ADVANTAGES AND DISADVANTAGES OF BAYESIAN METHODS FOR OBTAINING XRF NET INTENSITIES

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ABSTRACT

A method of extracting net intensities for the element peaks in an X-ray fluorescence (XRF) spectrum based on Bayes Theorem will be reviewed and discussed. The method has several advantages, among them that the total counts are preserved and that the a priori information is incorporated in a natural manner. These make it, for example, less sensitive to errors in the peak position, widths, and alpha/beta ratios. However, there are also disadvantages. The preservation of total counts means that spurious peaks, such as those from crystallite diffraction, will have their counts included in one or more of the element peaks.

We present the results of applying a Bayesian deconvolution method to several XRF spectra and compare them to conventional methods. The spectra are selected to illustrate both the advantages and disadvantages of this method. Errors introduced by variations in the functions used to model the peak shapes are investigated. Quantitative comparisons are also made by using the net intensities from each method in standardless analysis.

INTRODUCTION

A number of deconvolution methods based on Bayes Theorem have been developed. Such methods can be applied to X-ray spectra for extracting net intensities and are also referred to as maximum likelihood methods. They have advantages for this purpose that are discussed below. For a more thorough explanation of deconvolution methods and how the probability-based methods of various authors relate to the method used here, the reader is referred to the excellent book by Jansson (1997). Chapter 4 on modern constrained nonlinear methods includes mention of the approach employed in this work, which is taken from the work of Kennett, Prestwich, and Robertson (Kennett et al., 1978). Direct application of the method to X-ray emission spectra from electron excitation has been developed by Eggert and Scholz (1986) and by Shinkawa et al. (2005). This work will focus on X-ray fluorescence (XRF), that is X-ray emission spectra excited by X-ray photons. The method is used for XRF without modification and this paper will focus on its advantages and disadvantages in practical cases arising in XRF.

METHOD

In this work, three fitting methods for extracting net intensities were tried and compared. All of three methods used pure Gaussian functions without any tails or other asymmetries. The reference method was nonlinear least squares with all of the Gaussian parameters (amplitude, center position, and width) allowed to vary. The fitting procedure used the MRQMIN routine from Numerical Recipes (Press et al., 1986) that implements the Levenberg-Marquardt
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algorithm. The starting values for the fit were taken from the database of emission line energies and the energy resolution for the detector used to acquire the spectrum.

The first method being compared used linear least squares fitting of Gaussian functions with fixed center position and width. Since this method only provides values for the amplitude, the position and width were taken from the nonlinear least squares fits and were varied about these values to determine the sensitivity to errors in these parameters. The fits used the LFIT routine from *Numerical Recipes* (Press et al., 1986).

The second method compared was a deconvolution approach based on Bayes Theorem. It was implemented following the procedures given by Eggert and Scholz (1985) and proceeded for 15 iterations. Eggert and Scholz found that about 15 iterations maximum were required. This was checked by stopping after 5 iterations and the differences from the final results were a few tenths of a percent. The functions used for the *a priori* information in this method were the same as the functions used in the linear least squares fit. It was found in this work that a starting value of unity was adequate to insure convergence in 15 iterations for the spectra considered here.

The spectra used in the comparisons were obtained on a Pd-based white gold alloy #62 (Roentgenanalytik Messtechnik, Germany) and a CDA 903 Tin Bronze alloy (Brammer, USA). The CDA alloy was chosen because of the partially overlapped peaks from copper Kβ at 8905.4 eV and zinc Kα at 8631.5 eV. The white gold alloy was used to compare quantitative results using net intensities from the second and third methods. Its composition was well known and stable, and it contained a variety of elements all of which are well handled by the fundamental parameter standardless analysis used here. The details of our fundamental parameter calculations have been presented previously (Elam et al., 2004). Measurements were made with an Eagle III Spectrometer having a Rh tube operated at 40 kV and 90 μA. A 1 mm primary beam aperture was used with no filter. The detector was a Si(Li) unit with 12 μm Be window. Data collection employed a 17 ms time constant for the detector which resulted in a 40% dead time and data was collected for 400 live seconds. All specimens were presented to the instrument as received from the supplier (smooth, polished surfaces).

**RESULTS – NET INTENSITIES**

For fits to a single well-resolved peak, the only parameter obtained from either of the methods being compared is the amplitude. Throughout this work the amplitude is expressed as the integral under the Gaussian peak, which is directly related to the Gaussian amplitude. When the position and width parameters are taken from the nonlinear fits, the resulting amplitude from both methods is precisely the same as that from the nonlinear fits. However, when either of these “fixed” parameters differ from the reference value, the amplitude result is also different. Figure 1 shows the effect on the amplitude of changing these parameters.
As can be seen, the linear least squares result is dramatically more sensitive to deviations in the parameters. This results from the fact that the total counts are preserved in the Bayesian approach. The results in Figure 1 give a dramatic example of the advantage of the Bayesian method. The net intensities extracted from a single peak via this method will be accurate to within a few tenths of a percent relative for almost any reasonable choices of position and width.

