AN UPDATE TO NRLXRF AND NBSGSC

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ABSTRACT

The public-domain computer codes NRLXRF, developed at the Naval Research Laboratory (NRL), and NBSGSC, developed at the (then) National Bureau of Standards (NBS), were among the first and most important early realizations of the fundamental parameters (FP) method of analyzing X-ray fluorescence (XRF) spectra. However, it has been 20 years since NRLXRF was updated and more than 10 years since NBSGSC was released. We are attempting to revise and update these codes and combine them into a single, modular package to meet our respective needs for fundamental parameter calculations. The update, as presently planned, will comprise three components. The first is to incorporate the most recently available values for the parameters themselves. The main update will be to the X-ray absorption cross sections using the values of Hubbell and Seltzer [1] at high energies and the values of Henke, Gullikson, and Davis [2] at low energies. Other parameters will be updated as much as possible. The second component is to incorporate improvements in the calculation of excitation spectra from X-ray tubes. Finally, we plan to adapt the codes for multilayer samples using the work of De Boer [3].

INTRODUCTION

Both authors are active in the use of X-ray Fluorescence (XRF) for a variety of analytical purposes including routine analytical work, new instrument design, and method development. For these purposes, the so-called fundamental parameter (FP) method of analysis is often the preferred method. This was the motivation for the development of the computer codes NRLXRF and NBSGSC during the previous decades. Our current needs require continued development and improvement of this method. For analytical work, the use of FP methods may provide more accurate results over a wider range of compositions and matrices. New instrument design requires the predictive capabilities of FP to predict intensities in the early design phase before constructing hardware. In addition, new instruments, such as environmental sensors, work in a wide variety of uncontrolled conditions, making FP the method of choice for analysis of spectra.

We have undertaken to significantly upgrade the fundamental parameters portions of these older computer codes and to take advantage of the increased accuracy of the parameters available. The accuracy of the parameters is a significant limitation on the accuracy of FP calculations. In addition, improvements have been made in the calculation of electron-excited X-ray spectra such as those from X-ray tubes typically used to excite XRF spectra. Finally, extensions of the Sherman equations for application to multilayer samples are now available in analytical form. These three improvements comprise the three stages of the project to update the FP codes at NRL and NIST: parameters, X-ray tube spectra, and the reformulated Sherman equations.
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GOALS AND CHOICES

The goals for the project were to produce modular, portable, and maintainable computer codes, to take advantage of updated atomic parameters, and to include an improved calculation of the spectrum from X-ray tubes. The new codes are written in C++ with object-oriented design wherever possible and the ultimate addition of a graphical user interface in mind. The codes are written in a manner independent of machine and operating system so they can be easily adapted to any host machine. They are also written in modular fashion to be adaptable to the variety of tasks and instruments used and developed by the authors.

To update the atomic parameters, the so-called “fundamental parameters”, only values available in the literature were used. No additional measurements were made as part of this work. The calculation of spectra from X-ray tubes was based on recent work in electron microprobe analysis. Advantage was taken of improvements in the methods and accuracy over the last decade. The FP algorithm itself was taken from NRLXRF, which is fast and versatile. It handles mixtures of compounds and particulate samples rather than simple elemental compositions and can be extended to multilayer samples by incorporating the analytical solutions to Sherman’s equations derived by De Boer [3]. Finally, the newer and more complete IUPAC notation is used for X-ray emission lines. Siegbahn notation is included as well, since it is still more familiar and convenient for most spectroscopists.

PARAMETER DATABASE

The fundamental parameters method relies on the use of equations that express the intensity of X-ray emission in terms of parameters that are independent of a particular sample. These parameters fall into two categories: instrument parameters and atomic parameters. Instrument parameters can be measured using any of several methods or are known a priori, e.g., detector angle. The remaining parameters are associated with the elements of which the sample is composed and describe the X-ray properties of these elements. The properties of the elements together with the elemental composition of the sample can then be used to compute the expected X-ray emission of the sample. The computations can be iterated to determine the composition of an unknown sample.

