs 73-77
1st insert
(brass)
2nd insert
(brass)
3rd insert
(aluminum)
K = 5950
K = 5954
K = 5946
K = 5947
343.05 (7.4 d)
345.59 (9.1 d)
344.00 (12.7 d)
P / microwatt
2002 day
320
295
270
245
220
195
170
145
120
95
70
125
130
135
140
145
150
155
160
165

Run 73

1st insertion

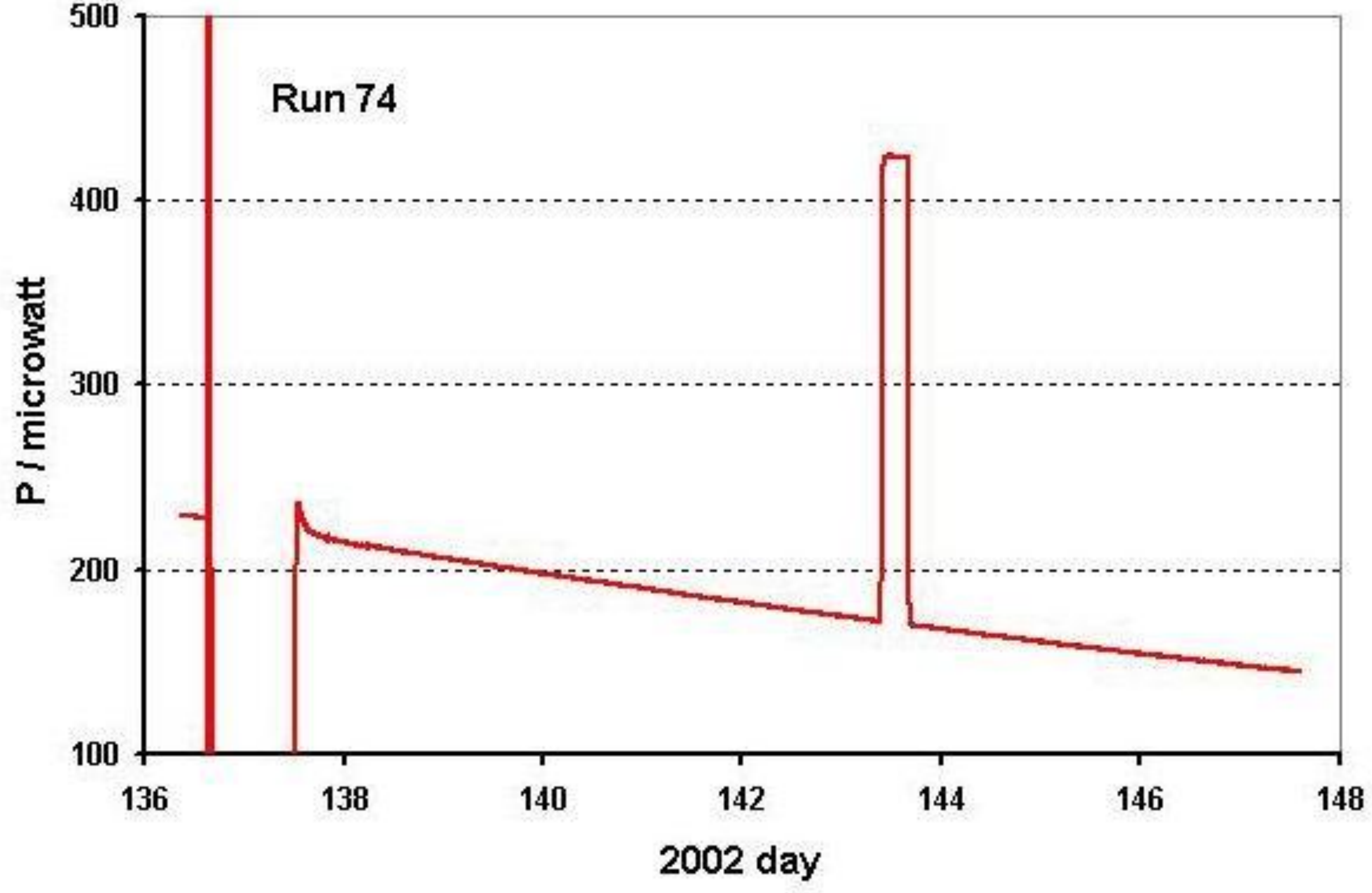
(brass)

