CALIBRATION OF ELECTRON SPECTROMETER ENERGY SCALES FOR AES AND XPS

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The calibration of the energy scale of electron spectrometers for Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) is important for the routine identification of elements and chemical binding states. For most current work on chemical binding states in XPS a calibration accurate to ± 0.1 eV will generally suffice but, for AES, where the chemical state effects are stronger, ± 0.2 eV is, in general, adequate.

With this requirement in mind a calibration methodology for XPS was established at NPL in 1984 [1]. In this work the X-rays were the natural, unmonochromated Al Kα and Mg Kα sources and the analyser was operated at an intrinsic resolution of 0.25 eV so that instrumental distortions of the peak shapes could be ignored. Furthermore, the spectrometer was operated to scan the spectrum with one retarding potential so that this potential had a precise 1:1 correspondence with the energy scale and no relativistic corrections were required. The energy scale was thus traceable to the UK national standards of voltage for 1984 and this was later upgraded [2] to the scale defined by the 1990 Josephson constant.

In this work the binding energies of the major peaks for clean copper, silver and gold were determined relative to the Fermi edge of nickel to accuracies of ± 0.01 and ± 0.02 eV. The peak energies, given in Table 1 were defined by fitting parabolas to the top 5% of the peak. In an interlaboratory test of many instruments [3] it was found that peak repeatabilities were typically ± 0.024 eV and, after calibration, peaks such as the Cu LMM Auger electron peak could be established accurately within ± 0.035 eV [4]. Prior to this calibration ± 0.4 eV was more typical [3]. In this work it was recommended to use the Au $4f_{7/2}$ and Cu $2p_{3/2}$ peaks as both were intense, sharp and at opposite ends of the energy scale.

In studies of alternative approaches we have considered reflected electron beams [5] and spectrometers operated in the constant ΔE/E mode [6]. The former involves the problem of energy transfers from the electron to the reflecting atom(s) and the latter the breakdown of the 1:1 correspondence of voltage with energy due to relativistic terms.

In more recent spectrometers Powell [7] has shown that the use of monochromators leads to shifts between the Auger and X-ray photoelectron peaks since the precise X-ray photon energy now depends on the monochromator settings and may be varied over a range of 0.4 eV. For instruments with monochromators the Auger electron peaks in the above calibration should be ignored.

Table 1
Absolute values of calibration core level binding energies (eV) [2] for unmonochromated X-rays

	Al Kα†	Mg Kα
Cu 3p	75.14 ± 0.02	75.13 ± 0.02
Au $4f_{7/2}$‡	83.98 ± 0.02	84.00 ± 0.01
Ag $3d_{5/2}$§	368.26 ± 0.02	368.27 ± 0.01
Cu L_3MM	567.96 ± 0.02	334.94 ± 0.01
Cu $2p_{3/2}$	932.67 ± 0.02	932.66 ± 0.02
Ag M_4NN	1128.78 ± 0.02	895.75 ± 0.02

† Al Kα-Mg Kα = 223.02 eV.
‡ Au $4f_{7/2}$ Al Kα BE lowered by Au $4f_{5/2}$ tail.
§ Ag $3d_{5/2}$ Mg Kα BE raised by Ag $3d_{3/2}$ X-ray satellite

Table 2
Calibration kinetic energies (eV) for Auger Electron peaks in the direct mode at high resolution. The first uncertainty shows the one standard deviation of the repeatability of the data and the second the accuracy of the measurement chain. A further ± 0.03 eV arises from the uncertainties of the X-ray energies used to define the Fermi level.

	E_K (Fermi level)
Cu $M_{2,3}$ VV†	61.16 ± 0.04 ± 0.03 63.44 ± 0.04 ± 0.03
Au $N_{6,7}$ VV†	70.10 ± 0.04 ± 0.03 72.21 ± 0.04 ± 0.03
Ag M_4 NN	357.81 ± 0.01 ± 0.02
Cu L_3 VV	918.62 ± 0.01 ± 0.02
Au $M_5N_{6,7}N_{6,7}$‡	2015.57 ± 0.05 ± 0.04

† For the copper and gold low energy doublets a tangent intercept has been used.
‡ This peak is on a very high background. If the background slope increases so will the energy of the peak and *vice versa*. This value is for a 5 keV electron beam incident at 30° to the sample surface normal. The position of the peak with the background removed is 0.07 eV lower than this value, as found, for instance, in XPS where the Bremsstrahlung radiation has been used.

For Auger electron spectroscopy the above philosophy was repeated [8] and peak positions were established as shown in Table 2. In this work one cannot measure the true Fermi level but this was inferred from the XPS measurements cited above and estimates of the effective X-ray energies. More recent detailed measurements of these photon energies give values 0.01 eV and 0.02 eV higher for Al and Mg, respectively but with uncertainties of ± 0.01 eV [9]. These confirm the values in Table 2 within the cited errors. For AES systems used at poor energy resolution the energies of these peaks shift [8]. It is recommended that the high and low energy peaks in copper be used for calibration and that, as in Table 2, energies are referred to the Fermi and not the vacuum level.

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