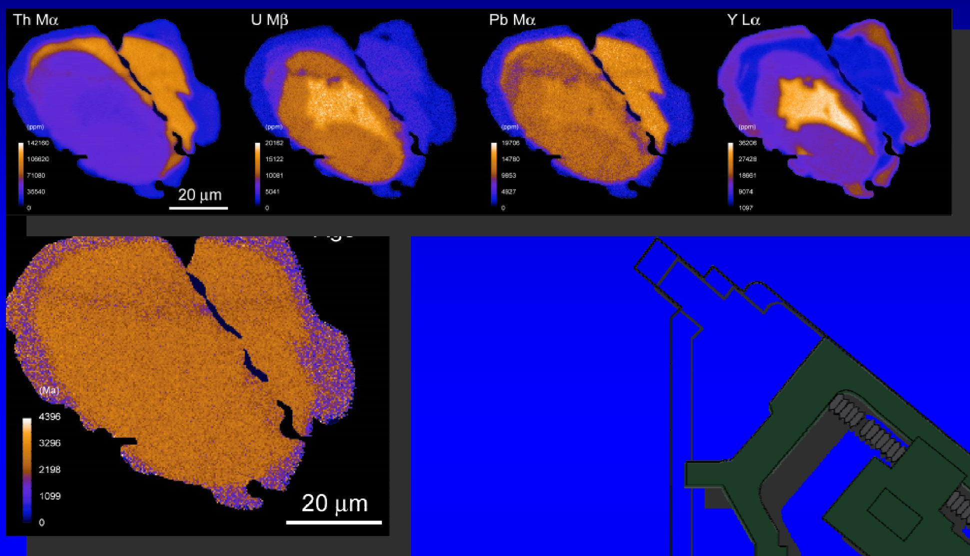
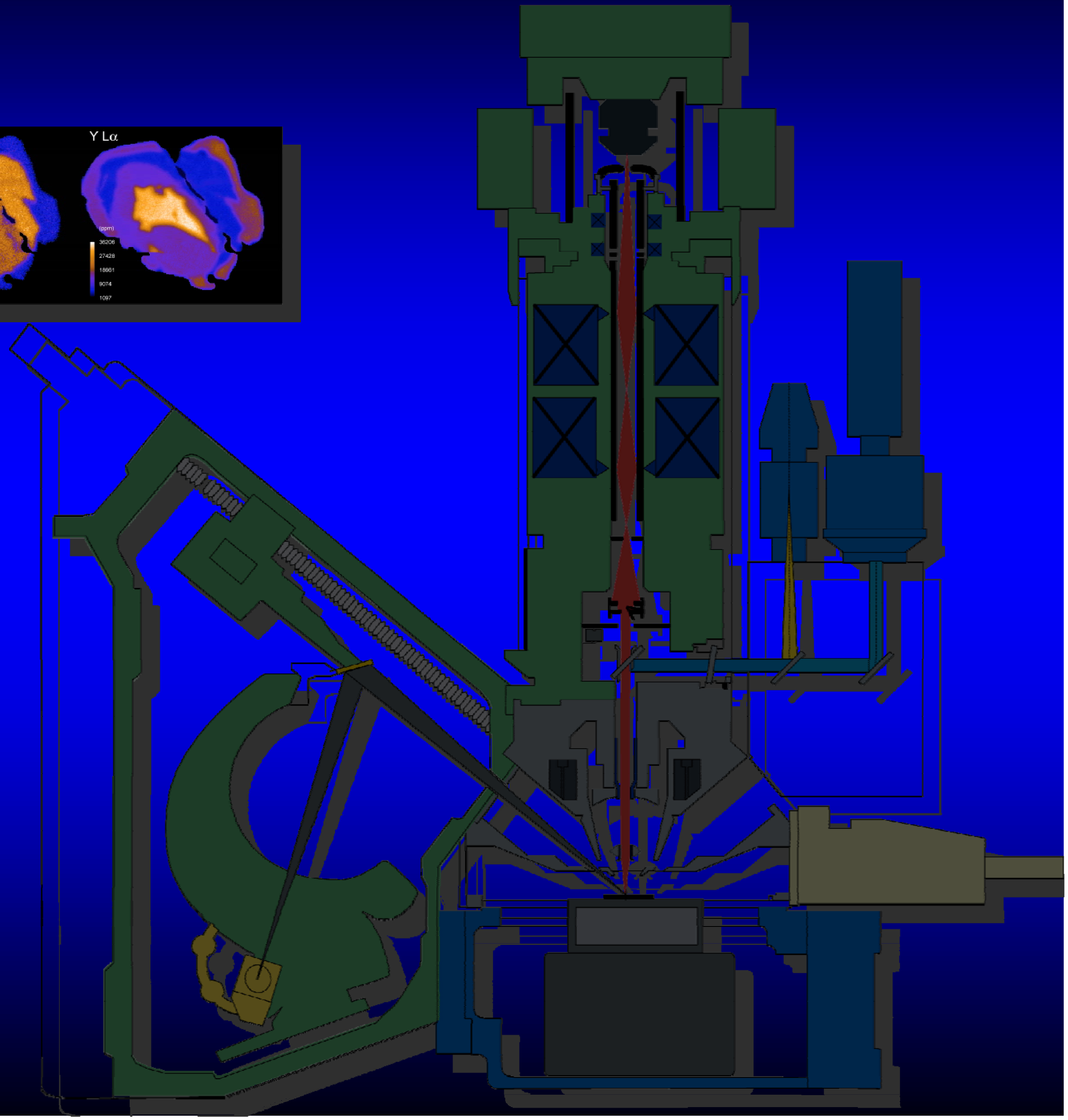
Analysis of Trace Elements in Complex Samples - U, Pb, Th in monazite





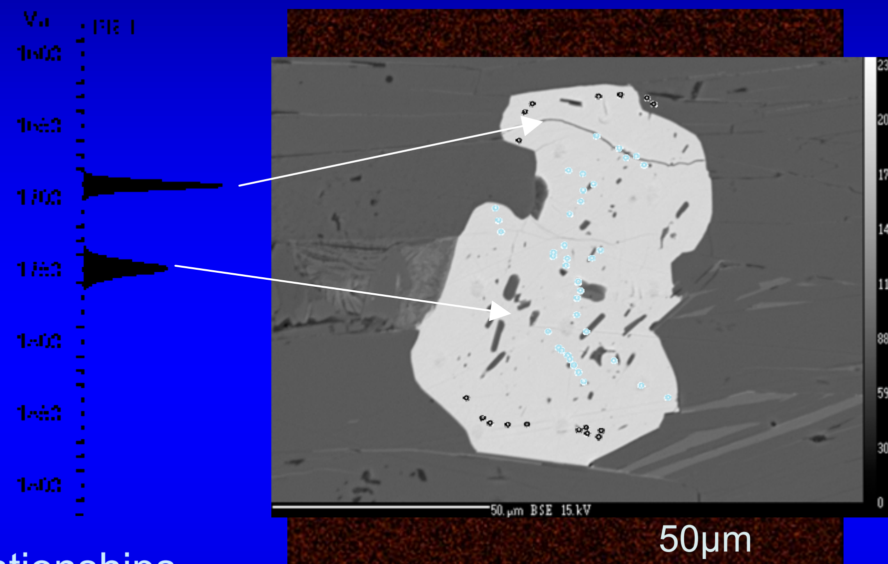
Geosciences

Geochronology – traditionally using isotopic/mass-spectrometric techniques

- IDTIMS
- Ion Probe

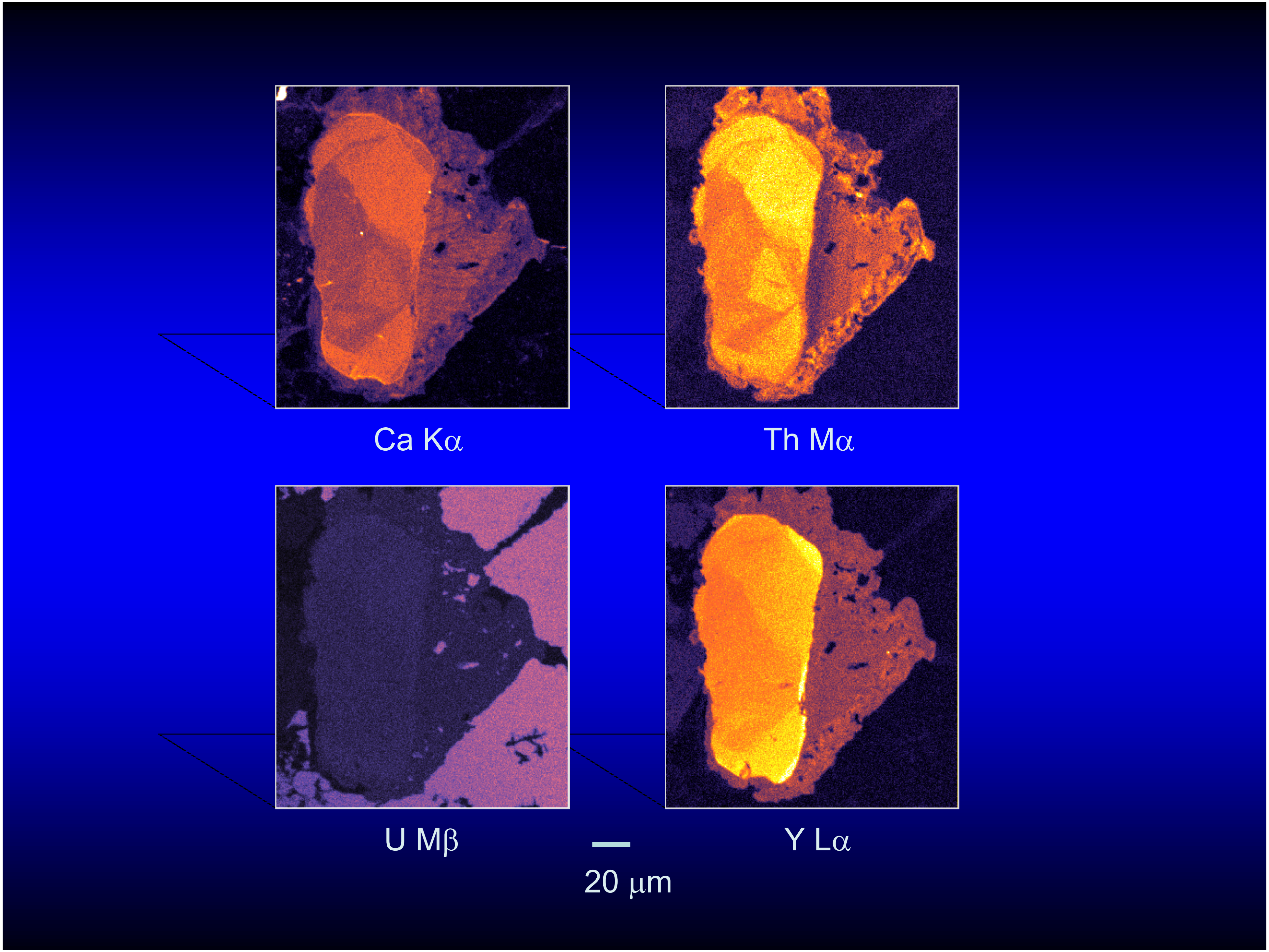
Electron Microprobe (EPMA)

- High spatial resolution
  access to ultra-thin rims,
  micro-domains, and inclusions
- In-situ: relate composition (and age) to
  micro/macro-structure and mineral
  paragenesis
- Non-destructive
- Integrated spatial / compositional / age relationships



Monazite: LREE-phosphate with Th and U (→ radiogenic Pb)

Dating events { Common accessory phase in many rocks
Fabric former
Dissolution/re-precipitation reactions result in polygenetic nature,
and ties into overall reaction history


Ca Kα
Th Mα
U Mβ
Y Lα
20 μm

Radiogenic Pb accumulates as a function of Th and U decay constants and time…

$$Pb = \left[\frac{Th}{232}\left(e^{\lambda^{232}t} - 1\right)\right]208 + \left[\frac{U}{238}0.9928\left(e^{\lambda^{238}t} - 1\right)\right]206 + \left[\frac{U}{235}0.0072\left(e^{\lambda^{235}t} - 1\right)\right]207$$

$Pb = concentration\ \ Pb(ppm)$

$Th = concentration\ \ Th(ppm)$

$U = concentration\ \ U(ppm)$

$\tau = age(years)$

$\lambda^{232} = Th^{232}$ decay constant (4.95E-11/yr)

$\lambda^{238} = U^{238}$ decay constant (1.55E-10/yr)

$\lambda^{235} = U^{235}$ decay constant (9.85E-10/yr)

Chimera

Mirriam-Webster

chi·me·ra

Pronunciation: kī-mîr'ə

Function: *noun*

Etymology: Latin *chimaera,* from Greek *chimaira* she-goat, chimera;

- **a: a fire-breathing she-monster in Greek mythology having a lion's head, a goat's body, and a serpent's tail b: an imaginary monster compounded of incongruous parts**

2. **an illusion or fabrication of the mind; *especially*: an unrealizable dream <a fancy, a *chimera* in my brain, troubles me in my prayer** -- John Donne>

From U, Th, and Pb concentrations, we can calculate dates

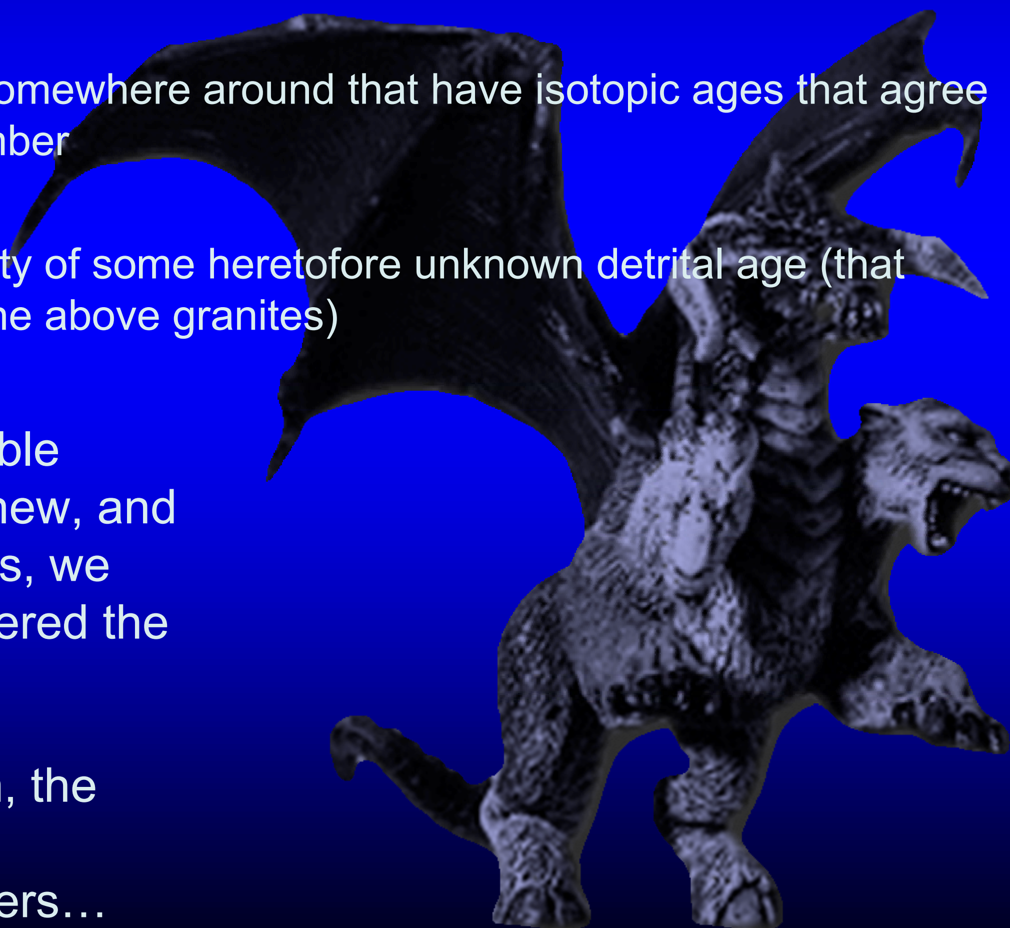
Systematic error - Can yield amazing results, requiring (or allowing) fantastic interpretations

Seeming truths –

- There are always granites somewhere around that have isotopic ages that agree with this number or that number
- There is always the possibility of some heretofore unknown detrital age (that usually agrees with one of the above granites)

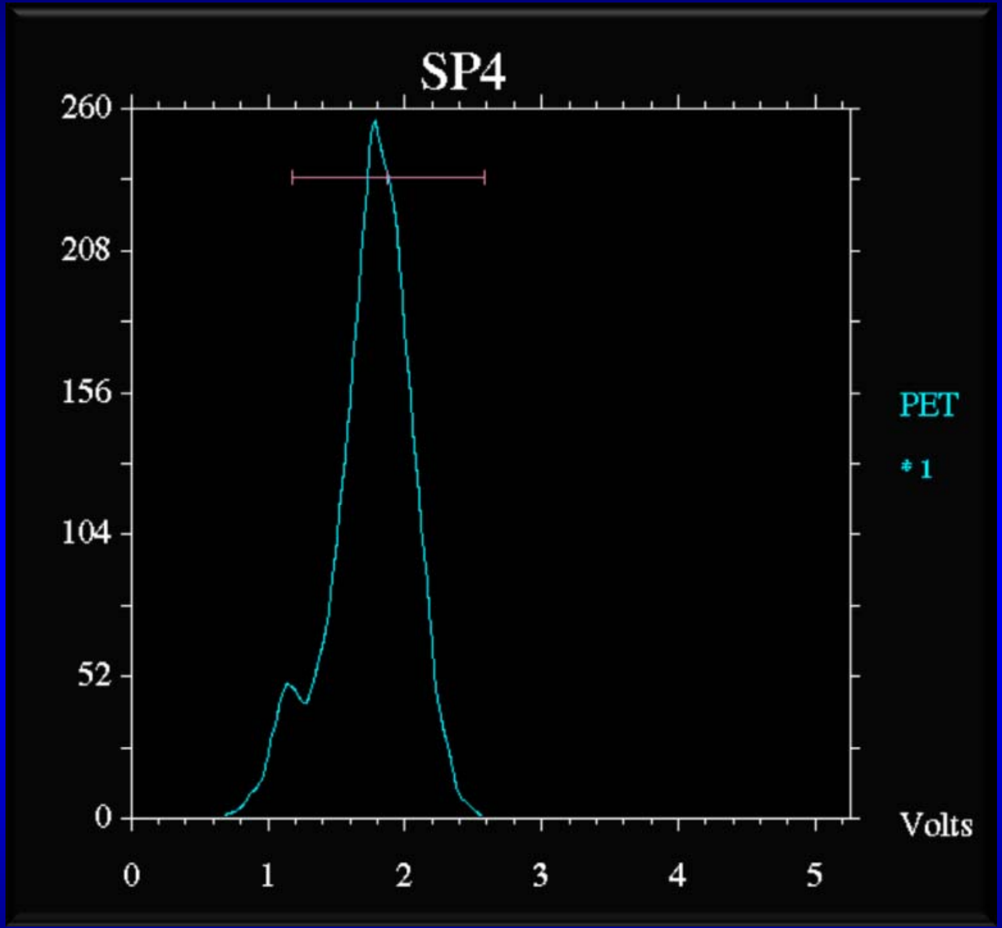
Before we concoct remarkable geochemical processes or new, and implausible tectonic histories, we have to insure we have covered the analytical bases…

The lower the concentration, the more everything about the measurement process matters…



Puzzler…

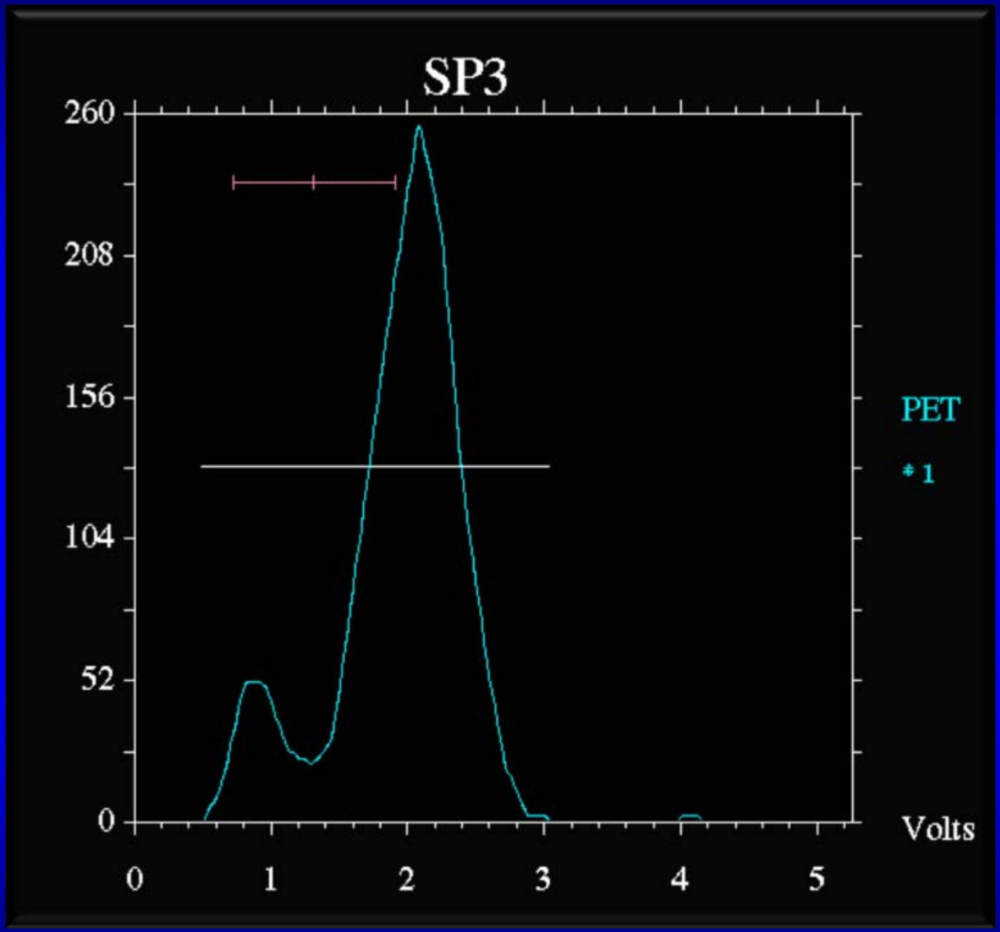
U Mβ = 3.336 keV
PET-P10 (3 bars)



Ar K-edge = 3.202 keV

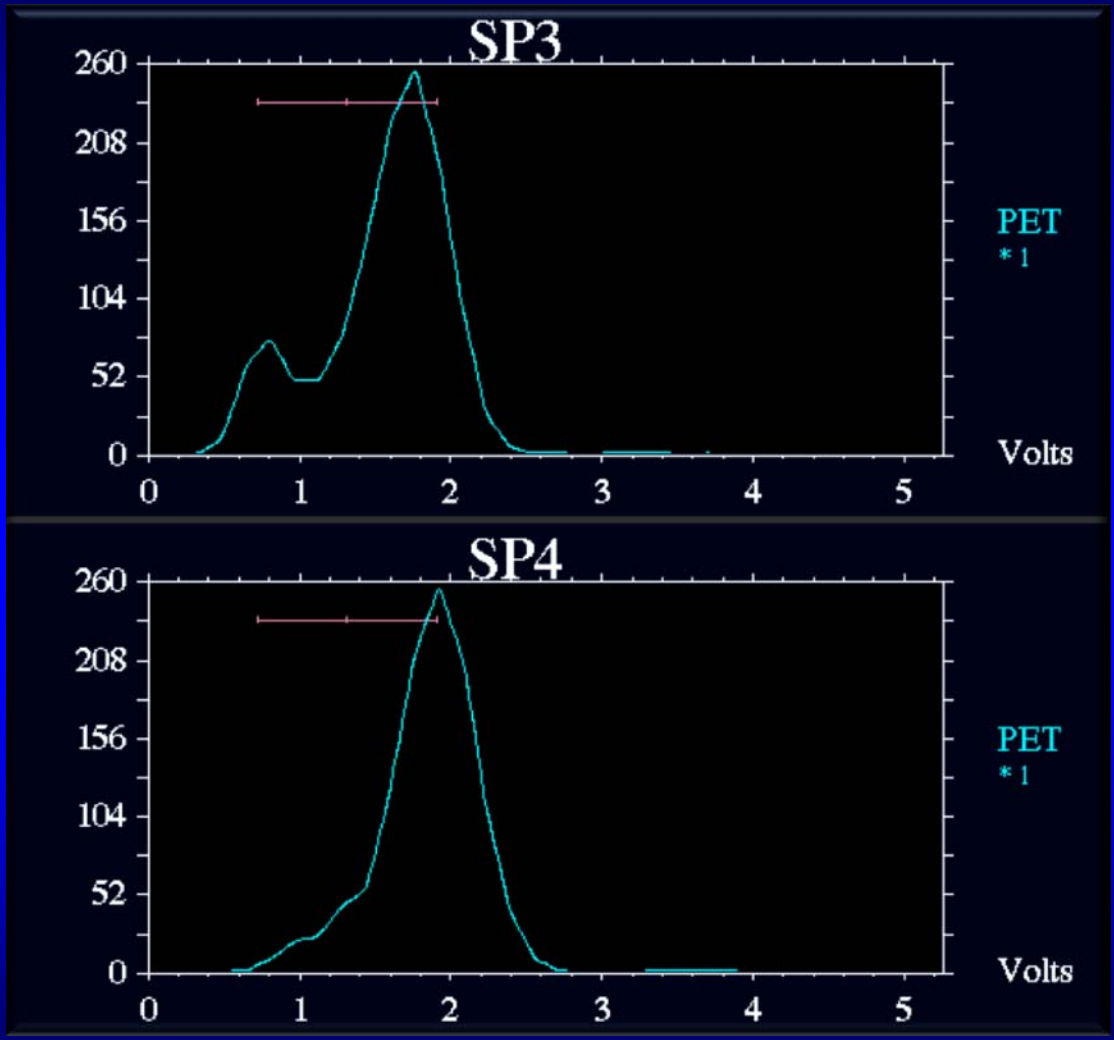
Puzzler…

Pb Mα = 2.345 keV
PET-P10 (3 bars)