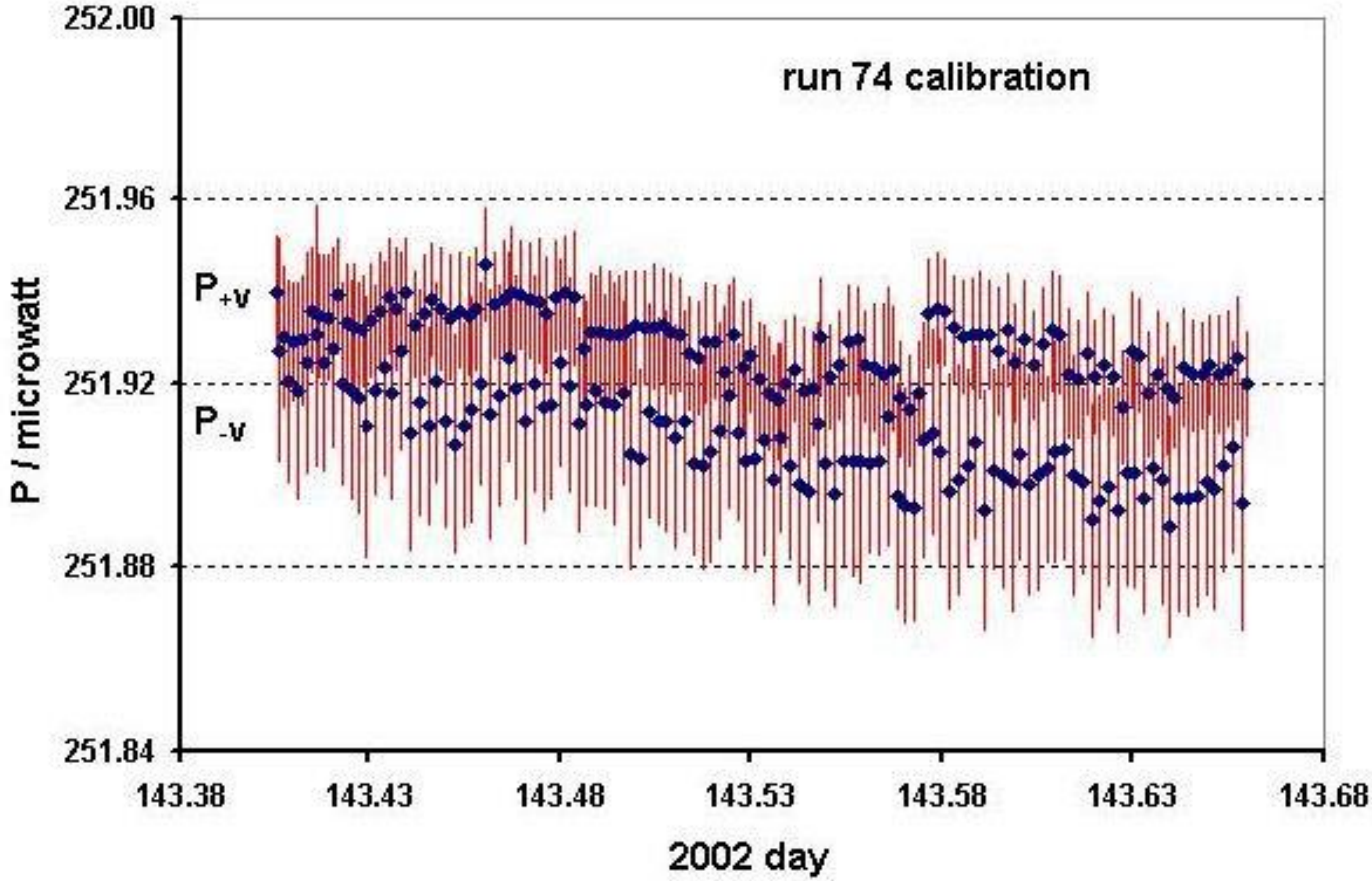


Run 74

