



The active background method in XPS data peak-fitting

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Abstract

A practical implementation of the *active* background method is introduced, one which 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 method provides better fits than the static method.

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

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

- One of the background types is chosen depending on the shape of the spectrum. 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 through 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.

- Sometimes it is necessary to make additional 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 from the whole spectrum.¹

The term *static* is employed for the traditional method in the sense that 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 contrasts with the *active* method, where the background shape and intensity is defined during peak-fitting. Figure 1 shows a Au $4p_{3/2}$ 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 Shirley-type step at the peak, the removal of the linear dependence leaves behind a flat background on both sides since, for this particular case, the slope of the background on the left is the same as 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.

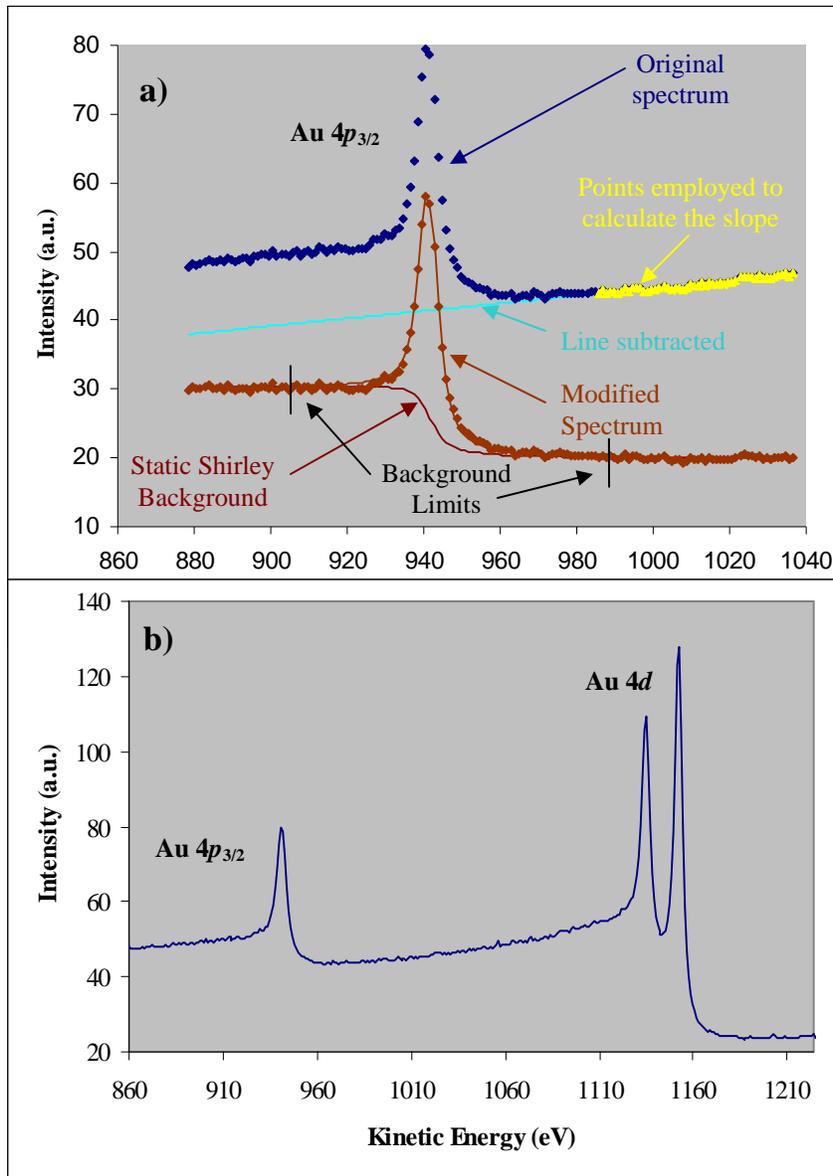


Figure 1. a) Au 4p_{3/2} XPS spectrum from a clean gold surface. Some of the steps employed for the static iterative Shirley background removal are shown. b) This figure illustrates that the Au 4p_{3/2} peak rides on the decreasing background of the 4d peak.

