

## CALCULATED AUGER SENSITIVITY FACTORS COMPARED TO EXPERIMENTAL HANDBOOK VALUES

Susan MROCKOWSKI

*Midwest Research Microscopy Inc., 5510 West Florist Avenue, Milwaukee, Wisconsin 53218, USA*

and

David LICHTMAN

*Physics Department and Surface Studies Laboratory, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin 53201, USA*

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A pseudo-first principles technique for Auger quantitation was used to calculate relative Auger yields. These yields were compared to the experimental sensitivity factors found in the *Handbook of Auger Electron Spectroscopy*. In cases where pure element standards are readily available, theory agreed quite well with experiment 95% of the time. However, when pure element standards are not available, such as the lanthanide series and the light elements from  $Z = 7$  to 12, large deviations exist. Plots of the calculated yields for 3, 5 and 10 kV primary beams are superimposed upon the Handbook sensitivity factor graphs and the reasons for the similarities and differences are discussed.

### 1. Introduction

Even though some experimental quantitative Auger yield data can be found in the research literature, almost everyone who does quantitative AES uses empirical sensitivity factors taken from the *Handbook of Auger Electron Spectroscopy* [1]. Quantitation of AES data using pseudo-first principles correction factors has been shown to be another viable technique when applied to several binary metal systems [2]. Although parts of this technique are based on empirical equations, the method relates observed Auger signals to basic materials properties and to instrument conditions. We have now extended the calculations to cover most of the periodic table so that significant comparisons can be made with the handbook curves. Although the details to this approach have already been presented [2], they will be summarized here for completeness.

The "first principles" procedure [2] states that the Auger electron current  $I_i$  for the UVW Auger transition of the  $i$ th element can be expressed as:

$$I_i(\text{UVW}) = I_p \rho(\text{UVW}) T \sigma(E_p, E_c) R N_i(X_i) \lambda_i(X_i) r_i(E_p, X_i) X_i, \quad (1)$$

where  $I_p$  is the primary electron current,  $\rho(\text{UVW})$  the UVW Auger transition probability,  $T$  the instrument response function,  $\sigma(E_p, E_c)$  the ionization cross section which is a function of the primary energy  $E_p$  and the critical energy for ionization  $E_c$ ,  $R$  a surface roughness factor,  $N_i$  the elemental atomic density,  $\lambda_i$  the elemental electron escape depth,  $r_i$  the electron backscatter coefficient, and  $X_i$  the atom fraction of the  $i$ th component in the volume analyzed.

When attempting quantitation of Auger spectroscopy data, relative Auger yield rather than absolute yield is usually sufficient. To determine relative elemental Auger yields, it will be assumed that  $T$  is constant above 200 eV because for electrons with energies above 200 eV, the multiplier gain is relatively constant. The surface roughness factor  $R$  will be assumed to be unity. Then, for a pure element with  $X_i = 1$ , the Auger yield is a combination of the elemental values for the ionization cross section, the Auger transition probability, the atomic density, the electron escape depth, and the backscattering factor. In this way, the relative Auger yield for a particular elemental transition at a given primary energy is given by eq. (2):

$$I_i/I_p \propto \rho\sigma N\lambda r. \quad (2)$$

The Auger transition probability ( $\rho$ ) is given by Burhop [3] as:

$$\rho = 1 - Z^4/(Z^4 + a), \quad (3)$$

where  $Z$  is the atomic number,  $a = 1.12 \times 10^6$  for K electrons and  $6.4 \times 10^7$  for L electrons. From the data given in Goldstein and Yakowitz [4], for M electrons  $a = 5.9 \times 10^8$ .

The following expression is given by DuCharme and Gerlach [5] for the ionization cross section ( $\sigma$ ) of a given subshell  $u$ :

$$\sigma_u = \left( \frac{n_u \sigma_0}{E_c^2 U} \right) \left( \frac{U-1}{U+1} \right)^{3/2} \left\{ 1 + \frac{2}{3} \left( 1 - \frac{1}{2U} \right) \ln [2.7 + (U-1)^{1/2}] \right\}, \quad (4)$$

where  $\sigma_u$  is the ionization cross section of the  $u$ th level (in  $\text{cm}^2$ ),  $n_u$  the electron population in the target atom subshell,  $\sigma_0 = 6.56 \times 10^{-14}$  and  $U = E_p/E_c$ . The cross section values were not adjusted for the effect of Coster-Kronig transitions because previous calculations [2] showed their final contribution to Auger quantitation is small.

