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The active background method in XPS data peak fitting

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Content

Abstract

In this Internal Report is introduced a practical implementation of the *active* background method. This is employed for fitting photoelectric spectra, such as in X-ray (XPS) or Ultraviolet (UPS) Photoelectron Spectroscopy. In contrast with the standard or *static* approach in which the background is defined prior to peak-fitting, the *active* background intensity and shape are defined during the peak-fitting process. The active provides better fits than the static method.

I. The traditional or *static* background method in XPS data peak-fitting

Quantifying the intensity of peaks in x-ray photoelectron spectroscopy (XPS) data requires properly modeling the background signal. There are various background types, namely Shirley, Tougaard, lineal, exponential and polynomial, that are employed in a case by case basis. The standard or traditional peak-fitting methodology has the following distinguishable characteristics:

- One of the background types is chosen depending on its shape. Some software allows for a certain predefined combination of two of them.
- Two points, one at each side of the main features of the spectra (i.e., at each side of the peak or peaks), are chosen. The background is forced to pass though these two points.
- The background is first subtracted from the original data and then the modified, backgroundless spectrum, is peak-fitted. In some commercially available software, the user

is allowed to manually modify the background by adding a polynomial contribution and forcing the background to pass through additional intermediate points.

- Some times it is necessary to make extra corrections to the data before peak fitting. For example, if the background on the right (high kinetic energy side) shows a non-negligible slope, it is necessary to fit a straight line in that region and subtract the extrapolated line to the whole spectrum.[1]

The term *static* is employed for the traditional method since the background does not play an active role during peak fitting since, as mentioned in the third point above, it is subtracted prior to peak-fitting. This contrast with the *active* method, where the background shape and intensity is defined during peak-fitting. Figure 1 shows a Au 4$p_{3/2}$ spectrum from a clean sample. Under the *static* methodology, a line going through the points on the right of the peak is extrapolated and subtracted to the whole spectrum. Besides the step at the peak, this leaves a flat background on both sides since, for this particular case, the slope of the background on the left is the same to that on the right. The remaining stepwise background shape is subtracted employing the iterative Shirley method.[2] The remaining feature is then fitted with a singlet peak.

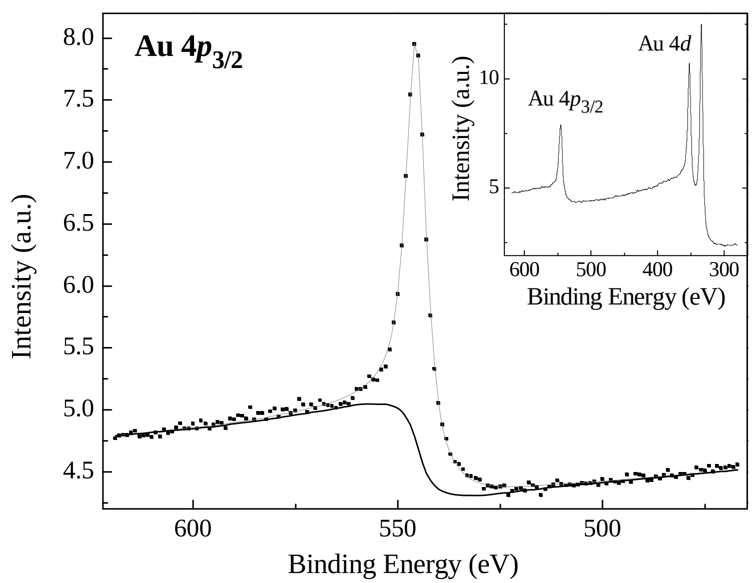

Figure 1. Au 4$p_{3/2}$ XPS spectrum from a clean gold surface. The inset shows that this peak rides on the background of the 4*d* peak. The background employed is the sum of a baseline, a linear term, and Shirley ($k_{Shirley}$ = 0.032 eV^{-1}). The slope of the background is the same at both sides of the peak.