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. For the example shown in Figure 1, the functions are a singlet peak, a constant term, a linear term, and an iterative-Shirley background. The contribution from each term is found through an optimization process. Since the parameters of the peak change during the fitting process, the relative contributions from the constant, linear, and Shirley backgrounds also change. The background shape and intensity vary during the fitting process. If the position of the proposed peak is off, as illustrated in Figure 2a for the same data as 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 2b. For this particular example, the static and the active background methods provide essentially the same fit. As shown in the next section, this is not the case for most spectra.

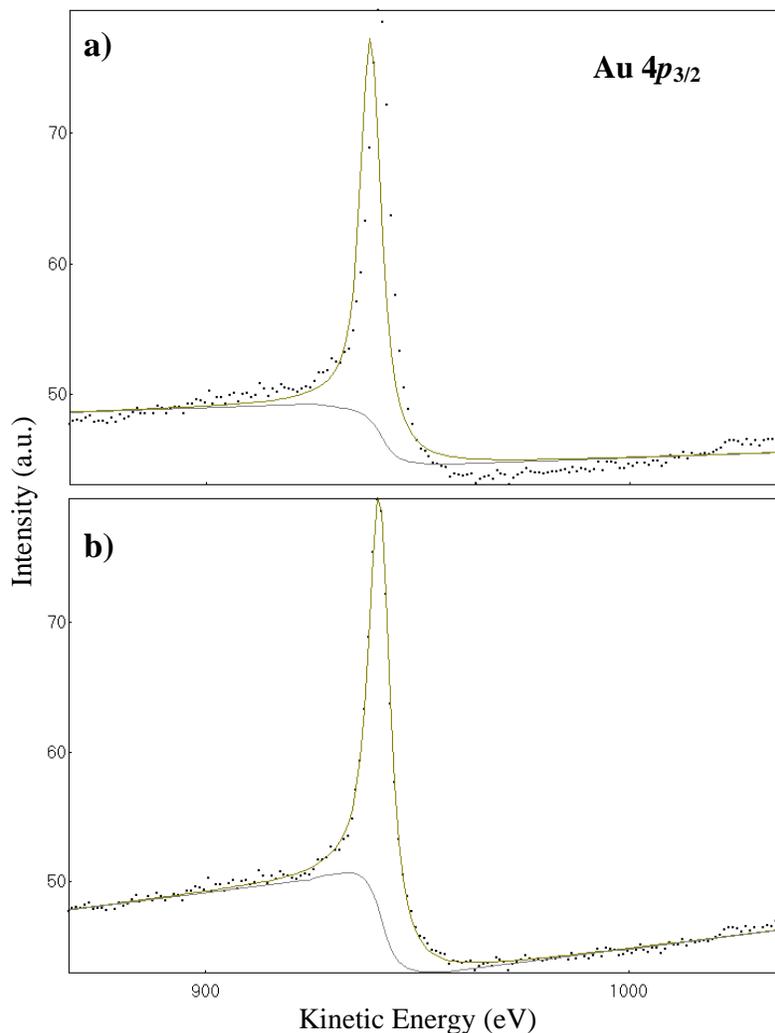


Figure 2. a) The same Au $4p_{3/2}$ spectrum as in Figure 1. Pictured is the first iteration of the *active* background fit illustrating how the background varies in an *active* manner responding to the position of the peak. The background is not the same as in (b), but it evolves to be the same as the fit is optimized. b) Optimized fit employing the active method. The background employed is the sum of a baseline, a linear term, and Shirley ($k_{\text{Shirley}} = 0.032 \text{ eV}^{-1}$). The slope of the background is the same on both sides of the peak. The fit is slightly better than in Figure 1a; the area 28.8 a.u., however, is slightly larger than in the static case (26.9 a.u.).

The *active* background method has been implemented in the software **AAnalyzer**[®].³ Under the active method, choosing various backgrounds to work simultaneously can be as easy as selecting the corresponding checkboxes. This is illustrated in Figure 3, which shows the parameters tab for the fit shown in Figure 2b. Note that the “Baseline” (constant term), “1st Order” (linear term), and “Shirley” backgrounds are chosen within the “Active Background” group box. The number of iterations for the Shirley background was set to six.