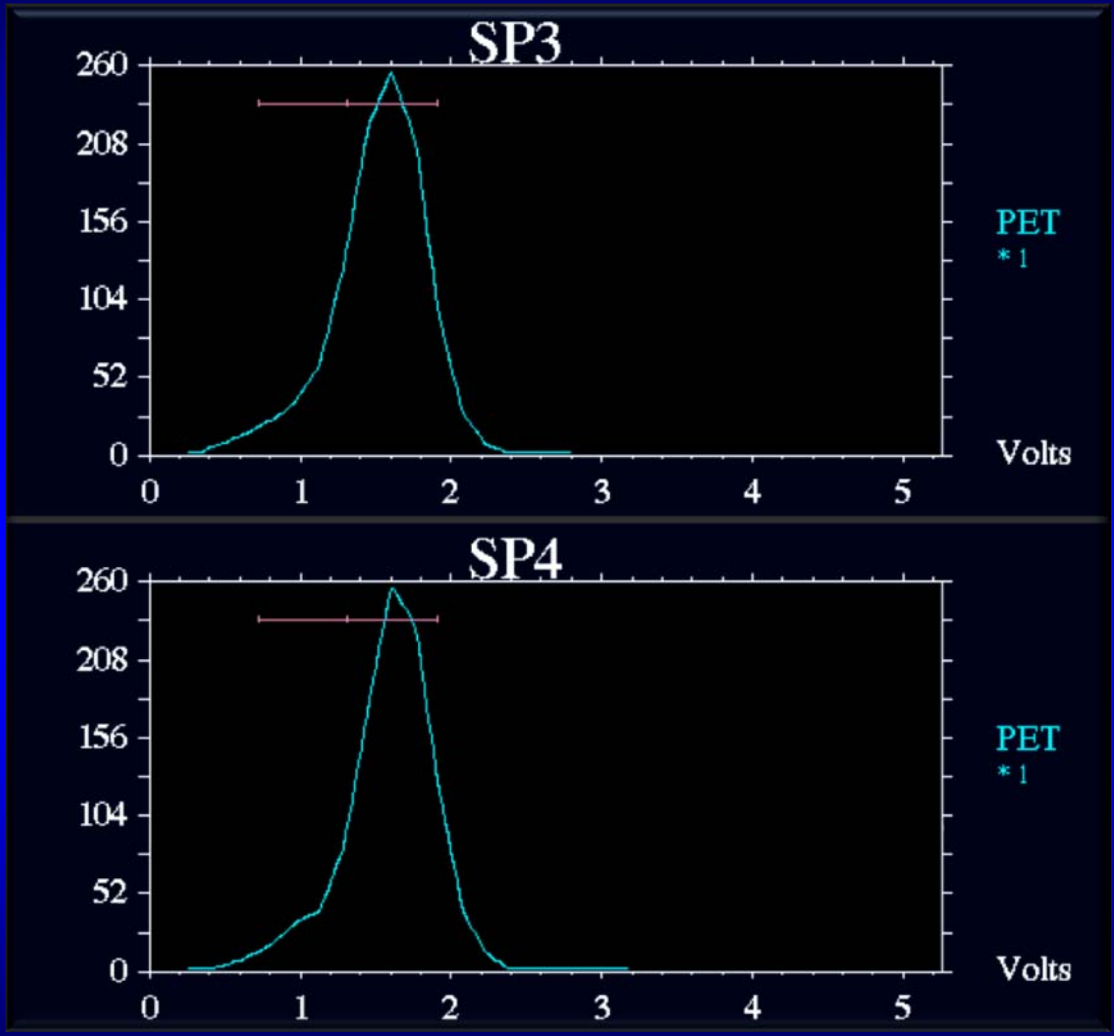


Ar K-edge = 3.202 keV

Two spectrometers, same line, crystals
Same counter gas, pressure, PHA conditions



Two spectrometers, same line, crystals
Same counter gas, pressure, PHA conditions



One day later, without changing any parameters…but we have done something

Pb values

	peak	bkg	Pk/bkg	Pb
	(cps/nA)	(cps/nA)		(ppm)
initial	0.29600	0.19882	1.48881	1715
after cleaning	0.31461	0.22177	1.41861	1662

In this instance, the resulting age difference …40 Ma

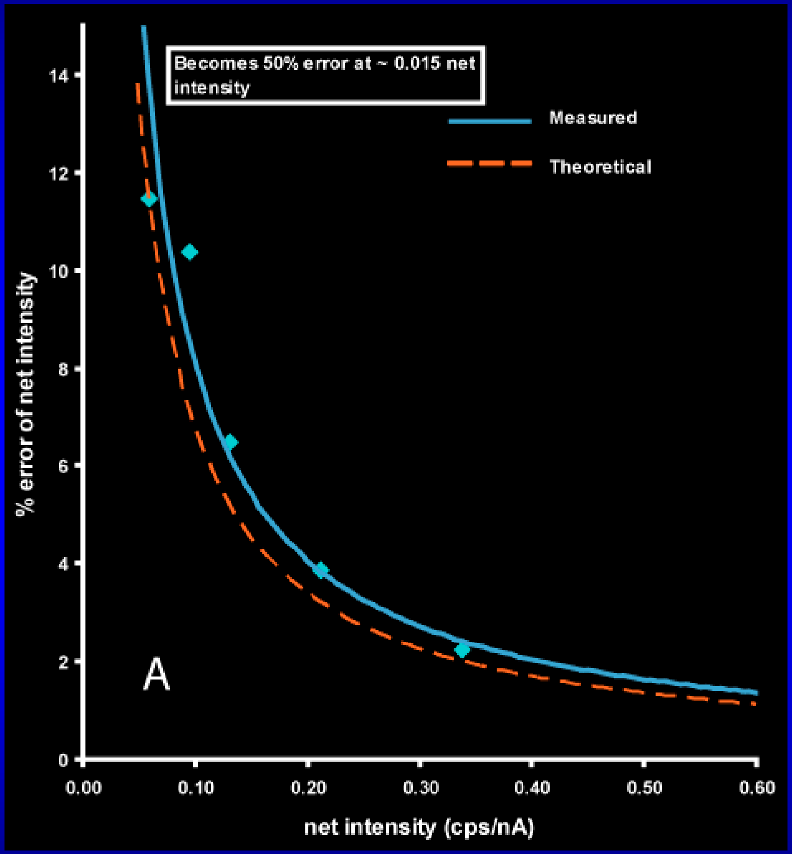
EPMA: What is the data?

- Ages?
- Concentration?
- X-Ray intensities?

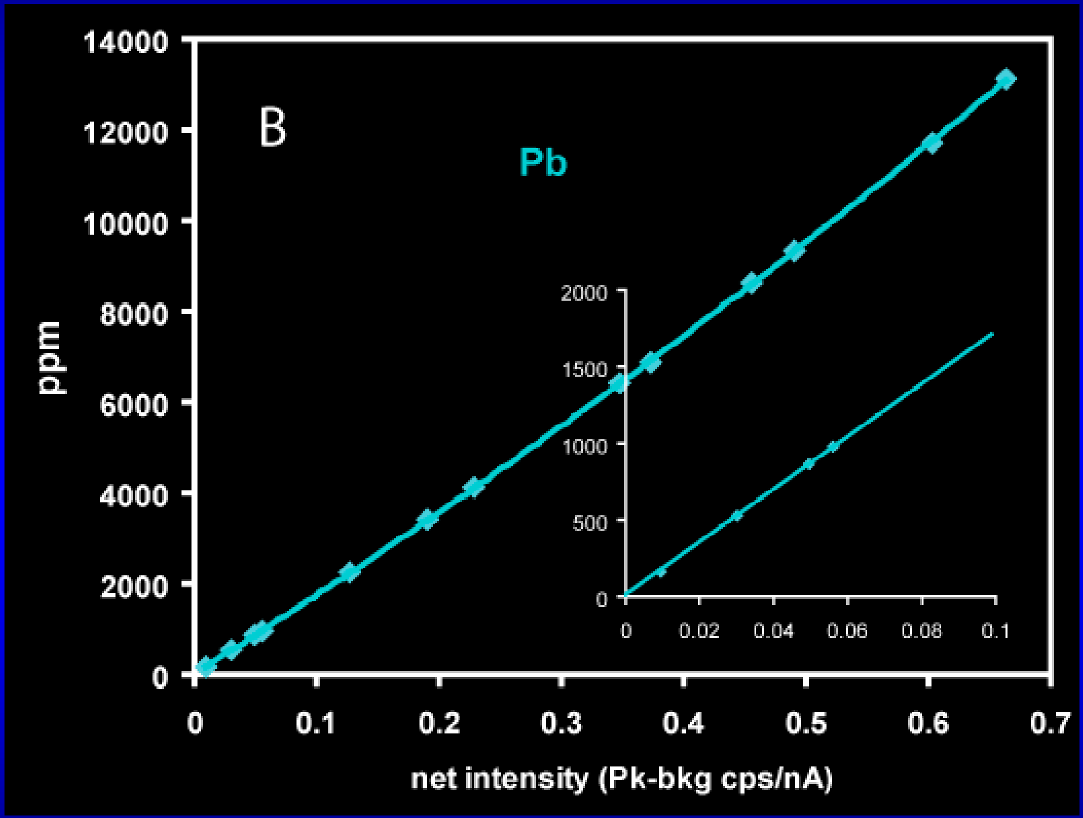
Enamored with precision

We have access to instruments that can produce fantastically precise numbers which can be wildly inaccurate

We have to try to understand all the potential sources of error



Becomes 50% error at ~ 0.015 net intensity
Measured
Theoretical
A
% error of net intensity
net intensity (cps/nA)
0
2
4
6
8
10
12
14
0.00
0.10
0.20
0.30
0.40
0.50
0.60


B
Pb
ppm
net intensity (Pk-bkg cps/nA)
0
2000
4000
6000
8000
10000
12000
14000
0.1
0.2
0.3
0.4
0.5
0.6
0.7
500
1000
1500
0.02
0.04
0.06
0.08

Analytical details:
Two essential aspects to be considered

- The sample
  - X-rays microanalysis: electron beam / specimen interactions and X-ray physics.

- The instrument
  - Measurement variables –
    - counts
    - current
    - time

In situ analysis of accessory minerals for geochronology: monazite xenotime

Grains are often small, 10s of μm or less
Grains are usually zoned compositionally, with remarkable complexity

Thin rims are important

Complex materials containing REEs, actinides, and multiple substitutional possibilities = lots of emission lines and absorption edges

Excitation of REE L lines results in energetic X-ray emission - efficient fluorescence

Phosphates are beam sensitive

Selected measurement issues

Background estimation

shape, etc.

Interferences

Peak

Background

Fluorescence interferences

Peak shift

Trace elements at high spatial resolution = high beam current density (sample damage, charge dynamics)

Selected measurement issues

Detectors

Counting chain – how do we really get the cps value?

- Counts?
- nA?
- seconds?

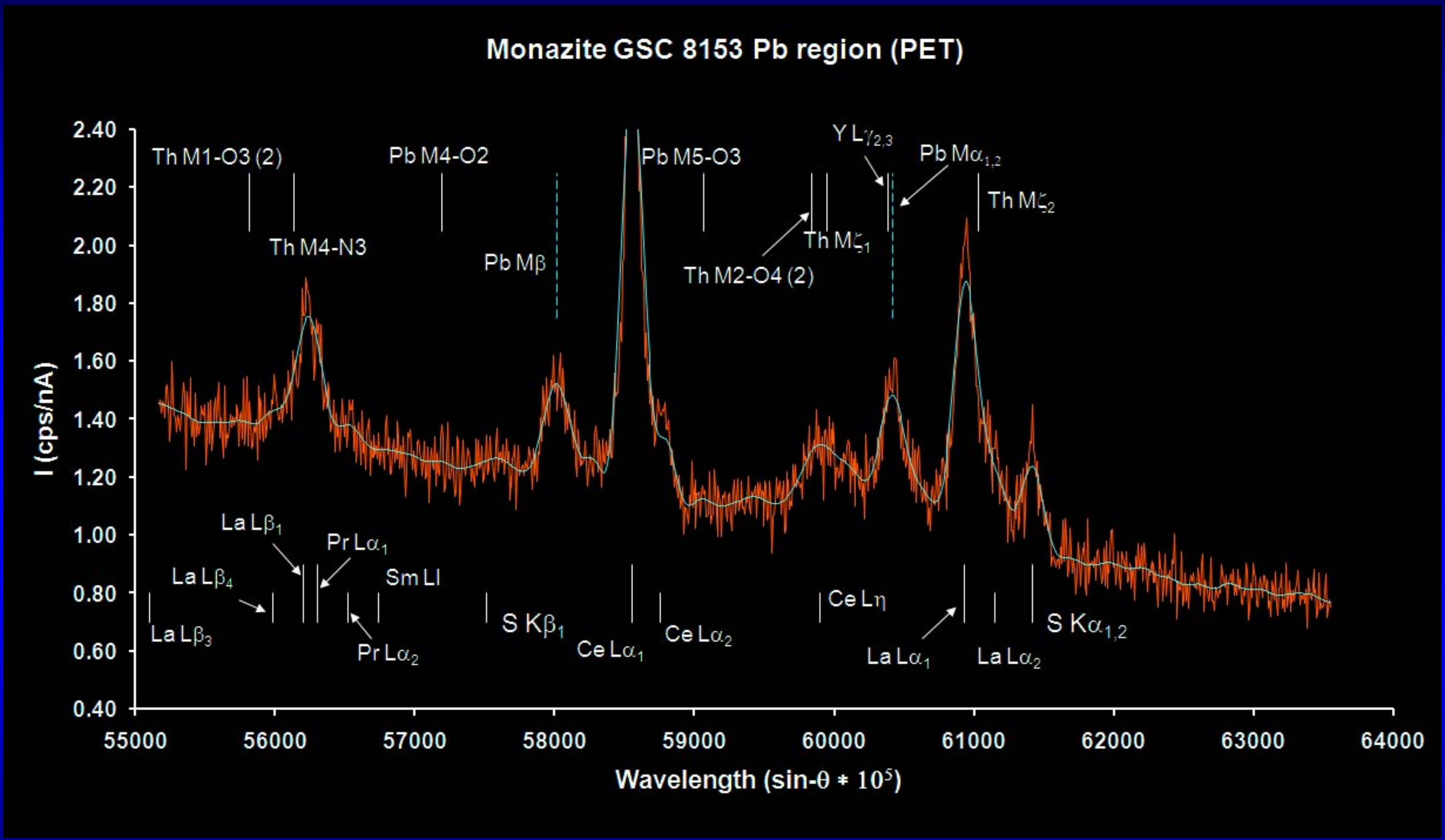
Temporal changes

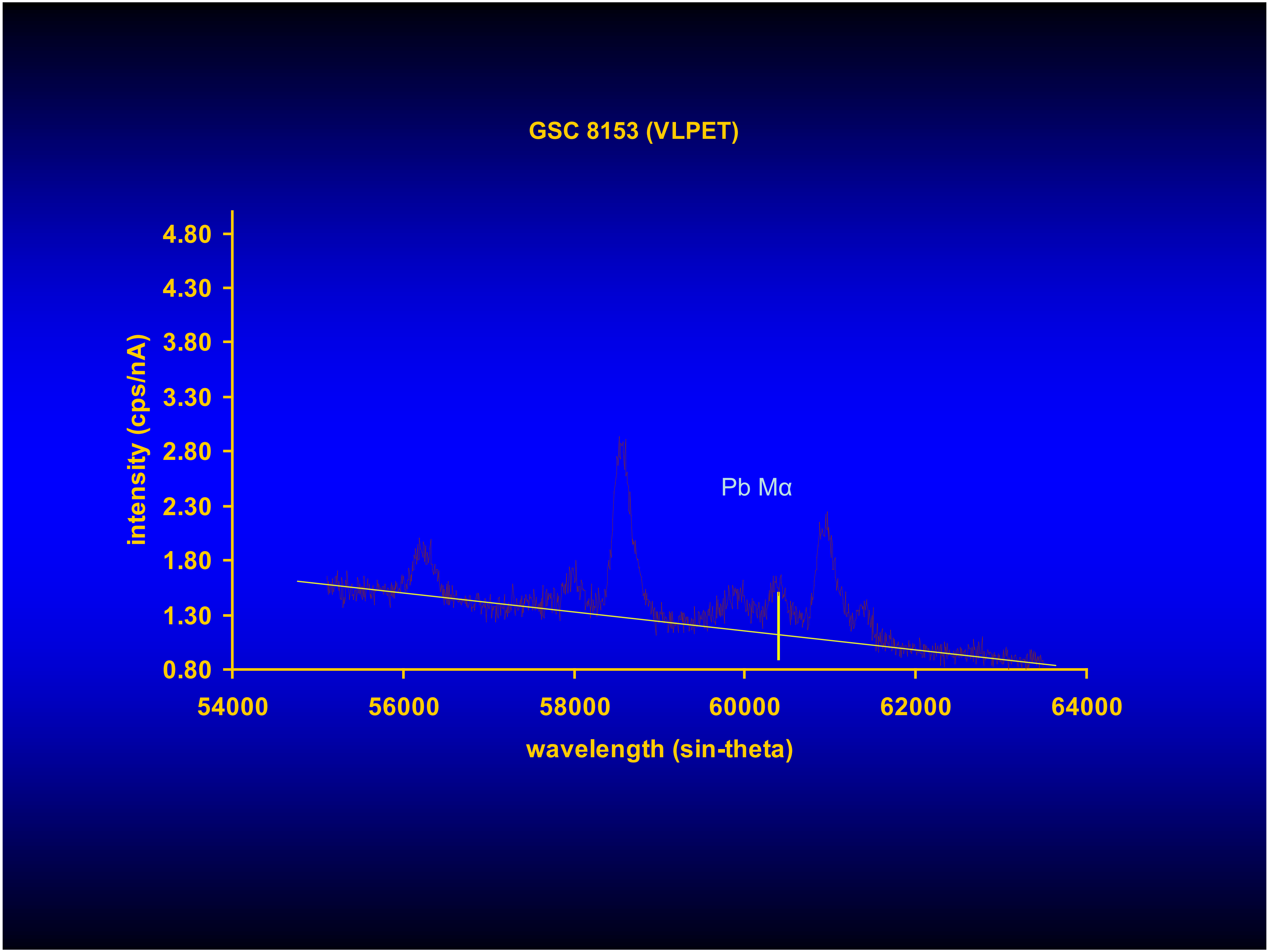
- Trace elements = long count times

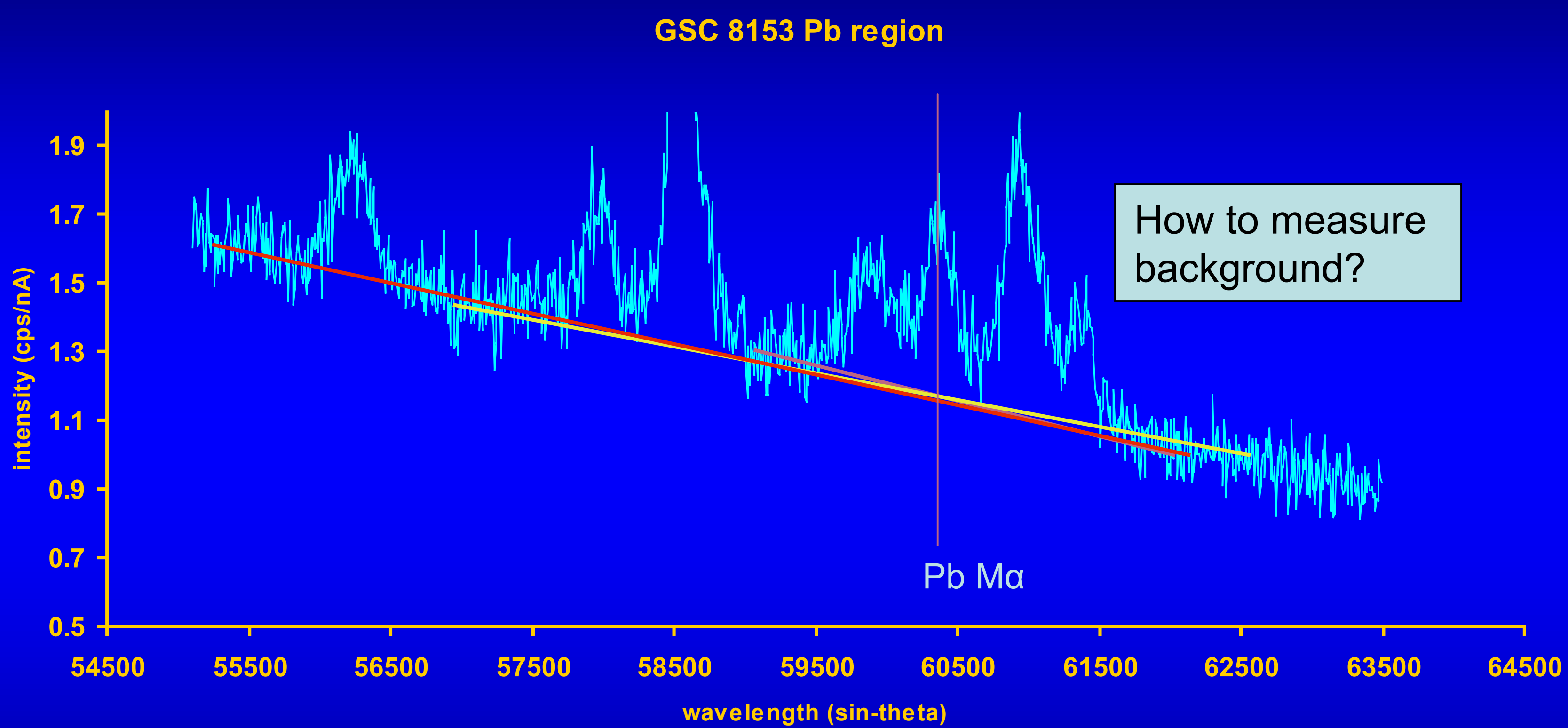
Measurement issues:

Background estimation

Curvature – PbMα or PbMβ measurement


Monazite GSC 8153 Pb region (PET)
I (cps/nA)
Wavelength (sin-θ * 10^5)
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
55000
56000
57000
58000
59000
60000
61000
62000
63000
64000
Th M1-O3 (2)
Th M4-N3
Pb M4-O2
Pb Mβ
Pb M5-O3
Th M2-O4 (2)
Th Mζ1
Y Lγ2,3
Pb Mα1,2
Th Mζ2
La Lβ1
Pr Lα1
La Lβ4
Sm Ll
La Lβ3
Pr Lα2
S Kβ1
Ce Lα1
Ce Lα2
Ce Lη
La Lα1
La Lα2
S Kα1,2


GSC 8153 (VLPET)
intensity (cps/nA)
4.80
4.30
3.80
3.30
2.80
2.30
1.80
1.30
0.80
54000
56000
58000
60000
62000
64000
wavelength (sin-theta)
Pb Mα


GSC 8153 Pb region
intensity (cps/nA)
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
54500
55500
56500
57500
58500
59500
60500
61500
62500
63500
64500
wavelength (sin-theta)
Pb Mα
How to measure background?

