

REPORT

XPS: Binding Energy Calibration of Electron Spectrometers 4 - An Assessment of Effects for Different X-ray Sources, Analyser Resolutions and Angles of Emission and of the Overall Uncertainties

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XPS: BINDING ENERGY CALIBRATION OF ELECTRON SPECTROMETERS 4 - AN ASSESSMENT OF EFFECTS FOR DIFFERENT X-RAY SOURCES, ANALYSER RESOLUTIONS AND ANGLES OF EMISSION AND OF THE OVERALL UNCERTAINTIES

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ABSTRACT

A detailed analysis is made of the binding energy calibration of X-ray photoelectron spectrometers when using monochromated Al K α X-rays and both unmonochromated Al and Mg K α X-rays. The binding energies of the peaks for Cu 2p $_{3/2}$, Ag 3d $_{5/2}$ and Au 4f $_{7/2}$, as well as for the Ni and Ag Fermi edges are measured at high resolution using monochromated Al K α X-rays. The binding energy shifts of the peaks are then calculated for this source, and also for the Al and Mg unmonochromated X-ray sources, using full synthetic K α X-ray structures, as a function of Gaussian spectrometer energy resolutions in the range 0 to 1.5 eV. For all three X-ray sources, the relative binding energies for the Cu 2p $_{3/2}$ and Au 4f $_{7/2}$ peaks are contained within ± 0.015 eV but the effects for Ag 3d $_{5/2}$ are stronger and the containment range increases to ± 0.026 eV for all three peaks. Further data and calculations are provided for surface core level shifts and here it is found necessary to restrict emission angles to less than 56° for all the peak separations to be restricted to the above ± 0.026 eV. Instrumental effects in certain cases may give rise to additional larger or smaller effects. Non-optimised settings for monochromators can show further shifts of up to ± 0.2 eV.

The uncertainties associated with the above calibration are then analysed to show how the uncertainty at 95% confidence varies across the binding energy range. Example calculations show that 7 repeats of the Cu 2p $_{3/2}$ and Au 4f $_{7/2}$ binding energies may be used to define the peak repeatability and that 1, 2 or 4 measurements should then be made for each calibration peak to define the calibration. The precise number of measurements to be used depends on the peak energy repeatability and the required confidence limits for the calibration. In practical situations, however, it is likely that the greatest uncertainty in the binding energy scale arises from the drift in the electronics between calibrations.

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

For the use of reference data banks of chemical state information in X-ray photoelectron spectroscopy (XPS),⁽¹⁻⁴⁾ electron spectrometers need to be calibrated with a binding energy scale accuracy in the range 0.1 to 0.3 eV. The required accuracy for a particular laboratory will depend on a judgement of the capability of the particular instrument and the accuracy requirements for the data interpretation. In the present paper we shall study many of the contributions to the corrections for, and to the uncertainties of, the binding energy scale so that the user has a framework in which to make the necessary corrections and informed judgements. What we shall not do, in the present paper, is discuss the requirements for data interpretation in particular chemical environments.

In the first major study of energy calibration in XPS, Powell et al⁽⁵⁾ showed that, in common use, the binding energies of the Cu 2p_{3/2} and Au 4f_{7/2} peaks scattered over a range of 2 eV and of 1 eV, respectively. By 1984 Anthony and Seah⁽⁶⁾, in a second survey, showed that things had not improved greatly. Combined with this second survey, Anthony and Seah⁽⁷⁾ provided traceable calibration energies for the peaks, some of which are shown in Table 1, using a least squares fit of a parabola to the top 5% of the peak. Using these data to establish the offset and voltage scaling errors for each respondent in the second survey, they showed that the reported data could be corrected or recalibrated. For each respondent the standard deviations of the individual differences between these corrected values and the reference values was only 0.033 eV. This compared favourably with the average Cu 2p_{3/2} peak repeatability of 0.024 eV. An alternative use of these data was to calibrate each spectrometer using the measured Cu 2p_{3/2} and Au 4f_{7/2} peak positions and then to evaluate the accuracy of the measured and then recalibrated Cu LMM peak energy. The Cu LMM peak is at an energy approximately mid-way between the Cu 2p_{3/2} and Au 4f_{7/2} energies and so is a useful test of the linearity of spectrometer energy scales. The average deviation and the standard deviation of the scatter of the recalibrated Cu LMM data were -0.002 eV and 0.035 eV, respectively⁽⁸⁾, showing that instruments exhibited no significant non-linearities. In that study all of the spectrometers had unmonochromated X-ray sources and most of the data were evaluated from graphical plots in which some precision may inevitably have been lost.

The data of Anthony and Seah⁽⁷⁾ were adjusted for the international alignment of voltage scales in 1990⁽⁹⁾ and a selection of the data is given in Table 1. The adjustment reduced all energy values by 8.065 ppm. More recently Powell⁽¹⁰⁾ has conducted a further survey showing that, when calibrating spectrometers with a monochromator, the use of Auger electron peaks should be avoided. He notes that the average X-ray energy transmitted by the monochromator, if optimised at the K α_1 energy,^(11,12) will be 0.138 eV higher than the average energy of an unmonochromated source. Powell⁽¹⁰⁾ observed that the measured binding energy of Auger electron peaks appeared to be 0.130 $\pm$ 0.084 eV too high (with a range from -0.05 eV to 0.32 eV) confirming that the average X-ray energy from the monochromator is higher than the average energy for an unmonochromated X-ray source. The scatter of these data was higher than that for unmonochromated sources and may indicate a variability of the monochromated X-ray energy which we shall address later.

It is important to remember that the data in Table 1 were generated using unmonochromated Al and Mg X-rays and with an electron spectrometer resolution described by a full width at half maximum (FWHM) intensity of 0.3 eV. The instrument used there was easy to calibrate since the energy scale was scanned using a single power supply giving a 1:1 correspondence between energy changes and voltage changes of this supply. Two other aspects make those measurements reliable. Firstly, measurements were only made using unmonochromated X-ray sources which flood the whole 9 mm by 1 mm area of the sample analysed by the

spectrometer⁽¹³⁾ in a way that makes the measured peak energies insensitive to the sample position. This insensitivity is very important. Secondly, the X-ray distribution in the unmonochromated X-rays is not thought to vary significantly from instrument to instrument. The use of a higher energy resolution monochromator to obtain data, as we shall see later, could have degraded this reliability. Modern instruments are more complex than this early instrument and so are not as easy to establish for a reference calibration, however they do have a greater performance for practical work. They also have monochromated Al X-rays and both better and worse energy resolution. All of these instruments require calibration and they therefore need traceability to the data of Table 1.

A further issue to those above is that the data in the original study⁽⁷⁾ could only be recorded for angles of emission in the range 30° to 60° and may not be as accurate outside that range. The reason for this concern originally arose from the effects of surface atom core level shifts. Citrin et al⁽¹⁴⁾ show that the relevant peaks from Cu, Ag and Au are composed of a bulk component and a component arising from the surface layer at a lower binding energy. The energy shifts they measured for the surface component are given in Table 2. The relative intensities of the surface and bulk components, I_s and I_b , were given by the approximate simple relation

$$I_s/I_b = \exp \{d/(\lambda \cos \theta)\} - 1 \quad (1)$$

where d/λ is the thickness of the surface layer, in units of the attenuation length of the relevant electrons, and θ is the angle of emission from the surface normal. In Table 2 we give their values of I_s/I_b at $\theta=0^\circ$ and at 60° . Their data were measured using a monochromated X-ray source of high energy resolution, for evaporated films deposited *in situ* onto optically flat glass⁽¹⁴⁾. Those samples differ from the materials traditionally used for calibration, and used to generate the data in Table 1, as they are (a) not sputtered and (b) will have a (111) surface texture. It may, therefore, be that the intensity of the surface core level shifts are not the same for the rough polycrystalline foils used for energy calibration as for the films of Citrin et al⁽¹⁴⁾. In summary, therefore we have calibration data for unmonochromated Al and Mg K α X-ray sources for a spectrometer at 0.3 eV resolution and at 45° emission angle. These data have worked well in earlier tests but, for general use, we need a clear extension for (i) monochromated Al X-rays, (ii) spectrometer resolutions in the range 0 to 1.5 eV and (iii) the effects of angle of emission from 0° to some maximum acceptable angle. We then need a procedure within which to conduct a calibration. Finally we need a way of assessing the uncertainties arising from that calibration at both the calibration energies and at intermediate energies in order that analysts can know the accuracy of their calibrated spectrometer binding energy scale.

In order to provide the extension of the calibration data of Table 1, we present here high resolution data recorded with monochromated Al K α X-rays for the Cu, Ag and Au calibration peaks as well as for the Fermi levels of Ni and Ag used in defining the zero position of the binding energy scale. We couple these data with convolutions for the unmonochromated X-ray lineshapes and for Gaussian spectrometer resolutions in the range 0 to 1.5 eV. This analysis shows how the peak positions and energy separations alter with X-ray source and spectrometer resolution. A further analysis, coupled with data for the effect of surface core level shifts on the positions of the peaks with angle of emission, define a practical working range of emission angles for calibration. These analyses show that Table 1 values may be used, within a certain level of further uncertainty, for a defined range of angles for spectrometers with resolutions in the range 0 to 1.5 eV for the three popular X-ray sources.

These issues are followed by an analysis of the uncertainties for calibrations at 95% confidence for instruments with energy scales that are either known to be linear or for which a linearity test is necessary. This allows an assessment of the calibration accuracy for an instrument immediately after calibration for work at the highest accuracy. In practice, the electronic supplies of most instruments will drift so that the accuracy progressively deteriorates with time. For routine work, therefore, where calibrations are made at intervals of a month or more, this drift may dominate the other uncertainty contributions. The present work covers all of these issues so that users can judge for themselves how best to effect the calibrations to achieve an appropriate accuracy for their work. In this work we do not seek to question the accuracy of Table 1. That is covered in part 5 of this series⁽¹⁵⁾.

To conduct a calibration a procedure needs to be established. Below we outline what a typical calibration procedure for regular routine analytical work could be. If we assume that the user has no knowledge of the instrument we may consider a procedure, as shown in the flow chart of Fig 1 which contains elements of Powell's description⁽¹⁰⁾ and of a draft ISO standard⁽¹⁶⁾. In calibrating any scale, in general, it is best to ensure, as a minimum, that there are calibration points near the ends of the scale and a point near the middle to confirm scale linearity. The Au 4f_{7/2} and Cu 2p_{3/2} peaks satisfy the first criterion and the Cu LMM and Ag 3d_{5/2} peaks the second. As shown in the top six items in Fig 1, first we obtain polycrystalline foil samples of these materials which are mounted in the instrument, are cleaned by ion sputtering and are analysed for a particular chosen set of operating conditions of X-ray anode, pass energy, lens settings, slit settings etc. Each choice of settings for which an accurate energy calibration is required should be considered separately since there are few principles of design which ensure that calibrations under one condition must be valid for other conditions. For some instruments it may be found that for any given pass energy, the binding energies of a given peak do indeed always coincide for all X-ray sources, slit and lens settings but the user will need to confirm that such an agreement occurs to the level of accuracy required.

We have now reached the first decision point in Fig 1. If this is the first calibration, we need to know the precision with which peaks may be located. For this, a number of separate measurements, typically 7, are made of the Cu 2p_{3/2} and Au 4f_{7/2} peak energy. The peak energy itself may be found by several methods^(10,17) and the standard deviation of these measurements, σ_R , often called the peak energy repeatability, is then determined as shown in the YES branch of the first decision loop in Fig 1. Measurements are then made for the Cu 2p_{3/2} and Au 4f_{7/2} peaks to establish the calibration of the binding energy scale, with additional measurements of the Cu LMM or Ag 3d_{5/2} peak to establish the linearity of that scale. If the scale is linear, or if the out-of-linearity energy error is acceptable, the calibration method is established with an uncertainty, at 95% confidence, typically in the range 2 to 4 times σ_R depending on the number of measurements made. This provides the data to recalibrate the instrument. If the repeatability and linearity are known, one follows the NO decision path directly to the calibration and correction of the energy scale. Immediately after the calibration, the energy scale will start to drift and the effects of that drift and the above uncertainty combine to provide the total uncertainty. If this drift is known one can set a calibration interval appropriate for the accuracy required. If not, one must follow the NO path of the second decision loop and evaluate the drift to set that calibration interval. Now the user can set the calibration tolerance limit which is often a compromise between achieving the most accurate result whilst not having to repeat the calibrations too often. Thus, in the last stages of the flow chart in Fig 1, the calibration interval is defined to be compatible with the drift rate and the desired tolerance limits, $\pm\delta$.

Table 3 provides values for some of the above parameters, with two numerical examples, to serve as a guide. A number of different terms occur in Table 3 and these will be introduced as we proceed through this study. We now consider instrumental and other terms which may contribute to the uncertainties in the energy calibrations and in the utilisation of Table 1. By understanding how these effects occur, the user can develop methods which lead to improved measurements and can complete their own version of Table 3.

2 THE EFFECTS OF DIFFERENT X-RAY SOURCES AND DIFFERENT SPECTROMETER RESOLUTIONS ON THE Cu AND Au PEAK ENERGIES

2(a) Acquisition of experimental data

Experimental data in this paper were all recorded using a VG Scientific ESCALAB II with a model 210, 5-detector analyser. The samples were polycrystalline Cu, Ag, Au and Ni foils, cleaned by 5 keV argon ion sputtering and confirmed to be clean by survey spectra in which the heights of the C 1s and O 1s peaks were less than 1% of those of the main metal peaks. Unless otherwise stated, all spectra were recorded at 10 eV pass energy with the 6 mm slit settings and the transfer lens operated at a magnification, M , of 3. This is a common operating condition used by analysts although it is not necessarily a common condition for reference work from NPL. We start below to consider issues concerning the monochromator.

2(b) Setting the sample position with the monochromator

In this spectrometer the X-ray monochromator produces a line image on the sample with a geometry as shown in Fig 2, the line being normal to the plane of the figure. The line is approximately 1 mm wide and the entrance slit of the analyser, when re-imaged back on the sample to define the analytical area, is 2 mm wide. These two dimensions are in the plane of Fig 2. From this geometry, a vertical shift of the sample, ΔZ , leads to a shift of the monochromator line across the acceptance area of the spectrometer at the sample surface. This shift, ΔS , is given by

$$\Delta S = \Delta Z (\tan 23^\circ + \tan 15^\circ) \quad (2)$$

The shift ΔW of the line, across the dispersion plane normal to the spectrometer axis, is given by

$$\Delta W = \Delta S \cos 15^\circ \quad (3)$$

From Eqs (2) and (3) we obtain

$$\Delta W = 0.669 \Delta Z \quad (4)$$

The dispersion of this spectrometer is calculated elsewhere⁽¹⁸⁾. The energy shift, ΔE , is given there by

$$\frac{\Delta E}{\Delta W} = \frac{E_p M}{2r_o} \quad (5)$$

where E_p is the pass energy and r_o is the mean radius of the spherical sectors. For an r_o value of 150 mm and the values cited above, the apparent energy shift with height is given by

$$\frac{\Delta E}{\Delta Z} = 0.067 \text{ eV/mm} \quad (6)$$

In addition to the shift from Eq (6) we shall see a shift due to the dispersion of the monochromator itself, where the higher energy X-rays are emphasised at the highest sample position. To avoid this, some manufacturers use a different geometry or designs of the type described by Coxon et al⁽¹⁹⁾ which avoid imaging the spectrometer dispersion onto the sample.

Figure 3 shows spectra for the Au 4f_{7/2} peak for sample heights increasing by 0.5 mm. The peak energy shifts by 0.36 eV for a height increase of 3 mm with the highest kinetic energy recorded at the highest position, as expected from the spectrometer dispersion calculation. Note, however that the shift is 0.053 eV/mm higher than expected from Eq (6) due to the contribution of the monochromator dispersion.

Figure 3 shows that for the peak energy to be accurate to, say, 0.025 eV, the sample surface needs to be reset here to a height accuracy of 0.2 mm. In repeatability tests analysts tend to use one of two procedures: (a) set the sample to the same manipulator position, or (b) maximise the spectral intensity. Method (a) gives very good apparent repeatability but, of course, only relates to another sample if that sample's surface height is accurately the same from the same manipulator position. More importantly, if the Cu and Au samples have thicknesses of 0.5 mm and 0.1 mm, respectively, the Cu peak is always lowered in binding energy by 0.054 eV with respect to that for Au. This may lead to systematic errors much larger than σ_R when using the erroneous method (a). Method (b) is, in general, more realistic but here the intensity only drops to 85% of the maximum value for height changes of ± 0.9 mm. Optimisation within 85% of the maximum intensity thus causes peak shifts of ξ_1 , where $\xi_1 = \pm 0.115$ eV. It is likely, therefore, that in this and many other instruments of this type, traditional procedures of sample positioning could still lead, at 95% confidence, to uncertainties of the binding energy scale of ± 0.1 eV. Better values may routinely be achieved in monochromated instruments designed to place the sample surface very accurately, or where smaller slits are used, or where the spectrometer dispersion is not imaged onto the sample. Better values may also be obtained if the X-rays are incident in a plane at right angles to the spectrometer dispersion direction. Of course, for accurate work here we may also use smaller slits, as discussed later, but we illustrate the effects by using the conditions normally adopted by analysts.

The above energy shifts arise from both the monochromator dispersion and the spectrometer dispersion. The latter causes the energy shift to change in magnitude with the slit size, the lens magnification and the pass energy. In a system with no stray magnetic fields and operated in the constant ΔE mode with a constant lens magnification this leads to an energy shift which is independent of the electron kinetic energy, ie in terms of the energy calibration, the voltage scaling remains correct but photoelectron peak energies will have changed by, say, ± 0.1 eV. Whether the effect is larger or smaller in any given spectrometer depends on the particular instrument design, the settings chosen and the extent to which the spectrometer dispersion is imaged onto the sample surface.

If stray magnetic fields are present, the monochromator will sample different regions of the input slit at different electron energies and now the voltage scaling may appear to depart from unity by up to 150 ppm depending on the conditions. Stronger fields would cause the

imaged input slit to drift completely away from the monochromator line so that, at low kinetic energy, considerable intensity is lost and the problem becomes easily diagnosed. In the present work, the stray magnetic field is predicted to cause a peak shift of less than 0.01 eV over the binding energy range from 0 eV to 1000 eV⁽²⁰⁾.

2(c) Setting the monochromator

The main X-ray feature used in the monochromator is the Al $K\alpha_1$ and $K\alpha_2$ doublet illustrated by Schweppe et al⁽¹¹⁾. These X-rays are diffracted using quartz crystals with the X-rays incident at 11.5° to the crystal surface normal⁽²¹⁾. Diffraction can occur at many angles but only for X-rays of different energies. If the optimum setting gives an angle of θ and diffracts X-rays of energy E , then the energy change, ΔE , for a change $\Delta\theta$ in θ is⁽²¹⁾

$$\Delta E/\Delta\theta = -E \tan \theta \quad (7)$$

This gives an energy change of 5.3 eV per degree change in θ .

Figure 4 shows the measured spectra for the Au $4f_{7/2}$ peak as the monochromator diffraction condition is changed. Here we fix a gold sample horizontally, as before, but this sample is a thin strip 0.5 mm wide suspended beyond the sample mount so that X-rays missing the sample only produce photoelectrons outside the acceptance region of the spectrometer. Below the sample is a clear space of 150 mm. This arrangement reduces the effects of both the spectrometer and monochromator dispersions so reducing the peak FWHM from 0.73 eV in Fig 3 to 0.6 eV here. The spectra shown have θ changed by -0.028° , -0.015° , 0° , 0.016° and 0.029° from the optimum. This is achieved by moving the X-ray anode and tilting the monochromating crystal. The energy shifts are therefore expected to be -0.15 eV, -0.08 eV, 0 eV, 0.08 eV and 0.15 eV, respectively. These compare with measured energy shifts of -0.16 eV, -0.05 eV, 0 eV, 0.09 eV and 0.23 eV, respectively. This correlation serves to make the point that, for intensities within 85% of the maximum attainable (a condition which probably is better than the routine operation of monochromators in many practical environments), the peak of the X-ray emission intensity may vary over a total range of 0.20 eV. Inset in Fig 4 is the $K\alpha_{1,2}$ line structure proposed by Klauber⁽¹²⁾ from which the monochromator filters X-rays.

It should be emphasised that, whereas the effect in the previous section may depend on the particular instrument and its settings, the effect noted here arises simply from the problem of selecting a narrow band of X-rays from a line of significant intrinsic width. It is an effect general to all monochromated instruments. Clearly, the average energy of the monochromated X-rays can be varied over a range of 0.2 eV whilst the intensity performance remains within the manufacturer's specification.

We may summarise the above two sections by noting that the setting of the monochromator itself may allow the average X-ray energy transmitted to be variable so that photoelectron peak energies are measured anywhere within an interval of $\pm\xi_2$ where $\xi_2 = 0.1$ eV. This means that whilst the energies of Auger electron peaks are well defined in kinetic energy, E_K , the kinetic energies of the photoelectron peaks are uncertain within a range of 0.2 eV. We may show this by denoting the average energy of the transmitted X-rays by $h\nu$, close to some fixed mean energy, $h\nu_0$, where

$$h\nu = h\nu_0 \pm \xi_2 \quad (8)$$

The Fermi level referenced kinetic energy of the zero of the binding energy scale of the photoelectrons is then given by

$$E_K = h\nu_0 \pm \xi_2 \quad (9)$$

Thus, if the acquisition computer software has been set assuming ξ_2 is zero, the measured binding energies of all peaks are shifted from their true value by a constant amount in the range $\pm\xi_2$. This means that differences in binding energies are unaffected but absolute binding energies and Auger parameters may be in error by up to $\pm\xi_2$ where, in the present work using the 85% intensity criterion, $\xi_2 = 0.1$ eV. A similar effect occurs through changes in the diffracting crystal temperature. The quartz lattice changes by 12.2 ppm per degree Kelvin so that a 0.1 eV energy reduction occurs in $h\nu$ if the crystal warms by 5 K. Such warming can occur, if the crystal is not temperature stabilised, by radiation from the filament for the X-ray gun or by changes in the ambient environment (eg sunshine). This type of drift gives a time varying factor to ξ_2 which may be systematic and repeatable under some circumstances (eg a calibration at start-up may be repeatable from day to day but be different from that at the end of a working day).

Even if the monochromator is correctly set, as noted earlier, a further shift of $\pm\xi_1$ may occur due to the mis-alignment of the monochromator within the spectrometer's imaged entrance slit. In certain cases this shift is independent of the measured energy and simply adds to the effect of ξ_2 . In the present work ξ_1 is also shown to be of the order of 0.1 eV, again for setting the intensity within 85% of the maximum attainable. For spectrometers where the lens magnification alters with the energy measured, or where there may be stray magnetic fields, ξ_1 will be energy dependent and peaks at different energies may appear to exhibit different errors. Where this is not the case, we can summarise the above by noting that the energies of Auger electron peaks may vary in the range $\pm\xi_1$, the energies of photoelectron peaks by $\pm(\xi_1 + \xi_2)$, the energy separation of photoelectron and Auger electron peaks by $\pm\xi_2$, whereas the energy separations of photoelectron peaks are generally unaffected unless the monochromator crystal temperature changes.

2(d) Monochromated data

To reduce some of the above mentioned dispersion effects in order to achieve high resolution spectra, samples of Cu, Ag and Au were made as 0.5 mm strips. These were aligned parallel to the imaged slit of the spectrometer defining the effective analytical area and mounted as described in the previous section. The virtual image of the slit, defining the analysis area at the sample surface plane, is 5 mm long by 2 mm wide so that these samples, when set to an angle of emission, α , of zero, occupy only 25% of the analytical area defined by the spectrometer. The samples were all sputtered using 5 keV argon ions until the carbon and oxygen 1s peak heights were less than 1% of those of the main metal peaks. The central region of these spectra for Cu, Ag and Au are given in Figs 5(a), (b) and (c) for 10 eV pass energy and 6 mm slit settings.

The spectrum for the Ni Fermi edge is shown in Fig 6(a) but that for Ag was unfortunately rather weak and so, instead we use data from Gelius⁽²²⁾, shown in Fig 6(b). This has an order of magnitude higher intensity whilst retaining comparable energy resolution. Added to the data are analytical fits for Ni and Ag described by Gaussian distributions about the Fermi edge:

$$I_{Ni} = 5.601 + 200.25(1-0.24257E) \left[1 + \operatorname{erf}\left\{E/(2^{1/2} \times 0.1556)\right\} \right] \quad (10)$$

for $-10 \leq E \leq 1.0$ eV and

$$I_{Ag} = 51.30 + 662.95(1-0.03965E) \left[1 + \operatorname{erf}\left\{E/(2^{1/2} \times 0.1314)\right\} \right] \quad (11)$$

for $-10 \leq E \leq 1.4$ eV where E , here, is the binding energy from the zero set at the centre of the respective Fermi edge functions. We are not concerned here with the absolute positions of these edges and peaks but the shifts that each exhibits as a result of its peak shape when we use different spectrometer resolutions or X-ray lineshapes. The issues of the absolute energies are dealt with in paper 5⁽¹⁵⁾. The above data give FWHMs of the Fermi edge resolution of 0.36 eV and 0.31 eV, respectively. At the present time few practical analytical XPS data will have significantly higher resolutions than presented here except for data recorded using synchrotrons or He I or II radiation.

