Instrumental technique

XPS peak fitting

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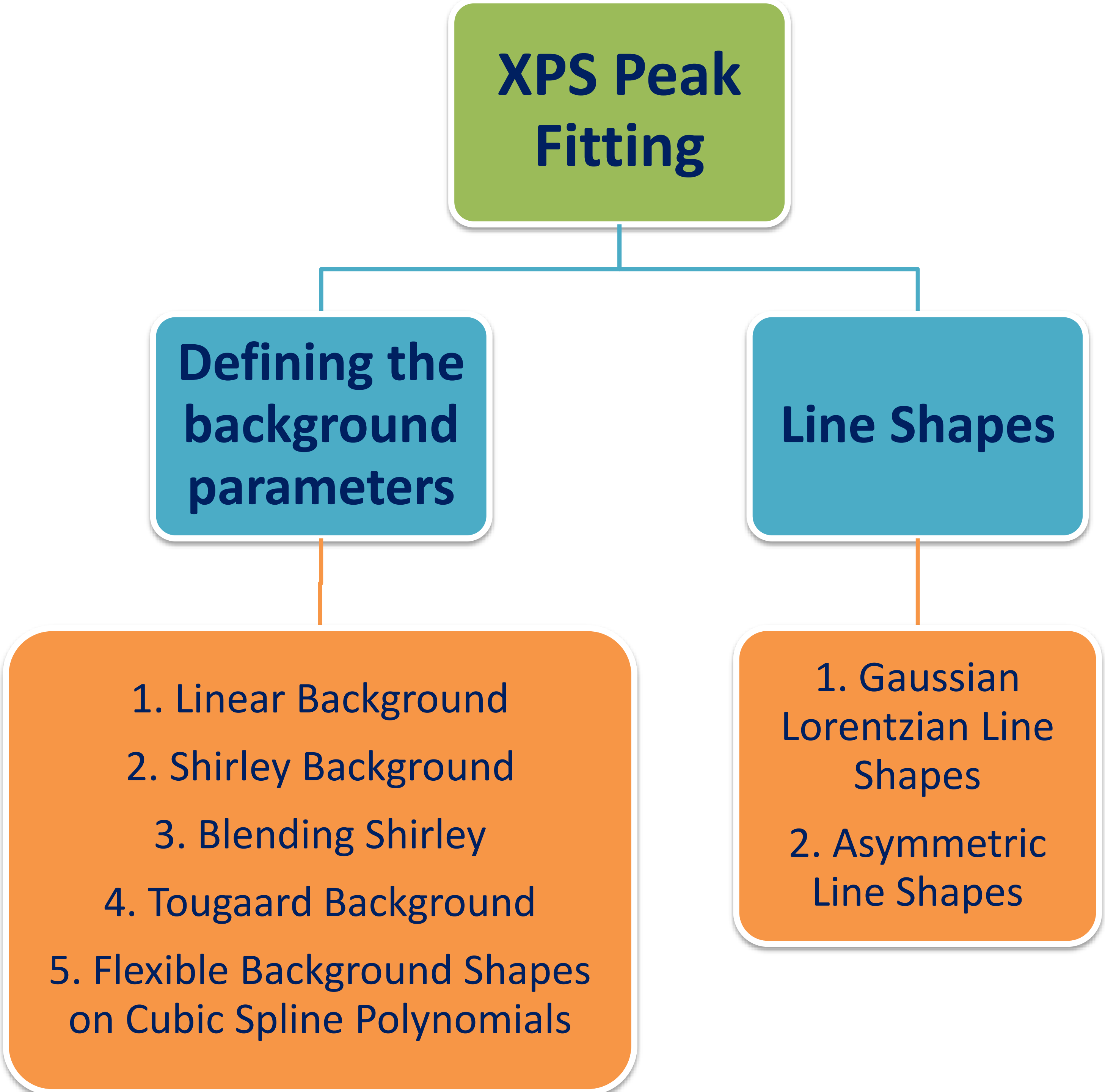