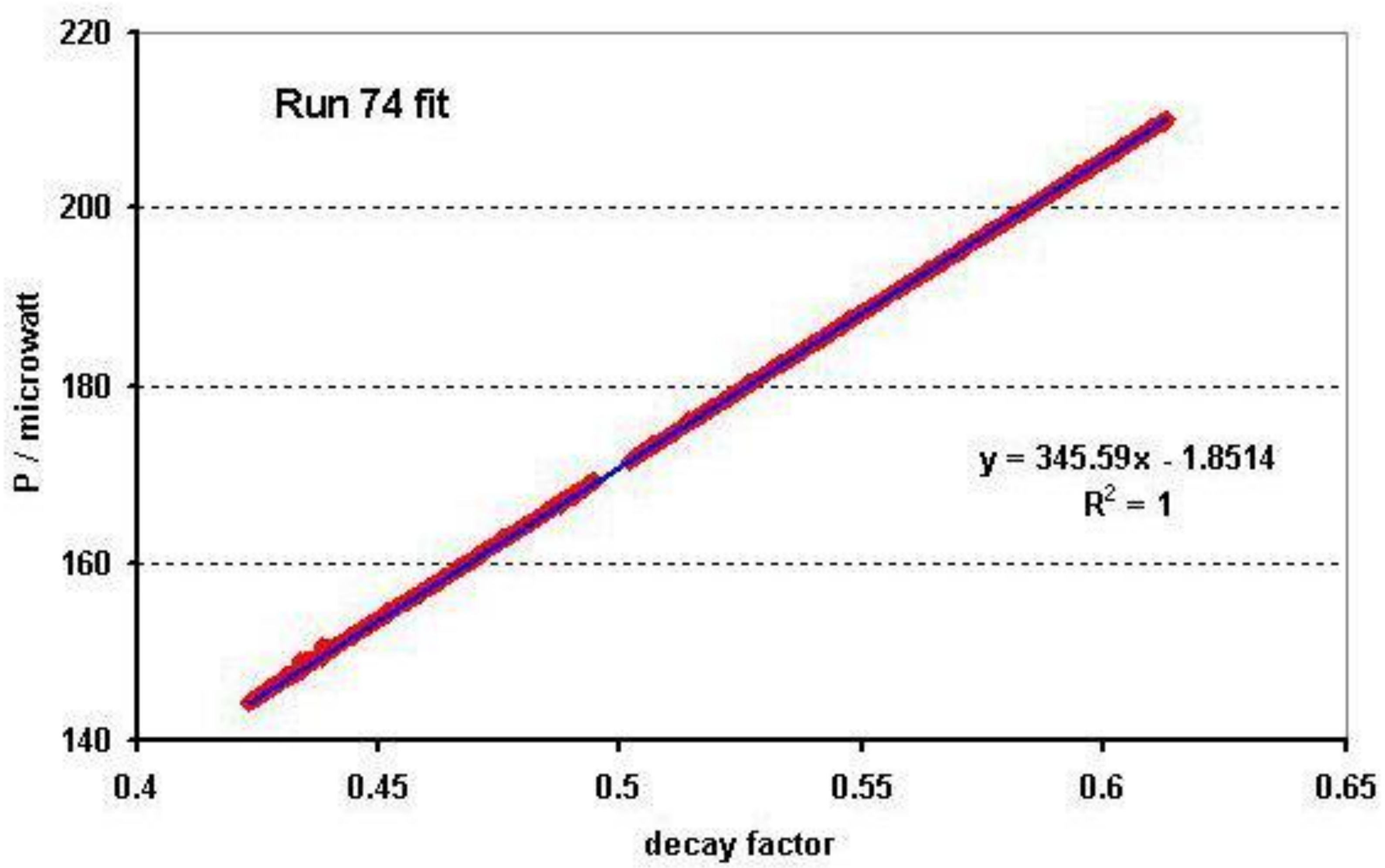
2nd insertion

(brass)