II. The *active* background method

An alternative for treating the background is the *active* method. The active approach is applied by first constructing a series of functions in the fitting energy range. In the example shown in Figure 1, the functions are a singlet peak, a constant term, a linear term, and an iterative-Shirley background. Then, the contribution from each term is found through an optimization process. Since the parameters of the peak changes during the fitting process, the relative contributions from the constant, linear, and Shirley backgrounds also changes. The background shape and intensity vary during the fitting process. If the position of the proposed peak is off, as illustrated in Figure 2 for the same data shown in Figure 1, the background is modified to minimize the fitting error for that particular position of the proposed peak. As the peak-fitting procedure continues, the shape of the background evolves to that shown in Figure 1.

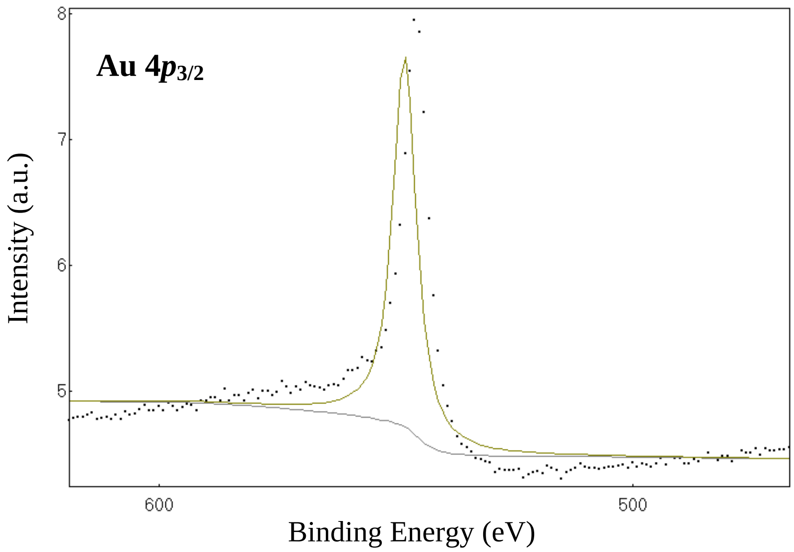

Figure 2. Same Au 4$p_{3/2}$ spectrum as in Figure 1. It illustrates how the background changes together with the peak in an *active* manner.

For the data shown in Figure 1, both the static and the active background methods provide essentially the same fit. As shown in the next section, this is hardly the case in most spectra.

The *active* background method has been implemented in the software ***AAnalyzer®***.[3] Under the active method, choosing various backgrounds to work simultaneously could be as easy as selecting the corresponding checkboxes. This is illustrated in Figure 3, which shows the parameters tab for the fit in Figure 1. Note that the "Baseline" (constant term), "1st Order" (linear term), and "Shirley" background are chosen within the "Active Background" group box. The number of iterations for the Shirley background was set to six.

