

Simulation of Electron Probe Microanalysis for the Purposes of Automated Material Identification—Initial Evaluation of Available Monte Carlo Tools

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INTRODUCTION

Analysis of small samples and material surfaces has progressed rapidly with the development of the scanning electron microscope (SEM) over the past half-century. SEM can produce images of surface features and can determine heterogeneous phases and other morphological information at much higher resolution than traditional (optical) microscopes. The X-rays given off by the interaction of the electron beam with a sample provide additional information to characterize the sample by identification of the electron transitions occurring in it. This last feature is often of secondary importance to SEM spectroscopists but forms the basis for the work under this project.

Automation of the SEM process allows generation of as many as 1,000 particle records per hour during unattended, automated runs. However, interpretation of the images, as well as verification of fidelity, must still be done individually by researchers trained and equipped to make such interpretations. Furthermore, a myriad of adjustments and exceptions must be noted that require separate calculations using empirical or semi-empirical models. Thus, the automation of imaging has not resulted in the automation of image analysis or X-ray spectrum analysis.

Measuring the chemical composition and crystallographic phase of small samples using X-rays in SEM instruments is termed electron probe microanalysis (EPMA). EPMA is performed via either wavelength-dispersive X-ray spectroscopy, where X-rays of selected wavelengths are counted, or energy-dispersive X-ray spectroscopy, where X-rays of all wavelengths are counted. By focusing an electron beam to a diameter of a few nanometers and measuring fluorescent X-rays produced by the sample when it is struck by electrons, an analyst can determine which elements are present (qualitative analysis) with a spatial resolution well below 1 μm . Depending on the electron beam energy used, most of the elements in the periodic table can be reliably detected this way. The problem of accurately measuring the relative elemental abundances (quantitative analysis) is much harder and has only been conducted acceptably for cases in which the sample is flat, highly polished, perpendicular relative to the beam, and chemically uniform. When these conditions are met, the chemical composition can be measured with great precision. However, we should note that most real-world samples do not conform to these restrictions.

The purpose of this ongoing project is to exploit the Monte Carlo (MC) method to simulate X-ray spectra of small samples; such simulations will enable rapid determination of sample properties, including both qualitative and quantitative chemical analysis. The underlying physics of this signal-generation process is reasonably well understood, and MC codes have been used to predict both the electron-scattering distribution and emitted X-rays. That is, for samples of known composition and simple geometry, code inputs can be devised to reproduce the X-ray spectra that are observed.

In this work, we endeavor to advance such simulation capability to evaluate progressively more complex samples and to provide rapid and automated analysis. To achieve these goals, we have focused our initial efforts on evaluation of existing MC codes. We discuss several existing codes, in the following sections, paying particular attention to their suitability for handling the problems that we seek to investigate. Following this discussion is an outline of the path forward for this research and its intended outcome.

EXISTING MONTE CARLO CODES

Four different codes have been investigated for performing this work: DTSA-II [1], ITS6 [2], MCNP [3], and PENELOPE [4,5]. Another coupled electron/photon transport code, EGS5 [6], was not evaluated directly for this work, but its published capabilities were compared with those of the other four transport codes evaluated. Below is a brief overview of some of the strengths and weaknesses of these codes, as they pertain to this work.

DTSA-II, developed at the National Institute of Standards and Technology (NIST), has an easy-to-use graphical user interface and easily simulates detector response. It is written in Java and has no adjoint or parallel computation ability or documented variance-reduction methods. The developers have significant experience performing EPMA quantitative analysis that has led to many unique features being incorporated into the code such as reading spectral files produced by most SEMs and the simulation of detector response.

The ITS6 code was developed at Sandia National Laboratory. The major attractions to ITS6 are its ability to perform coupled electron/photon adjoint calculations and its parallel capability. However, its interaction data are not up to par when simulations of M and N shell X-rays are needed.

The electron transport capability in MCNP, developed at Los Alamos National Laboratory, is based on early versions of ITS. However, with the release of MCNP6, this capability has been significantly improved beyond that of ITS6. Attractions to MCNP6 are these improvements in modeling X-ray production, particularly for the L and M shells, and its parallel capability. However, the X-rays from the N shell are not modeled; only the primary X-rays produced by each shell are modeled (e.g. $M_{\alpha 1}$ and $M_{\alpha 2}$). Additional improvements are the ability to transition to single event transport of electrons from the traditional condensed history technique at a single user-specified energy and the ability to transport photons and electrons below 1 keV. The capabilities of EGS5 are very similar to that of MCNP5 (not MCNP6), so it has not been as thoroughly investigated as the other codes mentioned.

