Effect of the Silicon Drift Detector on EDAX Standardless Quant Methods

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Abstract: Two standardless quantitative methods for evaluating EDS X-ray spectra were investigated in regards their basic metrics. Both methods have similar total errors, but the error contributions are from different sources. In the P/B-based method, error is more related to counting statistics and therefore can benefit from high count rates achievable with modern silicon drift detectors. To reduce systematic uncertainties in the net-count-based standardless approach, measured values need to be supported by data in a previously measured database. Using the P/B-based method, it is now possible to achieve standardless EDS quantification within ±10% relative deviation from true composition for 95% of results.

Keywords: X-ray spectra, standardless EDS quantification, silicon drift detector, P/B PeBaZAF Quant, eZAF Quant

Introduction

When used with a scanning electron microscope (SEM), energy-dispersive X-ray spectrometry (EDS) offers the microscopist significant analytical capabilities. For example, the operator can obtain distribution maps that are color-coded according to elements or phases present in the analyzed material. If more analytical details are needed, it is necessary to analyze the X-ray spectra from each distinguishable multi-element phase. From these spectra, quantitative values for the amounts of elements within each phase can be estimated. Sophisticated physical models, algorithms, and computer programs are needed to do this. The resultant uncertainties are a combination of the "precision" of the measured data and the "accuracy" available from the measurement setup, fundamental atomic databases, and the correctness of the matrix-correction models employed to convert X-ray peak intensities into values for the amounts of elements in the specimen. While standardless quantitative analysis had been developed and accomplished for many years using conventional Si(Li) EDS detection systems, the advent of silicon drift detectors (SDDs) has the potential to improve this type of analysis. Since the SDD can count over 100 times faster than the older Si(Li) detector, the SDD can quickly provide enough counts in X-ray peaks and background to significantly reduce the experimental scatter and improve the "precision" of the measurements.

In this article two standardless methods used in EDAX software are compared without and with the high-count rate provided by an SDD. One of these methods, which depends more on the number of counts collected (counting statistics), benefits significantly from the SDD.

Materials and Methods

Element identification is the first step toward getting a proper view of the sample composition. No Quant model would be able to calculate the element concentrations properly if the assumption about which elements are present in the sample is incorrect or wrongly evaluated. This is why EXpertID [1] is used with all EDAX spectra evaluation software to automatically identify the elements present. This procedure includes iterative evaluation of the residual spectrum, which is the measured minus the reconstructed spectrum, to find small peaks which were not detected in other ways.

Data from the spectrum. Figure 1 shows a simulated [2] spectrum of GaP with indications of how raw data are obtained for the two different Quant methods used in EDAX standardless analysis software (following the definitions in [3]). One method is based on evaluation of the measured net-counts of element peaks above the background (P=measured counts minus the background, shown in "green"). The other method is based on peak-to-background ratios (P/B=P divided by background, shown as "green" divided by "purple"). In both cases, the measured P and P/B values are greater with higher element concentrations in the sample. But there is usually no linear relationship between element concentration and measured element X-ray signal; moreover, other elements can cause large inter-element effects. For both methods, the measured input values for the quantification calculation (net intensities or P/B) require the X-ray background to be subtracted from the gross peak. In the case of the P/B method, the peak intensity must also be divided by the background; thus, accurate background values are particularly important. If element lines overlap, a deconvolution of the peaks is required.

Among the methods for determining the background, EDAX uses the physics-based bremsstrahlung calculation [4,5] and a pure mathematical background approximation method,
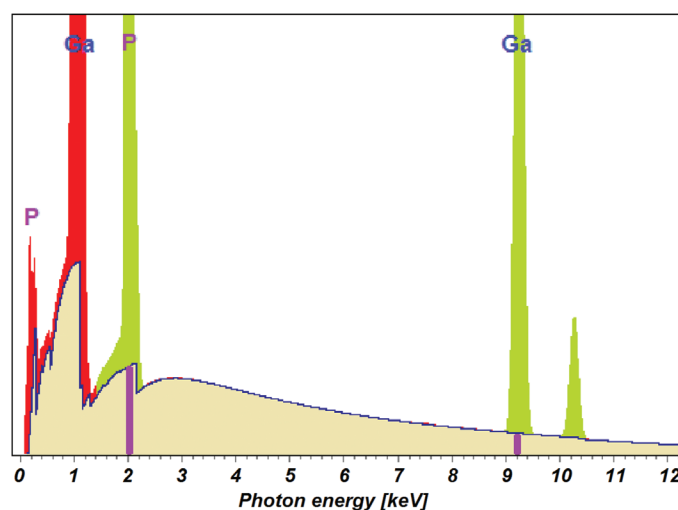

