A Beginners Guide to XPS

XPS Instrumentation

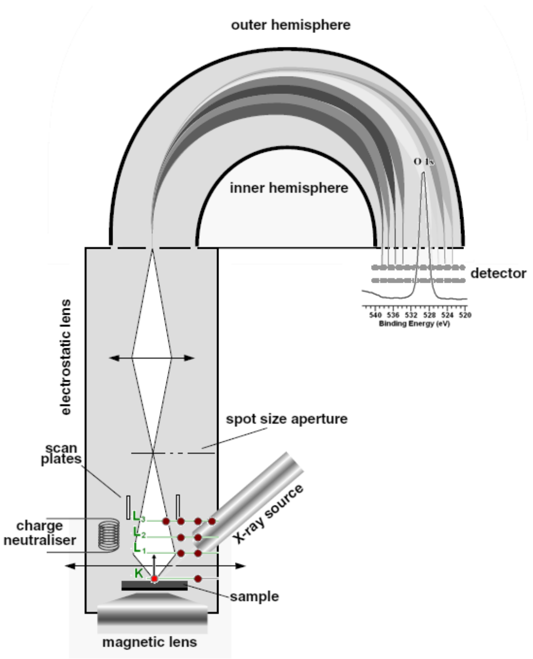

outer hemisphere
inner hemisphere
O 1s
detector
540 536 532 528 524 520
Binding Energy (eV)
electrostatic lens
spot size aperture
scan plates
charge neutraliser
L_3
L_2
L_1
K
X-ray source
sample
magnetic lens

Figure 1: Schematic of an XPS instrument.

Photoemission occurs when photon energy is transferred to electrons within bound-states of atoms causing the electron to gain sufficient kinetic energy to escape into the vacuum chamber.

An XPS instrument (Figure 1) includes an

1. Vacuum chamber to allow the free movement of electrons emitted from a sample.
2. An x-ray source to provide photons of a known energy.
3. An energy analyser, the function of which is to allow electrons with a given kinetic energy to pass through to a detection system.
4. A transfer lens system to gather photoelectrons and focus the electron beam into an energy analyser.
5. A charge compensation mechanism used to prevent a dynamic build-up of negative charge at the sample position which would result from the photoemission of electrons.
6. A stage for positioning the sample beneath the x-ray flux such that photoemission can be measured by the detectors after passing through both the lens and analyser components of the instrument.

An x-ray photoelectron spectrum is a sequence of measurements, where each measurement records the numbers electrons of a given energy for a specific time interval. The objective is to measure counts per second (CPS) as a function of kinetic energy (eV) of emission for electrons from atoms in the surface material. Measured in units of CPSeV, variation in intensity for electrons with differing emission energies provides a means for characterising the electronic state of atoms within the sample from which electrons are emitted and offers quantifiable information about the surface composition.

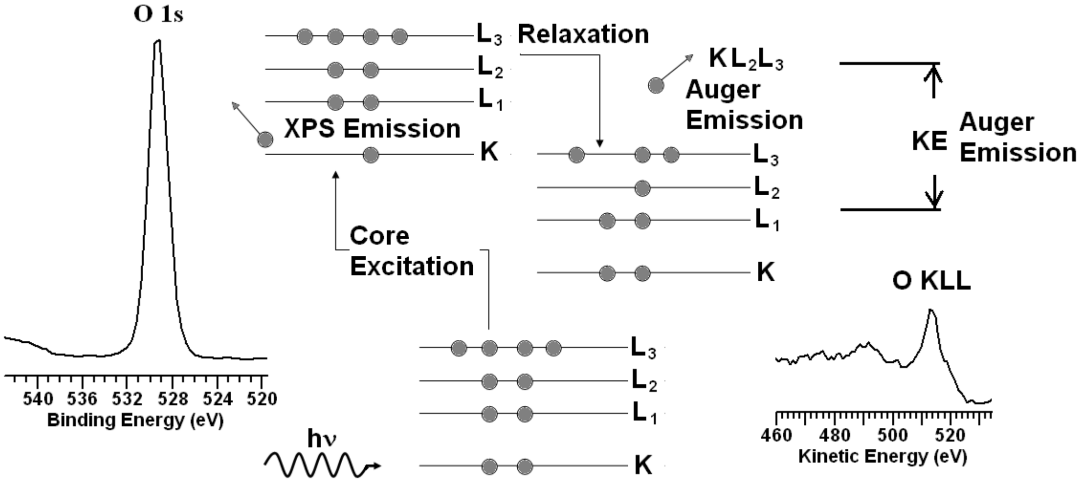


Figure 2: Excitation of core-level K-shell electron by photoionisation.

XPS instrumentation measures the kinetic energy $E_{ke}$for the photoelectrons. Electrons within atoms are characterised by an internally referenced binding energy E_{be} determined by the chemical environment for an atom. In the case of electrons emitted from bound states of atoms in an ideal conducting sample, the kinetic energy, the binding energy E_{be} and the photon energy $h\nu$ for an instrument with work function ϕ is given by

$$E_{ke} = h\nu - E_{be} - \phi$$

The key point here is the energy fundamental to excitation by photons measured by XPS instrumentation is kinetic energy. For photoelectron primary peaks the kinetic energy for these peaks, from the perspective of the instrument, changes with photon energy. From the perspective of the material analysed, sampling depth (see below) is also dependent on kinetic energy for the electrons, so changing the photon energy also changes the potential volume of sample from which primary photoemission is measured. Nevertheless, the kinetic energy for the photo-emitted electrons at point of excitation determines the depth from within the sample emission can be recorded. While binding energy is of primary interest to the analyst, understanding the influence of kinetic energy on instruments and samples is important for a successful measurement.

For the case of Auger emission (Figure 2), the relationship between the excitation source and the kinetic energy for the emitted electron is lost. Auger emission due to photoionisation generates electron emission with kinetic energy determined not by the photon energy, but by the difference between two bound electron states of the ion resulting from photoemission. Following the convention in XPS to use positive values for binding energy, the kinetic energy for Auger photoemission measured by an XPS instrument is

$$E_{ke} = -(E_{be}[Initial] - E_{be}[Final]) - \phi$$

Both $E_{be}[Initial]$ and $E_{be}[Final]$ are binding energies for ions created by photoionisation and are therefore absolute energies characteristic of these ions independent of the ionizing radiation energy.