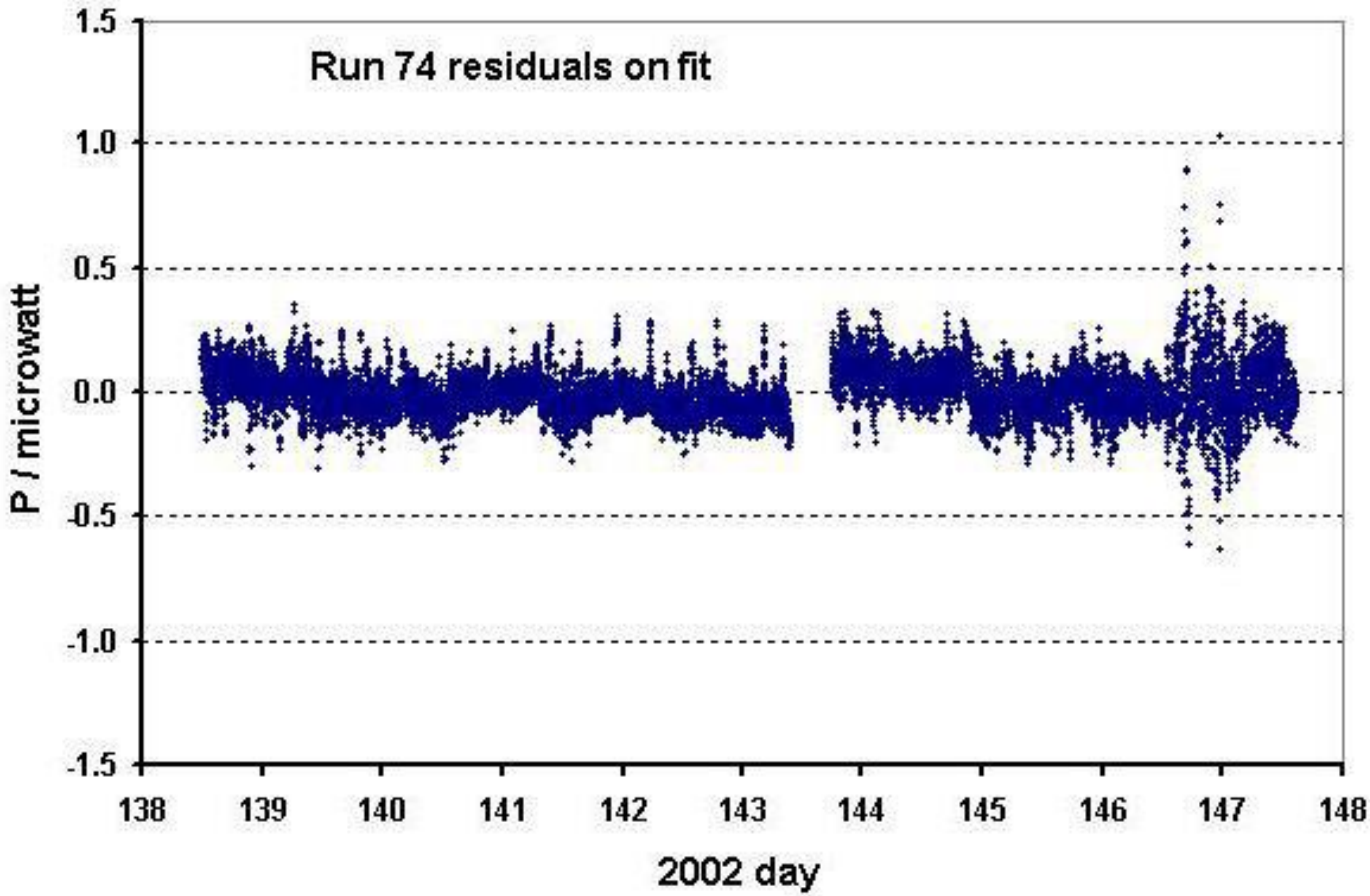


Run 74 calibration

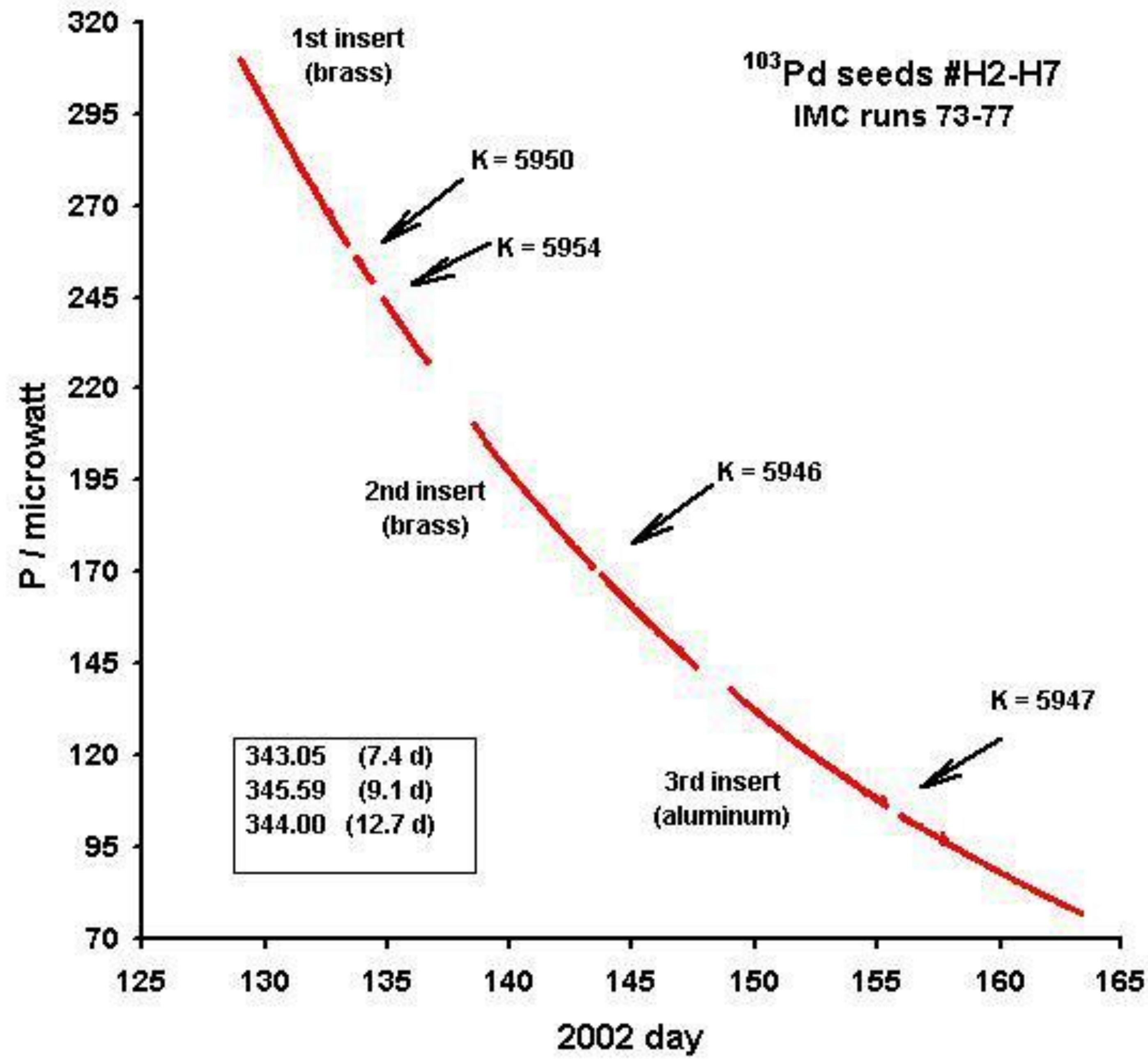


Run 74 fit
y = 345.59x - 1.8514
$R^2 = 1$
P / microwatt
decay factor
220
200
180
160
140
0.4
0.45
0.5
0.55
0.6
0.65

Run 74 fit



Run 74 residuals on fit
P / microwatt
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
138
139
140
141
142
143
144
145
146
147
148
2002 day



