The effect of electron transmission function on calculated Auger sensitivity factors

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It has been shown previously that calculated sensitivity factors can be used in some cases for quantification of Auger electron spectroscopy data. Internal calibration had been recommended for accurate quantification of transitions with energy < 200 eV. In this study, the effect of various electron transmission functions on calculated Auger electron spectroscopy sensitivity factors is investigated. Spectrometer resolution and its relation to intrinsic peak width are also discussed. The transmission function-corrected calculated sensitivity factors are compared to several available empirical handbook sensitivity factors. There is now improved reliability on the use of calculated values for the quantification of transitions at the lower end of the energy spectrum. When conductive, high-purity standards are routinely available, calculated and experimental sensitivity factors correlate well. There is a considerable difference when high-purity standards are not available as in the light element and lanthanide series. If accurate quantification is required and internal standards are not available, the Auger electron emission current should be correlated to the area under the peak for Auger spectra taken in the direct mode rather than peak-to-peak height measurements in the derivative mode.

I. INTRODUCTION

It has been shown previously[1-3] that calculated sensitivity factors can be used in some cases for quantification of Auger electron spectroscopy data. The earlier publications showed that when conductive, high-purity standards were available, calculated and experimental sensitivity factors correlate well. There is a considerable difference, sometimes an order of magnitude, when high-purity standards were not available as in the light element and lanthanide series. Internal calibration had been recommended for accurate quantification of transitions with an energy < 200 eV because the previous calculated values did not include factors to account for the transmission function of the spectrometer or for the electron multiplier gain variation with electron energy.

Despite the fact that the intensities were not corrected for the spectrometer transmission function, the values were used by a number of outside laboratories (in addition to our laboratory) with successful results.[4,5] Indeed, Weisz *et al.*[4] found that the only sensitivity factors which appeared to give "correct" zinc oxide quantification results were the calculated factors in Ref. 3. When they used the factors from the *Handbook of Auger Electron Spectroscopy*,[6] they calculated $< 20\%$ oxygen of the oxygen surface of ZnO. The experimental sensitivity factors that they determined for zinc and oxygen were within 10% of the calculated values in Ref. 3.

In this study, the calculated sensitivity factors will be combined with transmission function and electron multiplier gain corrections that are typical for many types of experimental conditions. The revised calculated factors will then be compared to experimentally determined sensitivity factors and differences and similarities will be discussed.

II. CALCULATION OF RELATIVE AUGER YIELD

The Auger electron current I_i for the UVW Auger transition of the ith element can be expressed as

$$I_i(\mathrm{UVW}) = I_p \rho(\mathrm{UVW}) T D \sigma(E_p, E_c) R N_i(X_i) \lambda(X_i) r(E_p, X_i) X_i, \quad (1)$$

where I_p is the primary electron current, $\rho(\mathrm{UVW})$ is the UVW Auger transition probability, T the instrument response function which is a function of the energy of the Auger electron E_x, D the detector efficiency, $\sigma(E_p, E_c)$ 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, λ the elemental electron attenuation length, r the electron backscatter coefficient, and X_i the atom fraction of the ith component in the volume analyzed.

The mathematical equations used to determine the value for each of the components in Eq. (1) have been published previously[2]; also discussed previously[3] are the assumptions made in the determination of each component. The specific equations used for the calculations will, however, be briefly reiterated here for completeness.

The Auger transition probability ρ is given by Burhop[7] as

$$\rho = 1 - Z^4/(Z^4 + a), \quad (2)$$

where Z is the atomic number, $a = 1.12 \times 10^6$ for K electrons and 6.4×10^7 for L electrons. From the data given in Goldstein and Yakowitz,[8] for M electrons $a = 5.9 \times 10^8$. This equation represents a simplification of the process because the probability as calculated here gives a total Auger probability for all level u transitions. The use of this equation implies that the ratio of the probabilities for the most intense transitions is equal to the ratio of the probabilities for the total level u transition.

The following expression from Gryzinski[9] is used by DuCharme and Gerlach[10] for the ionization cross section (σ) of a given subshell u:

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

where σ_u is the ionization cross section of the uth level (in cm^2), n_u the electron population in the target atom subshell, $\sigma_0 = 6.56\times10^{-14}$, and $U = E_p/E_c$. The cross-section values were not adjusted for the effect of Coster–Kronig transitions because previous calculations[1] for a gold–copper binary system showed that the difference in using a Coster–Kronig transition-adjusted cross-section ratio versus an uncorrected cross-section ratio was $<2\%$.

