Effective attenuation lengths for quantitative determination of surface composition by Auger-electron spectroscopy and X-ray photoelectron spectroscopy

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Abstract

The effective attenuation length (EAL) is normally used in place of the inelastic mean free path (IMFP) to account for elastic-scattering effects when describing the attenuation of Auger electrons and photoelectrons from a planar substrate by an overlayer film. An EAL for quantitative determination of surface composition by Auger-electron spectroscopy (AES) or X-ray photoelectron spectroscopy (XPS) is similarly useful to account for elastic-scattering effects on the signal intensities. We calculated these EALs for four elemental solids (Si, Cu, Ag, and Au) and for energies between 160 eV and 1.4 keV. The XPS calculations were made for two instrumental configurations while the AES calculations were made from the XPS formalism after “switching off” the XPS anisotropy. The EALs for quantitative determination of surface composition by AES and XPS were weak functions of emission angle for emission angles between 0 and 50°. The ratios of the average values of these EALs to the corresponding IMFPs could be fitted to a second-order function of the single-scattering albedo, a convenient measure of the strength of elastic-scattering effects. EALs for quantitative determination of surface composition by AES and XPS for other materials can be simply found from this relationship.
Keywords: Quantitative determination of surface composition by AES and XPS; Theory of AES and XPS signal-electron transport in surface region of solids; Effective attenuation lengths for quantitative applications of AES and XPS; Analytical expressions for effective attenuation lengths.

1. Introduction

Measured peak intensities for quantitative analyses by X-ray photoelectron spectroscopy (XPS) and Auger-electron spectroscopy (AES) are known to be affected by the elastic scattering of signal electrons by atoms in the surface region of a solid [1,2]. On the other hand, the common formalism for both spectroscopies is founded on the assumption that elastic scattering has a minor effect on the measured intensities and that this effect can therefore be neglected. Accounting for multiple elastic-scattering events along an electron trajectory generally complicates the analytical formalism, and algorithms that include these events (for example, Monte Carlo simulations) are often very slow and unsuitable for routine analyses. A practical approach that can help circumvent the theoretical complications of elastic scattering is the use of a parameter termed the effective attenuation length (EAL) that may be used for different purposes [3].

The attenuation length (AL) (ref. [4], definition 4.34) is commonly understood as a measure of the opacity of a solid with respect to a parallel beam of radiation or particles. This term is inappropriate for describing attenuation of a beam of monoenergetic electrons impinging on a solid since some electrons can be removed from the beam by elastic- as well as inelastic-scattering events. The probability of inelastic-scattering events in the solid can be described by the inelastic mean free path (IMFP) for the specified solid and electron energy (ref [4], definition 4.243).
Attenuation of electrons in a solid can usefully be accounted for by a single parameter, the EAL. The EAL is defined as the “parameter which, when introduced in place of the inelastic mean free path into an expression derived for AES and XPS on the assumption that elastic scattering effects are negligible for a given quantitative application, will correct that expression for elastic scattering effects” (ref. [4], definition 4.35). Two explanatory Notes accompany this definition. First, the EAL may have different values for different quantitative applications of AES and XPS. However, the most common use of EAL is in the determination of overlayer-film thicknesses from measurements of the changes of substrate Auger-electron or photoelectron signal intensities after deposition of a film or as a function of emission angle. For emission angles up to about 60° (with respect to the surface normal), it is often satisfactory to use a single value for this parameter. For larger emission angles, the EAL can depend on this angle. Second, since there are different uses of the EAL, it is recommended that users specify clearly the particular application and the definition of the parameter for that application (e.g., by giving an equation or by providing a reference to a particular source).

The EAL, \( L_{TH} \), for measuring the thickness of an overlayer film from changes of substrate AES or XPS peak intensities can be obtained as an average of values for a suitable range of overlayer-film thicknesses, \( t_1, t_2, \ldots, t_n \) (see for example ref. [1], p. 283, or ref. [2], p. 235):

\[
L_{TH} = \frac{1}{n} \sum_{i=1}^{n} \frac{1}{\cos \alpha} \left[ \ln \int_{0}^{\infty} \phi(z, \alpha) dz - \ln \int_{t_i}^{\infty} \phi(z, \alpha) dz \right].
\]

In Eq. (1), \( \alpha \) is the photoelectron or Auger-electron emission angle with respect to the surface normal and \( \phi(z, \alpha) \) is the emission depth distribution function (EMDDDF). This function is defined as the “probability that the particle or radiation leaving the surface in a specified state and in a given direction originated from a specified depth measured normally from the surface.
into the material” (ref. [4], definition 4.161). Predictive formulas have been published that provide EALs for determining overlayer thicknesses [5-9]. These EALs can also be obtained from a National Institute of Standards and Technology (NIST) database [10] and can be computed with simulated AES or XPS intensities from another NIST database [11-13].

Another important application of AES and XPS is the determination of the surface composition of a given sample. Elastic-scattering effects modify peak intensities from the values expected if these effects are neglected. These modifications can be described by use of an EAL in place of the IMFP in the formalism for quantitative determination of surface composition by XPS and AES. We emphasize that this EAL, sometime termed the EAL for quantitative analysis (ref. [1], p. 289), is generally different from the EAL used for determining the thickness of an overlayer film. We show here how ratios of EALs for quantitative analysis to the corresponding IMFPs for representative peaks from Si, Cu, Ag, and Au vary with measurement conditions, particularly the electron emission angle.

Previous papers [1,3,6,14-18] have reported evaluations of elastic-scattering effects on AES and XPS peak intensities from various elemental solids. Seah [19] has summarized the basic equations for quantitative analyses by AES and XPS and has utilized the empirical expressions developed by Seah and Gilmore [20] for describing elastic-scattering effects. These expressions were based on the early Monte Carlo calculations of Jablonski for many photoelectron lines excited by Mg Kα and Al Kα X-rays and for many XPS configurations [14]. The basic equations for quantitative analysis by AES and XPS provide a convenient basis for the calculation of average-matrix relative sensitivity factors that are useful for minimizing errors due to matrix factors in quantitative analyses by AES and XPS [19]. We have published what we consider to be improved expressions for describing elastic-scattering effects that were also based on the early Jablonski simulations [17]. We later developed more accurate formulae
for this purpose from Monte Carlo simulations that were repeated with differential elastic-scattering cross sections obtained from a more accurate scattering potential [18].

