XMI-MSIM: a general Monte Carlo simulation of energy-dispersive X-ray fluorescence spectrometers

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Outline

1. Monte Carlo simulation of energy dispersive X-ray fluorescence (ED-XRF) spectrometers
2. XMI-MSIM
3. Examples
4. Quantification using Monte Carlo simulations
Monte Carlo simulation of energy dispersive X-ray fluorescence (ED-XRF) spectrometers
A general Monte Carlo simulation of ED-XRF spectrometers

Basic idea: given a description of sample, excitation conditions and detector setup, predict the response of ED-XRF experiments

Why?

- Optimize and design experimental setups *in silico*
- Dose calculation
- Estimation of detection limits
- Quantification
- Didactic tool!
A general Monte Carlo simulation of ED-XRF spectrometers

How?

- Simulates the fate of individual photons
- Trajectories are modelled as a sequence of straight steps.
- At the end of each step, an interaction will occur, leading to a change in direction and energy
Initial photon properties:
• Energy
• Degree of linear polarization
• Intensity (weight)
• Direction
• Discrete or continuous
Sample properties:
• position and orientation
• $n$ parallel layers
• Thickness
• Density
• Composition
Detector properties:
- position and orientation
- crystal
- window
- zero/gain
- Collimator (optional)
Step size?
Atom type?
Interaction type?
Fluorescence line?
New direction?
Selection of step length

Based on the Lambert-Beer law

Find the largest index $m$, for which still holds:

$$R \leq \prod_{i=1}^{m-1} \exp(-\mu_i \rho_i S_{\text{max}}) \left(1 - \exp(-\mu_m \rho_m S_{\text{max}}^m)\right)$$

The actual steplength is calculated as:

$$S = -\frac{\ln\left(\frac{1 - R}{\prod_{i=1}^{m-1} \exp(-\mu_i \rho_i S_{\text{max}})}\right)}{\mu_m \rho_m} + \sum_{i=1}^{m-1} S_{\text{max}}$$
Step size?
Atom type?
Interaction type?
Fluorescence line?
New direction?

Selection of atom type
Choose atom type while still valid:

$$\sum_{i=1}^{k} w_i m_i \leq R < \sum_{i=1}^{k+1} w_i m_i$$

with:

$$m_i = \frac{\mu_i}{\sum_{m=1}^{n} w_m' u_m^i}$$
Selection of interaction type

\[
\begin{align*}
0 & \leq R < \frac{\tau_z}{\mu_z} & \text{photoelectric effect} \\
\frac{\tau_z}{\mu_z} & \leq R < \frac{\tau_z + \sigma_{RZ}}{\mu_z} & \text{Rayleigh scattering} \\
\frac{\tau_z + \sigma_{RZ}}{\mu_z} & \leq R < 1 & \text{Compton scattering}
\end{align*}
\]
The Monte Carlo simulation allows for interactions in the absorption coefficient range, only photoelectric effects occur. The cross sections associated with absorption and excitation terms from Eq. (10) is required. The generator as an interaction type, depending upon the atom species and the excitation energy, uses the absorption coefficient of the atom species and the excitation energy, using the absorption coefficient of the atom species and the excitation energy. The correction of the composition weights using the absorption coefficient allows for interactions in the absorption coefficient range.
Chapter 5. A general MC simulation of ED-XRF spectrometers: forward methodology

\[
\begin{align*}
\text{KL}_2: & \quad 0 \leq R < p_{KL2} \\
\text{KL}_3: & \quad p_{KL2} \leq R < p_{KL2} + p_{KL3} \\
\text{KM}_2: & \quad p_{KL2} + p_{KL3} \leq R < p_{KL2} + p_{KL3} + p_{KM2} \\
\text{KM}_3: & \quad p_{KL2} + p_{KL3} + p_{KM2} \leq R < p_{KL2} + p_{KL3} + p_{KM2} + p_{KM3} \\
\vdots &
\end{align*}
\]

with \( p_X \) corresponding to the radiative emission rates of line \( X \). Similar equations can be derived for the L- and M-subshells. Up to 320 K-, L-, and M-line sets are taken into account for each element of the periodic table.

