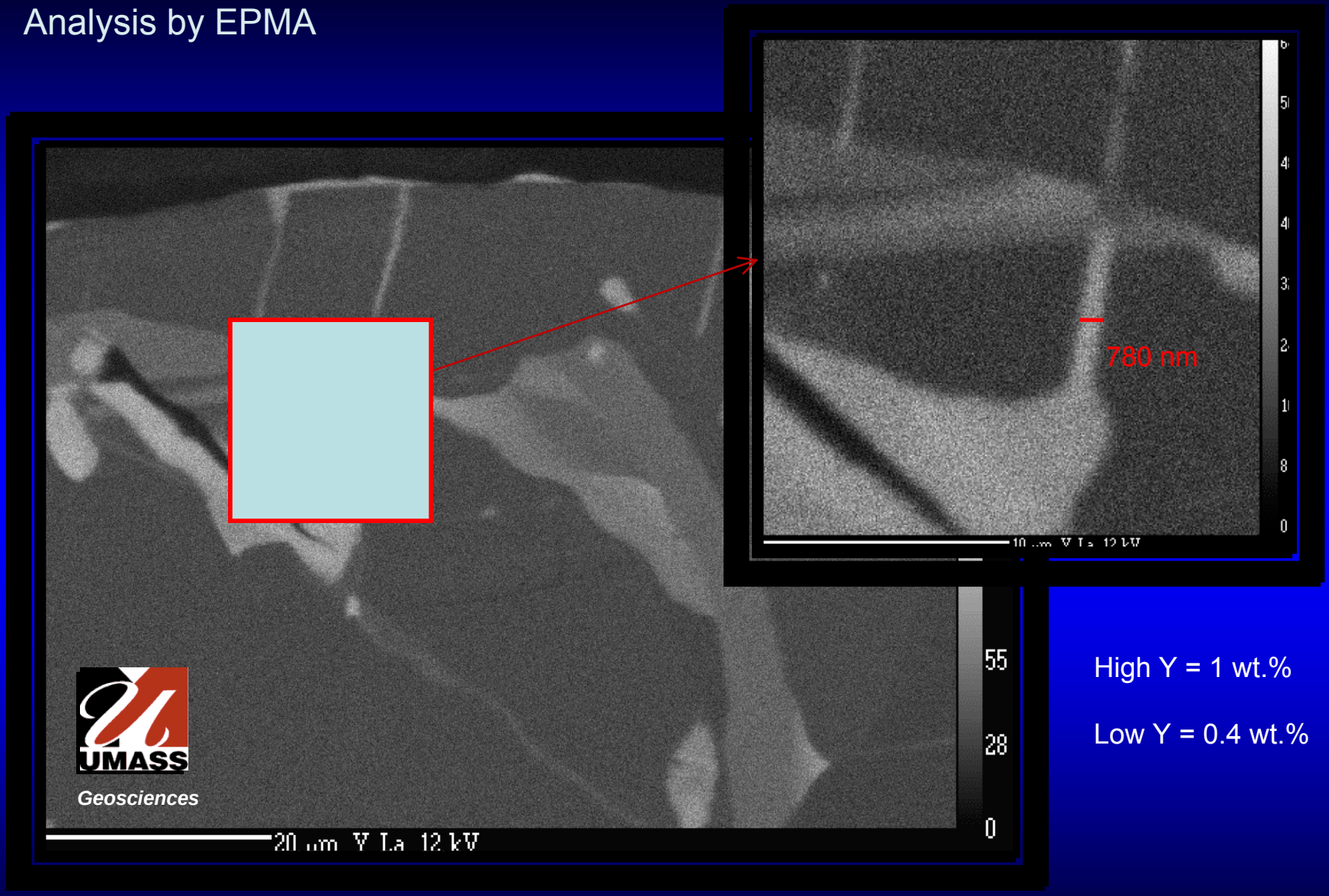
Practical Considerations in Trace Element Analysis by EPMA



High Y = 1 wt.%

Low Y = 0.4 wt.%

100 nA, 12 kV, 50 ms/pixel

Considerations:

Precision = counts

Accuracy = accurate net intensity
background measurement
peak measurement
interferences on peak and background
- elements in the phase of interest
- lines fluoresced from adjacent phases or compositional domains

Solutions:

Precision = current and count time – *Not the problem*
Improved sensitivity (lower MDL), more efficient spectrometers, higher, more stable currents

Accuracy =
Sample preparation and coating are critical
Map! Know the layout of the environment
High resolution WDS scanning
evaluation must be commensurate with the sensitivity of the analysis!

Minimize drift (contamination, dynamic charge effects, source stability, etc.) and beam damage (high current density)

Background measurement – must account for background shape
Spectrometer efficiency
Natural Bremmstrahlung
Watch for 'holes'

Peak measurement - watch for interferences – peak tails
Accurate interference corrections

Be wary of fluorescence at a distance
Induced by characteristic radiation
Induced by continuum – especially from high Z phases

Zr in rutile (thermometry)

Relatively low spatial resolution analysis

20 kV, 200nA, 5 spectrometer integration, 600 sec. acquisitions *Integrating PET, two LPETs, and 2 VLPETs*

= Single point detection limit of 14ppm (3σ) for Zr

= Grain average yields an overall detection limit of 3 ppm (3σ) for 15 points, and 4 ppm (3σ) for 10 points

Solutions:

Accuracy =

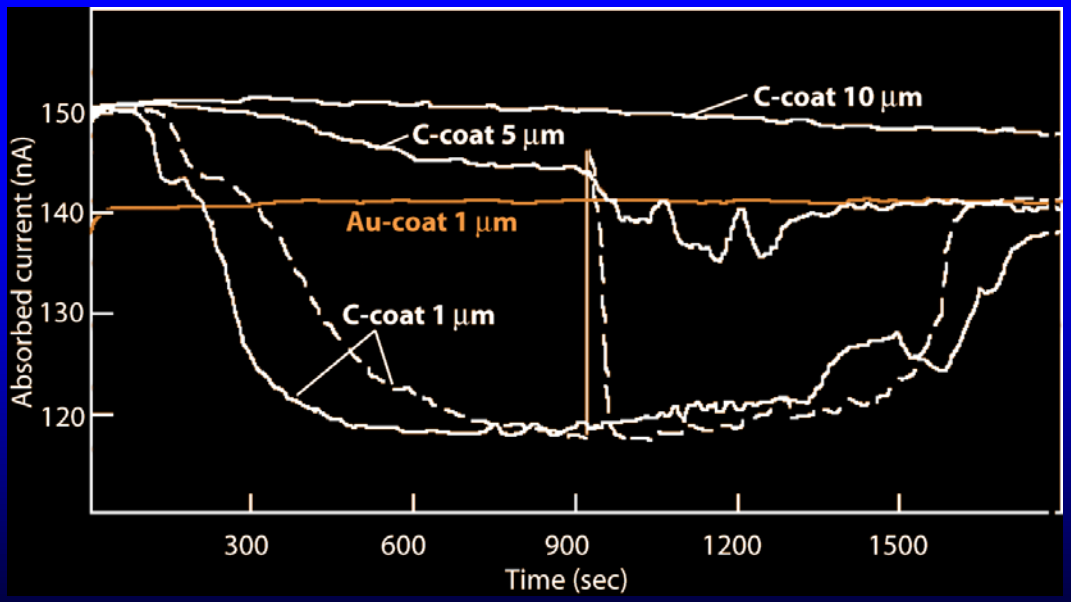
Sample preparation and coating are critical

A few brief thoughts on sample preparation –

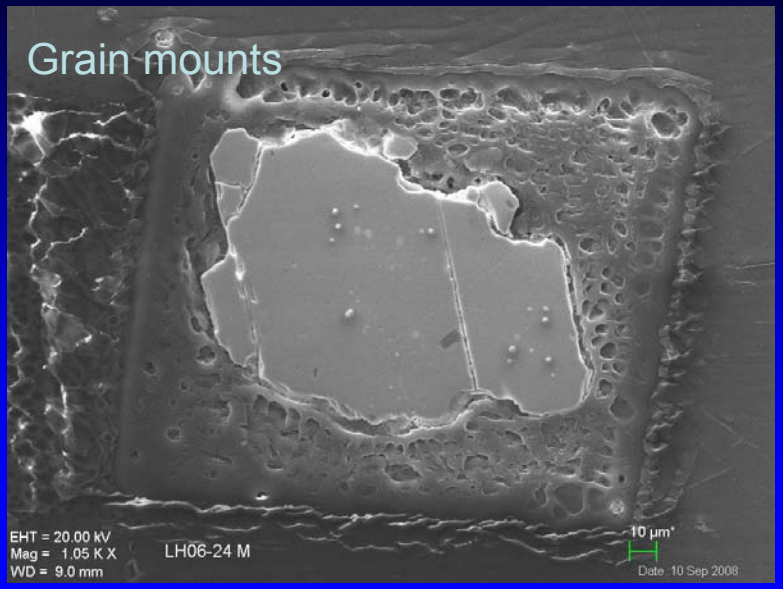
Trace element analysis (precision = counts) *very high current (voltage?)*
*very long count t*imes

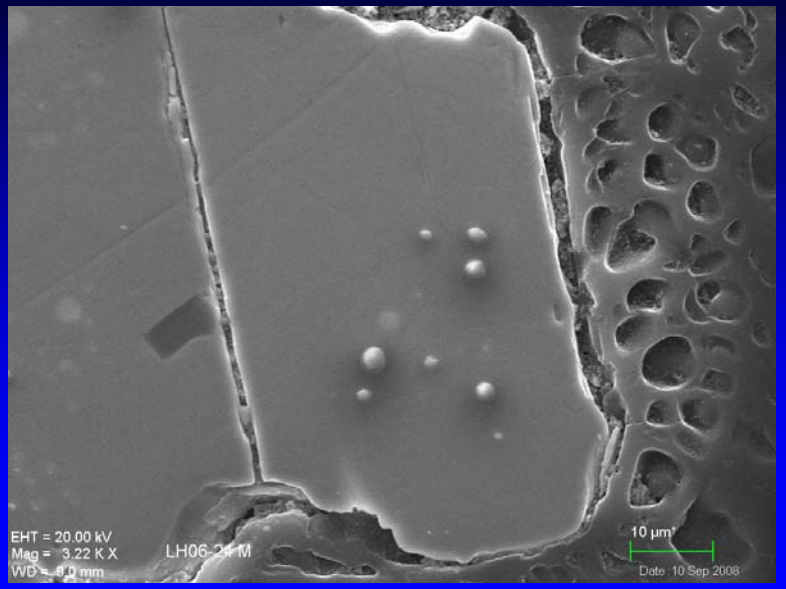
Must consider the sample
- High current density
- Beam damage
- Internal charge effects

