Qualitative Analysis Blunders: the Perils of Automatic Peak Identification in EDS Analysis

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Automatic Qualitative Analysis (Peak ID)

- **The critical first step in any EDS analysis: correctly identifying the elements responsible for the peaks**
- Can we trust automatic qualitative analysis (peak identification) to <u>always</u> identify peaks of <u>major</u> constituents correctly?
  - **Major: Concentration, $C > 0.1$ mass fraction (>10 weight %)**
  - **Minor: $0.01 \leq C \leq 0.1$ (1 to 10 weight %)**
  - **Trace: $C < 0.01$ (< 1 weight %)**

Automatic Qualitative Analysis (Peak ID)

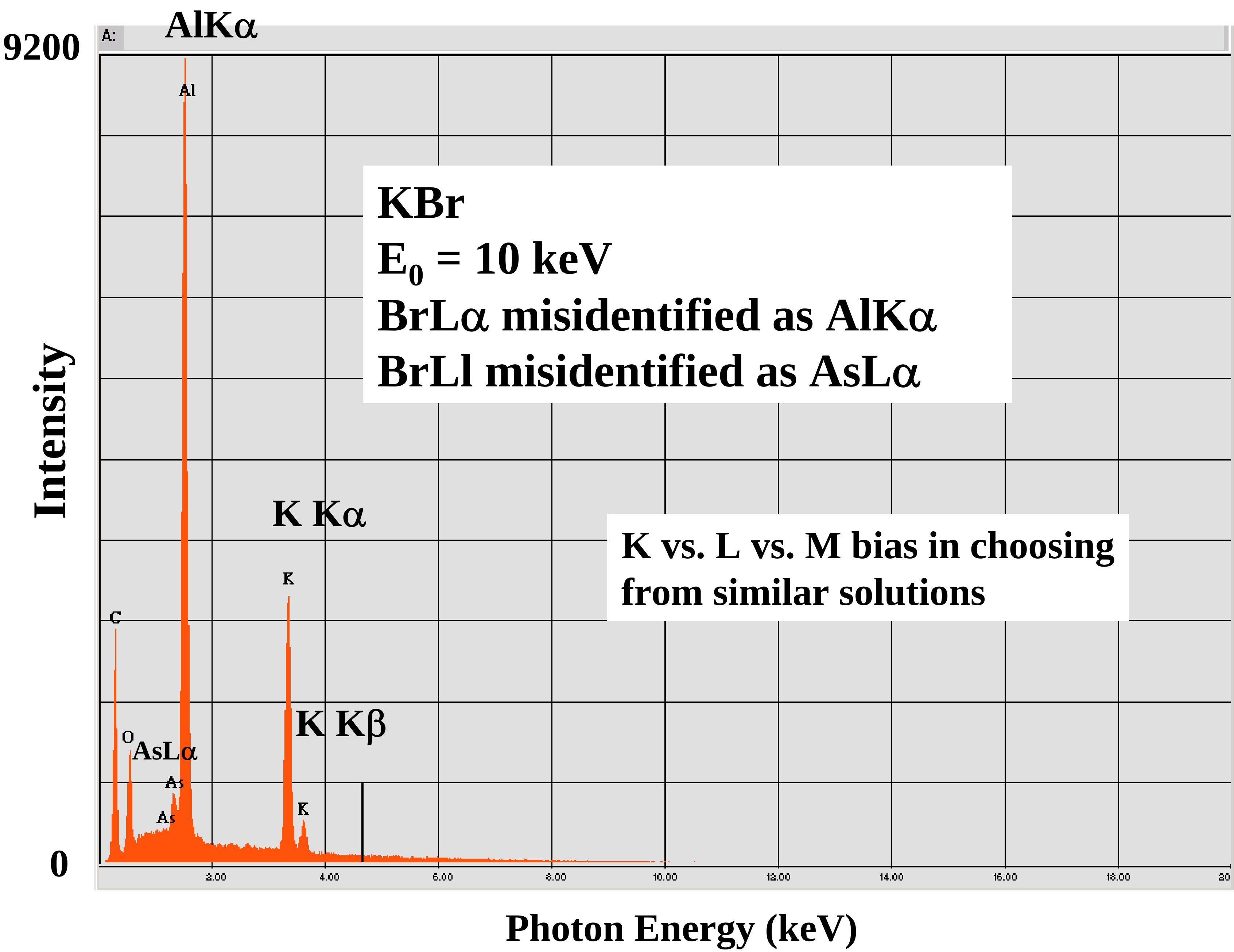
- Test automatic peak ID of commercial systems for the easiest case: **major constituents**
  - **big peaks (high peak-to-background)**
  - **high counting statistics**
  - **no interferences**
  - **simple spectra**
- **Results on Peak ID of major constituents presented at M&M 2004, 2005, and 2006 conferences. Papers published:**
- 1. Dale E. Newbury, "Misidentification of Major Constituents by Automatic Qualitative Energy Dispersive X-ray Microanalysis: A Problem that Threatens the Credibility of the Analytical Community", Microscopy and Microanalysis (2005) 11, 545-561.
- 2. Dale E. Newbury, "Mistakes Encountered during Automatic Peak Identification in Low Beam Energy X-ray Microanalysis," SCANNING, v 29 (2007) 137-151.

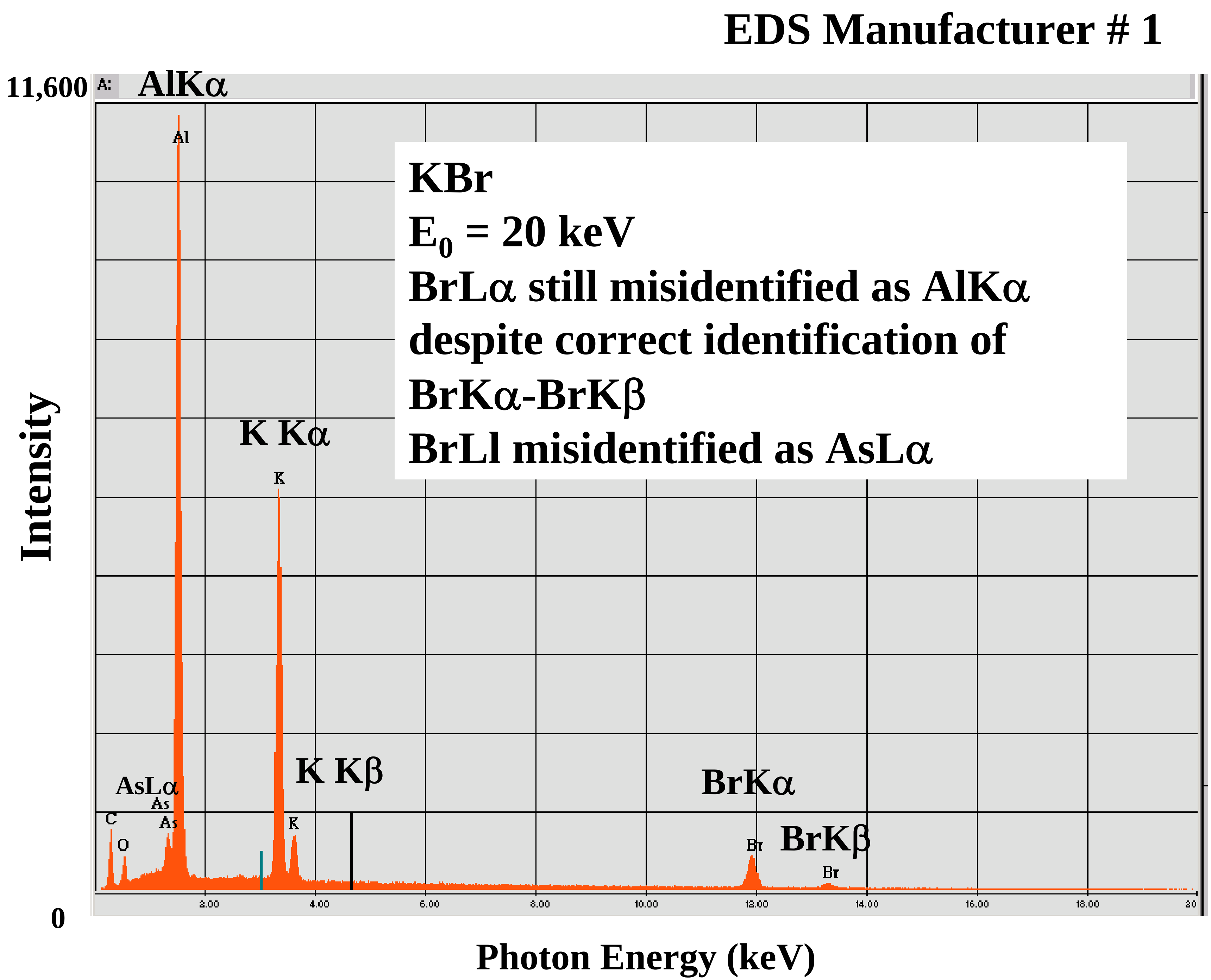
Testing Automatic Peak Identification

Protocol

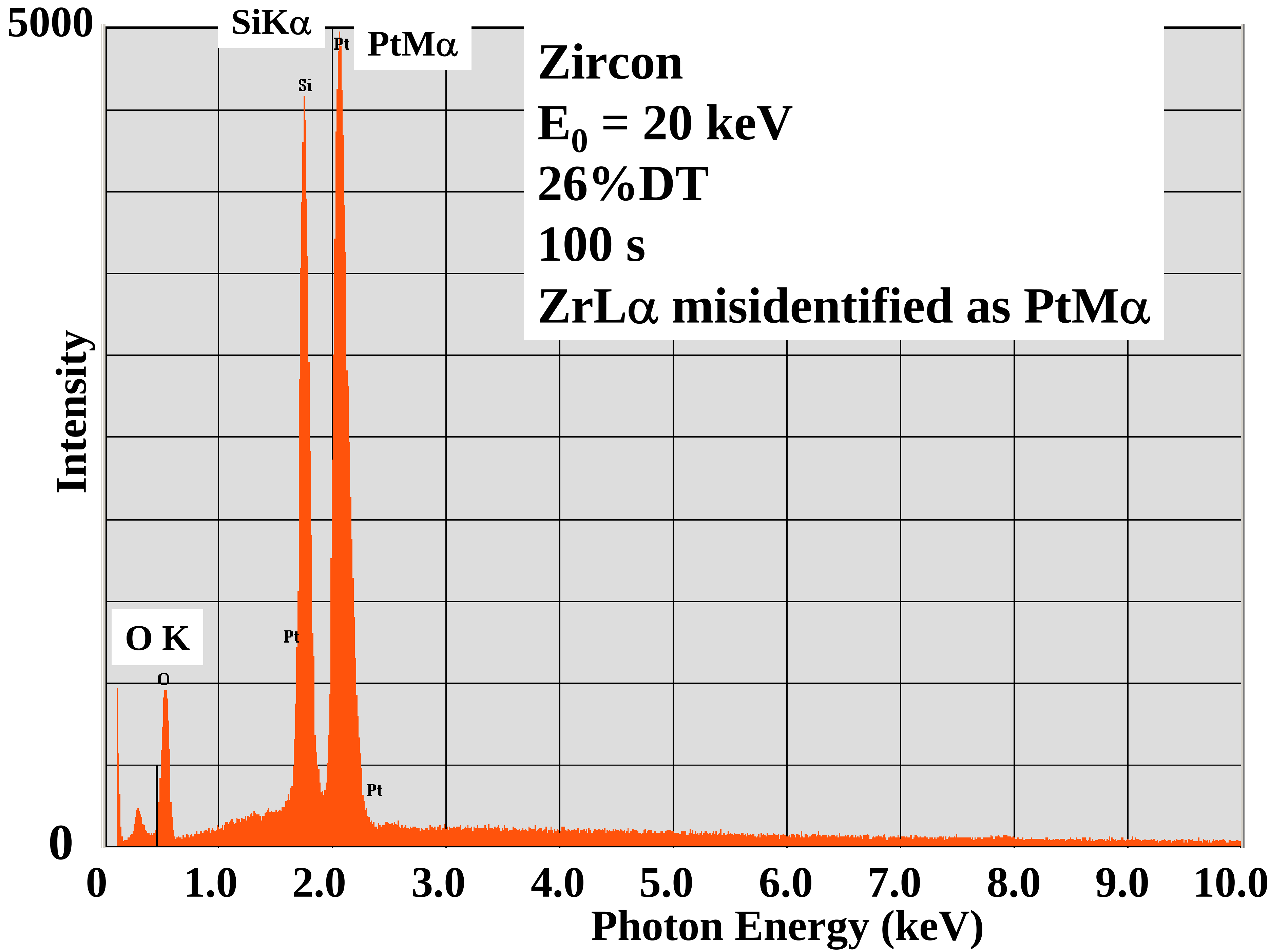
1. Select the pulse processing time constant to operate at optimum resolution for the particular EDS system.
2. Calibrate the EDS system (e.g., CuL and CuKα, preferably AlK and CuKα) and check the peak channel locations of some intermediate peaks, e.g., SiK, CaKα, TiKα, FeKα
3. Select a beam current to keep deadtime below 20%.
4. Obtain at least 1,000 counts in the peak channel for the peaks of interest.

