On the Use of Monte Carlo Based Methods to EDXRF Quantitative Analysis

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Abstract

The center for engineering applications of radioisotopes X-ray fluorescence (CEARXRF) graphic user interface (GUI)-Based monte carlo library least squares (MCLLS) code is demonstrated with results from the micro-focused EDXRF analyzer, which can be used to calculate elemental weight fractions in metal alloys or rock samples accurately, by library least-squares regression of the measured X-ray spectrum with computer-generated elemental spectra. An elemental stratified sampling variance reduction technique has been implemented in the CEARXRF code (version 5). In this case it refers to using the same number of histories for each element X-ray spectrum so that the same statistics are appropriate for each calculated library, which intends to improve the statistical precision of each elemental library spectrum within the measured sample. And an improved Si (Li) detector response function (DRF) has been optimized on the micro-focused XRF analyzer and the parameters are obtained based on regression on pure elemental experimental spectra. It was demonstrated that MCLLS approach can greatly improve the accuracy of elemental analysis results.

Introduction

X-ray fluorescence (XRF), a relatively simple, inexpensive, and non-destructive elemental analysis technique, is widely used for chemical compositional analysis in many fields including the oil and gas industry. For example, in core analysis, X-ray fluorescence is often used to determine a mineral’s elemental content in a rock sample extracted from the subsurface. Elemental concentrations are then converted to mineralogy volumes by assuming certain standard formulas and constraints for mineral composition. A commercial petroleum analyzer is also available for sulfur and chlorine analysis in hydrocarbon samples.

The measurement system requires an X-ray source, which may be radioisotopes such as ⁵⁵Fe, ¹⁰⁹Cd, ²⁴⁴Cm, or an X-ray tube. The second major component is the detector and associated data acquisition electronic system, which must be designed to produce electrical pulses that vary with the energy of the incident x-rays. Most laboratory EDXRF instruments still use liquid nitrogen-cooled Si(Li) detectors; while bench-top instruments usually have proportional counters, or newer Peltier cooled PIN diode detectors, but historically sodium iodide (NaI) detectors were common. Some handheld devices use other detectors such as mercuric iodide, CdTe, and CdZnTe, in addition to PIN diode devices, depending largely on the X-ray energy of the elements of interest. The most recent and fastest-growing detector technology is the Peltier cooled silicon drift detector (SDD), which are available in some laboratory-grade EDXRF instruments. The third component of the system is the measurement target or test sample for activation, which is often positioned on the other side of both X-ray source and detector. The x-rays emanated from the source hit the sample, interact with the elements and generate characteristic x-rays, which are then scattered and detected by the detector to accumulate a measurement spectrum within a limited time.

The measured characteristic X-ray spectrum using such a system as described is de-convolved to obtain the elemental composition quantitatively. For those traditional analysis methods, two steps are needed to make a quantitative analysis [He 1992]:

1) The intensity or intensity ratios of photoelectric peaks of the X-ray lines from elements of interest in the sample are estimated;
2) Peak intensities are converted to elemental weight fractions using corrections methods for “matrix effect”.

Four methods are typically used to obtain intensity ratios: spectrum stripping, peak integration, de-convolution and least-squares fit [Bertin 1978, Gardner 1997]. Spectrum stripping is not very accurate and
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also difficult to use because errors accumulate as the stripping proceeds. Integration and de-convolution basically share the same principle but are applied differently. They both use a detector-response model to mathematically calculate the peak intensity. The accuracy of these two methods depends on the accuracy of the detector-response model. Limited by their functionality, overlapping peaks can not be resolved by these two methods, and only parts of the spectral information are used. The least-squares fit method solves the problem but introduces the new difficulty of experimentally acquiring elemental library spectra, which are the key parts of the least-squares fit method.

The matrix effect causes changes in secondary X-ray yield or intensity, the energy or shape of the signal of an element as compared to these quantities in a pure element, i.e., any changes in the chemical composition of the sample will affect the library spectrum, both intensity ratio and spectral shape. Corrections methods for quantification of elemental weight fractions can be handled with one of two methods: the empirical coefficients method and the fundamental parameters method.

A detailed review of the empirical coefficients method can be found in literature [Bertin 1978 and Jenkins 1988]. The disadvantage lies in the requirement of measurements on a number of carefully prepared standard samples to determine the empirical coefficients, which is very time consuming and expensive. In addition, these empirical coefficients are often system specific and not transferable to other systems.