The accuracy of the atomic parameters is crucial to the accuracy of the FP method. In particular, the X-ray absorption cross sections contribute directly to the quality of the results. Other parameters, e.g., Coster-Kronig transition probabilities, produce smaller effects and high accuracy is not required. However, the better the parameters, the more useful the calculations will be and the greater the accuracy that can be achieved.

The authors undertook to produce a consistent set of parameters optimized for FP calculations using values available in the literature. The required parameters are given in Table 1. A detailed description of the database containing these parameters is being published elsewhere [4]. The most important parameters are the X-ray absorption and scattering cross sections. The values of Berger and Hubbell [1] were used above 1 keV since they were assembled using the NIST database of experimental measurements. These values are not available below 1 keV, so they were extended using the optical constants of Henke, Gullikson, and Davis [2], which are
believed to be the most complete and recent values at that low energy range. The values for f2, the anomalous term in the atomic scattering factor, were converted to absorption cross sections using the method given by the authors and smoothly joined to the Berger and Hubbell photoabsorption values at 1 keV. The values for coherent and incoherent scattering from Berger and Hubbell were extrapolated using linear fits to the data just above 1 keV.

Table 1. Parameters required for fundamental parameters calculation of XRF spectra.
Parameters are required for each element in any sample under investigation.

<table>
<thead>
<tr>
<th>Atomic number</th>
<th>Photoabsorption cross sections (versus energy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic weight</td>
<td>Coherent scattering cross section (versus energy)</td>
</tr>
<tr>
<td>Pure element density</td>
<td>Incoherent scattering cross section (versus energy)</td>
</tr>
<tr>
<td>X-ray absorption edges</td>
<td>Coster-Kronig transition probabilities</td>
</tr>
<tr>
<td>Energy</td>
<td>X-ray emission lines</td>
</tr>
<tr>
<td>Jump ratio</td>
<td>Energy</td>
</tr>
<tr>
<td>Fluorescence yield</td>
<td>Relative intensity</td>
</tr>
</tbody>
</table>

The remaining parameters listed in Table 1 were obtained from the literature, using what were the authors’ (admittedly subjective) judgements in the selection. Where possible, experimental data was used as the basis for evaluation. A complete list of the sources for the data and the manipulations performed, if any, are given in Reference 4.

X-RAY TUBE SPECTRA

Any FP calculation requires knowledge of the radiation used to excite the X-ray emission from the sample. Since X-ray tubes are usually used for this purpose, the ability to calculate the spectrum from common X-ray tubes is the starting point for a FP program. Both NRLXRF and NBSGSC contain algorithms for this purpose. The routine in NRLXRF is based on measurements of a variety of X-ray tubes and empirical fits to the interaction of electrons with the tube target [5]. The algorithm in NBSGSC is based on measurements made with electron microprobes and uses a calculation of the continuum radiation and the ratio of characteristic lines to the continuum. This algorithm has been described in detail by Pella, Feng, and Small [6] and was updated for M and L series lines [7].

Many improvements in the calculation of X-ray spectra via electron excitation have been made in recent years, motivated by the use of analytical electron microscopes. This work takes advantage of this progress to calculate the continuum and characteristic line emission from X-ray tubes for use in FP calculations. Atomic parameters from the new database compiled by the authors were used for these calculations to further improve their accuracy.

Production of continuum X-rays by incident electrons was investigated by Small et al. [8] who produced an empirical fit to the dependence on atomic number, incident electron energy (or voltage), and emitted photon energy. Their correction for photon absorption in the target is a simplified version of the Philibert model [9] given by Heinrich and Yakowitz [10]. Small et al. also give a parameterized version of the electron backscatter correction. Trincavelli, Castellano, and Riveros [11] recently published a new empirical fit to the bremsstrahlung cross section...
similar to that of Small et al. but with a new term to account for the observed behavior at low atomic number and with slightly adjusted coefficients. However, unlike Small, et al., they do not give a value for the constant necessary to convert their values to absolute cross sections. Use of the factor $3 \times 10^{-10}$ gives good agreement with measured X-ray tube spectra and with the values of Small et al. Since the cross section of Trincavelli, et al. should work better at low atomic number, it was used in place of the cross section of Small et al. for this work. All of the corrections used in this work were those given by Small, et al. as described above.

