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## **A System for the Intensity Calibration of Electron Spectrometers**

**M P Seah**

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### 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 m<sup>2</sup> 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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Approved on behalf of Chief Executive, NPL,  
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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  $I_0$  is given by

$$I_A(E) = I_o \int_{\phi} \int_{\theta} \int_E T(E'-E, E, \theta, \phi) n_A(E', \theta, \phi) D(E') dE' \sin\theta d\theta d\phi \quad (1)$$

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  $\theta, \phi$ .  $T(E-E, E, \theta, \phi)$  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

$$\int T(E'-E, E, \theta, \phi) n_A(E', \theta, \phi) D(E') dE' = T(E, \theta, \phi) n_A(E, \theta, \phi) D(E) \Delta E \quad (2)$$

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,

$$I_A(E) = I_o \Delta E D(E) \int_{\phi} \int_{\theta} T(E, \theta, \phi) n_A(E, \theta, \phi) \sin\theta d\theta d\phi \quad (3)$$

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

$$n_A(E, \theta, \phi) = n_A(E, 0, 0) \cos\theta \quad (4)$$

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

$$I_A(E) = I_o Q_A(E) n_A(E, 0, 0) \quad (5)$$

Thus

$$Q_A(E) = \Delta E D(E) \int_{\phi} \int_{\theta} T(E, \theta, \phi) \sin\theta \cos\theta d\theta d\phi \quad (6)$$

It is useful, conceptually, to think of this as



$$Q_A(E) = F_A(E) \overline{\cos\theta} \quad \text{sr eV} \quad (7)$$

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

$$\overline{\cos\theta} = \frac{\int_{\phi} \int_{\theta} T(E,\theta,\phi) \cos\theta \sin\theta \, d\theta \, d\phi}{\int_{\phi} \int_{\theta} T(E,\theta,\phi) \sin\theta \, d\theta \, d\phi} \quad (8)$$

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

$$\Omega = \int_{\phi} \int_{\theta} T(E,\theta,\phi) \sin\theta \, d\theta \, d\phi \quad \text{sr} \quad (10)$$

$F_A(E)$  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  $\overline{\cos\theta}$  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

$$Q_A(E) = K E D(E) \int_{\phi} \int_{\theta} T(E,\theta,\phi) \sin\theta \cos\theta \, d\theta \, d\phi \quad (11)$$

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  $42^\circ$  from the spectrometer axis the above integral becomes [17]

$$Q_A(E) = K 2\pi \Delta\alpha \cos\alpha \sin 84^\circ W E D(E) \quad (12)$$

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

$$Q_A(E) \propto E D(E) \quad (13)$$

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  $En_A(E)$  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]

$$Q_A(E) = K 2\pi \cos\theta (1 - \cos\beta) W E D(E) \quad (14)$$

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

$$F_A(E) = Q_A(E)/\cos\theta = K \pi\beta^2 W E D(E) \quad (15)$$

## 2(b) X-ray Photoelectron Spectrometers

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

$$I_X^u(E) = J_0^u \int_{y \times \phi} \int_{\theta} \int_{E'} T(E' - E, E, \theta, \phi, x, y) n_X(E', \theta, \phi) D(E') dE' \quad (16)$$

$$d\theta d\phi dx dy$$

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  $\cos\alpha$  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

$$I_X^u(E) = J_0^u \Delta E D(E) n(E, 0, 0) \int_{y \times \phi} \int_{\theta} T(E, \theta, \phi, x, y) \sin\theta \cos\theta d\theta d\phi dx dy \quad (17)$$

As before, we may write

$$I_X^u(E) = J_o^u Q_X^u(E) n_X(E,0,0) \quad (18)$$

and

$$Q_X^u(E) = \Delta E D(E) \int_y \int_x \int_\phi \int_\theta T(E,\theta,\phi,x,y) \sin\theta \cos\theta \, d\theta \, d\phi \, dx \, dy \quad (19)$$

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,

$$Q_X^u(E) = C Q_A(E) \quad (20)$$

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

$$Q_X^u(E) = K C 2\pi (1-\cos\beta) W E E(E) \quad (21)$$

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  $J_o^u$  is replaced by,  $J_o^m$ , 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  $Q_X^m(E)$  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]:

$$X_A = \frac{I_{A1}/I_{A1}^\infty}{\sum_i I_{i1}/I_{i1}^\infty} \quad (22)$$

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  $I_{A1}^\infty$  etc are unimportant provided that they are all measured under the same conditions. If the  $I_A^\infty$  values are from a second, reference instrument with superscript R, we write

$$X_A = \frac{I_A^S Q_A^R / I_A^{R\infty} Q_A^S}{\sum_i I_i^S Q_i^R / I_i^{R\infty} Q_i^S} \quad (23)$$

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 ion sputter cleaned reference materials SCAA 87 of Cu, Ag and Au [1] using a measured or constant beam current of  $I_o$  (nA). These spectra, corrected for the dead time (if known) [22],  $I_{Ai}^S(E)$ , then give  $Q_{Ai}^S(E)$  from Eq (5). First

$$Q_{Ai}^S(E) = \frac{I_{Ai}^S(E)}{I_o n_{Ai}^R(E,0,0)} \quad i = \text{Cu, Ag, Au} \quad (24)$$

and then

$$Q_A^S(E) = \frac{1}{3} \sum_i Q_{Ai}^S(E) \quad (25)$$