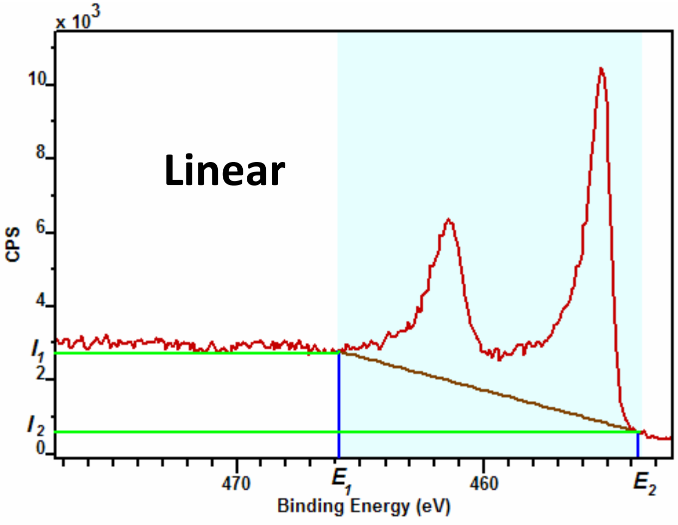
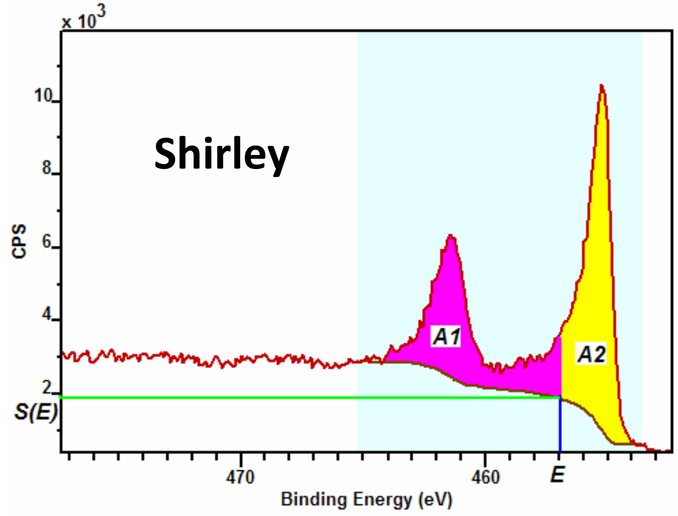
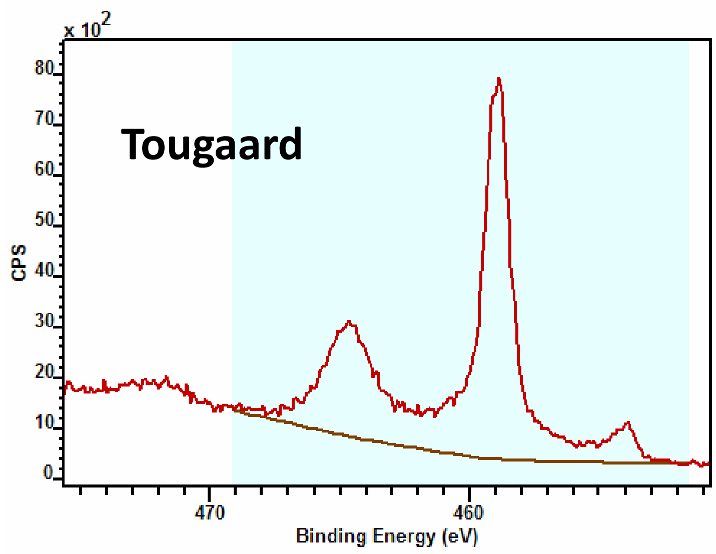