Backscatter correction factors are calculated from an empirical equation by Reuter[11] that is used by Hall and Morabito[12]:

$$r_i = 1 + 2.8(1 - 0.9E_c/E_p)\eta, \quad (4)$$

where

$$\eta = -0.0254 + 0.016Z - 0.000\,186Z^2 + 8.3\times10^{-7}Z^3. \quad (5)$$

The use of this equation implies that the backscattering parameter is not a function of the angle of the impinging electron beam. Research and calculations by Ichimura and Shimizu[13] have shown that this is not strictly true. They present Monte Carlo calculations for the change in r as a function of the reduced energy U, the atomic number Z, and the angle of the incident electron beam. When their calculations are used for $Z = 40$ and $U = 4$, the value of r changes by $<10\%$ for the angle of electron incidence ranging from 0° to 45°. Therefore, for simplicity, the equation of Reuter will be used. An additional implication of the results of the calculations of Ichimura and Shimizu is that for the first-order comparison being done in this study, there is very little angular dependence on relative yields. Therefore, relative yields of systems with different electron beam/analyzer axis geometries can be compared as a first approximation.

The attenuation length of an electron is proportional to its inelastic mean free path. Seah and Dench[14] have presented an empirical equation for the inelastic mean free path:

$$\lambda = A(N^{-1/3})(E_x^{-2}) + B(E_x/N)^{1/2}, \quad (6)$$

where λ is the electron attenuation length in nm, $A = 538$ eV^2, $B = 0.41$ $nm^{-1/2}$, N is the atomic density in atoms/nm^3, and E_x is the energy of the Auger electron. Atomic densities can be found in Kittel.[15]

The calculated yields are tabulated in Ref. 3. The roughness factor was assumed to be unity. Figure 1 is a plot of σ, N, λ, r, and ρ for a 10-keV primary electron beam excitation in order to illustrate the relative strength of each facet of the correction. The factor that 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 backscattering factor and Auger transition probability are also smoothly varying functions but have comparatively little effect on the overall Auger yield. The atomic density and the electron attenuation length (which is in part a function of atomic density) have a relatively large effect on the total yield. In the earlier publications, the instrument response

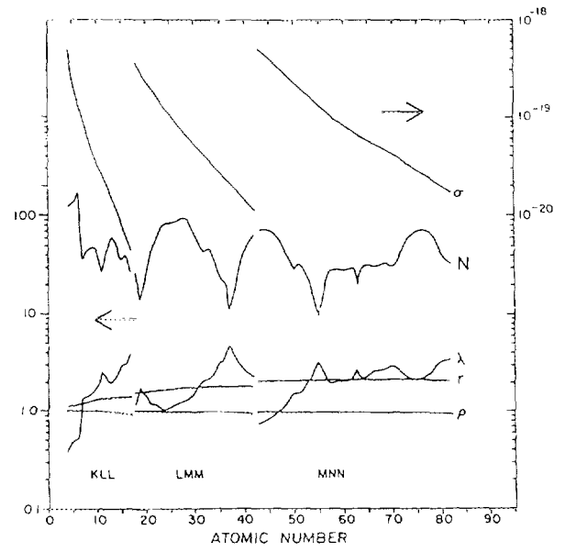

FIG. 1. Ionization cross section $\sigma(cm^2)$, atomic density N (atoms/nm^3), electron attenuation length λ (nm), backscattering factor r, and Auger transition probability ρ vs atomic number for a 10-keV primary electron beam.

function T was assumed to be constant for all Auger peaks above 200 eV.

The results obtained with that assumption were that there was good agreement between theory and experiment when conductive, pure atomic standards were readily obtainable. There was a large discrepancy when such standards were not available as in the light element and lanthanide series. The only major areas that did not correlate to this pattern were those peaks below 300 eV. It was assumed that this relatively poor low-energy agreement was due to the instrument response function.

A cylindrical mirror analyzer (CMA) is the most common electron spectrometer in commercial Auger systems. It is generally operated in the constant resolution mode with $\Delta E/E$ as constant (typically 0.5%–0.6%); this effect helps to increase the signal from the generally lower intensity higher energy Auger electron peaks. Under this mode of operation, the transmission increases with energy E, i.e., the transmission is proportional to E. According to Seah,[16] however, a linear transmission function is valid only when the Auger electron signal is proportional to the area under a direct spectrum peak. The effective transmission function changes if the signal is regarded as proportional to the peak height with a direct spectrum peak or if the signal is regarded as proportional to the peak-to-peak height in the derivative mode.