The paper is structured as follows: We first derive expressions for the EALs for quantitative determination of surface composition by XPS and AES from the mathematical formalism for each technique (Section 2) and analytical theory for electron transport in solids (Section 3). For brevity, we will refer to these EALs as “EALs for quantitative analysis,” as in our previous publications [3,6]. In Section 4, we report calculations of EALs for quantitative analysis by XPS for photoelectron lines from Si, Cu, Ag, and Au excited by Mg and Al Kα X-rays. These calculations were made for two XPS configurations. EALs for quantitative analysis by AES were obtained for hypothetical Auger lines with kinetic energies equal to those of the photoelectrons after “switching off” the XPS anisotropy. Finally, we develop a predictive equation with which EALs for quantitative analysis by AES or XPS can be determined for any material.

2. Mathematical formalism of Auger-electron spectroscopy and X-ray photoelectron spectroscopy

2.1. X-ray photoelectron spectroscopy

Let us first briefly outline the main assumption made in the formalism of quantitative XPS. It is generally accepted that attenuation and scattering of X-rays in the surface region of a sample can be ignored. The direction of X-rays incident on a sample and the X-ray intensity in the shallow surface region responsible for the detected XPS signal intensity are approximately constant (see Fig. 1). However, it is now well known that the elastic-scattering of the photoelectrons should not be neglected [1,2,14–20]. In addition to photoelectrons emitted
in the direction towards the analyzer (trajectory A in Fig. 1), photoelectrons emitted in other
directions have a finite probability of reaching the analyzer (e.g., trajectories B and C in Fig.
1). Using the concept of the EMMDF, we can write the photoelectron signal intensity from a
layer at depth \( z \) with thickness \( dz \) as

\[
dI_x = \Delta \Omega T D_e F_x A N \sigma_x \phi(z, \alpha) \, dz
\]

where \( \Delta \Omega \) is the solid acceptance angle of the analyzer, \( T \) is the transmission function of the
analyzer, \( D_e \) is the detector efficiency, \( F_x \) is the flux of incident X-rays, \( A \) is the analysis area,
\( N \) is the atomic density (the number of analyzed atoms per unit volume), \( \sigma_x \) is the photoemission
cross section, and \( \phi(z, \alpha) \) is the EMDDF [1,2,14-18]. Typically, the irradiated area is larger
than the analysis area and we can then assume that the following approximate relation holds:

\[
A \cong A_0 / \cos \alpha,
\]

where \( A_0 \) is the sample area viewed by the analyzer for photoemission normal to the surface.

From Eqs. (2) and (3), we obtain

\[
I_x = \Delta \Omega T D_e F_x A_0 N \frac{\sigma_x}{\cos \alpha} \int_0^\infty \phi(z, \alpha) \, dz.
\]

If elastic-scattering of the photoelectrons is neglected (the so-called straight-line
approximation (SLA)), the EMDDF is given by

\[
\phi_{SLA}(z, \alpha) = \frac{d\sigma_x/d\Omega}{\sigma_x} \exp \left( -\frac{z}{\lambda_{in} \cos \alpha} \right),
\]

where \( d\sigma_x/d\Omega \) is the differential photoemission cross section and \( \lambda_{in} \) is the IMFP of the
photoelectrons in the sample. In Eq. (5), the term containing the photoemission cross sections
describes the probability density function for photoemission in a given direction, while the
exponential term describes the probability of a photoelectron leaving the surface without energy
loss. From Eqs. (2), (3) and (5), we obtain an equation for the photoelectron signal intensity from a theoretical model in which elastic-scattering events are ignored:

\[ I_x^{SLA} = \Delta \Omega \, T \, D_e F_x A_0 N \frac{d\sigma_x}{d\Omega} \lambda_{in}. \]  

(6)

Since the 1970s, slightly different modifications of Eq. (6) have typically been used in quantitative XPS [21-24].

Let us rewrite Eq. (4) in the following form:

\[ I_x = \Delta \Omega \, T \, D_e F_x A_0 N \left( \frac{d\sigma_x}{d\Omega} \right) \left( \frac{\sigma_x}{d\sigma_x/d\Omega} \frac{1}{\cos \alpha} \int_0^\infty \phi(z, \alpha) dz \right). \]  

(7)

The expression in brackets in Eq. (7) is equivalent to the IMFP in Eq. (6) based on the SLA. This expression can thus be used in place of the IMFP in Eq. (6) to account for elastic-scattering events. We can then define an EAL for quantitative analysis by XPS, \( L_{XPS} \), as

\[ L_{XPS} = \frac{\sigma_x}{d\sigma_x/d\Omega} \frac{1}{\cos \alpha} \int_0^\infty \phi(z, \alpha)dz \]  

(8)

Equation (8) can be rewritten in another form. We have

\[ \int_0^\infty \phi^{SLA} (z, \alpha) dz = \frac{d\sigma_x/d\Omega}{\sigma_x} \lambda_{in} \cos \alpha. \]  

(9)

From Eqs. (8) and (9), we obtain

\[ L_{XPS} = \lambda_{in} \frac{\int_0^\infty \phi(z, \alpha) dz}{\int_0^\infty \phi^{SLA}(z, \alpha) dz}. \]  

(10)

Equation (10) is particularly convenient when the EAL is calculated from a theoretical model that provides EMDDFs in arbitrary units. For example, the EAL can be obtained from Monte
Carlo simulations of photoelectron transport in which EMDDFs are calculated after “switching-on” the elastic scattering of photoelectrons, and then from the same strategy after “switching-off” these events.

2.2. Auger electron spectroscopy

Figure 2 illustrates the creation of Auger electrons in a thin layer of thickness $dz$ at a depth $z$ in a sample following inner-shell ionizations induced by an incident electron beam, and possible Auger-electron trajectories and elastic-scattering events along these trajectories. In contrast to the case of the incident X-ray beam in XPS (Fig. 1), attenuation and scattering of the primary electrons is generally not negligible. Consequently, electrons that ionize the inner shells of atoms in the surface region may arrive from all directions in space, not just from the primary-beam direction. However, emission of Auger electrons is commonly assumed to be isotropic. The angular and energy distributions of incident and scattered electrons varies strongly with depth. As a result, the Auger-electron production rate can vary strongly with depth. This variation may be non-negligible in the surface region of the sample (i.e., the region that contributes to the detected Auger-electron signal). The variation in the Auger-electron production rate with depth is described by the excitation depth distribution function (EXDDF). This EXDDF is defined as the “probability that specified excitations are created at specified depths measured normally from a surface into the material by a beam of specified particles or radiation incident on the surface in a given direction” (ref. [4], definition 4.162).