Figure 1: Two different quantification models, one based on evaluation of the measured net-counts of element peaks (green) and the other based on peak-to-background (P/B) ratios (green divided by purple).

SNIP [6]. Mathematical background methods are not suitable for P/B based quantification [4] because the absorption jumps at large peaks are not easily determined, but knowledge of them is required for correct calculation of proper P/B values. Peak deconvolution is performed with a probability-theory-based Bayesian algorithm [7,8]. Background calculation and peak deconvolution procedures are also core components of the EXpertID initial qualitative analysis of measured spectra. Also required are incomplete charge collection and pile-up corrections to the spectrum; these are related to the detector properties and the pulse processing electronics.

Corrections for matrix effects. Two methods are available in EDAX software to convert the raw data (P or P/B) to element concentrations for bulk samples: the net-counts procedure called eZAF and the P/B-based termed PeBaZAF. Both correction procedures employ aspects of the well-known ZAF corrections [9]. The ZAF abbreviation stands for atomic number correction (Z), absorption correction (A), and secondary fluorescence correction (F).

ZAF method basics. A classical (very simplified) formula, where N_i stands for the measured net-counts of characteristic radiation (ch) and c_i are the unknown weight fractions for elements i, is:

$$N_{a,i}^{ch} = c_{a,i} \; \varepsilon_i \; it \frac{d\Omega}{4\pi} \omega_i q_i \;\; (Z\,A\,F)_{a,i}^{ch} \tag{1}$$

where ε_i is the detector efficiency, and $it\dfrac{d\Omega}{4\pi}$ is the product of the electron microscope beam-current, the measurement time, and the solid angle. The index a stands for "all" elements and indicates those values that depend on the amounts of the other elements in the specimen. ω_i is the fluorescence yield, the fraction of ionizations that result in emission of an X-ray photon, and q_i is the transition probability of an evaluated line in a line series (for example, the Kα part of K-series). An iteration is required to solve the equation system. In Equation 1, the Z describes the generated X-rays by primary electron interactions inside of the sample. The A and F factors consider the loss of X-rays due to absorption in the sample and the enhancement by secondary fluorescence caused by other generated X-rays with higher photon energies. But with classical standards-based notation, the measured net counts of the unknown sample are always related to the measured net counts from a standard sample; this is the k-ratio of standards-based analysis. We can modify Equation 1 to:

$$\frac{N_{a,i}^{s}}{N_i^{st}} = k_{a,i} = c_{a,i} \frac{(ZAF)_{a,i}^{s}}{(ZAF)_i^{st}} \tag{2}$$

Where s is for the sample and st stands for standard, usually a pure element standard, measured under the same conditions. Several factors cancel out because they are usually the same for measurements of the standard and the sample. With further simplification Equation 2 becomes:

$$k_{a,i} = c_{a,i} \;\; (ZAF')_{a,i} \tag{3}$$

The ZAF' factors are now all correction factors relative to the pure element standard. It is possible to take the k-ratio and divide by ZAF' factors to get the weight fractions of the elements in the unknown. The ZAF' notation of Equation 3 is still used in

standardless quantification results to keep it somehow consistent with the classical standards-based formula. Nevertheless, since no standards were measured, the pure-element-related k-ratio is actually calculated via a model; it is not a really a measured value.