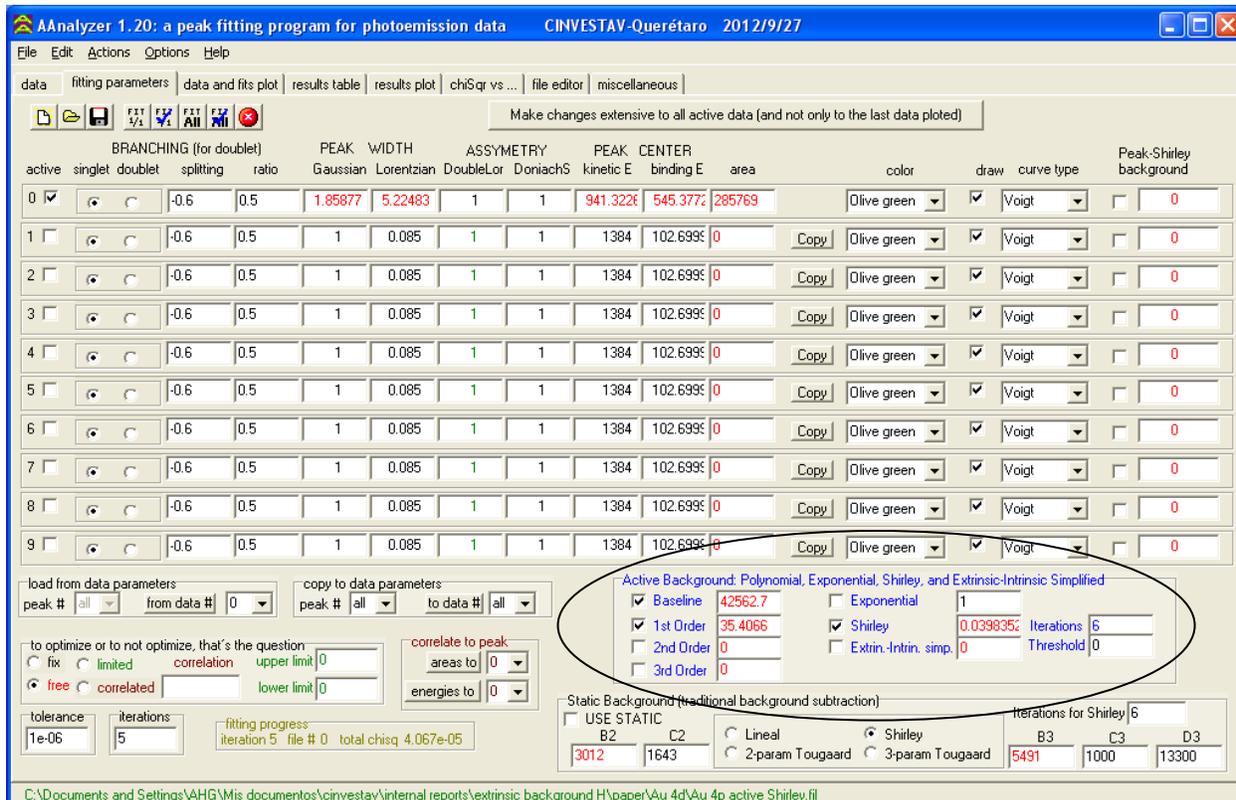


Figure 3. The “fitting parameters” tab of AAnalyzer, showing the parameters employed for the fit shown in Figure 1. As indicated in the box next to the Shirley parameter box, six iterations were employed to generate the background. This number was chosen since, generally, further iterations have negligible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

The implementation of the active background, and its importance, had been covered 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 background type, the Peak-Shirley background (last column in Figure 3), that can also be used in an active way. 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 and a detailed description can be found elsewhere.⁶

The *Extrinsic-Intrinsic Simplified* background is described in Reference ⁷, where it is shown 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 always better, and often 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, with the static method it is necessary to choose two points, one at each side of the spectrum features or peaks. The operator has to guarantee or assume that there is no appreciable contribution to the signal at those two points from any of the peaks. The method

does not allow the consideration of peaks that extend beyond either 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 peaks that extend beyond the chosen points. The active method should be employed when the data contains a peak that extends beyond the measurement range. 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 is well known, the traditional (static) 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 a simultaneous combination of backgrounds. For example, the strength of a linear 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 (linear, Shirley, Tougaard, etc.), or a fixed combination of them.
- When the background is subtracted before peak-fitting, the Poisson-character of the data is no longer applicable, so the uncertainty of the peak parameters cannot be calculated employing the covariant matrix method.⁹
- The operator might forget about the background once it has been subtracted, which can lead to errors in the static method. In the active method, the changing role of the background is accounted for as the operator considers other 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 look, both fitting methods, static and active, 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.