The Auger-electron signal intensity from a thin layer at a depth $z$ is given by

$$dl_A = \Delta \Omega T_D e \Phi(z, E_0, \theta_0) \phi(z, \alpha) dz,$$

(11)
where $\Phi(z, E_0, \theta_0)$ is the EXDDF, $E_0$ is the primary-electron energy, and $\theta_0$ is the angle of incidence of the primary beam with respect to the sample normal. The total Auger-electron signal intensity is obtained by integration of Eq. (11) [25,26]:

$$I_A = \Delta \Omega T D e \int_0^\infty \Phi(z, E_0, \theta_0) \phi(z, \alpha) dz .$$

(12)

The influence of elastic and inelastic scattering of the primary electrons is taken into account by introduction of the backscattering correction factor, $R$ (ref. [4], definitions 7.2 and 7.3),

$$R = \frac{I_A}{I_A^{(id)}},$$

(13)

where $I_A^{(id)}$ is the Auger-electron signal intensity from an idealized model in which Auger electrons are created following ionizations due to primary electrons assumed to have a constant energy ($E_0$) and constant direction (defined by $\theta_0$). $I_A^{(id)}$ is given by

$$I_A^{(id)} = \Delta \Omega T D e \int_0^\infty \Phi^{(id)}(E_0, \theta_0) \phi(z, \alpha) dz ,$$

(14)

where $\Phi^{(id)}$ is the EXDDF for the assumed idealized model. Consequently,

$$I_A = \Delta \Omega T D e R \int_0^\infty \Phi^{(id)}(E_0, \theta_0) \phi(z, \alpha) dz .$$

(15)

The EXDDF for the number of Auger electrons created by the primary beam in the idealized case per unit layer thickness is given by [25,26]

$$\Phi^{(id)}(E_0, \theta_0) = I_0 P_A \sigma_i(E_0) N \sec \theta_0 ,$$

(16)
where $I_0$ is the primary-beam current, $P_A$ is the probability that a specified Auger transition follows the inner-shell ionization, and $\sigma_i(E_0)$ is the relevant cross section for inner-shell ionization. From Eqs. (15) and (16), we have

$$I_A = \Delta \Omega D_e R I_0 P_A \sigma_i(E_0) N \sec \theta_0 \int_0^\infty \phi(z, \alpha) dz. \quad (17)$$

Due to the fact that emission of Auger electrons is isotropic, the EMDDF from the SLA has the form

$$\phi^{SLA}(z, \alpha) = \frac{1}{4\pi} \exp \left( -\frac{z}{\lambda_{in} \cos \alpha} \right). \quad (18)$$

If elastic scattering of the Auger electrons is neglected, we obtain

$$I_A^{SLA} = \frac{\Delta \Omega}{4\pi} T D_e R P_A I_0 \sigma_i(E_0) N \lambda_{in} \sec \theta_0 \cos \alpha. \quad (19)$$

Let us rewrite Eq. (17) as follows:

$$I_A = \Delta \Omega D_e R I_0 P_A \sigma_i(E_0) N \left( \frac{4\pi}{\cos \alpha} \int_0^\infty \phi(z, \alpha) dz \right) \sec \theta_0 \cos \alpha. \quad (20)$$

On comparison of Eqs. (19) and (20), we see that the IMFP in Eq. (19) can be replaced by the expression in brackets in Eq. (20) to take elastic scattering of the Auger electrons into account. The EAL for quantitative analysis by AES, $L_{AES}$, is then

$$L_{AES} = \frac{4\pi}{\cos \alpha} \int_0^\infty \phi(z, \alpha) dz \quad (21)$$

This expression can be generalized to
We note that $L_{AES}$ from Eq. (22) is defined similarly as the EAL for quantitative analysis by XPS [see Eq. (10)].

3. Analytical theory of electron transport in solids

Parameters describing the transport of photoelectrons and Auger electrons in the surface region of solids can be obtained from two theoretical approaches: (i) Monte Carlo simulations, and (ii) expressions derived from analytical transport theories. The present analysis is based on solution of the kinetic Boltzmann equation within the so-called transport approximation [27-32]. Results obtained from this approach agree very well with corresponding results from Monte Carlo simulations [27-32] yet the programs implementing the analytical theory are much faster.

As shown in the previous section, we need to know EMDDFs for a particular sample and a given experimental configuration to calculate EALs for quantitative analysis by XPS and AES. We first briefly summarize the relevant algorithms from the transport theory for XPS.

Since emission of photoelectrons is anisotropic, we have to determine the probability density function of photoelectron emission angles with respect to the direction of X-rays (see Fig. 1). This distribution is expressed by the differential photoemission cross section. Differential photoemission cross sections derived within the so-called dipole approximation for unpolarized X-rays can be safely used if the photoelectron kinetic energies do not exceed 2000 eV [33,34]:

$$\frac{d\sigma_x}{d\Omega} = \frac{\sigma_x}{4\pi} \left( 1 - \frac{\beta}{2} P_2(\cos \Theta) \right) = \frac{\sigma_x}{4\pi} \left[ 1 - \frac{\beta}{4} (3 \cos^2 \Theta - 1) \right].$$ (23)
where $\beta$ is the asymmetry parameter [35,36] and $\Theta$ is the angle between the X-ray direction and the direction of the analyzer (Fig. 1). The EMDDF derived within the transport approximation has the following general form [1,3,31,32]:

$$\phi(z,\alpha) = \phi_i(z,\alpha,\omega) - \frac{\beta}{4} \phi_a(z,\alpha,\theta_x,\psi,\omega),$$

(24)

where $\phi_i(z,\alpha,\omega)$ is the isotropic part of the EMDDF (corresponding to the assumption that the photoelectron emission is isotropic), $\phi_a(z,\alpha,\theta_x,\psi,\omega)$ is the anisotropic contribution, $\beta$ is the asymmetry parameter, $\theta_x$ is the X-ray incidence angle with respect to the surface normal (Fig. 1), $\psi$ is the angle between the X-ray direction and the axis of the analyzer (Fig. 1), and $\omega$ is the so-called single-scattering albedo [1-3,5-9]. The latter parameter is a convenient measure of the relative strengths of elastic and inelastic scattering in the sample material:

$$\omega = \frac{\lambda_{in}}{\lambda_{in} + \lambda_{tr}},$$

(25)

where $\lambda_{tr}$ is the transport mean free path related to the differential elastic-scattering cross section, $d\sigma_{el}/d\Omega$ [37]:

$$\lambda_{tr} = \left(2\pi N \int_0^\pi (1 - \cos \theta) \frac{d\sigma_{el}}{d\Omega} \sin \theta d\theta\right)^{-1}.$$