Photoemission by the Auger process and photoemission by direct coupling of photons with bound states of atoms means changing the photon energy when measuring equivalent samples results in a shift in relative energy for photoemission lines from these two different sources for peaks in an XP spectrum.

Surface Sensitivity and Sampling Depth

XPS is a **surface sensitive** technique. That is to say, photoemission without energy loss is restricted to the top few nanometres of the interface between the sample and the vacuum. While x-rays penetrate the sample to a greater depth, scattering of emitted electrons by electrons located between the depth within the sample of emission and the vacuum/sample interface limits the intensity of primary photoelectron peaks to depths which depend on the emission energy of electrons. For example, photons with energy 1486.6 eV, characteristic of an aluminium anode x-ray gun, generate 95% of emission electrons from depths less than 10 nm. The maximum sampling depth for photons with energy 1486.6 eV is therefore less than 10 nm, and depending on the binding energy for an atom from which the photoemission originates, the sampling depth can be significantly less than 10 nm.

Primary photoelectron peaks (Figure 3) are the sum of all electrons collected by the detection system emitted from a sample surface into the vacuum for which no energy is lost following excitation by photoionisation other than the work function of the instrument.

Electron scattering of an emitted electron by electrons associated with surface material may occur as emission electrons move from an atom deep in the sample before arriving in the vacuum chamber of an XPS instrument. Electron scattering may be elastic or inelastic. **Inelastic scattering** of the photoelectron causes a reduction in the kinetic energy of a photoelectron from the initial excitation energy. Inelastic electron scattering during a photoemission experiment results in a significant proportion of the photoemission signal assigned as background in nature (Figure 3).

Primary photoemission intensity, which can be linked to specific elements and chemical states within elements, is superimposed on the inelastic scattered background signal. Quantification of sample material requires an estimate for the background contribution to the intensity over the energy interval associated with a primary photoemission peak. That is, sample composition is estimated using background subtracted peak intensity.

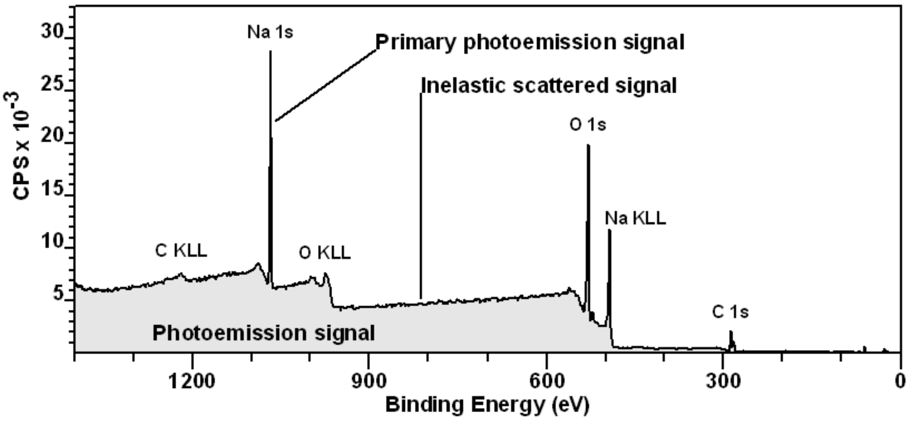


Figure 3: Photoemission signal includes background intensity due to inelastic scattering of photo-ionised electrons appearing within a spectrum at energies different from the primary photoemission peaks.

Since XPS has a limited sampling depth, the angle of the sample with respect to the direction of the extraction optics for the analyser is a factor in the measurement process. Tilting a sample with respect to the analyser axis alters the volume of material from which a spectrum is collected. Figure 4 illustrates the relationship between sample tilt and the volume of material from which electrons are collected during photoemission measurements. If the sample normal and the axis for the analyser are in the same direction, the angle of tilt is considered to be zero. Increasing the angle between the sample normal and the analyser axis causes changes to the volume sampled resulting in a reduction in the depth from which photoemission is recorded. Figure 4 shows the mechanism by which tilting a sample selects for surface layers as the angle increases.

Figure 5 contains spectra from a layered sample where nominally the layers are ppHex on SiO_2. The amount of Si and O as evidenced by the O 1s, Si 2s and Si 2p peaks relative to the C 1s ppHex contribution for three different angles shows SiO_2 is beneath a layer of ppHex. As the angle of tilt increases the O 1s, Si 2s and Si 2p peaks from the SiO_2 substrate reduce relative to C 1s, hence the SiO_2 is seen to be significantly reduced in the outermost layer of the material.

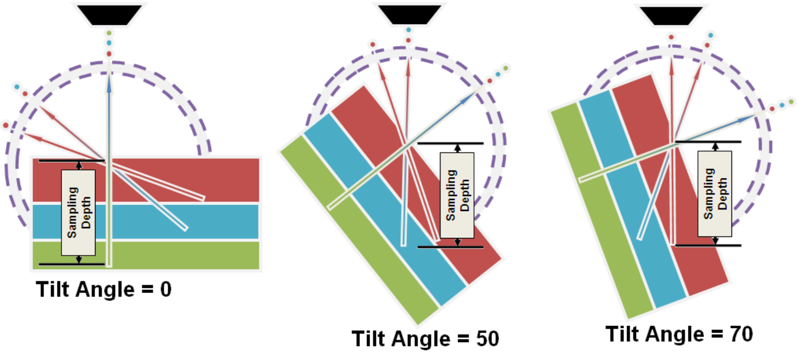


Figure 4: An idealised layered material analysed at three different angle of sample tilt with respect to the analyser acceptance angle.

