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The Physical Basis for Quantitative Surface Analysis by Auger Electron Spectroscopy and X-Ray Photoelectron Spectroscopy

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ABSTRACT: A review is given of the physical basis for quantitative surface analysis by Auger electron spectroscopy (AES) and by X-ray photoelectron spectroscopy (XPS) or electron spectroscopy for chemical analysis (ESCA). The principal topics discussed are: the feasibility of surface analysis, approaches to surface analysis, description of models and data for surface analysis by AES and XPS, analytical methods, intensity measurements, practical considerations, applications, and reference materials.

KEY WORDS: quantitative analysis, materials, analysis, Auger electrons, spectroscopy, X-ray spectroscopy

A substantial number of reviews have been published in the past few years on the application of Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) (also known as electron spectroscopy for chemical analysis or ESCA) to the analysis of solid surfaces [*1–22*].[2] Most analyses of surfaces to date have been qualitative rather than quantitative, but there is now an increasing desire to quantify the measurements made by AES and XPS and to use this information for problem solving in analytical laboratories and for the development, evaluation, and control of processes and products [*23*].

The purpose of this review is to describe the physical basis for quantitative surface analysis by AES and XPS. A summary will be given of the models that have been used to describe the measurements and of the

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[2]The italic numbers in brackets refer to the list of references appended to this paper.

uncertainties in their application. Consideration will be given to the factors that should be considered when measurements are made of the intensities of AES and XPS spectral features. Examples will be given of the applications of the various methods to the analysis of metal, alloy, and compound surfaces. At the end, a brief description will be given of a plan for the development of "reference sources" that could be useful for intensity calibrations of AES and XPS instruments. At the beginning, however, it is desirable to describe what is meant by the phrase "quantitative surface analysis."

Are Analyses of Surfaces Possible?

It is obvious that the intensities of observed AES and XPS spectral features are measures of elemental abundance. The key question is, of course, can the observed intensities be converted to elemental concentrations? If the answer to this question is "yes," what are the preferred analytical methods for different situations and what are the expected accuracies of the derived concentrations?

These questions are posed because the author has encountered skepticism, misapprehension, and confusion concerning the present and potential feasibility of quantitative surface analysis. Indeed, like other areas of controversy, there are vocal optimists and pessimists. The source of confusion is largely due to ambiguity in the meaning of the term "quantitative surface analysis" coupled in some cases with an implicit hope or expectation that an analysis of any sample surface should be possible with high relative accuracy (say 0.1 to 1 percent) to be useful.

There would be little confusion (or interest) if the surface composition of a sample were the same as the bulk composition. Indeed, the importance of measuring a surface composition stems from the actual or possible *inhomogeneity* of a sample in the direction normal to the surface. The variation of composition with depth may occur over distances comparable to or much greater than atomic dimensions. In addition, the sample may be laterally inhomogeneous; the local composition may vary in a plane parallel to the surface as well as normal to the surface. It is clear, then, that one cannot make a meaningful determination of surface composition without knowledge of the sample structure, in some cases on an atomic scale. It is also important in this context to remember that the intensity of the AES or XPS spectral features (that is, the measure of the surface composition) depends on sample properties (for example, the total inelastic mean free path for the electrons of interest and the surface roughness) and on the instrumental geometry (for example, the angle between the sample surface and the direction to the electron energy analyzer). The measure of the surface composition therefore will depend both on the sample structure and the conditions of measurement. Thus, it can be difficult or impossible

to determine "the" surface composition of an arbitrary sample from an AES or XPS measurement alone. The pessimists do indeed have a case.

Fortunately, perhaps, there are many analytical situations in which there is information concerning the sample and its properties in addition to that obtained from the simplest AES or XPS measurement. The sample, for example, could be a semiconductor device, a manufactured metal part, a polymer, a dispersed catalyst, or a single crystal. In each of these cases, there would be reasonable assumptions or expectations concerning the degree of homogeneity of the sample, and these expectations could be tested in several ways. Inhomogeneities in the plane of the sample could be examined with a scanning Auger spectrometer. The nature of inhomogeneities normal to the surface over a depth range comparable to atomic dimensions could be detected either from intensity measurements made as a function of takeoff angle or from the relative intensities of two lines from the same element with different energies and thus different inelastic mean free paths. The presence of inhomogeneities normal to the surface for larger depths could be examined by "depth profiling" or sputtering of the sample surface. It is therefore possible to use prior information or to obtain information concerning the sample homogeneity to define desirable AES or XPS measurement conditions and to interpret properly the intensity data so obtained.

There are also analytical situations in which one does not need a "complete" analysis of the surface; different kinds of analysis can be made, depending on the problem to be solved. One important analytical problem is the determination of the presence or absence of a key material or contaminant within specified limits. The sample could contain a single phase, and the problem could be to determine the concentration of impurities or deposits in the surface region. The sample of interest also could contain two phases, a homogeneous substrate and some amount of oxide, contaminants, or deposits on the surface. Thermodynamic considerations may indicate that small amounts of bulk impurities, for example, may diffuse to the sample surface on heating. The problem in this case is to process the sample in some way to reduce the concentration of the surface impurity below a defined level, as determined by an AES or XPS measurement with a known sensitivity. Another important analytical problem is the determination of the surface composition of a bicomponent system. The problem is to determine the extent to which the surface, the "outermost" layers of atoms, is enriched by one of the components, perhaps as a function of sputtering or annealing.

The answer to the principal question posed at the beginning of this section is a qualified "yes." Examples will be given of practical applications where quantitative analyses of surface have been made. Although it may not be possible to use AES or XPS alone to analyze the surface of a multiphase, inhomogeneous sample, there are ample grounds for asserting that

defensible analyses of simpler surfaces have been made (although, as we shall see later, the accuracy of some measurements is not well established). The name of the game is surely to develop reliable methods and procedures for AES and XPS so that surface analyses of known accuracy can be obtained. The goal is to relate an analysis of a sample (with consideration of sample type, available instrumentation, and adequate methodology) to solve a problem or to answer a question at an acceptable cost.