XPS Peak Fitting
Defining the background parameters
Line Shapes
1. Linear Background
2. Shirley Background
3. Blending Shirley
4. Tougaard Background
5. Flexible Background Shapes on Cubic Spline Polynomials
1. Gaussian Lorentzian Line Shapes
2. Asymmetric Line Shapes

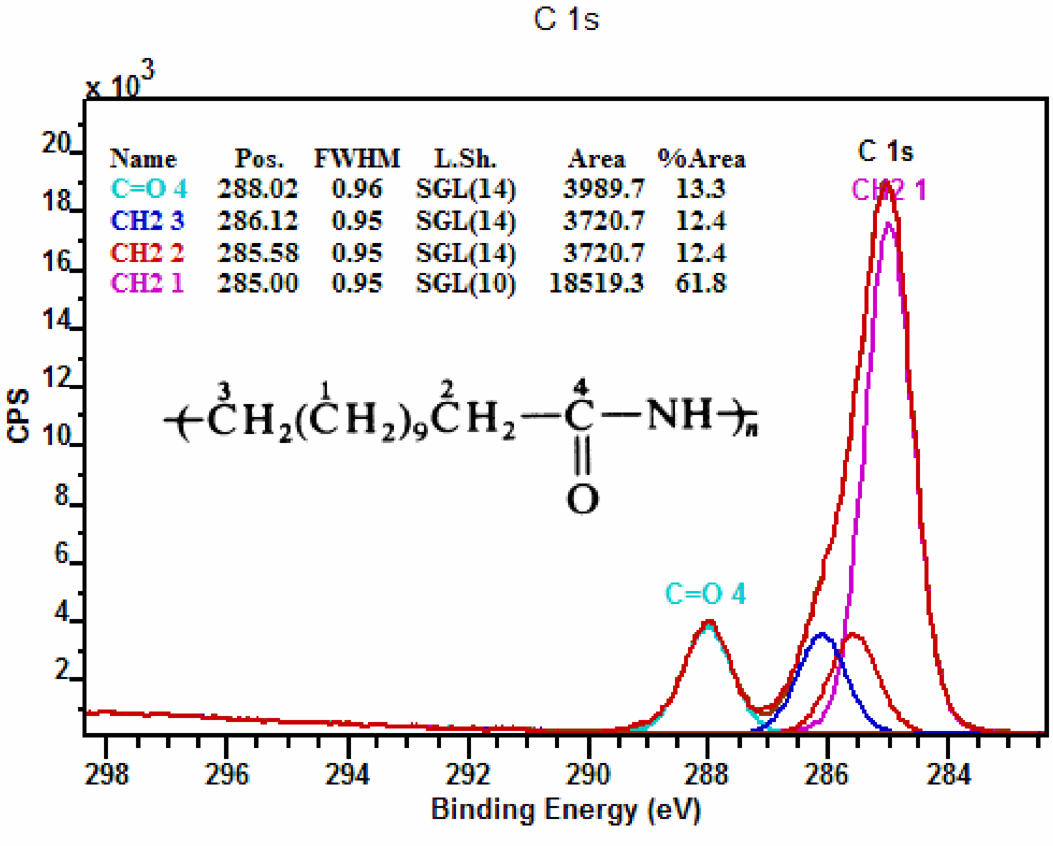
An comparison between commonly used peak background







Why peak fitting is essential tool for XPS data analysis?



-Backgrounds to spectra containing both doublet pairs coupled with a variety of chemical shifts represent the greatest challenge to modeling XPS spectra.

- All the peaks modeled in Figure 1 are due to chemical shifts. Electrons ejected from s-subshells generally appear as chemically shifted primary peaks.

Figure 1: C 1s region measured from a nylon sample.

