ED-XRF SPECTRUM EVALUATION AND QUANTITATIVE ANALYSIS USING MULTIVARIATE AND NONLINEAR TECHNIQUES

P. Van Espen, P. Lemberge
Micro and Trace Analysis Center (MiTAC)
University of Antwerp, Universiteitsplein 1, B 2610 Antwerp, Belgium

ABSTRACT
Exploiting the knowledge about the physical processes involved in XRF and the tremendous computing power available, we can overcome the two main drawbacks of ED-XRF: the matrix effects and the spectral overlap. Using nonlinear least-squares fitting using Gauss or Voigt profiles modified with step and tail functions, entire spectra can be evaluated very accurately in a few seconds. The net peak areas obtained can then be used as input to a quantitative fundamental parameter method. Alternatively, multivariate linear methods such as PLS regression can be used to relate the spectral data directly to analyte concentrations, avoiding the explicit spectrum evaluation step. The PLS method is capable of dealing simultaneously with the peak overlap and the absorption and enhancement effects. However, the PLS method requires a large number of standards during the calibration stage. These standards can be generated via Monte Carlo simulation. Simulated spectra of multi-element samples excited with polychromatic x-rays can be generated in a few minutes. The use of the Monte Carlo method in the PLS calibration requires the knowledge of the detector response function and the Monte Carlo method relies basically on the same data as the fundamental parameter method.

INTRODUCTION
Two aspects of x-ray fluorescence (XRF) hinder a straightforward analytical use: matrix effects and spectral interference. Both energy-dispersive (ED) and wavelength-dispersive (WD) XRF share the first problem. Peak overlap, although also existing in WD-XRF, is especially a problem in ED-XRF. On the other hand the physics of XRF is very well known and readily applicable. One can predict the x-ray intensities for a given sample from first principles and use the reverse relation to estimate the sample composition from measured intensities. This can be considered as a true advantage of XRF over other analytical techniques having either a sound physical background that is not useful in practice or no applicable physical model at all. ED-XRF even has a small advantage over WD-XRF in this respect, because it is much easier to model the detector response of a solid state detector than of a crystal spectrometer.

Compared to 10 or even 5 years ago we have formidable computer power available by a simple desktop PC. This implies that we can combine now the physics of XRF using the appropriate mathematical tools and this processing power to overcome these inherent drawbacks of XRF.

For quantitative analysis the fundamental parameter method has proven to be very useful and accurate. It has gained the status of the de facto “standard method” in XRF. The fundamental parameter method relies on the accurate estimation of the net intensities of the characteristic lines
in the spectrum. We found that spectrum evaluation procedures based on nonlinear least-squares
fitting are very useful for this. Because XRF is a technique with very large dynamic range (trace
constituents determination at ppm level together with major elements at the % level) the fitting
function must be very accurate. The use of an incorrect or incomplete fitting function results in
considerable bias in the estimates of the net peak areas (systematic errors), especially for small
peaks in the vicinity of large ones. The addition of step and tail functions to the basic Gaussian
peak shape drastically improves the ability of the nonlinear least-squares procedures to fit
complex, high intensity x-ray spectra.

The combination of spectrum evaluation by nonlinear least-squares fitting and quantitative
analysis using the fundamental parameter method delivers accurate concentration estimates for a
large variety of samples and experimental conditions but still has one major disadvantage. It is a
procedure with a high and steep learning curve. The theoretical background of the method is
difficult and any decision of the operator can drastically influence the outcome of the method.

In an attempt to overcome this practical problem, a few laboratories[1][2] have successfully
introduced multivariate methods from chemometrics into the field of XRF. Especially partial
least squares regression (PLS) has proven to be useful in this respect. The PLS method basically
consists of a multivariate linear relation between the concentrations of (one or more) constituents
and the measured spectral data. An explicit evaluation of the spectrum is not required. In contrast
to the fundamental parameter model, the PLS model does not contain any XRF-specific relations.
The price to be paid for this is that the PLS method requires a large number of standards. One
way to deal with this requirement, as will be shown in this paper, is the use of Monte-Carlo
procedures to simulate “standards” rather than to measure them.

