Exploiting the Speed of the Silicon Drift Detector to Open New Measurement Opportunities in Particle Analysis

Dale E. Newbury

National Institute of Standards and Technology

Gaithersburg, MD 20899-8370

dale.newbury@nist.gov

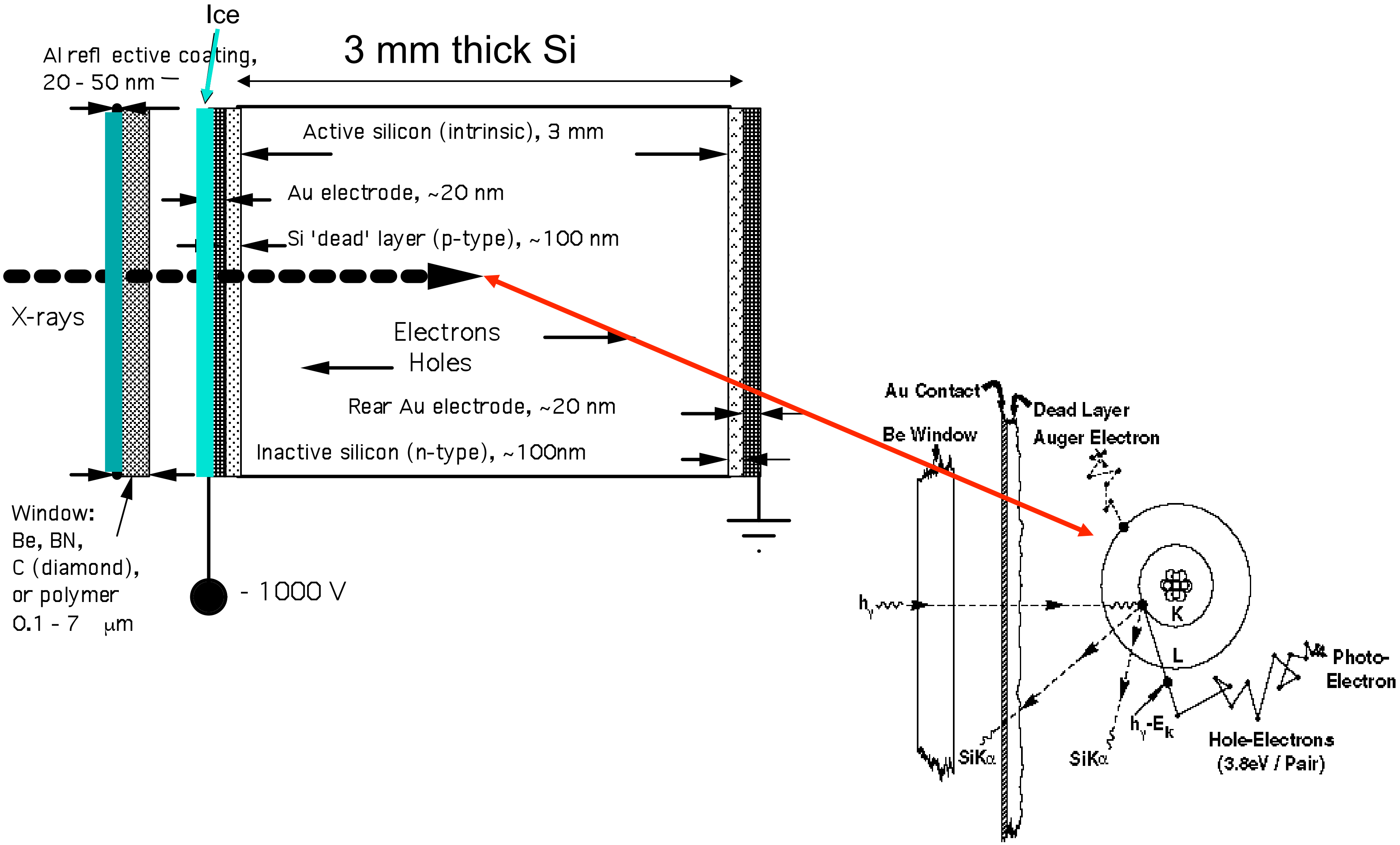
We are experiencing an extraordinary and wonderful convergence of technologies that open new measurement opportunities in particle analysis

- **The silicon drift detector energy dispersive x-ray spectrometer (SDD-EDS)**

Fitzgerald, R, Keil, K. and Heinrich, K. Science v 159 (1968) 528

“Solid-State Energy-Dispersion Spectrometer for Electron-Microprobe X-ray Analysis”

Si(Li)-EDS



Ice

3 mm thick Si

Al reflective coating,
20 - 50 nm

Active silicon (intrinsic), 3 mm

Au electrode, ~20 nm

Si 'dead' layer (p-type), ~100 nm

X-rays

Electrons

Holes

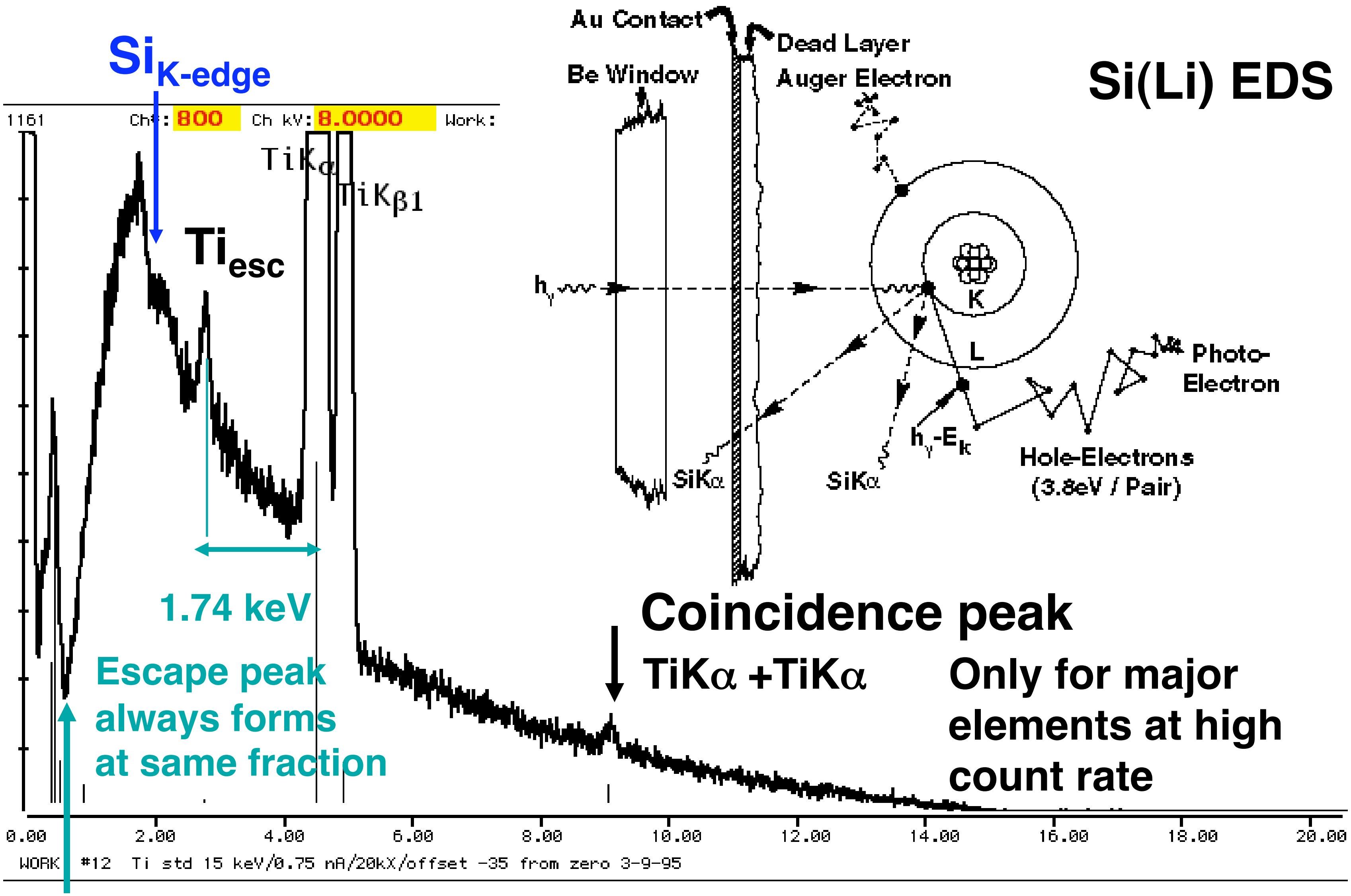
Rear Au electrode, ~20 nm

Inactive silicon (n-type), ~100nm

Window:
Be, BN,
C (diamond),
or polymer
0.1 - 7 μm

- 1000 V

Si(Li) EDS



Intensity

$Si_{K\text{-edge}}$

Ti_{esc}

1.74 keV

Escape peak always forms at same fraction

Coincidence peak

TiKα +TiKα

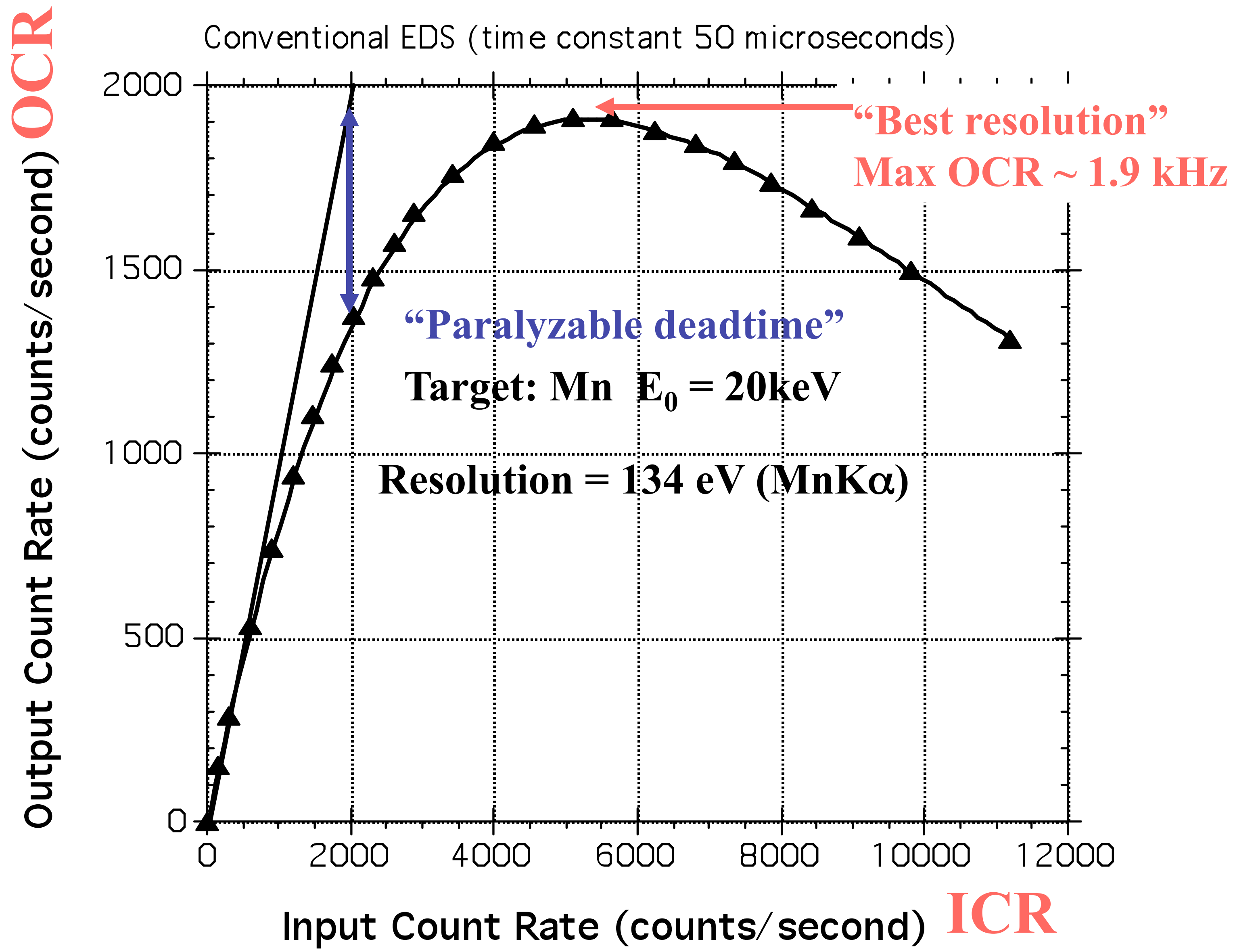
Only for major elements at high count rate

Drastic decrease in detector efficiency

Photon Energy (keV)

Spectrum appears to be continuously measured at all energies, but it is actually one photon at a time: paralyzable deadtime

Current State-of-the Art Si(Li)-EDS (30 mm^2)



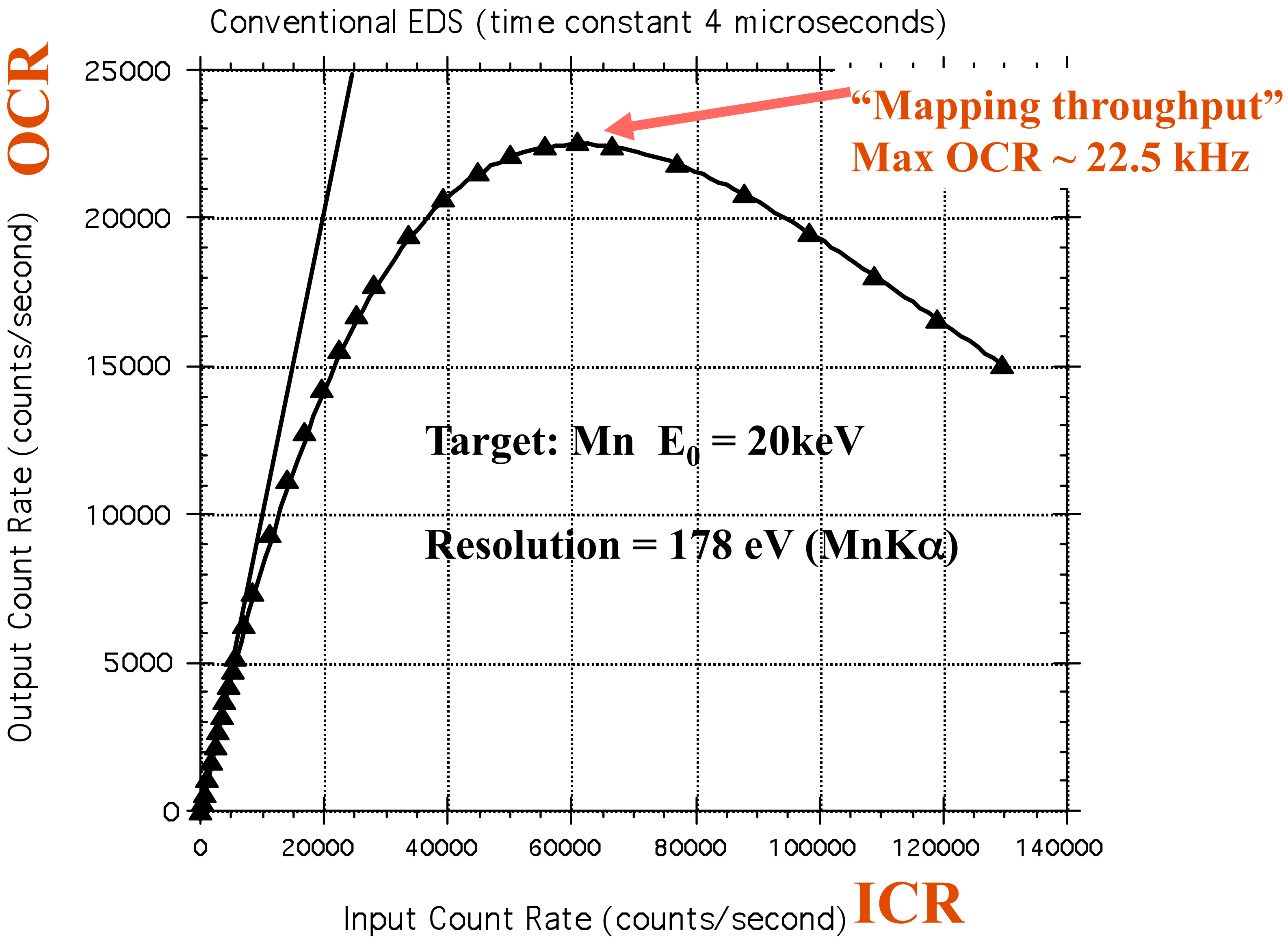
“Best resolution”
Max OCR ~ 1.9 kHz

“Paralyzable deadtime”

Target: Mn E_0 = 20keV

Resolution = 134 eV (MnKα)

Current State-of-the Art Si(Li)-EDS (30 mm^2)

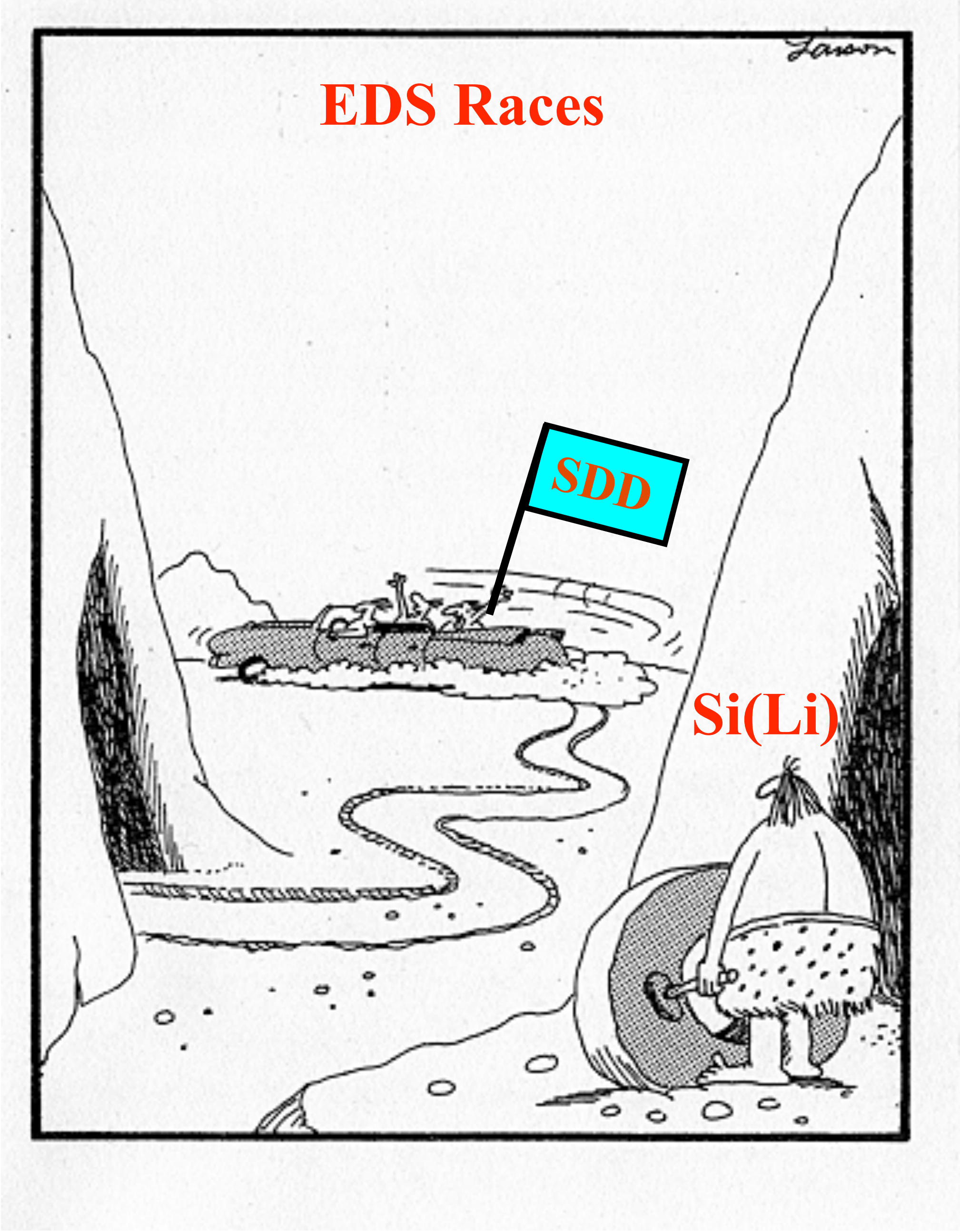


"Mapping throughput"
Max OCR ~ 22.5 kHz

Target: Mn $E_0 = 20keV$

Resolution = 178 eV (MnKα)

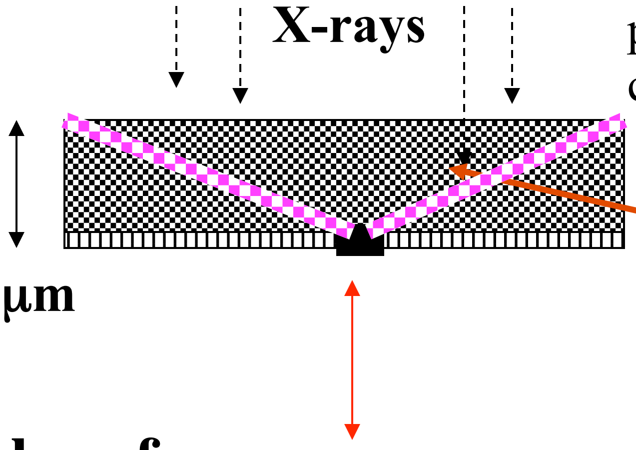
Silicon Drift Detector (SDD) EDS

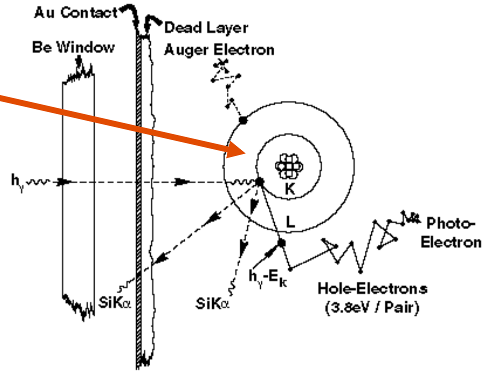


Silicon Drift Detector: Same detection physics as Si(Li)-EDS, but a radically different design

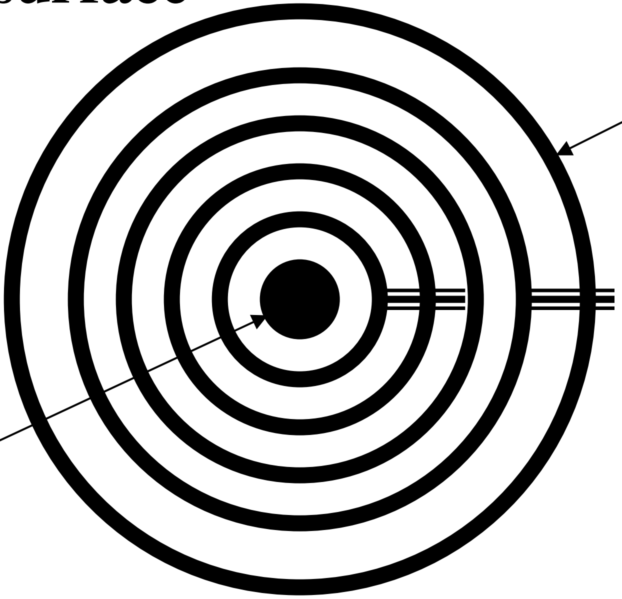
X-ray absorption and ejection of photoelectron; inelastic scattering creates electron-hole pairs.