A more relevant situation is shown in Figure 2 in the spectrum of the CDA 903 Tin Bronze alloy. The alloy is nominally 88% copper and only 4% zinc. The zinc Kα line is thus partially hidden under the left side of the copper Kβ line (region inside gray box in the figure). Figure 3 shows a nonlinear least squares fit of two Gaussians to this region of the spectrum. Note that the fit is very good, as expected, with all of the fit values falling within the 1-σ statistical error bars of the measured spectrum points. The fit was to 81 data points, used 6 parameters, and resulted in a reduced chi squared of 2.03. A perfect fit would yield a reduced chi squared of 1. The positions deviate from the recent tabulated values of Deslattes et al. (2003) by +2.9 eV for the zinc Kα line and -0.2 eV for the copper Kβ line. The other fit results are given in Table I. Note that the amplitude values are for the integral (corresponding to the net line intensity) and the width values are full-width at half-maximum (FWHM).
Figure 2. Spectrum of a CDA 903 Tin Bronze alloy. The region inside the gray box shows the zinc $K\alpha$ line partially hidden under the left side of the copper $K\beta$ line.

Table I. Results of a nonlinear least squares fit to the boxed region of the spectrum in Figure 2, as shown in Figure 3. The fit used two Gaussian functions with all parameters varied (6 parameters). Amplitudes are expressed as the integral under the Gaussian function and widths are full-width at half-maximum (FWHM).

<table>
<thead>
<tr>
<th></th>
<th>zinc $K\alpha$</th>
<th>copper $K\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amplitude</td>
<td>1481k</td>
<td>3854k</td>
</tr>
<tr>
<td>Position</td>
<td>8634.1 eV</td>
<td>8905.2 eV</td>
</tr>
<tr>
<td>Width</td>
<td>193.6 eV</td>
<td>187.1 eV</td>
</tr>
</tbody>
</table>
For both the linear least squares fit and Bayesian deconvolution applied to this overlap situation the only result parameters are the two amplitudes. If the positions and widths of the Gaussian functions are set to the values obtained from the nonlinear fit, then both approaches yield the same amplitudes as the nonlinear fit. However, the two approaches have different behavior if the position and width deviate from the best-fit values. The effects of these deviations are the subject of the next sections.
to +66 eV from the reference value). The blue solid curve is the spectrum and the dashed curves are the fit results.

The most sensitive parameter in these types of fits is the center position of the Gaussian functions. Accordingly, this parameter was varied over a considerable range. The larger peak position (Position 2 in the figures) was varied because of its dramatic effect on the amplitude of the smaller peak. The curves resulting from the fits are plotted in Figure 4 for both types of fit and for the extremes of the range of parameter variation. This shows the effects in exaggerated detail. It is apparent from these plots that the Bayesian method has less variation in the amplitude of the larger peak, as expected from the discussion above. However, the effect on the smaller peak is not so obvious.

To quantify the effects for smaller and more reasonable variations in the position of the larger peak, the amplitude errors were calculated against the reference amplitudes from the nonlinear fit. The results of this analysis are shown in Figure 5 for both the linear least squares (on the left side in the figure) and Bayesian methods (on the right side). The upper panels on both sides show the errors from varying only the position of the larger peak. The error for the larger peak amplitude (err 2 in the figure) exhibits the same behavior as in Figure 1. However, the error in the smaller peak amplitude (err 1 in the figure) changes monotonically and is roughly linear for small variations. The behavior and even the slope are similar for the linear least squares and Bayesian methods, indicating the effect of errors in the larger peak position on the smaller peak amplitude are intrinsic to the procedure and cannot be avoided by either of these methods.

Figure 5. Errors in the fit amplitudes versus the reference values as a function of the position of the larger peak in the fitting function. Results for the linear least squares fit are in the left panels.
and for Bayesian deconvolution in the right panels. The error in the amplitude of the larger peak is err 2 while that for the smaller peak is err 1. The lower panels show the effect of varying both peak positions with fixed separation, as a function of the smaller peak position.

The lower panels in Figure 5 show the effect of varying both peak positions together. This would be the case, for example, if the spectrum had an energy calibration error. The spacing between the center positions was kept fixed at the value from the nonlinear fit. The errors are plotted against the position of the lower energy (smaller) peak. The behavior is similar to that in the upper panels but is more pronounced, leading to larger errors for the same shift.

