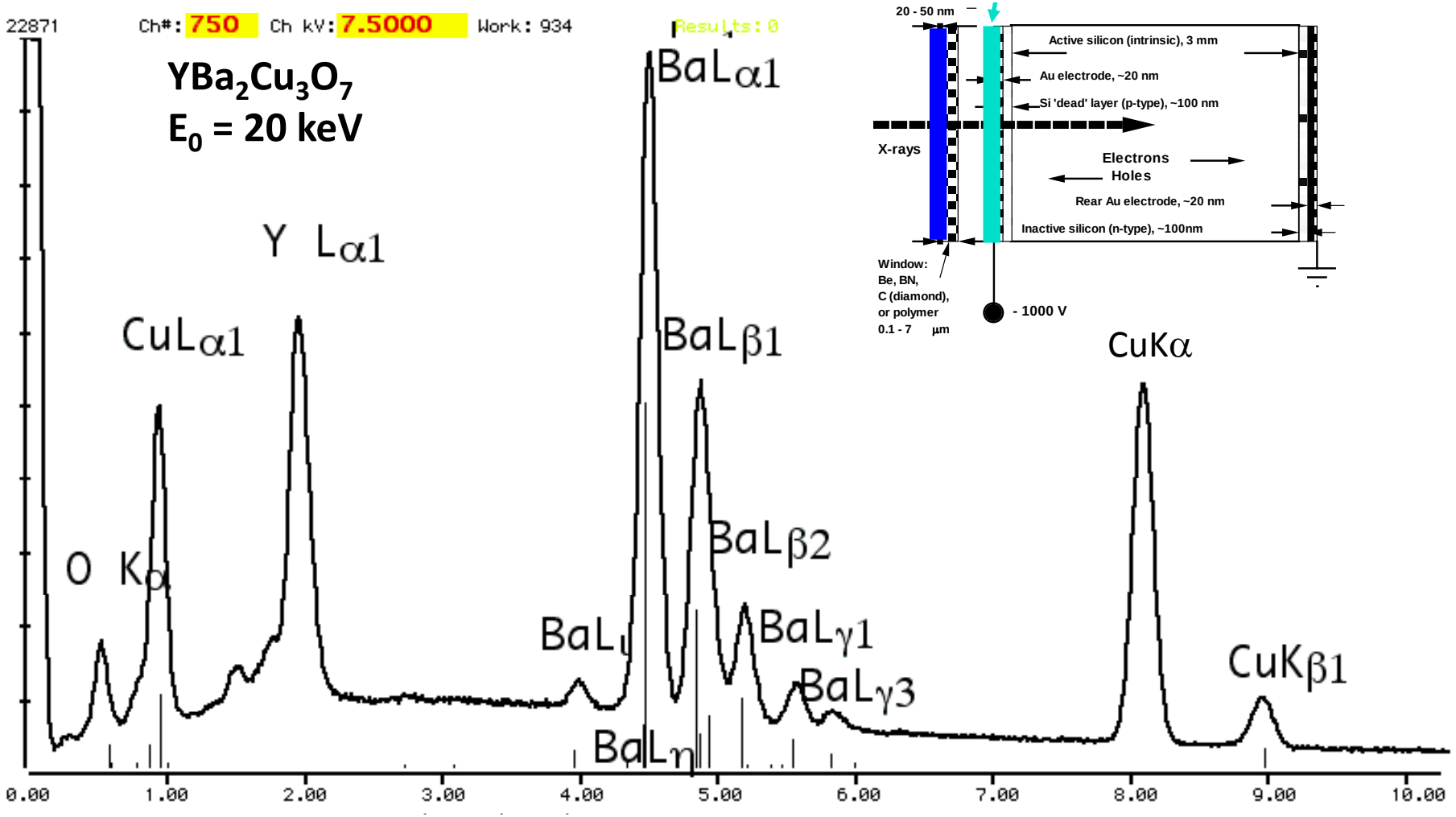
2012: How is most SEM/EDS "Quantitative Analysis" performed? By means of "Standardless Analysis"!



EDS records the entire spectrum. It is very appealing to directly and "quantitatively" compare the x-ray intensities of different elements in a single EDS measurement.

