Quantitative Electron Probe Microanalysis (EPMA): Doing It Right and Doing It Wrong!

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The objective: accurate analysis

- “Accuracy” [finding the “correct” value(s)] is actually considered to be an archaic concept. The preferred concept is an “error budget” associated with each reported value.
- BUT, what happens when we test a method against “absolute” standards, i.e., those prepared and characterized by absolute methods that are traceable to fundamental standards. In chemistry, “absolute” means gravimetry and/or methods that count individual atoms. For spatially-resolved analytical methods like electron probe microanalysis, we require lateral and depth microscopic homogeneity (best determined by the statistics of extensive EPMA analyses) and the best possible knowledge of the composition, determined by independent, absolute methods, such as separation chemistry and gravimetry. There are not many of these materials, about 25 worldwide, but they provide the most rigorous test. Augment with stoichiometric compounds.
- How well does EPMA match independent “absolute” results?

Quantitative EPMA

Two "zeroth" order conditions must be fulfilled:

1. The specimen must have no factors other than composition differences affecting the measured x-ray intensities. Geometric factors (surface irregularities) must be eliminated by careful polishing (NO ETCHING).

2. The specimen must be homogeneous over the interaction volume (dimensions ~ 1 micrometer) that the beam excites. Heterogeneous specimens (e.g., a thin film on a substrate) can be quantified, but advanced calculational procedures are necessary.

The Key to Quantitative EPMA

The best "accuracy" and the most <u>predictable</u> quantitative EPMA procedure (i.e., best understood error budget) is obtained by analyzing the unknown against standards.

1. The SAME elemental x-ray PEAK is measured in the unknown and standard UNDER THE SAME CONDITIONS:

Beam energy, E_0
Known dose (product of beam current and time)
X-ray Take-off Angle, ψ
Spectrometer efficiency and performance

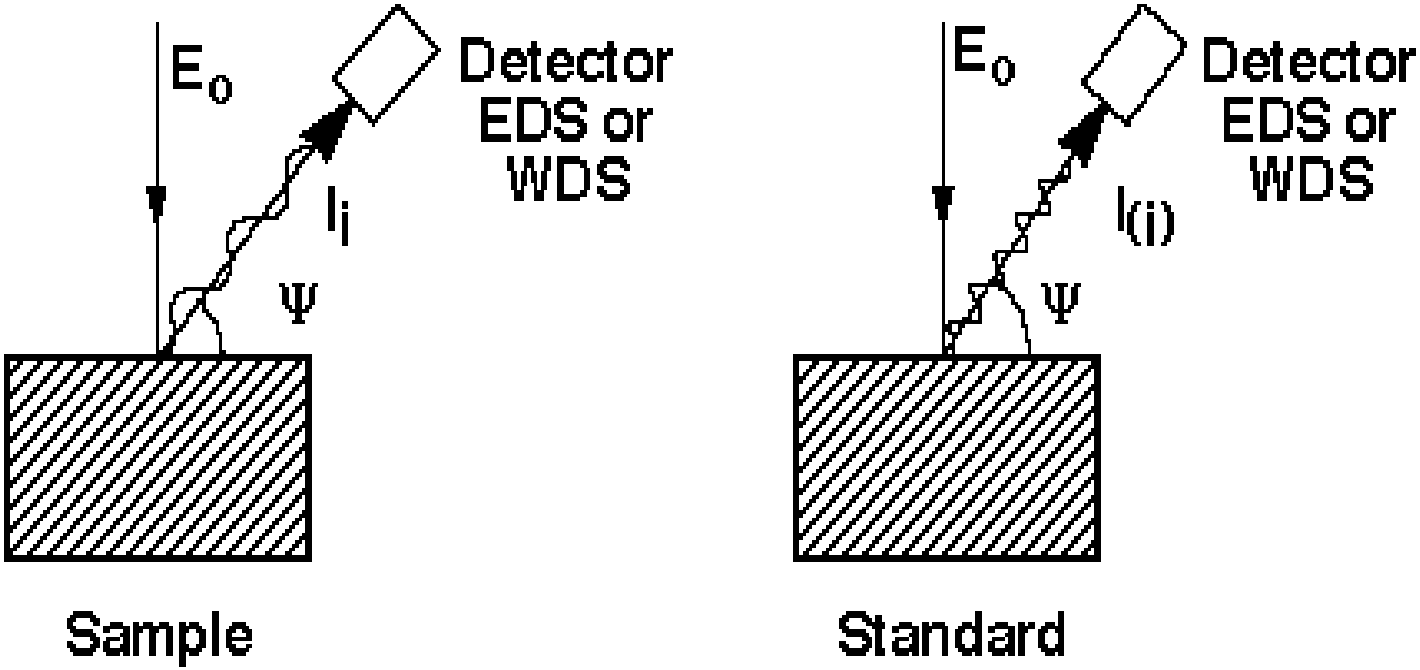
2. The characteristic intensity under the peak is extracted.

3. The ratio of intensities (k-value) between the unknown sample composition and standard is the starting point for quantitative analysis:

$$k = i_{sample}/i_{std} \qquad C_a \approx k_a \text{ (first order)}$$

4. Matrix corrections convert k to C.

The Most Important Step in Achieving Quantitative X-ray Microanalysis



$$k = i_{sample} / i_{std}$$

For each element being analyzed, measure the same X-ray peak in the unknown and a standard under identical conditions of beam energy, known dose, and spectrometer efficiency.

Impact of Spectrometer Efficiency, ε

$$I_{measured} = I_{generated} * f(\chi) * \varepsilon$$

$f(\chi)$ is the absorption factor in the target, sample or standard

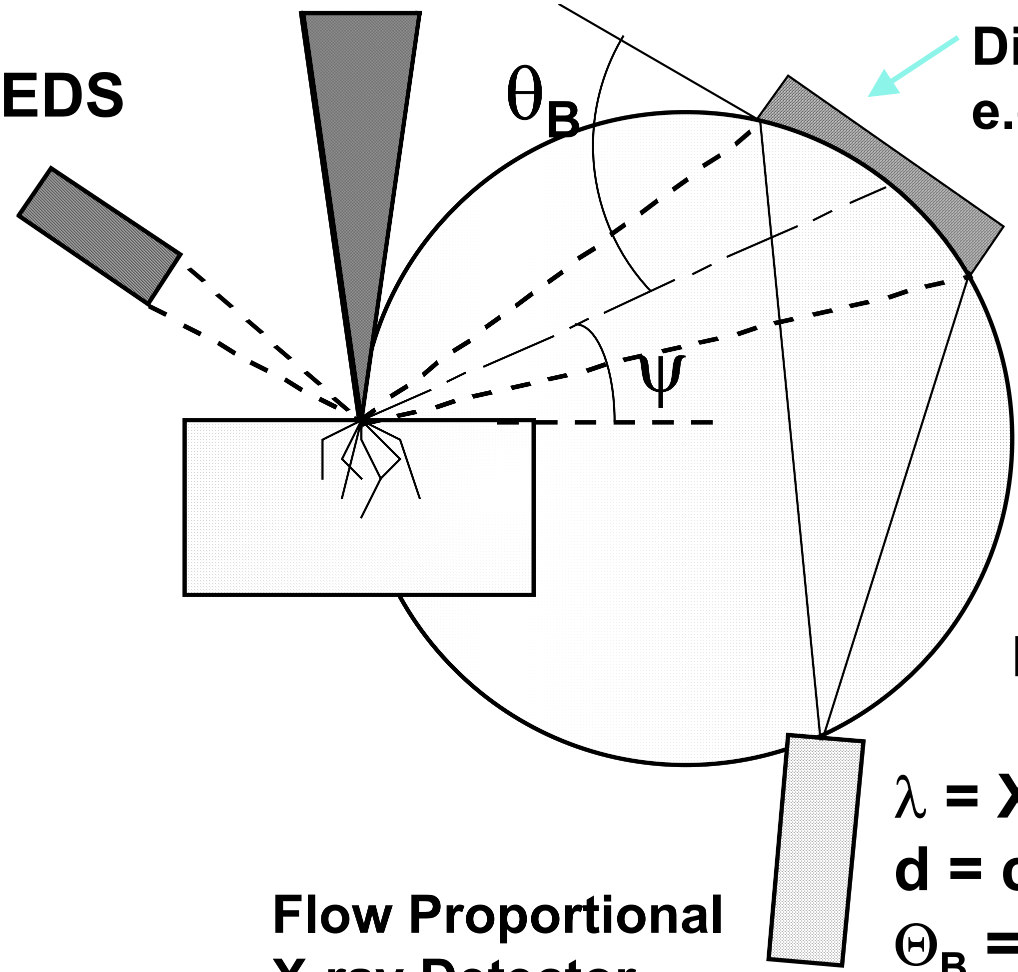
$$k = i_{sample} / i_{standard}$$

$$= (I_{generated} * f(\chi) * \varepsilon)_{sample} /(I_{generated} * f(\chi) * \varepsilon)_{std}$$

Spectrometer efficiency ε cancels quantitatively when the k-ratio is measured because exactly the same X-ray energy is measured for both! The efficiency does NOT cancel in standardless!

This k-value procedure originated with the EPMA/WDS

Wavelength Dispersive X-ray Spectrometry



EDS

Diffraction Crystal
e.g., LiF, PET, multilayer

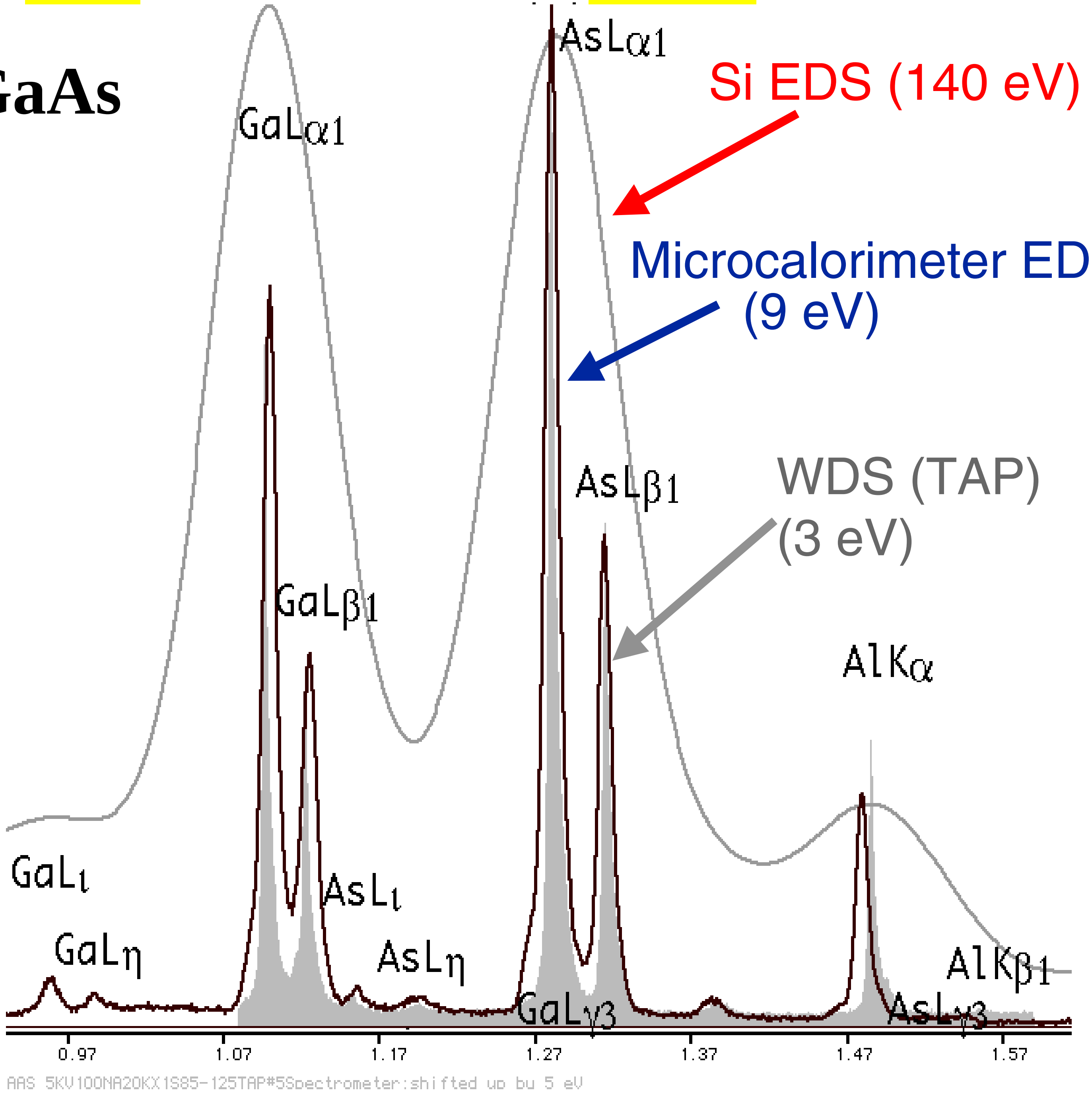
Focussing circle

$$n \lambda = 2d \sin \Theta_B$$

λ = X-ray wavelength
d = crystal plane spacing
Θ_B = Bragg angle

Flow Proportional
X-ray Detector

AlGaAs



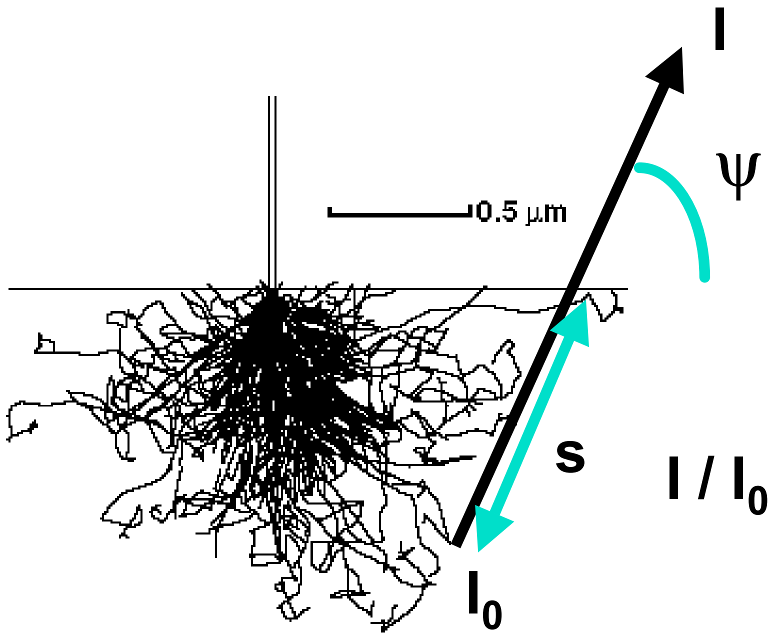
Si EDS (140 eV)

Microcalorimeter EDS
(9 eV)

WDS (TAP)
(3 eV)

Several processes modify x-ray generation and propagation. These processes depend on the composition of the matrix. (“Matrix effects”)

Z: Electron backscattering, η, removes electrons that could have continued to make characteristic x-rays.