EDS Manufacturer # 1

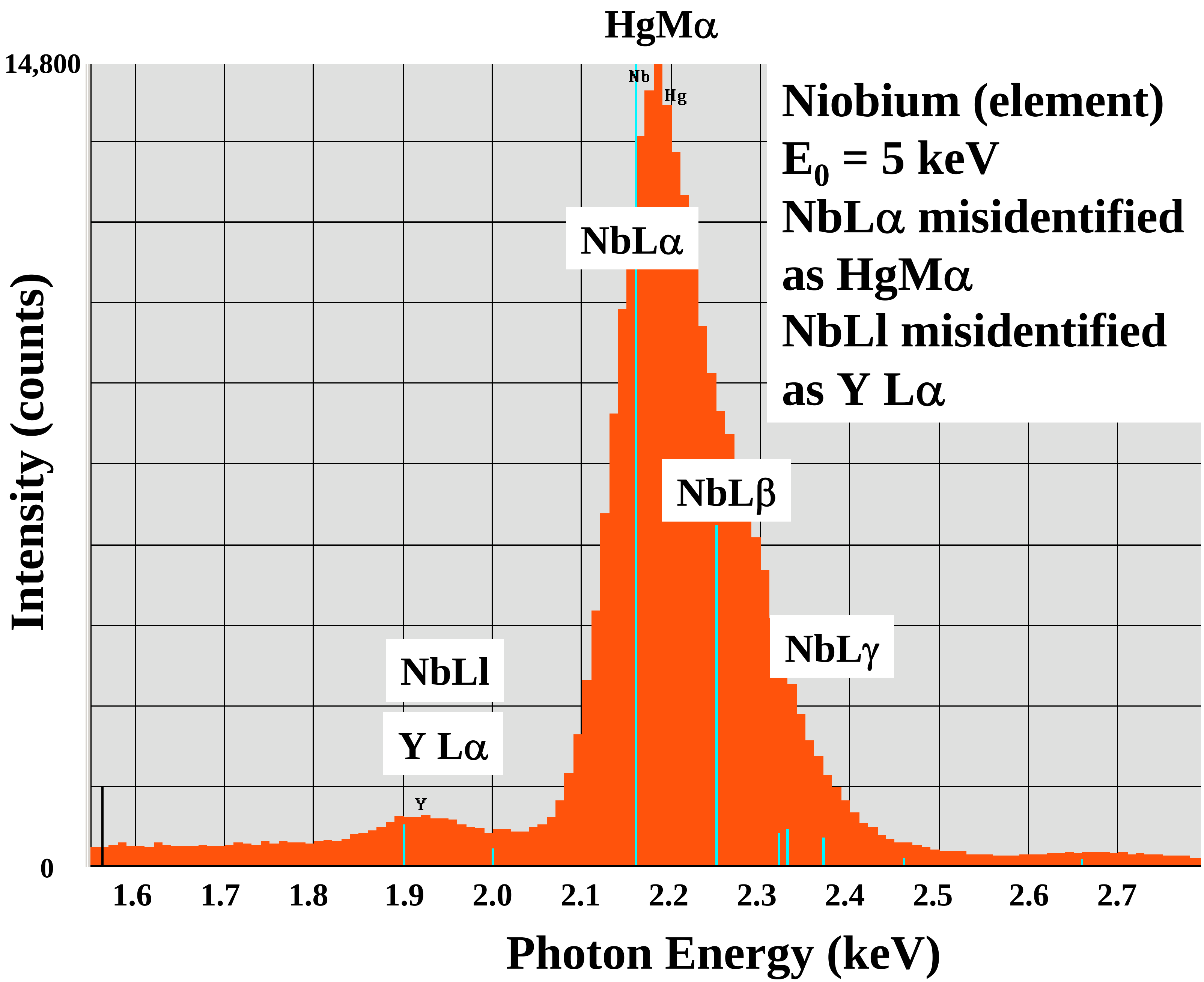




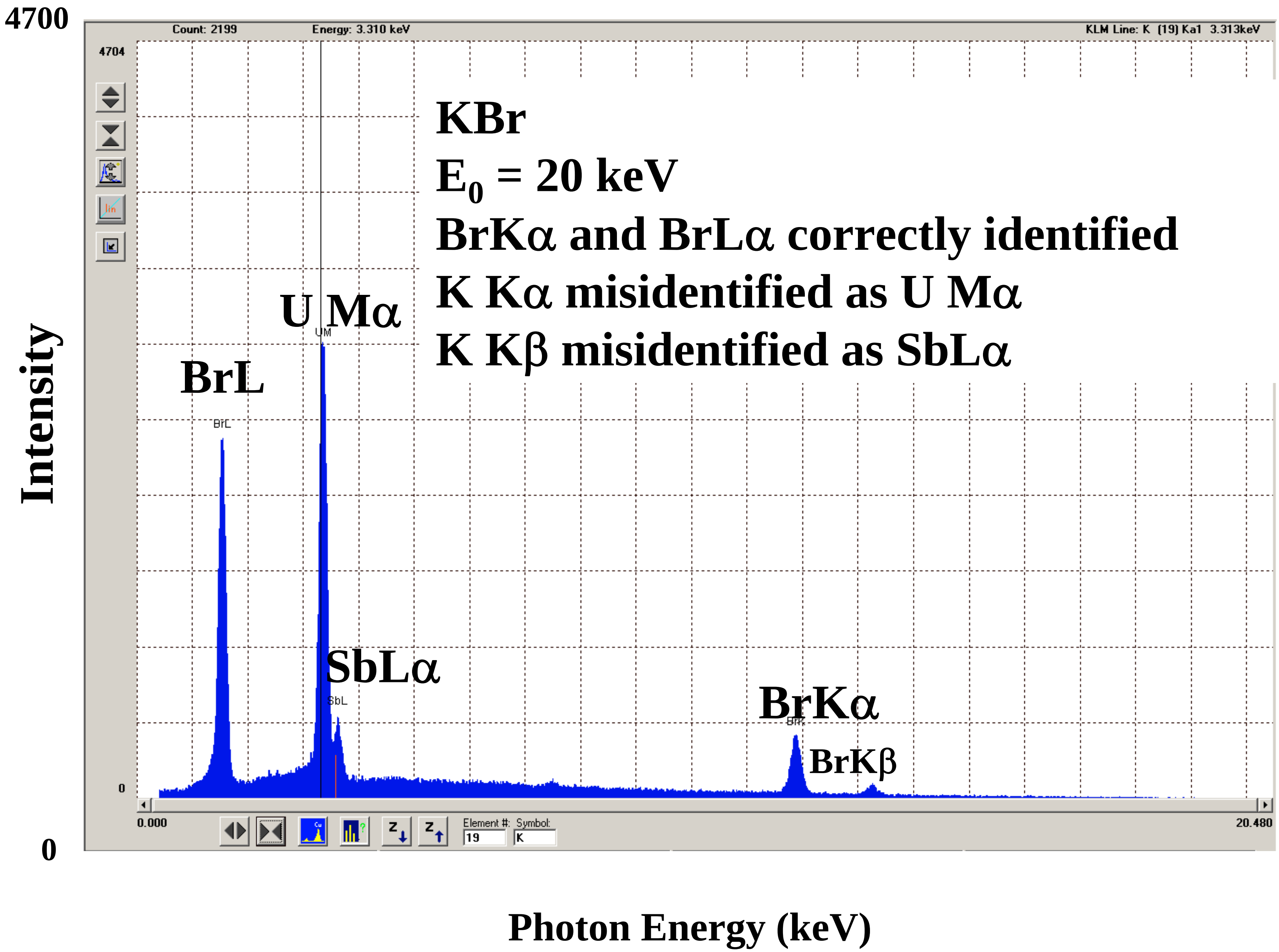
EDS Manufacturer # 1
11,600
A:
AlKα
Al
KBr
E₀ = 20 keV
BrLα still misidentified as AlKα
despite correct identification of
BrKα-BrKβ
BrLl misidentified as AsLα
K Kα
K
K Kβ
K
AsLα
As
As
C
O
BrKα
Br
BrKβ
Br
Intensity
0
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20
Photon Energy (keV)



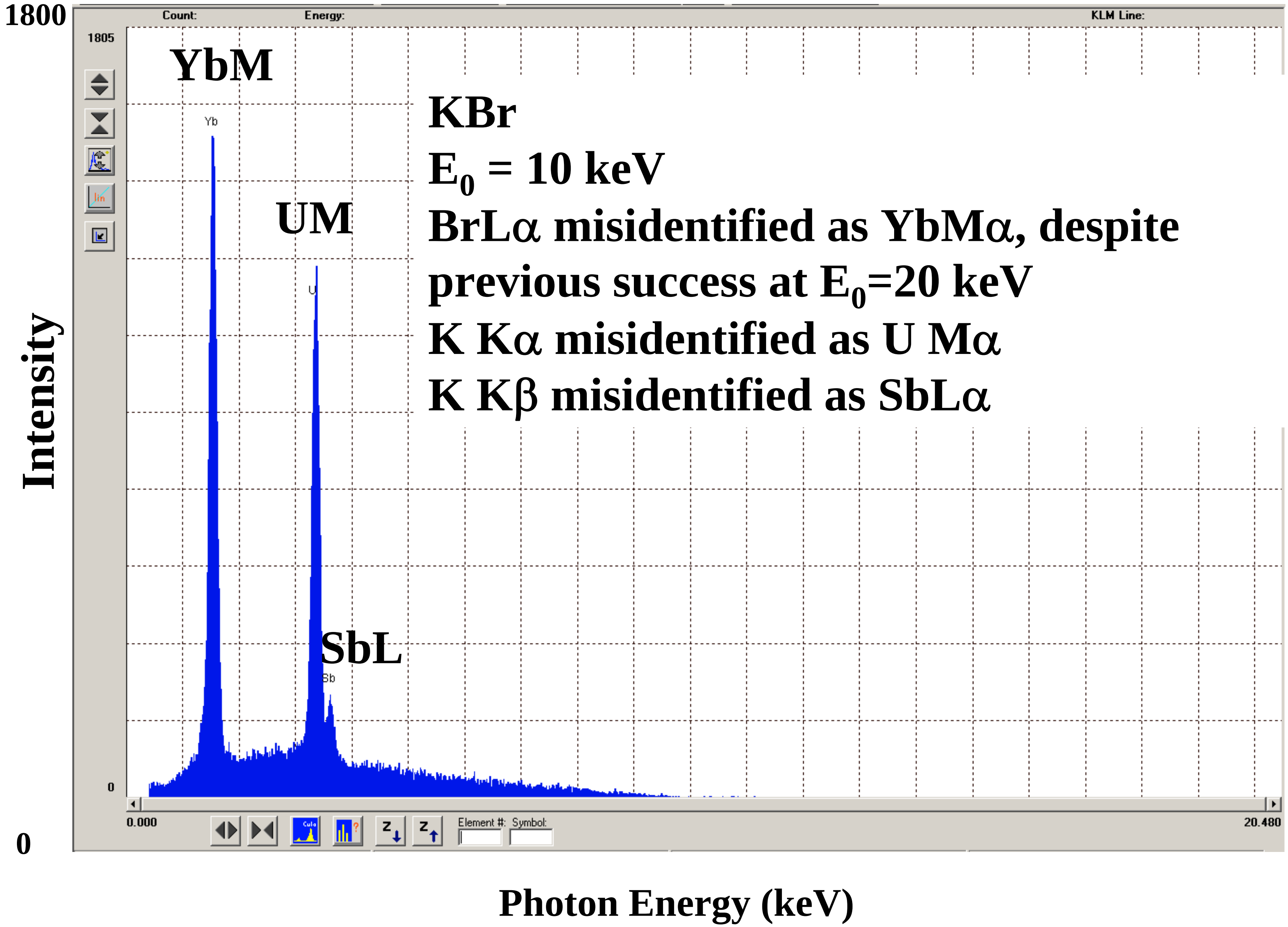
5000
0
SiKα
PtMα
Si
Pt
Zircon
E0 = 20 keV
26%DT
100 s
ZrLα misidentified as PtMα
O K
O
Pt
Pt
Intensity
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
Photon Energy (keV)


HgMα
14,800
0
Nb
Hg
Niobium (element)
E_0 = 5 keV
NbLα misidentified
as HgMα
NbLl misidentified
as Y Lα
NbLα
NbLβ
NbLγ
NbLl
Y Lα
Y
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
Intensity (counts)
Photon Energy (keV)

EDS Manufacturer # 2



EDS Manufacturer # 2



KBr

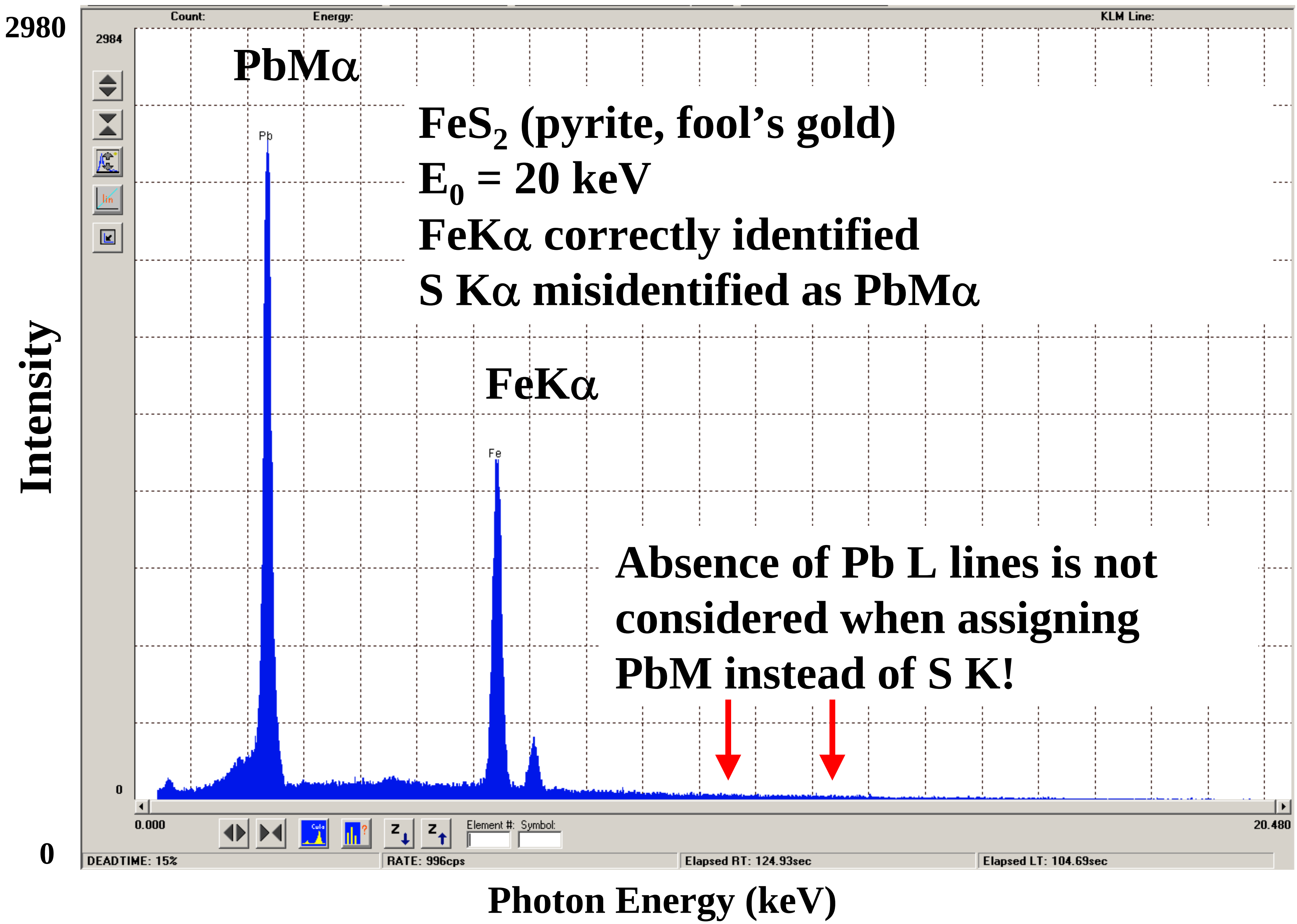
E_0 = 10 keV

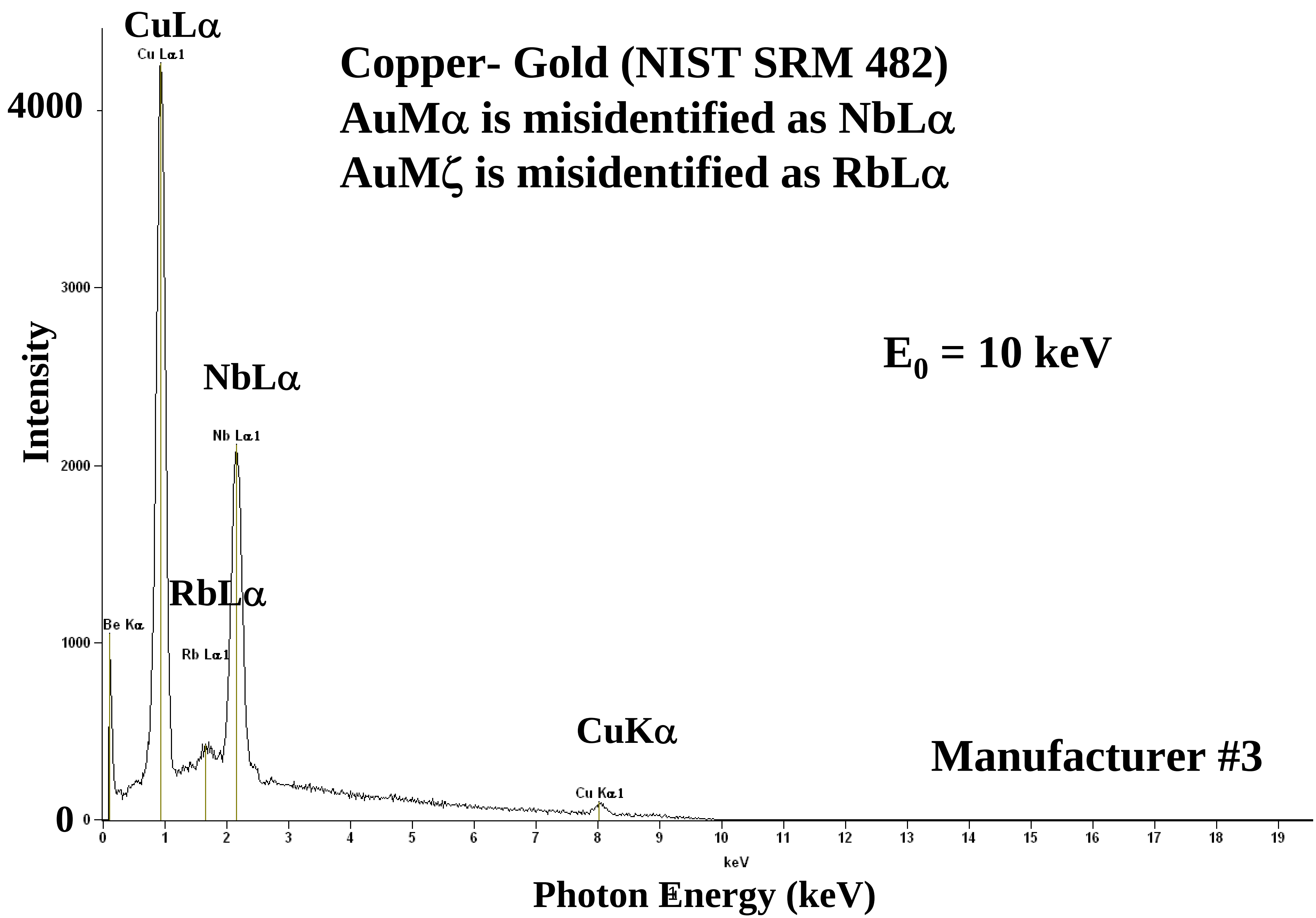
BrLα misidentified as YbMα, despite previous success at E_0=20 keV

