DEVELOPMENT OF A MONTE CARLO – LIBRARY LEAST-SQUARES (MCLLS) CODE PACKAGE FOR THE EDXRF INVERSE PROBLEM

Robin P. Gardner and Weijun Guo

Center for Engineering Applications of Radioisotopes (CEAR)
Nuclear Engineering Department, PO Box 7909
North Carolina State University
Raleigh, NC 27695

ABSTRACT

The Monte Carlo – Library Least-Squares (MCLLS) approach has now been developed, implemented, and tested for solving the inverse problem of EDXRF sample analysis. It consists of a linear library least-squares (LLS) code and a comprehensive Monte Carlo code named CEARXRF that is capable of calculating the unknown sample spectrum, all the elemental library spectra in the sample, and the differential operators for each library spectrum with respect to each element. Two codes with Graphical User Interface (GUI) have been designed to implement the MCLLS approach and benchmark results are presented for the two stainless steel samples; SS304 and SS316. The results are accurate, the system is easy to use, and all indications are that this approach will be very useful for the EDXRF practitioner.

INTRODUCTION

EDXRF sample analysis is confronted with two primary problems: (1) the determination of X-ray intensities from the sample and (2) the determination of elemental composition from the sample X-ray intensities. Both of these problems become more acute as the atomic numbers of the elements of interest get closer together. In this case the first problem becomes difficult because the characteristic X-ray peaks become overlapped for even the highest resolution detectors. The second problem becomes more difficult in this case due to the nonlinear matrix interferences becoming more acute (for example, the K absorption edge of one elemental component may lie between the $K\alpha$ and $K\beta$ X rays of another, which can cause drastic changes in the effective ratio of the detected $K\alpha$ and $K\beta$ X rays of the element of interest). The Monte Carlo – Library Least-Squares (MCLLS) approach automatically provides an excellent solution to both of these problems. The main disadvantage of this approach in the past has been the difficulty in the practical application of this approach. The present code and GUI development is aimed at solving this problem for the EDXRF practitioner.

The MCLLS approach basically consists of using a Monte Carlo code with fundamental parameters to simulate the X-ray spectral response to a sample of known (or assumed known) composition. Monte Carlo simulation extends the practical use of fundamental parameters to cases in which the system geometry and excitation source spectra are
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otherwise difficult to describe by conventional deterministic methods. In the course of this simulation individual elemental library spectra are also produced and are subsequently used in a linear library least-squares (LLS) calculation for elemental composition. If the calculated elemental amounts are not close enough to the assumed values, iterations are performed until they are. The mathematical tools required for the MCLLS approach are an accurate and user-friendly Monte Carlo code and a library least-squares code. CEAR personnel have been working on these two tools since the mid 1970’s for EDXRF analysis. The present CEARXRF Monte Carlo code was designed for this purpose and has a number of features that make it ideal for this application. This includes: (1) a general geometry package, (2) use of detector response functions for increased accuracy and variance reduction, (3) the differential operator technique for efficient iteration when estimates of sample composition are inaccurate, and (4) use of other variance reduction methods for optimum calculational efficiency. Recent work on the LLS code includes an off-line method for correcting spectra for pulse pile up based on the Monte Carlo code CEARPPU. This work is described in the paper by Guo, Gardner, and Li [1] in this Proceedings. Benchmark and other sample results are given that indicate the accuracy and power of the proposed code package.

THE MONTE CARLO – LIBRARY LEAST-SQUARES (MCLLS) APPROACH

The Monte Carlo – Library Least-Squares (MCLLS) approach essentially consists of the following steps.

Step 1. With an assumed sample composition that has been obtained with a suitable qualitative and approximate quantitative analysis, Monte Carlo simulation is performed to give the predicted spectrum of the unknown sample mixture, the individual library spectra of each element in the sample, and the differential operators for each library spectrum with respect to each element.

Step 2. With the library spectra obtained in Step 1 or Step 3 a library least-squares analysis (LLS) is performed to give a calculated set of elemental amounts.