SDDs are thin!





SDD Backsurface



SDDs have a complex back surface electrode structure. Applied potential creates internal radial collection channel

Ring electrodes

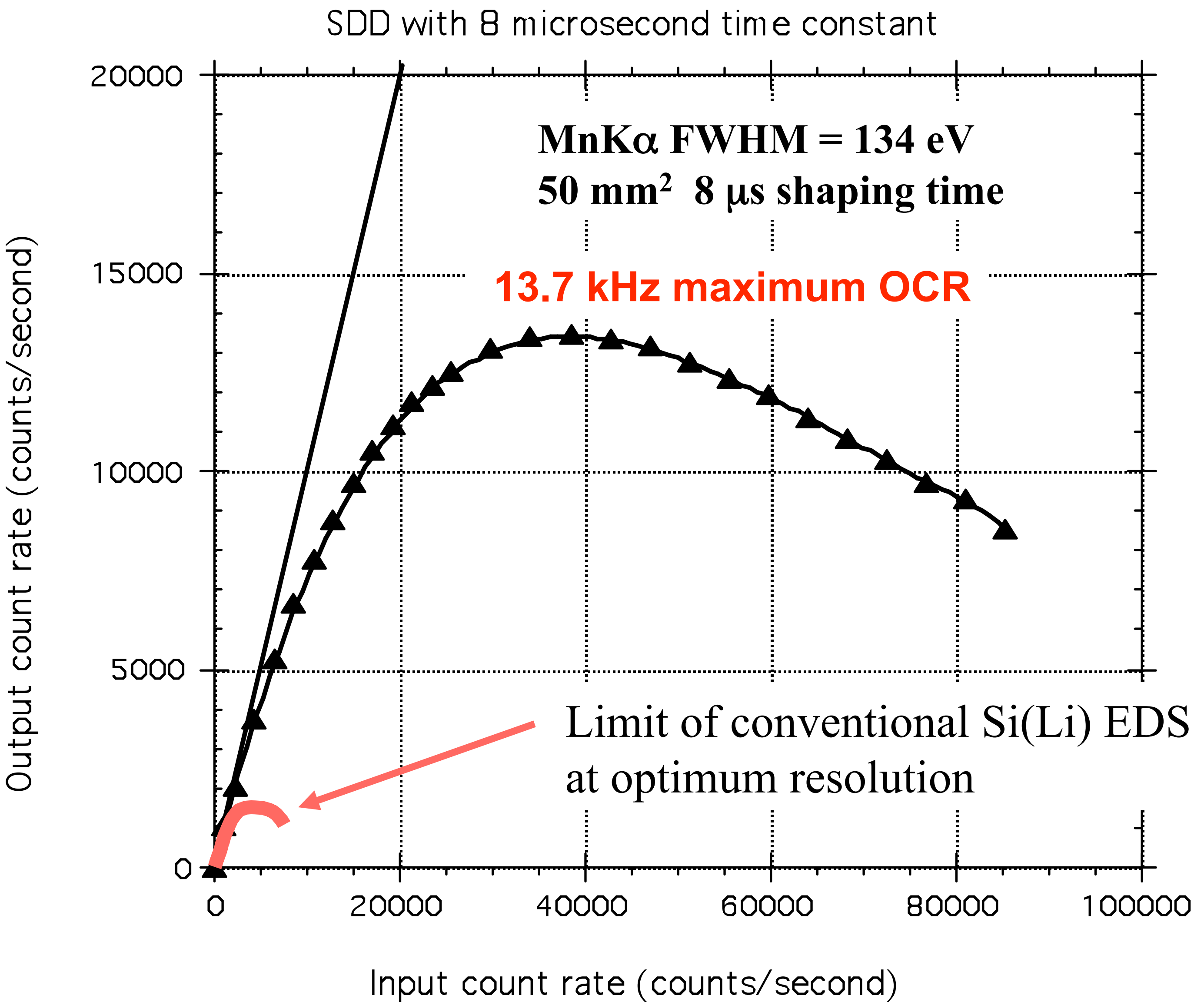
≡ Resistor bridge

Central anode, 80 µm diameter

Active area 5 mm^2 to 100 mm^2

The anode of an SDD is ~ 0.005 mm^2 for a 50 mm^2 detector, about 1/10,000 the area of EDS

Radiant Detectors LLC (Third Generation SDD)


SDD with 8 microsecond time constant

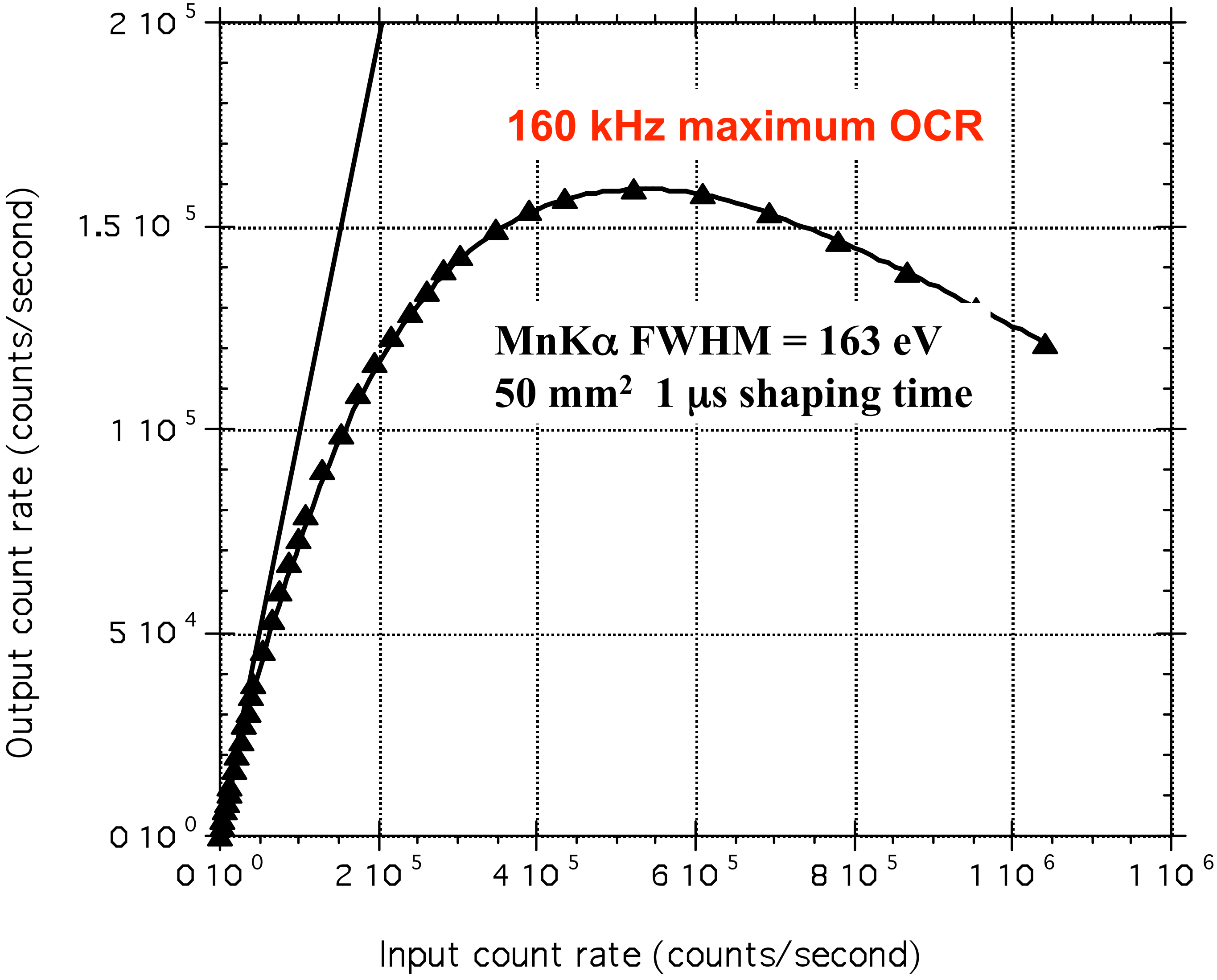
MnKα FWHM = 134 eV

50 mm^2 8 μs shaping time

13.7 kHz maximum OCR

Limit of conventional Si(Li) EDS at optimum resolution

Radiant Detectors LLC (Third Generation SDD)



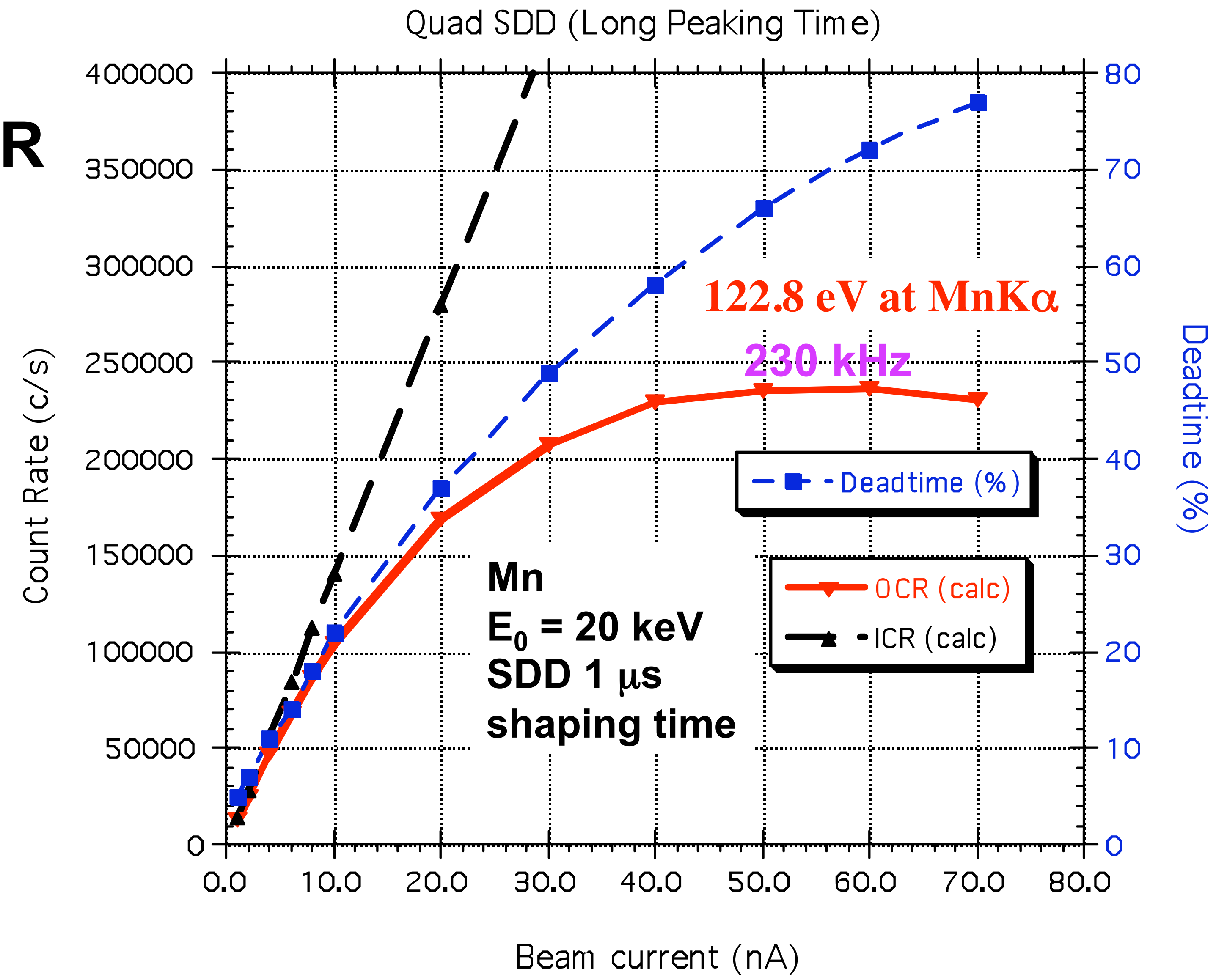
SDD 1 microsecond time constant

160 kHz maximum OCR

MnKα FWHM = 163 eV
50 mm^2 1 μs shaping time

Bruker (Fourth Generation SDD; Cluster of four 10 mm^2 SDDs)

OCR


Quad SDD (Long Peaking Time)

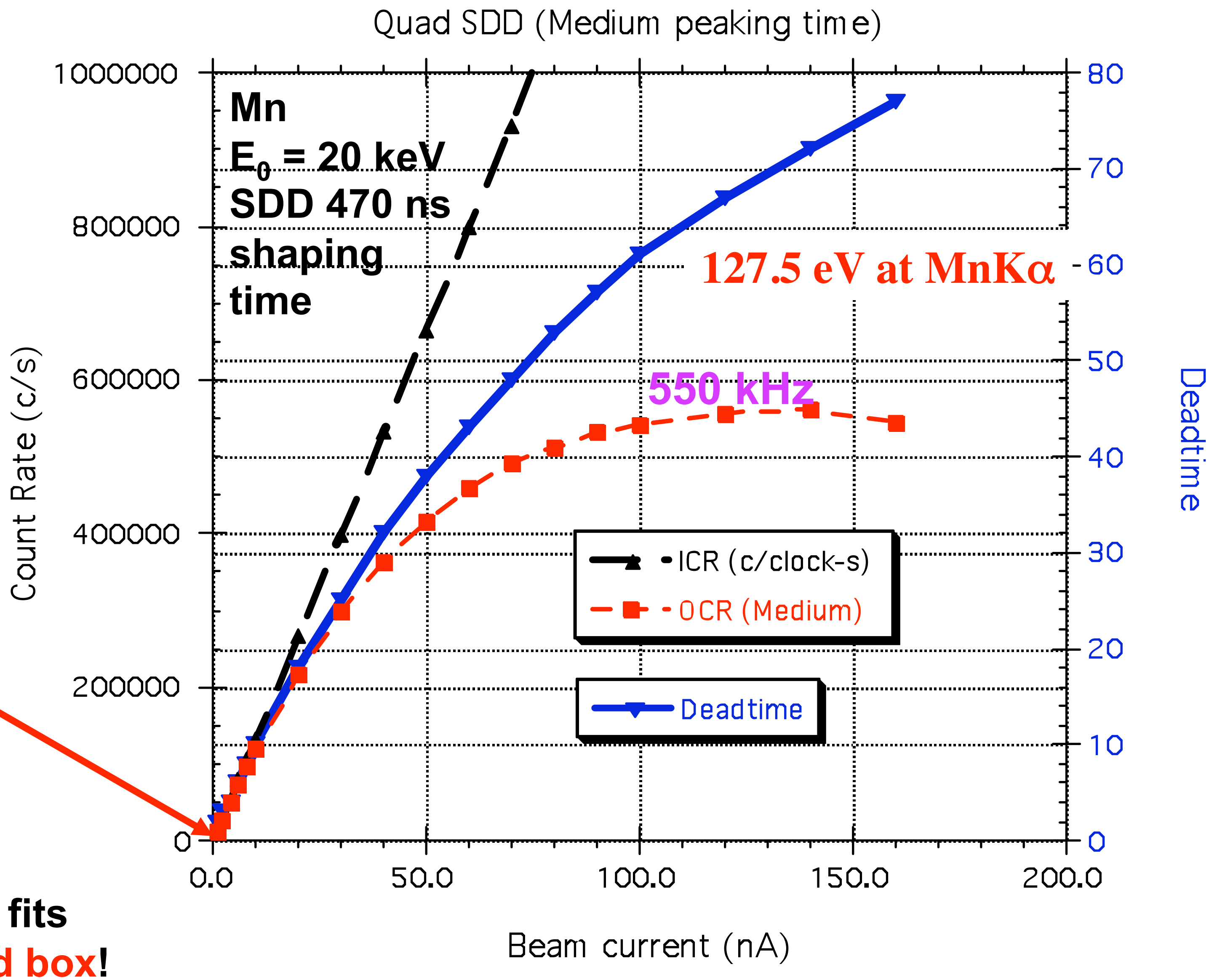
122.8 eV at MnKα

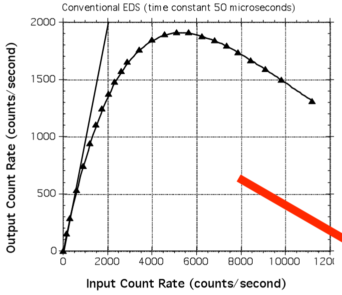
230 kHz

Mn
E_0 = 20 keV
SDD 1 μs
shaping time

Bruker (Fourth Generation SDD; Cluster of four 10 mm^2 SDDs)

OCR

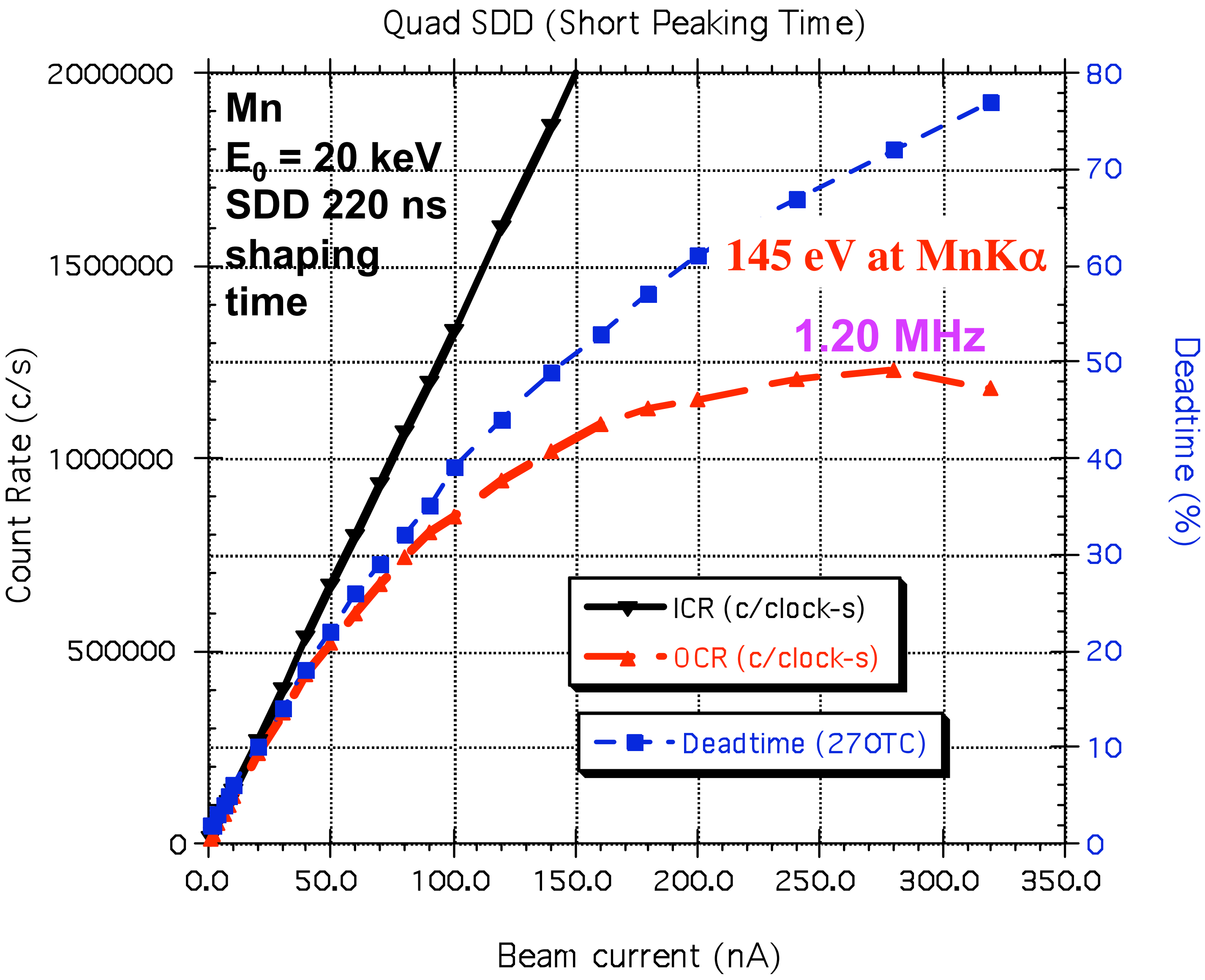




For Si(Li) at 129 eV, the entire OCR vs nA graph fits inside the first red box!