Approaches to Quantitative Surface Analysis by AES and XPS

There are three approaches that have been proposed for the quantitative analysis of surfaces: (*a*) standards, (*b*) elemental sensitivity factors, and (*c*) a first-principles model. All three approaches have their advantages and disadvantages (but none can be used effectively without defining the analytical problem and assessing the sample homogeneity, as discussed earlier).

Analysis with local standards can be useful if samples with a limited range of compositions are to be analyzed routinely. It then becomes practicable to manufacture a limited number of reference standards with compositions encompassing those that are likely to be encountered in practice. An important condition is that the surface composition of the reference standard can be determined readily from the starting material and processing conditions. Another condition is that the reference surface can be regenerated reliably with multiple use. If these conditions can be fulfilled, the surface composition of the unknown sample can be deduced by interpolation.

The use of local standards is not feasible for most applications on account of the cost and the difficulty of preparing satisfactory standards in the surface compositions similar to those of the unknown samples. There does, however, appear to be a need for reference samples that could be used either to check the results of the other two approaches for surface analysis or to determine the working sensitivity of AES or XPS instruments. Reference samples of the latter type will be discussed further.

The use of elemental sensitivity factors for surface analysis by AES or XPS has been proposed and developed by a number of authors [*24–34*]. Extensive measurements have been made by Wagner [*24*] and by Jorgensen and Berthou [*25,26*] to intercompare XPS intensities from many elements in a variety of compounds. These authors have developed a relative intensity scale in which elemental intensities were referenced to the fluorine 1*s* intensity. Berthou and Jorgensen [*28*] have developed a similar scale for the intensities of Auger features observed in an XPS instrument. For this case, the Auger intensities will depend on the relative amounts of magnesium $K\alpha$ X-rays and of bremsstrahlung and will thus vary with the voltage on the X-ray tube. Most applications of elemental sensitivity factors

for AES, however, are based on measurements for pure elements recorded under essentially similar conditions. The intensity of the most intense feature for each element often is given relative to the intensity of the silver $M_{45}VV$ Auger transition [*31-33*].

The third approach, the use of a so-called "first-principles" model, relates observed AES or XPS intensities to basic material properties and to measurement conditions with a simple three-step model for electron creation, transport to the surface, and detection [*35-66*]. Certain simplifying assumptions and approximations are made in the analysis in order to obtain results that can be readily compared with experiment. Although lack of necessary data (of sufficient accuracy) and the greater complexity in handling the model (compared to the other two approaches) have prevented widespread use, the insight provided by the model description has in fact led to improved methodology. It now seems likely that measured elemental sensitivity factors used in conjunction with a satisfactory model will be useful in a number of analytical situations.

A First-Principles Model for Auger Spectroscopy and ESCA

We will consider the simplest possible case, a homogeneous surface irradiated by X-rays or by electrons, in order to summarize the essential points of the model description and to show how it can be applied. Detailed descriptions of the various situations that are likely to be encountered in practice and generalizations of the model are discussed elsewhere [*22,27, 37,41,51,64*].

For ESCA, the attenuation length for the incident X-rays is assumed to be much greater than the inelastic mean free path for the detected photoelectrons. Effects due to reflection or refraction of X-rays and electrons will be disregarded since such effects are expected to be small for common conditions of operation. For AES, the incident electron energy is assumed to be high enough so that the incident beam is not degraded substantially in energy over depths from the surface corresponding to about five times the inelastic mean free path of the detected Auger electrons. These assumptions are reasonable for most applications.

Photoelectrons and Auger electrons are assumed to travel along straight-line paths from their point of creation to the surface. No account is taken of elastic electron scattering or diffraction in crystals. The implicit assumption is made that as many electrons will be elastically scattered through some angle into the direction of the analyzer as will be scattered out of this direction through the same angle. This approximation is satisfactory in an infinite medium and is considered plausible near a surface when electrons are detected at nongrazing angles of emergence and when small-angle elastic scattering predominates over large-angle elastic scattering.

Possible spatial or directional anisotropies in the cross sections for inelastic scattering of the detected electrons are not included.

We finally assume that the sample is smooth on an atomic scale. Effects of roughness will be described later.

With these assumptions, the current of photoelectrons in an XPS experiment can be written in the form [22,35]

$$I_s(E_{i,X}) = I(\hbar\omega)N_i\sigma_i(\hbar\omega, \theta, X)\lambda_s(E_i)F(E_i, E_a)T(E_i, E_a)D(E_a)G_A \quad (1)$$

where

- $I_s(E_{i,X})$ = measured current of photoelectrons of kinetic energy E_i (level X of the ith species) from the sample s,
- $I(\hbar\omega)$ = X-ray flux on the sample at the characteristic energy $\hbar\omega$,
- N_i = volume density of atoms of the ith species,
- $\sigma_i(\hbar\omega, \theta, X)$ = differential photoionization cross section for the shell X of the ith species at the X-ray energy $\hbar\omega$ and for the electron ejection angle θ,
- $\lambda_s(E_i)$ = total inelastic mean free path in the sample for electrons of kinetic energy E_i,
- $F(E_i, E_a)$ = an electron-optical factor that may be present if the photoelectrons are decelerated from their initial energy E_i to some energy E_a before entering the energy analyzer,
- $T(E_i, E_a)$ = transmission function of the analyzer and is written in this form if the analysis energy E_a is a function of the initial energy E_i,
- $D(E_a)$ = efficiency of the detector either at the energy E_a or at $E_a + E_b$, where E_b is an additional energy given to the electrons after dispersion in the analyzer, and
- G_A = a geometrical factor that takes account of the area of the sample irradiated by X-rays and viewed by the analyzer, and the solid angle of acceptance of the analyzer.

A similar equation can be written to describe the current of Auger electrons in an AES experiment [27,51]

$$I_s(E_{i,XYZ}) = I(E_0)N_i\sigma_i(E_0, E_X)r_{s,i}(E_0, E_X)$$

$$\times \nu_{s,i}(W_j, X)\gamma_i(XYZ)\lambda_s(E_i)F(E_i, E_a)T(E_i, E_a)D(E_a)G_B \quad (2)$$

where

- $I_s(E_{i,XYZ})$ = measured current of Auger electrons from the sample s of kinetic energy E_i resulting from the XYZ Auger transition,

$I(E_0)$ = current incident on the sample at the energy E_0,
$\sigma_i(E_0, E_X)$ = cross section for ionization of the level X in the sample with binding energy E_X at the incident energy E_0,
$r_{s,i}(E_0, E_X)$ = correction for the additional ionization of electrons in the level X of the ith species due to backscattered electrons,
$\nu_{s,i}(W_j, X)$ = correction for additional ionization of electrons in the level X due to Auger and Coster-Kronig transitions that can occur after ionization of electrons in other levels W_j,
$\gamma_i(XYZ)$ = probability that an atom ionized in the X level will decay through an XYZ Auger transition, and
G_B = a geometrical factor analogous to G_A.