A: X-ray absorption within the specimen reduces the intensity emitted.

$$I / I_0 = \exp[\,-(\mu/\rho)\ \rho s]$$

F: absorption of x-rays occurs by photoelectric process, ionizing an inner shell. Decay of this state produces x-rays of absorbing atom

To a first approximation (C = mass concentration),

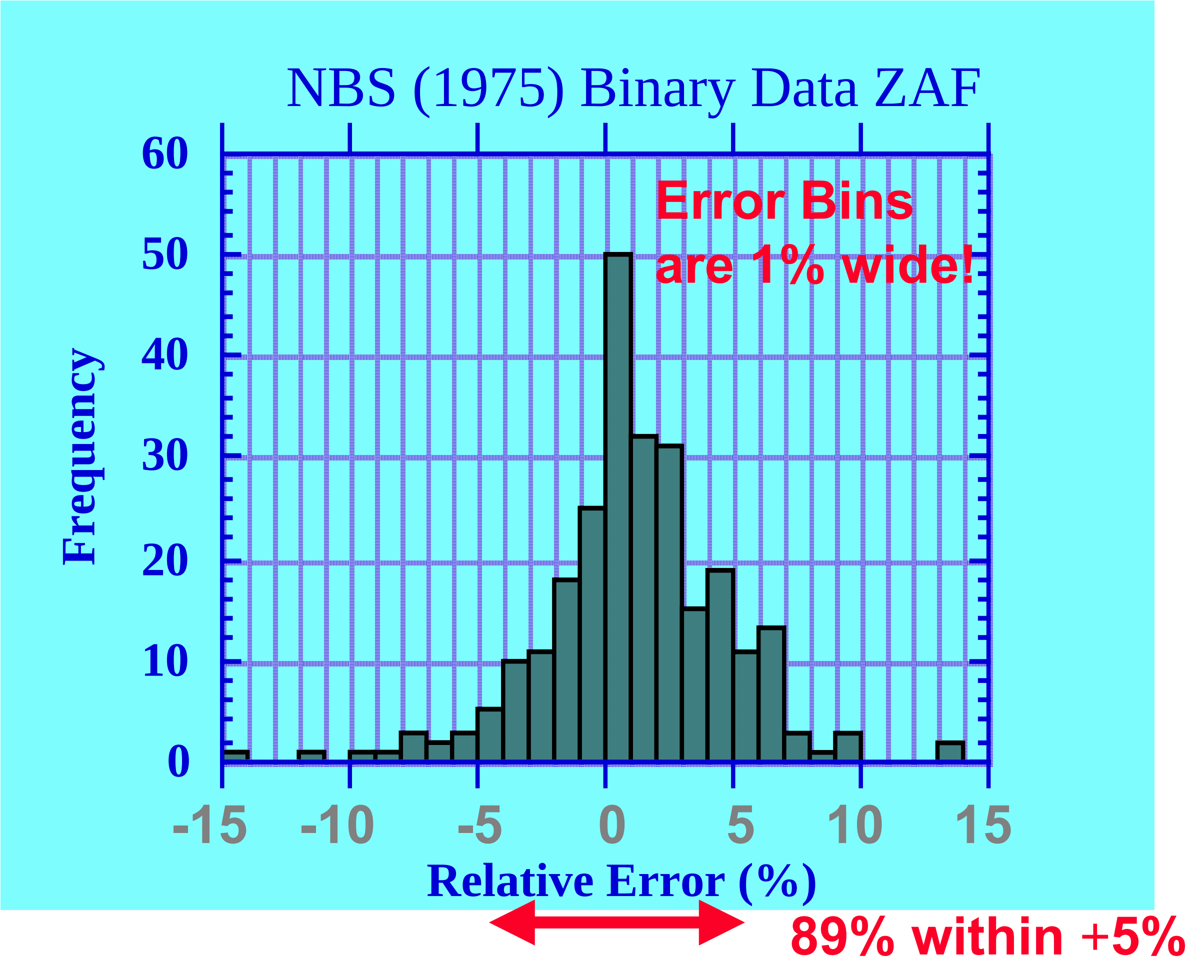
$$C_{sample} / C_{std} \sim i_{sample} / i_{std} = k$$

Matrix correction factors (Z, A, F, c) are calculated from first principles physics and empirical experiments:

$$C_{sample} / C_{std} = k\ Z\ A\ F\ c$$

Z = atomic number correction
A = absorption correction
F = characteristic fluorescence correction
c = continuum fluorescence correction

Error Distribution for Analysis with Standards and ZAF



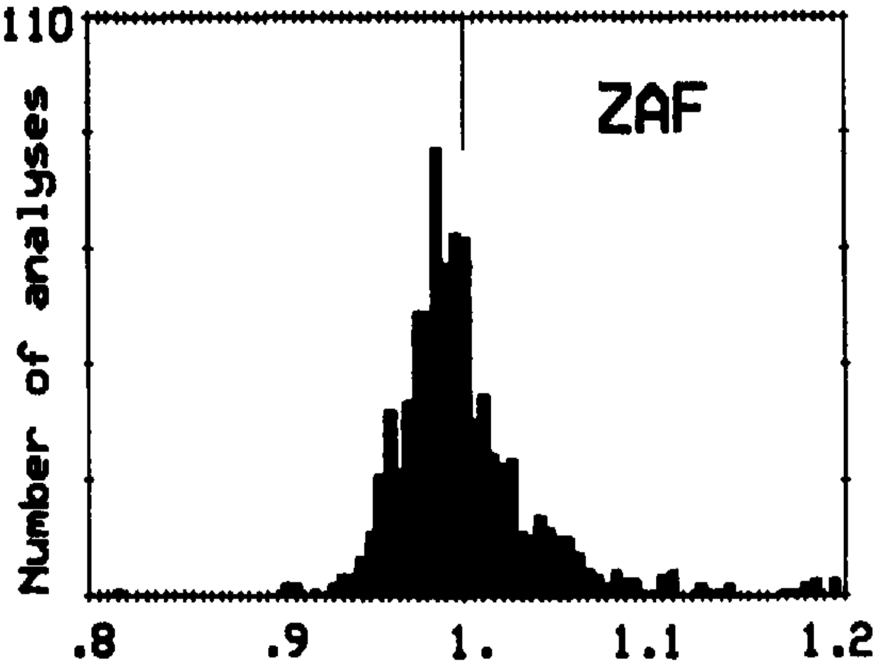
Error Bins are 1% wide!

89% within ±5%

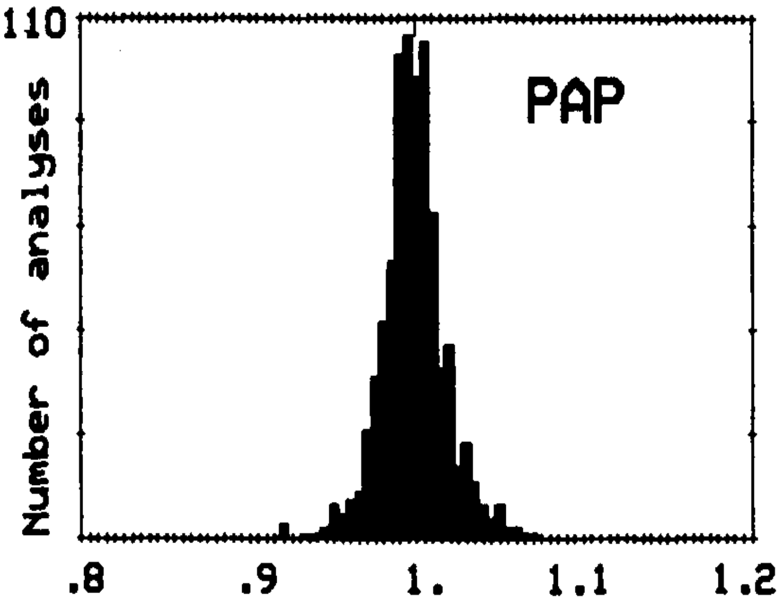
Heinrich and Yakowitz (1975) WDS results
Binary alloys analyzed with pure element standards.

Subsequent developments in the last 30 years have narrowed the error distribution even further:

95% within ±5% relative (element standards)
95% within ±2% relative (alloy standards)



Relative error



Relative error

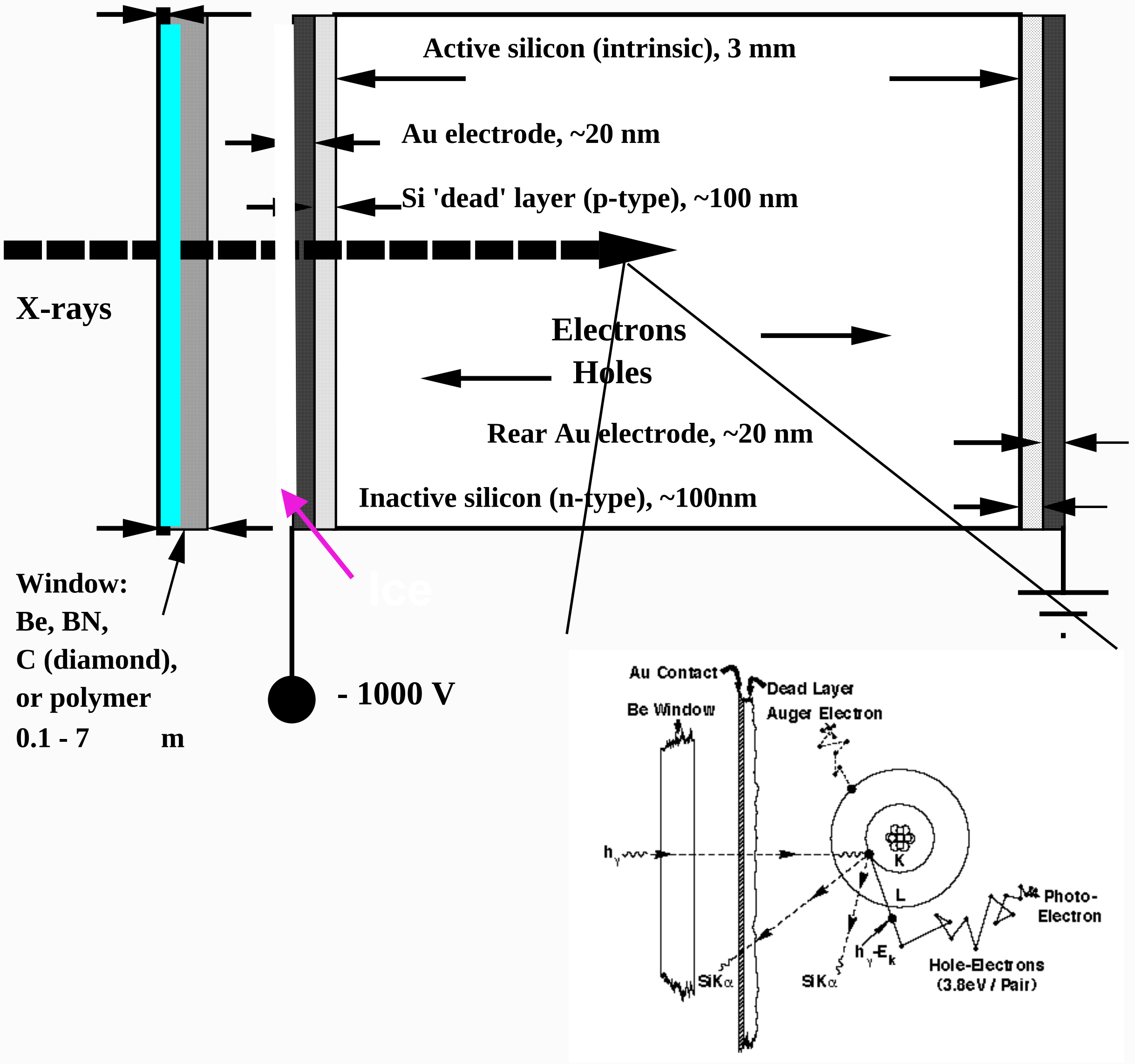
Pouchou and Pichoir, in Electron Probe Quantitation, eds. Heinrich and Newbury, (Plenum, New York, 1991) 31

With a great technique (EPMA) in place, what has gone wrong?

- “We used to use EPMA all of the time for critical materials analysis problems, but recently the results from our central research facility do not seem to have the accuracy we need!” (The EPMA was replaced with an SEM/EDS system).
- “The chemical formula based on our SEM/EDS results bears no resemblance to x-ray diffraction results, but the EPMA results you gave us agree closely with the crystal chemistry/diffraction analysis.”