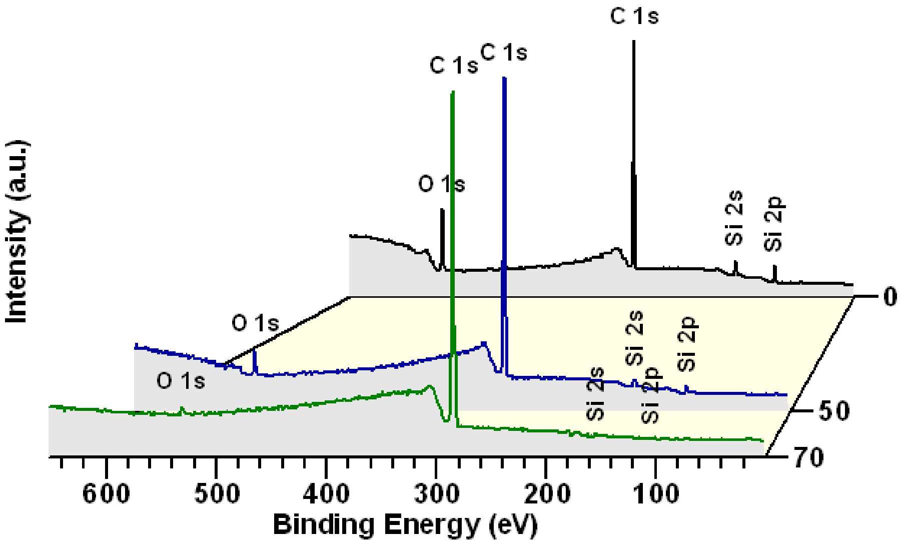


Figure 5: ppHex layer on SiO_2 measured from the same sample tilted with respect to the analyser acceptance angle by 0^o, 50^o and 70^o.

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 typically 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 potential at the surface. Given a fixed potential α at the surface, binding energy for photo-emitted electrons can be measured by removing the potential from the basic XPS energy relationship. Thus, for insulting samples for which charge compensation is performed during an experiment, the basic relationship relating binding energy and kinetic energy changes from

$$E_{ke} = h\nu - E_{be} - \phi$$

to

$$E_{be} = h\nu - E_{ke} - \phi - \alpha$$

The data in Figure 6 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 differ between the two spectra by 5 eV. Without effective charge compensation the potential at the surface may change with time, hence the measured kinetic energy for a photoemission line may change as a function of elapse time between measuring two peaks.

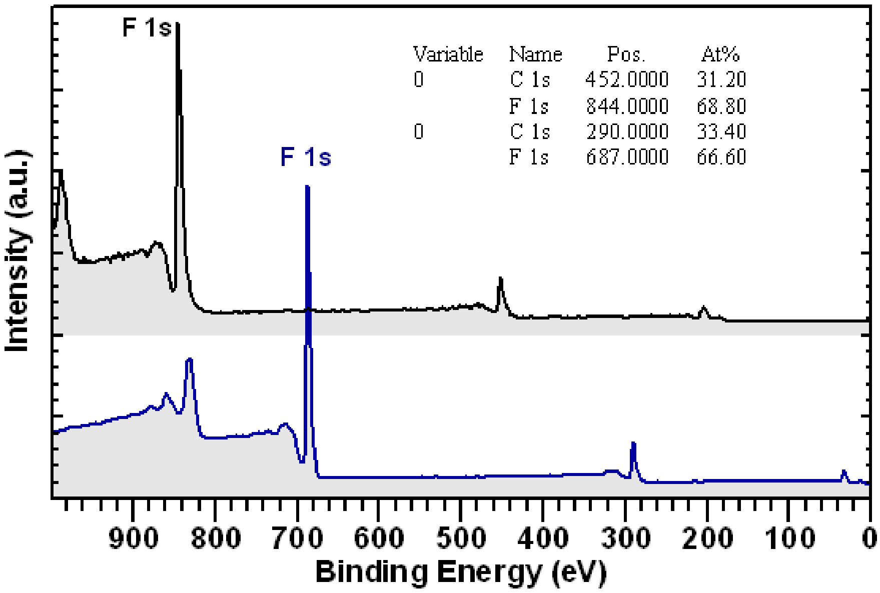


Figure 6: Insulating sample before and after charge compensation.

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.

Physical interpretation of spectral features

Survey Spectra

Definition: A ***survey spectrum*** refers to a measurement over an extended energy interval designed to assess general peak structure in the electron emission intensity in response to incremental changes in acceptance energy for the electron spectrometer. The principal goal for survey data is to assess a sample in terms of elemental composition. Survey data are typically performed using a low energy resolution mode for the electron spectrometer. Emission peaks are typically broadened to allow increased transmission for electron at a given measurement energy, which in turn permits short acquisition times using large steps in energy between recording the count rate.

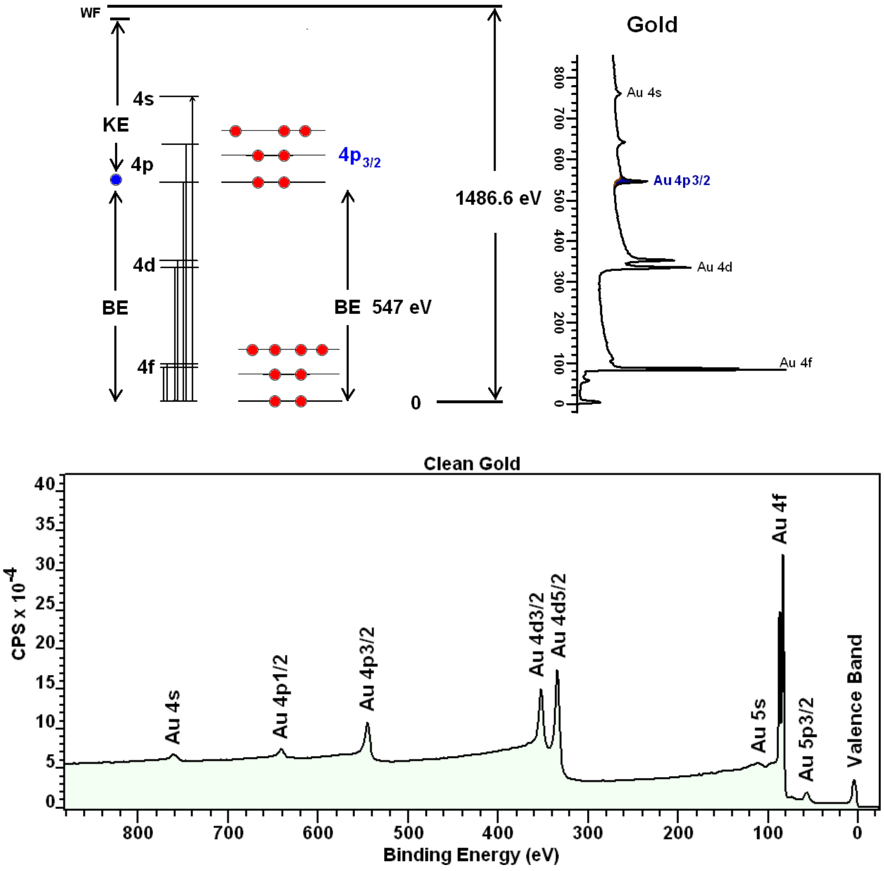


Figure 7: Example of a survey spectrum from a gold sample. Only involves emission peaks from one element.