Backscatter correction factors are calculated from an empirical equation by Reuter [6] that is used by Hall and Morabito [7]:

$$r_i = 1 + 2.8(1 - 0.9E_c/E_p)\eta, \quad (5)$$

where

$$\eta = -0.0254 + 0.016Z - 0.000186Z^2 + 8.3 \times 10^{-7}Z^3. \quad (6)$$

The escape depth of an electron is proportional to its inelastic mean free path. Seah and Dench [8] have presented an empirical equation for the

inelastic mean free path:

$$\lambda_i = A(N^{-1/3})(E_x^{-2}) + B(E_x/N)^{1/2}, \quad (7)$$

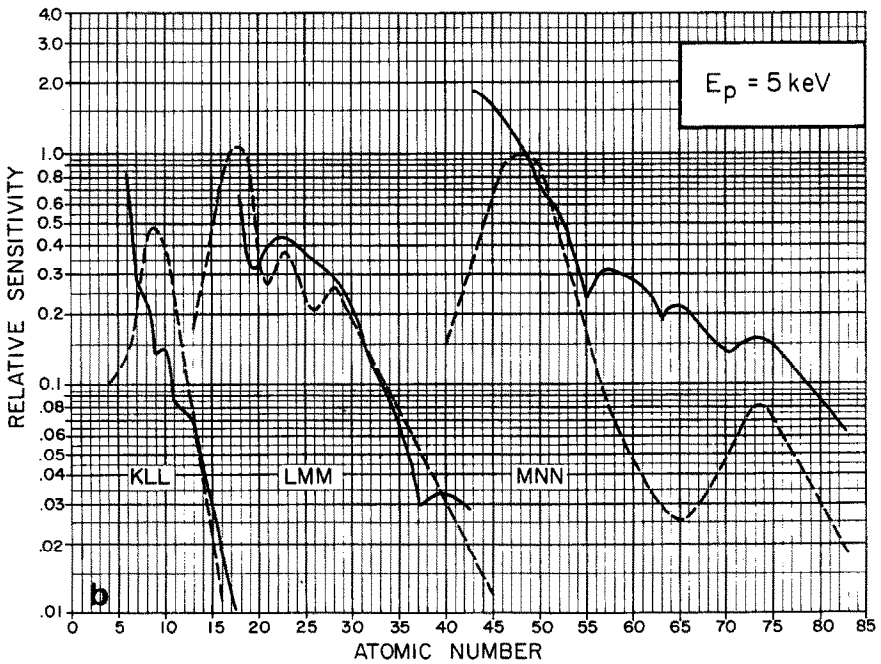
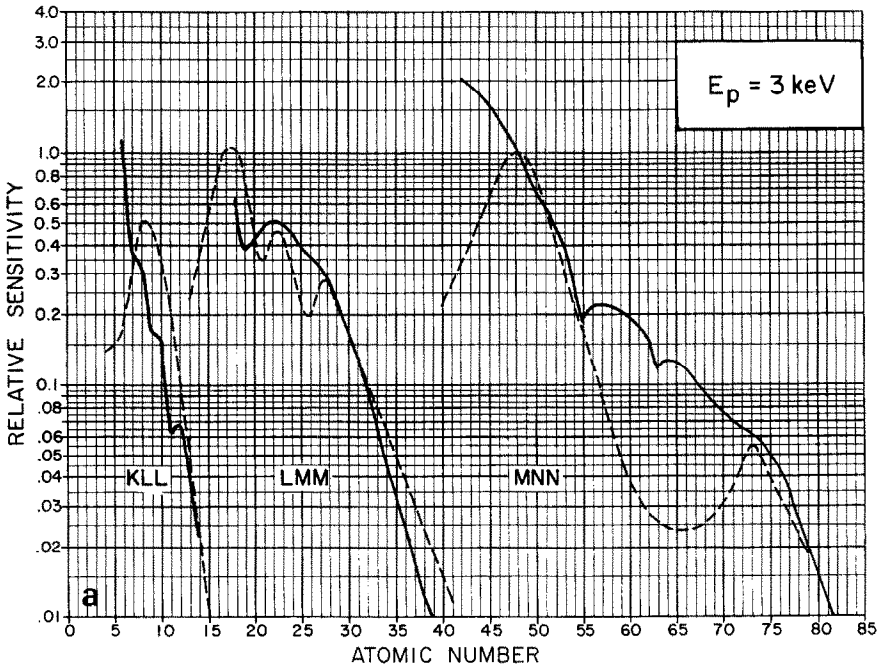
where  $\lambda_i$  is the inelastic mean free path in nm,  $A = 538 \text{ eV}^2$ ,  $B = 0.41 \text{ nm}^{-1/2} \text{ eV}^{-1/2}$ ,  $N$  is the atomic density in atoms/nm<sup>3</sup>, and  $E_x$  is the energy of the Auger electron. Atomic densities can be found in Kittel [9].