What are these people using?
SEM/EDS with Standardless Analysis

The Monolithic Semiconductor Energy Dispersive X-ray Spectrometer



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

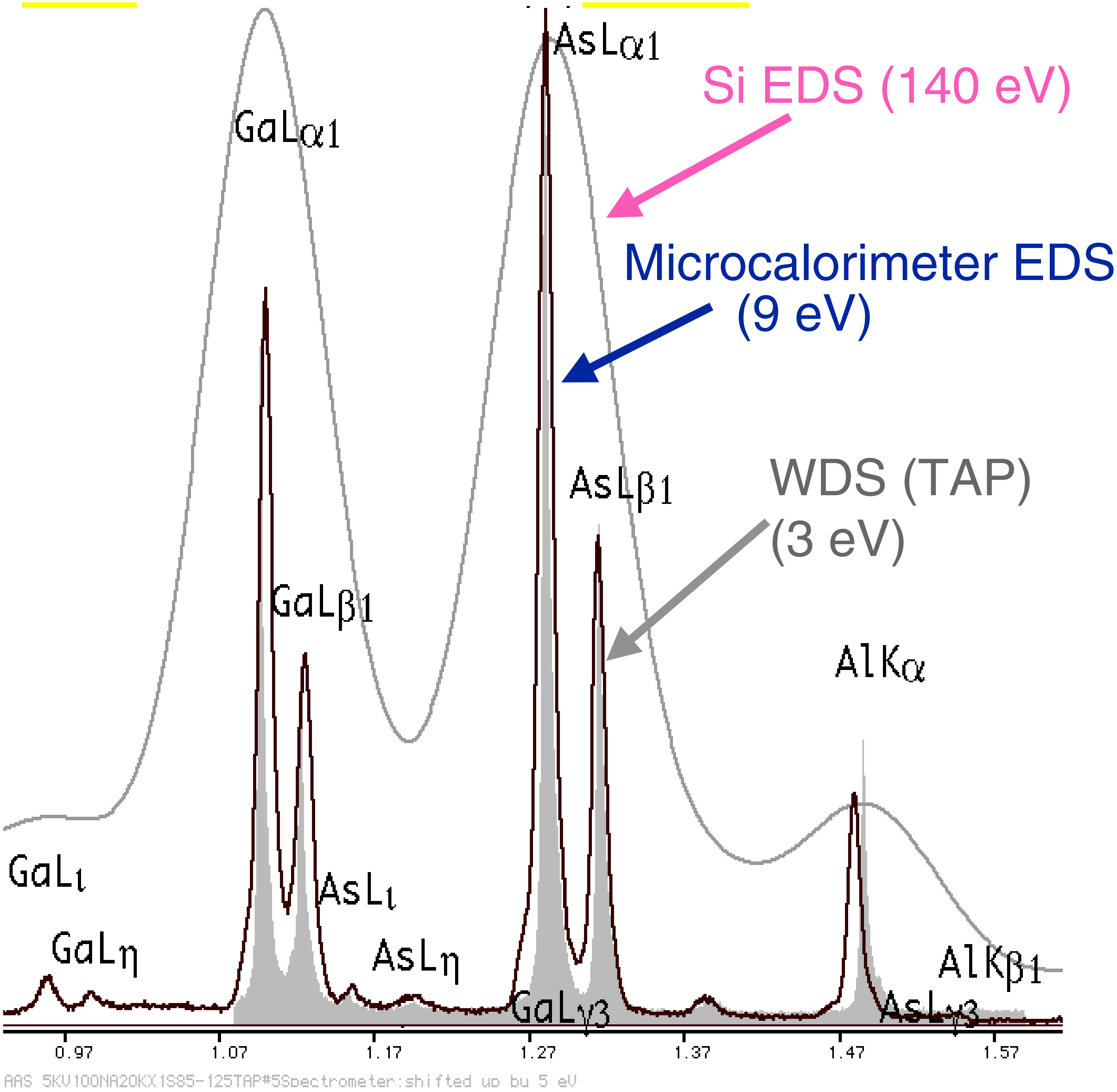
Rear Au electrode, ~20 nm

Inactive silicon (n-type), ~100nm

Ice

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

- 1000 V



Si EDS (140 eV)

Microcalorimeter EDS (9 eV)

WDS (TAP) (3 eV)

Can SEM/EDS be quantitative?

Quantitative Electron Probe Microanalysis by Energy Dispersive X-ray Spectrometry (NIST SRM 482 Au-Cu Microprobe Standards)

Cu Conc.	Analysis	Rel Err	Au Conc	Analysis	Rel Err
19.8w/o	19.8	0.0%	80.1w/o	79.0	- 1.4%
					total = 98.8%
39.6	39.9	+0.8%	60.3	59.4	- 1.6%
					total = 99.3%
59.9	60.5	+1.0%	40.1	40.2	+ 0.1%
					total = 100.7%
79.8	79.7	-0.1%	20.0	19.9	- 1.2%
					total = 99.6%

These errors are well within the error distribution seen with WDS.

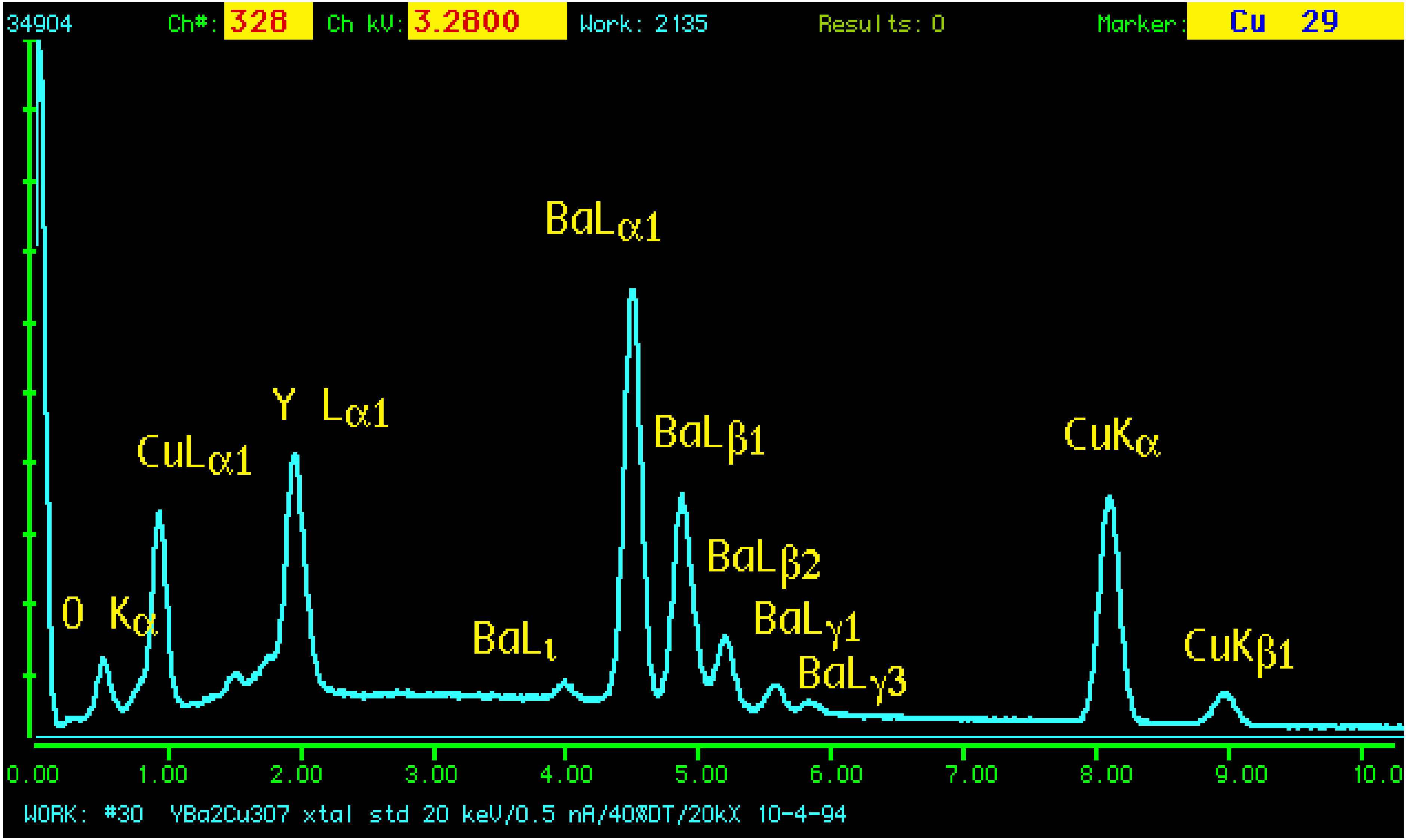
Relative error = 100%x(measured - true) / true
Beam energy: 20 keV
Standards: pure elements
Matrix corrections: NIST ZAF

Classic Standards + ZAF Analysis

1. Error distribution histogram allows an estimate of the systematic errors. Conservative: 95% within ± 5% relative
2. Counting statistics provide an estimate of the random error.
3. For EDS, standards can be archived, with a good measurement quality assurance procedure in place.
4. The analytical total is a valuable piece of information. It may indicate deviations in analytical conditions due to the instrument (dose, spectrometer efficiency, etc.), but it may also indicate a missing, unanalyzed element.

With such a great procedure as standards+ZAF to follow, why has "standardless analysis" arisen in EDS practice and become so popular?
How "accurate" is standardless analysis?

EDS lets us see ALL of the spectrum ALL of the time. Inter-element comparisons are readily available and tempting.



WORK: #30 YBa2Cu3O7 xtal std 20 keV/0.5 nA/40%DT/20kX 10-4-94

What Is “Standardless” Analysis?

1. Measure the EDS spectrum of sample ONLY.
Ease of operation
2. No need to measure standards. No need to know electron dose accurately, or at all. Only beam energy is required.
3. Quantify the unknown by using first principles physics to calculate equivalent standard intensities, including effect of detector efficiency.
OR
4. Use a library of remotely measured standards (one energy) and apply first principles physics to provide standards missing from the suite and correction to different beam energy, spectrometer efficiency, tilt, etc.
5. Either way, the analytical total is ALWAYS 100%.
(Is this good or bad?)

Steel Analysis: Standardless

```
Spectrum Label:  Substrate steel 1 20 keV/0.5 nA/300kX  6-29-94
Standardless Analysis
Take-Off Angle:  40.00
Beam Entry Angle:  90.00
Beam keV:  20.00
Number of elements:        4
Elem & Line  k-Value    Conc.    AtNo Fact.    Absorp Fact    Fluor
SiKA1    0.0040    0.0084    0.8900    0.4579    0.0013
CrKA1    0.2001    0.1880    1.0035    0.9890    0.1758
FeKA1    0.6396    0.7180    1.0028    0.9693    0.0111
NiKA1    0.0716    0.0856    0.9870    0.9017    0.0000

Analysis Total is 1.0000
```

Is automatic scaling to a 100% total good or bad?

- Automatic scaling can lead to complete analytical nonsense unless everything is included!!
- In the conventional ZAF + standards route the total is rarely exactly 100%. Each element is determined separately against a standard, so the error inherent in each measurement is cumulative in the total. Typically when everything is measured (with oxygen by assumed stoichiometry), the total falls within 99% to 101%. Outside 98% to 102% the analyst should look for error sources that are out of control.
- A missing element will show up as a deviation in the analytical total. For example, if a metal with oxide inclusions is analyzed and an oxide is measured but analyzed as a metal, the analytical total will be low, e.g., ~80% for iron oxide.

How good are the commercial implementations of standardless analysis?

- The manufacturer is unlikely to have rigorously tested the procedure. Stainless steel is the likely example.
- In a few cases, we have.

Testing Standardless Analysis

Analysis Conditions:

Beam energy: 20 keV
X-ray range: 1 keV - 12 keV

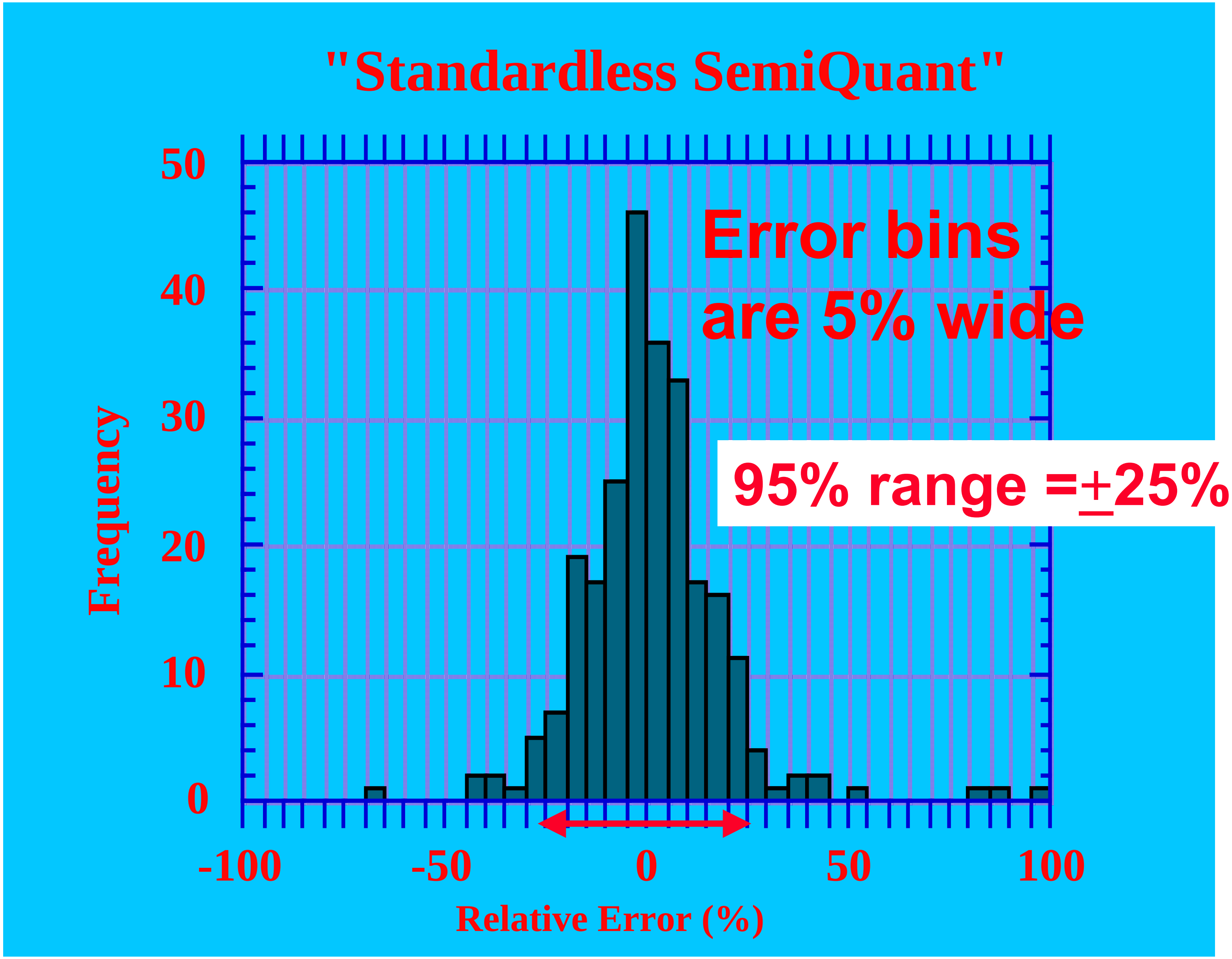
Test Materials:

- Standard Reference Materials (SRMs),
- Research Materials (RMs)
- Glasses
- Compounds: e.g., PbSe, InP, GaTe, PbTe, GaP, FeS, ZnS, CuS, GaAs, CdTe, HgTe, KCl, KBr, KI

Analysis:

- **Test all combinations of K, L, and M lines**
- **Calculate oxygen by stoichiometry; not included in the error distributions**