The fundamental parameters (FP) method was initially proposed in the early 1950s and investigated further [Criss and Birks 1968; Gillam and Heal 1952]. It attempts to model the sample matrix effect with a complete mathematical model. In principle, the fundamental parameters method is an absolute method and does not require measurements on standard samples. As the required calculations are extremely complex, the practical application of this approach usually makes use of pure element standards and the X-ray intensity ratio, that of the unknown sample to that of the pure element standard, to cancel some number of unknown fundamental parameters that are required and simplify the calculation. The shortcoming of this method requires intensive calibration and complicated calculation. In practice, a series of “type standards” is needed to perform a calibration. This means that the procedure is acceptable for process control, but not for analysis of unknown samples. The limitation to the accuracy of the analysis is determined by whether the fluorescence intensities can determined with high precision and the complexity of enormous variety of theoretical and empirical approximations.

The Monte Carlo-based library least-squares (MCLLS) approach to XRF elemental analysis solved the two problems (peak intensity and matrix effect) simultaneously by performing least squares regression of the measured spectrum with computer-generated elemental library spectra [R. P. Gardner 2006, F. Li 2008]. The system can accurately determine elemental concentrations because the Monte Carlo-computed library spectra are generated according to assumed compositions and matrix effects are corrected inherently. Variance reduction techniques, such as differential operators and elemental stratified sampling, were applied to speed up the process. As an integrated component, a GUI program was developed to analyze the measured spectrum both qualitatively and quantitatively. Firstly, elemental types are identified by the GUI program based on the characteristic X-ray peak energies and associated weight fractions (initial guesses) are obtained by analyzing the peak intensity and corresponding X-ray fluorescence yields. Then, a specific-purpose Monte Carlo simulation code generates the elemental libraries for all elements based on the initial guesses and are further processed by X-ray Detector Response Functions (DRFs).

Together with any other required background libraries, these library spectra are then used in the least-squares regression with the measured sample spectra to provide better estimates the concentrations of all elements in the sample. Using the estimated values as inputs, iterations of such procedure are run until the least-squares estimated values agree with the previous guesses or within tolerated limits. The iterative procedure is accelerated by the use of Differential Operators (1st and 2nd order of perturbation derivatives from Monte Carlo Simulation) which can be used to calculate the new elemental spectra by Taylor series expansion, avoiding the time-consuming Monte Carlo simulation and quantifies the matrix effect in near real time. It is a very powerful variance reduction method and also useful for elemental sensitivity study and system optimization [Lee 1999, Li 2008].

In summary, the components of MCLLS approach to XRF elemental analysis include:
The specific-purpose Monte Carlo simulation code for forward generation of the necessary elemental library spectra for the XRF spectrum LLS calculation

- Generation of detector-response functions (DRF) for detectors with linear or non-linear responses for Monte Carlo simulation of pulse-height spectra
- Use of the differential operator (DO) technique with Monte Carlo pre-calculations to make the necessary iterations for non-linear responses practical
- Use of GUI-based analyzer software in the MCLLS approach to provide accurate results both qualitatively and quantitatively

In the specific-purpose Monte Carlo simulation code, stratified sampling was implemented as an enhanced sampling technique from all elements’ population in the measured sample. If elemental concentrations vary greatly within the sample especially for trace elements, stratified sampling will ensure simulation results can be made with equal accuracy in all elemental spectra in the sample.

**System Treated**

Micro-focused XRF is an elemental analysis technique which uses doubly curved crystal (DCC) optics to enhance measurement intensities by capturing X-rays from a divergent source and redirecting them into an intense focused beam on the surface of the product. Figure 1 shows the diagram of Micro-focused XRF spectrometry used to perform XRF measurement in consumer products of interest.

The major benefit is that monochromatic excitation eliminates the X-ray scattering background under the fluorescence peaks, greatly enhancing detection performance. This new analytical approach results in detection limits in the parts-per-billion (ppb) range for many elements of interest in a variety of commercial materials.

Monte Carlo Simulation and Variance Reduction

A Monte Carlo method is a computational algorithm which relies on repeated random sampling to approach its asymptotic results (by central limit theorem) and all problems solved by Monte Carlo are essentially equivalent to integrations [I. Lux and L. Koblinger, 1990].

