

## Peak Location in X-Ray Photoelectron Spectroscopy

C. J. Powell

Surface and Microanalysis Science Division, National Institute of Standards  
and Technology, Gaithersburg, MD 20899, USA  
e-mail: cpowell@enh.nist.gov

The determination of peak position is an important part of x-ray photoelectron spectroscopy (XPS), and most instruments have software available for this purpose. An analyst can generally choose one of several functions for the lines (such as Lorentzian, Gaussian, asymmetric Gaussian, and mixed Lorentzian-Gaussian) and several functions for the background (such as linear, Shirley, and Tougaard) for fitting measured spectra and thus deriving peak positions and intensities.

This presentation will in two parts. In the first part, I will address sources of random and systematic error that can be encountered in fitting lines used for the calibration of the instrumental binding-energy scale (the Au 4f<sub>7/2</sub>, Ag 3d<sub>5/2</sub>, and Cu 2p<sub>3/2</sub> lines). These lines have a small amount of natural asymmetry, and there can thus be a systematic error when fits are made to these lines with symmetrical functions (particularly when using unmonochromated x rays). The effects of line asymmetry were essentially eliminated in the measurements of line positions at the UK National Physical Laboratory [1] from fits of a quadratic function to the top 5% of each peak. In practical calibrations, however, it is more convenient to use instrumental software for this purpose.

I will show random and systematic errors resulting from fits of both symmetrical and asymmetrical functions to illustrative Cu 2p<sub>3/2</sub> spectra measured with unmonochromated Al x rays. The fits were made in each case using different fractions of the line (that is, different numbers of points comprising the peak). For calibration purposes, it is desired to locate the peak positions as accurately and precisely as

possible, and to avoid systematic errors caused by backgrounds with non-zero slopes [2].

As expected, use of symmetrical functions gave poor fits (as judged from plots of residuals and systematic errors in peak location) when groups of points comprising more than about 20% of the peak were fitted. A larger fraction of the peak (50% or more) could be used to obtain high-quality fits with an asymmetrical Gaussian function. In the latter fits, the random and systematic errors were much smaller than those found in fits with symmetrical functions. The asymmetric Gaussian function thus appears to be a suitable and convenient choice for peak location in calibration experiments.

In the second part of the talk, I will report on a pilot study to evaluate prototype standard test data (STD) for XPS [3]. The STD were simulations of overlapping carbon 1s XPS spectra, and were designed to assess data analysis procedures for determining peak position and intensity. The STD simulated a range of analytical situations that are encountered in practice, such as varying degrees of peak overlap, varying relative peak intensities, and varying levels of random noise.

The STD were constructed from selected C 1s spectra of polymers that had a single "main" C 1s peak. The spectra were smoothed and then fitted with fifth-degree spline functions. In most cases, the STD were constructed by adding the modeled spectra for two polymers to simulate a spectrum of overlapping C 1s peaks that might be measured from a specimen consisting of two separate phases. Different pairs of polymer spectra were used to represent different types of binary specimens with varying degrees of peak overlap, varying relative intensities of the two

peaks, and varying levels of absolute intensities for the combined spectra (i.e., amount of random (Poisson) noise). The factorial-based design had three levels for peak overlap: a) no shoulder present, b) shoulder present, c) valley present. The design had three levels for relative intensities of the peaks: a) peak 1-high/peak 2-low, b) peak 1-low/peak 2-high, c) peaks 1 and 2 approximately equal. The design also had two levels for absolute peak intensity: a low intensity level with twice the Poisson noise of the high intensity level. For each spectrum with a given amount of peak overlap, given relative intensities of the two peaks and a given level for the absolute intensity, Poisson noise was added in replicate to simulate multiple experimental measurements of the same specimen. In addition to spectra for two overlapping C 1s peaks, spectra were simulated for single C 1s peaks at the two levels of absolute peak intensity to provide the "null case" in the factorial design.

A number of surface scientists in industry, academia and government were asked to use their data analysis procedures to estimate peak parameters (position and intensity) and to estimate the uncertainties of the peak parameters. In analyzing the spectra, participants had to choose whether one or two peaks were present, and which fitting function, background correction, and initial parameters to use. I will give a report on preliminary results of the pilot study, particularly: (a) the variability in peak parameter estimates from the individual analyst (reported anonymously) using his/her chosen data analysis procedures, as well as from different analysts using their data analysis procedures, (b) parameter uncertainty estimates, (c) the types of operator choices, and (d) overall impressions of the study.

1. M. T. Anthony and M. P. Seah, *Surf. Interface Anal.* 6, 95 (1984).
2. C. J. Powell, *Surf. Interface Anal.* 23, 121 (1995).
3. Work performed in collaboration with J. M. Conny and L. A. Currie of NIST.