A System for the Intensity Calibration of Electron Spectrometers

M P Seah

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M P Seah
Division of Materials Metrology
National Physical Laboratory
Teddington
Middlesex TW11 0LW
United Kingdom

ABSTRACT

A system for the calibration of the intensity/energy response function for electron spectrometers used in Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) is described. The basic physical principles of a complete system are detailed to show how the data are derived and how the calibrations may be made traceable to the SI system. The calibration method gives an accurate energy dependence of the intensity/energy response function which is the functional dependence presently needed for analytical work. For AES this gives a reproducibility demonstrated below 2% and for XPS at 4%. For AES this is also made traceable in absolute sense, where the response function is given in sr eV units, to an accuracy of 6%. For XPS the units of the response function are also sr eV for focused X-ray monochromators but for diffuse unmonochromated X-ray sources m² sr eV units are more appropriate. Accurate traceability for XPS exists for all terms except the X-ray source production efficiency. The full traceability is important for those studying absolute cross sections but is usually unimportant where quantification procedures involve any normalisation procedures.
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1 INTRODUCTION

For quantitative analysis using Auger or X-ray photoelectron spectroscopies the electron spectrometer requires intensity calibration. Without some form of intensity calibration errors of more than a factor of 2 may occur [1-4]. The extent to which intensity calibration is necessary depends on the type of quantitative analytical procedure being used.

In the simplest aspect of calibration, if we wish to note the relative dilute amounts of an element in two similar samples, it may be sufficient to know that the relevant instrument intensity scale has been stable over the period of the analysis. If a simple quantification is required and reference materials are analysed with the samples, stability may be required over a slightly longer period [5]. If the reference data have been acquired into a local data bank either a long term stability is required or a method to monitor a relative intensity/energy response function is necessary. If the instrument is switched between high energy or spatial resolutions and a high sensitivity mode further conversions are needed and, if published data banks [6] are used, the necessity to relate calibrations spreads more widely. For all of these uses a relative spectrometer intensity/energy response function is adequate. However, if we wish to use the Tougaard background subtraction method [7] or theoretically derived cross-sections or other parameters we shall need the true shape of the intensity/energy response function although we may not need an absolute intensity scale. If we wish to compare results fully with theory to confirm the theory or to make other basic measurements we need a fully quantitative intensity scale. The present paper sets down how these calibrations may be efficiently completed.

In the literature we may find several examples of calibration methods. Many of these rely on an assumption about electron optics which, at first sight, may seem quite reasonable but which, if tested experimentally, are found to be rather poor approximations. Usually they involve a short-cut in method which gives a moderate result but does not give a result in which the accuracy may be improved. In early work Seah [8] showed that the dependence of spectral intensity on the spectrometer pass energy, $E_p$, and the electron kinetic energy, $E$, was as $E_p f(E_p / E)$. This has been used by Hemminger et al [9] to rationalise data from different operating conditions to within a standard deviation of some 20%. Carazza and Leon [10] use a similar approach but unfortunately the simple relation is not very accurate as stray magnetic fields, the effect of the detector [11] etc are all ignored [2]. In the AES work of Langeron [12] similar effects are also ignored. An alternative approach has been from theoretical AES and XPS intensities [2,13]. There are many other works but none has found universal acceptance since most methods are difficult and lack traceability. Some useful background may be found in the work of Weng et al [14]. This is not really a criticism of any of this early work, it merely shows how difficult and important the problem is.

In the next section we present the basic parameters affecting intensities in electron spectrometers for AES and XPS and then follow this with a description of the calibration procedure.

2 SPECTROMETER TRANSMISSION TERMS

2(a) Auger Electron Spectrometers

The energy spectrum in Auger electron spectroscopy, $I_A(E)$ that is measured for a given sample for a small, focused electron beam of current $I_o$ is given by
\[ I_A(E) = I_o \int_0^\infty \int_0^\pi T(E',E,\theta,\phi) \; n_A(E',\theta,\phi) \; D(E') \; dE' \; \sin \theta \; d\theta \; d\phi \]  

(1)

where the subscript A is for AES, E is the electron energy measured with respect to the Fermi level and \( I_A(E) \) is the measured current.

Here \( \theta \) and \( \phi \) are the polar and azimuthal angles, \( n_A(E,\theta,\phi) \) is the true energy spectral current per unit incident current, per unit solid angle and per eV emitted in the direction \( \theta,\phi \). \( T(E,E',\theta,\phi) \) is the fractional transmission term into each elemental solid angle for the electron analyser and \( D(E') \) the efficiency of the whole detection system for electrons of energy \( E' \). The convolution of \( T(E'-E,E,\theta,\phi) \) with \( n_A(E',\theta,\phi) \) is important from the point of view of the energy resolution of the measured spectrum but, for our present studies, we may write this convolution simply as

\[ \int T(E'-E,E,\theta,\phi) \; n_A(E',\theta,\phi) \; D(E') \; dE' = T(E,\theta,\phi) \; n_A(E,\theta,\phi) D(E) \Delta E \]  

(2)

where \( \Delta E \) is not the measured energy resolution of the spectrometer but is an energy width which, in many cases, is defined by the output slit. In many spectrometers the measured resolution is defined by terms involving angular dispersion, machining tolerances and the output slit width [16]. The effects of the angular dispersion and machining tolerances are simply to transfer intensity which would appear at one energy to an intensity in a nearby energy channel so that, as the spectrum is scanned, the overall intensity is unchanged. A non zero output slit width, however, allows a given element of \( n_A(E',\theta,\phi) \) to be counted in several channels, hence the dependence in Eq (2) on the \( \Delta E \) term, as defined. For multi-detector spectrometers Eq (1) is simply evaluated for each discrete detector and the result is summed.