Linear Background (I)

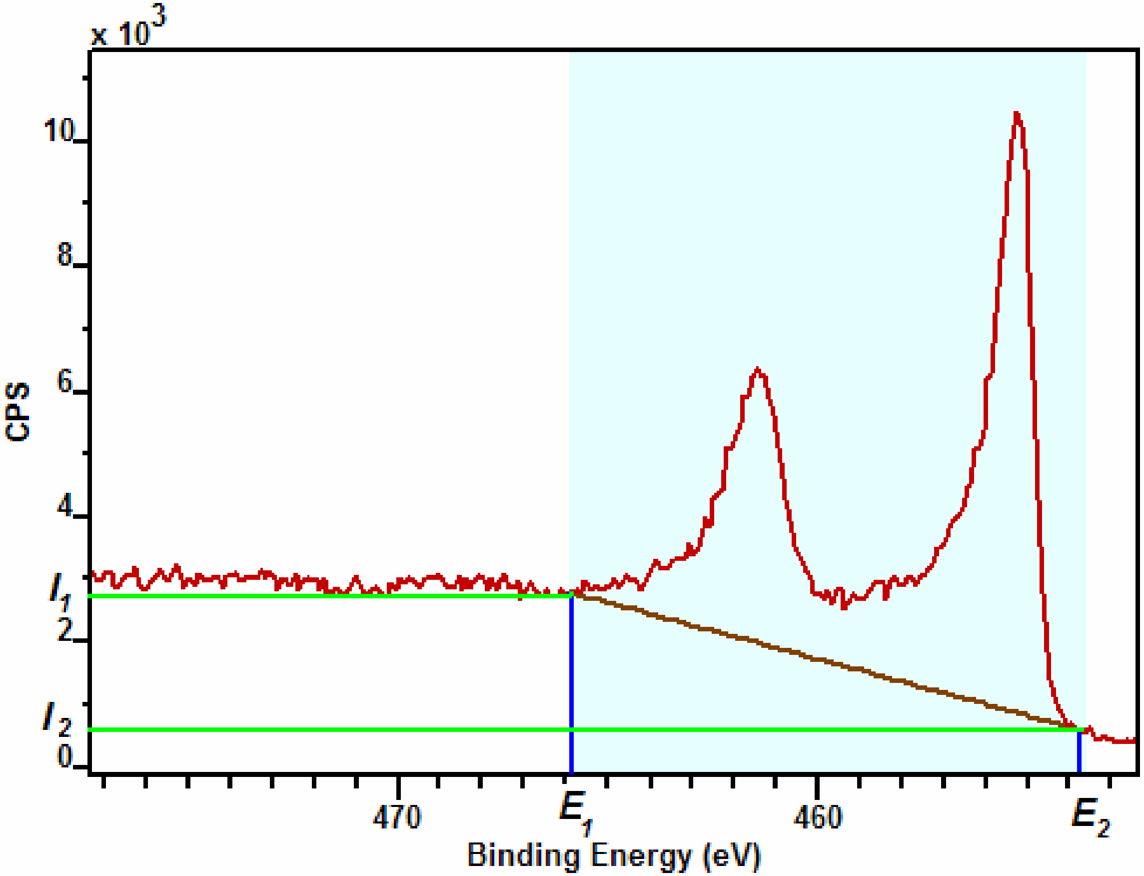


Figure 2: Example of a linear background type applied to a Ti 2p doublet pair.

- C 1s peaks can be approximated by a linear background type:

$$L(E) = I_1 \frac{(E_2 - E)}{(E_2 - E_1)} + I_2 \frac{(E - E_1)}{(E_2 - E_1)}$$

Where:

E_1 and E_2 are two distinct energies and I_1 and I_2 are two intensity values

Shirley Background (S)