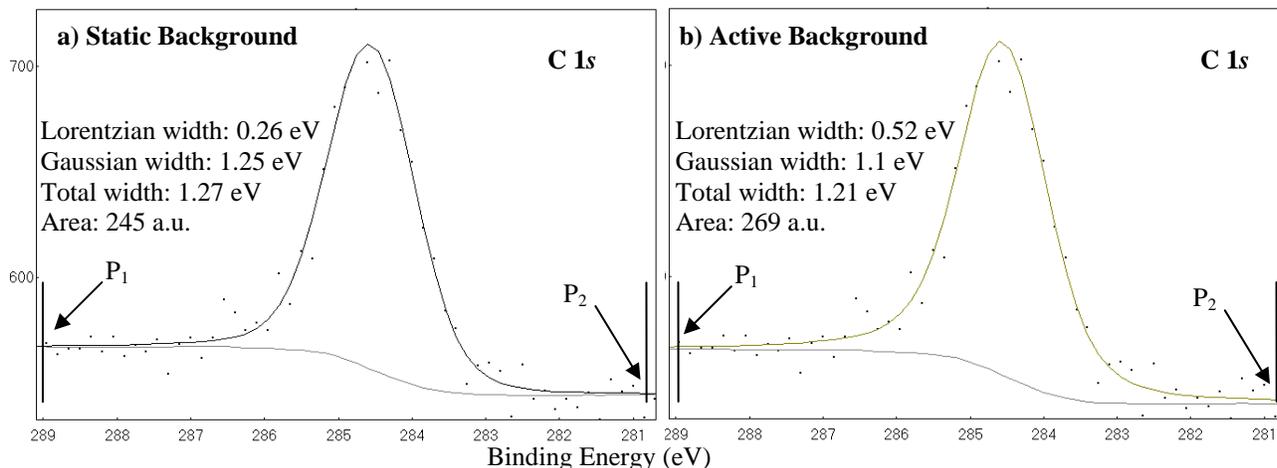


Figure 4. Fitting of a C 1s peak with the background treated a) using the static method (first subtracted and then fitted) and b) using the active method (optimized during the fitting process). Although the fits look equally good, the difference in the peak area is ~10%. The background is the main source of the difference. Using the active method, the background is allowed to go below the signal at the chosen end 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 be considerably prolonged. This is exemplified in Figure 5 with an Fe 2p spectrum. (The asymmetry in Figure 5 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 ratio restriction is applied (see inset in Figure 5a). Another important difference is that the ratio of the intensities of the oxidized and metallic peaks changes by 50%. This would directly affect the assessment of the thickness of the oxide layer by about that same percentage.