SPECTRUM EVALUATION

The aim of spectrum evaluation is to obtain unbiased, minimum variance, estimates of the net
intensities (peak areas) of the fluorescence lines. Fitting an appropriate mathematical function to
the spectral data can do this. The parameters of this function are chosen so that the weighted sum
of squared differences between the measured spectral data \( y_i \) and the fitting function \( y(i) \) are
minimal. This object function is known as chi-square:

\[
\chi^2 = \sum_{i=n}^{m} \frac{1}{w_i} [y(i) - y_i]^2
\]

(1)

The fitting function generally consists of two parts, one that describes the continuum and one that
deals with the characteristic lines.

\[
y(i) = y_{\text{cont}}(i) + \sum_{j=\text{elements}} A_j \left( \sum_{k=\text{lines}} R_{jk} P(i, E_{jk}) \right)
\]

(2)
The inner summation runs over the number of $K$ and/or $L$ lines of each element with $R_{jk}$ the relative contribution of line $k$ of element $j$. The outer summation runs over all elements with the linear parameter $A_j$ being the total intensity of element $j$. $P(i,E_{jk})$ is a function that describes the shape of the x-ray line with energy $E_{jk}$. A typical implementation of $P(i,E_{jk})$ consists of a Gaussian

$$
P = G(i,E_{jk}) = \frac{Gain}{\sigma_{jk}\sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{E(i) - E_{jk}}{\sigma_{jk}} \right)^2 \right]$$

in which the width and position obey the energy and resolution calibration functions of the spectrometer:

$$
E(i) = Zero + Gain \times i
$$

$$
\sigma_{jk} = \left( \frac{Noise}{\sqrt{2 \ln 2}} \right)^2 + \varepsilon Fano E_{jk}^{\nu^2}
$$

The fitting function is linear in the net peak area parameter $A_j$, but nonlinear in the parameters Zero, Gain, Noise and Fano so that a nonlinear least-squares procedure is required. In successive approximations the values of the parameters are altered until the minimum in $\chi^2$ is reached. A spectrum evaluation procedure based on these principles is very flexible since lines of one element can be grouped in various ways, e.g. a multiplet for all lines of an element or separately for $K\alpha$ and $K\beta$ lines. Escape and sum peaks can be incorporated easily. However, the quality of the results depends highly on the accuracy of the model or the ability of the fitting function to describe the observed spectrum. Figure 1a shows part of the x-ray spectrum of NIST SRM 1106. The spectrum is obtained with a TN SpecTrace 5000 ED-XRF (TN SpecTrace, Round Rock, TX, USA) equipped with a Rh x-ray tube operated at 30 kV, 0.1 mA and a Si(Li) detector having a resolution of 160 eV at Mn-$K\alpha$. The spectrum is fitted using a polynomial continuum and a Gaussian peak shape. Due to the principle of least squares the difference between fit and spectrum at the low energy side of the intense Cu $K\alpha$ line is filled up by increasing the intensity of the Ni $K\alpha$ lines. Any concentration estimate based on the Ni $K\alpha$ intensity will therefore be extensively overestimated.

To improve the spectrum evaluation procedure for this type of spectral data, a mathematical model that takes into account the deviation from the Gaussian peak shape must be used. Such a model includes a step and tail function to describe the low energy tailing due to incomplete charge collection in the detector.

$$
P(i,E_{jk}) = G(i,E_{jk}) + f_s S(i,E_{jk}) + f_T T(i,E_{jk})
$$
in which $G(i,E_{jk})$ is the Gaussian as in equation (3) and $f_S$ and $f_T$ are (linear) parameters representing the fraction of photons that gives rise to a step and tail contribution. The step and tail functions can be written as follows:

$$S(i,E_{jk}) = \frac{\text{Gain}}{2E_{jk}} \text{erfc} \left[ \frac{E(i)-E_{jk}}{\sqrt{2}\sigma} \right]$$

$$T(i,E_{jk}) = \frac{\text{Gain}}{2\gamma \sigma \exp \left[ -\frac{1}{2\gamma^2} \right] \text{erfc} \left[ \frac{E(i)-E_{jk}}{\gamma \sigma} \right] \text{erfc} \left[ \frac{E(i)-E_{jk}}{\sqrt{2}\sigma} + \frac{1}{\sqrt{2}\gamma} \right]}$$

Fig. 1 A Part of the ED-XRF spectrum of a NIST 1106 brass SRM. A polynomial is used to represent the continuum. The peaks are fitted with simple Gaussians. The Ni Kα intensity is significantly overestimated.