The correction for backscattering can be defined as

$$r_{s,i}(E_0, E_X) = 1 + R_{s,i}(E_0, E_X)$$

where

$$R_{s,i}(E_0,E_X) = \frac{1}{I(E_0)\sigma_i(E_0,E_X)}\int_{E_X}^{E_0} I_{B,s}(E)\sigma_i(E,E_X)dE \tag{3}$$

and where $I_{B,s}(E)$ is the current of backscattered electrons in the surface region of the sample as a function of electron energy E. For small depths from the surface (say five times the total inelastic mean free path), $I_{B,s}(E)$ in the sample can be approximated by the current of backscattered electrons emitted into the vacuum and measured by the electron energy analyzer. The correction for additional ionization of the level X resulting from the decay of vacancies in all shells W_j of higher binding energy $E_{W,j}$ is defined as

$$\nu_{s,i}(W_j,X) = 1 + V_{s,i}(W_j,X)$$

where

$$V_{s,i}(W_j,X) = \frac{\Sigma_j\sigma_i(E_0,E_{W,j})[1 + R_{s,i}(E_0,E_{W,j})]\gamma_j(W,X)}{\sigma_i(E_0,E_X)[1 + R_{s,i}(E_0,E_x)]} \tag{4}$$

where $\gamma_j(W,X)$ is the probability that a vacancy in shell W will be transferred to shell X. The summation in the numerator of Eq 4 is taken over all shells that can be ionized by electrons of energy E_0.

Equations 1 and 2 can be expressed in the simpler forms

$$I_s(E_{i,X}) = AN_i\sigma_i(\hbar\omega,\theta,X)\lambda_s(E_i)H(E_i,E_a) \tag{5}$$

and

$$I_s(E_{i,XYZ}) = BN_i\sigma_i(E_0,E_X)r_{s,i}(E_0,E_X)v_{s,i}(W_j,X) \times \gamma_i(XYZ)\lambda_s(E_i)H(E_i,E_a) \quad (6)$$

for XPS and AES, respectively. The factor A represents the product of $I(\hbar\omega)$ and G_A while the factor B represents the product of $I(E_0)$ and G_B; these factors describe the excitation conditions for XPS and AES, respectively, and are usually constant for a measurement on a single sample. The factor $H(E_i,E_a)$ represents the product of the factors $F(E_i,E_a)T(E_i,E_a)$ and $D(E_a)$ and is a property of the system used for energy analysis and electron detection; this factor should be constant for repetitive measurements of the same type involving emitted electrons of any energy E_i and analyzed electrons of energy E_a.

Operationally, the observed electron current in AES and XPS is the product of five distinguishable factors. One factor represents the excitation conditions (Factors A and B in Eqs 5 and 6). A second factor is N_i, the concentration of atoms of the ith species; this quantity is determined either in absolute terms or in relation to the concentration of other atomic species. A third factor contains quantities that depend for the most part only on atomic properties of the ith species (the terms $\sigma_i(\hbar\omega,\theta,X)$, $\sigma_i(E_0,E_X)$, and $\gamma_i(XYZ)$ in Eqs 5 and 6). A fourth factor contains quantities that depend on the properties of the matrix s as well as those of the ith species (the terms $\lambda_s(E_i)$, $r_{s,i}(E_0,E_X)$, and $v_{s,i}(W_j,X)$ in Eqs 5 and 6). The final factor is the instrument response function $H(E_i,E_a)$. The last three factors are the ones of importance in most quantitative measurements and these will now be discussed briefly in turn.

Atomic Properties

The differential cross section for photoionization $\sigma_i(\hbar\omega,\theta,X)$ is proportional to $\sigma_i(\hbar\omega,X)F(\theta,X,\hbar\omega)$, where $\sigma_i(\hbar\omega,X)$ is the total cross section for photoionization from the level X by X-rays of energy $\hbar\omega$, and $F(\theta,X,\hbar\omega)$ is an angular asymmetry factor, a function of X and the angle θ between the directions of the incident X-rays and the ejected photoelectron. Calculations of $\sigma_i(\hbar\omega,X)$ for levels of the element that can be excited by the $K\alpha$ lines of magnesium and aluminum have been reported recently by Scofield [*67*]. These calculated cross sections are for free atoms but agree with experimental measurements for solids (typically better than 10 percent) as long as the X-ray energy is at least about 500 eV greater than the threshold energy for ionization [*68*]; relative values of cross sections are probably more reliable. There will, however, be small (several percent) modulations of the atomic photoionization cross sections caused by interference effects from the neighboring atoms, particularly near ionization thresholds [*69*].

The angular asymmetry factor $F(\theta,X,\hbar\omega)$ is given by [*70*]

$$F(\theta,X,\hbar\omega) = 1 + \frac{\beta(X,\hbar\omega)}{2}\left(\frac{3\sin^2\theta}{2} - 1\right) \quad (7)$$

where $\beta(X,\hbar\omega)$ is an asymmetry parameter.

If $\theta = 90$ deg, a common experimental situation, Eq 7 is reduced to

$$F(90,X,\hbar\omega) = 1 + \beta(X,\hbar\omega)/4 \quad (8)$$

Reilman et al [71] have calculated values of $\beta(X,\hbar\omega)$ for aluminum and magnesium $K\alpha$ X-rays and the atomic levels X that can be photoionized by this radiation. Plots of their values of $\beta(X,\hbar\omega)$ are shown in Fig. 1 as a function of atomic number; $\beta(X,\hbar\omega)$ is 2 for photoionization from s subshells. It can be seen that $\beta(X,\hbar\omega)$ varies from about 0.7 to 2 and thus $F(90,X,\hbar\omega)$ is typically between 1.18 and 1.5.