Seah[16] presents a lengthy discussion on the change of effective transmission function under these circumstances based upon the intrinsic peak widths and the spectrometer resolution. For a resolution of 0.6%, the ΔE for a 200-eV peak is 1.2 eV; the ΔE for a 2000-eV peak is 12 eV. Therefore, at higher energies the spectrometer resolution dominates over the peak width of the signal. According to Seah, at lower energies (<150 eV) the effective transmission is proportional to E for all modes of operation. At higher energies

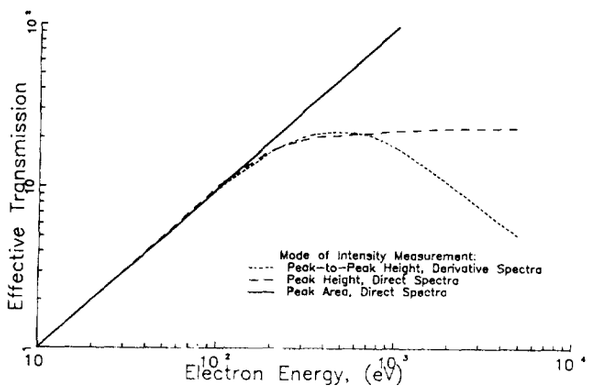

FIG. 2. Spectrometer transmission functions from Seah (Ref. 16).

the effective transmission function is (i) proportional to E for peak area measurements, (ii) is constant for peak height measurements if the energy is greater than approximately 300 eV, and (iii) is proportional to E^{-1} for differential peak height measurements if the energy is greater than ~800 eV. The peak width used by Seah[16] in these presentations is 1.5 eV.

Another parameter included in the instrument response function is the electron multiplier gain variation with electron energy. Above ~200 eV the multiplier gain becomes constant. It is assumed that there is no first dynode bias.

A plot of effective transmission functions from Seah[16] is shown in Fig. 2. A typical plot of the multiplier gain versus electron energy[6] is shown in Fig. 3. These parameters will be multiplied together and combined with data from previous publications in order to determine the effect of these corrections on the calculated sensitivity factor values. The data will then be compared to experimental data published by Physical Electronics[6] and by JEOL.[17]

Experimental data utilizing a 10-keV primary electron beam for excitation and perpendicular detector/electron beam configuration has been published by JEOL[17] using peak areas as the measure of generated Auger electron intensity. Under these conditions, the appropriate transmission function is linear with energy as shown in Fig. 2. Calculated values are determined by multiplying the previously published 10-keV primary excitation yield by the energy of the Auger electron and by the multiplier gain shown in Fig. 3. The data were normalized so that the sensitivity factor for the Cu *LMM* transition was equal to 1.25. The results obtained are illustrated in Fig. 4.

Experimental data utilizing a 10-keV primary electron beam for excitation and perpendicular detector/electron beam configuration have been published by JEOL[17] using the direct spectra peak height as the measure of generated Auger electron intensity. Using these conditions, the transmission function is linear with electron energy until ~350 eV; it is then roughly constant. Calculated values are determined by multiplying primary excitation yield by the appropriate transmission function shown in Fig. 2 and by the multiplier gain shown in Fig. 3. The data were normalized so that the sensitivity factor for the Cu *LMM* transition was equal to 0.20. The results obtained are illustrated in Fig. 5.

Experimental data employing a 10-keV primary electron beam for excitation and a perpendicular detector/electron beam configuration have been published by JEOL[17] and a collinear configuration has been published by Physical Electronics[6] using derivative peak-to-peak heights as the indicator of generated Auger electron intensity. Under these conditions, the transmission function goes through a maximum at ~500 eV. Calculated values are determined by multiplying the previously published 10-keV primary excitation yield by the appropriate transmission function shown in Fig. 2 and by the multiplier gain shown in Fig. 3. The data were normalized so that the sensitivity factor for the Cu *LMM* transition was equal to 0.20. The results obtained are illustrated in Fig. 6.

