

Basic Quantification of XPS Spectra

XPS counts electrons ejected from a sample surface when irradiated by x-rays. A spectrum representing the number of electrons recorded at a sequence of energies includes both a contribution from a background signal and also resonance peaks characteristic of the bound states of the electrons in the surface atoms. The resonance peaks above the background are the significant features in an XPS spectrum (Figure 1).

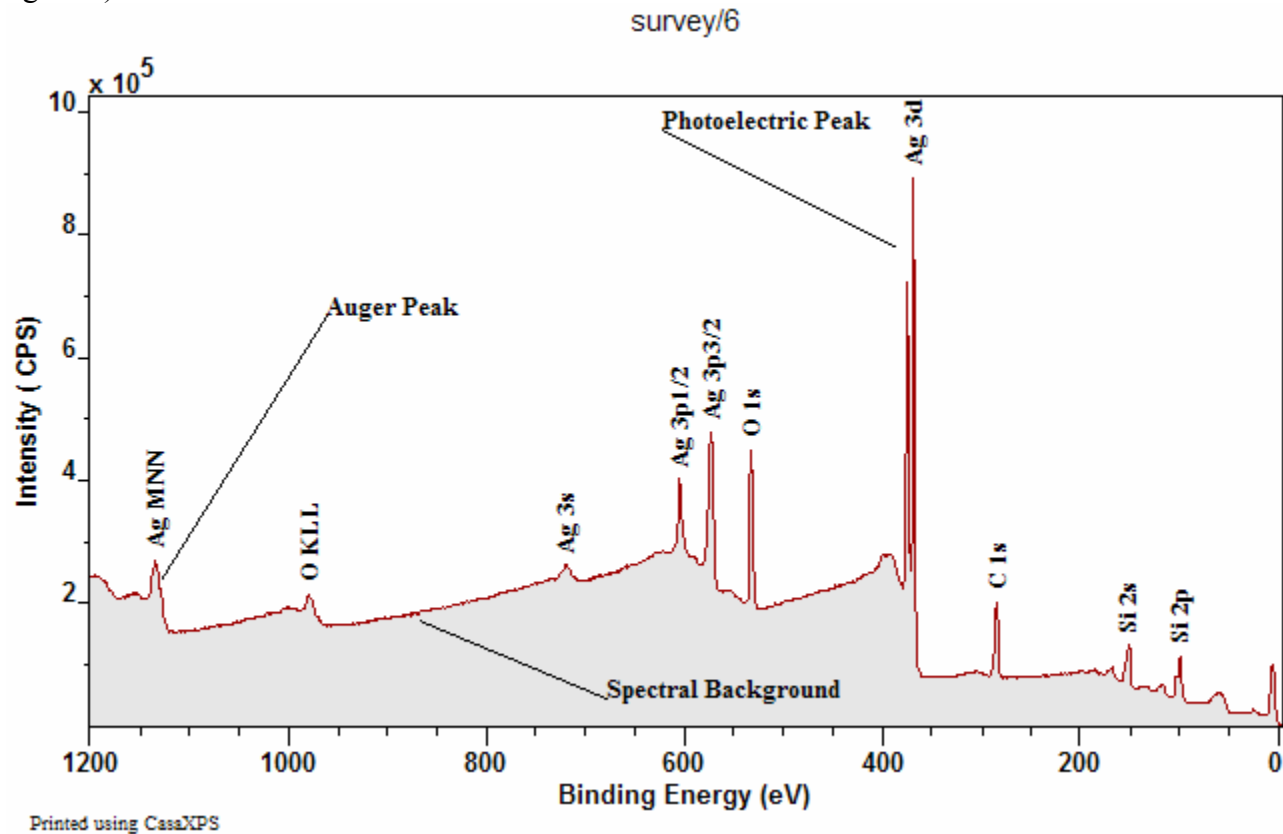


Figure 1: XPS and Auger peaks appear above a background of scattered electrons.