Thus,

\[ I_A(E) = I_o \; \Delta E \; D(E) \int_0^\pi T(E,\theta,\phi) \; n_A(E,\theta,\phi) \; \sin \theta \; d\theta \; d\phi \]  

(3)

From earlier studies [15] it is a reasonable approximation to express \( n_A(E,\theta,\phi) \) using

\[ n_A(E,\theta,\phi) = n_A(E,0,0) \; \cos \theta \]  

(4)

We now express all of the instrumental terms in one spectrometer total intensity/energy response function, \( Q(E) \), via the equation

\[ I_A(E) = I_o \; Q_A(E) \; n_A(E,0,0) \]  

(5)

Thus

\[ Q_A(E) = \Delta E \; D(E) \int_0^\pi T(E,\theta,\phi) \; \sin \theta \; \cos \theta \; d\theta \; d\phi \]  

(6)

It is useful, conceptually, to think of this as
\[ Q_A(E) = F_A(E) \cos \theta \quad \text{sr eV} \quad (7) \]

where \( F_A(E) \) is the analyser intensity/energy transmission and \( \cos \theta \) an average value of \( \cos \theta \) which allows for the analyser's efficiency in capturing the spectral intensity in the instrumental situation. Clearly

\[
\cos \theta = \frac{\iiint T(E, \theta, \phi) \cos \theta \sin \theta \, d\theta \, d\phi}{\iiint T(E, \theta, \phi) \sin \theta \, d\theta \, d\phi} \quad (8)
\]

We may now write

\[ F_A(E) = \Delta E \, D(E) \, \Omega \quad \text{sr eV} \quad (9) \]

where the effective solid angle of the instrument is given by

\[ \Omega = \iiint T(E, \theta, \phi) \sin \theta \, d\theta \, d\phi \quad \text{sr} \quad (10) \]

\( F_A(E) \) is the intensity/energy response of the analyser wherever it is placed whereas \( Q_A(E) \) is the intensity/energy response function of the spectrometer as an analytical instrument. For those simply requiring the energy dependence and not the absolute value of their spectrometer response, the distinction between \( F_A(E) \) and \( Q_A(E) \) is irrelevant since \( \cos \theta \) very rarely depends on \( E \). The \( \cos \theta \) term is included since a spectrometer set at a given angle \( \theta \) will necessarily measure a weaker spectrum than one at zero polar emission angle as though its efficiency were lower. For simple analyses it is \( Q_A(E) \) that is directly required.

Note that the SI units of both \( F_A(E) \) and \( Q_A(E) \) are sr eV. The units of \( n_A(E) \) are, of course, electrons per unit solid angle per eV per electron so that the integral over the whole space and energy scale simply gives the dimensionless secondary electron emission coefficient.

As discussed in the Introduction, for some experiments we need to know that \( Q_A(E) \) is not changing with time, whereas for others that the dependence of \( Q_A(E) \) on \( E \) is accurately known but with precise units of the measure that are unimportant and finally, for the last group, that \( Q_A(E) \) as a function of \( E \) is accurately known in sr eV. The accuracy for statements that may be made for each of these three instances inevitably degrades through these three, respective, measures since each, of course, includes the errors of its predecessor. The simplest measure is clearly the best, provided that it truly gives the information required.

It is worth considering some illustrative spectrometer behaviours. In AES studies it is common to use spectrometers in the constant \( \Delta E/E \) mode (often known as constant or fixed retarding ratio). If \( \Delta E/E = K \) then

\[ Q_A(E) = K \, E \, D(E) \iiint T(E, \theta, \phi) \sin \theta \, \cos \theta \, d\theta \, d\phi \quad (11) \]

For a cylindrical mirror analyser (CMA) with its axis at an angle \( \alpha \) to the surface normal and with an angular acceptance of \( \pm \Delta \alpha \) about the mean angle of 42° from the spectrometer axis the above integral becomes [17].
\[ Q_A(E) = K \ 2\pi \ \Delta\alpha \ \cos\alpha \ \sin\theta^0 \ W \ E \ D(E) \]  \hspace{1cm} (12)

where \( W \) is the total transmission of all of the meshes and \( K \), it should be remembered, derives from \( \Delta E \) and not the measured energy resolution. For a given spectrometer the terms \( K, \Delta\alpha, \cos\alpha, W \) etc may all be combined into a proportionality constant so that

\[ Q_A(E) \propto E \ D(E) \]  \hspace{1cm} (13)

Often the effect of \( D(E) \) is ignored and so \( Q_A(E) \) is thought to be proportional to \( E \) and so, in the literature, readers will see spectra with the intensity axis marked as \( E n_A(E) \) where really \( Q_A(E) \) \( n_A(E) \) is meant.

For a spherical sector analyser (SSA) with an input lens of cone semiangle \( \beta \), set at some general angle of emission, \( \theta \), larger than \( \beta \), we similarly find [17]

\[ Q_A(E) = K \ 2\pi \ \cos\theta \ (1 - \cos\beta) \ W \ E \ D(E) \]  \hspace{1cm} (14)

which reduces to Eq (13) as above. For angle-resolved measurements with a small \( \beta \) one would not use \( Q_A(E) \), but \( Q_A(E)/\cos\theta \) or \( F_A(E) \). Thus

\[ F_A(E) = Q_A(E)/\cos\theta = K \pi\beta^2 \ W \ E \ D(E) \]  \hspace{1cm} (15)