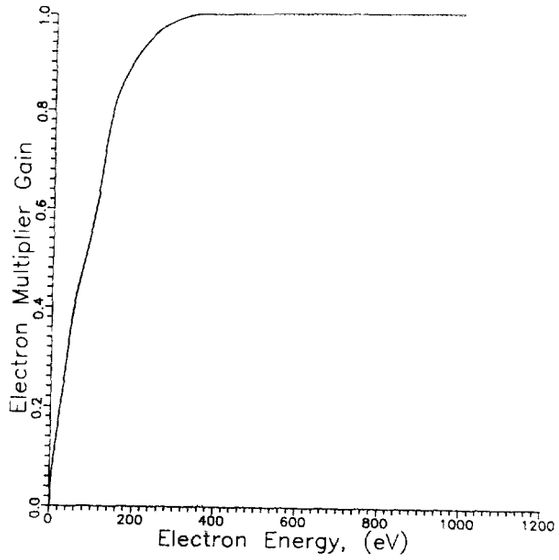

FIG. 3. Typical plot of the electron multiplier gain variation with electron energy from Davis *et al.* (Ref. 6).

The calculated data plotted in the figures were normalized to only one point across the entire Periodic Table; this is contrary to the earlier publications where different normalization factors were used in an attempt to account for different peak shapes in the derivative spectra. Copper was chosen as the normalization point rather than the standard silver for a number of reasons. The shape of the silver doublet peak obtained after differentiation is very difficult to relate to the original area under the curve. There is more inherent uncertainty in calculated *MNN* transitions than in *KLL* or in *LMM* transitions because for heavier atoms the influence of multiple collisions becomes increasingly difficult to predict. It is therefore preferred to normalize to a peak with more equal positive and negative excursions, with clean polished conductive standards readily available, with preferably a *KLL* or *LMM* transition, and at a high enough energy such that the multiplier gain is in the constant region. The copper *LMM* transition was chosen as a compromise of these features.

III. RESULTS

From an inspection of Figs. 4–6, it appears that the "best fit" of theory to experiment occurs for the direct spectra/

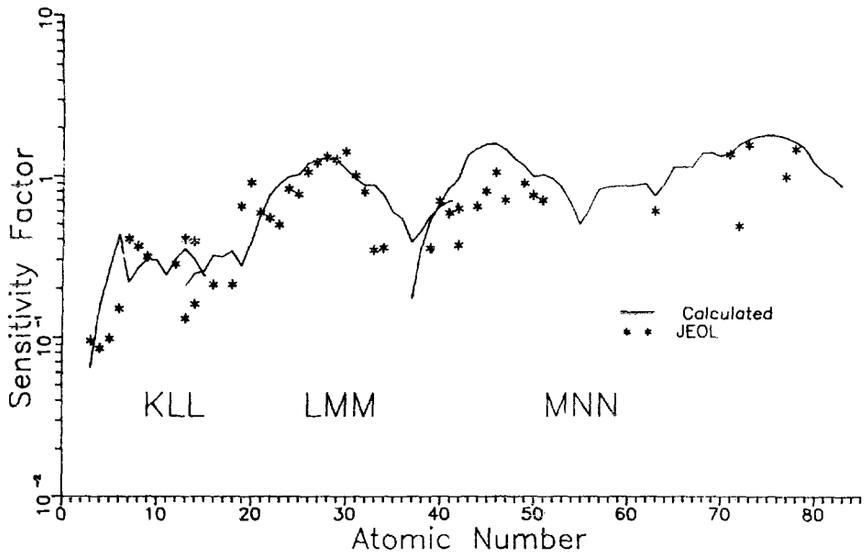

FIG. 4. Experimental [from Sekine *et al.*, (Ref. 17)] vs calculated sensitivity factors using peak areas (from data taken in the direct mode) as the measure of Auger electron emission intensity. Primary beam = 10 keV, perpendicular detector/electron beam configuration.

peak area measurement of Auger electron intensity, Fig. 4.

Figure 6 illustrates the differences in calculated sensitivity factors and experimental sensitivity factors for data taken in the derivative mode by Physical Electronics and JEOL. It is immediately apparent from this figure that the low-energy correction is not of the proper magnitude. The low-energy variations are quite large, indicating that there is sometimes as much as an order of magnitude difference between the calculated and experimental data. The agreement between JEOL and Physical Electronics was, however, quite good. This indicates some level of universality between the relative yields of different instruments even though they have different multipliers and gun/analyzer geometries. There is, therefore, more confidence in the use of the first approximation of Reuter's backscattering formula.

Figure 5 is a plot of the experimental sensitivity factors from JEOL obtained by measuring the peak height of a direct spectra. Once again, the low-energy transition corrections are of insufficient magnitude for a good correlation. With this exception, the overall fit is somewhat better in Fig. 5 than in Fig. 6. It is not reasonable to quantify the agreement in the data sets because there is an expected disparity for those elements that do not have pure, conductive standards such as the light element and lanthanide series.