Using these equations, a “first principles” relative sensitivity factor can be calculated for any transition (above 200 eV) for any primary energy. A discussion of the possible errors that can arise by the use of this technique has been presented [2]. The use of sensitivity factors to obtain atomic percent concentrations is outlined in the appendix. Calculations similar to these have been done by Staib and Staudenmaier [10]. They have published yield curves for 3 and 10 keV primary beam transitions, and although their calculations yield similar values to those arrived at here, they did not compare their calculations to the *Handbook* data.

## 2. Results

Using this approach, values of  $\rho\sigma N\lambda r$  for major Auger transitions above 200 eV were calculated for primary voltages of 3, 5 and 10 kV. These values were normalized to the *Handbook* aluminum sensitivity factor for the KLL transitions, to zinc for the LMM transitions, and to antimony for the MNN transitions at the respective primary voltages. The *Handbook* normalizes everything to the silver MNN peak generated with a 3 kV primary beam; this procedure was not used here because the first principles method assumes that all Auger peaks are of the same general shape and normalizing each transition group to an element in that group is an attempt to account for peak shape changes that occur from transition group to transition group. Normalization for each respective primary voltage is done within each transition group to reduce any error that may be inherent in the cross section values.

A plot of the calculated yields is superimposed on the *Handbook* sensitivity factors graph for 3, 5 and 10 kV primary voltages in figs. 1a–1c. In fig. 2, each parameter in the theoretical equation is plotted as a function of atomic number for the 10 kV transitions. It can be seen from fig. 2 that the factor which is most responsible for the overall range of the yield curve is the ionization cross section which can vary by as much as three orders of magnitude. The cross section values smoothly decrease with increasing atomic number for a given transition. The backscattering factor and Auger transition probability are also smoothly varying functions but have comparatively little effect on the overall Auger yield. In fig. 1, minima are present in the theoretical yield lines. Comparison with fig. 2 shows that these minima are due to variations in the atomic density factor  $N$  and are not due to any periodic characteristics (such as