It is worth noting the absence of the KL\(_1\) transition in Eq. (5.14). This transition is not accounted for owing to its multipole nature and its subsequent extreme weakness.

After the selection of the linetype and the corresponding energy, the new direction of the photon is calculated taking into account the isotropic nature of the fluorescence production:

\[
\theta_i = \arccos \left( \frac{2R - 1}{R} \right) \\
\phi_i = 2\pi \frac{R}{R}
\]

where \( R \) has the aforementioned meaning.

5.5.7 Cascade effect

As in single cascade event may lead to a photo process: if the precursory transition type is radiative, and if the fluorescence yield selection step is favorable, then a second fluorescence photon is being produced. An example of such a process looks as follows:

1. Initial K-shell excitation
2. A radiative transition produces a KL\(_3\) photon and a vacancy in the L\(_3\) shell
3. The fluorescence yield of the L\(_3\) shell is favorable, leading to a new radiative transition
4. The vacancy created in the M\(_5\) shell is giving rise to a new secondary cascade event

In this case, the code will create an additional photon (offsetting) which will be considered by the program as any other photon. Note that it is possible that these shells may...
Chapter 5. A general MC simulation of ED-XRF spectrometers: trajectory (from next step of the trajectory is calculated. In case the photon is not absorbed at the current interaction point: fluorescence line? interaction type? atom type? Scattered photons: according to appropriate inverse cumulative distribution functions. When the photon leaves the simulated volume, the new coordinates of the photon become at the next interaction point:

\[
\begin{bmatrix}
\sin \Theta_{i+1} \cos \Phi_{i+1} \\
\sin \Theta_{i+1} \sin \Phi_{i+1} \\
\cos \Theta_{i+1}
\end{bmatrix} =
\begin{bmatrix}
\cos \Theta_i \cos \Phi_i & -\sin \Phi_i & \sin \Theta_i \cos \Phi_i \\
\cos \Theta_i \sin \Phi_i & \cos \Phi_i & \sin \Theta_i \sin \Phi_i \\
-\sin \Theta_i & 0 & \cos \Theta_i
\end{bmatrix}
\begin{bmatrix}
\sin \theta_i \cos \phi_i \\
\sin \theta_i \sin \phi_i \\
\cos \theta_i
\end{bmatrix}
\]

\[
x_{i+1} = x_i + S_{i+1} \sin \Theta_{i+1} \cos \Phi_{i+1} \\
y_{i+1} = y_i + S_{i+1} \sin \Theta_{i+1} \sin \Phi_{i+1} \\
z_{i+1} = z_i + S_{i+1} \cos \Theta_{i+1}
\]

Fluorescence line? New direction?
Step size?
Atom type?
Interaction type?
Fluorescence line?
New direction?
Photon termination

- After each interaction, a new stepsize will be calculated and so on...

- The procedure stops when the photon is either absorbed by the sample or leaves it.

- Upon leaving the sample, a check is performed to determine whether or not the photon hit the detector.
Brute force algorithm: inefficient

- Very large number of photons must be simulated
- Possible loss of photons due to thin, low absorbent samples, low fluorescence yields, and detector geometry
- Usually requires supercomputer
Brute force algorithm: inefficient

- Very large number of photons must be simulated
- Possible loss of photons due to thin, low absorbent samples, low fluorescence yields, and detector geometry
- Usually requires supercomputer

Variance reduction
1. Step size selection
2. Forced detection
3. Exclusion of non-radiative transitions

10000 fold efficiency increase!
XMI-MSIM
XMI-MSIM

• Based on *msim*, developed by Laszlo Vincze

• Fortran 77 and C

• Command-line only

• Advanced variance reduction techniques

• Impressive execution speed due to tables with inverse cumulative distribution data