How do we know the analysis is correct ?

Analysis of elemental concentration

Test against secondary standard of
“known” composition

Secondary must be appropriate for
monazite, etc.

- REE phosphate
- Th
- U

Very difficult to find or make homogeneous trace
element secondary standard

How do we know the analysis is correct ?

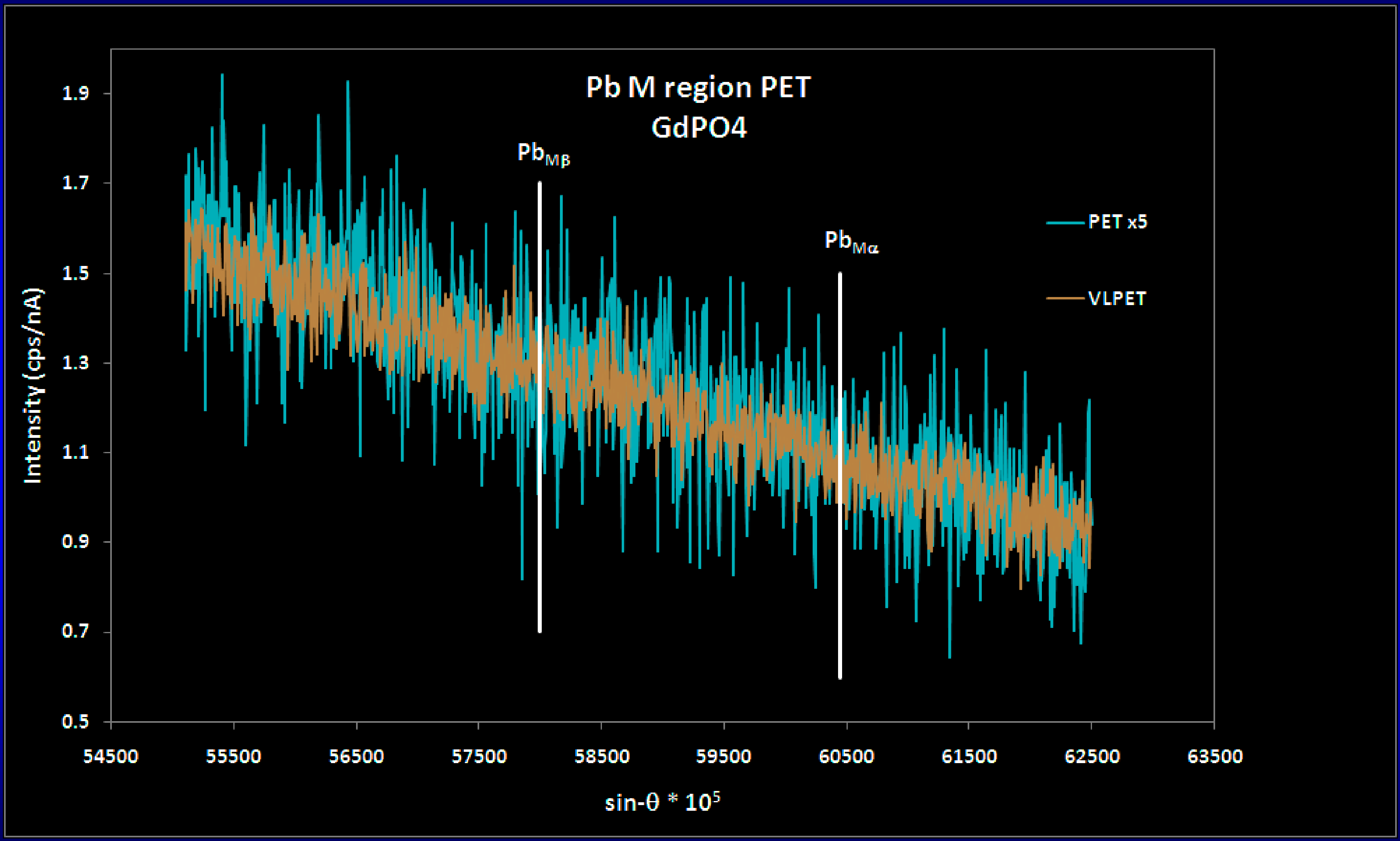
A place to start…

If you can't check against a known value, then try for a zero result in something appropriate that doesn't have any of the trace element of interest (blank).

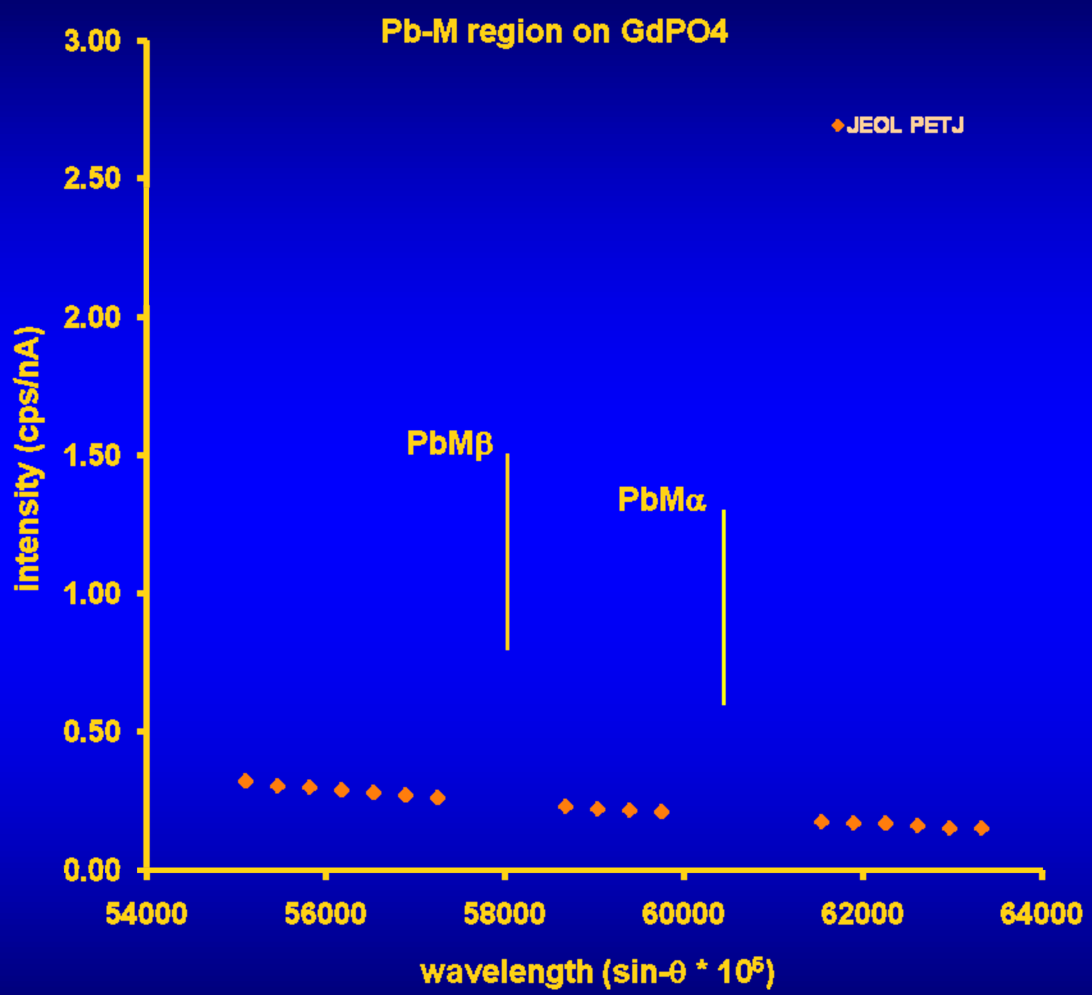
Clearly,
"If you can't analyze something, then see if you can analyze nothing…"

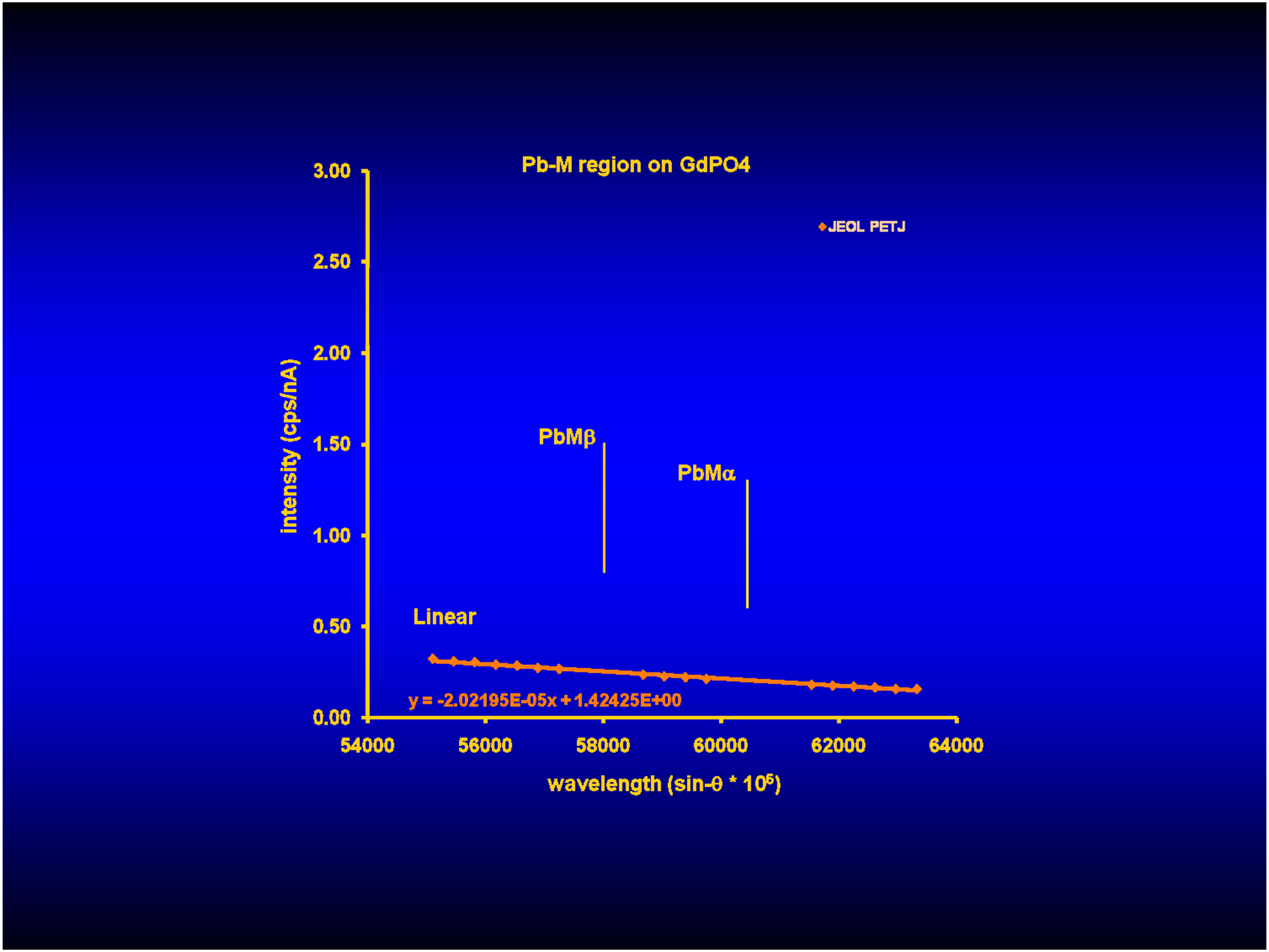
"Because, if you can't do nothing right, then you can't do anything."

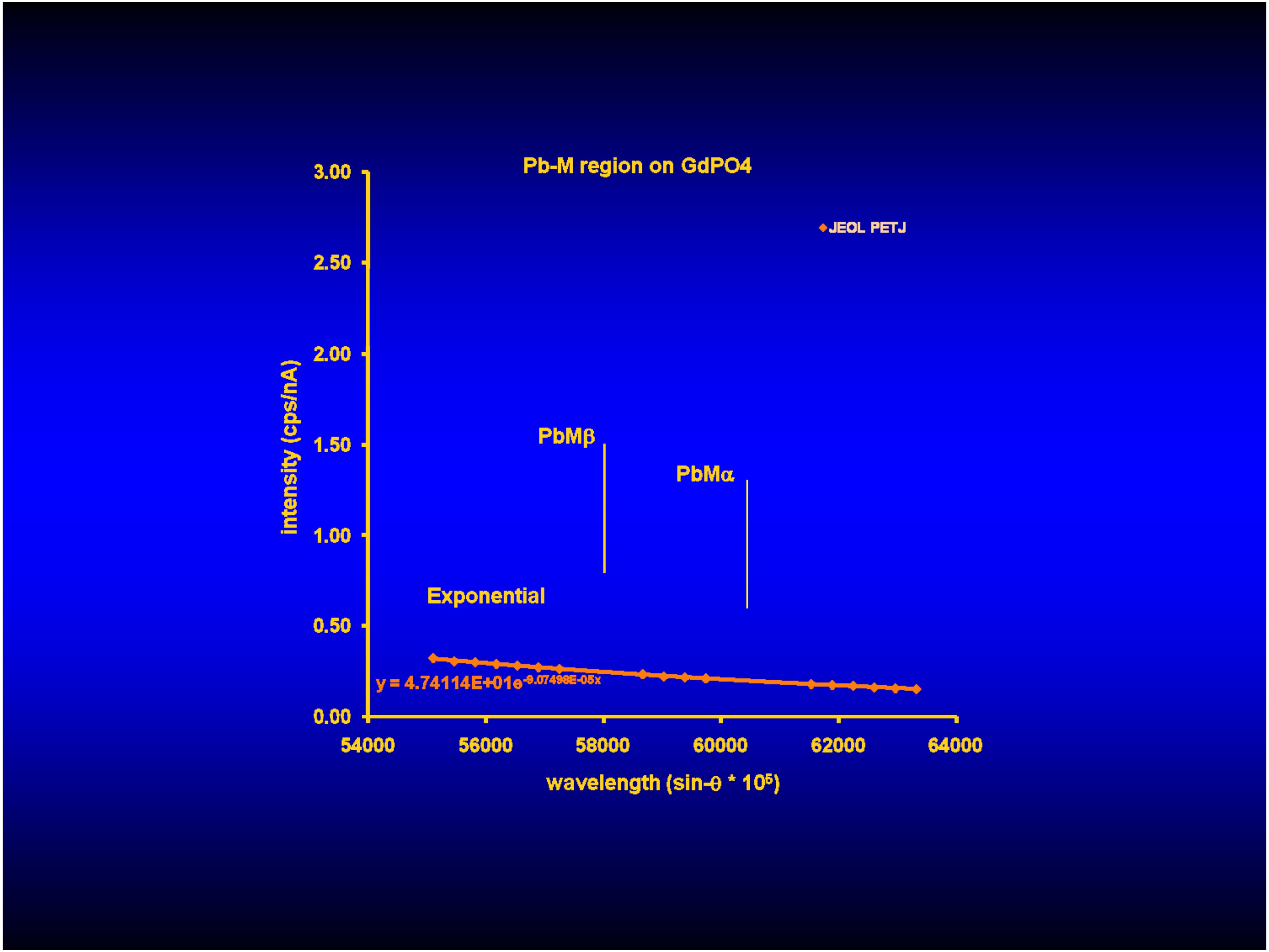
Lets start by looking at a "peakless" Pb M region in monazite
Strip away the interferences and look at background shape

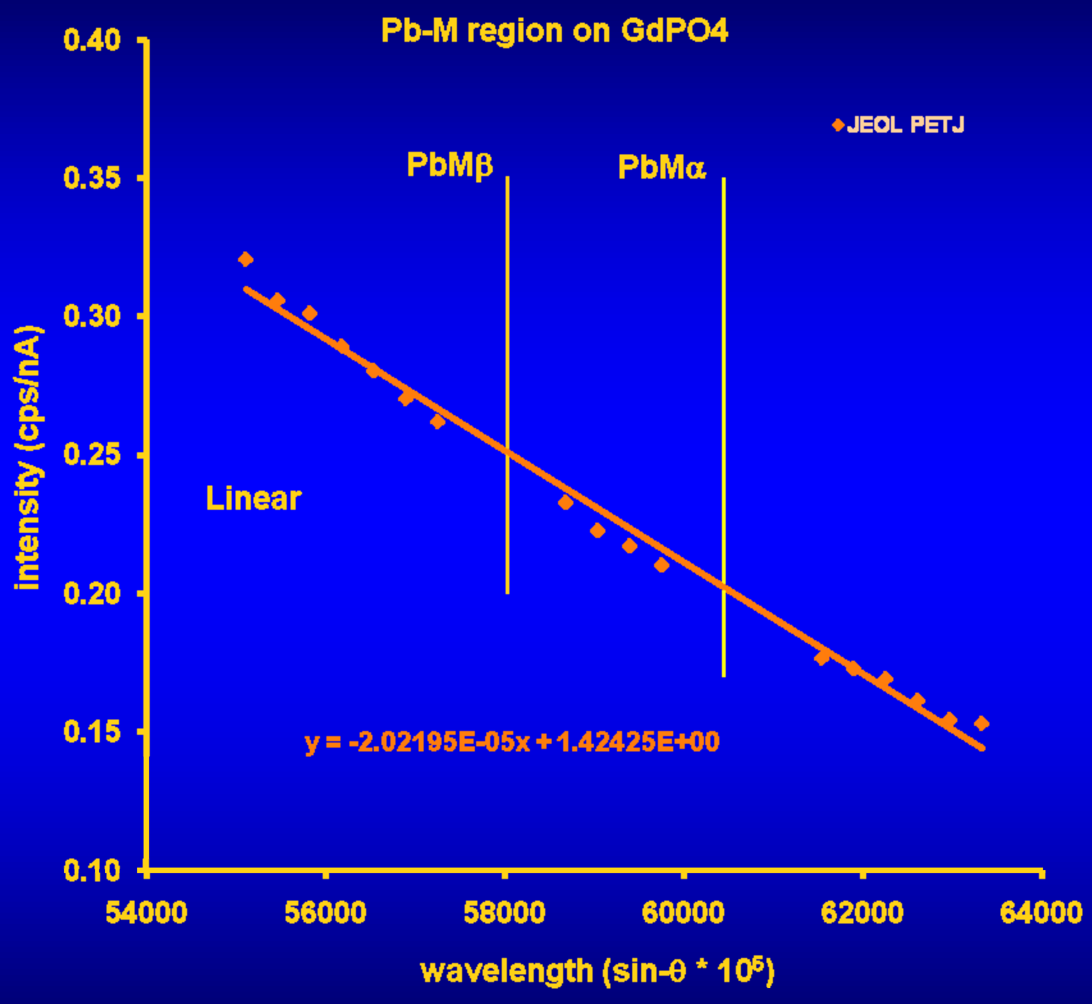


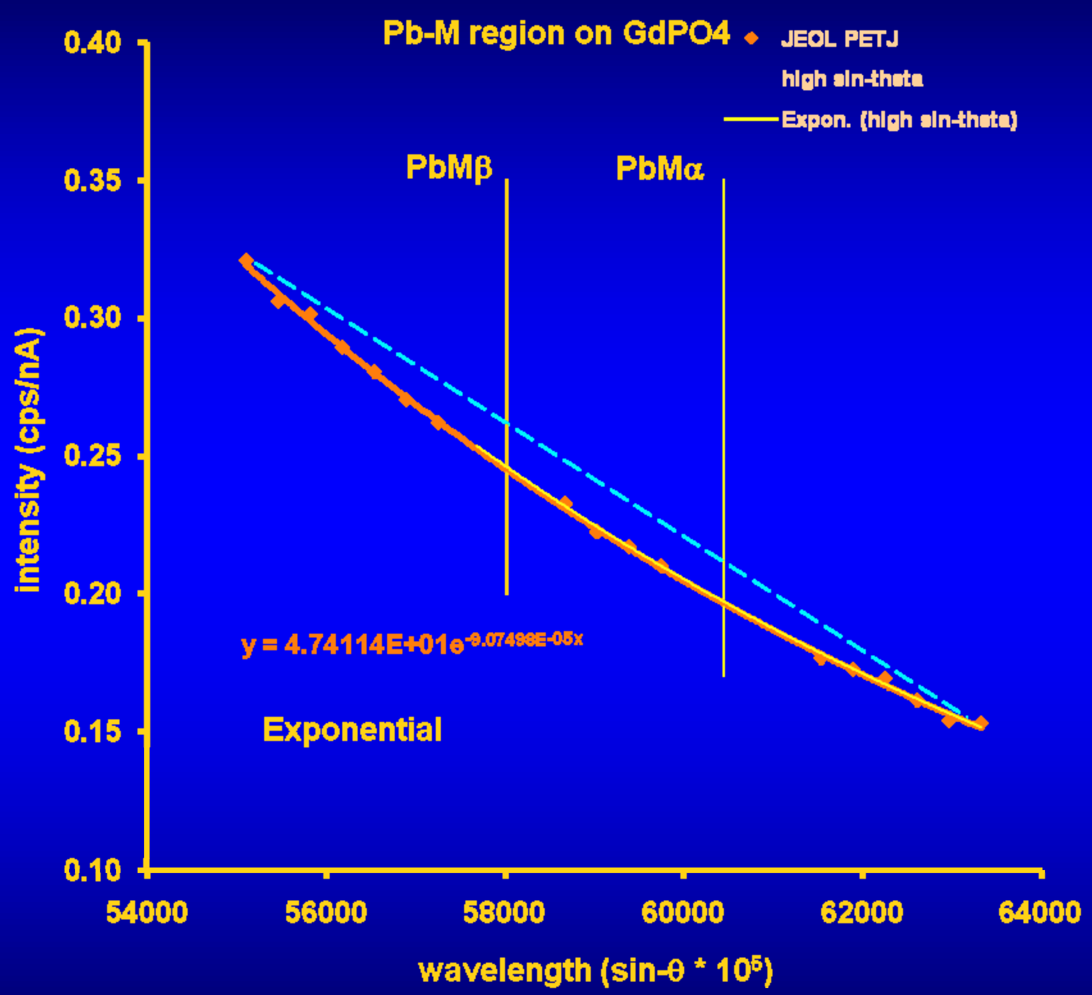
Let's look at this with very high precision




Pb-M region on GdPO4
JEOL PETJ
intensity (cps/nA)
3.00
2.50
2.00
1.50
1.00
0.50
0.00
PbMβ
PbMα
Linear
y = -2.02195E-05x + 1.42425E+00
54000
56000
58000
60000
62000
64000
wavelength (sin-θ * 10^5)

