ORIGINAL PAPER





Simulating electron-excited energy dispersive X-ray spectra with the NIST DTSA-II open-source software platform

Dale E. Newbury¹ · Nicholas W. M. Ritchie¹

Received: 18 May 2022 / Accepted: 9 June 2022

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Abstract

NIST DTSA-II is a free, open access, and fully-documented comprehensive software platform for electron-excited X-ray microanalysis with energy dispersive spectrometry (EDS), including tools for quantification, measurement optimization, and spectrum simulation. EDS simulation utilizes a Monte Carlo electron trajectory simulation that includes characteristic and continuum X-ray generation, self-absorption, EDS window absorption, and energy-to-charge conversion leading to peak broadening. Spectra are simulated on an absolute basis considering electron dose and spectrometer parameters. Simulated and measured spectra agree within $\pm 25\%$ relative for K-shell and L-shell characteristic X-ray peaks from 1 to 11 keV, while the predicted M-shell intensity was found to exceed the measured value by a factor of 1.4–2.2 from 1 to 3 keV. The X-ray continuum (bremsstrahlung) intensity agreed within $\pm 10\%$ over the photon energy range from 1 to 10 keV for elements from boron to bismuth. Simulated spectra can be used to develop analytical strategy, such as assessing detection of trace constituents.

Introduction

Electron-excited X-ray microanalysis with energy dispersive spectrometry (EDS) is a widely used technique for quantitative elemental characterization at the micrometer to nanometer spatial scale [1]. Quantitative analysis proceeds by first extracting the characteristic X-ray intensities for each element from the X-ray continuum (bremsstrahlung) background and from any contributions from peaks of similar energy arising from other elements. The intensity for each element in the unknown is ratioed (forming the "k-ratio") to the intensity measured for that element in a standard, which may be a pure element or a stoichiometric compound for those elements that are reactive or are not solid or stable in a vacuum under electron bombardment, e.g., MgO, CaF₂, KCl, etc., with all measurements performed at the same beam energy, EDS parameters, and known dose. Commercial software supports the collection, interpretation, and quantification of EDS spectra. However, commercial software is often considered company proprietary and not available without a license, and thus cannot satisfy the requirement for publication in journals that demand open

access to experimental data such as EDS spectra and the software used to process those spectra to produce the results to be published. In response to this need, NIST has developed "DTSA-II" as an open access, fully-documented, and freely available comprehensive software platform for EDS quantification, measurement optimization, and spectrum simulation [2]. As a quantification tool, DTSA-II has been widely tested, including for challenging analytical situations involving severe peak interference, low atomic number elements, trace constituents, and low beam energy analysis [3–7].

DTSA-II includes an EDS simulation function based upon a Monte Carlo electron trajectory simulation. The trajectory of a beam electron in the target is followed incrementally with a step length determined by the elastic scattering cross-section, and with elastic scattering angles statistically selected with appropriate weighting. Energy loss along each segment of the trajectory due to inelastic scattering is calculated from the continuous energy loss approximation. At any elastic scattering location, the position coordinates $\{x, y, z\}$ and the velocity components $\{v_x,v_v,v_z\}$ of the electron are known as well as the remaining kinetic energy E_i . Comparison of the position coordinates to the surface(s) of the target enables determination of backscattering events, and progressive energy loss sets the ultimate travel within the target. For EDS spectrum simulation, the probabilities of characteristic and continuum (bremsstrahlung) X-ray production along the trajectory segment are calculated



Dale E. Newbury dale.newbury@nist.gov

¹ National Institute of Standards and Technology, Gaithersburg, MD 20899, USA

and then subjected to absorption along the path to the detector to yield the contribution to the emitted spectrum [8–10]. DTSA-II contains several specimen geometry "set pieces" for structured bulk and particle targets where the user can specify target composition(s) and feature dimensions as well as instrument parameters (e.g., beam energy, dose, and EDS parameters). Structured bulk" targets include: (1) a film on a bulk substrate; (2) a layer of defined thickness buried at a specified depth; (3) a rectangular prism intersecting the surface; and (4) the electron beam of defined size placed at a specified distance from a vertical interface between two materials. The user can also modify the embedded Monte Carlo code to simulate other target geometries of interest.

