

REPORT

XPS: Binding Energy Calibration of Electron Spectrometers 5 - A Re-Evaluation of the Reference Energies

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November 1997

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ABSTRACT

The binding energies of the calibration peaks for X-ray photoelectron spectroscopy, Cu 2p_{3/2}, Ag 3d_{5/2} and Au 4f_{7/2}, have been reassessed based on the traceable data recorded in 1984 using unmonochromated X-rays and an analyser resolution of 0.3 eV. The changes in those energies for different X-ray sources and analyser resolutions have been calculated and the results compared with further data including work with monochromatic Al X-rays recorded at high energy resolution referred to the Fermi edge measured for Ag. A consistent set of data is presented for the calibration and assessment of photo-electron spectrometers with energy resolutions in the range 0 eV to 1.5 eV, when used with unmonochromated Al or Mg X-rays or monochromated Al X-rays.

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ISSN 1361-4061

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Approved on behalf of Managing Director, NPL, by Dr C Lea,
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1 INTRODUCTION

For many years XPS instrument binding energy scales have been calibrated using the tabulated binding energies for the Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks given in Table 1^(1,2). These peaks are chosen as they are at either end of the binding energy scale normally used. Tests for linearity are then made using the CuLMM Auger electron peak or, for systems with monochromators, the Ag $3d_{5/2}$ peak⁽³⁾.

The data in Table 1 are derived in earlier work⁽⁴⁾ after corrections for the re-definition of voltage using the 1990 Josephson constant⁽¹⁾. Additionally, a small correction was made to the Ag $3d_{5/2}$ peak energy. In the original study the peak energies were measured using a scale which was traceably related to the national voltage scale with an uncertainty estimated at 11 ppm. The energies of the peaks were defined by a parabola fit (quadratic) to the top 5% of the intensity of the peak. The zero of the binding energy scale was, in turn, defined by a similar fit to the negative peak in the differential of the measured Ni Fermi edge using unmonochromated Mg X-rays. In the earlier work only unmonochromated X-rays were used and the data for the Ni Fermi edge, using the Al X-rays, had an uncertainty approximately double that for the Mg X-rays. In that work the standard deviation for measurement of the binding energies of the copper and gold peaks as a function of repositioning, sputtering and so on were typically 4 meV. In all of the data, the greatest uncertainty occurred in the setting of the zero of the binding energy scale.

The procedure used to define the zero point of the binding energy scale involved the assumption that the nickel Fermi edge could be approximated by a step function. This step function is convolved with the X-ray lineshape of the unmonochromated X-ray source during the measurement. For an ideal step function, the differential of the measured spectrum, with respect to energy, would re-create the lineshape of the X-ray source. Thus, the position of the peak in the differential would reflect the Fermi edge energy in the same way as the peaks directly reflect the binding energies for the Cu $2p_{3/2}$, Ag $3d_{5/2}$ and Au $4f_{7/2}$ core levels. Since the nickel Fermi edge is approximately a step function at the upper edge of a conduction band with a density of occupied states that rises with energy, instead of being constant, a correction was included for estimating the nickel differential peak energy superimposed on a varying background slope.

Whilst the above procedure was repeatable and defined, there were uncertainties which could have led to systematic errors which were not defined. These arose from the use of the Ni Fermi edge which was known to have structure⁽⁵⁾ which may have led to some error in the establishment of the zero value for the binding energy scale⁽⁶⁾. The Pd Fermi edge was also analysed but found to be less repeatable. Shown in Table 2 are the binding energy values of Bird and Swift⁽⁷⁾ determined using unmonochromated Al X-rays with reference to the Pd $3d_{5/2}$ peak. They then determined the binding energy of this peak with respect to the Pd Fermi edge, at the 50% intensity level, using monochromatic Al X-rays. This latter procedure removes any effects of the X-ray satellite peaks which would add uncertainty to the result for the Fermi edge. The calibration of the energy scale in their work was made by adjustments to give the energy separation between peaks, using Al $K\alpha$ and Ag β X-rays, in agreement with the data of Bearden⁽⁸⁾ and of Cohen and Taylor⁽⁹⁾. For the present purposes this is sufficiently accurate to note that the value of the binding energy for Au $4f_{7/2}$ peak agrees well with the value derived by Anthony and Seah⁽⁴⁾, although no details of the sample geometry were given.

The agreement with the data for unmonochromated Al X-rays in Tables 1 and 2, however, may be fortuitous. Calculation of the density of states at the Ni Fermi edge show structure likely to lead to a setting of the zero energy at a small positive binding energy^(5,10,11) which could lead to the values in Table 1 all being, say, 0.05 eV too low. It is not known if this shift is significant and so this is addressed in the present work. It is also not known if the

sputtering and subsequent room temperature annealing of the Ni is significant in changing this density of states at the surface and if so, to what depth.

It has been proposed that the Ag Fermi edge is a much better measure of the zero of the binding energy scale than that for Ni since the density of states is closer to the step function sought earlier. Ag was not used earlier as the intensity is a factor of 8 weaker than that for Ni and so the data are more difficult to measure. Measurements of the Ag Fermi edge are not straightforward with unmonochromated X-rays since the relatively intense 4d electron peak places satellites from the $K\alpha_{3,4}$ X-rays just where the Fermi edge measurements are needed. However, with monochromatic Al X-rays good measurements are possible and an Ag Fermi edge resolution of 0.27 eV has been measured⁽¹²⁾. Since the present work was started, recent studies have shown that 0.25 eV can be attained⁽¹³⁾. In studies using He I radiation at 21.2 eV, Stadnik et al⁽¹⁴⁾ demonstrate an unstructured Fermi edge with 5.2 meV analyser resolution at 14K.

The present work thus aims to repeat some of the earlier calibration work but, using modern instruments of higher sensitivity, which can give better precision to the data. For the absolute calibration of the energy scale, however, we shall rely on the original study⁽¹⁾.

From the point of view of practical analysis, where instruments are calibrated using Table 1 and data for chemical states or shift energies are then reported, those chemical states or shift energies will be reliably attained on any other instrument also calibrated using Table 1. Any systematic errors of offset or energy scaling, incorporated in Table 1, become eliminated in the use of the same Table for both instruments. Thus, chemical shifts may be reliably interpreted. A more important issue, for practical analysis, is the difference between the values for the two unmonochromated sources in Table 1 and whether these differences are significant. A further requirement is a Table of values to use for a monochromatic Al X-ray source.

