Fundamental Parameters For Microanalysis

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In order to perform quantitative X-ray microanalysis many parameters, representing the various stages of X-ray generation and transport through the specimen at the chosen experimental conditions, must be known for all of the elements that might be encountered. Although ideally quantification is done by reference to standards so that only the functional variation of these parameters is required, in current practice it is increasingly necessary to work in situations where standardization is impossible and consequently where absolute magnitudes must be known. The quality and quantity of data that is now available varies widely.

Ionization cross sections

Although the amount of experimental data is limited, particularly in the energy range between 1 and 20 keV, a critical assessment has concluded that for K-shell excitations both the magnitude of the cross-section σ and its variation with energy are adequately well known for overvoltages greater than about $2^{1,2}$. For L- and M- shell excitations, however, and in all cases when the operational over-voltage is less than 2, the situation is much less satisfactory. In the energy range below 100 keV there are only published L-shell ionization cross-sections for six elements (compared with data for 18 k-shells), and none at all for M-shells. With the increasing interest in performing X-ray microanalysis at low beam energies, and consequently at low over-voltages, there is a demonstrated need for systematic work in this topic. While the measurement of cross-sections at high beam energies is relatively straightforward, since the use of electron transparent foils simplifies the calculations particularly when bremsstrahlung production is employed as an internal standard, at low beam energies detailed simulations must be performed in order to extract the desired data from experimental measurements.

Fluorescent yields

Fluorescent yields are the least well known parameters amongst those that are of interest. Since the X-ray yield is proportional to the product of the fluorescent yield ω and the cross-section σ the uncertainly in the fluorescent yields directly impacts the accuracy of absolute cross-section determinations. Although the variation of fluorescent yields for K-shell excitations is fairly well established for atomic numbers greater than 10, for lower atomic numbers, and for the L- and M-shell excitations there is little theoretical or published experimental data. An additional complexity, that so far has not been taken seriously into account, is the likelihood that the magnitude of the fluorescent yield is itself chemically sensitive. Estimates of the variation suggest that a 20% change between the value for an element and the corresponding value for that element in a compound is possible.[3] Since the measurement of the fluorescent yield is a complicated matter it may be preferable to consider only the product of $\sigma\omega$ rather than to attempt to separate the two.

Electron stopping power

The electron stopping power determines the depth and lateral distribution of X-ray production within the specimen, and hence affects the magnitude of the generation, absorption and the backscatter correction terms. Experimental stopping power data for a variety of elements and compounds are now available over the energy range from 1 eV to 10 keV.[1] A comparison of the measured data for elements with stopping power values computed from the Bethe expression and employing one of the accepted expressions for the mean ionization potential J shows that the simple analytic model is adequately accurate down to energies of the order of 3J, but for lower energies significantly underestimates the stopping power. The application of the Bethe expression to compounds, using values of J derived from the mean average atomic number of the material, results in stopping power values which can be substantially in error at all energies compared to measured values. However, the experimental data shows that stopping powers are additive at all except perhaps the lowest energies (<100 eV) and hence if a comprehensive collection of elemental data can be assembled then the necessary values for any arbitrary compound can be generated as needed.

Backscattered and Secondary Electron yields

Although neither the backscattered electron yield η nor the secondary electron yield δ appear directly in the computations for microanalysis, these parameters are an important metric of the electron-solid interaction and a sensitive test of the accuracy of Monte Carlo and other simulations of the interaction. A survey of published data contains values of η and δ for about half of the elements in the periodic table over at least some of the energy range from 10 eV to 20 eV.[1] The spread in experimental values is generally higher than desirable, and even for the most exhaustively studied materials such as aluminum or copper it still is not possible to state a value of either η and δ with a precision of better than ±5%. It is thus still not possible to answer even such long-standing questions as to whether the variation of η with atomic number is smoothly monotonic or if there are discontinuities as shells are filled.[4] There are apparently no more than a couple of measurements of η and δ for compounds, and consequently there is no way to test any of the various predictions of these parameters for complex materials as compared to their elemental constituents.

In summary, a considerable body of experimental data on ionization cross-sections, fluorescent yields, stopping powers, and electron yields is now in place, but the coverage of the data with respect to atomic number and energy is usually sparse and for many quite common elements there still is apparently no measured data at all. For compounds, again even those of technological or industrial importance, the situation is much worse as there is insufficient data even to make it possible to evaluate the accuracy of analytic approximations or fits to the desired parameters. A systematic program to measure the parameters discussed here is urgently required, particularly to obtain values at the low energies and low over-voltages which characterize much of the current applications of electron-beam microanalysis. ∎

1.	Joy DC, SCANNING 17, (1995), 270. A complete copy of this compilation is available on request from the author. SE and BSE data may be accessed at http://www.nsctoronto.com/nissei-sangyo.

2.	CJ Powell, NBS Special Publication 460, (1970),97

3.	CA Quarles and L Estep, Phys.Rev.A34, (1986), 2488.

4.	H Bishop, Ph..D Thesis, University of Cambridge, 1963

5.	Oak Ridge National Laboratory is operated by Lockheed Martin Energy Research Corp. for the U..S. Department of Energy under contract number DE-AC05-96OR22464

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