The total cross section per atom for ionization $\sigma_i(E_0,E_X)$ of an inner-shell electron of binding energy E_X by an incident electron of energy E_0 can be expressed in the form [72]

$$\sigma_i(E_0,E_X)E_X^2 = 6.51 \times 10^{-14} Z_X b_X \ln(c_X U_X)/U_X \quad \text{cm}^2\text{eV}^2 \quad (9)$$

where Z_X is the number of electrons in the X subshell, b_X and c_X are parameters, and $U_X = E_0/E_X$. The available cross section data for inner-shell ionization is rather limited in scope and is of uncertain accuracy, but it has been analyzed recently to yield the following "preferred" values of

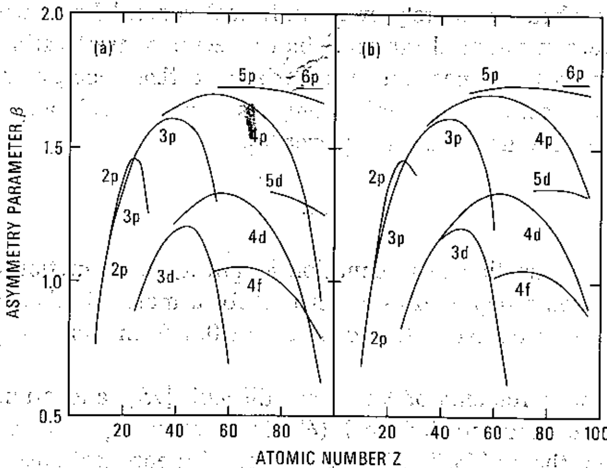

FIG. 1—*Values of the asymmetry parameter β to be used in Eqs 7 and 8 as a function of atomic number, as calculated by Reilman et al* [71]. *Values of β are plotted for different subshells and for the* Kα *radiation of* (a) *magnesium and* (b) *aluminum.*

b_X and c_X [72,73]. For the case of K-shell ionization, the values $b_K \sim 0.9$ and $c_K \sim 0.60$ to 0.75 appear to be useful for light atoms in the range $4 < U_K < 25$. The situation for L_{23}-shell ionization is less certain, but the values $b_{L_{23}} \sim 0.5$ to 0.6 and $c_{L_{23}} \sim 1$ seem reasonable choices for $U_{L_{23}} \gtrsim 20$ while the values $b_{L_{23}} \sim 0.6$ to 0.9 and $c_{L_{23}} \sim 0.6$ seem appropriate for $4 < U_{L_{23}} \lesssim 20$. Equation 9 is not expected to be valid for $U_X < 4$ and other expressions become useful in this range [73]. Little cross section data exists for ionization from the M, N, and O shells of medium- and high-Z atoms.

A review of X-ray fluorescence yields and of Auger and Coster-Kronig transition probabilities has been published by Bambynek et al [74]. For shells of binding energy less than about 1500 eV, the region of greatest practical interest in AES, the X-ray fluorescence yield is small (less than 5 percent). The Auger transition probability $\gamma_i(XYZ)$ can therefore be assumed to be unity for most applications. The fluorescence yield has been shown to depend on chemical environment for inner shells where the vacancy is filled from the valence band; this effect, however, is not expected to be significant in AES.

Matrix Properties

Experimental data for the total inelastic mean free path or attenuation length for low-energy electrons in solids has been reviewed recently by Powell [75]. Early measurements for a few elements and compounds suggested that this quantity did not vary appreciably amongst these materials and that the variation of inelastic mean free path with electron energy could be described adequately by a "universal curve." Later work showed that there were substantial (greater than a factor of two) variations of attenuation length from material to material at a fixed energy and that the universal curve could be regarded only as a very rough approximation. Some workers have used a simple power law

$$\lambda_s = KE_i^n \qquad (10)$$

to describe the variation of attenuation length λ_s as a function of electron energy E_i, K being regarded as a constant for a material. The value of the exponent n has been estimated to be about 0.5 from fits to experimental data.

Accurate measurements of $\lambda_s(E_i)$ are difficult [75], and attempts therefore have been made to deduce $\lambda_s(E_i)$ from other types of experimental data and from theory [75,76]. There is a sound theoretical basis for writing an expression for $\lambda_s(E_i)$, valid for $E_i \gtrsim 200$ eV, in the form

$$\lambda_s = E_i/[a_s(\ln E_i + b_s)] \qquad (11)$$

where a_s and b_s are constants for a particular material. Penn [*76*] has computed values of a_s and b_s for "free-electron-like" elements, those for which the most probable type of inelastic scattering is plasmon excitation. His values of λ_s for these elements for $E_i = 1000$ eV are plotted as solid circles in Fig. 2 as a function of atomic number; these values are believed accurate to about 5 percent [*76*]. Estimates of λ_s for other elements at $E_i = 1000$ eV are shown as open circles in Fig. 2 and these are believed to have an uncertainty of about 40 percent [*76*]. If the concept of a universal curve was valid, the points in Fig. 2 would lie on a line parallel to the abscissa.

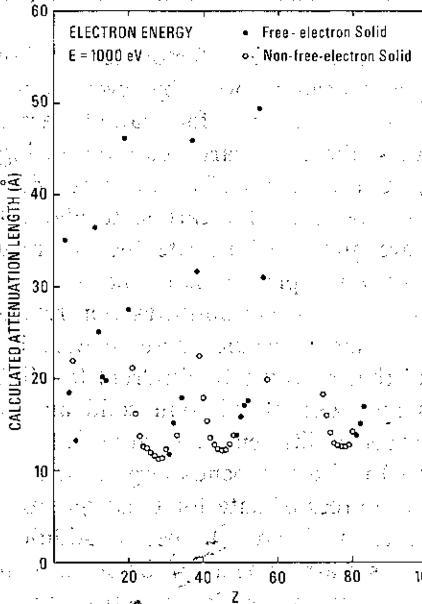

FIG. 2—*Calculated values of the electron attenuation length for inelastic scattering in elemental solids as a function of atomic number Z, according to the results of Penn* [76]. *The attenuation lengths have been calculated for a fixed electron energy of 1000 eV. The solid circles denote results for free-electron-like solids which are expected to be more accurate than the estimates shown as open circles for nonfree-electron-like solids.*

It is seen, however, that, although many of the points lie between 10 and 20 Å, there are a substantial number of points outside this range. There is, of course, no physical reason why attenuation lengths should be material-independent; in fact, theory shows that the parameters a_s and b_s of Eq 11 depend on electron density in the solid for free-electron-like solids [*76*].