The PENELOPE code was developed at the University of Barcelona by physicists interested in both high- and low-energy physics applications. This code seems to contain the most comprehensive and up-to-date physics models of all the codes assessed relative to electron transport. The developers have provided a package specifically tailored to SEM simulations (PENEPMA), which includes certain helpful features, such as a routine to perform Gaussian energy broadening of the calculated line spectrum in a manner similar to that of an actual silicon drift detector (SDD). Besides the superior X-ray fluorescence production data, PENELOPE has two advantages over the other transport codes considered. First, it has implemented the forced collisions variance reduction technique for electrons and, more specifically, for interactions that produce fluorescent X-rays. MCNP6 and ITS6 provide the option to increase the interaction cross section or fluorescence yield but not the option to force these interactions in thin materials that are typical of samples analyzed in an SEM. Second, PENELOPE uses a combination of condensed history and single event transport that balances accuracy and speed. Two drawbacks are that (1) normal use requires some additional programming by the user if anything beyond simple sources or tallies are required and (2) PENELOPE is not capable of parallel computation.

Based on the facts presented in this brief discussion, MCNP6 and PENELOPE were selected as the two leading contenders to perform the type of computational EPMA needed for this project. The choices are primarily based on the level of detail in the physics models, variance reduction techniques, and parallel processing capability.

COMPARISON OF COMPUTATIONAL RESULTS AND MEASUREMENT

A number of simulations have been performed to compare these transport codes, and the results produced

by each code have been compared with each other and to measurements. The results of one typical comparison will be presented next. In this comparison, a 25 keV electron beam is directed at a 2 μm thick sample of U_3O_8 , which has a density of 8.3 g/cm^3 and a radius of 5.08 cm. The photons that leave the sample in the direction opposite the electron beam are tallied on an energy group structure from 1 to 20.5 keV with 10 eV bins. The X-ray spectrum tallied by each of these codes is plotted in Fig. 1. There are two major differences between the calculated X-ray spectra. First, MCNP6 does not produce the same characteristic X-ray lines as PENELOPE. For example, around 3 keV, MCNP6 only produces two of the lines created when electrons cascade down to vacancies in the M electron shell. Second, the number of characteristic X-rays produced by MCNP6 is much smaller than the number produced by PENELOPE.

Presented in Fig. 1 is a comparison between two radiation transport codes, and clear differences are evident. To determine which one, if either, is correct, a comparison between these computational results and a measurement is required. However, before this comparison can be made, the computational results must be convolved with a detector response function to account for the Gaussian energy broadening of the photon peaks. This was accomplished via the utility provided with the PENEPMA package (for the MCNP6 and PENELOPE results). A typical energy resolution for a typical SDD detector used in EPMA is a full width at half maximum (FWHM) of 132 eV for the Mn $K_{\alpha 1}$ characteristic X-ray (~5.899 keV). The algorithm for Gaussian energy broadening provided with PENEPMA produces a FWHM of 145 eV for the Mn $K_{\alpha 1}$ characteristic X-ray. The detector responses produced from the calculated spectra in Fig. 1 are plotted in Fig. 2.

Also plotted in Fig. 2 is the measured X-ray spectrum produced by a 25 keV electron beam on a sample of U_3O_8 . The measured spectrum was normalized such that the magnitude of the largest peak ($M_{\alpha 1}$, ~3.1 keV) exactly matches the magnitude of the PENELOPE calculation because the computational results are presented on a per-source electron basis and the number of electrons used in the measurement are unknown.

The results in Fig. 2 indicate that PENELOPE is performing much better than MCNP6 when compared to experiment. However, there are clearly differences between the PENELOPE results and the measurement that need to be resolved. More accurate details about the experimental measurement, which was performed by NIST, have been requested. If significant differences exist between the PENELOPE and MCNP6 model and the actual experimental geometry, they likely will account for at least some of the differences seen in Fig. 2.

CONCLUSIONS

At this point, PENELOPE has been shown to be the best code for EPMA simulations, due primarily to its superior modeling of fluorescent X-ray production, variance reduction capabilities tailored to EPMA simulations, and the results presented in Fig. 2 (and similar results not presented here). Obviously, the differences between the PENELOPE results and the measured spectrum in Fig. 2 need to be investigated further before a quantitative statement about the bias between PENELOPE and measurement can be made.

As stated in the introduction, the purpose of this project is to exploit MC simulations of X-ray spectra to enable rapid determination of properties of small samples. This will be accomplished using inverse analysis, so the next phase of this work involves construction of algorithms for inverse analysis using MC. At this point, the leading candidate for this development is PENELOPE.

