IMPLEMENTATION OF THE MONTE CARLO-LIBRARY LEAST-SQUARES APPROACH TO ENERGY DISPERSIVE X-RAY FLUORESCENCE ANALYSIS

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ABSTRACT

An integrated Monte Carlo-Library Least-Squares (MCLLS) System has been developed and implemented to model the complete spectral response of energy-dispersive X-ray fluorescence (EDXRF) spectrometers and perform an inverse elemental analysis by an iterated Library Least-Squares method when an initial guess is provided. This software is a visualization system developed on the Borland C++ Builder platform and has a user-friendly interface to accomplish all qualitative and quantitative tasks easily. The software enables users to run the forward Monte Carlo simulation (if necessary) or use previously obtained Monte Carlo results that include differential operators and complete the sample composition inverse analysis just by selecting several modes of operation and providing simple inputs. An overview of the software is illustrated with experimental results on standard reference materials.

INTRODUCTION

The XRF analysis problem has always consisted of two parts [1,2]: (1) determination of X-ray intensities and (2) determination of elemental amounts from the sample X-ray intensities. For the first part, one of the methods available to determine X-ray intensities is the use of peak areas while another is the use of the entire spectrum that is obtained by using X-ray elemental libraries with the linear library least-squares (LLS) approach. The problem with using peak areas is that many peaks from different elements cannot be de-convolved even when detectors with excellent resolution are used. The LLS approach [3] has the advantage that this problem is circumvented entirely and all of the available spectral data is utilized. Actually, using all of the spectral data [4] can reduce the standard deviations of the elemental analysis by as much as 2.5 to 3 times over the use of only the peaks. This is the case because although the peaks contain more useful information, the continuum parts of the spectrum also contain useful information, albeit much less than the peaks. The LLS approach is the most fundamental one and automatically gives the standard deviations for the X-ray intensities that are calculated. The limitation with this approach is that it is valid only for linear analysis.

For the second part, the determination of elemental amounts in XRF analysis must account for the non-linearity introduced by matrix effects. In the past this has been done by empirical, semi-empirical, and theoretical approaches. The deterministic equations developed by Sherman [5,6] and others have been adapted to predict the non-linear matrix effects that give rise to non-linear X-ray intensities. Sherman derived equations that accounted for primary, secondary (element A excites element B), and tertiary (element A excites element B which in turn excites element C) excitations for entrance thin-beam source excitation and exit thin-beam detection. Scattered
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radiation is ignored in Sherman’s treatment and actual application of these theoretical equations to wide-beam (the usual case in practice) cases has apparently been only for primary and secondary excitations. Monte Carlo simulation of the fundamental physics of X-ray excitation and detection offers a more versatile, general, and accurate approach for treating the non-linearity of matrix effects. Scattered radiation and any order of excitation are easily treated, as is any complicated geometry (including broad beam) of the source-sample-detector configuration.

The MCLLS system developed contains three advanced technologies developed by CEAR researchers since 1970 including a comprehensive and accurate Monte Carlo forward simulation code, CEARXRF5, that includes differential operators and uses the detector response function approach; differential operators, which is a very powerful method for measurement sensitivity study and spectral extrapolation; and the detector response function, which is required. An improved Si(Li) detector response function model over the energy range from 5 to 60 keV and an accurate Germanium detector response function have been developed at CEAR and implemented in this integrated system.

Benchmark results on standard reference materials (two stainless steel samples from NIST and two aluminum alloy samples from Alcoa) are provided for a simple reproducible prototype system using a $^{109}$Cd radioisotope source and a Si(Li) detector. The results show excellent agreement between our calculated sample compositions with those of the reference standards and the approach is very fast. The software is easy to use with user-friendly features and has the capability to accomplish all related tasks in a visualization environment. It can be a powerful tool for EDXRF analysts.

**MONTE CARLO-LIBRARY LEAST-SQUARES APPROACH: THEORY AND COMPONENTS**

The MCLLS approach basically consists of seven parts: (1) using a reproducible experimental configuration, (2) correcting any pulse pile up distortion (if necessary), (3) qualitative and semi-quantitative analyses to determine the elemental initial guess composition (thus providing the initial guess for the Monte Carlo simulation code CEARXRF), (4) use of the Monte Carlo simulation code CEARXRF to simulate the problem based on the initial guess (pre-calculations can be made if the general composition is known), (5) use of detector response functions to transform the flux library spectra obtained from the simulation code into pulse height library spectra ("real" spectra), (6) using the library least-squares (LLS) method to fit the experimental spectrum with library spectra and experimental background, and (7) use of differential operators to achieve optimum efficiency if multiple iterations are needed.