A point which we must bear in mind is that we appear to measure shifts in the reference binding energies as we alter the spectrometer resolution or as we alter the X-ray source by changing the X-rays or adding or subtracting X-ray satellites. The binding energies do not of course shift as a result of these changes, it is only our measure of that energy that may change. Thus, if we find that all the peaks shift in the same way except for the Fermi edge measurement as, say, a function of resolution, it would not be helpful to provide a Table such as Table 1 with lots of correction terms since these correction terms would all cancel out in defining chemical state energies. Of course, all of the peaks do not shift by exactly the same amount but it is shown in part 4⁽¹⁵⁾ of this programme that, for many conditions, the separation of the Au 4f_{7/2} and Cu 2p_{3/2} peak energies is reasonably consistent. It may, therefore, be best to measure the absolute binding energy for the Au 4f_{7/2} peak at good energy resolution using monochromatic Al X-rays and then to refer all binding energies to the energy of that peak for other X-ray sources or spectrometer resolutions. We shall analyse the data with these approaches in mind. In the next section we provide the basic experimental methods. The straightforward approach of our original work⁽⁴⁾ is not possible here and so certain compromises must be made to achieve adequate data. The data and a discussion of their interpretation then follows in the experimental section.

2 EXPERIMENT

Measurements are reported in this work of the binding energies of the Cu 2p_{3/2}, Ag 3d_{5/2} and Au 4f_{7/2} peaks and of the Ni and Ag Fermi edges. The samples are all of metal foils cleaned by *in situ* sputtering with argon ions until the carbon and oxygen 1s peaks are reduced close to the noise level of the spectra. Detailed measurements have been made using a VG ESCALAB II instrument and these results have then been confirmed with separate data using a Scienta ESCA-300.

2.1 MEASUREMENTS WITH THE VG ESCALAB II

Measurements in the VG ESCALAB II were made using the traditional unmonochromated Al and Mg X-ray sources as well as a monochromator with a 120 mm diameter spherically bent diffracting crystal on a 500 mm Rowland circle. This crystal produced a line focus of X-rays, approximately 7 mm long by 1 mm wide. The orientation of this line coincided with the virtual image of the entrance slit for the spectrometer which was 5 mm long by 2 mm wide at the sample. The general arrangement of the system is as shown in Fig 2 of reference (16) except that the analyser has been replaced by a model 210 analyser with 5 channel electron multipliers.

Also shown in Fig 2 of reference (16) is the measurement circuit for the determination of the peak energies. The spectrometer's control circuits are used for the data acquisition but the energy scale is subsequently corrected by the measurement of the voltage difference, V , between precision temperature-stabilised resistors linked to the hemisphere voltages and so arranged that V reflects the electron energy at all pass energies. In this way the kinetic energy of electrons, E_K , is given by

$$E_K = AeV + B \quad (1)$$

where A is a constant factor just less than 1250 and B is the spectrometer work function which is typically in the range 4 eV and 5 eV. The use of this approach eliminates small changes in the spectrometer pass energy and any non-linearity of the supply voltages between the digital-to-analogue converter defining the spectral abscissa and the voltages at the hemispheres defining the energy of the electrons. The values for A and B are determined from Eq (1) by substitution of the V values measured for the Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks using unmonochromated Mg $K\alpha$ X-rays. The kinetic energies of these peaks have been determined earlier⁽⁴⁾ and their energy separations may be determined without reference to the location of the Fermi level zero in order to determine A . In this work we do not need to determine the value of B . Detailed calculations of the effects of the Mg X-ray lineshape and the analyser resolution⁽¹⁵⁾ show that the Cu to Au separation in this case only changes by 2 meV for resolutions in the range 0 eV to 0.75 eV. The earlier work⁽⁴⁾ used a resolution of 0.3 eV so that, for the 0.2 eV resolution used here, the separation changes by less than 1 meV from the values in Table 1.

The locations of the Cu $2p_{3/2}$, Ag $3d_{5/2}$ and Au $4f_{7/2}$ peaks for the unmonochromated Mg X-ray source using Eq (1) repeat from day-to-day with a standard deviation of 7 meV. These data are recorded for 10 eV pass energy with the 6 mm input and output slits. The resolution under this condition is calculated to be 0.2 eV. Dwell times per channel were typically between 3 and 50 seconds. These data have a high reliability since the energy of the X-rays emitted does not vary with time and the X-rays fully fill the 5 mm by 2 mm analytical area of the spectrometer at the sample. Measurements in this instrument with the monochromator, however, are not so robust to the measurement conditions and require more care. It is shown elsewhere⁽¹⁵⁾ that the mean energy of the X-rays focused by the monochromator varies with the crystal alignment and also that the measured energy depends on the part of the entrance slit of the spectrometer into which the emitted electrons are focused by the input lens. This slit forms a virtual image at the sample of 5 mm by 2 mm in the non-dispersion and dispersion planes, respectively. The 1 mm line of the monochromated X-rays can then sample different portions of the spectrometer dispersion for different settings of the sample height. Using 10 eV pass energy and the 6 mm slits with the input lens set at a magnification of 3, the peak shift for Au $4f_{7/2}$ was measured earlier as 120 meV per mm change in sample height⁽¹⁵⁾.

In this work the metal foil thicknesses ranged from 0.06 mm for Au to 0.27 mm for Ni. In order to set the stage height correctly for each sample, the position of the analysed surface was monitored using an electrical wire probe contact. This gave a long-term repeatability

standard deviation for positioning both inside and outside the vacuum system of ± 0.013 mm. This uncertainty leads to a standard uncertainty of 1.6 meV in the kinetic energies as a result of these errors of alignment.

2.2 MEASUREMENTS WITH THE SCIENTA ESCA-300

The measurements with the Scienta instrument were limited to the use of the monochromatic Al X-ray source. All data were recorded using 150 eV pass energy with input slits of 0.8 mm width and 30 mm length. The resolution under these conditions is calculated to be 0.2 eV⁽¹²⁾. This is the same resolution as was used for most of the VG Scientific ESCALAB II data. However, here the X-ray power could be raised to 4 kW to generate significantly more intensity in the monochromated spectra.