Boundaries and edge preservation

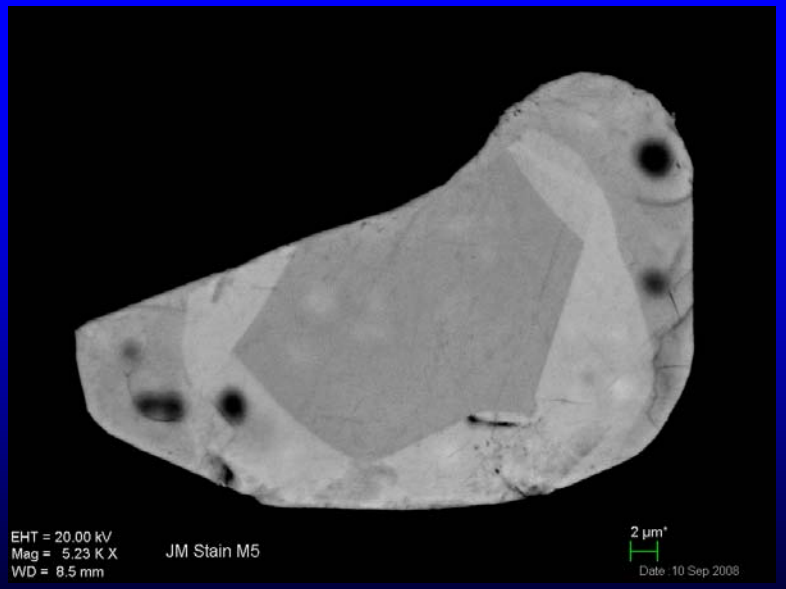


Grain mounts





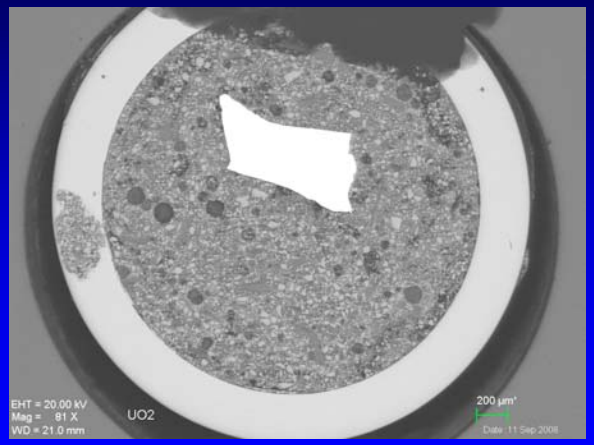
Thin sections – *in situ analysis*!

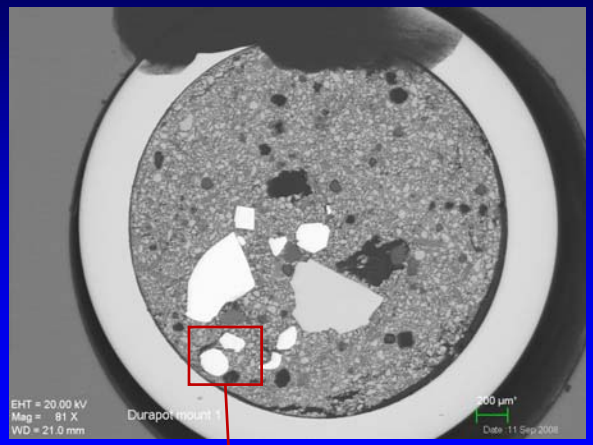


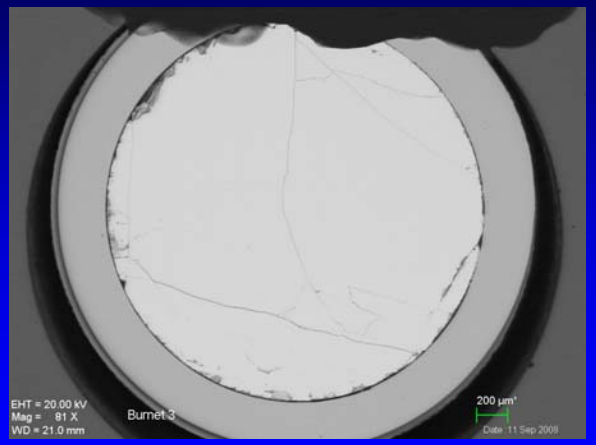
Grain mounts

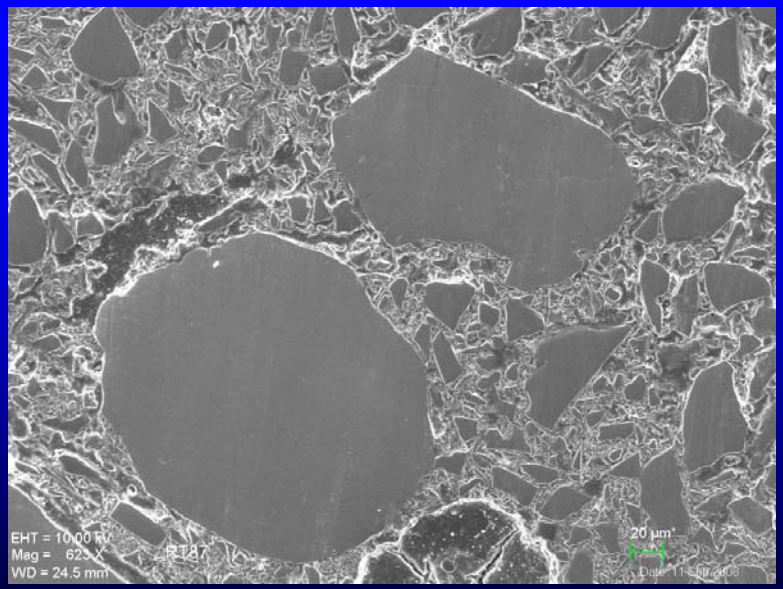
Potting - Casting ceramics

Micro-drill, press fit, and Ni-epoxy





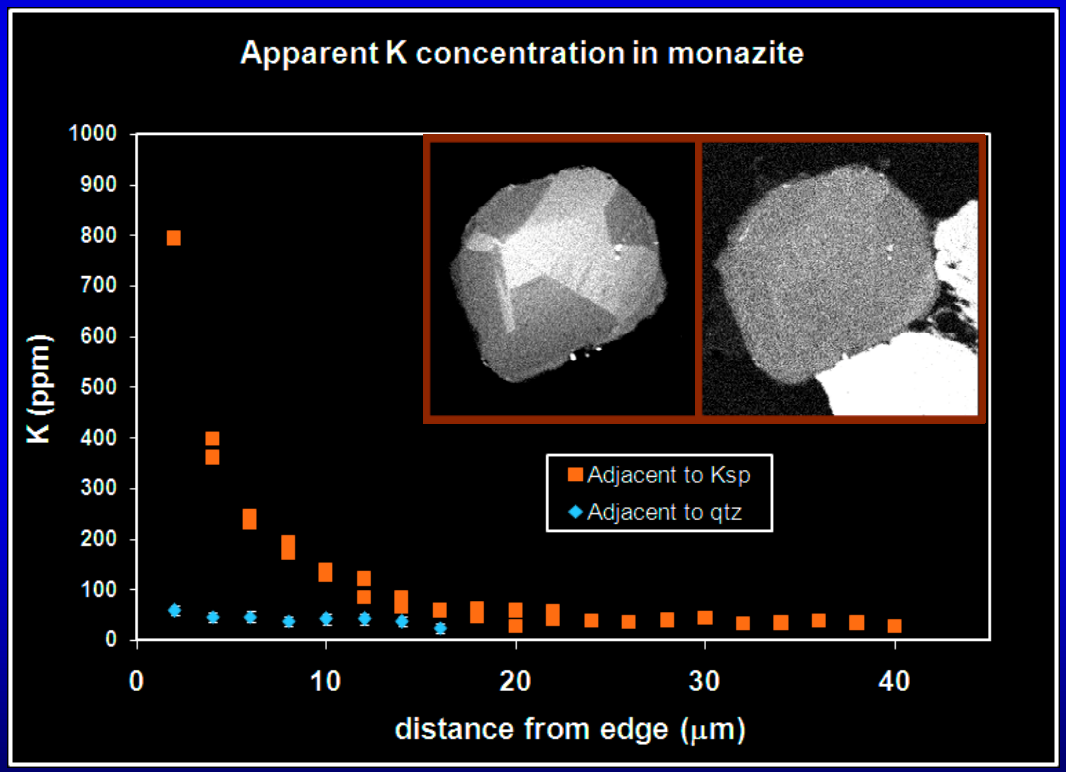


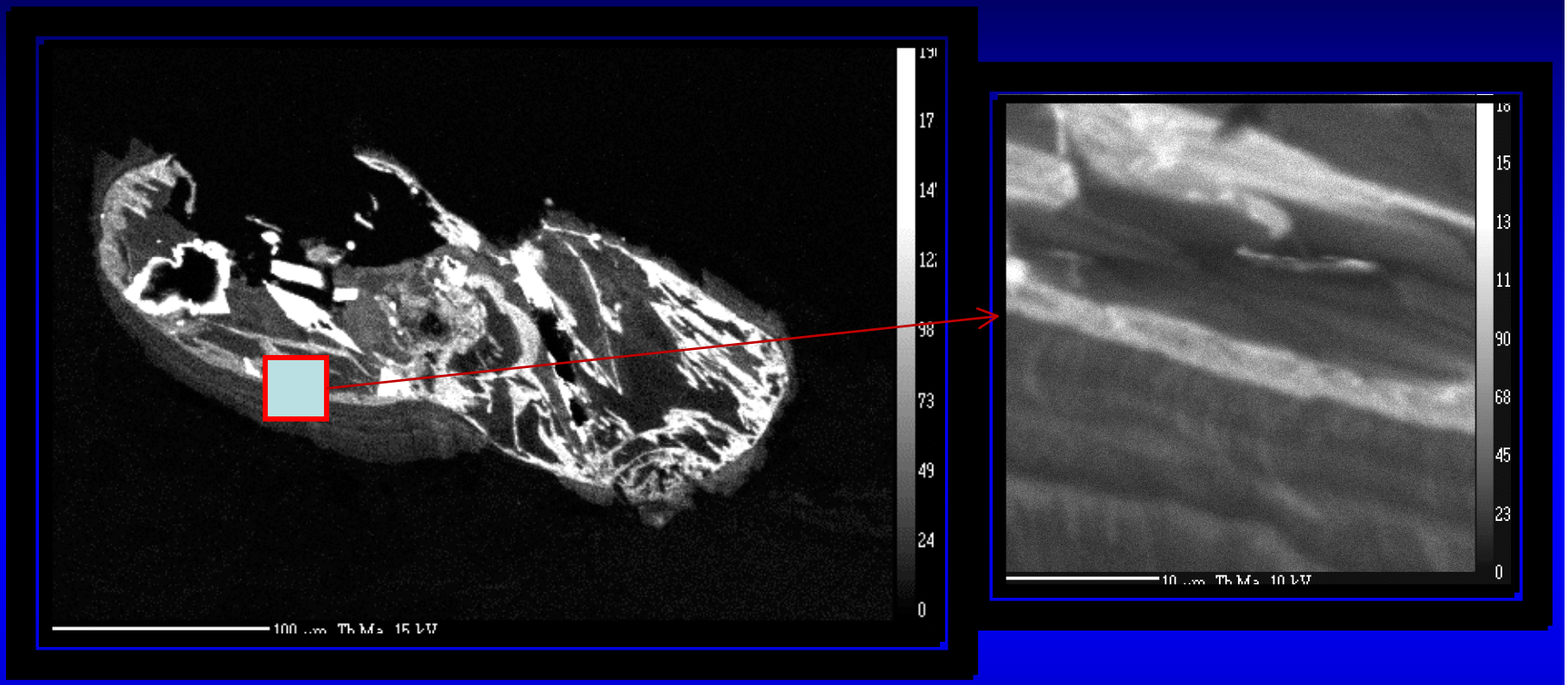


Solutions:

Accuracy =

Map! Know the layout of the environment



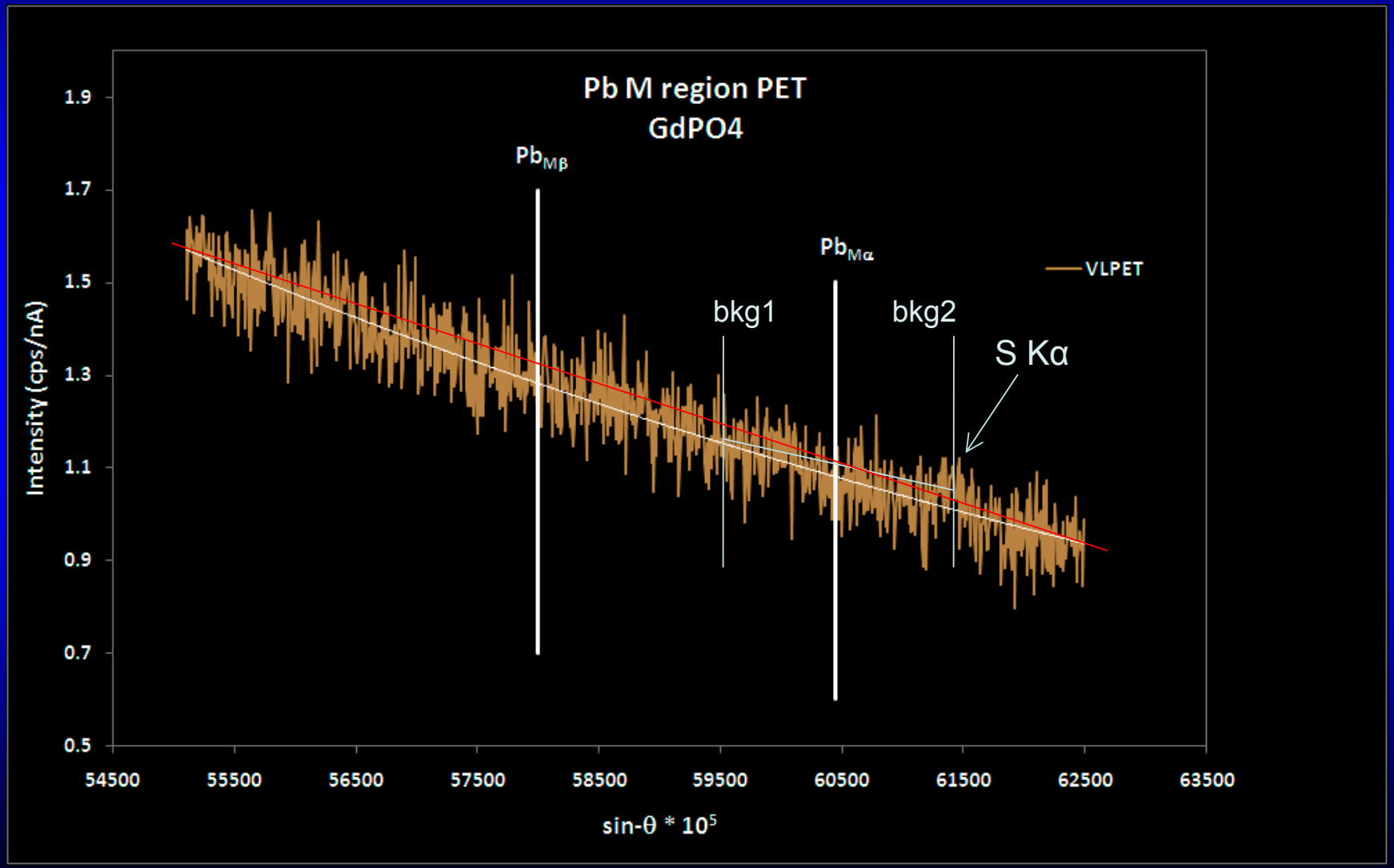

17
14
12
98
73
49
24
0
15
13
11
90
68
45
23
0

Solutions:

Accuracy =

High resolution WDS scanning

evaluation must be commensurate with the sensitivity of the analysis!



Solutions:

Accuracy =

Minimize drift (contamination, dynamic charge effects, source stability, etc.) and beam damage (high current density)

Peak measurement - watch for interferences – peak tails

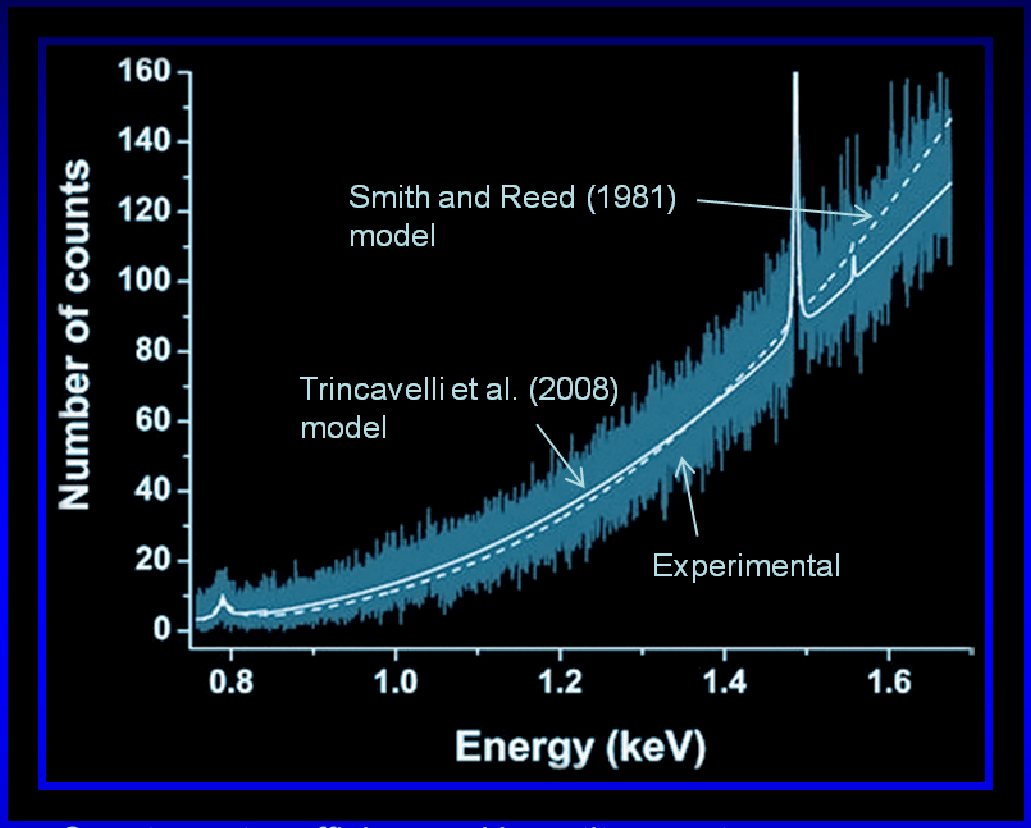
Accurate interference corrections

Background measurement – must account for background shape

Spectrometer efficiency

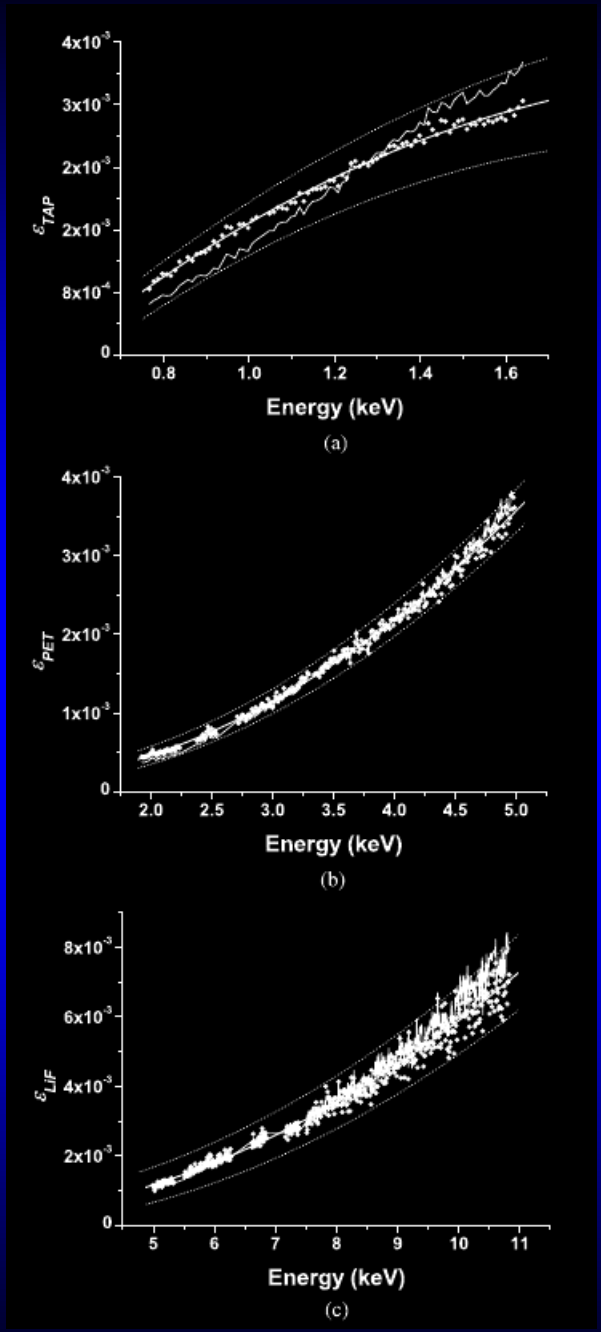
Natural Bremmstrahlung

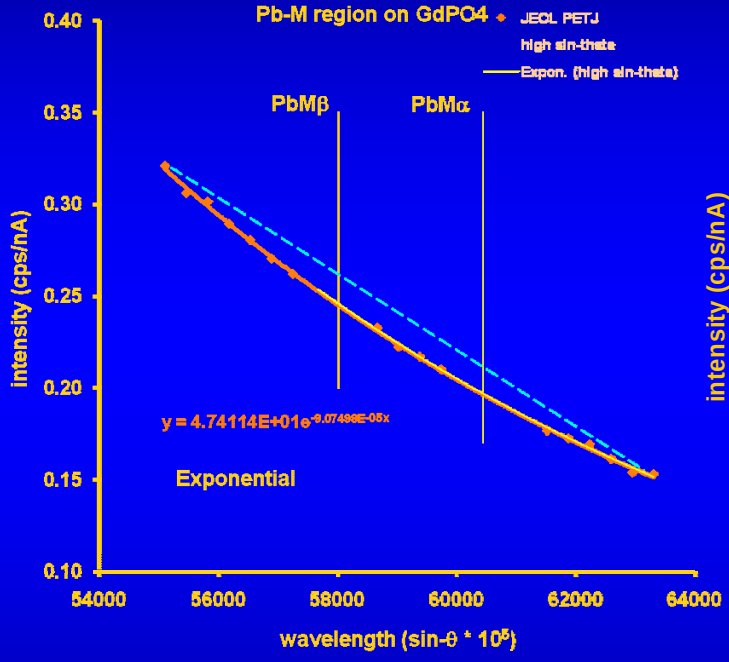
Watch for ‘holes’