Bruker (Fourth Generation SDD; Cluster of four 10 mm^2 SDDs)

OCR



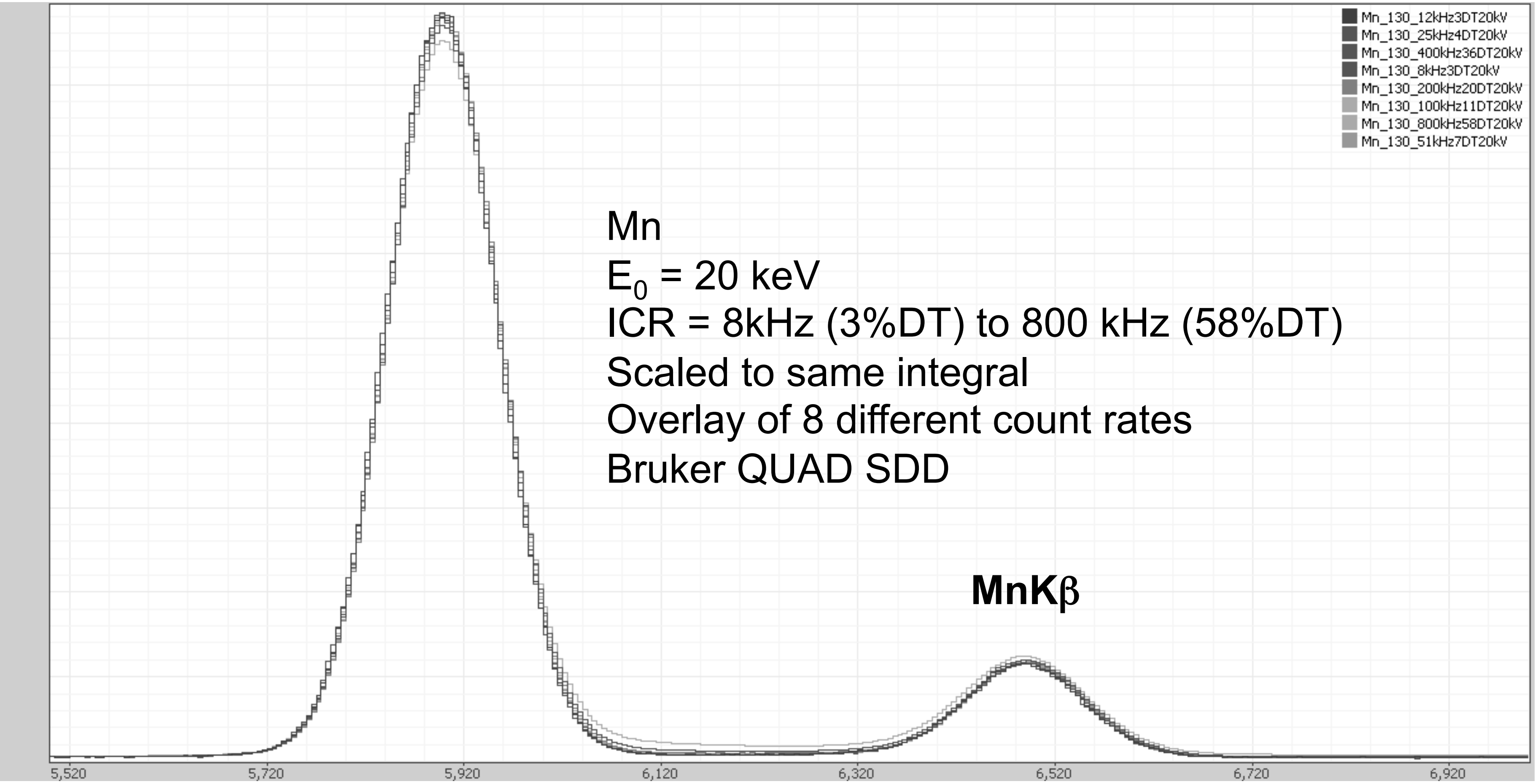
Quad SDD (Short Peaking Time)

Mn
E_0 = 20 keV
SDD 220 ns shaping time

145 eV at MnKα

1.20 MHz

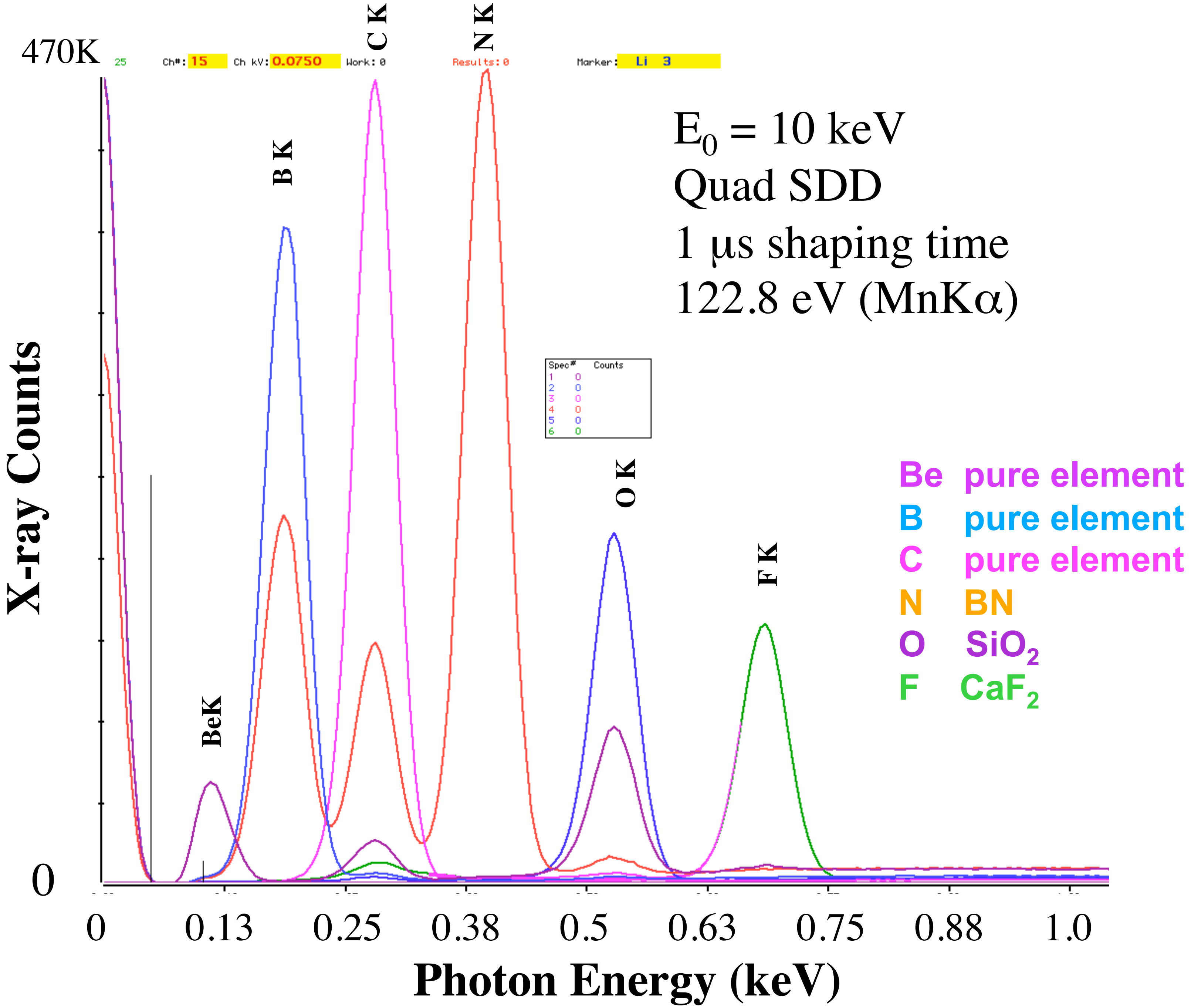
Extraordinary peak stability, FWHM and peak channel



MnKα

MnKβ

Mn
E_0 = 20 keV
ICR = 8kHz (3%DT) to 800 kHz (58%DT)
Scaled to same integral
Overlay of 8 different count rates
Bruker QUAD SDD



E_0 = 10 keV
Quad SDD
1 μs shaping time
122.8 eV (MnKα)

We are experiencing an extraordinary and wonderful convergence of technologies that open new measurement opportunities in particle analysis

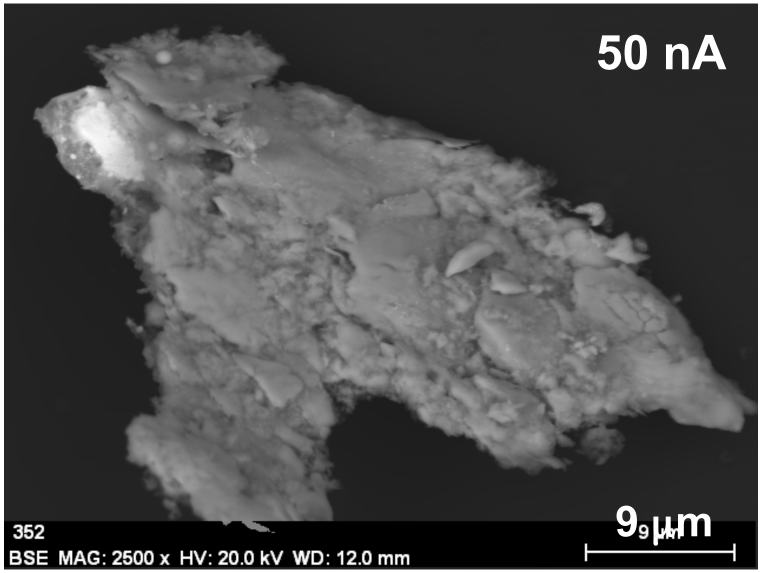
- **The silicon drift detector energy dispersive x-ray spectrometer (SDD-EDS)**
- **The thermal field emission gun SEM gives both high brightness and high total beam current:**

  10 nA in 40 nm

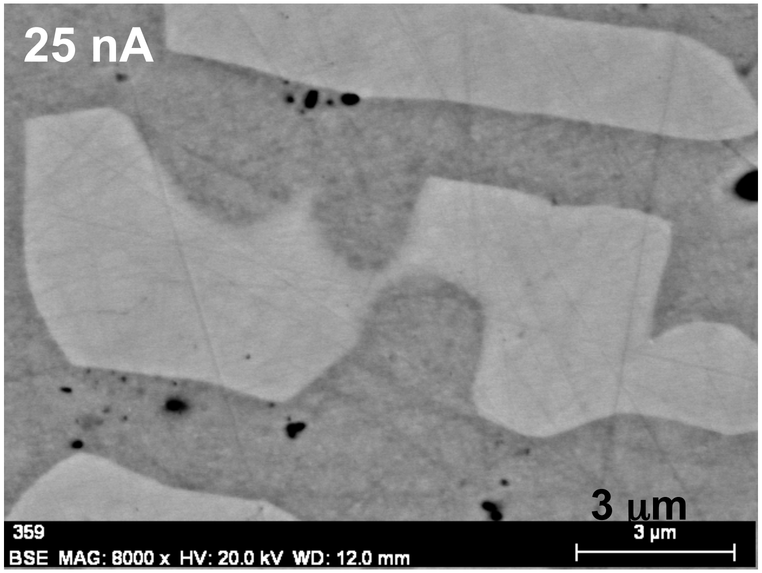
  100 nA in 100 nm

SEM-BSE images

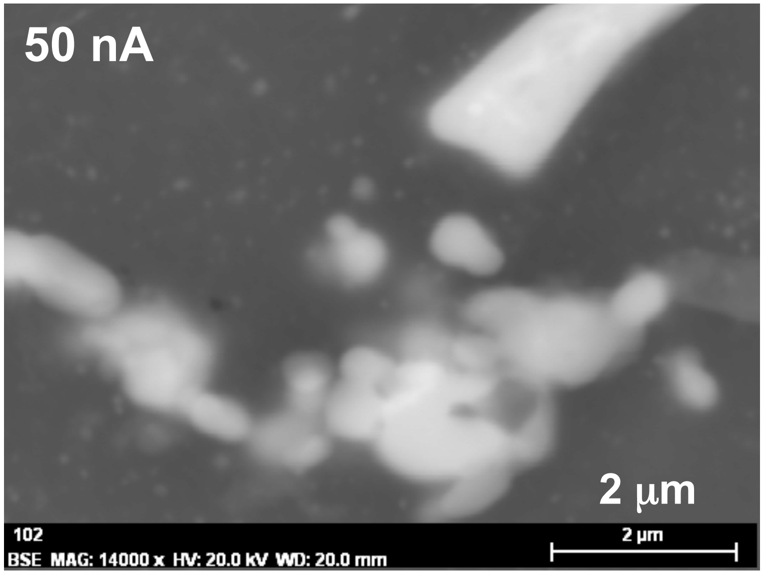
Brass particle



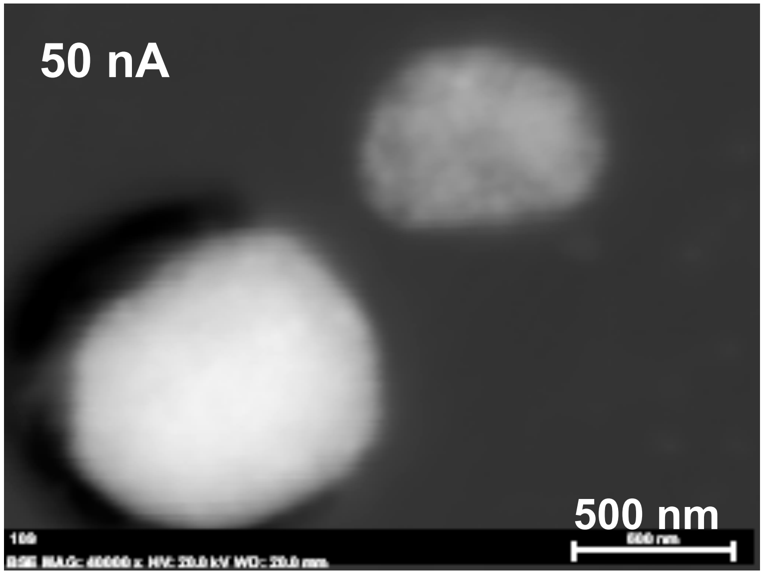
Zr-37Pd



Al alloy (2024-T6)



Al alloy (2024-T6)



We are experiencing an extraordinary and wonderful convergence of technologies that open new measurement opportunities in particle analysis

- **The silicon drift detector energy dispersive x-ray spectrometer (SDD-EDS)**
- **The thermal field emission gun SEM gives both high brightness and high total beam current:**
  10 nA in 40 nm

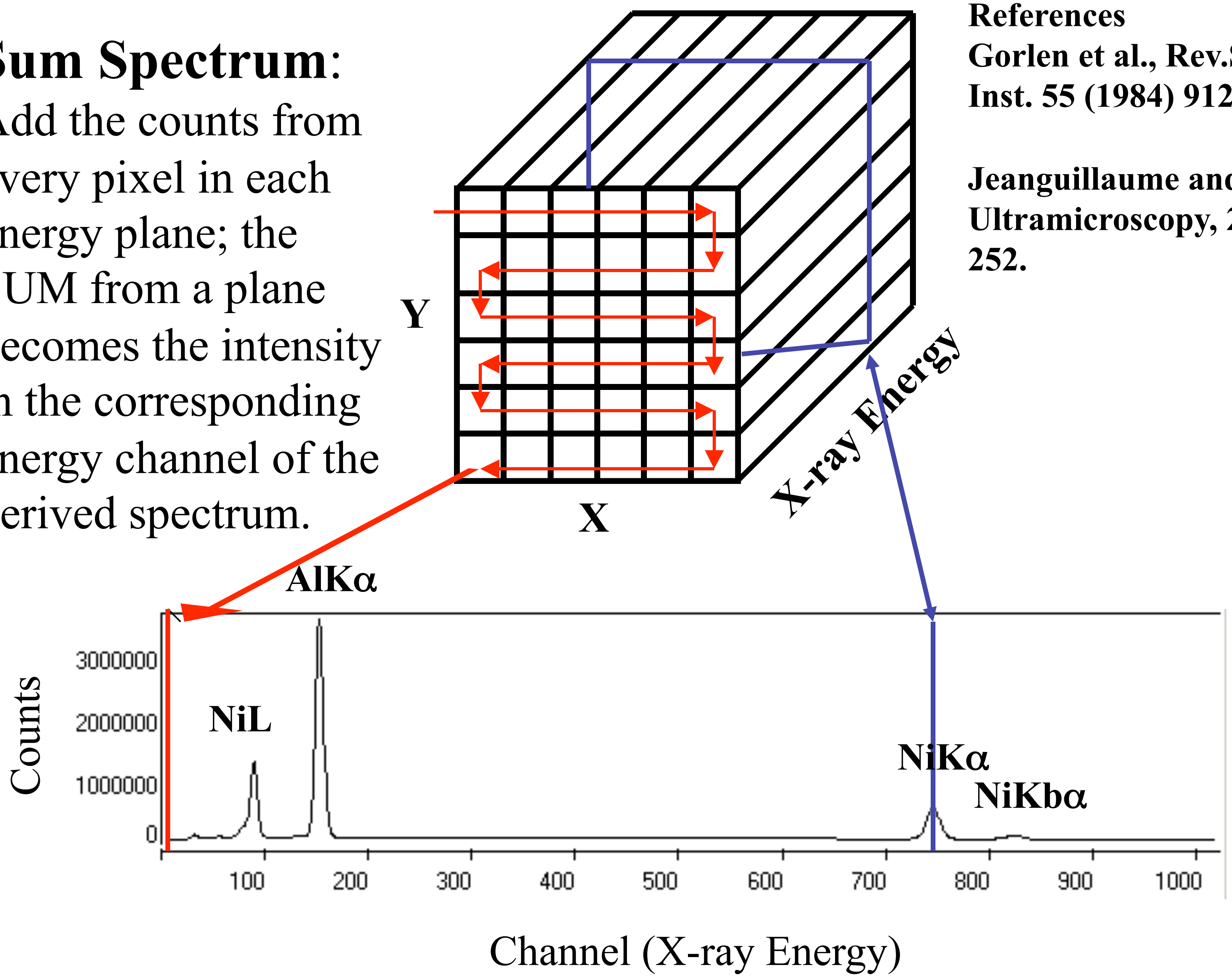
  100 nA in 100 nm
- **Mapping data collection in x-ray spectrum image (XSI) mode; record 4096 5-eV channels at each pixel, capturing all possible compositional information within performance of SDD-EDS and dose. Highly effective data mining software tools [NIST Lispix (Dave Bright) and Sandia Multivariate (Kotula and Keenan)]**

Derived x-ray spectra are calculated from measured spectra within the cube.

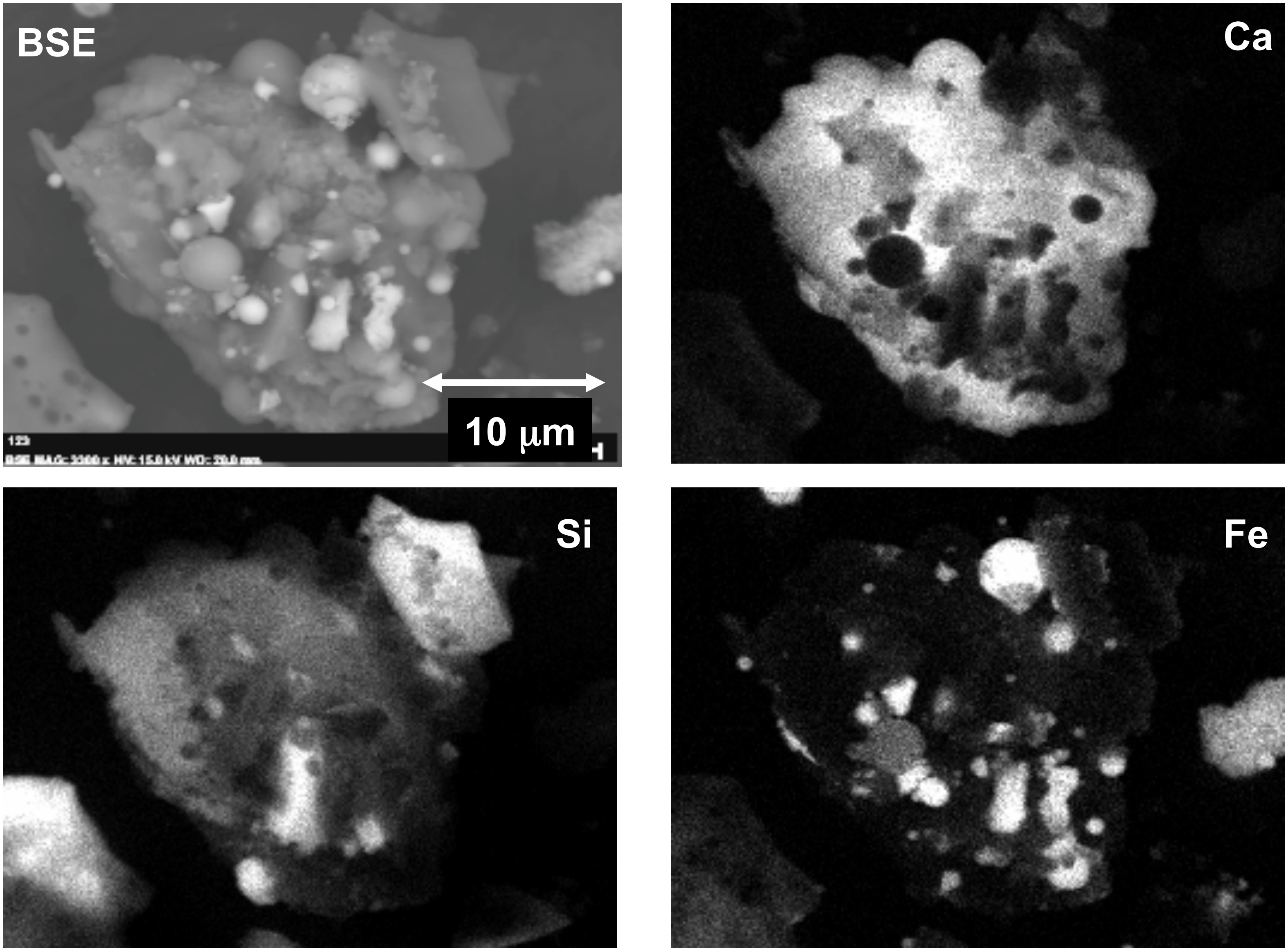
Sum Spectrum:
Add the counts from every pixel in each energy plane; the SUM from a plane becomes the intensity in the corresponding energy channel of the derived spectrum.