The design of the Scienta ESCA-300 differs from that of the VG Scientific ESCALAB II in one important aspect in regard to the geometry of the monochromator. Here the monochromator beam is arranged to lie in a plane through the analyser lens axis and the non-dispersive direction of the virtual analyser slit image on the sample. In the VG Scientific ESCALAB II the monochromator beam is in the plane through the analyser lens axis and the dispersion direction of that slit. Thus, in the Scienta ESCA-300, as the sample is moved to and from the analyser, the X-rays illuminate approximately the same region of dispersion in the slit. The shift in the peak energies with sample position are therefore expected to be small. Tests for the Ag 3d_{5/2} peak showed that the peak energy was kept within a range of ± 5 meV for ± 2 mm sample movement, ± 3 meV for angles of emission from 10° to 80° and ± 5 meV over 4½ hours of test.

Data are reported here using the energies defined by the Scienta electronics. This scale is shown to be linear with energy and so may be re-calibrated, as described later, in the present work.

3 RESULTS AND DISCUSSION

3.1 THE VG SCIENTIFIC ESCALAB II DATA

In the previous analysis of the VG ESCA 3 data leading to the published binding energy values, the measured kinetic energies were as shown in Table 3⁽¹⁾. These led to the values given in Table 1 after rounding and allowing for the relevant X-ray energies. Table 3, rather than Table 1, will be used for the traceable calibration to reduce rounding errors.

In the first experiment, samples of Cu, Ag, Au and Ni were cleaned by ion sputtering and then analysed using the unmonochromated Mg X-ray source. As noted earlier, this was done for a pass energy of 10 eV with 6 mm slits and a lens magnification of 3 to give 0.2 eV energy resolution. These data were used to establish the spectrometer calibration traceably to the data in Tables 1 and 3. The peak energies were defined by a parabola (quadratic) fit to the top 5% of the peak and were defined in terms of the DVM voltage V given in Eq (1). The Fermi edge position was defined by fitting the function given by Eq (10) in reference (15) and by the differential and tangent method also described there. The function to describe the shape at the Fermi edge is the product of a linearly rising density of states and the integral of a Gaussian resolution edge function described by

$$I_{Ni} = C + D(1 - FE_B) \left[1 + \operatorname{erf} \left\{ E_B / (2^{1/2} \sigma) \right\} \right] \quad (2)$$

where E_B is the binding energy referred to the edge of the step, σ is the standard deviation of the Gaussian and C , D and F are fitting parameters. The differential and tangent method uses the negative differential of the Fermi edge. Instead of determining simply the peak of

this differential, a correction is made to allow for the effect of the changing background. A chord is drawn between the half-height positions at either side of the peak and the point of contact of a parallel tangent is taken to be the energy of the peak⁽¹⁵⁾. Figure 1 shows the Ni Fermi edge using Mg K α X-rays and the negative differential of the spectrum with the tangent peak energy determination. The fit to Eq (2) and the tangent to the differential give two measures of the Fermi edge energies as the "fit" value and the tangent/differential or "t/d" value, respectively. These are reported below.

Following the measurements for Cu, Ag, Au and Ni using the unmonochromated Mg X-rays, similar measurements were made with the monochromatic Al X-rays. To check for drift of the spectrometer energy scale, further data for Mg X-rays were recorded followed by additional measurements with the monochromator and so on. The peak energies were determined as noted above by fitting the parabola to the top 5% of the peaks as acquired by the VG data system but those energies were then corrected by the use of the DVM and Eq (1).

Results for the data using Mg X-rays were consistent from day to day with a standard deviation of 7 meV. The calibration of the parameter A was made using the Cu 2p_{3/2} and Au 4f_{7/2} peak energy differences in Table 3. For the time being we shall assume the Au 4f_{7/2} peak energy to be at 84.000 eV and simply work with the binding energy differences. The results of these calculations are given in Table 4. In order to calibrate the parameter A, it should be noted that the present data are for a spectrometer resolution of 0.2 eV at 15° emission angle whereas the data in Table 3 are for 0.3 eV and 45° emission angle. Fortunately, as shown in Fig 16(b) of reference (15) this change requires no corrections for the Mg X-rays. We shall frequently refer to Figs 16(b) and (c) of reference (15) and so, for convenience, they are reproduced in Figs 2(a) and (b). The Cu 2p_{3/2} to Au 4f_{7/2} binding energy separation using the Mg X-ray data from Table 3 is thus 848.659 eV. We may also use the separation from the unmonochromated Al X-ray data of Table 3. This gives a value of 848.684 eV but this must be reduced by 0.005 eV, deduced from Fig 2(a), to be relevant for Mg X-rays and 15° angle of emission. Averaging these two determinations of the Cu 2p_{3/2} to Au 4f_{7/2} separations gives a value of 848.669 eV for 15° emission angle and 0.2 eV resolution. This leads directly to a value of the factor A and so to the data for Cu, Ag, Au and the Ni Fermi edge binding energies given in Table 4. Thus, the traceability of Table 4 is via the earlier determination of binding energies for both Al and Mg unmonochromated X-rays and the calculations given in Fig 2(a).

The results in Table 4 are consistent with those of Table 1 at the 95% confidence level but still leave the correct position of the Fermi level zero of energy to be defined.

The data for the monochromatic Al X-rays, recorded amongst the data for Mg X-rays is converted using the same value of the factor A but showed an effective X-ray energy which slowly fell from 233.022 eV above the effective Mg X-ray energy to 232.976 eV above that energy after a day of measurements. This fall in energy arises due to the heating of the non-stabilised diffracting crystal by a few degrees, which increases its lattice spacing by some 30 ppm. These measurements, using the above value of A and setting the Au 4f_{7/2} peak at 84.000 eV binding energy give, directly, the results shown in Table 5.

So far the results of Tables 4 and 5 depend on a determination of the factor A from the data recorded in the original calibration together with an arbitrary reference setting the Au 4f_{7/2} binding energy at 84.000 eV. To obtain adequate signal to define the energy of the Ag Fermi level we have had to increase the pass energy to 20 eV. Measurements of the relative positions of the Ni and Ag Fermi levels were now made by using the monochromatic Al X-rays at the same settings, apart from pass energy, as previously. The Ni and Ag Fermi levels, shown in Fig 3, were then measured.