The center for Engineering Applications of Radioisotopes (CEAR) in North Carolina State University has a long history of research on Monte Carlo simulation on XRF. Monte Carlo Simulation application in the EDXRF spectrometer design and optimization is feasible and has been reported by many researchers [He 1992, Ao and Gardner 1995; Lee et al. 2001; Guo and Gardner 2004; Gardner and Li 2006; Li and Gardner 2008]. A specific-purpose Monte Carlo code (CEARXRF) for simulating the total and individual library spectral responses of all elements, has been developed by CEAR researchers including complete X-ray photon interactions of X-rays. And it has been recently upgraded, with several key improvements including: an easy-to-use interface, a faster geometry tracking package, versatile source definition, variance reduction...
techniques, a new cross section loading method and updated database (EPDL97), four times faster than the previous version, while keeping all the capabilities of the previous version such as Differential Operators (DO) [Lee 1999]. Coincidence sampling etc. Table 1 briefly summarizes the key features of the CEARXRF code and other general purpose Monte Carlo codes with respect to the EDXRF simulation (Guo and Gardner, 2004).

Table 1 Comparison table for features of CEARXRF-5 and several general purpose Monte Carlo simulation codes

<table>
<thead>
<tr>
<th>CODE</th>
<th>CEARXRF 5</th>
<th>EGS4</th>
<th>ITS 3.0</th>
<th>MCNP 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Establishment</td>
<td>NCSU, USA</td>
<td>SLAC, USA</td>
<td>KEK, Japan</td>
<td>SAND, USA</td>
</tr>
<tr>
<td>Particles</td>
<td>Photon</td>
<td>Photon/Electron</td>
<td>Photon/electron</td>
<td>Neutron/Photon/electron</td>
</tr>
<tr>
<td>Elements(Z)</td>
<td>1-100</td>
<td>1-100</td>
<td>1-100</td>
<td>1-94</td>
</tr>
<tr>
<td>Energy Regime</td>
<td>1kev-1 MeV</td>
<td>1kev – 100Gev</td>
<td>1kev-100Gev</td>
<td>1kev-100Gev</td>
</tr>
<tr>
<td>XRF Physics</td>
<td>All shells.</td>
<td>(K_{\alpha 1}, K_{\alpha 2}, K_{\beta 1}, K_{\beta 2}) and L</td>
<td>All K and L, Average M and N</td>
<td>(K_{\alpha 1}, K_{\alpha 2}, K_{\beta 1}, K_{\beta 2}) and average L</td>
</tr>
<tr>
<td>Photon Physics</td>
<td>PE, Incob, Coh, Doppler, Polarization</td>
<td>Same + Pair</td>
<td>Same- Doppler Polarization</td>
<td>Same – Polarization</td>
</tr>
<tr>
<td>Geometry</td>
<td>General</td>
<td>General</td>
<td>General</td>
<td>General</td>
</tr>
<tr>
<td>Variance Reduction</td>
<td>Powerful</td>
<td>Basically analog</td>
<td>Few and simple</td>
<td>Powerful for transport analog for spectra</td>
</tr>
<tr>
<td>Correlated Sampling</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes (from MCNP version 4B)</td>
</tr>
<tr>
<td>Library spectra</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Differential Operators</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>X-ray Coincidence simulation</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
</tbody>
</table>

This specific-purpose Monte Carlo code is suitable to use for photon energy up to 1MeV, various source form factors, and arbitrary geometry setup. It can provide the following components to be used in XRF analytical process.

- Total spectral responses of X-ray flux incident on detector surfaces
- Individual elemental spectral responses on detector surfaces
- Differential operators or elemental perturbation derivatives (1st and 2nd order)
- Coincidence X-rays simulation spectra for dual detector configuration

To improve the statistics of characteristic X-ray for those trace elements, at each interaction site, all chemical elements in that region are forced to interact with photon and a proper weight adjustment is made for each emitted X-ray photon [Cashwell and Everett 1959].

The adjustment of photon weight (W) is based on each element’s interaction probability with the photon at a specific energy (E), which is determined by macroscopic cross section \(\Sigma_i(E)\). For a test sample with density (\(\rho\)), the macroscopic cross section for an individual element (i) is calculated by:

\[
\Sigma_i(E) = \rho N_A \frac{f_i \sigma_i(E)}{A_i}
\]

Where \(\sigma_i(E)\) is the microscopic cross section for element i, and \(A_i\) is the atomic mass in units of gram/mole and \(N_A\) is Avogadro’s number \((6.022 \times 10^{23} \text{ mol}^{-1})\), and \(f_i\) is elemental weight fraction, \(i=1\ldots n\).