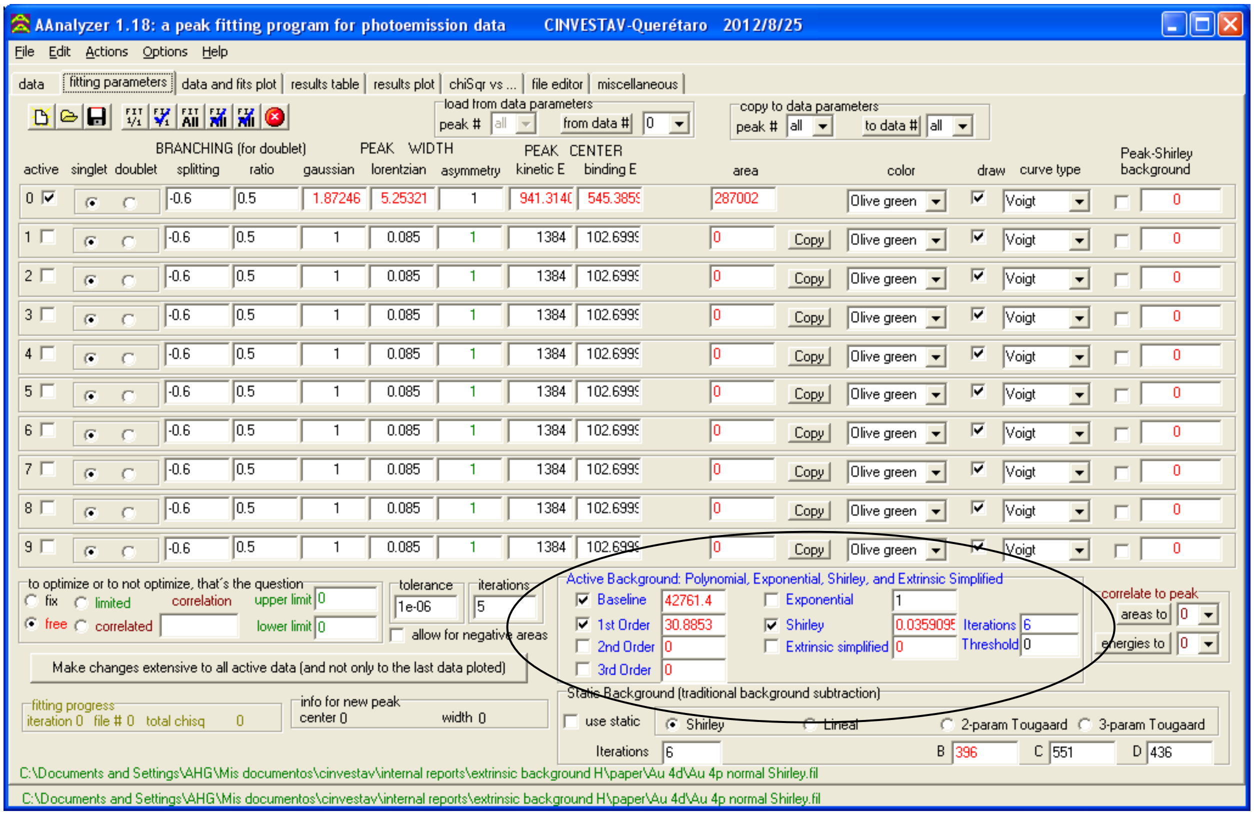

Figure 3. Tab of the software AAnalyzer showing the parameters employed for the fit shown in Figure 1. As indicated in the box next to the Shirley parameter box, six iterations were employed to generate the background. This number was chosen since further iterations have negligible effects on the background.

The implementation of the active background, and its importance, had been suggested in other reports.[4,5] It should be mentioned that, besides those in the Active Background group box (circled in Figure 3), there is another active background type, the Peak-Shirley background (last column in Figure 3). This is a variant of the Shirley method that *does not require iterations*. Its form is very similar to that suggested in another report.[5] A detailed description can be found elsewhere.[6]

The Extrinsic Simplified background is described in Reference 7, which shows a number of examples in which this is combined with the Shirley and 1st order backgrounds under the active method.

III. Active versus static background

The *active* method is usually much better than the traditional or *static* method for the treatment of the background in photoemission data analysis. The advantages of the active method are many:

- The area of the peaks is usually underestimated when the static method is employed. As mentioned above, under the static method it is necessary to choose two points, one at each side of the spectrum features or peaks. The operator has to guaranty or to assume that there is no appreciable contribution to the signal at those two points from any of the peaks. The method does not allow for considering peaks that extend beyond any of the chosen points. In contrast, the active treatment does not restrain this possibility since the strength of the background can be varied to account for contributions from extended peaks. The active method should to be employed when the data is acquired with a too-short energy range, when one of the peaks extends beyond the spectrum limits. The extent of the errors incurred by using the static method in the quantification of the peak intensity is illustrated in Reference [8].

