Standardless EDS Analysis – The Influence of X-ray Detector Models

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Outline

- Background
- Detector modeling
  - Detector components, charge collection
- Analytical and Monte-Carlo models
  - Description of X-Tracker program
- Examples of modeling
- Applications to real situations and spectra
- Future prospects
Effects on Standardless Analysis - 1

- Quantitative Analysis (FP, ZAF, etc.)
  - conversion of intensities to concs.
- Detector Efficiency assumptions
  - Active volume
  - Entrance/Interfacial layer
  - Front contact
  - Window + coating absorption
  - Misc. artifacts such as carbon, ice, etc., can all affect detector efficiency as f(energy)
  - Counting loss from escape and sum peaks

Effects on Standardless Analysis - 2

- Spectrum Artifacts
  - extraction of net peak intensities
  - Peak shifts
    - Detector degradation
  - Peak tails
    - Incomplete charge collection
  - Background models
    - Window, contact & dead layer absorption steps
    - Carbon and ice contamination steps
    - Electron escape at varying energies
  - Blank corrections
    - Trace peaks of passivation layers, contacts, back contacts and charge traps
  - Escape peaks
    - Loss of fluorescent X-rays from detector material
Technology Evolution

1960's through 80's
- Au contact, No Interfacial Layer
- P/B 3,000:1
- Tail 0.2%

Since 1990
- Ni contact, Interfacial Layer
- P/B >10,000 : 1
- Tail < 0.1%

Current Low-Energy Technology - Be Spectrum

Spectrum acquired with a Si(Li) on an SEM
Be-K peak is at 110 eV with a FWHM = 38 eV
Other Detectors

- **HPGe**
  - Ni contact
  - Interfacial Layer
  - P/B >10,000 : 1
  - Tail 0.15%

- **Thin-Film Detector**
  - Boron contact
  - No Interfacial Layer
  - P/B 2,000 : 1
  - Tail < 0.2%

Simplified Model of Si(Li) Detector

1. X-Rays enter through the aperture in the Collimator
2. X-Ray interactions take place in the Metal Contact and the Interfacial Layer
3. Low Energy X-rays (<5 keV) will interact in the front region of the Sensitive Volume
4. X-rays above ~10 keV will scatter and can reach the Side Walls
5. X-Rays with energy >20 keV will reach the Back Contact
6. At each X-ray interaction point we evaluate the number of electrons produced (Photoelectrons and subsequent Auger electrons)
Processes Considered in the Model

Source of X-rays

- Scattered X-ray
  - Photoelectron

X-ray scattering governed by Klein-Nishina angular distribution probabilities + Compton electrons

Photoelectric absorption produces a photoelectron with a defined range

Photoelectron ionizes as it loses energy

Silicon (for example) de-excites

Fluorescent Si X-rays & Auger electrons are produced

All these processes produce small volumes of charge

At low temperatures the charge thermalizes in a few microns

As temperatures approach room temperature this can be of the order of a hundred microns

Both energetic electrons and thermal electrons can be lost to the surfaces

Volumes of Charge produced

Both Si X-rays and Scattered X-rays escape

“Hot” Electrons lost directly to surfaces

Thermal Electrons lost to surfaces

Movement of Charge to Form the Signal

- Ionization produces electron-hole pairs as charge carriers
  - Si(Li), HPGe & PIN detectors collect both carriers
    - X-Tracker uses the Hecht Equation to establish the Charge Collection Efficiency
  - SDD and CCD are “single-carrier” detectors
    - SDD’s use a “Drift Field” to move the charge to the anode
    - CCD’s store charge in each pixel prior to readout

Electron-hole pairs created by incident photon
The charge cloud expands through diffusion:
- In bulk regions the range is small compared with total volume.
- In surface regions charge can be lost to edges:
  - Charge can be lost in the front contact region.
  - Charge can be lost in the interfacial layer.
  - Suitable chemistry of the interfacial layer can support a “reflection” of charge (the electron component) and be transparent to the holes.
- The most important factor for low-energy spectroscopy is the value of the “Reflection Coefficient” (RC) for different detectors.
- Low values of RC correlate with incomplete charge collection & low-energy tails.
- Loss of hot electrons directly to the contact, & the gain of electrons from the contact to the bulk, governs the low-energy background.

Reflection Coefficient Model:

\[
\eta(X) = \begin{cases} 
1 & \text{if } x = R \\
0.5 & \text{if } x = 0 
\end{cases}
\]

Boundary Conditions:
- \( \eta(X) = 1 \) when \( x = R \)
- \( \eta(X) = 0.5 \) when \( x = 0 \)

Typical Values:
- \( R = 0.2 \, \mu\text{m} \)
- \( r = 0.9 \)

Model developed by:
- Madden et al. (1990)
- Goto (1993)
- Scholze & Ulm (1994)
The Interfacial Layer

- The interfacial layer is key part of Si(Li) structure
- Typically about 5 – 20 nm thick
- Has the properties of a semiconductor
- Thin enough to transmit low-energy X rays
- Thick enough to absorb electrons
- Must support high electric field
- Transparent to holes

Shockley-Ramo Theorem

\[ dQ^* = -(eN_0 / L) \times (dx_e + dx_h) \]  

(1)

where \( dQ^* \) is the induced charge, \( N_0 \) is the initial number of electron-hole pairs, \( L \) is the detector depth, and \( e \) is the electronic charge, under a uniform field gradient.