EDS spectrum simulation can provide the microanalyst with a critical tool for developing appropriate analytical strategy when dealing with a new complex composition. It is generally unlikely that a known reference material of the appropriate multi-element composition that is also homogeneous on microscopic scale will be available to evaluate the EDS measurement situation. DTSA-II can provide simulated spectra to fill this need, enabling "desktop experiments" to aid in experimental design. With DTSA-II, the X-ray intensity is calculated on an absolute basis so that the simulated EDS spectrum can be directly compared to the measured spectrum based upon the user's specification of the electron dose (beam current \times EDS live time) and the EDS parameters (solid angle and isolation window materials). In this report examples of simulated spectra are compared to measured spectra.

An initial version of EDS simulation was included in the original version of DTSA-II [8]. Enhancements that have been subsequently made to DTSA-II include:

- Algorithms:
 - Bote-Salvat ionization cross-sections [11]
 - Chantler mass absorption coefficients (MACs) enhanced with Sabattuci MACs (Z>92) [12, 13, 14]
 - Relaxation rates from Cullen's RELAX program [15]
- Elements from Z=93 to Z=99 [16]
- New geometries including "buried layers"
- Simulation of variable pressure mode
- Enhanced output
 - Output of the emitted spectrum intensity
 - Fractional Emission Depths and Volumes
- Enhanced Monte Carlo scripting in mcSimulate3.py
 - ZAF calculation
 - Energy deposition
 - Many different sample models including horizontal and vertical layers, moguls, sphere beds, rough surfaces, scratched surfaces, rippled surfaces, two particles on a substrate and others.
 - Additional output modes including $\varphi(\rho z)$, voxelated, continuum images, backscatter depth and others.

Materials and methods

Materials examined in this study included pure elements and stoichiometric compounds as well as prepared polished samples procured from commercial vendors. Multi-constituent materials included NIST (https://www.nist.gov/srm) Standard Reference Materials (SRM) SRM 481 (Gold-Silver alloys), SRM 482 (Gold-Copper alloys), SRM 470 (Mineral Glasses), and SRMs 1871, 1872, 1873, and 1875 (Microanalysis Glasses), all of which were specifically developed to achieve microscopic homogeneity for use by the microanalysis community. These SRMs fulfill the definition of a Certified Reference Material (CRM), which is a reference material characterized by a metrologically valid procedure for one or more specified properties, accompanied by a certificate that provides the value of the specified property, its associated uncertainty, and a statement of metrological traceability [17]. Additionally, Reference Materials (RM), which are defined as a material, sufficiently homogeneous and stable with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process, were used, including other microanalysis glasses under development.

Electron-excited X-ray spectrometry was performed using the JEOL 8500F thermal field emission electron probe microanalyzer. Over the period of these measurements, two different EDS systems were used: (1) a Bruker QUAD system with four 10 mm² silicon drift detectors at a 72 mm specimen-to-detector distance and (2) a Bruker Quantax XFlash single 30 mm² silicon drift detector at a 60 mm specimen-to-detector distance.

Results

Comparing Simulated and Measured Absolute Intensity EDS Spectra

EDS spectra were collected using Bruker Esprit software and exported in the ISO/EMSA standard [18] spectral format for subsequent processing with the NIST DTSA-II software for comparison to simulated spectra [2]. For each measurement condition in this study, a sufficient electron dose was utilized so that the total spectrum count, integrated from a threshold of 0.1 keV to the incident beam energy, E_0 , generally exceeded 2.5 million counts.