K Kα misidentified as U Mα

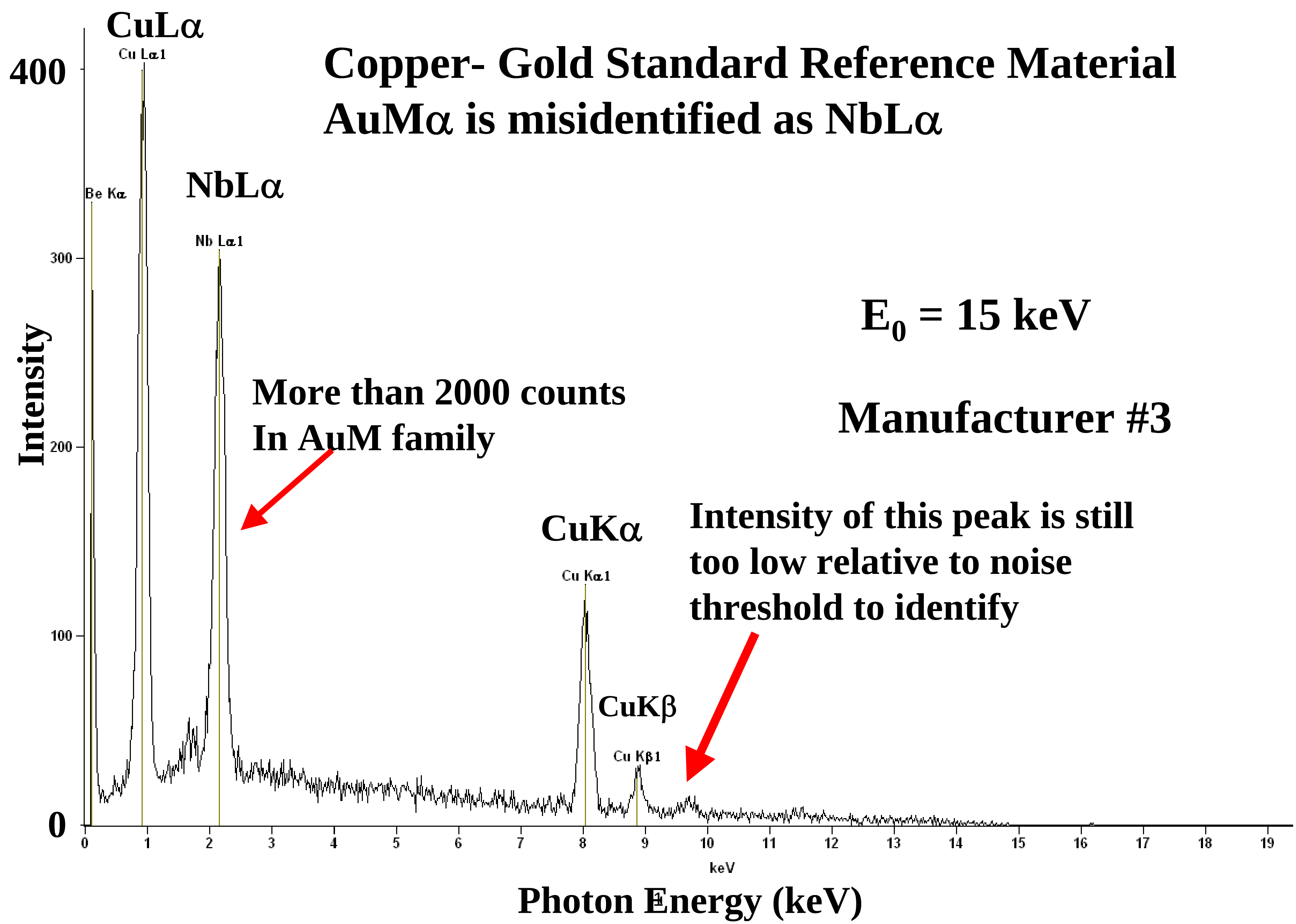
K Kβ misidentified as SbLα

EDS Manufacturer # 2





Copper- Gold (NIST SRM 482)
AuMα is misidentified as NbLα
AuMζ is misidentified as RbLα
E0 = 10 keV
Manufacturer #3
CuLα
Cu Lα1
NbLα
Nb Lα1
RbLα
Rb Lα1
Be Kα
CuKα
Cu Kα1
Intensity
4000
3000
2000
1000
0
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
keV
Photon Energy (keV)

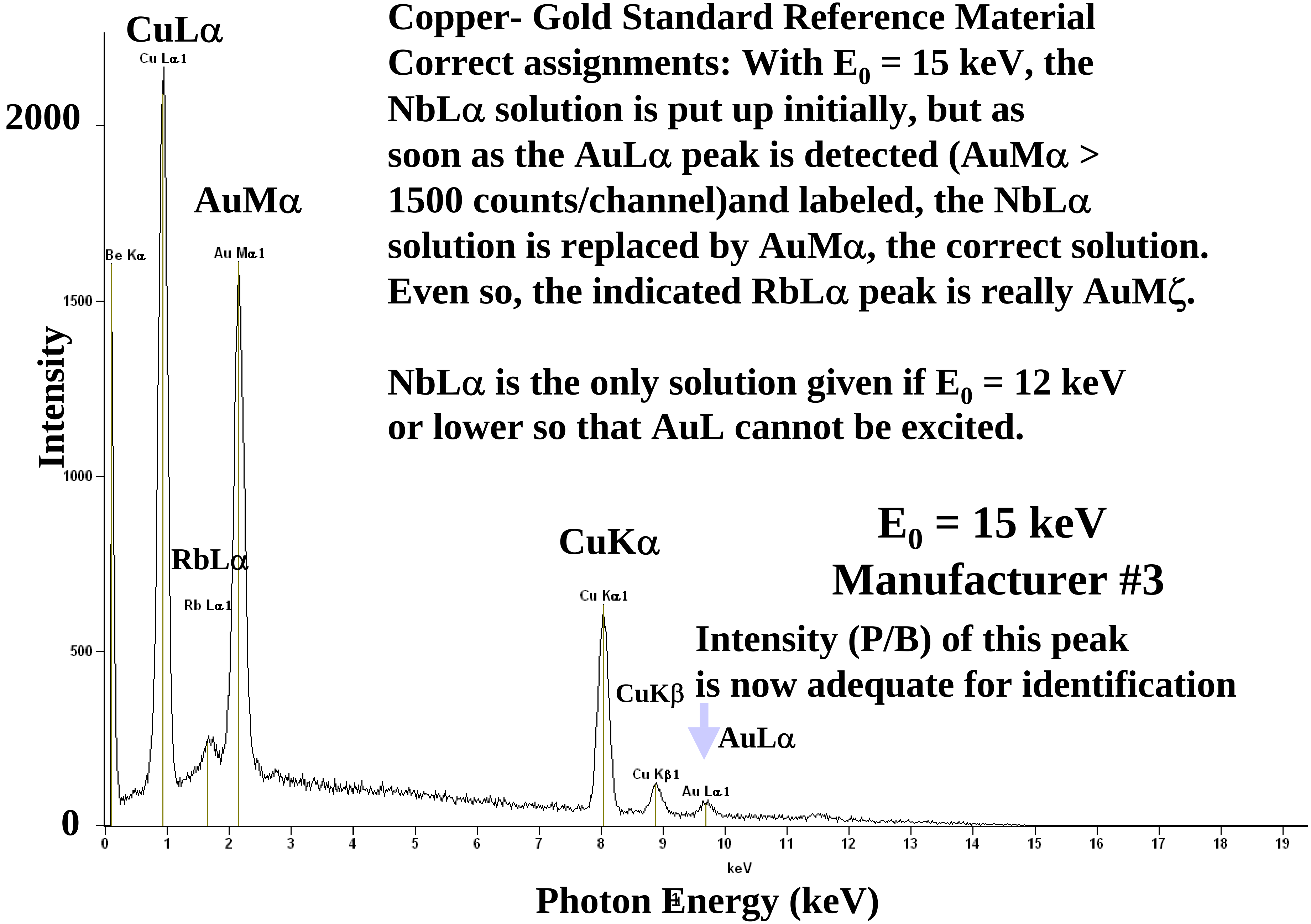


Copper- Gold Standard Reference Material
AuMα is misidentified as NbLα
CuLα
Cu Lα1
400
Be Kα
NbLα
Nb Lα1
300
200
100
0
Intensity
E0 = 15 keV
Manufacturer #3
More than 2000 counts
In AuM family
CuKα
Cu Kα1
Intensity of this peak is still
too low relative to noise
threshold to identify
CuKβ
Cu Kβ1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
keV
Photon Energy (keV)

Copper- Gold Standard Reference Material

Correct assignments: With E_0 = 15 keV, the NbLα solution is put up initially, but as soon as the AuLα peak is detected (AuMα > 1500 counts/channel)and labeled, the NbLα solution is replaced by AuMα, the correct solution. Even so, the indicated RbLα peak is really AuMζ.

NbLα is the only solution given if E_0 = 12 keV or lower so that AuL cannot be excited.



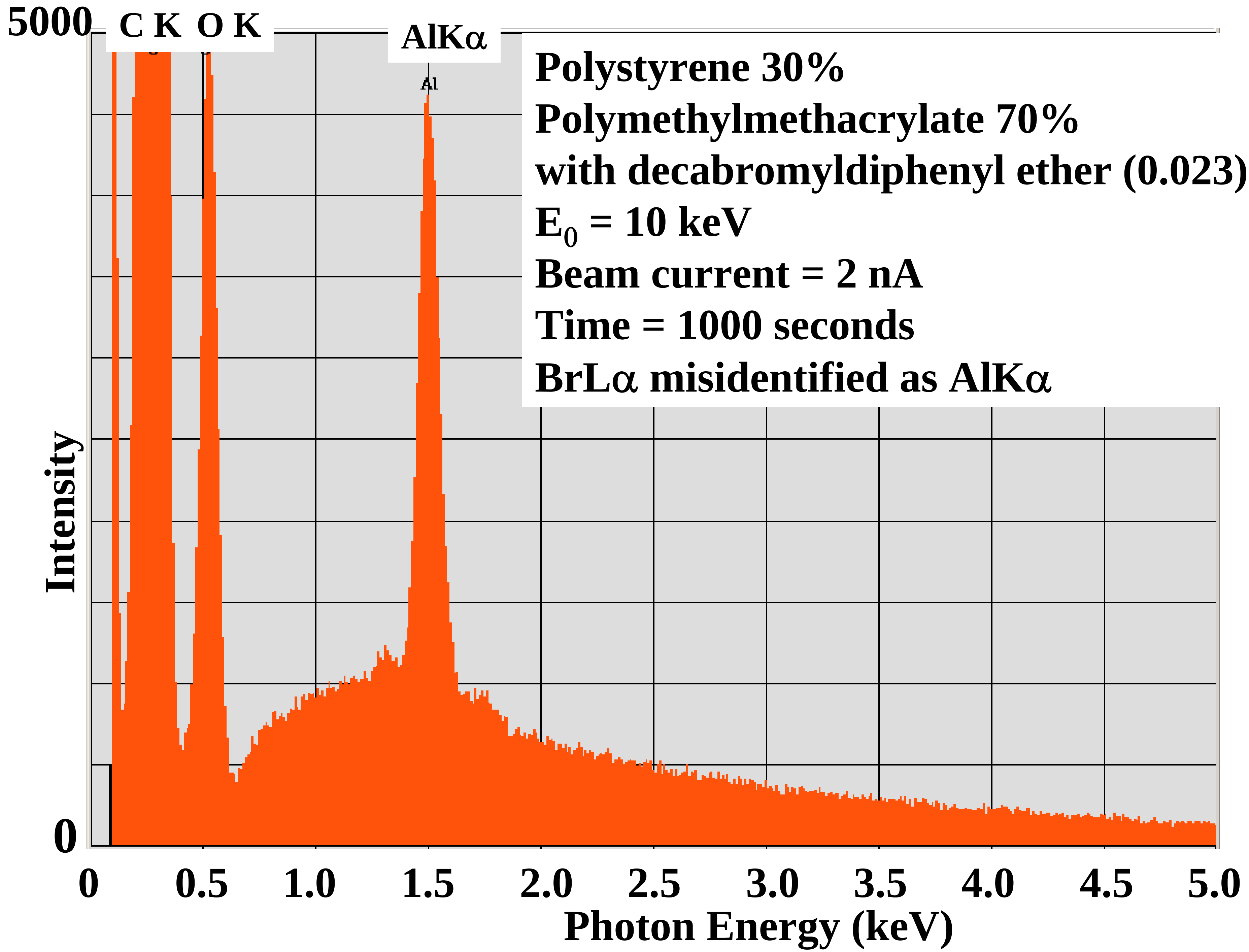
Possible Troublemakers
(Closely spaced K-L-M peaks; not necessarily a complete list!)

- **0.390-0.395 keV** — **N K (0.392); ScLα (0.395)**
- **0.510-0.525 keV** — **O K (0.523); V Lα (0.511)**
- **0.670-0.710 keV** — **F K (0.677); FeLα (0.705)**
- **0.845-0.855 keV** — **NeKα (0.848); NiLα (0.851)**
- **1.00-1.05 keV** — **NaKα (1.041); ZnLα (1.012); PmMα (1.032)**
- **1.20-1.30 keV** — **MgKα (1.253); AsLα (1.282); TbMα (1.246)**
- **1.45-1.55 keV** — **AlKα (1.487); BrLα (1.480); YbMα (1.521)**
- **1.70-1.80 keV** — **SiKα (1.740); TaMα (1.709); W Mα (1.774)**
- **2.00-2.05 keV** — **PKα (2.013); ZrLα (2.042); PtMα (2.048)**
- **2.10-2.20 keV** — **NbLα (2.166); AuMα (2.120); HgMα (2.191)**
- **2.28-2.35 keV** — **S Kα (2.307); MoLα (2.293); PbMα (2.342)**
- **2.40-2.45 keV** — **TcLα (2.424); BiMα (2.419)**
- **2.60-2.70 keV** — **ClKα (2.621); RhLα (2.696)**
- **2.95-3.00 keV** — **ArKα (2.956); AgLα (2.983); ThMα_1 (2.996)**
- **3.10-3.20 keV** — **CdLα (3.132); U Mα_1 (3.170)**
- **3.25-3.35 keV** — **K Kα (3.312); InLα (3.285); U Mβ (3.336)**
- **4.45-4.55 keV** — **TiKα (4.510); BaLα (4.467)**
- **4.90-5.00 keV** — **TiKβ (4.931); V Kα (4.949)**