The Fermi level data for Ni and Ag were fitted using the function of Eq (2) as shown in Fig 3. As is clear, the fitted functions are excellent descriptions of the data. Different values of C, D and F are required for Ni and Ag, as discussed earlier⁽¹⁵⁾. Four Ni spectra were measured, interspaced with three Ag spectra. To allow for drift in the energies, the difference between each bracketing pair of Ni results and the intervening Ag measurement were calculated. This gave three values for the separations of the Fermi levels defined by the fits to Eq (2) for Ni and Ag, Ni FE(fit) and Ag FE(fit), respectively. If the Ag value, Ag FE(fit), is assumed to give the true zero of binding energy, we find

$$\text{Ni FE(fit)} = 0.038 \pm 0.005 \text{ eV} \quad (3)$$

This value is valid for monochromatic Al K α X-rays and an analyser with 0.4 eV resolution. However, if we use the differential with the tangent construction for the Ni data, we find

$$\text{Ni FE(t/d)} = 0.027 \pm 0.005 \text{ eV} \quad (4)$$

with respect to the fit position for Ag, Ag FE(fit).

The edge resolution in terms of the full width at half maximum (FWHM) of the Gaussian function of Eq (2) was now 0.54 eV. If we use the above values to define the zero of binding energy, Table 5 may be recalculated as in Table 6. We see that values are typically 0.01 eV lower than the unmonochromated values in Table 1 and that the position of the Ni Fermi edge using the differential method appears to have approximately compensated for the difference in position of the Ni and Ag edges. A similar value to Eq (3) for the shift between the Fermi edges of Ni and Ag, of 0.045 ± 0.005 eV has also recently been reported⁽¹⁷⁾.

The measurements for the Ag Fermi edge require some hours to record and so complete sets of all measurements reported in this work, in one day, are not possible. Checks are made using Mg X-rays within each set of data and each anode is pre-heated for 3/4h to 1h before recording data. Hence the experiments have been structured in stages as described. In the final experiment, measurements were made of the Ag Fermi edge and the Au 4f_{7/2} peak energy with monochromatic Al X-rays using 20 eV pass energy. The energy calibrations, both before and after recording the data, were checked with Cu, Ag and Au data using the Mg X-rays. The results of two measurements for both the Ag Fermi edge and the Au 4f_{7/2} binding energy, corrected for the previously established monochromator drift rate with time gave:

$$\text{Au } 4f_{7/2} = 83.981 \pm 0.004 \text{ eV} \quad (5)$$

This value is valid for monochromatic Al K α X-rays and an analyser with 0.4 eV resolution and 15° emission angle.

Before resolving the data of Table 6 further, we now consider the results using the Scienta ESCA-300.

3.2 THE SCIENTA ESCA-300 DATA

Here measurements were made of the Cu 2p_{3/2}, Ag 3d_{5/2}, Au 4f_{7/2} and Ag FE(fit) energies. All of the data except that for the Ag Fermi edge were recorded using the monochromator at 14 keV with 25 mA emission current, and the analyser at 150 eV pass energy, with 0.8 mm slits and 45° emission angle. Unfortunately, the weakness of the Ag Fermi edge required the X-ray source current to be increased to 250 mA for that spectrum. If this is done without care, the size of the X-ray source may change and the X-ray lineshape and energy focused by the monochromator will then also change. The intensity was therefore increased by increasing the emission from the X-ray electron source whilst maintaining its focus on the rotating anode. Tests for the Ag 3d_{5/2} peak using this protocol for the power increasing from

50 mA to 250 mA with the 0.3 mm slits to avoid detector saturation, showed a scatter of less than 1 meV in the measured binding energy.

The measurements here followed the above pattern in the order Cu 2p_{3/2}, Ag 3d_{5/2}, Au 4f_{7/2}, followed by a repeat of the series, a measurement of the Ag Fermi edge and two further repeats of the Cu, Ag, Au series. The average standard deviation of the Cu, Ag and Au peak binding energies was 3 meV and the data, shifted to zero for the Ag Fermi edge, are given in Table 7 in the left hand column titled "Data as recorded". These data have a voltage scaling error since the instrument had not been calibrated for some time. If we assume the data in Table 3 to be correct we may re-calibrate the voltage scale for these data by correcting the Cu 2p_{3/2} to Au 4f_{7/2} calibration separation using Fig 2(a). This gives a separation of 848.657 eV for monochromatic X-rays, an analyser resolution of 0.2 eV and an emission angle of 45°. Calibration using this separation gives the data scaled up by 52.3 ppm in the right hand column of Table 7.

3.3 CONSISTENCY OF DATA

It is not easy to consider the consistency of the data of Tables 1, 4, 6 and 7 directly since they use different X-rays, analyser resolutions and angles of emission. We start by considering the binding energy differences between the Cu 2p_{3/2} and Au 4f_{7/2} peaks and also between the Ag 3d_{5/2} and Au 4f_{7/2} peaks. It is these peaks that are recommended for calibrations^(1,3,18) and so a measure of the consistency here may indicate the best achievable values in careful analysis. As a reference condition we shall convert all data so far reported here to a spectrometer using monochromatic Al X-rays with 0.2 eV resolution and 45° angle of emission, as shown in Table 8, in order to consider consistency. For these conversions we use the data of Figs 2(a) and (b). This is rather tedious but the data are clear. The Cu 2p_{3/2} - Au 4f_{7/2} difference for the Table 3 data averaged between the unmonochromated Al and Mg X-ray sources, converted to 0.2 eV resolution and 45° angle of emission, is 848.657 eV. This calibration was used for Tables 4 and 7 and so the separations derived from these tables must also give this figure. However, the scatter of the data is still meaningful.

In addition to the earlier data, we have made one further experiment with the VG ESCALAB II with 10 eV pass energy and 15° emission angle using the unmonochromated Mg and Al X-rays. Here we make binding energy measurements for the Au 4f_{7/2}, Ag 3d_{5/2} and Cu 2p_{3/2} peaks using Mg X-rays followed by further measurements with the Al X-rays and so on to a total of five measurements for each peak. These data appear in Table 8 as "Supplementary Mg" and "Supplementary Al" data.