A reproducible prototype configuration for the EDXRF measurement was designed for Si(Li) and Ge detectors. This reproducible prototype keeps the distance from source to detector and source emission angle fixed and produces reliable experimental spectra for the same measurement conditions. It consists of a base, which is placed on the detector, four-source holders (two sets with 45° and 60° with respect to the horizontal), and a cap to hold the sample.

After the detection system (detector is cooled with liquid nitrogen) has been assembled and the source and sample are placed on the experimental arrangement, an MCA (multiple channel
analyzer) system is used to record the energy of each photon that has scattered (incoherent scattering and coherent scattering) or been produced/emitted from the sample by X-ray fluorescence interaction. The source, target, and detection systems are kept in place and the experiment runs for a sufficiently long time so that the counting statistical errors are low enough to permit further accurate library least-squares analysis and then the X-ray spectral response to an unknown sample (such as stainless steel, aluminum alloy, etc.) is obtained.

In high counting rate measurements, the spectrum may be distorted because of pulse pile-up—two or more pulses may occur within a time so small that the MCA can not discriminate each pulse individually, but recognizes them as a single usually larger pulse. In order to correct the distortion of the spectrum, a CEAR Pulse Pile-Up program (CEARPUP—forward PPU calculation code or CEARIPPU—inverse PPU calculation code) is used to handle this problem and obtain the “true” spectrum [7,8].

From the experimental spectral peak energies, one can identify the elements that are in the sample by comparing them with the element’s characteristic X-ray energies. Through matching of the peak energy one by one for each peak, most elements with high weight fraction in the sample can be identified. Some “missed” elements may not be found in the sample spectrum but can be identified from the residual spectrum after the first run of the library least-squares fit. The XRF Qualitative Analyzer and XRF Query (X-ray fluorescence yield query) have been developed to provide an easy way to find these peaks and determine the elements contained in the sample. The area below each X-ray fluorescence peak gives information about the amounts of each element, which will be the initial guesses for weight compositions that are used as the input for the CEARXRF simulation code.

The Monte Carlo code CEARXRF (now version 5) is used to simulate the X-ray spectral response to the sample with assumed composition based on the initial compositional guess for the sample. Monte Carlo simulation extends the practical use of fundamental parameters to cases in which the system geometry and excitation source spectra are otherwise difficult to describe by conventional deterministic methods. In the course of this simulation individual elemental library flux spectra and library differential spectra with respect to each other are produced. The general simulation time is an hour.

The detector response function is needed to transform these flux spectra into “real” pulse height spectra because flux spectra are not like the spectra actually observed with the MCA. To develop these “real” spectra, the effects of the detector response function of interest need to be convolved onto the flux spectra. Therefore, SILIDRF for Si(Li) detector or GEDRF for Ge detector is used to calculate the detector response function for each detector, respectively. Figure 1 (left plot) shows the flux spectrum (dotted) and its transformed “real” spectrum (solid line) after Si(Li) detector response function. The right hand plot shows the full spectrum and components of the detector response function, which is composed of the following five parts [9]:

1. Gaussian-shaped full energy peak,
2. Gaussian-shaped Si escape peak,
3. a flat continuum from zero to full energy,
4. a long-term exponential function on the low-energy side of the full-energy peak, and
5. a short-term exponential function on the low-energy side of the full-energy peak.

In Figure 2, the long-term exponential function and short-term exponential function on the low-energy side of the full-energy peak are shown together as “tail” in the dotted line.

Those library spectra together with a background (noise) spectrum (see Figure 2) are then normalized and used to fit the experimental spectrum by a linear library least-squares (LLS) calculation for elemental composition. If the calculated elemental amounts are not close enough to the initial guesses, then a new assumption on the element composition is made. Iteration is needed to get closer results. It can be done by running the simulation again using the new guesses to get updated library spectra and continue to get fitted results as stated as above. And this process can be iterated as many times as possible to get converged composition values for all elements, or a criterion can be set to stop the process when it is met.

Another important approach called differential operators is an efficient variance reduction technique because it accounts for matrix-effect correction directly instead of having to simulate the whole problem again by Monte Carlo. CEARXR F produces not only the elemental library flux spectra, but also provides the first and second derivative differential operators with respect to each element in the sample, which can be used to generate a new set of library flux spectra based on Taylor Series Expansion (the process takes only several seconds), thus eliminating the necessity to rerun the CEARXR F code, which is a relatively slow process (typically an hour for 100 million histories). Note that the differential operators approach is a very important addition in that it allows one to use the Monte Carlo simulation code only once for each separate class of samples, for example, once for a wide range of stainless steels. Differential operators are as follows.

\[ R(w_{1,x}, w_{2,x}, \ldots, w_{n,x}) = R(w_{1,0}, w_{2,0}, \ldots, w_{n,0}) + \sum_i \frac{\partial R}{\partial w_{i,x}} \bigg|_{x=0} (w_{i,x} - w_{i,0}) + O(w_x - w_0)^2 \]
The remaining mathematical tool required for the MCLLS approach is a library least-squares code that is capable of using the elemental library spectra together with a background (possibly experimental) spectrum to fit an unknown sample spectrum to obtain elemental amounts. The CEARLLS code is a fast and accurate linear library least squares code that obtains the best linear unbiased estimate of each element composition and linear correlation between all elements and each element relative to the sample.