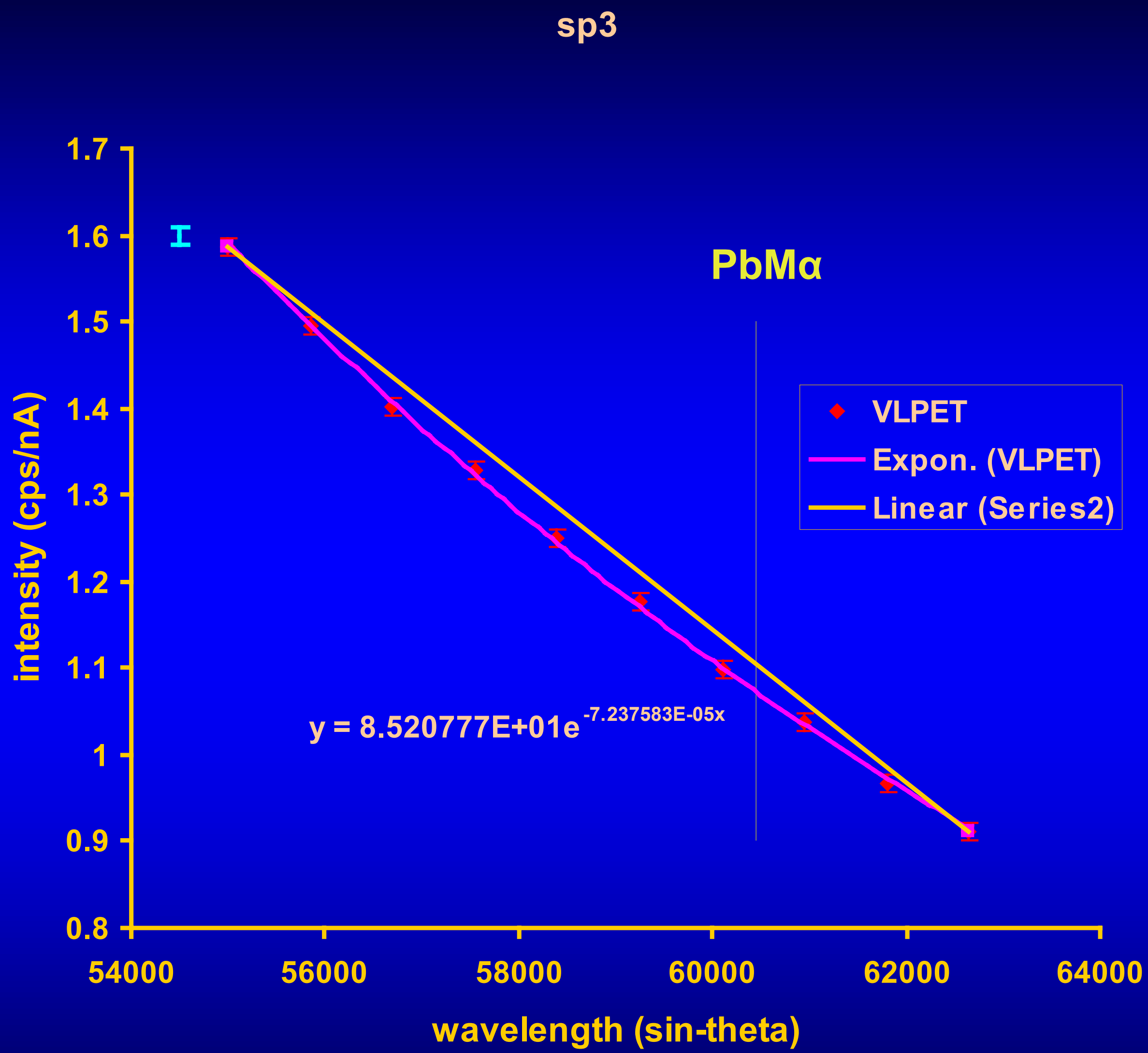

Pb-M region on GdPO4
JEOL PETJ
3.00
2.50
2.00
1.50
1.00
0.50
0.00
intensity (cps/nA)
PbMβ
PbMα
Exponential
y = 4.74114E+01e-9.07498E-05x
54000
56000
58000
60000
62000
64000
wavelength (sin-θ * 10^5)

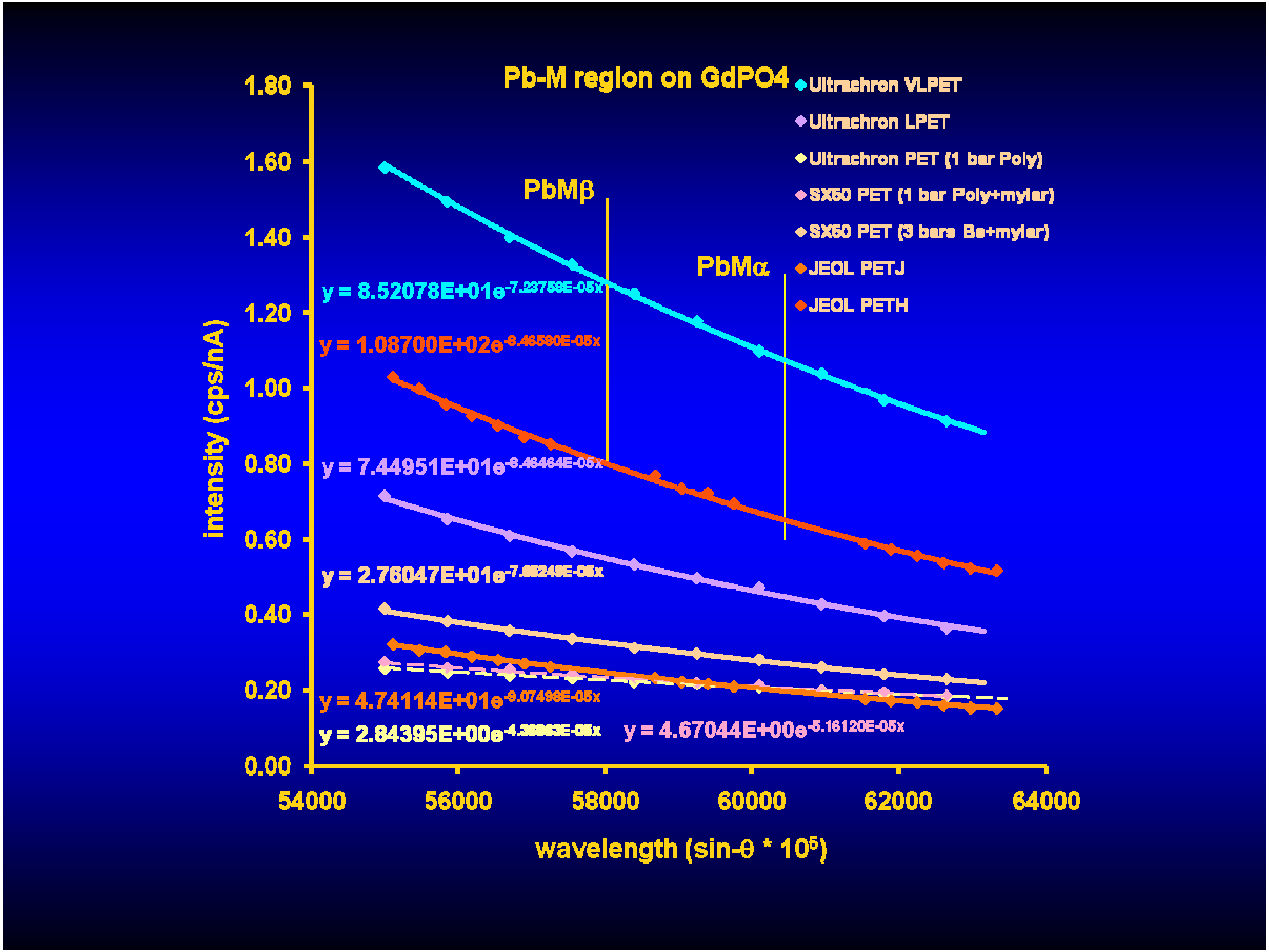

Pb-M region on GdPO4
JEOL PETJ
PbMβ
PbMα
Linear
y = -2.02195E-05x + 1.42425E+00
intensity (cps/nA)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
54000
56000
58000
60000
62000
64000
wavelength (sin-θ * 10^5)

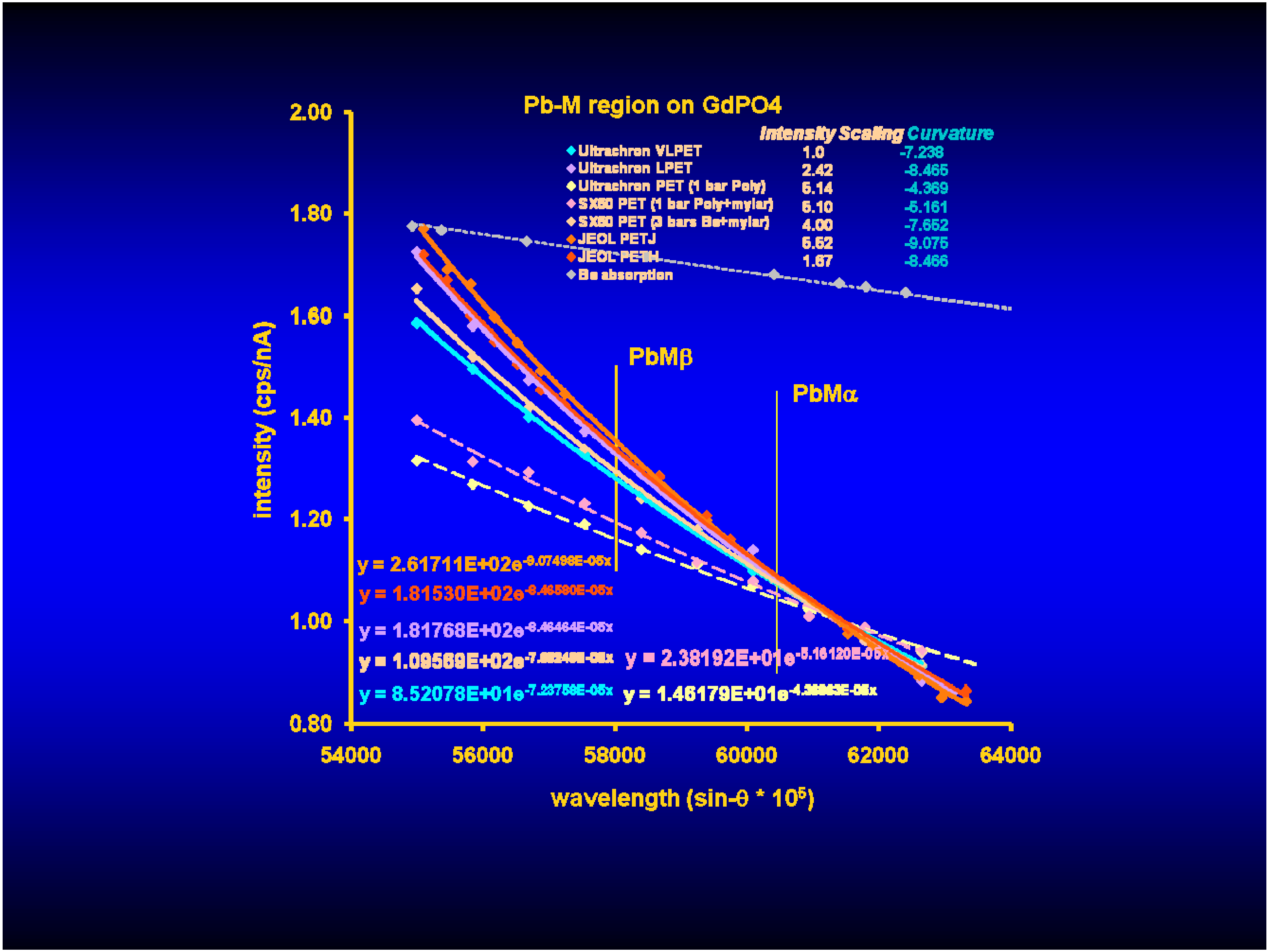


Pb-M region on GdPO4
JEOL PETJ
high sin-theta
Expon. (high sin-theta)
PbMβ
PbMα
y = 4.74114E+01e-9.07498E-05x
Exponential
intensity (cps/nA)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
54000
56000
58000
60000
62000
64000
wavelength (sin-θ * 10^5)

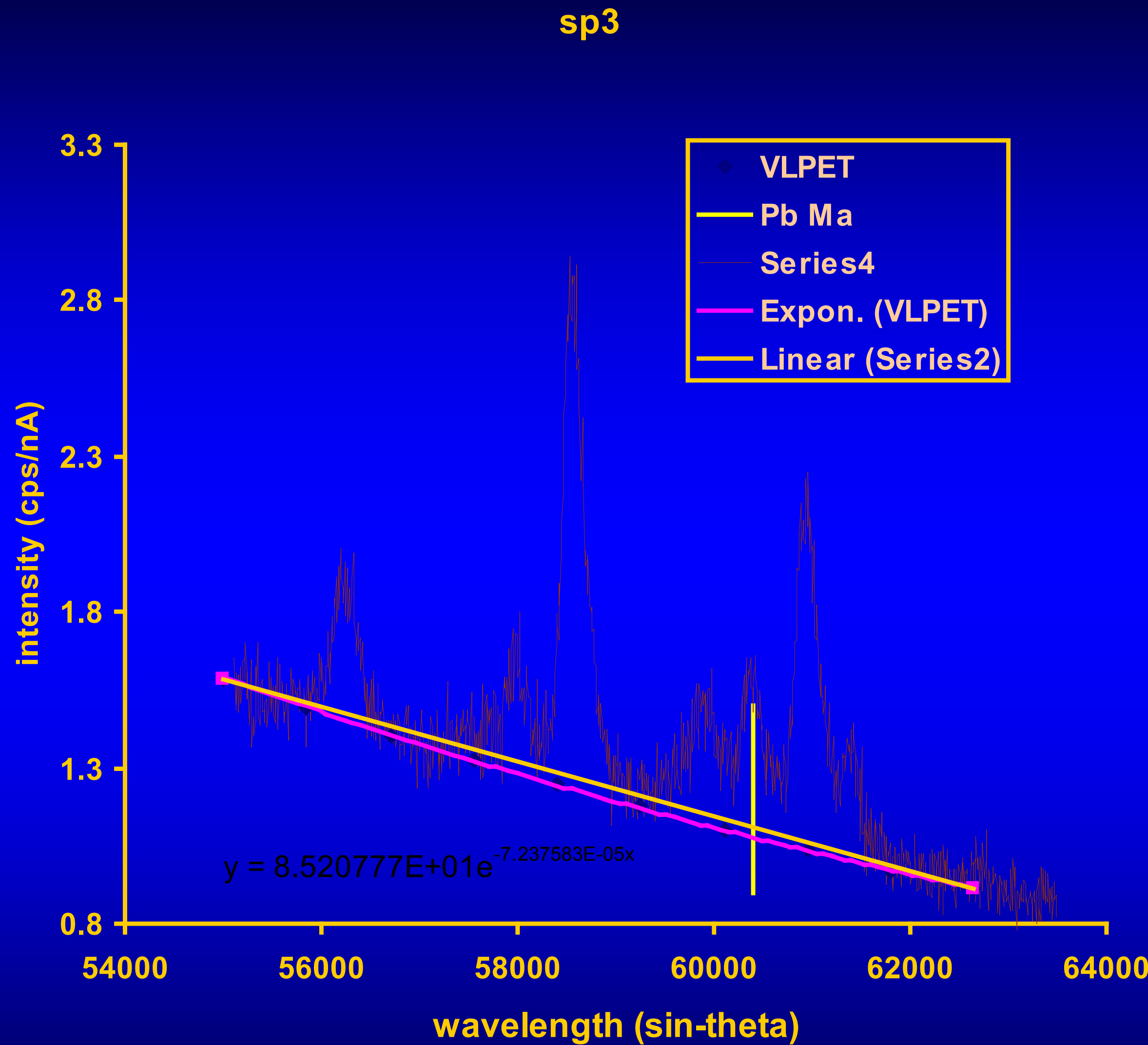
GdPO4 Pb region (PET)



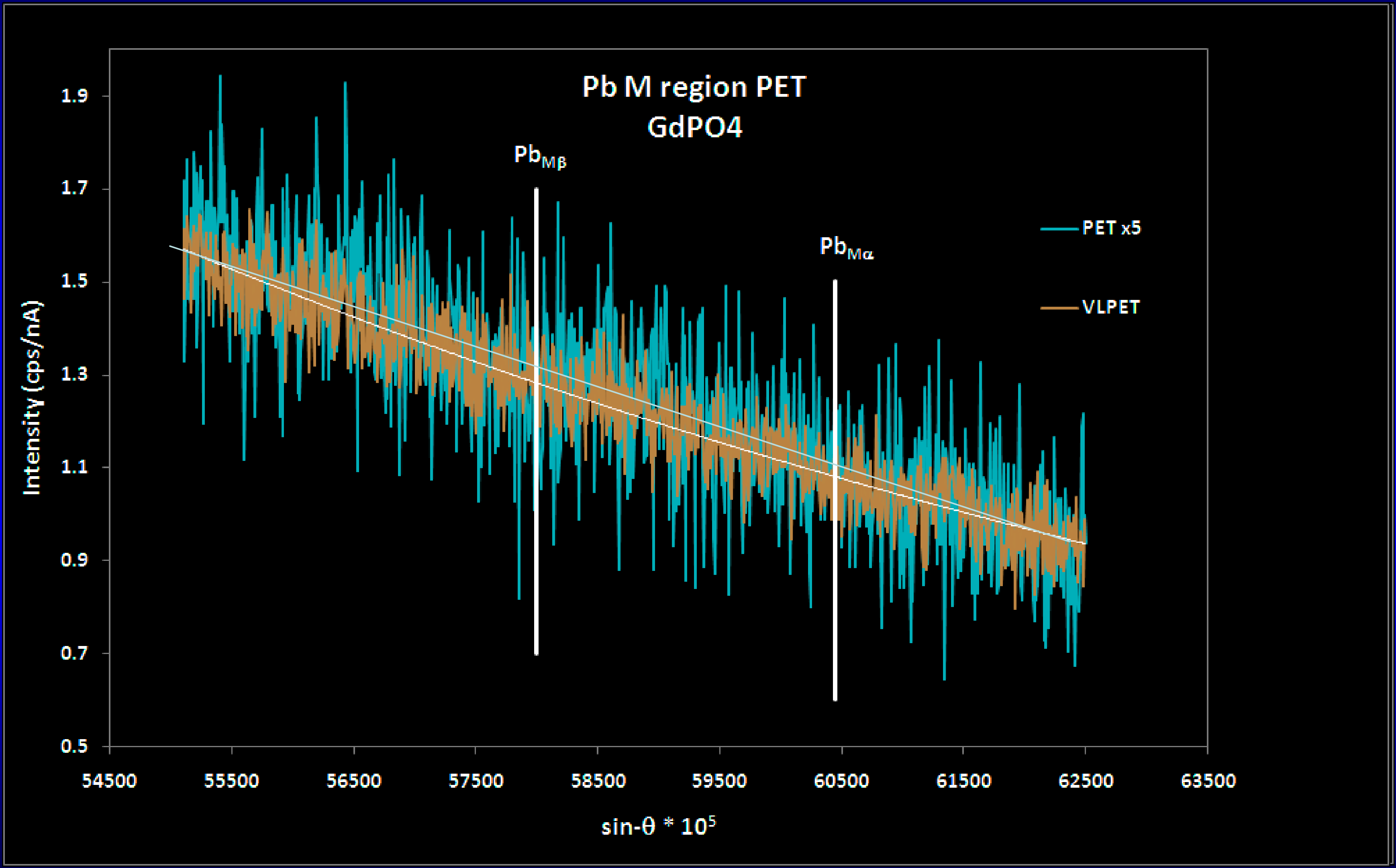

Pb-M region on GdPO4
Ultrachron VLPET
Ultrachron LPET
Ultrachron PET (1 bar Poly)
SX50 PET (1 bar Poly+mylar)
SX50 PET (3 bars Be+mylar)
JEOL PETJ
JEOL PETH
PbMβ
PbMα
y = 8.52078E+01e-7.23758E-05x
y = 1.08700E+02e-6.46580E-05x
y = 7.44951E+01e-6.46464E-05x
y = 2.76047E+01e-7.88249E-05x
y = 4.74114E+01e-9.07498E-05x
y = 2.84395E+00e-4.38963E-05x
y = 4.67044E+00e-5.16120E-05x
intensity (cps/nA)
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
54000
56000
58000
60000
62000
64000
wavelength (sin-θ * 10^5)

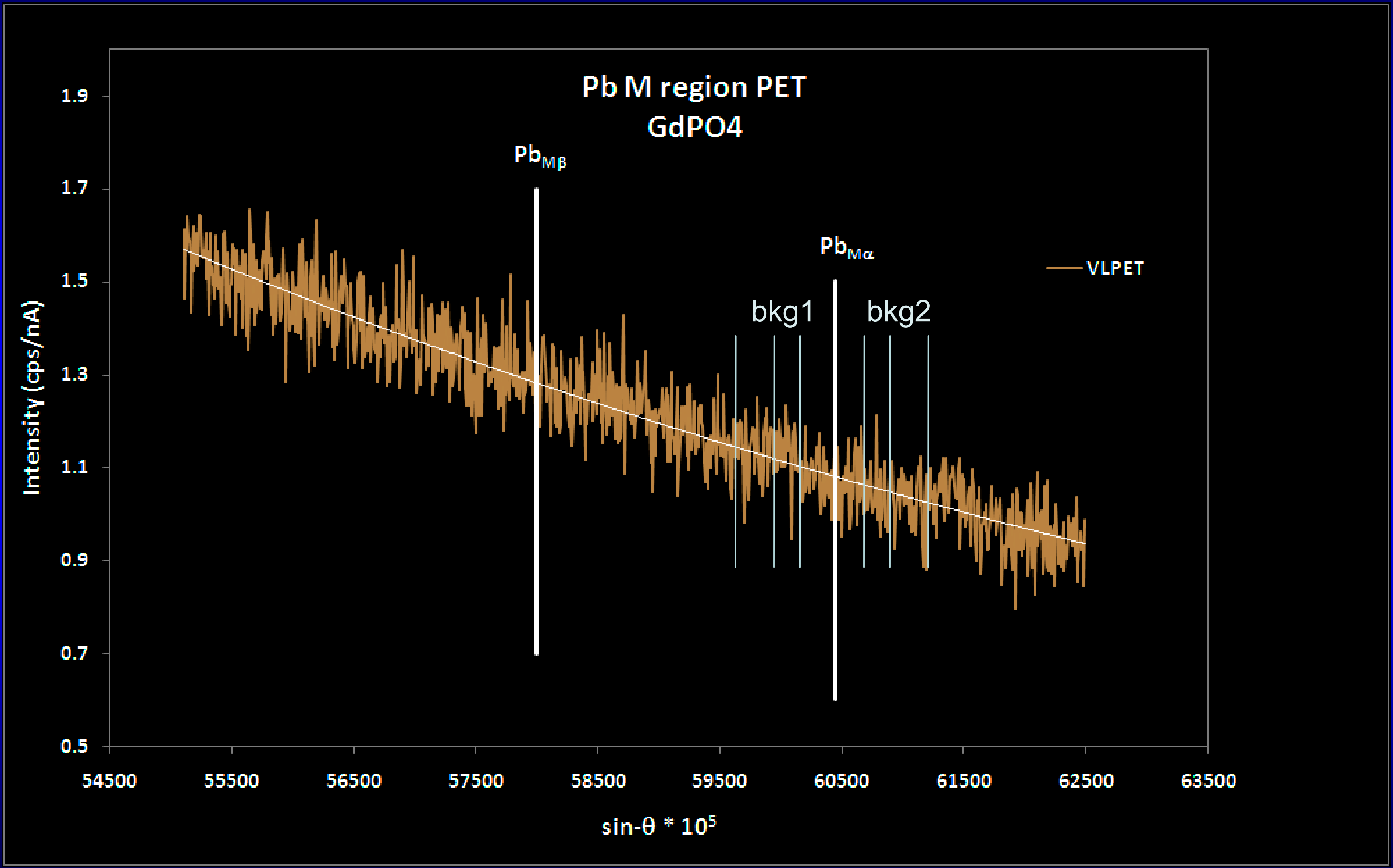

Pb-M region on GdPO4
Intensity Scaling Curvature
Ultrachron VLPET 1.0 -7.238
Ultrachron LPET 2.42 -8.465
Ultrachron PET (1 bar Poly) 6.14 -4.369
SX50 PET (1 bar Poly+mylar) 6.10 -5.161
SX50 PET (3 bars Be+mylar) 4.00 -7.652
JEOL PETJ 6.62 -9.075
JEOL PETH 1.67 -8.466
Be absorption
PbMβ
PbMα
y = 2.61711E+02e-9.07498E-05x
y = 1.81530E+02e-8.46590E-05x
y = 1.81768E+02e-8.46464E-05x
y = 1.09569E+02e
y = 2.38192E+01e-5.16120E-05x
y = 8.52078E+01e-7.23758E-05x
y = 1.46179E+01e
intensity (cps/nA)
2.00
1.80
1.60
1.40
1.20
1.00
0.80
54000
56000
58000
60000
62000
64000
wavelength (sin-θ * 10⁵)