B The same spectrum is fitted but the peaks are represented by a Gaussian with a tail and step function. A more realistic estimate of the small Ni peaks in the vicinity of the large Cu and Zn lines is obtained.

The functions are normalized, i.e. the integral of the function over the spectrum equals unity. The parameter $\gamma$ is an extra nonlinear parameter, modeling the width of the tail. To keep the number of parameters to be estimated during the least-squares fit as low as possible, $f_S$, $f_T$ and $\gamma$ are expressed as functions of the energy. This functional relation is fitted rather than the value for each peak individually. Spectrum evaluation based on this fitting model gives more reliable results than simple Gaussians. This is illustrated in figure 1b where the same spectrum as in
figure 1a is fitted using step and tail functions for the Cu and Zn Kα and Kβ lines. Previously, since only Gaussians are used to describe the peak profiles, the tail and step parts of the peaks are accounted for by shifting the polynomial background function upwards (to model the step part) and by increasing the intensities of the Ni peak (to model the tail part). Although this provides the lowest χ² value it is clear the continuum and the Ni intensity are not realistically estimated. By including a step and tail function in the peak model a much more realistic estimate is obtained for the Ni Kα line and the continuum. A further improvement is possible by replacing the Gaussian by a Voigt profile, which is the convolution of a Lorentz and a Gauss function. This is only necessary when the natural width of the x-ray line becomes substantial compared to the detector resolution, e.g. for the K-lines of the elements above Ba. With the current processing power (Intel Pentium II 450 MHz) fitting entire spectra using Gaussians with tail and step functions can be done in seconds. Still, minutes are required when Voigt profiles are considered. Apart from delivering unbiased estimates of the net peak intensities, which are used in a fundamental parameter algorithm to obtain concentration estimates, the least-squares method delivers an accurate peak shape function which can be implemented in a detector response function to convolute simulated spectra. This will be shown further on in this paper.

MONTE CARLO SIMULATION

During a Monte Carlo simulation the fate of a large number of exciting photons interacting with the specimen is followed. The Monte-Carlo method uses the same physical parameters and processes as the fundamental parameter method but at an individual microscopic level to predict the intensities of characteristic lines. Different from the fundamental parameter approach, the Monte Carlo procedure is capable of dealing correctly with coherent and incoherent scattering phenomena. The data generated by a Monte Carlo process can be considered as a spectrum seen by a detector with infinitely good resolution. Figure 2a shows such a spectrum obtained with the Monte Carlo simulation code developed in our laboratory.[5] The spectrum is simulated assuming that the sample has the composition of NIST 1106 and is excited by a Rh x-ray tube operated at 35 kV. A remarkable feature that is observed in this simulated spectrum is the tail-line structure on the low energy side of the major K lines of Cu and Zn. They are due to fluorescent photons that undergo incoherent scattering in the sample before being detected. The observation of these features in the simulated spectrum is simply the consequence of the treating each photon individually and following all the processes that it can undergo. They resemble very much the tailing function observed in the first part of this paper. This is an indication that not only secondary processes in the detector but also radiative phenomena taking place in the sample contribute to the overall peak shape.

In figure 2b the simulated spectrum of the NIST 1106 SRM after convolution with the detector response function is shown. The importance of the correct detector response function becomes evident from this figure. Due to the tail and step contribution of all photons, the apparent continuum at the low energy part of the convoluted spectrum is much higher than in the simulated spectrum seen by an ideal detector. Because the absolute intensity used in the experimental setup is unknown (i.e. number of exciting photons produced per mA of tube current applied) the intensity of the simulated spectrum is adjusted by multiplying each channel with a constant factor. Thus by combining a Monte Carlo simulation code based on fundamental
parameters with a detector response function obtained experimentally by nonlinear least-squares fitting, spectra can be simulated that agree very well with measured spectra. The Monte Carlo spectrum simulation and subsequent convolution of a multi-component sample excited by polychromatic radiation, although computationally demanding, can be performed in a few minutes time with today's fast PC's. For example, the spectrum simulation and convolution of a brass sample containing 8 elements using 73000 excitation photons takes about 1 minute on an Intel Pentium II 450 MHz). In principle the Monte Carlo simulation technique can be used directly in a quantitative analysis scheme. We use the Monte Carlo technique to simulate "standards" that are used to build a multivariate calibration model as discussed in the next section.