The scatter of the Ag 3d_{5/2} - Au 4f_{7/2} data in Table 8 shows an excellent standard deviation of 5 meV. Typically 3 meV will arise from each of the two peaks involved. Linearity tests^(3,18) use a peak such as Ag 3d_{5/2} between the Cu 2p_{3/2} and Au 4f_{7/2} energies. The standard deviation of the Cu 2p_{3/2} - Au 4f_{7/2} binding energy difference is 10 meV. This larger value appears to have scaled up with the increased energy separation. For linearity checks, the final ratio in Table 8 is relevant. This ratio gives a value of 0.3349329 with a standard deviation of scatter of 0.0000059. Such a scatter implies a standard deviation in the precision of defining the peak energies of 3 meV for each of the three peaks. We assume, in deducing this 3 meV figure that the uncertainties are equally distributed and that all of the instrumental measurements involved no linearity errors. If linearity errors existed, the summation of this error and the precision of defining the peak energies could only add up to the 3 meV figure. In Table 8 are results for three very different instruments, a VG Scientific ESCA3, the VG Scientific ESCALAB II and the Scienta ESCA-300. The average values of the final ratios in Table 8, of 0.3349363, 0.3349318 and 0.3349305 indicate divergencies from the mean equivalent to errors of less than 3 meV in locating the energy of the Ag 3d_{5/2} peak relative to the Au 4f_{7/2} and Cu 2p_{3/2} peaks. These results show that the measurements reported here, corrected by the data of Fig 2 allow excellent X-ray source to X-ray source and instrument to instrument consistency.

For those wishing to conduct energy scale linearity tests at accuracies better than expressed by $U_{95}^c(\epsilon_{2,3})$ in reference (15), this shows that a significant improvement is possible. If the mean values in Table 8 are used together with the corrections of Fig 2, Eq (45) in reference (15) may be used with the final term of 0.026 eV reduced by half to 0.013 eV. This should only be applied with spectrometer resolutions of 0.4 eV or less since resolutions, in general, will only be approximated by the Gaussian lineshapes assumed both here and in reference (15).

In the above we have three values for the Au $4f_{7/2}$ binding energy given in Tables 6 and 7 and Eq (5). Converting the value in Table 7 to 15° emission using the data of Fig 14 of reference (15) scaled for the relevant angles and the for factor of 0.72 discussed in reference (15) leads to an increase in the Table 7 value of 4 meV. The average of these three values for the Au $4f_{7/2}$ binding energy gives, for 15° angle of emission:

$$\text{Au } 4f_{7/2} = 83.969 \pm 0.016 \text{ eV} \quad (15^\circ) \quad (6)$$

or, for 45° angle of emission,

$$\text{Au } 4f_{7/2} = 83.965 \pm 0.016 \text{ eV} \quad (45^\circ) \quad (7)$$

Here the uncertainty is the standard deviation of the three measurements. Adoption of these values leads to a slight modification of Table 6. However, rather than proliferate the number of tables we shall consider final tables for the three X-ray sources at a resolution of 0.3 eV and 45° emission angle. We chose the 45° emission angle as this is at the centre of the range proposed in a recent draft ISO standard⁽¹⁸⁾ for binding energy calibration. Table 9 gives this final result for monochromatic Al X-rays using Eq (7) and the average peak separations from Table 8. In Table 9 we also give the data for unmonochromated Al and Mg X-rays calculated using the data of Fig 2 and reference (15). Binding energies for other conditions may be calculated from this table using the data of Fig 2 and further data in reference (15). This is rather tedious and so we simply note that in the range for angles of emission, θ , between 0° and 56° one should add an energy E_c to the values in Table 9 where, approximately

$$E_c = 0.017 (\sec 45^\circ - \sec \theta) \quad (8)$$

With this correction, calculations for the binding energies of all three levels for all three X-ray sources and for analyser resolutions in the range 0.2 eV to 0.4 eV have a mean divergence from Table 9 of -0.001 eV with a standard deviation of scatter of 0.004 eV. For 0° and 56° angles of emission, E_c is 0.007 eV and -0.007 eV, respectively, and for many practical purposes may be ignored. For the measurement of chemical shifts analyser resolutions are usually set in the range 0.2 eV to 0.4 eV and so for practical work Table 9 now replaces Table 1.

The uncertainties in Table 9 reflect the standard deviations from Eq (7), Table 8 and the 11 ppm uncertainty of the original calibration. The values of Table 9 are consistent with those of Table 1 with a small displacement of the zero position of the binding energy scale. More significantly, the differences between the Al and Mg data for unmonochromated X-rays have been reconciled and a table for monochromatic Al X-rays added.

4 CONCLUSIONS

Measurements have been made of the Cu $2p_{3/2}$, Ag $3d_{5/2}$ and Au $4f_{7/2}$ peak binding energy calibration values with improved sensitivity to ensure consistency of these values for different spectrometer operating conditions and different X-ray sources. Measurements under various conditions may be related using data from paper 4 of this series⁽¹⁵⁾. This enables the relative

position of the Ag 3d_{5/2} peak between the Cu 2p_{3/2} and Au 4f_{7/2} peaks to be confirmed with a standard deviation of 5 meV.

Measurements under various conditions and for two different spectrometers use our earlier work^(1,4) to provide overall traceability and allow reference to the Ag Fermi edge not available in the earlier work. This study is summarised in the Table 9 which, together with Fig 2 here or Fig 16 in reference (15) allows calibration of most XPS instrument binding energy scales. This reconciles small differences seen previously between the Al and Mg unmonochromated X-ray data and adds data for monochromatic Al X-rays.

ACKNOWLEDGEMENTS

The authors would like to thank Dr C J Powell for raising the issues concerning the Fermi edge measurement. The work in this paper was supported under contract with the UK Department of Trade and Industry as part of the National Measurement System Valid Analytical Measurement Programme.

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Table 1

Calibration binding energies, eV, for X-ray photoelectron spectrometers after 1 January 1990. The uncertainties represent the one standard deviation values, after Seah⁽¹⁾.