Figure 7 is a survey spectrum from a clean gold sample showing emission peaks due to Al x-rays using a monochromator to limit photon energy to 1486.7 eV. Emission count-rates were recorded after steps of 1 eV adjustments to the emission energy accepted by a hemispherical analyser working in Fixed Analyser Transmission (FAT) mode with a pass energy of 80 eV.

XPS of gold using an Al x-ray source energy filtered using a monochromator causes emission from a limited number of core-level electrons within the gold atoms. None of the inner core electrons of gold with assignments of 1s, 2s, 2p, 3s, 3p and 3d are observed through emission of electrons by photons with energy 1486.7 eV, as these inner core electrons require more energy than 1486.7 eV to escape from a gold atom, hence these inner core electrons of gold cannot be measured by XPS using an Al anode.

A clean gold sample is an ideal example of a homogeneous sample. The data in Figure 8 is measured from a powder containing several elements and includes contaminants such as carbon and sodium. Nevertheless, XPS of K_2HPO_4 powder is expected to result in almost identical spectra. Moving the analysis position within a well prepared powder sample does not alter the spectra. In this sense, the K_2HPO_4 powder can be considered homogeneous to XPS.

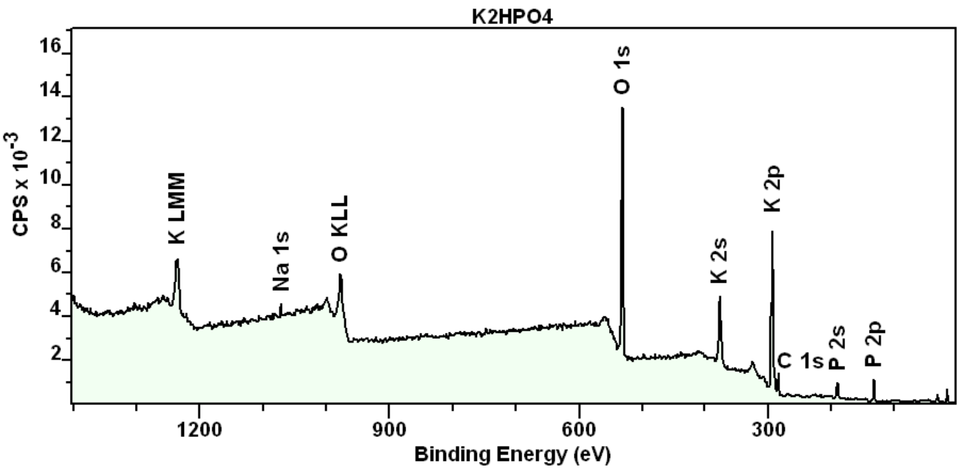
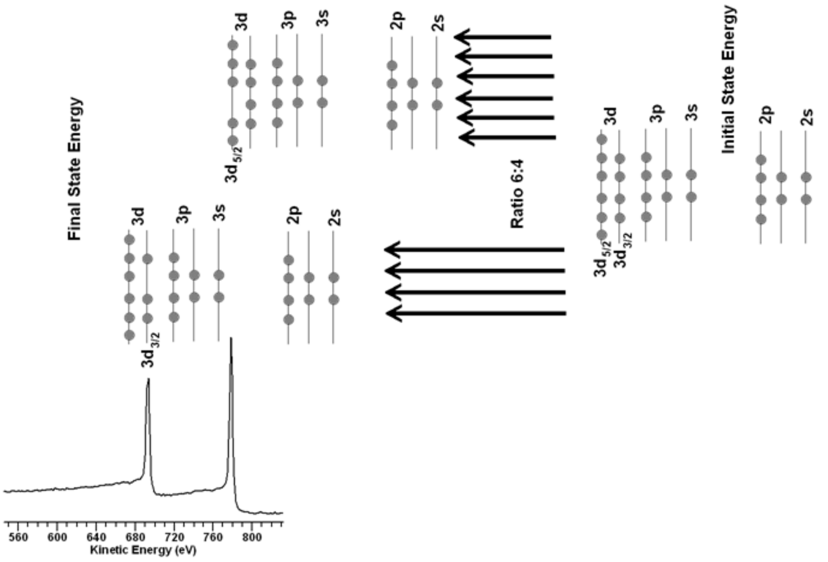


Figure 8: Example of a survey spectrum with multiple elements within the sample surface.

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 phosphorus, both the P 2s and P 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, and therefore in principle the RSF, 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 phosphorus, say, is determined from either the P 2s or the P 2p transitions. More generally, the peak areas for transitions from different elements must be scaled too. A set of relative sensitivity factors (RSF) 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.



Understanding Relative Sensitivity Factors for Doublet Transitions

An electron spectrum is essentially obtained by monitoring a signal representing the number of electrons emitted from a sample over a range of kinetic energies. The energy for these electrons, when excited using a given photon energy, depends on the difference between the initial state for the electronic system and the final state. If both initial and final states of the electronic system are well defined, a single peak appears in the spectrum. Well defined electronic states exist for systems in which all the electrons are paired with respect to orbital and spin angular momentum. The initial state for the electronic system offers a common energy level for all transitions. When an electron is emitted from the initial state due to the absorption of a photon, the electrons emerge with kinetic energies characteristic of the final states available to the electronic system and therefore XPS peaks represent the excitation energies open to the final states. Since these final states include electronic sub-shells with unpaired electrons, the spin-orbit coupling of the orbital and spin angular moment results in the splitting of the energy levels otherwise identical in terms of common principal and orbital angular momentum. Thus, instead of a single energy level for a final state, the final state splits into two states referred to in XPS as doublet pairs. To differentiate between these XPS peaks, labels are assigned to the peaks based on the hole in the final state electronic configuration. Since these final states, even when split by spin-orbit interactions, are still degenerate in the sense that more than one electronic state results in the same energy for the system, three quantum numbers are sufficient to identify the final state for the x-ray excited system. Specifying the three quantum numbers in the format nlj both uniquely identifies the transition responsible for a peak in the spectrum and offers information regarding the degeneracy of the electronic state involved. The relative intensity of these doublet pair peaks linked by the quantum numbers nl is determined from the $j = l \pm \frac{1}{2}$ quantum number. Doublet peaks appear with intensities in the ratio $2j_1+1 : 2j_2+1$. Thus p-orbital doublet peaks are assigned j quantum numbers 1/2 and 3/2 and appear with relative intensities in the ratio 1:2.