What is "Standardless Analysis"?

- "Standardless Analysis" – with EDS we measure the entire x-ray spectrum (~ 0.1 keV to E_0, E_0 up to 30 keV). "Standardless Analysis" attempts to quantitatively compares the suite of different elements within a single spectrum.
  - 1. "First principles" standardless: uses only physical calculations of the x-ray generation, propagation, and detection for quantification. (RARE; e.g., NIST-NIH DTSA Classic)

Calculate this

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

Measure this

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

ε = EDS efficiency

Stainless Steel Analysis: Standardless Analysis

Spectrum Label: Substrate steel 1 20 keV/0.5 nA/300kX 6-29-94 offset=-30
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.	Z	A	F
SiKA1	0.0040	0.0084	0.8900	0.4579	1.0013
CrKA1	0.2001	0.1880	1.0035	0.9890	1.1758
FeKA1	0.6396	0.7180	1.0028	0.9693	1.0111
NiKA1	0.0716	0.0856	0.9870	0.9017	1.0000
		Σ = 1.0000			

The Analysis Total (sum of all constituents) is exactly 1.0000
Is this result comforting?

Stainless Steel Analysis: Standardless Analysis

Spectrum Label: Substrate steel 1 20 keV/0.5 nA/300kX 6-29-94 offset=-30
Standardless Analysis
Take-Off Angle: 40.00
Beam Entry Angle: 90.00
Beam keV: 20.00
Number of elements: 4

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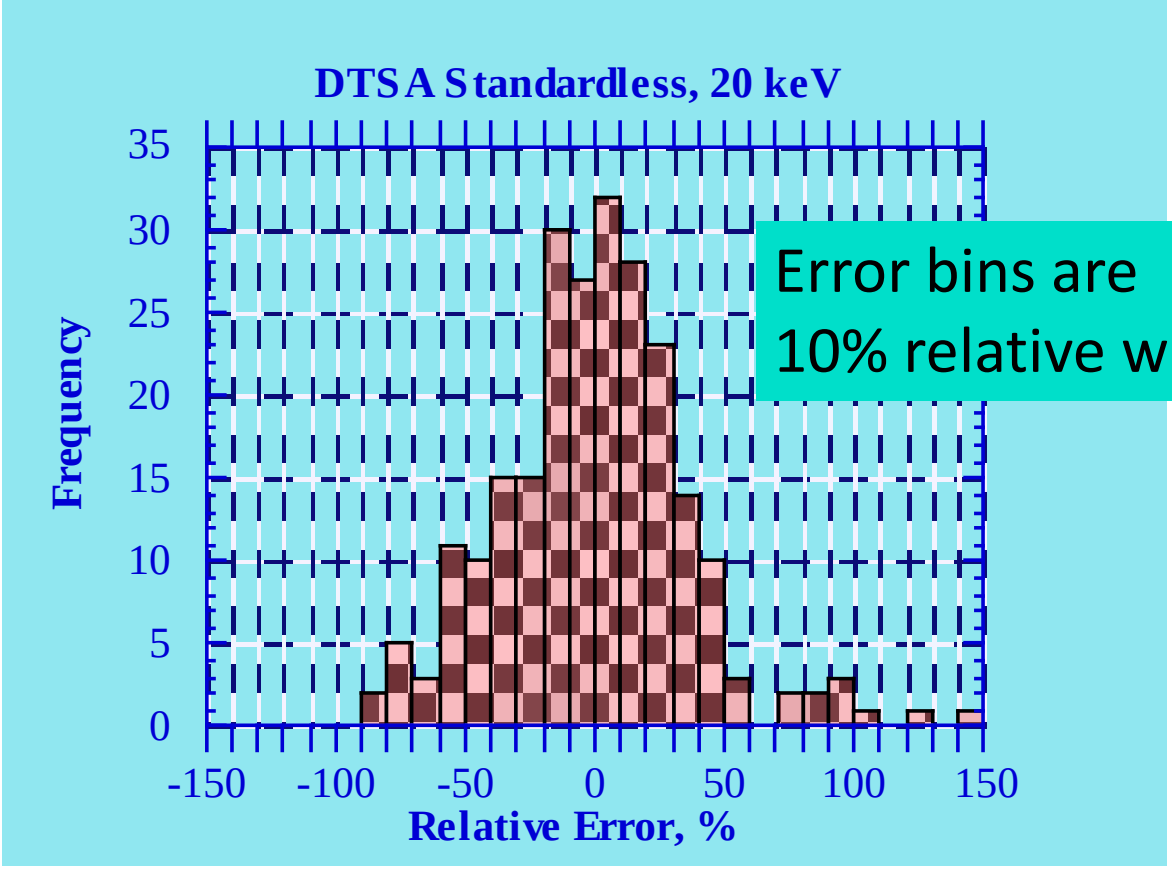
		Σ = 1.0000			