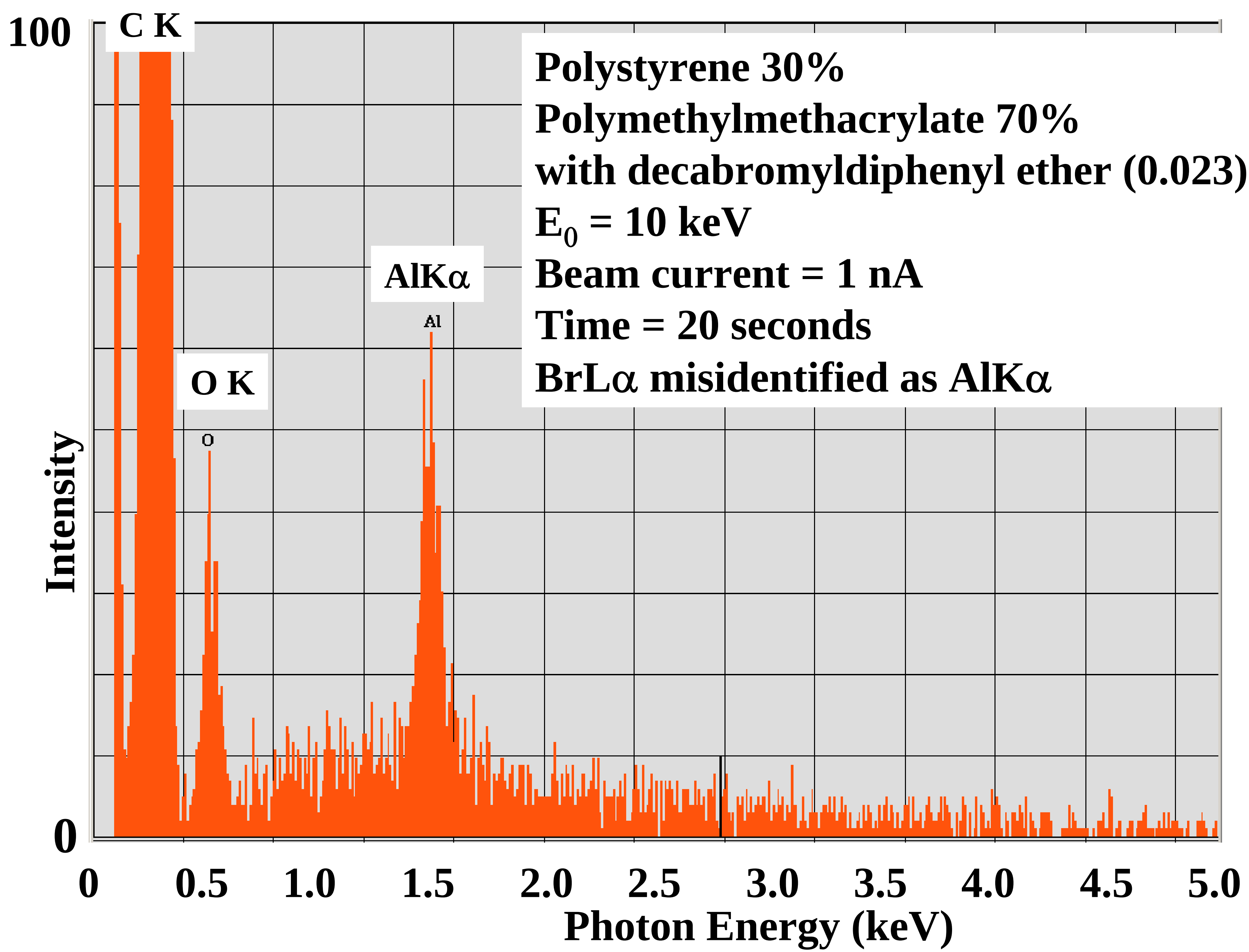
Directly observed

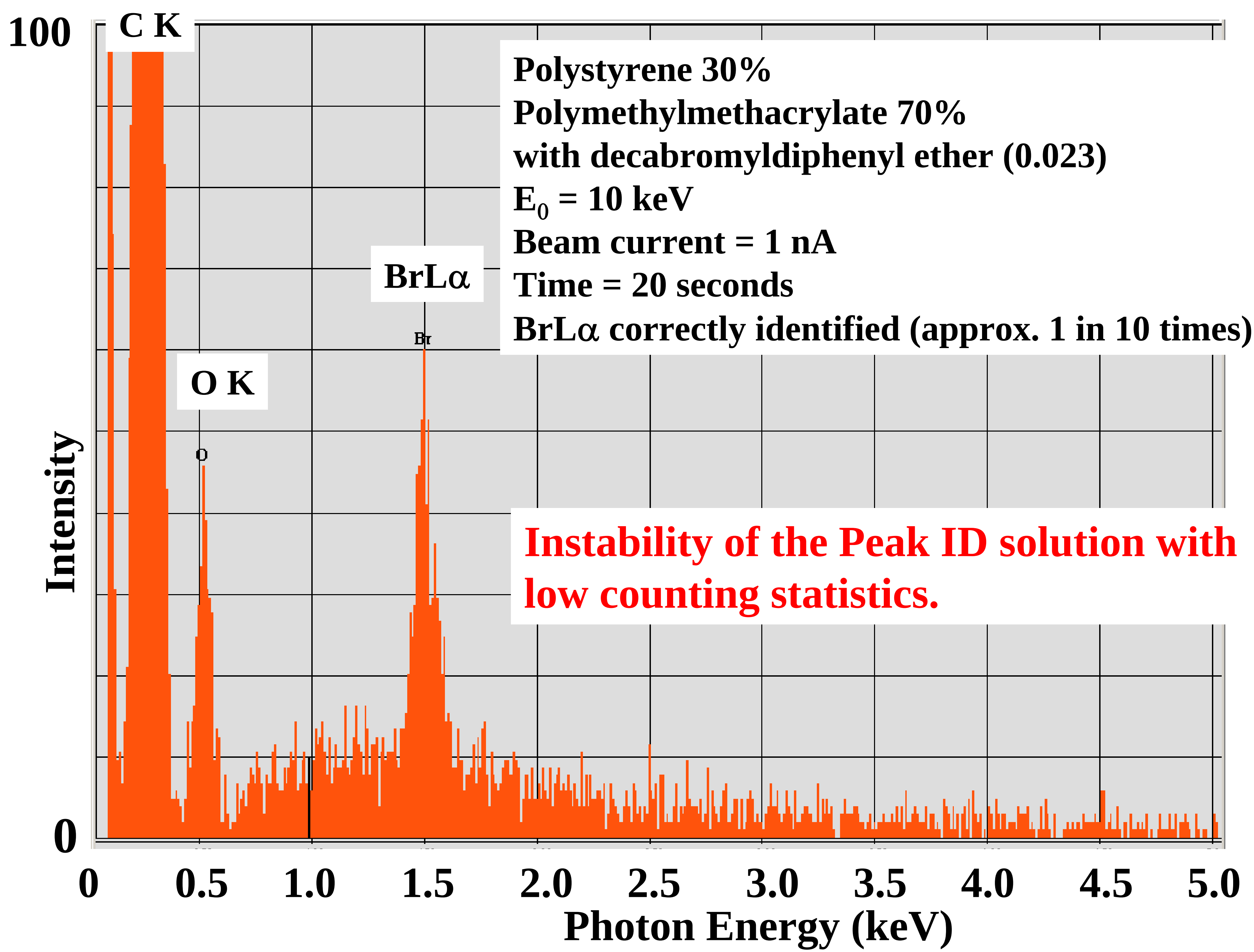
Peak ID for Minor ($0.01 \leq C \leq 0.1$ mass fraction) and Trace ($C < 0.01$ mass fraction) Constituents

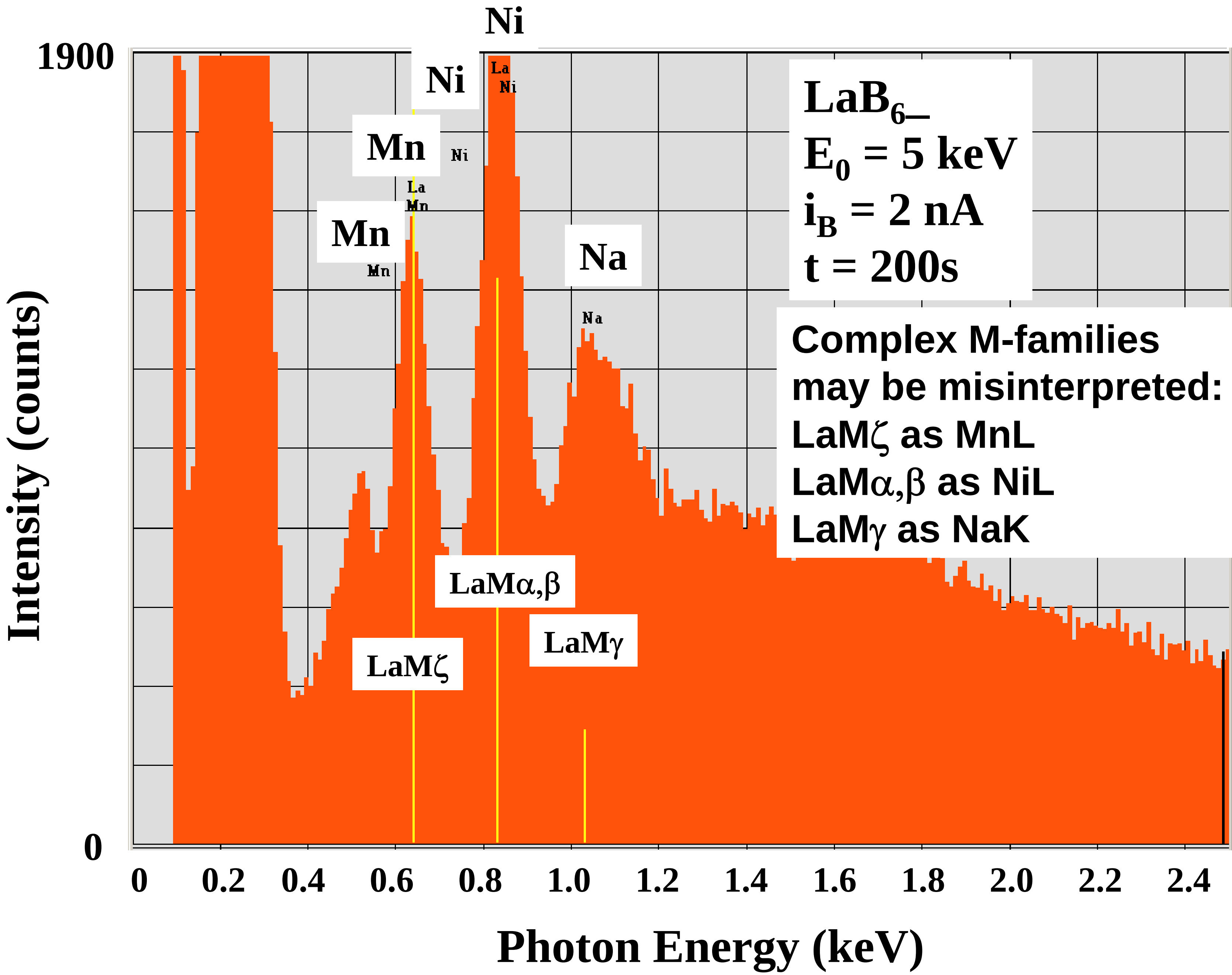
- Things only get worse because of lower peak-to-background
- Round up the usual suspects (Table)
- Additional problems are found that lead to false positives
  - Not recognizing minor family members, Ll, M_2N_4
  - Ignoring M-family solution (despite having data!)
  - Escape and sum peaks misinterpreted



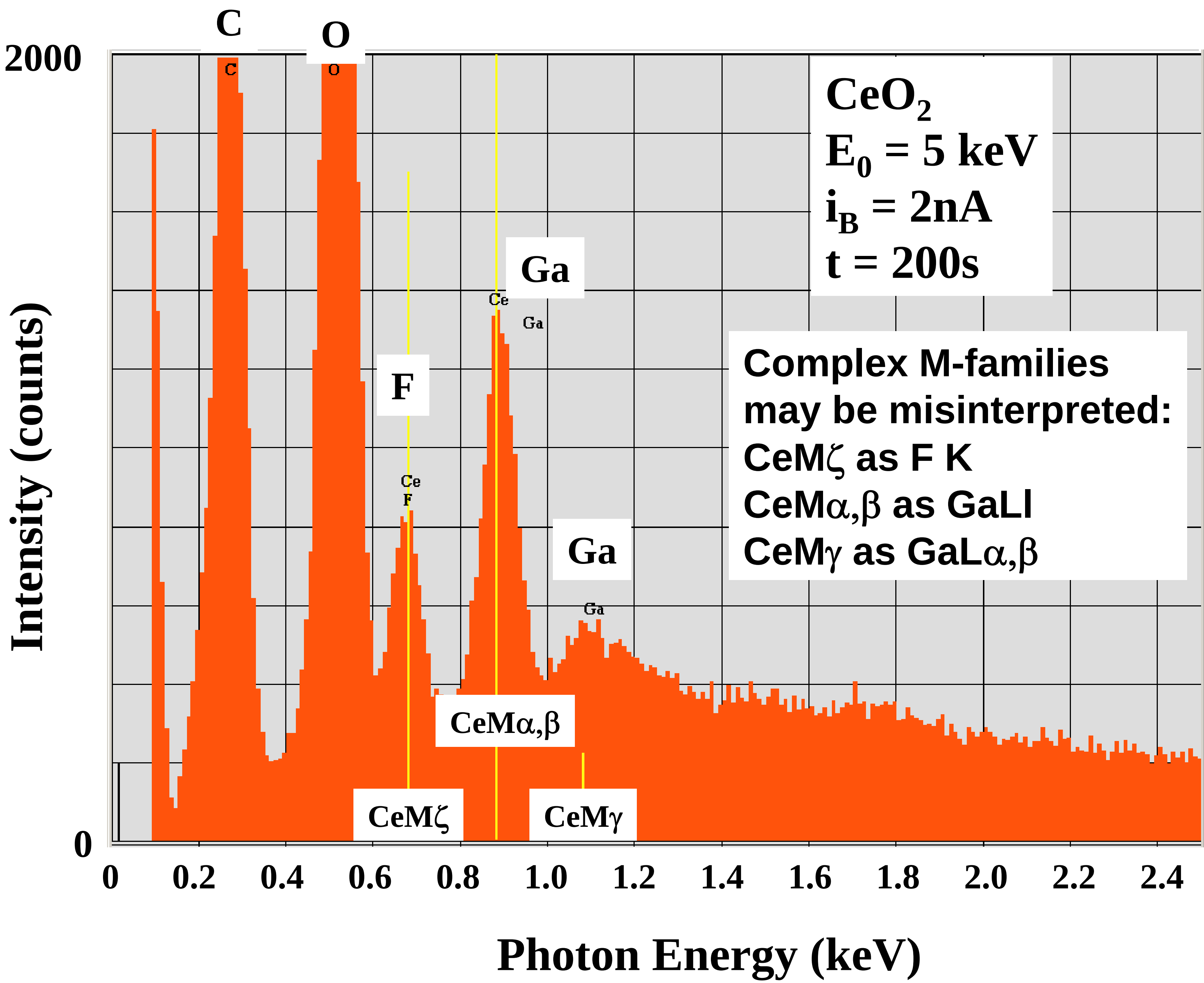
5000
0
C K
O K
AlKα
Al
Polystyrene 30%
Polymethylmethacrylate 70%
with decabromyldiphenyl ether (0.023)
E_0 = 10 keV
Beam current = 2 nA
Time = 1000 seconds
BrLα misidentified as AlKα
Intensity
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Photon Energy (keV)


Polystyrene 30%
Polymethylmethacrylate 70%
with decabromyldiphenyl ether (0.023)
E_0 = 10 keV
Beam current = 1 nA
Time = 20 seconds
BrLα misidentified as AlKα
C K
O K
AlKα
O
Al
100
0
Intensity
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
Photon Energy (keV)


100
C K
Polystyrene 30%
Polymethylmethacrylate 70%
with decabromyldiphenyl ether (0.023)
E0 = 10 keV
Beam current = 1 nA
Time = 20 seconds
BrLα correctly identified (approx. 1 in 10 times)
BrLα
Br
O K
O
Intensity
Instability of the Peak ID solution with low counting statistics.
0
0 0.5 1.0 1.5 2.0 2.5 3.0 3.5 4.0 4.5 5.0
Photon Energy (keV)

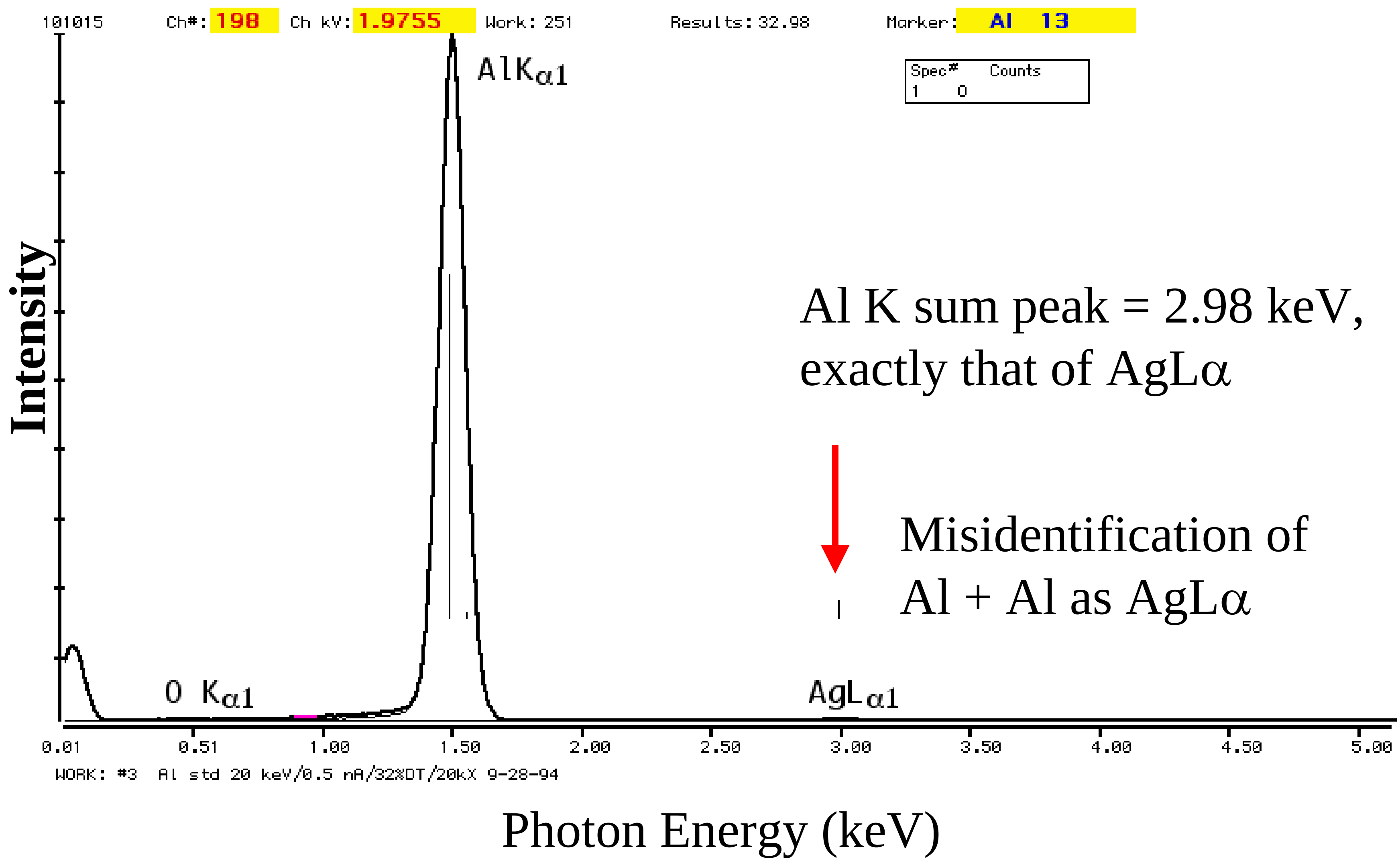


1900
0
Intensity (counts)
Ni
Ni
Mn
Mn
Na
La
Ni
Ni
La
Mn
Mn
Na
LaB6
E0 = 5 keV
iB = 2 nA
t = 200s
Complex M-families may be misinterpreted:
LaMζ as MnL
LaMα,β as NiL
LaMγ as NaK
LaMα,β
LaMγ
LaMζ
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4
Photon Energy (keV)