Similar intensity ratios and differing energy separations are common features of doublet peaks in XPS spectra. Final states with s symmetry do not appear as doublets, e.g. Au 4s.

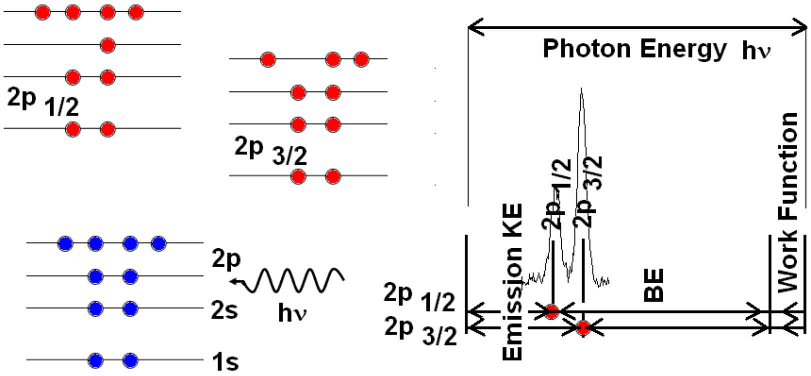


Figure 9: Excitation of L-shell electron resulting in doublet emission peaks.

When quantifying XPS spectra, RSFs are used to scale the measured peak areas so variations in the peak areas are representative of the amount of material in the sample surface. An element library typically contains lists of RSFs for XPS transitions. For some transitions more than one peak appears in the data in the form of doublet pairs and, in the case of the default CasaXPS library, three entries are available for each set of doublet peaks: one entry for the combined use of both doublet peaks in a quantification table and two entries for situations where only one of the two possible peaks are used in the quantification. A common cause of erroneous quantification is the inappropriate use of these optional RSF entries.

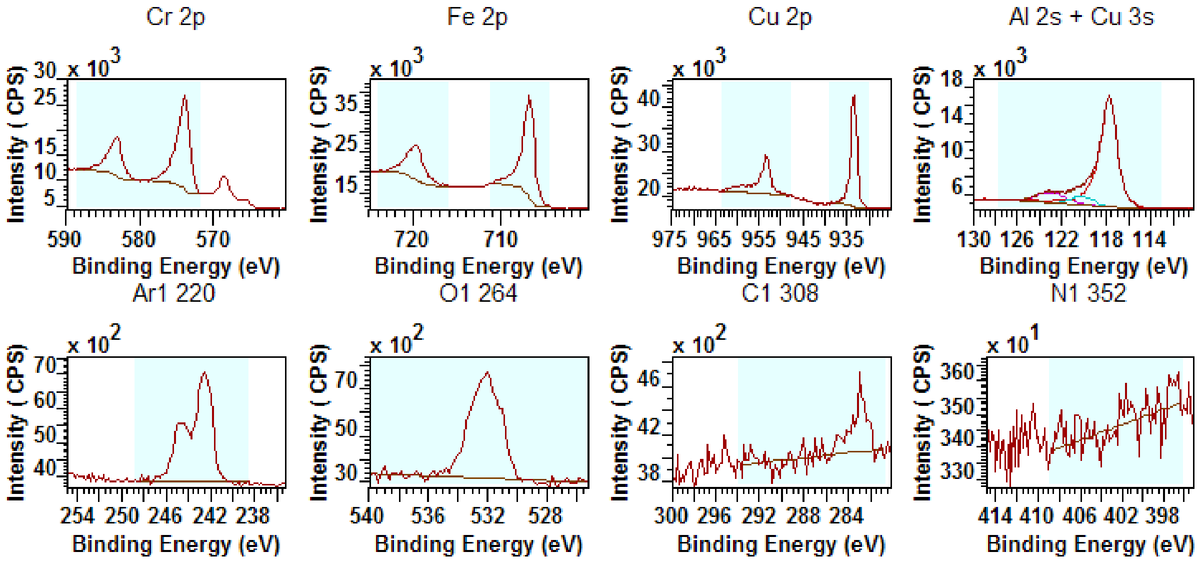


Figure 10: Example of quantification regions and components used to quantify peak areas.

The data in Figure 10 are a set of high resolution spectra where quantification regions and components are used to calculate the area for the peaks. These data illustrate some of the issues associated with XPS quantification as the data includes singlet peaks in the form of O 1s, C 1s, Al 2s and N 1s; as well as doublet pairs: Cr 2p, Cu 2p, Ar 2p and Fe 2p. These spectra are sufficiently complex to involve overlaps such as the Al 2s and Cu 3s, while the Cu 2p1/2 peak includes signal from a Cr Auger line. When creating a table of percentage atomic concentrations it is important to select the correct RSF for the peak area chosen to measure the given element.

Table 1: Quantification table showing RSFs used to scale the raw peak areas.

Name	R.S.F.	% Conc.
Cr 2p 1/2	10.6041	2.9
Cr 2p 3/2	10.6041	6.2
Fe 2p 1/2	14.8912	2.2
Fe 2p 3/2	14.8912	4.5
Cu 2p 3/2	15.0634	4.4
Al 2s Metal	0.753	61.4
Al 2s Ox	0.753	5.1
Ar 2p	2.65797	5.5
O 1s	2.93	6.2
C1s	1	1.5
N1s	1.8	0.2

When measuring a transition, from the perspective of signal to noise, it is better to include both peaks from a doublet pair. For the data in Figure 10, the Fe 2p, Cr 2p and Ar 2p transitions are free of interference from other peaks and therefore simple integration regions can be used to measure the peak areas. The Ar 2p doublet peaks overlap each other, however the Cr 2p and Fe 2p peaks do not overlap, thus separate quantification regions are used to measure the area for these resolved doublet peaks. Even though separate regions are used to estimate the peak areas for the two peaks in each of the Cr 2p and the Fe 2p transitions, total RSFs for these transitions are used to scale the raw area calculated from the regions. Similarly, the total RSF is used to scale the Ar 2p doublet peaks, because both peaks from the doublet are used in calculating the peak area for argon. On the other hand, since the Cu 2p1/2 peak overlaps with the Cr LMM Auger transition, only the Cu 2p3/2 peak can be used with ease and so the reduced RSF must be applied to scale the peak area. The quantification table in Table 1 lists the regions and components used to calculate the atomic concentrations together with the RSFs for each transition.