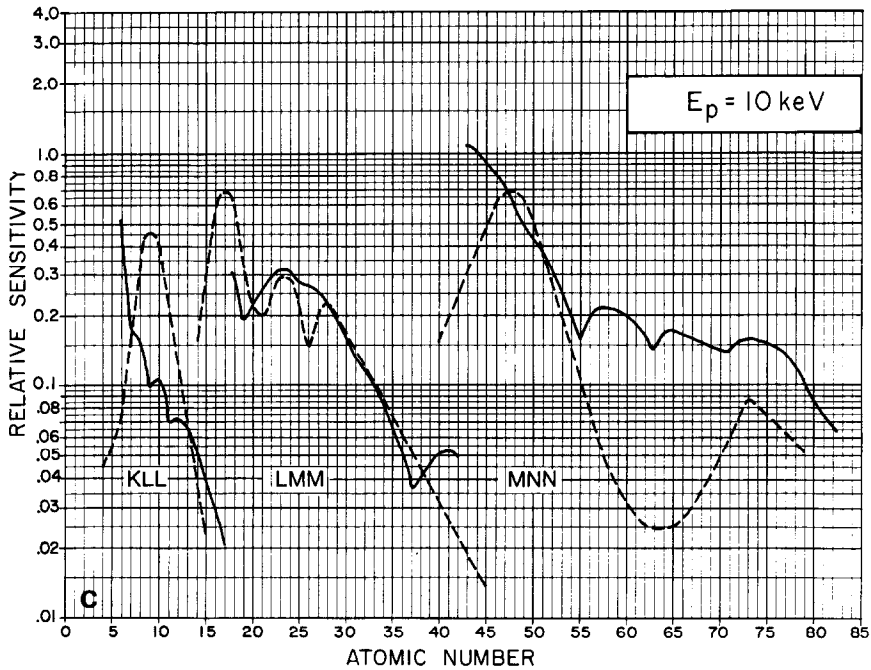


Fig. 1. Calculated Auger yields (—) compared to Handbook sensitivity factors (---): (a) 3 kV primary beam; (b) 5 kV primary beam; (c) 10 kV primary beam.

ionization energy) as might have been anticipated. The electron escape depth, which is an inverse function of atomic density, shows maxima in the same locations.

In comparing “first principles” corrections to experimental data in the *Handbook*, there is good agreement from  $Z = 13-17$  for the KLL transitions. In the 13–15 range, high purity elemental standards are readily available. There is a deviation for the KLL transitions in the range of  $Z = 6-11$ ; except for carbon, elemental standards are an impossibility in this range and the experimental data presented in the *Handbook* may not be accurate. The density used for the yield calculation of carbon was the density corresponding to diamond,  $176 \text{ atoms/nm}^3$ . The atomic density of graphite is  $113 \text{ atoms/nm}^3$  and for quantitation of samples which are graphitic in nature, a yield factor reduced by 0.64 should be used. This difference is not sufficient to explain the factor of 5 discrepancy between the *Handbook* sensitivity factor and the first principles calculation; this difference may be due to an experimental standard whose surface region is not “perfectly dense”. Clearly, quantitation of samples containing carbon as an adsorbed hydrocarbon or as an impurity element is not straightforward.

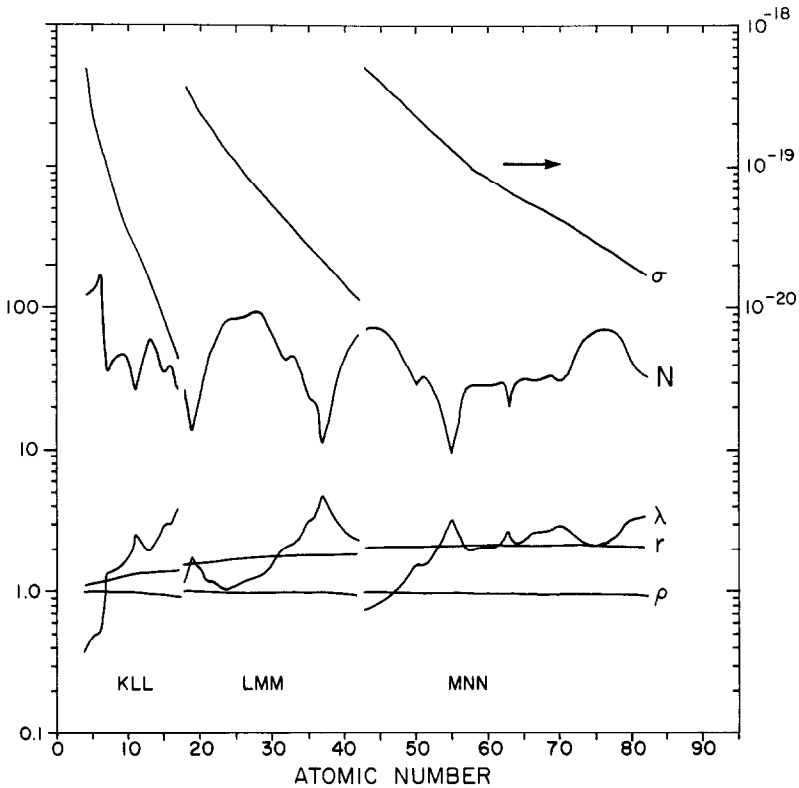


Fig. 2. Ionization cross section  $\sigma$ , atomic density  $N$ , electron escape depth  $\lambda$ , backscattering factor  $r$ , and Auger transition probability  $\rho$ , versus atomic number for 10 kV primary beam.