The Analysis Total (sum of all constituents) is exactly 1.0000
Is this result comforting?
NO! The loss of any connection to the electron dose means the calculated Concentrations must be normalized to unity to have any meaning.

True “First Principles” Standardless Analysis
DTSA Classic “Standardless Miracle” (Fiori, Swyt and Myklebust)

Newbury, D. E., Swyt, C. R., and Myklebust, R. L., "'Standardless' Quantitative Electron Probe Microanalysis with Energy-Dispersive X-ray Spectrometry: Is It Worth the Risk?", Analytical Chemistry, 67 (1995) 1866-1871.



The errors here are 10 times worse than analysis with standards. The 95% range is ±50% relative.

Conditions: SRMs, RMs, and stoichiometric compounds; E_0 =20 keV; photon energies above 0.9 keV (CuL); oxygen by assumed stoichiometry but not included in distribution

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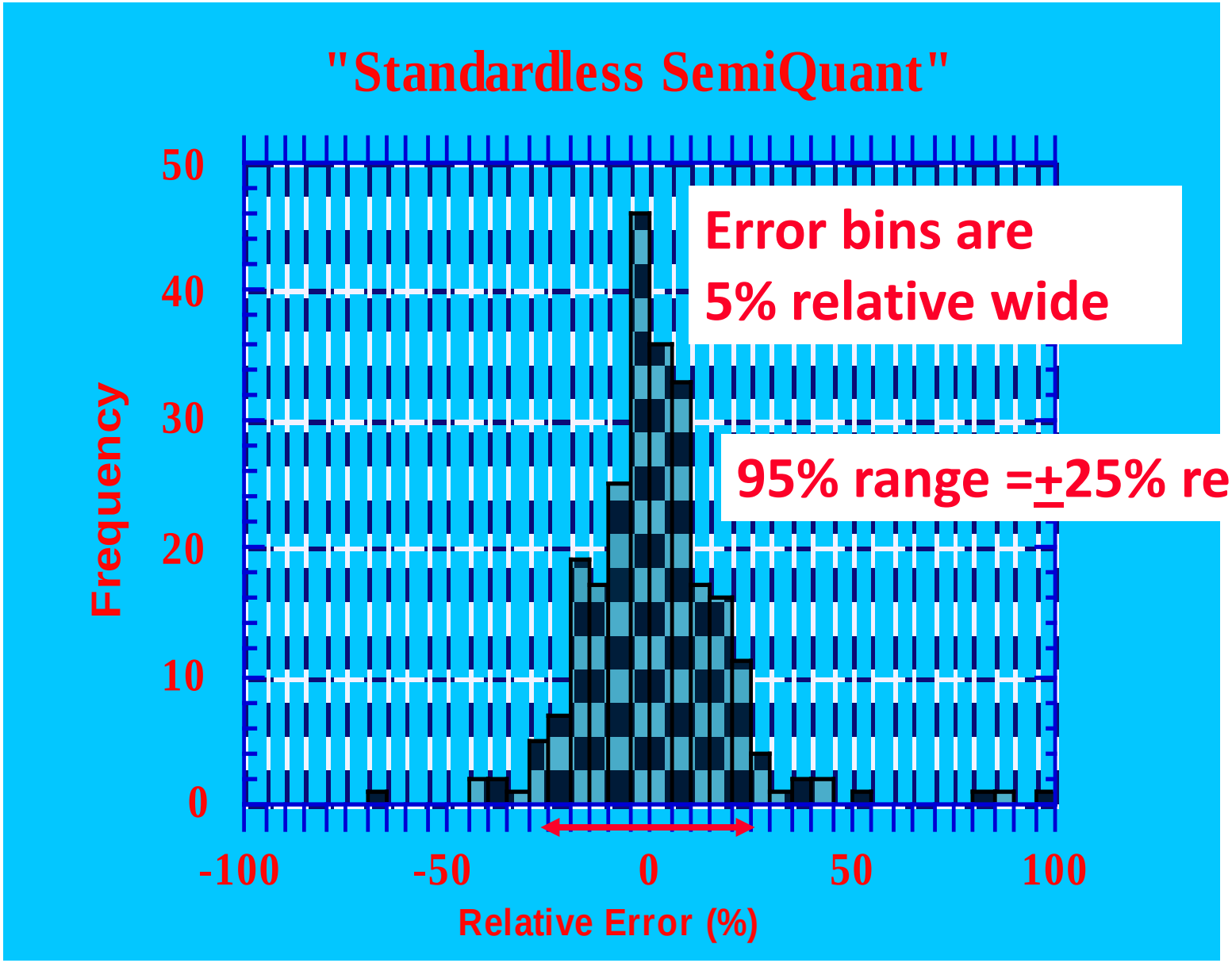
  - 1. “First principles” standardless: uses only physical calculations of the x-ray generation, propagation, and detection for quantification. (RARE; e.g., NIST-NIH DTSA Classic)
  - 2. “Remote Standards” standardless: A library of spectra is measured on a suite of known standards (elements, binary compounds) at several beam energies with a known EDS detector. This library is used to estimate standard intensities appropriate to the local measurement environment (E_0, take-off angle, and local detector efficiency), followed by matrix corrections. Final results must be normalized because of the loss of dose information.