References
Gorlen et al., Rev.Sci. Inst. 55 (1984) 912.

Jeanguillaume and Colliex, Ultramicroscopy, 28 (1989) 252.



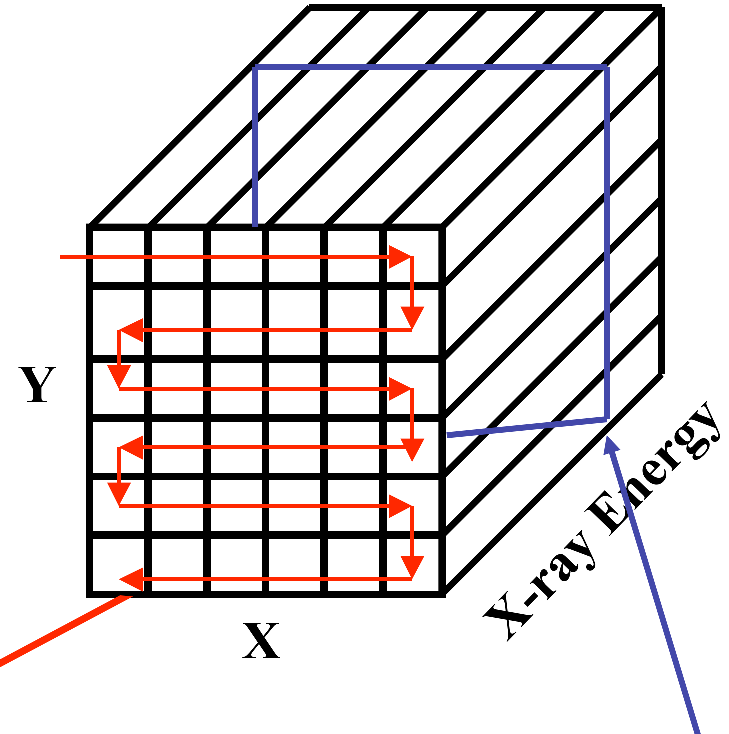
Fly ash from coal-fired power plant (economizer stage)



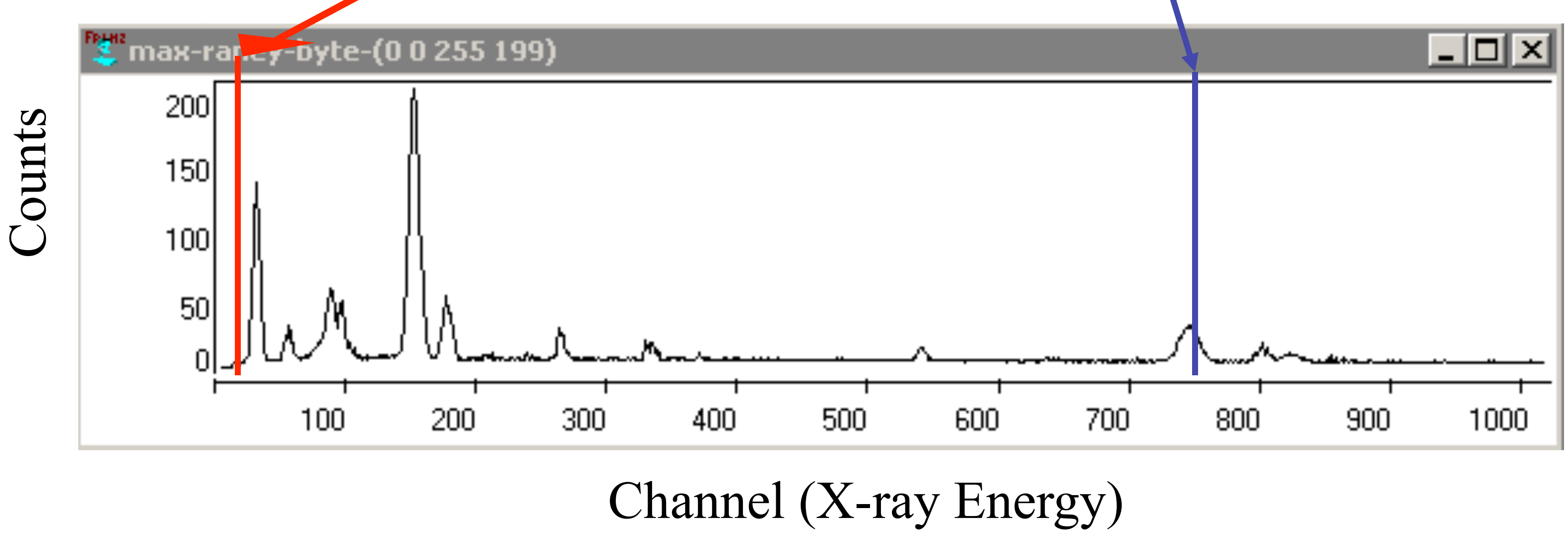
E_0 = 20 keV; 40 nA; OCR 300 kHz; res 145 eV; 14% deadtime; 256x192 pixels; 1 ms/pixel = 50 s

Maximum Pixel Spectrum

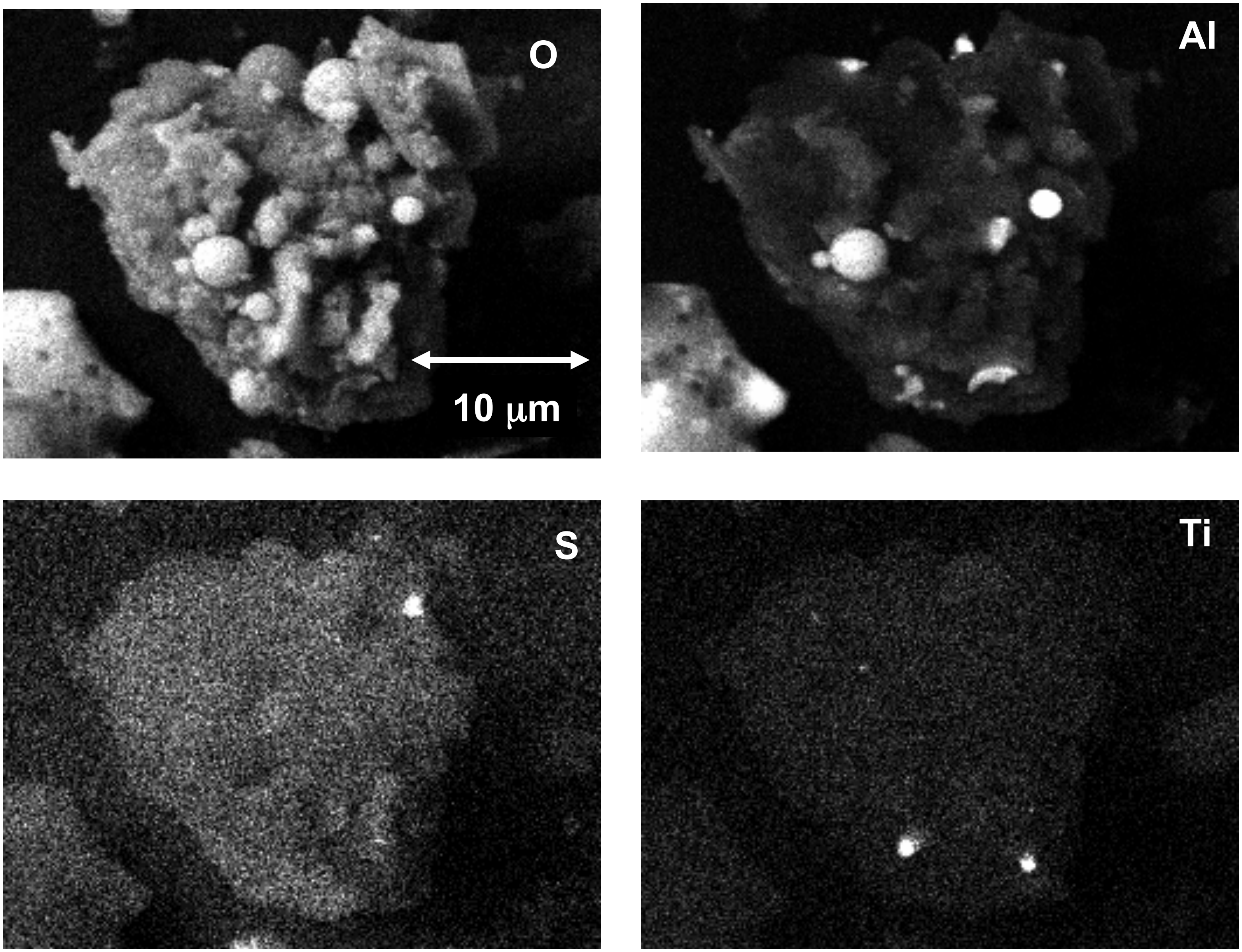
Bright and Newbury,
J. Microscopy,
216 (2004) 186



Test every pixel in an energy plane to find the MAXIMUM value. This maximum value
becomes the intensity in the corresponding energy channel of the derived Maximum Pixel Spectrum.



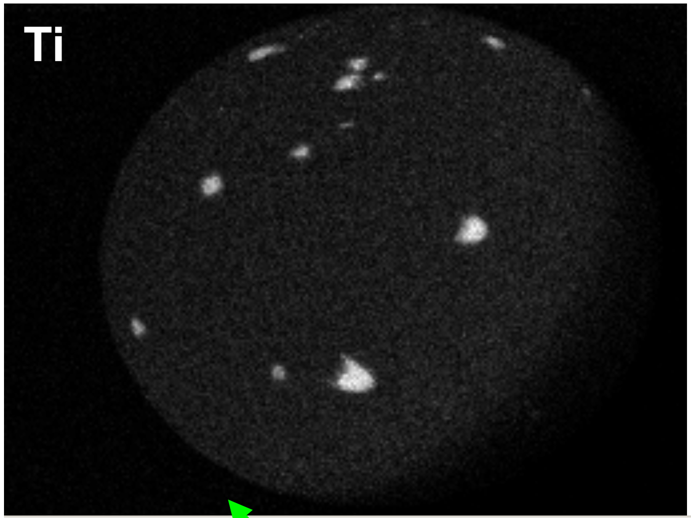
Fly ash from coal-fired power plant (economizer stage)

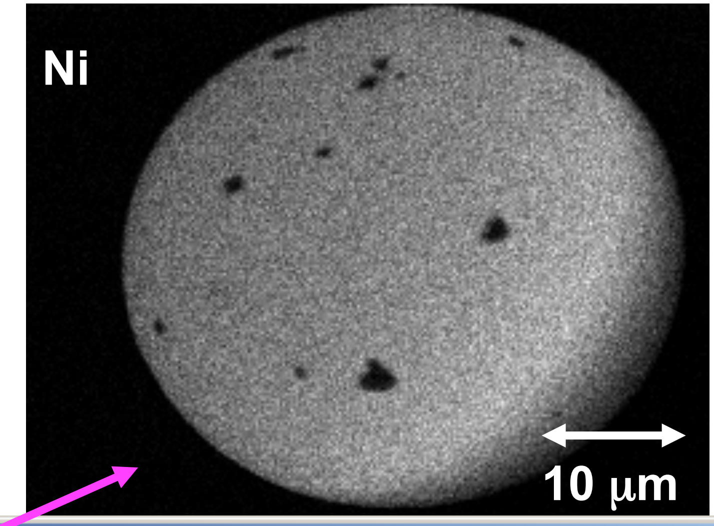


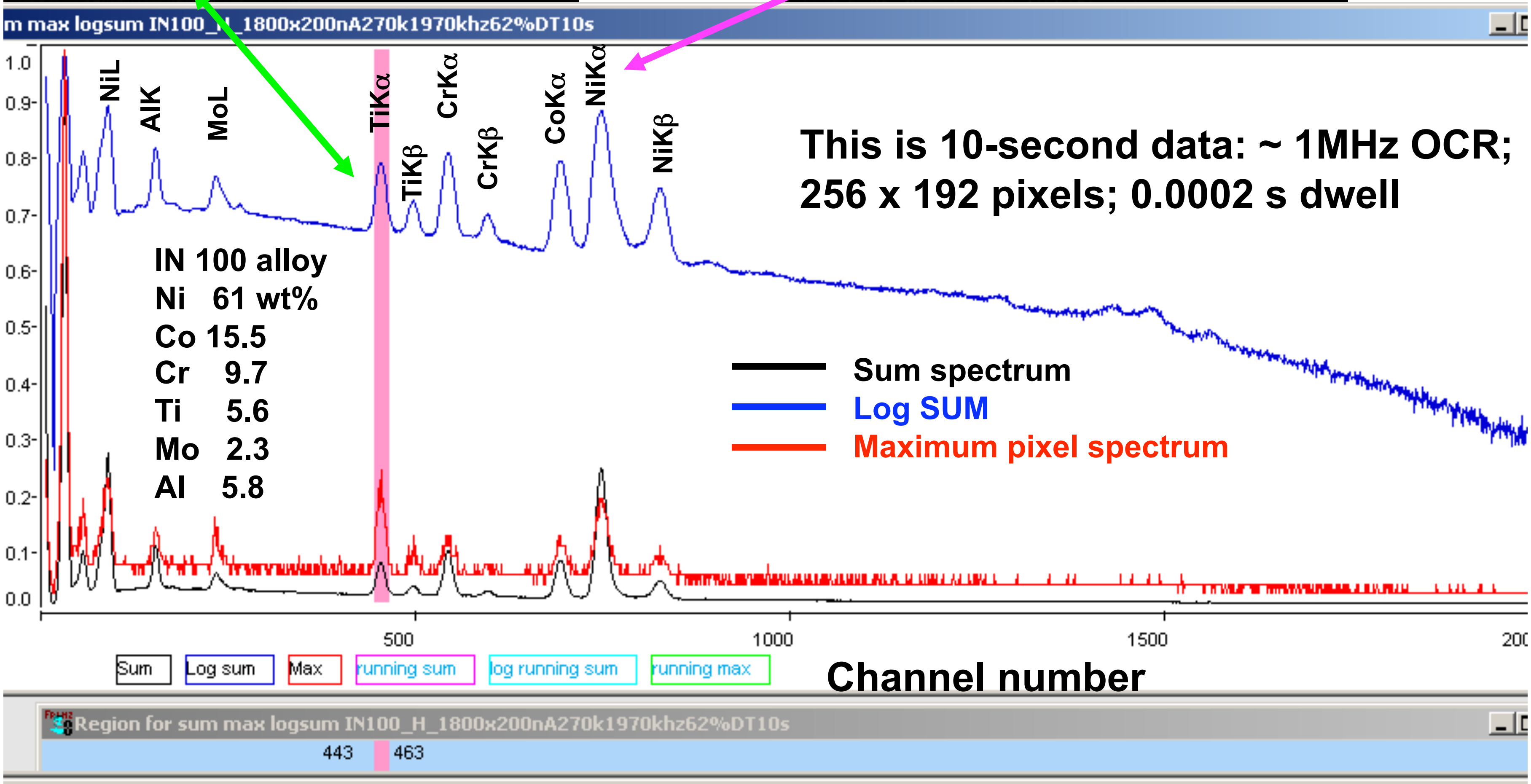
E_0 = 20 keV; 40 nA; OCR 300 kHz; res 145 eV; 14% deadtime;
256x192 pixels; 1 ms/pixel = 50 s

Pull out all the stops: what can we accomplish in ~ 10 seconds in XSI mapping ?

- E_0 = 20 keV; i_B = 100nA
- SDD-EDS: 220 ns time constant (145 eV at MnKα); ~ 1 MHz output count rate; ~ 40% deadtime
- Full image resolution 256x192 pixels
- 200 microseconds/pixel dwell
- Total XSI map time = 9.8 seconds







This is 10-second data: ~ 1MHz OCR; 256 x 192 pixels; 0.0002 s dwell

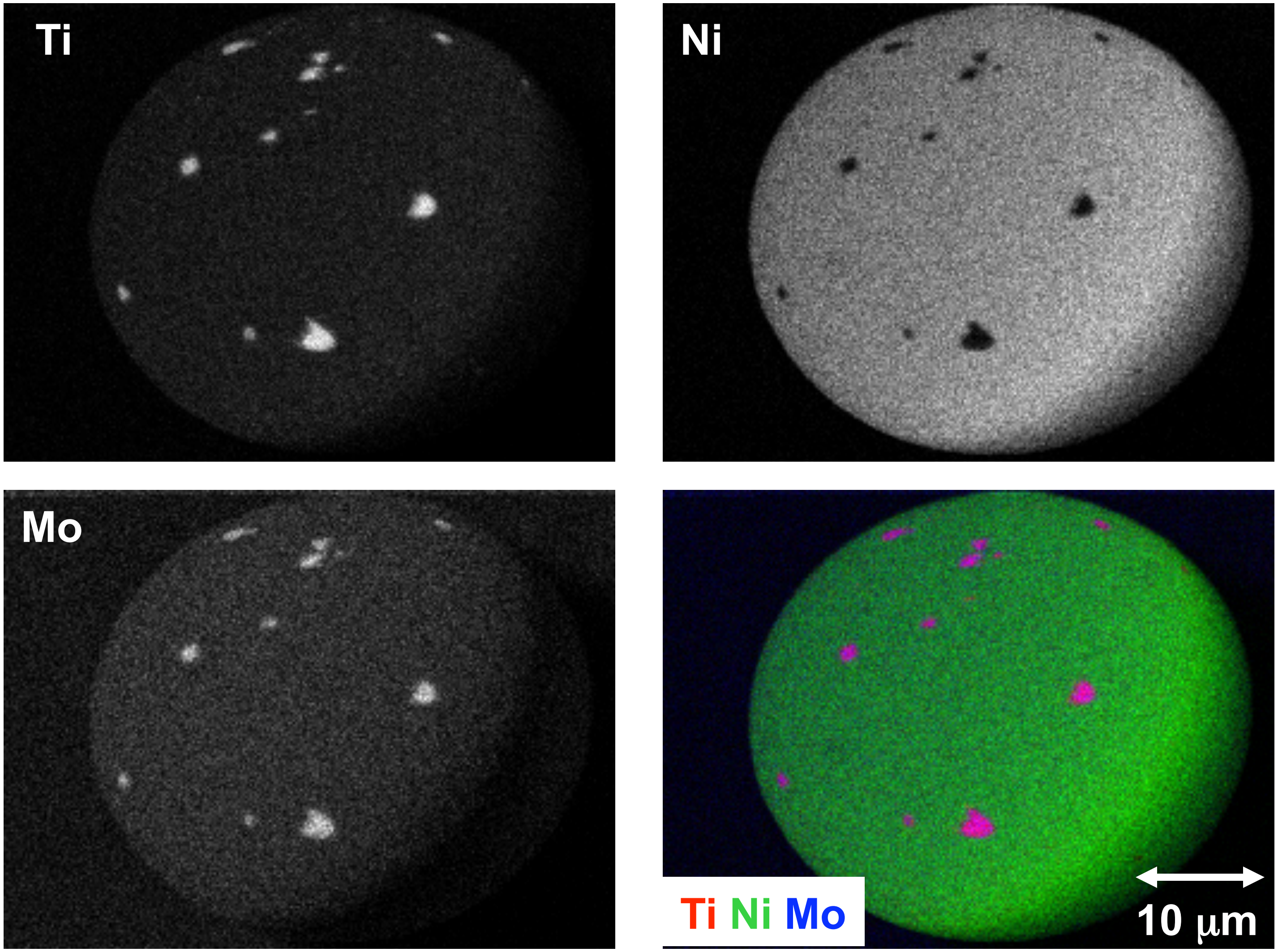
IN 100 alloy

Ni	61 wt%
Co	15.5
Cr	9.7
Ti	5.6
Mo	2.3
Al	5.8

- Sum spectrum
- Log SUM
- Maximum pixel spectrum

IN100 (Ni-Co-Cr-Ti-Mo-Al alloy)

This is 10-second data: ~ 1MHz OCR; 256 x 192 pixels; 0.0002 s dwell



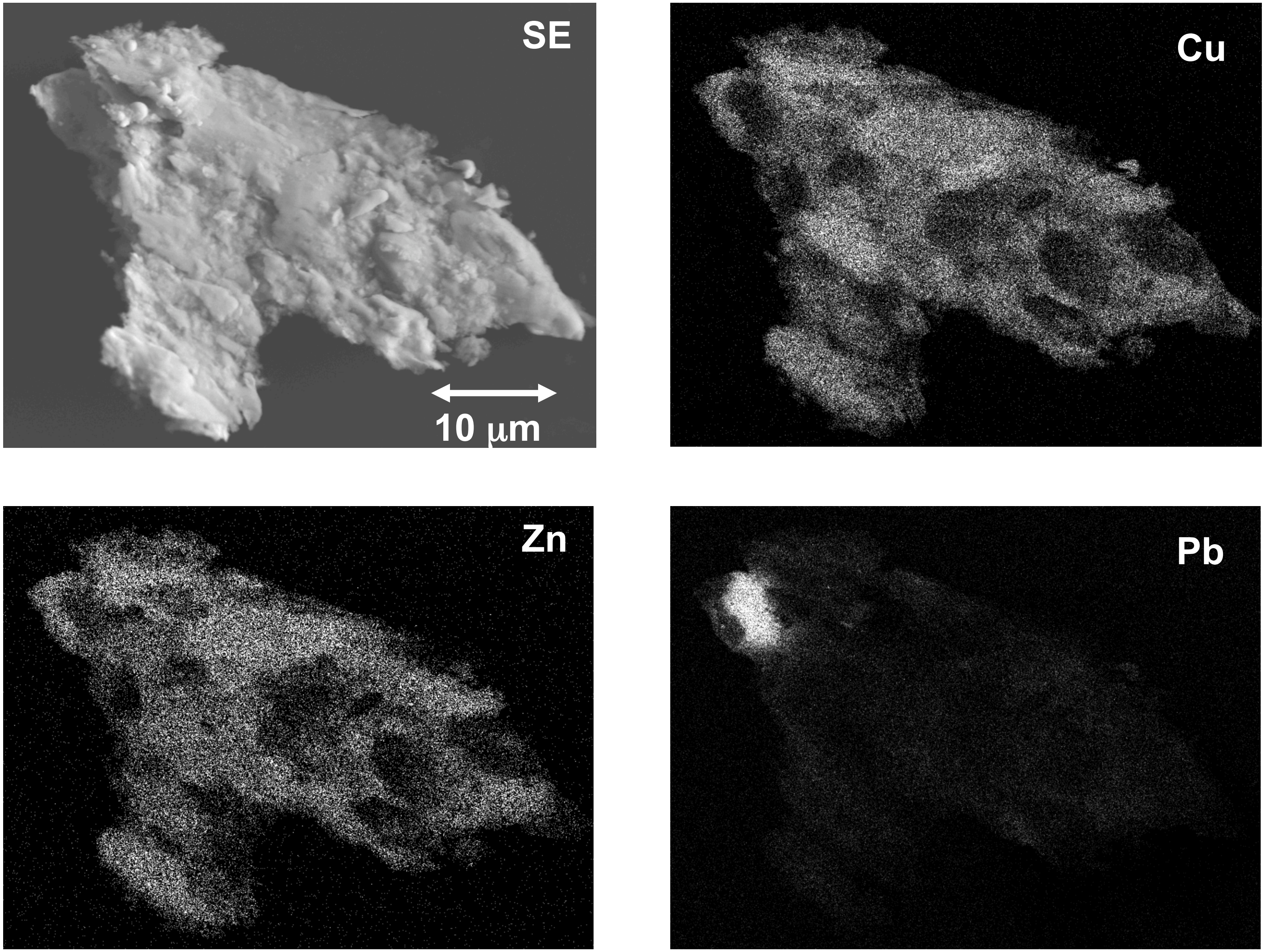
IN 100 alloy

Ni	61 wt%
Co	15.5
Cr	9.7
Ti	5.6
Mo	2.3
Al	5.8

Pull out all the stops: what can we accomplish in ~ 10 seconds in XSI mapping ?