The eZAF method. In this article a generically standardless-based correction factor notation is always used. The atomic number correction Z, which is in two parts, is no longer a "correction" but a calculation of primarily excited X-rays [9]. There is a calculated integral over energy-dependent cross sections that considers the stopping power for electrons in the sample, the energy lost from incident electrons. This is the S-factor calculation for all electron-generated X-ray photons. The second part of the Z factor is a separate backscatter "correction," the R-factor [3,9], which compensates for electrons escaping the sample and not generating X-rays. One can derive from Equation (1):

$$N_{a,i}^{ch} = c_{a,i} \; \varepsilon_i \; it \frac{d\Omega}{4\pi} \omega_i q_i \; S_{a,i}^{ch} \;\; (R\,A\,F)_{a,i}^{ch} \tag{4}$$

The dead-time corrected measurement time is known, but it is not usually possible to determine the beam-current exactly in an SEM. There is one more unknown parameter than the available equations, thus it is necessary to use the additional constraint that the sum of all concentrations must equal 100%. But it is possible to determine the unknown parameter indirectly with a separate reference measurement on a pure element sample under the same conditions. In the latter case, the results can be calculated as un-normalized compositions.

The eZAF method uses a Z and R calculation that follows the fundamental work by Love & Scott [10]. The absorption correction used is based on the Sewell/Love/Scott "Quadrilateral" model for estimating the curve of generated X-rays as a function of depth [11]. In the absorption correction, a more recent database of mass absorption coefficients (MACs) by Elam et al. [12] is also used. This is important because these MAC values can strongly affect the absorption correction. The fluorescence correction is based on [13].

Figure 2 shows a HfNi sample spectrum, and Figure 3 shows the evaluation of the spectrum with a k-ratio-based result presentation versus generic standardless notation. The internal correction calculation is same using identical models. Therefore, the results are same. The difference in the upper table is that the k-ratio notation is assuming smaller corrections in relation to an estimated pure element measurement. But this measurement was actually not performed and therefore the algorithm has calculated the k-ratio, based on a theoretical model. In the lower table of Figure 3, the correction factors in relation to generated X-rays are actually greater because standard measurements were not performed. Based on different estimated corrections, the calculated systematic error estimations are different. In the standardless notation, all R- and A-corrections are less than 1.0 (a loss from primary excited X-rays), and all F-corrections are greater than 1.0 (an enhancement of primarily excited X-rays). This is not what happens with k-ratio of ZAF' notation where everything is compared to pure element standards. In the standardless case, the k-ratio is a fake. It was never really measured.

The P/B method. The EDAX PeBaZAF is a P/B-method following the basic ZAF approaches, but in this case a precise measurement must be made of the bremsstrahlung background. The basic relation is given by writing Equation 4 for
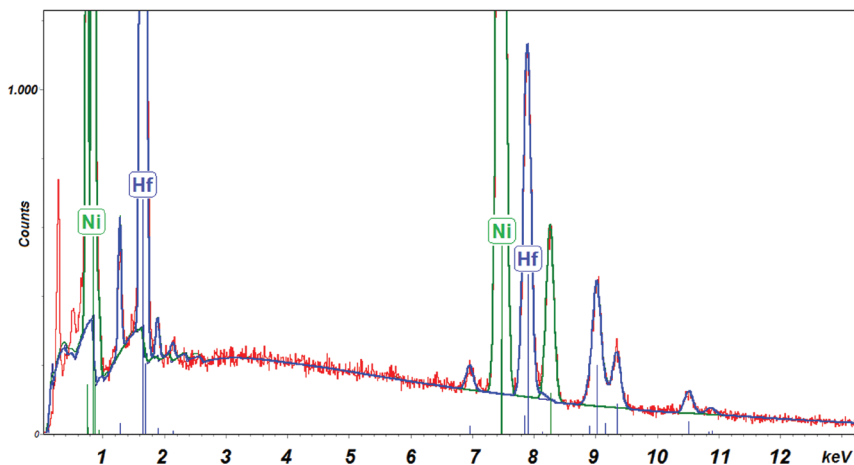
Figure 2: Spectrum from a Ni/Hf sample acquired with an SDD. Accelerating voltage=20 kV; counting time=30 seconds; count rate 13 kcps. Calculated background and spectrum reconstruction are shown.

both P and B and dividing the equations. Thus, $(P/B)_i$ represents the number of net characteristic (*ch*) peak counts divided by the measured bremsstrahlung (*br*) at the same energy:

$$(P/B)_{a,i} = c_{a,i}\ \omega_i q_i\ \frac{S_{a,i}^{ch}}{S_{a,i}^{br}}\ \frac{(R\ A\ F)_{a,i}^{ch}}{(R\ A)_{a,i}^{br}} \qquad (5)$$