Peak	Al K α	Mg K α
Au 4f _{7/2}	83.98 $\pm$ 0.02	84.00 $\pm$ 0.01
Ag 3d _{5/2}	368.26 $\pm$ 0.02	368.27 $\pm$ 0.01
Cu L ₃ MM	567.96 $\pm$ 0.02	334.94 $\pm$ 0.01
Cu 2p _{3/2}	932.67 $\pm$ 0.02	932.66 $\pm$ 0.02

Note: data are for 0.3 eV analyser resolution and 45° angle of emission.

Table 2

Calibration binding energies, eV, from Bird and Swift⁽⁷⁾. The uncertainties are probable errors in which the main contribution is the uncertainty in the calibration of the voltage scaling.

Peak	Al K α
Au 4f _{7/2}	83.98 $\pm$ 0.02
Ag 3d _{5/2}	368.21 $\pm$ 0.03
Cu L ₃ MM	567.97 $\pm$ 0.04
Cu 2p _{3/2}	932.66 $\pm$ 0.06

Table 3

Kinetic energy values, eV, measured in reference (4) and corrected according to reference (1). The uncertainties represent the one standard deviation values.

Peak	Mg K α	Al K α
Ni FE(t/d)	1199.328 $\pm$ 0.011	
Au 4f _{7/2}	1115.323 $\pm$ 0.005	1348.357 $\pm$ 0.006
Ag 3d _{5/2}	831.058 $\pm$ 0.004	1064.086 $\pm$ 0.004
Cu 2p _{3/2}	266.664 $\pm$ 0.004	499.673 $\pm$ 0.007

Note: data are for 0.3 eV analyser resolution and 45° angle of emission.

Table 4

Binding energy values, eV, determined using the VG ESCALAB II for Mg K α X-rays and an analyser resolution of 0.2 eV derived using the data of Table 3 to calibrate the voltage scaling. The uncertainties represent the one standard deviation of the measurement repeatability. The data are referenced to an Au 4f_{7/2} value of 84.000 eV.

Peak	Mg K α
Ni FE(fit)	0.062 $\pm$ 0.001
Ni FE(t/d)	0.029 $\pm$ 0.005
Au 4f _{7/2}	84.000 $\pm$ 0.009
Ag 3d _{5/2}	368.255 $\pm$ 0.005
Cu 2p _{3/2}	932.670 $\pm$ 0.006

Note: the data are for 15° angle of emission

Table 5

Binding energy values, eV, determined using the VG ESCALAB II for monochromatic Al X-rays and an analyser resolution of 0.2 eV derived at the same time as the data of Table 4. The uncertainties represent the one standard deviation of the measurement repeatability. The data are referenced to an Au 4f_{7/2} value of 84.000 eV.

Peak	Al mono K α
Ni FE(fit)	0.064 $\pm$ 0.004
Ni FE(t/d)	0.053 $\pm$ 0.004
Au 4f _{7/2}	84.000 $\pm$ 0.001
Ag 3d _{5/2}	368.249 $\pm$ 0.010
Cu 2p _{3/2}	932.681 $\pm$ 0.002

Note: the data are for 15° angle of emission.

Table 6

Binding energy values, eV, determined from Table 5 corrected using Eqs (3) or (4) for monochromatic Al X-rays. The uncertainties represent the one standard deviation values of Eq (3) combined with those of Table 5.

Peak	Al mono K α
Ag FE(fit)	0.000
Ni FE(fit)	0.038 ± 0.005
Ni FE(t/d)	0.027 ± 0.005
Au 4f _{7/2}	83.974 ± 0.005
Ag 3d _{5/2}	368.223 ± 0.011
Cu 2p _{3/2}	932.655 ± 0.005

Note: the data are for 0.2 eV analyser resolution and 15° angle of emission.

Table 7

Binding energy values, eV, determined using the Scienta ESCA-300 with monochromatic Al K α radiation and an analyser resolution of 0.2 eV.

The uncertainties of the "Data as recorded", are the one standard deviations of the measurement repeatability. The standard uncertainties of the "Data scaled up by 52.3 ppm" include the uncertainty of the binding energy zero position and of the Cu 2p_{3/2} - Au 4f_{7/2} separation from Table 8.

Peak	Data as recorded	Data scaled up by 52.3 ppm
Ag FE(fit)	0.000 ± 0.003	0.000
Au 4f _{7/2}	83.943 ± 0.004	83.947 ± 0.005
Ag 3d _{5/2}	368.169 ± 0.001	368.188 ± 0.005
Cu 2p _{3/2}	932.555 ± 0.005	932.604 ± 0.012

Note: the data are for 45° angle of emission.

Table 8

Binding energy separations, eV, for peaks referred to the Au 4f_{7/2} peak.
The data are corrected to be appropriate for monochromated Al X-rays with the spectrometer set at 0.2 eV resolution and an angle of emission of 45°.

Peaks	Table 3 (Mg)	Table 3 (Al)	Table 4	Table 5	Table 7	Supplementary Mg	Supplementary Al	Mean ± SD
(Ag 3d _{5/2} - Au 4f _{7/2})	284.243	284.250	284.240	284.250	284.241	284.249	284.239	284.245 ± 0.005
(Cu 2p _{3/2} - Au 4f _{7/2})	848.647	848.667	848.659	848.676	848.657	848.653	848.668	848.661 ± 0.010
$\left(\frac{\text{Ag } 3d_{5/2} - \text{Au } 4f_{7/2}}{\text{Cu } 2p_{3/2} - \text{Au } 4f_{7/2}} \right)$	0.3349359	0.3349366	0.3349286	0.3349332	0.3349303	0.3349416	0.3349238	0.3349329 ± 0.0000059

Table 9

Recommended binding energies, eV, for peaks for a spectrometer of 0.2 eV to 0.4 eV resolution and an angle of emission of 45°.