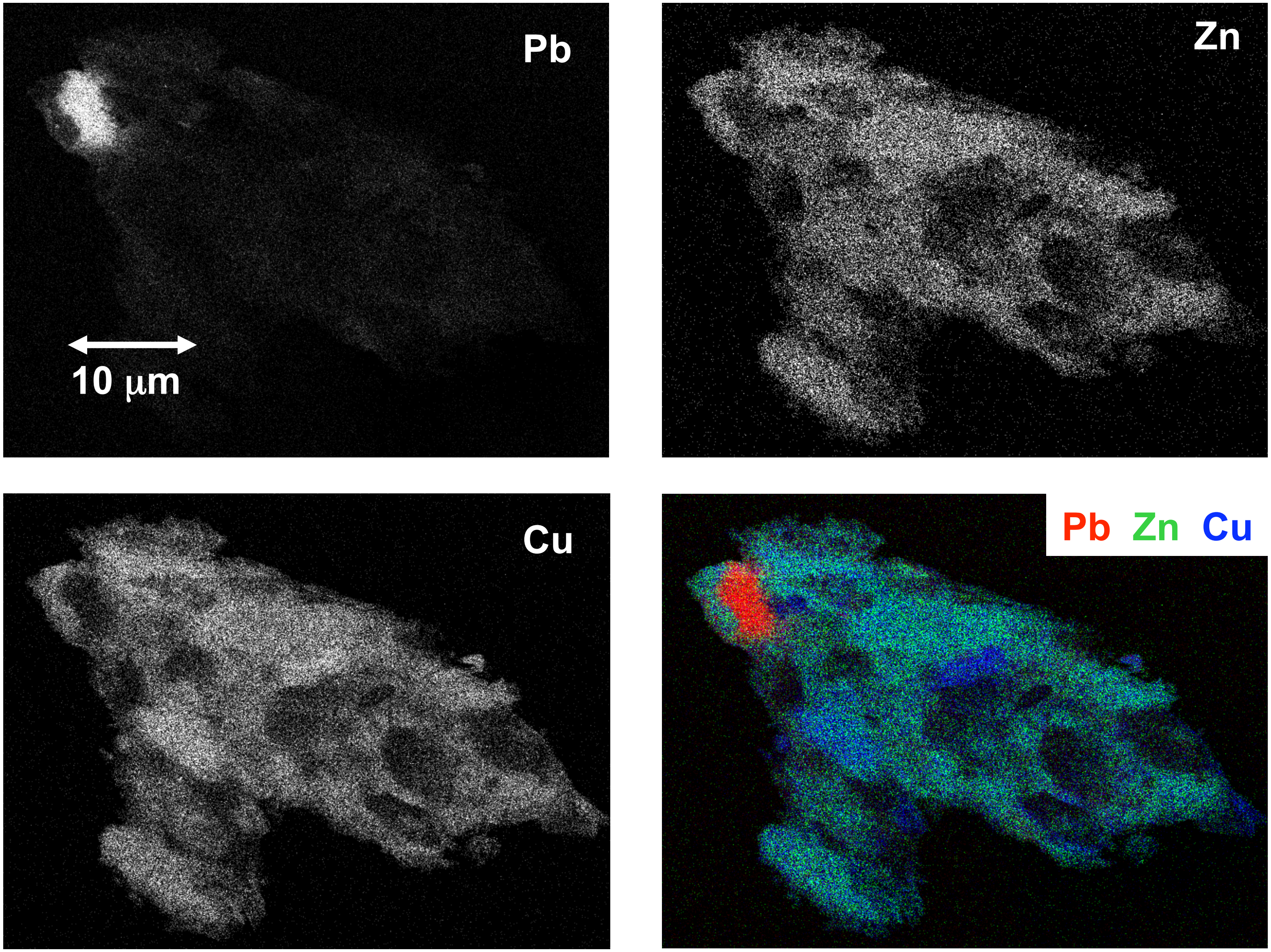
- E_0 = 20 keV; i_B = 50nA
- SDD-EDS: 220 ns time constant (145 eV at MnKα); ~ 500 kHz output count rate; ~ 30% deadtime
- Full image resolution 640x480 pixels
- 16 microseconds/pixel dwell
- Total XSI map time = 4.9 seconds

Brass Particle: E_0 = 20 keV; 50nA; OCR=465kHz 20% deadtime; 640x480;
16 microseconds/pixel; **4.9** seconds for complete XSI



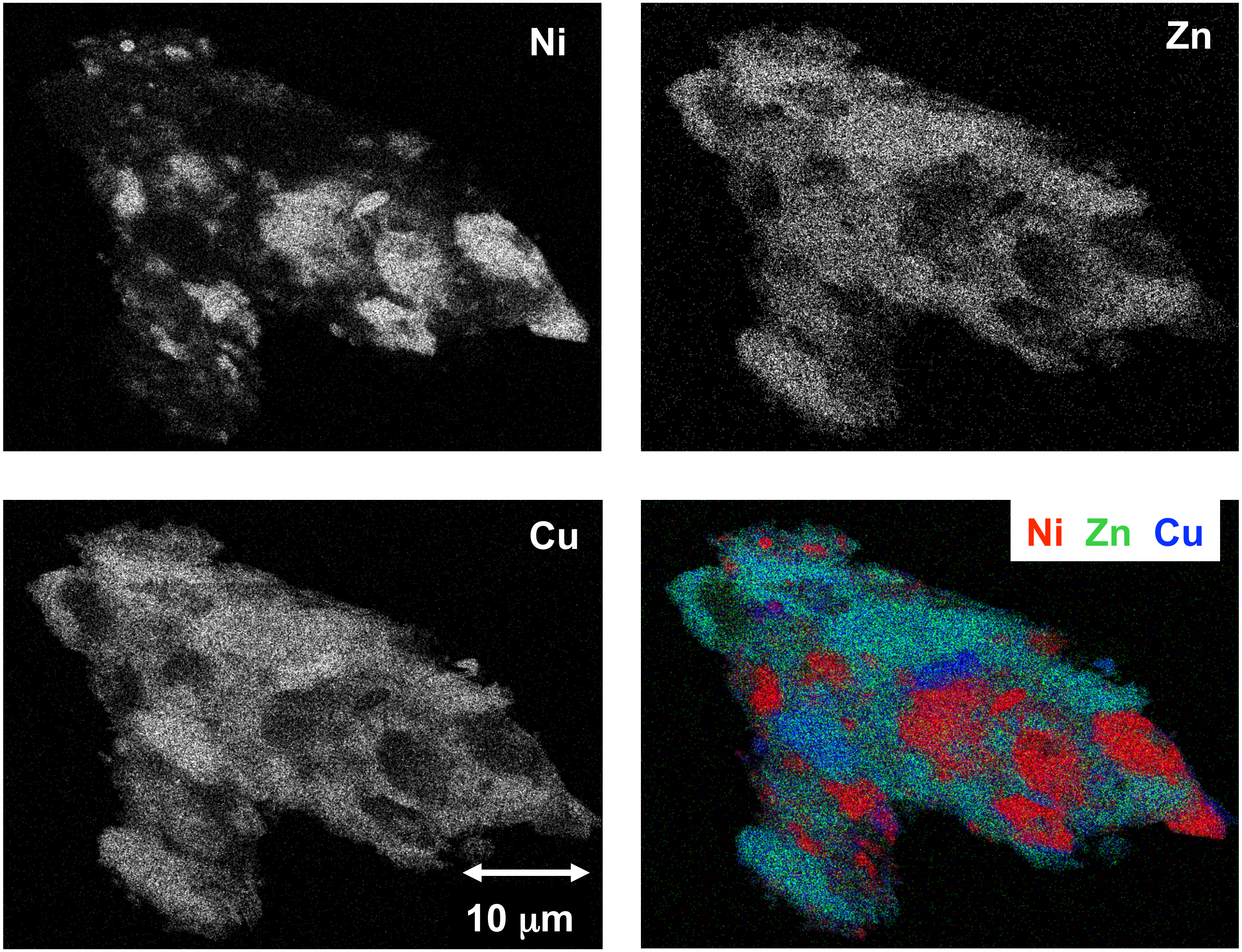
In 5 seconds, XSI reveals the major constituents of the particle, plus some surprises!

Brass Particle: E_0 = 20 keV; 50nA; OCR=465kHz 20% deadtime; 640x480; **16** microseconds/pixel; **4.9** seconds for XSI



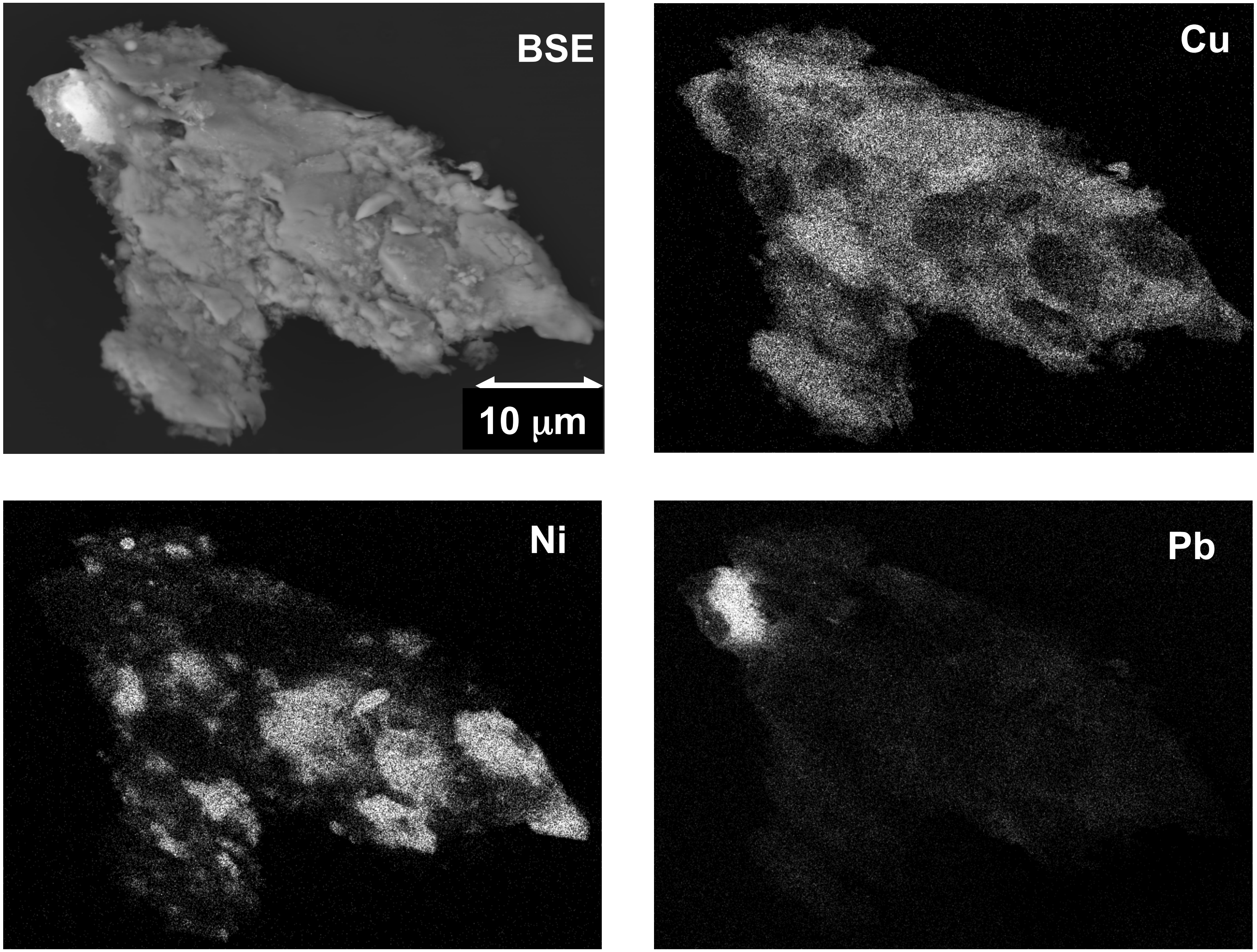
In 5 seconds, XSI reveals the major constituents of the particle, plus some surprises!

Brass Particle: E_0 = 20 keV; 50nA; OCR=465kHz 20% deadtime; 640x480; **16** microseconds/pixel; **4.9** seconds for complete XSI



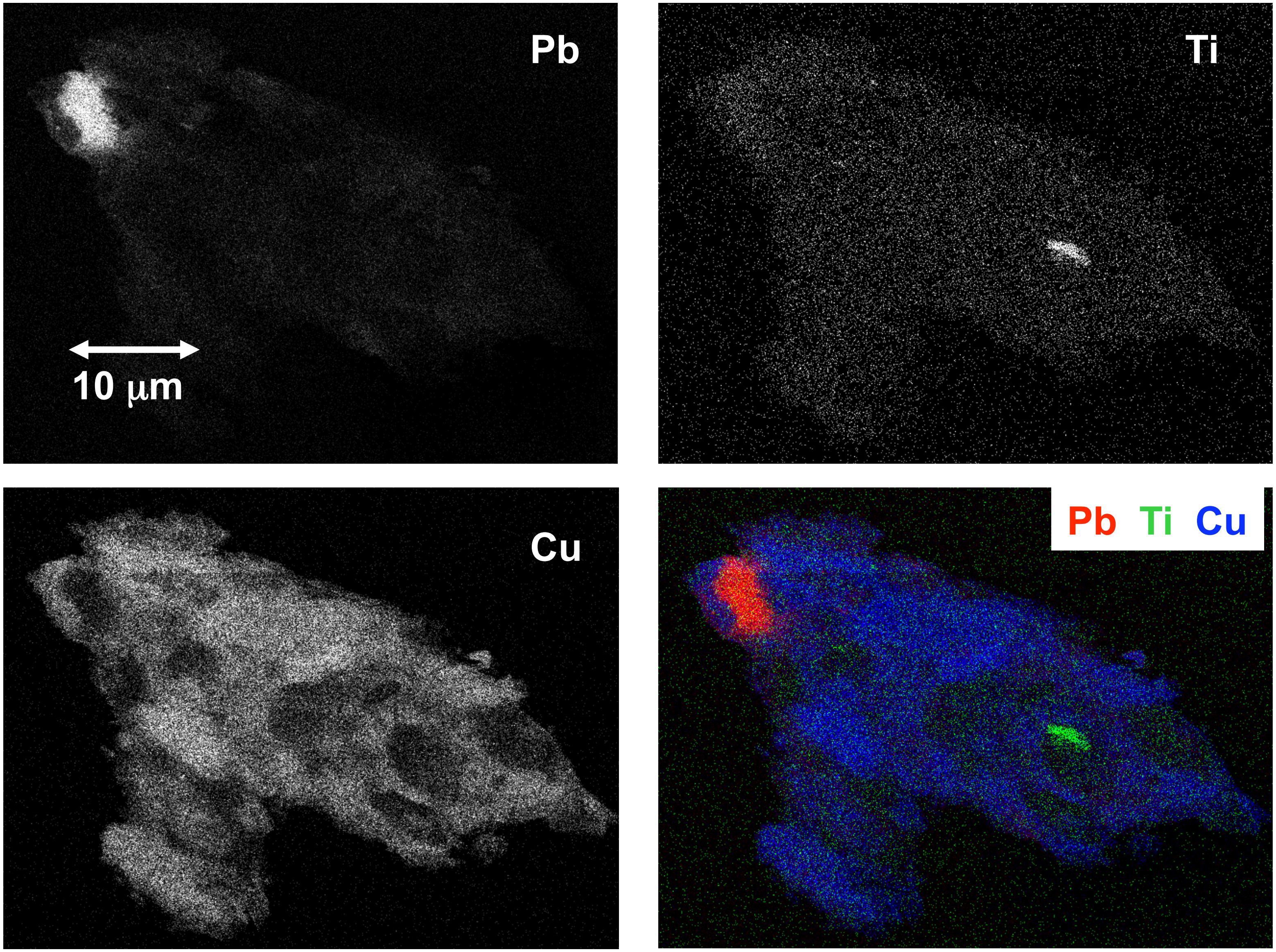
In 5 seconds, XSI reveals the major constituents of the particle, plus some surprises!