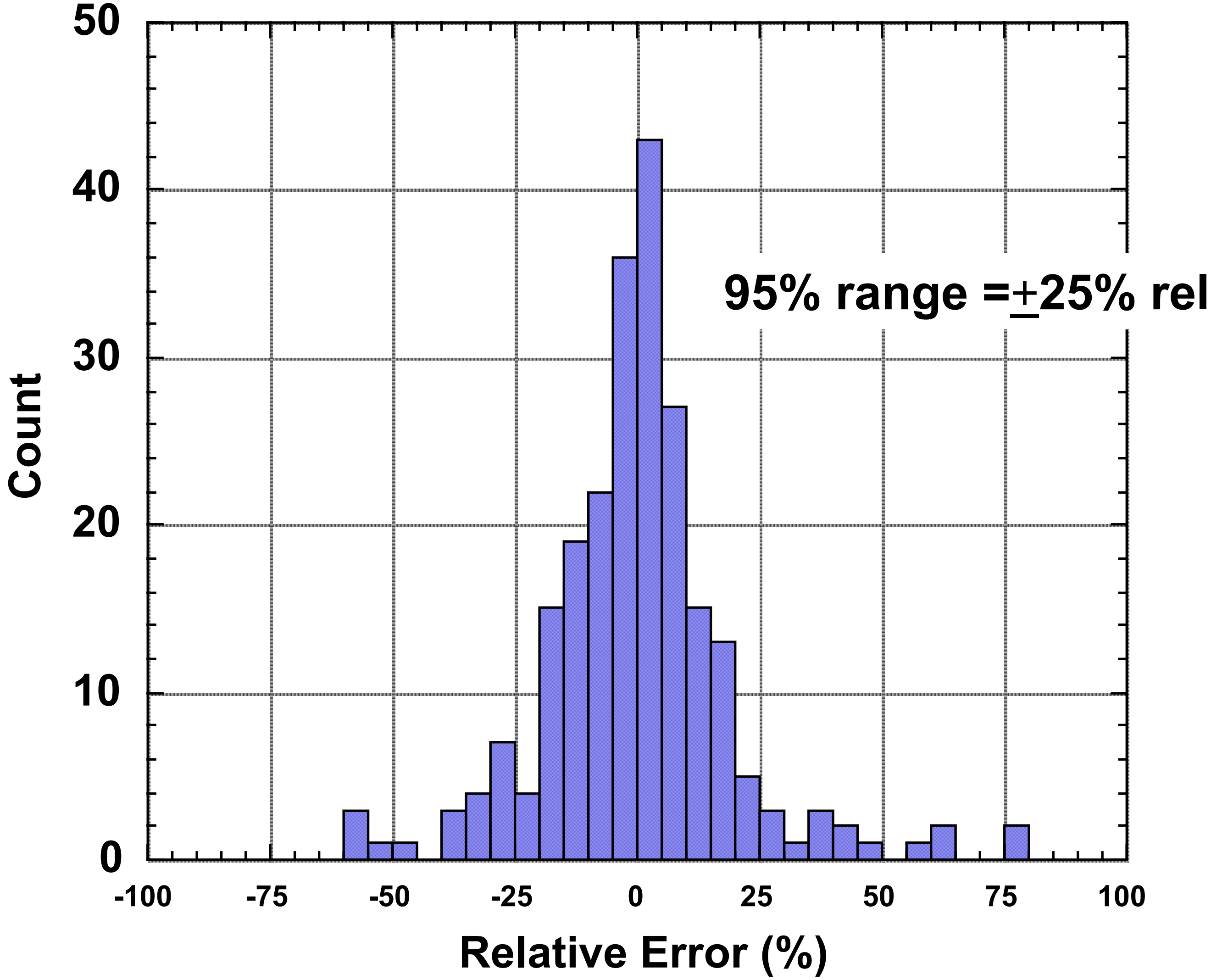
Error Distribution for a Commercial Standardless Analysis



Error bins are 5% wide

95% range =±25% rel

Standardless Analysis Vendor 2



95% range = ±25% rel

SEM/EDS Stds/ZAF Analysis of a $YBa_2Cu_3O_7$ Single Crystal

	Y (true)	Ba (true)	Cu (true)	
	13.3 w/o	41.2 w/o	28.6 w/o	
Stds	13.8 (+ 4%)	41.1 (-0.2%)	28.1 (-2%)	Cu-K
ZAF	$Y_1Ba_2Cu_3O_{6.4}$			

(Standards: Y and Cu as metal; Ba from a glass)

“Standardless” Analyses of a $YBa_2Cu_3O_7$ Single Crystal

Standardless Analyses on two different systems:

M1	17.3 (+30%)	40.0 (-3%)	26.7 (-7%)	Cu-K
	$Y_2Ba_3Cu_4O_{10}$			
M1	15.8 (+19%)	36.2 (-12%)	31.6 (+10%)	Cu-L
	$Y_2Ba_3Cu_6O_{12}$			
M2	16.5 (+24%)	38.7 (-6%)	28.7 (+0.4%)	Cu-K
	$Y_2Ba_3Cu_5O_{11}$			
M2	16.8 (+26%)	39.5 (-4%)	27.6 (-3.5%)	Cu-L
	$Y_4Ba_6Cu_9O_{21}$			

Oxygen calculated by method of assumed stoichiometry

What goes into the generated intensity?

$$I_{ch} = (\omega\ N_A\ \rho\ C_i\ /A)\ R \int_{E_0}^{E_c} (Q\ /\ (dE/ds)\ dE$$

ω = fluorescence yield N_A = Avogadro's number

ρ = density C_i = mass concentration of i

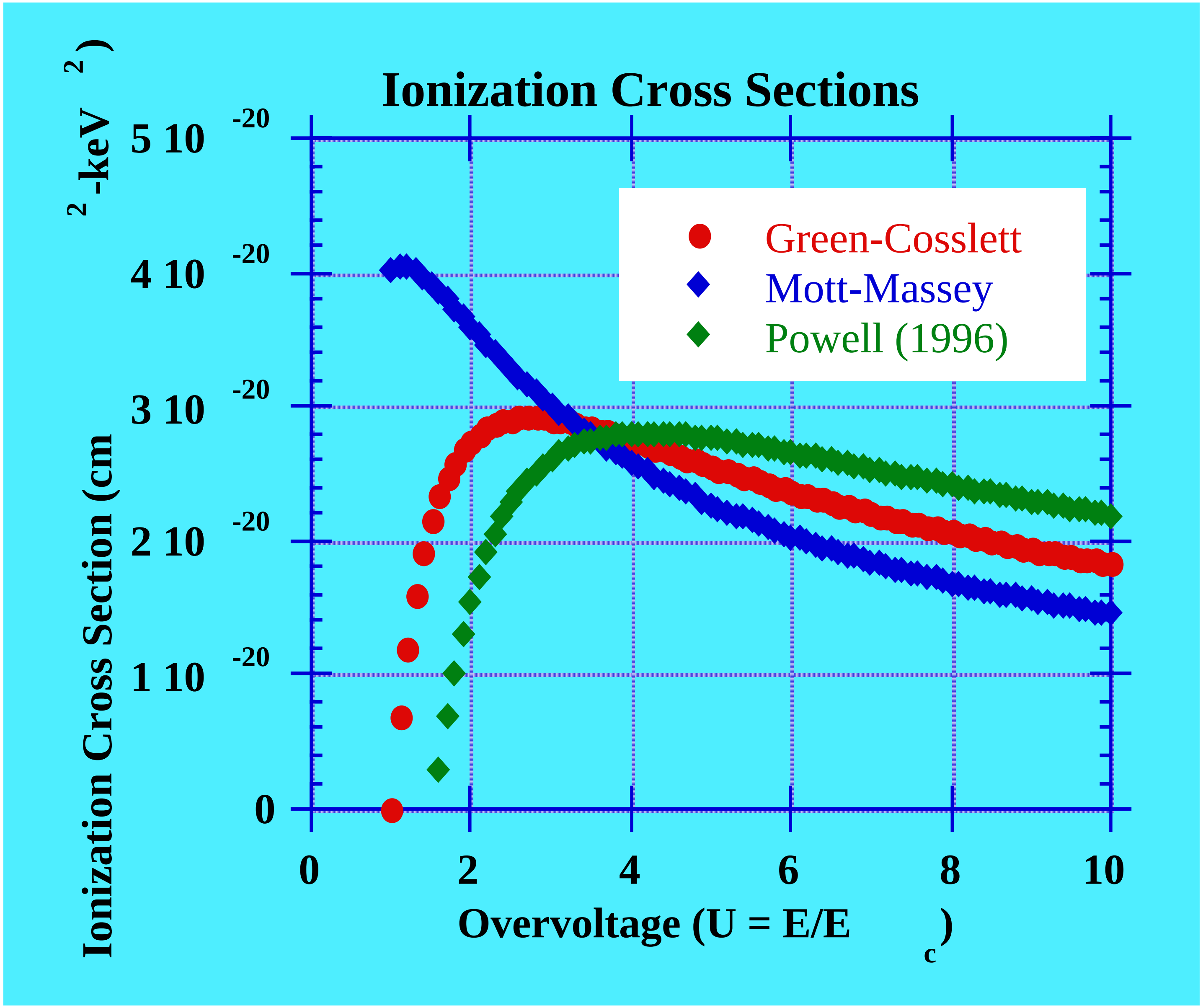
A = atomic weight   R = backscatter loss