GSC 8153 scan vs $GdPO_4$



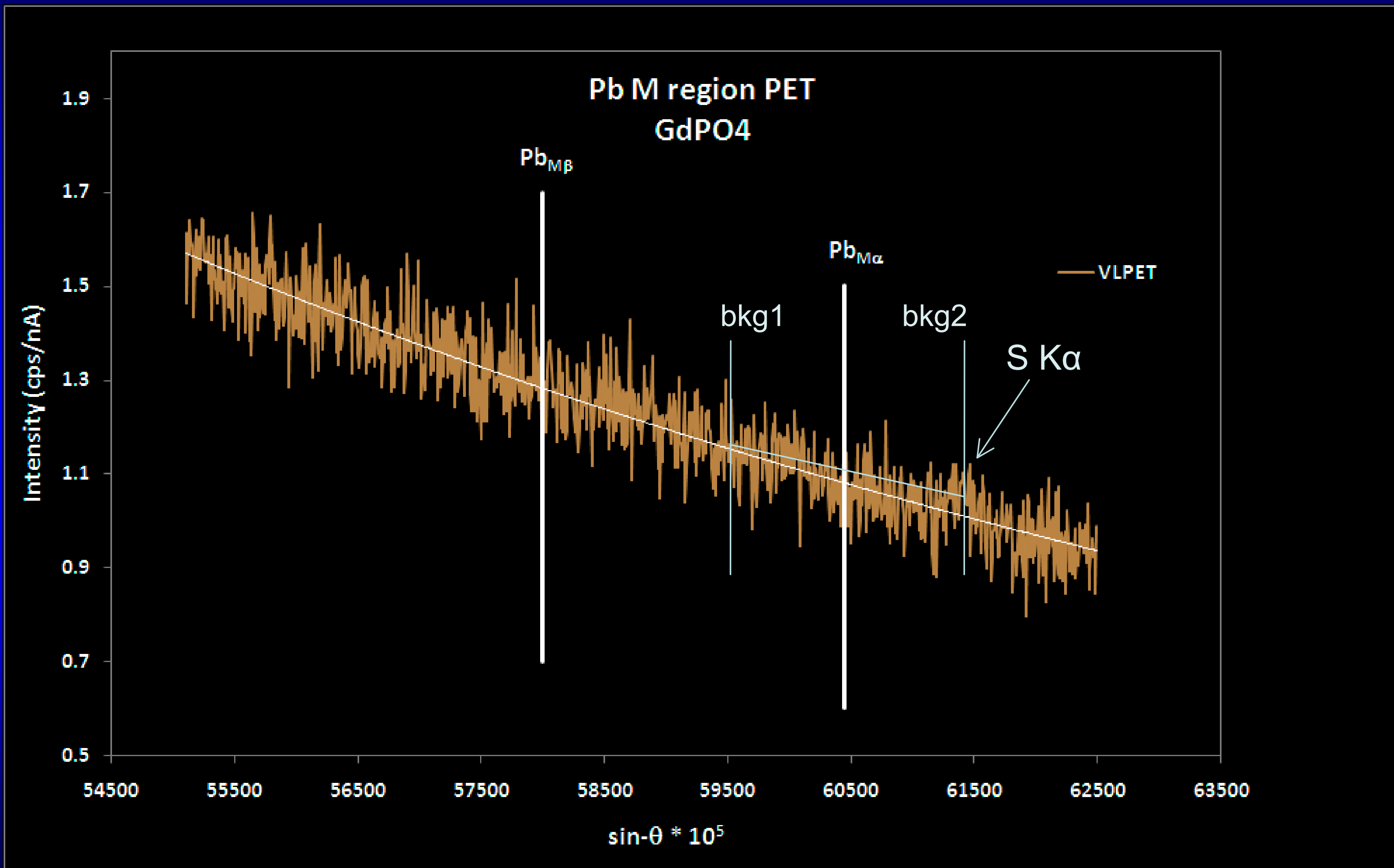
“peakless” Pb M region in monazite
Strip away the interferences and look at background shape



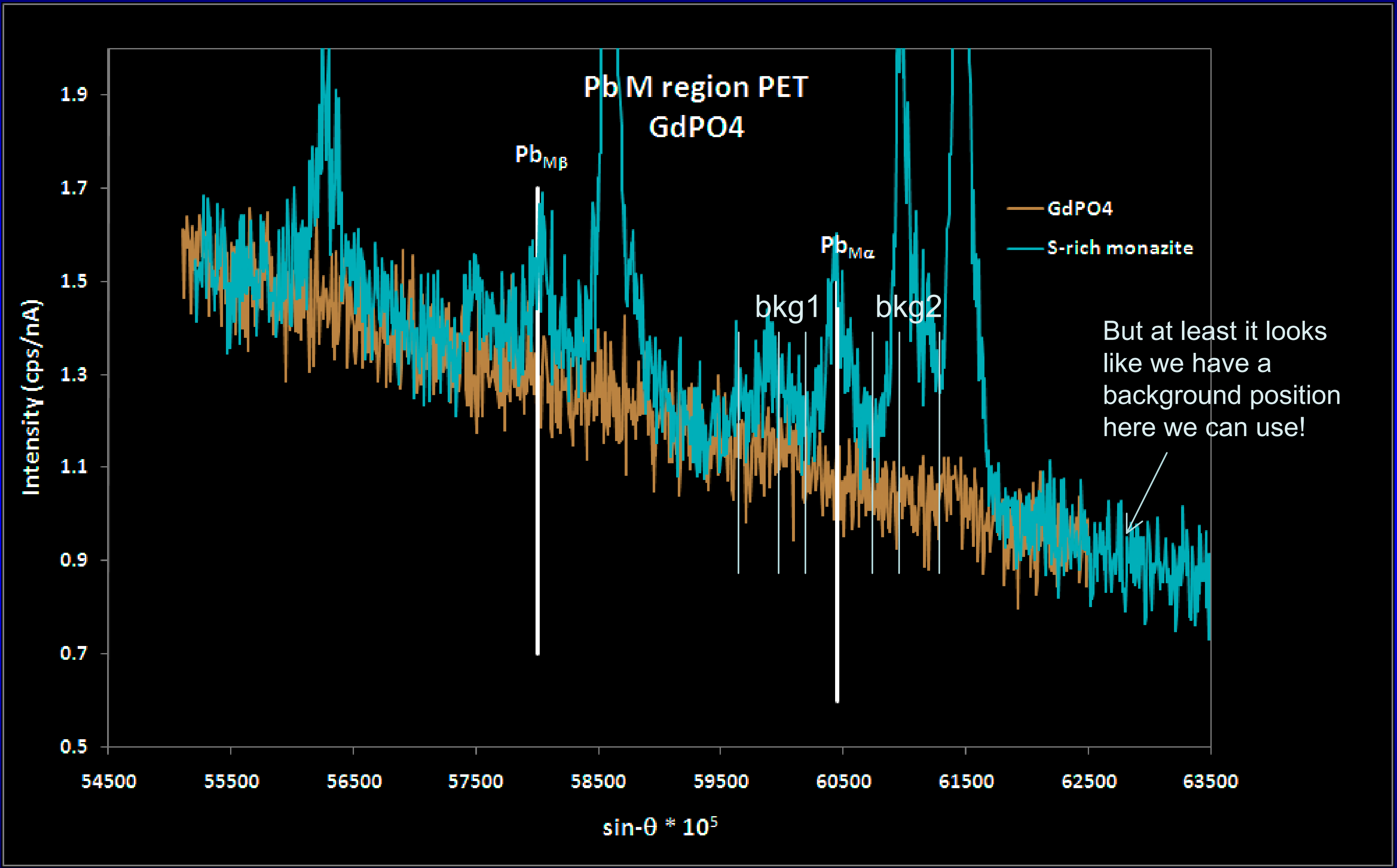


Pb M region PET
GdPO4
Pb$_{M\beta}$
Pb$_{M\alpha}$
bkg1
bkg2
VLPET
Intensity (cps/nA)
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
54500
55500
56500
57500
58500
59500
60500
61500
62500
63500
sin-θ * 10^5

Background offsets (sinθ*10[5])	Pb ppm	sd
+/- 200	2	12
+/- 500	-40	14
+/- 1000	-79	7
+/- 2000	-54	6
Regressed	-4	10



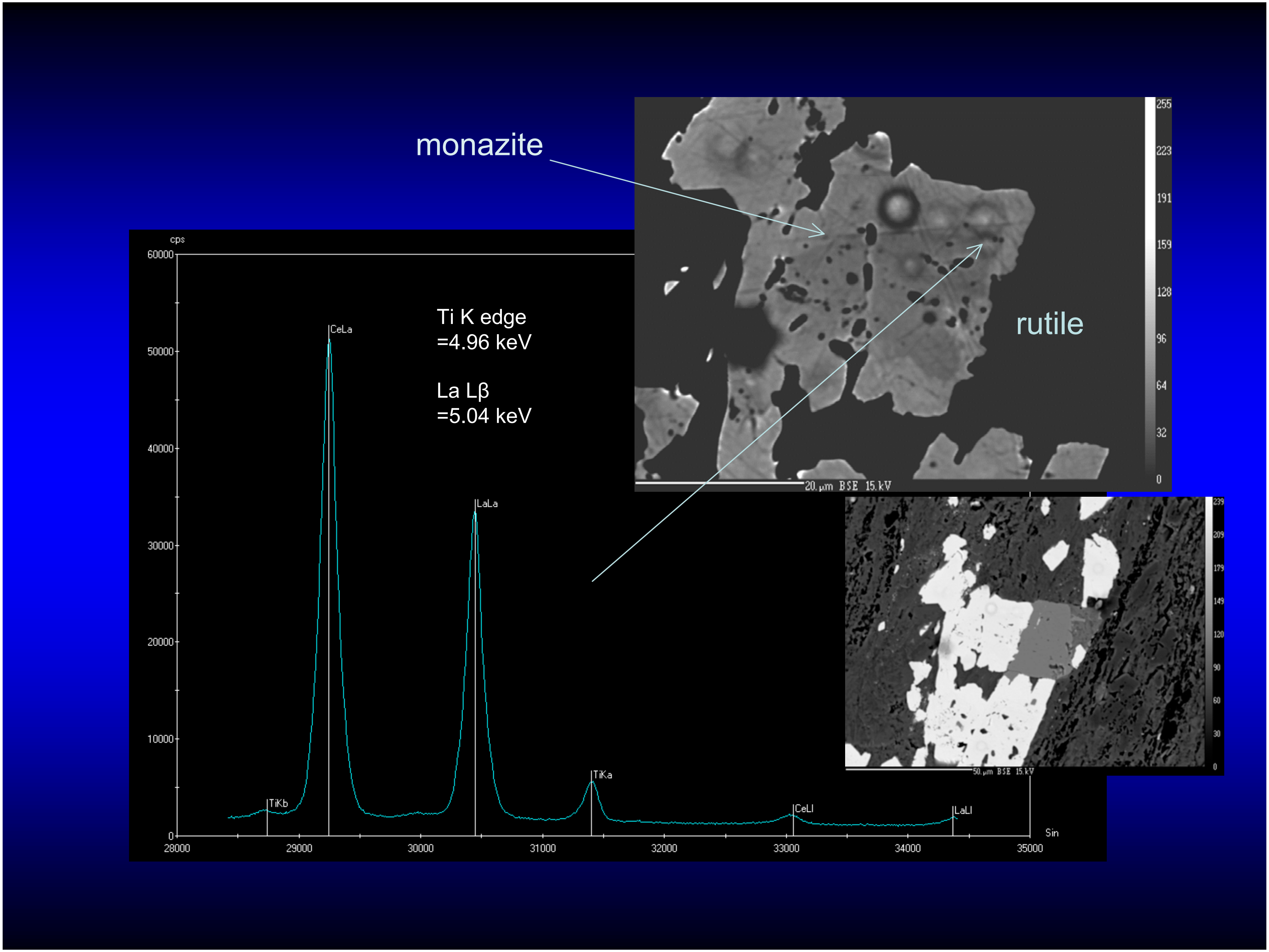
Pb M region PET
GdPO4
PbMβ
PbMα
bkg1
bkg2
S Kα
VLPET
Intensity (cps/nA)
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
54500
55500
56500
57500
58500
59500
60500
61500
62500
63500
sin-θ * 10^5

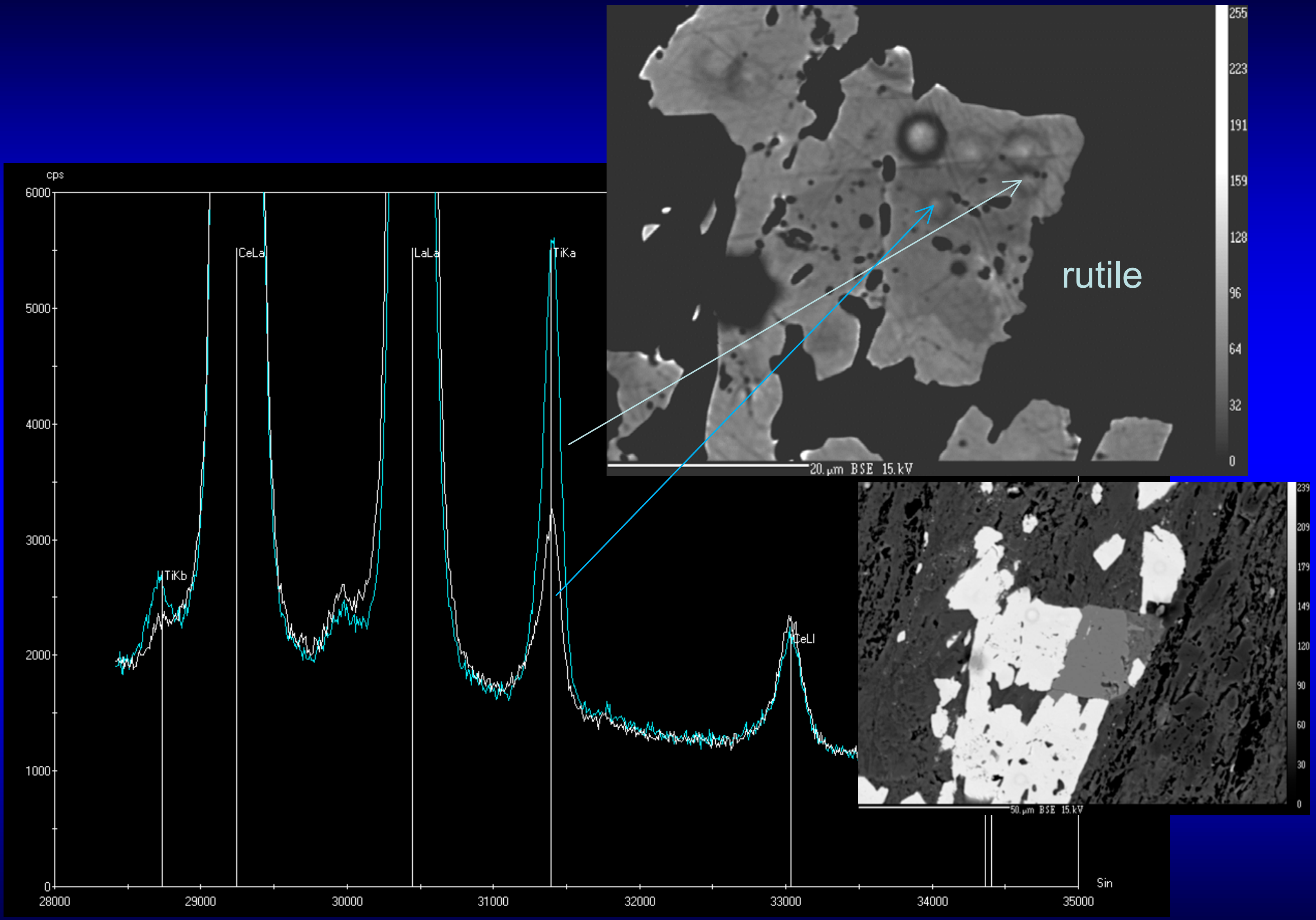


Pb M region PET
GdPO4
$Pb_{M\beta}$
$Pb_{M\alpha}$
bkg1
bkg2
GdPO4
S-rich monazite
But at least it looks like we have a background position here we can use!
Intensity (cps/nA)
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
54500
55500
56500
57500
58500
59500
60500
61500
62500
63500
sin-θ * 10^5

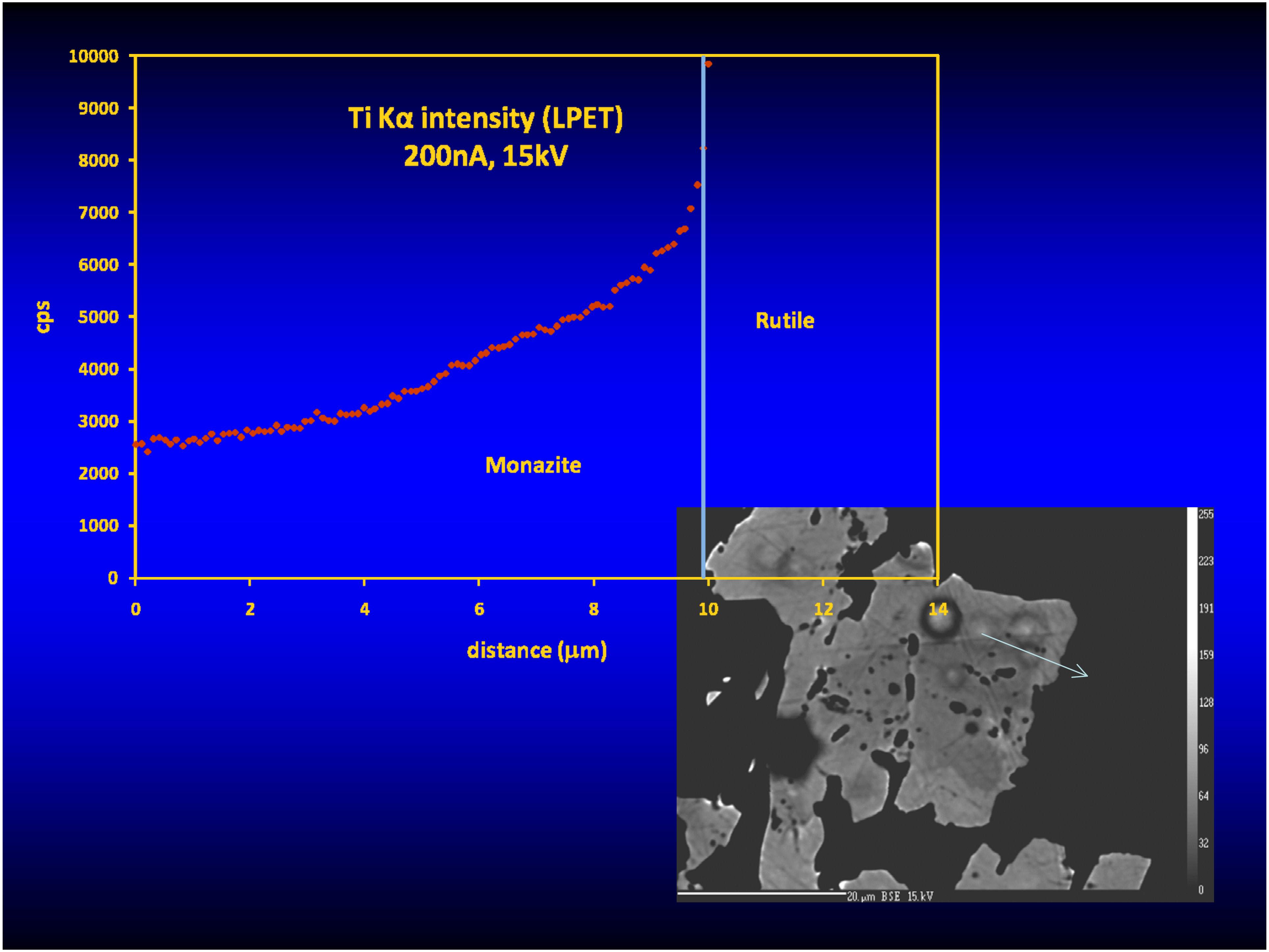
Similar exercise for sulfur…

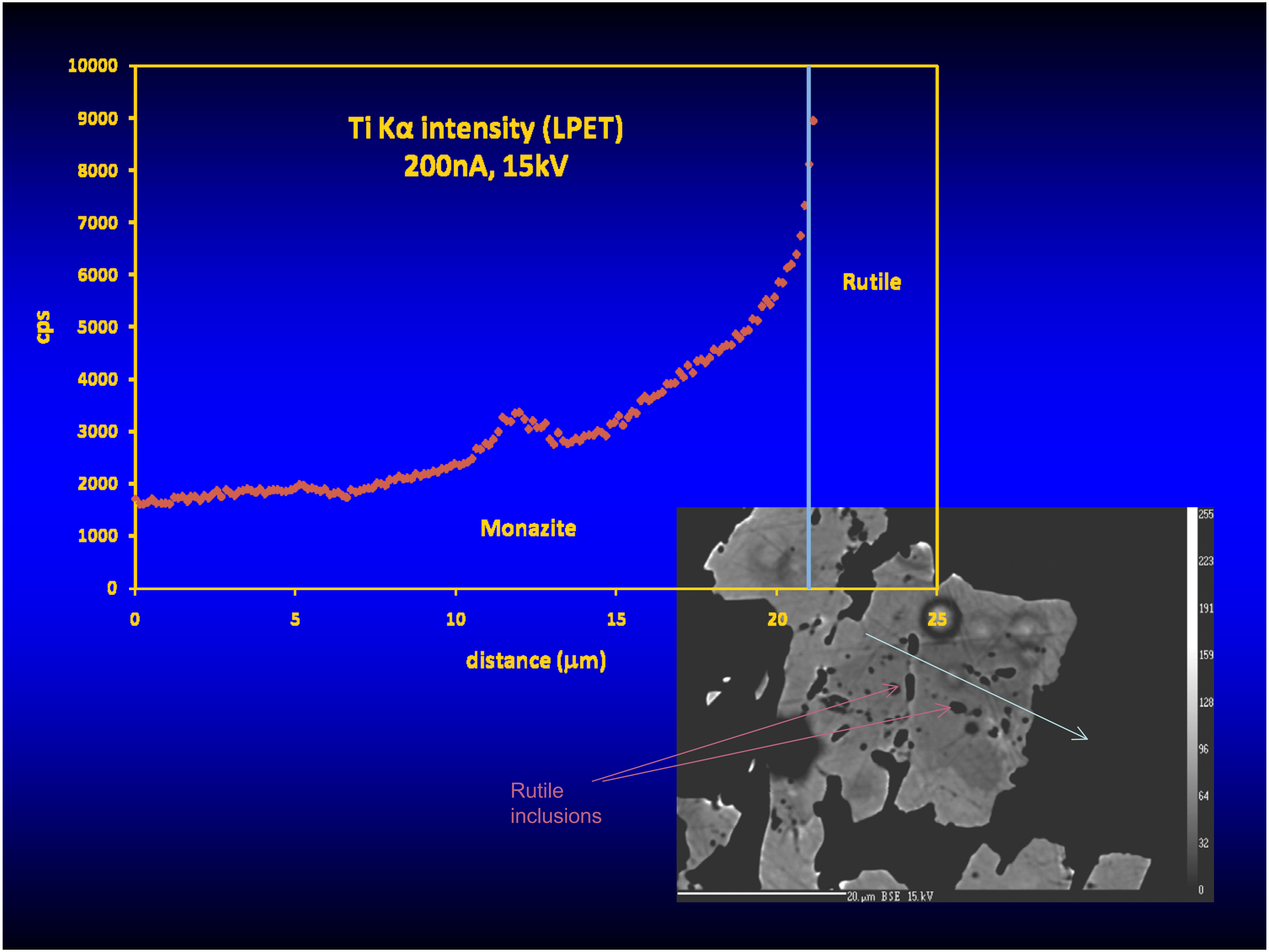
Background offsets ($sin\theta*10^5$)	S ppm	sd
+/- 500	39	2
Regressed	53	4


monazite
rutile
Ti K edge
=4.96 keV
La Lβ
=5.04 keV
cps
60000
50000
40000
30000
20000
10000
0
28000
29000
30000
31000
32000
33000
34000
35000
Sin
TiKb
CeLa
LaLa
TiKa
CeLl
LaLl
20 μm BSE 15.kV
255
223
191
159
128
96
64
32
0
50 μm BSE 15.kV
239
209
179
149
120
90
60
30
0



cps
6000
5000
4000
3000
2000
1000
0
28000
29000
30000
31000
32000
33000
34000
35000
Sin
TiKb
CeLa
LaLa
TiKa
CeLl
rutile
20.μm BSE 15.kV
50.μm BSE 15.kV