2(e) The effect of different sources and different spectrometer resolutions

Instead of making measurements with different sources we calculate the effect using the data in Figs 5 and 6 to study the energy shifts resulting from different conditions. If all peaks shifted in the same way, irrespective of the magnitude of the shift, we would know that the calibration table shown in Table 1 could be applied to all conditions. In a similar study for AES⁽²³⁾ it was shown, however, that the resolution did affect the measured peak energies within 0.025 eV, for spectrometer resolutions with a Gaussian lineshape with a FWHM less than 1 eV.

In this study we have generated synthetic line structures for the unmonochromated X-ray sources with component intensities generally as described by Klauber⁽¹²⁾ for Mg and Al X-rays. We have, in fact, generated three sets of such sources: (a) directly as Klauber's⁽¹²⁾ data, (b) Klauber's data modified to give the line separations of Schweppe at al⁽¹¹⁾ with the $K\alpha_2$ at -0.251 eV and -0.413 eV with respect to the $K\alpha_1$ line position for Mg and Al, respectively, and (c) a revised set, empirically adjusted, so that sets of monochromated and unmonochromated data recorded using this instrument with the same operating conditions agree with each other. Sets (a) and (c) are mainly developed to ensure that the satellites are correctly described whereas set (b) takes account of the recent X-ray measurements of the $K\alpha_1$ and $K\alpha_2$ separations⁽¹¹⁾. Figure 7 shows example data for the Zn 2p_{3/2} photoelectrons using unmonochromated and monochromated Al X-rays. Zn is chosen as it gives a very clear test of the method. The satellite removal uses the unmonochromated data and deconvolves the lineshapes using the above set (c). In Fig 7(a) are shown the unmonochromated data as the upper curve and the monochromated and deconvolved unmonochromated data as the overlapped lower curves. The expanded region in Fig 7(b) shows the near peak region with the monochromated data as the noisier of the two lower curves. The closeness of these curves shows the X-ray source structures to be correct. It should be stressed here that the comparison data are recorded with the same energy resolution as each other and that this process is not designed here to reduce the spectrometer peak width contribution. We invert the above process in Fig 7(c) where we see the monochromated and unmonochromated data with, superimposed, the unmonochromated data convolved with the Mg and Al $K\alpha$ lineshapes described above as set (c). This excellent agreement between the unmonochromated data and the monochromated data convolved with set (c) is confirmed for the Ti, Cu and Zn 2p_{3/2} peaks, the Ag, Cd, In and Sn 3d_{5/2} peaks and the Pt and Au 4f_{7/2}

peaks, showing that set (c), by convolution with the monochromated data, accurately generates the unmonochromated results. This group of elements all have sharp well resolved peaks which provide a critical test of the data.

The experimental data of Fig 5 may thus be used to represent data recorded using a monochromator set with its central energy coincident with the centre of the $K\alpha_1$ X-ray line. Convolution with the sets of X-ray lineshapes then generates spectra for unmonochromated sources. This gives the positions of the peaks used for the calibration for instruments for all three X-ray sources at high resolution. We may now study the energy shifts of these peaks for changes in the spectrometer resolution in the range 0.1 to 1.5 eV. Few users study chemical state data at poorer resolutions than 1.5 eV. In this work we shall only use Gaussian spectrometer lineshapes and shall always refer to the resolution in terms of the FWHM of that lineshape in eV. Furthermore, we shall only provide calculations for the constant pass energy mode in which this resolution is constant over the full binding energy range. Other shapes of spectrometer resolution function may give significantly different results. The above convolutions provide an accurate measure of the peak shifts but do not give the absolute values of binding energy. For that we must use Table 1, as described later. All convolutions were made at 25 meV channel intervals except the Ni and Ag Fermi edge data which were at 5 meV intervals using the analytic functions.

As before, we define the peak energies by a parabola (ie quadratic) fit to the top 5% of the photoelectron peak. The results for the three variants of the X-ray source lineshapes noted above, for each of the Mg and Al $K\alpha$ X-ray sources, are within 0.005 eV and so, to avoid confusion we only provide the results of calculations for the set (c) since this very accurately links the experimental monochromated and unmonochromated data. Figure 8 shows the data of Fig 5 convolved with the Mg and Al unmonochromated X-ray source functions. Figure 9 shows the calculated peak energies for monochromated Al X-rays and unmonochromated Al and Mg X-rays for resolutions up to 1.5 eV. These are referred to the high resolution position using monochromated X-rays aligned with the $K\alpha_1$ energy. Figure 9(a) shows the data for the Cu $2p_{3/2}$ peak, Fig 9(b) that for the Ag $3d_{5/2}$ peak and Fig 9(c) that for the Au $4f_{7/2}$ peak. Note that the effects for each peak are broadly similar. At poor resolution we would expect the unmonochromated Mg and Al X-ray data, respectively, to be at 0.088 eV and 0.138 eV higher binding energies than that for the monochromated source, as these are the separations of the $K\alpha_{1,2}$ centroids from the $K\alpha_1$ energy position. This is, in fact what is calculated.

The changes of peak energy with resolution are not, in practice, what an analyst will measure for the reasons described below. In practice, the analyst changes the resolution in order to achieve the best compromise of signal intensity and peak shape by changing the pass energy to one of some 3 to 6 available settings. For each pass energy a number of electronic trims and offsets will have been adjusted by the manufacturer to ensure that the peaks "line-up" at different pass energies. Thus, effectively, the binding energy zero is re-established by this "lining-up" for each pass energy. We, therefore, consider energy differences at each resolution, for a given X-ray source, rather than the absolute values shown in Fig 9.

Figure 10 shows these differences, for Ag and Au referenced to Cu and Ag referenced to Au, as the changes from the value appropriate for Mg X-rays using a spectrometer with a resolution of 0.3 eV. This reference is simply taken for the conditions of Table 1 where the Mg X-ray data are more accurate than those for unmonochromated Al. Cu referenced to Au is not given as this is simply the converse of Au referred to Cu. Over the range of 0 to 1.5 eV resolution we see that the data for the monochromated Al X-rays and the unmonochromated Al and Mg X-rays, are always within a range ± 9 meV at any given

resolution. Over the same range of energy resolution, the standard deviations of the Au to Cu peak separations is 4 meV whereas that for Ag to either Au or Cu is 9 meV. The Ag peak gives a larger extreme range for the variation of energy differences since that peak is intrinsically narrower than those for Cu or Au. It is clear, therefore, from Fig 10(b) that Cu $2p_{3/2}$ and Au $4f_{7/2}$ are stable reference peaks for energy calibration over the resolution range 0 to 1.5 eV.

Note that if the Cu, Ag and Au peaks were all the same shape, the plots in Fig 10 would be coincident at zero separation. It is only the changes in shape that cause the differences observed. The intrinsic core levels, of course, all have unique binding energies but the measured binding energies shift as a function of the broadening by the spectrometer and by the use of unmonochromated sources. If the Fermi edge was a step function broadened by the same lineshape as the peaks, this zero of binding energy would also shift by an identical amount so that all measured binding energies would be unaltered. It is clear from the above that all peaks actually have different shapes but that shifts from the Mg X-ray results are less than 9 meV for Cu and Au and broader peaks but this value degrades to 19 meV for the narrower Ag peak. From Fig 10, therefore, working only with energy differences, one could clearly apply the data in Table 1 for all sources, using the Mg data, by adding, in quadrature, a further standard deviation of 0.008 eV or using the Al data with a further 0.010 eV. This would cover the spectrometer resolution range 0 to 1.5 eV.

In addition to the three peaks shown in Fig 5 we should also consider the effects for the Fermi level data of Fig 6. Here we have a choice of two methods for determining the zero of the binding energy. In the first survey⁽⁵⁾, the point on the curve at which the intensity above the background has fallen to 50% is used to define the Fermi level energy. In the later survey, Anthony and Seah⁽⁷⁾ using both that method and the differential method of Asami⁽²⁴⁾, showed that the latter gave a more repeatable measure with a standard deviation of 0.011 eV for the Mg $K\alpha$ X-ray source. In using Asami's method it was noted that a varying background existed behind the differential peak and, to allow for this, a tangent was taken to the differential peak to define the peak position. The tangent was parallel to a line through points at the half height from background either side of the peak, Figure 11(a) shows the data of Fig 6(a) convolved with the Mg $K\alpha$ lineshape together with the differential and the tangent peak location method. This result is very close to that observed previously⁽⁷⁾. Figure 11(b) shows this differential peak position for the three X-ray sources for the Ni Fermi level and, in Fig 11(c), the result for the monochromator for the Ag Fermi level. The other sources cannot be used for the Ag Fermi level since the intense 4d valence band electrons combine with the $K\alpha_{3,4}$ X-ray satellites to produce intense and varying spectral structure just where the Fermi edge is sought. The ordinate energy has the zero defined at $E=0$ in Eqs (10) and (11). The position of the differential peak, without the tangent construction, and the position of the 50% intensity point were more sensitive to the spectrometer resolution and tended to occur at higher kinetic energies. In Fig 11(d) we show the result for a step function Fermi edge. What these results show is that the sharper the peak the greater the shift and that this shift, at its greatest, is 0.138 eV for unmonochromated Al and 0.088 eV for unmonochromated Mg $K\alpha$ X-rays for an ideal step function.

Figure 12 shows the positions of the Cu, Ag and Au peaks referred to the Ni and Ag Fermi levels estimated by the differential and tangent method. In Fig 12(a) the ordinate energy has been set to zero for the Mg X-ray results at 0.3 eV resolution. The plots using the 50% intensity point and the differential with no tangent show somewhat greater shifts. The results of Fig 12 are what would be obtained for straightforward calibrations at different resolutions. This would indicate a total variation in the measured binding energies of Au $4f_{7/2}$ and Cu $2p_{3/2}$ in a range of less than 0.09 eV when referenced to the Ni Fermi level.

This large range arises because of the large apparent shifts of the Fermi levels. In deriving primary calibrations, a simple scheme is to refer the Au 4f_{7/2} binding energy to the Ag Fermi edge using a monochromatic source and an analyser resolution of 0.4 eV or less and then to refer all other peaks to the Au 4f_{7/2} binding energy⁽¹⁵⁾. In this way the variations in the binding energies for Cu and Au peaks are all within ± 0.01 eV.

Of course the core levels are not actually moving in energy, it is our measure using the top of the peak. If we had used the centroid, the shift would be zero. However, the practical problem of measuring the centroids would give much poorer precision than the implied gain in accuracy. This is because the intrinsic X-ray and core level lines have Lorentzian-like tails which, in practice, are arbitrarily truncated when the peak fitting and necessary background subtraction calculations are made. These tails, unfortunately, contribute very strongly to the centroid energy.

It is clear from Figs 9(a), 9(c), 10(b) and 12 that the Cu 2p_{3/2} and Au 4f_{7/2} peaks are excellent for providing energy calibrations, with single values accurate within a range ± 0.008 eV for spectrometer resolutions in the range 0 to 1.5 eV when using monochromated Al or unmonochromated Mg X-rays. This range degrades to ± 0.011 eV for unmonochromated Al X-rays. These results are more than adequate for practical calibrations.

We may summarise this section as follows. The data for binding energy calibration in Table 1 may be extended to all sources as well as spectrometers in the resolution range up to 1.5 eV by adding a further 10 meV in quadrature to the standard deviations shown. Taking previous roundings into account, all of the one standard deviation uncertainties become 0.02 eV.

The above studies all relate to data recorded at an angle of emission of 0° but Table 1 refers to an angle of emission of 45°. We consider, below, some effects of altering this angle.

3 THE EFFECTS OF SURFACE CORE LEVEL SHIFTS

Surface core level shifts are important, as noted above, since the relative intensity of the shifted peak for the surface atoms increases as the angle of emission increases. This causes the measured peak binding energy to decrease. We, therefore, analyse the effect here. A very full account of the surface core level shifts is provided by Citrin et al⁽¹⁴⁾. We shall use much of their data here but note that the present rough, sputtered polycrystalline samples may show less effect for the angle of emission than Citrin et al's polycrystalline films prepared by evaporation onto optically flat glass. We assume that, as described by Citrin et al, the measured peak is the sum of a bulk peak and a peak due to surface atoms at the energy shift given in Table 2.

It is clear in Citrin et al's work that both the peak and the background behind the peak are scaled together for the surface contribution. We, therefore, first simulate Citrin et al's data to predict the effect of changing the emission angle from 0° to 60°. We simply use the spectra of Fig 5 which are measured for an angle of emission of 0°. Then, to simulate the spectrum at 60°, we add the same spectrum shifted by the surface core level shift to lower binding energy, as given in Table 2, and scaled by the increase in intensity of the surface peak from Eq (1), using the best fit values of d/λ , given in Table 2, for 5° intervals between 0° and 60°. These combined spectra are also convolved with the unmonochromated Al and Mg K α X-ray structures and all are then convolved with the Gaussian resolution functions in the range 0 to 1.5 eV. These calculations show how the measured peak energies change as a result of the

effects of surface core level shifts. For presentational purposes we may simplify the large amount of angular data from these calculations as follows. From Eq (1), for small values of I_s/I_b , it can be shown that I_s/I_b is proportional to $(d/\lambda \cos\theta)$ and that the shift of the peak in energy is proportional to I_s/I_b . Thus we expect, for small values of I_s/I_b , that the binding energy of the peak is given by $E_B(\theta)$ where

$$E_B(\theta) = E_B(0) - s(\sec\theta - 1) \quad (12)$$

In the arrangement of Eq (12), the parameter s has units of eV and will indicate the shift to lower binding energy between 0° and 60° . In all of the cases calculated here, the simple approximation of Eq (12) happens to be a valid description of the full calculation to within 1 meV even though I_s/I_b in Citrin et al's data is not always small. In Fig 13 we show an example of the linearity with $\sec\theta$ for the Au $4f_{7/2}$ peak at 0.3 eV resolution using Mg X-rays. We now plot the difference in the peak positions at 0° and 60° for each X-ray source and resolution in Fig 14. Figures 14(a) and (b) show, for all sources, that the Cu $2p_{3/2}$ and Ag $3d_{5/2}$ peaks shift to lower binding energy by around 0.035 eV and 0.013 eV, respectively. However, Fig 14(c) shows that the results for the Au $4f_{7/2}$ peak are much more variable. Note that these data are deduced for Citrin et al's evaporated films.

For our sputtered polycrystalline metal foils we have not measured data using the monochromator since, as we saw earlier, shifts of the sample of 50 μm during tilting to change the angle of emission, could mask the effect being studied. Instead, we measure data for angles of emission in the range 0 to 60° , using the unmonochromated sources to flood the full analytical area seen by the spectrometer. Beyond 60° the sample is not large enough to be guaranteed to fill this analytical area with an even emission and so data are restricted to angles at or below 60° . Data were recorded at both 10 eV pass energy and 5 eV pass energy, which produce 0.1 eV and 0.05 eV resolutions, respectively, to confirm that there were no problems arising from the spectrometer dispersion. The average results for s from these angular measurements at 5 eV and 10 eV pass energies, for the four peaks of Table 1, are shown in Table 4. An example plot for the Cu $2p_{3/2}$, Ag $3d_{5/2}$ and Au $4f_{7/2}$ peaks using Mg X-rays and 5 eV pass energy is given in Fig 15 with least squares fits to Eq (12). The scatter of data about Eq (12) was the same as the scatter of repeated data at $\theta=0^\circ$ and these scatters, in turn, contribute to the one standard deviation uncertainties in the values of s in Table 4. At the extreme right of Table 4 we show the predictions using Citrin et al's data reduced to 72%. The figure of 72% is deduced by matching the prediction with the experimental data and may arise through the effects of sputtering, morphology or topography. The predictions show no difference between the unmonochromated Al and Mg data and so in the central columns we show the averages of the Al and Mg data. The divergence between the measured and calculated s values has a standard deviation of 9 meV, consistent with the uncertainties in the experimental s values.

Note that the spectrometer dispersion terms could, in some instruments, produce an effect like Eq (12). For a sample being tilted in front of the X-ray source, first one edge of the sample is closest and then, as the angle of emission exceeds an angle around 45° , the other edge becomes closest. Bearing in mind that the distance of the unmonochromated X-ray source from the sample can be as low as 13 mm, the intensity excess at the lower edge of the acceptance area and the deficit at the upper edge can be significant and will alter with the sample tilt angle. In many spectrometers this acceptance area is the virtual image of the entrance slit to the spherical sectors in which electrons originating from different points appear to have slightly different energies. These differences in intensities may thus cause an apparent peak shift to higher or lower kinetic energies as the angle of emission increases. This is similar to the effect expected for surface core level shifts but, having an instrumental

origin, would be similar for all peaks and would change with the instrument operating conditions. In the present work we have confirmed that this effect is negligible by using both 5 eV and 10 eV pass energies and by confirming the uniformity of the X-ray intensity with a scanned 0.5 mm sample.

The variations in measured binding energies arising from surface core level shifts may be kept to a minimum by restricting the angle of emission used to between 0° and $\theta_{\max}$. Since the reference data of Table 1 were acquired at 45° emission, this may be done by setting

$$\sec \theta_{\max} - \sec 45^\circ = \sec 45^\circ - \sec \theta^\circ \quad (13)$$

Hence $\theta_{\max}$ is 56° . From the calculations shown in Fig 14(c) it is clear that at 56° and with Citrin et al's effect reduced to 72% by the surface morphology or other difference of these samples. The data and calculations above are for a 0.05 eV resolution spectrometer setting. We may see what happens as a function of resolution between 0° and 56° from Fig 14 where the ordinate should be reduced by a factor of 0.72, as discussed above, and a further factor of 0.79 for the angular restriction. The full reduction is therefore a factor of 0.57. Thus, the Cu $2p_{3/2}$ and Ag $3d_{5/2}$ peaks typically shift by 0.020 eV and 0.007 eV to lower binding energies, respectively, for all resolutions between 0° and 56° emission angle. The effect for Au is rather stronger with a shift of up to 0.026 eV at the poorest resolutions. Thus, the total range of surface core level shift effects is 26 meV. These effects are all systematic, as are those for resolution at 0° emission in Fig 10. Thus, these uncertainties are not to be summed in quadrature but are added linearly to those in Fig 10. In Fig 16 we recalculate the data of Fig 10 for 0° and add the calculations for 45° and 56° emission angles. The reason for calculating data for 45° is that the reference data in Table 1 are recorded at that angle. Thus, in Fig 16 the full data set are calculated as shifts from a reference position for Mg X-rays at 0.3 eV resolution and 45° emission. It is clear from Eq (12) that for 0° emission the measured binding energies are increased by 0.30s whereas at 56° they are reduced by 0.27s where s here is the value appropriate for Citrin et al's material. Fig 16 shows us that the effects of the surface core level shifts tend to counter the asymmetric effects of the intrinsic peak shapes and the asymmetric unmonochromated X-ray lines to reduce the magnitude of the changes in the binding energy separations of Cu and Au and their dependence on analyser resolution. The overall result is such that we see a range of values that encompasses emission angles between 0 and 56° and certain of the X-ray sources, as shown in Table 5. It is clear that calibrations using the Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks with unmonochromated sources only involve a total range of ± 0.012 eV of uncertainty in establishing the energy scale but that tests including the Ag $3d_{5/2}$ energy for linearity, or for monochromatic Al X-rays, will extend this range to 0.027 eV. For more accurate work all the above corrections to the Table 1 reference data are necessary, however, these corrections are approaching the original one standard deviation of the uncertainties of that data and little may be gained. Generally, for very accurate work a shift from some local internal reference is used rather than an absolute energy.

Figure 16 shows that the values in Table 1 could be made more consistent with each other. This is discussed in part 5⁽¹⁵⁾. Additionally the accurate use of the linearity test using the Ag $3d_{5/2}$ peak, where the corrections of Fig 16 are used, show that the linearity can be established within a one standard deviation value of 5 meV⁽¹⁵⁾.

We may thus summarise this section with the recommendation that the sample orientation used for calibration is the same as that used for the samples for which analytical data are to be recorded, or is limited to angles of emission of less than 56° where the total effect of surface core level shifts on the energy separations of the Cu, Ag and Au reference levels for

these samples is seen to be less than ± 0.027 meV for all X-ray sources and for spectrometer resolutions of less than 1.5 eV. It must also be clear, however, that at the level of accuracy discussed here, any peak energies in a data bank are similarly affected by the angle of emission. Some of these shifts may be to higher binding energy and so the total error for identifying a particular chemical state may appear to be significantly greater than the calibration error.

4 THE UNCERTAINTY OF THE CALIBRATION AT THE CALIBRATION POINTS

Uncertainties in calibration systems are well treated in general texts of fitting and statistical analysis. However, for the energy calibration of X-ray photoelectron spectrometers, only Powell has provided any general analysis⁽¹⁰⁾, and Cumpson et al⁽¹⁷⁾ calculations on the accuracy of peak fitting.

In this section we assume that the calibration of the spectrometer energy scale has been made using several measures of each of the Cu 2p_{3/2} and Au 4f_{7/2} peaks. This analysis will be based on that supposition but may be readily transferred to any other scenario. There are two aspects of the uncertainty, (i) the uncertainty of the calibration values to use for the instrument settings selected and (ii) the uncertainty of making the calibration in the instrument concerned. Sections 2 and 3 deal with most aspects of item (i). The remaining issue is dealt with in paper 5⁽¹⁵⁾. In this section we consider item (ii) in more detail.

The uncertainty of making the calibration in the instrument will involve the uncertainty with which the Cu 2p_{3/2} and Au 4f_{7/2} peak energies may each be determined. There are generally four components to this uncertainty, (i) drift of the electronics over the sample-to-sample measurement time; (ii) the sample-to-sample variation of the core level binding energy; (iii) the change in the measured core level binding energy with sample position coupled with the precision of resetting the sample position for different samples and (iv) the precision associated with the energy value derived from least squares fitting the parabola to the top of the relevant photoelectron peak. As we have seen, where monochromators are used there may be an additional contribution from the drift in the effective X-ray energy of the source. In practice, items (i) and (ii) are very small and (iv) should be a few meV. For more than 40000 counts in the peaks the Poissonian counting statistics should ensure that the contribution to (iv) is less than 6 meV at one standard deviation⁽¹⁷⁾. Item (iii) is often thought to be small since the sample, when replaced, reproduces the same peak energy. However, as we have seen, replacing the same sample to the same sample stage co-ordinates is not always the same as replacing the sample by a proper placement procedure. The latter will not usually be given in terms of the stage co-ordinates, but in terms of the maximisation of an intensity, the focus of a microscope image or some such alignment procedure. As we have shown earlier, for some monochromators a standard deviation of 0.1 eV could arise from such a procedure, but it is not clear how any significant standard deviation occurs when unmonochromated sources are used.

For unmonochromated sources, in the second survey,⁽⁶⁾ the repeatability for the Cu 2p_{3/2} peak, found by graphical means was, on average 0.024 eV. In the more recent study by Powell⁽¹⁰⁾, the repeatability for unmonochromated sources had fallen to 0.007 eV and that for monochromators was also 0.007 eV. Powell, however, notes that these small repeatabilities do not fully reflect the true sample-to-sample repeatabilities in the manner described above since most of the data did not include the re-positioning needed for repeatability measurements. It would therefore seem reasonable that present-day repeatabilities, at one standard deviation, are typically more than 0.007 eV but less than the 0.024 eV of 1984. In

work at NPL with unmonochromated sources values of 0.005 eV are fairly typical at counting levels above 50000 at the peak.

If we record m_1 measurements of a calibration peak number 1 in Table 1 with calibration energy E_{refl} we may determine the experimental standard deviation, $\sigma(m_1)$ from the relation

$$\sigma(m_1)^2 = \frac{1}{m_1 - 1} \sum_{i=1}^{m_1} (E_{1i} - \bar{E}_{1m})^2 \quad (14)$$

where $\bar{E}_{1m}$ is the mean value of the m_1 measurements, E_{1i} for peak 1. In the text above, $\sigma(m_1)$ is what we have called the repeatability standard deviation, σ_R , and this is usually measured using between 4 and 7 measures of the peak energy. The value of the measured position of E_{refl} can now be cited as

$$\bar{E}_{1m} \pm U_{95}^c(E_1) \quad (15)$$

where $\pm U_{95}^c(E_1)$ is the expanded uncertainty defining the interval with 95% confidence of the mean value cited as $\bar{E}_{1m}$. Strictly $U_{95}^c(E_1)$ should be written $U_{95}^c(\bar{E}_{1m})$ but $U_{95}^c(E_1)$ will be used to reduce the proliferation of superscripts and subscripts. Thus, at the binding energy E_{refl} , in order to correct the measured value to obtain an estimate of the true value we must add the binding energy correction $\Delta(E_1)$ where

$$\Delta(E_1) = \bar{E}_{1m} - E_{\text{refl}} \pm U_{95}^c(E_1) \quad (16)$$

and $U_{95}^c(E_1)$ is given by

$$U_{95}^c(E_1) = t_{m_1-1} \sigma(m_1)/m_1^{1/2} \quad (17)$$

Here t_{m_1-1} is Student's t factor for m_1-1 degrees of freedom. Equation (17) gives the uncertainty as the expanded standard deviation where the expansion is the Student factor for a two sided distribution at 95% confidence and m_1-1 degrees of freedom. In this last sentence, by standard deviation we mean, of course, standard deviation of the mean, $\sigma(m_1)/m_1^{1/2}$, not of the population, $\sigma(m_1)$.