And the total macroscopic cross section \(\Sigma(E)\) is calculated by,
\[ \Sigma_i(E) = \rho N \sum_{i=1}^{n} \frac{f_i \sigma_i(E)}{A_i} \]

Then, the probability of an element elected to interact with the photon is determined by \( P_i(E) \).

\[ P_i(E) = \frac{\Sigma_i(E)}{\Sigma_i(E)} = \frac{f_i \sigma_i(E)}{A_i \sum_{i=1}^{n} \frac{f_i \sigma_i(E)}{A_i}} \]

For analog sampling, the trace elements with very low-weight fraction \( f_i \) have less opportunity to be sampled compared to those elements with higher concentrations. Then, the statistical precision for these trace elements will be much worse since there is always a limit for number of simulation (history number). The problem can be more severe especially when there is not adequate history number due to time constraint. In these cases, some events won’t be sampled and the elemental library spectra are not correct to represent the true values.

Stratified sampling can improve this situation by forcing all elements to interact with the photon and adjusting the particle weight appropriately. Supposed that there are “n” elements in the sample, one photon will split to “n” photon particles with new weight \( W' \). Assume \( W_0 \) is the source photon weight before splitting, the weight of each resulting photon is:

\[ W_i' = W_0 \frac{\Sigma_i(E)}{\Sigma_i(E)} \frac{f_i \sigma_i(E)}{A_i \sum_{i=1}^{n} \frac{f_i \sigma_i(E)}{A_i}} \]

The total weight of photon before and after splitting is conserved and stratified sampling should produce the same results as analog sampling.

In the Monte Carlo simulation code, it can only track one particle at a time, the property (energy, weight, position, direction, etc.) of each split photon is pushed into a “last in, first out” also known as LIFO stack and retrieved to track its life cycle after the current photon particle completes.

**Detector Response Function**

The Detector Response Function (DRF) is defined as the pulse height distribution for incident mono-energetic x-ray, usually indicated by \( R(E', E) \), where \( E' \) is the pulse height energy and \( E \) is the incident X-ray energy. The energy spectrum from Monte Carlo simulation code is denoted as flux spectrum \( \Phi(e) \) and the convolution of \( \Phi(e) \) and DRFs is defined as the integral of the product of two functions after one is reversed and shifted. As such, pulse height spectrum is a particular kind of integral transform,

\[ \text{PulseHeight} = (\Phi * DRF)(E) = \int_{E_{\text{min}}}^{E_{\text{max}}} \Phi(e)DRF(E - e)de \]

The MCLLS approach requires a complete set of accurate response functions of the Si (Li) detector for different incident energy. While Monte Carlo models predict the photon spectra incident on the detector, the DRF can be used to generate the pulse-height spectra from these photon flux spectra. This is a powerful variance reduction technique to speed up the overall process. A semi-empirical response function model for Si(Li) detector was developed for this purpose [Yacout et al 1986], which consists of four major components: (1) Gaussian-shaped full-energy peak, (2) Gaussian-shaped Si escape peak, (3) flat continuum from zero to full energy, and (4) an exponential tail located on the low-energy side of the full-energy peak. The authors improved the model to consider multiple incident X-rays and the model can be written as:
\[ R(E, E') = \sum_{i=1}^{n} \{ A_i(E_i)G[E_i, E', \sigma(E_i)] + A_2(E_i)G[E_i - 1.74, E', \sigma(E_i - 1.74)] \} \]
\[ \ldots + A_3(E_i)A_4(E_i) \exp[\alpha(E_i)(E_i - E')] \times F[E_i, E', \sigma(E_i)] \}\]

Where \( E_i \) is incident X-ray energy in KeV for incident energy i (K\( \alpha \) or K\( \beta \) etc.), and \( E' \) is the portion of the energy deposited in X-ray detector. \( G(E_i, E', \sigma(E_i)) \) is defined as a Gaussian function with its peak standard resolution (\( \sigma \)), representing both the Gaussian-shape full-energy peak and Si escape peak. \( F(E_i, E', \sigma(E_i)) \) is given by an error function (erf), representing the flat continuum and exponential-tail terms, and \( \alpha(E_i) \) is the exponential exponent.

\[ G[E_i, E', \sigma(E_i)] = \exp[-\frac{(E'-E_i)^2}{2\sigma^2}] \]
\[ F[E_i, E', \sigma(E_i)] = \pi \times \text{erfc}[-\frac{(E'-E_i)^2}{\sqrt{2}\sigma^2}] \]

As shown in the model, \( n \) is the number of incident X-ray energies. For example, two incident energies are commonly observed corresponding to K\( \alpha \) and K\( \beta \) peaks. For these cases, \( n=2 \). This model can also be used in those cases with more incident energies such as L\( \alpha \) and L\( \beta \) x-rays that are also recorded together with K shell x-rays. The linear parameters (denoted as \( A_1, A_2, A_3 \ldots \)) are the normalized response function constants such that:

\[ \int R(E, E')dE' = 1 \]

In this work, the excitation source is a 17.5 keV mono-energetic X-ray using doubly curved crystal (DCC) X-ray optics [Z. Chen et al. 2002, 2008]. Eleven high-purity thick element targets (Al, Si, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, and Pb) were used. A total of 11 spectra containing multiple X-ray energy lines were investigated. All spectra were measured with the Si(Li) cylindrical detector crystal having a thickness of 0.45mm and radius of 1.27mm.