Penn [*76*] has found that b_s for most materials lies between -1 and -3. For 200 eV $\leq E_i \leq$ 2400 eV, the range of practical interest in most AES

and XPS, $\ln E_i$ lies between 5.3 and 7.8. If the approximation $b_s = -2.3$ is made, Eq 11 simplifies to

$$\lambda_s \approx E_i / a_s (\ln E_i - 2.3) \tag{12}$$

with at most an error of 14 percent in ratios of values of λ_s at different energies in the same material.

The calculations of $\lambda_s(E_i)$ by Penn are for a homogeneous, infinite solid. It is possible that the effective value of $\lambda_s(E_i)$ could vary with distance from a surface or interface, for distances on an atomic scale, but the effects of any such variation have not been fully evaluated for quantitative AES and XPS [*77,78*].

Determinations of the correction factor for backscattered electrons, $r_{s,i}(E_0,E_X)$ in Eq 6, have been reported by several authors [*53,56,79-81*]. The results of Smith and Gallon [*80*], for example, are given in Fig. 3 and show that $r_{s,i}$ increases almost linearly with increasing values of $U_X = E_0/E_X$, for $2 \leq U_X < 10$. Values of $r_{s,i}$ increase with increasing atomic number, varying from about 1.1 for carbon to about 1.8 for gold at $U_X = 3$. These values are given to illustrate the observed trends when the incident beam strikes the sample normally and when the Auger spectrum is measured with a low-energy-electron-diffraction retarding-field analyzer. It would be expected that $r_{s,i}$ would increase with increasing angles of incidence [*82,83*] and that $r_{s,i}$ could be different for different experimental configurations (with analyzers of different solid angles of acceptance or with sample and analyzer in different orientations).

The factor $v_{s,i}(W_j,X)$ in Eq 6 depends largely on the atomic parameters γ_j and σ_i in Eq 4; the sources of data for these quantities have been given in the previous subsection. There will be, in addition, an effect of the matrix through $r_{s,i}$. This matrix effect will be small if the binding energies of the levels $E_{W,j}$ (Eq 4) are not too different from the binding energy E_X.

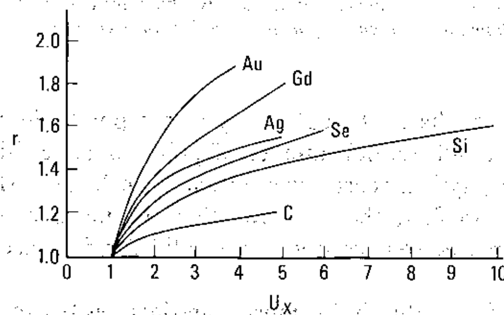

FIG. 3—*Plots of values of the backscattering correction factor* $r_{s,i}(E_0, E_X)$ *for several elements as a function of* $U_X = E_0/E_X$ *obtained by Smith and Gallon* [80].

Instrument Response Function

Most commercial AES and XPS instruments have electrostatic deflection-type analyzers to disperse the electrons. For these analyzers, the transmission function $T(E_a)$ is a linear function of electron energy in the analyzer, E_a [*84*]. The factor $F(E_i,E_a)$ in Eqs 1 and 2 describes how intensities are modified if electrons are decelerated from the energy E_i to E_a before energy analysis. This factor is known for the electron-optical systems of some instruments but is not always known for instruments with proprietary designs.

A draft recommended practice "Describing and Specifying Electrostatic Electron Spectrometers," prepared by C. E. Kuyatt of the National Bureau of Standards, is now under consideration by ASTM Committee E-42 on Surface Analysis. This draft practice gives the dependence of the product $F(E_i,E_a)T(E_i,E_a)$ on E_i for several configurations of an analyzer system consisting of apertures, deceleration lenses, and a dispersing element. Table 1 shows these values.

TABLE 1—*Expected dependence of the product* $F(E_i, E_a)T(E_i, E_a)$ *on* E_i *for several configurations of an electrostatic electron energy analyzer system consisting of apertures, electron lenses to decelerate electrons from an initial energy* E_i *to an analysis energy* E_a, *and a dispersing element (analyzer). The analyzer can operate with* E_a *fixed or with* E_a *proportional to* E_i. *Taken from the ASTM E-42 draft recommended practice "Describing and Specifying Electrostatic Electron Spectrometers" prepared by C. E. Kuyatt.*

Configuration	$F(E_i, E_a)T(E_i, E_a)$
Sample → apertures → analyzer ($E_a = E_i$)	αE_i
Sample → lens and apertures → analyzer ($E_a \alpha E_i$)	αE_i
Sample → lenses → apertures → analyzer (E_a = constant)	$\alpha 1/E_i$
Sample → apertures → lenses → analyzer (E_a = constant)	constant

The final factor to be considered is the detector efficiency $D(E_a)$. The variation of efficiency with the energy of the electrons striking the multiplier depends on the type of multiplier but should not be large as long as the incident energy is greater than a few hundred electron volts. The magnitude of the efficiency (and perhaps the variation of efficiency with energy) may change with time, particularly if the multiplier is exposed to active gases.

Analytical Methods

A number of procedures have been proposed for different analytical situations.

Information concerning homogeneity or inhomogeneity normal to the surface can be obtained from the variation of spectral intensities with take-off angle (AES and XPS) and with incident energy (AES). Similar information can be obtained from comparisons of the relative intensities of two or more features of different kinetic energy from the sample with corresponding intensities from a reference sample (AES and XPS). A scanning Auger electron spectrometer can be used to determine the degree of homogeneity or inhomogeneity parallel to the surface. The equations given earlier can be generalized to these more complex situations [*1,22,27,31,37, 41,49,51,52,58,59,64,85*].