(26)

where $\theta$ is the polar elastic-scattering angle. Detailed expressions for the contributions $\phi_i(z,\alpha,\omega)$ and $\phi_a(z,\alpha,\theta_x,\psi,\omega)$ in Eq. (24) are published elsewhere [1,3,31,32]. On integration of the EMDDF, we obtain [3,29,31]

$$\int_0^\infty \phi(z,\alpha) dz = \frac{\mu \omega \lambda_{tr}}{4\pi} \left[\frac{H(\mu,\omega)}{(1 - \omega)^{1/2}} - \frac{\beta}{4} (3 \cos^2 \psi - 1)\right]$$

(27)
where \( \mu = \cos \alpha \) and \( H(\mu, \omega) \) is the Chandrasekhar function. Equation (27) can be rewritten in a more compact form [29]:

\[
\int_{0}^{\infty} \phi(z, \alpha) \, dz = \lambda_{\text{in}} \cos \alpha \frac{Q_x}{4\pi} \left[ 1 - \frac{\beta_{\text{eff}}}{4} (3 \cos^2 \psi - 1) \right],
\]

(28)

where

\[ Q_x = (1 - \omega)(D_1 + D_2), \]

(29)

\[ \beta_{\text{eff}} = \beta \frac{1 - \omega}{Q_x}, \]

(30)

\[ D_1 = \frac{H(\mu, \omega)}{(1 - \omega)^{1/2}}, \]

(31)

and

\[ D_2 = \frac{\beta \omega}{16} (3 \cos^2 \theta_x - 1) H(\mu, \omega) \int_{0}^{1} \frac{xH(x, \omega)}{x + \mu} (3x^2 - 1) \, dx. \]

(32)

Equation (29) is further simplified by taking advantage of the fact that \( D_1 \gg D_2 \) and thus the quantity \( D_2 \) can be omitted [29]. For the dipole approximation, the integral of the EMDDF for the SLA model is obtained from Eq. (28) in the limit \( \omega \to 0 \):

\[
\int_{0}^{\infty} \phi^{\text{SLA}}(z, \alpha) \, dz = \frac{1}{4\pi} \lambda_{\text{in}} \cos \alpha \left[ 1 - \frac{\beta}{4} (3 \cos^2 \psi - 1) \right].
\]

(33)

The EAL for quantitative analysis by XPS can be obtained by introducing Eqs. (28) and (33) into Eq. (10) [1,3]:
After introducing Eqs (29) and (30) into Eq. (34), we obtain a general analytical expression for the EAL for quantitative analysis by XPS that is convenient for use as a correction parameter in practical analysis:

\[
L_{XPS} = \lambda_{in} Q_x \frac{1 - (\beta_{eff}/4)(3 \cos^2 \psi - 1)}{1 - (\beta/4)(3 \cos^2 \psi - 1)}. \tag{34}
\]

Furthermore, for the “magic angle” configuration in which \(3 \cos^2 \psi - 1 = 0\) (i.e., \(\psi = 54.7^\circ\)), Eq. (35) simplifies to

\[
L_{XPS} = \lambda_{in} (1 - \omega) \left[ 1 - \frac{1 - (1 - \omega)^{-1/2}H(\mu, \omega)}{1 - (\beta/4)(3 \cos^2 \psi - 1)} \right]. \tag{35}
\]

Since Auger-electron emission is assumed to be isotropic, the EMDDF for AES is equal to the isotropic part of Eq. (24).

\[
\phi(z, \alpha) = \phi_i(z, \alpha, \omega). \tag{37}
\]

The integral of the EMDDF for AES is obtained by introducing \(\beta = 0\) into Eq. (27) which simplifies then to

\[
\int_0^\infty \phi(z, \alpha) dz = \frac{\mu \omega \lambda_{tr}}{4\pi} \frac{H(\mu, \omega)}{(1 - \omega)^{1/2}} = \frac{1}{4\pi} \lambda_{in} \mu (1 - \omega)^{1/2} H(\mu, \omega). \tag{38}
\]

In the limit \(\omega \to 0\), Eq. (38) provides the EMDDF for AES based on the SLA model:

\[
\int_0^\infty \phi^{SLA}(z, \alpha) dz = \frac{1}{4\pi} \lambda_{in} \cos \alpha. \tag{39}
\]

As follows from Eqs. (22), (38) and (39), the EAL for quantitative analysis by AES is:
\[ L_{AES} = \lambda_{in} (1 - \omega)^{1/2} H(\mu, \omega) = \lambda_{in} Q_{AES}. \] (40)

We note that the EAL for quantitative analysis by AES is equal to the EAL for quantitative analysis by XPS for the “magic-angle” configuration [Eq. (36)]. In other XPS configurations, this conclusion may be not valid. This problem is approached in the next section.

4. Results and discussion

Our calculations of EALs for quantitative analysis by XPS were performed using Eq. (35) or Eq. (36) for the magic-angle XPS configuration. We considered four illustrative elemental solids, Si, Cu, Ag, and Au, and photoionization by the commonly used Mg K\(\alpha\) and Al K\(\alpha\) X-ray sources. We selected the following photoelectron lines for our analysis:

Si: 2s\(1/2\) and 2p\(3/2\)

Cu: 2s\(1/2\), 2p\(3/2\) and 3p\(3/2\)

Ag: 3s\(1/2\), 3p\(3/2\), 3d\(5/2\) and 4s\(1/2\)

Au: 4s\(1/2\), 4p\(3/2\), 4d\(5/2\) and 4d\(7/2\).

The EAL calculations were performed for two experimental configurations:

A. The “magic-angle” configuration in which there is a fixed angle \(\psi = 54.7^\circ\) (Fig. 1) and the photoelectron emission angle \(\alpha\) is varied. For this experimental configuration, it is generally possible to rotate the sample while the X-ray source and the analyzer are mounted in fixed positions.

B. The X-ray source is fixed normal to the sample surface while the emission angle \(\alpha\) can be varied. This configuration can be realized in spectrometers with movable analyzers.

The material parameters needed for the EAL calculations were taken from the following literature sources that were judged to be the most reliable: IMFPs from Tanuma et al. [38], asymmetry parameters from Trzhaskovskaya et al. [35,36], transport mean free paths from
Salvat et al. [39], and binding energies from Williams [40]. The Chandrasekhar function was calculated from a recently published algorithm [41,42]. Table 1 shows the material parameters used in the present analysis.