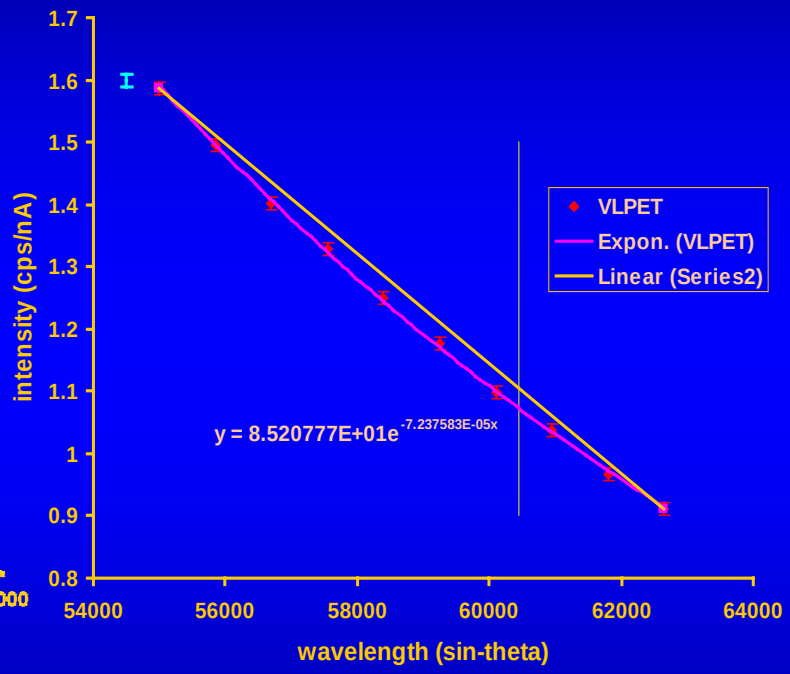
Spectrometer efficiency: Hematite spectrum (TAP)Trincavelli et al., 2008

$$\varepsilon_{\mathrm{WDS}}(E) = \frac{N_{\mathrm{WDS}}^{grouped}(E)(i\Delta t)_{\mathrm{EDS}}}{N_{\mathrm{EDS}}(E)(i\Delta t)_{\mathrm{WDS}}} \frac{\Delta\Omega_{\mathrm{EDS}}}{4\pi} \varepsilon'_{\mathrm{EDS}}(E)$$

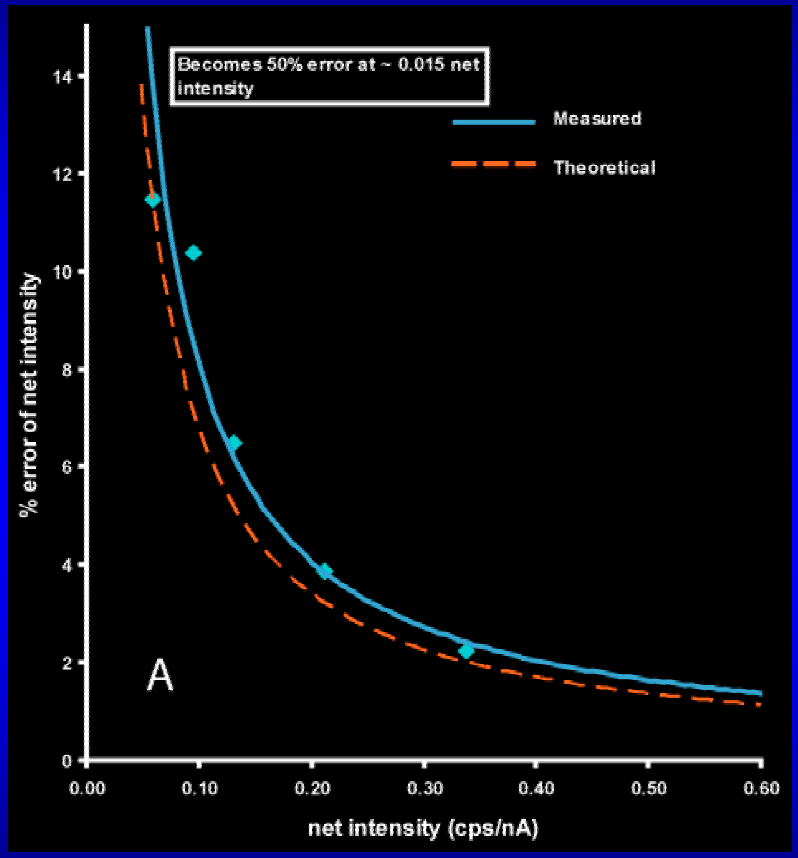



Pb-M region on GdPO4
JEOL PETJ high sin-theta
Expon. (high sin-theta)
PbMβ
PbMα
y = 4.74114E+01e-9.07498E-05x
Exponential
intensity (cps/nA)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
54000
56000
58000
60000
62000
64000
wavelength (sin-θ * 10^5)

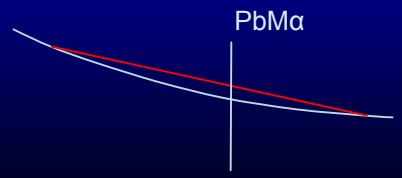
sp3

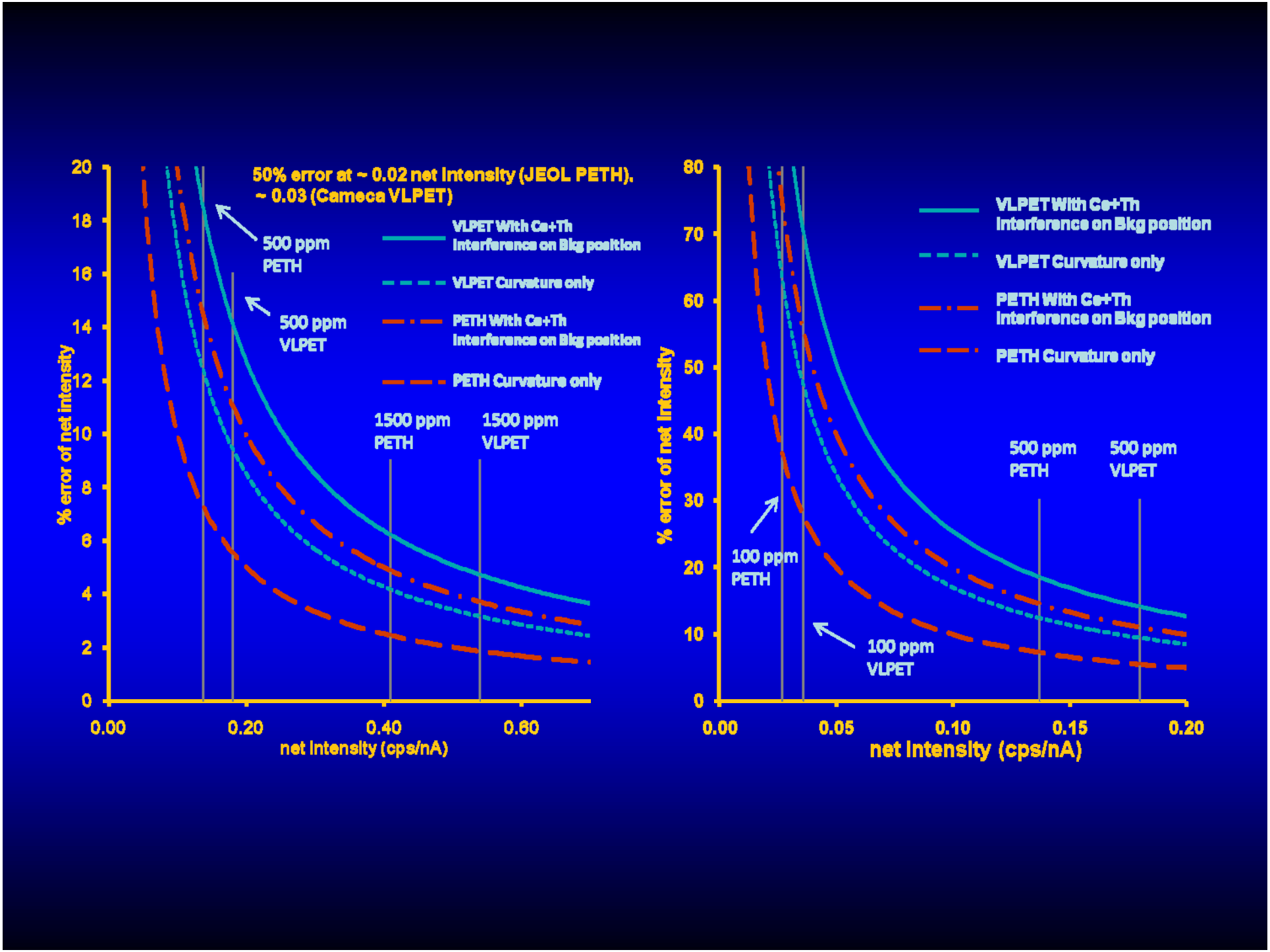

intensity (cps/nA)
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
54000
56000
58000
60000
62000
64000
wavelength (sin-theta)
y = 8.520777E+01e-7.237583E-05x
VLPET
Expon. (VLPET)
Linear (Series2)