- The relative contributions of the Gaussian and Lorentzian widths to the FWHM of the peaks are dependent on the fitting energy range when the static method is employed. As shown below, this is not the case for the active approach.
- As it is well known, the iterative-Shirley background algorithm fails for some types of spectra. An example is provided below. Another issue is that it takes longer to converge, that is, more iterations are required with the static than with the active method.
- The active treatment allows for a combination of backgrounds: the strength of a lineal background employed simultaneously with a Shirley background can be decided by the optimization process. In contrast, the static method requires that the operator chooses *one* among the background types available (lineal, Shirley, Tougaard, etc.), or a fixed combination of them.
- When the background is subtracted before peak-fitting, the Poisson-character of the data is not longer applicable, so the uncertainty on the peak parameters cannot be calculated employing the covariant matrix method.[9]
- There are other issues, such that the operator might forget about the background once it has been subtracted. In the active method, the changing role of the background is accounted as the operator considers different options during peak-fitting.
- Last, but not least, the active method *always* provides better fits than the static method.

III.1. **Underestimation of the peak area with the static method**

Figure 4 shows an example in which the use of the static method seems harmless since the background at both sides of the peak is apparently flat. At first sight, both fitting methods, static and actve, provide approximately the same fit. However, the difference in the calculated area is ~ 10%. This is because, in the static method, the background is forced to pass through the points P_1 & P_2 (shown in the figure). In contrast, in the active approach the peak is allowed to have a (small) contribution at those points, so the background is slightly lower, resulting in a larger area of the peak.

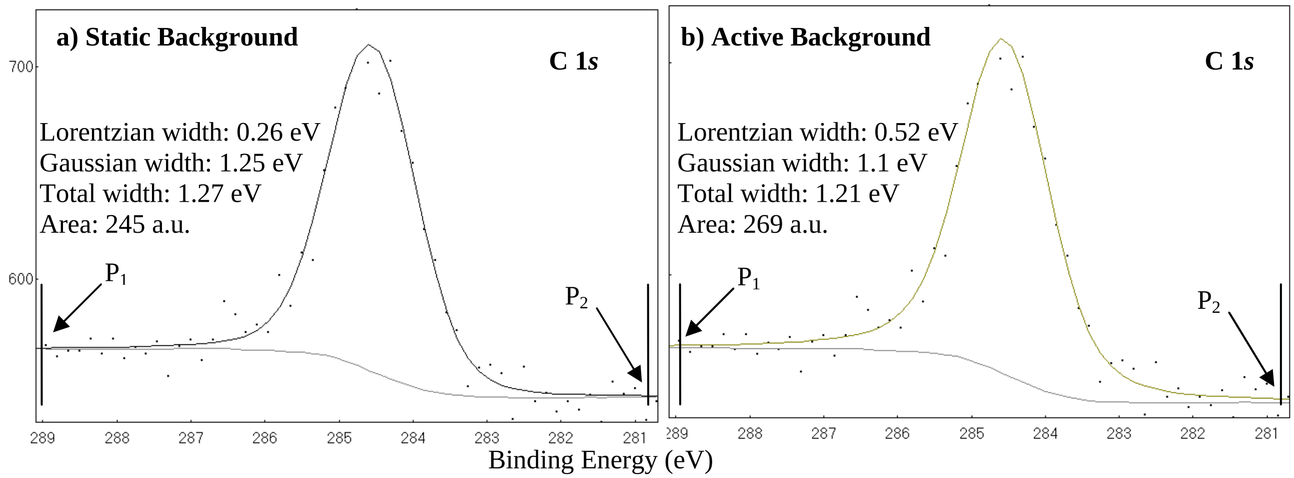

Figure 4. Fitting of a C 1s peak with the background treated a) in a static (first subtracted and then fitted) and b) in an active way (optimized during the fitting process). Although both fits looks equally good, the change in the area is ~ 10%. The main difference comes from the background. In the second case, the background is allowed to go below the signal at the chosen points (P_1 at 288.8 and P_2 at 280.9 eV). This freedom allowed for larger values of the Lorentzian width during the optimization process.