Peak	Al mono	Mg	Al
Au 4f _{7/2}	83.96 ± 0.01	83.96 ± 0.01	83.96 ± 0.01
Ag 3d _{5/2}	368.21 ± 0.01	368.23 ± 0.01	368.23 ± 0.01
Cu 2p _{3/2}	932.63 ± 0.02	932.63 ± 0.02	932.64 ± 0.02

CAPTIONS

- Fig 1 The Fermi edge region of Ni for Mg $K\alpha$ X-rays together with the negative differential with the tangent construction to define the differential peak energy.
- Fig 2 Change in the binding energy separations as a function of the spectrometer resolution for the three X-ray sources, (a) Au $4f_{7/2}$ minus Cu $2p_{3/2}$ and (b) Ag $3d_{5/2}$ minus Au $4f_{7/2}$. The positions are given as binding energy shifts from the Mg X-ray value at a resolution of 0.3 eV for an emission angle of 45° . The data are presented for 0° (- - -), 45° (—) and 56° (-·-·-) emission angles⁽¹⁵⁾. The lineshapes defining the spectrometer resolution are Gaussian. In practice the lineshapes may differ from this and so an unknown error may occur, especially at the poorer resolutions.
- Fig 3 The Ni and Ag Fermi levels recorded at 20 eV pass energy and 0° angle of emission with the VG ESCALAB II for monochromated Al X-rays, together with the fitted functions. Note that the Ni and Ag spectra have, respectively, 40s and 140s dwell time per channel. For presentation, the Ag spectrum has been scaled up by 2.5 times.

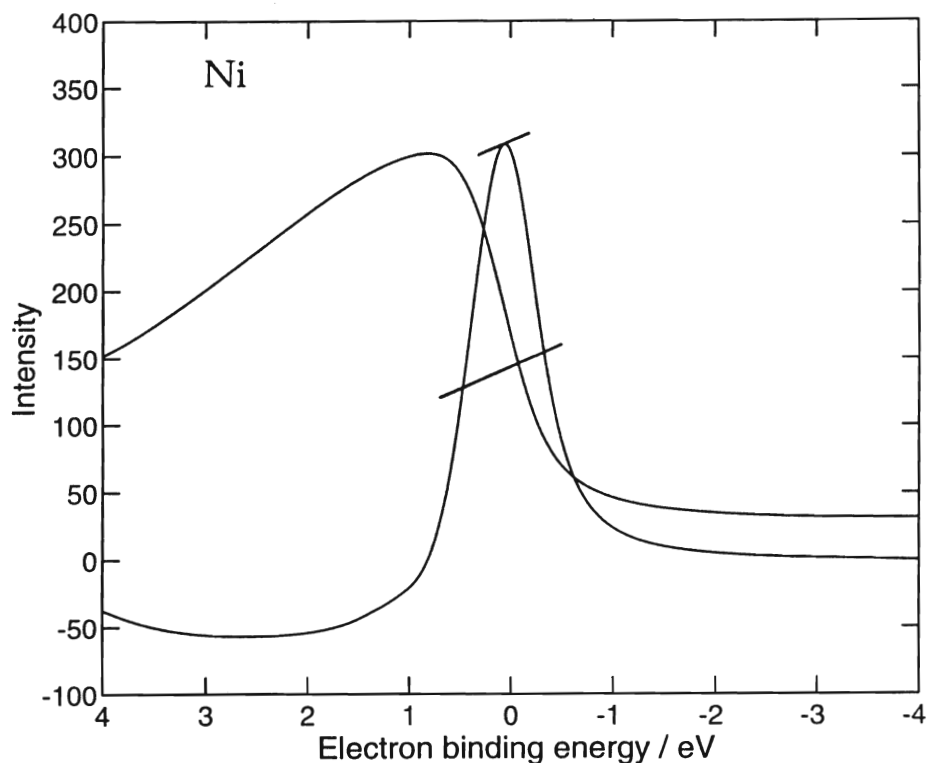


Fig 1 The Fermi edge region of Ni for Mg K α X-rays together with the negative differential with the tangent construction to define the differential peak energy.

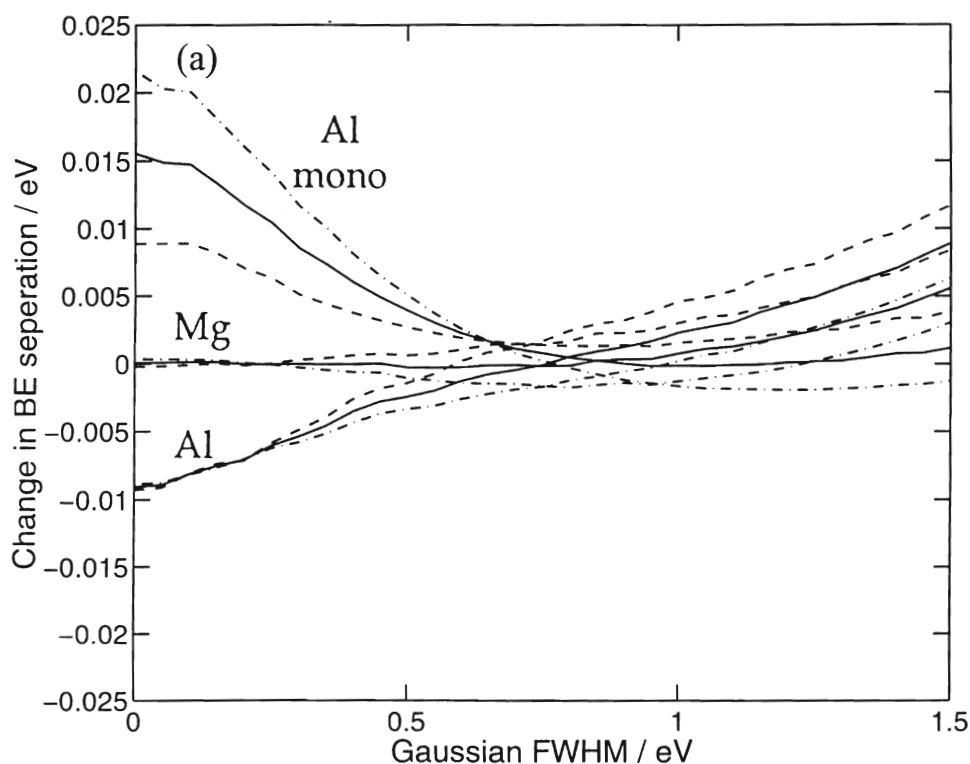


Fig 2 Change in the binding energy separations as a function of the spectrometer resolution for the three X-ray sources, (a) Au 4f_{7/2} minus Cu 2p_{3/2} and (b) Ag 3d_{5/2} minus Au 4f_{7/2}. The positions are given as binding energy shifts from the Mg X-ray value at a resolution of 0.3 eV for an emission angle of 45°. The data are presented for 0° (---), 45° (—) and 56° (- · - ·) emission angles⁽¹⁵⁾. The lineshapes defining the spectrometer resolution are Gaussian. In practice the lineshapes may differ from this and so an unknown error may occur, especially at the poorer resolutions.