IV. DISCUSSION

The calculated sensitivity factors of Mroczkowski and Lichtman[1-3] have been criticized to some extent in the literature.[16,18,19] It is felt that the most serious criticism in principle deals with the initial assumption of a constant instrument response function. Other facets of the criticism are either not valid or are not a significant adjustment relative to other errors inherent in the calculated values.[20]

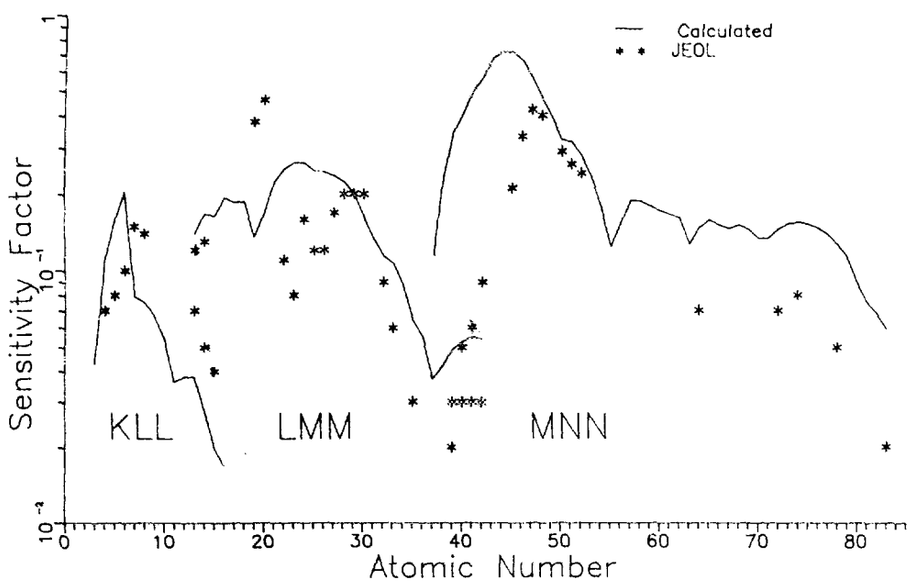

FIG. 5. Experimental [from Sekine *et al.* (Ref. 17)] vs calculated sensitivity factors using peak heights (from data taken in the direct mode) as the measure of Auger electron emission intensity. Primary beam = 10 keV, perpendicular detector/electron beam configuration.

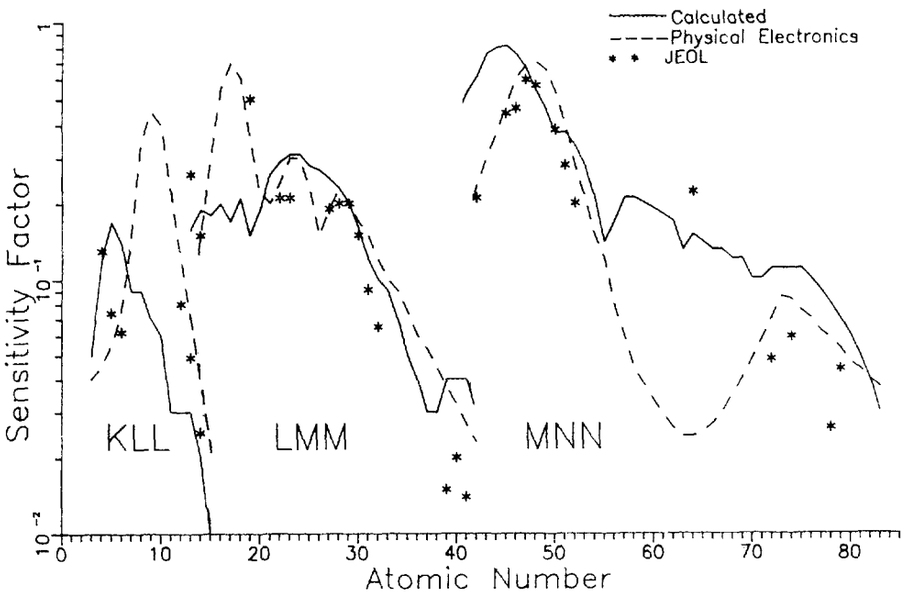

FIG. 6. Experimental [from Sekine *et al.* (Ref. 17) and Davis *et al.* (Ref. 6)] vs calculated sensitivity factors using peak-to-peak heights in the derivative mode as the measure of Auger electron emission intensity. Primary beam = 10 keV, perpendicular detector/electron beam configuration for Sekine, coaxial detector/electron beam configuration for Davis.