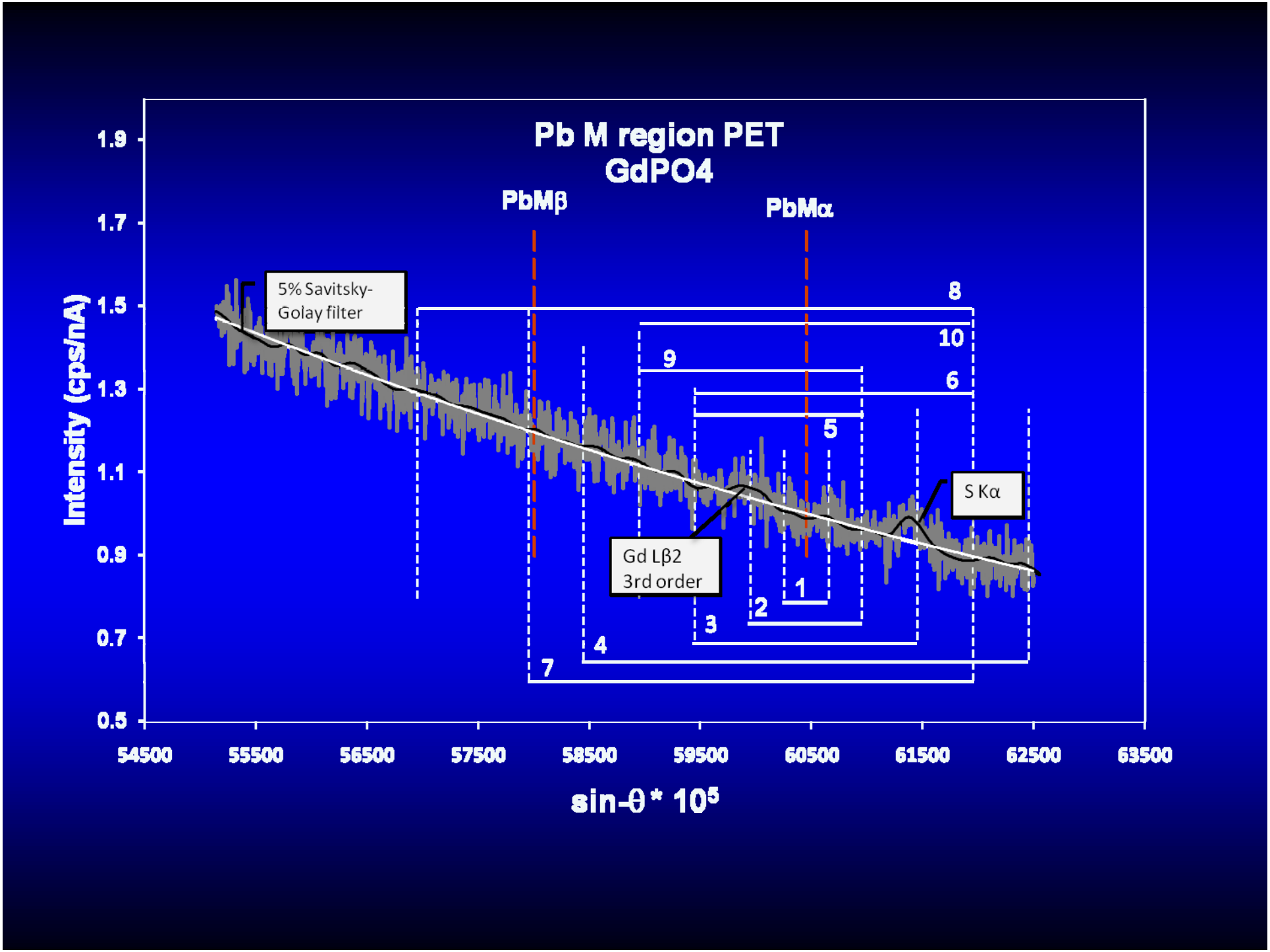
Errors - Background shape

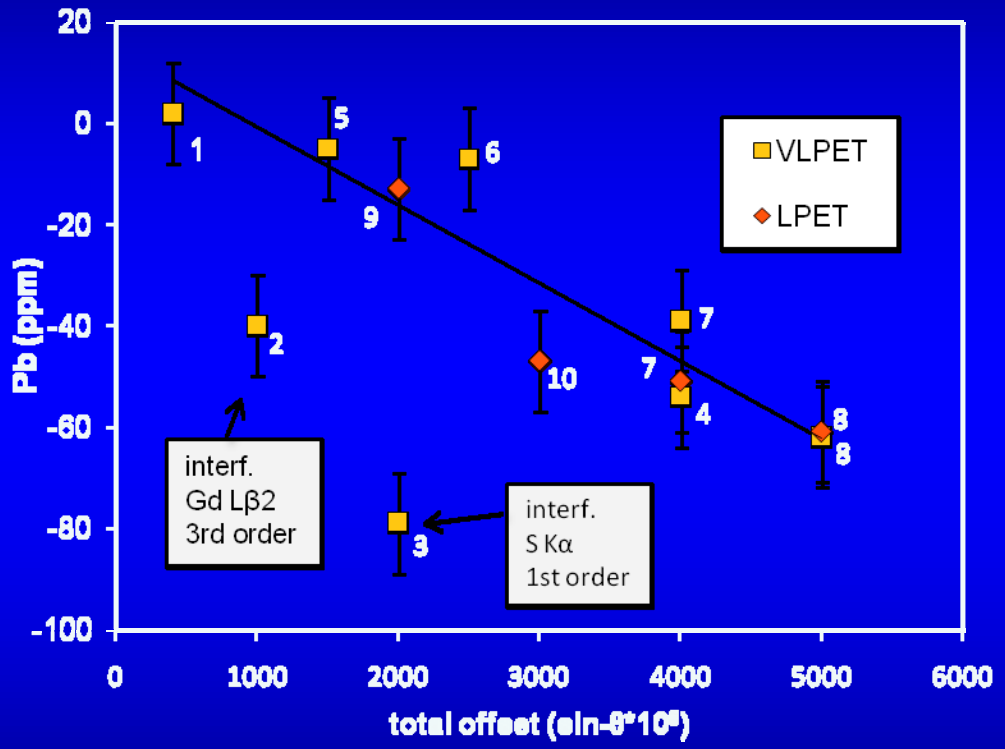


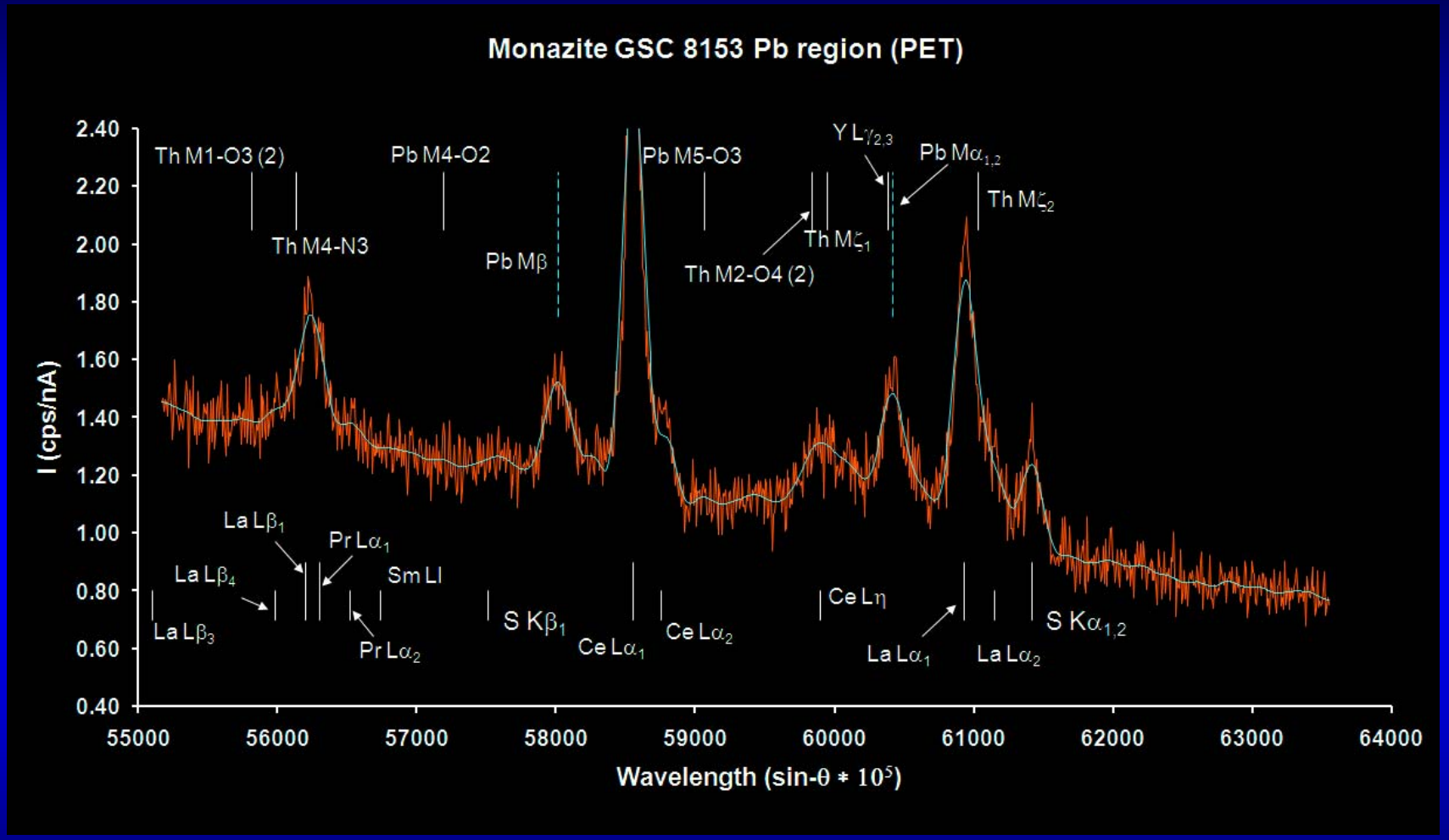
Error due to improper background model for PbMα as peak intensity is lowered (lower concentration)