In Table 1 we have listed peak number 1 as the Au $4f_{7/2}$ peak and peak number 4 as the Cu $2p_{3/2}$ peak but Eqs (14) to (17) can, of course, be applied to any peak. In Table 6 we show how $U_{95}^c(E_1)/\sigma(m_1)$ rapidly reduces as m_1 increases, together with an example for $U_{95}^c(E_1)$ with $\sigma(m_1) = 0.020$ eV.

At the present time it is not known if this uncertainty is energy dependent. For unmonochromated sources, in our original calibrations⁽⁷⁾, the standard deviations of the Cu $2p_{3/2}$ peak for sample movement by 5 mm towards the analyser, by rotation through 30° of tilt and removal, sputtering and annealing were 0.005 eV, 0.004 eV and 0.005 eV, respectively. It is not easy to see where any significantly greater uncertainties could arise but, in practice they do appear to be present in many studies. It may be that some stainless steel holders have residual magnetism or that, through contamination, they have developed significant contact potentials. At this time we do not know the source of poor repeatabilities. For monochromated sources the sample position affects the energy to an extent which depends on the analyser dispersion imaged back onto the sample surface. For those

spectrometers where the lens magnification between the sample and the analyser changes as the electron energy is scanned⁽²⁵⁾, the uncertainties associated with the sample position will change with energy. Thus, for that class of spectrometer, at least, we expect $\sigma(m_1)$ not to be the same as $\sigma(m_4)$ (or $\sigma(m_2)$ or $\sigma(m_3)$). Thus, for the Cu $2p_{3/2}$ peak

$$U_{95}^c(E_4) = t_{m_1-1} \sigma(m_4)/m_4^{1/2} \quad (18)$$

In a suggested procedure⁽¹⁰⁾ for energy calibration in XPS a number of measurements of the Cu $2p_{3/2}$ peak are made with re-positioning to define the repeatability standard deviation and then further measurements are made of the Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks to conduct the calibration. These further measurements may be made at any later time that a calibration is required. In a second procedure⁽¹⁶⁾ the repeatability standard deviation is also determined for the Au $4f_{7/2}$ peak using the same number of measurements as for the Cu $2p_{3/2}$ peak. We now denote the first number of measurements to define the repeatabilities of the Au and Cu peaks, peaks 1 and 4, as k_1 and k_4 and the latter numbers for subsequent routine calibration measurements as m_1 and m_4 . Powell⁽¹⁰⁾ suggests, as an example, that k_4 is 7 and $m_1 = m_4 = 2$. In the ISO draft⁽¹⁶⁾, additional repeatability data are required for the Au $4f_{7/2}$ peak. Thus $k_1 = k_4 = 7$. We may use these data several ways, to illustrate the calculations of uncertainty contributions below. Cases 1 and 3 refer to Powell's suggestions and cases 2 and 4 the ISO draft suggestions.

Case 1: The k_4 repeatability data for the Cu $2p_{3/2}$ peaks are recorded at a very different time from the m_4 and m_1 calibration data for the Cu $2p_{3/2}$ and the Au $4f_{7/2}$ peaks. Additionally it is known that the repeatabilities for the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks are the same as each other.

We calculate first the repeatability standard deviation, σ_R , of the k_4 measurements of the Cu $2p_{3/2}$ peak

$$\sigma_R^2 = \frac{1}{k_4-1} \sum_{j=1}^{k_4} (E_{4j} - \bar{E}_{4k})^2 \quad (19)$$

where $\bar{E}_{4k}$ is the mean value of the k_4 measurements, E_{4j} , for peak 4. The measured position of the Cu $2p_{3/2}$ peak is then given by

$$\bar{E}_{4m} \pm U_{95}^c(E_4) \quad (20)$$

where $\bar{E}_{4m}$ is the mean of the m_4 measurements for peak 4 and

$$U_{95}^c(E_4) = t_{m_4+k_4-2} \sigma(m_4, k_4)/m_4^{1/2} \quad (21)$$

This equation may seem complicated but it simply reads, as Eqs (16) and (17), that the uncertainty is the expanded standard deviation of the mean and that the latter is simply $m_4^{-1/2}$ times the population standard deviation $\sigma(m_4, k_4)$. Adding the k_4 data to the m_4 measurements has given a better estimate of the population standard deviation and so has improved the uncertainty via Student's term. It has not, however, had the leverage that one gets from measurements in the m_4 distribution to define the mean. The value of $\sigma(m_4, k_4)$ is given by

$$\{\sigma(m_4, k_4)\}^2 = \frac{1}{m_4 + k_4 - 2} \left\{ \sum_{i=1}^{m_4} (E_{4i} - \bar{E}_{4m})^2 + \sum_{j=1}^{k_4} (E_{4j} - \bar{E}_{4k})^2 \right\} \quad (22)$$

Similarly, the binding energy of the Au 4f_{7/2} peaks is given by Eq (15) and

$$U_{95}^c(E_1) = t_{m_1+k_1-2} \sigma(m_1, k_1) / m_1^{1/2} \quad (23)$$

If $m_1 = m_4 = m$, and k_4 is much larger than m we may simplify the above equations by an approximation which will overestimate the uncertainties, but reduce the calculation effort, by replacing $\sigma(m_1, k_4)$ and $\sigma(m_4, k_4)$ by σ_R from Eq (19). Thus,

$$U_{95}^c(E_1) = U_{95}^c(E_4) \leq t_{k_4-1} \sigma_R / m^{1/2} \quad (24)$$

Values of $U_{95}^c(E_4)/\sigma_R$ are given in Table 7. For $k_4 \geq 5$ and $k_4 \geq 2m$, Eq (24) is less than 9% greater than Eq (21) or (23) and so is a useful approximation. Using Table 7 we highlight three useful conditions; $k_4 = 7$ and $m_1 = m_4 = m = 1, 2$ or 3 . In these cases $U_{95}^c(E_1) = U_{95}^c(E_4)$, and both are then $2.4\sigma_R$ ($m = 1$), $1.7\sigma_R$ ($m = 2$) or $1.4\sigma_R$ ($m = 3$), respectively.

Case 2: A situation as case 1 but the repeatabilities of the Cu 2p_{3/2} and Au 4f_{7/2} peaks are not known to be the same.

In this situation we need k_1 repeatability measurements for the Au 4f_{7/2} peak in addition to the k_4 for the Cu 2p_{3/2} peak. $U_{95}^c(E_4)$ is given in Eq (21) and $U_{95}^c(E_1)$ is given by an equivalent equation with all of the "4"s replaced by "1"s. A simple equation such as Eq (24) could be written where, to be safe, σ_R is the greater of the values determined for the Cu 2p_{3/2} and Au 4f_{7/2} peaks. Values of $U_{95}^c(E_4)/\sigma_R$ and $U_{95}^c(E_1)/\sigma_R$ may be found in Table 7 and the numerical examples again give, for $k_1 = k_4 = 7$

$$U_{95}^c(E_1) = U_{95}^c(E_4) = 2.4\sigma_R \text{ for } m = 1 \quad (25)$$

$$U_{95}^c(E_1) = U_{95}^c(E_4) = 1.7\sigma_R \text{ for } m = 2 \quad (26)$$

Case 3: A situation as in case 1 but where the m_4 calibration data for the Cu 2p_{3/2} peak are recorded sequentially to the k_4 repeatability data.

The result for $U_{95}^c(E_1)$ remains as in Eq (23) but $U_{95}^c(E_4)$ improves to

$$U_{95}^c(E_4) = t_{m_4+k_4-1} \sigma(m_4 + k_4) / (m_4 + k_4)^{1/2} \quad (27)$$

where the mean value for E_4 , $\bar{E}_4$, is now calculated for the complete set of $m_4 + k_4$ measurements. Values are shown in Table 8. Compared with case 1 we see that the uncertainties for the Cu 2p_{3/2} are roughly halved through the greater number of data defining E_4 .

Case 4: A situation as in case 2 but where the m_1 and m_4 calibration data for the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks are recorded sequentially to the k_1 and k_4 repeatability data.

In this situation $U_{95}^c(E_4)$ is as given in Eq (27) and $U_{95}^c(E_1)$ is given by an equivalent equation with all the "4"s replaced by "1"s. As in case 2, to be safe, σ_R is taken as the greater of the values determined for the Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks. In this case $U_{95}^c(E_1)$ is taken to be equal to $U_{95}^c(E_4)$ and both may be evaluated from Table 8. Compared with case 2 we see that the uncertainties for the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks are roughly halved through the greater number of data defining $\bar{E}_1$ and $\bar{E}_4$.

We may summarise this section by noting that cases 1 and 2 are the cases which will typically apply to an instrument being routinely calibrated using the NO decision route in the centre of Fig 1 where the repeatability and linearity are already determined. In cases 1 and 2 three conditions are worth highlighting; $k_4 = 7$ and $m = 1, 2$ or 3 . For $m=1, 2$ and 3 , both $U_{95}^c(E_1)$ and $U_{95}^c(E_4)$ are $2.4 \sigma_R$, $1.75 \sigma_R$ and $1.4 \sigma_R$, respectively. It will be seen later that, for practical work there is not usually a lot of point in trying to reduce $U_{95}^c(E_1)$ or $U_{95}^c(E_4)$ much further. Cases 3 and 4 apply where the YES decision was taken at the centre of Fig 1 and the repeatability is determined at the same time as the first calibration, improving the Cu $2p_{3/2}$ measurement in case 3 and both the Au $4f_{7/2}$ and Cu $2p_{3/2}$ measurements in case 4. We shall deal with some numerical implications of these different cases in the next section.

5 THE UNCERTAINTY OF THE CALIBRATION AT A GENERAL ENERGY, E

5(a) Case of a measured binding energy scale that is known to have a linear energy scale correction

From section 4 we have values of the uncertainties, at 95% confidence, for the energy scale corrections, $\Delta(E)$ at the calibration energies E_{ref1} and E_{ref4} from Eqs (21), (23), (24) or (27). We first assume that, by some independent means, we know that

$$\Delta(E) = aE + b \quad (28)$$

where a and b are constants, ie the energy scale corrections vary linearly with energy. If we define Δ_i as $\Delta(E_i)$ from Eq (16) without the associated uncertainty then

$$\Delta_1 = \bar{E}_1 - E_{ref1} \quad (29)$$

and

$$\Delta_4 = \bar{E}_4 - E_{ref1} \quad (30)$$

The constant a , which is the energy scaling error, is given by

$$a = \frac{\Delta_1 - \Delta_4}{E_{ref4} - E_{ref1}} \quad (31)$$

and b , which is the zero offset error, is given by

$$b = \frac{\Delta_4 E_{\text{ref1}} - \Delta_1 E_{\text{ref4}}}{E_{\text{ref4}} - E_{\text{ref1}}} \quad (32)$$

where the E_{ref} values are given in Table 1. In this case the uncertainty at any energy, E , is given by

$$\{U_{95}^c(E)\}^2 = \left\{ \frac{E_{\text{ref4}} - E}{E_{\text{ref4}} - E_{\text{ref1}}} U_{95}^c(E_1) \right\}^2 + \left\{ \frac{E - E_{\text{ref1}}}{E_{\text{ref4}} - E_{\text{ref1}}} U_{95}^c(E_4) \right\}^2 \quad (33)$$

For the case of $m_1 = m_4 = m$ and $k_1 = k_4$ or where the repeatabilities of the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks are the same and $k_4 \gg m_4$,

$$U_{95}^c(E) = \frac{t_{k_4-1} \sigma_R}{m^{0.5}} \frac{\{(E_{\text{ref4}} - E)^2 + (E - E_{\text{ref1}})^2\}^{1/2}}{(E_{\text{ref4}} - E_{\text{ref1}})} \quad (34)$$

This function has the value given in Eq (24) at $E = E_{\text{ref1}}$ or E_{ref4} , has a minimum of $2^{-1/2}$ times this value at an energy midway between E_{ref1} and E_{ref4} and reaches 1.2 times this value at $E = 1070$ eV.

Calculations based on Eq (33) are shown in Fig 17. The upper curve shows the result for $U_{95}^c(E)/\sigma(m_4, k_4)$ for a routine calibration where $m_1 = m_4 = 2$ and $k_4 = 7$ (ie case 1 of section 4), whereas the lower curve shows the result where the repeatability data for Cu are recorded at the same time as the calibration so that m_4 and k_4 are additive (ie case 3 of section 4). From Fig 17 for the case 1, upper curve, it is clear that the ordinate value is below 2 for $E \leq 1070$. The ordinate is for a $t_{k_4-1}/m^{1/2}$ value of 1.67 so we may use this, or Eq (33), to write a simple upper limit to $U_{95}^c(E)$ for $E \leq 1070$ as

$$U_{95}^c(E) \leq \frac{1.2 t_{k_4-1} \sigma_R}{m^{1/2}} \quad (35)$$

Comparison with Eq (24) shows that the uncertainty increases by a factor of up to 1.2 as E moves outside the energy range E_{ref1} to E_{ref2} but within the range 0 eV to 1070 eV.

Note that Eq (33) reduces to Eq (8) of Powell's analysis⁽¹⁰⁾ only for the case that the number of measurements for Cu $2p_{3/2}$ and Au $4f_{7/2}$ is equal (ie k_4 is zero and $m_1 = m_4 = m$) and the repeatabilities of the Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks are the same. Thus, Eq (33) reduces to

$$U_{95}^c(E) = t_{m_1+m_4-2} \frac{\sigma(m_1, m_4)}{m^{1/2}} \frac{\{(E_{\text{ref4}} - E)^2 + (E - E_{\text{ref1}})^2\}^{1/2}}{E_{\text{ref4}} - E_{\text{ref1}}} \quad (36)$$

We now need to write M as the sum of m_1 and m_4 and $\bar{E}$ as the mean of E_{ref4} and E_{ref1} . Thus,

$$U_{95}^c(E) = t_{M-2} \left\{ \frac{1}{M} + \frac{4(E-\bar{E})^2}{M(E_{\text{ref4}} - E_{\text{ref1}})^2} \right\}^{\frac{1}{4}} \sigma(m_1, m_4) \quad (37)$$

This is equivalent to Powell's Eq (8) where M here is his m and the second term in curly brackets is his V . However, if as in Powell's method⁽¹⁰⁾ m_1 and m_4 are not equal, by using the case 3 situation where m_4 is effectively m_1 plus k_4 ,

$$U_{95}^c(E) = t_{M-2} \left\{ \frac{1}{M} + \left(\frac{1}{m_1} + \frac{1}{m_4} \right) \frac{(E - E_{\text{av}})^2}{(E_{\text{ref4}} - E_{\text{ref1}})^2} \right\}^{\frac{1}{4}} \sigma(m_1, m_4) \quad (38)$$

where E_{av} is now the energy for the average of m_4 measures of E_{ref4} and the m_1 measures of E_{ref1} . This function has a minimum at E_{av} , as shown by the lower curve in Fig 17, rather than the $\bar{E}$ indicated in Powell's analysis.

5(b) Case of a measured energy scale that is not known to have a linear energy scale correction

To check if Eq (28) is valid, an out-of-linearity error is deduced by measuring the binding energy E_3 of the Cu L_3VV peak (peak 3 in Table 1) or E_2 of the Ag $3d_{5/2}$ peak (peak 2 in Table 1). Either peak may be used for unmonochromated sources although use of the Cu L_3VV peak will save having to prepare an Ag sample as well as the Cu and Au. For monochromated systems, the shifts we saw in Fig 4 mean that the effective binding energies of Auger electron peaks, when using monochromators, may be uncertain within $\pm \xi_2$ from Eq (9). Thus, for monochromated systems we must use the Ag $3d_{5/2}$ peak. With these recommendations we shall denote the energies etc of these two peaks, with their appropriate choice by $E_{2,3}$, where the subscript 2,3 indicates a choice of peak 2 and peak 3. Thus, from m_1 , $m_{2,3}$ and m_4 measurements of the positions of the three peaks, we have Δ_1 and Δ_4 from Eqs (29) and (30) and

$$\Delta_{2,3} = \bar{E}_{2,3} - E_{\text{ref2,3}} \quad (39)$$

If the scale is linear we would find the out-of-linearity contribution, $\epsilon_{2,3}$ given below, as zero, where

$$\epsilon_{2,3} = \Delta_{2,3} - \left[\frac{\Delta_1(E_{\text{ref4}} - E_{\text{ref2,3}}) + \Delta_4(E_{\text{ref2,3}} - E_{\text{ref1}})}{E_{\text{ref4}} - E_{\text{ref1}}} \right] \quad (40)$$

Of course, $\epsilon_{2,3}$ will not be identically zero but, should, if the scale is linear, be within limits defined by the uncertainties in Δ_1 , $\Delta_{2,3}$ and Δ_4 and the uncertainty, $U_{95}^1(E_{2,3})$, of the $E_{\text{ref2,3}}$ energy with respect to the E_{ref1} and E_{ref4} energies. $U_{95}^1(E_2)$ may be deduced from Fig 16 and Table 5 to be 0.026 eV for resolutions in the range 0 to 1.5 eV and angles of emission less than 56° if the calibration is made from a Table with no corrections for resolution or emission angle. In part 5 we note how, with these corrections, $U_{95}^1(E_2)$ may be reduced to 0.013 eV. The value of $U_{95}^1(E_3)$ may be calculated from the data in Table 4 and ref (23) to be 0.020 eV. To simplify the algebra we shall assume that these peaks all have the same number of measurements m

and the same measurement uncertainties $U_{95}^c(E_1)$. The uncertainty associated with $\epsilon_{2,3}$, $U_{95}^c(\epsilon_{2,3})$ is given by the square root of the quadrature sum of $U_{95}^c(E_{\text{ref}2,3})$ for the calibration from Eq (33), the uncertainty $U_{95}^c(E_1)$ for measuring the energy of peak 2 or 3 and $U_{95}^1(\epsilon_{2,3})$ representing the uncertainty of the $E_{\text{ref}2,3}$ energy with respect to the $E_{\text{ref}1}$ and $E_{\text{ref}4}$ energies. Thus,

$$\{U_{95}^c(\epsilon_2)\}^2 = \{1.25 U_{95}^c(E_1)\}^2 + \{U_{95}^1(E_2)\}^2 \text{ for monochromated Al X-rays} \quad (41)$$

$$\{U_{95}^c(\epsilon_3)\}^2 = \{1.23 U_{95}^c(E_1)\}^2 + \{U_{95}^1(E_3)\}^2 \text{ for unmonochromated Al X-rays} \quad (42)$$

$$\{U_{95}^c(\epsilon_3)\}^2 = \{1.26 U_{95}^c(E_1)\}^2 + \{U_{95}^1(E_3)\}^2 \text{ for unmonochromated Mg X-rays} \quad (43)$$

For simplicity we may apply Eq (43), as the worst case, for all sources. For our case where $k_1 = k_{2,3} = k_4 = 7$.

$$\begin{aligned} U_{95}^c(E_1) &= \frac{t_6 \sigma_R}{7^{1/4}} \\ &= 0.92 \sigma_R \end{aligned} \quad (44)$$

and

$$U_{95}^c(\epsilon_{2,3}) = \left\{ (1.2 \sigma_R)^2 + (0.026)^2 \right\}^{1/2} \quad (45)$$

Thus, if $\epsilon_{2,3}$ is less than $U_{95}^c(\epsilon_{2,3})$ we may assume the scale to be linear. For the example shown in Table 3, where σ_R is 0.020 eV we find that $U_{95}^c(\epsilon_{2,3})$ is 0.035 eV. These values assume there to be no error in Table 1. We shall consider this aspect later in paper 5⁽¹⁵⁾.

If $\epsilon_{2,3}$ is more than $U_{95}^c(\epsilon_{2,3})$ the scale is non-linear. The natural extension from the linear energy scale correction is to assume

$$\Delta(E) = b + aE + cE^2 \quad (46)$$

where a , b and c are constants. This and more complex cases are not usually considered in texts since the design of the system should produce only the result of Eq (28) and any deviation from that result may indicate a more serious instrument malfunction. However, we now analyse the uncertainty on the basis of Eq (46) with the calibration defined at the Au 4f_{7/2} peak (E_1), the Cu 2p_{3/2} peak (E_4) and an intermediate peak E_2 or E_3 . Solving the three simultaneous equations from Eq (46) gives values for a , b and c rather more complex than Eqs (31) and (32) and an overall uncertainty $U_{95}^{cl}(E)$ where the 'l' superscript denotes the linearity consideration and the 'c' superscript the Au 4f_{7/2} and Cu 2p_{3/2} calibration contribution. Thus,

$$\begin{aligned}
\left\{U_{95}^{\text{cl}}(E)\right\}^2 &= \left\{\frac{(E-E_{\text{ref}2,3})(E-E_{\text{ref}4})}{(E_{\text{ref}1}-E_{\text{ref}2,3})(E_{\text{ref}1}-E_{\text{ref}4})}\right\}^2 U_{95}^{\text{c}}(E_1)^2 \\
&+ \left\{\frac{(E-E_{\text{ref}1})(E-E_{\text{ref}4})}{(E_{\text{ref}2,3}-E_{\text{ref}1})(E_{\text{ref}2,3}-E_{\text{ref}4})}\right\}^2 U_{95}^{\text{c}}(E_{2,3})^2 + \left\{\frac{(E-E_{\text{ref}1})(E-E_{\text{ref}2,3})}{(E_{\text{ref}4}-E_{\text{ref}1})(E_{\text{ref}4}-E_{\text{ref}2,3})}\right\}^2 U_{95}^{\text{c}}(E_4)^2
\end{aligned} \quad (47)$$

which, for the case of $m_1 = m_{2,3} = m_4 = m$ and $k_1 = k_{2,3} = k_4$ or where the repeatabilities of the Cu 2p_{3/2}, Au 4f_{7/2} and Cu LMM or Ag 3d_{5/2} peaks are the same and $k_4 \gg m_4$, Eq (47) simplifies to

$$\begin{aligned}
U_{95}^{\text{cl}}(E) &= \frac{t_{k_4-1} \sigma_R}{m^{1/2}} \left\{ \left[\frac{(E-E_{\text{ref}2,3})(E-E_{\text{ref}4})}{(E_{\text{ref}1}-E_{\text{ref}2,3})(E_{\text{ref}1}-E_{\text{ref}4})} \right]^2 + \left[\frac{(E-E_{\text{ref}1})(E-E_{\text{ref}4})}{(E_{\text{ref}2,3}-E_{\text{ref}1})(E_{\text{ref}2,3}-E_{\text{ref}4})} \right]^2 \right. \\
&\quad \left. + \left[\frac{(E-E_{\text{ref}1})(E-E_{\text{ref}2,3})}{(E_{\text{ref}4}-E_{\text{ref}1})(E_{\text{ref}4}-E_{\text{ref}2,3})} \right]^2 \right\}^{1/2}
\end{aligned} \quad (48)$$

The result for $U_{95}^{\text{cl}}(E)/t_{k_4-1} \sigma_R m^{-1/2}$ is shown in Fig 18 for the three possible numerical values of $E_{2,3}$ given in Table 1. We see that the result is typically unity but is always less than 1.5 for $E \leq 1040$ eV. Few data are required beyond this range and so we adopt the useful approximation

$$U_{95}^{\text{cl}}(E) \leq U_{95}^{\text{cl}} = \frac{1.5 t_{k_4-1} \sigma_R}{m^{1/2}} \quad (49)$$

which is slightly worse than Eq (35) as a result of the uncertainty in the linearity.

Values of $t_{k_4-1}/m^{1/2}$ are given in Table 7. For 7 repeats of the three calibration peaks, $k_1 = k_{2,3} = k_4 = 7$ we find for $0 \leq E \leq 1040$ eV, the overall uncertainty is given by

$$U_{95}^{\text{cl}} = 3.7 \sigma_R \text{ for } m = 1 \quad (50)$$

$$= 2.6 \sigma_R \text{ for } m = 2 \quad (51)$$

Mean values of $U_{95}^{\text{cl}}(E)$ are, of course, lower. It is clear from Table 7 that increasing k_4 is only weakly beneficial (but the data need only be recorded once) compared with the effect of increasing m .

If $\epsilon_{2,3}$ is not less than $U_{95}^c(\epsilon_{2,3})$ but is small, calibrations are still valid but $\epsilon_{2,3}$ must be included in the uncertainty of the calibration. If the energy scale error is assumed to have a second order dependence on E , the non-linearity contribution would maximise at $1.15 \epsilon_{2,3}$ and minimise at $-1.15 \epsilon_{2,3}$ in the binding energy range 0 eV to 1100 eV. Again, a third order energy scale error is contained within $\pm 1.2 \epsilon_{2,3}$. The total energy scale uncertainty, U_{95} , is thus usefully given by

$$U_{95} = \left[\left\{ U_{95}^{cl}(E) \right\}^2 + 1.2 | \epsilon_{2,3} |^2 \right]^{1/2} \quad (52)$$

In Table 3 we show examples where U_{95} is calculated using Eqs (52) and (50) or (51) with both σ_R and ϵ_2 or ϵ_3 measured to be 0.020 eV.