EDS spectra were simulated with the DTSA-II Monte Carlo procedure for the bulk, homogeneous material case [2]. At least 6000 trajectories were calculated for each condition simulated in this study. The DTSA-II simulation for $SrTiO_3$ with 0.001 Ca required 450 s to complete 6000 trajectories when performed on an OptiPlex 7060 pc platform, including calculation of primary characteristic and continuum X-rays as well as characteristic- and continuum-induced secondary fluorescence. Simulated spectra were then compared to measured spectra using the functions within DTSA-II that integrate intensities over user-defined regions-of-interest, including the "peak background" tool which measures the characteristic X-ray peak intensity above the bremsstrahlung background. Figure 1 shows the spectrum simulated for SrTiO₃ at a beam energy $E_0 = 20$ keV as-emitted from the target following absorption within the interaction volume (upper plot, red trace). The characteristic X-ray peaks are plotted as a single channel 5 eV in width, which is similar to the natural peak width. The X-ray spectrum after absorption by the spectrometer isolation window and after the energy-to-charge conversion process of the EDS (upper plot, blue trace) reveals the substantial broadening of the characteristic peaks, the principal EDS artifact. For the Ti K-L_{2,3} the full peak width at half peak intensity (FWHM) is 115 eV for an EDS with resolution specified as 130 eV FWHM at Mn K-L_{2.3}. In the lower plot, the simulated spectrum (blue trace) for SrTiO₃ is overlaid for comparison to the spectrum measured (red trace) for the specified dose and EDS parameters. Numerical comparisons between simulated (Monte Carlo calculation) and measured (experimental) absolute intensities for various features are shown as the ratio "MC/EXP", e.g., Ti K-L_{2.3} (MC/EXP = 1.02); Sr L-family (1.05); O K-L (1.30). The continuum background at various energies varies from MC/



Fig.1 (Upper plot) Simulated as-emitted spectrum (red trace) of $SrTiO_3$ at $E_0 = 20$ keV and simulated as-detected spectrum (blue trace); note peak broadening as a result of energy-to-charge conver-

sion. (Lower plot) Overlay of simulated (blue) and measured (red) EDS spectra of SrTiO₃ at $E_0 = 20$ keV with selected numerical comparison of characteristic X-ray peaks and continuum energy bands



EXP = 0.915 for the band 1.0–1.2 keV to MC/EXP = 0.999 for the band 7.0–7.2 keV.

Figure 2 shows the comparison of simulated and measured spectra for a spectrum containing K-, L-, and Mfamily characteristic X-ray peaks: NIST Standard Reference Material (SRM) 482 Au–Cu alloys: (40Au-60Cu) at $E_0 = 20$ keV. Comparison points include Cu K-L_{2,3} (MC/ EXP = 1.04); Cu L-family (0.745); Au L₃-M_{4,5} (1.10); and Au M-family (1.45). The correspondence for the continuum background over various energy bands is: 1.1–1.3 keV (MC/ EXP = 0.962); 4–4.2 keV (1.04); 6.0–6.2 keV (1.06); and 10–10.2 keV (1.04). Although the simulated and measured absolute characteristic X-ray intensities show significant deviation for the Cu L-family and the Au M-family, the ratio of k-ratios, k-simulated/k-measured, is 0.965 for the Cu L-family and 1.004 for the Au M-family.

Extensive comparisons of simulated and measured spectra at $E_0 = 20$ keV of pure elements, stoichiometric compounds, and reference materials certified for homogeneity at the microscopic scale revealed agreement within $\pm 25\%$ relative (i.e., MC/EXP ranged from 0.75 to 1.25) for K-shell and L-shell characteristic X-ray peaks in the photon energy range 1–11 keV [19]. The predicted M-shell intensity was found to exceed the measured value by a factor of 1.4–2.2 in the range 1–3 keV. The X-ray continuum (bremsstrahlung) intensity was found to agree within $\pm 10\%$ over the photon energy range from 1 to 10 keV for elements from boron to bismuth.

Discussion

Within the limits of accuracy revealed by the extensive comparison of simulated and measured EDS spectra, DTSA-II can be used to simulate EDS spectra for target composition(s) and measurement conditions of interest to the analyst. As an example, consider the problem of measuring a trace element, arbitrarily defined as a constituent present at a mass concentration below 0.01 (1 wt%), in a matrix of interest. Figure 3 (upper plot, red trace) shows a simulated spectrum for SrTiO₃ with 0.001 (0.1 wt%) Ca at $E_0 = 20$ keV for measurement conditions (dose and EDS solid angle) that yielded 13.8 million counts integrated from 0.1 to 20 keV. The Ca K-L_{2,3} peak is visible by inspection. Reducing the mass concentration of Ca by a factor of 5 to 0.0002 (0.02 wt%), as shown in Fig. 3 (upper plot, blue trace), yields a Ca K- $L_{2,3}$ peak that is effectively lost in the statistical noise of the continuum and not likely to be detected in a visual inspection. The lower plot in Fig. 3 shows the effect on the visibility of the peak for 0.001 Ca by changing the dose by factors of 0.1 (yielding 1.38 million counts) and 100 (138 million counts). Although trace peaks may be lost to visual inspection in the statistical noise of the continuum, peak fitting with DTSA-II can often quantitatively recover trace constituents that produce low peak-to-background signals if adequate spectral counts are accumulated. The effectiveness