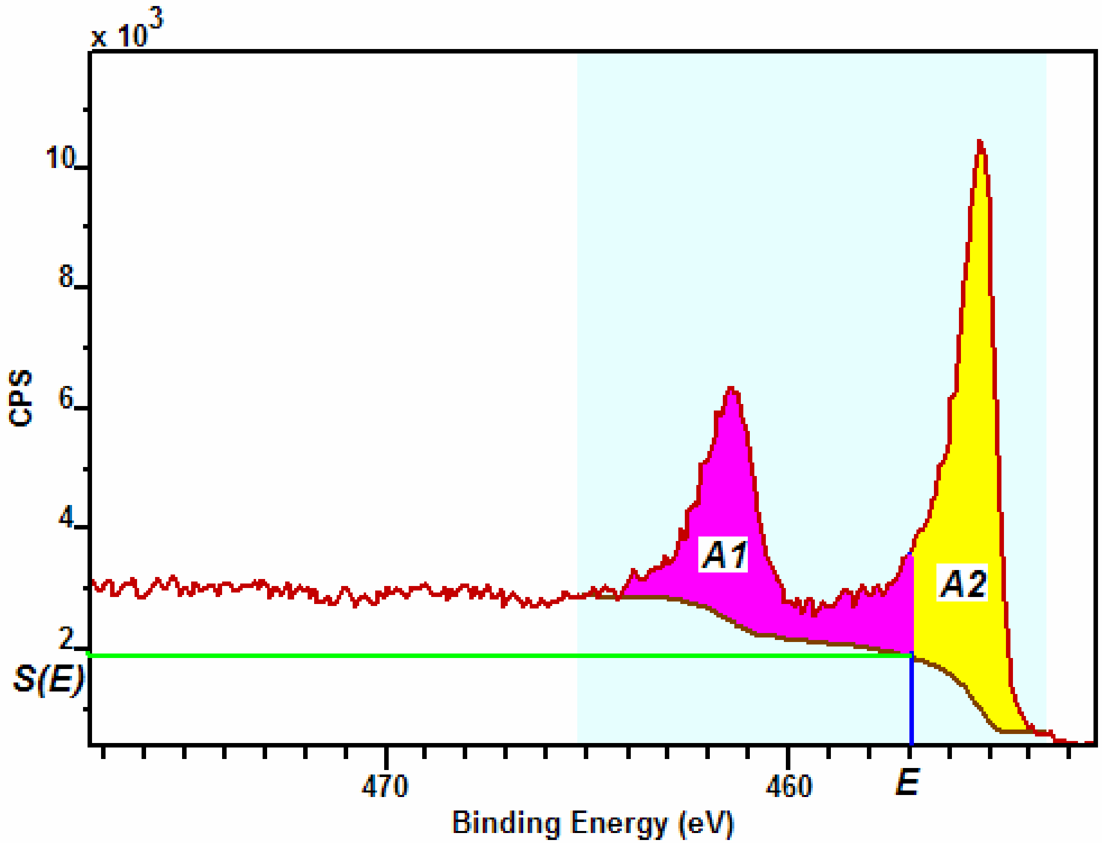


Figure 3: A Shirley background computed from a Ti 2p spectrum.

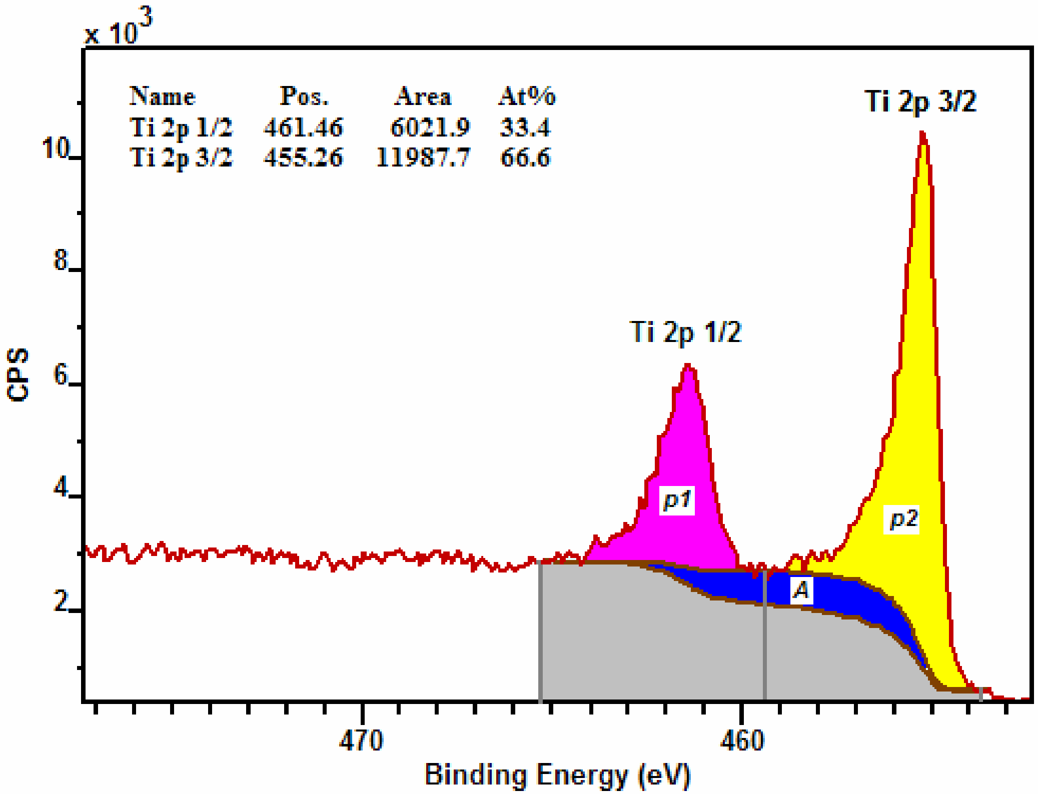
-The Shirley algorithm uses information about the spectrum to construct a background sensitive to changed in the data.