![Graph](image.png)

**Fig. 2** A Result of the Monte Carlo simulation of the photon interaction of a Rh x-ray tube with a sample having the composition of NIST 1106 SRM brass. B The same spectrum as in A now convoluted with the detector response function of a real detector system (solid line) and the measured spectrum of the NIST 1106 SRM (dots).

**MULTIVARIATE REGRESSION**

In multivariate regression a relation is established between a two matrices $X$ and $Y$. The $X$ ($n \times p$) matrix represents the spectral data, with $n$ measured spectra each having $p$ x-ray intensities (channels). The $Y$ ($n \times m$) matrix holds the concentrations of $m$ analytes in the $n$ samples. One of the most powerful methods to build this relation is partial least squares regression (PLS). PLS uses two outer relations and one inner relation. The outer relations describe the decomposition of the $X$ and the $Y$ matrix:
\[ X = TP' + E = \sum_{a=1}^{A} t_a p_a' + E \]  \hspace{1cm} (9) \\
\[ Y = UQ' + F = \sum_{a=0}^{A} u_a q_a' + F \]  \hspace{1cm} (10)

in which T and U are the scores matrices while P and Q are the loadings matrices, A represents the number of latent variables retained in the PLS model. The matrices E and F contain the residuals, e.g. respectively the part of the original spectral data and the concentration data not accounted for when A latent variables are used. The inner relation is written as:

\[ u_a = b_a t_a \hspace{1cm} a = 1 \ldots A \]  \hspace{1cm} (11)

from which the regression coefficients are obtained. This operation can be seen as a least squares fit between the X block and the Y block scores. The ultimate PLS model can be written as:

\[ Y = TBQ' + F' \]  \hspace{1cm} (12)

The quality of the calibration model can be judged by the root mean square error of prediction (RMSEP):

\[ \text{RMSEP} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (\hat{y}_i - y_i)^2} \]  \hspace{1cm} (13)

in which \( \hat{y}_i \) is the PLS predicted concentration and \( y_i \) is the true concentration in standard \( i \). The RMSEP value is calculated via cross-validation.\textsuperscript{[6]} The number of latent variables A retained in the model is of crucial importance and its optimum value must be determined. Therefore the RMSEP value is calculated for an increasing number of latent variables. Next, the RMSEP value is plotted as a function of latent variables included in the model. The number of latent variables corresponding to a minimum or plateau is said to be optimal.

The method involves a calibration step in which a large number of standards are used to build and validate the model and the actual analysis step in which the model is applied to spectra of unknown samples. The spectrum evaluation and subsequent application of empirical or semi-empirical methods encountered in traditional ED-XRF quantitative analysis is contained in one single step when PLS is used. This methodology offers an increased flexibility of ED-XRF towards portable instruments and online analysis. Details on the PLS method can be found in the literature.\textsuperscript{[6][7][8]} The PLS method has been applied successfully to a number of ED-XRF problems\textsuperscript{[9][10][11]} but its general applicability is hindered by the large number of standards with widely varying compositions the method requires. In this work we propose to use the Monte Carlo method discussed in the previous section as an alternative to measured samples.
To illustrate the combination of PLS and Monte Carlo simulation the method is used for the analysis of brasses. In total, 35 brass compositions serve as input for the Monte Carlo simulation program. The composition of the brasses is determined by random selection of values from the element concentration ranges represented in Table 1. The experimental settings correspond to a TN Spectrace 5000 ED-XRF instrument equipped with a Rh x-ray tube operated at 35 kV. The use of a Rh filter (0.05 mm) and a collimator are taken into account by the software package. The Si(Li) detector response function applied in the detector convolution is based on a modified Gaussian as explained in the first part of this paper.

For each of the elements a PLS model is built. To increase the accuracy in PLS prediction two data pre-treatment methods are applied to the data: mean centring and mean centring + square root pre-processing. The PLS models having the best predictive properties, as determined by the RMSEP value, are ultimately used.

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration range (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>50 - 100</td>
</tr>
<tr>
<td>Zn</td>
<td>5 - 40</td>
</tr>
<tr>
<td>Pb</td>
<td>0.001 - 4</td>
</tr>
<tr>
<td>Sn</td>
<td>0.001 - 1.5</td>
</tr>
<tr>
<td>Ni</td>
<td>0.001 - 0.2</td>
</tr>
<tr>
<td>Mn</td>
<td>0.001 - 0.1</td>
</tr>
<tr>
<td>Fe</td>
<td>0.001 - 0.05</td>
</tr>
</tbody>
</table>

Table 1: Element concentration ranges used to compose the 35 brass calibration standards used in the Monte Carlo program for the simulation of spectra.