Integrating eqn (1): 

\[ Q^* = eN_0 \]  

(2)

Charge Trapping

- Charge traps caused by impurities or defects such as missing atoms in the crystal lattice or interstitial atoms.
- In the presence of charge traps, induced charge is a function of the distance over which the charge travels.
- The density and location of the charge traps can give rise to spurious peaks in the spectrum.
**Hecht Equation**

\[ Q^* = \frac{eN_0}{L} \left[ \nu_h \tau_h \left( 1 - \exp \left( -\frac{x_i}{\nu_h \tau_h} \right) \right) + \nu_e \tau_e \left( 1 - \exp \left( -\frac{x_i - L}{\nu_e \tau_e} \right) \right) \right] \]

- \(\nu\) is the charge carrier velocity (mobility), \(\tau\) is the charge carrier lifetime,
- \(x_i\) is the interaction depth from the cathode,
- \(L\) is the detector thickness
- \(e\) and \(h\) subscripts represent electrons and holes respectively

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**Default Values for X-Tracker**

Electron mobility, \(\nu_e = 2.1 \times 10^4\) cm\(^2\)/V·s,
Hole mobility, \(\nu_h = 1.1 \times 10^4\) cm\(^2\)/V·s,
Electron lifetime, \(\tau_e = 1.0 \times 10^{-4}\) seconds,
Hole lifetime, \(\tau_h = 7.0 \times 10^{-7}\) seconds.

Mobility values are from Table 11.1 in Knoll (2000) for silicon at 77 °K.
Lifetime values for silicon were supplied by Rob Sareen (personal comm.)

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**X-Tracker Program - Fe-55 Source**

Simulation screen for x-ray scattering of Mn-Ka,β photons

Dimensions in microns

Close-up of surface region
X-Tracker Program - Cd-109 Source

Simulation screen for x-ray scattering of Ag-Kα,β photons

Dimensions in microns

X-Tracker - Electron Scatter Plots

Scattering of 4.1 keV photoelectrons

Dimensions in microns

Scattering of 20 keV photoelectrons
Charge Collection Efficiency

**Hecht Equation parameters:**
- Electron mobility: \(2.1 \times 10^4 \text{ cm}^2/\text{V-s}\)
- Hole mobility: \(1.1 \times 10^4 \text{ cm}^2/\text{V-s}\)
- Electron Lifetime: 1e-4 seconds
- Hole Lifetime: 7e-7 seconds

**Low (equal) settings**
- Electron mobility: \(1 \times 10^4 \text{ cm}^2/\text{V-s}\)
- Hole mobility: \(1 \times 10^4 \text{ cm}^2/\text{V-s}\)
- Electron Lifetime: 1e-7 seconds
- Hole Lifetime: 1e-7 seconds

**Default settings**
- Electron mobility: \(2.1 \times 10^4 \text{ cm}^2/\text{V-s}\)
- Hole mobility: \(1.1 \times 10^4 \text{ cm}^2/\text{V-s}\)
- Electron Lifetime: 1e-4 seconds
- Hole Lifetime: 7e-7 seconds

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X-Tracker Program - Flow Chart

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Efficiency is never 100% in settings with low electron mobility and lifetime, and therefore the peaks are downshifted in energy.

Efficiency <100% away from surface if hole carriers not included, and so peaks are downshifted and have low-energy tails.
Electron Ranges in Silicon

Relative Contributions of Photon Interactions in Si
Fe-55 Spectra Sims for 3 Reflection Coefficients

All hot electron escape events off
Almost no background when RC=0.9

\[ \eta(X) = \eta(X) + r[1 - \eta(X)] \]

\[ \eta(X) = \eta(X) = 0.5 \text{ when distance from center of charge to contact (x) is zero, and Reflection Coefficient (r) is zero.} \]

Simulated B-F-Al Spectra for 3 Reflection Coefficients

As RC decreases from 0.9 to 0, peaks downshift & tails appear
Simulation of Pb Passivation Artifact

Side walls must be passivated to reduce excessive surface currents

Cd-109 source with 1 micron side wall passivation

Pb peaks can interfere with trace analysis

Simulation of Cu Back Contact Artifact

Inactive silicon region required to absorb copper back-contact fluorescence

Cd-109 source with and without intervening 0.5 mm of inactive silicon, which absorbs any contact fluorescence

Cu peaks can interfere with trace analysis
Modeling Charge Trapping Artifact

Defects in silicon crystal can cause charge trapping and spurious artifact peaks

“Ghost peaks” simulated with 100-micron cubic void 1000 microns below surface & 100 microns from center

Defects modeled at constant depth give fixed energy-loss “Ghost Peaks”

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Spectrum Simulations for 3 Windows & Windowless

0-10 keV Flat Top Spectra

Ni-L3 edge

3mm Si(LI) Detector with 10 nm Ni front contact

Shows good agreement with transmission curves, except for Ni contact edge, plus Gaussian spreading and Poisson noise

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Comparison of Three Different Contact Materials

Al & Ni are very similar, but lower background than Au, with no fluorescence.