Q = ionization cross section

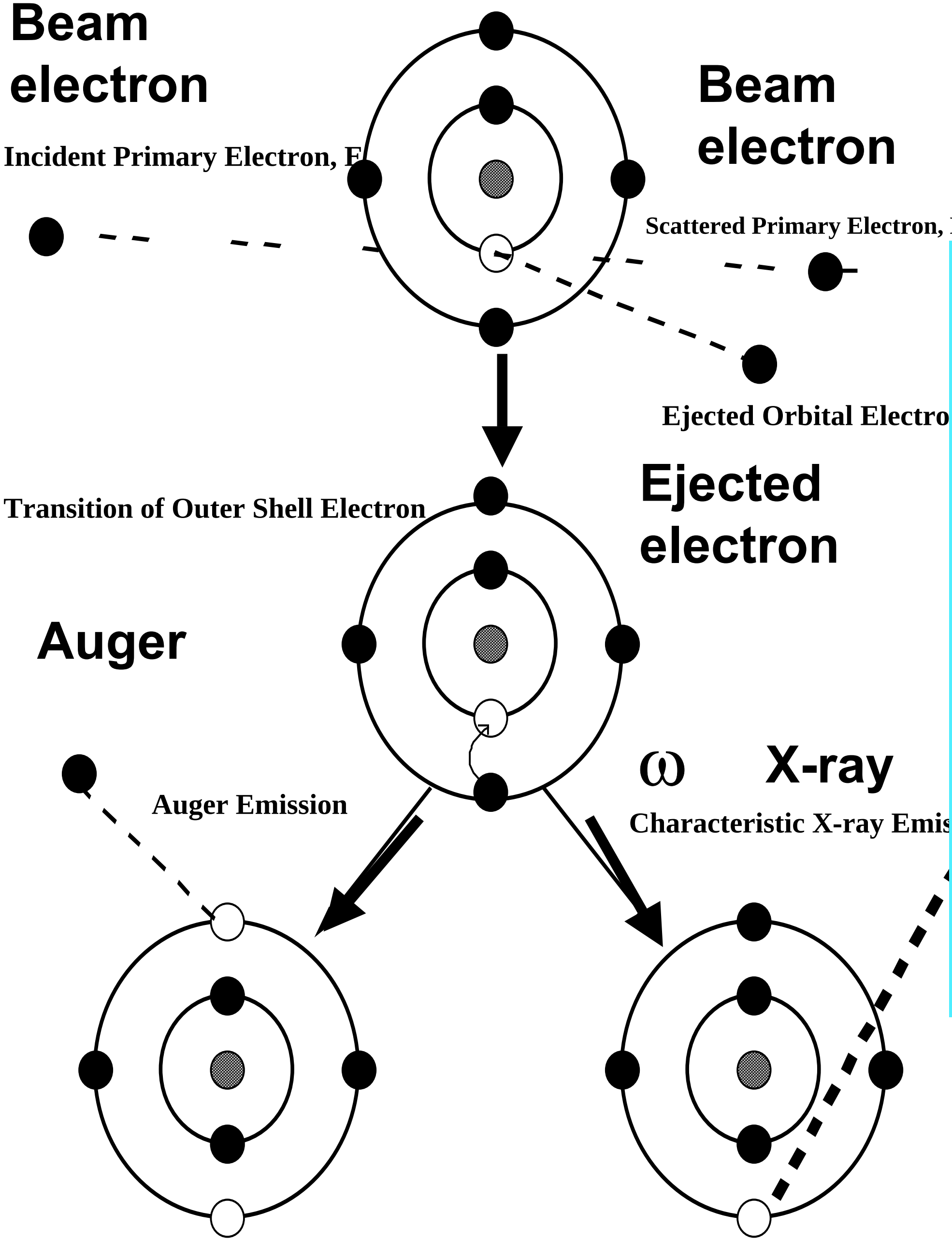
dE/ds = rate of energy loss

E_0 = incident beam energy E_c = excitation energy

Cross Section for Inner Shell Ionization



Fluorescence Yield



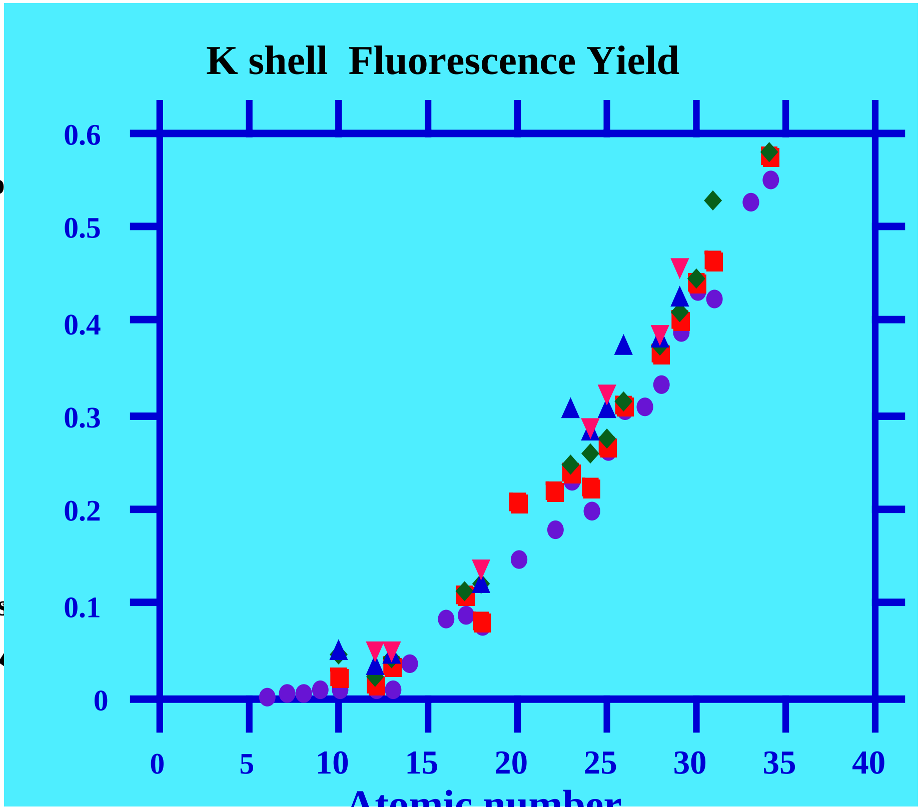
Beam electron

Beam electron

Ejected electron

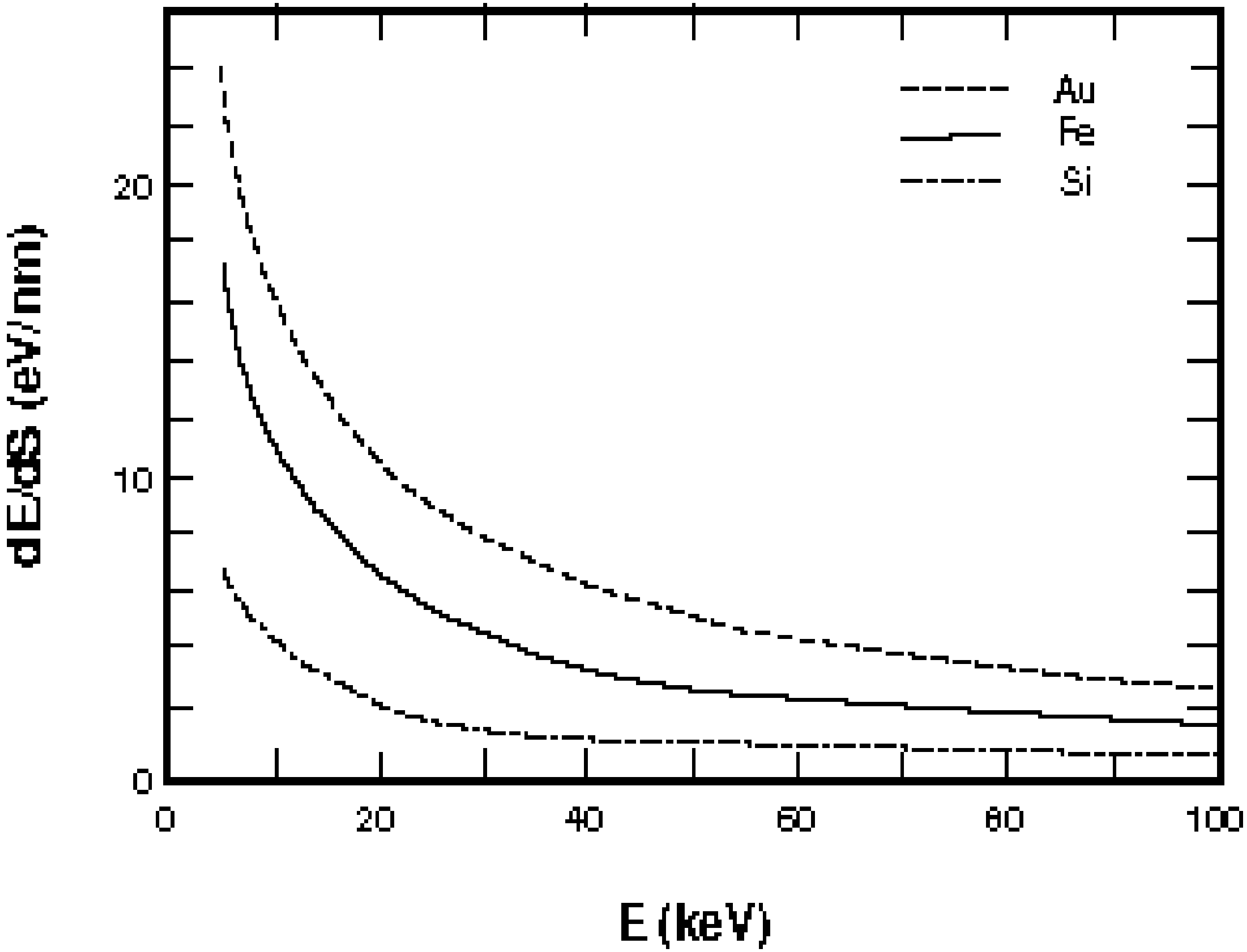
Auger

ω **X-ray**

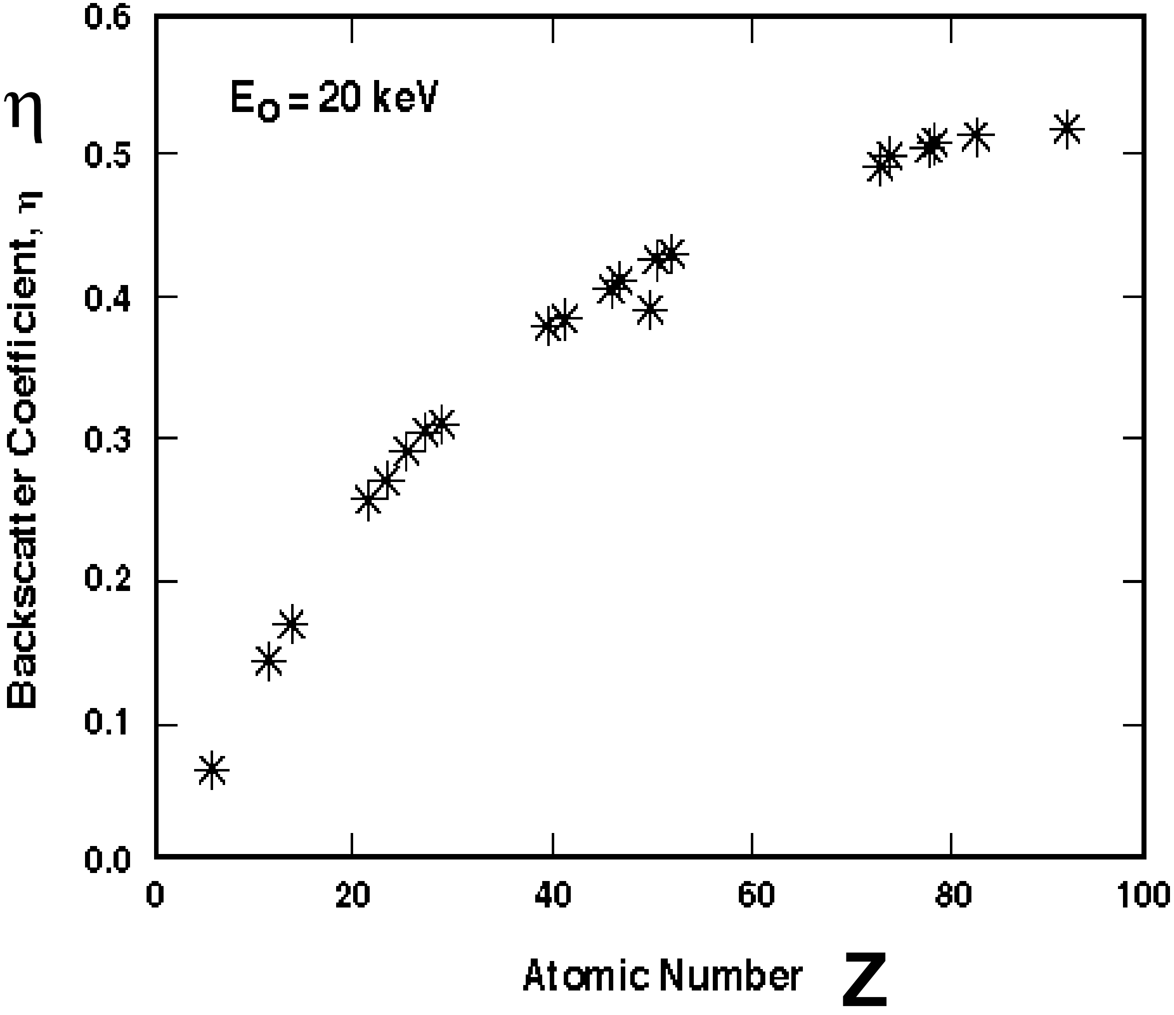


$$I_x \approx Q * \omega$$

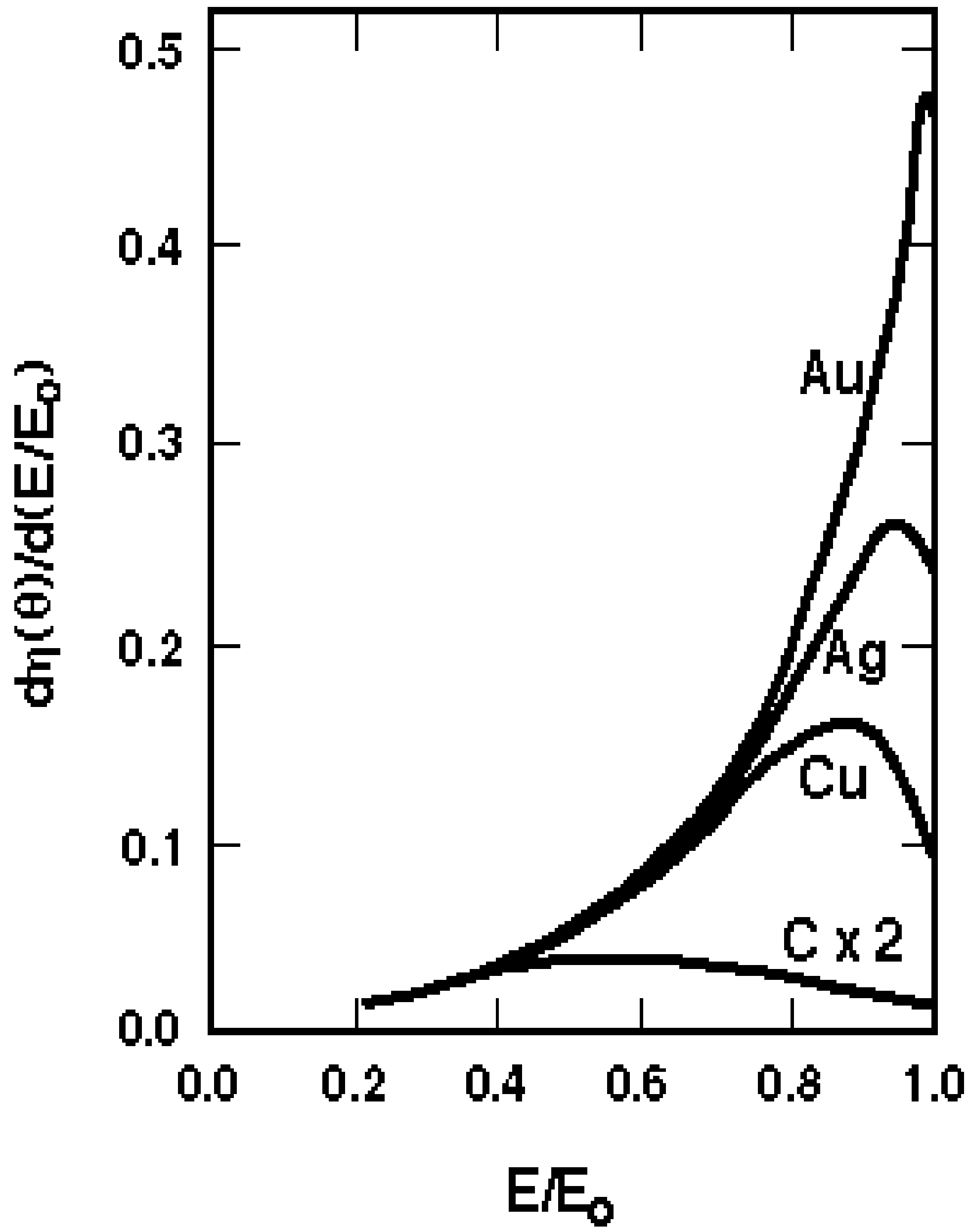
Energy Loss



Backscatter Loss: Backscatter Coefficient

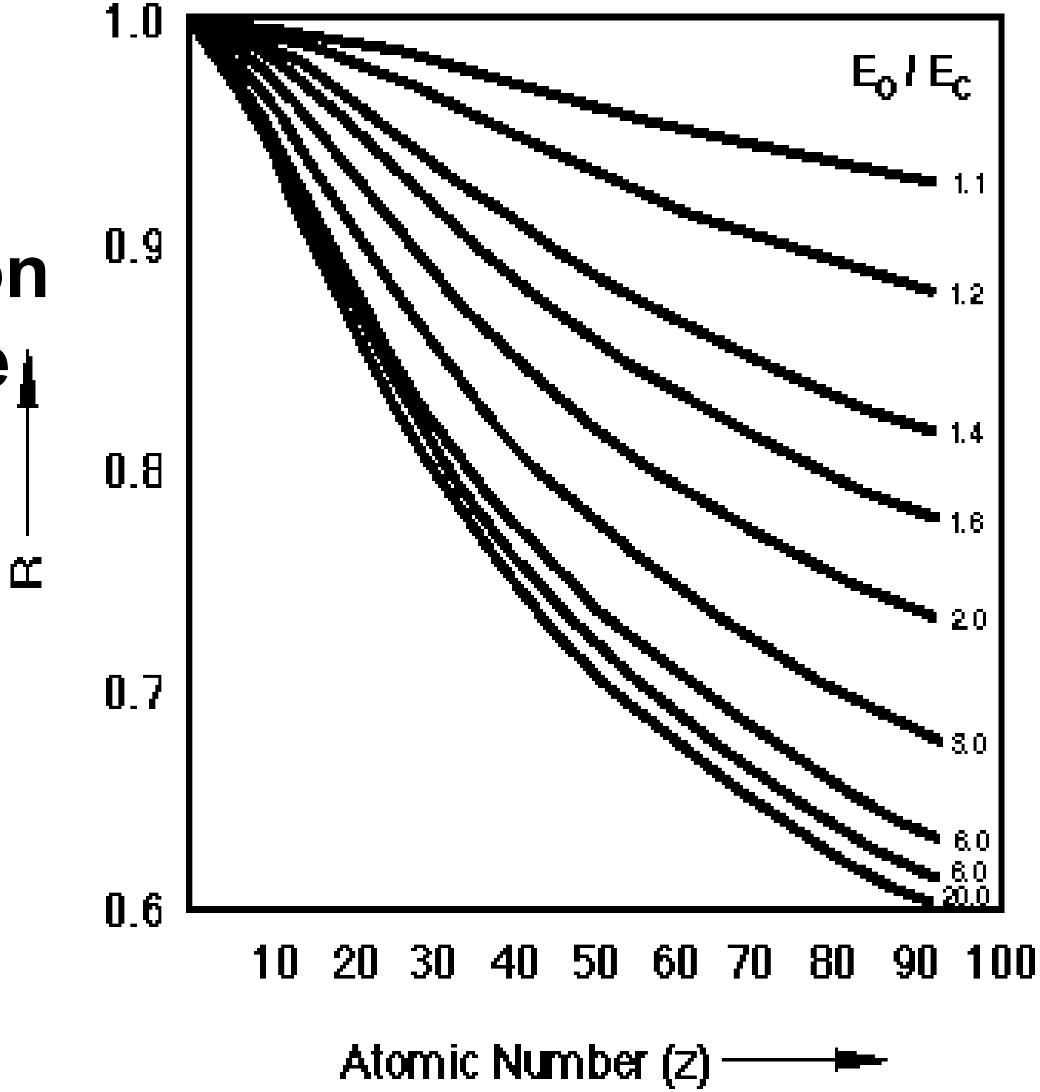