An integrated Monte Carlo-library least-squares visualized system has been developed to complete the simulation of EDXRF (with the CEARXRF code as an integral part) and performs all related data analysis under a single system. The advantages are it is easy to use with a user-friendly graphical user interface—all tasks can be completed with a few inputs and clicks with the help of an accompanying manual, and it is comprehensive—Monte Carlo simulation and all data analysis can be done in this integrated software system platform.

**XRF Quantitative Analyzer**

Figure 3 shows the main interface of the XRF Quantitative Analyzer. There are four panels:
1. Basic controls panel: the user can load a simulation input file and run the Monte Carlo simulation code implemented in the system (CEARXRF5). Subsequently the library least-squares program can be run from this panel.

2. Advanced controls panel: in addition, the software provides 10 modules (or more in the future) for advanced analysis including: (1) an XRF qualitative analyzer: preliminary determination of element and initial guesses for Monte Carlo simulation; (2) XRF data query searches the X-ray fluorescence yields for a specific element (atomic number); (3) initial guess: generate or modify initial guesses for each element in the sample tested, together with XRF Qualitative Analyzer, etc.

3. Spectral analysis panel: the fitted spectrum and original spectrum are shown here.

4. LLS fitted results: the fitted results are shown in this region with weight fraction estimates of each element together with the standard deviations and their linear correlation with respect to each other. The user can click the “Linear CC” button to toggle between fitted weight fractions and linear correlations.

Figure 3. Main display of the XRF Quantitative Analyzer.

XRF Qualitative Analyzer and XRF Query

The XRF Qualitative Analyzer described here is used to provide an easy method for a preliminarily determination of the composition of a sample from experimental spectra. Figure 4
shows typical analysis results for a stainless steel (C1152A) sample with a $^{109}$Cd excitation source. From this figure, we can see that the primary components contained in the C1152A sample are Cr(24), Fe(26), Ni(28), Nb(41), and Mo(42). Ag X-ray peaks are also observed, which come from the backscatter of the $^{109}$Cd source from the sample. These are not all of the elements in the SS304; other elements like Mn, Co, and Cu are also present in the sample, but their peaks are not observed because of their relatively small amounts. These elements may be found from the residuals plot. Figure 5 shows the XRF Query results for lead (Pb-82).

**EXPERIMENTAL RESULTS ON STANDARD REFERENCE MATERIALS**

*MCLLS fitted spectra*

In this paper, two stainless steel (C1152a and C1151a—standard reference materials from NIST) and two aluminum alloy samples from Alcoa are excited with the X-ray source $^{109}$Cd and Monte Carlo simulations are performed according to the experimental arrangement. The libraries from the simulation are used in the MCLLS approach to fit the experimental spectra. An iterative scheme based on the MCLLS differential operator approach is used on these samples until satisfactory results are obtained. The fitted results with experimental spectra are shown in Figures 6 and 7 and they indicate that the fits are both accurate and reliable.

Figure 4. Preliminary results for C1152A with $^{109}$Cd source from XRF Qualitative Analyzer and XRF Query.
These fitted results for standard reference material C1152a are shown in Table I and are seen to be very close to the reference values for the major elements Cr, Fe, and Ni. The MCLLS approach is shown to be a general and accurate approach for the inverse XRF material composition measurement.
Table I. Fitted result for C1152A.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fit results (%)</th>
<th>Reference value (%)</th>
<th>Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>16.78</td>
<td>17.76</td>
<td>0.98</td>
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<tr>
<td>Fe</td>
<td>69.21</td>
<td>69.52</td>
<td>0.31</td>
</tr>
<tr>
<td>Ni</td>
<td>10.71</td>
<td>10.86</td>
<td>0.15</td>
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DISCUSSION, CONCLUSION, AND FUTURE WORK

Benchmark results on standard reference materials (stainless steel samples from NIST and aluminum alloy samples from Alcoa) are provided for a simple reproducible prototype system using a $^{109}$Cd radioisotope source and a Si(Li) detector. The results show good agreement between our calculated sample compositions with those of the reference standards and the approach is very fast. The software is easy to use with user-friendly features and has the capability to accomplish all related tasks in a visualization environment. It can be a powerful tool for EDXRF analysts. The CEARXRF Monte Carlo code has been modified to include coincidence counting of K and L X-rays for future applications to the analysis of high atomic number elements [10].

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REFERENCES