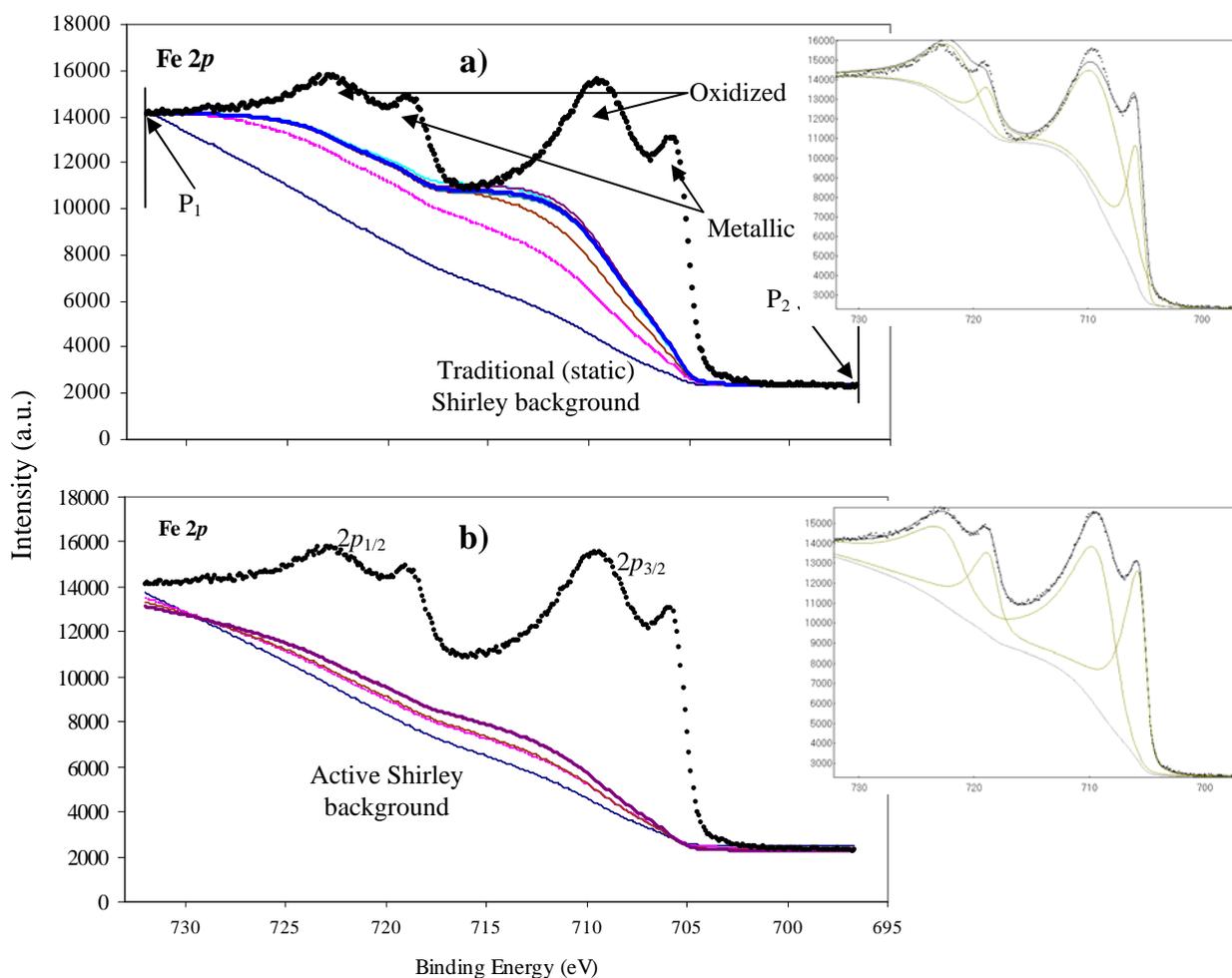


Figure 5. Fe 2*p* XPS spectrum from an iron substrate with a thin iron oxide layer. The Shirley background is shown for various iterations for the a) static method, and b) active method. The thicker lines correspond to the final convergence shape. The background takes longer to converge and arrives at a very different value with the static method. The reason is that, under this method, the background is obligated to go through the point P₁. The active method allows for the possibility that a peak could contribute to the signal at that position. This is indeed the case, as the data was acquired over an energy range that was not wide enough. The insets show that the fit is much better with the active than with the static method.

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

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

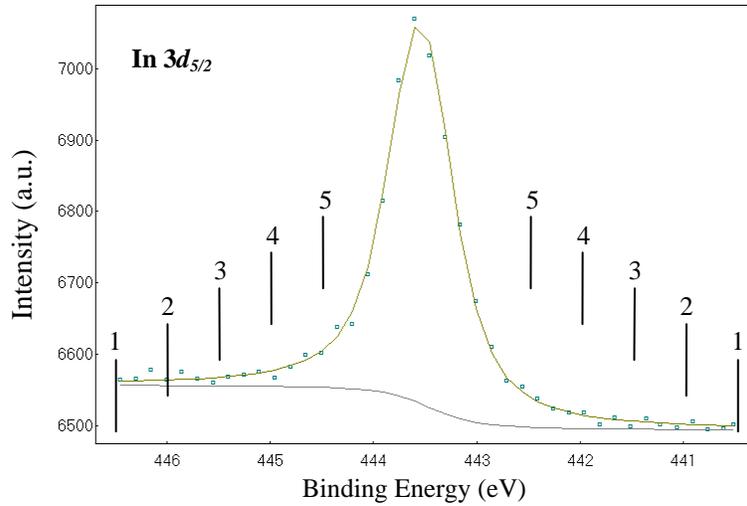


Figure 6. In $3d_{5/2}$ spectrum (dots). The pairs of vertical lines indicate the energy range over which peak-fitting was carried out. The results of the fits for the different energy ranges, and employing both the static and active background methods, are shown in Figure 7. In this figure, the lines correspond to the fit carried out employing the active background method and the energy range 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 peak height and the Lorentzian and Gaussian widths were allowed to vary during the analysis process to optimize the fit. Besides being underestimated, the area assessed with the static method has a large dependence on the fitting range. Likewise, the Lorentzian and Gaussian widths also show a large dispersion when the static method is employed.