<table>
<thead>
<tr>
<th></th>
<th>NIST 1106</th>
<th></th>
<th>NIST 1108</th>
<th></th>
<th>NIST 1115</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Calc</td>
<td></td>
<td>Calc</td>
<td></td>
<td>Calc</td>
</tr>
<tr>
<td>Cu</td>
<td>55.07</td>
<td>59.08</td>
<td>61.26</td>
<td>64.95</td>
<td>82.47</td>
<td>87.96</td>
</tr>
<tr>
<td>Zn</td>
<td>38.88</td>
<td>40.08</td>
<td>33.23</td>
<td>34.42</td>
<td>11.78</td>
<td>11.73</td>
</tr>
<tr>
<td>Pb</td>
<td>0.14</td>
<td>0.063</td>
<td>0.14</td>
<td>0.063</td>
<td>0.06</td>
<td>0.013</td>
</tr>
<tr>
<td>Sn</td>
<td>0.74</td>
<td>0.74</td>
<td>0.37</td>
<td>0.39</td>
<td>0.08</td>
<td>0.1</td>
</tr>
<tr>
<td>Ni</td>
<td>0.01</td>
<td>0.033</td>
<td>0.033</td>
<td>0.02</td>
<td>0.02</td>
<td>0.074</td>
</tr>
<tr>
<td>Mn</td>
<td>-0.014</td>
<td>0.025</td>
<td>0.011</td>
<td>0.025</td>
<td>-0.047</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.27</td>
<td>0.05</td>
<td>0.21</td>
<td>0.05</td>
<td>0.35</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Table 2: Certified and PLS predicted concentrations of elements in brass.

Figure 3 shows the effect of increasing the number of latent variables on the predicted versus given concentrations in the case of Pb. It is obvious that one latent variable only is not enough model the relationship between spectra and Pb concentration. Adding an extra latent variable
results in an accurate model that describes the relationship correctly. The RMSEP curve in figure 3A reaches a plateau when three latent variables are retained in the model. Figure 3D shows that the precision of the prediction has further improved. Including more latent variables in the PLS model doesn’t improve the RMSEP value. In fact, including too many latent variables leads to overfit meaning that the PLS model is tailored specifically for the standards in the calibration set, i.e. the noise in the data is modelled as well.

![Pb RMSEP plot](image)

**Fig. 3** A RMSEP plot for Pb determination in brass. B PLS prediction of Pb concentrations using one latent variable versus given Pb concentrations in the calibration set. C and D show the predicted versus given Pb concentrations for respectively 2 and 3 latent variables retained in the model.

After validation, the different PLS models are used to determine the element concentrations in real samples. Therefore three NIST standard reference materials (NIST 1106, NIST 1108 and NIST 1115) are measured using the TN SpecTrace 5000. The same operating conditions are applied as in the Monte Carlo simulations and the intensities were scaled using NIST 1106 SRM. Table 2 shows the certified element concentrations and the PLS predicted concentrations.
Investigation of table 2 reveals some systematic errors, especially for Cu and Pb for which the predicted concentrations are too low compared to the certified ones. The general accuracy and precision of the method still needs to be optimized. Improvement of the scaling between measured and simulated spectrum is mandatory. Also, the parameters of the detector response need to be in agreement with the detection conditions such as the pulse shaping time applied.

CONCLUSIONS

Desktop and portable PC's nowadays have tremendous computer power. This makes it possible to implement new data treatment techniques. One such application we discuss in this paper is the non-linear least square fitting using modified Gaussians or Voight profiles taking into account the low energy tailing of peaks to fit complete ED-XRF spectra. This improved fitting procedure leads to more accurate quantitative results.

Another application we present is the combination Monte Carlo simulation and partial least square regression (PLS). This method enables the direct transformation of spectra into element concentrations. The large number of standards needed to create an accurate PLS model is solved by simulating the standards. The PLS-Monte Carlo method is used for the analysis of brass samples. Results show that the major elements in brass are determined with a relative error below 10%. Further optimization of the method is required.

REFERENCES