Compared to the eZAF formula, some parameters dropped out of Equation 5 so that the number of unknown variables is equal to the number of equations. The solution does not require normalization of the composition values so that they sum to 100%. There is no physical effect to generate bremsstrahlung radiation by other X-rays (all bremsstrahlung is generated by charged particles), thus there is no F-factor for the bremsstrahlung model. This P/B model has been developed and improved from the 1980s until today [3,13,2,14]. All ZAF factors within Equation 5, except the F-correction, are ratios between characteristic radiation and bremsstrahlung.

Comparison of the two methods. Both approaches have advantages and disadvantages. The original design idea was that the P/B would always be the method of choice if the sample surface is not flat (particles, rough surfaces) because many effects in excitation and absorption cancel out. But during early work with this method, it was found that the P/B produced good accuracy [15] in general, even for flat specimens. The challenge with PeBaZAF method is to extract the proper P/B values from a measured spectrum. An accurate background determination is required at the same

energy as the peak, and the EDAX software provides this with an iterative bremsstrahlung calculation [4]. But the small number of counts in the measured background intensity (B) significantly influences the value of P/B, causing the PeBaZAF to exhibit a worse value of precision compared to eZAF. This means that PeBaZAF has poorer repeatability, which is detrimental for comparison tasks. On the other hand, the ZAF correction in the PeBaZAF is smaller (correction factors are closer to 1), leading to fewer systematic errors and good mean accuracy. The eZAF method exhibits larger correction factors, which reduces accuracy, but it has better precision. So one could say these two methods are "complementary" [16].

To evaluate the expected uncertainty with these quantitative measurements, an error parameter was calculated for each result. The parameter Err% is based on company software that combines the level of systematic error in the quantitative method with the level of precision in the measurement. Thus, if the number of counts is large enough, the precision part will be small, leaving Err% to report primarily the systematic error, which includes uncertainties with the inputs for, and the formulation of, the ZAF matrix correction method.

Results

Figure 4 shows how the accuracy and precision of these methods play out in an analysis of GaP. The top two tables show results with a low total number of counts typical of a Si(Li) spectrometer. The eZAF method has relatively large correction factors, which results in relatively large systematic errors, but the precision in

Figure 3: Two ways of representing standardless ZAF results. (top) Net-count-based eZAF analysis of a Ni/Hf sample with "classical" k-ratio notation; all corrections are in relation to estimated "pure" element standards (Equation 3). (bottom) Generic standardless notation where all corrections are in relation to primary electron excited X-rays (Equation 4). The standardless unnormalized results were obtained using a single reference measurement made on pure Cu to determine the absolute relation. Note that the measurement input and the final analytical results are identical. The difference is only the notation of presented factors. The calculated error is based on different assumptions for each correction. Only the second view is a correct depiction of the corrections employed in standardless case.
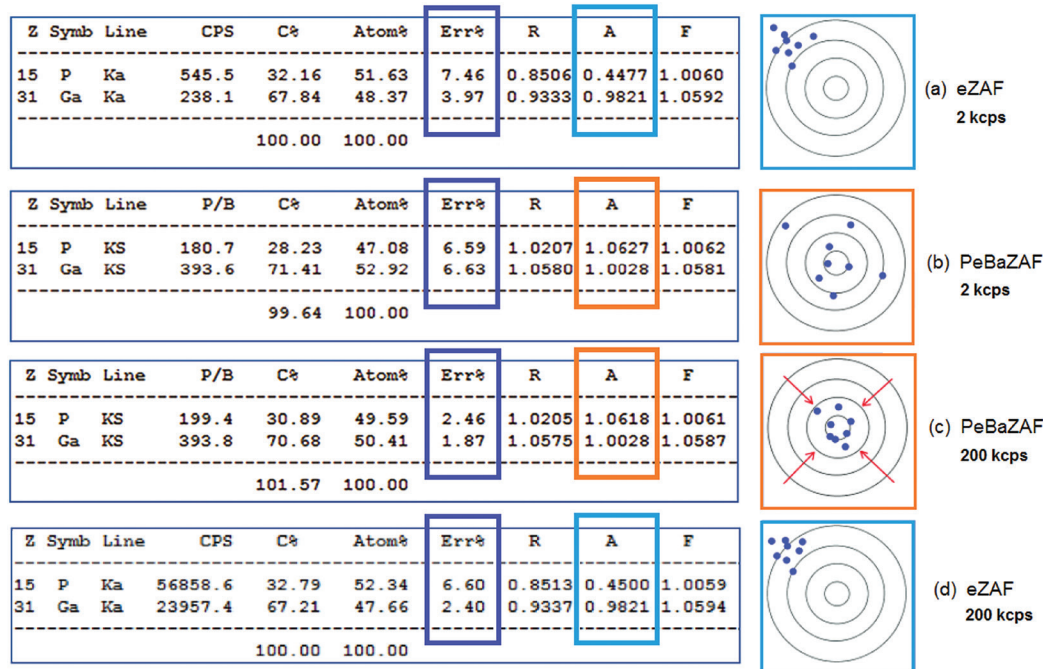
Z	Symb	Line	CPS	C%	Atom%	Err%	R	A	F
15	P	Ka	545.5	32.16	51.63	7.46	0.8506	0.4477	1.0060
31	Ga	Ka	238.1	67.84	48.37	3.97	0.9333	0.9821	1.0592
				100.00	100.00				