Brass Particle: E_0 = 20 keV; 50nA; OCR=465kHz 20% deadtime; 640x480; **16** microseconds/pixel; **4.9** seconds for complete XSI



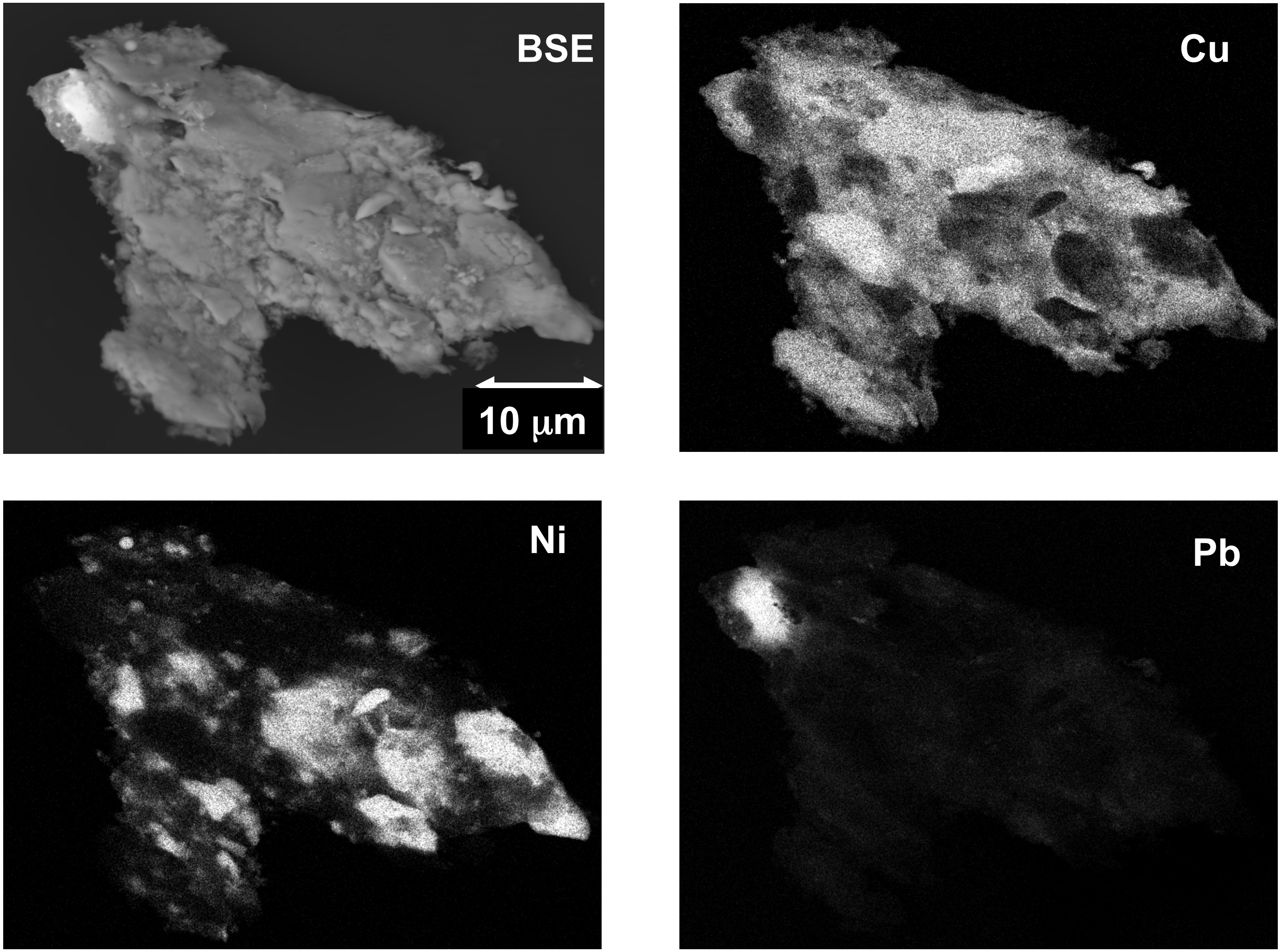
SEM-BSE reveals the Pb but not the Ni (ΔZ = 1 relative to Cu)

Brass Particle: E_0 = 20 keV; 50nA; OCR=465kHz 20% deadtime; 640x480;
16 microseconds/pixel; **4.9** seconds for XSI



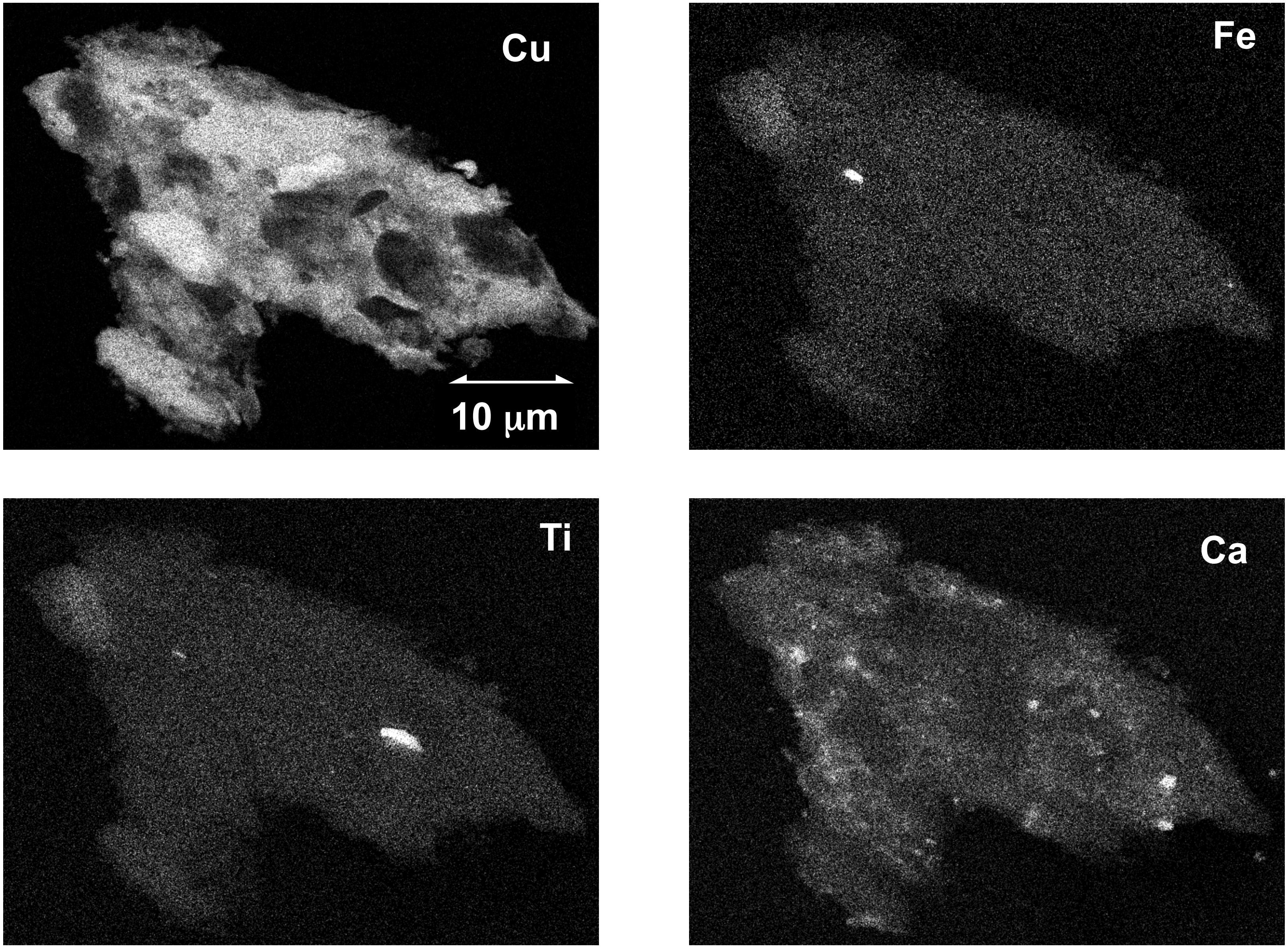
In 5 seconds, XSI reveals the major constituents of the particle, plus some surprises!

Brass Particle: E_0 = 20 keV; 50nA; OCR=465kHz 20% deadtime; 640x480; **256** microseconds/pixel; **79** seconds for complete XSI



With 79 seconds, XSI reveals deep gray level range and compositional structures!

Brass Particle: E_0 = 20 keV; 50nA; OCR=465kHz 20% deadtime; 640x480;
256 microseconds/pixel; **79** seconds for complete XSI

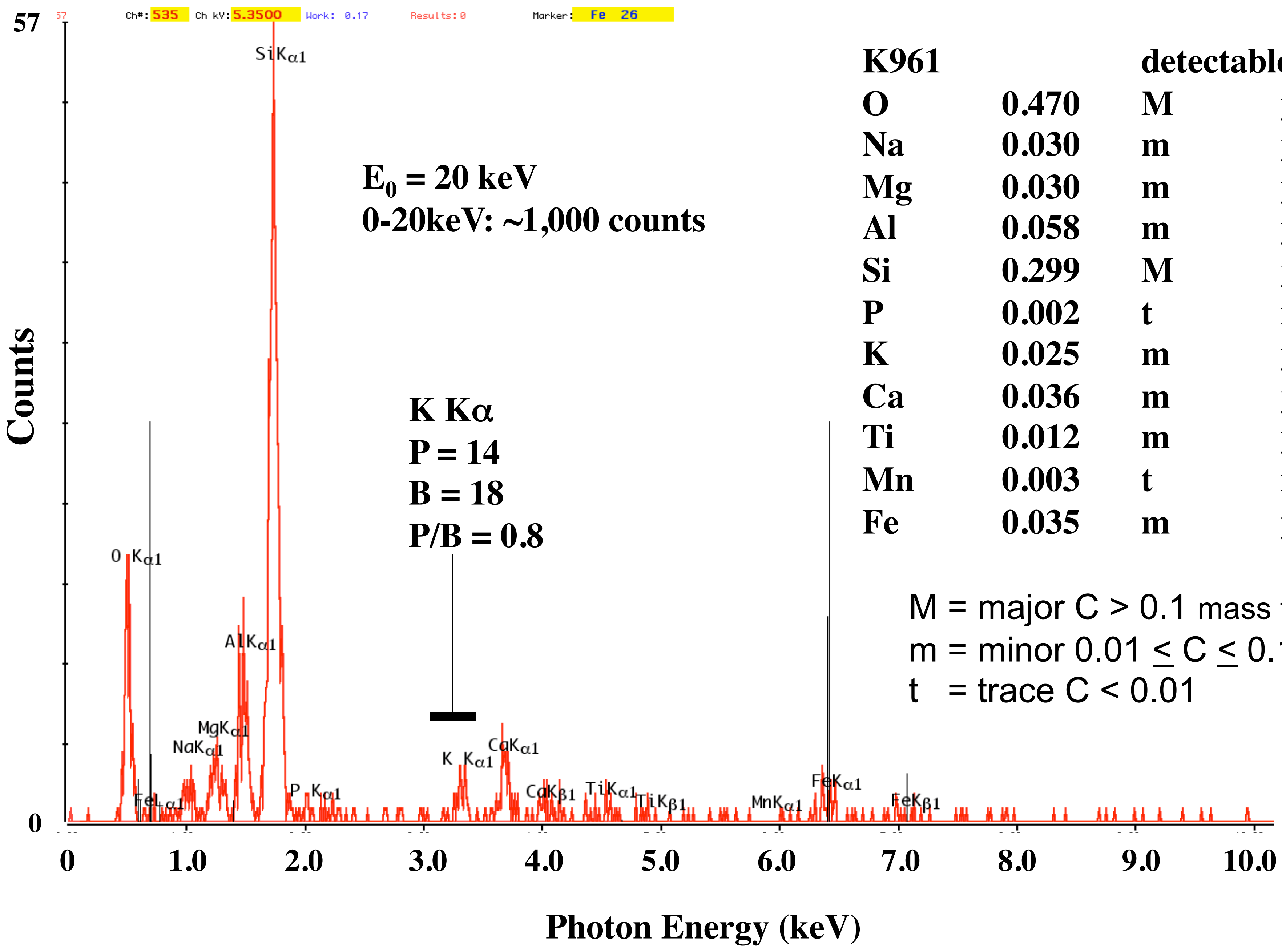


With 79 seconds, XSI reveals deep gray level range and more surprises!

Future particle analysis strategy with SDD-EDS and tFEG-SEM

- Instead of collecting an “average” EDS spectrum during an overscan that inevitably ignores particle microstructure, collect a small XSI (e.g., 64x64 pixel, 1 ms dwell = 4 s)
- A single-pixel spectrum at 1 MHz OCR and 1 ms dwell contains ~1,000 counts. Is this useful?

Desktop Spectrum Analyzer (DTSA) Simulation



E_0 = 20 keV
0-20keV: ~1,000 counts

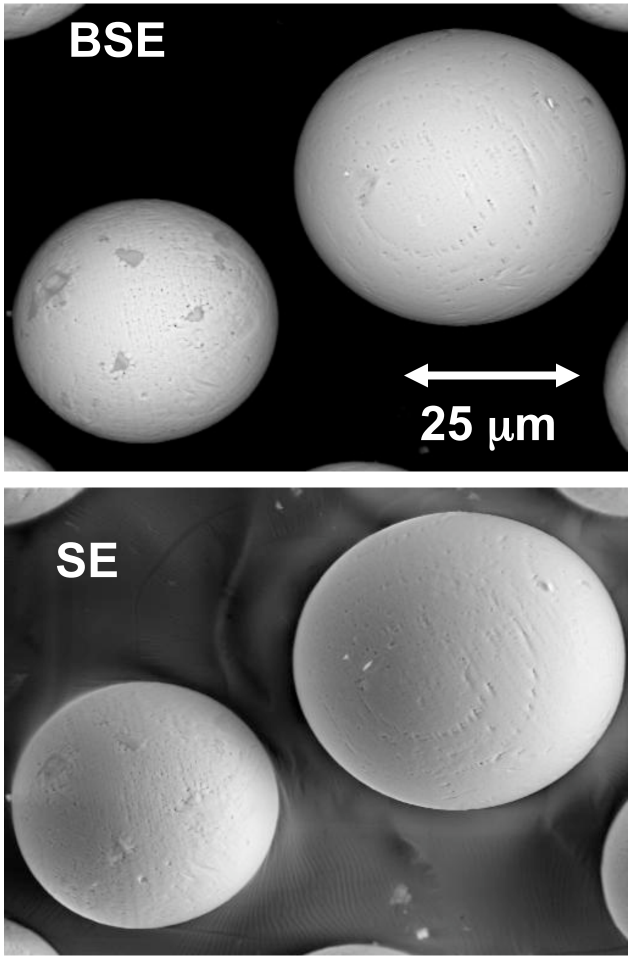
K Kα
P = 14
B = 18
P/B = 0.8

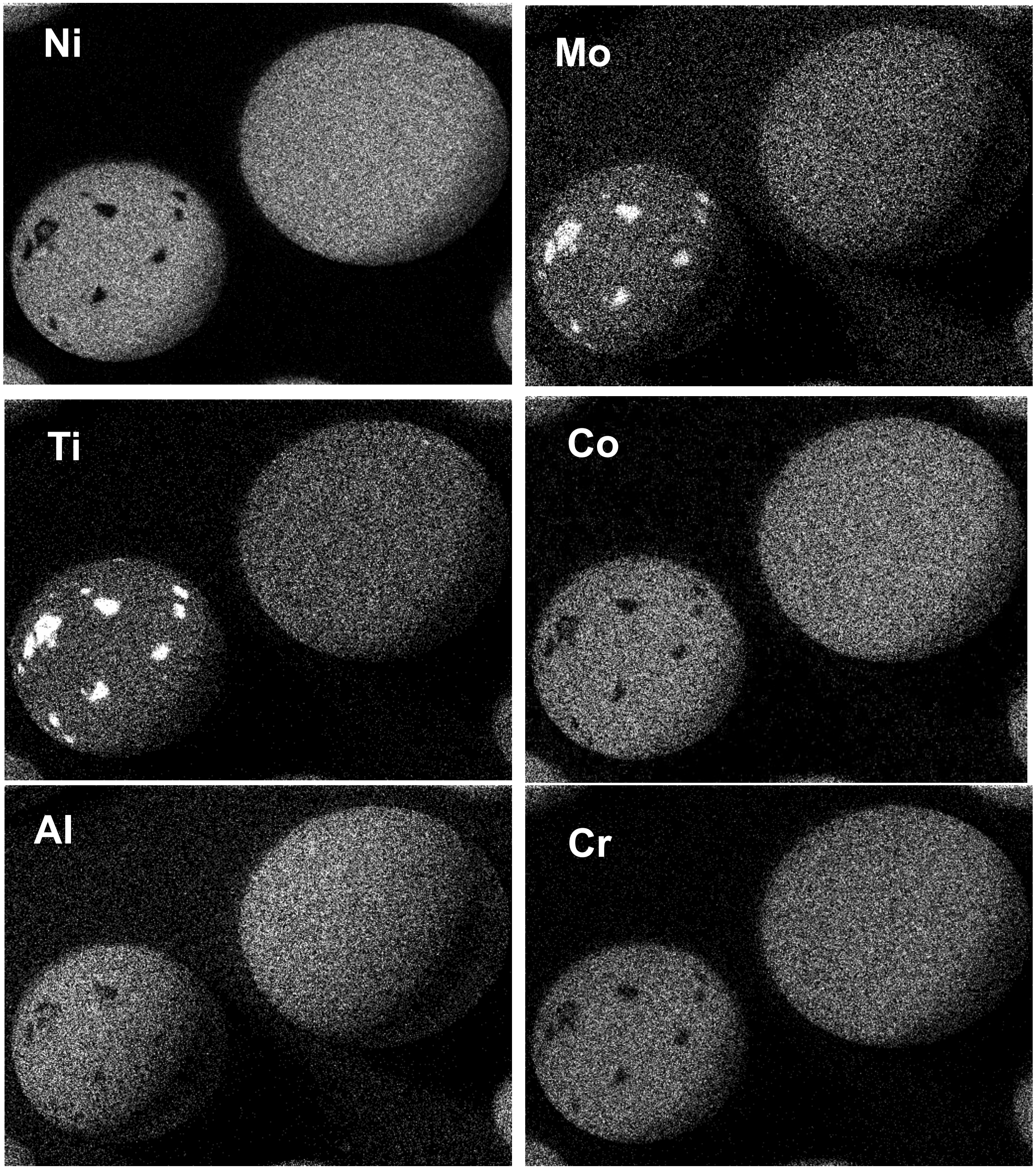
K961		detectable?	
O	0.470	M	y
Na	0.030	m	y
Mg	0.030	m	y
Al	0.058	m	y
Si	0.299	M	y
P	0.002	t	n
K	0.025	m	y
Ca	0.036	m	y
Ti	0.012	m	y
Mn	0.003	t	n
Fe	0.035	m	y

M = major C > 0.1 mass frac.
m = minor $0.01 \leq C \leq 0.1$
t = trace C < 0.01

Future particle analysis strategy with SDD-EDS and tFEG-SEM

- Instead of collecting an “average” EDS spectrum during an overscan that inevitably ignores particle microstructure, collect a small XSI (e.g., 64x64 pixel, 1 ms dwell = 4 s)
- A single-pixel spectrum at 1 MHz OCR and 1 ms dwell contains ~1,000 counts. Is this useful? **YES!**
- Now we have a storage problem (raw, 8 Mbyte/particle; compressed, ~1 Mbyte/particle) if we want to accumulate a large particle database, 10,000 particles or more
- We also have an information retrieval problem, e.g., which particles have interesting heterogeneity? Need for fast AutoLispix!!





E_0 = 20 keV
i = 50 nA
512x384 pixels
64 μs/pixel
13 s XSI

Future particle analysis strategy with SDD-EDS and tFEG-SEM

- Instead of collecting an “average” EDS spectrum during an overscan that inevitably ignores particle microstructure, collect a small XSI (e.g., 64x64 pixel, 1 ms dwell = 4 s)
- A single-pixel spectrum at 1 MHz OCR and 1 ms dwell contains ~1,000 counts. Is this useful? **YES!**
- Now we have a storage problem (raw, 8 Mbyte/particle; compressed, ~1 Mbyte/particle) if we want to accumulate a large particle database, e.g., 10,000 particles or more.
- We also have an information retrieval problem, e.g., finding which particles have interesting heterogeneity? Need for fast AutoLispix!
- **Having problems like these makes it interesting to come to work in the morning!!**

Limits of Detection

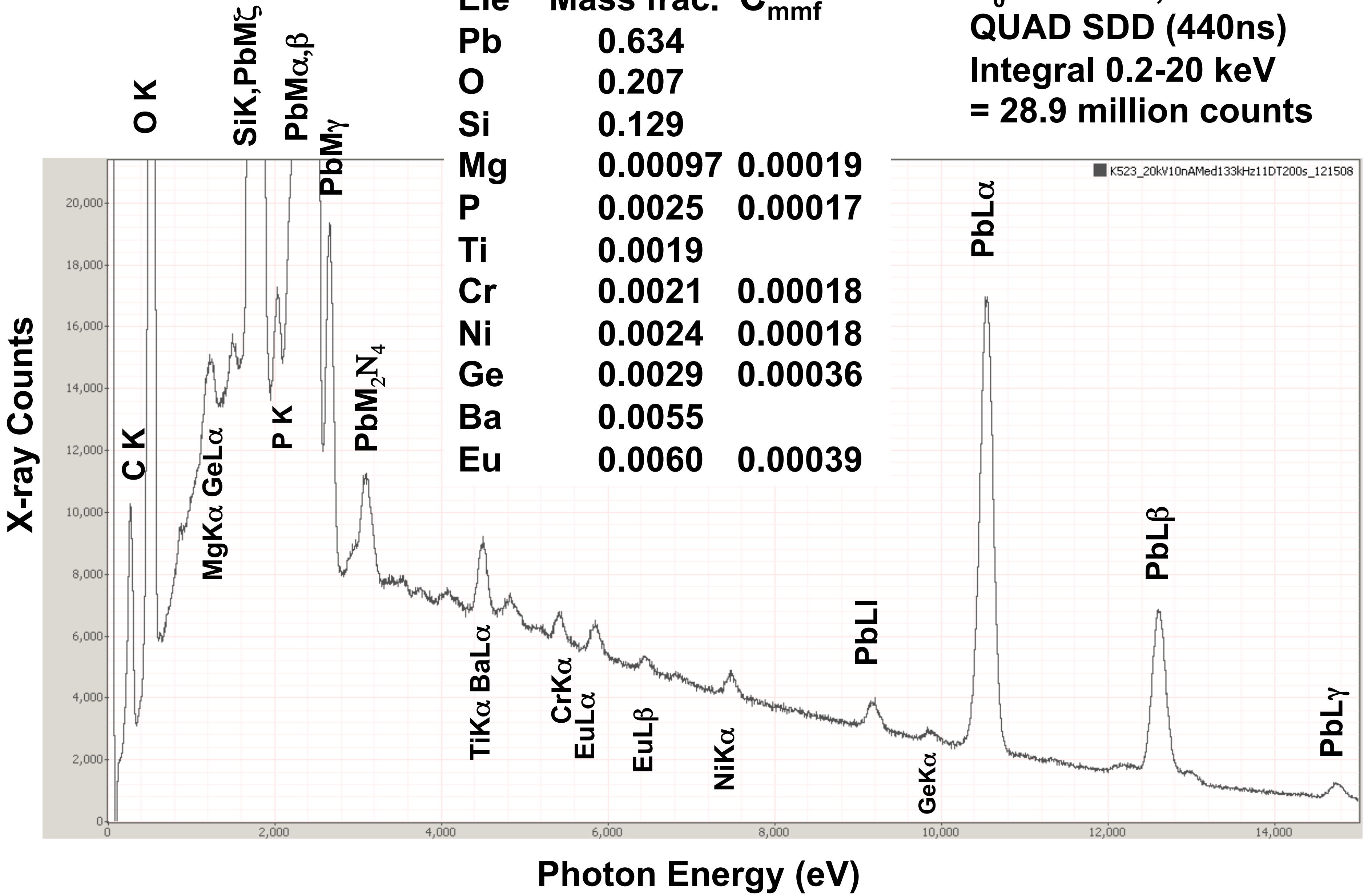
- With high beam current and SDD-EDS, we can accumulate extremely high count spectra, 10 M – 100 M counts, in a short time.
- We can now work with extraordinary precision (<u>but not necessarily improved accuracy</u>).
- We can now routinely achieve limits of detection at the 500 parts per million level, or lower!
- $C_{mmf} = [3B^{1/2}/(P\text{-}B)]\ C_{std}$