### 2(b) X-ray Photoelectron Spectrometers

As an analogue to the situation for AES, the measured spectrum for unmonochromated sources \( (u) \) is given by

\[
I_X^u(E) = J_0^u \int \int \int \int T(E' - E, E, \theta, \phi, x, y) \ n_X(E', \theta, \phi) \ D(E') \ dE' \\
\times \ d\theta \ d\phi \ dx \ dy
\]  \hspace{1cm} (16)

where the co-ordinate system \( x,y \) is over the surface of a solid, here assumed to be homogeneous, \( n_X(E',\theta,\phi) \) is the true energy spectral intensity of electrons per unit incident photon, per unit solid angle and per eV emitted in the direction \( \theta,\phi \). \( J_0^u \) is the incident photon rate per unit area of the surface and is equal to the product of the photon fluence and \( \cos\theta \) where \( \alpha \) is the angle of incidence of the photons. Of course, if \( J_0^u \) depends on \( x \) and \( y \), as it generally does in practice, then \( J_0^u \) must move to the right of the integral signs. As before, ignoring the effects of line broadening and the uniformity of the photon distribution we have

\[ I_X^u(E) = J_0^u \Delta E \ D(E) \ n(E,0,0) \int \int \int T(E,\theta,\phi, x, y) \ \sin\theta \ \cos\theta \ d\theta \ d\phi \ dx \ dy \]  \hspace{1cm} (17)
As before, we may write

\[ I_X^u(E) = \int_0^u Q_X^u(E) n_X(E,0,0) \]  

(18)

and

\[ Q_X^u(E) = \Delta E D(E) \iint T(E,\theta,\phi,x,y) \sin \theta \cos \theta \ d\theta \ d\phi \ dx \ dy \]  

(19)

The units of \( Q_X^u \) are \( m^2 \text{ sr eV} \) equivalent along the surface normal.

If the spectrometer accepts electrons from a well defined area \( C \) perpendicular to the spectrometer axis,

\[ Q_X^u(E) = C Q_A(E) \]  

(20)

and we may use Eqs (7) to (10).

For the example of our hemispherical spectrometer used in the constant \( \Delta E/E \) mode, if it accepts electrons from a well defined area \( C \), perpendicular to its entrance lens

\[ Q_X^u(E) = K C 2\pi (1-\cos \beta) W E E(E) \]  

(21)

where the \( \cos \theta \) appearing in Eqs (14) and (19) has cancelled with the \( \cos \theta \) from the area of analysis on the sample (assuming a sample area of greater than \( C \sec \theta \) evenly illuminated by photons). We assume also that the full cone angle of electrons from the lens is passed by the dispersing hemispheres. \( Q_X^u(E) \) in this case may be identified with the Etendue [18] of the spectrometer and again gives the approximation of Eq (13). Note now that for angle-resolved XPS \( Q_X^u(E) \) does not depend on \( \cos \theta \) as did \( Q_A(E) \) and so \( Q_X^u(E) \) is used directly.

For focused monochromatic sources \( J_0^u \) is replaced by, \( J_0^m \), the total number of photons per second into the spot rather than per unit area. Equation (16) then becomes an analogue of Eq (1) and the dimensions of \( Q_X^u(E) \) are \( \text{sr eV} \).

3 THE INTENSITY CALIBRATION SYSTEM

3(a) **Background**

The basic philosophy of this calibration system is that by the use of Eqs (5), (18) and the counterpart of the latter for monochromators, AES and XPS instruments may be calibrated for their intensity scales so that work on one instrument under one set of operating parameters may be related to work on another instrument of a different design and using different operating parameters.

In AES or XPS if we have certain sensitivity factors \( I_{A1}^\infty \) for element A on instrument 1 and wish to quantify a spectrum recorded on the same instrument under the same conditions, it is common to use an equation of the type [19]:

\[ I_{AI} = I_{A1}^\infty \times \text{calibration factor}. \]
\[ X_A = \frac{I_{A1}}{I_1} \]  

(22)

where \( X_A \) is the sought after atomic fraction of element A. Some equations include matrix factors etc but two aspects are important in Eq (22): (i) the use of ratios means that the beam current or photon flux is unimportant, provided that it is constant and (ii) the absolute values of \( I_{A1} \) etc are unimportant provided that they are all measured under the same conditions. If the \( I_{A1}^S \) values are from a second, reference instrument with superscript R, we write

\[ X_A = \frac{I_{A1}^S Q_A^R / I_1^R Q_1^S}{\sum_i I_i^S Q_i^R / I_i^R Q_i^S} \]  

(23)

where the superscript, S, denotes the analytical instrument. Again, the ratios remove the need for an absolute scale for any of the terms. What is important is that we may define the energy dependencies of \( Q_A^R \), \( Q_A^S \) or \( Q_X^R \), \( Q_X^S \) accurately. If we wish to use the Tougaard background subtraction method [7] and theoretical predictions of cross sections then we need to be able to convert spectra to have the correct energy dependence and, for this, we only need the accurate energy dependencies of \( Q_A^S(E) \) or \( Q_X^S(E) \). Absolute values are not necessary for these calculations. However, if we develop absolute methods without normalisation or if we wish to correlate with some theoretical predictions, then the absolute values may be required. As it is not too difficult we shall therefore work with absolute values as discussed later.

The present calibration system acts as described above and gives an accurate energy dependence of Q(E) which, by using three separate samples provides an internal consistency test which for AES can show scatters of less than 2\% [1] and for XPS scatters of less than 4\% [2]. The absolute value of Q(E) is not known very accurately, as described in section 4 but, as will be shown, this absolute value is actually extremely useful in assessing basic values of theoretical parameters [20].

3(b) Structure for AES

It is easiest to start with the structure of the calibration method for AES. The analyst first records good quality spectra using a 5 keV electron beam at 30° angle of incidence, as detailed elsewhere [21], for the inert gas sputter cleaned reference materials SCAA 87 of Cu, Ag and Au [1] using a measured or constant beam current of \( I_0 \) (nA). These spectra, corrected for the dead time (if known) [22], \( I_{A1}^R(E) \), then give \( Q_A^S(E) \) from Eq (5). First

\[ Q_{A1}^S(E) = \frac{I_{A1}^S(E)}{I_0 N_{A1}^R(E,0,0)} \]  

(24)

\[ i = \text{Cu, Ag, Au} \]

and then

\[ Q_A^S(E) = \frac{1}{3} \sum_i Q_{A1}^S(E) \]  

(25)
The reference spectra $n^R_{AI}(E,0,0)$ have been derived and tested over a long period of research at NPL and are very accurately known in terms of a relative unit $i_A$ whose dimensions are electrons sr$^{-1}$ eV$^{-1}$ per electron. We give the value of $i_A$ in section 4. In Eq (25) $Q^S_{A}(E)$ is accurately derived in counts/second per nA per $i_A$, i.e. counts s$^{-1}$ nA$^{-1}$ i$^{-1}$ units, known as A$_o$ units or less accurately, as we shall see, in sr eV units. Below we derive the values of the relative units in terms of SI units. To clarify the derivation, the units of measures in equations are shown following the item in square brackets.