Step 3. If the calculated elemental amounts of Step 2 are significantly different from the initial assumed amounts, Steps 1 and 2 are repeated using the calculated elemental amounts as the new assumed composition for Step 1. If the calculated elemental amounts are close to the initial assumed amounts, the differential operators obtained in Step 1 are used to correct the elemental library spectra obtained there and Step 2 is repeated. When the calculated elemental amounts become essentially the same as the initial values, the problem is solved. This procedure is shown in schematic form in Figure 1.

This approach requires a Monte Carlo simulation code that is capable of accurately simulating the unknown sample spectrum, the individual elemental library spectra, and the differential operators for each elemental library spectrum with respect to each element. It also requires a linear library least-squares (LLS) code that is capable of using the elemental library spectra with an unknown sample mixture spectrum to obtain the elemental amounts. A qualitative code is required for identifying the elemental components of the unknown sample mixture. A GUI called XRF Qual + XRF Query has been designed and tested for this purpose. A second GUI called XLLS has been designed and tested for accomplishing the linear library least-squares function. The Monte Carlo
code CEARXRF designed for this purpose, the library least-squares (LLS) approach, and the differential operators approach are discussed in subsequent separate sections. Then example results are given for this approach for two stainless steel samples (SS304 and SS 316). 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.

Figure 1. Schematic Diagram of the Monte Carlo – Library Least-Squares Approach.

THE LIBRARY LEAST-SQUARES (LLS) APPROACH

The library least-squares (LLS) approach for determining elemental gamma-ray (or X-ray) intensities has been around for a long time [2] and has a number of advantages. This includes: (1) it is the most fundamental approach; (2) it is capable of giving the most accurate results possible since the entire spectrum can be used; (3) it automatically provides an estimate of the standard deviation of each calculated elemental amount in the presence of all other components; and (4) peak interferences are automatically accounted for. The only disadvantage is that elemental libraries must be available for all elements present in the sample of interest. In the present case these libraries are provided by Monte Carlo simulation rather than by experiment, so this disadvantage has been substantially decreased.

The LLS approach assumes that the measurement process is linear – that is, the intensities of each element multiplied by the counts in every channel or pulse-height energy bin per unit element intensity summed over all elements adds to the counts (in a least-squares sense) in the unknown mixture sample. For each channel i (or energy bin) this is mathematically stated as:

$$y_i = \sum_{j=1}^{m} x_j a_{ij} + E_i, \ i = 1, n$$

Where $y_i$ is the counts of the unknown sample mixture in channel i, $a_{ij}$ are the library spectra or counts in channel i of element j in the unknown sample mixture, and $E_i$ is the random error in counts in channel i, m is the total number of chemical elements consisting of the sample and n is the total number of energy channels of the Multi-Channel Analyzer (MCA). The reduced chi-square value ($\chi^2$) is formed from:
\[ \chi^2 = \frac{1}{n-m} \sum_{i=1}^{n} \frac{E_{i}^2}{\sigma_i^2} \]

Where \( \sigma_i^2 \) is the variance of \( y_i \) and is usually taken as Poisson distributed and, therefore, equal to \( y_i \). The \( x_j \) are found by minimizing the reduced chi-square value. This is done in the usual way by setting the derivative of the reduced chi-square value with respect to each \( x_j \) equal to zero to obtain a system of \( m \) equations. These equations can be solved simultaneously by matrix inversion to find the \( x_j \). The LLS code developed here provides the calculated elemental amounts and their standard deviations, the reduced chi-square value, and the residuals of the experimental minus the calculated sample spectra. The residuals are important in that elements that have been missed in the analysis can be easily identified. A good reference for the derivation of these formulas is the paper by Arinc, Wielopolski, and Gardner [3].

**MONTE CARLO SIMULATION CODE - CEARXRF**

The Monte Carlo simulation method is becoming more and more important in many fields of design and analysis with the help of faster computers and improved physics models. It has the powerful capability for accurately modeling almost arbitrarily complex geometry and automatically taking into account inter-elemental effects with no extra mathematical complexity. These features make the Monte Carlo simulation an ideal tool in the field of EDXRF for both instruments design and optimization. With the application of the MCLLS approach that we have been working on for a long time, the simulation results can be used for quantitative EDXRF analysis in an iterative fashion.