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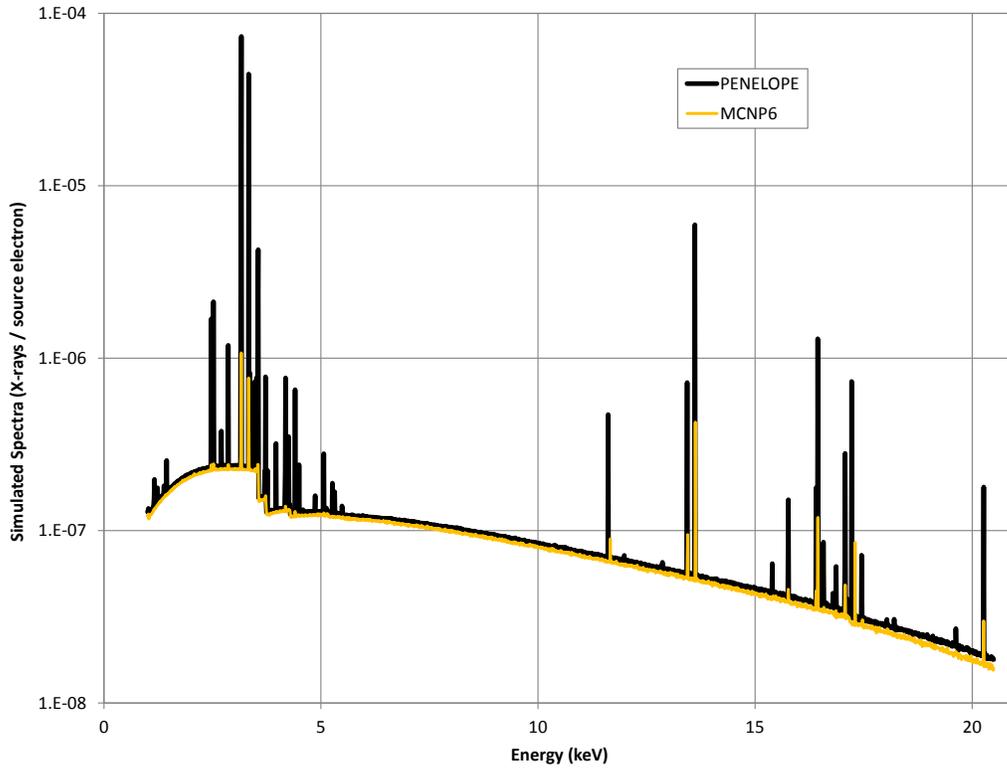


Fig. 1. U_3O_8 X-Ray Spectra Simulated by MCNP6 and PENELOPE.

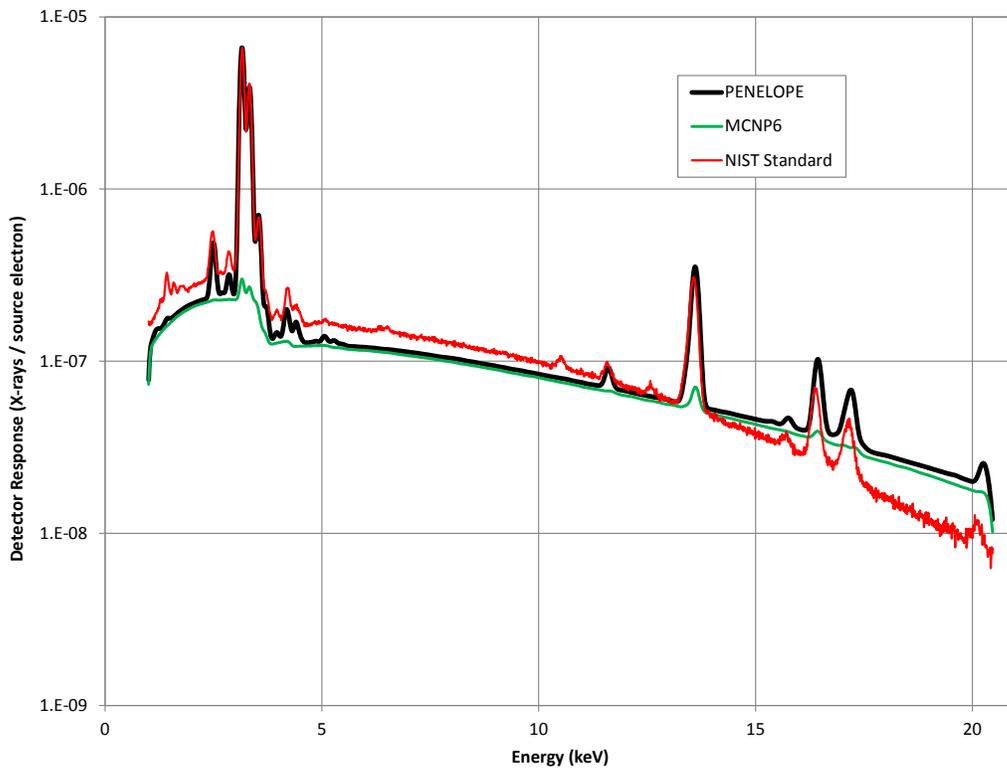


Fig. 2. U_3O_8 X-Ray Detector Response Measured by NIST and Simulated by MCNP6 and PENELOPE.