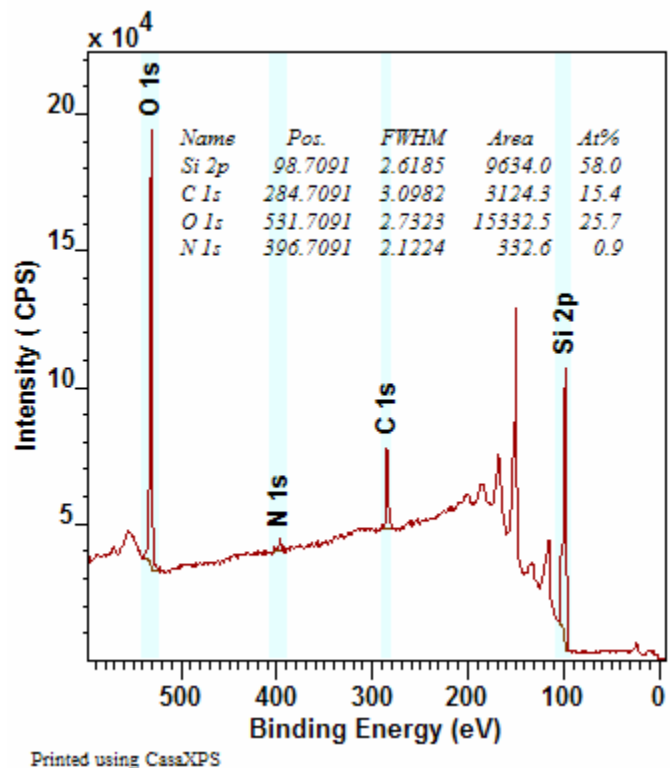


Figure 2: Quantification regions

XPS spectra are, for the most part, quantified in terms of peak intensities and peak positions. The peak intensities measure how much of a material is at the surface, while the peak positions indicate the elemental and chemical composition.

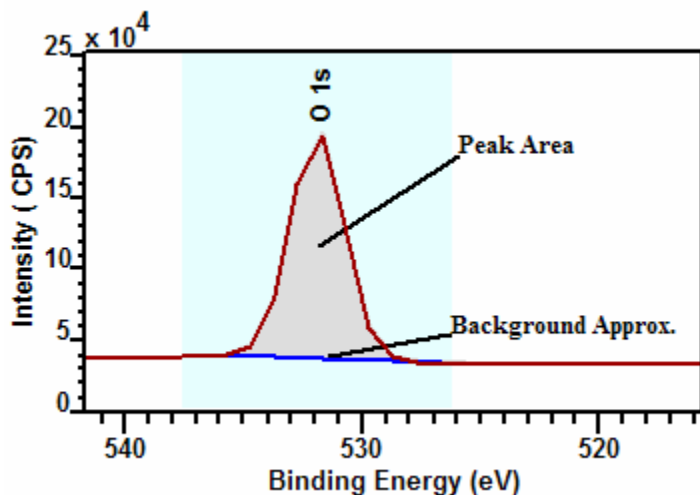
Other values, such as the full width at half maximum (FWHM) are useful indicators of chemical state changes and physical influences. That is, broadening of a peak may indicate: a change in the number of chemical bonds contributing to a peak shape, a change in the sample condition (x-ray damage) and/or differential charging of the surface (localised differences in the charge state of the surface).

The underlying assumption when quantifying XPS spectra is that the number of electrons recorded is proportional to the number of atoms in a given state. The basic tool for measuring the number of electrons recorded for an atomic state is the quantification region. Figure 2 illustrates a survey spectrum where the surface is characterised using a quantification table based upon values computed from regions. The primary objectives of the quantification region are to define the range of energies over which the signal can be attributed to the transition of interest and to specify the type of approximation appropriate for the removal of background signal not belonging to the peak.

