

K-Alpha: Energy Scale Linearity and Calibration

Key Words

- Surface Analysis
- Energy Scale Calibration
- Energy Scale Stability
- Monochromator Alignment



Accurate calibration of the energy scale in an XPS spectrometer is essential for the reliable determination of chemical states.

The Thermo Scientific K-Alpha from has calibration standards built into the sample stage so that they are always available for checking the instrument's condition. These standards include copper, silver and gold which are used to calibrate the energy scale.

The Avantage data system controls all aspects of the operation of K-Alpha, including routines that are designed to ensure that the instrument is always operating at its peak performance. One of these routines rapidly calibrates the binding energy scale. The procedure can be performed frequently because it is rapid (taking only a few minutes) and it does not require the user to load the standard samples. It would not be unreasonable for a user to check the calibration of the instrument once each week.

With increasing requirements for traceability, particularly in the QA and QC areas, the ability to perform regular calibration checks and automatically log the results is seen as an important requirement of an analytical instrument such as this.

The Data Collection Procedure

The data is collected using a procedure similar to that described in Reference 1, the reference binding energies are also taken from this document. Each of the three standard samples is cleaned by sputtering with argon ions prior to the collection of the XPS spectral regions shown in Table 1.

Peak	Reference Binding Energy (eV)	Scan Start Energy (eV)	Scan End Energy (eV)	Step Size (meV)
Au 4f _{7/2}	83.96	82	86	50
Ag 3d _{5/2}	368.21	366	370	50
Cu 2p _{3/2}	932.62	930	934	50
Cu L ₃ VV	567.93	566	570	50

Table 1: The spectral regions and scan ranges used for the data collection

As described in Reference 1, to determine the position of the peak maximum, the top of each peak is fitted to a parabolic function using a least squares method. The position of the maximum is then calculated from the parabolic function. Figure 1 shows the Ag 3d_{5/2} peak collected by K-Alpha and Figure 2 shows the top part of the peak fitted with a parabola from which the position of the peak maximum was determined.

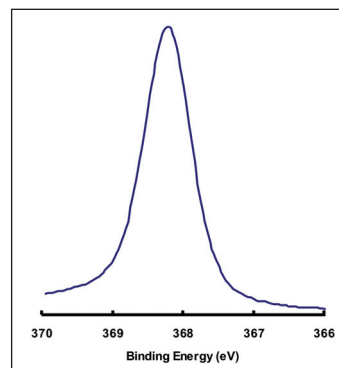


Figure 1: The Ag 3d_{5/2} peak

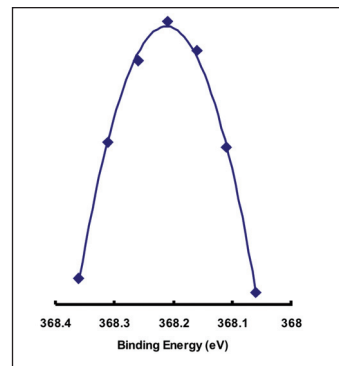


Figure 2: The top of the Ag 3d_{5/2} peak and the parabolic curve fitted to the experimental data

This procedure is repeated with the Au 4f_{7/2} and Cu 2p_{3/2} peaks. The binding energy scale is then adjusted in both gain and offset to minimize the binding energy error at the three XPS binding energies listed in Table 1. The Cu L₃VV peak position will be used later.

Constancy of the Binding Energy

Having calibrated the instrument using this automated procedure, data were collected from each of the three standard samples 100 times. The period over which these data were collected was about 2 days. This is a test of the short-term stability of the energy scale. During this process, the data collection and peak position measurement procedures were the same as in the calibration process but no changes were made to the calibration of the instrument.