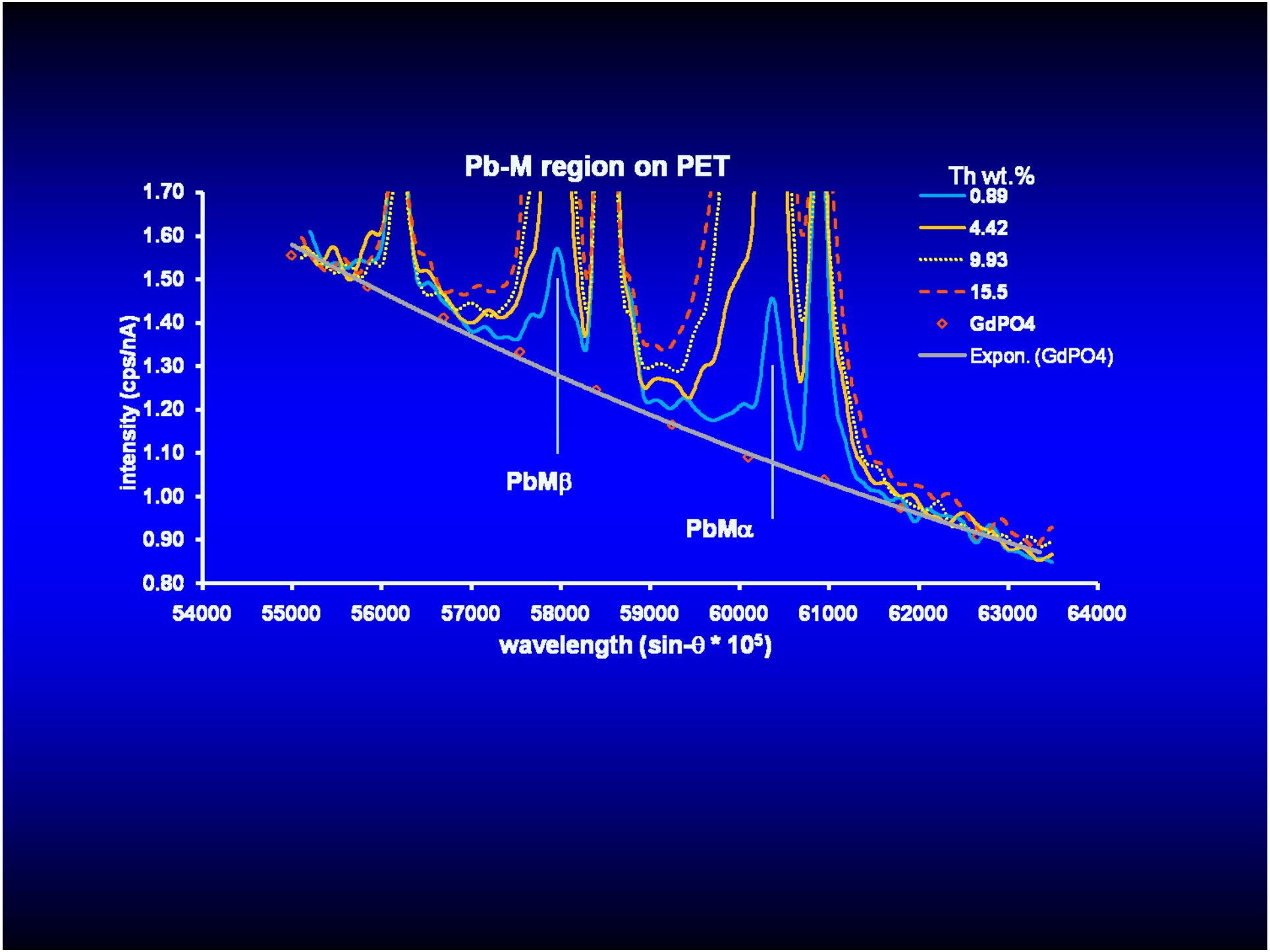



50% error at ~ 0.02 net intensity (JEOL PETH).
~ 0.03 (Cameca VLPET)
500 ppm PETH
500 ppm VLPET
1500 ppm PETH
1500 ppm VLPET
VLPET With Ce+Th Interference on Bkg position
VLPET Curvature only
PETH With Ce+Th Interference on Bkg position
PETH Curvature only
% error of net intensity
net intensity (cps/nA)
0
2
4
6
8
10
12
14
16
18
20
0.00
0.20
0.40
0.60
100 ppm PETH
100 ppm VLPET
500 ppm PETH
500 ppm VLPET
0
10
20
30
40
50
60
70
80
0.00
0.05
0.10
0.15
0.20

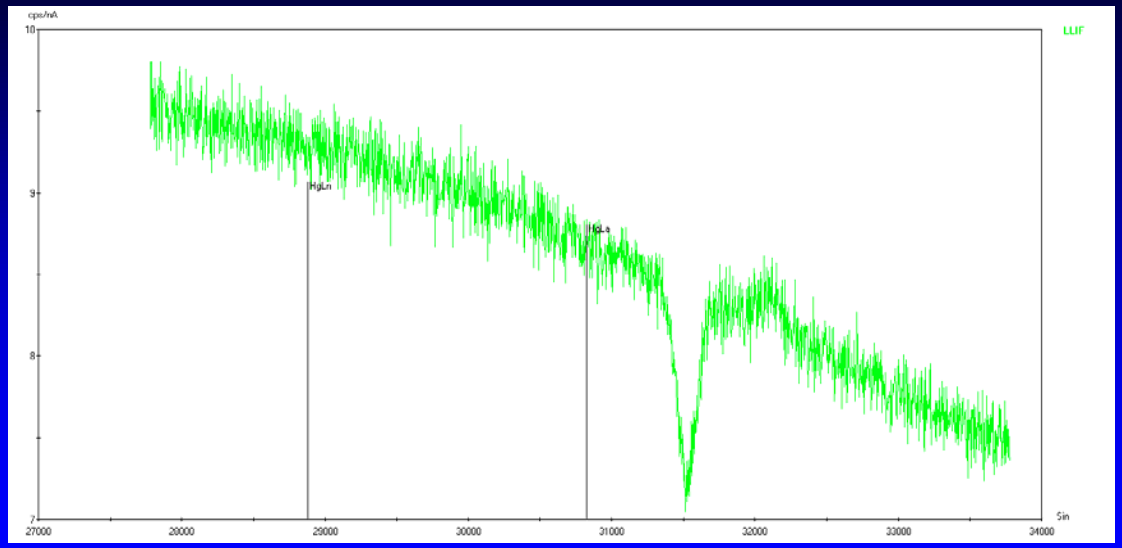

Pb M region PET
GdPO4
PbMβ
PbMα
5% Savitsky-Golay filter
Gd Lβ2 3rd order
S Kα
1
2
3
4
5
6
7
8
9
10
Intensity (cps/nA)
1.9
1.7
1.5
1.3
1.1
0.9
0.7
0.5
54500
55500
56500
57500
58500
59500
60500
61500
62500
63500
sin-θ * 10⁵

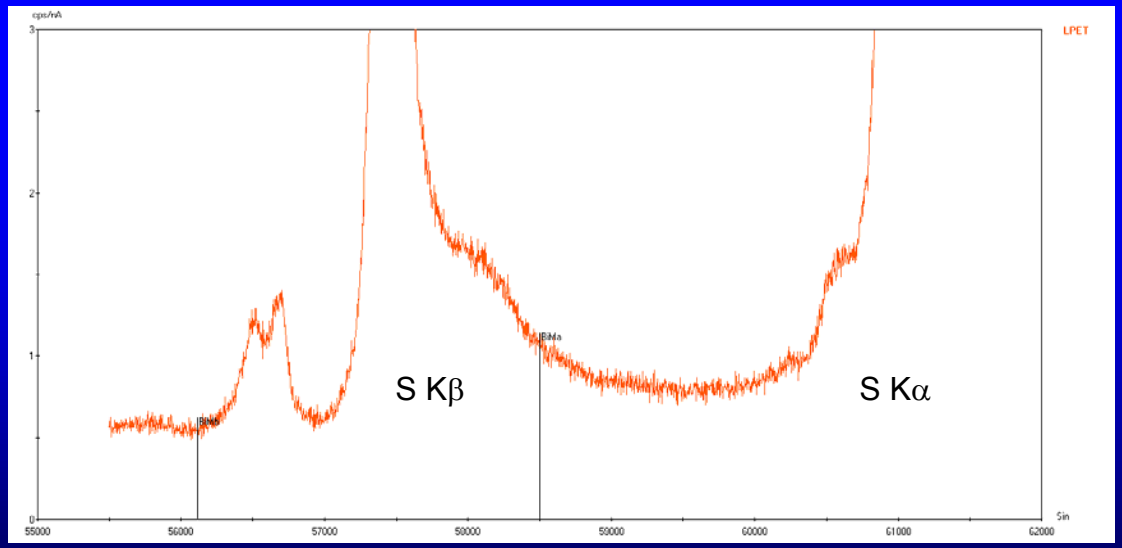

20
0
-20
-40
-60
-80
-100
Pb (ppm)
0
1000
2000
3000
4000
5000
6000
total offset (sin-θ*10⁵)
VLPET
LPET
1
2
3
4
5
6
7
7
8
8
9
10
interf.
Gd Lβ2
3rd order
interf.
S Kα
1st order


Monazite GSC 8153 Pb region (PET)
I (cps/nA)
Wavelength (sin-θ * 10^5)
Th M1-O3 (2)
Th M4-N3
Pb M4-O2
Pb Mβ
Pb M5-O3
Th M2-O4 (2)
Y Lγ2,3
Th Mζ1
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


Pb-M region on PET
Th wt.%
0.89
4.42
9.93
15.5
GdPO4
Expon. (GdPO4)
PbMβ
PbMα
intensity (cps/nA)
1.70
1.60
1.50
1.40
1.30
1.20
1.10
1.00
0.90
0.80
54000
55000
56000
57000
58000
59000
60000
61000
62000
63000
64000
wavelength (sin-θ * 10^5)

LLIF





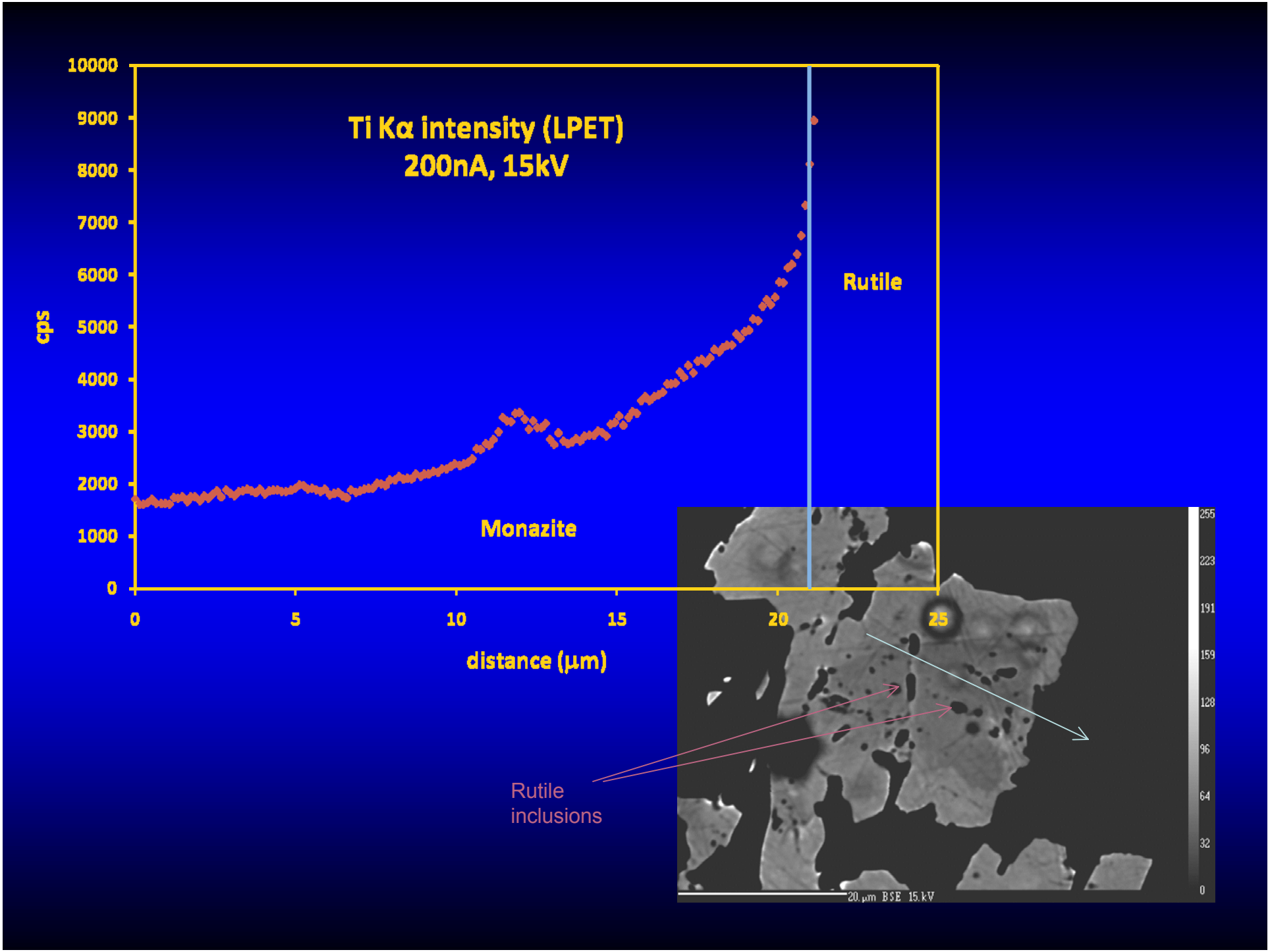
Bi measurement in sulfides and satellites of sulfur diagram lines,