How to Compare Samples

A direct comparison of peak areas is not a recommended means of comparing samples for the following reasons. An XPS spectrum is a combination of the number of electrons leaving the sample surface and the ability of the instrumentation to record these electrons; not all the electrons emitted from the sample are recorded by the instrument. Further, the efficiency with which emitted electrons are

recorded depends on the kinetic energy of the electrons, which in turn depends on the operating mode of the instrument. As a result, the best way to compare XPS intensities is via, so called, percentage atomic concentrations. The key feature of these percentage atomic concentrations is the representation of the intensities as a percentage, that is, the ratio of the intensity to the total intensity of electrons in the measurement. Should the experimental conditions change in anyway between measurements, for example the x-ray gun power output, then peak intensities would change in an absolute sense, but all else being equal, would remain constant in relative terms.



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Figure 3: O 1s Region

Quantification Parameters

Regions | Components | Data Editor | Report Spec. | RPT Report

survey/3 Calc Max

Regions	A	B	C	D
Name	Si 2p	C 1s	O 1s	N 1s
R.S.F.	0.817	1	2.93	1.8
Start	107.681	290.883	539.7	407.179
End	92.0543	279.378	522.516	389.065
BG Type	Shirley	Shirley	Shirley	Linear
Av. Width	0	0	0	2
St. Offset	0	0	0	0
End Offset	0	0	0	0
Cross Se...	299, 54...	299, ...	299, 5...	299, 542...
Tag	Si 2p	C 1s	O 1s	N 1s
Area	9634.0	3124.3	15332.5	332.6
Std Dev ...	0	0	0	0
fwhm	2.61846	3.09819	2.73225	2.12241
Position	98.7091	284.709	531.709	396.709
% Conce...	57.99	15.37	25.73	0.91
Max Height	101708.5	29472.1	16005...	4107.5
Min Height	-268.6	0.0	0.0	-945.4
Peak to ...	58.95	13.92	25.80	1.33

Create Calculate Error Bars Delete

Create From Labels Save Regions ... Copy and Paste

Intensity Calibration

Automatic Update

STO RCL RST

Figure 4: Regions Property Page.

Relative Intensity of Peaks in XPS

Each element has a range of electronic states open to excitation by the x-rays. For an element such as silicon, both the Si 2s and Si 2p transitions are of suitable intensity for use in quantification. The rule for selecting a transition is to choose the transition for a given element for which the peak area is the largest, subject to the peak being free from other interfering peaks.

Transitions from different electronic states from the same element vary in peak area. Therefore, the peak areas calculated from the data must be scaled to ensure the same quantity of silicon, say, is determined from either the Si 2s or the Si 2p transitions. More generally, the peak areas for transitions from different elements must be scaled too. A set of relative sensitivity factors are necessary for transitions within an element and also for all elements, where the sensitivity factors are designed to scale the measured areas so that meaningful atomic concentrations can be obtained, regardless of the peak chosen.

Quantification of the spectrum in Figure 2 requires the selection of one transition per element. Figure 3 illustrates the area targeted by the region defined for the O 1s transition; similar regions are defined for the C 1s, N 1s and Si 2p transitions leading to the quantification table displayed over the data in Figure 2. The Regions property page shown in Figure 4 provides the basic mechanism for creating and updating the region parameters influencing the computed peak area. Relative sensitivity factors are also entered on the Regions property page. The computed intensities are adjusted for

instrument transmission and escape depth corrections, resulting in the displayed quantification table in Figure 2.