Whether users should be concerned if $\epsilon_{2,3}$ is greater than $U_{95}^c(\epsilon_{2,3})$, showing a non-linear scale, depends on the value of $\epsilon_{2,3}$ and the tolerance limits with which they wish to work. In equipment at NPL, σ_R is approximately 0.005 eV so that from Eq (45) $U_{95}^c(\epsilon_{2,3})$ is 0.027 eV. For many users, a value of $\epsilon_{2,3}$ of 0.04 eV, which would clearly indicate a non-linear scale, could still be accommodated within tolerance limits of ± 0.1 eV. This is evident since they would have accepted the result, as passing the linearity criterion etc, if σ_R had the worse value of 0.020 eV, as in Table 3. What the above equations allow us to do is define the limit to which we may work. Providing this is better than we need we are safe. However, the situation is usually not as good as we have described above due to drift in the electronic supplies discussed below.

6 THE UNCERTAINTY OF THE CALIBRATION AT A TIME SIGNIFICANTLY AFTER CONDUCTING A CALIBRATION

The uncertainties given above, U_{95} and U_{95}^{cl} are only valid for the instrument for a period in which the drift of the calibration is significantly less than the values of U_{95} and U_{95}^{cl} . In practice, most users cannot afford the time to recalibrate their instruments at intervals of less than a month or two. As an example, in our equipment we find that σ_R is approximately 0.005 eV so that, for $m = 1$, Eq (50) gives a U_{95}^{cl} value of 0.02 eV. However, for those instruments with σ_R values of 0.020 eV, U_{95}^{cl} could be 0.074 eV, as shown in Table 3. For those trying to work to a calibration limit of ± 0.1 eV clearly the former can allow more drift to occur than the latter.

Figure 19 shows a typical calibration plot using Table 1 values for our equipment with both the Al and Mg unmonochromated X-rays. The ordinate shows Δ_1 and Δ_4 from Eqs (29) and (30), recorded with m_1 and m_4 both unity. A number of these calibration plots have been recorded for both Al and Mg unmonochromated X-rays using 50 eV pass energy, 6 mm slits and an angle of emission of 15° . This is a setting for high intensity studies at the moderate resolution of 1 eV. Calibrations are made prior to recording sets of data and are therefore not as regular as would be made in an analytical laboratory. From Fig 16(b) we see that the separation of the Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks changes by less than 2 meV on moving from Mg to Al unmonochromated X-rays at this resolution and so we "modify" the Table 1 values for the Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks to be 932.665 eV and 83.990 eV, respectively for both X-ray sources. As can be seen from Fig 19, this instrument, as all others, actually measures kinetic energies, E_K , which are converted to binding energies E_B using the simple relation

$$E_B = h\nu - E_K \quad (53)$$

Using the above modified binding energies and values of the effective X-ray energies, $h\nu$, of 1486.58 eV and 1253.56 eV for Al and Mg X-rays, respectively,⁽¹⁸⁾ we obtain four reference kinetic energy values as follows. For Cu 2p_{3/2}, using Mg and Al X-rays we get 320.895 eV and 553.915 eV, respectively and for Au 4f_{7/2} using Mg and Al X-rays 1169.570 eV and 1402.590 eV, respectively. We now use these four reference calibration values to study the four monthly calibrations of this instrument made so far in 1997. First we calculate the difference between the measured kinetic energy data and the reference energies, Δ_i , as a set of four results for each calibration. Next, we make a correction according to Eq (28) using a least squares fit to these differences as a function of kinetic energy. The residual difference between the Δ_i and the least squares fit using Eq (28), reflects the contributions of random errors in the fitting of the single peaks, systematic errors in the reference energies and non-linearity in the instrument's energy scale. In Fig 20 we plot these residual differences. The average of the modulus of the errors of the individual results, is 4 meV. The average of the residuals for the four calibration points, with their standard deviations in ascending kinetic energy order, are -3 ± 3 meV, 4 ± 5 meV, -1 ± 7 meV and 0 ± 5 meV, respectively. These errors and scatters are consistent with our value of σ_R noted above of 5 meV, mainly arising from the statistics of peak fitting. These very small mean errors are the reason for considering the reference values above to meV precision. It is interesting to note that these data show a very linear energy scale, enabling a calibration with one unmonochromated X-ray source to provide the calibration for the other source. For the data in Fig 20 we may try this and use the data from the Al X-ray source to study the increased error associated with the two point calibration from the Mg X-ray source and vice versa. For either X-ray source, the average of the modulus of the errors increases from the above 4 meV to only 8 meV. Where users are confident of the operation of their equipment from studies such as these and where the extra 4 meV of error is not significant, the saving of effort in calibration using only one source could be worthwhile.

The above results cannot be used to correct the absolute values of Table 1 since equivalent consistency would be obtained if the Cu 2p_{3/2} data were homogenised at 932.66 eV and the Au 4f_{7/2} data at, say, 84.00 eV. What the results do show is that, at a resolution of 1.0 eV and for 15° emission angle, the Cu binding energy minus the Au binding energy for Mg X-rays is 6 ± 10 meV higher than the similar measure for Al X-rays. This compares favourably with the 2 meV value in Fig 16(b). Additionally at 1 eV resolution, the difference in the effective X-ray energies is then 233.02 eV with an uncertainty of ± 0.01 eV at 1 eV resolution and 95% confidence.

This apparent accuracy of calibration of ± 0.01 eV at 95% confidence seems fine but how long does it last? Although the VG-ESCALAB II instrument, used for Figs 19 and 20, is recalibrated after each calibration measurement, we have data for before and after each calibration so that we can determine the long term drift as if no recalibrations had been made. The drift in the manufacturer's energy scale, in this case, appears to be roughly proportional to kinetic energy so that the drift at 0 eV binding energy is worst. After fitting new components in the voltage supply chain about 2 years ago, the drift values were initially 0.1 eV per month, whereas over the last year the average rate has been 0.005 eV per month with a short term drift of 0.025 eV per month. To achieve this, the electronic unit for the spectrometer voltage supplies is left on continually. For accurate measurements we do not use the manufacturer's energy scale⁽¹⁵⁾ but the records of that scale may be used for illustrative purposes as if the instrument were being used for routine analysis with tolerance limits $\pm \delta$, at 95% confidence, of ± 0.1 eV. Three weeks after recalibration, our 0.02 eV value

for U_{95}^{cl} becomes comparable to the error caused by the drift and the value of U_{95}^{cl} is only important for critical experiments which then have to be conducted within two weeks of a calibration. For such a calibration, an uncertainty of ± 0.03 eV could be cited. For a tolerance limit of 0.1 eV and the U_{95}^c value of 0.02 eV, the drift rate of 0.025 eV per month indicates a calibration interval for our instrument of less than 3 months.

Figure 21 shows a schematic control chart to illustrate behaviour relating to an instrument with σ_R at the more common value of 0.02 eV, as shown in Table 3. Using $m = 2$ we see from Eq (51) error bars for U_{95}^{cl} of 0.052 eV. Figure 21 shows synthetic measurements of Δ_1 and Δ_4 and how the drift may occur in an instrument originally calibrated in January and monitored monthly but left unchanged after each calibration measurement. The average drift is 0.025 eV per month, as in Table 1, but note that a tolerance limit of 0.1 eV would require calibrations every 3 weeks as the drift is erratic. A choice of 0.2 eV has therefore been used in Fig 21. Of course, each measurement allows a recalibration anyway, even if it is done retrospectively. If the instrument is recalibrated it is still instructive to add the cumulative corrections as in Fig 21 to see if drift is steady, erratic or correlated with particular events in the spectrometer environment. Figure 21 is schematic but is introduced to emphasise (i) how the drift added to U_{95}^{cl} must be less than the tolerance limit, (ii) that drift, as components age, is probably largely in one direction and (iii) that drift rates may not be uniform on a month-by-month basis. Unfortunately, measured data for different instruments is presently far too sparse to give any guidance to the values to expect in practice.

7 CITING THE ACCURACY OF A MEASUREMENT USING A CALIBRATED INSTRUMENT

When a new measurement is made, the cited accuracy for the peak is the tolerance limit, $\pm\delta$, if no uncertainty is associated with the measurement of the new peak itself. If the peak is comparable to the reference peaks, the uncertainty for this peak, ignoring the calibration, will be $U_{95}^c(E_1)$, as given in Eq (24) with $m = 1$. For a k_4 value of 7, from Table 7, we find this uncertainty to be $2.4 \sigma_R$. This uncertainty occurs in addition to the calibration uncertainty. For a σ_R value of 5 meV, this 0.012 eV may normally be ignored since the instrument should be operating significantly within the 0.1 or 0.2 eV tolerance limit.

In practice the new peak may not be a strong, separate sharp peak but a peak in one chemical state to be separated by peak synthesis from similar peaks in other chemical states. The uncertainties can now be much larger due to the problems of peak fitting. Here the effects of noise become more important⁽²⁷⁾ but, even in the absence of noise, errors of 0.1 eV may occur due to the inadequacies of some commercial software⁽²⁸⁾.

A last topic of importance here is that many samples studied by XPS are insulators and the charging potential then needs definition. At an accuracy of 0.1 eV, opinions differ⁽²⁹⁾ concerning the best system for reference and so absolute accuracies are difficult to define. Energy differences, however, may still be established accurately, as defined above.

8 CONCLUSIONS

Binding energy calibration of X-ray photoelectron spectrometers is relatively straightforward using unmonochromated Al or Mg X-rays. For the use of monochromators analysts should

satisfy themselves that they have adequate procedures for use of the monochromator to achieve binding energy repeatabilities suitable for their work. Without such procedures variations for binding energies may exceed ± 0.2 eV and, for Auger parameters, ± 0.1 eV.

Calculations are provided to give traceability between data recorded using monochromated Al X-rays and unmonochromated Al or Mg X-rays as a function of the Gaussian resolution of the electron spectrometer in the range from 0 to 1.5 eV FWHM. It is shown that accurate reference values are only determined for resolutions better than 0.4 eV. However, calibrations over the resolution range 0 to 1.5 eV, and for angles of emission in the range 0° to 56° , may be made using the Cu $2p_{3/2}$ and Au $4f_{7/2}$ reference energies such as those in Table 1. Note that Table 1 is the subject of further work in paper 5⁽¹⁵⁾. Measurements of the surface core level shifts show results weaker than those of Citrin et al⁽¹⁴⁾ thought to be due to the use of sputtered rough polycrystalline foils instead of their evaporated films on glass. For angles of emission below 56° the effects of these shifts are contained within the range ± 0.027 eV.

An analysis of the uncertainties of measurement at 95% confidence, U_{95} , provides general and simplified equations for calibration in terms of an estimate of the instrumental repeatability standard deviation σ_R . These appear in Eq (52) with Eq (48), (49), (50) or (51) with seven measurements of the Cu $2p_{3/2}$ and Au $4f_{7/2}$ peaks and either the Cu LMM or Ag $3d_{5/2}$ peak to define σ_R , provide the first calibration and confirm the energy scale linearity. For subsequent regular calibrations only the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks are used, the number of repeats of these, m , depending on the value of U_{95} needed. Usually m is taken as one or two, as shown in Eqs (50) and (51). It is thought that the σ_R values obtained for unmonochromated sources may sometimes be lower than those found using monochromated X-rays.

An illustration is provided of instrumental drift to show that in normal analytical work this drift may provide a much greater uncertainty than U_{95} , above. This drift may often be the effect that defines the tolerance limit that may be used in practice.

ACKNOWLEDGEMENTS

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Table 1

Calibration binding energies, E_{refn} eV, for X-ray photoelectron spectrometers after 1 January 1990. The uncertainties represent the one standard deviation values, after Seah⁽⁹⁾

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

Notes

- (a) Al K α - Mg K α = 233.02 eV
 (b) Data recorded at a spectrometer resolution of 0.3 eV using unmonochromated X-rays

Table 2

Surface Atom Core level Shift Data of Citrin et al⁽¹⁴⁾

Peak	Surface shift, BE, eV	d/ λ	I _s /I _b (0°)	I _s /I _b (60°)
Cu 2p _{3/2}	-0.241	0.143	0.136	0.374
Ag 3d _{5/2}	-0.076	0.162	0.164	0.409
Au 4f _{7/2}	-0.398	0.122	0.130	0.274

Table 3 - Contributions to an error budget for regular binding energy calibration. The uncertainties are at 95% confidence. The examples illustrate the effect of choices on the accuracy of calibration and the required interval between recalibrations. The data are for an instrument where prior calibration has determined σ_R and ε_2 or ε_3 all as 0.020 eV.

Item	Symbol	Calculated from	Examples		
			For high accuracy	For lower accuracy	
tolerance limits, eV	$\pm \delta$	Choice	± 0.1	± 0.2	
repeatability standard deviation, eV	σ_R	Eq (19)	0.020	0.020	
number of times each pair of spectra is acquired	m	Choice of $m = 1$ or 2	$m = 1$	$m = 2$	$m = 2$
uncertainty of calibration measurements, eV	U_{95}^c	Eqs (50) or (51)	0.074	0.052	0.052
measure of scale non-linearity, eV	ε_2 or ε_3	Eq (40)	0.020	0.020	0.020
uncertainty of energy scale after calibration, eV	U_{95}	Eq (52)	0.078	0.057	0.057
maximum allowable drift between calibrations, eV	$\pm (\delta - U_{95})$	δ and U_{95}	± 0.022	± 0.043	± 0.143
maximum calibration interval (for a steady drift rate of 0.025 eV per month), months	-	Section 6	0.9	1.7	5.7
chosen calibration interval, months	-	variability in observed drift behaviour	Decided to be impractical	1	4

Table 4

Values of the parameter s for surface atom core level shifts (meV), measured at high resolution, with their associated one standard deviation uncertainties

Peak number n	Assignment	Experiment			0.72x Prediction			
		Al K α	Mg K α	Av Al, Mg	Av Al, Mg unmono	Al K α	Mg K α	Al mono
1	Au 4f _{7/2}	24 $\pm$ 6	38 $\pm$ 5	31 $\pm$ 10	23	22	23	7
2	Ag 3d _{5/2}	8 $\pm$ 4	11 $\pm$ 5	10 $\pm$ 4	9	9	9	9
3	Cu L ₃ MM	12 $\pm$ 5	6 $\pm$ 6	9 $\pm$ 6				
4	Cu 2p _{3/2}	11 $\pm$ 4	18 $\pm$ 7	14 $\pm$ 6	23	23	24	22

Table 5

Total range of peak separation energies, x , expressed as $\pm x$ meV from the values at the reference condition of 0.3 eV resolution for Mg X-rays, for angles of emission in the range 0 to 56° and spectrometer resolutions in the range 0 to 1.5 eV

Peaks	Al K α	Mg K α	Al mono
Ag 3d _{5/2} - Cu 2p _{3/2}	27	25	23
Au 4f _{7/2} - Cu 2p _{3/2}	12	8	22
Ag 3d _{5/2} - Au 4f _{7/2}	21	21	26

Table 6

Values of $U_{95}^c(E_1)/\sigma(m_1)$ or $t_{m_1-1}/m_1^{1/2}$ from Eq (17) and $U_{95}^c(E_1)$ for $\sigma(m_1) = 0.020$ eV for 95% confidence. This shows how an increasing number of measurements, m_1 , rapidly reduces the uncertainty

m_1	1	2	3	4	5	6	7	8	10	20	50	100
$t_{m_1-1}/m_1^{0.5}$	∞	12.706	3.043	1.837	1.241	1.050	0.925	0.836	0.715	0.468	0.284	0.198
$U_{95}^c(E_1), \text{ eV}$	∞	0.254	0.061	0.037	0.025	0.021	0.019	0.017	0.014	0.009	0.006	0.004

Table 7

Values of $U_{95}^c(E_4)/\sigma_R$ or $t_{k_4-1}/m^{1/2}$ from Eq (24) for uncertainties defined by k_4 measurements at a different time to the m measurements as in Cases 1 and 2

m	k_4				
	5	7	10	20	50
1	2.776	2.447	2.262	2.093	2.008
2	1.963	1.730	1.599	1.480	1.420
3	1.603	1.413	1.306	1.208	1.159
4	1.388	1.224	1.131	1.047	1.004
5	1.241	1.094	1.012	0.936	0.898

Table 8

Values of $U_{95}^c(E_4)/\sigma(m_4+k_4)$ or $t_{k_4+m_4-1}/(m_4+k_4)^{1/2}$ as in Eq (27) for uncertainties defined by k_4 measurements at the same time as the m measurements as in Cases 3 and 4

m	k_4				
	5	7	10	20	50
1	1.050	0.836	0.672	0.455	0.281
2	0.925	0.769	0.635	0.443	0.278
3	0.836	0.715	0.604	0.432	0.276
4	0.769	0.672	0.577	0.422	0.273
5	0.715	0.635	0.554	0.413	0.270

FIGURE CAPTIONS

- Fig 1 Flow chart for a possible calibration procedure.
- Fig 2 Geometry of the monochromator analysis.
- Fig 3 Measured kinetic energy for Au 4f_{7/2} photoelectrons using monochromated Al X-rays with 10 eV pass energy, 6 mm slits and a lens magnification of 3. The peaks are seen to shift to higher apparent kinetic energy as the sample is raised by successive 0.5 mm increments. In this study the sample is 10 mm by 10 mm, aligned horizontally.
- Fig 4 Measured kinetic energy for Au 4f_{7/2} photoelectrons using monochromated Al X-rays with 10 eV pass energy, 6 mm slits, a lens magnification of 3 and a 0.5 mm wide sample. The spectra are recorded for the X-ray anode moved by approximately 0.5 mm increments and the diffraction condition re-optimised by adjusting the crystal tilt. The diffraction angles for the peaks reading from the left are at -0.028°, -0.015°, 0°, 0.016° and 0.029° away from optimum, respectively. Inset is shown the Kα_{2,3} line structure for Al⁽¹²⁾ with 1 eV markers.
- Fig 5 Details of the spectra for (a) Cu 2p_{1/2,3/2}, (b) Ag 3d_{3/2,5/2} and (c) Au 4f_{5/2,7/2} peaks using the monochromator with zero angle of emission.
- Fig 6 Details of the Fermi edge measurements for (a) Ni and (b) Ag⁽²²⁾ together with the fits of Eqs (10) and (11) showing edge resolutions of 0.36 eV and 0.31 eV, respectively. The binding energy zero is defined by the fit. The measured data extend to 15 eV binding energy.
- Fig 7 Zn 2p_{3/2} photoelectron peak. (a) monochromated and unmonochromated spectra using Al X-rays, as recorded, as well as the unmonochromated spectrum with deconvolution of the peak and satellites. The unmonochromated spectrum is uppermost. (b) detail of (a) showing the near peak region (the monochromated spectrum shows greater noise than the deconvoluted unmonochromated spectrum). (c) monochromated spectrum using Al X-rays and its convolute with the Al and Mg X-ray peak structures to simulate unmonochromated spectra, overlaid on the experimental unmonochromated spectra. The Mg spectra are uppermost and the unmonochromated Al data are lowest, except at the peak where the order is reversed.
- Fig 8 Details of the spectra for (a) Cu 2p_{3/2}, (b) Ag 3d_{3/2,5/2} and (c) Au 4f_{5/2,7/2}, as in Fig 5 together with the convolutions for the unmonochromated Mg and Al X-ray sources. The latter is the dashed spectrum with the satellites displaced farthest from the peaks towards low binding energies.

- Fig 9 Relative binding energies derived from the peak energies as a function of spectrometer resolution for the three X-ray sources, (a) Cu $2p_{3/2}$, (b) Ag $3d_{5/2}$ and (c) Au $4f_{7/2}$. The ordinate is given as binding energy shifts from the high resolution energy using monochromated X-rays aligned with the $K\alpha_1$ energy. The resolution is assumed to be determined by a Gaussian lineshape. In practice this is only an approximate description of the behaviour and the plot may involve increasing error as the resolution degrades.
- Fig 10 Change in the binding energy separations as a function of the spectrometer resolution for the three X-ray sources, (a) Ag $3d_{5/2}$ minus Cu $2p_{3/2}$, (b) Au $4f_{7/2}$ minus Cu $2p_{3/2}$ and (c) Ag $3d_{5/2}$ minus Au $4f_{7/2}$ from the data of Fig 5. Note the scale expansion of 5 times compared with Fig 9. The ordinate is given as the binding energy shift from the Mg X-ray value at a resolution of 0.3 eV.
- Fig 11 Fermi edge data as a function of the spectrometer energy resolution, (a) the Ni Fermi edge from Fig 6(a) convolved with the Mg $K\alpha$ X-ray structure and its differential with the tangent construction to define the differential peak energy, (b) the differential peak energy for Ni for the three X-ray sources, (c) the differential peak energy for Ag for monochromated Al X-rays, (d) the differential peak energy for a step function. Note that the ordinate here is referenced to the zeros of Eqs (10) and (11) which are not the same⁽¹⁵⁾.
- Fig 12 Cu, Ag and Au binding energies referred to the measured Fermi edge peak energy at that resolution, as a function of the spectrometer resolution for the three peaks. (a) Ni with three X-ray sources, the unmonochromated Al is always uppermost, followed by unmonochromated Mg and finally monochromated Al as shown for Cu, (b) Ag with monochromated Al X-rays. In (a) the ordinate is set to zero for the Mg data at 0.3 eV resolution.
- Fig 13 An example of the calculated angular dependence of the binding energy shift of the Au $4f_{7/2}$ peak at 0.3 eV resolution, using Mg X-rays. This shows the near linear dependence on $\sec\theta$. These calculations are valid for Citrin et al's data and diverge from linearity by less than 1 meV.
- Fig 14 The predicted peak binding energy shifts to simulate Citrin et al's data for evaporated films for an angular change between 0° and 60° for all X-ray sources for (a) Cu $2p_{3/2}$, (b) Ag $3d_{5/2}$ and (c) Au $4f_{7/2}$. These use the data at 0° from Fig 5 as well as that data shifted as shown in Table 2, scaled using Eq (1) and then added to the original data to form a new spectrum appropriate to 60° .
- Fig 15 The measured peak binding energy shift using 5 eV pass energy as a function of the angle of emission for unmonochromated Mg X-rays for Cu $2p_{3/2}$ (●), Ag $3d_{5/2}$ (+) and Au $4f_{7/2}$ (x).

- Fig 16 Data as in Fig 10 but for 0° (---), 45° (—) and 56° (- . - . - .) emission angles. The data are for the change in the binding energy separations as a function of the spectrometer resolution for the three X-ray sources, (a) Ag $3d_{5/2}$ minus Cu $2p_{3/2}$, (b) Au $4f_{7/2}$ minus Cu $2p_{3/2}$ and (c) Ag $3d_{5/2}$ minus Au $4f_{7/2}$. The ordinate is the binding energy shift from the Mg X-ray value at a resolution of 0.3 eV for an emission angle of 45° (the data in Fig 10 are for 0° only and are referenced to the Mg X-ray value at 0.3 eV in those data). The X-ray source may be identified from Fig 10.
- Fig 17 The uncertainty at 95% confidence from Eq (33) for the case where calibrations have been made at E_1 and E_4 and the energy scale is known to be linear. The upper curve shows the uncertainty given by $U_{95}^c(E)/\sigma(m_4, k_4)$ for case 1 of section 4 with $m_1 = m_4 = 2$ and $k_4 = 7$ whereas the lower curve is for case 3 where k_4 can be added to m_4 . The vertical lines show the energies E_{ref1} and E_{ref4} .
- Fig 18 The uncertainty at 95% confidence for the case where the energy scale obeys Eq (46) and calibrations have been made for Au $4f_{7/2}$, Cu $2p_{3/2}$ and Cu LMM or Ag $3d_{5/2}$. The ordinate is $U_{95}^{cl}(E)m^{1/2}/t_{k-1}\sigma_R$ from Eq (48) and it is assumed that the same number of measurements and the same uncertainty applies to each peak. The three curves relate to the three $E_{ref2,3}$ values in Table 1. Note that the ordinate in this Fig is not the same as in Fig 17.
- Fig 19 A typical calibration plot for the VG ESCALAB II. The ordinate values are Δ_1 and Δ_4 from Eqs (29) and (30) for unmonochromated Al and Mg X-rays using the reference values of Table 1.
- Fig 20 Residual errors from four re-calibrations using mean values for the reference binding energies for the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks for the Al and Mg X-rays. The different symbols relate to each calibration in the chronological order ●, x, + and o.
- Fig 21 Schematic of an energy calibration control chart showing the calibration status of an X-ray photoelectron spectrometer after Seah⁽²⁶⁾. The plotted points are synthetic values of Δ_1 and Δ_4 from Eqs (29) and (30) which are defined as the differences between the measured binding energies and the tabulated binding energies for the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks. These are shown as a function of time for an instrument originally calibrated in January and which should have been recalibrated, according to Table 3, in May. The values used in this Fig are $m = 2$ and $\delta = 0.2$ eV, as shown in Table 3. If the measured calibration data had been used to re-calibrate the instrument each month, the 95% confidence tolerance limit could be reduced to ± 0.16 eV.