• 4 publications between 1993-1999
XMI-MSIM

- Collaboration between Ghent University and ESRF
- Goal: rewrite *msim* from scratch and create plug-in for PyMca → Quantification!
- First commit: August 16, 2010
- Development hosted on Github
- GPLv3 license

XMI-MSIM: new features

- Simulation of XRF M-lines
- Cascade effect
- Detector escape peaks
- Detector pulse pile-up simulation
- Custom detector response functions
- Collimator support
- Multithreading
- MPI
- OpenCL
- Graphical user interface
- Comprehensive documentation!
Dependencies

- Written in Fortran 2003 and C
- OpenMP
- xraylib ➔ poster!
- hdf5
- libxml2
- libxslt
- FGSL or easyRNG
- Graphical User Interface: Gtk+3 and Gtkmm-PLplot
- MPI (optional)

Platform support

- Mac OS X: 64-bit Intel native app bundle for Yosemite and later
- Windows: 32-bit and 64-bit installers available
- Linux: 64-bit RPM/DEB packages available for CentOS/ScientificLinux/Fedora and Debian/Ubuntu
- Installer size: 2.0 GB HDF5 data file!
- Memory usage: varies between 14 MB and 1.5 GB
Examples
Stainless steel NIST SRM 1155

- $E_{\text{exc}} = 16$ keV
- 300 s RT
- $\rho_{\text{deg}} \sim 92\%$
- $10 \times 10 \mu m^2$

enhancement!
detector pile-up
Lead-base bearing metal NIST SRM 1132

16 keV
1500 s RT
$\rho_{\text{deg}} \sim 92 \%$
$10 \times 10 \, \mu\text{m}^2$

L$\rightarrow$M cascade
Multicomponent glass NIST SRM 1412

- 16 keV
- 1500 s RT
- $p_{\text{deg}} \sim 92\%$
- 60 x 60 µm²

Gaussian excitation profile
29 keV
1500 s RT
$p_{\text{deg}} \sim 92\%$
$10 \times 10 \mu m^2$

K$\rightarrow$L cascade
Compton escape peak
Quantification using iterative Monte Carlo simulations
• Alternative for fundamental parameter based quantification
• Produces spectrum: direct verification of results
• Arbitrary high interaction orders
• Scatter enhancement
• Implemented as a plug-in for PyMca

XMI-MSIM-PyMca
NIST SRM 1155
stainless steel

Schoonjans et al. *Spectrochimica Acta B*, 82, 2013, 36-41

<table>
<thead>
<tr>
<th>Element</th>
<th>NIST</th>
<th>XMI-MSIM PyMca</th>
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</thead>
<tbody>
<tr>
<td>Cr</td>
<td>18.37%</td>
<td>18.37%</td>
</tr>
<tr>
<td>Mn</td>
<td>1.62%</td>
<td>1.92%</td>
</tr>
<tr>
<td>Fe</td>
<td>64.31%</td>
<td>65.72%</td>
</tr>
<tr>
<td>Co</td>
<td>1090 ppm</td>
<td>5325 ppm</td>
</tr>
<tr>
<td>Ni</td>
<td>12.35%</td>
<td>12.63%</td>
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<tr>
<td>Cu</td>
<td>1750 ppm</td>
<td>2184 ppm</td>
</tr>
<tr>
<td>W*</td>
<td>1100 ppm</td>
<td>1183 ppm</td>
</tr>
<tr>
<td>Pb*</td>
<td>10 ppm</td>
<td>75 ppm</td>
</tr>
</tbody>
</table>
NIST SRM 1412

multicomponent glass

Schoonjans et al. *Spectrochimica Acta B*, 82, 2013, 36-41
Goodfellow
Nickel Silver rod

Schoonjans et al. Spectrochimica Acta B, 82, 2013, 36-41
Thank you!