CEARXRF, a FORTRAN code for Monte Carlo simulation of EDXRF instruments, has been developed and continuously improved by researchers at the Center for Engineering Applications of Radioisotopes (CEAR) [4-7]. CEARXRF was first implemented on Sun Unix workstations in FORTRAN 77 and then ported to the Cygwin platform of the PC Windows system. The major motivations for developing CEARXRF are:

- Simulating Monte Carlo elemental library spectra for quantitative EDXRF multi-elemental analysis;
- Investigating the matrix effect with simulated differential responses of sample and library spectra;
- Optimizing the EDXRF spectrometer configuration by improving the measurement sensitivity. This can be done by analyzing a series of simulated sample spectra that are reliable and accurate approximations for experimental spectra with the CEARXRF code after it has been benchmarked with experimental data.

Several key components are necessary to ensure accurate Monte Carlo simulation results for EDXRF instruments. These include a general geometry package, complete photon transport physics (especially for the low-energy X-ray regime), random number generation algorithms, sampling schemes, and variance reduction techniques (including detector response functions to convolve an incident photon flux on the detector surface to a spectrum with detector artifacts, such as escape peaks). Compared to several general
purpose Monte Carlo simulation codes, CEARXRF has unique and powerful features for EDXRF applications. Comparisons with other codes are given in Table.1.

A geometry-modeling package, called HERMETOR [8], is used to characterize the geometry of the EDXRF analyzer for photon tracking. A complex three-dimensional heterogeneous system can be defined by HERMETOR through a simple and verifiable input format. An approach that combines boundary representation and constructive solid geometry techniques is employed in this treatment. The geometry input file can be plotted for any two-dimensional cross-section view (as shown in Figure 2) with a self-supporting code called HGEMPLOT and this is a reliable and convenient way to verify the accuracy of the geometry input file.

Detailed physics models for photoelectric absorption, incoherent scattering, and coherent scattering are coded for both polarized and unpolarized photons. The photon cross sections for all elements ($Z=1-94$) in the energy range 1-150 keV are from the MCNP photon library based on the ENDF/V database. The electron binding effects become apparent in Compton scattering when the photon energy is lower than a few hundred keV. One of the electron binding effects is the Doppler broadening effect in which the Compton scattered photon energy is broadened by the pre-collision motion of the bound electron. Neglecting this Doppler broadening effect in Compton scattering may result in incorrect Compton scattering profiles in a photon-excited XRF spectrum. A method similar to that in the expanded EGS4 code is adopted to incorporate the Doppler broadening effect into the CEARXRF code. The Hartree-Fock Compton profiles, calculated in the frame of the impulse approximation theory are used to handle the Doppler broadening of Compton-scattered photon energies. For bibliography information, Table 2 lists the references for the physics data library.

The XRF pulse-height spectrum is predicted by convolving the detector-incident X-Ray spectral flux, simulated by the CEARXRF code, with a detector response function (DRF). Figure 3 compares the incident flux and the corresponding convolved spectrum. A semi-empirical DRF for a Si(Li) detector [9] and a low-energy photon germanium detector
[10-12] are presently available with the CEARXRF simulation. These DRF models have the following features: (1) a Gaussian-shaped full-energy peak, (2) a Gaussian-shaped Si or Ge escape peak, (3) a flat continuum from zero to full energy, and (4) an exponential tail located on the low-energy side of the full-energy peak. The values of the model parameters were obtained by nonlinear least-squares fitting of the pulse-height spectra from a number of pure-element samples excited by various radioisotope sources. Simple functional forms of the separable parts of the detected X-Ray pulse-height spectrum as functions of incident energy were summed to produce the generalized response function.

DIFFERENTIAL OPERATOR

The Differential Operator method is discussed in the literature [13-15]. It is a very powerful method for measurement sensitivity study and system optimization. For EDXRF instruments, it becomes a powerful technique for quantifying the matrix effect when combined with MCLLS. The Monte Carlo - Differential Operator approach was implemented in CEARXRF for simulating differential responses of both sample and elemental library spectra for variations of elemental concentrations [16]. By using the Taylor series expansion, these differential responses can be used for spectra adjustment according to possible weight fraction differences between initial guess values used for Monte Carlo simulation and true values of the unknown sample. This is potentially a very accurate approach for taking account the nonlinear EDXRF response due to inter-elemental absorption-enhancement effects.