Non-linear regression code was used to determine the linear and nonlinear parameters of the response function. Initial guesses of the nonlinear parameters are provided prior to the fitting and the code calculated the optimized coefficients for the model to represent the experimental library spectra the best. The fitting reduced chi-square values for each element target are included in table 2. Figure 2 shows fitted model spectrum with its components for nickel the measured DRF response compared. It is demonstrated that the semi-empirical DRF model fits experimental values very well.

<table>
<thead>
<tr>
<th>Element</th>
<th>Reduced chi-Square values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>6.59</td>
</tr>
<tr>
<td>Si</td>
<td>5.73</td>
</tr>
<tr>
<td>Ti</td>
<td>6.24</td>
</tr>
<tr>
<td>V</td>
<td>6.35</td>
</tr>
<tr>
<td>Cr</td>
<td>6.1</td>
</tr>
<tr>
<td>Mn</td>
<td>5.77</td>
</tr>
<tr>
<td>Co</td>
<td>4.56</td>
</tr>
<tr>
<td>Ni</td>
<td>4.48</td>
</tr>
<tr>
<td>Cu</td>
<td>3.56</td>
</tr>
<tr>
<td>Zn</td>
<td>3.42</td>
</tr>
<tr>
<td>Pb</td>
<td>9.75</td>
</tr>
</tbody>
</table>
Results and Analysis

The Monte Carlo based Library Least-Squares (MCLLS) approach was successfully implemented on the micro-focused EDXRF Analyzer and the accuracy of the system was benchmarked using a plastic substrate (base layer with 20mm in thickness and 1.5g/cm$^3$ in density) and a thin layer of paint sample with known composition: Ti (~16%), Br (~0.03%), Fe (~0.02%), Pb (~0.015%) and the remaining elements are C and H. Another plastic substrate without paint layer was used to measure the background spectrum.

The excitation source is a 17.5 keV mono-energetic X-ray source generated by DCC. The X-ray spectrum was obtained with a Si detector crystal (0.45mm in thickness and 1.27mm in radius). As shown in figure 3, the substrate plus paint spectrum is the target sample spectrum to be fitted. The surface analysis of the paint layer elemental compositions takes 150 seconds of measurement time. And the substrate spectrum without paint serves as a background spectrum and takes 30 seconds of measurement time. All paint elemental spectra (Ti, Br, Pb, and Fe) are the fitting components – generated by Monte Carlo Simulation & the DRF process.
The spectral regression results are shown in figure 4. The calculated weight fractions are demonstrated in table 3. The comparisons of the calculated weight fractions with known values and the fitted spectra with experimental spectra indicate that the CEARXRF GUI-Based MCLLS Code is very accurate.

<table>
<thead>
<tr>
<th>Element</th>
<th>Fit results (%)</th>
<th>Reference value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>16.21</td>
<td>16</td>
</tr>
<tr>
<td>Br</td>
<td>0.028</td>
<td>0.03</td>
</tr>
<tr>
<td>Pb</td>
<td>0.016</td>
<td>0.015</td>
</tr>
<tr>
<td>Fe</td>
<td>0.025</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Figure 4 Original experimental spectrum compared with fitted spectrum

Conclusions

The Monte Carlo simulation code CEARXRF was upgraded to have better user-friendly input configuration and it runs much faster than previous code because several variance reduction techniques have been implemented such as elemental stratified sampling. The advantage of stratified sampling over analog sampling method is able to improve the statistical precision for elements with low-weight fractions and guarantee that each element in the sample has similar statistical precision, which is especially important for accuracy of trace elements in the sample. The Monte Carlo code generates computed elemental library spectra needed to fit the measured spectrum and estimate the weight fraction of each element in the sample, intended to correct the matrix effect of XRF elemental analysis following an iterative Least Squares regression. The procedure was implemented on a micro-focused XRF analyzer system and an improved detector response functions were optimized for such system. DRF is defined as a probability density function \( R(E,E') \), where \( E' \) is incident energy and \( E \) is the vector of pulse-height energies. The results of benchmarked experiments show that the Monte Carlo based library least squares method is very accurate.

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