Our final expressions for the EAL for quantitative XPS [Eqs. (35) and (36)] were derived on the assumption that the parameters \( D_1 \) and \( D_2 \) defined by Eqs. (31) and (32) satisfy the inequality \( D_1 \gg D_2 \). This assumption was based on an analysis of signal intensities of \( s \) photoelectrons in an experimental configuration with a movable X-ray source [29]. Let us consider this issue for the more common experimental configurations considered here and for our selected photoelectron lines. Exemplary results of the values of \( D_2/D_1 \) for Au \( 4s_{1/2}, 4p_{3/2}, 4d_{5/2}, \) and \( 4f_{7/2} \) photoelectrons are shown in Fig. 3 as a function of photoelectron emission angle, \( \alpha \). We see that the ratio \( D_2/D_1 \) calculated for both experimental configurations is always smaller than 0.01. Similar results were obtained for the other solids.

In a recent work, EALs for overlayer-thickness determination were calculated from Eq. (1) for the “magic-angle” configuration using different theoretical models [9]. General conclusions from these calculations were the following: (i) the EALs obtained from different Monte Carlo strategies and from the transport approximation formalism were in good agreement, (ii) the EALs were practically independent of the emission angle up to \( \alpha \approx 50^\circ \); (iii) the EALs increased strongly with emission angle for \( \alpha > 50^\circ \), and (iv) the EALs in the range \( 0^\circ \leq \alpha \leq 50^\circ \) depended very weakly on the maximum considered thickness (for thicknesses corresponding to 90 %, 95 % and 99 % of the total signal intensity from a thin film). These thicknesses correspond to different measures of the information depth (ref. [4], definition 4.246).

We first compare EALs for overlayer-thickness determination, \( L_{TH} \), calculated for our photoelectron lines with Eq. (1) as in ref. [9] from the transport approximation formalism with EALs for quantitative analysis by XPS, \( L_{XPS} \), obtained from Eq. (36). These comparisons were
made as a function of photoelectron emission angle for the magic-angle configuration (i.e., \( \psi = 55^\circ \) in Fig. 1). The results for XPS with Mg K\( \alpha \) X-rays are shown in Figs. 4 to 6 where it is convenient to show ratios of each EAL to the corresponding IMFP to indicate the extent to which each ratio departs from unity (i.e., the strength of elastic-scattering effects for each application). Values of \( L_{TH} \) were calculated assuming a maximum film thickness corresponding to the 95% information depth and with photoemission cross sections given by Eq. (23).

Figures 4 to 6 show that the EALs for the two experimental applications, \( L_{TH} \) and \( L_{XPS} \), are distinctly different. Both \( L_{TH} \) and \( L_{XPS} \) depend weakly on emission angle up to about \( \alpha = 50^\circ \). However, values of \( L_{XPS} \) are closer to the corresponding IMFPs compared to values of \( L_{TH} \). For emission angles exceeding 50°, values of \( L_{XPS} \) decrease with increasing emission angle while values of \( L_{TH} \) increase substantially with emission angle. We note here that values of \( L_{XPS} \) and \( L_{TH} \) are numerically equal for each line at a particular emission angle, typically about 75°. Our results thus indicate the importance of the Note following the ISO definition of the EAL, namely that the EAL can have different values for different quantitative applications of AES and XPS. Qualitatively similar results were obtained for XPS with Al K\( \alpha \) X-rays, and are shown as Figs. S1 to S3 in the Supporting Information.

We now consider experimental XPS configurations in which the X-rays are incident normally on the sample and the angle between the X-ray beam and the analyzer axis is variable (i.e., \( \theta_i = 0^\circ \) and \( \psi = \alpha \) in Fig. 1). We will make comparisons of EALs for quantitative XPS, \( L_{XPS} \), now calculated from Eq. (35) with EALs for quantitative AES, \( L_{AES} \), calculated from Eq. (40). For convenience, the latter values were determined for hypothetical Auger electrons with kinetic energies equal to the energies of our photoelectron lines after “switching off” the anisotropy (i.e., by assuming that the asymmetry parameter, \( \beta = 0 \)). In this way, we can examine the influence of isotropic emission of Auger electrons which is the main difference from photoemission.
The dotted lines in Figures 7 to 9 show plots of the ratios of the EAL for quantitative XPS to the corresponding IMFPs as a function of photoelectron emission angle for our photoelectron lines excited by Mg Kα X-rays in the movable-analyzer configuration. We see that the ratios can differ appreciably from unity, particularly for emission angles, $\alpha$, less than 30°. For the $s$ lines with the largest values of the asymmetry parameter (nearly 2; see Table 1), the ratios reach 77.12, 71.7, 28.1, and 33.3 for the Si 2$s_{1/2}$, Cu 2$s_{1/2}$, Ag 3$s_{1/2}$ and Ag 4$s_{1/2}$ lines, respectively, at $\alpha = 0°$. This result is due to the fact that the signal intensity predicted by the common formalism is very small (equal to zero for $\beta = 2$) while the intensity is considerably increased by elastic collisions of the photoelectrons. Fortunately, in typical experimental configurations, an analyzer is not normally positioned so close to the X-ray source, and thus these large values would not be encountered in practical analysis. For emission angles larger than 30°, the ratios in Figs. 7 to 9 can still exceed unity. For example, $L_{\text{XPS}} / \lambda_{\text{m}} = 1.48$ for Cu 2$S_{1/2}$ photoelectrons when $\alpha = 30°$ [see Fig. 7(c)]. For still larger emission angles, the ratios become less than unity. Qualitatively similar results were obtained for XPS with Al Kα X-rays, and are shown as Figs. S4 to S6 in the Supporting Information.

The solid lines in Figs. 7 to 9 show the emission-angle dependence of the ratios of EALs for quantitative AES, $L_{\text{AES}}$, calculated from Eq. (40) to the corresponding IMFPs. As follows from Eqs. (36) and (40), the EALs for quantitative AES are identical to the EALs for quantitative XPS in the magic-angle configuration that were shown in Figs. 4 to 6. As expected, the solid and dotted lines in Figs. 7 to 9 intersect at the magic angle $\psi_M = 54.7°$.

While the ratios $L_{\text{XPS}} / \lambda_{\text{m}}$ and $L_{\text{AES}} / \lambda_{\text{m}}$ in Figs. 7 to 9 are generally different, the values are similar for a limited range of emission angles, $50° < \alpha < 60°$ or, equivalently, $50° < \psi < 60°$. Since the angle between the X-ray source and the analyzer axis is generally within this range for many XPS instruments, we now consider the possibility of deriving a predictive formula that would provide EALs for quantitative analysis by AES, $L_{\text{AES}}$, and for quantitative
XPS with the magic-angle configuration, $L_{XPS}$. We have previously derived predictive formulae for the EAL for overlayer-thickness measurements [7,9].