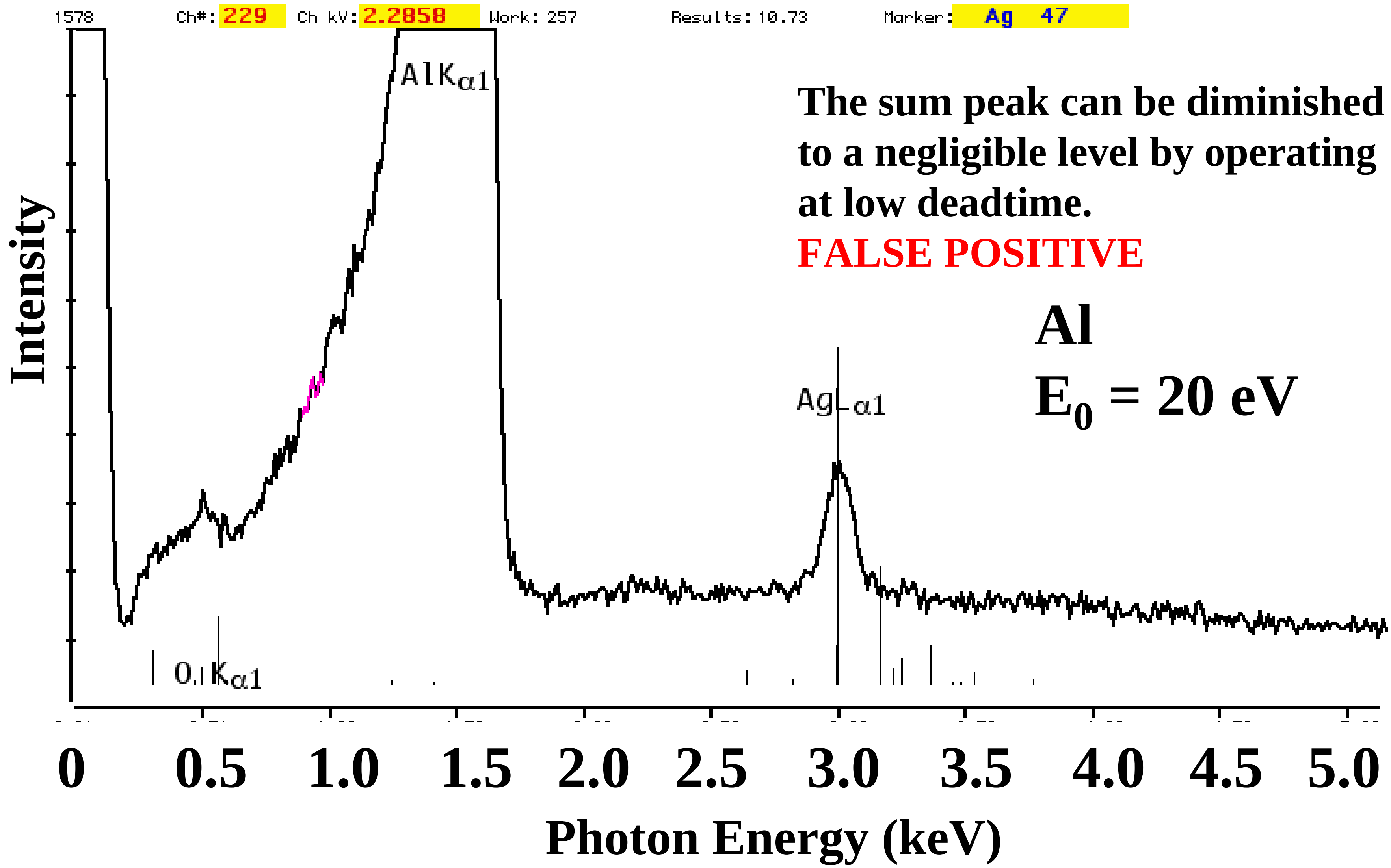


C
O
2000
0
CeO$_2$
E_0 = 5 keV
i_B = 2nA
t = 200s
Ga
Ce
Ga
F
Ce
F
Ga
Ga
Complex M-families may be misinterpreted:
CeMζ as F K
CeMα,β as GaLl
CeMγ as GaLα,β
CeMα,β
CeMζ
CeMγ
Intensity (counts)
0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4
Photon Energy (keV)

Incorrect identification of sum peak by automatic qualitative analysis



Incorrect identification of sum peak by automatic qualitative analysis

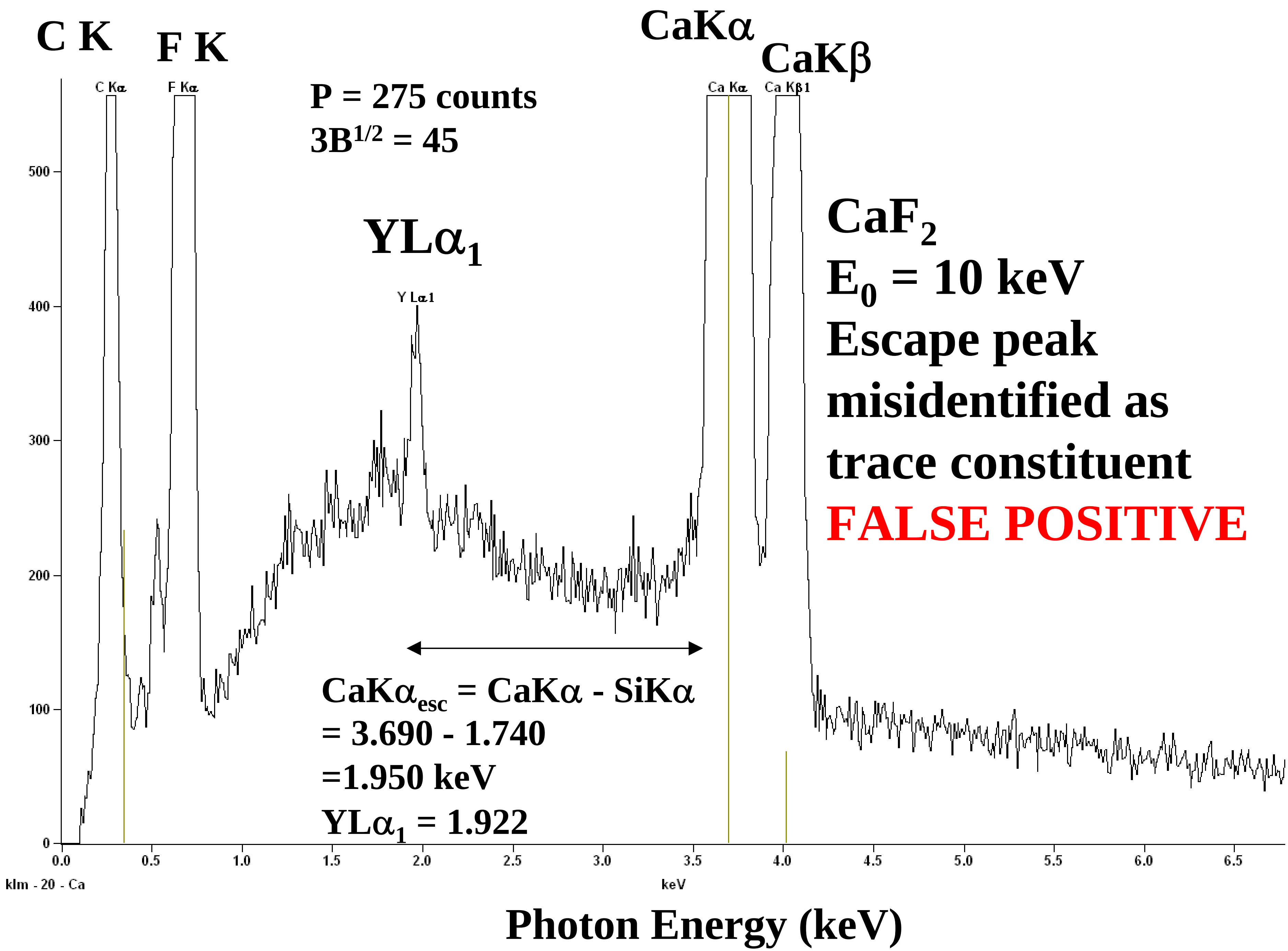


The sum peak can be diminished to a negligible level by operating at low deadtime.

FALSE POSITIVE

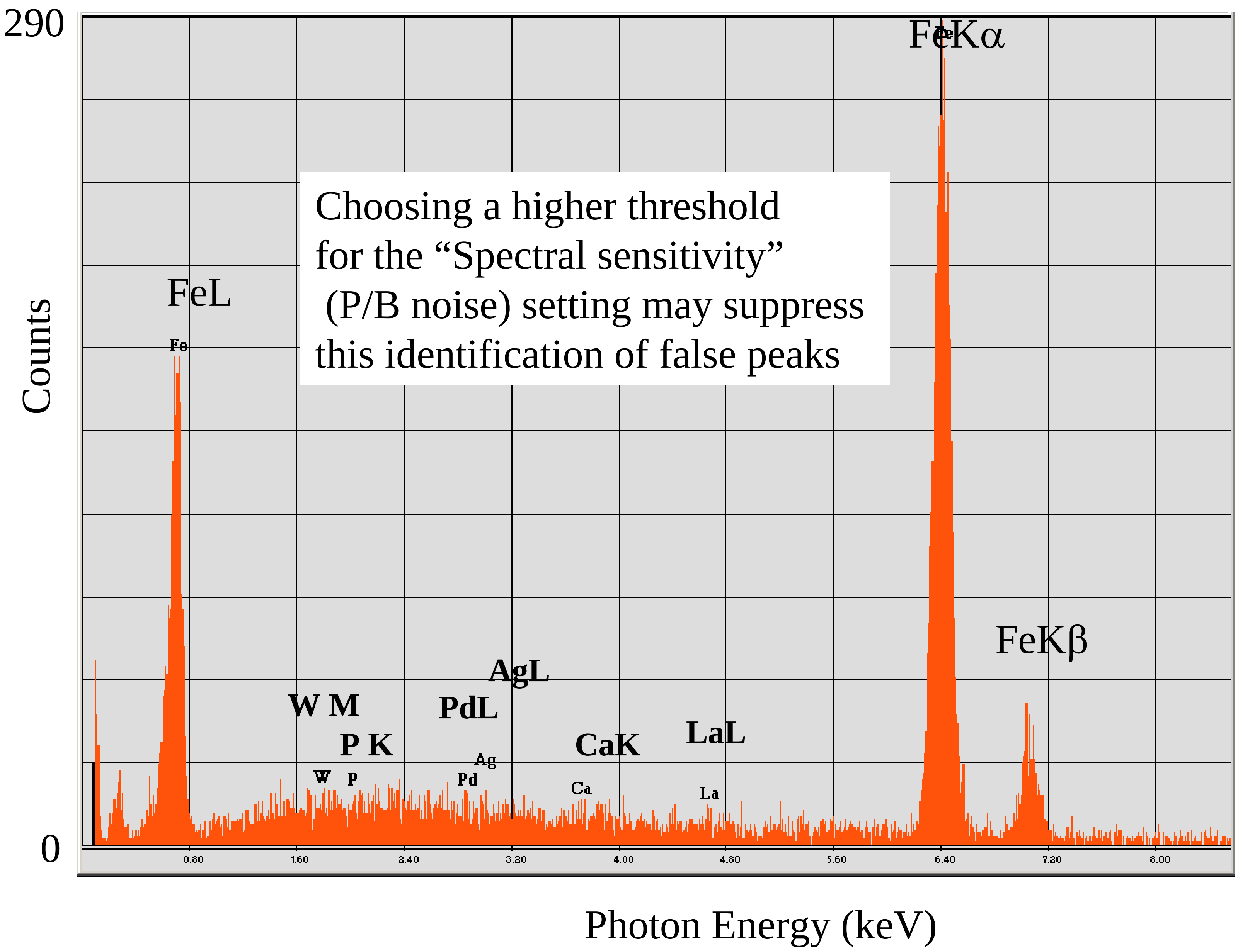
Al

E_0 = 20 eV

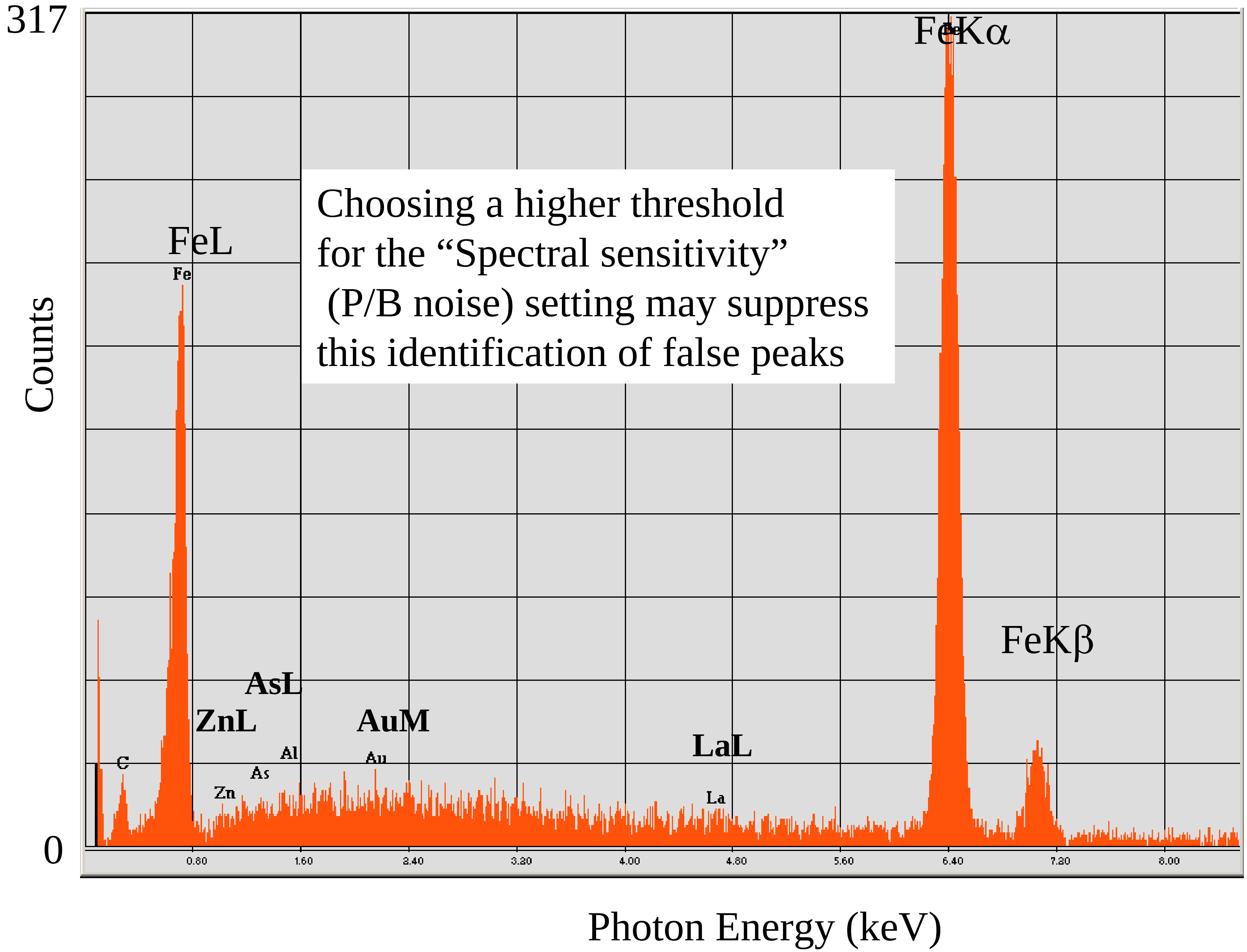


C K
F K
CaKα
CaKβ
C Kα
F Kα
Ca Kα
Ca Kβ1
P = 275 counts
3B^1/2 = 45
YLα1
Y Lα1
CaF2
E0 = 10 keV
Escape peak
misidentified as
trace constituent
FALSE POSITIVE
CaKαesc = CaKα - SiKα
= 3.690 - 1.740
=1.950 keV
YLα1 = 1.922
0
100
200
300
400
500
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
klm - 20 - Ca
keV
Photon Energy (keV)

Sensitivity to False Peaks: Unstable Solution Changes with Time



Sensitivity to False Peaks: Unstable Solution Changes with Time



Choosing a higher threshold for the "Spectral sensitivity" (P/B noise) setting may suppress this identification of false peaks