(a) eZAF 2 kcps

Z	Symb	Line	P/B	C%	Atom%	Err%	R	A	F
15	P	KS	180.7	28.23	47.08	6.59	1.0207	1.0627	1.0062
31	Ga	KS	393.6	71.41	52.92	6.63	1.0580	1.0028	1.0581
				99.64	100.00				

(b) PeBaZAF 2 kcps

Z	Symb	Line	P/B	C%	Atom%	Err%	R	A	F
15	P	KS	199.4	30.89	49.59	2.46	1.0205	1.0618	1.0061
31	Ga	KS	393.8	70.68	50.41	1.87	1.0575	1.0028	1.0587
				101.57	100.00				

(c) PeBaZAF 200 kcps

Z	Symb	Line	CPS	C%	Atom%	Err%	R	A	F
15	P	Ka	56858.6	32.79	52.34	6.60	0.8513	0.4500	1.0059
31	Ga	Ka	23957.4	67.21	47.66	2.40	0.9337	0.9821	1.0594
				100.00	100.00				

(d) eZAF 200 kcps

Figure 4: Effect of count rate. Internally calculated errors Err% are marked with dark blue boxes (considering systematic+random errors). The top two analyses are for low-count measurements (30 seconds, 2 kcps): (a) eZAF method and (b) PeBaZAF method. Lower two analyses show results obtained with 100 times higher counts (200 kcps): (c) PeBaZAF and (d) eZAF. Both methods have similar total error for low counts. The PeBaZAF (P/B) method improves in precision and total error with higher counts. The eZAF method is hampered by the same high correction factors that limited accuracy at lower counts, and the total error improves only marginally.

the method is good (Figure 4a). The PeBaZAF method has better accuracy, but repeated values are more widely scattered, causing worse precision (Figure 4b). Under these conditions, the calculated total error (Err%) is similar for both methods.

When the same sample is analyzed 100 times longer or with a count rate 100 times greater (for example, 200 kcps with an SDD versus 2 kcps with an Si(Li) detector), the precision improves for the PeBaZAF method (Figure 4c). This causes repeat analyses to be closer to the correct value. For the eZAF method the calculated error does not improve much, if at all, with higher count rates because the systematic errors in the correction factors still dominate (Figure 4d).

Figures 5 and 6 show the results of PeBaZAF standardless EDS analyses on 269 multi-element specimens containing various amounts of elements with atomic numbers from Z = 6 to Z = 83. For this group of test specimens, the relative deviation from the correct values was smaller than±13.7% for 95% of the results.

Thus, it is possible to improve the error factor for the PeBaZAF method with more counts in the spectrum, which leads to more counts in the background and better overall precision. Since the use of an SDD spectrometer makes spectrum acquisition at high count rates routine, the PeBaZAF method now has a significant advantage.