Backscatter Loss: Backscatter Energy



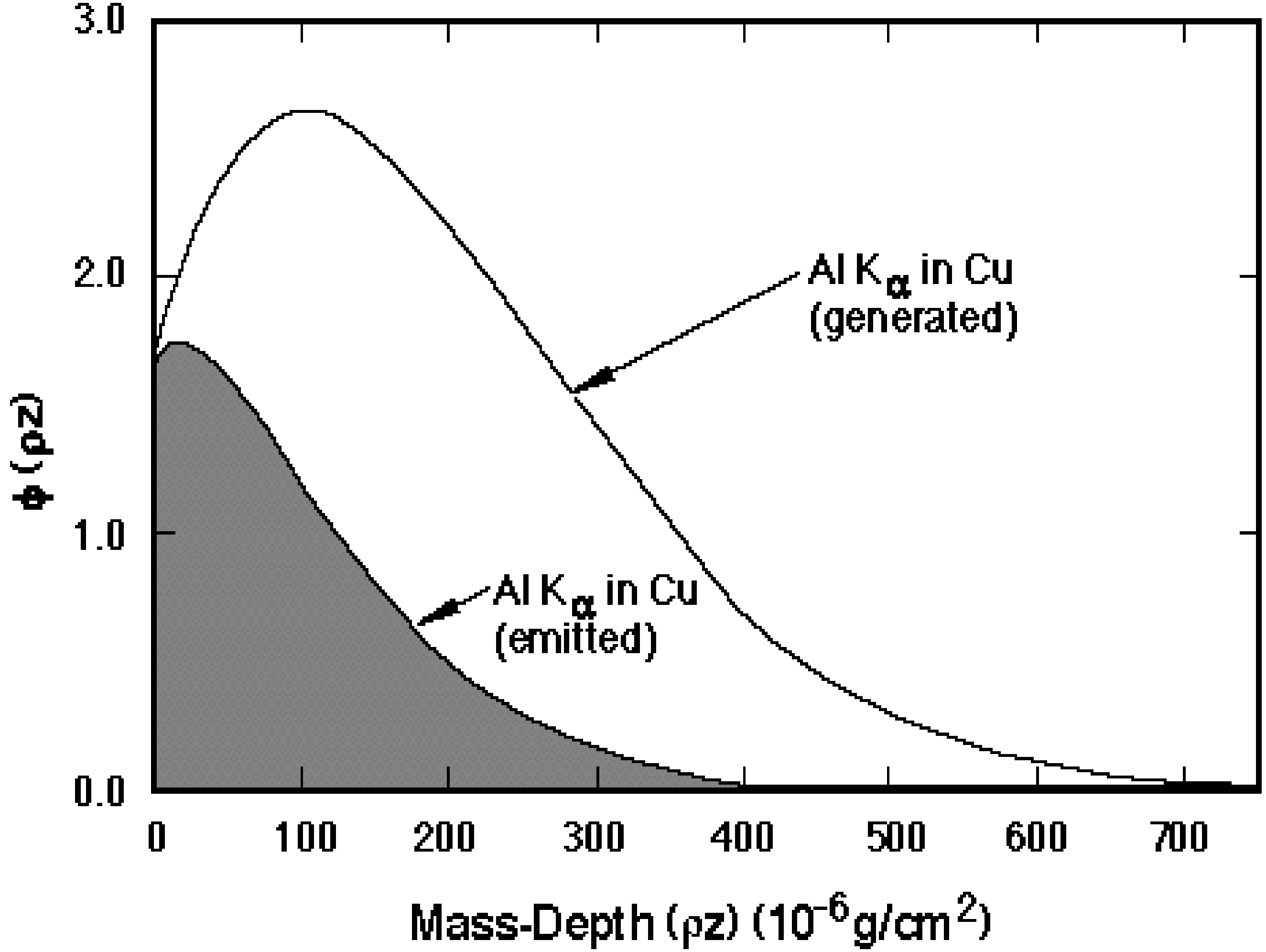
Backscatter Loss: R factor

R = Fraction of possible ionization actually deposited in target

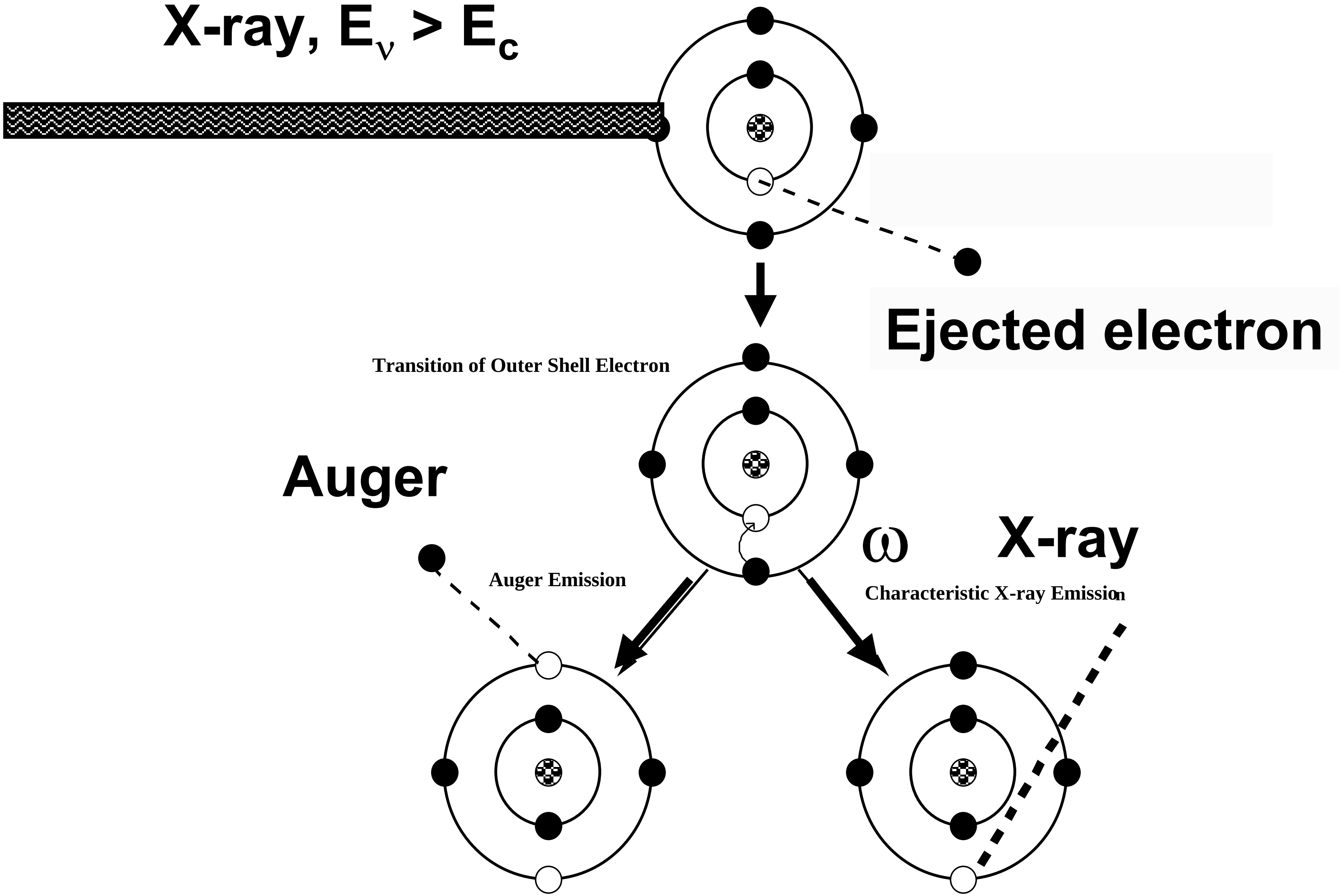


X-ray Absorption

$$I / I_0 = \exp[-(\mu/\rho)\,\rho\, s]$$



Secondary Fluorescence



X-ray, $E_\nu > E_c$

Ejected electron

Transition of Outer Shell Electron

Auger

ω

X-ray

Auger Emission

Characteristic X-ray Emission

Spectrometer Efficiency, ε

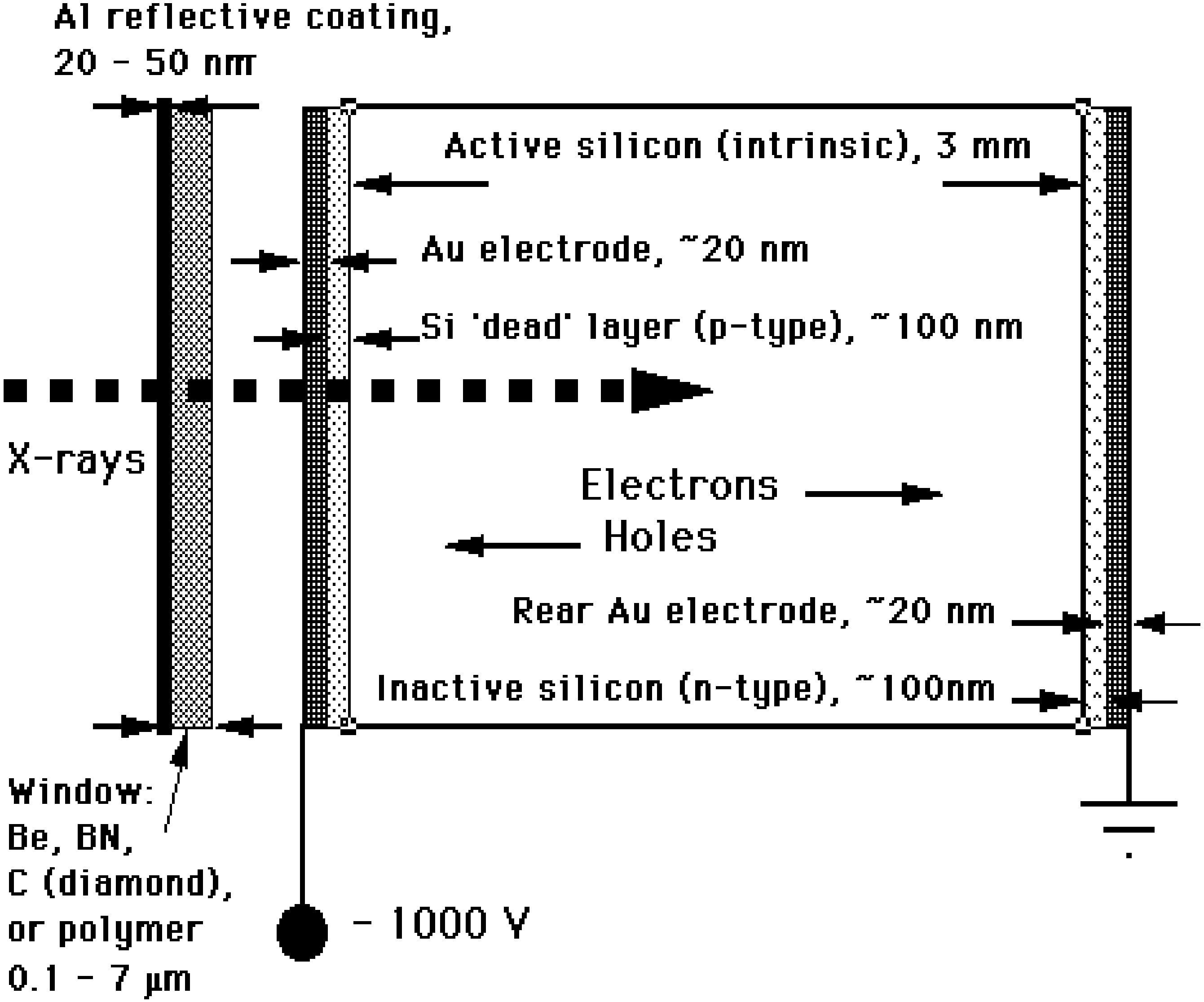
$$I_{measured} = I_{generated} * f(x) * \varepsilon$$