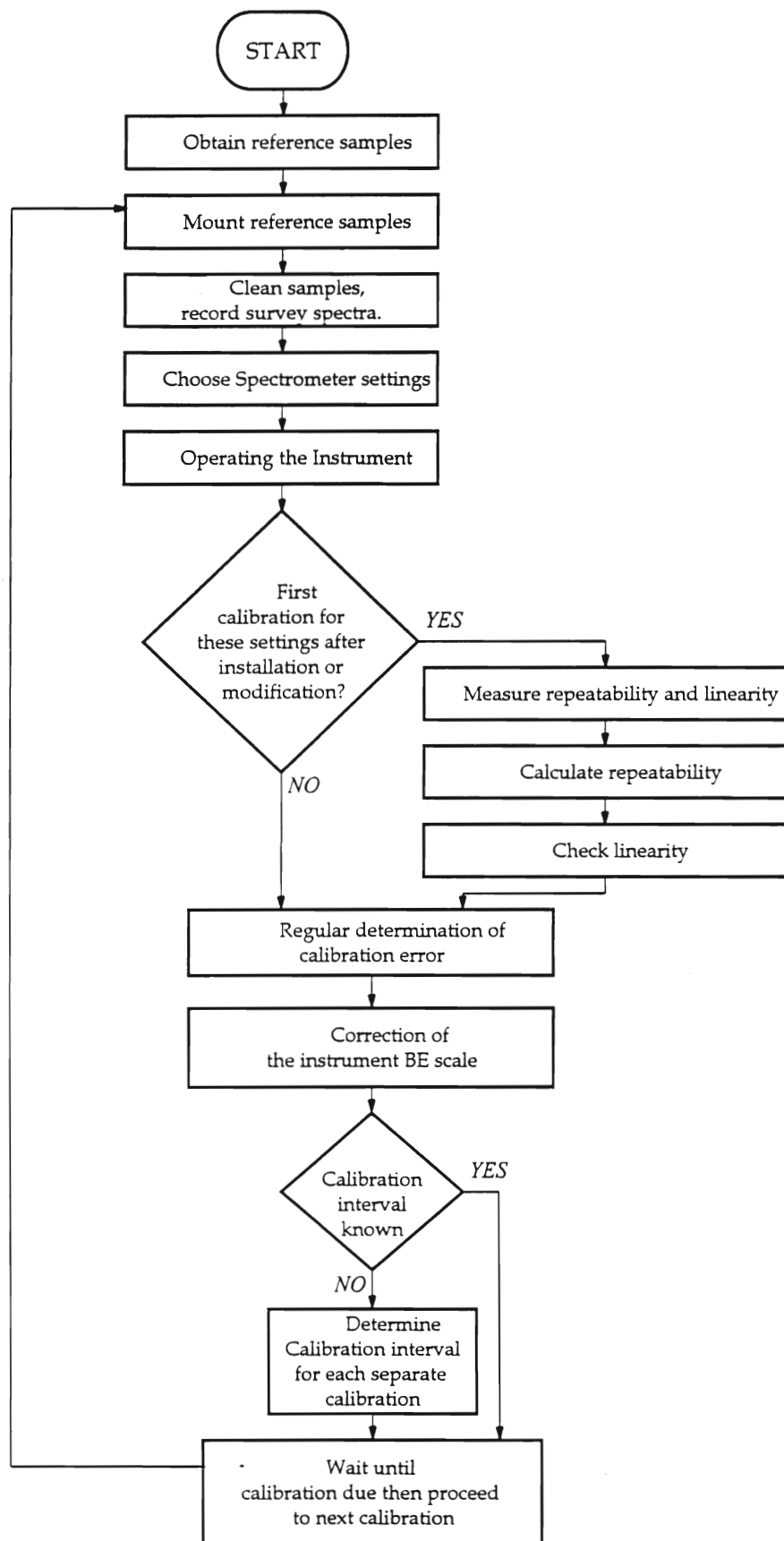


Fig 1

Flow chart for a possible calibration procedure.

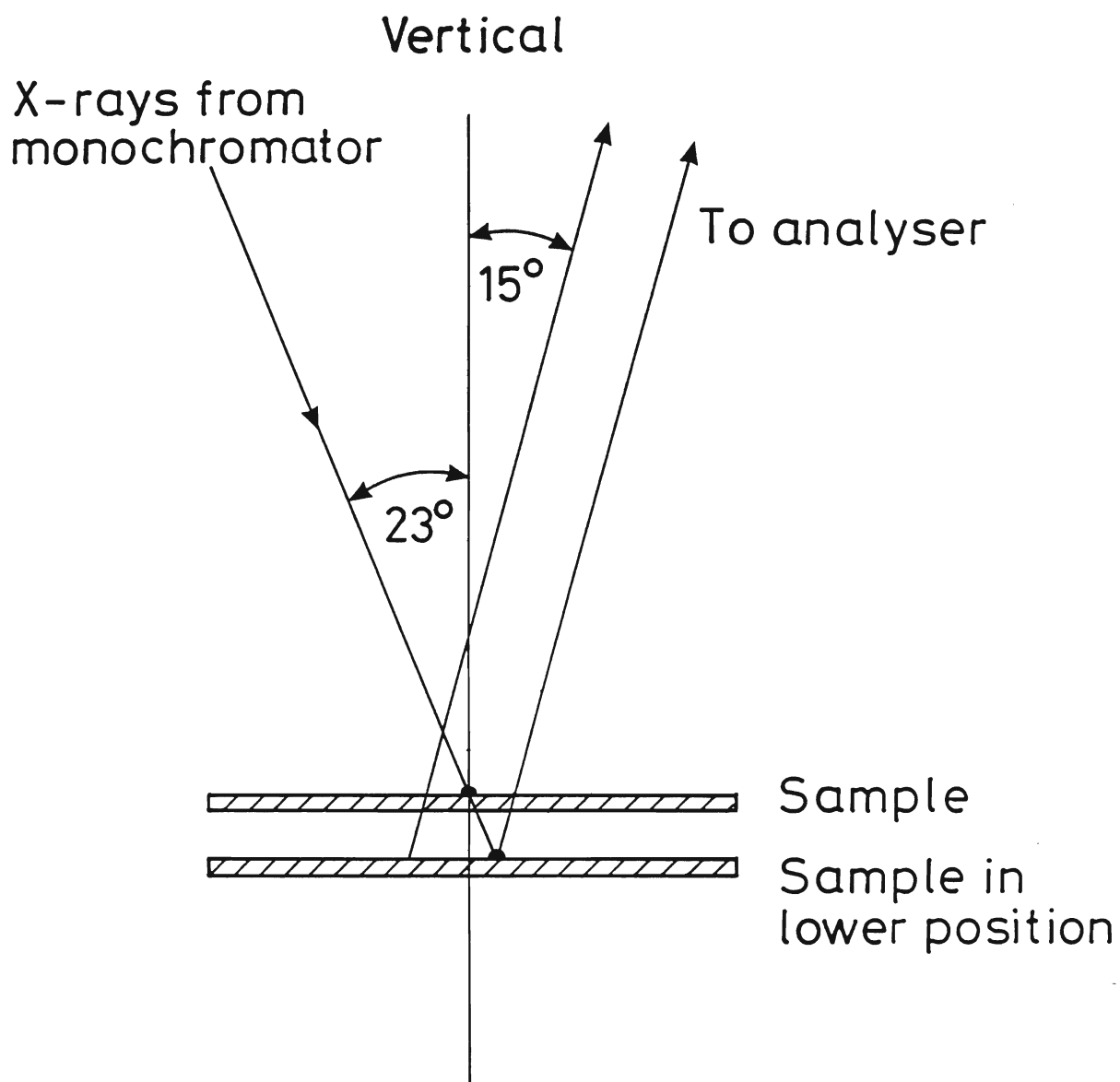


Fig 2 Geometry of the monochromator analysis.

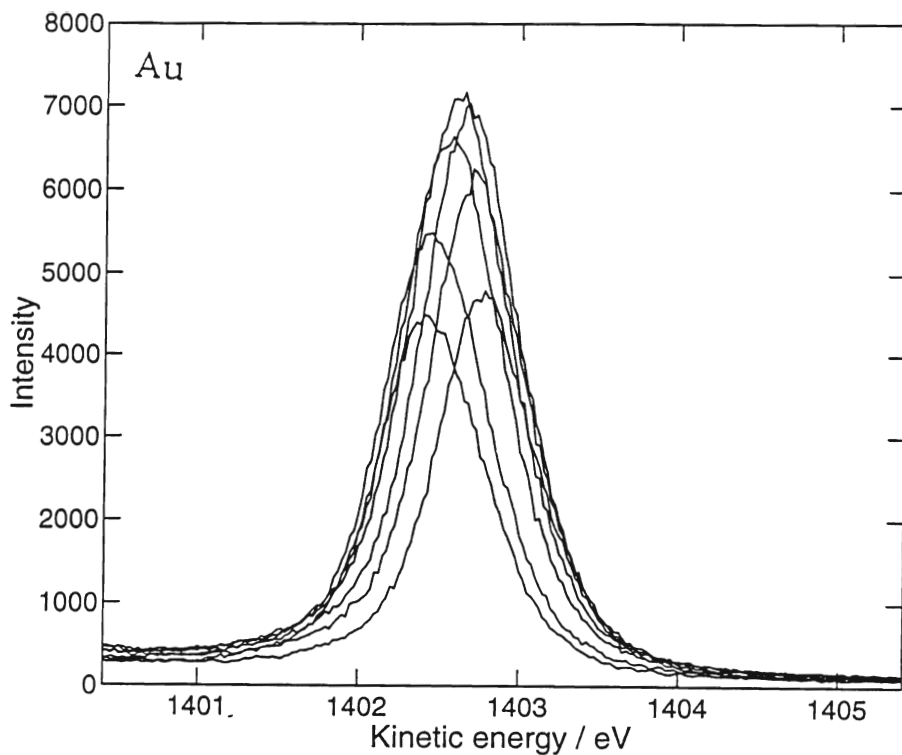


Fig 3

Measured kinetic energy for Au $4f_{7/2}$ photoelectrons using monochromated Al X-rays with 10 eV pass energy, 6 mm slits and a lens magnification of 3. The peaks are seen to shift to higher apparent kinetic energy as the sample is raised by successive 0.5 mm increments. In this study the sample is 10 mm by 10 mm aligned horizontally.

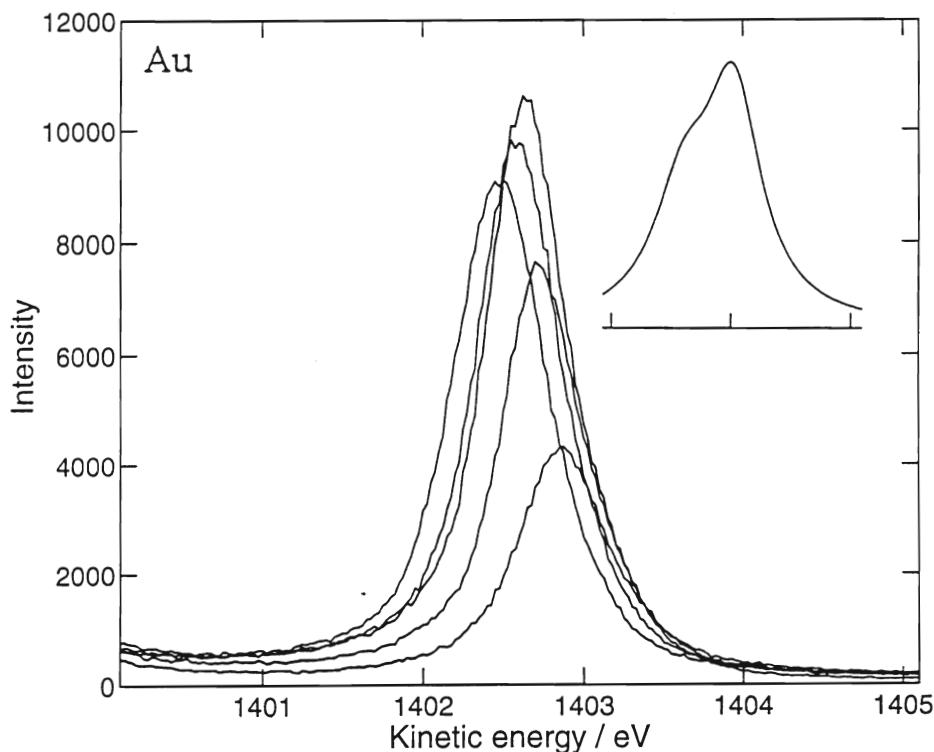


Fig 4

Measured kinetic energy for Au $4f_{7/2}$ photoelectrons using monochromated Al X-rays with 10 eV pass energy, 6 mm slits, a lens magnification of 3 and a 0.5 mm wide sample. The spectra are recorded for the X-ray anode moved by approximately 0.5 mm increments and the diffraction condition re-optimised by adjusting the crystal tilt. The diffraction angles for the peaks reading from the left are at -0.028° , -0.015° , 0° , 0.016° and 0.029° away from optimum, respectively. Inset is shown the $K\alpha_{2,3}$ line structure for $Al^{(12)}$ with 1 eV markers.

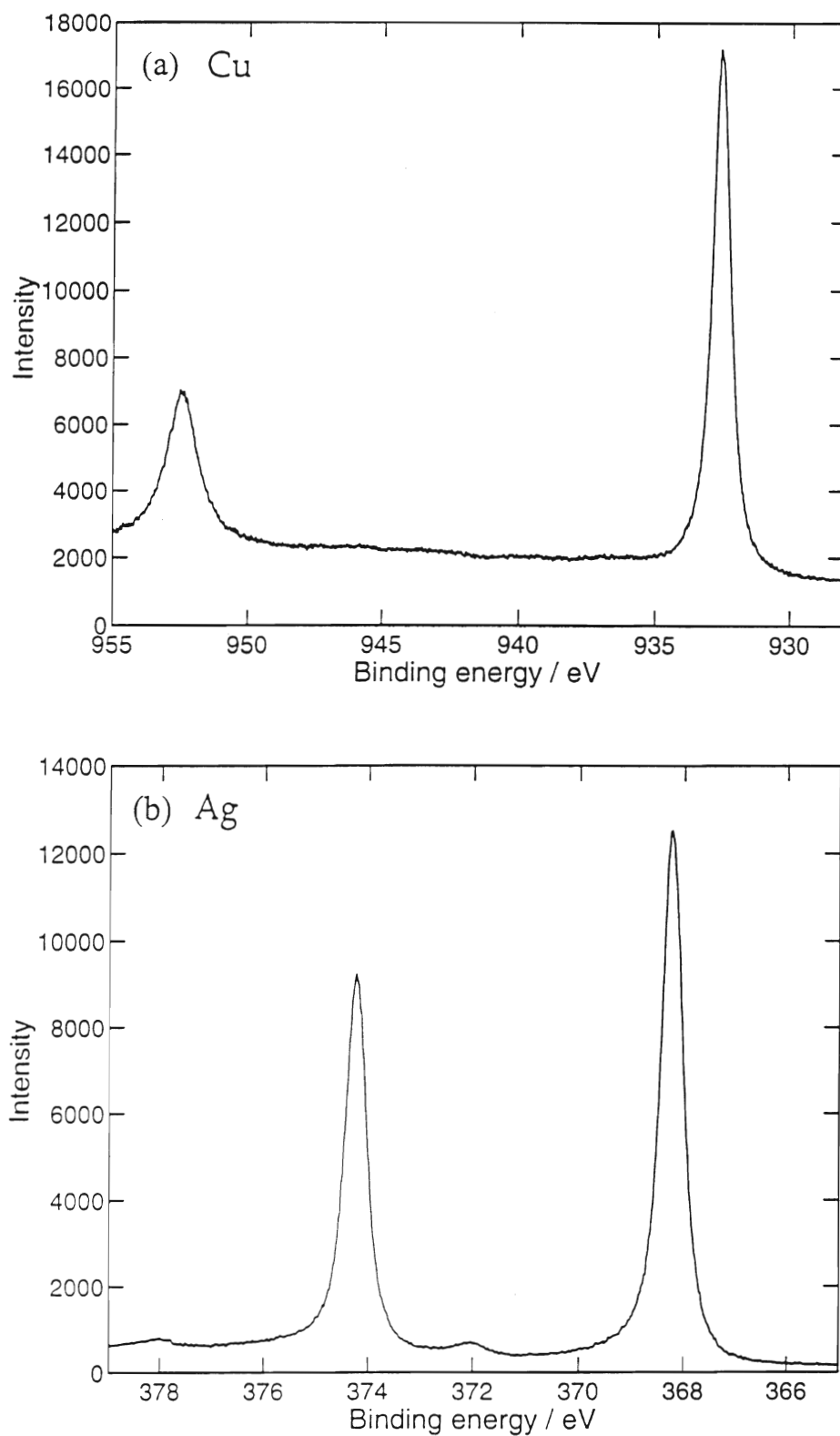


Fig 5

Details of the spectra for (a) Cu $2p_{1/2,3/2}$, (b) Ag $3d_{3/2,5/2}$ and (c) Au $4f_{5/2,7/2}$ peaks using the monochromator with zero angle of emission.

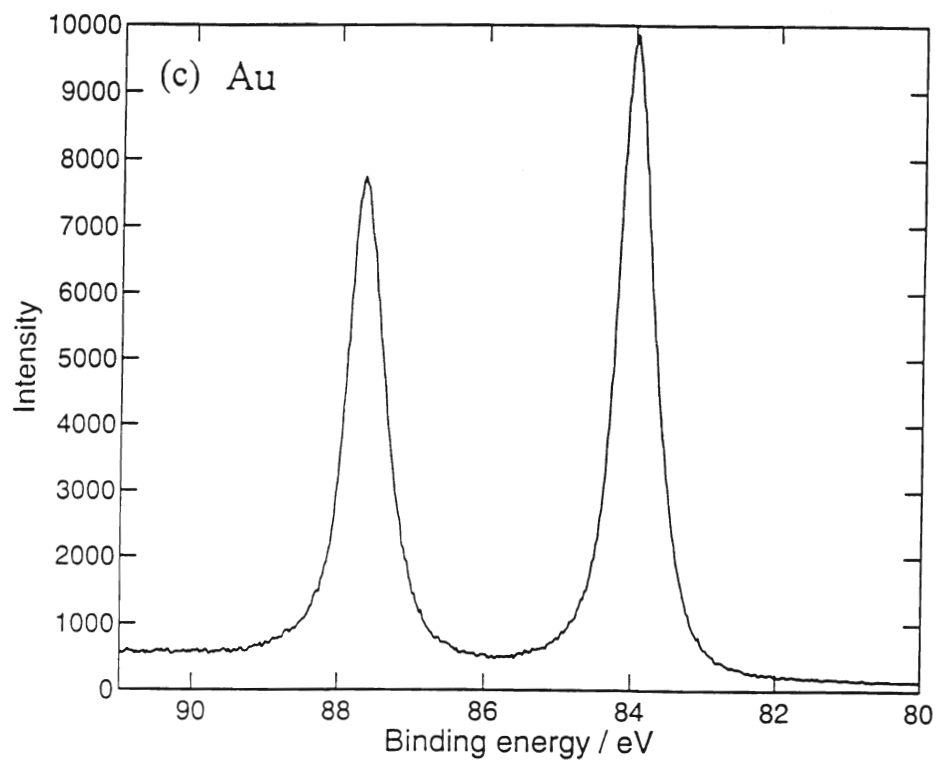


Fig 5 Details of the spectra for (a) Cu 2p_{1/2,3/2}, (b) Ag 3d_{3/2,5/2} and (c) Au 4f_{5/2,7/2} peaks using the monochromator with zero angle of emission.

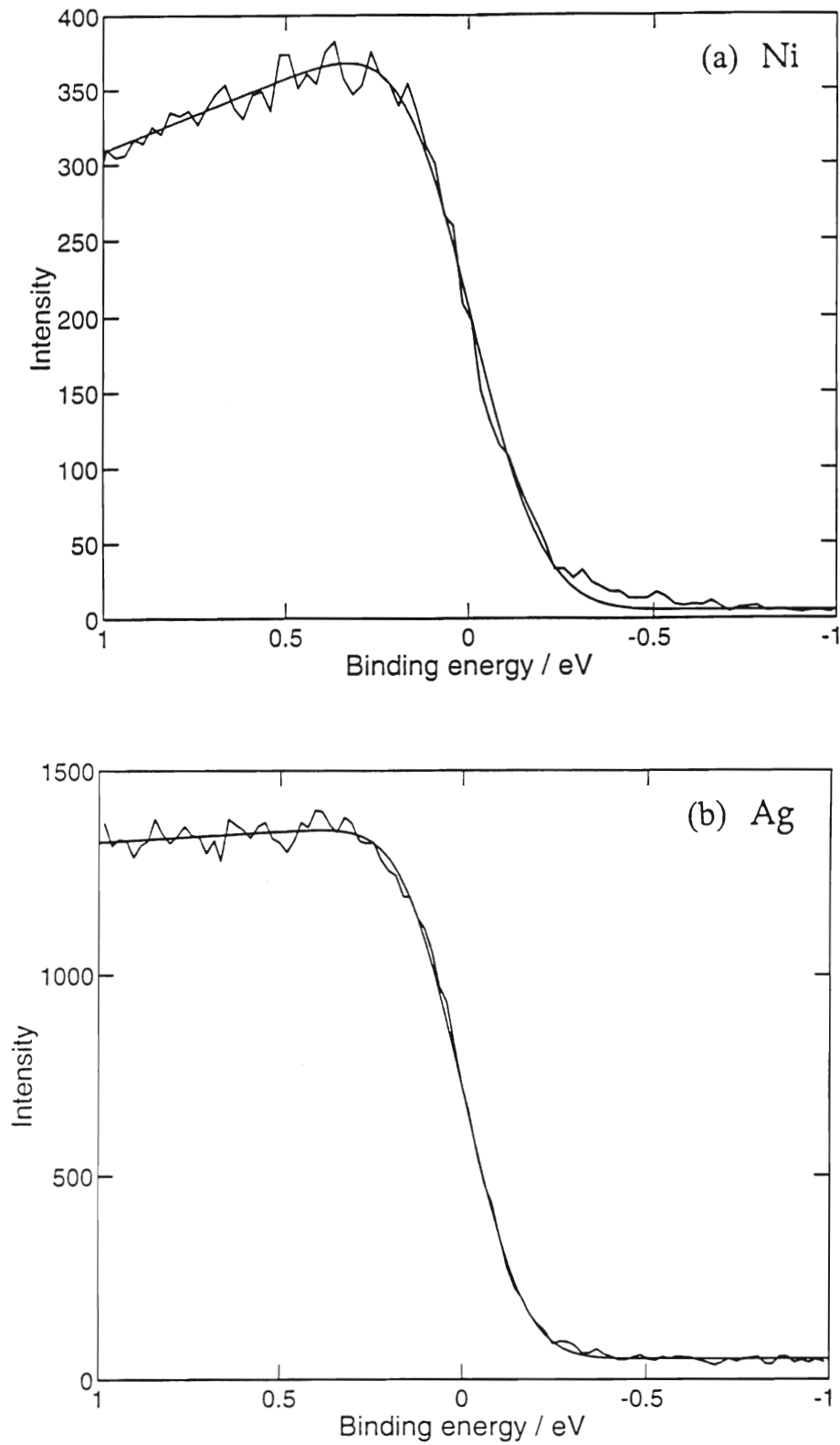


Fig 6

Details of the Fermi edge measurements for (a) Ni and (b) $\text{Ag}^{(22)}$ together with the fits of Eqs (10) and (11) showing edge resolutions of 0.36 eV and 0.31 eV, respectively. The binding energy zero is defined by the fit. The measured data extend to 15 eV binding energy.