Solutions:

Accuracy =

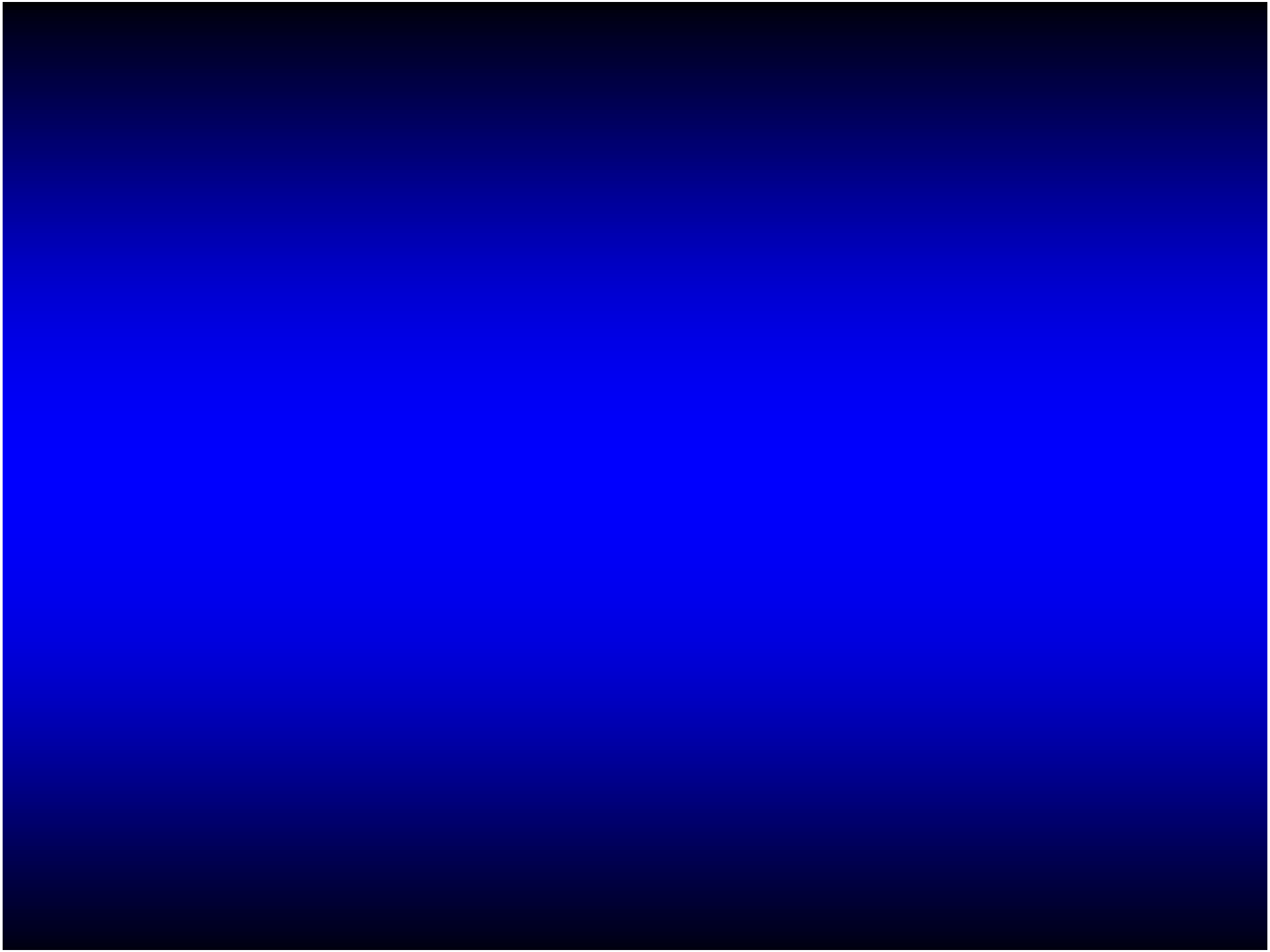
Be wary of fluorescence at a distance

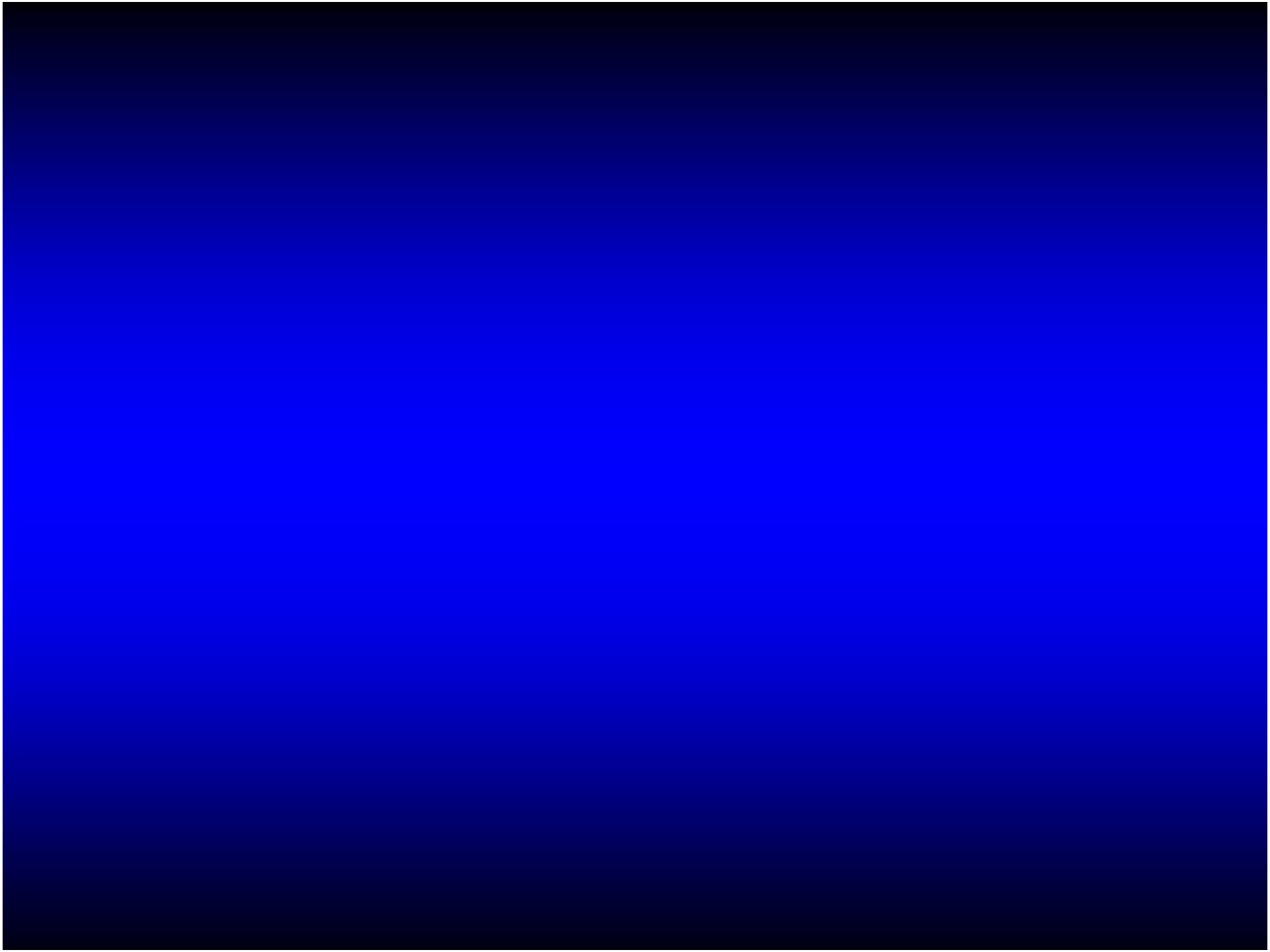
- Induced by characteristic radiation
- Induced by continuum – especially from high Z phases