-The essential feature of the Shirley algorithm is the iterative determination of a background using the areas marked A1 and A2 to compute the background intensity S(E) at energy E:

$$S(E) = I_2 + \kappa \frac{A2(E)}{(A1(E) + A2(E))}$$

Where κ is $(I_2 - I_1)$

Some problems encountered during shirley background usage



-A common problem with using a Shirley background over such an extended range is that the algorithm produces a background curve that cuts through the data.

Figure 4: Metallic Ti modeled using two regions each defining a Shirley background (upper curve). The lower background curve is the Shirley background computed using the combined peaks. The At% column is computed using an RSF of unity for both peaks in the doublet pair, hence the 1:2 ratio in peak areas p1 and p2.

Blending Shirley and Linear Backgrounds (OS)

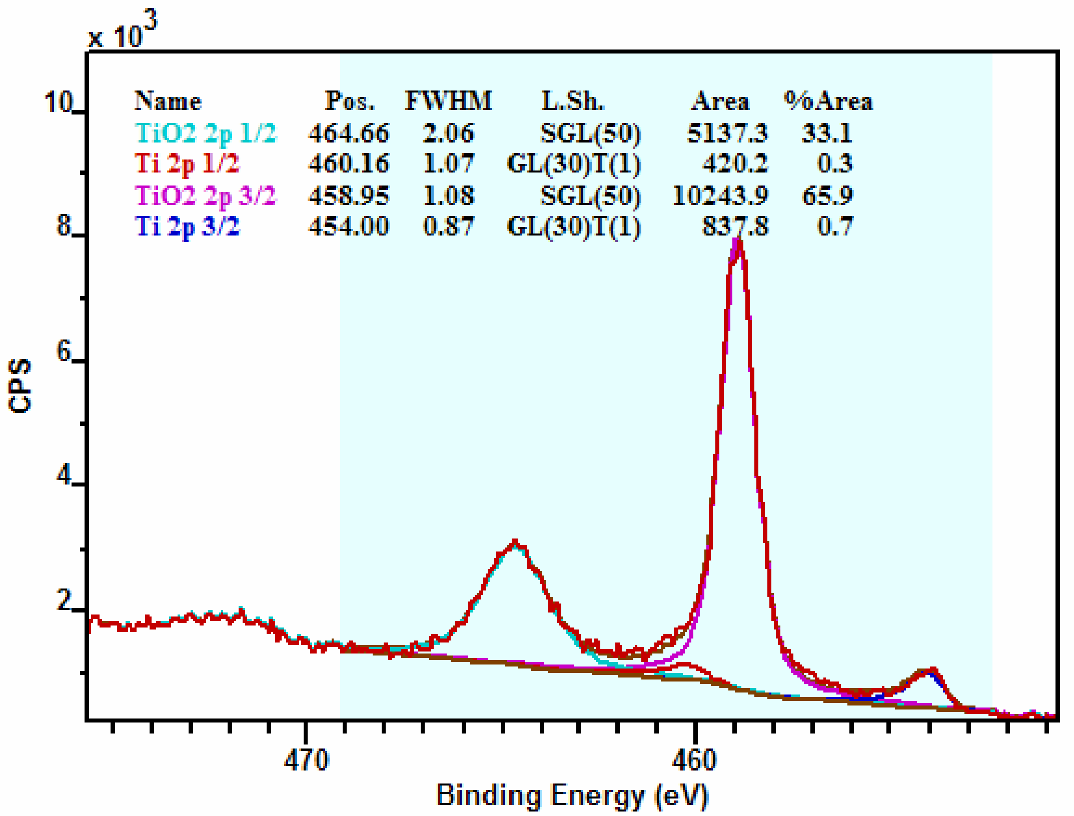


Figure 5: Chemically shifted Ti 2p doublet pairs.

-Use of a pure linear or a pure Shirley background over the same interval would require the intensity ratio to be violated and as such represents a less wrong solution used when peak fitting the data.

The background for OS is calculated from a blend of a Shirley and linear backgrounds:

$$OS(E:\lambda,\delta) = S(E-\delta)(1-\lambda) + L(E)\lambda$$

Tougaard Background (t)

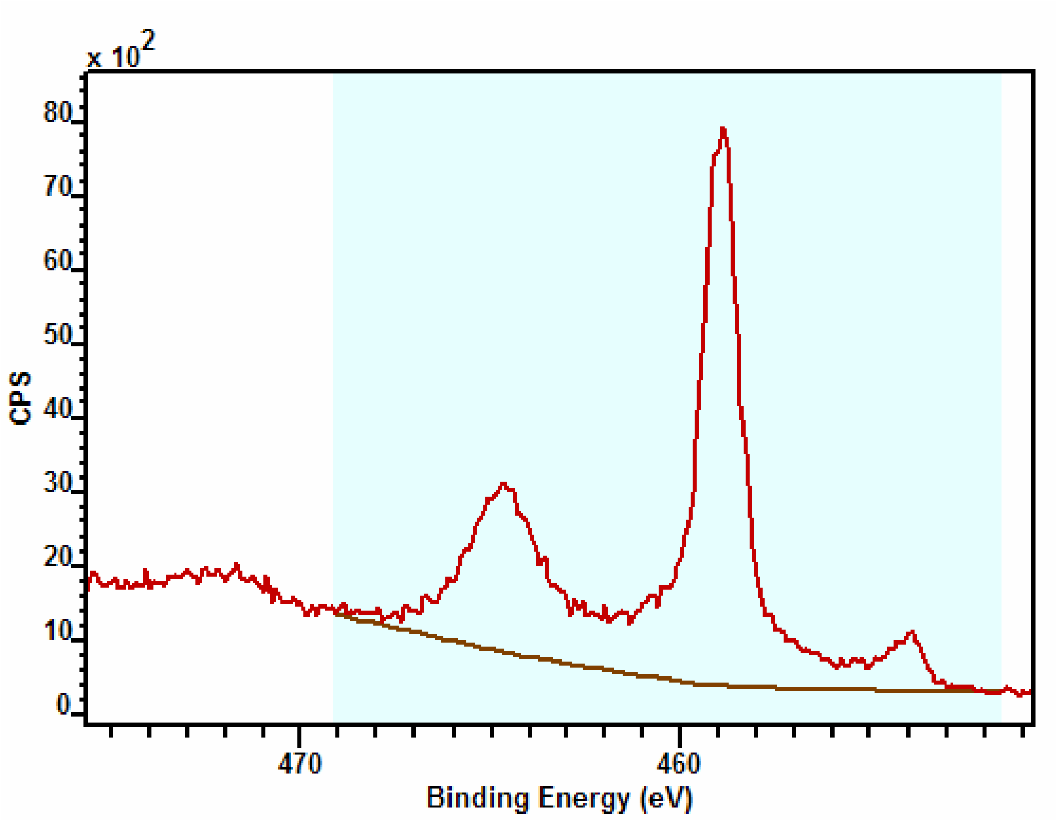


Figure 6: Universal Cross Section Tougaard background.