The problem might be more serious for asymmetric peaks for which the tail on the left could prolong considerably. This is exemplified in Figure 5 with a Fe 2*p* spectrum. (The asymmetry in Figures 5 and 8 was accounted for through the double-Lorentzian line shape described in Reference 10). Although the signal is already flat for binding energies above 730 eV, the analysis performed with the active background method shows that the last peak to the left extends well beyond 732.5 eV, the left extreme of the energy range in which the data was acquired. The inset in Figure 5b shows that the fit done with the active background method is excellent, even when the 1:2 ratio for the intensity of the $2p_{1/2}$ and $2p_{3/2}$ branches is forced during the fitting. A good fit is not possible with the static method if the branching ration restriction is applied (see inset in Figure 5a). Another important difference is that the ratio of the intensities of the oxide and metallic peaks changes by 50%. This would directly affect the assessment of the thickness of the oxide layer by about that same percentage.

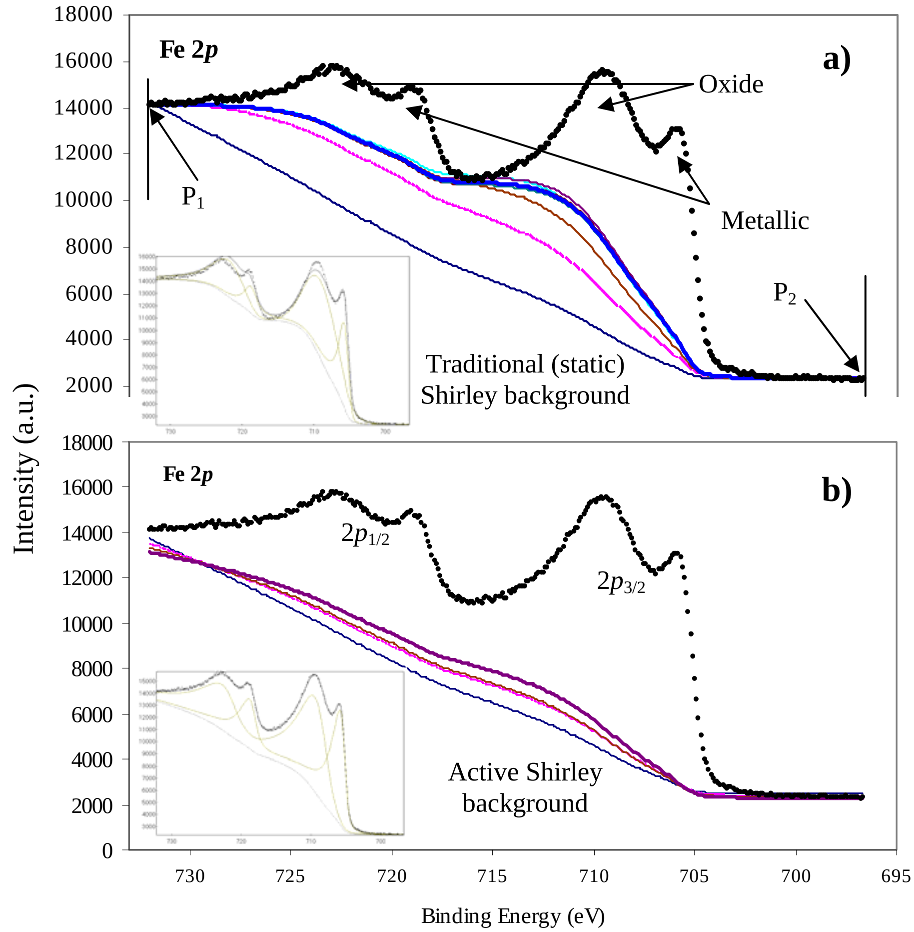

Figure 5. Fe 2*p* XPS spectrum from a iron substrate with a thin iron oxide layer. The Shirley background is shown for various iterations for the a) traditional, static method, and b) for the active method. The thicker lines correspond to the final convergence shape. The background takes longer to converge and does it to a very different value with the static method. The reason is that, under this method, the background is obligated to go through the point P_1. The active method allows for the possibility that a peak could contribute to the signal at that position. This is the case since the data was acquired with a too-short energy range.