Formally we should rewrite Eq (5)

$$Q^S_{AI}(E) = \frac{I^S_{AI}(E) \ [\text{counts s}^{-1}]}{I_o \ [\text{counts s}^{-1}] \ n^R_{AI}(E,0,0) \ [\text{sr eV}]} \quad \text{sr eV} \quad (26)$$

$$= \frac{I^S_{AI}(E) \ [\text{counts s}^{-1}] \ 10^9 \text{e}^{}}{I_o \ [\text{nA}] \ n^R_{AI}(E,0,0) \ [i_A \ \text{units}] \ i_A} \quad \text{sr eV} \quad (27)$$

$$= \frac{I^S_{AI}(E) \ [\text{counts s}^{-1}]}{I_o \ [\text{nA}] \ n^R_{AI}(E,0,0) \ [i_A \ \text{units}] \ A_o \ \text{units}} \quad (28)$$

where

$$1_{A_o} = 10^9 \text{e}/i_A \quad \text{sr eV} \quad (29)$$

The Cu reference spectrum for AES is shown in Fig 1 in both $i_A$ and sr$^{-1}$ eV$^{-1}$ units. The Cu, Ag and Au spectra are very similar to those given in Fig 12 of reference [23]. Figure 2 shows a calibration plot using these spectra for a VG ESCALAB with a 5 CEM 210 analyser used for establishing an AES data bank. The upper plot gives $Q^S_{A}(E)$ in A$_o$ units and the lower in sr eV using the conversion factor of section 4.

The above shows the simple outline of the calibration system [24]. To provide a certificated calibration, as required in accredited laboratories under the NAMAS [25] or equivalent systems using ISO guide 25 [26], the software running the calibration must be tamper-proof (no software is every fully tamper-proof but it should involve a non-trivial effort) and the system should reasonably protect against the problems of internal scattering in the analyser, cross-contamination or failure to clean the samples, poor energy calibration etc. For these reasons the reference spectra are only released to the public within the licensed software package for spectrometer calibration [24].

The software package provides $Q^S_{A}(E)$ in A$_o$ units at 1 eV energy intervals, in kinetic energy referenced to the Fermi level from 20 eV to 2500 eV as a VAMAS format digital file [27] as well as a hardcopy certificate with the value of $Q^S_{A}(1000)$, for checking calibration-to-calibration consistency, and with values for the internal scattering as a fraction of the background in the Cu spectrum at 879 eV and of the Ag spectrum at 329 eV [28,29].

To diagnose the consistency of the calibrations we also evaluate the three values [1,2]
\[ \bar{R}_i = \frac{\sum Q_{AI}^S(E)/Q_A^S(E)}{E_{\text{max}} - E_{\text{min}} + 1} \quad i = \text{Cu,Ag,Au} \quad (30) \]

where \( E_{\text{max}} \) and \( E_{\text{min}} \) represent the upper and lower limits of the calibration energy range.

These \( \bar{R}_i \) values show the extent to which the measured spectral absolute intensities may be retained from sample to sample. These are measures of the quality of the setting up procedures and the robustness of the instrument for the user. The \( \bar{R}_i \) values should, of course be unity but in a recent inter-laboratory study the \( \bar{R}_i \) values scattered by some 5% around unity. Another measure of the response function shape consistency is \( r \) [1,2] were

\[ r^2 = \sum \sum \left( \frac{Q_{AI}^S(E)}{\bar{R}_i Q_A^S(E)} - 1 \right)^2 \times 3 \times (E_{\text{max}} - E_{\text{min}} + 1) \quad (31) \]

The parameter \( r \) characterises the scatter of the individual calibrations about the mean.

The 3 is valid if Cu, Ag and Au are all used. The calibration is possible also just using Cu and Ag and then the 3 is, of course, reduced to 2. The \( r \) value should ideally be zero. In a recent inter-laboratory [1] study an average \( r \) value of 3% was found for the energy range 10 to 2500 eV. This value had contributions from some spectrometers known to exhibit internal scattering [28]. Scattering increases the \( r \) value. Thus, if we only consider spectrometers with low scattering the average \( r \) value is around 2%.

Having established \( Q_A^S(E) \) how does the analyst proceed? With measured spectra, \( I_{AI}^S(E) \) counts/second, using the same instrumental operating conditions as used to produce \( Q_A^S(E) \) we generate

\[ n_{AI}^S(E) = \frac{I_{AI}^S(E)}{I_o Q_A^S(E)} \quad (32) \]

where, if \( I_o \) is in nA the \( n_{AI}^S(E) \) are returned in the original \( i_A \) units as the reference spectra. Using the value of \( I_o \) given in section 4 this means that the corrected spectra are in electrons emitted per incident electron per steradian per eV. The analyst now has absolute spectra!