Ferron *et al.*[18] and Seah[16] feel that the use of a single Auger transition probability for all transitions with the same core level introduces serious errors in the quantification scheme. Payling[19] and Ferron[21] estimated the fraction of each transition with the same initially ionized core level by dividing the peak-to-peak height of the Auger line of interest by the sum of the peak-to-peak heights of the Auger lines sharing the same general *xyy* nomenclature. The validity of this technique is questionable because different electron attenuation lengths, ionization cross sections, transmission functions, and multiplier functions would also be of importance in determining the difference in peak heights within one group. Although admittedly the transition probability for a KL_1L_2 transition is not the same as that for a KL_2L_2 transition, it seems obvious from Fig. 1 that as long as the most intense transitions are chosen, the error is less than is inherent in other parameters, such as the ionization cross section.

Both Ferron[21] and Payling[19] state that the transmission should be a linear function with energy. The publication by Seah[16] and the data presented here show that this is not true in cases where direct spectra peak height measurement or derivative spectra peak-to-peak height data are utilized. The basic good agreement shown in Fig. 4 illustrates that the major correction factor of σ, N, λ, r, ρ, and the multiplier gain function (assuming no first dynode bias) are basically correct. The deviation between theory and experiment increases when direct spectra peak heights are used and increases still more when derivative spectra peak-to-peak heights are used as a measure of Auger electron emission intensity.

Seah[16] states the assumptions used in his plot of the effective transmission functions for the various analysis modes. The plots shown in Fig. 2 were for a peak of intrinsic width of 1.5 eV. He explains that as the intrinsic width is increased, the departures from the early linearity occur at proportionately higher energies. Intrinsic widths of many Auger peaks are typically 1.5–4.0 eV, so deviations are expected to occur. The effect of the modulation amplitude in derivative spectra is also very much related to the inherent peak width; this factor induces an expected larger difference in calculated and experimental sensitivity factor values as illustrated in Fig. 6.

Goldstein *et al.*[22] propose a universal curve so that peak-to-peak heights can be used to accurately determine the relative atomic concentration using Auger spectroscopy. It is their feeling that the available sensitivity data required for quantification were not always measured with sufficient instrumental resolution.

V. CONCLUSIONS

Calculations were done in order to determine the effect of various electron transmission functions of a spectrometer and the electron multiplier gain variation with electron energy. In general, good correlation between theory and experiment was obtained when the Auger electron emission intensity was assumed to be proportional to the area under the peak for spectra taken in the direct mode. However, uncertainties in the transmission function and the effect of intrinsic peak width introduce possible sources of error when using derivative spectra. Based upon the data obtained and the knowledge that higher energy peaks have a generally higher intrinsic width, a transmission function like that shown in Fig. 2 for Auger intensity measured as the peak height in the direct mode may more accurately represent the function that should be used when derivative spectra are recorded. If this is indeed correct, the data presented in the earlier publications[2,3] are essentially still valid because the transmission function is assumed constant for energies above 200 eV.

Another interesting facet of the effect of the transmission function can be realized if the plots in Fig. 2 are compared to the relative order of importance of the individual parameters shown in Fig 1. The majority of the strong Auger transitions

occur in the range 0–1000 eV. If one looks at the plot of effective transmission functions for a spectra in the derivative mode in the range from 200 to almost 900 eV, the function is essentially constant relative to the changes in the ionization cross section, electron attenuation length, and atomic density. If one realizes that peak widths over 1.5 eV will cause the derivative transmission function to be slightly higher than the E^{-1} function shown in Fig. 2, it becomes apparent that for transitions in the range from 200 to almost 1000 eV the transmission function is essentially constant, even for the evaluation of the spectra taken in the derivative mode.

The increasing use of computerized data handling should help to alleviate difficulties currently encountered in quantitative Auger analysis because the trend in that area is toward the measurement of relative Auger electron emission intensities based upon area under the peak taken in the direct mode. The use of calculated sensitivity factors is reliable when peak areas are used. Although the effective transmission function can be taken as constant in the range 200–900 eV, internal calibrations are recommended as discussed by Goldstein *et al.*[22] when derivative spectra are recorded in order to account for the proper high-energy (>1000 eV) and low-energy (<200 eV) instrument response functions. Calculated sensitivity factors, corrected for the proper electron multiplier effect and the proper effective transmission function, are viable parameters that should be used for quantification of Auger electron spectroscopy data when internal standards are not available.

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