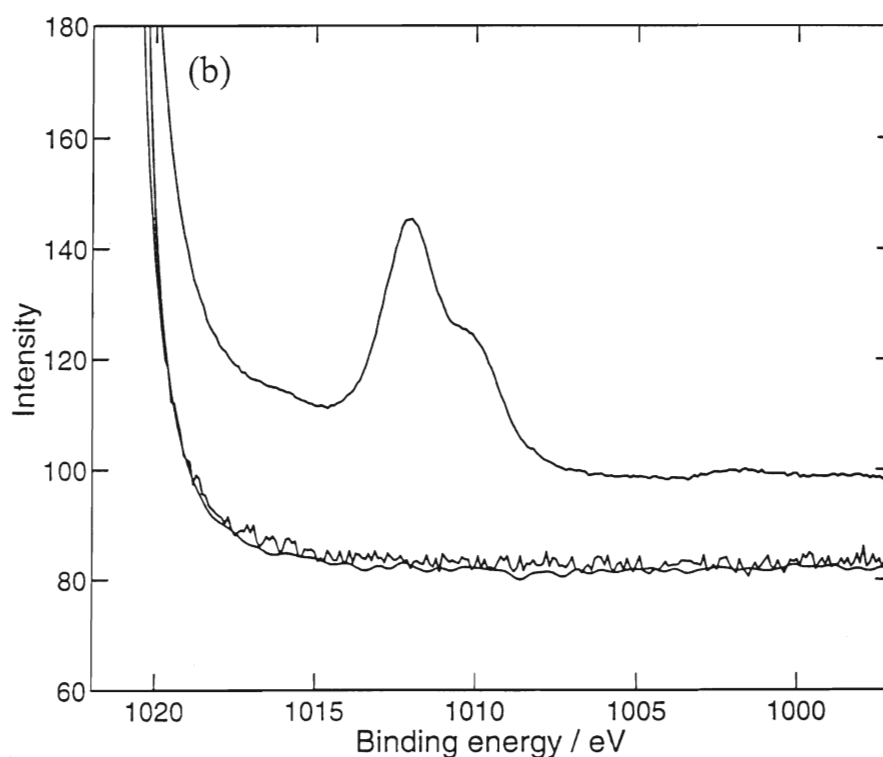
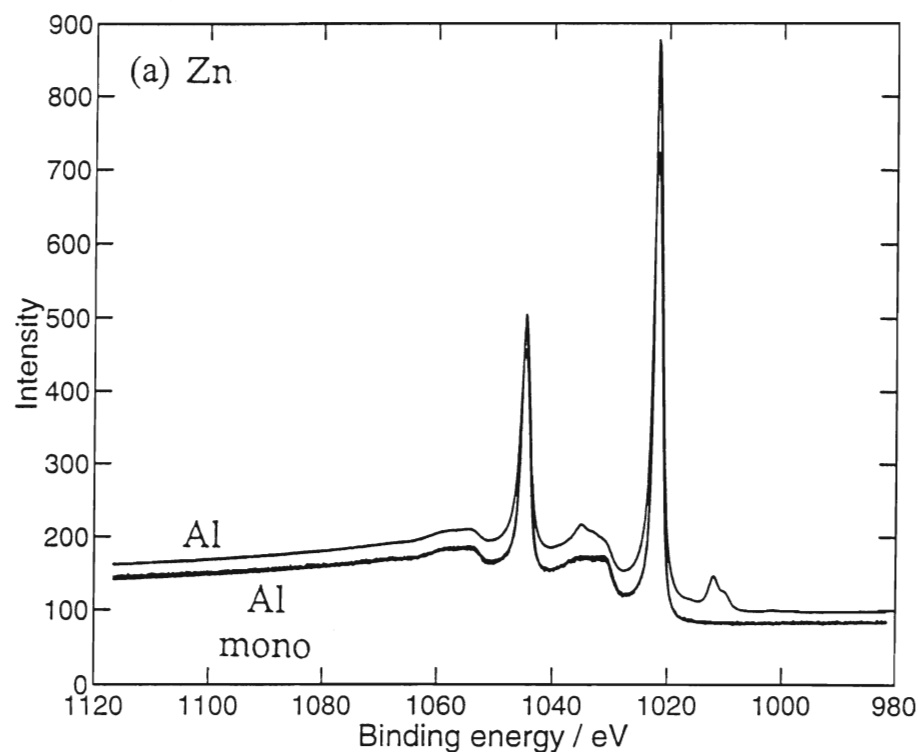


Fig 7

$2p_{3/2}$ photoelectron peak for Zn. (a) monochromated and unmonochromated spectra using Al X-rays, as recorded, as well as the unmonochromated spectrum with deconvolution of the peak and satellites. The unmonochromated spectrum is uppermost. (b) detail of (a) showing the near peak region (the monochromated spectrum shows greater noise than the deconvoluted unmonochromated spectrum). (c) monochromated spectrum using Al X-rays and its convolute with the Al and Mg X-ray peak structures to simulate unmonochromated spectra, overlaid on the experimental unmonochromated spectra. The Mg spectra are uppermost and the unmonochromated Al data are lowest, except at the peak where the order is reversed.

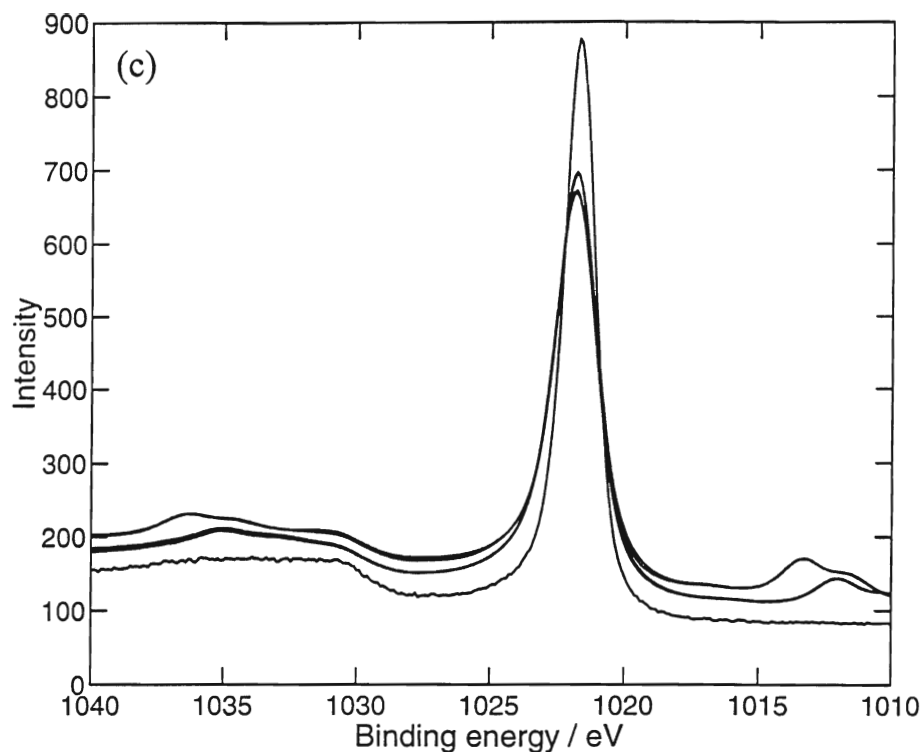


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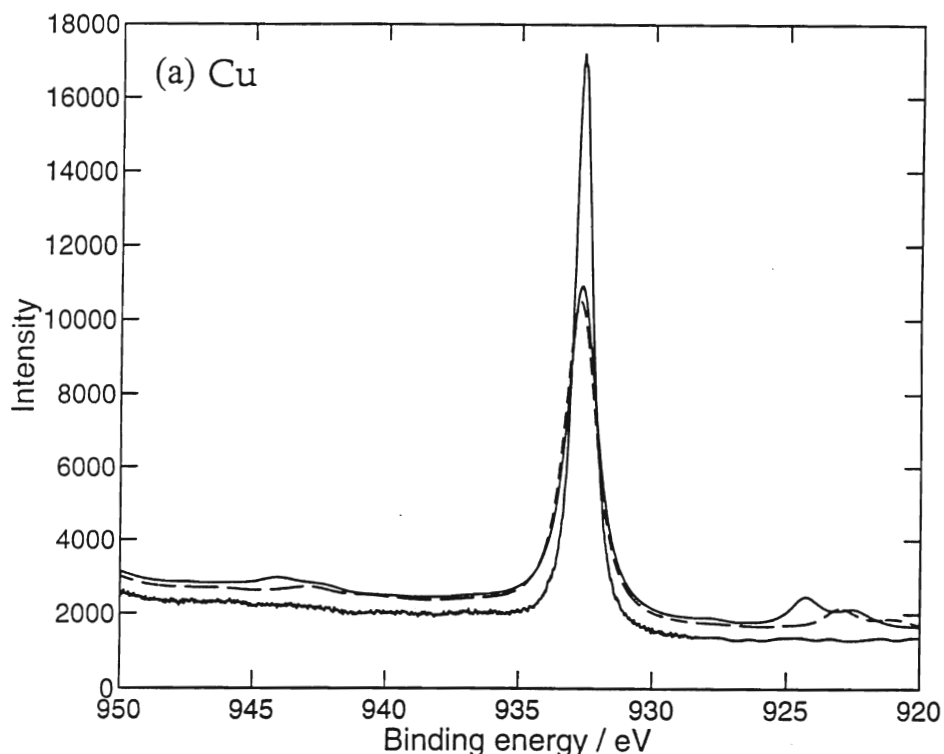


Fig 8

Details of the spectra for (a) Cu $2p_{3/2}$, (b) Ag $3d_{3/2,5/2}$ and (c) Au $4f_{5/2,7/2}$ as in Fig 5 together with the convolutions for the unmonochromated Mg and Al X-ray sources. The latter is the dashed spectrum with the satellites displaced farthest from the peaks towards low binding energies.

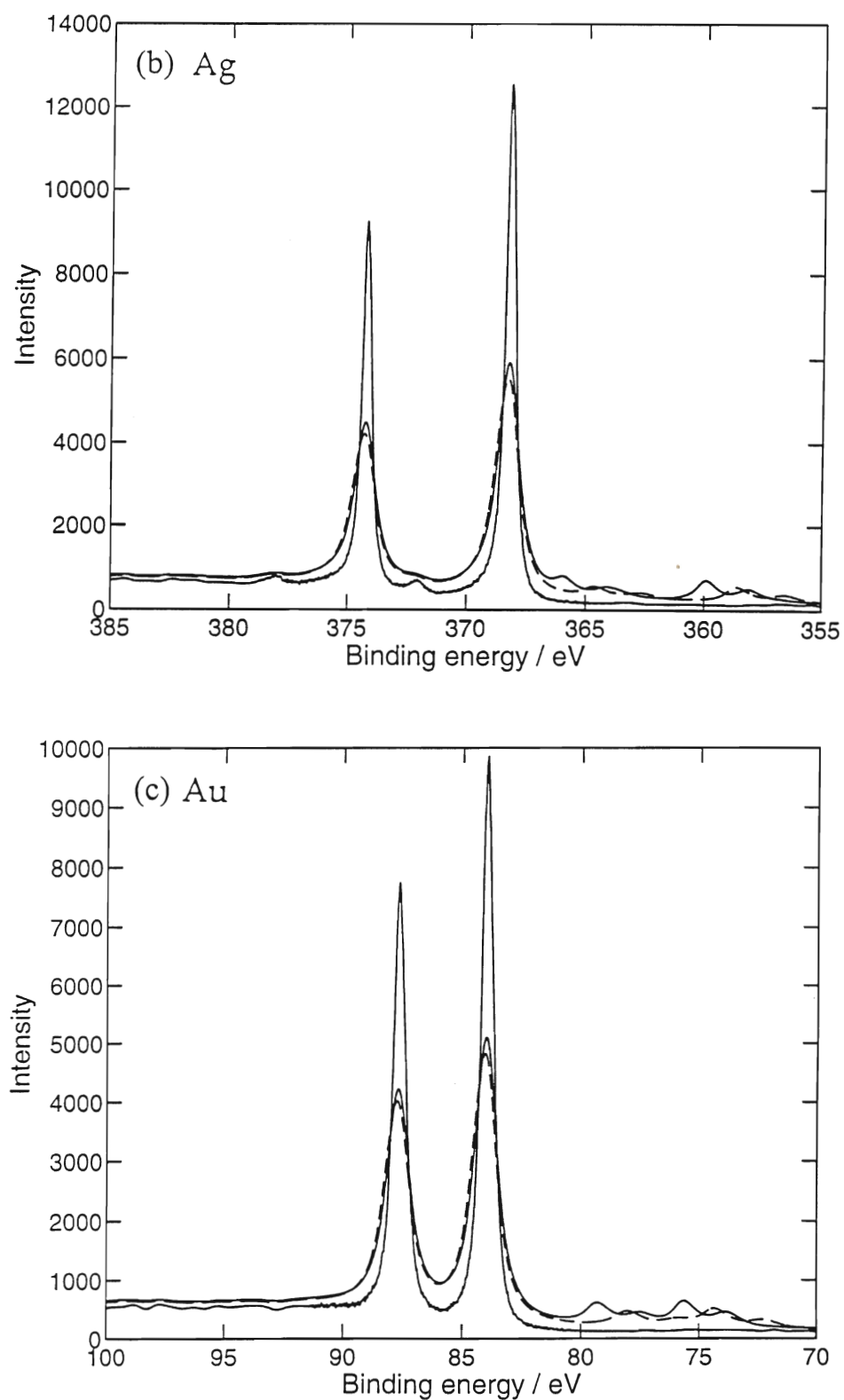


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Details of the spectra for (a) $\text{Cu } 2p_{3/2}$, (b) $\text{Ag } 3d_{3/2,5/2}$ and (c) $\text{Au } 4f_{5/2,7/2}$ as in Fig 5 together with the convolutions for the unmonochromated Mg and Al X-ray sources. The latter is the dashed spectrum with the satellites displaced farthest from the peaks towards low binding energies.

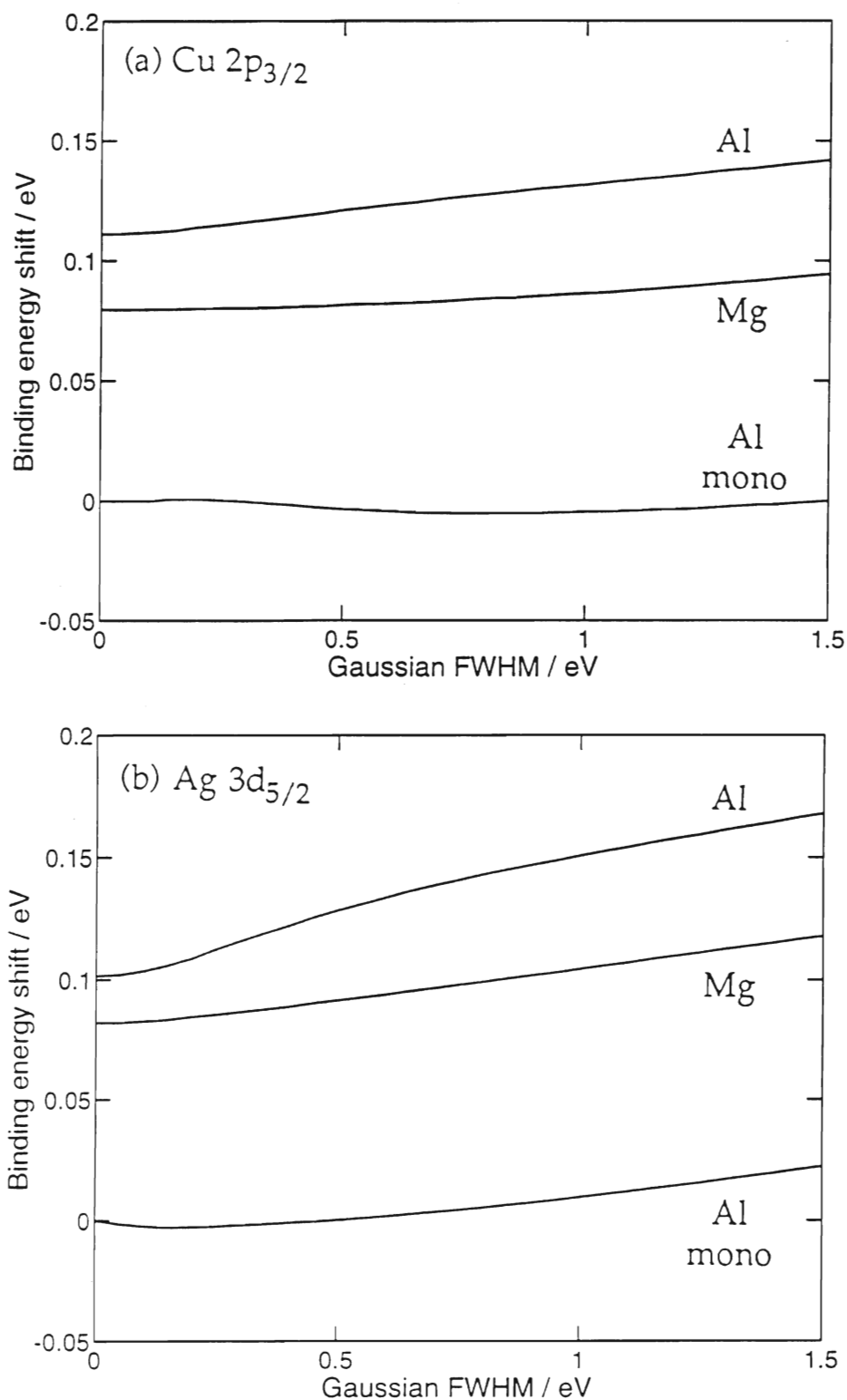


Fig 9

Relative binding energies derived from the peak energies as a function of spectrometer resolution for the three X-ray sources, (a) Cu $2p_{3/2}$, (b) Ag $3d_{5/2}$ and (c) Au $4f_{7/2}$. The ordinate is given as binding energy shifts from the high resolution energy using monochromated X-rays aligned with the $K\alpha_1$ energy. The resolution is assumed to be determined by a Gaussian lineshape. In practice this is only an approximate description of the behaviour and the plot may involve increasing error as the resolution degrades.

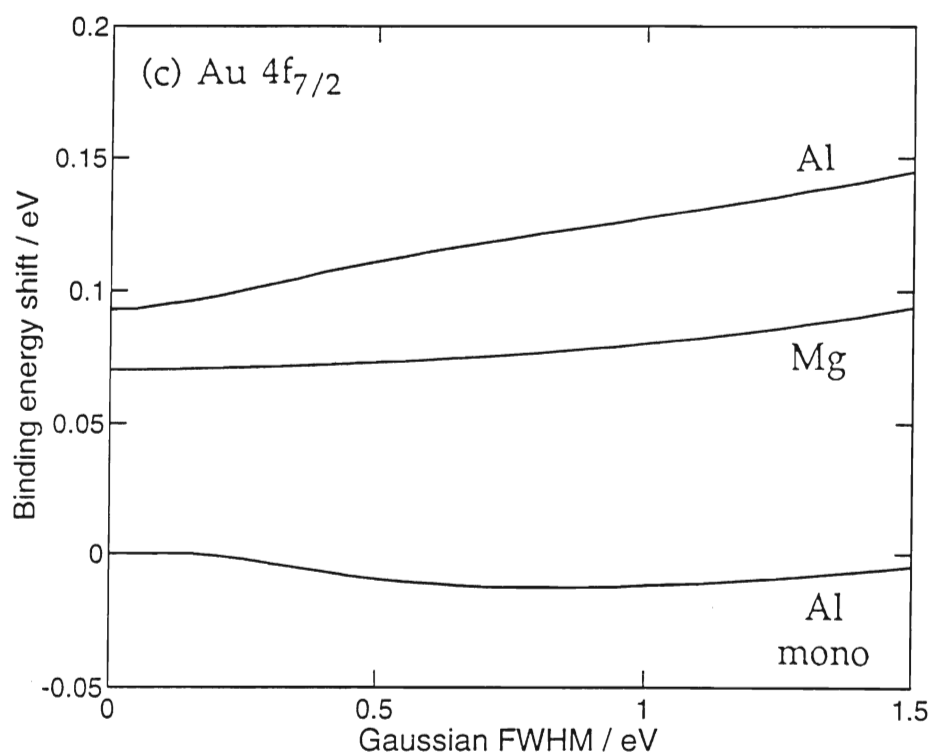


Fig 9 Relative binding energies derived from the peak energies as a function of spectrometer resolution for the three X-ray sources, (a) Cu 2p_{3/2}, (b) Ag 3d_{5/2} and (c) Au 4f_{7/2}. The ordinate is given as binding energy shifts from the high resolution energy using monochromated X-rays aligned with the K α ₁ energy. The resolution is assumed to be determined by a Gaussian lineshape. In practice this is only an approximate description of the behaviour and the plot may involve increasing error as the resolution degrades.

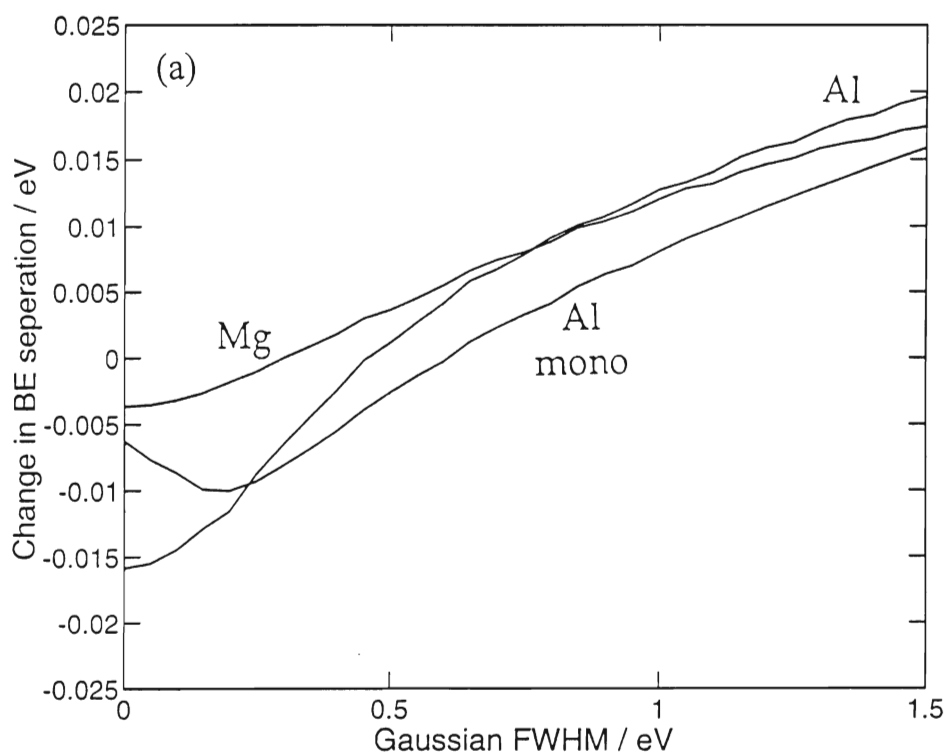


Fig 10 Change in the binding energy separations as a function of the spectrometer resolution for the three X-ray sources, (a) Ag 3d_{5/2} minus Cu 2p_{3/2}, (b) Au 4f_{7/2} minus Cu 2p_{3/2} and (c) Ag 3d_{5/2} minus Au 4f_{7/2} from the data of Fig 5. Note the scale expansion of 5 times compared with Fig 9. The positions are given as binding energy shifts from the Mg X-ray value at a resolution of 0.3 eV.

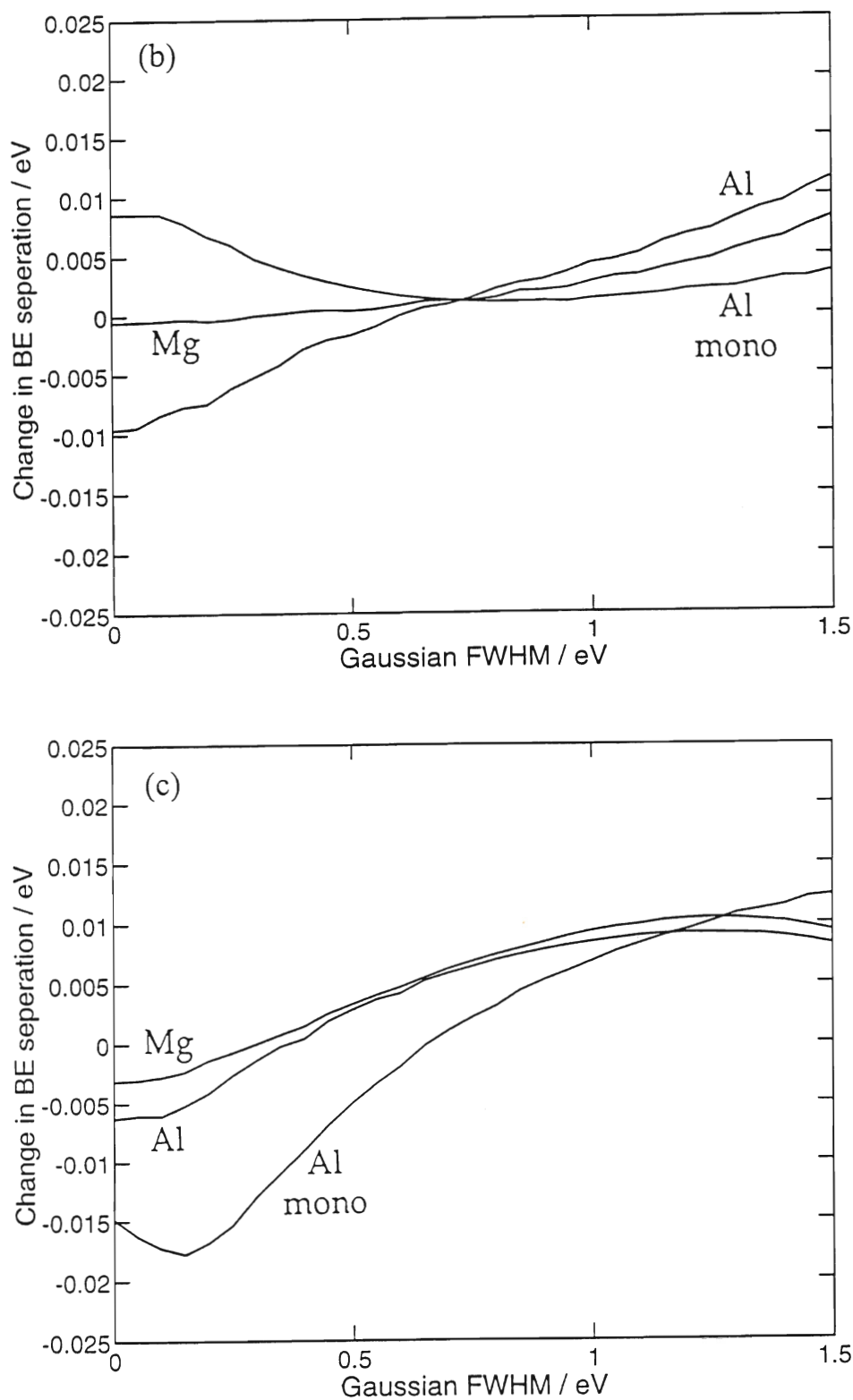


Fig 10

Change in the binding energy separations as a function of the spectrometer resolution for the three X-ray sources, (a) Ag $3d_{5/2}$ minus Cu $2p_{3/2}$, (b) Au $4f_{7/2}$ minus Cu $2p_{3/2}$ and (c) Ag $3d_{5/2}$ minus Au $4f_{7/2}$ from the data of Fig 5. Note the scale expansion of 5 times compared with Fig 9. The positions are given as binding energy shifts from the Mg X-ray value at a resolution of 0.3 eV.