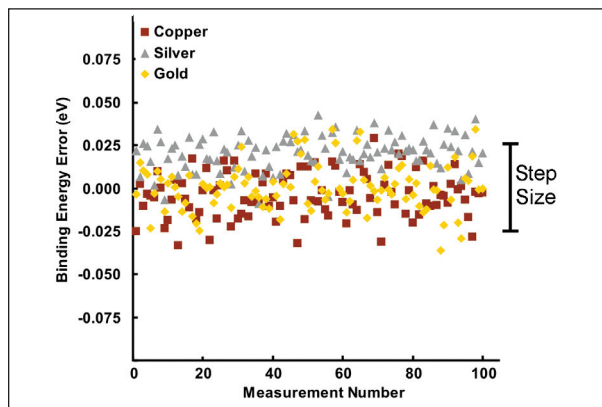


Figure 3: The deviation of the measured binding energy from the reference values for copper, silver and gold, each measured 100 times. The deviation is compared with the binding energy step size (50 meV) used in the measurements.

Figure 3 shows the deviation of the position of the peak maximum from the reference binding energy values shown in Table 1 for each metal and for each measurement.

It will be seen from this figure that the total spread of the data in this figure is only slightly more than the step size used to collect the data.

Analysis of the data in Figure 2 shows that the mean error in the peak position is 6 meV, and the standard deviation of the distribution of the errors is 16 meV so the (3sigma) value of 48 meV is very close to the step size used for the acquisition.

The Effective Photon Energy

The fact that the Cu L₃VV peak was measured in the procedure used here means that we can calculate the effective photon energy of the incident X-rays. Following the procedure in Reference 1, the deviation of the measured peak position for Cu L₃VV from the reference value of 567.93 eV is equal to the difference in the photon energy from 1486.61 eV, $\Delta(h\nu)$. From this, it is possible to calculate the effective photon energy for each of the 100 measurements taken, see Figure 4.

Reference 1 states that the value for $\Delta(h\nu)$ should lie within the range 0 to 0.2 eV (i.e. the photon energy should be in the range 1486.61 to 1486.81 eV). These limits are indicated in Figure 4. Should the calculated values be

outside this range then it may be necessary to adjust the monochromator crystal alignment to set the Bragg angle correctly. This procedure is, of course, computer controlled in K-Alpha.

In this case, the calculated values were all well within the desired range and there is no trend seen in the data. Therefore, the crystal is well aligned.

The mean photon energy was calculated to be 1486.69 eV with a standard deviation of 24 meV and the total spread in the data was 109 meV.

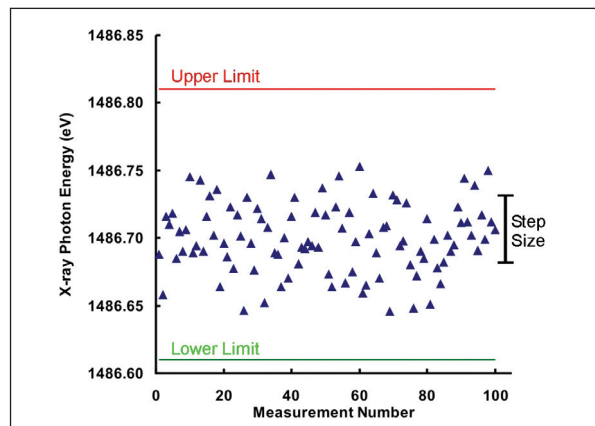


Figure 4: The X-ray photon energy calculated for each of the measurements

Conclusions

The automated instrument calibration routine in K-Alpha, using samples built into the sample stage, is a rapid and efficient method to ensure that the instrument is well calibrated. The routine can be run unattended and so does not need to interrupt normal workflow.

Following calibration, the accuracy and precision of the binding energy is excellent, as can be seen from Figure 3.

The Advantage data system maintains a log of the calibration events ensuring good traceability.

Not only are the binding energies measured but, by measuring the copper Auger peak, it is possible to check the energy of the X-ray photons giving a good indication of the state of alignment of the X-ray monochromator crystal.

The user is informed when a calibration procedure is required and warned if the instrument should fall outside of its preset performance limits.

This is just one of the reasons why users of K-Alpha can have the utmost confidence in the quality of their data.

References

1. International Standard ISO 15472, 'Surface chemical analysis - X-ray photoelectron spectrometers - Calibration of energy scales' 2001

www.thermo.com/surfaceanalysis

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