Error Distribution for a Commercial Standardless Analysis: **1995**



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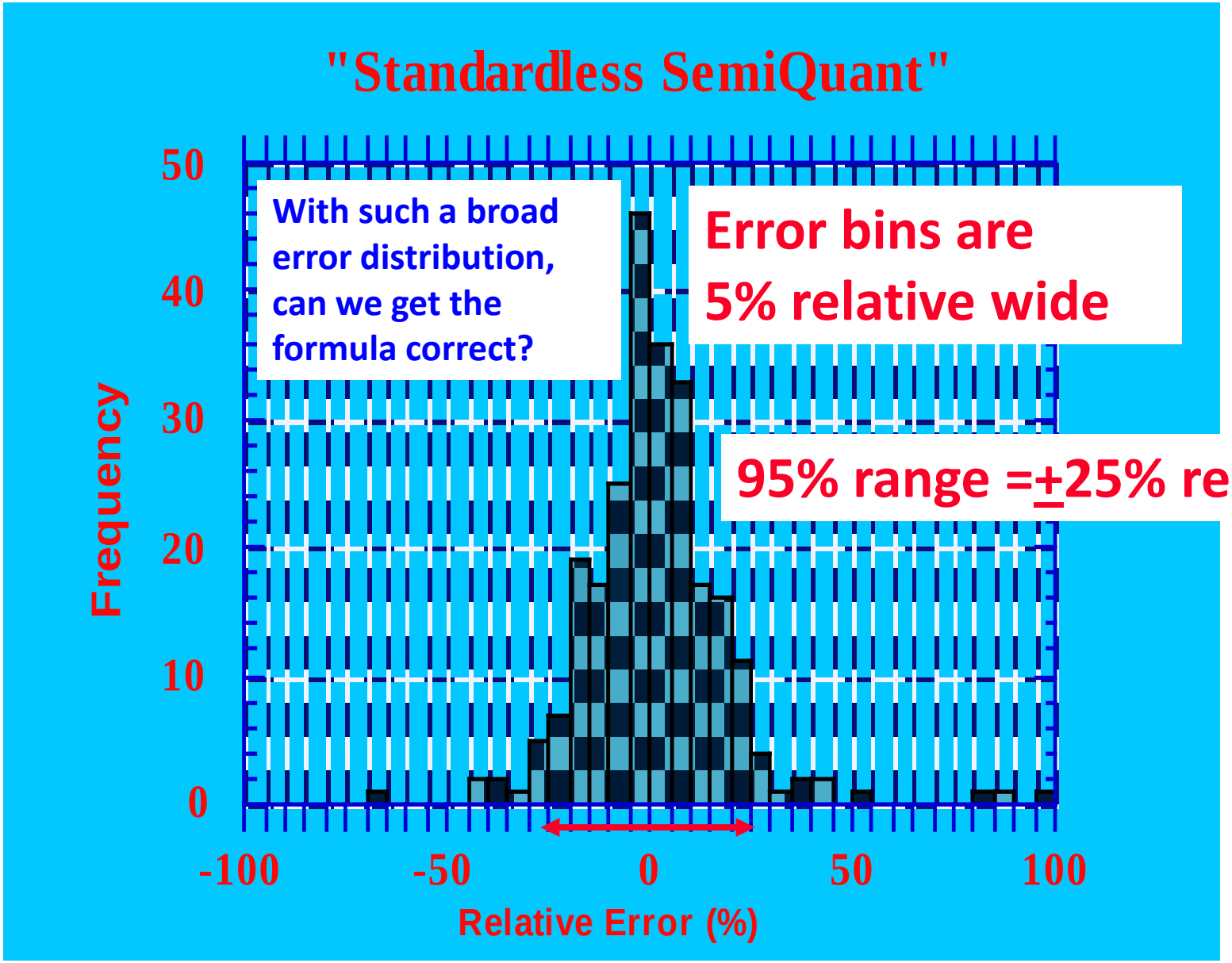