For homogeneous samples, Eqs 5, 11, and 12 can be used to compare measured XPS intensities $I_1(E_i)$ and $I_2(E_i)$ for the same transition of the *same atom* in *different compounds* or *alloys*

$$\frac{I_1(E_i)}{I_2(E_i)} = \frac{N_1\lambda_1(E_i)}{N_2\lambda_2(E_i)} \approx \frac{N_1 a_2}{N_2 a_1} \tag{13}$$

Equation 13 was derived on the assumptions that the photoelectron energy will be essentially the same (E_i) in the different compounds and that the instrumental response function $H(E_i,E_a)$ will be the same for both measurements. The attenuation lengths at E_i in the two samples will be $\lambda_1(E_i)$ and $\lambda_2(E_i)$ which are proportional to a_2 and a_1, respectively. The use of uncorrected elemental sensitivity factors involves the implicit assumption that $\lambda_i(E_i) \approx \lambda_2(E_i)$. If this assumption is made, relative atomic concentrations can be readily obtained from measured intensities with Eq 13.

Equations 5, 11, and 12 can also be used to compare XPS intensities $I_1(E_1)$ and $I_2(E_2)$ from transitions for *different atoms* in the *same compound* or *alloy*

$$\frac{I_1(E_1)}{I_2(E_2)} = \frac{N_1\sigma_1\lambda_s(E_1)H(E_1,E_a)}{N_2\sigma_2\lambda_s(E_2)H(E_2,E_a)} = \frac{N_1\sigma_1E_1(\ln E_2 + b_s)H(E_1,E_a)}{N_2\sigma_2E_2(\ln E_1 + b_s)H(E_2,E_a)} \tag{14}$$

In general, the photoelectrons from atoms 1 and 2 will emerge with different kinetic energies E_1 and thus different attenuation lengths $\lambda_s(E_1)$ and $\lambda_s(E_2)$ in the sample s. The advantage of Eq 14 is that absolute values for the attenuation lengths are not needed; rather, one needs only the variations of λ_s with E_i which is given by Eqs 11 and 12. On the other hand, use of Eq 14 requires knowledge of the differential photoionization cross sections σ_1 and σ_2 and of the instrumental response function $H(E_1,E_a)$ and $H(E_2,E_a)$ for the particular measurement.

Equations 13 and 14 can be generalized for specific models of inhomogeneous surfaces. Analogous equations can also be written using Eq 6 with AES intensities.

A problem with the analogous forms of Eqs 13 and 14 for Auger electron spectroscopy is that there are *two* parameters, the attenuation length and the backscattering factor, that can affect the analysis significantly. Hall et al [*34*] have found that the variation of these factors with composition can modify the signals from the major peaks proportionally. They write, for a two-component alloy containing elements A and B with relative concentrations c_A and c_B $(0 \leq c \leq 1)$

$$I_A = I_A{}^0 c_A f(c_A) \tag{15a}$$

and

$$I_B = I_B{}^0 c_B f(c_B) \tag{15b}$$

where I_A and I_B are measured intensities of the AES features for each element and $I_A{}^0$ and $I_B{}^0$ are measured intensities for the pure elements. The functions $f(c_A)$ and $f(c_B)$ are written as linear functions of composition

$$f(c_A) = 1 + ac_B \tag{16a}$$

and

$$f(c_B) = 1 + b(c_A) \tag{16b}$$

where the parameters a and b are yet to be determined. Hall et al find that the linear approximation (Eq 16) is satisfactory for a number of alloy systems and that $b \approx -a$. The surface concentration can be written in the form

$$c_A = \frac{I_A}{I_A + I_B P_{\text{rel}}} \tag{17}$$

where

$$P_{\text{rel}} \approx \frac{I_A{}^0}{I_B{}^0}(1 + a) \tag{18}$$

The constant P_{rel} can be determined experimentally from surfaces of known composition or from specific atomic and matrix properties [*66*]. This approach has been found to be useful for over a dozen alloy systems [*34,66*].

We emphasize again that the use of the various analytical approaches described here is based at least implicitly on a specific structural model of the sample surface. In many cases, however, numerical results are pre-

sented for "the" composition of a surface without explicit recognition being given to sample homogeneity and to defining the volume (sample area and sample depth) being probed under the specific conditions of measurement.

Intensity Measurements

Whatever the procedure used for quantitative surface analysis by AES or XPS, it is necessary to make meaningful determinations of the intensities of selected spectral features in the raw data. A rigorous intensity measurement can be difficult, but shortcuts proposed for simplicity and experimental convenience can lead to appreciable systematic errors. We will therefore review here the physical factors that affect the measured spectra.

Figure 4 illustrates a "typical" feature in an XPS experiment [*50*]. This example has been selected for the favorable case where most of the observed intensity is in a relatively sharp line. Subsidiary structure at lower electron kinetic energies is due to inelastic scattering of the emerging photoelectrons. These features appear on a background due to the multiple inelastic scattering of photoelectrons of initially higher kinetic energy, and, in instruments without an X-ray monochromator, to photoemission by bremsstrahlung from the X-ray source. The problem is to determine the XPS intensity corresponding to the cross section $\sigma_i(\hbar\omega,\theta,X)$ in Eq 5 with proper regard to the background, to the XPS line shape, to inelastic scattering, and to "shake-up" or final-state effects [*10*].

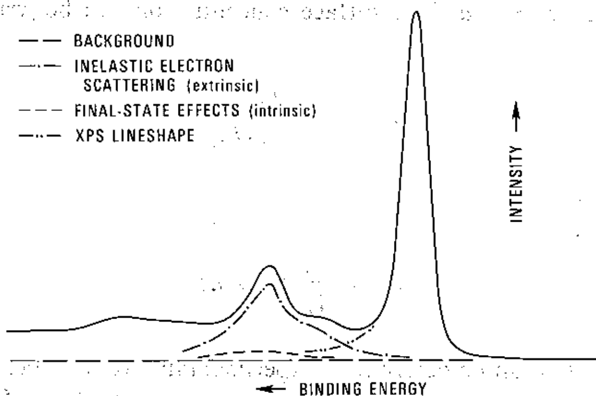

FIG. 4—*Schematic diagram of an observed XPS line (solid line)* [50]. *The long-dashed line (— —) represents an extrapolation of the background from high to low electron energies; the dot-dashed line (-·-) represents the contribution due to single inelastic scattering; the short-dashed line (---) represents the contribution due to shake-up processes; and the double-dot-dashed line (-··-) represents the line shape of the parent XPS feature.*

Over the region of the main XPS line and its associated structures, the background can be located by simple analytic extrapolation, as indicated by the long-dashed line in Fig. 4. No structure is expected in the background, as defined previously, except in the unlikely event of a weak XPS signal from a minor constituent or impurity (whose presence could be made evident by characteristic features at other electron energies).