For the case of overlayer-thickness measurements, we took advantage of the fact that the needed EAL, $L_{TH}$, varies weakly with photoelectron emission angle in the range, $0^\circ < \alpha < 50^\circ$. In that range, a mean value can be calculated from the individual EAL values

$$< L_{TH} >= \frac{1}{m} \sum_{k=1}^{m} L_{TH}^{(k)},$$

(41)

where $m$ is the number of emission angles. The ratio

$$R_{TH} = \frac{< L_{TH} >}{\lambda_{m}}$$

(42)

turned out to be a linear function of the single-scattering albedo, $\omega$, for a group of photoelectron lines and Auger transitions [7,9]:

$$R_{TH} = 1 - A_{TH} \omega.$$  

(43)

The value of the parameter $A_{TH} = 0.738$ was obtained in a recent evaluation [9].

We now consider whether a similar procedure can be applied for the EALs for quantitative analysis by AES and XPS. As follows from Figs. 4 to 9, the EALs, $L_{XPS}$ and $L_{AES}$, are also weak functions of emission angle in the range $0^\circ < \alpha < 50^\circ$. It is then useful to calculate average EALs:

$$< L_{XPS} > = \frac{1}{m} \sum_{k=1}^{m} L_{XPS}^{(k)},$$  

(44a)

and

$$< L_{AES} > = \frac{1}{m} \sum_{k=1}^{m} L_{AES}^{(k)},$$  

(44b)

where the EALs, $L_{XPS}$ and $L_{AES}$ are calculated from Eqs. (36) and Eq. (40), respectively, for each photoelectron line and for each X-ray source, and the averaging in Eqs. (44a) and (44b) is made over the $m = 51$ uniformly distributed values of emission angle between 0 and 50°.
Let us introduce the following notation:

\[ R_{QA} = \frac{<L_{XPS}>}{\lambda_{in}} = \frac{<L_{AES}>}{\lambda_{in}}. \] (45)

Values of the ratio \( R_{QA} \) calculated for the photoelectron lines considered here are plotted as symbols in Fig. 10 as a function of the single-scattering albedo, \( \omega \), for each line (Table 1). We note that these data points are located along a curve that deviates slightly from linearity. We therefore have fitted the points with a second-degree polynomial:

\[ R_{QA} = 1 - A_{QA}\omega - B_{QA}\omega^2, \] (46)

where \( A_{QA} \) and \( B_{QA} \) are parameters that were found to be \( A_{QA} = 0.147 \) and \( B_{QA} = 0.164 \). The resulting fit is shown as the solid line in Fig. 10, and the root-mean-square deviation of the points from the curve was 0.085 %. Equation (46) is thus a useful formula for predicting EALs for quantitative AES and XPS analyses. This formula is valid for XPS experimental configurations close to the magic-angle configuration, i.e., those configurations for which the angle between the direction of X-rays and the analyzer direction is close to 54.7°, i.e., between 50° and 60°. For AES, this formula is valid for any experimental configuration. If the XPS configuration differs appreciably from the magic-angle configuration, the EAL for quantitative XPS should be calculated from Eq. (35).

The dot-dashed line in Fig. 10 is a plot of the ratio \( R_{TH} \) for determination of overlayer thickness as a function of \( \omega \) from Eq. (43) with \( A_{TH} = 0.738 \) [9]. We see a considerable difference between values of the ratio \( R_{QA} \) for determination of surface composition from Eq. (46) and the corresponding values of the ratio \( R_{TH} \) for measurement of overlayer thickness. EALs for one quantitative application obviously should not be used for another. For example, EALs from a NIST database [10] and predictive formulae [7-9] that are intended for use in measuring thicknesses of overlayer films on planar substrates should not be used for calculation of average-matrix relative sensitivity factors [19]. To avoid confusion, users of EALs should
clearly specify the particular application, the EAL definition, and the source of the EAL data. An interested reader is referred to a published Table that lists different quantitative applications of AES and XPS and analytical expressions for the EALs corresponding to these applications [43].

Equation (46) should be valid for XPS with Mg Kα and Al Kα X-rays or for Auger energies up to 1.5 keV. This conclusion follows from the fact that Eq. (24) was derived from the assumption that the dipole approximation was valid. For larger electron kinetic energies, Eq. (24) should also include an additional term that takes non-dipolar effects into account [44]. Nevertheless, the inclusion of this term had only a very minor effect on calculated values of the EAL for overlayer-thickness measurements involving energies up to about 5 keV. We therefore tentatively assume that Eq. (46) might also be valid for energies up to 5 keV; this assumption will be analyzed in the future. For larger kinetic energies, Eqs. (24) and (27) may not be valid. We also point out that our analysis is for XPS with unpolarized X-rays. This approach is relevant for laboratory X-ray sources and is also considered appropriate for circularly polarized synchrotron radiation. A different formalism for the photoelectron signal intensity would be required for the linearly polarized X-rays available from synchrotron-radiation sources since photoemission cross sections for unpolarized and linearly polarized radiation can differ considerably [35]. A separate study is planned for this problem.

5. Summary
The EAL has long been employed as a parameter for describing the attenuation of Auger electrons and photoelectrons from a planar substrate material by an overlayer film. According to the ISO definition, the EAL is used in an expression in place of the IMFP to correct that expression for elastic-scattering effects [4]. We show here that an EAL for quantitative analysis by AES and XPS can also be defined, consistent with the ISO definition, to give information on changes of photoelectron and Auger-electron intensities due to elastic scattering of the signal electrons. We utilized an analytical theory of electron transport based on the kinetic Boltzmann equation to derive expressions for the EALs for quantitative analysis by XPS and AES; this approach gives results for other parameters similar to those from Monte Carlo simulations [27-32]. Illustrative calculations of the EALs for quantitative analysis were made for photoelectrons excited by unpolarized Mg and Al Kα X-rays in four elemental solids, Si, Cu, Ag, and Au. These calculations were made for two XPS configurations, one in which there was a fixed angle of 55° between the X-ray direction and the direction of the analyzer (the “magic-angle” configuration) and the other in which the X-ray source was fixed normal to the sample surface. We considered photoelectron emission angles, α, between 0 and 85°.

For the magic-angle XPS configuration, we found that ratios of the EALs for quantitative XPS, \( L_{XPS} \), to the corresponding IMFPs were less than unity, but closer to unity than the ratios of the EALs for overlayer-thickness measurement, \( L_{TH} \), to the IMFPs. Both \( L_{XPS} \) and \( L_{TH} \) depended weakly on emission angle up to about 50°. For larger emission angles, values of \( L_{XPS} \) decreased while values of \( L_{TH} \) increased significantly.