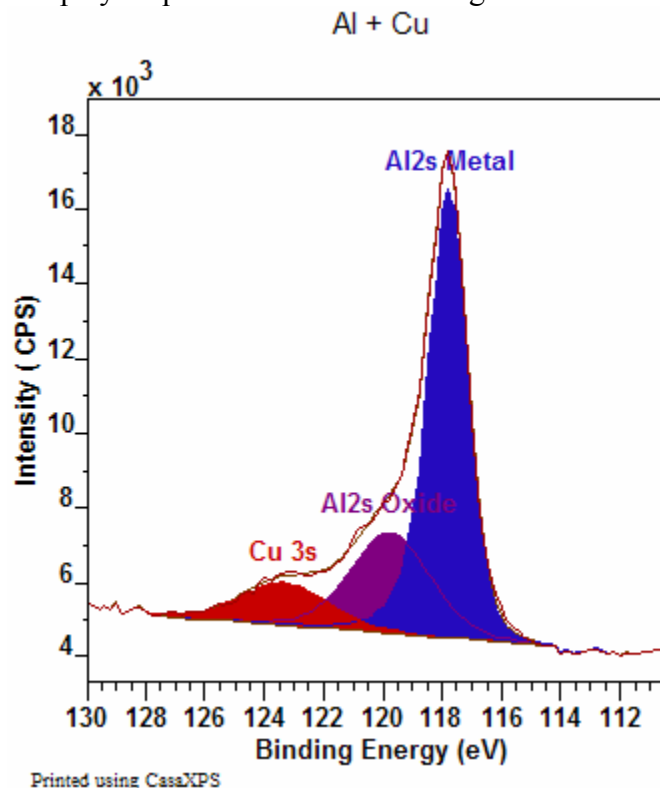


Figure 5: Aluminium and Copper both in evidence at the surface.

Quantification regions are useful for isolated peaks, however not all samples will offer clearly resolved peaks. A typical example of interfering peaks is any material containing both aluminium and copper. When using the standard magnesium or aluminium x-ray anodes, the only aluminium photoelectric

peaks available for measuring the amount of aluminium in the sample are Al 2s and Al 2p. Unfortunately, both aluminium peaks appear at almost the same binding energy as the Cu 3s and Cu 3p transitions, therefore estimating the intensity of the aluminium in the sample requires a means of modelling the data envelope resulting from these overlapping transitions illustrated in Figure 5.

Overlapping Peaks

Techniques for modelling data envelopes not only apply to separating elemental information, such as the copper and aluminium intensities in Figure 5, but also apply to chemical state information about the aluminium itself. Intensities for the aluminium oxide and metallic states in Figure 5 are measured using synthetic line-shapes or components. An XPS spectrum typically include multiple transitions for each element; while useful to identify the composition of the sample, the abundance of transitions frequently lead to interference between peaks and therefore introduces the need to construct peak models. Figure 6 illustrates a spectrum where a thin layer of silver on silicon (University of Iowa, Jukna, Baltrusaitis and Virzonis, 2007, unpublished work) introduces an interference with the Si 2p transition from the Ag 4s transition.

The subject of peak-fitting data is complex. A model is typically created from a set of Gaussian/Lorentzian line-shapes, however without careful construction involving parameter constraints, the resulting fit, regardless of how accurate a representation of the data, may be of no significance from a physical perspective. The subject of peak fitting XPS spectra is dealt with in detail elsewhere.

Peak models are created using the Components property page on the Quantification Parameters dialog window shown in Figure 7. A range of line-shapes are available for constructing the peak models including both symmetric and asymmetric functional forms. The intensities modelled using these synthetic line-shapes are scaled using RSFs and quantification using both components and regions are offered on the Report Spec property page of CasaXPS.