The spectra are always in exactly the same intensity units irrespective of the beam current, channel dwell time, slit selection, constant \( \Delta E \) or constant \( \Delta E/E \) mode, pass energy or retardation ratio etc etc as they have all been accounted for. The only aspect that will change is the spectral resolution and the noise. In practice, of course, surface roughness will alter the measured intensity but now the instrument is calibrated such that the roughness effect may be measured. Note that although the \( I_{AI}^S(E) \) spectra for calibrating \( Q_A^S(E) \) are for \( i = \text{Cu, Ag and Au} \) using a 5 keV electron beam at 30° to the surface normal, the \( I_{AI}^S(E) \) for Eq (32) may be at any energy on any material. Figure 3 thus shows a spectrum for selenium recorded for a 10 keV beam which, after correction for \( Q_A^S(E) \), may be plotted with an absolute ordinate. The relative orientation of the spectrometer and surface may change but then, if the absolute intensity is to be maintained, a correction for cos \( \theta \) must be made using Eq (8).
3(c) The direct approach

The structure for XPS follows that for AES but uses the inert gas ion sputter cleaned reference materials SCAA90 of Cu, Ag and Au [2]. Here we cannot measure the photon flux. We may only measure the emission for the X-ray source generator $I_X^S$(mA). For unmonochromated Al or Mg sources a 12 kV anode voltage is used and for monochromated sources the normal working voltage. The angle of incidence of the X-rays is between 0 and 50° and the angle of emission of the electrons into the spectrometer between 0 and 50°, as detailed in references [2],[21] and [23]. These limits are set by the requirement that the spectra change shape by less than 2% over this range [23,30]. The spectra, corrected for dead time, if known, $I_j^i$(E), then give $Q_X^S(E)$ according to Eq (18):

$$Q_X^{iS}(E) = \frac{I_X^{iS}(E)}{J_o^S n_X^{iR}(E,0,0)}$$  \hspace{1cm} i = Cu,Ag,Au  \hspace{2.2cm} (33)$$

However, we do not know $J_o^u$ the number of photons s⁻¹ m⁻² and its counter part $J_o^m$, we only know that $J_o^u$ and $J_o^m$ are propositional to the X-ray source generator emission current $I_j[\text{mA}]$. Thus

$$J_0^i = J_1^i I_0^i$$  \hspace{1.2cm} j = u, m  \hspace{2.2cm} (34)$$

where $J_0^i$ is the production rate of unmonochromated X-rays at the sample in photons s⁻¹ m⁻² per mA of emission current and $J_1^i$ is its counterpart with a monochromator. $J_1^i$ is not an absolute parameter but will vary with the source, will vary from instrument to instrument and may vary with time as the anode ages. It will, however, be constant in any given spectrum and does not vary with E. Thus, we shall use

$$Q_X^{iS}(E) = \frac{I_X^{iS}(E)}{I_0^{iS} n_X^{iR}(E,0,0)}$$  \hspace{1.2cm} i = Cu,Ag,Au  \hspace{2.2cm} (35)$$

In Eq (33) the units of $Q_X^{iS}(E)$ are m² sr eV for $j = u$ and sr eV for $j = m$. In Eq (35) however the units are $X_0$ units as discussed below. As before we average to determine the intensity/energy response function, $Q_X^{iS}(E)$

$$Q_X^S(E) = \frac{1}{3} \sum_i Q_X^{iS}(E)$$  \hspace{1cm} i = Cu, Ag, Au  \hspace{2.2cm} (36)$$

The reference spectra used here, n_Xi(E, 0, 0) have, like the Auger electron reference spectra been used over a long time at NPL and are known accurately in terms of a relative unit, $i_X$, whose dimensions are electrons sr⁻¹ eV⁻¹ per photon (this is the counterpart of $i_A$, which is really electrons sr⁻¹ eV⁻¹ per electron). Unlike the case for AES we cannot measure the conversion factor for $i_X$ accurately at the present time. Thus, $Q_X^{iS}(E)$ is accurately derived in counts/second per mA of emission per $i_X$, ie counts s⁻¹ mA⁻¹ sr⁻¹ eV⁻¹ units, known as $X_0$ units. The value of the $X_0$ unit depends on the radiation and so strictly should be labelled $X_0^j$, however for brevity the superscript $j$ will be omitted.

The reference spectra for XPS are very similar to those given in Figs 15 of reference [23]. Figure 4 gives an example for Cu using Al Kα radiation. Figure 5 shows a calibration plot
for the same instrument as in Fig 2 under the same operating conditions but for XPS. The NPL software system [31] provides $Q_X^{1S}(E)$ in $X_o$ units at 1 eV energy intervals in kinetic energy referenced to the Fermi level within the energy range 130 eV to 1600 eV as a VAMAS format digital file [27] as well as a hardcopy certificate with the value of $Q_X^{1S}(1000)$ as for AES. In a similar manner to AES the internal scattering is diagnosed as a fraction of the background at 879 eV in Cu and 329 eV in Ag as well as 1075 eV in Ag using Al Kα radiation and 842 eV in Ag using Mg Kα radiation. Values of $\bar{R}_1$ and $R^2$ are also given using analogues of the Eqs (30) and (31).

Typical values of $\bar{R}_1$ scatter by 6% around unity and typical values of $r$ are 3% [2]. Here, as well as checking the energy calibration it is important to ensure that the spectra are free from anode cross talk, oxygen Kα ghosts etc [2]. This is all checked in the software.

As with the case for AES, when the user correctly applies the calibration values of $Q_X^S(E)$ to their measured spectra, $I_{Ai}^S(E)$, they will generate true spectra $n_{Ai}(E)$ in the $i_X$ units described in section 4(d).

3(c)(ii) The indirect approach

The above methods give calibrations for AES and XPS, using the instruments in their normal way, in $A_o$ and $X_o$ units. An alternative method for XPS, if an electron gun is provided, is to use the AES method with a 5 keV electron gun at 30° to the surface normal for the XPS calibration. Care must now be exercised to ensure that the electron beam mimics the X-ray source. For unmonochromated sources which flood the sample the best approximation is to raster the electron beam or defocus it to cover an area larger than the acceptance area of the spectrometer. If rastering is used, a problem which tends not to be recognised is that the dead time correction should be made for each instant of the raster as the instantaneous count rates change, sometimes being higher than average and sometimes lower. To correct the measured intensity the intensity first needs to be scaled up by the ratio of the raster area, $C_r$, to the acceptance area, $C_a$, then the dead time correction [22] is applied and the intensity is scaled back down to give $I_{Ai}^S(E)$. Now we have

$$Q_{X_i}^{uS}(E) = \frac{I_{Ai}^S(E) \cdot C_r}{I_o^S \cdot n_{Ai}(E,0,0)}$$

(i = Cu,Ag,Au)  \hspace{1cm} (37)

and so on. Here the units of $Q_{X_i}^{uS}(E)$ are $m^2$ counts/second per nA per $i_A$ known as $m^2 A_o$ units which may be converted to $m^2$ sr eV units. This, therefore, characterises the spectrometer irrespective of X-ray source efficiency and by comparison with the direct approach allows a partial conversion between $A_o$ and $X_o$ units. Note, however that the $X_o$ unit is unique to a given instrument and depends on the design of the X-ray source as discussed later.