For the XPS configuration with the X-rays normally incident on the sample, the ratios of \( L_{XPS} \) to the IMFP could be appreciably greater than unity, particularly for emission angles less than 30°. For larger emission angles, the ratios decreased and became equal to the corresponding ratios for the magic-angle configuration at an emission angle of 55°. 

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Values of the EAL for quantitative AES, $L_{AES}$, were obtained for hypothetical Auger electrons with kinetic energies equal to those of our photoelectrons after “switching off” the XPS anisotropy (i.e., by assuming that the asymmetry parameter $\beta = 0$ in the XPS formalism). As expected, values of $L_{AES}$ were equal to values of $L_{XPS}$ for the magic-angle configuration. While the ratios of $L_{XPS}$ and $L_{AES}$ to the IMFPs are generally different, the values are similar for a limited range of emission angles emission angles, $50^\circ < \alpha < 60^\circ$ or, equivalently, if angles between the X-ray direction and the analyzer direction were between $50^\circ$ and $60^\circ$.

We previously found that ratios of $L_{TH}$ values to the IMFPs were a linear function of the single-scattering albedo, $\omega$, a convenient measure of the strength of elastic-scattering effects in a material [7,9]. This linear relation enabled values of $L_{TH}$ to be estimated from $\omega$ which can be determined from IMFPs and transport mean free paths (TMFPs) [cf. Eq. (25)]. IMFPs are available from a NIST database [45] while TMFPs can be obtained from two other NIST databases [10,11]. We found here that ratios of our $L_{XPS}$ and $L_{AES}$ values for emission angles between $50^\circ$ and $60^\circ$ to the corresponding IMFPs could be fitted to a second-order polynomial as a function of $\omega$. Values of $L_{XPS}$ and $L_{AES}$ can thus be similarly found for any material. Our predictive equation for $L_{XPS}$ and $L_{AES}$ is useful for XPS configurations in which the angle between the X-ray direction and the analyzer direction is between $50^\circ$ and $60^\circ$. The predictive equation is valid for any AES experimental configuration. We expect this formula to be useful for photoelectron kinetic energies and Auger energies between 160 eV and 1.5 keV.

Finally, we emphasize that EALs for quantitative determination of surface composition by AES and XPS are numerically different from EALs for determination of the thicknesses of overlayer films on planar substrates. For example, EALs developed for calculating film thicknesses should not be used for calculating average-matrix relative sensitivity factors.
References


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web address: http://cpc.cs.qub.ac.uk/summaries/AEWW_v1_0.html


Table 1. Kinetic energies, inelastic mean free paths, transport mean free paths, values of the single-scattering albedo, \( \omega \), and values of the asymmetry parameter, \( \beta \), for the photoelectron lines considered in the present work.

<table>
<thead>
<tr>
<th>Line</th>
<th>( E_k ) (eV)</th>
<th>( \lambda_{in} ) (nm)</th>
<th>( \lambda_{tr} ) (nm)</th>
<th>( \omega )</th>
<th>( \beta )</th>
</tr>
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<td>Mg K( \alpha ) radiation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td>Si 2s( \frac{1}{2} )</td>
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<td>17.336</td>
<td>0.1332</td>
<td>1.997</td>
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<td>Si 2p( \frac{3}{2} )</td>
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<td>2.758</td>
<td>18.528</td>
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<td>Cu 2s( \frac{1}{2} )</td>
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<td>0.565</td>
<td>0.717</td>
<td>0.4404</td>
<td>1.990</td>
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<td>Cu 2p( \frac{3}{2} )</td>
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<td>0.795</td>
<td>1.045</td>
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<td>1.364</td>
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<td>Cu 3p( \frac{3}{2} )</td>
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<td>4.845</td>
<td>0.2988</td>
<td>1.561</td>
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<td>0.920</td>
<td>1.714</td>
<td>0.3492</td>
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<td>Ag 3p( \frac{3}{2} )</td>
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<td>1.710</td>
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<td>1.266</td>
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<td>Au 4f( \frac{7}{2} )</td>
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<td>1.511</td>
<td>2.777</td>
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<td>Au 4d( \frac{5}{2} )</td>
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<td>1.731</td>
<td>3.273</td>
<td>0.3459</td>
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\(^{a}\)Taken from ref. [38]  
\(^{b}\)Calculated from ELSEPA program [39]  
\(^{c}\)Interpolated values from refs [35,36]
Figure Captions

Fig. 1. Diagram illustrating photoelectron emission and the notation used.

Fig. 2. Diagram illustrating Auger-electron emission and the notation used.

Fig. 3. Dependence of the ratio of parameters $D_2$ and $D_1$ defined by Eqs. (32) and (31), respectively, on the photoelectron emission angle. Solid line: Au 4s$_{1/2}$ photoelectrons; dotted line: Au 4p$_{3/2}$ photoelectrons; dashed line: Au 4d$_{5/2}$ photoelectrons; dot-dashed line: Au 4f$_{7/2}$ photoelectrons. (a) The “magic-angle” experimental configuration, and (b) the experimental configuration with a movable analyzer.

Fig. 4. Comparison of ratios of EALs to the IMFP for two XPS analytical applications as a function of photoelectron emission angle that were calculated for the “magic-angle” experimental configuration. Solid line: the ratio of the EAL for quantitative XPS analysis to the IMFP [$\frac{L_{XPS}}{\lambda_{in}}$ calculated from Eq. (36)]; dotted line: the ratio of the EAL for overlayer-thickness measurement to the IMFP derived from Eq. (1) using the formalism described in ref. [9]. (a) Si 2s$_{1/2}$ photoelectrons; (b) Si 2p$_{3/2}$ photoelectrons; (c) Cu 2s$_{1/2}$ photoelectrons; and (d) Cu 2p$_{3/2}$ photoelectrons.

Fig. 5. The same as Fig. 4 except for Ag 2s$_{1/2}$, Ag 3p$_{3/2}$, Ag 3d$_{5/2}$ and Ag 4s$_{1/2}$ photoelectrons.

Fig. 6. The same as Fig. 4 except for Au 4s$_{1/2}$, Au 4p$_{3/2}$, Au 4d$_{5/2}$ and Au 4f$_{7/2}$ photoelectrons.
Fig. 7. Comparison of ratios of EALs to the IMFP for quantitative analysis by XPS and AES as a function of electron emission angle that were calculated for an experimental configuration in which Mg Kα X-rays are normally incident on the sample and the analyzer moves (i.e., $\alpha = \psi$ in Fig. 1). Dotted line: the ratio of the EAL for quantitative analysis by XPS to the IMFP [$L_{XPS}/\lambda_{in}$ calculated from Eq. (35)]; solid line: the ratio of the EAL for quantitative analysis by AES to the IMFP [$L_{AES}/\lambda_{in}$ calculated from Eq. (40)]. (a) Si 2s$_{1/2}$ photoelectrons; (b) Si 2p$_{3/2}$ photoelectrons; (c) Cu 2s$_{1/2}$ photoelectrons; and (d) Cu 2p$_{3/2}$ photoelectrons.