More Detail of Fe-55 Spectrum with Ni Contact

Note: photoelectron shelf starts at 1.75 keV & Auger at 4.2 keV.
Fe-55 Spectrum with Ni Contact - Linear Scale

Note: photoelectron shelf starts at 1.75 keV & Auger at 4.2 keV

Modeling 200 nm Al window coating step in background
X-Tracker vs. analytical model with “flat” spectrum source from 0 to 5 keV

Inaccurate background modeling produces Al artifact “peak”
1 Micron Carbon Window Spectra
X-Tracker modeling with "flat" spectrum source from 0 to 1 keV

0-1 keV Flat Source with 1 micron Carbon Window

Counts

Energy (keV)

0.00 0.20 0.40 0.60 0.80 1.00

0-1 keV spectrum windowless
0-1 keV with 1 micron carbon window

1 um carbon window edge

"Normal" background fit
C-K Gaussian fit to net spectrum

Background fit start at 185 eV
Background fit start at 185 eV plus 1 micron C window
Real Ni Standard Spectrum with Carbon Peak
Incorrect Analytical Background Model gives Too Much Carbon in ZAF Analysis

<table>
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<tr>
<th>Elmt</th>
<th>Line</th>
<th>Intensity (c/s)</th>
<th>Conc (wt%)</th>
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<tr>
<td>C</td>
<td>Ka</td>
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<td>2.564</td>
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<tr>
<td>O</td>
<td>Ka</td>
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<tr>
<td>Mn</td>
<td>Ka</td>
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<td>1.086</td>
</tr>
<tr>
<td>Fe</td>
<td>Ka</td>
<td>19.60</td>
<td>1.543</td>
</tr>
<tr>
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<td>Ka</td>
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</tr>
<tr>
<td>Cu</td>
<td>Ka</td>
<td>148.47</td>
<td>31.615</td>
</tr>
</tbody>
</table>

Background fit w/o Carbon Layer
Carbon peak is over estimated

Background fit with Carbon
Background removed – No "peak"

Carbon Spectra under Various Conditions

Carbon Spectra at Different Peaking Times

Counts

Energy (keV)

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Carbon Peak Spectra Simulations with X-Tracker

Peak Shapes Qualitatively Model Experiment
Probably Not True Reason for Peak Distortion in this Case!

1 Micron Ice Layer Spectra
X-Tracker vs. analytical models with “flat” spectrum from 0 to 5 keV

(1) 0-5 keV Flat Source with 1 Micron Ice Layer
(2) “Normal” background fit without Ice Layer included
(3) O-K Gaussian fit to net spectrum from (2)
(4) “Good” background fit using Ice Layer Model

Backgrounds & Peak Models Generated Analytically
Compare Real to Simulated 1% Mg-99% Al Spectra

X-Tracker Modeling gives Mathematical fit - Not necessarily correct Physics!

Artificial modeling of Mg-Al peaks gives approx. fit to real spectrum

Mg-Al Spectrum Processing

X-Tracker modeling real spectrum with severe low-energy tailing on Al peak

Inaccurate peak modeling produces high Mg “peak” intensities
Comparing Real & Simulated Fe-55 Spectra

- Red bars: Experimental Fe-55 spectrum
- Black line: Simulated X-Tracker spectrum

Zero strob noise peaks
Step at 1.75 keV
Al Kα1, Al Kα2
Ga Kα1, Ga Kα2
Si Kα1
Ge Kα1, Ge Kα2
Ca Kα1
Mn-K Escape Peaks
Step at 1.75 keV
Mn Kα1
Mn Kα2
Radiative K-LL Auger Peaks?

Counts vs. Energy (keV)

Comparing Real & Simulated Cd-109 Spectra

- Red: Real Cd-109 spectrum
- Blue: Simulated Cd-109 spectrum

Low & high ends match, but background is 5-10x higher in real spectrum
Monochromatic 1.8 keV spectrum

Comparison of Monochromatic Source Spectra with Simulation

Counts

Energy (keV)

Monochromatic 3 keV spectrum

Comparison of Monochromatic Source Spectra with Simulation

Counts

Energy (keV)

Spectrum courtesy of B. Beckhoff, PTB
Monochromatic 6 keV spectrum

Comparison of Monochromatic Source Spectra with Simulations

Monochromatic 10 keV spectrum

Comparison of Monochromatic Source Spectra and Simulation
Conclusions and Future

- Detector modeling can predict or explain many spectral features & artifacts.
- Understanding these effects can improve the quality of Standardless Analysis.
- Combining Monte-Carlo and Analytical models yields advantages.
- More sophisticated modeling could predict detector responses before design is complete.
- Extend model to other detector types (SDD, CCD, etc.) and higher energies.

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