In the LMM transitions, good agreement is seen in the range from  $Z = 27-33$ , where once again good standards are readily available. Agreement is also good in the range from  $Z = 18-23$  although the *Handbook* sensitivity factors predicted for the phosphorus, sulfur, chlorine, and argon transitions may be slightly high – once again good experimental data are not possible with these elements. In the range from  $Z = 37$  to  $40$ , the LMM transition experimental sensitivity factors differ from the theoretical values; here, the handbook spectra show large impurity peaks. A discrepancy arises in the  $Z = 25-26$  range. Experimental data for this region show a minimum; at this point the theory shows only a very slight minimum and the reason for the differences is not obvious.

For the MNN transition, there is good agreement in the range from  $Z = 48-55$  and from  $Z = 73-82$ . There is a very large discrepancy from  $Z = 56-72$ ; this area encompasses the lanthanide series where, in the *Handbook*,

the impurity peaks are often substantially larger than the Auger peaks from the MNN transition of the standard itself. Because of the accuracy of the  $Z = 48-55$  and the  $Z = 73-82$  regions, and the probable improved accuracy in the  $Z = 56-72$  range when the first principles calculations are used, the discrepancy that exists in the range from  $Z = 43-47$  is not trivial to explain. However, inspecting the *Handbook* spectra, it appears that the yield of the silver and ruthenium is indeed higher than that of cadmium, as theory predicts. Simultaneously, it appears that the experimental yield of palladium and rhodium is lower than that of cadmium, contrary to theory.

The *Handbook* factors are from experimental data based upon the analysis of "real" standards which were scribed in-situ and ion bombarded to clean the surfaces. The first principles method used here assumes an atomistically smooth surface of perfectly dense material. The function that is responsible for minima in the calculated curves is the atomic density; therefore any less than perfect surface topography can have a detrimental effect on experimental yield determination. The surface roughness factor,  $R$ , which was assumed to be unity should have some other value for a sputtered surface. The *Handbook* data may essentially take this factor into account for those elements that oxidize strongly and must be sputtered extensively to obtain a "clean" surface.

### 3. Conclusions

Auger yields that were obtained by calculations from a pseudo-first principles technique were compared to the relative sensitivity factors in the *Handbook of Auger Electron Spectroscopy*. The theoretical yields agreed quite well with the experimental yields in all cases where pure element standards are readily available, except for atomic numbers 25, 26, 45 and 46. There were significant discrepancies between theory and experiment when the *Handbook* spectra exhibited large impurity peaks or when the standard could not be obtained in elementally pure form. It is possible that for these elements, the sensitivity factors reported in the *Handbook* may need adjustment. The largest discrepancies exist for the light elements in the range from carbon to sodium and for the lanthanide series. Because the correction factor responsible for minima in the theoretical yield line is the atomic density, it is possible that the differences observed for  $Z = 25, 26, 45$  and  $46$  are due to localized surface density alteration caused by ion bombardment of the samples.

### Appendix

As outlined in the *Handbook of Auger Electron Spectroscopy* [1] relative sensitivity factors (yields) can be used to calculate concentrations of elements

above atomic number 2. The atomic concentration can be expressed as:

$$X_i = \frac{I_i/S_i d_i}{\sum_{\alpha} I_{\alpha}/S_{\alpha} d_{\alpha}}, \quad (\text{A.1})$$

where  $X_i$  is the atomic concentration of element  $i$ ,  $I_i$  the peak-to-peak intensity,  $S_i$  the relative sensitivity of element  $i$ , and  $d_i$  is a scale factor defined by

$$d_i = L_i i_p, \quad (\text{A.2})$$

where  $L_i$  is the lock-in amplifier sensitivity and  $i_p$  is the primary beam current. It is assumed the modulation voltage is held constant.

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