Fig.2 (Upper plot)) Comparison of the simulated and measured EDS spectra of SRM 482: 40Au-60Cu alloy at $E_0 = 20$ keV with the intensity ratio Monte Carlo/Experimental ("MC/EXP") shown for the

principal characteristic X-ray peaks; (Lower plot) expanded intensity scale showing comparison MC/EXP of the bremsstrahlung X-ray intensity in selected energy regions



Fig. 3 (Upper plot) Simulated spectra at E0=20 keV and at a dose that produces 13.8 million counts integrated from 0.1 to 20 keV for SrTiO₃ with trace Ca: 0.001 mass concentration (0.1 wt%) (red trace) and 0.0002 mass concentration (0.02 wt%) (blue trace); (lower plot)

of this procedure can be tested with simulated spectra. Appropriate pure element and stoichiometric compound "standards" are simulated with DTSA-II, e.g., O (MgO); Ca (CaF₂); Ti; and Sr (SrF₂) for Ca in SrTiO₃, and then used with the quantitative analysis module of DTSA-II exactly as would be the case for measured spectra of the unknown and standards. Results for quantifying trace Ca in are presented in Table 1. When simulating spectra with DTSA-II, the user has the option to determine a specified number of statistically different spectra at the nominal dose, thus simulating the effect of making replicate measurements. The mean Ca concentration of 10 replicates is

simulated spectra for SrTiO₃ with 0.001 Ca at two different doses that produce 1.38 million counts (red) and 138 million counts (blue) integrated from 0.1 to 20 keV

presented and the relative deviation from expected value (RDEV) is determined:

 $RDEV = [(analyzed value - true value)/true value] \times 100\%$

where the "true value" in this case is the Ca concentration that has been simulated. The effect of the counting statistics on the analysis is revealed by the range of values, given as maximum and minimum, and the standard deviation of the distribution of the replicates. For Ca at a concentration of 0.001 mass fraction (0.1 wt%), the standard deviation for 10

Table 1 Results of DTSA-II quantitative analysis of simulated spectra of $SrTiO_3$ with trace Ca using simulated standards (MgO, CaF_2 , Ti and SrF_2)

Ca conc. simulated	0.1–20 keV spectrum integral (counts)	Mean conc (10 replicates)	RDEV	Maximum conc in 10 replicates	Minimum conc in 10 replicates	σ (10 replicates)	$\sigma_{relative}$ (10 replicates)
0.001	1.38 million	0.00105	5%	0.00139	0.000907	0.000141	13.4%
0.001	13.8 million	0.000988	-1.2%	0.00106	0.000892	0.000055	5.6%
0.001	138 million	0.00102	2%	0.00104	0.000995	0.000014	1.4%
0.0002	1.38 million	0.000210	5%	0.000467	0.0000473	0.000134	64%
0.0002	13.8 million	0.000177	-11%	0.000231	0.000105	0.0000438	25%
0.0002	138 million	0.000192	-4%	0.000213	0.000172	0.0000127	6.6%
Blank	138 million	0.000015	NA	0.000026	0.000002	0.0000068	45%



replicates is 13.4% and the range of values, maximum-tominimum, spans a factor of 1.5. For Ca at a concentration of 0.0002 mass fraction (0.02 wt) at the lowest dose, the relative standard deviation is 64% and the range of values, maximum-to-minimum, spans a factor of 10, indicating the need for much higher counts to achieve a robust result. At the highest dose, the relative standard deviation is reduced to 6.6% and range of maximum-to-minimum values is reduced to 1.2.