Note the peak model used to measure the Al 2s includes a component representing the contribution of the Cu 3s transition to the Al 2s spectrum in Figure 10. Copper is measured using the Cu 2p3/2 peak therefore the RSF for the Cu 3s component is set to zero hence the component does not appear in Table 1.

By way of example, an alternative quantification regime might be to use only one of the two possible Fe 2p doublet peaks. The quantification in Table 2 removes the Fe 2p1/2 region from the calculation by setting the RSF to zero, whilst adjusting the Fe 2p3/2 RSF to accommodate the absence of the Fe 2p1/2 peak area from the calculation. Since the ratio of 2p doublet peaks should be 2:1, the RSF for the Fe 2p3/2 region is two thirds of the total RSF used in Table 1. In Table 1, the percentage atomic concentration for Fe is split between the two Fe 2p doublet peaks, whereas in Table 2 the entire Fe 2p contribution is estimated using the Fe 2p3/2 and therefore the same amount of Fe is measured via either approach.

A common misunderstanding is to use both peaks in the calculation, but still assign RSFs for the individual peaks in the doublet. The consequence of using both peaks and the specific RSFs to the individual peaks in the doublet is the contribution from Fe to the quantification table would be incorrectly increased by a factor of two.

Note: the RSFs used in both Table 1 and Table 2 are Scofield cross-sections adjusted for angular distribution corrections for an instrument with angle of 90º between the analyser and x-ray source.

Table 2: Fe 2p 3/2 peak is used without the area from the Fe 2p1/2.

Name	R.S.F.	% Conc.
Cr 2p 1/2	10.6041	2.9
Cr 2p 3/2	10.6041	6.2
Fe 2p 3/2	9.8064	6.8
Cu 2p 3/2	15.0634	4.4
Al 2s Metal	0.753	61.3
Al 2s Ox	0.753	5.1
Ar 2p	2.65797	5.5
O 1s	2.93	6.2
C1s	1	1.5
N1s	1.8	0.2

To further illustrate the issues associated with the uses of the three RSFs allocated to doublet peaks in the default element library, consider the three possible options available when quantifying the Cr 2p doublet shown in Figures 11, 12 and 13. Table 3 shows that the corrected area when measured using any of these three options is approximately the same.

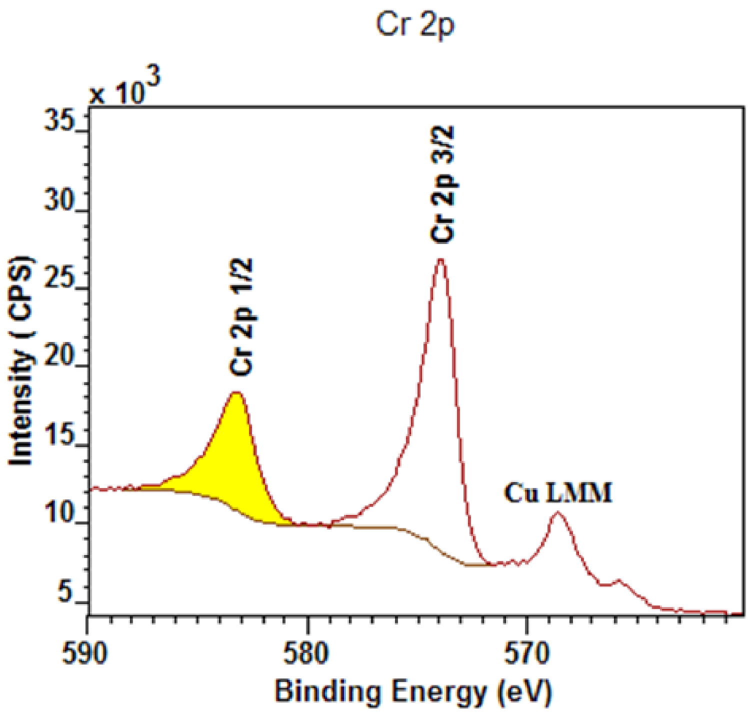


Figure 11: Intensity for Cr calculated from the Cr 2p1/2 transition.

Cr 2p1/2 RSF	Raw Area
3.60721	19234.8

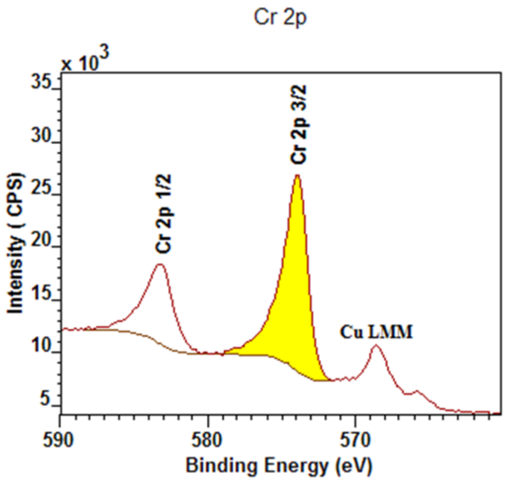


Figure 12 Intensity for Cr calculated from the Cr 2p3/2 transition.

Cr 2p3/2 RSF	Raw Area
6.9697	40871.9

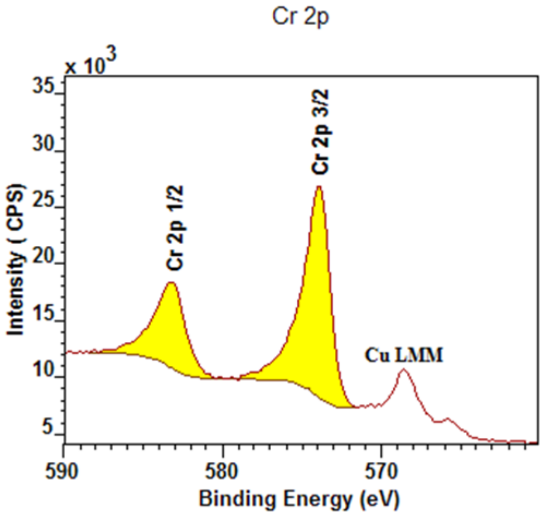


Figure 13: Intensity for Cr calculated from both peaks in the doublet.