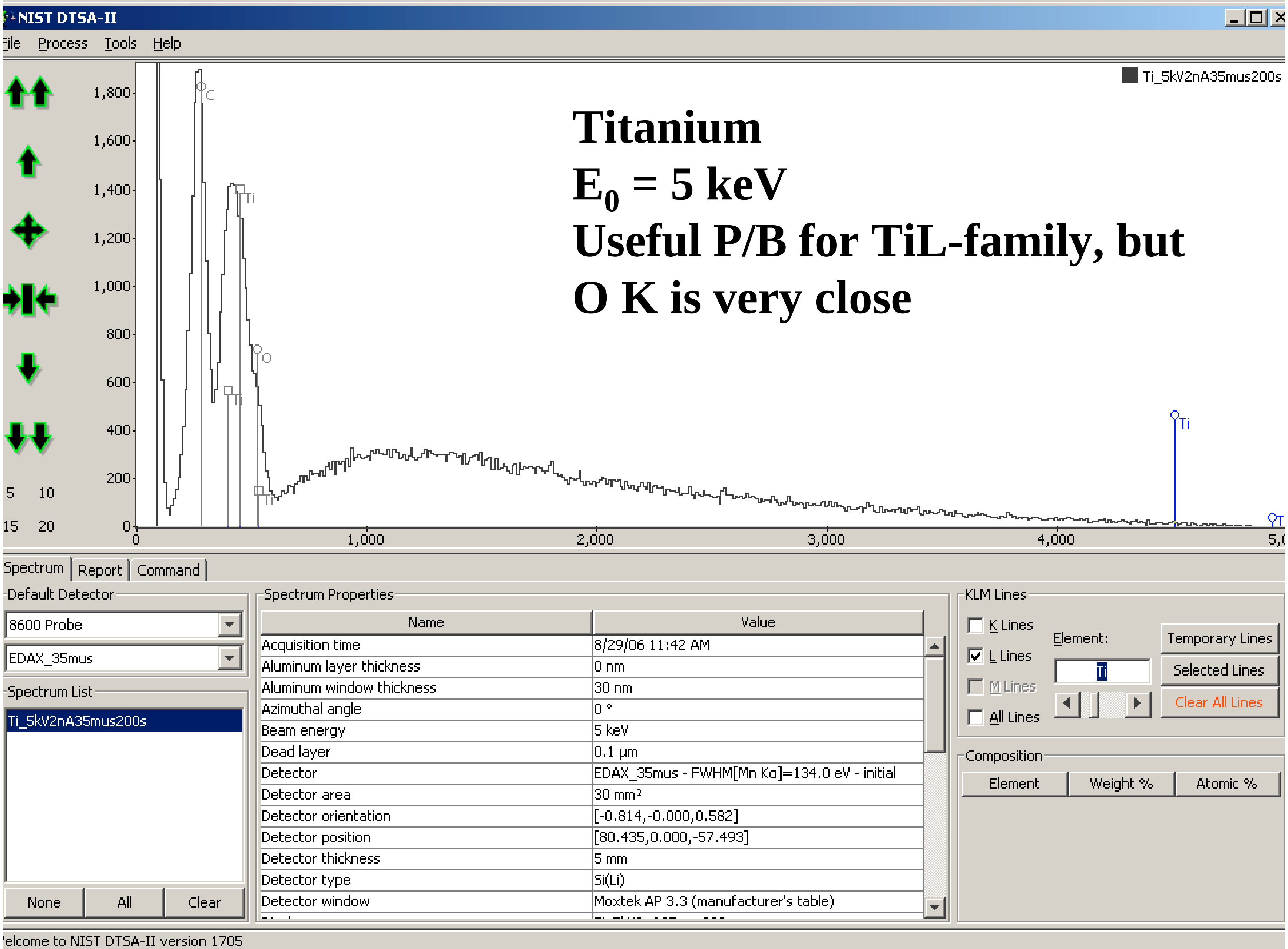
Peak ID for Low Voltage Microanalysis ($E_0 \leq 5$ keV)

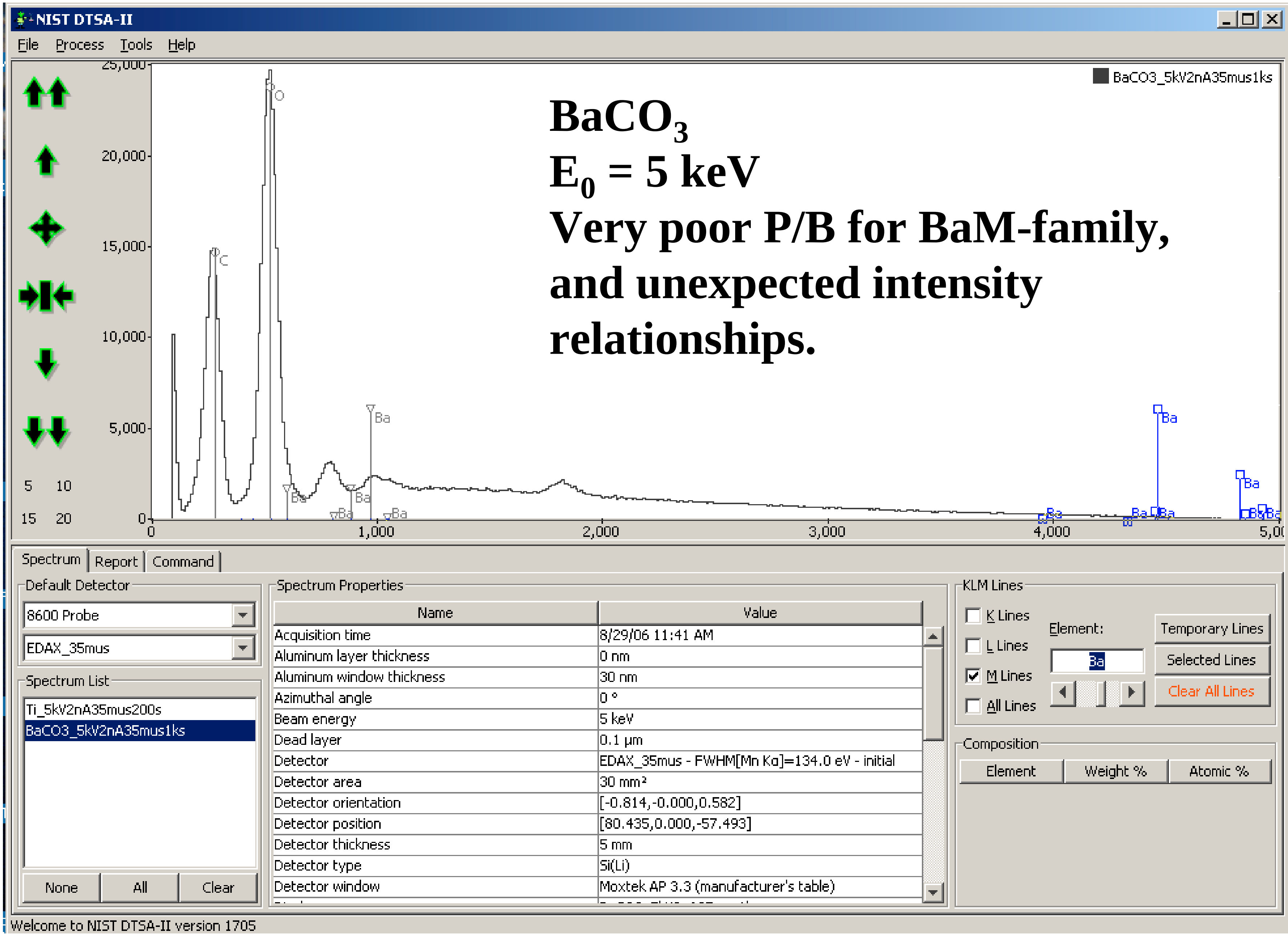
- E_0 = 5 keV is the lowest energy for which the entire Periodic Table (except H, He, Li) is accessible by EDS, although some elements are just barely detectable, e.g., Cs, Ba
- Operating with LVSEM conditions ($E_0 \leq 5$ keV) eliminates K- and L- shell information critical for robust peak ID obtained from peaks with photon energies > 5 keV.
- Unfamiliar L- and M- shells must be used instead.
- The fluorescence yield of these low photon energy L- and M- shell peaks is often very low, resulting in low P/B, even from pure elements
- The intensity relationships among family members may behave in unexpected ways.
- As E_0 is reduced below 5 keV, significant portions of the Periodic Table become inaccessible by EDS, even for pure elements

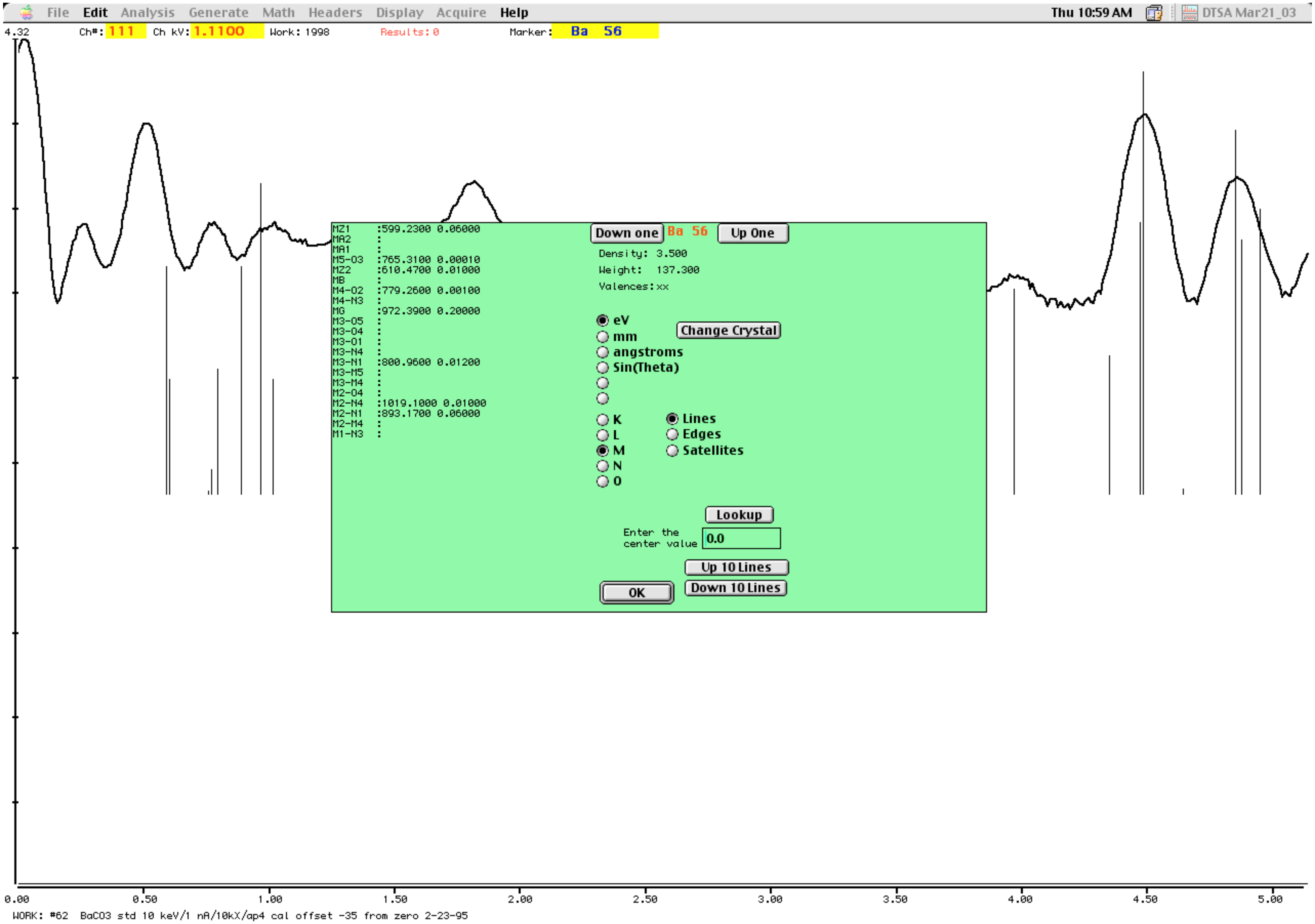
Titanium

E_0 = 5 keV

Useful P/B for TiL-family, but O K is very close




NIST DTSA-II
File Process Tools Help
BaCO3_5kV2nA35mus1ks
BaCO3
E0 = 5 keV
Very poor P/B for BaM-family,
and unexpected intensity
relationships.
25,000
20,000
15,000
10,000
5,000
0
1,000
2,000
3,000
4,000
O
C
Ba
Spectrum
Report
Command
Default Detector
8600 Probe
EDAX_35mus
Spectrum List
Ti_5kV2nA35mus200s
BaCO3_5kV2nA35mus1ks
None
All
Clear
Spectrum Properties
Name
Value
Acquisition time
8/29/06 11:41 AM
Aluminum layer thickness
0 nm
Aluminum window thickness
30 nm
Azimuthal angle
0 °
Beam energy
5 keV
Dead layer
0.1 µm
Detector
EDAX_35mus - FWHM[Mn Kα]=134.0 eV - initial
Detector area
30 mm²
Detector orientation
[-0.814,-0.000,0.582]
Detector position
[80.435,0.000,-57.493]
Detector thickness
5 mm
Detector type
Si(Li)
Detector window
Moxtek AP 3.3 (manufacturer's table)
KLM Lines
K Lines
L Lines
M Lines
All Lines
Element:
Ba
Temporary Lines
Selected Lines
Clear All Lines
Composition
Element
Weight %
Atomic %
Welcome to NIST DTSA-II version 1705

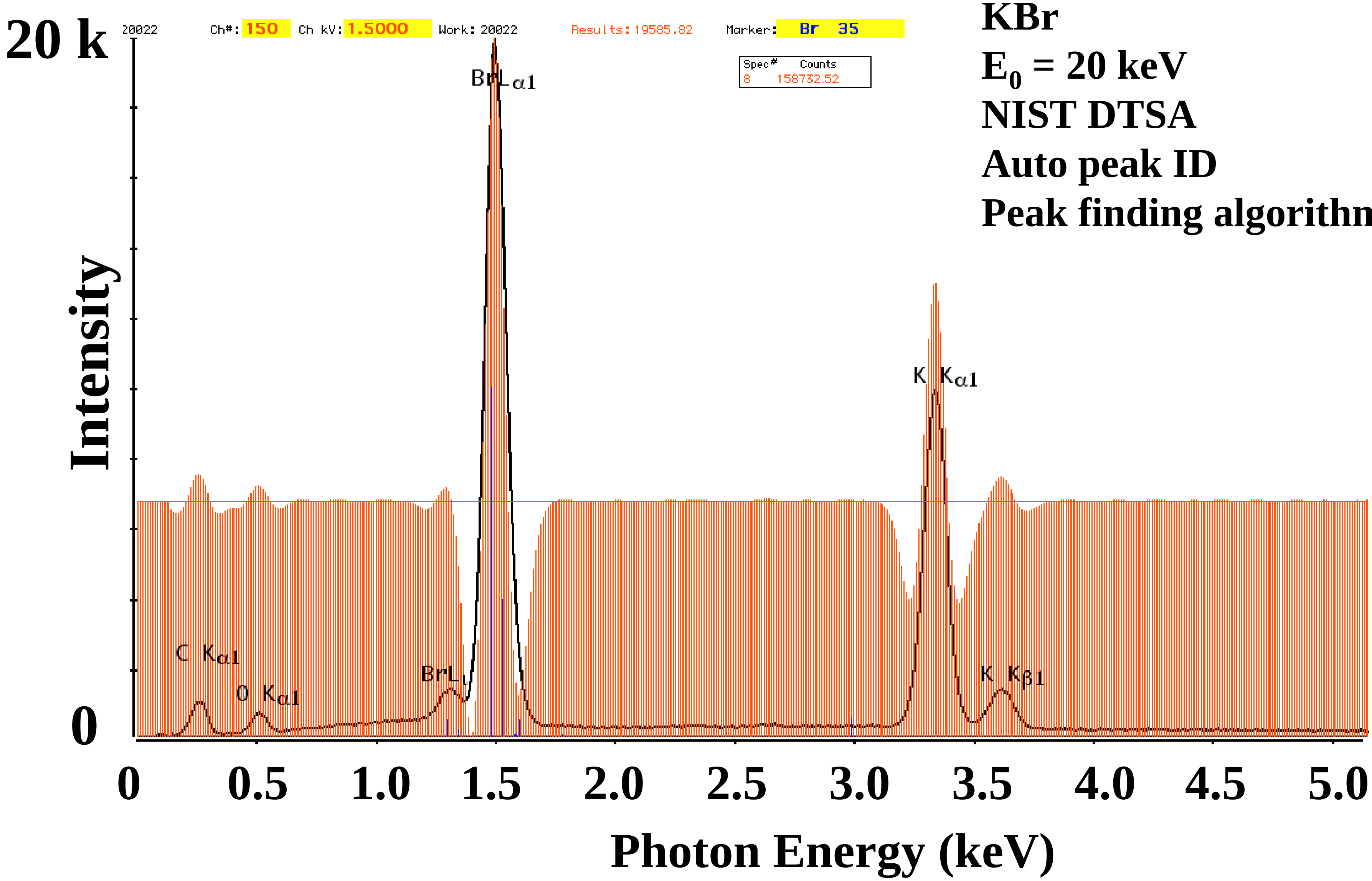

File Edit Analysis Generate Math Headers Display Acquire Help
Thu 10:59 AM
DTSA Mar21_03
4.32
Ch#: 111
Ch kV: 1.1100
Work: 1998
Results: 0
Marker: Ba 56
MZ1 :599.2300 0.06000
MA2 :
MA1 :
M5-O3 :765.3100 0.00010
MZ2 :610.4700 0.01000
MB :
M4-O2 :779.2600 0.00100
M4-N3 :
MG :972.3900 0.20000
M3-O5 :
M3-O4 :
M3-O1 :
M3-N4 :
M3-N1 :800.9600 0.01200
M3-M5 :
M3-M4 :
M2-O4 :
M2-N4 :1019.1000 0.01000
M2-N1 :893.1700 0.06000
M2-M4 :
M1-N3 :
Down one
Ba 56
Up One
Density: 3.500
Weight: 137.300
Valences: xx
eV
mm
angstroms
Sin(Theta)
Change Crystal
K
L
M
N
O
Lines
Edges
Satellites
Lookup
Enter the center value
0.0
Up 10 Lines
Down 10 Lines
OK
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
WORK: #62 BaCO3 std 10 keV/1 nA/10kX/ap4 cal offset -35 from zero 2-23-95

Why does automatic Peak ID fail?