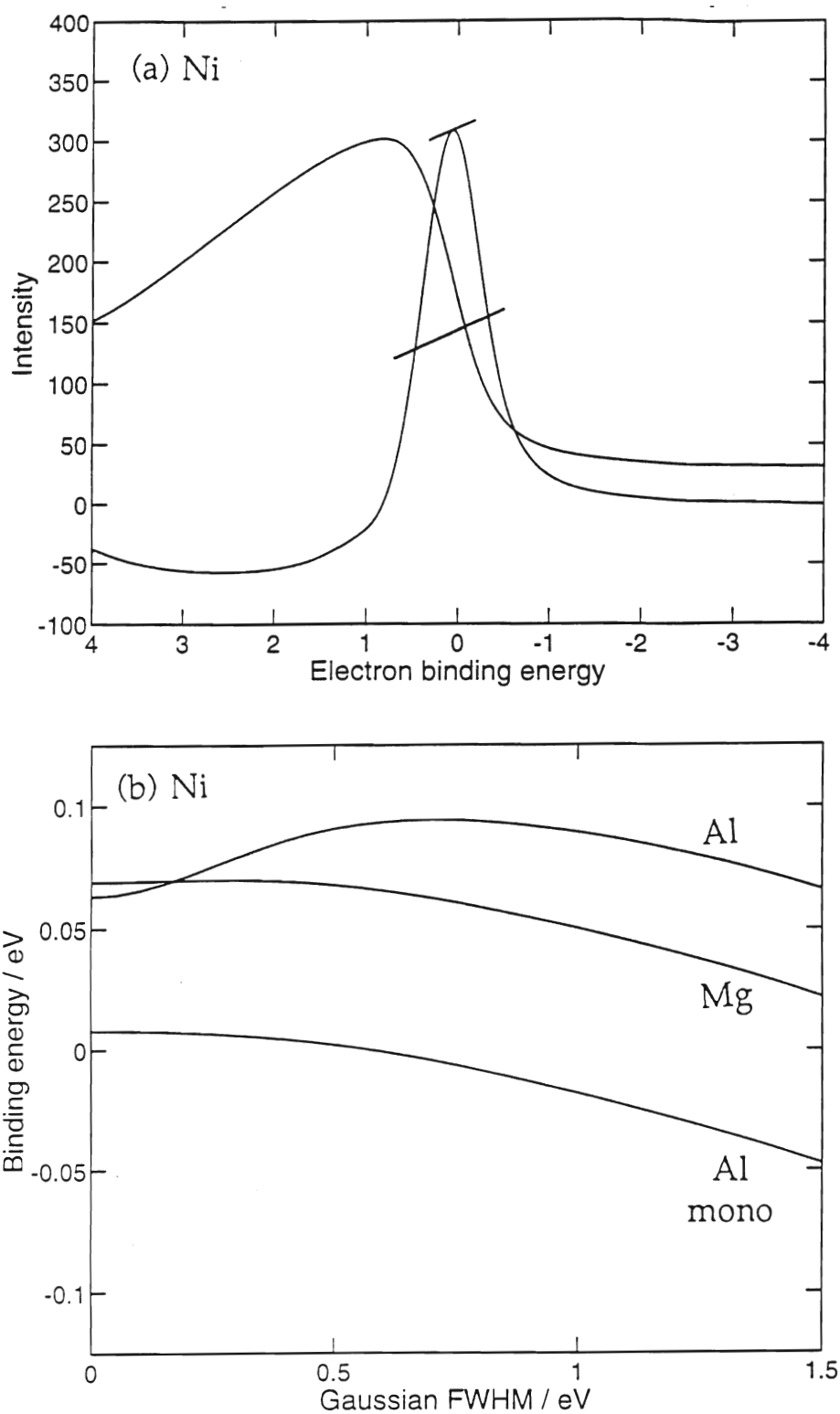


Fig 11

Fermi edge data as a function of the spectrometer energy resolution, (a) the Ni Fermi edge from Fig 6(a) convolved with the Mg $K\alpha$ X-ray structure and its differential with the tangent construction to define the differential peak energy, (b) the differential peak energy for Ni for the three X-ray sources, (c) the differential peak energy for Ag for monochromated Al X-rays, (d) the differential peak energy for a step function. Note that the ordinate here is referenced to the zeros of Eqs (10) and (11) which are not the same⁽¹⁵⁾.

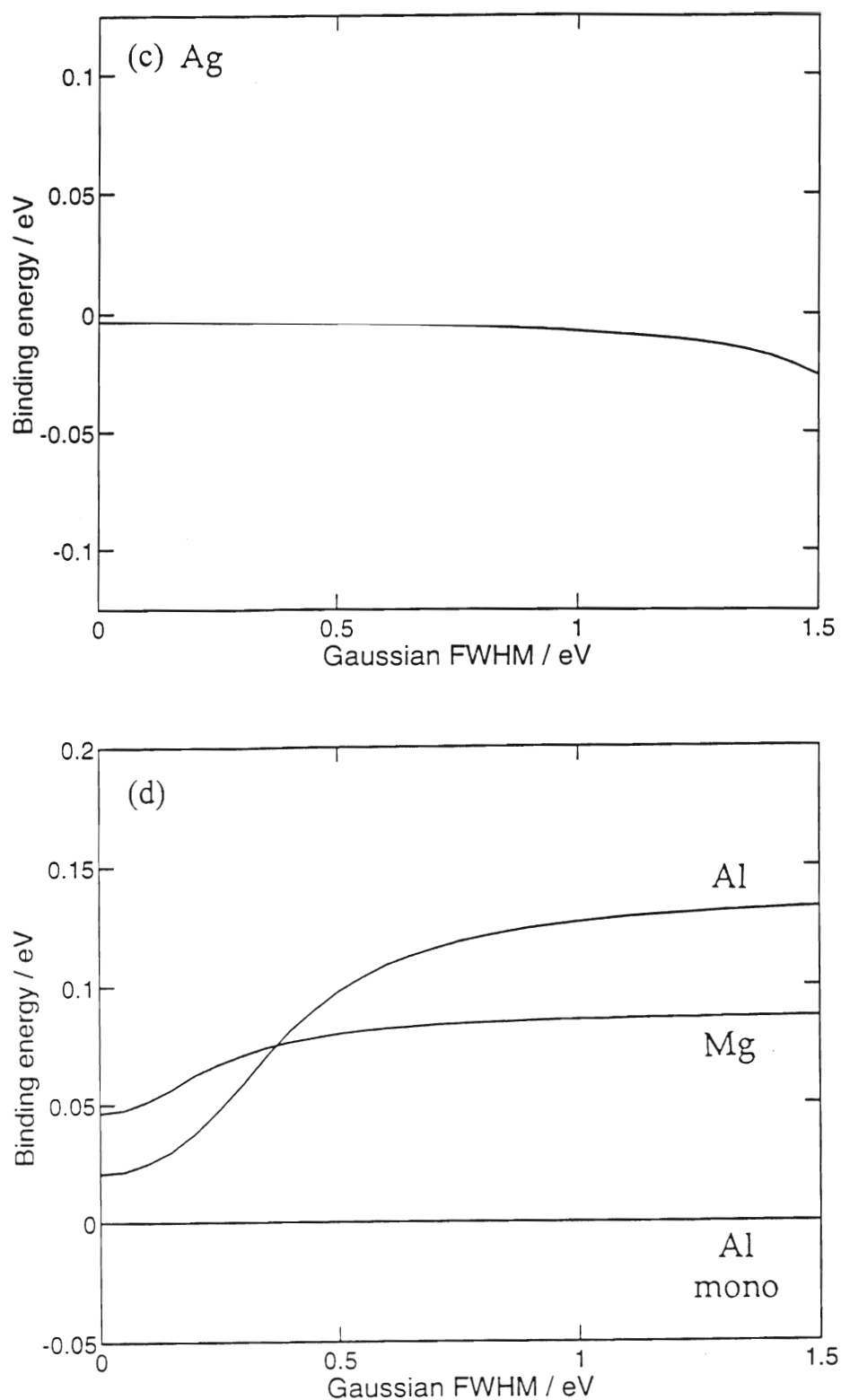


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Fermi edge data as a function of the spectrometer energy resolution, (a) the Ni Fermi edge from Fig 6(a) convoluted with the Mg K α X-ray structure and its differential with the tangent construction to define the differential peak energy, (b) the differential peak energy for Ni for the three X-ray sources, (c) the differential peak energy for Ag for monochromated Al X-rays, (d) the differential peak energy for a step function. Note that the ordinate here is referenced to the zero of Eqs (10) and (11).

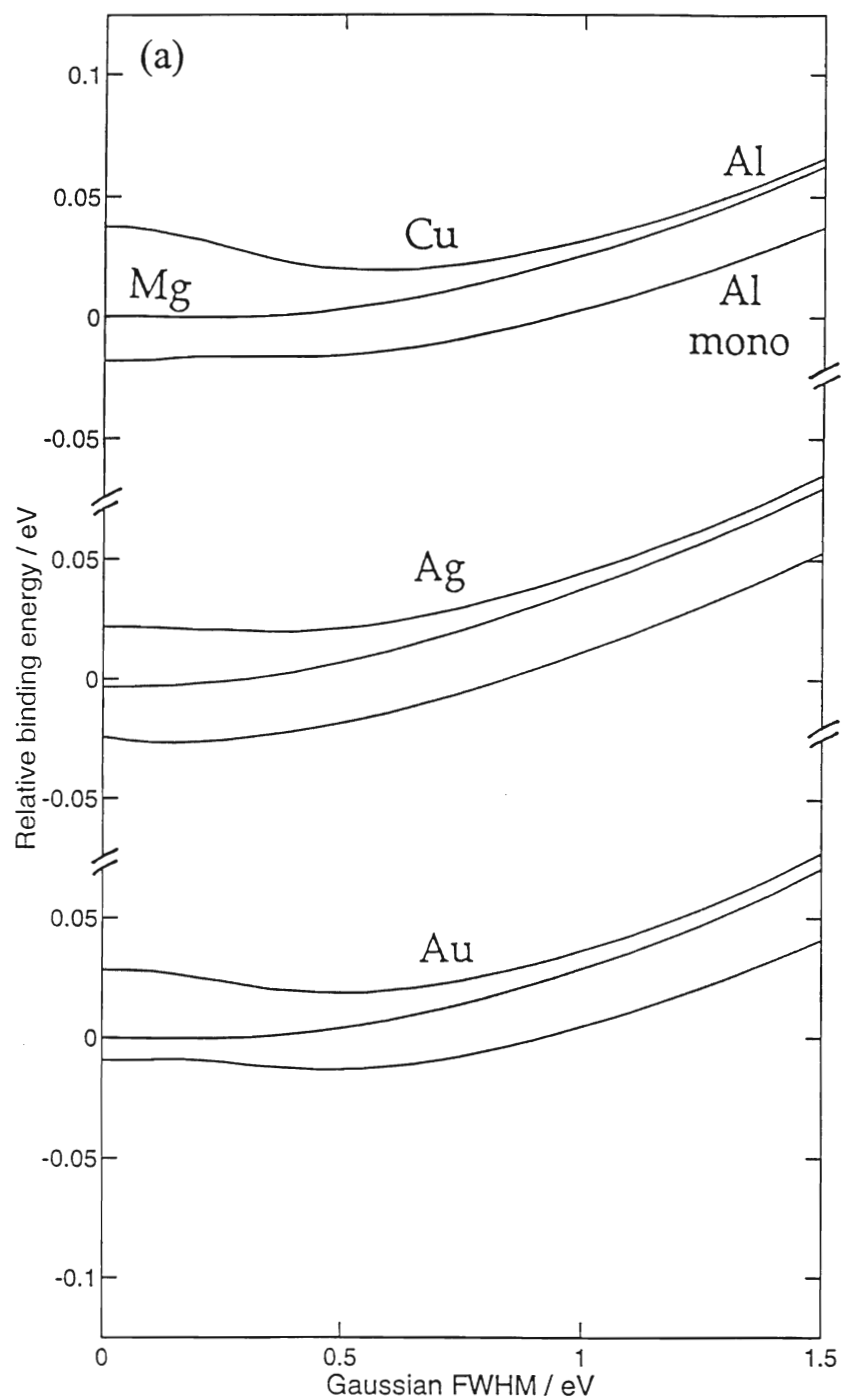


Fig 12

Cu, Ag and Au binding energies referred to the measured Fermi edge peak energy at that resolution, as a function of the spectrometer resolution for the three peaks. (a) Ni with three X-ray sources, the unmonochromated Al is always uppermost, followed by unmonochromated Mg and finally monochromated Al as shown for Cu, (b) Ag with monochromated Al X-rays. In (a) the ordinate is set to zero for the Mg data at 0.3 eV resolution.

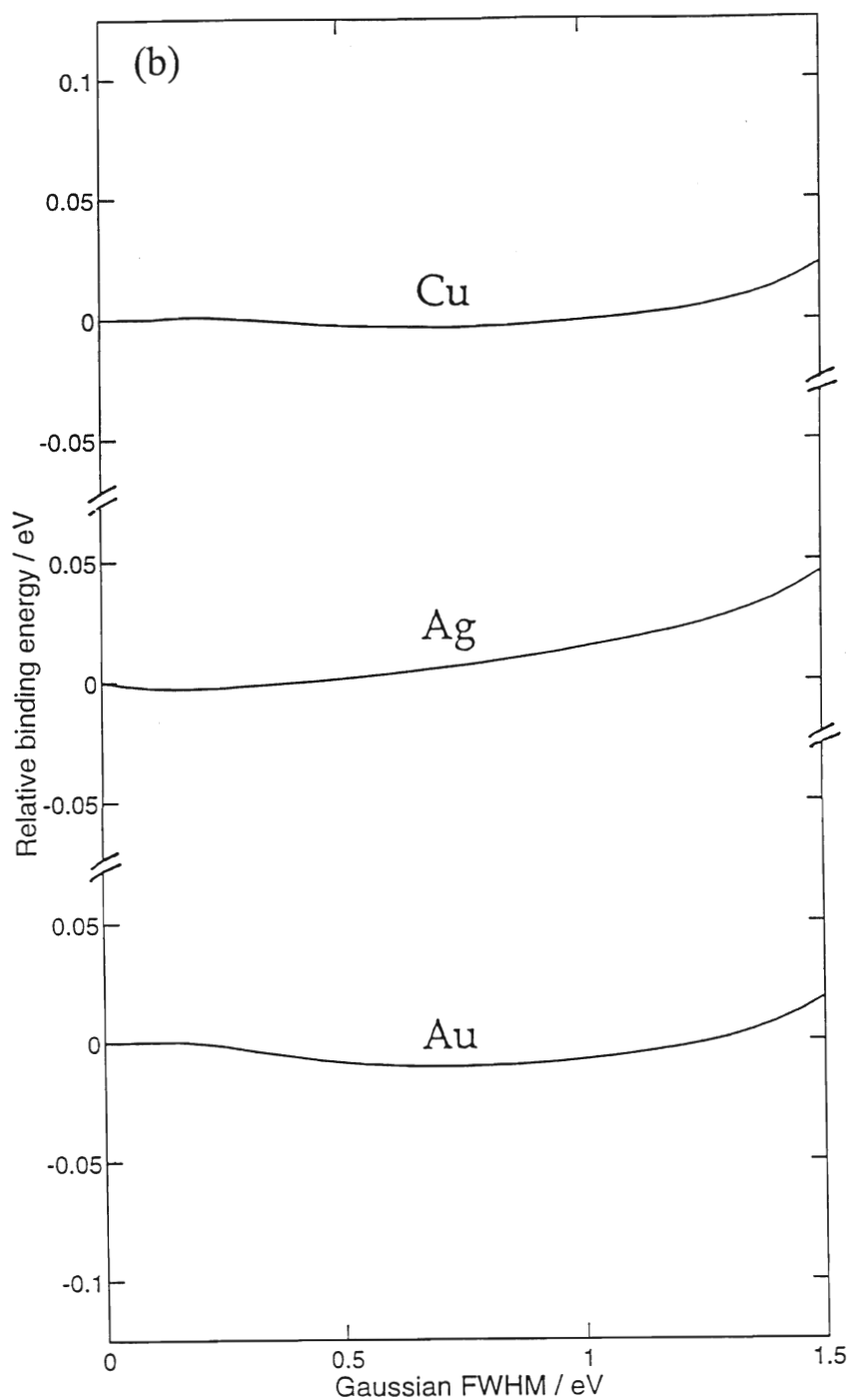


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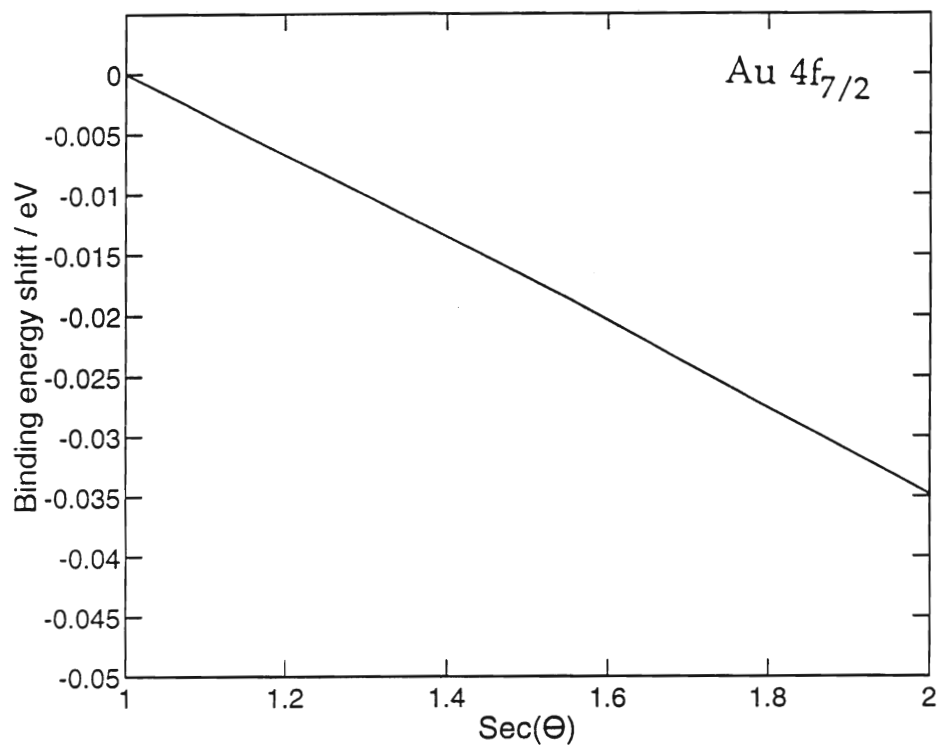


Fig 13

An example of the calculated angular dependence of the binding energy shift of the Au $4f_{7/2}$ peak at 0.3 eV resolution, using Mg X-rays. This shows the near linear dependence on $\sec\theta$. These calculations are valid for Citrin et al's data and diverge from linearity by less than 1 meV.

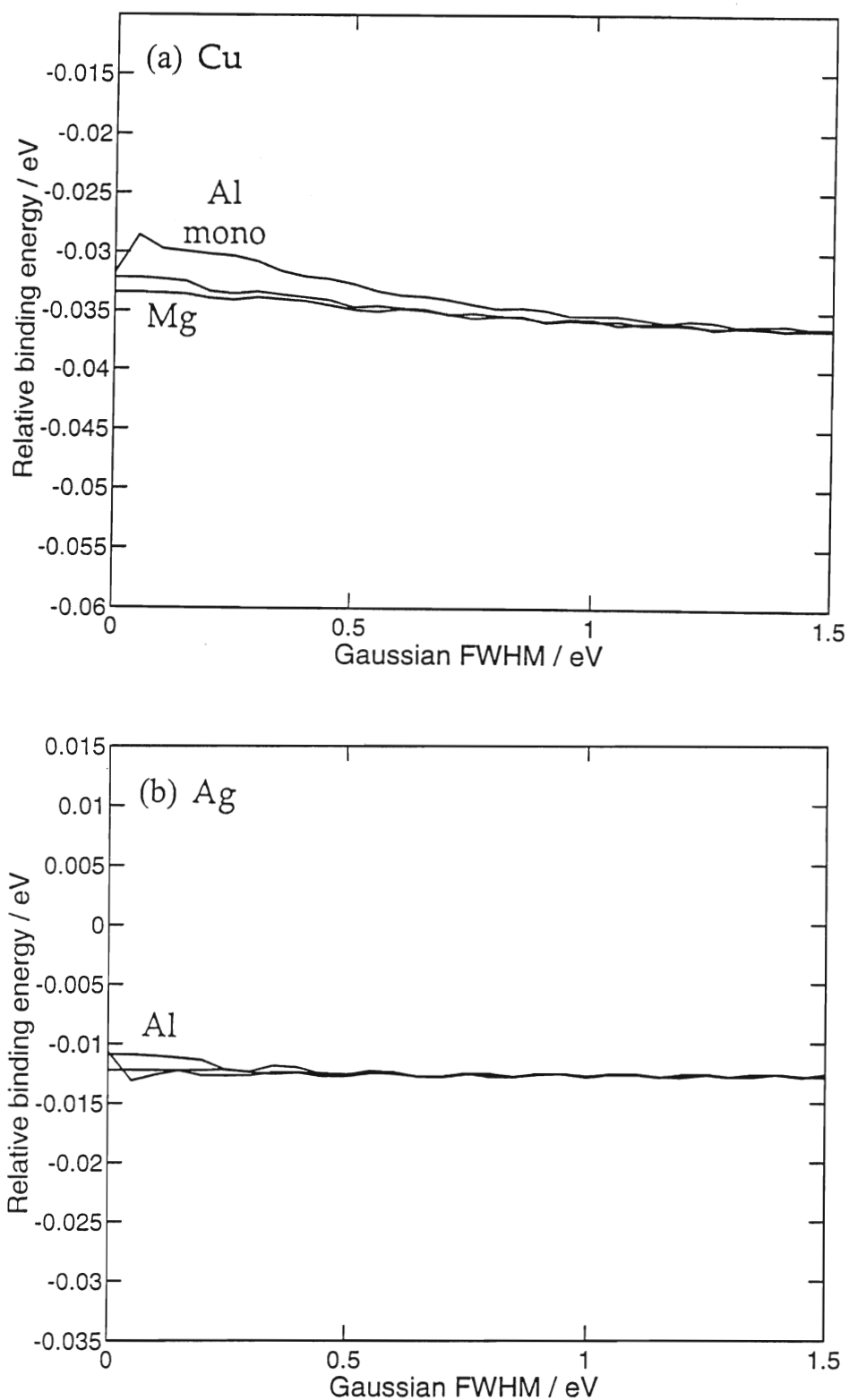


Fig 14

The predicted peak binding energy shifts to simulate Citrin et al's data for evaporated films for an angular change between 0° and 60° for all X-ray sources for (a) Cu $2p_{3/2}$, (b) Ag $3d_{5/2}$ and (c) Au $4f_{7/2}$. These use the data at 0° from Fig 5 as well as that data shifted as shown in Table 2, scaled using Eq (1) and then added to the original data to form a new spectrum appropriate to 60° .

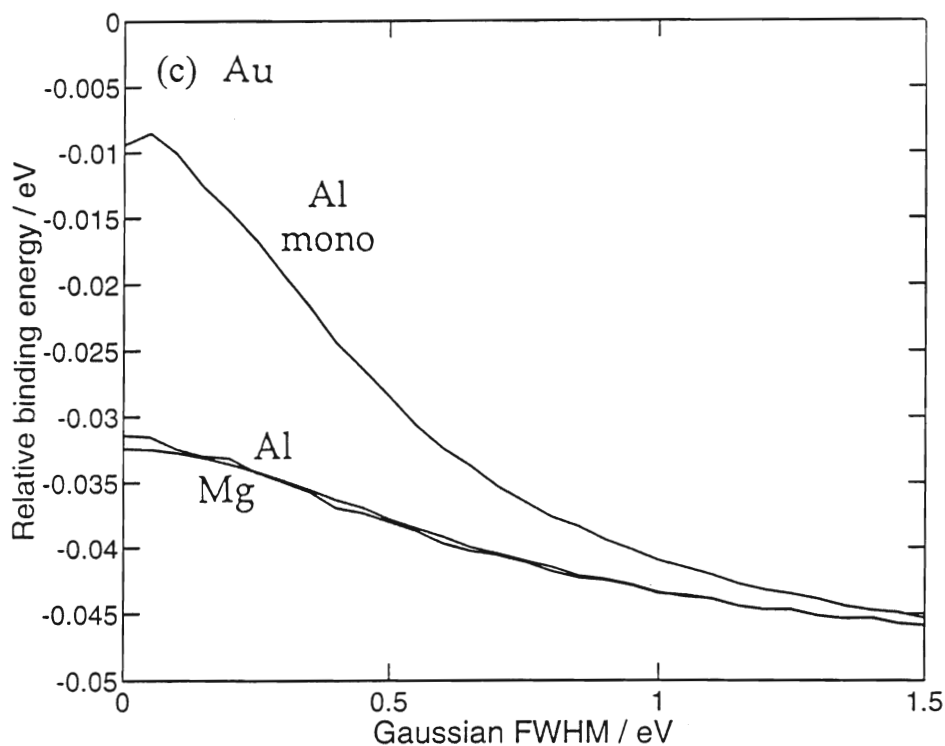


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The predicted peak binding energy shifts to simulate Citrin et al's data for evaporated films for an angular change between 0° and 60° for all X-ray sources for (a) Cu $2p_{3/2}$, (b) Ag $3d_{5/2}$ and (c) Au $4f_{7/2}$. These use the data at 0° from Fig 5 as well as that data shifted as shown in Table 2, scaled using Eq (1) and then added to the original data to form a new spectrum appropriate to 60° .