The XPS intensity of interest is constrained by several factors. First, the intensity of the structures due to single inelastic scattering is known to be approximately equal to the intensity of the parent XPS line [*77,78,86*]. For solids in which the most probable inelastic scattering events are due to bulk and surface plasmon excitation, it is possible to make a plausible estimate of the line profile, as represented by the dot-dashed curve in Fig. 4. Second, there will be finite intensity due to final-state or shake-up processes in which other electrons of the solid are excited in addition to the photoelectron from the core level. The fractional intensity of such processes is not, in general, well known, although for metals it could be as high as 15 to 30 percent of the parent XPS line intensity [*87,88*]; this contribution is represented schematically as the short-dashed line in Fig. 4. Finally, the shape of the parent XPS line is expected to be asymmetrical [*89*]. The form of the asymmetry can be expressed as

$$I(\epsilon) = \frac{\cos\left[\frac{\pi\alpha}{2} + (1 - \alpha)\arctan\frac{\epsilon}{\gamma}\right]}{[\epsilon^2 + \gamma^2]^{(1-\alpha)/2}} \tag{19}$$

where $I(\epsilon)$ is the intensity of the line as a function of energy ϵ, 2γ is the natural width (full width at half maximum) of the core level due to lifetime broadening, and α is an asymmetry parameter. The parameter α is large for conductors with a large density of states at the Fermi level (for example, transition metals) and is zero for insulators; this parameter is also a matrix property in that it changes with composition (for example, in an alloy) [*90*]. The values of α encountered in practice range from 0 to 0.3. Equation 19 is plotted in Fig. 5 for the relatively small value of $\alpha = 0.11$ and for two typical values of the parameter γ. It can be seen that a substantial fraction of the total intensity of the line occurs in the tails extending to low kinetic energy; this fraction is greater for larger values of α.

Similar considerations apply to the determination of AES intensities. The problem in this case is made more difficult by changes in AES line shape with different chemical environments (for transitions involving valence-band electrons) and by the expectation that final-state or shake-up effects will be more severe than in XPS since the emitting atom is left doubly ionized. Also, AES transitions involving valence-band electrons (the transitions commonly observed) are often broader than the peaks ob-

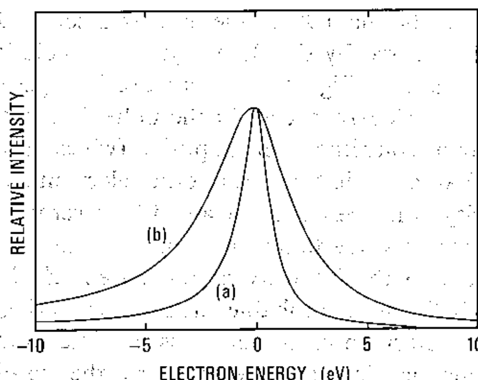

FIG. 5—*Plot of Eq 19 with* $\alpha = 0.11$ *and for* $2\gamma = 1.4$ *eV* (*Curve* (a)) *and* $2\gamma = 4.0$ *eV* (*Curve* (b)).

served in XPS, and it can be more difficult to decompose the observed AES intensity into its several components.

There is no simple, general prescription that allows a determination of AES and XPS intensities with proper regard paid to all of the factors just described. Useful progress, however, has been made recently in the development of objective methods for determining several of the relevant factors. Sickafus [*91*] and Houston [*92*] have developed analog and digital procedures, respectively, for the determination of the background in AES data. Hesse et al [*93*] have used a smoothing spline algorithm with AES data for interpolation purposes; this method is useful for peak location but does not give the background as defined previously. Methods for deconvoluting observed spectra for the effects of inelastic electron scattering have been reviewed by Madden and Houston [*94*]. This approach is convenient in AES where the characteristic energy-loss spectrum for the sample at an incident electron energy close to that for an AES feature can be readily measured; for XPS, however, use must be made of inelastic-scattering data in the literature which may not, in general, be appropriate for the experimental XPS geometry and the electron energies of interest. Analog and digital integration methods for the determination of total AES intensities have been described by Grant et al [*95*] and by Springer and Pocker [*96*], respectively; Grant et al [*97*] have shown that the total AES intensity is required rather than a measurement of the peak-to-peak heights of features in the usually measured derivative of the electron energy distribution. An analog method for the determination of XPS intensities has been discussed by Powell and Larson [*50*]. While the methods described briefly here have varying degrees of uncertainty for the determination of $I_s(E_{i,X})$ in Eq 5 or $I_s(E_{i,XYZ})$ in Eq 6 (and the systematic errors have not

been well established), it is likely that ratios of intensities, with each intensity measured by the same method, have appreciably less systematic error than the individual intensities.

Practical Considerations

Up to this point, it has been assumed that the actual conditions of analysis fulfill the assumptions made in the earlier descriptions of the AES and XPS processes. In practice, of course, these assumptions may not be valid, and we discuss factors here which should be kept in mind in practical measurements. The magnitude of the resulting error in a surface analysis can only be assessed by a more detailed characterization of the sample and the conditions of measurement in the specific analytical situation.

Practical surfaces are not smooth on an atomic scale, and finite roughness has been found to affect both the AES and XPS intensity as well as the angular distribution [*22,41,98,99*]. The roughness of a sample could affect the intensities of different spectral features in a proportional way, at least approximately, but comparison of intensities for different samples (that is, the unknown and a reference) may be subject to appreciable error unless the samples had a similar surface topography.