Simulated EDS spectra can be used to predict the accuracy of analysis when severe peak overlaps occur, such as the mutual interference of the S K-family, Mo L-family, and Pb M-family at 2.3 keV or the Ti K-family and the Ba L-family at 4.5 keV. Mixtures involving various relative concentration ratios of the elements of interest can be simulated and then "solved" by applying DTSA-II quantification with appropriate simulated standards for peak fitting. Simulated EDS spectra can also be used in comparison to measured spectra to examine artifacts in the EDS detection process. The only artifact included in the DTSA-II simulation is peak broadening due to the photon energyto-charge conversion process. By overlaying simulated and measured spectra, artifacts such as incomplete charge collection, manifested as a distortion on the low energy side of a peak, and coincidence peaks can be detected. Simulate spectra can also be used to assess the capability of peak fitting to deal with interfering peaks, especially when one of the mutually interfering constituents is present at a much lower concentration.

While the accuracy of the DTSA-II simulation is adequate for the absolute intensities of K- and L-shell X-rays and continuum X-rays, the M-shell intensity is consistently overestimated by a significant factor. The EDS spectrum simulation is fundamentally based on an approach in which the atoms in a material can be treated as independent non-interacting entities. This approximation works best for the ionization of tightly bound inner shells which are filled by electrons from other tightly bound shells. M-shells are less tightly bound than K- or L-shells and most ionizations are filled by even less tightly bound N-shell electrons. This means that M-family X-rays are less well modeled with an atomistic approach. Furthermore, there are five M-shells compared to three L-shells and one K-shell. Ionizations in any of these five shells can lead to many possible X-rays depending upon which outer shell fills the ionization. This leads to many different lines with a variety of line intensities dependent on ionization cross-section and relaxation rates. Data on the relaxation rates is not as accurate as for K-shell transitions. Furthermore, M-family lines tend to fall in an energy range which is naturally hard to model because of uncertainties in mass-absorption coefficients, fluorescence yields and detector efficiency. The net result is larger model uncertainties which result in larger model errors for M-family lines.

There are two approaches that could improve the accuracy of the simulation for M-shell and N-shell characteristic X-rays, which are of increasing importance because of the improved low photon energy (< 1 keV) performance of EDS and the rise of interest in low beam energy analysis ($E_0 \leq 5$ keV) enabled by improved SEM performance. First, better first-principle physical models will be incorporated in DTSA-II as they become available. Second, a semi-empirical approach could be used. We could measure many of the required parameters directly from measured X-ray spectra and adapt these measured values to alternative samples and measurement conditions. This is similar to the way some EDS vendors approach "standardless analysis". Many parameters in the model are independent of the incident electron beam energy. We could measure parameters like relative weights of lines, i.e., the X-ray intensity on a sub-shell basis, and use these to calibrate a locally trained model. This model could be adapted to detectors with different performance characteristics albeit with loss of accuracy. We are pursuing this approach in on-going research efforts.

Summary

The DTSA-II simulation function can predict absolute intensities of EDS spectra within $\pm 25\%$ relative for K-shell and L-shell characteristic X-ray peaks in the photon energy range 1–11 keV, while the predicted M-shell intensity was found to exceed the measured value by a factor of 1.4–2.2 in the range 1–3 keV. The X-ray continuum (bremsstrahlung) intensity was found to agree within $\pm 10\%$ over the photon energy range from 1 to 10 keV for elements from boron to bismuth. Simulated EDS spectra provide the analyst with the basis for developing analytical strategy when dealing with difficult measurement problems, such as estimating the dose needed to detect and measure trace constituents or estimating analytical accuracy when severe peak overlap occurs.

Acknowledgements This work was conducted by the authors as part of their official duties as employees of the National Institute of Standards and Technology of the US. Department of Commerce. Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Data availability Data available at: https://datapub.nist.gov/od/id/mds2-2608.

Code availability NIST DTSA-II software available at: https://www.nist.gov/services-resources/software/nist-dtsa-ii.

Declarations

Conflict of interest The authors certify that they have no conflicts of interest based on any aspect of this work.

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