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

<table>
<thead>
<tr>
<th>CODE</th>
<th>CEARXRF</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>SAND, USA</td>
<td>LANL, USA</td>
</tr>
<tr>
<td>KEK, Japan</td>
<td>KEK, Japan</td>
<td>KEK, Japan</td>
<td>KEK, Japan</td>
<td></td>
</tr>
<tr>
<td>NRCC, Canada</td>
<td>NRCC, Canada</td>
<td>NRCC, Canada</td>
<td>NRCC, Canada</td>
<td></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>1-94</td>
<td>1-100</td>
<td>1-100</td>
<td>1-94</td>
</tr>
<tr>
<td>Energy Regime</td>
<td>1-150 keV</td>
<td>1keV – 100 GeV</td>
<td>1kev-100Gev</td>
<td>1kev-100Gev</td>
</tr>
<tr>
<td>XRF Physics</td>
<td>All K and All L</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 4B)</td>
</tr>
<tr>
<td>Library spectra</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Differential Responses</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>
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</table>
Table 2. Table for the physics data libraries used in the CEARXRF code and their related references

<table>
<thead>
<tr>
<th>Physics</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photo-electric total absorption cross section</td>
<td>[17]</td>
</tr>
<tr>
<td>Angular Distribution</td>
<td>[17]</td>
</tr>
<tr>
<td>Atomic Form Factors</td>
<td>[18]</td>
</tr>
<tr>
<td>Cross section</td>
<td>[17]</td>
</tr>
<tr>
<td>Coherent Scattering</td>
<td></td>
</tr>
<tr>
<td>Incoherent Scattering</td>
<td>[18]</td>
</tr>
<tr>
<td>Cross section</td>
<td>[17]</td>
</tr>
<tr>
<td>Angular Distribution</td>
<td>[18]</td>
</tr>
<tr>
<td>Incoherent Scattering Function</td>
<td>[18]</td>
</tr>
<tr>
<td>shell-wise photoelectric absorption cross sections</td>
<td>[20]</td>
</tr>
<tr>
<td>Doppler broadening effect</td>
<td>[19]</td>
</tr>
<tr>
<td>Auger, Coster-Kronig, and total fluorescence yields</td>
<td>[21]</td>
</tr>
<tr>
<td>K and L emission rates</td>
<td>[22, 23]</td>
</tr>
<tr>
<td>Ionization energy levels</td>
<td>[24]</td>
</tr>
</tbody>
</table>

The calculation principle for the Differential Operator approach is as following. Mathematically, the spectral response can be expressed as the average value of each photon history weight that is scored by the detector. So, differential spectral responses to variations of elemental concentrations are also equal to average values of derivatives of photon weights with respect to variations of elemental weight fractions. The process of photon history track can be treated as multiple steps. The photon weight is adjusted with a correction factor for each step. The mathematical equation is:

\[ w_n = w_{n-1} \cdot f_n \]

So the derivative of the photon weight can be expressed as:

\[ \frac{\partial w_n}{\partial \alpha_j} = \frac{\partial w_{n-1}}{\partial \alpha_j} f_n + \frac{\partial f_n}{\partial \alpha_j} w_{n-1} \]

At the end of each step, the incident photon either escapes or reacts with constituent elemental atoms until the history is terminated according to certain rules or scored by a detector. To calculate the derivative of the photon weight, all four possible scenarios have been considered [25].

1. Escape, the photon escapes from a region without interaction
2. Reaction, path length determination in a region
3. Reaction element selection: the element of interest is selected
4. Reaction element selection: an element other than the element of interest is selected

SAMPLE RESULTS

To verify the previously described MCLLS approach, two standard stainless steel slab samples with 3mm thickness, SS304 and SS316, respectively, were measured with a low-energy Germanium detector (2” x 20mm). A 10 mCi Cd-109 radioisotope point source was used for excitation. The spectrometer geometry is plotted in Figure 4.
The major elements composing stainless steel is Fe. The coexistence of Cr and Ni in the stainless steel sample makes them well suitable to demonstrate matrix effects of EDXRF measurements. The dominant X-ray lines and K absorption edges for these three elements are presented in Figure 5. It is obvious that Cr is a strong absorber for Fe and Ni lines and Fe has the same effect on Cr lines.