The treatment of the characteristic lines used herein is based on recent work by Armstrong, Newbury, and Carpenter [12]. They discovered that the dominant factor in determining agreement with the measurements was the form used for the ionization cross section. The forms of various other corrections produced maximum effects of less than a few percent. Their evaluation of the cross sections for K shell excitation indicates that the cross sections of Pouchou and Pichoir [13] give good agreement with measurements. The cross-section can be integrated analytically if the form of the stopping power is a polynomial in energy. The form of the stopping power chosen for this work was that of Love, Cox, and Scott [14], which contains terms in the square root and first power of energy.

RESULTS

New calculations were performed for X-ray tube geometries identical to those measured by Brown, Gilfrich, and Peckerar [15], who performed absolute intensity measurements on tungsten and chromium target X-ray tubes at 45 kV operating voltage. The results of the calculations were compared to the measurements without adjustments of any kind. However, the constant in the continuum production was chosen to agree with these measurements overall (see above). Since they were included in the parameter files distributed with NRLXRF, these measurements were available to the authors in machine-readable form and extensive comparisons could be made. Many other measurements of X-ray tube output have been performed but the results were not available in machine-readable form.

Figure 1 is a plot of the continuum from a tungsten-target X-ray tube as a function of photon energy. The outputs of NRLXRF and NBSGSC are also plotted. The version of NRLXRF used was dated August 1979 and contained all of the recommended updates as of that date. NBSGSC was version 6 with the absorption coefficients of Heinrich chosen. The values were converted to units of electron volts for the photon energy and to units of photons per keV per steradian per incident electron for all spectra. These units are the direct output of the computer codes used for the new calculation. As can be seen from Fig. 1, the results have improved with time. NRLXRF provides the worst agreement and is the oldest. NBSGSC is better and more recent. The new calculation provides even better agreement. All of the calculations have the correct overall shape, but the new calculation agrees substantially better in the change at the absorption edges, which is probably due to the improved database.
Figure 1. Plot of continuum output of tungsten-target X-ray tube. Calculations from this work, NRLXRF and NBSGSC are compared to measurements.

Comparisons of the characteristic line intensities are shown in Fig. 2. NRLXRF shows significant errors and only gives results for the L3-M5 and L2-M4 (L alpha and beta) lines of tungsten. NBSGSC provides intensities for many more lines and agrees well with the relative intensities. However, the intensities from NBSGSC had to be divided by the integral of the continuum to fit on the same plot with the other results [16]. The new calculation shows reasonable results and in particular gives better absolute intensities than the earlier algorithms.

Figure 2. Intensities of characteristic lines from a W-target X-ray tube. Comparisons as in Fig. 1.
PLANS

At the present time, the computer codes are almost ready to perform the first actual FP calculations of intensity from samples. The algorithm in NRLXRF must be converted to C++ and the output of the code verified and checked for accuracy with the new parameters. The equations can then be modified to use the forms derived by De Boer for multilayer samples. These equations are a modified version of the Sherman equation that gives the contribution of secondary fluorescence in an inhomogeneous sample consisting of layers of different composition and thickness. This form is readily adaptable to inclusion in the FP algorithm. For particulate samples, the corrections of Criss [17] will be included. Finally, a graphical user interface will be added to the program if time allows. This interface will be substantially more complex if multilayer samples must be described, since a composition and thickness for each layer must be included for a variable number of layers. Similar demands are made on the interface for particulate samples if the composition and particle size of each component can be specified separately. The program will evolve as time and effort permit and needs arise.

The results of this work, in the form of both a database and computer source code, will be made available to the public once the project is nearer completion and the necessary approvals have been obtained from the authors' institutions. It is hoped that the new codes will be used and tested under a variety of conditions and the feedback employed in future improvements.

REFERENCES