$$k = i_{sample} / i_{standard}$$

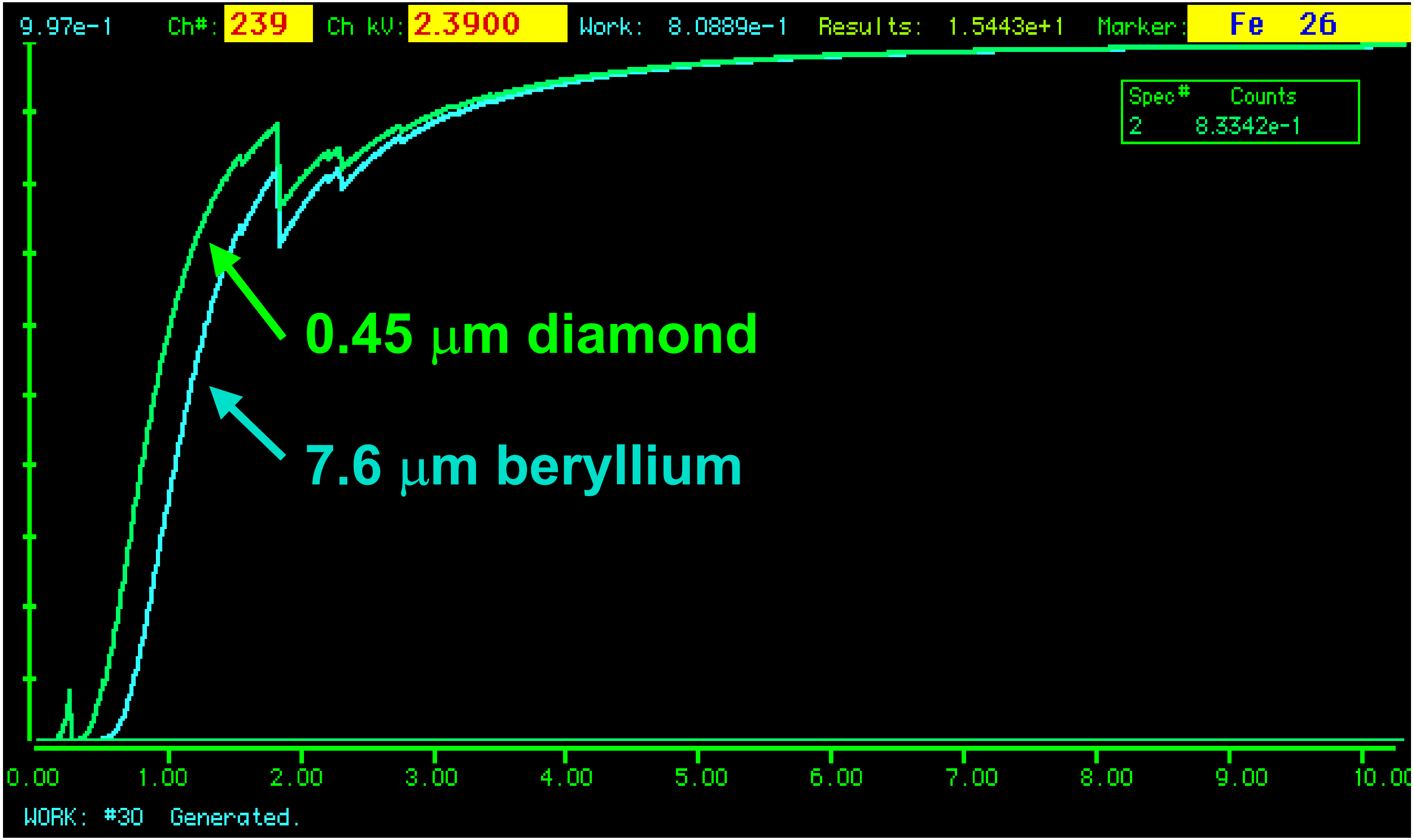
$$= (I_{generated} * f(x) * \varepsilon)_{sample} /(I_{generated} * f(x) * \varepsilon)_{std}$$

Spectrometer efficiency ε cancels quantitatively when the k-ratio is measured because exactly the same X-ray energy is measured for both! The efficiency does NOT cancel in standardless!

EDS Detector



Spectrometer Efficiency



9.97e-1 Ch#: 239 Ch kV: 2.3900 Work: 8.0889e-1 Results: 1.5443e+1 Marker: Fe 26

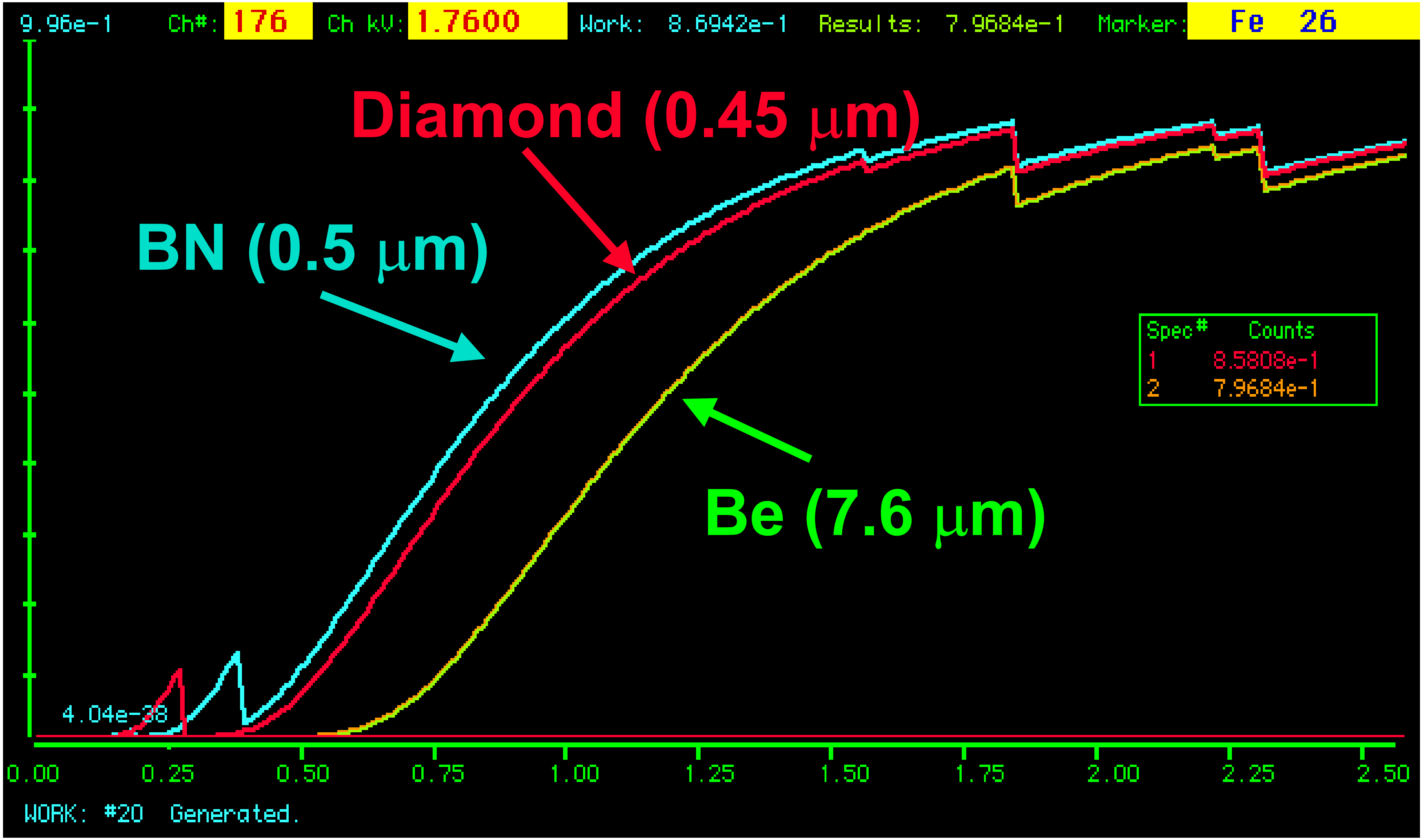
Spec#	Counts
2	8.3342e-1

WORK: #30 Generated.

0.45 µm diamond

7.6 µm beryllium

Spectrometer Efficiency: Low X-ray Energy



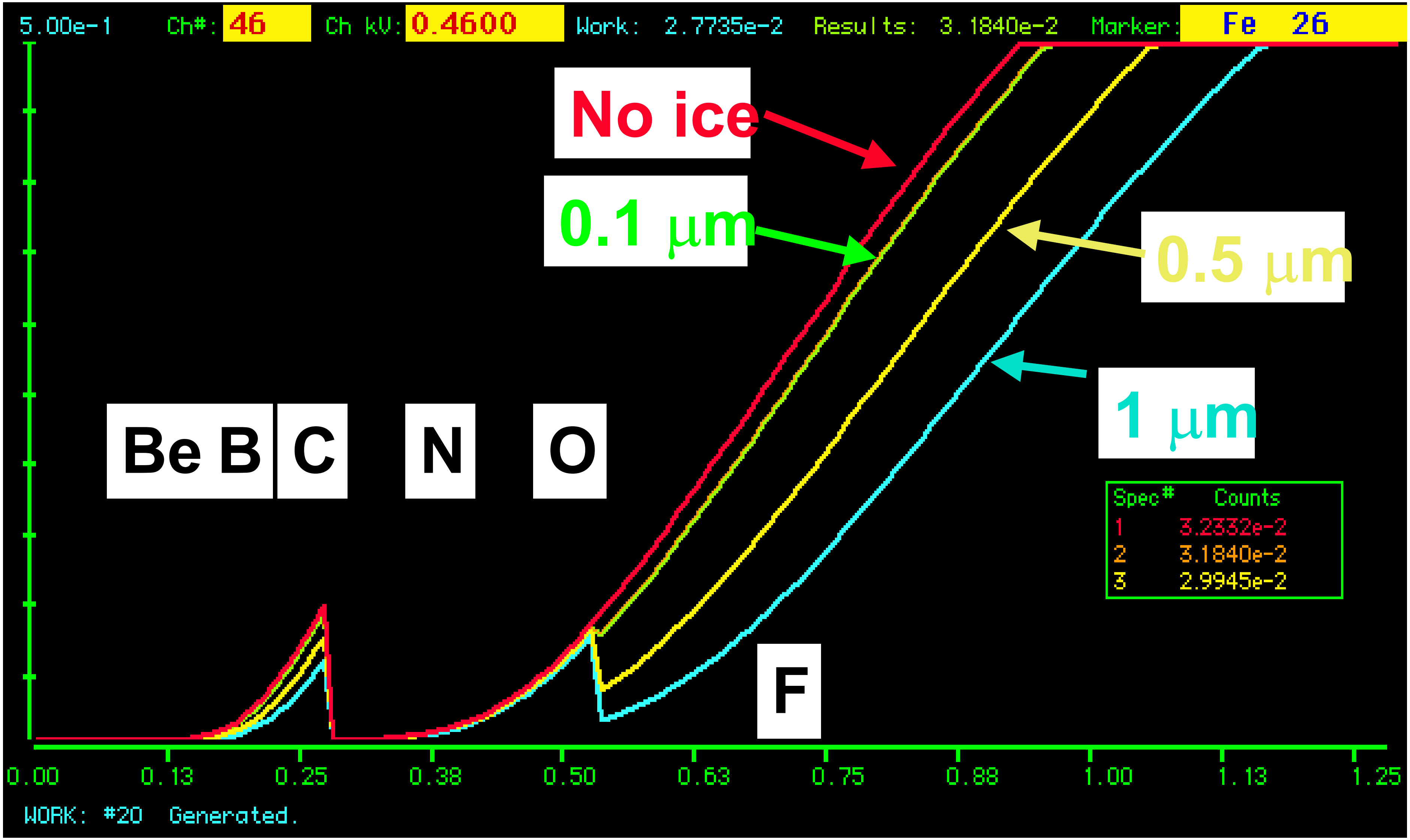
Diamond (0.45 μm)

BN (0.5 μm)

Be (7.6 μm)

Spectrometer Efficiency: Ice Build-Up

Diamond Window (0.45 µm thick)



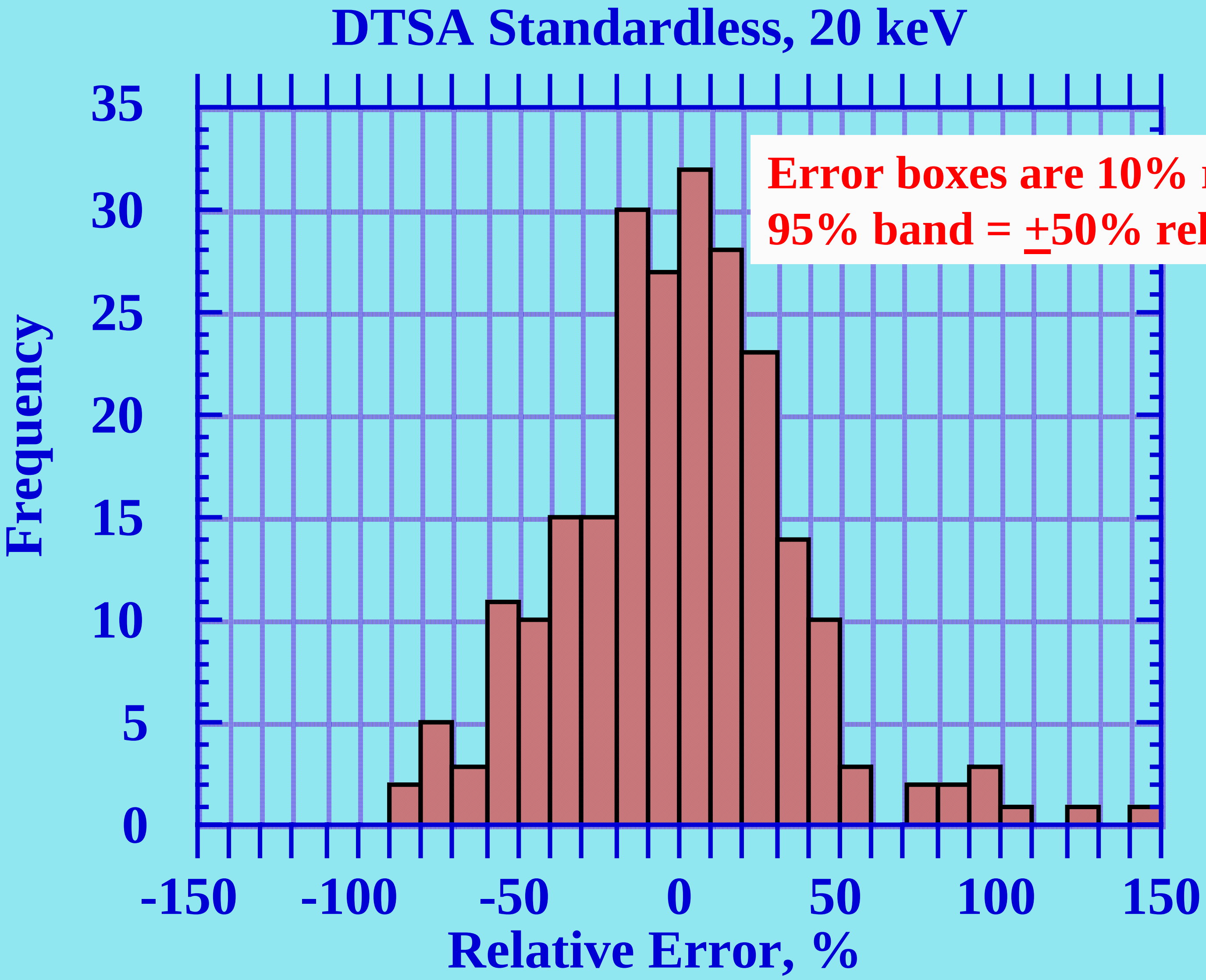
```
5.00e-1   Ch#: 46   Ch kV: 0.4600   Work:  2.7735e-2   Results:  3.1840e-2   Marker: Fe  26
```