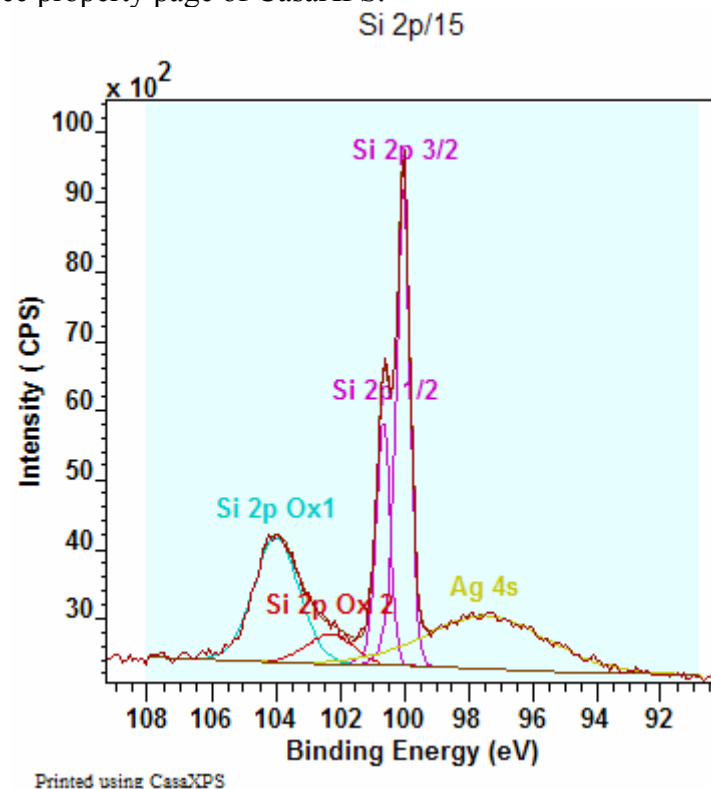


Figure 6: Elemental and oxide states of Silicon

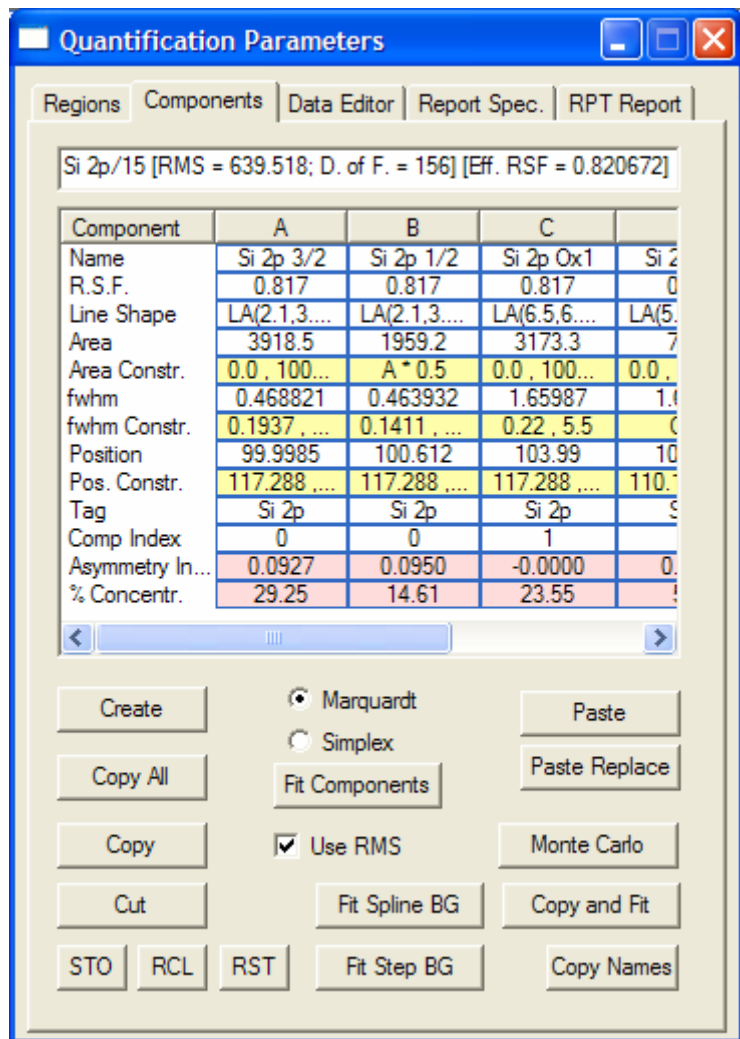


Figure 7: Components property page on the Quantification Parameters dialog window.