Total RSF	Raw Area
10.6041	60098.5

Table 3: Comparison of the intensities calculated from the three different combinations of peak area and RSF for the Cr 2p doublet illustrated in Figure 11, Figure 12 and Figure 13.

Peak Raw Area/(RSF*T*MFP)	RSF	Raw Area	Corrected Area
Cr 2p 1/2	3.60721	19234.8	125.455
Cr 2p 3/2	6.9697	40871.9	138.192
Both Cr 2p Peaks	10.6041	60098.5	133.555

Basic Quantification of XPS Spectra

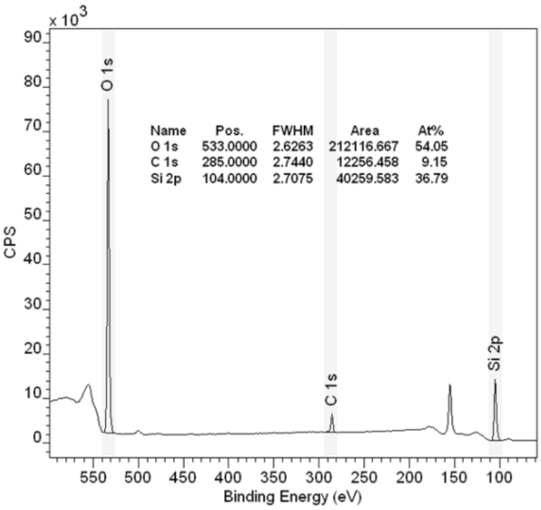
How to Compare Samples

A direct comparison of raw 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 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 any way 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.

Quantification Regions

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 when quantification of a surface is performed from an XPS spectrum (Figure 14).

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 across a surface (localised differences in the surface potential).



Name	Pos.	FWHM	Area	At%
O 1s	533.0000	2.6263	212116.667	54.05
C 1s	285.0000	2.7440	12256.458	9.15
Si 2p	104.0000	2.7075	40259.583	36.79

Figure 14: Quantification regions used to integrate signal above background corresponding to primary photoemission peaks.

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 14 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.

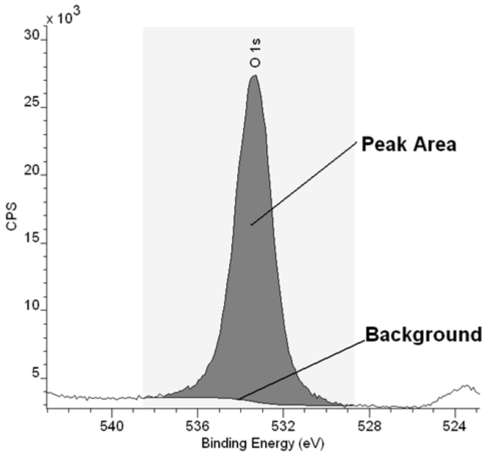


Figure 15: Primary photoemission peak due to oxygen electrons initially in a 1s core level. A background estimate is used to remove the signal due to inelastic scattering of electrons with initial kinetic energies greater than the O 1s primary peak.

Peak Models in XPS

Quantification regions are useful for isolated peaks. Unfortunately 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. Both aluminium peaks appear at almost the same binding energy as the Cu 3s and Cu 3p transitions. Thus estimating the intensity of the aluminium in a sample containing these elements requires a means of modelling the data envelope resulting from the overlapping transitions illustrated in Figure 16.

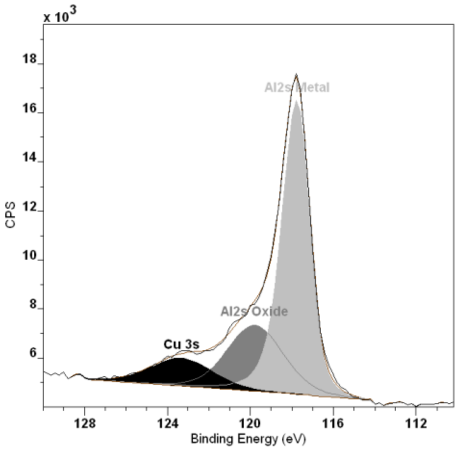


Figure 16: Aluminium and Copper both in evidence at the surface.

Techniques for modelling data envelopes not only apply to separating elemental information, such as the copper and aluminium intensities in Figure 16, but also apply to chemical state information about the aluminium itself. Intensities for the aluminium oxide and metallic states in Figure 16 are measured using synthetic line-shapes or components within a peak model. The problem of aluminium and copper is not unique. Even basic materials result in XPS spectra which typically include multiple transitions for each element and while useful in identifying the composition of the sample, the abundance of transitions frequently leads to interference between peaks and therefore introduces the need to construct peak models. Figure 17 further illustrates the point with a spectrum over the Si 2p energy interval from a sample with a thin layer of silver on silicon (University of Iowa, Jukna, Baltrusaitis and Virzonis, 2007, unpublished work). Samples such as these are all too common and quantification of such interfering Si 2p and Ag 4s intensities require the use of peak models.