Anisotropies in electron transport are to be expected in crystalline material. Diffraction effects have been observed in AES [*100*] and XPS [*22,41*]; in addition, Kikuchi patterns have been observed in AES as the angle of incidence of the primary beam was varied [*101*]. For polycrystalline surfaces, these angular anisotropies may be averaged out although there is no guarantee that this will always occur (on account of preferred orientation). Measurements of the angular anisotropies for AES and XPS from chemisorbed atoms on single-crystal surfaces can be analyzed to yield information on the local atomic structure of the adsorbates [*102,103*].

A frequent application of AES is for "depth profiling," the determination of surface composition as layers of the sample are removed by sputtering. Sputtering may modify the composition it is desired to measure, change the surface microtopography, and cause motion of surface and subsurface atoms [*104*]. Changes may occur in the AES line shape with varying chemical environment, and this needs to be considered in quantitative measurements [*105*]. The "chemical shifts" of both AES [*106*] and XPS [*107*] peaks can, however, be used to provide additional information to characterize interfaces.

Finally, improved accuracy and sensitivity cannot be obtained merely by increasing the total observation time with limits set only by the patience of the experimenter or the stability of the instrument. The surface composition may change with time through adsorption of gases and vapors from the residual vacuum. More importantly, the incident electron beam in AES may cause desorption of adsorbed gases, dissociation of molecules

and compounds, enhanced diffusion of near-surface species, and polymerization [*108*].

Applications

Quantitative information on surface composition has been obtained by AES and XPS in many laboratories for many different applications [*1–22*]. We can only indicate here the nature of the results in typical applications.

Both techniques have been used to measure the concentration of surface species (contaminants, adsorbates, and condensates) on an otherwise clean surface. The formalism described previously has been used to determine surface concentration, although, when applied to submonolayer phases, the use of a macroscopic electron attenuation length does not appear to be justified [*78*]. Nevertheless, observed AES and XPS signals for such thin films appear to correlate well with other estimates of surface coverage [*54*]. Ueda and Shimizu [*109*], for example, have used AES to determine the concentration of impurities that diffused to the surface of a silicon-iron sample on heating. Measurements such as these have been related to theories of surface segregation [*110*].

AES and XPS have been used to find the extent to which the surface composition of alloys is different from the bulk composition [*64,65,110–114*]; several of these authors have determined the variation of composition with depth from AES measurements with electrons of different kinetic energy (and thus attenuation length). The degree of surface enrichment of one species has been found to be dependent on sample treatments, such as sputtering, annealing, and exposure to gases and chemicals.

The surface composition of numerous compounds has been determined by Wagner using XPS [*69*]. Similar measurements have been made by AES [*31,32,61*].

AES has been used to measure the composition of dopants in silicon and other materials used in the semiconductor industry [*62,115,116*]. Measurements of this type have been used to obtain information on diffusion coefficients in semiconductor devices and in intermetallic films [*117,118*].

Depth profiling is used frequently to obtain relative elemental abundances by AES as the surface is eroded by sputtering. Johannessen et al [*106*] have used this technique to determine the stoichiometry of the silicon-silicon dioxide interface.

Finally, XPS has been used successfully for trace analyses in the parts-per-billion range [*119,120*]. This has been accomplished using surface enrichment methods.

The precision of the results in applications such as those described is often good (of the order of 1 percent), but the accuracy is not, in general, well established. Each experimenter has usually done as well as reasonably could be expected, but the state of the art in quantitative surface analysis

by AES and XPS has not advanced to the point where definitive statements of accuracy can be made for specific analytical situations. As mentioned earlier, the experimenter often does not know enough about the distribution of atoms in the surface region of the sample to be able to determine the accuracy.

This situation, however, is changing, and the outlook is encouraging. For the relatively simple case of impurities or an adlayer on a surface, the AES and XPS measurements can be readily compared with the results of independent measurements of surface coverage. Intercomparisons of XPS data such as those of Wagner [*69*] for many compounds show a high degree of internal consistency. These and similar AES and XPS measurements show a necessary degree of internal consistency and indicate the essential correctness and utility of the model description given here for many applications. Improved methods for the determination of the intensities of spectral features [*50*] are expected to yield improved accuracy.

Reference Materials

The models and methods described here can be used not only as a framework for surface analysis by AES and XPS but also can serve as a means to develop reference materials or reference sources which can be used to calibrate instruments and to validate the entire chain (sample preparation, measurement, data analysis) used to make surface analyses. Several types of reference materials are envisaged.

Pure materials (for example, metals) can be used to calibrate the energy and relative intensity scales of AES and XPS instruments. These materials can also be used to determine the instrument response function (the term $H(E_i, E_a)$ in Eqs 5 and 6) if the atomic and matrix properties of these samples are sufficiently well known. Finally, there is a need for materials to obtain the working sensitivity of an AES or XPS instrument for different areas of application; suitable materials could be ion-implanted silicon, oxides, glasses, or thin-film samples.

Conclusion

AES and XPS have been used extensively for qualitative analyses of surfaces but have been applied only recently for quantitative analyses. It seems likely that the pattern of development of these techniques for quantitative measurements will be similar to that of the electron-probe microanalyzer (EPMA). Since the latter instrument became commercially available, models and data for quantitative applications have been refined and extended extensively. I foresee a situation soon in which AES and XPS intensities will be analyzed by a procedure analogous to the *ZAF* method [*121*] for the EPMA. The *ZAF* method involves separate corrections

for the atomic number of detected element (Z), absorption of X-rays leaving the sample (A), and for additional ionization by fluorescence (F). It is clear from Eqs 5 and 6 that elemental concentrations of surface atomic species can be obtained from measured AES and XPS intensities with knowledge of atomic properties (ionization cross sections (AES and XPS) and Auger transition probabilities), electron attenuation lengths (AES and XPS), and of the backscattering correction (AES). I am therefore optimistic that there will be an increasing number of surface analyses of known accuracy made with AES and XPS in the coming years.

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DISCUSSION

A. Benninghoven[1] *(written discussion)*—My question concerns your table of practical considerations. Although you mention the effect of surface roughness and the crystal structure on the electron yield, you did not discuss the damaging effect of the electron beam. This would have a marked effect on the detectability of species such as hydrogen and oxygen.

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C. J. Powell (*author's closure*)—I agree that this should be another practical consideration in assessing the quantitative aspects of the AES technique.