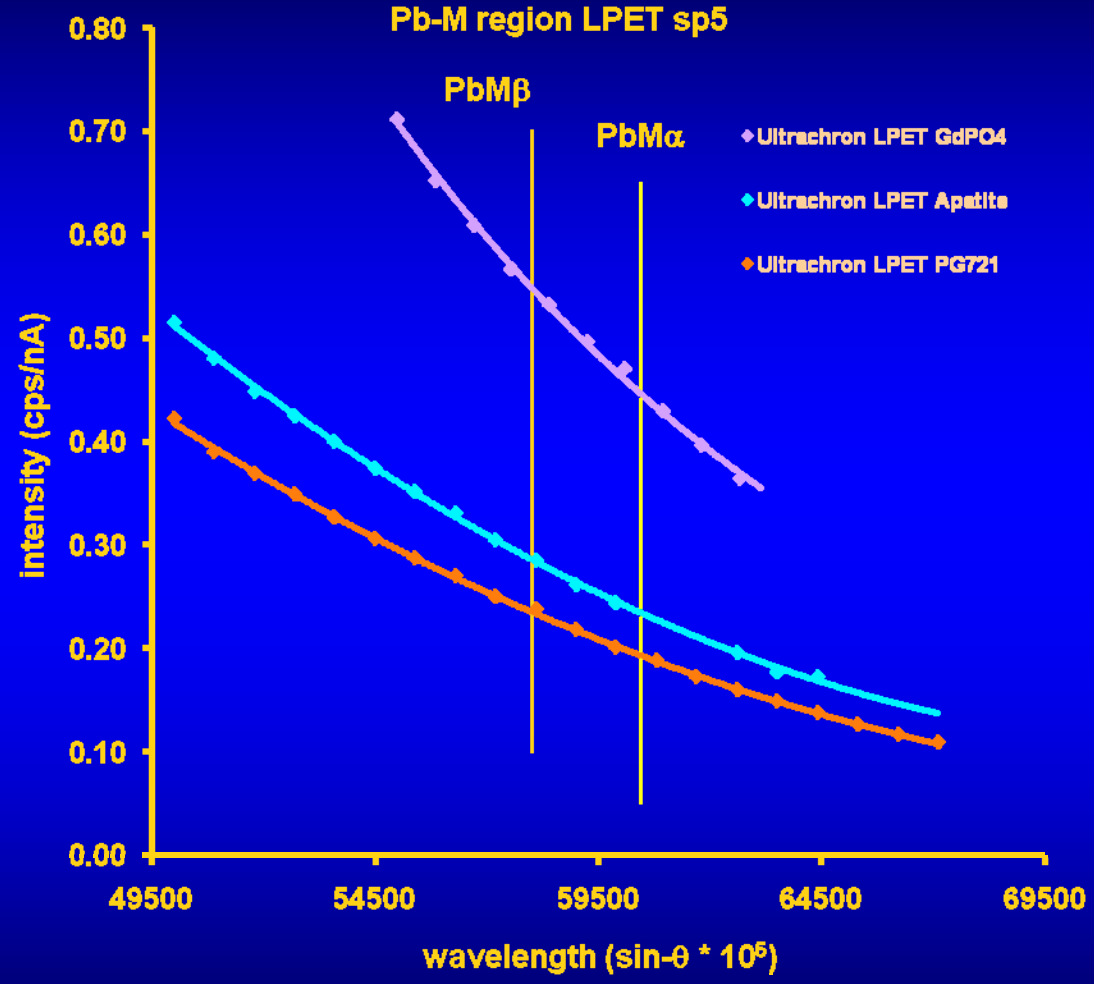

Ti Kα intensity (LPET)
200nA, 15kV
cps
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
0
5
10
15
20
25
distance (µm)
Monazite
Rutile
Rutile inclusions
255
223
191
159
128
96
64
32
0
20 µm BSE 15 kV

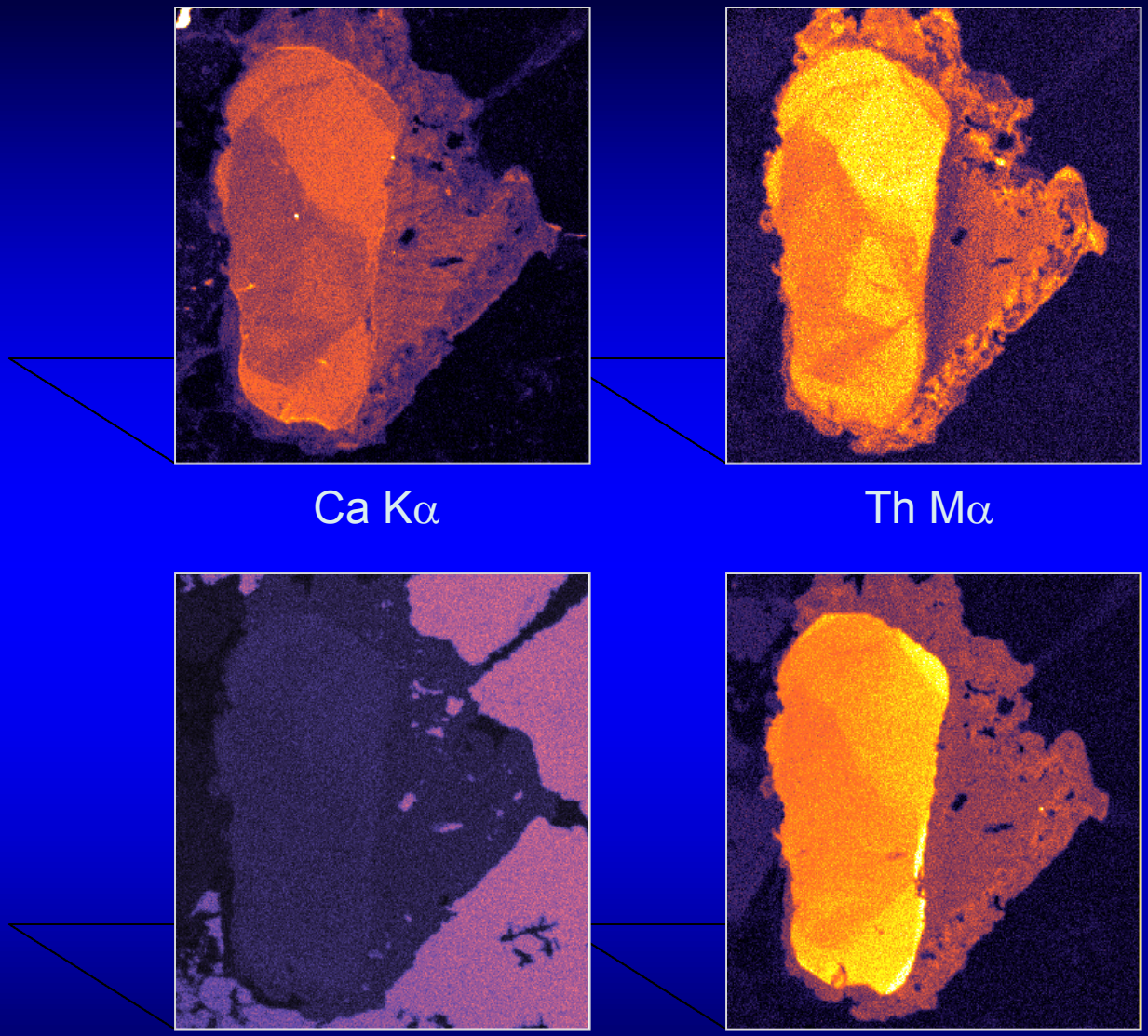
Dependable secondary standards for trace concentrations?

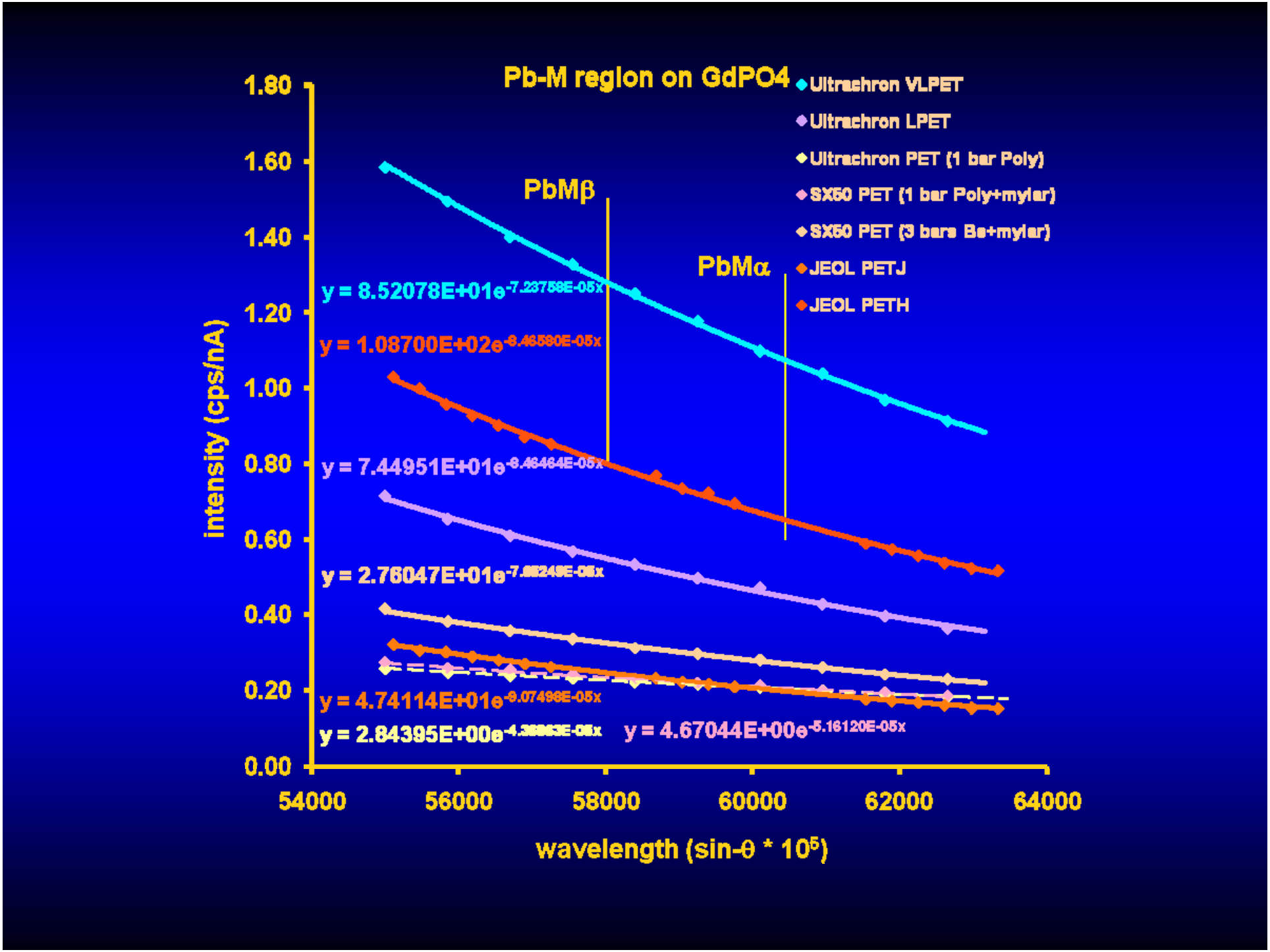
Ion probe?
LA-ICP-MS?






Pb-M region LPET sp5
PbMβ
PbMα
Ultrachron LPET GdPO4
Ultrachron LPET Apatite
Ultrachron LPET PG721
intensity (cps/nA)
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
49500
54500
59500
64500
69500
wavelength (sin-θ * 10⁵)


Ca Kα
Th Mα
U Mβ
Y Lα
20 μm


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-8.46590E-05x
y = 7.44951E+01e-8.46464E-05x
y = 2.76047E+01e-7.88249E-05x
y = 4.74114E+01e-9.07496E-05x
y = 2.84395E+00e-4.38863E-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 * 10⁵)