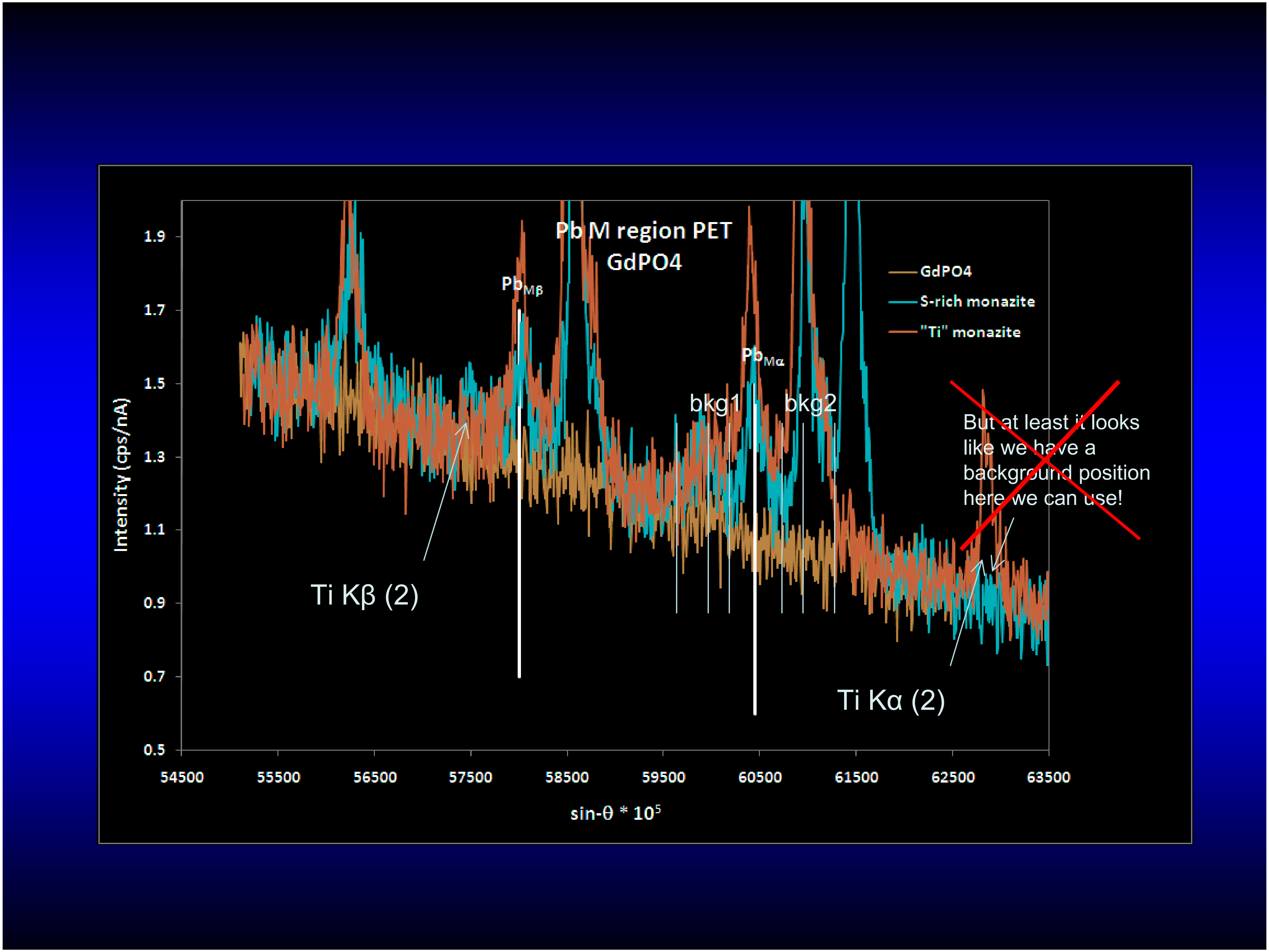

Ti Kα intensity (LPET)
200nA, 15kV
cps
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
2
4
6
8
10
12
14
distance (μm)
Monazite
Rutile
20 μm BSE 15 kV
255
223
191
159
128
96
64
32
0

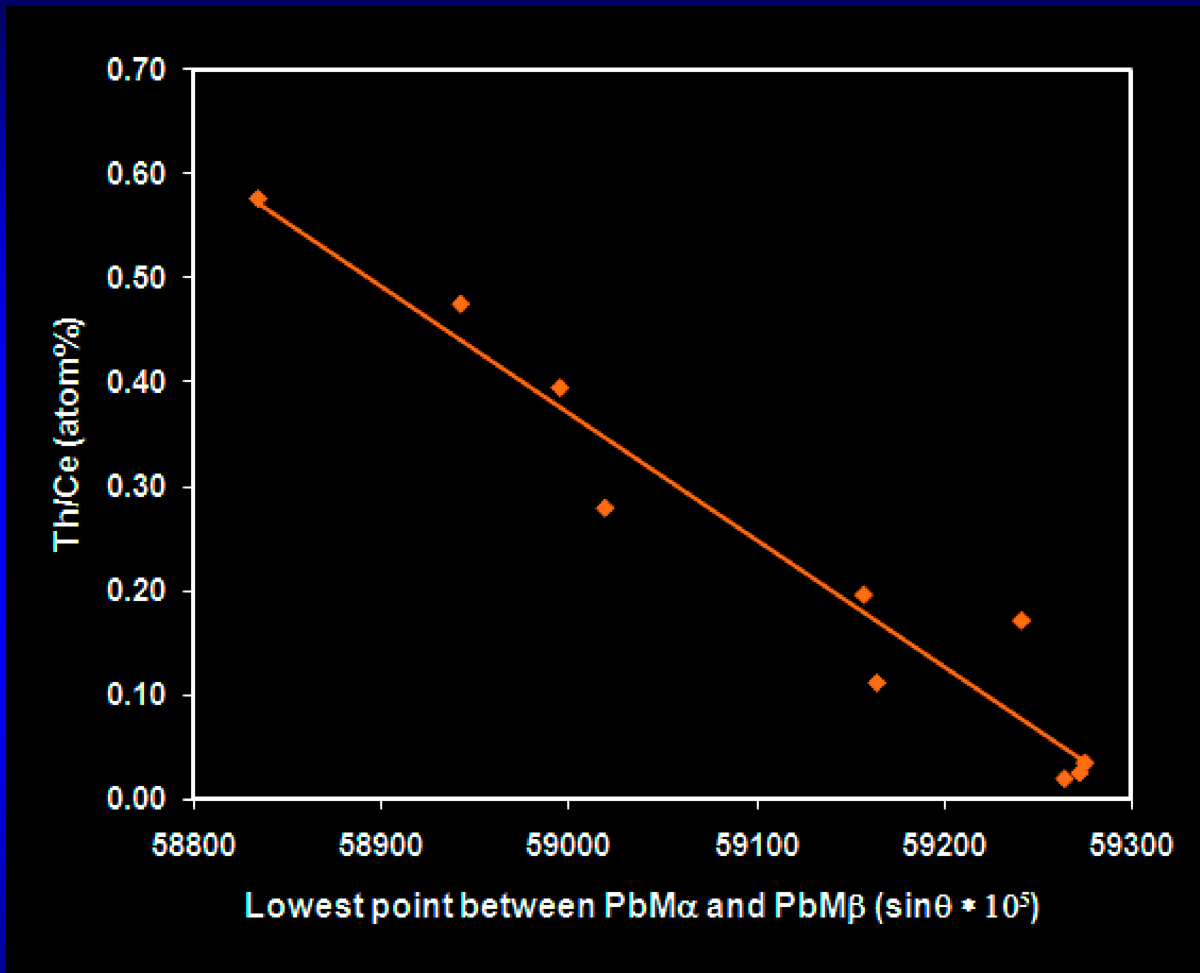

Ti Kα intensity (LPET)
200nA, 15kV
cps
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
5
10
15
20
25
distance (μm)
Monazite
Rutile
Rutile inclusions
20 μm BSE 15.kV
255
223
191
159
128
96
64
32
0

Mike, why are you telling us about titanium in monazite?

What does this have to do with anything?

Please stop


Pb M region PET
GdPO4
$Pb_{M\beta}$
$Pb_{M\alpha}$
bkg1
bkg2
Ti Kβ (2)
Ti Kα (2)
But at least it looks like we have a background position here we can use!
GdPO4
S-rich monazite
"Ti" monazite
Intensity (cps/nA)
sin-θ * 10^5
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
54500
55500
56500
57500
58500
59500
60500
61500
62500
63500



There is no reliable background
position between Pb Mα and PbMβ

So we have to model the background

Exponential fit

Linear 2-point fit

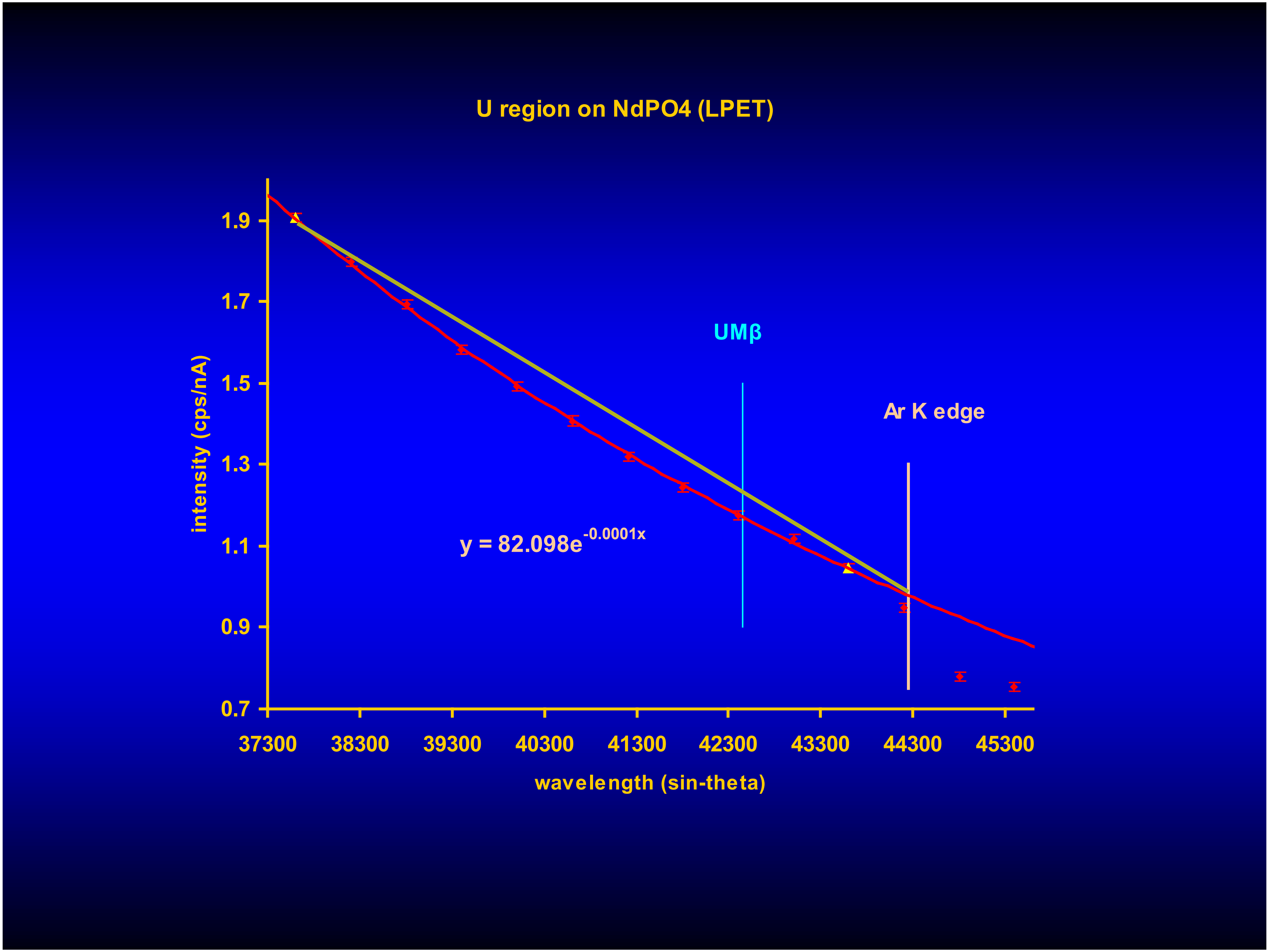
Linear 2-point fit

One located between PbMα and PbMβ

But note: the actual age difference will be less as you will also underestimate the U and Th ppm values = systematic error

	cps/nA
Pk	2.0000
Lin Bkg 1	1.1851
Lin Bkg 2	1.1585
Exp Bkg	1.14810

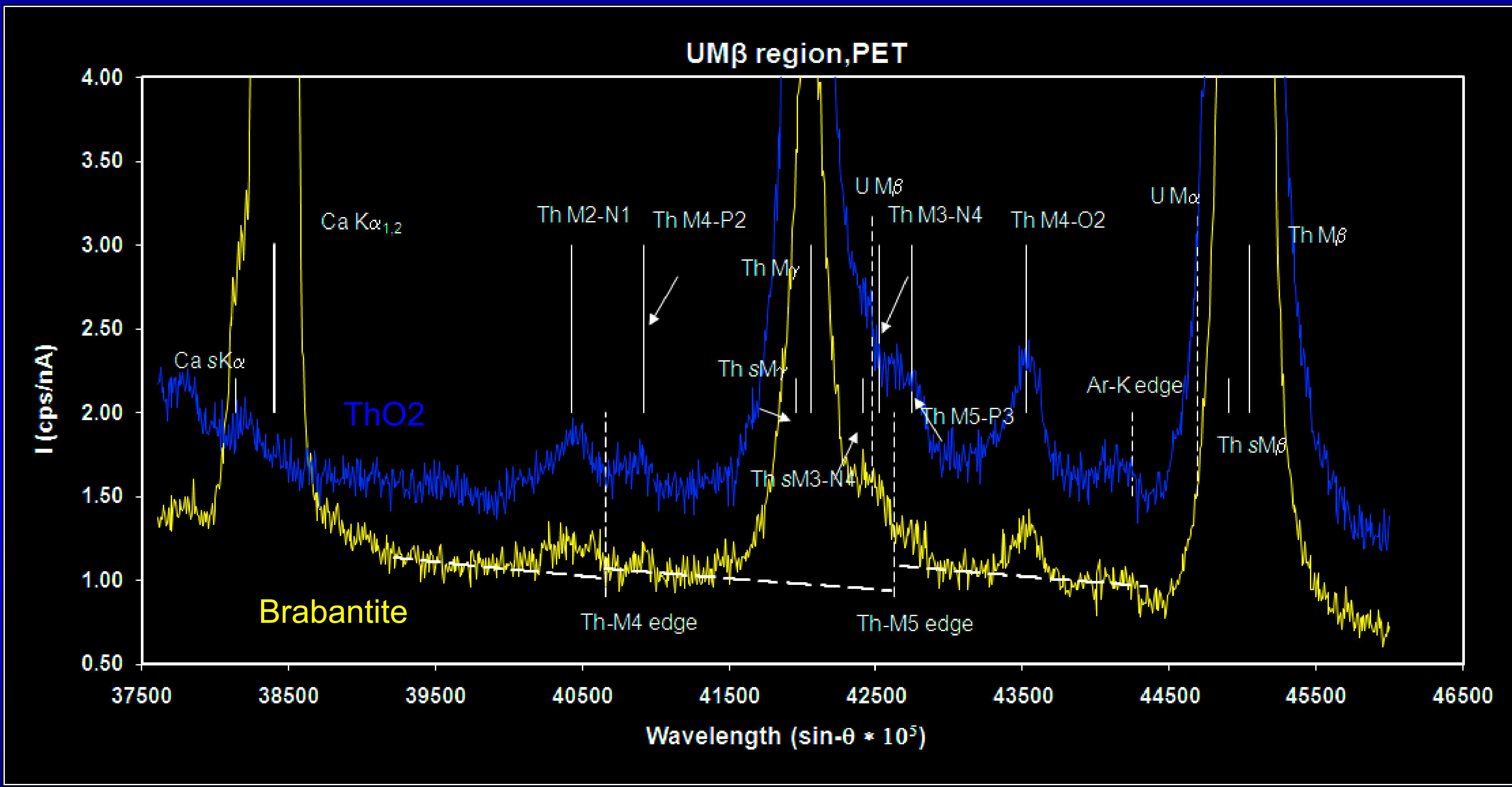
Pk – Bkg	cps/nA	% error	ppm	Age (Ma)
Lin Bkg 1	0.8149	4.3%	2692	1601
Lin Bkg 2	0.8415	1.2%	2752	1636
Exp Bkg	0.8519		2801	1665


U region on NdPO4 (LPET)
intensity (cps/nA)
1.9
1.7
1.5
1.3
1.1
0.9
0.7
UMβ
Ar K edge
y = 82.098e-0.0001x
37300
38300
39300
40300
41300
42300
43300
44300
45300
wavelength (sin-theta)

Open...
Exit
Inc
Dec
File
Zoom
16
16
4
Exp
Reg
Sp5
TChart
0
1
2
3
38,000
38,500
39,000
39,500
40,000
40,500
41,000
41,500
42,000
42,500
43,000
43,500
44,000
44,500
45,000
45,500
Peak Pos
42455
Change
L
R
BkgValue
ChiSq
Pk/Bkg
Curve
Raw
2.24060
0.1281
1.0559
-0.0864
SG
2.24890
0.0035
K 39452
2.91500
SavGol
On
Off
Selected
On
Off
BkgScale
On
Off
Probe
SX50
SX100Sun
SX100
LoadSelStd
ClearSel
CopyResult
-8.760E-05 x
4.526E+00
C:\MJJ\Talks\CAMCOR meeting 07\mzt scans\Mzt rim near rutile 2.txt

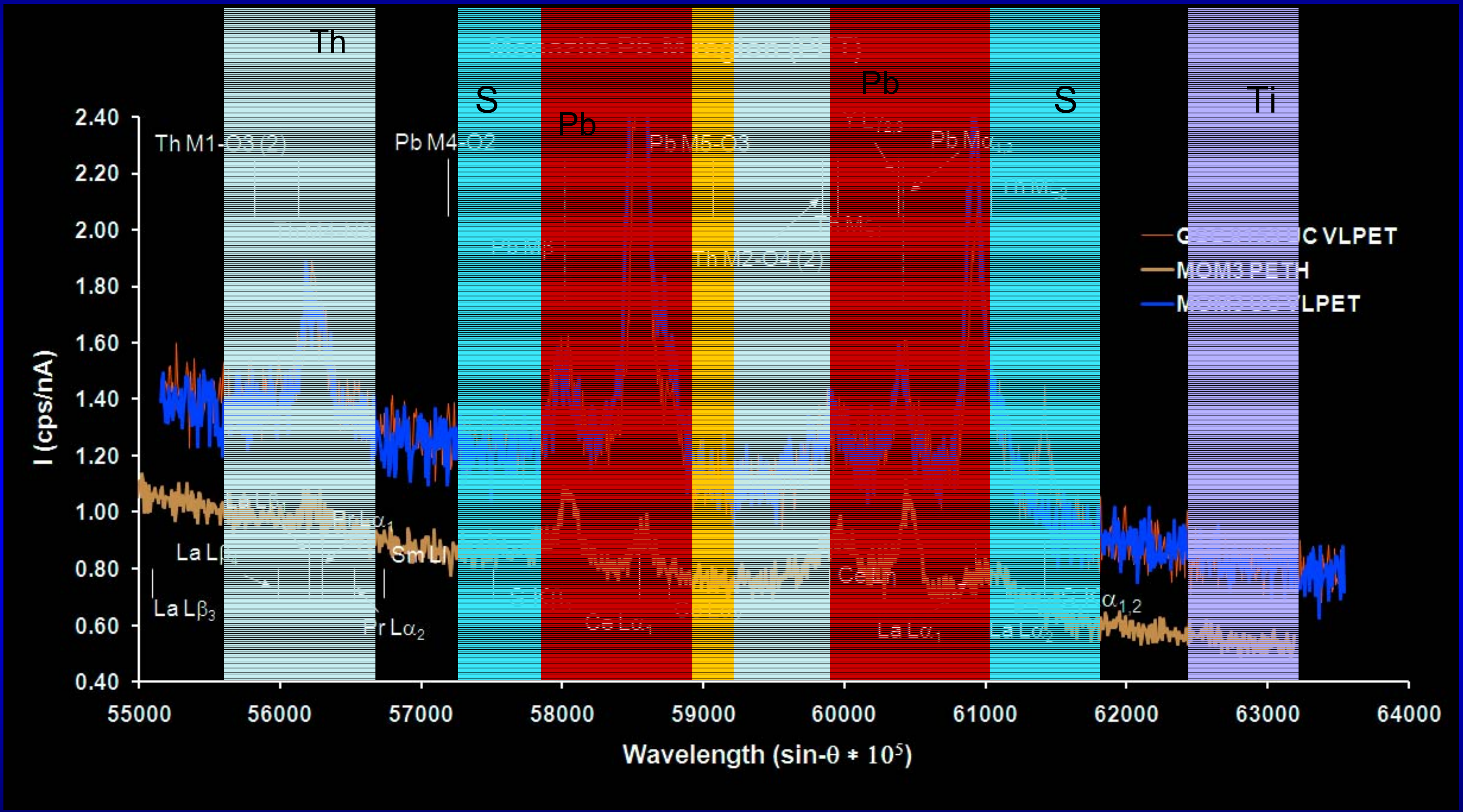
Th interferences on U-M region

Th absorption edges significant for high Th monazite



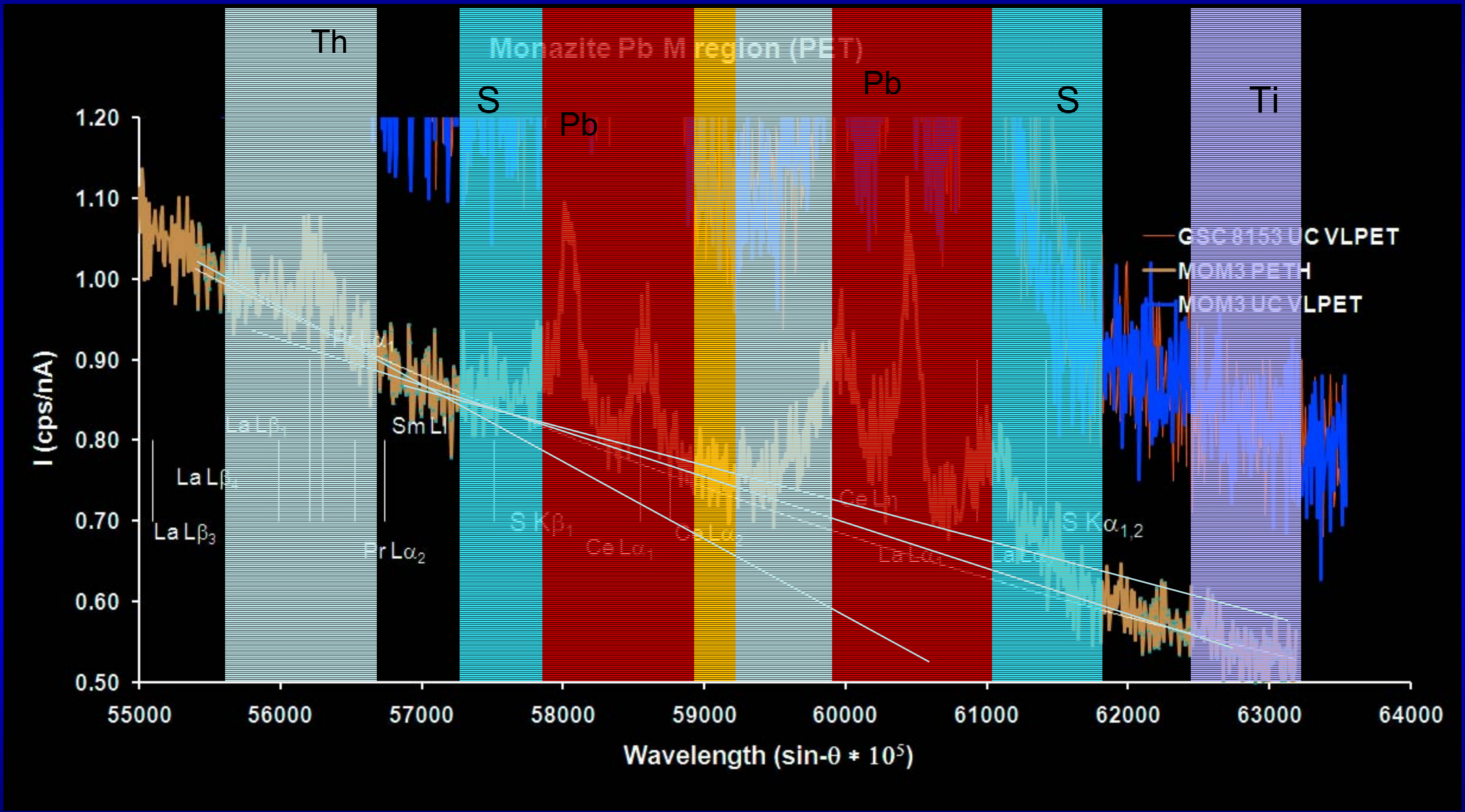
Measurement issues:

Interferences



Measurement issues:

Interferences



Measurement issues

Fluorescence interference

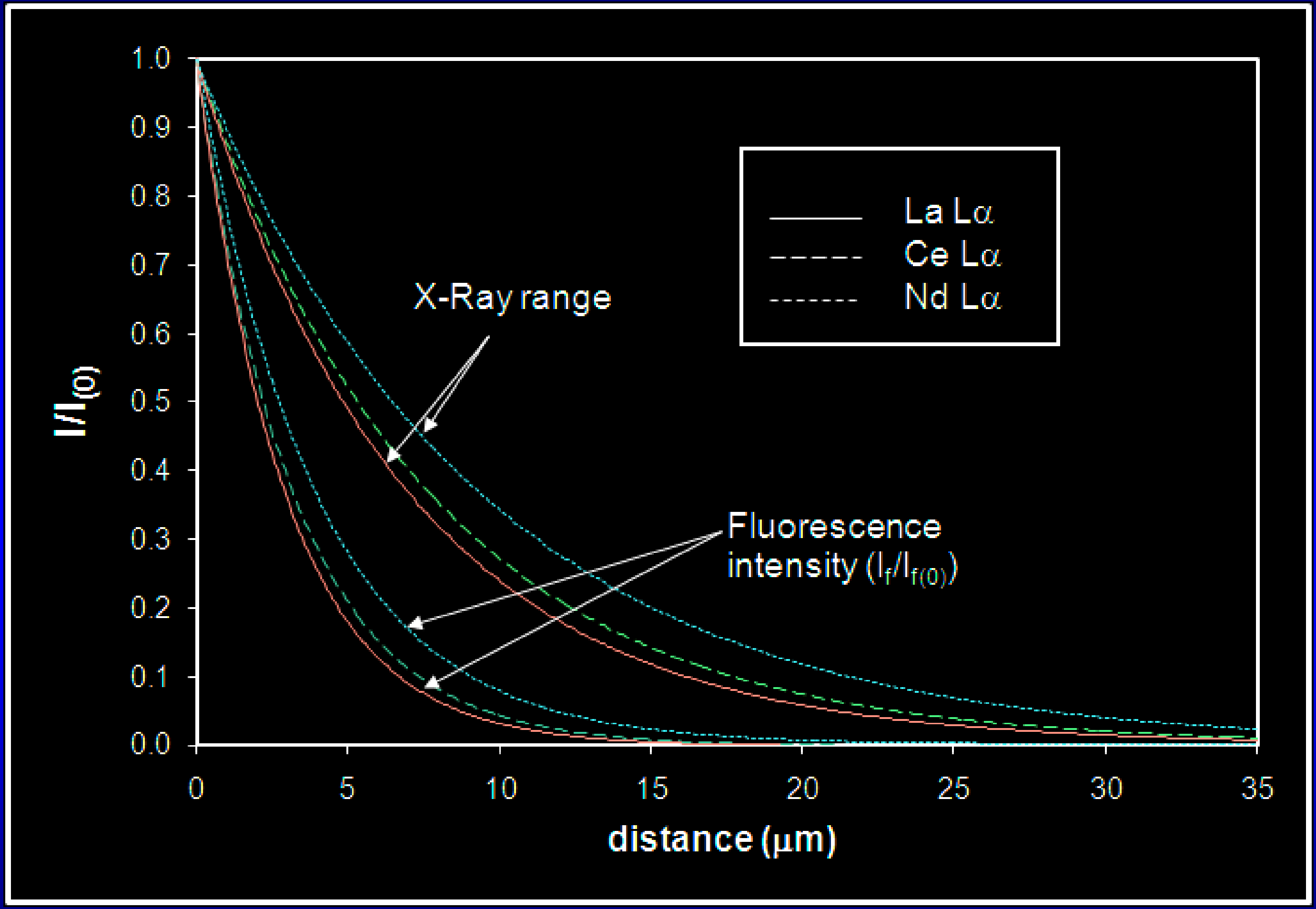
REE-L lines will fluoresce Ti Kα, K Kα, etc.

We have just seen some effects for Ti –

Rutile, ilmenite hosts or inclusions

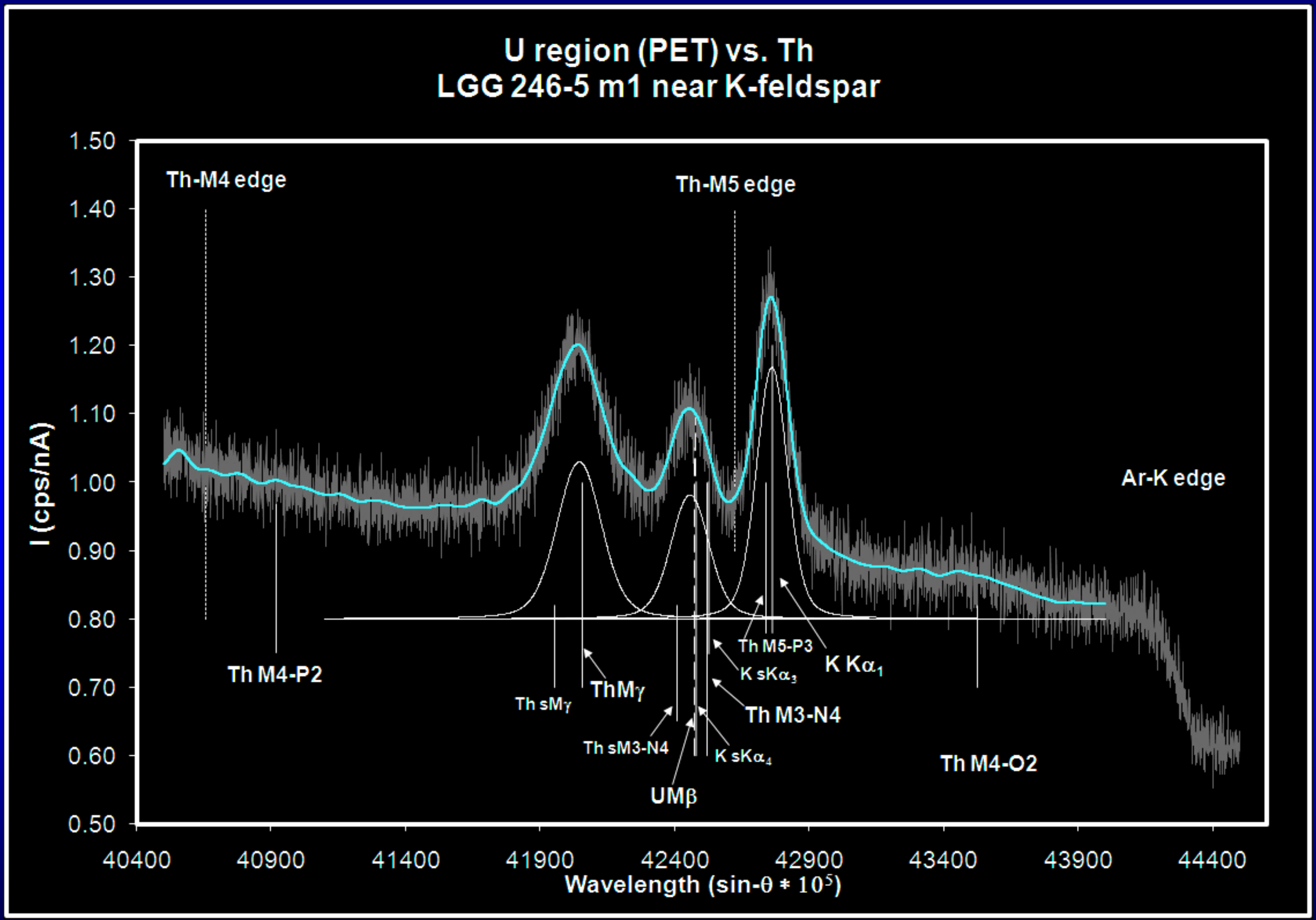
K-feldspar or mica hosted monazite?

Fluorescence range

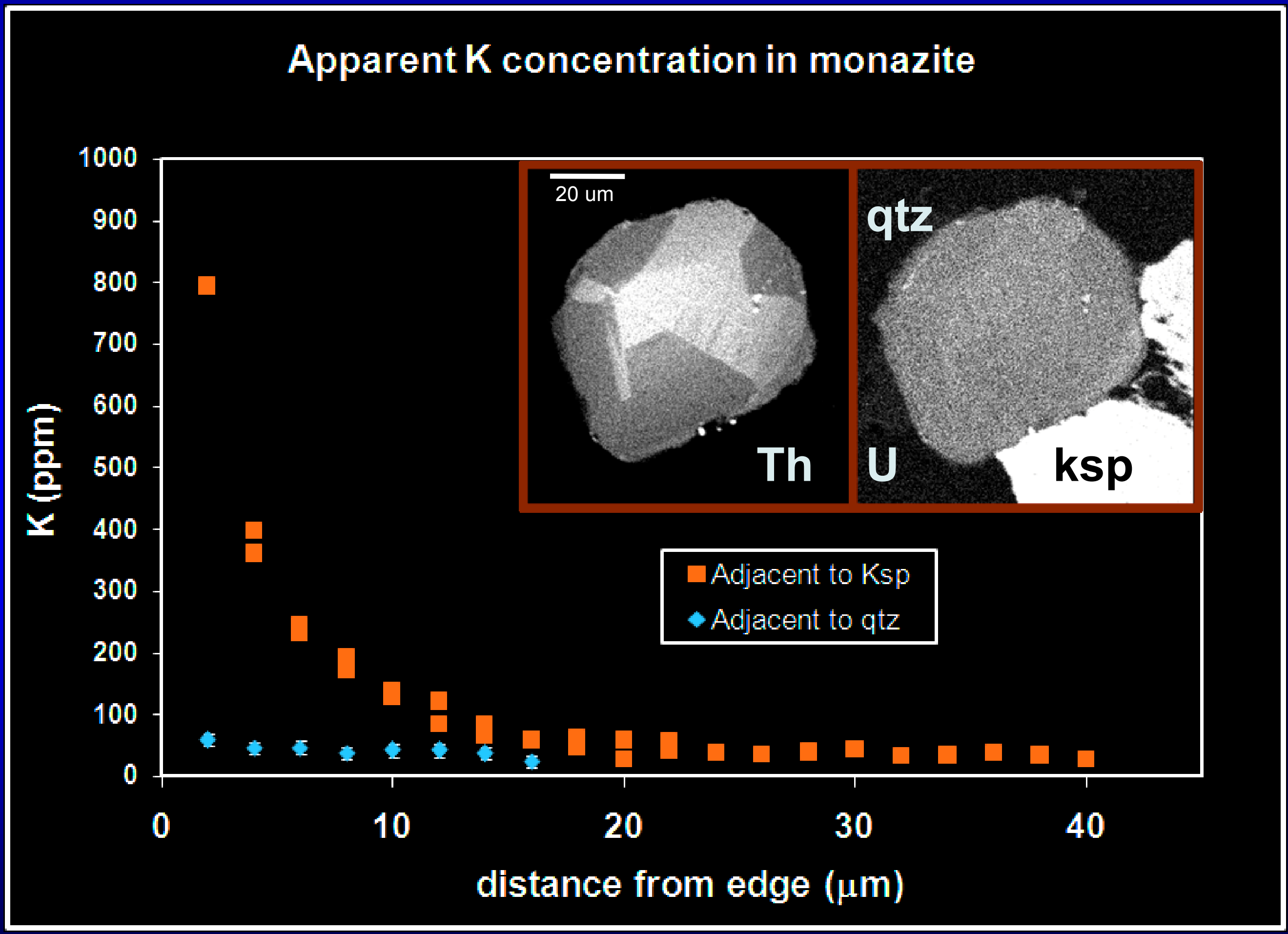


Interference effects

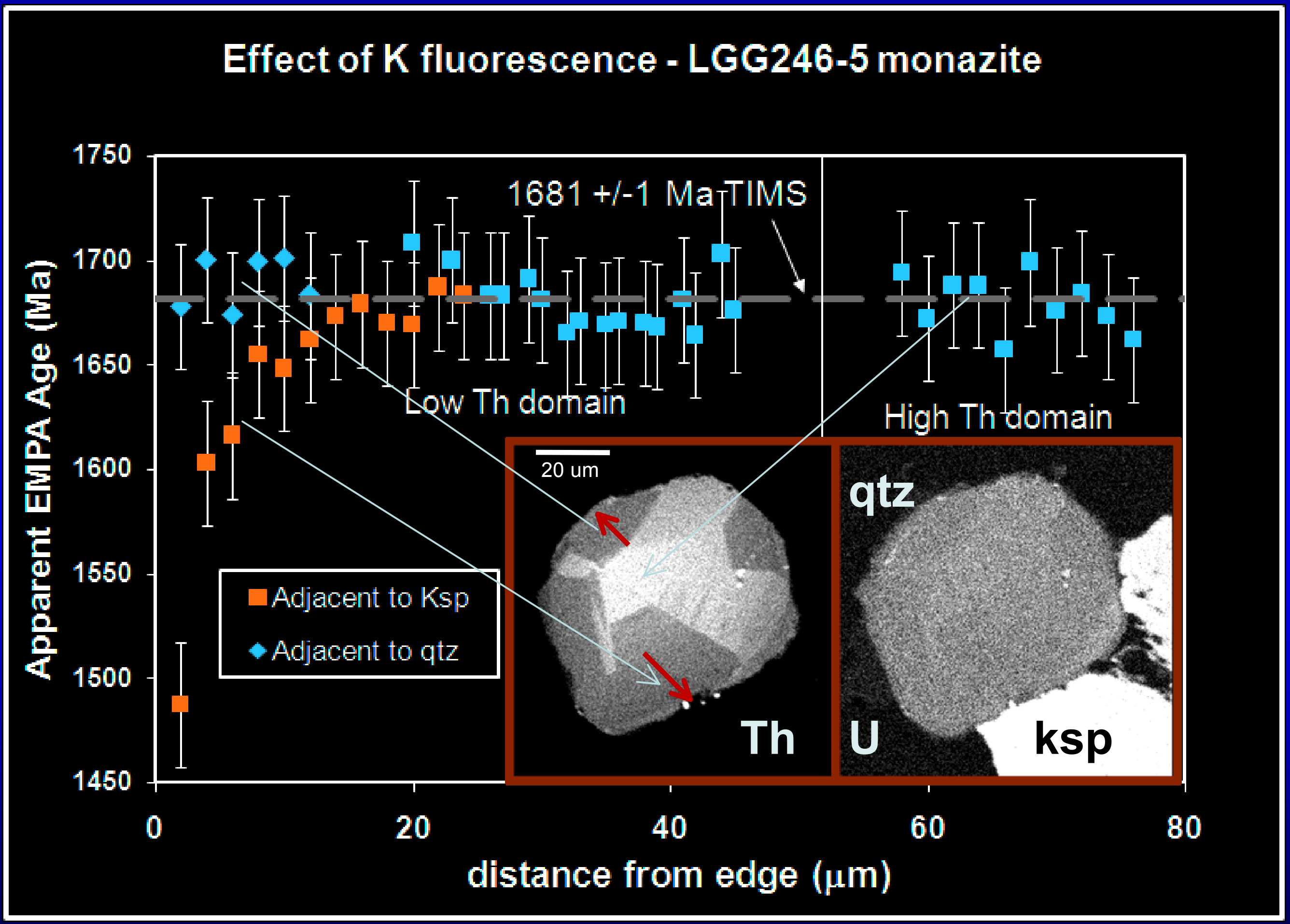
The case of mutual interference of first order lines



K fluorescence effect on U concentration



K fluorescence effect on apparent age



Measurement issues:

A nanoamp is a nanoamp?

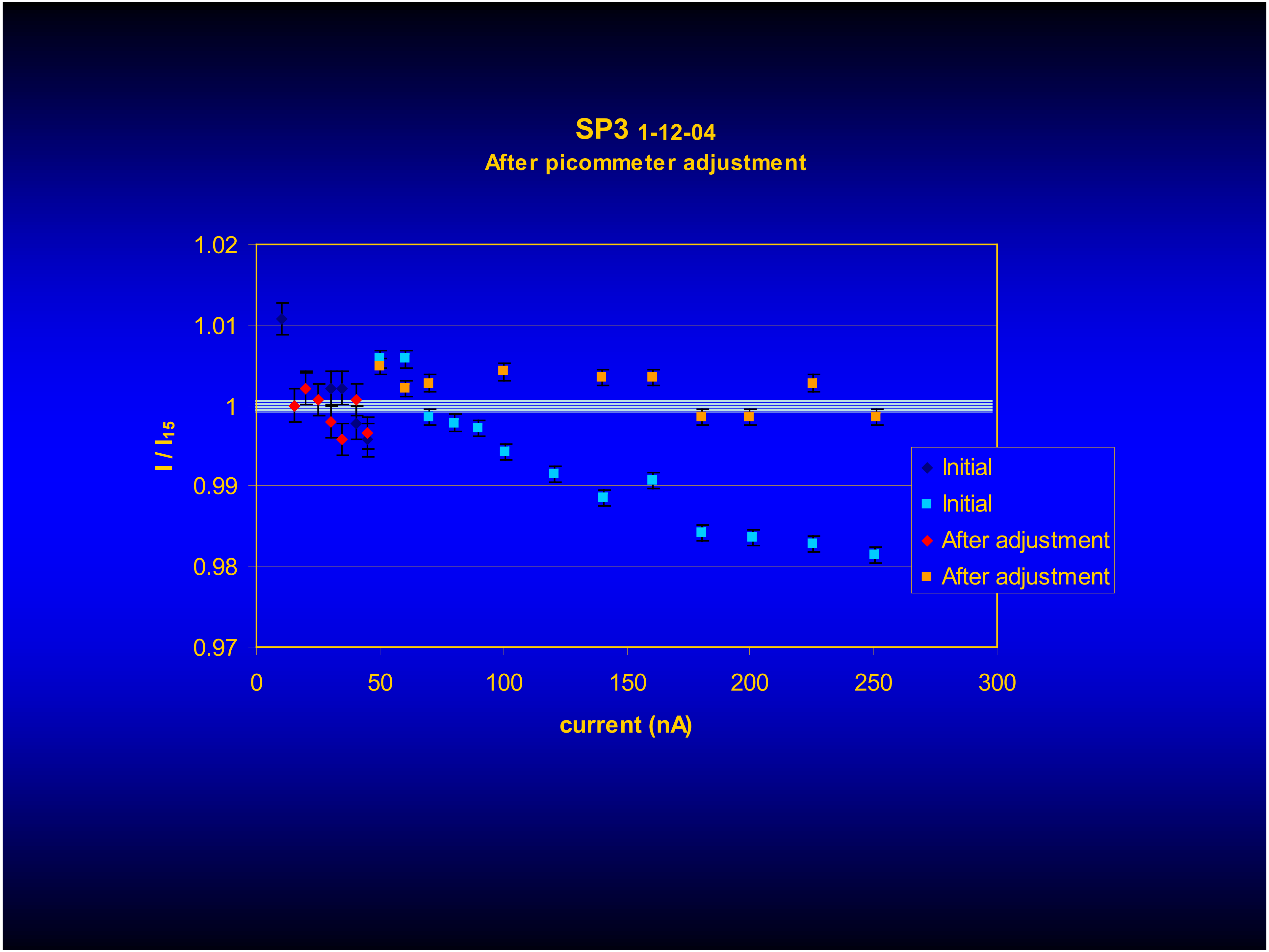
Depends on the range!

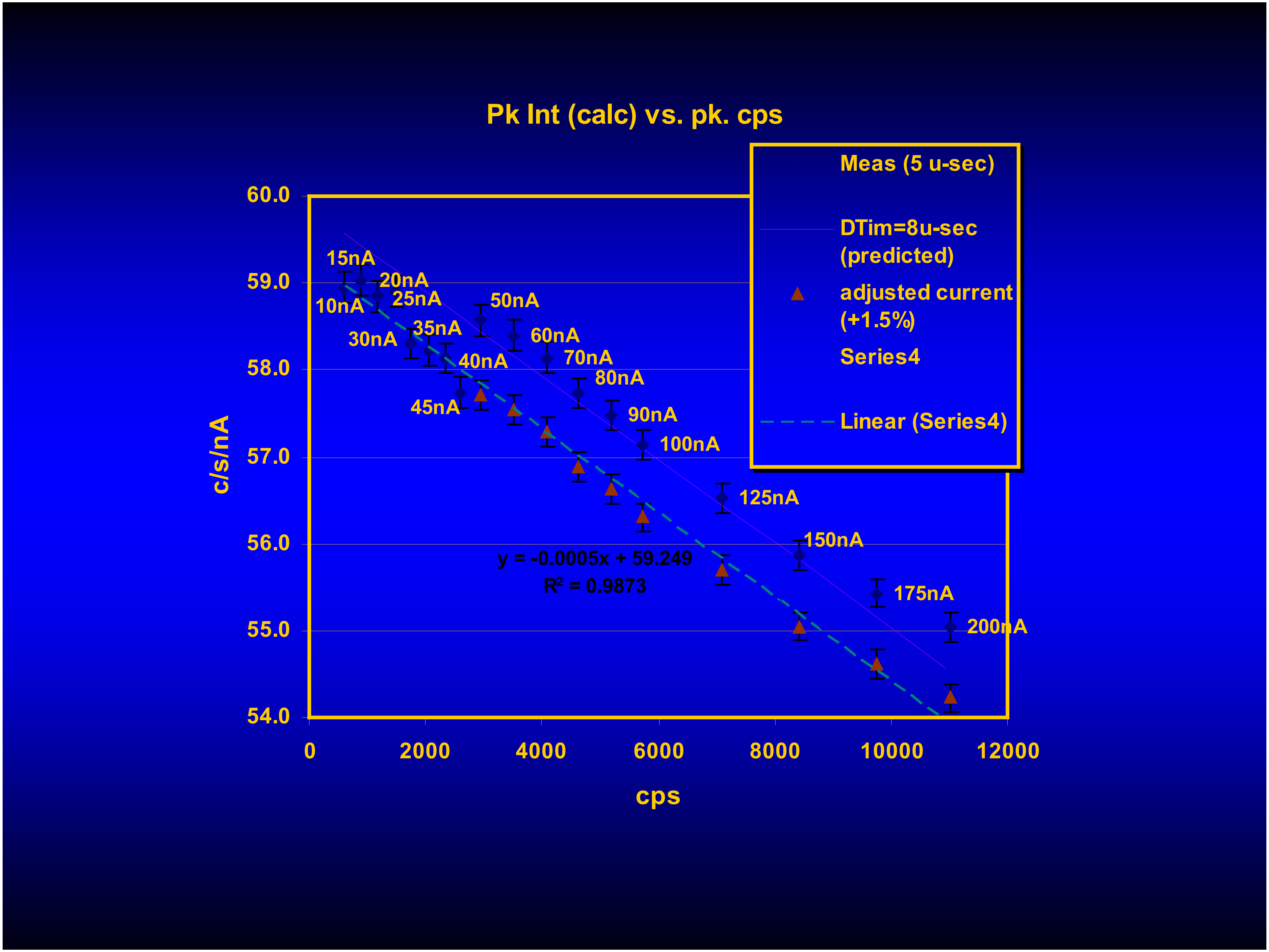
A millisecond is a millisecond?