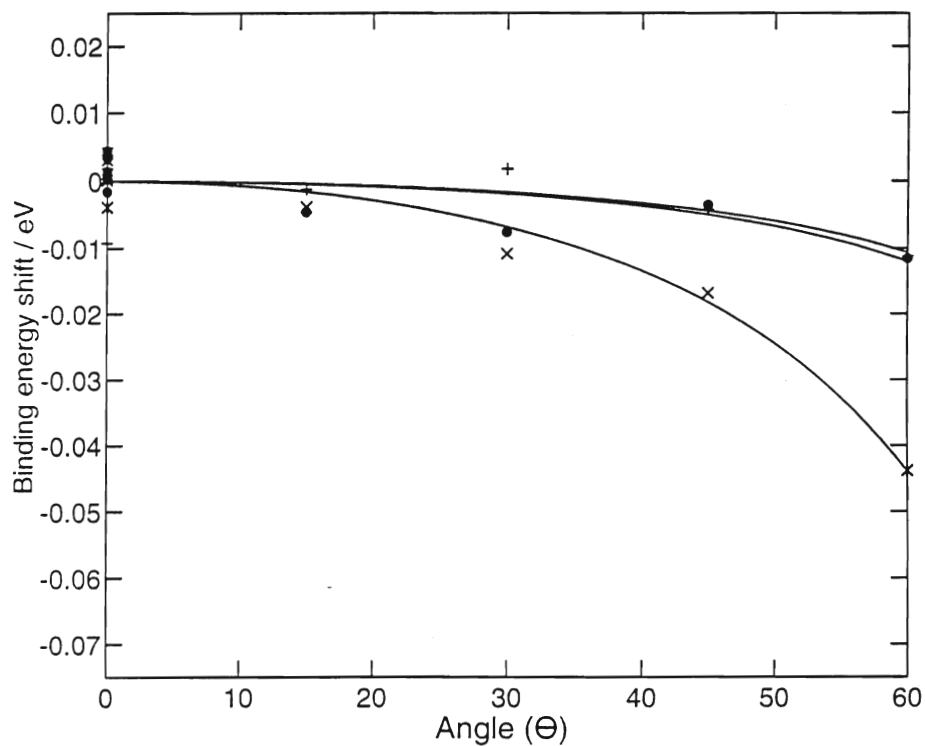


Fig 15

The measured peak position variation using 5 eV pass energy as a function of the angle of emission for unmonochromated Mg X-rays for Cu $2p_{3/2}$ (●), Ag $3d_{5/2}$ (+) and Au $4f_{7/2}$ (x).

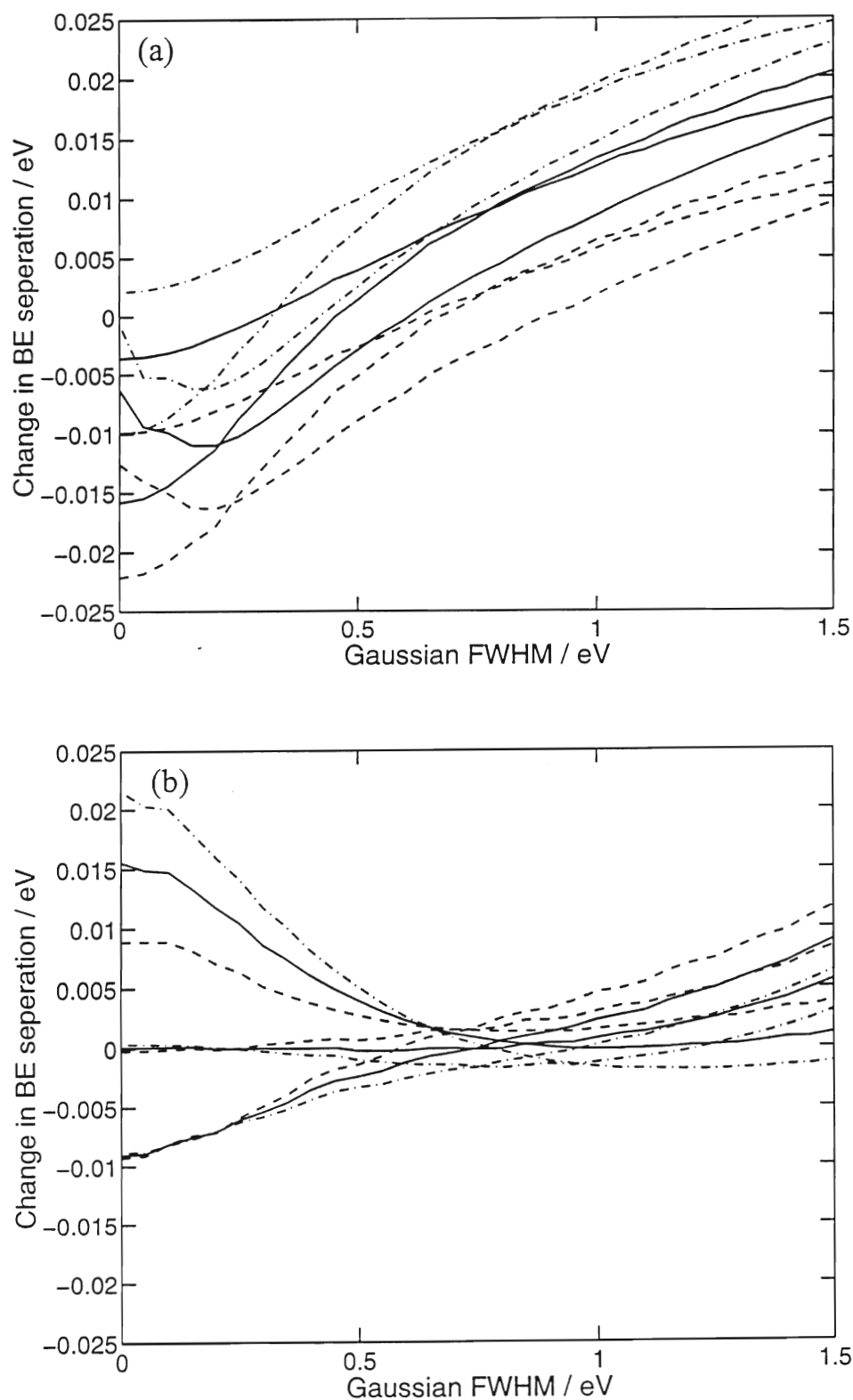


Fig 16

Data as in Fig 10 but for 0° (---), 45° (—) and 56° (- · - · -) emission angles. The data are for the change in the binding energy separations as a function of the spectrometer resolution for the three X-ray sources, (a) Ag $3d_{5/2}$ minus Cu $2p_{3/2}$, (b) Au $4f_{7/2}$ minus Cu $2p_{3/2}$ and (c) Ag $3d_{5/2}$ minus Au $4f_{7/2}$. The ordinate is the binding energy shift from the Mg X-ray value at a resolution of 0.3 eV for an emission angle of 45° (the data in Fig 10 are for 0° only and are referenced to the Mg X-ray value at 0.3 eV in those data). The X-ray source may be identified from Fig 10.

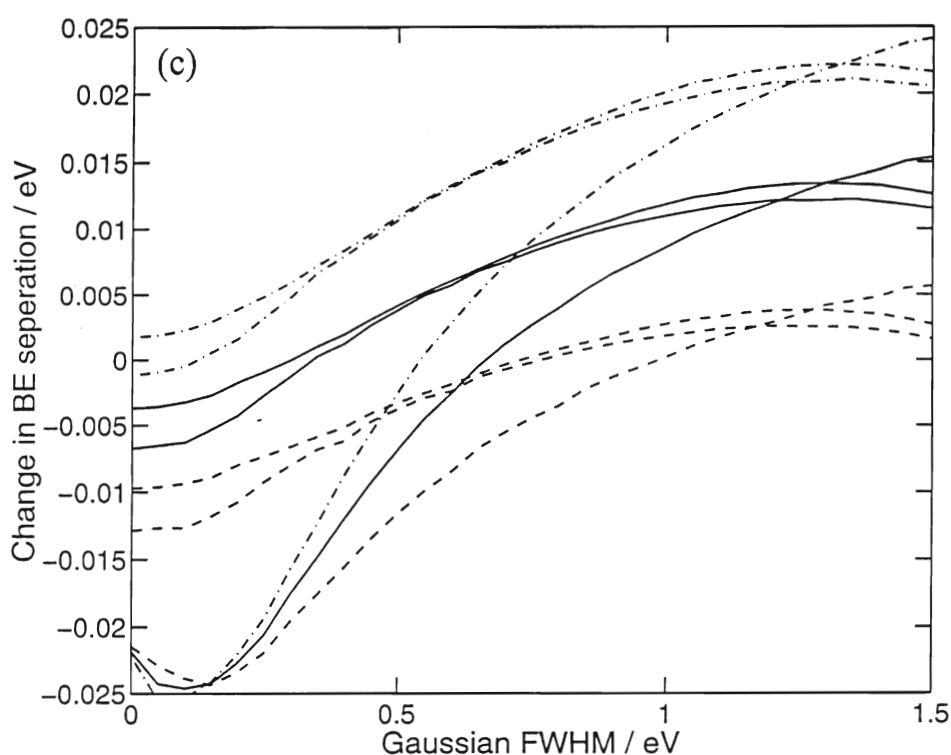


Fig 16

Data as in Fig 10 but for 0° (---), 45° (—) and 56° (- · - · -) emission angles. The data are for the change in the binding energy separations as a function of the spectrometer resolution for the three X-ray sources, (a) Ag $3d_{5/2}$ minus Cu $2p_{3/2}$, (b) Au $4f_{7/2}$ minus Cu $2p_{3/2}$ and (c) Ag $3d_{5/2}$ minus Au $4f_{7/2}$. The ordinate is the binding energy shift from the Mg X-ray value at a resolution of 0.3 eV for an emission angle of 45° (the data in Fig 10 are for 0° only and are referenced to the Mg X-ray value at 0.3 eV in those data). The X-ray source may be identified from Fig 10.

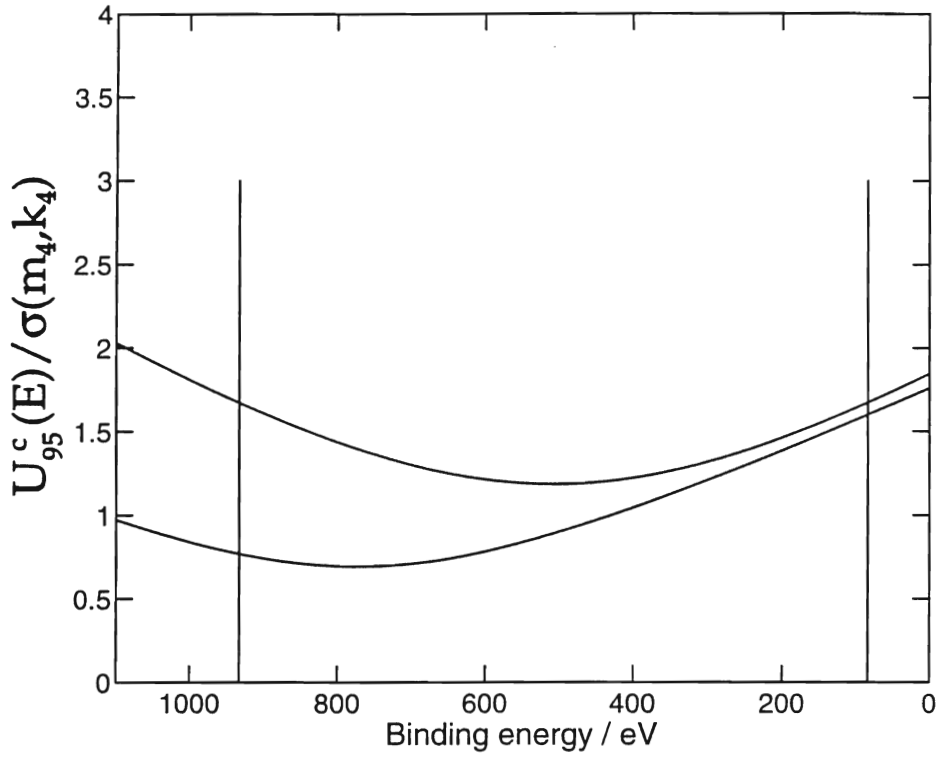


Fig 17

The uncertainty at 95% confidence from Eq (33) for the case where calibrations have been made at E_1 and E_4 and the energy scale is known to be linear. The upper curve shows the uncertainty given by $U_{95}^c(E)/\sigma(m_4, k_4)$ for case 1 of section 4 with $m_1 = m_4 = 2$ and $k_4 = 7$ whereas the lower curve is for case 3 where k_4 can be added to m_4 . The vertical lines show the energies E_{ref1} and E_{ref4} .

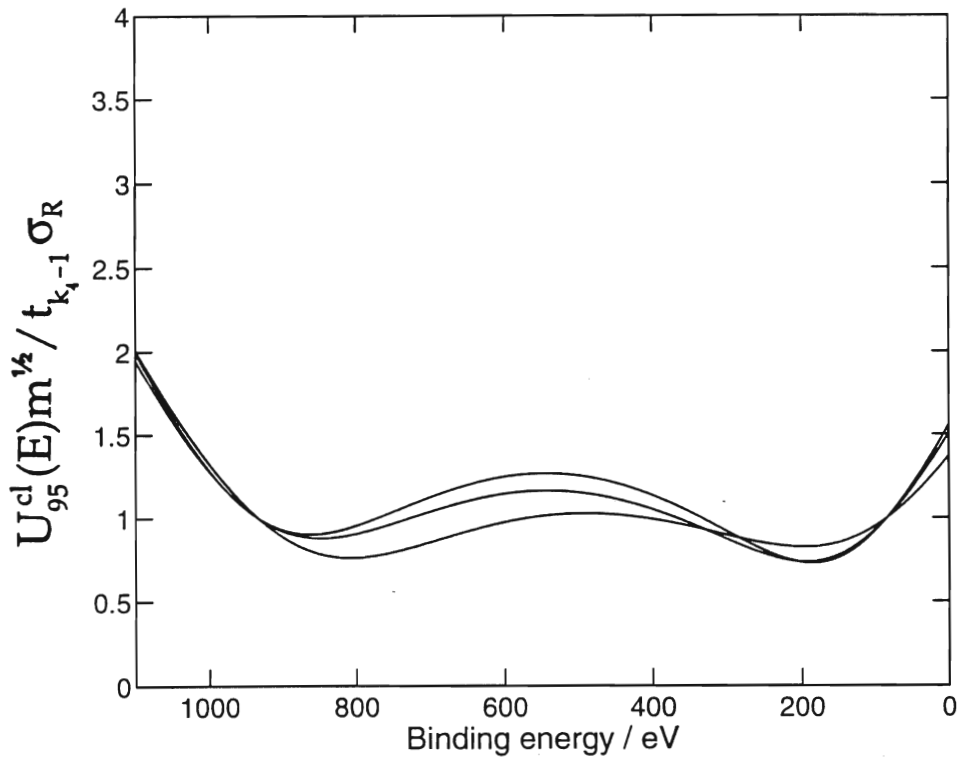


Fig 18

The uncertainty at 95% confidence for the case where the energy scale obeys Eq (46) and calibrations have been made for Au $4f_{7/2}$, Cu $2p_{3/2}$ and Cu LMM or Ag $3d_{5/2}$. The ordinate is $U_{95}^{cl}(E)m^{1/2}/t_{k_4-1}\sigma_R$ from Eq (48) and it is assumed that the same number of measurements and the same uncertainty applies to each peak. The three curves relate to the three $E_{ref2,3}$ values in Table 1. Note that the ordinate in this Fig is not the same as in Fig 17.

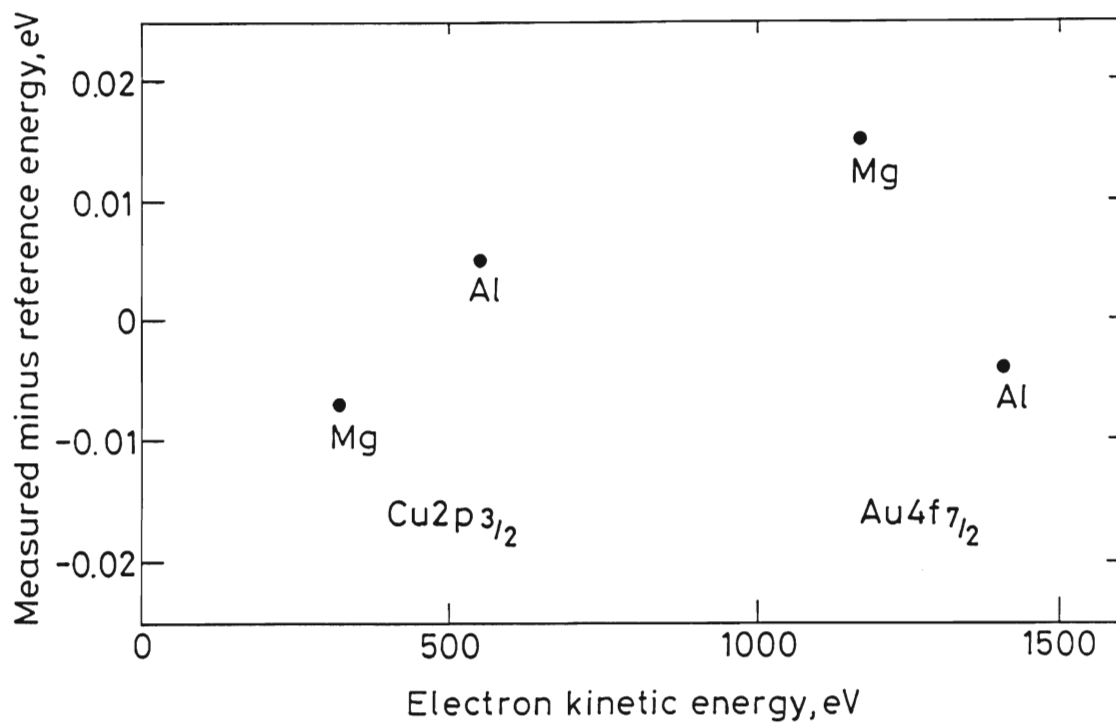


Fig 19 A typical calibration plot for the VG ESCALAB II. The ordinate values are Δ_1 and Δ_2 from Eqs (29) and (30) for unmonochromated Al and Mg X-rays using the reference values of Table 1.

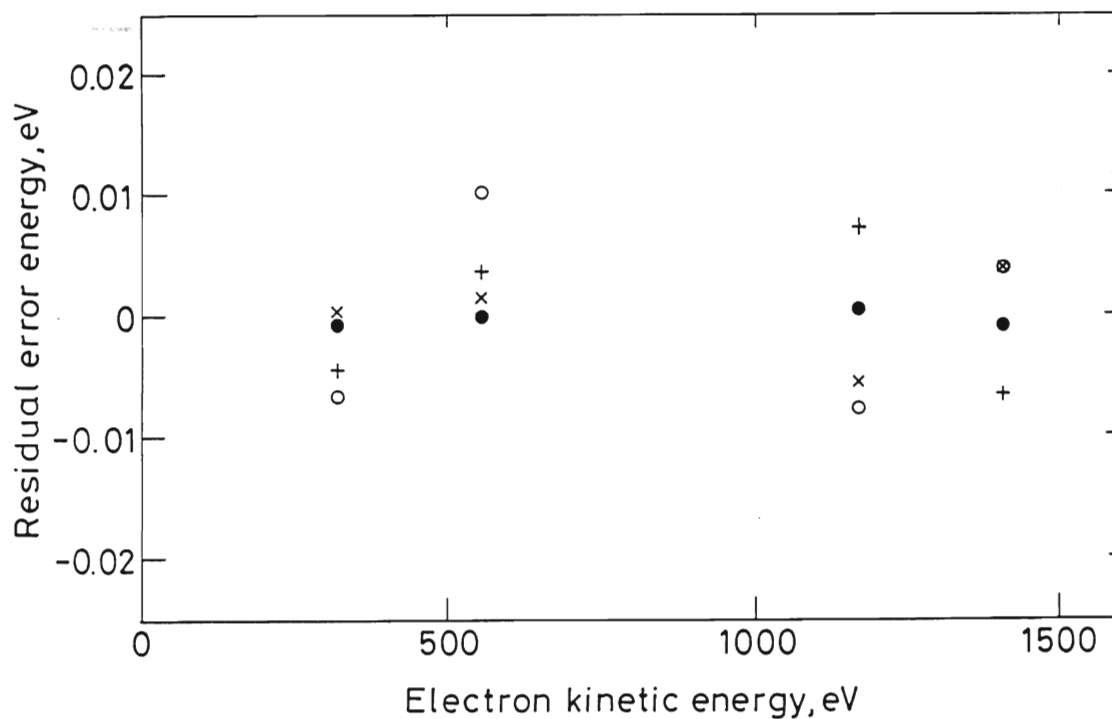


Fig 20 Residual errors from four re-calibrations using mean values for the reference binding energies for the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks for the Al and Mg X-rays. The different symbols relate to each calibration in the chronological order ●, x, + and o.

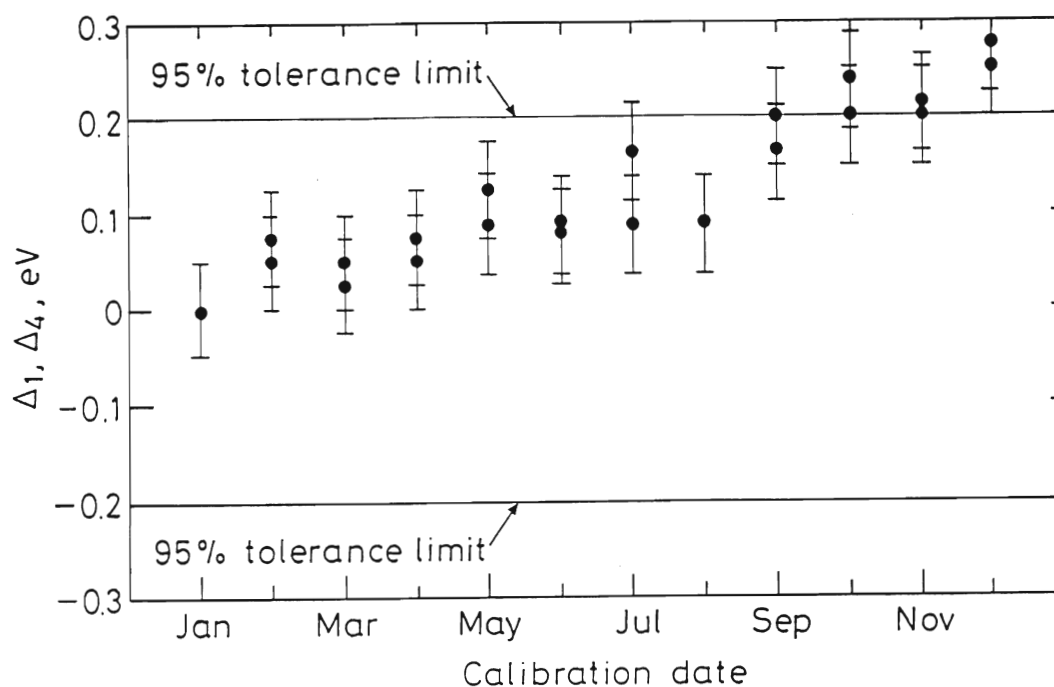


Fig 21

Schematic of an energy calibration control chart showing the calibration status of an X-ray photoelectron spectrometer after Seah⁽²⁶⁾. The plotted points are synthetic values of Δ_1 and Δ_4 from Eqs (29) and (30) which are defined as the differences between the measured binding energies and the tabulated binding energies for the Au 4f_{7/2} and Cu 2p_{3/2} peaks. These are shown as a function of time for an instrument originally calibrated in January and which should have been recalibrated, according to Table 3, in May. The values used in this Fig are $m = 2$ and $\delta = 0.2$ eV, as shown in Table 3. If the measured calibration data had been used to re-calibrate the instrument each month, the 95% confidence tolerance limit could be reduced to ± 0.16 eV.