Peak Positions

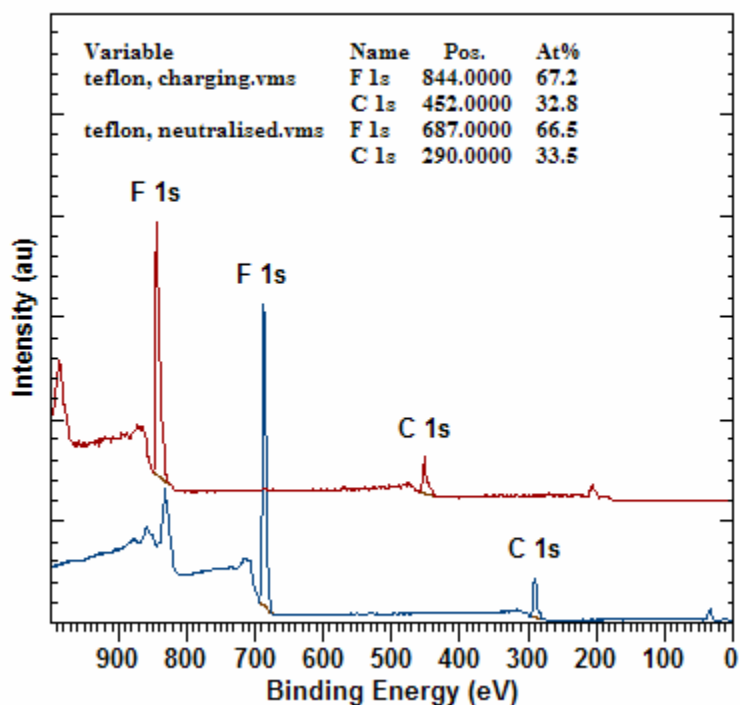
In principle, the peak positions in terms of binding energy provide information about the chemical state for a material. The data in Figure 6 provides evidence for at least three chemical states of silicon. Possible candidates for these silicon states might be SiO₂, Si₂O₃, SiO, Si₂O or Si, however an assignment based purely on the measured binding energies for the synthetic line-shapes relies on an accurate calibration for the energy scale. Further, the ability to calibrate the energy scale is dependent on the success of the charge compensation for the sample and the availability of a peak at known binding energy to provide a reference for shifting the energy scale.

Charge Compensation

The XPS technique relies on electrons leaving the sample. Unless these emitted electrons are replaced, the sample will charge relative to the instrument causing a retarding electric field at the sample surface. For conducting samples electrically connected to the instrument, the charge balance is easily restored, however for insulating materials electrons must be replaced via an external source. Insulating samples are normally electrically isolated from the instrument and low energy electrons and/or ions are introduced at the sample surface. The objective is to replace the photoelectrons to provide a steady state electrical environment from which the energy of the photoelectrons can be measured.

The data in Figure 8 shows spectra from PTFE (Teflon) acquired with and without charge compensation. The C 1s peaks are shifted by 162 eV between the two acquisition

conditions, but even more importantly, the separation between the C 1s and the F 1s peaks differs between the two spectra by 5 eV. Without effective charge compensation, the measured energy for a photoelectric line may change as a function of kinetic energy of the electrons.



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Figure 8: Insulating sample before and after charge compensation.

Charge compensation does not necessarily mean neutralization of the sample surface. The objective is to stabilize the sample surface to ensure the best peak shape, whilst also ensuring peak separation between transitions is independent of the energy at which the electrons are measured. Achieving a correct binding energy for a known transition is not necessarily the best indicator of good charge compensation. A properly charge compensated experiment typically requires shifting in binding energy using the Calibration property page, but the peak shapes are good and the relative peak positions are stable.

A nominally conducting material may need to be treated as an insulating sample. Oxide layers on metallic materials can transform a conducting material into an insulated surface. For example, aluminium metal oxidizes even in vacuum and a thin oxide layer behaves as an insulator.

Calibrating spectra in CasaXPS is performed using the Calibration property page on the Spectrum Processing dialog window.