Figures 6 and 7 show the same plots for variations in the width of the fitting functions. The results are similar to Figures 4 and 5 with the exception of the lower panels in Figure 7 where the widths are varied together. In this case, the linear least squares fit gives low values for the amplitudes regardless of the sign of the width deviation. Note that the errors are much less when both widths are varied than when only one is varied. The two widths were forced to be the same for this calculation, so the errors do not both go to zero in the linear fit. The Bayesian method still has one amplitude always larger and the other amplitude smaller than the reference value, which is a result of its property of preserving the overall counts. This implies that for some value of the width both amplitudes have the correct value. Of course, this width cannot be determined without knowing the correct answer so it is of little benefit.

Figure 6. Results of a linear least squares fit (left plot) and Bayesian deconvolution (right plot) when the width of the larger peak is shifted to two extremes of the range investigated (150 eV to 250 eV FWHM). The blue solid curve is the spectrum and the dashed curves are the fit results.
Figure 7. Errors in the fit amplitudes versus the reference values as a function of the width of the larger peak in the fitting function. Results for the linear least squares fit are in the left panels and for Bayesian deconvolution in the right panels. The error in the amplitude of the larger peak is err 2 while that for the smaller peak is err 1. The lower panels show the effect of varying both peak widths with both forced to be the same value.

RESULTS – QUANTITATIVE ANALYSIS

The question of what is the correct value for the net intensity is dependent on what information is desired. The actual number of photons emitted by atoms in the specimen is relevant when the associated atomic parameters are being measured or when calculations based on those atomic parameters are being used to determine elemental compositions. If composition is being determined by comparison with standards, it is more important to have a reproducible net intensity value than one that can be related precisely to the actual emission. In some sense the result of a fit that falls within the standard deviations of the measured data points is the best possible answer that can be obtained without resorting to a priori information.

As a further test, we have used the net intensities from the two methods to determine the elemental composition of a known material. A fully standardless method was used to avoid any comparison with other spectra. This implies that normalization to 100% was necessary to remove the geometric factor from the calculation. This test is designed to evaluate the net intensities rather than the atomic parameters, so the elements were restricted to those for which the best values of the parameters are available – that is, the elements that have been most thoroughly investigated by X-ray spectroscopy. This includes the 3-d transition metals and the
abundant heavier metals. In order to broaden our investigation to include L emission lines, we included a heavier element (gold) in the mix. Gold jewelry alloys are well characterized and stable, so an available specimen of this type was used. The palladium-based white gold alloy number 62 contains only gold, copper, zinc, palladium, and silver.

For the net intensity determination, the database values of the peak positions were used in the fitting functions and the width was taken as a fixed value of 150 eV. No attempt was made to adjust these values or to correct any errors in the energy calibration. In particular, the peak width was independent of energy. Both of these errors are expected to be significant and to be more important at higher energies. Peak assignments were also fixed and the net intensity was taken as the contribution to the fitting function from an individual diagram line for each element (the Kα1 line for all but gold, which used the Lα1 line). The intensity of the same diagram line was calculated using a fundamental parameters method that has been described previously (Elam et al. 2004). The composition was adjusted until the calculated intensities matched the intensities extracted from the spectrum.

The results of the standardless quantification are given in Table II together with the known composition of this alloy. The linear least squares values are not particularly good, since the widths are not a very good match and the positions are slightly in error due to an imperfect energy calibration of this spectrum. The Bayesian values are a dramatic improvement over the linear least squares except for the value for zinc.

Table II. Results of applying fundamental parameters standardless quantification to the net intensities from the spectrum in Figures 8 and 9 of a white gold alloy, together with the composition supplied by the manufacturer. The two methods of determining net intensities discussed in the text are compared.

<table>
<thead>
<tr>
<th></th>
<th>Linear Least Squares</th>
<th>Given</th>
<th>Bayes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rel Err</td>
<td>wt%</td>
<td>wt%</td>
</tr>
<tr>
<td>Cu</td>
<td>5.73</td>
<td>12.26</td>
<td>11.6</td>
</tr>
<tr>
<td>Zn</td>
<td>27.16</td>
<td>0.51</td>
<td>0.4</td>
</tr>
<tr>
<td>Au</td>
<td>11.65</td>
<td>61.41</td>
<td>55</td>
</tr>
<tr>
<td>Pd</td>
<td>-17.33</td>
<td>6.53</td>
<td>7.9</td>
</tr>
<tr>
<td>Ag</td>
<td>-22.84</td>
<td>19.29</td>
<td>25</td>
</tr>
</tbody>
</table>

The reason for this improvement can be seen in Figure 8 where the measured spectrum for the alloy is shown together with reconstructions based on the results of the two net intensity extraction methods. The plot is restricted to the region of the palladium and silver emission lines to clearly show the quality of the fit. Note that the Bayes curve (green in the figure) is higher than the linear least squares curve (red curve). This is because the position and width errors have a dramatic effect on the linear least squares fit, while the Bayes deconvolution preserves the total counts under the peaks. For these two elements, the fact that the counts are preserved seems to give a much better answer. The lower values from the linear least squares method makes the concentrations of those elements smaller, which affects the other elements via the normalization.
Figure 8. Spectrum of Pd White #62 white gold alloy in the region of the palladium and silver Kα emission lines. The blue curve is the measured spectrum, the red curve is the result of a linear least squares fit using Gaussian functions, and the green curve is the result of a Bayesian deconvolution. The positions of the functions are taken from the emission line energies and the width is fixed for all peaks at 150 eV. Note that the width is too small at this energy and that there is some error in the peak positions. This is done deliberately to illustrate the relative effects of these common errors (see text and Table II).