III.2. Dependence of the Lorentzian and Gaussian widths with the fitting energy range

The spectrum shown in Figure 6 for In $3d_{5/2}$ was fitted employing the five energy range sets indicated by the pairs of numbered vertical lines.

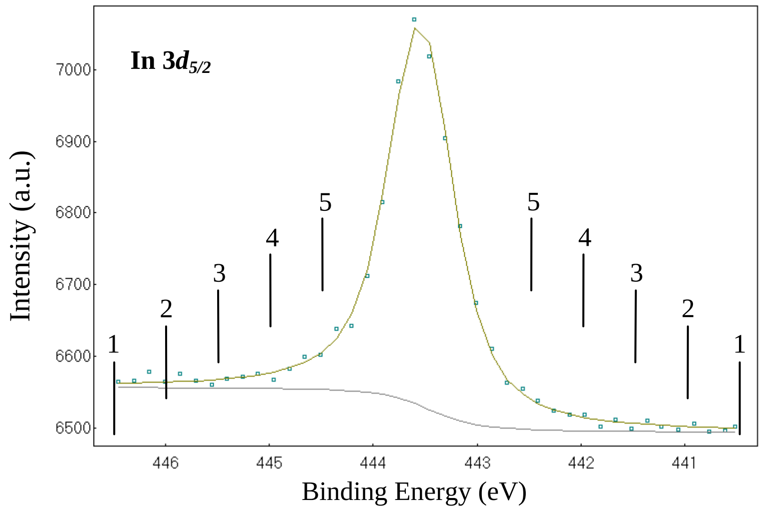

Figure 6. In 3$d_{5/2}$ spectrum (dots). The pairs of vertical lines indicate the energy range in which peak-fitting was carried out. The results of the fits for the different energy ranges, and employing both the static and active background methods, are shown in Figure 7 (the lines correspond to the fit carried out employing the active background method and the energy range corresponding to pair # 1).

Figure 7 shows the results of the fitting of the data shown in Figure 6 for the various energy ranges and employing both the static and active background methods. The height and the Lorentzian and Gaussian widths were allowed to vary during the analysis process to optimize the fit. Besides underestimated it, the area assessed with the static method has a large dependence with the fitting range. Likewise, the Lorentzian and Gaussian widths also shows a large dispersion when the static method is employed.

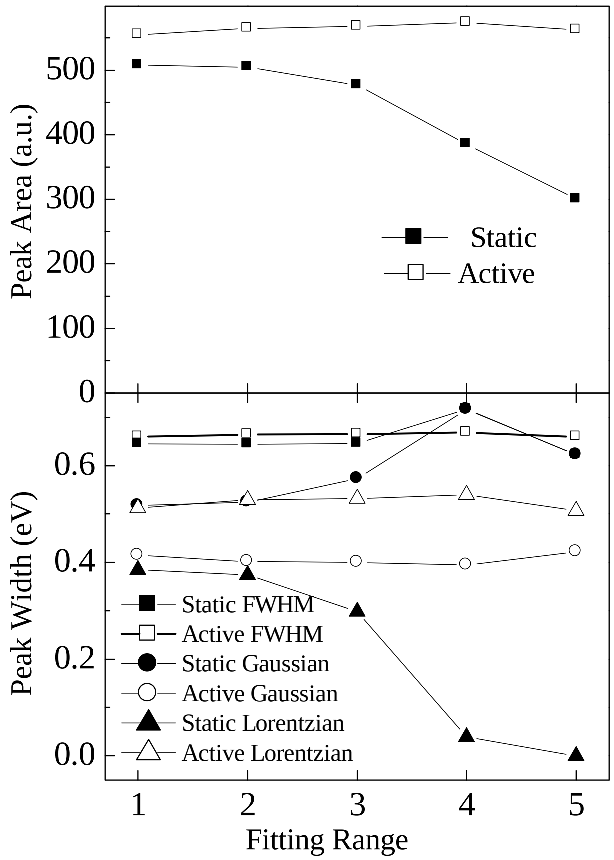

Figure 7. Results of the fits performed employing the static and active background methods for the data shown in Figure 6 using the various energy ranges there indicated. The results employing the active show much lower dispersion than with the static background method.