-Tougaard was designed as a practical background for general use and as such is almost certainly as incorrect as the Shirley and linear background types.

-The background is computed from the measured spectrum S(E) using the integral:

$$T(E) = \int_{E}^{\infty} F(E' - E) S(E') dE' .$$

Flexible Background Shapes based on Cubic Spline Polynomials

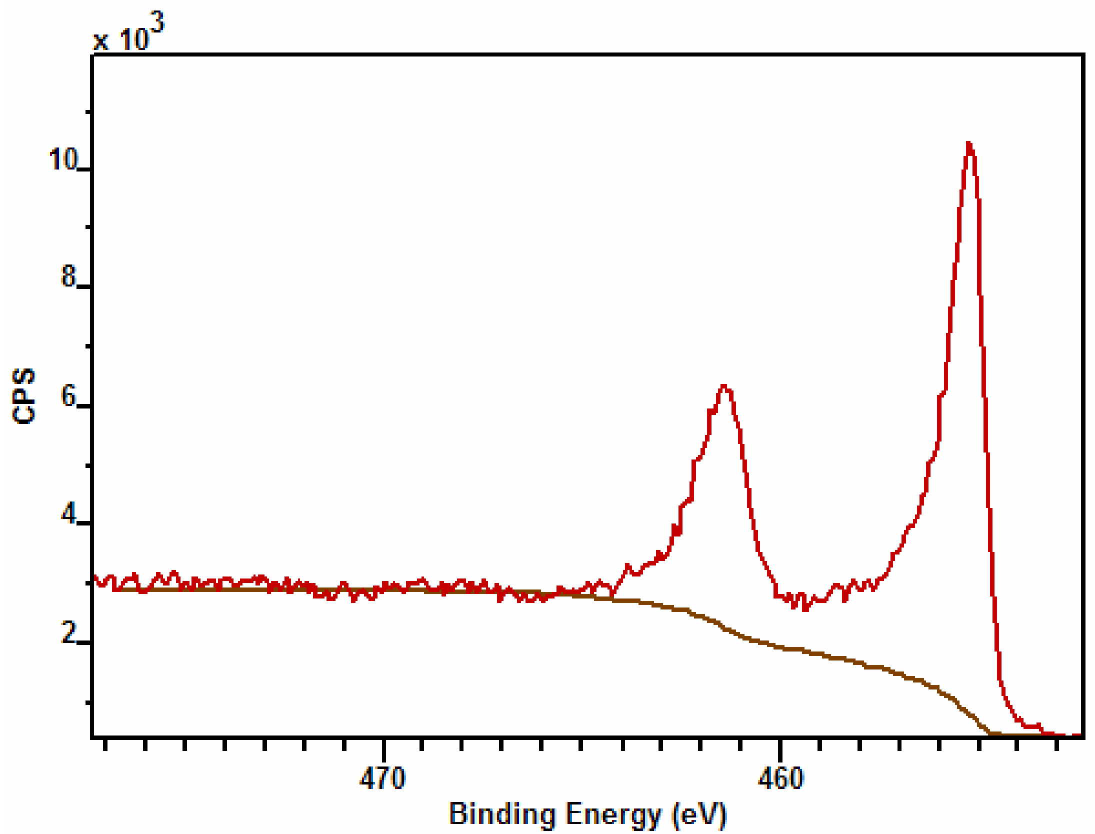


Figure 7: An E Tougaard background showing remarkable similarity to a Shirley background shape. The background shape is achieved by adopting a very broad Gaussian loss structure.

Thank you ☺