This example shows both the strength and the weakness of the Bayes method. While the improvement in the major elements is substantial, the minor element zinc has a larger disagreement. The reason can be seen in Figure 9 which is a similar plot for the region around the ZnKα emission line. It is affected by the gold L½ and copper Kβ lines that bracket it on either side. The gold L½ intensity is primarily determined by the gold Lα line since they both occur from L3 vacancies. Likewise the copper Kβ intensity is primarily determined by the copper Kα line. Since the width is incorrect, the copper Kβ line is not fit as well and some intensity remains at the left side of this peak. The linear least squares ignores this, since it is more heavily weighted at the position of the maximum in the Gaussian used to fit the zinc Kα line. However, the Bayes method preserves the total counts, so these counts must go someplace, and they wind up partially allocated to the Zn emission since it is independent of any other line. Neither method does a very good job for this element in this situation but the Bayes method is markedly worse. Simple improvements to the width and positions would improve the quantification results for both methods and with perfect matches both would give the same results.
Figure 9. Spectrum of Pd White #62 white gold alloy in the region of the gold L\(\nu\), copper K\(\beta\), and zinc K\(\alpha\) emission lines. The blue curve is the measured spectrum, the red curve is the result of a linear least squares fit using Gaussian functions, and the green curve is the result of a Bayesian deconvolution. Note the bump in the Bayes (green) curve near the Zn peak.

The \textit{a priori} information consisted of the function (pure Gaussian) and the ratios of the emission lines taken simply as the transition probabilities. This implied that each atomic level with a vacancy was fit individually. Thus the K lines had one fit parameter and the L lines had 3 fit parameters. This was of some importance in the fits of overlapped peaks, as shown in Table III, which gives the linear least squares results if the diagram lines are combined according to whether they are resolved in the spectrum (with K\(\alpha\) and K\(\beta\) lines fit with separate parameters, for example).

Table III. Results of standardless analysis as in Table II but with \textit{less a priori} information (more parameters in the fit).

<table>
<thead>
<tr>
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<th>Rel Err</th>
</tr>
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<tbody>
<tr>
<td>Cu</td>
<td>33.62</td>
</tr>
<tr>
<td>Zn</td>
<td>55.07</td>
</tr>
<tr>
<td>Au</td>
<td>21.08</td>
</tr>
<tr>
<td>Pd</td>
<td>-45.5</td>
</tr>
<tr>
<td>Ag</td>
<td>-48.07</td>
</tr>
</tbody>
</table>

CONCLUSIONS

Both of the methods for extracting net intensities of emission line peaks from an X-ray fluorescence spectrum discussed here, a method based on Bayesian deconvolution and a
traditional linear least squares (LSQ) fit were evaluated. The reference values were taken from nonlinear least squares fits that matched the spectrum to within the errors due to counting statistics. Both of the methods give comparable results and performance in ideal cases, such as for well-resolved peaks. The Bayesian method does much better over a wide range of parameter variations because it conserves total counts.

For the more difficult and more realistic situation of overlapped peaks, each method has slightly different errors when the positions or widths do not match the measured data. The linear least squares approach may have a slight advantage if the deviations are small. The Bayesian approach retains its advantages and performs much better if the deviations are larger. For spurious peak overlaps, conservation of counts is a disadvantage for the Bayesian methods. The spurious peak must be fit to get good results.

Typical net intensity errors for Bayes deconvolution of 2 peaks with incorrect positions or widths were determined for the overlap cases presented here, which are typical of energy dispersive X-ray spectroscopy. If the position is off by about 10 eV, the error in the overlapped peak intensities will be about 2% relative. If the width is off by about 10 eV, error will be about 1% relative.

When the net intensities are used together with the standardless fundamental parameters method to quantify the elements in a specimen, the results can be rather different. The Bayesian approach shows its strength when the peak positions and widths are not very well chosen by giving much better results for the major elements. However, it also shows its weakness under certain conditions when weak peaks fall under the major lines. If the fit is too large or too small, the minor element line intensity sometimes gets distorted by the counts that are missing in the fits to the overlapping lines. This is caused by a combination of the errors in the \textit{a priori} information (positions, widths, and relative intensities of the overlapped lines) and the conservation of total counts.

REFERENCES