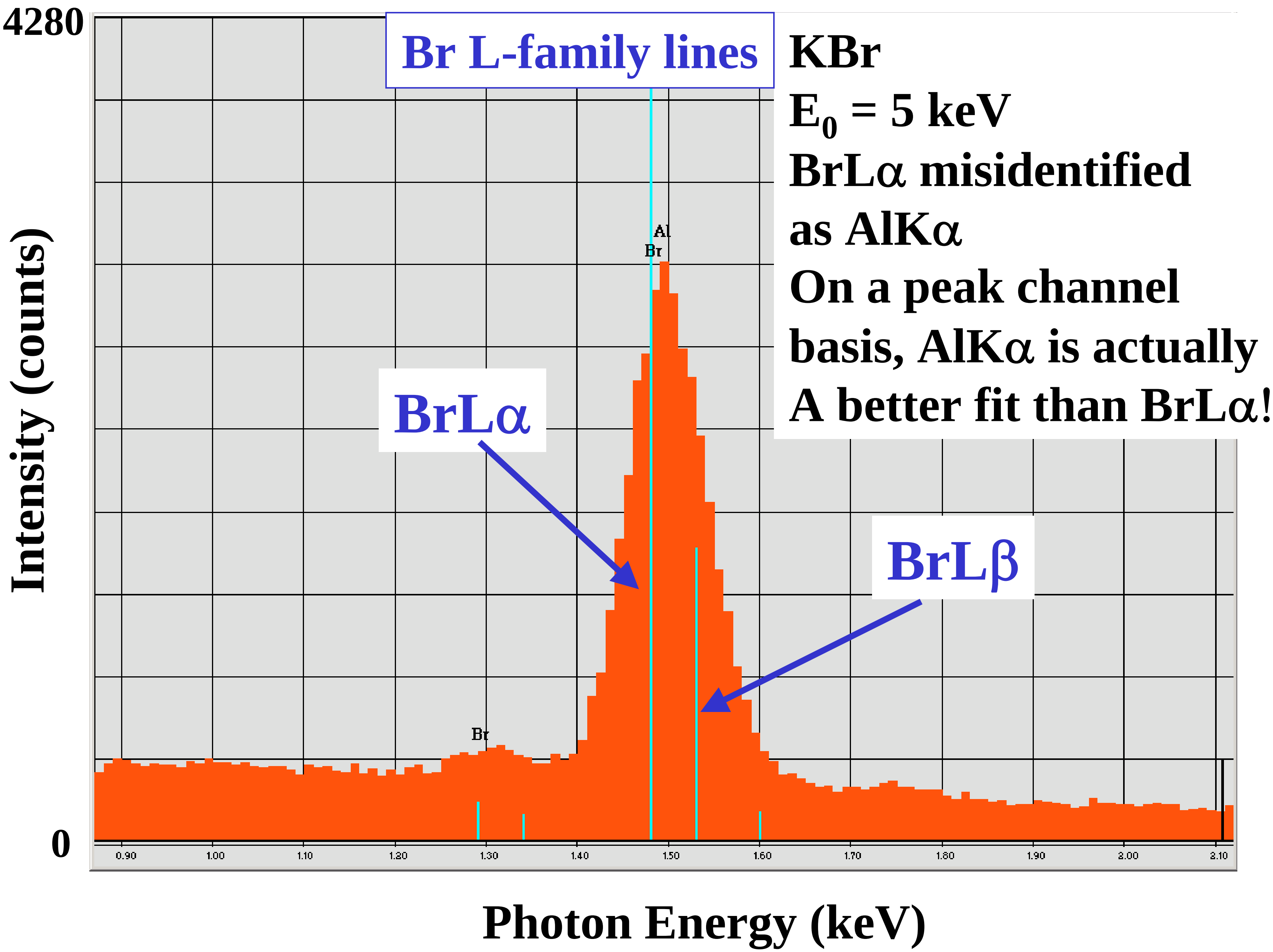
- Apparent reliance on the “single channel” solution

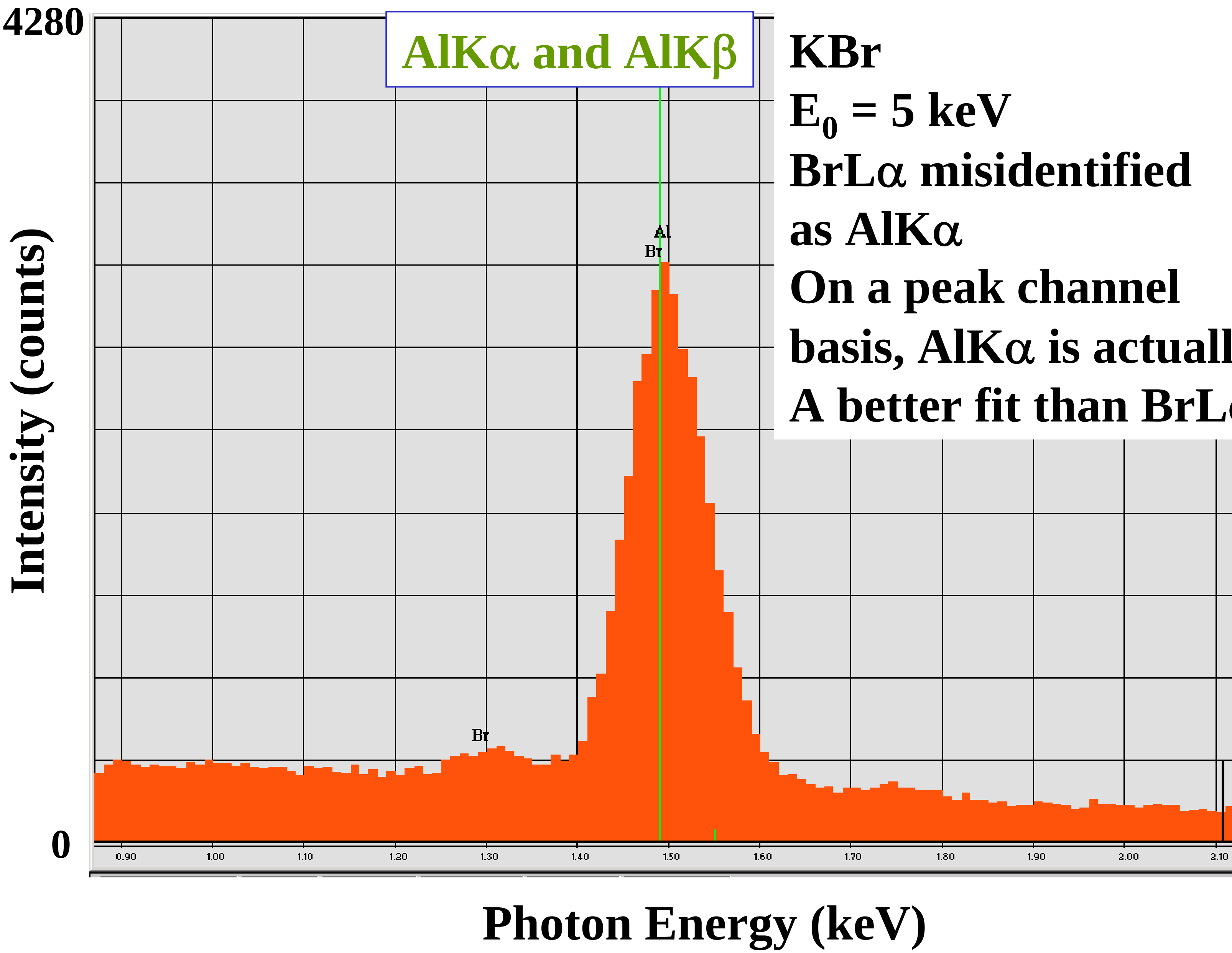
What is going on here? Basic Peak ID finds the peak channel only and then proceeds to a look-up table!