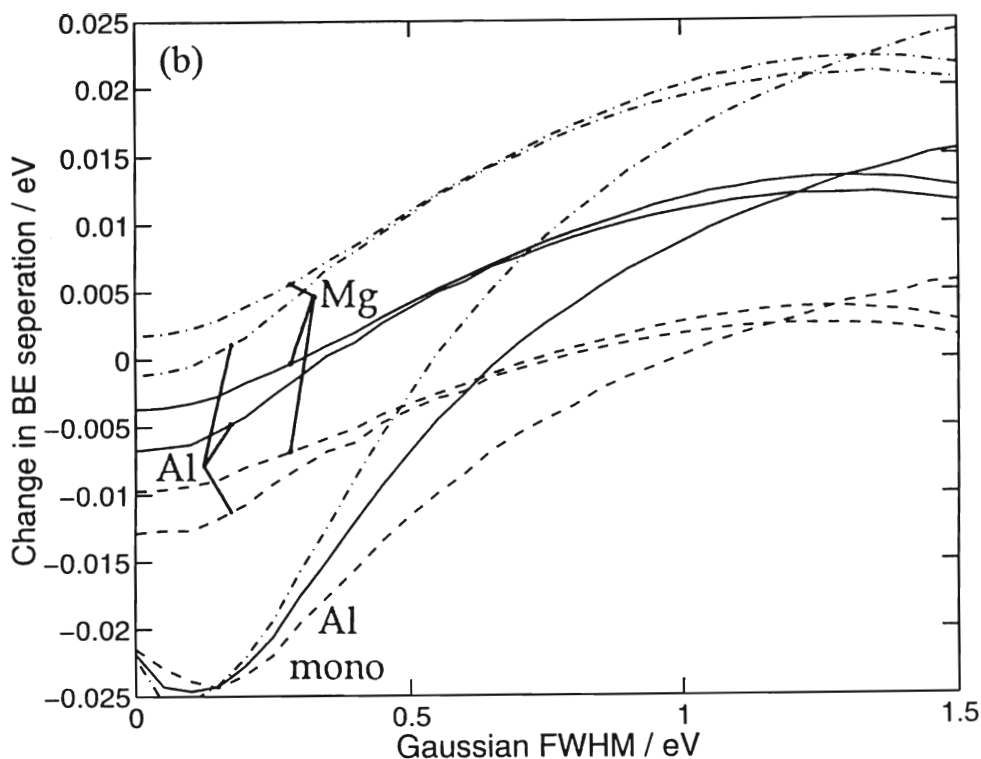


Fig 2 Change in the binding energy separations as a function of the spectrometer resolution for the three X-ray sources, (a) Au $4f_{7/2}$ minus Cu $2p_{3/2}$ and (b) Ag $3d_{5/2}$ minus Au $4f_{7/2}$. The positions are given as binding energy shifts from the Mg X-ray value at a resolution of 0.3 eV for an emission angle of 45° . The data are presented for 0° (---), 45° (—) and 56° (-·-·-) emission angles⁽¹⁵⁾. The lineshapes defining the spectrometer resolution are Gaussian. In practice the lineshapes may differ from this and so an unknown error may occur, especially at the poorer resolutions.

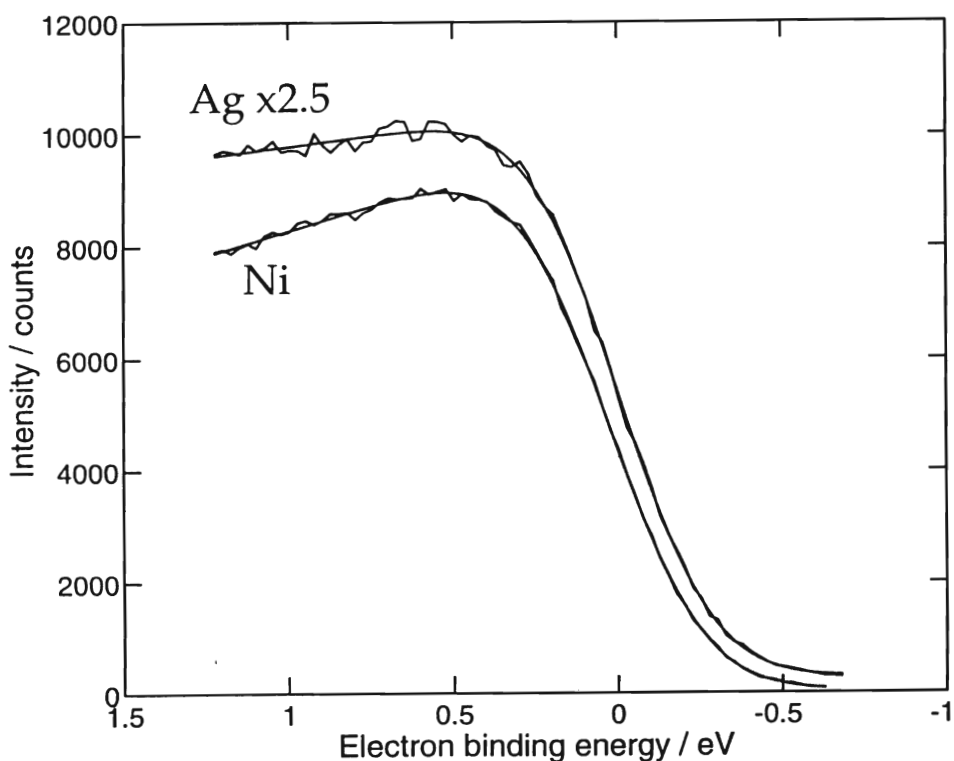


Fig 3 The Ni and Ag Fermi levels recorded at 20 eV pass energy and 0° angle of emission with the VG ESCALAB II for monochromated Al X-rays, together with the fitted functions. Note that the Ni and Ag spectra have, respectively, 40s and 140s dwell time per channel. For presentation, the Ag spectrum has been scaled up by 2.5 times.