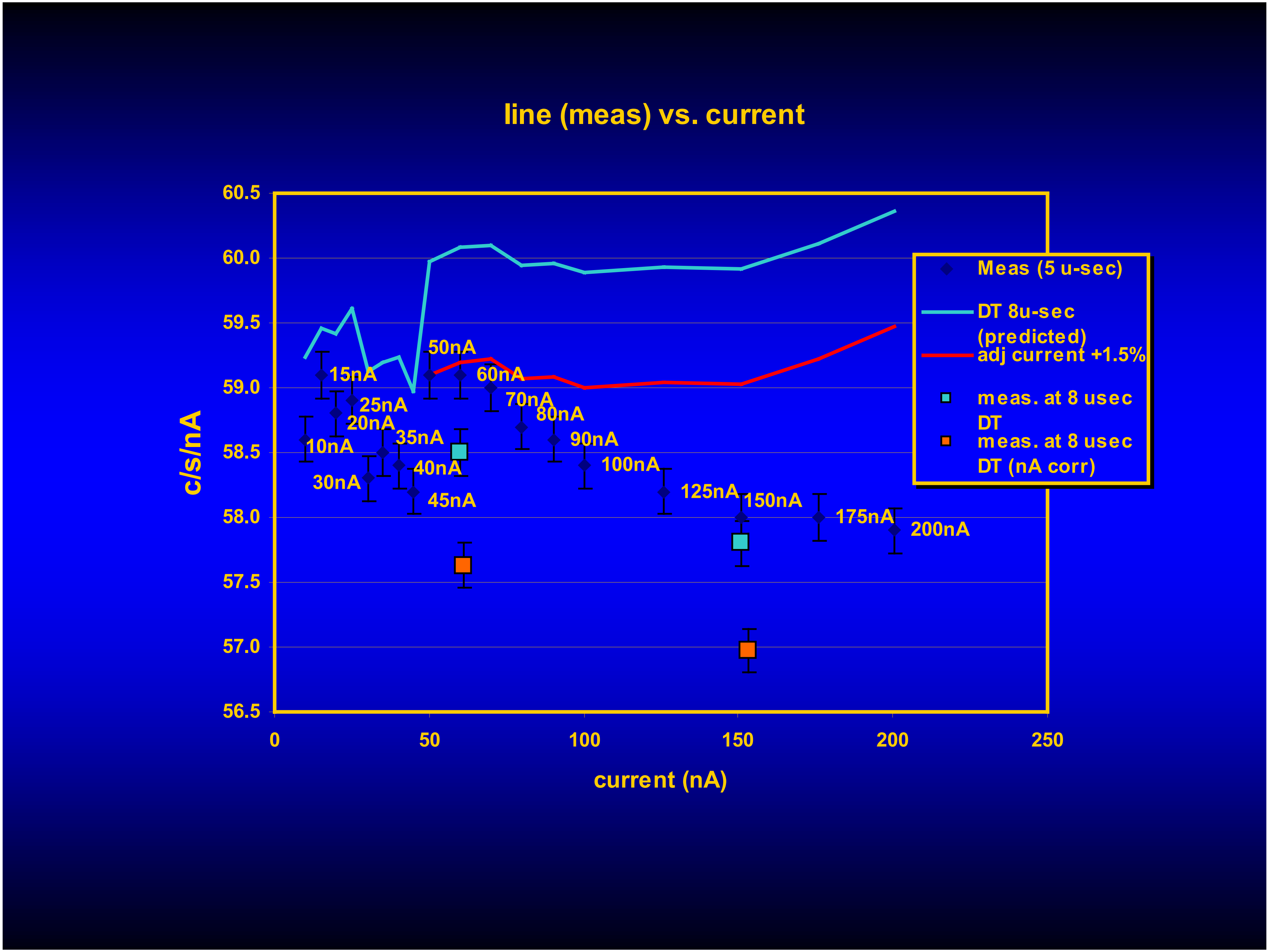
Depends on how you slice it!

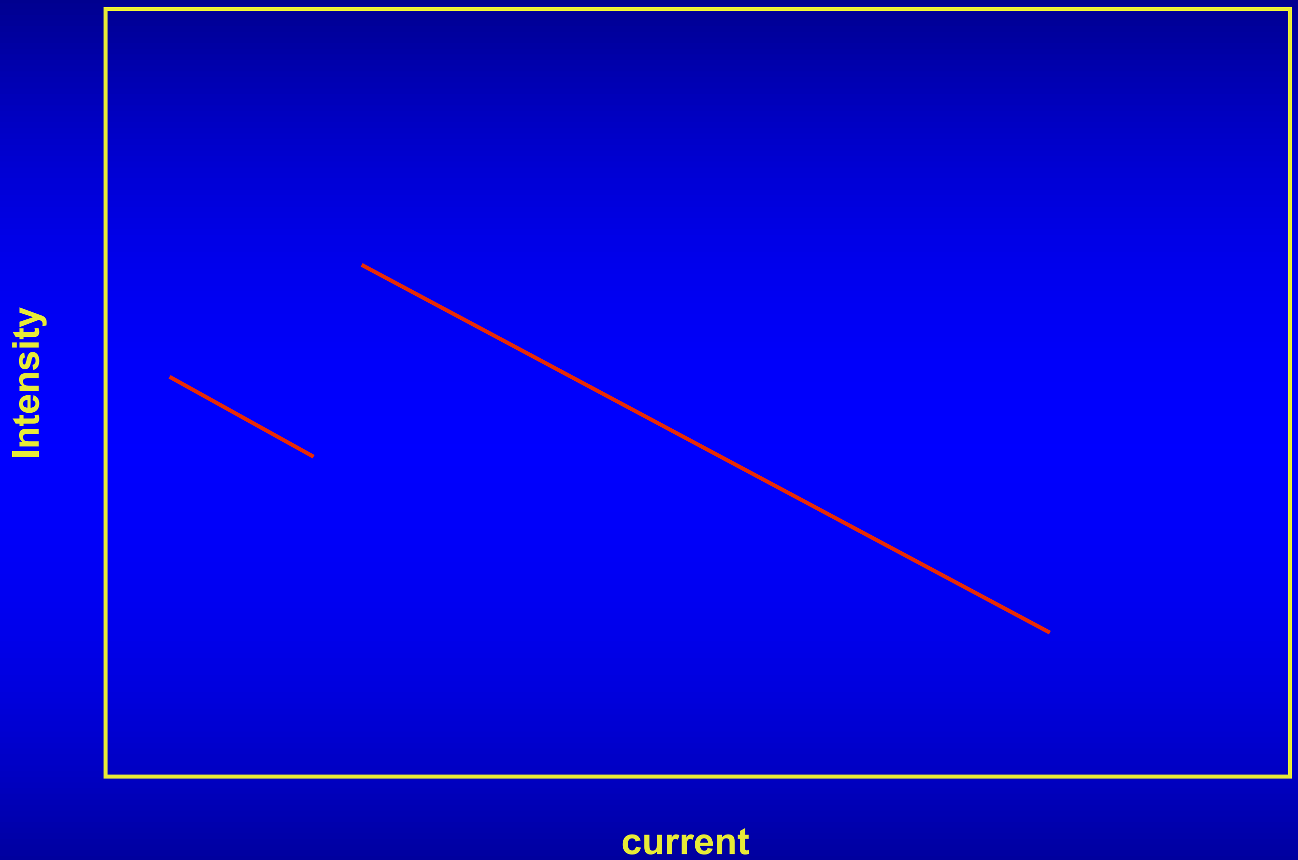
Counting linearity

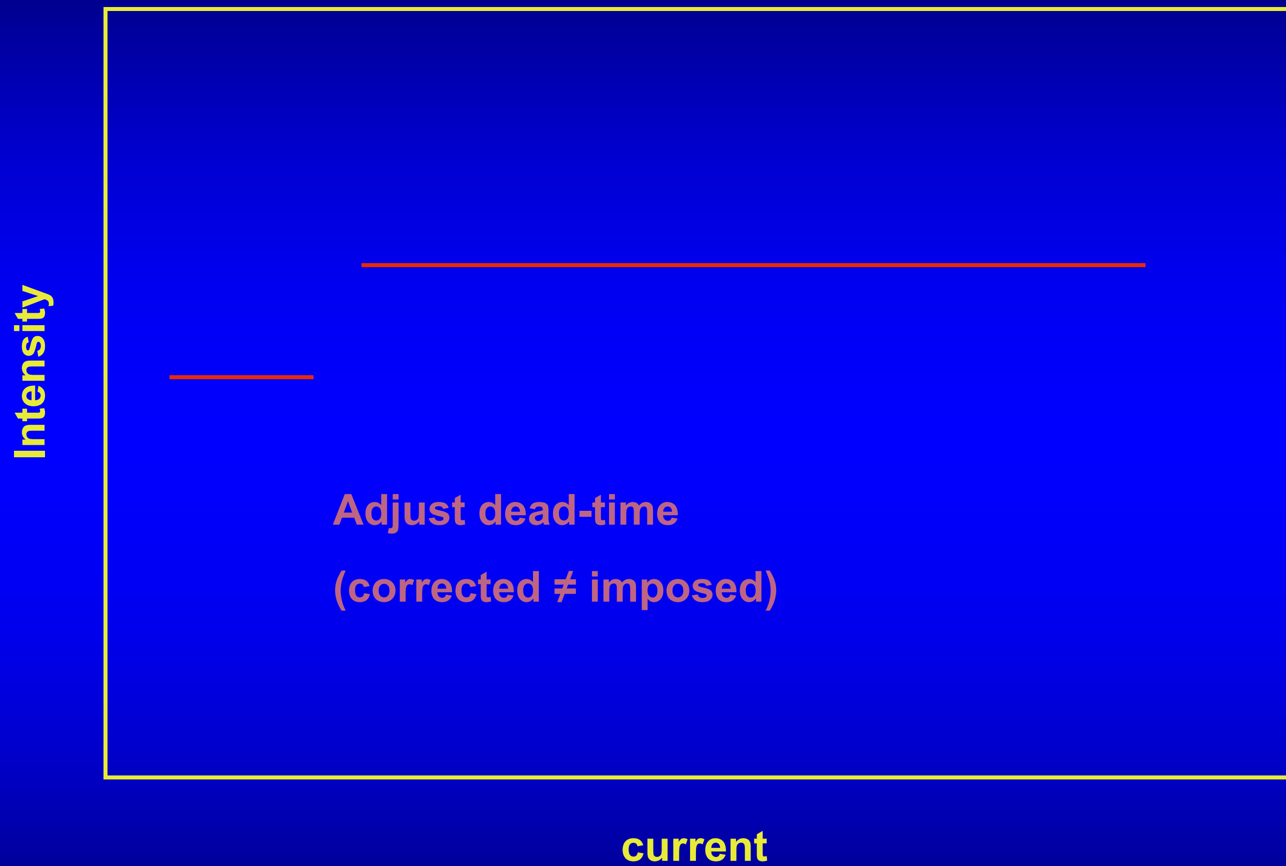
Calibrate at low current, analyze at high current

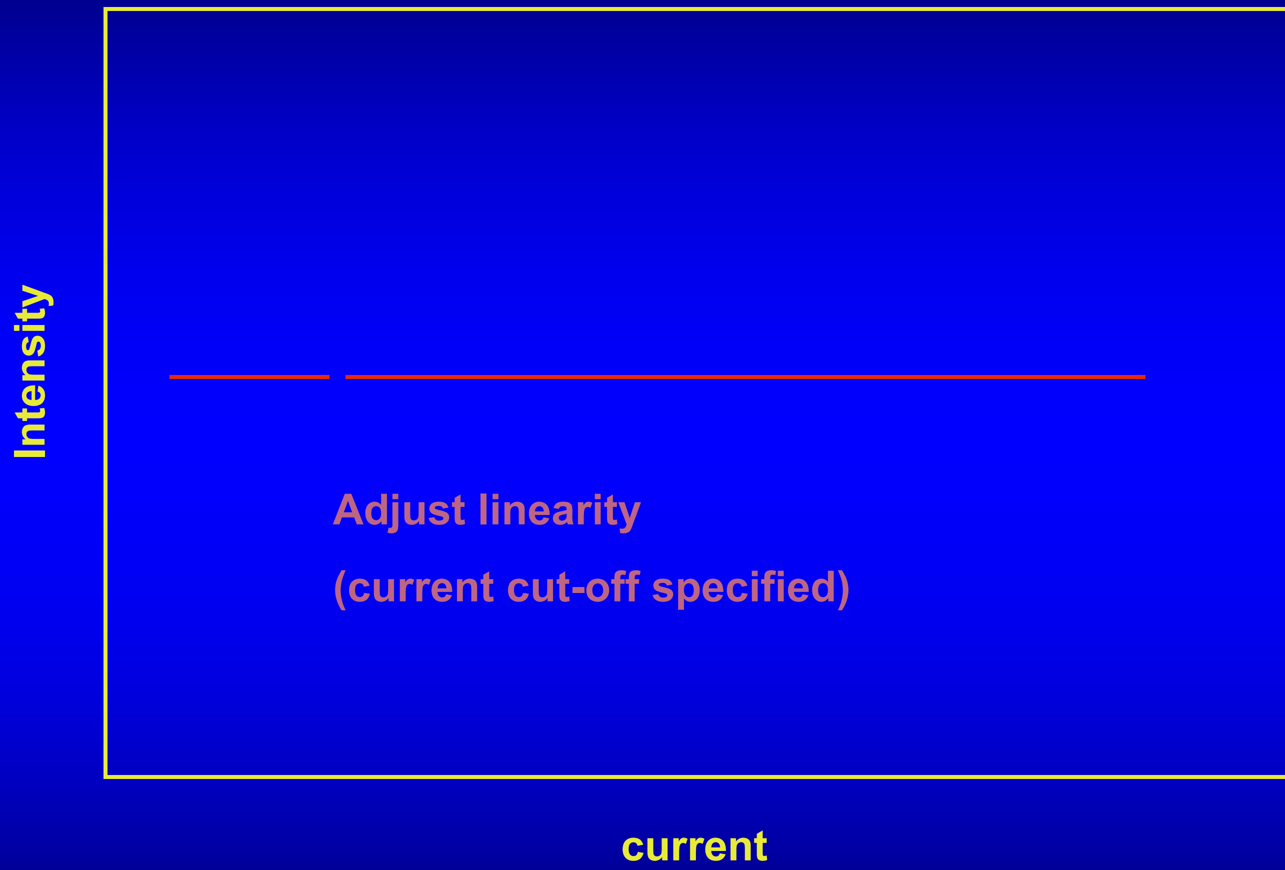

SP3 1-12-04
After picommeter adjustment
1.02
1.01
1
0.99
0.98
0.97
I / I15
0
50
100
150
200
250
300
current (nA)
Initial
Initial
After adjustment
After adjustment


Pk Int (calc) vs. pk. cps
60.0
59.0
58.0
57.0
56.0
55.0
54.0
c/s/nA
0
2000
4000
6000
8000
10000
12000
cps
15nA
20nA
10nA
25nA
50nA
30nA
35nA
60nA
40nA
70nA
80nA
45nA
90nA
100nA
125nA
150nA
175nA
200nA
y = -0.0005x + 59.249
R2 = 0.9873
Meas (5 u-sec)
DTim=8u-sec (predicted)
adjusted current (+1.5%)
Series4
Linear (Series4)


line (meas) vs. current
c/s/nA
current (nA)
60.5
60.0
59.5
59.0
58.5
58.0
57.5
57.0
56.5
0
50
100
150
200
250
10nA
15nA
20nA
25nA
30nA
35nA
40nA
45nA
50nA
60nA
70nA
80nA
90nA
100nA
125nA
150nA
175nA
200nA
Meas (5 u-sec)
DT 8u-sec (predicted)
adj current +1.5%
meas. at 8 usec DT
meas. at 8 usec DT (nA corr)


Intensity
current


Intensity
Adjust dead-time
(corrected ≠ imposed)
current

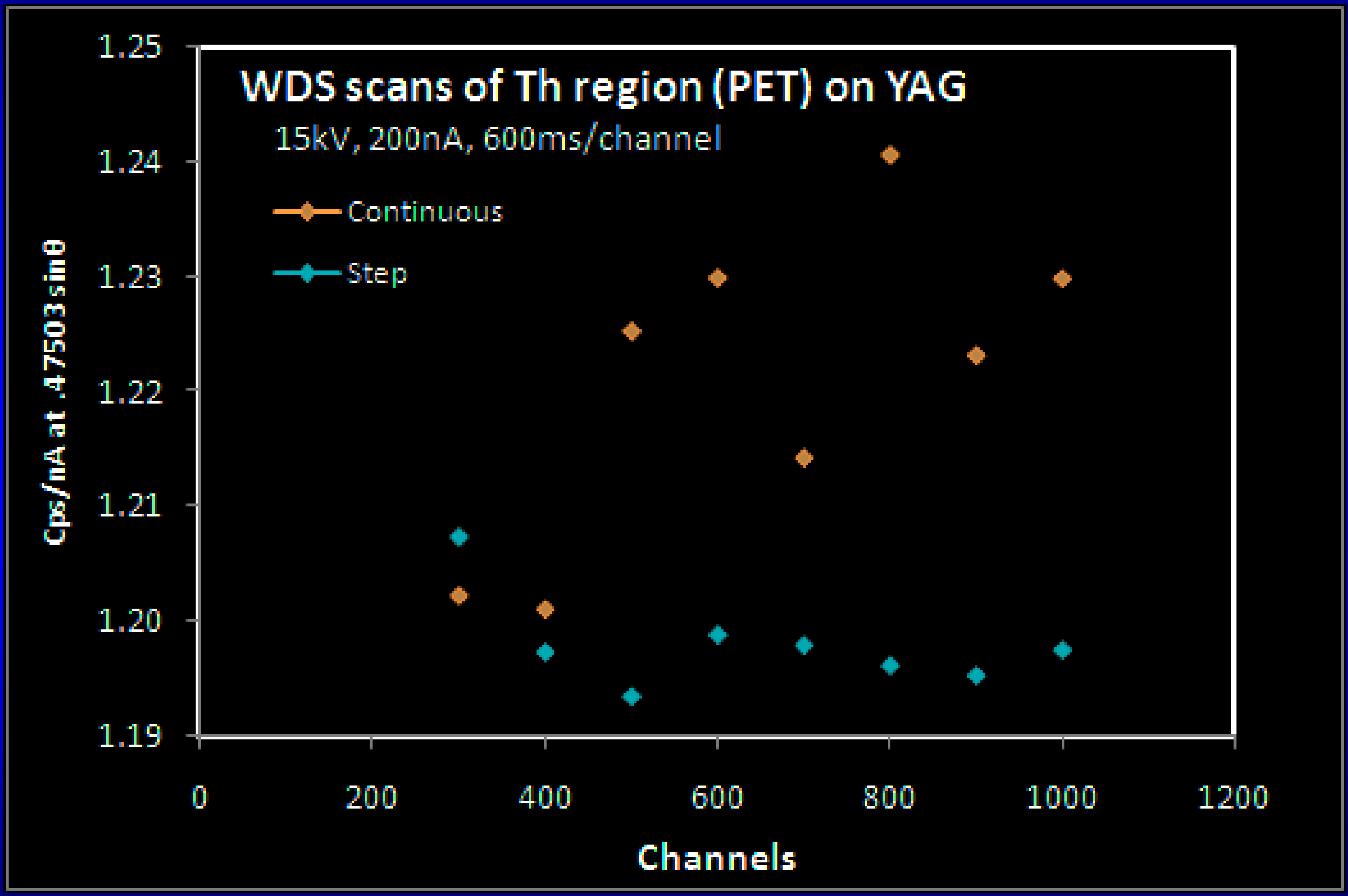

Intensity
Adjust linearity
(current cut-off specified)
current

Time

WDS scans, step scan vs. "continuous" scan

Time

WDS scans, step scan vs. “continuous” scan



Test the aspects you can…

Blanks

Consistent relative compositions

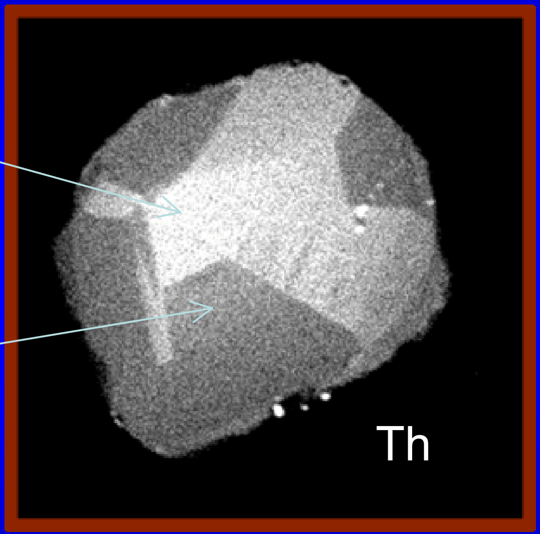
Consistency from session to session

Consistent relative compositions?
Test different compositions of the “same” materials

Monazite = same age in sector zones?
In this case, heterogeneity is good!

High Th = 7.9 wt.%
EPMA Age = 1676 +/- 4 Ma

Low Th = 4.3 wt.%
EPMA Age = 1679 +/-6 Ma



Bulk ID-TIMS ~ 1681Ma

Consistency

Test before, during and after trace element runs

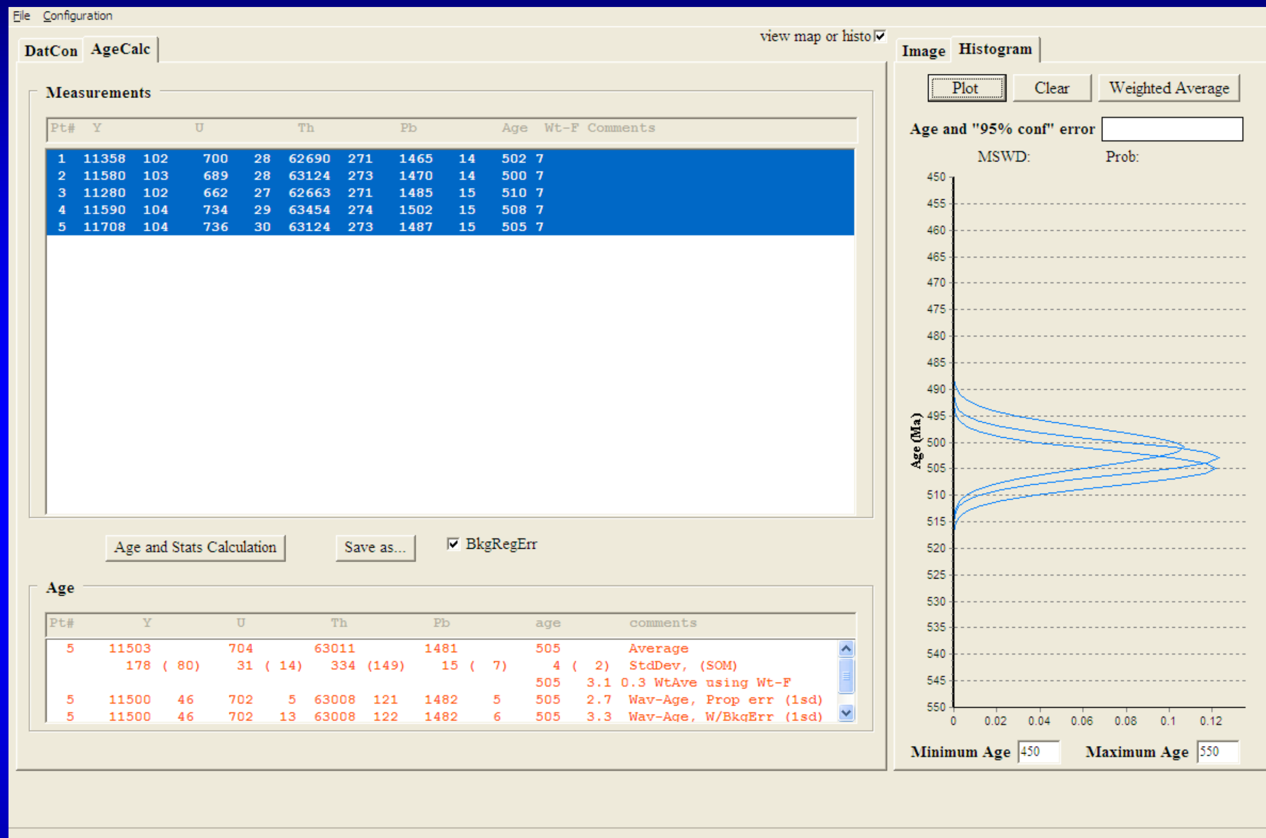
Does this tell you the results are correct (accurate)? No!

But you do get insight into when things go wrong (or at least change in a measurable way)

Calibration

Coating, etc.

Instrumental changes



File
Configuration
DatCon
AgeCalc
view map or histo
Measurements
Pt# Y U Th Pb Age Wt-F Comments
1 11358 102 700 28 62690 271 1465 14 502 7
2 11580 103 689 28 63124 273 1470 14 500 7
3 11280 102 662 27 62663 271 1485 15 510 7
4 11590 104 734 29 63454 274 1502 15 508 7
5 11708 104 736 30 63124 273 1487 15 505 7
Age and Stats Calculation
Save as...
BkgRegErr
Age
Pt# Y U Th Pb age comments
5 11503 704 63011 1481 505 Average
178 (80) 31 (14) 334 (149) 15 (7) 4 (2) StdDev, (SOM)
505 3.1 0.3 WtAve using Wt-F
5 11500 46 702 5 63008 121 1482 5 505 2.7 Wav-Age, Prop err (1sd)
5 11500 46 702 13 63008 122 1482 6 505 3.3 Wav-Age, W/BkgErr (1sd)
Image
Histogram
Plot
Clear
Weighted Average
Age and "95% conf" error
MSWD:
Prob:
Age (Ma)
Minimum Age 450
Maximum Age 550