$C_{mmf} = [3B^{1/2}/(P-B)]\ C_{std}$

K523

Ele	Mass frac.	C_{mmf}
Pb	0.634	
O	0.207	
Si	0.129	
Mg	0.00097	0.00019
P	0.0025	0.00017
Ti	0.0019	
Cr	0.0021	0.00018
Ni	0.0024	0.00018
Ge	0.0029	0.00036
Ba	0.0055	
Eu	0.0060	0.00039

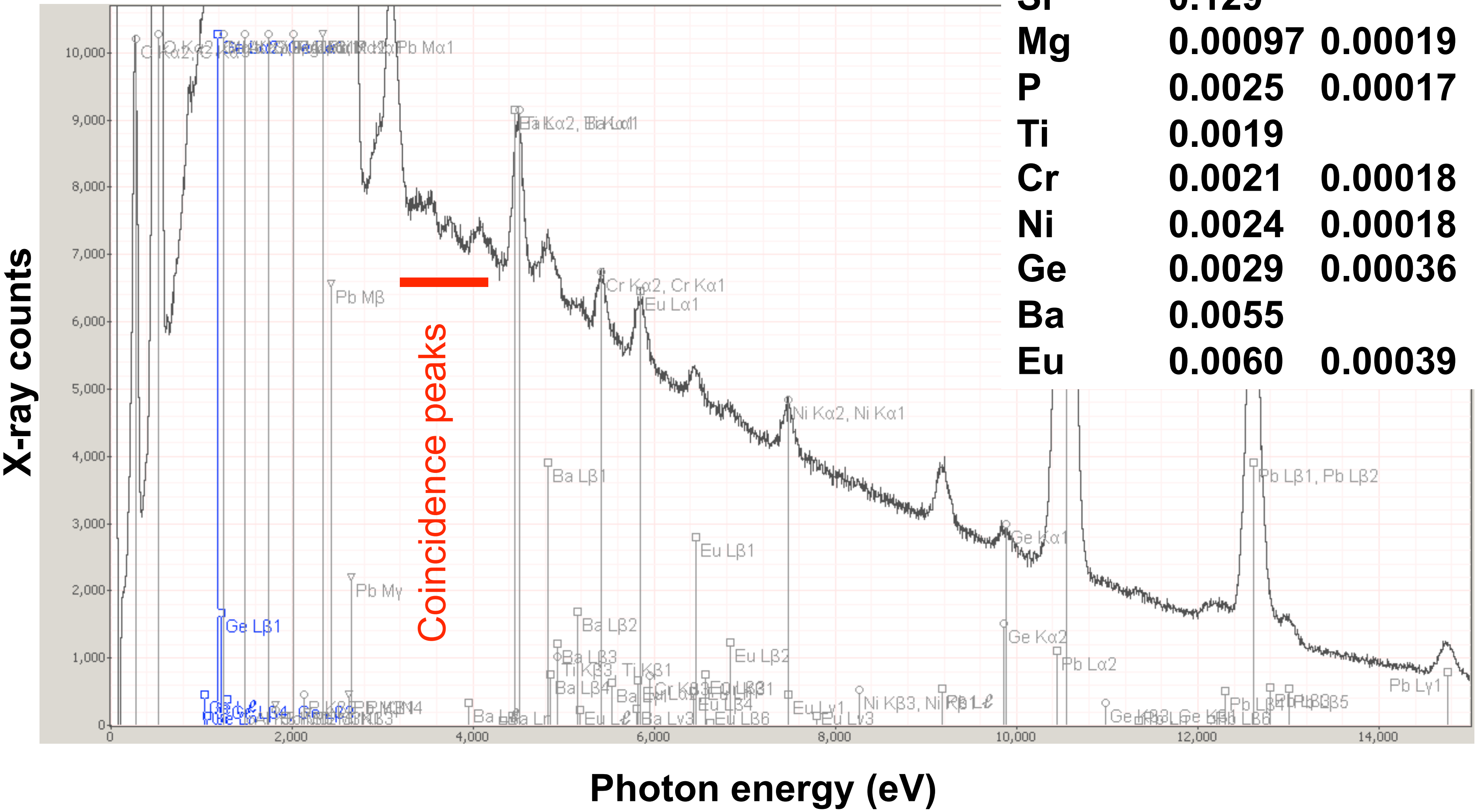
NIST Glass K523
E_0 = 20 keV; 200 s
QUAD SDD (440ns)
Integral 0.2-20 keV
= 28.9 million counts



$$C_{mmf} = [3B^{1/2}/(P-B)]\, C_{std}$$

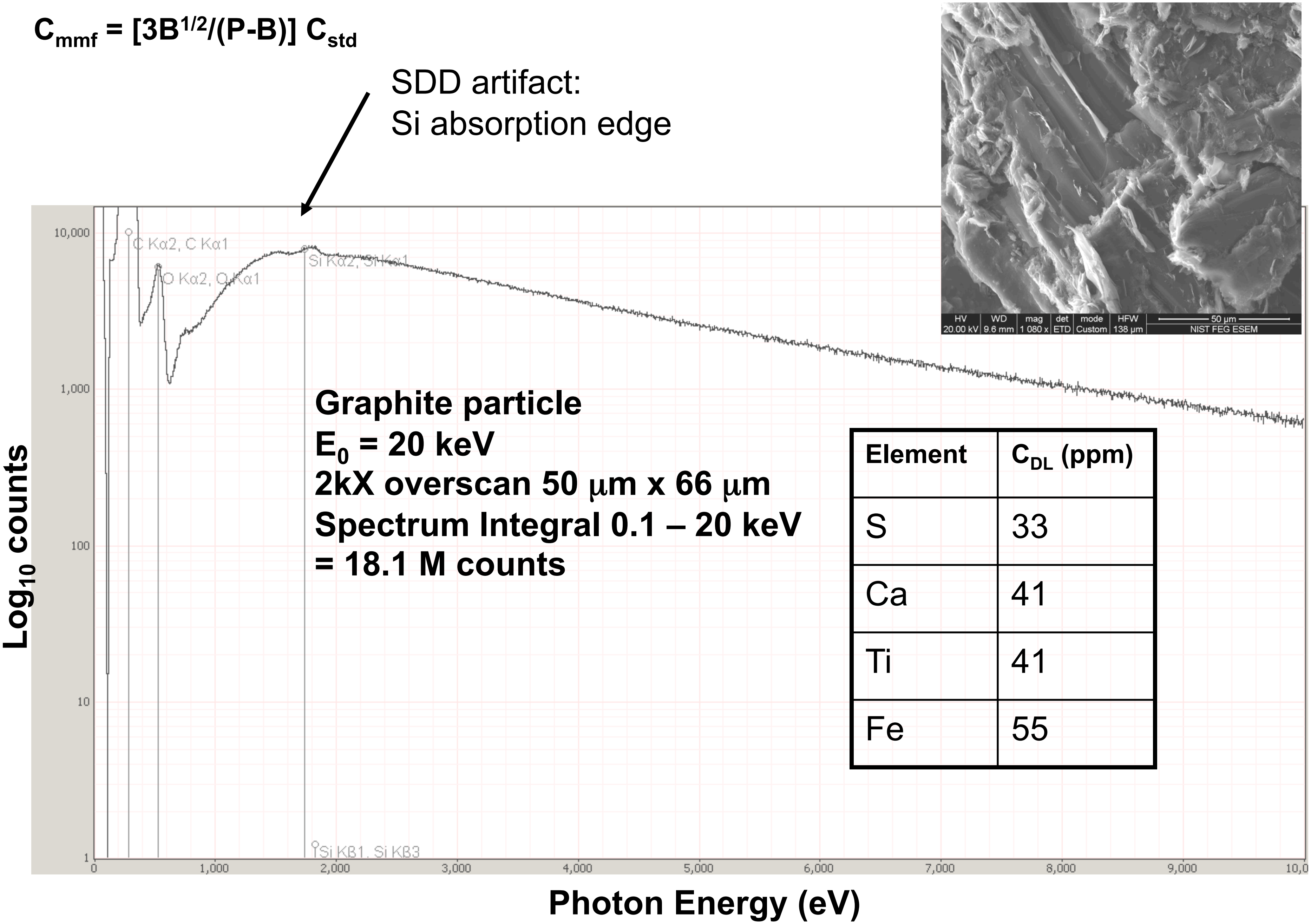
K523

Ele	Mass frac.	C_{mmf}
Pb	0.634	
O	0.207	
Si	0.129	
Mg	0.00097	0.00019
P	0.0025	0.00017
Ti	0.0019	
Cr	0.0021	0.00018
Ni	0.0024	0.00018
Ge	0.0029	0.00036
Ba	0.0055	
Eu	0.0060	0.00039



$C_{mmf} = [3B^{1/2}/(P-B)]\ C_{std}$

SDD artifact:
Si absorption edge



Graphite particle
E_0 = 20 keV
2kX overscan 50 μm x 66 μm
Spectrum Integral 0.1 – 20 keV
= 18.1 M counts

Element	**C_{DL} (ppm)**
S	33
Ca	41
Ti	41
Fe	55

Conclusions

- SDD-EDS, tFEG-SEM, and NIST Lispix provide a powerful new approach to particle analysis
- Future spectrum collection strategy should seek to retain access to particle heterogeneity information.
- Limits of detection can be pushed much lower within limits of patience

The Argyle Sweater (Scott Hilburn)

Second coming of “The Far Side?

http://www.theargylesweater.com/

The Argyle Sweater (Scott Hilburn)

Second coming
of "The Far Side?

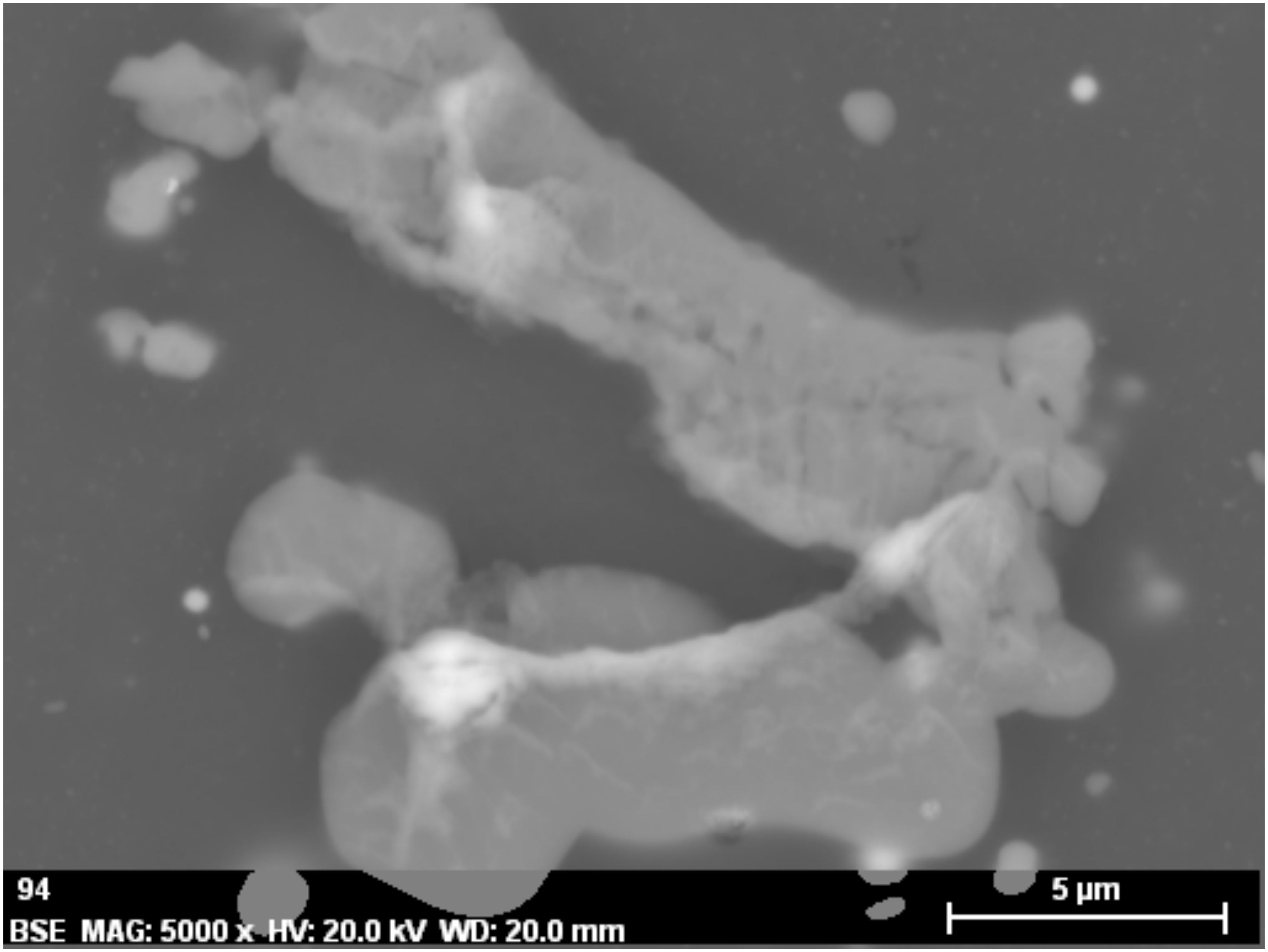
Only edgier!

http://www.theargylesweater.com/

Pull out all the stops: what can we accomplish in high spatial resolution/short time in XSI mapping ?

- E_0 = 20 keV; i_B = 10nA
- SDD-EDS: 470 ns time constant (127.5 eV at MnKα);
  ~ 250 kHz output count rate; ~ 30% deadtime
- Full image resolution 320x240 pixels
- 1 milliseconds/pixel dwell
- Total XSI map time = 77 seconds

Al alloy 2024 (T6)

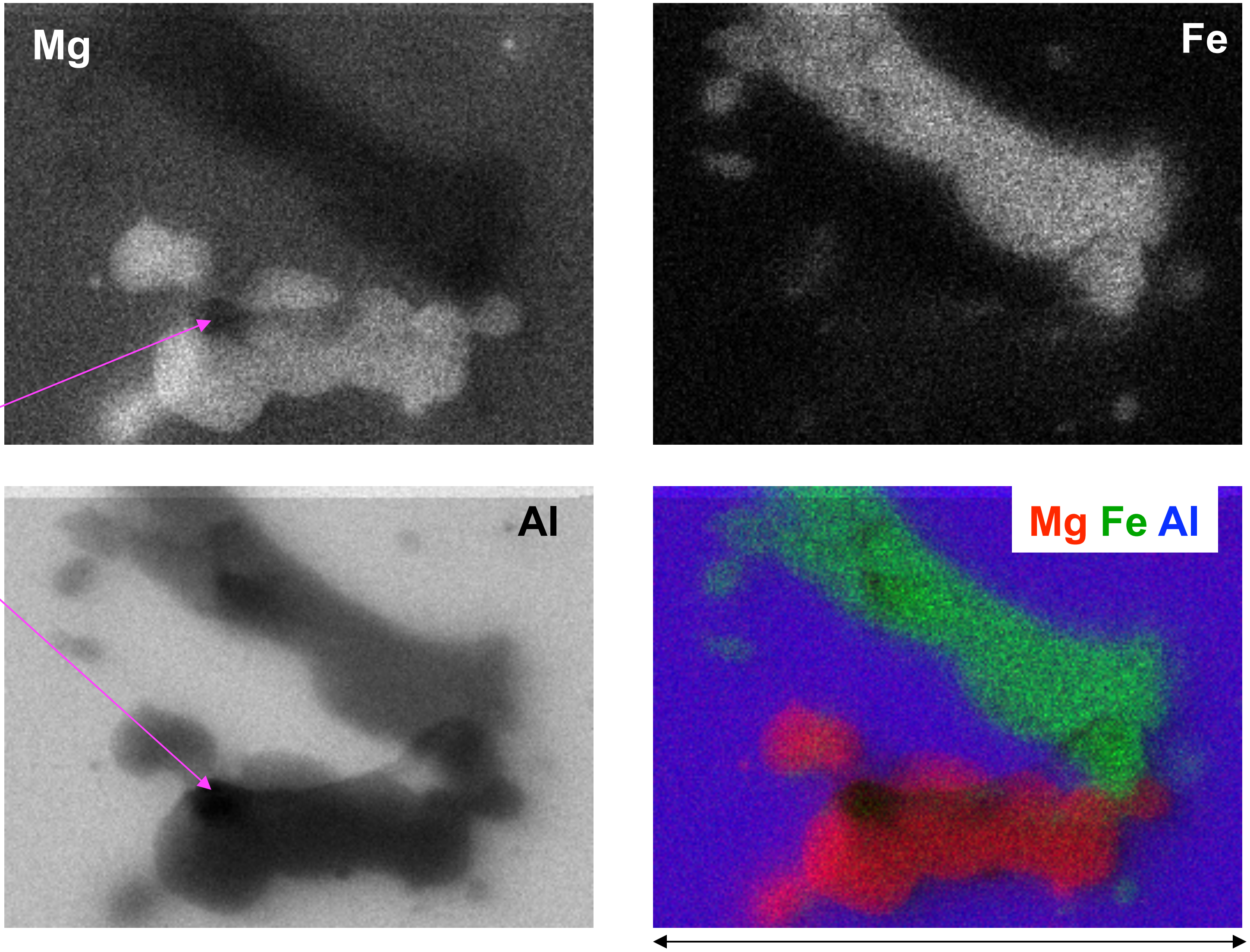


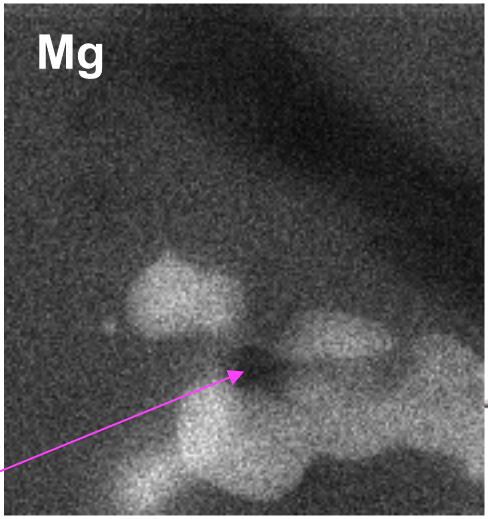
XSI SDD imaging is the way to study inhomogeneous particles!

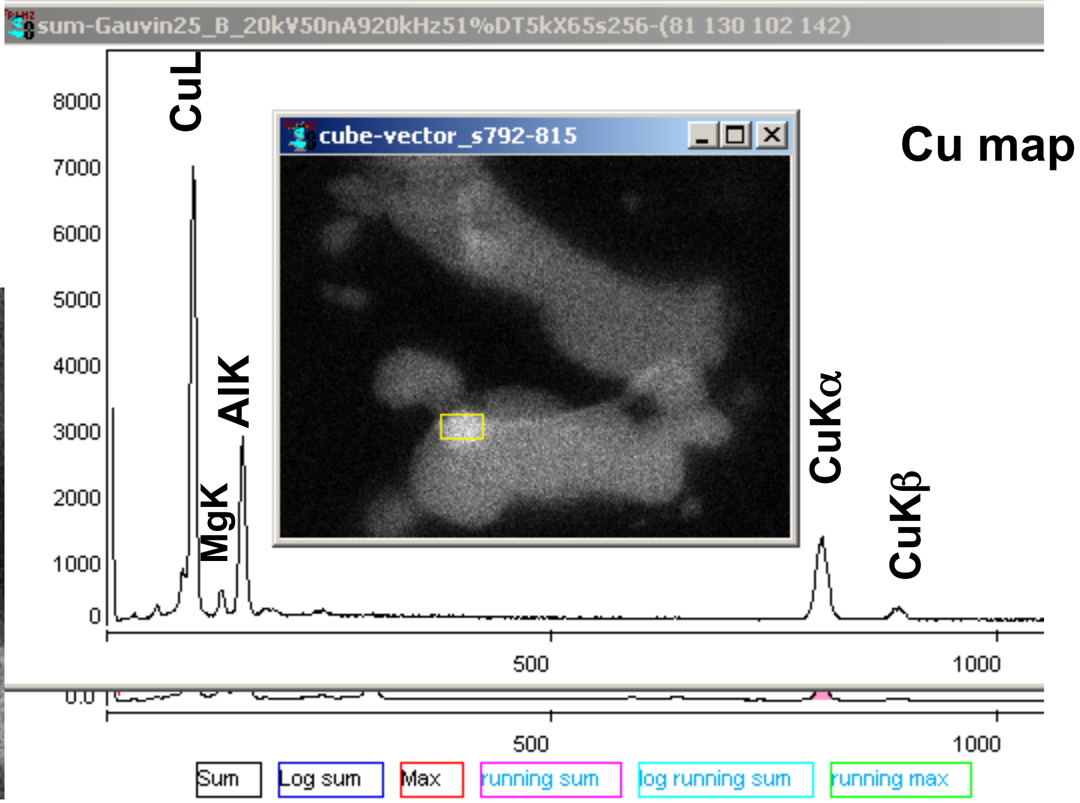
77 second
XSI data

Inclusions in
complex Al-alloy

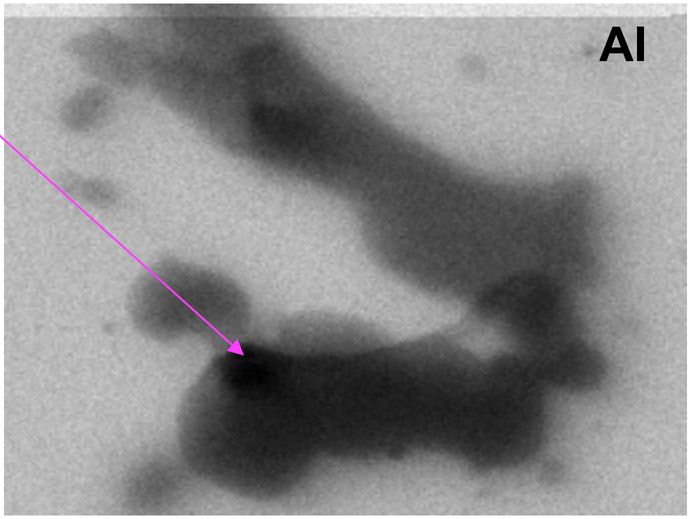
What is
this?