Discussion

The original PeBaZAF disadvantage, that it required higher than usual acquisition times, was reduced with the introduction of SDD detectors, where the count rate can be more than 2 orders of magnitude higher compared to the old Si(Li) detectors. This ability to offer more counts in the same collection time is clearly

a benefit to the PeBaZAF method. The test presented here shows that for 269 measurements of different multi-element specimens, 95% of the results were within ±13.7% of the known composition. This result is better than some published results for standardless EDS methods in [9,17]. Further development of this method is expected to improve the P/B-based standardless analysis to about ±10% relative deviation with 95% of the results [14].

The major uncertainties with the net-count-based eZAF approach are systematic errors in the ZAF correction calculations and errors related to the parameters used (for example, MACs). The example presented here shows larger corrections, especially for the absorption correction, for the eZAF method compared to the PeBaZAF method. It is possible to improve the uncertainties with the eZAF method by employing a measured standards database (this standardless method uses "remote standards" [18]), which makes this method behave in a manner closer to a true standards-based quantitative analysis.

Conclusion

Two standardless methods were compared in light of the high count rate capabilities of the silicon drift detector (SDD). The disadvantage in precision typical of the PeBaZAF method is mitigated when using the high count rates available with the SDD. The test presented here shows that for 269 measurements
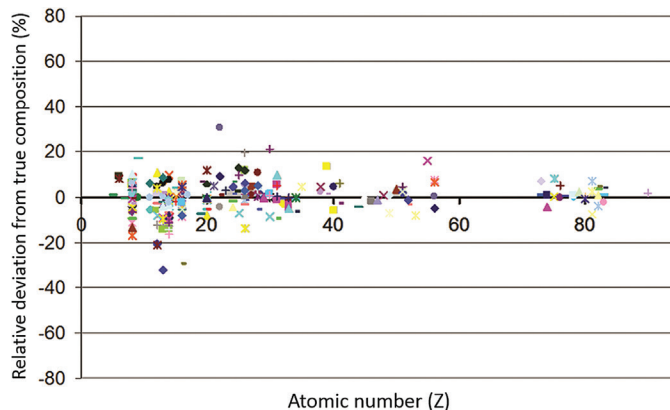

Figure 5: Results for 269 PeBaZAF standardless EDS analyses with an SDD on specimens containing various amounts of elements with atomic numbers from Z=6 to Z=83. The statistical evaluation of these results indicates that the relative deviation from correct values was better than±13.7% for 95% of results [14].
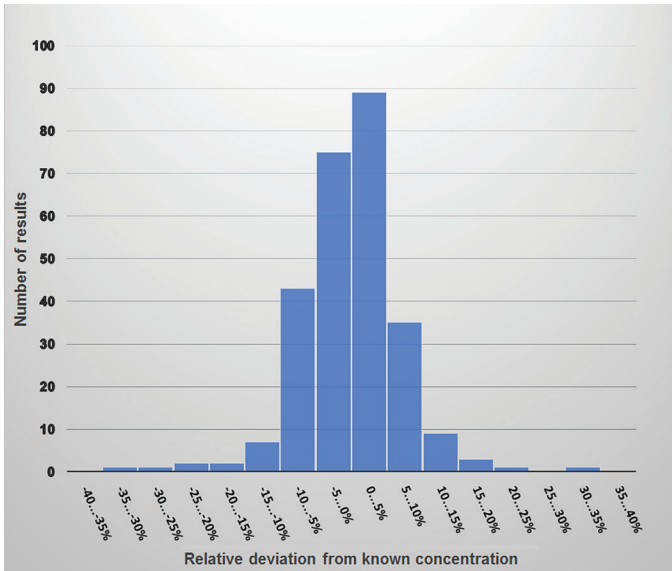
Figure 6: Error histogram for 269 PeBaZAF results showing the relative deviations from the true compositions. The central (largest) bar gives the number of results within the deviation range of from 0% to 5% of the true composition [14].

of different multi-element specimens, the PeBaZAF method yields 95% of the results within ±13.7% of the known composition. This is better than certain other standardless methods. The eZAF method should gain improved accuracy from a stored database of standards measurements.

Acknowledgements

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