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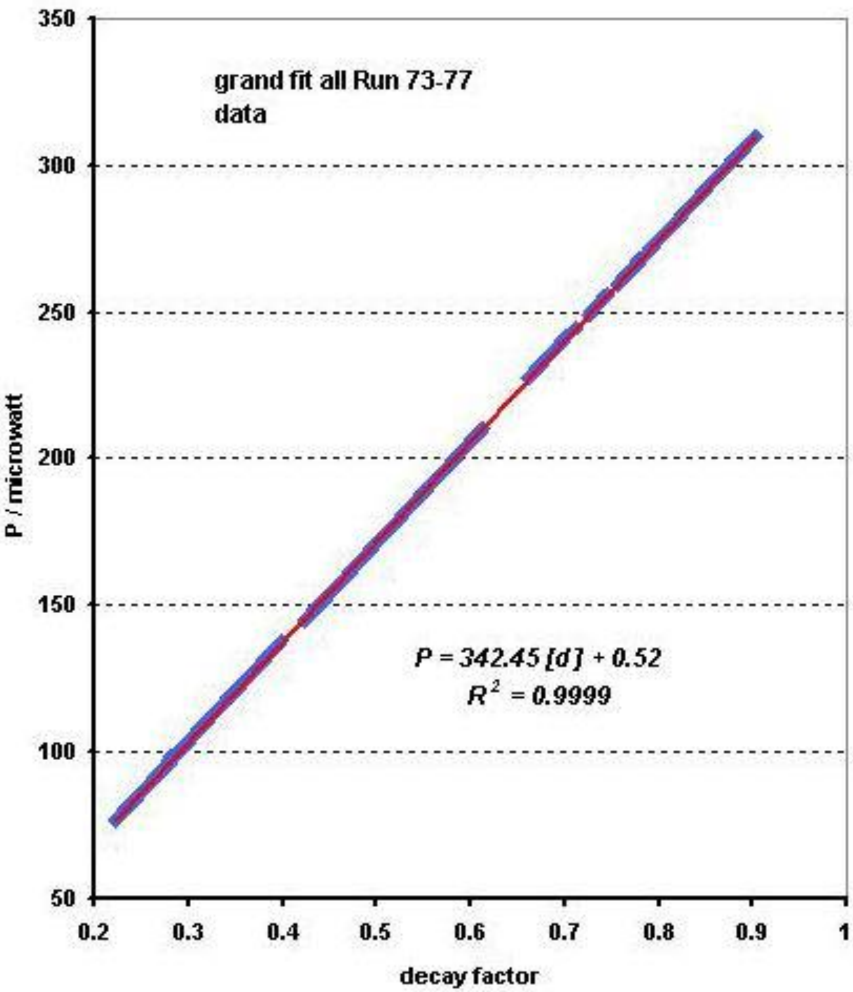
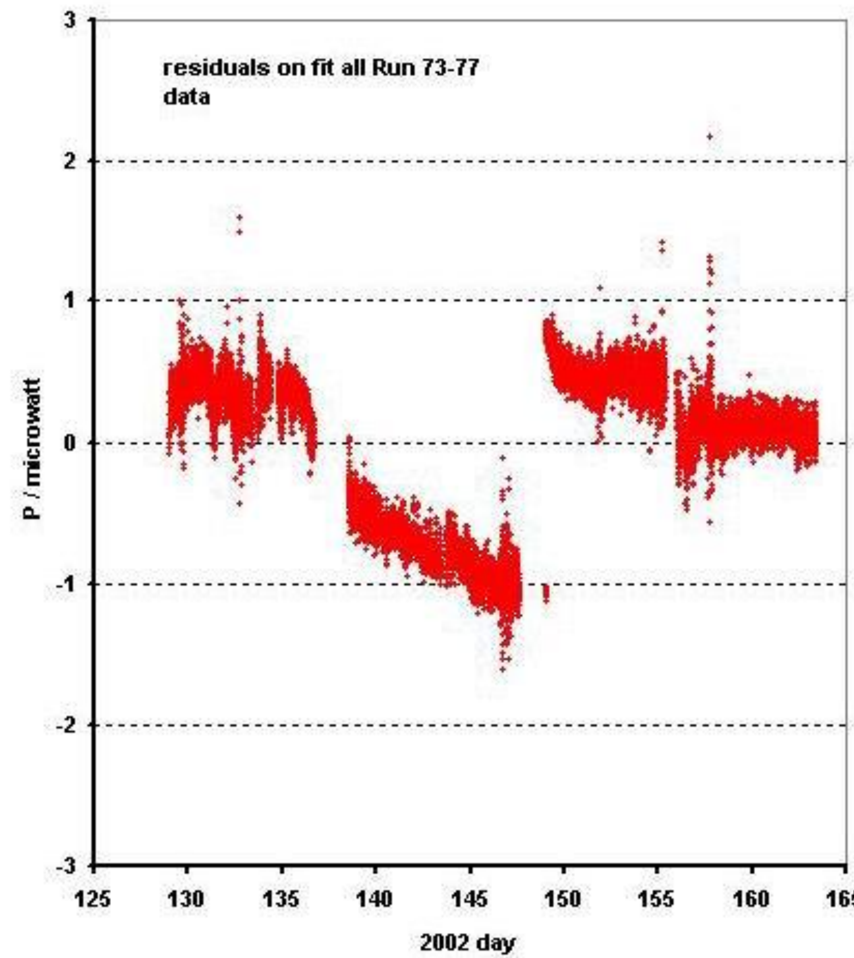
P / microwatt
2002 day
320
295
270
245
220
195
170
145
120
95
70
125
130
135
140
145
150
155
160
165



grand fit all Run 73-77 data
$P = 342.45 [d] + 0.52$
$R^2 = 0.9999$
P / microwatt
decay factor
350
300
250
200
150
100
50
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1



residuals on fit all Run 73-77 data
P / microwatt
2002 day
3
2
1
0
-1
-2
-3
125
130
135
140
145
150
155
160
165

Some concluding thoughts …

- **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, accuracy is in range of ± 1 or 2 percent**
  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

END