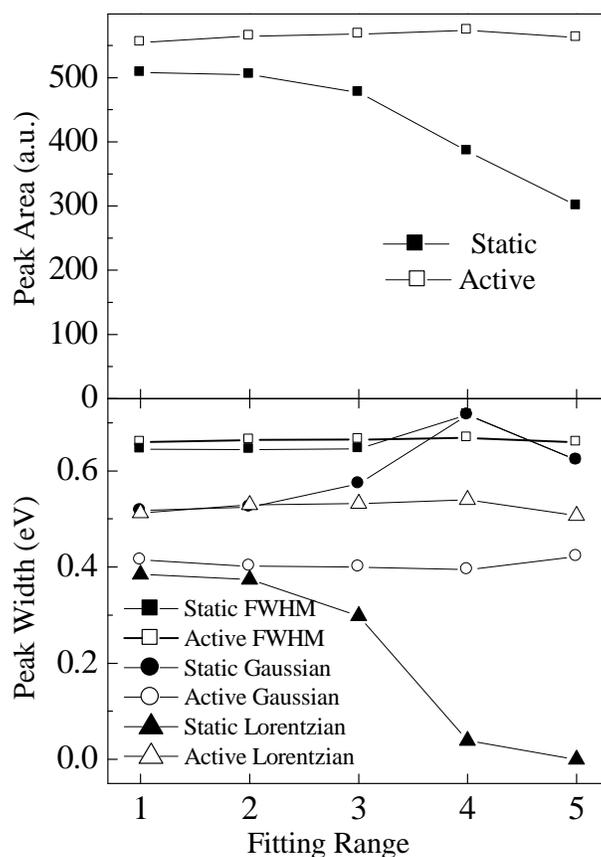


Figure 7. Results of the fits performed employing the static and active background methods for the data and energy ranges shown in Figure 6. The results employing the active method show much lower dispersion than with the static background method.

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 an Fe $2p$ spectrum from a clean iron surface. The static Shirley background does not converge and has large oscillations between even and odd iterations, whereas the active iterative-Shirley algorithm converges quickly to produce an excellent fit.

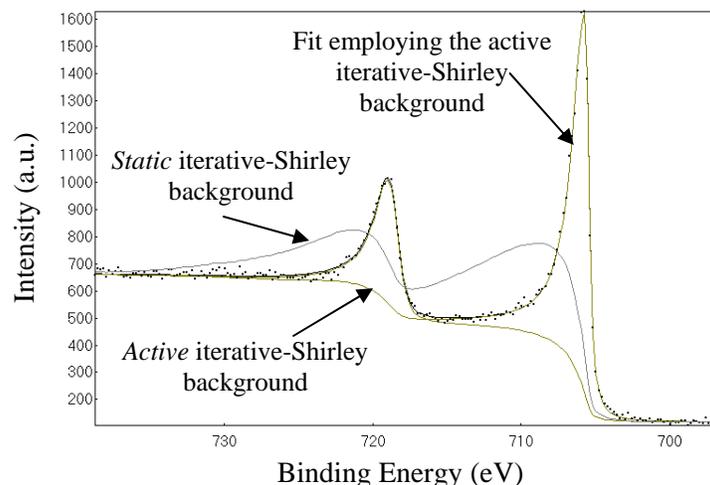


Figure 8. Fe 2*p* spectrum for a clean iron sample. It shows the lack of convergence of the traditional or static iterative-Shirley background method. The asymmetry was modeled with the Double-Lorentzian line shape.¹⁰

There are many advantages and no apparent drawbacks when the *active* method is employed instead of the traditional (*static*) background methodology. The active method provides better fits with much lower dependence on operator choices, such as the fitting energy range.

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