If the X-ray source is not a broad source but a focused monochromator, the measured energy dependence of $Q_{X_i}^{uS}(E)$ derived by the above approach may not be correct. Some spectrometers have an analytical area which is higher at one energy than another. If the analytical area is larger than the monochromated beam, the relative intensity/energy response functions for the unmonochromated to the monochromated source will broadly follow the variations in the spectrometer analytical area which involve a factor of 3 difference over the analytical energy range as shown by respondee 38 in Fig 14 of reference [2]. For monochromators, the electron beam should mimic, as closely as possible the X-ray spot or line pattern. For these systems, provided the analytical area is always larger than the X-ray spot or line we use
\[ Q_{X_{i}}^{mS}(E) = \frac{I_{A_{i}}^{S}(E)}{I_{o}^{S} n_{A_{i}}^{R}(E,0,0)} \quad i = \text{Cu,Ag,Au} \] (38)

where the units are counts/second per nA per \( i_{A} \) or \( A_{o} \) units and so on.

A failure to use the correct method may clearly lead to the errors of a factor of 3 noted above. It can, in practice, sometimes be very difficult to mimic the X-ray source with an electron beam and so for practical analytical work this indirect approach is not always to be recommended.

In both of these cases the measured spectra \( I_{A_{i}}^{S}(E) \) should generate true spectra \( n_{A_{i}}^{S}(E) \) in units related to the \( i_{X} \) units of the direct method.

4 VALUES OF THE DIMENSIONED UNITS

4(a) The \( i_{A} \) units

Some data exist in the literature [17] from which we may obtain an approximate value of \( i_{A} \). In the Appendix to reference [17] are discussions for a Varian 10 keV cylindrical mirror analyser (CMA) and a VG Microlab spherical sector analyser (SSA) in which the detector terms \( D(E) \) are unity.

4(a)i The Varian 10 keV CMA

The intensity on the background of copper at 950 eV, using a 5 keV electron beam at 30° angle of incidence, is 19.26 \( i_{A} \). The background in reference [17] at 45° angle of incidence is 4.26 pA/\( \mu \)A for a spectrometer where

\[ \int_{\Omega} T(E,\theta,\phi) \cos\theta \, d\Omega = 2\pi \Delta\alpha \cos\alpha \sin 84° W \] (39)

where the semi-angular acceptance, \( \Delta\alpha \), is estimated to be 0.077 radians and \( W \), the transmission of the two 90% transparent thin electroformed meshes on three solid support bars occupying 5% of the mesh area each, is 0.6885. We may now calculate \( Q_{A}(E) \) by two routes. From Eq (6) for an angle of incidence, \( \alpha \), of 30°

\[ Q_{A}(E) = \Delta E \, 2\pi \Delta\alpha \cos 30 \sin 84 \, W \] (40)

and from Eq (5) and the knowledge that the background at 950 eV for Cu using a 5 keV electron beam in a Varian CMA varies as \( \cos^{0.535} \alpha \) [32] then

\[ Q_{A}(E) = 4.26 \times 10^{-7} \left( \frac{\cos 30}{\cos 45} \right)^{0.535} \] (41)

Thus
\[ i_A = \frac{4.26 \times 10^{-6}}{19.26} \Delta E \frac{1}{2\pi \Delta \alpha \cos30 \sin84} \left( \frac{\cos30}{\cos45} \right)^{0.525} \] (42)

We do not know \( \Delta E \) accurately but, assuming that the designers allowed equal contributions to the design resolution of 0.25% from \( \Delta \alpha \) and from the output slit in quadrature, then \( \Delta E \) will be 1.679 eV. Thus

\[ i_A = 5.12 \times 10^{-7} \text{ electrons sr}^{-1} \text{ eV}^{-1} \text{ per electron} \] (43)

The uncertainty for this figure depends largely on the uncertainties in \( \Delta \alpha \) and \( \Delta E \), each estimated at 15%, so that the overall uncertainty is 20%.

4(a)ii The VG Microlab SSA

The background of Cu at 950 eV using a 5 keV electron beam in reference [17] at 45° angle of incidence for the VG Microlab with the 6 mm slits, the lens operated at a magnification of 3 and at a retardation ratio of 4, is 2.87 pA/μA where

\[ \int \int T(E,\theta,\phi) \sin \theta d\theta \, d\phi = 2\pi \cos15^\circ (1-\cos\beta) \, W \] (44)

where \( \beta \) is the input cone semi angle of the lens and the 15° is the emission angle from the surface normal. In reference [17] \( \beta \) was estimated at 12°. Analysis of the trajectories through the lens, using the SIMION program [33], shows that, whilst 12° is accepted by the lens, only 8° is accepted by the spherical sectors in the dispersion direction and 9° in the non-dispersion direction. \( W \), the combined transparency of the two meshes in the Microlab is approximately 0.98² since each wire wound mesh is of 98% transparency [34]. As above, from Eq (6)

\[ Q_A(E) = \Delta E \frac{2\pi \cos15^\circ (1-\cos8.5^\circ)}{W} \] (45)

and from Eq (5) and the knowledge that the background at 950 eV for Cu using a 5 keV electron beam in a VG SSA system varies as \( \sec^{0.465} \alpha \) [32] then

\[ Q_A(E) = \frac{2.87 \times 10^{-6}}{19.26} \left( \frac{\sec30}{\sec45} \right)^{0.465} \] (46)