To automate the process of the MCLLS approach, a software package with a graphical user interface has been developed. The XRayQual software is used for identifying the existence of specific elements in the sample based on the measured unknown EDXRF spectrum. A screenshot of the software is presented in Figure 6. XRayQual makes the routine task of energy calibration and element identification as easy as “point and click”. The implementation of advanced peak area integration algorithms is under development. The Monte Carlo simulation code CEARXRF is used for generating elemental library spectra and differential responses of these library spectra for variations of elemental concentrations. Figure 7 presents the simulated sample spectrum together with normalized elemental library spectra. It is clear that the information carriers of each element consist not only of the characteristic X-ray lines but also the peaks contributed by backscattered source photons. The quantitative results for two samples are listed in
Table 3. All results for elemental weight fractions fall in the nominal range of the standards. The least-squares fitted spectrum for SS316 is compared with the measured one in Figure 8. Based on the residuals plot, we can conclude that they are in good agreement.

![Image](image1.png)

**Figure 6.** XRayQual software screenshot.

![Image](image2.png)

**Figure 7.** Total sample and elemental library spectra.

![Image](image3.png)

**Figure 8.** Experimental and MCLLS calculated spectra with residuals.

<table>
<thead>
<tr>
<th></th>
<th>W.F.% (SS 304)</th>
<th>Nominal</th>
<th>W.F.% (SS 316)</th>
<th>Nominal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>18.4</td>
<td>18.0-20.0</td>
<td>16.4</td>
<td>16.0-18.0</td>
</tr>
<tr>
<td>Fe</td>
<td>68.2</td>
<td>60.0-70.0</td>
<td>64.5</td>
<td>60.0-70.0</td>
</tr>
<tr>
<td>Ni</td>
<td>8.1</td>
<td>8.0-12.0</td>
<td>11.4</td>
<td>10.0-14.0</td>
</tr>
<tr>
<td>Mo</td>
<td>0.4</td>
<td>-</td>
<td>2.8</td>
<td>2.0-3.0</td>
</tr>
</tbody>
</table>
Differential responses were simulated at the same time as library spectra with CEARXRF. The inter-elemental absorption-enhancement matrix effect causes the elemental libraries to be different for the same element in different samples. The Fe library for the SS304 sample is compared with that for SS316 in Figure 9. The differential response of the Fe library for the amount of Cr in the sample is presented in Figure 10. It is clear that Cr strongly absorbs Fe $K\alpha$ line and absorbs somewhat less of the Fe $K\beta$ line. This can be easily explained by looking at the photoelectric attenuation coefficient as a function of photon energy. Based on the Taylor series expansion, the following equation can be applied for the counts in each channel of the spectrum to be re-adjusted:

$$R(w_{1,x}, w_{2,x}, ..., w_{n,x}) = R(w_{1,0}, w_{2,0}, ..., w_{n,0}) + \sum \frac{\partial R}{\partial w_i} (w_{i,x} - w_{i,0}) + O(w_x - w_0)^2$$

The library spectrum calculated with Taylor series expansion is compared with the directly simulated spectrum with good agreement in Figure 11.

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Figure 9. Fe library spectra for SS316 and SS304 samples.

Figure 10. Differential operator response of the Fe library with respect to Cr amount in the sample.
DISCUSSION AND CONCLUSIONS

The results indicate that the proposed software system is accurate and user-friendly – at least for the benchmark cases investigated here. However, it is obvious that the system treated is not the usual case encountered in laboratory practice. There is a need to obtain detector response functions for detectors other than the LEPD Ge that is treated here. This would certainly include Si(Li) and SDD detectors and others in common use. There is also a need to treat exciting sources other than the radioisotope source Cd-109. This certainly includes typical X-ray tube spectra used in commercial systems. While this will require some additional effort, it is anticipated that this will be straightforward and that no unsolvable or even difficult problems will emerge. Work has already been initiated in these areas and the authors already have extensive previous experience that is pertinent to this effort. The authors have begun to contact commercial suppliers of EDXRF equipment to develop and demonstrate this software for their specific systems.

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