KBr
E_0 = 20 keV
NIST DTSA
Auto peak ID
Peak finding algorithm



Basic single channel Peak ID is vulnerable to convolution of family members



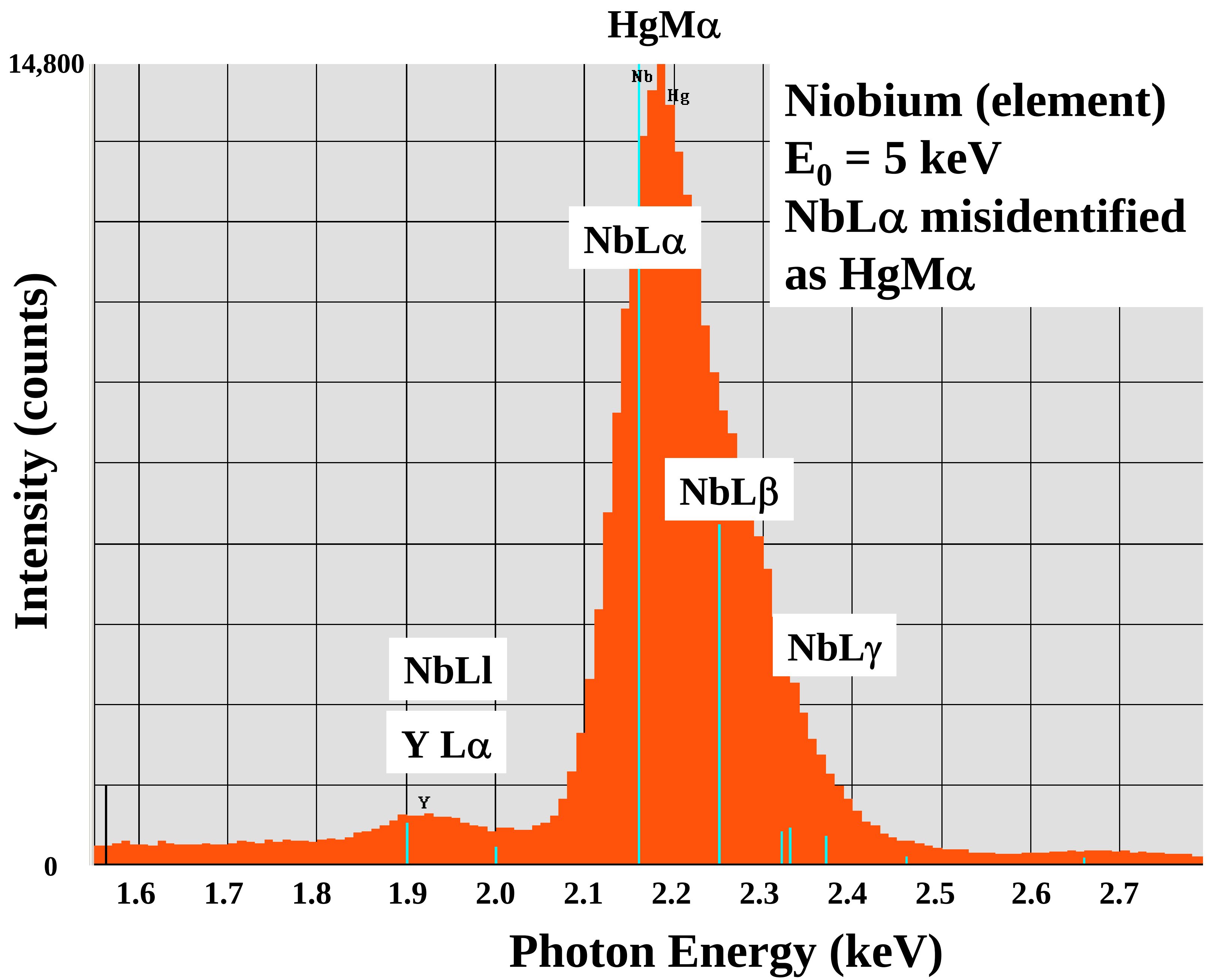


KBr

E_0 = 5 keV

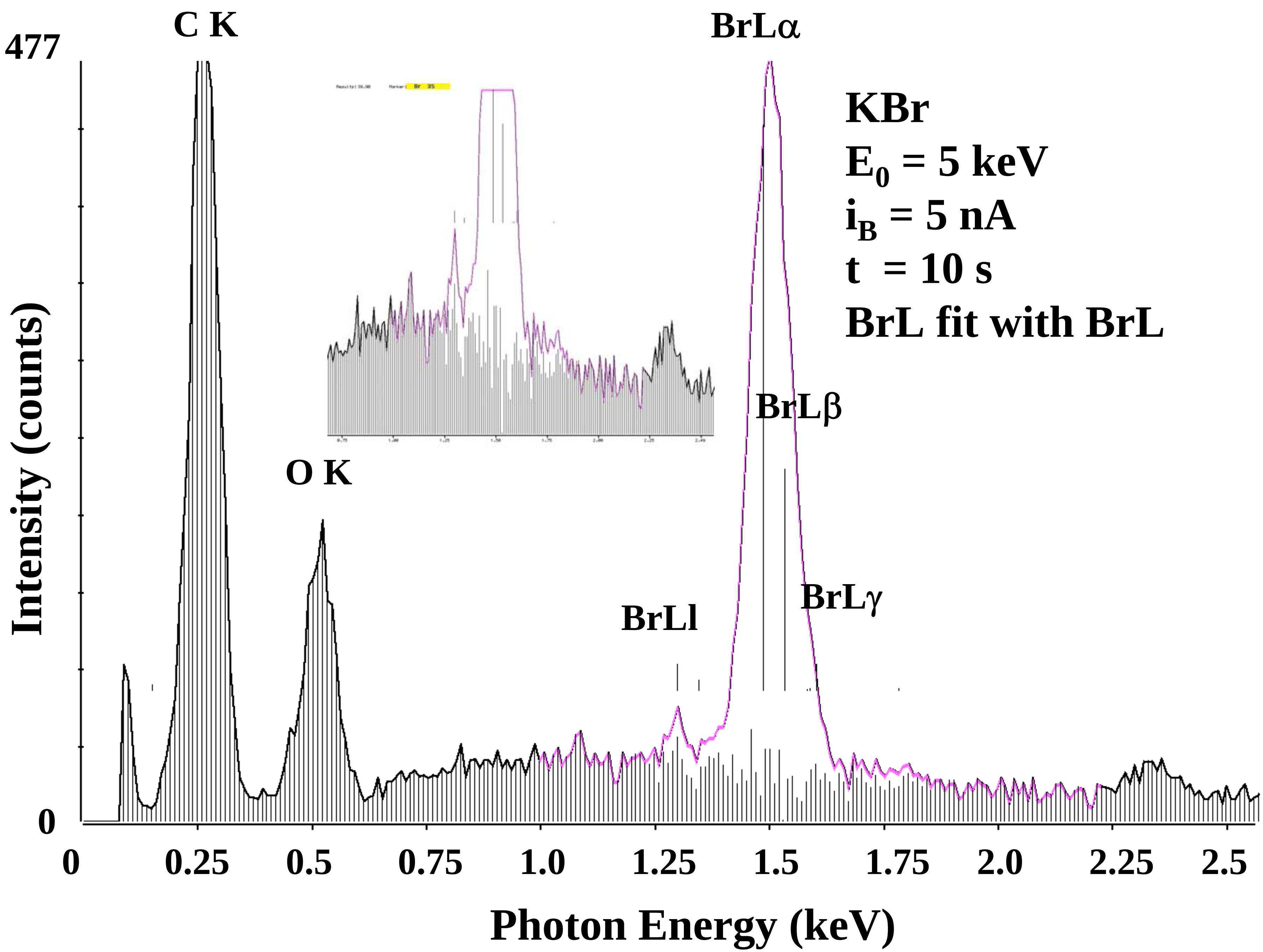
BrLα misidentified as AlKα

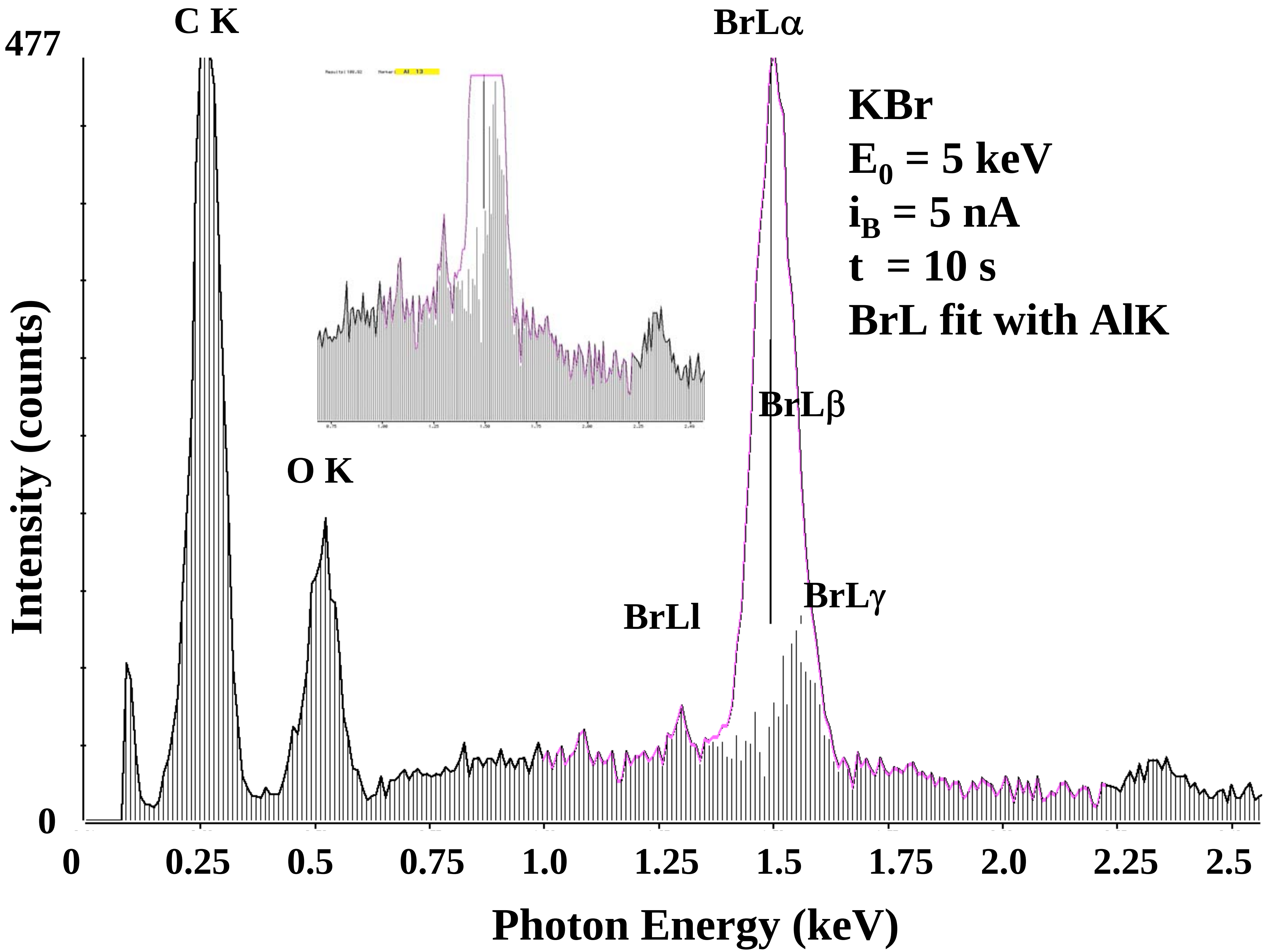
On a peak channel basis, AlKα is actually A better fit than BrLα!

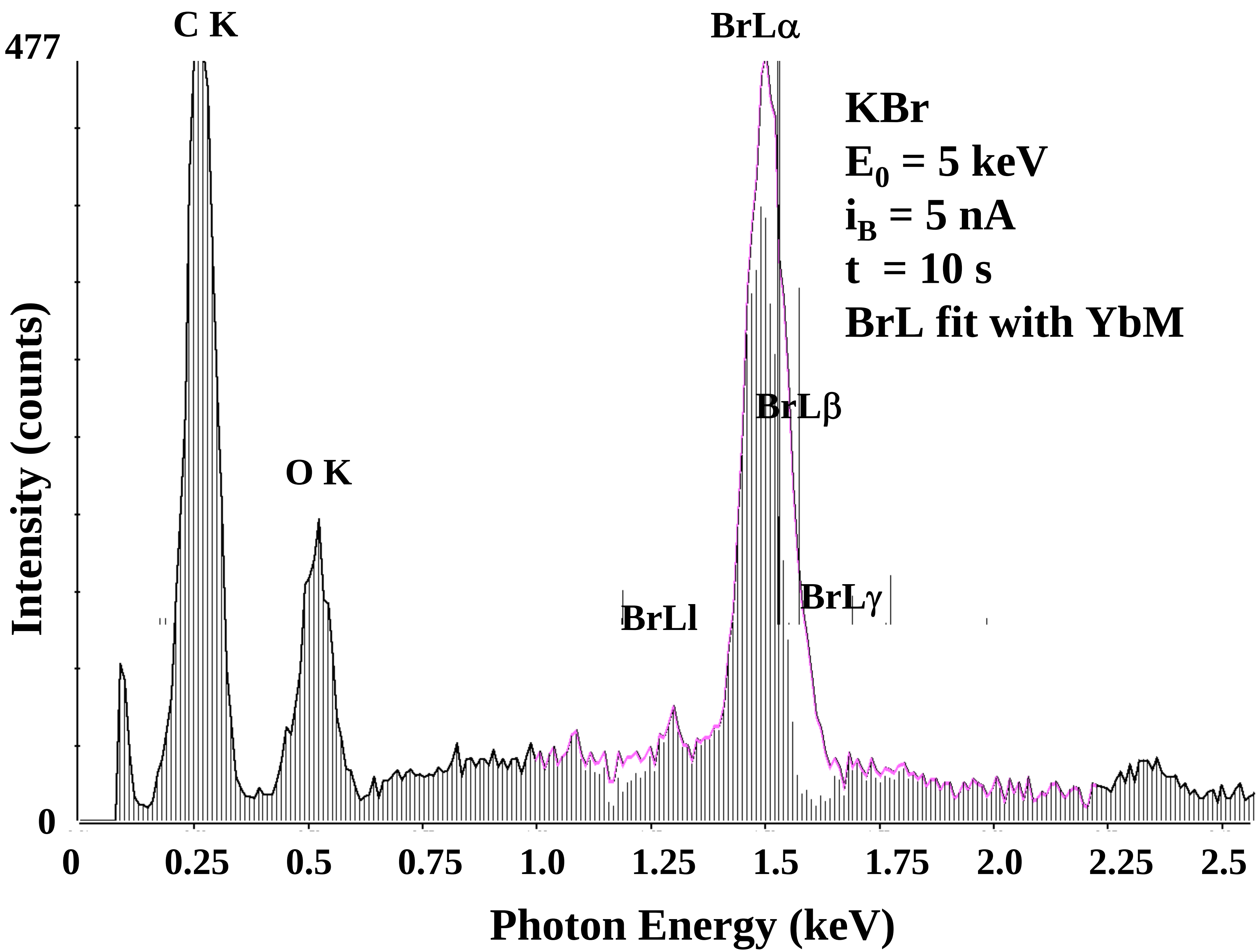

HgMα
14,800
0
Nb
Hg
Niobium (element)
E0 = 5 keV
NbLα misidentified
as HgMα
NbLα
NbLβ
NbLγ
NbLl
Y Lα
Y
Intensity (counts)
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
2.5
2.6
2.7
Photon Energy (keV)

A more robust approach: multiple linear least squares (MLLS) fitting

- Locate candidate peak
- Determine possible elemental families, e.g., AlK, BrL, YbM for E = ~1.5 keV
- Fit the peak reference over the full range of channels necessary to span family
- Test and compare residuals after fitting

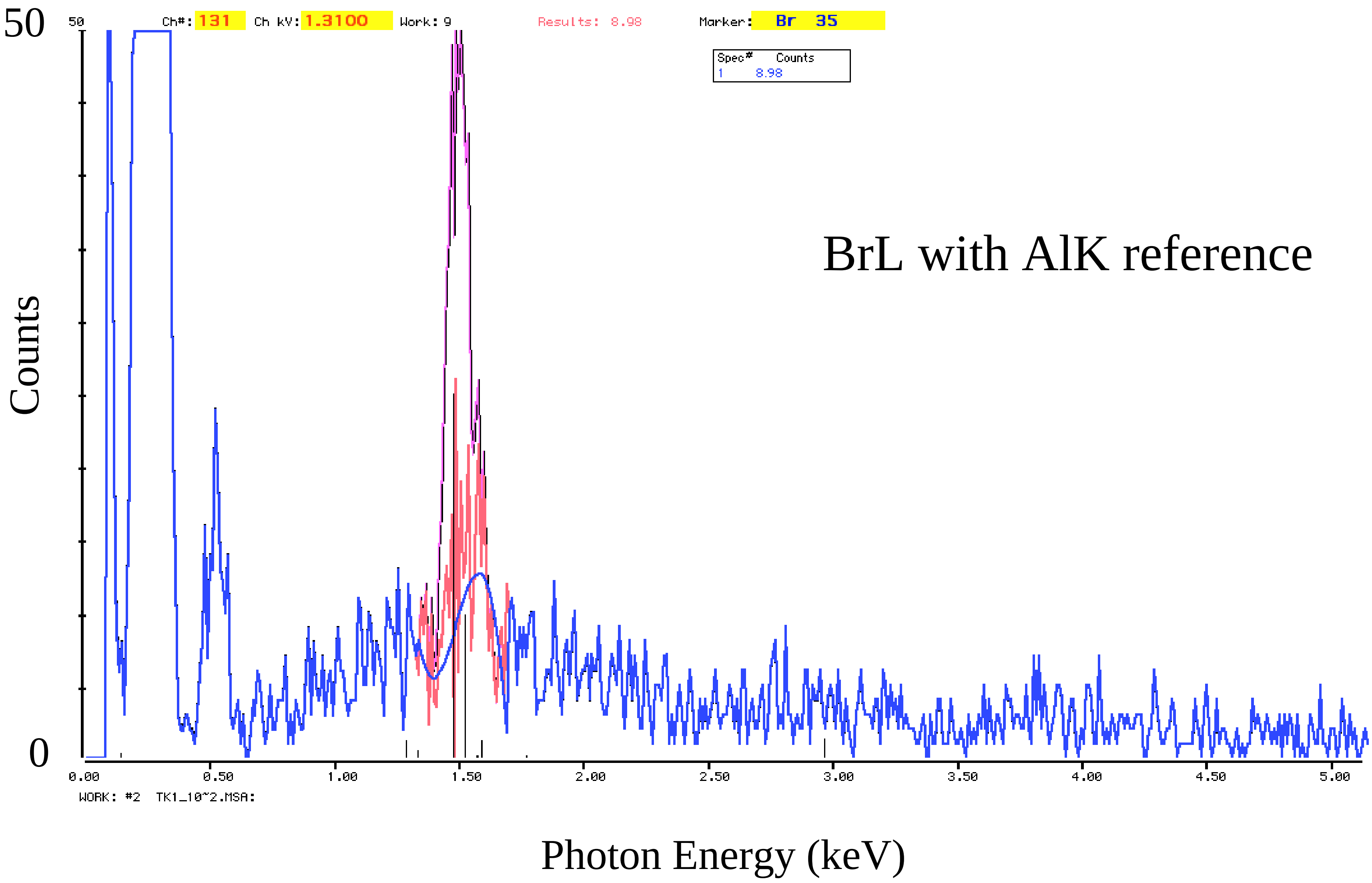

C K
BrLα
477
KBr
E_0 = 5 keV
i_B = 5 nA
t = 10 s
BrL fit with BrL
BrLβ
O K
Intensity (counts)
BrLγ
BrLl
0
0
0.25
0.5
0.75
1.0
1.25
1.5
1.75
2.0
2.25
2.5
Photon Energy (keV)


C K
477
BrLα
KBr
E_0 = 5 keV
i_B = 5 nA
t = 10 s
BrL fit with AlK
BrLβ
O K
BrLγ
BrLl
Intensity (counts)
0
0
0.25
0.5
0.75
1.0
1.25
1.5
1.75
2.0
2.25
2.5
Photon Energy (keV)

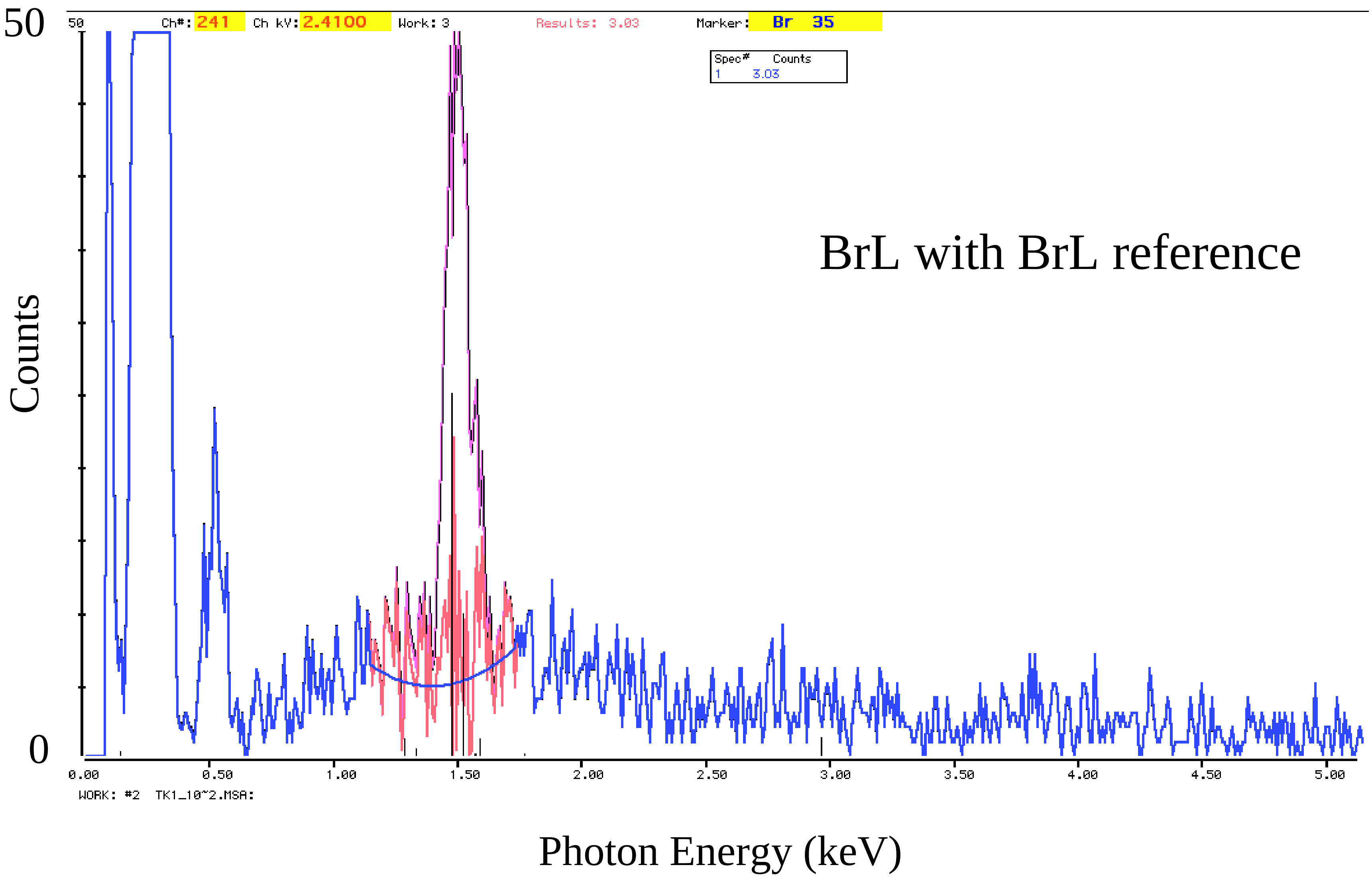


C K
BrLα
477
KBr
E_0 = 5 keV
i_B = 5 nA
t = 10 s
BrL fit with YbM
BrLβ
O K
BrLγ
BrLl
0
0
0.25
0.5
0.75
1.0
1.25
1.5
1.75
2.0
2.25
2.5
Intensity (counts)
Photon Energy (keV)

1/10 of the dose of the previous example



1/10 of the dose of the previous example



Summary of blunders observed with Automatic Peak Identification under conventional beam energy conditions ($10 \leq E_0 \leq 30$ keV)

- It is estimated that if the entire Periodic Table (except H, He, and Li) is in play, about 3% to 5% of automatic peak IDs of major elements result in blunders (e.g., SiK instead of TaM; AlK instead of BrL).
- These blunders are not random mistakes. The same element/peak in different systems will be consistently misidentified, e.g., AlK for BrL in various Br-compounds.
- These blunders occur despite high counting statistics.
- In some EDS systems, identifying a high energy K or L peak does not eliminate the blunder on the corresponding low energy L or M peak; e.g., ZnK-ZnL (NaK)
- Poor EDS calibration makes the problem much worse!!
- The problem is worse for minor and trace constituents
- The problem is worse for low voltage ($E_0 \leq 5$ keV) microanalysis