Thus,

\[ i_A = \frac{2.87 \times 10^{-6}}{19.26} \frac{1}{\Delta E \frac{\cos45}{\cos30} (1-\cos8.5) W} \left( \frac{\cos45}{\cos30} \right)^{0.465} \] (47)

In this spectrometer \( \Delta E \) is defined by a pair of 6 mm slits separated by a 10 mm gap on hemispheres of 150 mm radius. At a retardation ratio of 4, for 950 eV electrons, \( \Delta E \) is approximately 4.354 eV. Thus,
\[ i_A = 4.86 \times 10^{-7} \text{ electrons sr}^{-1} \text{ eV}^{-1} \text{ per electron} \quad (48) \]

This value of \( i_A \) is more accurate than the value using the Varian spectrometer since both the \( \Delta E \) and solid angle terms are better known. The solid angle term is probably accurate to 15% from the SIMION calculations but stray fields may cause some unknown error in the measurement. We have no such evidence but this spectrometer had not been as carefully characterised as the Metrology Spectrometers I and II. We therefore decided to repeat these measurements for the Metrology Spectrometer II which is similar to Metrology Spectrometer I but has the analyser replaced by a 5 CEM 210 analyser from VG Scientific.

4(a)iii  Metrology Spectrometer II

In order to obtain an accurate measure of the solid angle this spectrometer was used with the lens switched off. The entrance solid angle is then defined by a pair of 6 x 15 mm slits at 584 and 594 mm from the sample, respectively. By using a retardation ratio of 1 the meshes are in a field free region and an electrometer may be used at the output stage without affecting the field free region there. By measuring the spectral intensity emitted at 100 eV intervals from Cu excited by a 28.32 \( \mu \)A beam of 5 keV electrons at angles of incidence and emission of 30° and 16°, respectively, it was found that the ratio of the emitted current to that in the reference spectrum was

\[ \frac{I_A(E)}{I_0(E)} \frac{E}{n_A(E,0,0)} = \frac{(3.224 \pm 0.032)}{28.32 \times 10^{-10}} \quad (49) \]

where the uncertainty is the standard deviation of the mean value. From Eq (6) we have, since there are 5 output channels,

\[ Q_A(E) = 5 \times \Delta E \times \frac{6 \times 15}{594^2} \cos 16^\circ \text{ W sr eV} \quad (50) \]

where W includes the mesh transmission of (0.98)^2 and a small electron optical term of 0.946 for transmission of the 4 slits. Thus from Eq (5)

\[ i_A = \frac{3.224 \times 10^{-10} \times 594^2}{28.32 \times 0.1 \times 6 \times 15 \times \cos 16^\circ \times 0.98^2 \times 0.946} \text{ sr}^{-1} \text{ eV}^{-1} \]

\[ i_A = 5.11 \times 10^{-7} \text{ electrons sr}^{-1} \text{ eV}^{-1} \text{ per electron} \quad (51) \]

This final value is consistent with the earlier values and is estimated to have an accuracy of about 6%. In the rest of this work we therefore use

\[ i_A = (5.1 \pm 0.3) \times 10^{-7} \text{ electrons sr}^{-1} \text{ eV}^{-1} \text{ per electron} \quad (52) \]

4(b)  The A\(_o\) units

As described in section 3(b), \( Q_A(E) \) is accurately derived in A\(_o\) units. From above, therefore
1A_o unit = \(10^9\) e/i_A \(\text{sr eV}\)  
= \(3.14 \times 10^{-4}\) sr eV \(\text{(53)}\)

Thus, a conversion for A_o exists which is accurate to about 6%. We retain the A_o units to retain the higher relative accuracy.

4(c) The X_o units

The X_o unit derives from the use of Eq (35) to calibrate spectrometers instead of Eq (33). In Eq (33) \(Q_X^{f}(E)\) is in units of m^2 sr eV and sr eV, respectively, for unmonochromated and for focused monochromated sources. In Eq (35) the X_o units of \(Q_X^{m}(E)\) are counts s^{-1} mA^{-1} i_X^{-1}.

Using the indirect approach at NPL but the value of \(Q_X^{m}(E)\) of the Metrology Spectrometer II has been determined in a similar manner to \(Q_A(E)\) but by using a focused electron beam simulating the monochromator line source within the defined analytical area. In this spectrometer the analytical area, C, is independent of the analysed energy, E. Thus

\[Q_X^{m}(E) = Q_A(E)\] \(\text{(54)}\)

which is available accurately in A_o units and approximately in sr eV. Similarly, by rastering the electron beam to overfill the analytical area we also determine \(Q_X^{m}(E)\) in m^2A_o or m^2 sr eV units.

The true XPS spectra \(n_X^{i}(E,0,0)\) are in units of electrons sr^{-1} eV^{-1} per photon. The reference spectra \(n_X^{iR}(E,0,0)\) that we derive are in i_X units. From Eqs (18) and (35) we may write, using the superscript R for the reference work,

\[n_X^{iR}(E,0,0) = \frac{i_X^{iR}}{J_i^{iR}} \frac{i_X^{iR}}{Q_X^{iR}} \text{ electrons sr}^{-1}\text{eV}^{-1} \text{ per photon} \] \(\text{(55)}\)

\[= \frac{i_X^{iR}}{I_o^{iR} Q_X^{iR} ([m^2] A_o \text{ units})} i_X^{i} \text{ units}\]

where the units m^2 are put in brackets to signify that they are only included for \(j = u, i.e.\) for the unmonochromated sources. Thus, in the reference spectra

\[1 i_X^{i} \text{ unit} = \frac{1}{A_o J_i^{iR}} \text{ electrons sr}^{-1}\text{eV}^{-1} \text{ per photon} \] \(\text{(56)}\)

This reflects the unknown rate of production of the X-ray photons per mA of emission current incident on the sample for monochromated sources and per m^2 for unmonochromated sources.