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Standards-based and "Standardless" Analyses of a $YBa_2Cu_3O_7$ Single Crystal

Can the analyst get the correct formula? (Oxygen by assumed stoichiometry)

	Y (true) 13.3 w/o	Ba (true) 41.2 w/o	Cu (true) 28.6 w/o	
Standards	13.8 (+ 4%)	41.1 (-0.2%)	28.1 (-2%)	Cu-K
ZAF	$Y_1Ba_2Cu_3O_{6.4}$			
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
	$Y_4Ba_6Cu_9O_{21}$			

Standardless Analysis: Is it any better in 2012?
A few analyses from a current commercial standardless program

Analysis of Binary Sulfides with a commercial "standardless" analysis protocol.

FeS (Troilite): measured formula is FeS

FeS (meteoritic troilite)
Spectrum: Acquisition FeS troilite (STD MT C)

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]	Relative Error % (C norm)
Fe	26	K-ser	62.40	62.86	49.29	1.7	-1.1%
S	16	K-ser	36.86	37.14	50.71	1.3	+1.8%
Total:			99.26	100.00	100.00		

Standardless Analysis: Is it any better in 2012?
A few analyses from a current commercial standardless program

Analysis of Binary Sulfides with a commercial "standardless" analysis protocol.

FeS: measured formula is FeS

ZnS: measured formula is Zn_3S_2

CuS: measured formula is Cu_3S_2

And this is analysis with energetic K-peaks! These results are only one snapshot of the 2012 performance of one system. A more complete study is underway.

FeS (meteoritic troilite)
Spectrum: Acquisition FeS troilite (STD MT C)

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]	Relative Error % (C norm)
Fe	26	K-ser	62.40	62.86	49.29	1.7	-1.1%
S	16	K-ser	36.86	37.14	50.71	1.3	+1.8%
		Total:	99.26	100.00	100.00		

ZnS
Spectrum: Acquisition (ZnS (STD MT C)

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]	Relative Error % (C norm wt%)
Zn	30	K-ser	67.94	76.15	61.02	1.9	+14%
S	16	K-ser	21.28	23.85	38.98	0.8	-28%
		Total:	89.23	100.00	100.00		

CuS
Spectrum: Acquisition

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]	Relative Error % (C norm wt%)
Cu	29	K-ser	69.02	76.43	62.07	1.9	+15%
S	16	K-ser	21.29	23.57	37.93	0.8	-30%
		Total:	90.31	100.00	100.00		