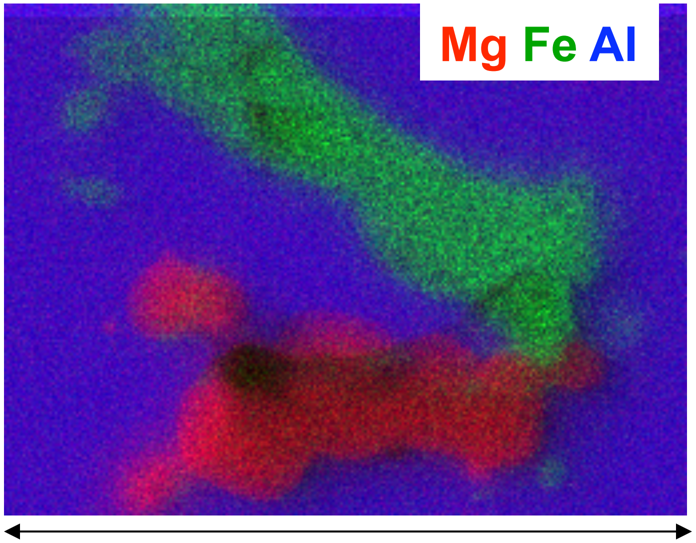






What is this?



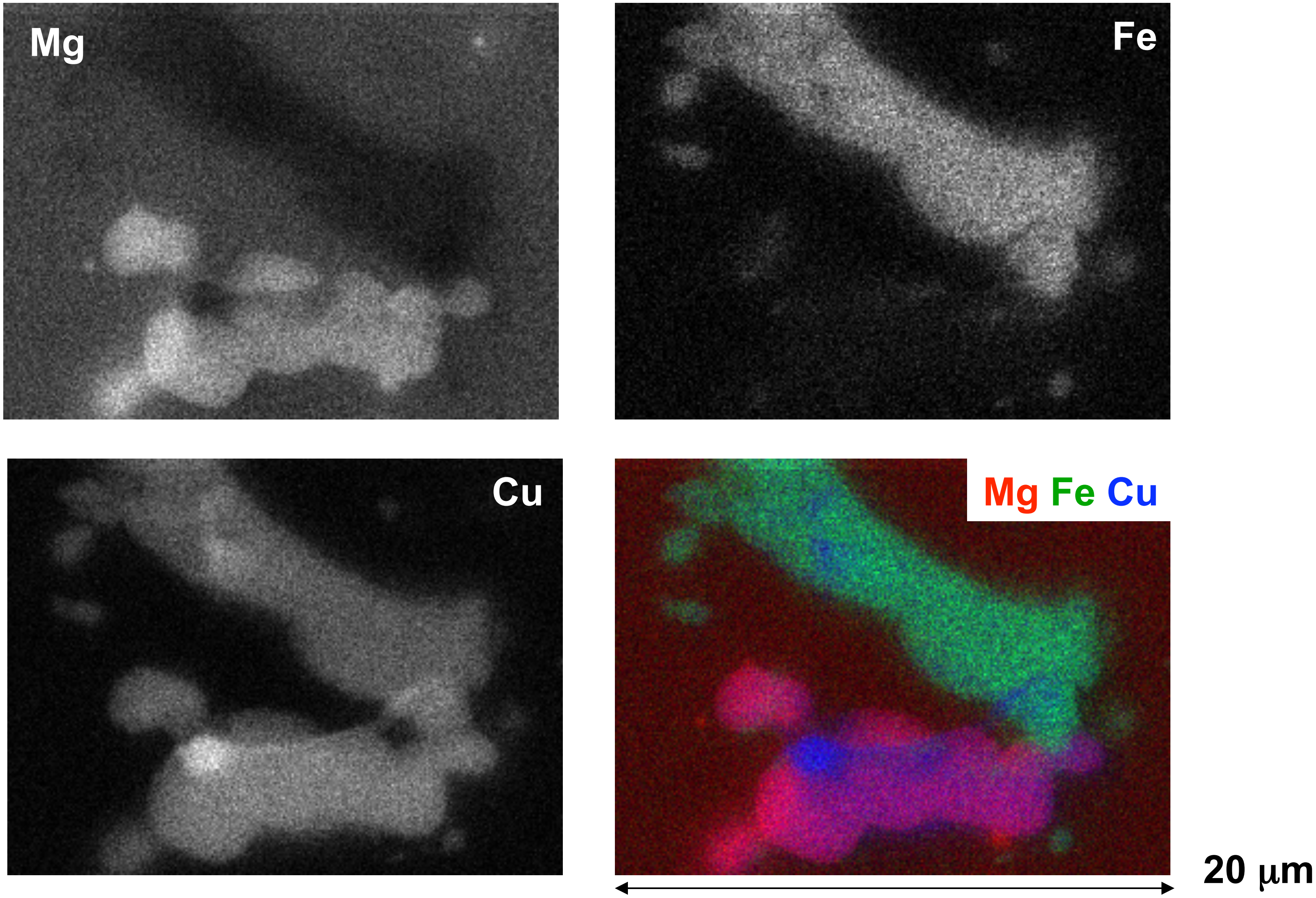


20 µm

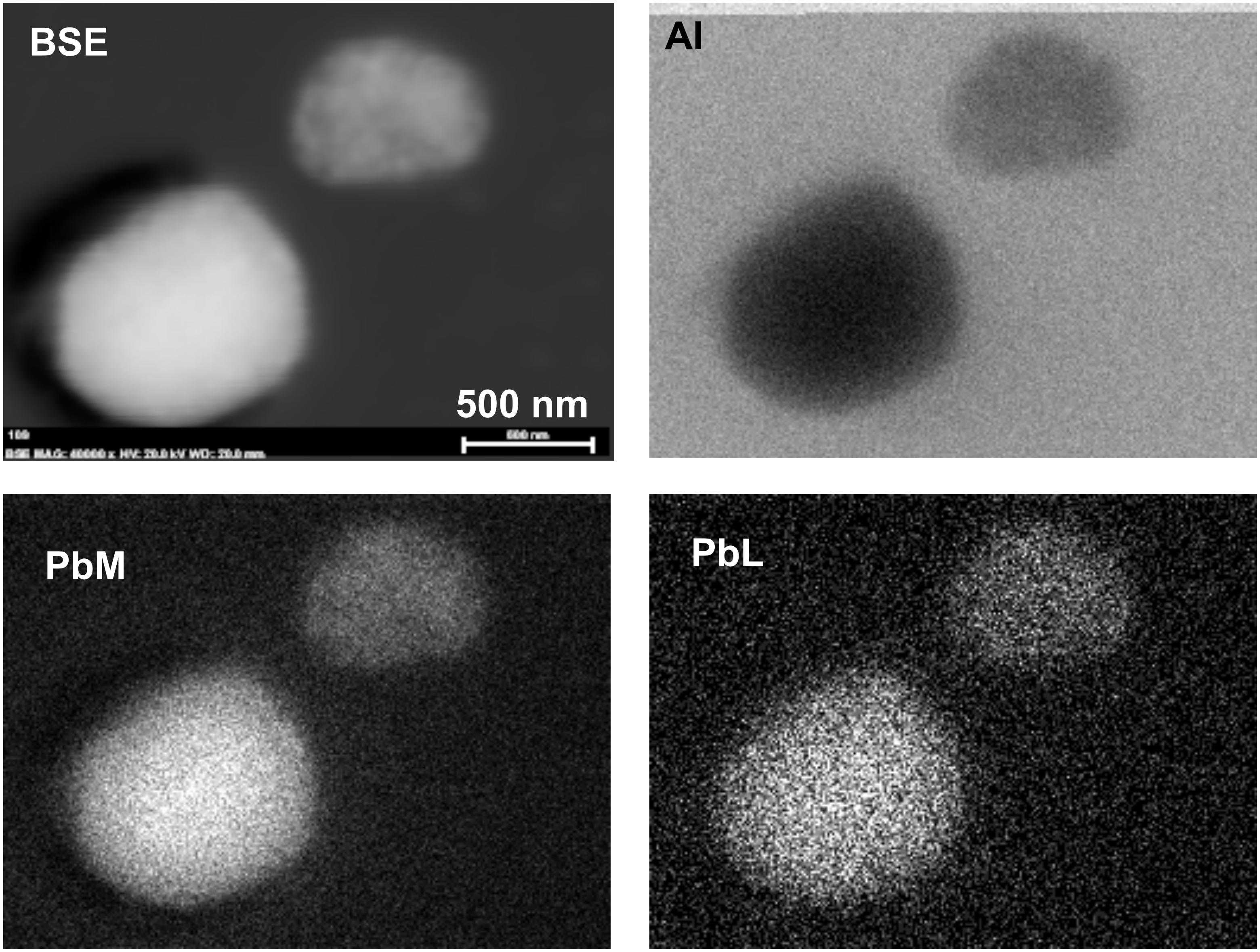
XSI SDD: Complete database enables detailed analysis

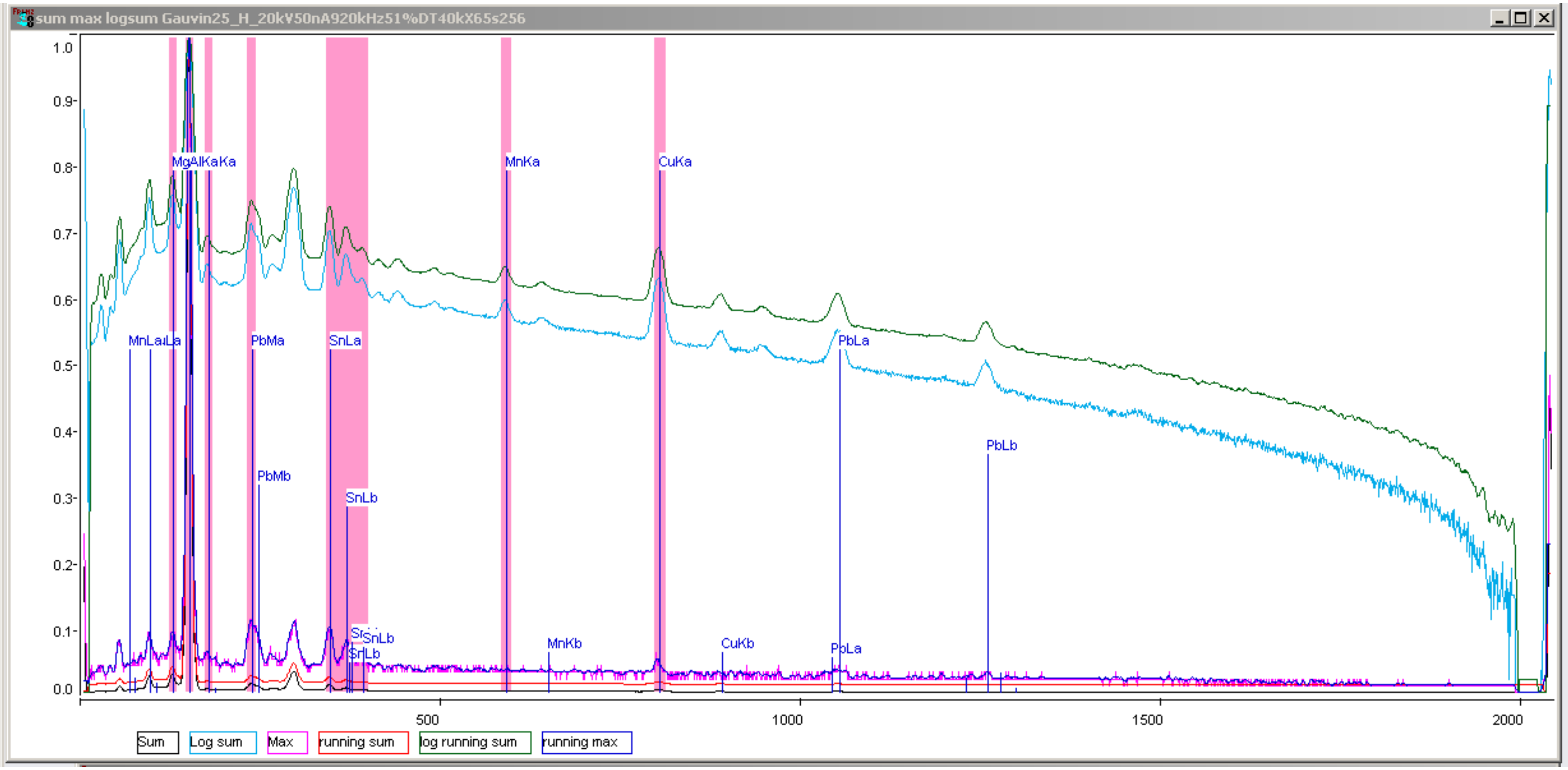
77 second
XSI data

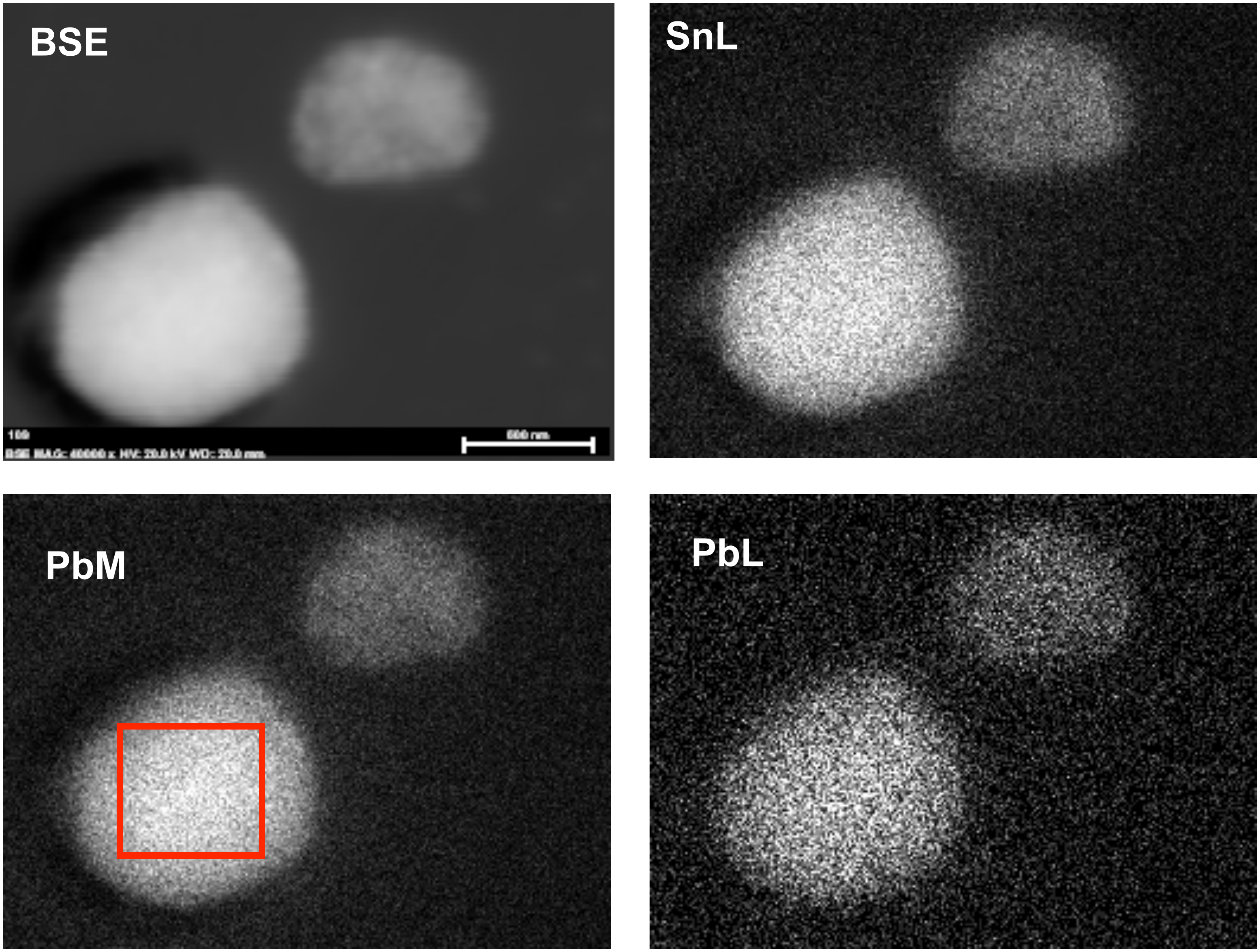
Inclusions in
complex Al-alloy

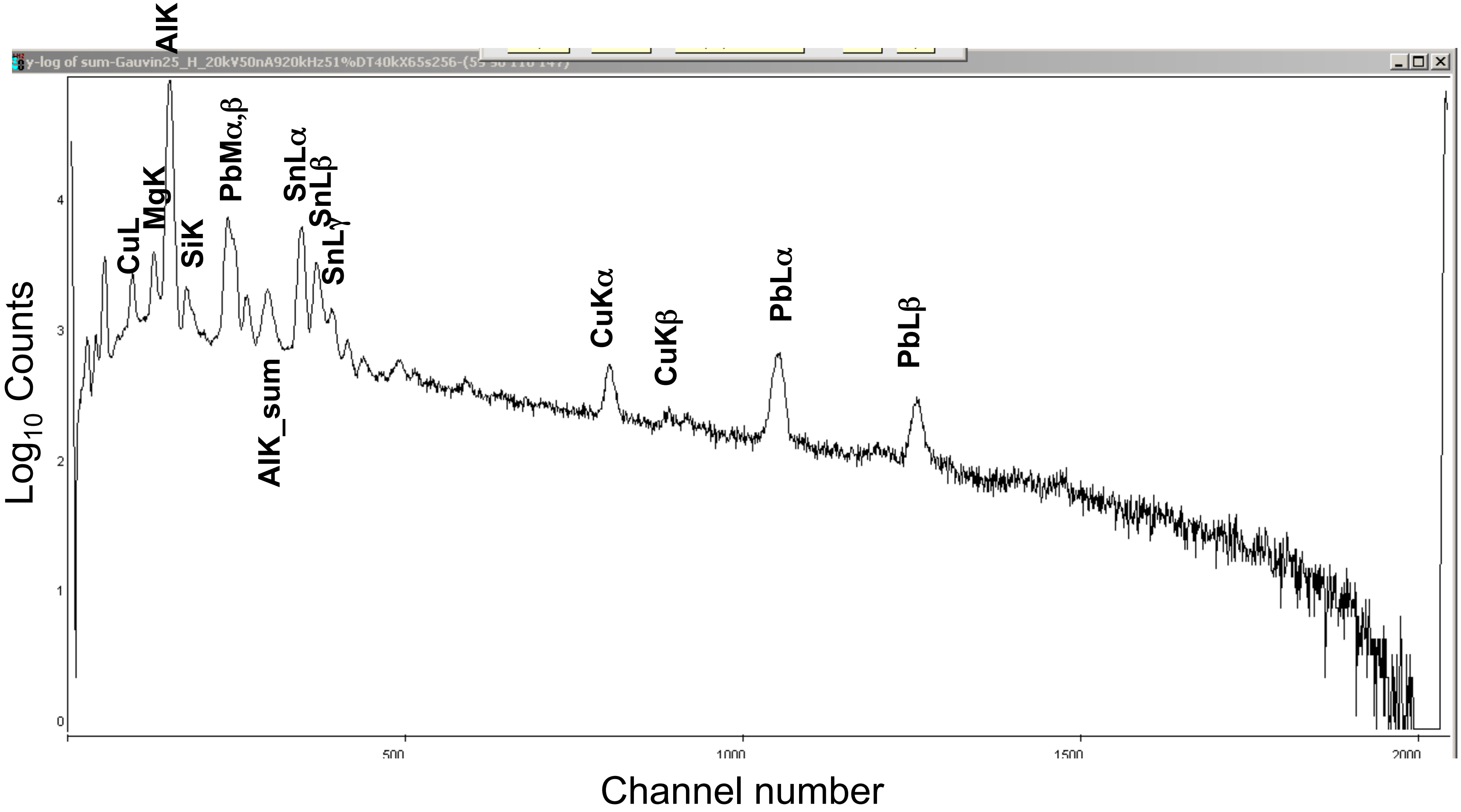


Finding the really unexpected in the complex Al 2024-T6 alloy!




sum max logsum Gauvin25_H_20kV50nA920kHz51%DT40kX65s256
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
500
1000
1500
2000
MgAlKaKa
MnKa
CuKa
MnLaLa
PbMa
SnLa
PbLa
PbLb
PbMb
SnLb
SnLb
SnLb
MnKb
CuKb
PbLa
Sum
Log sum
Max
running sum
log running sum
running max


BSE
SnL
PbM
PbL
600 nm
BSE MAG: 40000 x HV: 20.0 kV WD: 20.0 mm

y-log of sum-Gauvin25_H_20k¥50nA920kHz51%DT40kX65s256-(5
AlK
CuL
MgK
SiK
PbMα,β
AlK_sum
SnLα
SnLβ
SnLγ
CuKα
CuKβ
PbLα
PbLβ
Log10 Counts
0
1
2
3
4
500
1000
1500
2000
Channel number