Spec#	Counts
1	3.2332e-2
2	3.1840e-2
3	2.9945e-2

```
WORK: #20  Generated.
```

True (physics only) “first principles” standardless analysis

NIST DTSA

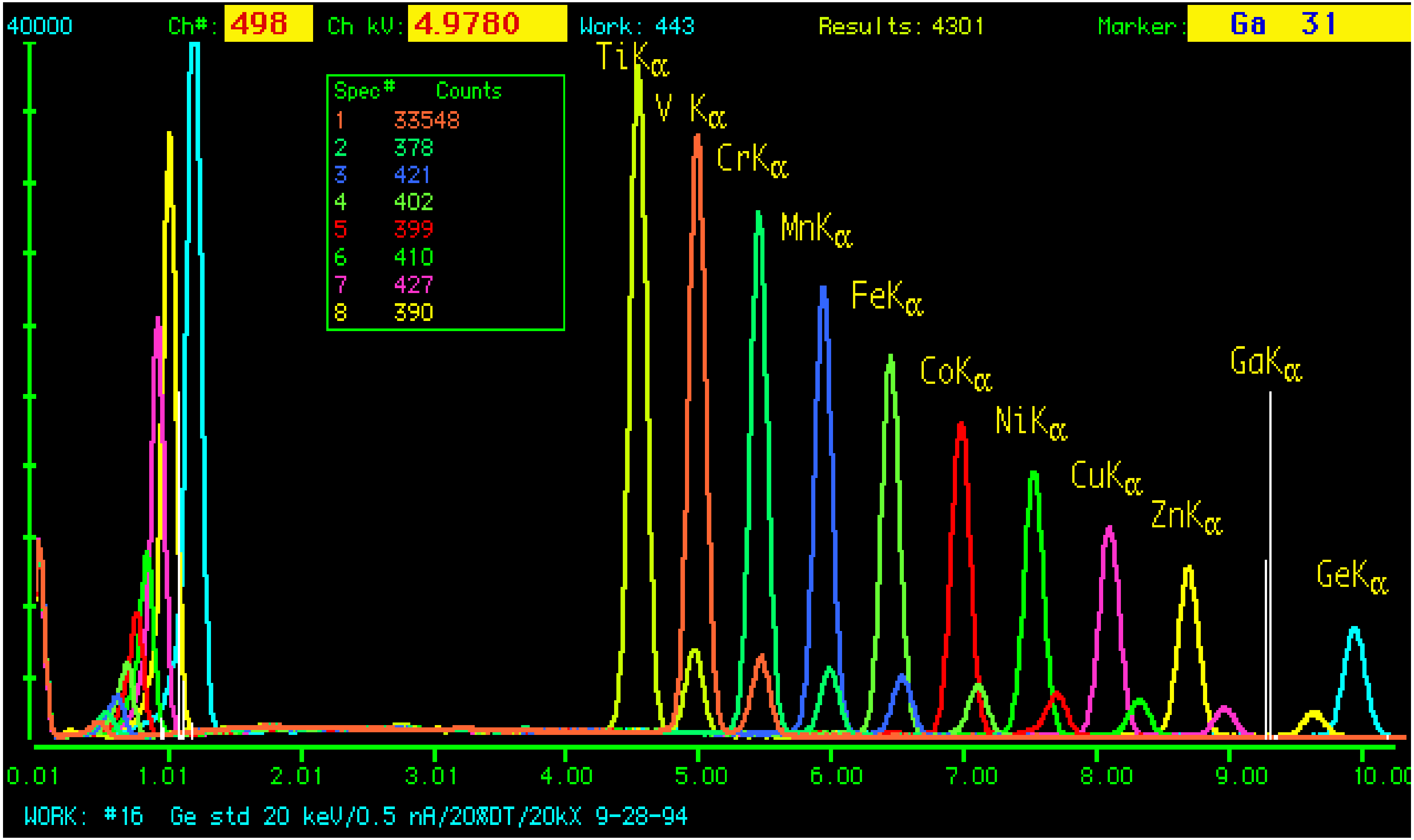


Error boxes are 10% relative wide:
95% band = ±50% relative

Approaches to Standardless Analysis: “Fitted Standards”

1. A suite of standards (K,L, M shell) is measured at one or more beam energies.
2. First principles physics calculations are used to supply elements missing from the suite with reference to those present, and to recalculate standard intensities for other beam energies, spectrometer windows (efficiency), and specimen tilts.
3. Results must be normalized, including calculation of oxygen by stoichiometry.

Measured Pure Element Standards (20 keV)

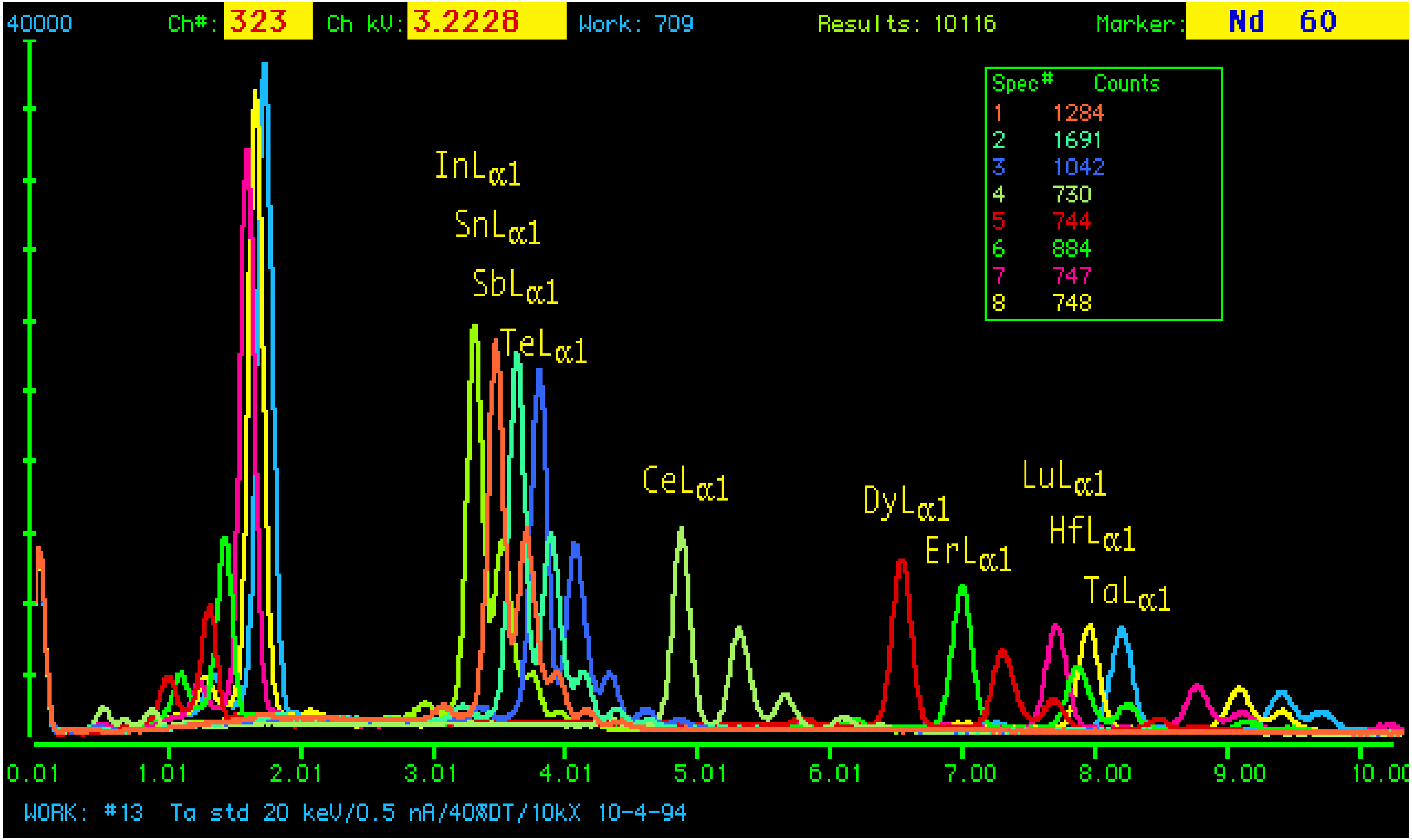


Ch#: 498 Ch kV: 4.9780 Work: 443 Results: 4301 Marker: Ga 31

Spec#	Counts
1	33548
2	378
3	421
4	402
5	399
6	410
7	427
8	390

WORK: #16 Ge std 20 keV/0.5 nA/20%DT/20kX 9-28-94

Measured Pure Element Standards at 20 keV

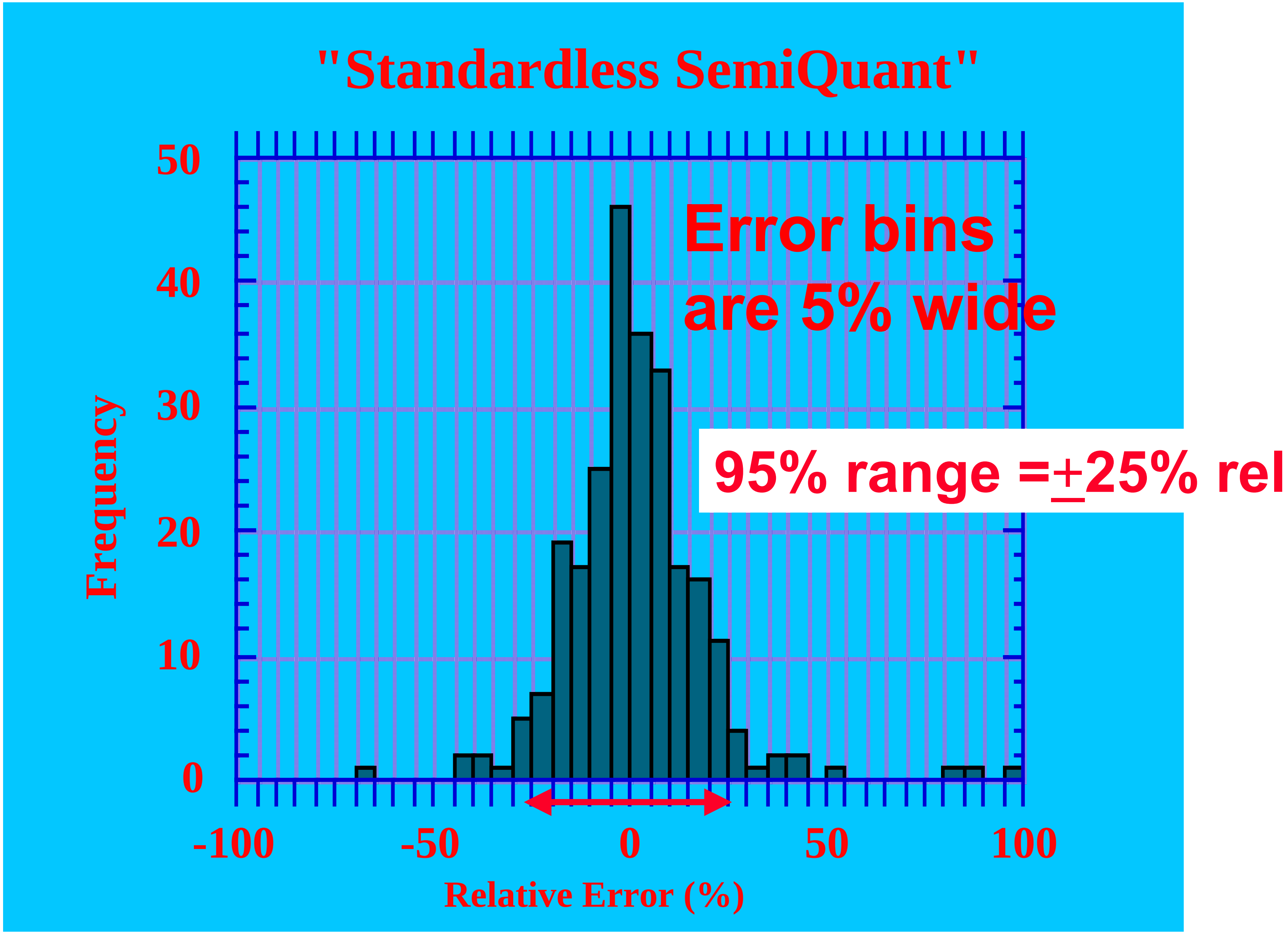


40000 Ch#: 323 Ch kV: 3.2228 Work: 709 Results: 10116 Marker: Nd 60

Spec#	Counts
1	1284
2	1691
3	1042
4	730
5	744
6	884
7	747
8	748

WORK: #13 Ta std 20 keV/0.5 nA/40%DT/10kX 10-4-94

Error Distribution for a Commercial Standardless Analysis



Error bins are 5% wide

95% range =±25% rel

Conclusions
What to do about standardless analysis?

1. If standardless analysis must be used for an unknown, report a realistic error estimate for the systematic error (ask manufacturer for an error histogram) or use the error histograms reported above, with a suitable caution.
2. If a known standard similar to the unknown is available, an error estimate can be based on analysis of the known.
3. Don’t report a numerical concentration. Use category names instead, for example:

Major: > 10%
Minor: 1 to 10%
Trace: < 1%

If a client requires a numerical value, do a full analysis with standards and ZAF!

Measuring the X-ray Intensities

- Wavelength dispersive spectrometry (WDS)
  - Based on x-ray diffraction from a crystal or artificial periodic structure, $n \lambda = 2 d \sin \theta$
  - High resolution (1 – 15 eV) separates most peak interferences and gives optimum limits of detection
  - Narrow instantaneous energy coverage requires scanning for qualitative analysis and background measurements
  - Variable efficiency (e.g., pressure) prevents archival standards measurements

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  - High resolution (1 – 15 eV) separates most peak interferences and gives optimum limits of detection
  - Narrow instantaneous energy coverage requires scanning for qualitative analysis and background measurements
  - Variable efficiency (e.g., pressure) prevents archival standards measurements
- Energy dispersive spectrometry (Si-EDS)
  - Based upon photoelectric capture and charge collection in a semiconductor crystal
  - Poor resolution [129 eV at MnKa (5890 eV); 70 – 170 eV across energy range] but has <u>continuous energy coverage</u> from 100 eV to 20 keV or more
  - Ideal for qualitative analysis and can perform quantitative analysis of major ($C > 0.1$) and minor ($0.01 \leq C \leq 0.1$)