Fig. 8. The same as Fig. 7 except for Ag 2s$_{1/2}$, Ag 3p$_{3/2}$, Ag 3d$_{5/2}$ and Ag 4s$_{1/2}$ photoelectrons.

Fig. 9. The same as Fig. 7 except for Au 4s$_{1/2}$, Au 4p$_{3/2}$, Au 4d$_{5/2}$ and Au 4f$_{7/2}$ photoelectrons.

Fig. 10. Comparison of predictive formulas for EALs for quantitative analysis by AES and XPS as described in the text and for overlayer-thickness determination. Symbols: Ratios $R_{QA}$ obtained from averaging the EALs for quantitative AES and XPS according to Eqs. (44) and (45); solid line: fit of Eq. (46) to the $R_{QA}$ values; dot-dashed line: predictive formula for EAL for measurements of an overlayer thickness according to Eq. (43) with $A_{TH} = 0.738$ [9].
Fig. 2
Fig. 3

$\psi = \psi_M \approx 55^\circ$

$\theta_x = 0^\circ$

Gold  Mg K$\alpha$

- Gold 4s$_{1/2}$
- Gold 4p$_{3/2}$
- Gold 4d$_{5/2}$
- Gold 4f$_{7/2}$
Fig. 4
Fig. 5
Fig. 6
Fig. 7
Fig. 8
Fig. 10
Supplementary Information for

Effective attenuation lengths for quantitative surface analysis by Auger-electron spectroscopy and X-ray photoelectron spectroscopy

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We present ratios of EALs for quantitative analysis by XPS and by AES to the corresponding IMFPs for XPS with Al Kα X-rays as a function of photoelectron emission angle like those shown in Figs. 4 to 9 for XPS with Mg Kα X-rays. All dependences are plotted in the same coordinates to facilitate comparisons.

Figures S1 to S3 show comparisons of ratios of the EAL for quantitative analysis by XPS, \( L_{XPS} \), to the IMFP with the ratio of the EAL for overlayer-thickness measurement, \( L_{TH} \), to the IMFP. The calculations were performed for the “magic-angle” XPS configuration. We see that these plots are practically identical to the corresponding plots shown in Figs. 4 to 6. One can notice that the emission-angle dependence of the ratio \( L_{TH}/\lambda_{in} \) differs slightly in Figs. S1(c) and S1(d) as compared to Figs. 4(c) and 4(d) in the vicinity of 85° (for Cu 2s\(_{1/2}\) and Cu 2p\(_{3/2}\) photoelectrons). The change of radiation from Mg Kα to Al Kα (which results in an
increase of photoelectron kinetic energies by 233 eV) does not affect our general conclusion that EALs determined for different quantitative XPS applications may differ considerably.

Figures S4 to S6 show comparisons of ratios of the EAL for quantitative analysis by AES to the IMFP (solid lines) as a function of electron emission angle to the ratios of the EAL for quantitative analysis by XPS to the IMFP (dotted lines) for an XPS configuration in which the X-rays are normally incident on the sample surface. Similar trends to those shown in Figs. 7 to 9 are visible. There are, however, noticeable differences in the magnitudes of the ratios \( L_{AES}/\lambda_{in} \) for emission angles less than about 30°, as shown in the plots for Ag 3p\(_{3/2}\) photoelectrons [Fig. S5(b) compared to Fig. 8(b)], Au 4s\(_{1/2}\) photoelectrons [Fig. S6(a) compared to Fig. 8(a)] and Au 4f\(_{7/2}\) photoelectrons [Fig. S6(b) compared to Fig. 9(b)].
Figure Captions

Fig. S1. Comparison of ratios of EALs to the IMFP for two XPS analytical applications as a function of photoelectron emission angle that were calculated for Al Kα radiation and the “magic-angle” experimental configuration. Solid line: the ratio of the EAL for quantitative XPS analysis to the IMFP [ratio $L_{XPS}/\lambda_{in}$ calculated from Eq. (36)]; dotted line: the ratio of the EAL for overlayer-thickness measurement to the IMFP derived from Eq. (1) using the formalism described in ref. [9]. (a) Si 2s$_{1/2}$ photoelectrons; (b) Si 2p$_{3/2}$ photoelectrons; (c) Cu 2s$_{1/2}$ photoelectrons; and (d) Cu 2p$_{3/2}$ photoelectrons.

Fig. S2. The same as Fig. S1 except for Ag 2s$_{1/2}$, Ag 3p$_{3/2}$, Ag 3d$_{5/2}$ and Ag 4s$_{1/2}$ photoelectrons.

Fig. S3. The same as Fig. S1 except for Au 4s$_{1/2}$, Au 4p$_{3/2}$, Au 4d$_{5/2}$ and Au 4f$_{7/2}$ photoelectrons.

Fig. S4. Comparison of ratios of EALs to the IMFP for quantitative analysis by XPS and AES as a function of electron emission angle that were calculated for an experimental configuration in which Al Kα X-rays are normally incident on the sample and the analyzer moves (i.e., $\alpha = \psi$ in Fig. 1). Dotted line: the ratio of the EAL for quantitative analysis by XPS to the IMFP [ratio $L_{XPS}/\lambda_{in}$ calculated from Eq. (35)]; solid line: the ratio of the EAL for quantitative analysis by AES to the IMFP [ratio $L_{AES}/\lambda_{in}$ calculated from Eq. (40)]. (a) Si 2s$_{1/2}$ photoelectrons; (b) Si 2p$_{3/2}$ photoelectrons; (c) Cu 2s$_{1/2}$ photoelectrons; and (d) Cu 2p$_{3/2}$ photoelectrons.

Fig. S5. The same as Fig. S4 except for Ag 2s$_{1/2}$, Ag 3p$_{3/2}$, Ag 3d$_{5/2}$ and Ag 4s$_{1/2}$ photoelectrons.

Fig. S6. The same as Fig. S4 except for Au 4s$_{1/2}$, Au 4p$_{3/2}$, Au 4d$_{5/2}$ and Au 4f$_{7/2}$ photoelectrons.
Fig. S1
Fig. S2
Fig. S3
Fig. S4
Fig. S5
Fig. S6