III.3. Convergence of the static iterative-Shirley background

For some spectra, when the energy range is large or it contains large sharp peaks with low regions in between, the traditional iterative-Shirley algorithm fails. This is illustrated in Figure 8 for a Fe 2*p* spectrum from a clean iron surface. The static Shirley background does not converge and have large oscillations between even and odd iterations.

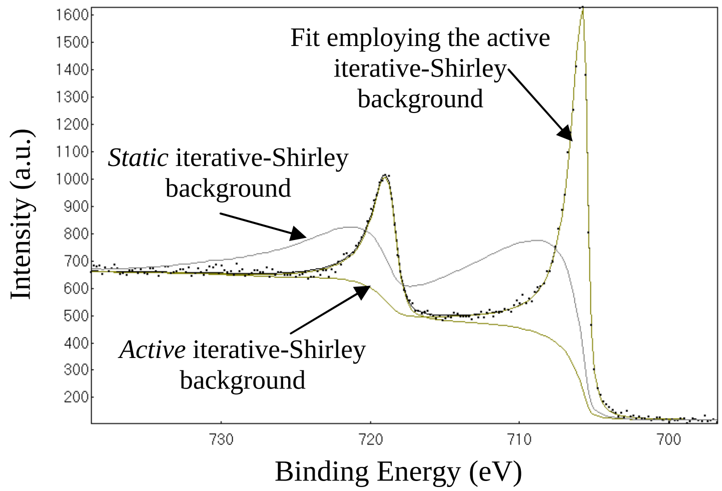

Figure 8. Fe 2*p* spectrum for a clean iron sample. It shows the lack of convergence of the traditional or static iterative-Shirley background method.

There are many advantages and no apparent drawbacks when the *active* is employed instead of the traditional (*static*) background methodology. Once the active method has been implemented, it can provide better fits with much lower dependence on operator-choices, such as the fitting energy range. This is also illustrated in Figure 7 of Reference 7 for different combination of the Shirley and the extrinsic-simplified backgrounds.

References

[1] S. Tougaard. Surface Science 216 (1989) 343-360

[2] P.M.A. Sherwood, in: D. Briggs, M.P. Seah (Eds.), Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, Wiley, Chichester, 1983 (Appendix 3).

[3] More information about the software can be found at ***www.rdataa.com/aanalyzer***.

[4] A.M. Salvi and J.E. Castle. J. Elec. Spec. Rel. Phen. 95 (1988) 45.

[5] J. Vegh. J. Elec. Spec. Rel. Phen. 46 (1988) 411.

[6] A. Herrera-Gomez. ‘‘The Peak-Shirley Background.’’ Internal Report. CINVESTAV-Unidad Queretaro (2011). http://www.qro.cinvestav.mx/~aherrera/reportesInternos/peakShirley.pdf

[7] A. Herrera-Gomez. “Simplified near-peak background for extrinsic and intrinsic electron scattering in XPS data peak-fitting.” To be submitted to J. Elec. Spec. Rel. Phen. (2012).

[8] J. Muñoz-Flores, A. Herrera-Gomez. “The static and the active background methods in XPS peak-fitting.” To be submitted to J. Elec. Spec. Rel. Phen. (2012).

[9] J. Muñoz-Flores, A. Herrera-Gomez. “Resolving overlapping peaks in ARXPS data: the effect of noise and fitting method.” J. Elec. Spec. Rel. Phen. 184 (2012) 533– 541, and references therin.

[10] A. Herrera-Gomez. “A double Lorentzian shape for asymmetric photoelectron peaks.” Internal Report. Cinvestav-Queretaro.(2011). http://www.qro.cinvestav.mx/~aherrera/reportesInternos/doubleLorentzian.pdf