Note that if, in the Metrology Spectrometer II, the monochromated and unmonochromated signals were of equal magnitude, the ratio i_X^{iR} unit to the i_X^{mR} unit is C_o or about \(10^{-5}\) m^2. Thus, the numerical values of n_X^{iR} are around \(10^5\) times those in n_X^{mR}. 

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We now calibrate instruments using Eq (35)

$$Q_X^S(E) = \frac{I_X^S(E)}{J_o^S n_X^R(E,0,0)} \text{ (m}^2\text{ sr eV)}$$  (57)

$$= \frac{I_X^S(E) \ [\text{counts s}^{-1}]}{J_1^S J_o^S [\text{mA}] n_X^R(E,0,0) [i_X^j \text{ units}]} \text{ (m}^2\text{ sr eV)}$$

$$= \frac{I_X^S(E) \ [\text{counts s}^{-1}]}{J_o^S [\text{mA}] n_X^R(E,0,0) [i_X^j \text{ units}]} \ X_o \text{ units}$$  (58)

Where

$$1 \ X_o^j \text{ unit} = \frac{J_1^R}{J_1^S} A_o \text{ (m}^2\text{ sr eV)}$$  (59)

Thus, the $X_o$ unit derives originally from the $A_o$ unit scaled by the ratio of the efficiencies of the reference and analytical instruments X-ray sources. Note that a highly efficient source would lead to a high value of $Q_X^S(E)$ in $X_o^j$ units, implying that $X_o^j$ must be less than unity. Note also that $J_1^R$ is fixed when the reference data are derived whereas $J_1^S$ will be the value at the time of calibration. $J_1^S$ may slowly reduce with time so that the value of $Q_X^S(E)$ falls with time (reflecting the lower performance of the analytical instrument) in $X_o^j$ units. In $(\text{m}^2\text{ sr eV})$ units $Q_X^S(E)$ is of course constant and it is the value of the $X_o^j$ unit which is becoming inflated.

Note that the above ratio of $i_X^j$ to $i_X^m$, being $C_s$, feeds through to the ratio $Q_X^S(E)$ to $Q_X^m(S(E)$ which, all else being equal, also has the ratio $C_s$. Thus $Q_X^S$ will be some $10^{-5}$ of $Q_X^m$, as indicated from Eqs (20) and (54).

4(d) **The $i_X^j$ units**

The analysts corrected spectra, $n_X^S(E,0,0)$ are given by

$$n_X^S(E,0,0) = \frac{I_X^S(E)}{I_o^S Q_X^S(E)}$$  (60)

$$= n_X^R(E,0,0)$$

Thus, the analyst's spectra have the same units and dimensions as the reference spectra, here in $i_X$ units.
5 CONCLUSIONS

A calibration system has been established which rapidly determines the energy dependence of the spectrometer intensity/energy response function in AES and XPS. The concept of the calibration system has been established and tested over a reasonable period to give reproducibilities below 2% for AES [1] and 4% for XPS [2]. The calibration is provided over the relevant range of kinetic energy as a VAMAS Format file at 1 eV intervals, together with a diagnosis of many of the possible spectrometer faults and the statistics of the calibration.

A unit system is defined which permits absolute calibrations and hence the conversion of analyst's spectra to an absolute basis in AES. In XPS a similar system is provided but with an unknown constant defined by the X-ray source production efficiency.

For calibrations in AES we use Eqs (24) and (25) to give $Q_A^S(E)$ at 1 eV intervals in units of $A_0$, traceable to sr eV via Eq (53). For calibrations in XPS we use Eqs (58) and (36) to give $Q_X(E)$ at 1 eV intervals in units of $X_0$ related to $m^2$ sr eV for unmonochromated and sr eV for monochromated sources via Eq (59).

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FIGURE CAPTIONS

Fig 1  The reference AES spectrum (a) $n_A(E,0,0)$, for Cu in $i_A$ and sr$^{-1}$ eV$^{-1}$ units. (b) shown in $E n_A(E,0,0)$ format in $E i_A$ or sr$^{-1}$ units.

Fig 2  Intensity/energy response function, $Q_A^S(E)$, for a VG ESCALAB with a 5 CEM 210 analyser, known as Metrology Spectrometer II operated with the input lens at unity magnification, 6 mm slits and a pass energy of 50 eV to give 1 eV resolution in the constant $\Delta E$ mode.

Fig 3  True spectrum of selenium using a 10 keV electron beam and the calibration from Fig 2, in the $E n_A(E,0,0)$ format of Fig 1(b).

Fig 4  The reference XPS spectrum for Cu using 12 kV Al Kα unmonochromated X-rays, in $i_X$ units.

Fig 5  Intensity/energy response function, $Q_X^{US}(E)$, for the Metrology Spectrometer II in the condition of Fig 2 with an analytical area of 6 mm by 15 mm at the sample.
Fig 1

The reference AES spectrum (a) $n_A(E,0,0)$, for Cu in $i_A$ and sr$^{-1}$ eV$^{-1}$ units. (b) shown in $E_{n_A}(E,0,0)$ format in $E_i^A$ or sr$^{-1}$ units.
Intensity/energy response function, $Q_A^S(E)$, for a VG ESCALAB with a 5 CEM 210 analyser, known as Metrology Spectrometer II operated with the input lens at unity magnification, 6 mm slits and a pass energy of 50 eV to give 1 eV resolution in the constant $\Delta E$ mode.
Fig 3  
True spectrum of selenium using a 10 keV electron beam and the calibration from Fig 2, in the $E_{n_A}(E,0,0)$ format of Fig 1(b).

Fig 4  
The reference XPS spectrum for Cu using 12 kV Al Kα unmonochromated X-rays, in $i_x$ units.
Fig 5  Intensity/energy response function, $Q^S_X(E)$, for the Metrology Spectrometer II in the condition of Fig 2 with an analytical area of 6 mm by 15 mm at the sample.