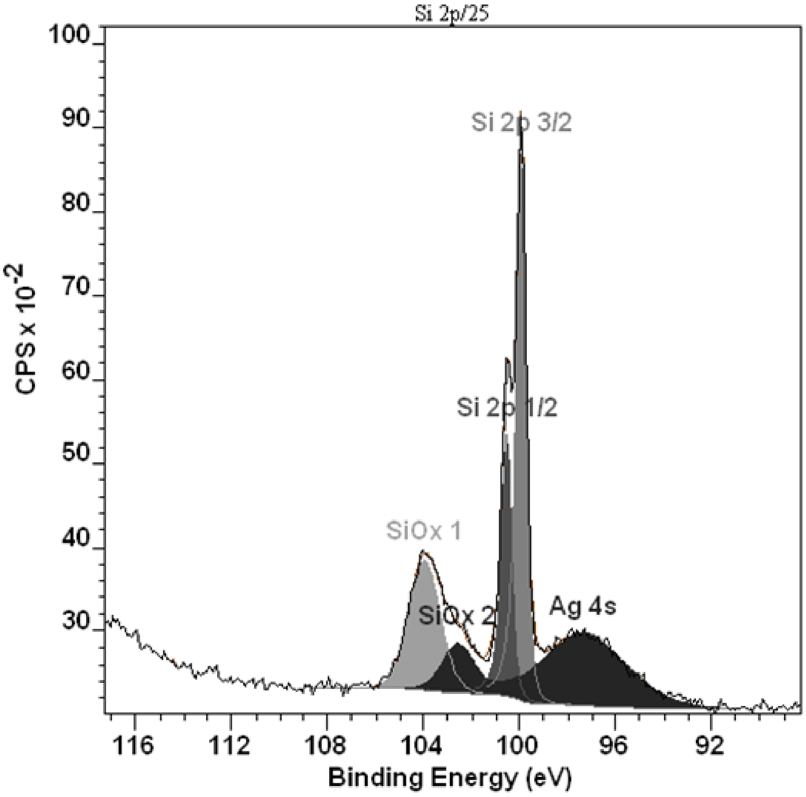
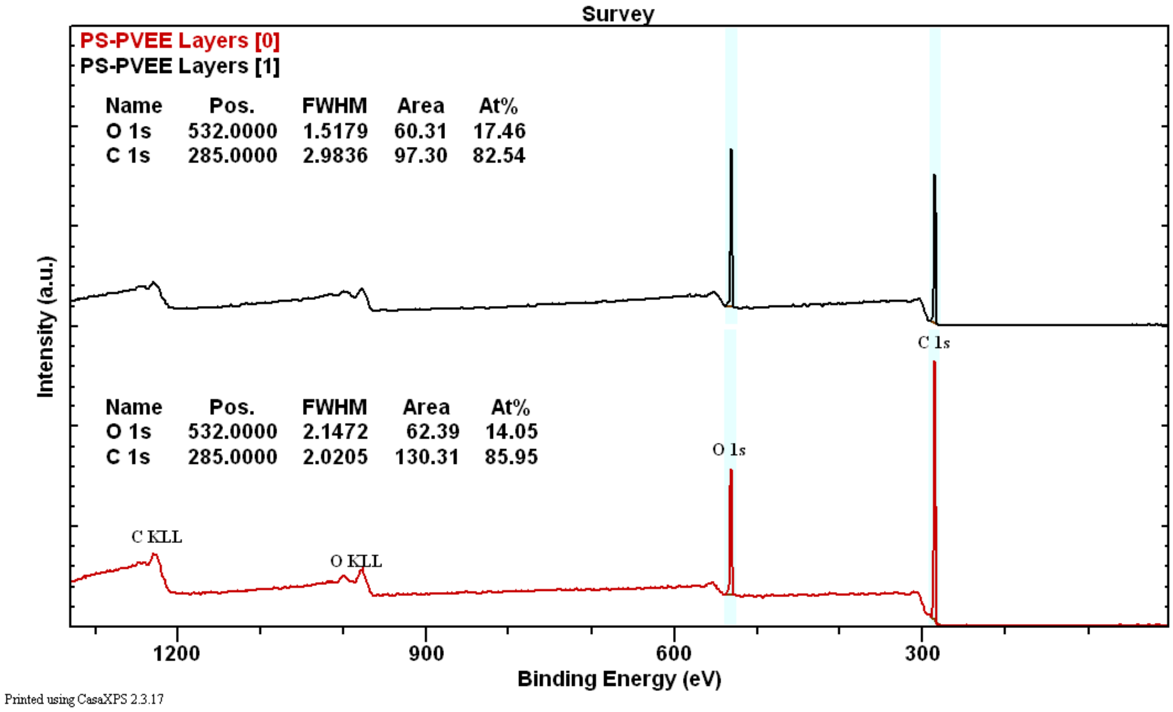


Figure 17: Elemental and oxide states of silicon overlapped by a silver peak Ag 4s.

The subject of peak-fitting data is complex. A model is typically created from a set of Voigt or approximations to Voigt line-shapes. Without careful model construction involving additional parameter constraints, the resulting fit, regardless of how accurate a representation of the data, may be of no significance from a physical perspective.

Survey Data

XPS survey spectra can be used to differentiate elemental composition between samples. The two spectra in Figure 18 are an example where two polymers are present in the top 10 nm of the surface. These samples are also constructed to form well defined layers designed to consist of poly (styrene) and poly (vinyl ethyl ether).



Name	Pos.	FWHM	Area	At%
O 1s	532.0000	1.5179	60.31	17.46
C 1s	285.0000	2.9836	97.30	82.54

Name	Pos.	FWHM	Area	At%
O 1s	532.0000	2.1472	62.39	14.05
C 1s	285.0000	2.0205	130.31	85.95

Figure 18: Survey spectra measured from layered PS PVEE polymer samples prepared by Graham Beamson for angle resolved XPS analysis.

Quantification tables in Figure 18 present the results of a straight forward data treatment. The relative amount of material at the surface is measured using two transitions C 1s and O 1s. These two transitions from a simple material appear as single peaks in an XPS spectrum. To estimate the amount of material at the surface quantification tables in Figure 18 displaying atomic concentration based on regions, for which signal above background counts is integrated directly from the data. The survey spectra contain additional peaks labelled C KLL and O KLL, but for the purposes of quantifying a sample, a set of peaks representative of the various elements must be identified, specified using regions and intensities computed using the parameters defined in these regions.

For these two spectra, photoelectron lines C 1s and O 1s are selected rather than any of these other peaks evident in Figure 18. The selection of these two transitions is made simply by virtue of these peaks are well resolved, that is, there are no interfering peaks from other transitions, and these two transitions for each of the two elements expected at the surface are the most intense peaks out of the set of photoelectron transitions due to these elements. The latter point ensures the best signal-to-noise relationship for measuring carbon and oxygen and therefore the greatest precision given the acquisition conditions used to collect these data.

The quantification tables in Figure 18 show a variation in these two measurements indicating the relative amount of carbon to oxygen is different between these two samples. In addition the FWHM for the C 1s peaks change significantly. The energy resolution typically used for a survey spectrum prevents detailed chemical state information from these data, nevertheless a change in the FWHM shown in Figure 18 suggests the carbon chemistry is not identical between these two measurements.

These two spectra in Figure 18 are measured from the same sample using two different take-off angles. By tilting the sample, electrons collected by the analyser can be made to favour the surface layers of a sample thus qualitatively these two angle resolved XPS measurements suggest the amount of oxygen relative to the carbon alters with depth. The empirical formulae in Figure 19 and Figure 20 suggest this variation is significant as PS contains no oxygen, while PVEE is expected to be responsible for oxygen signal in these samples.

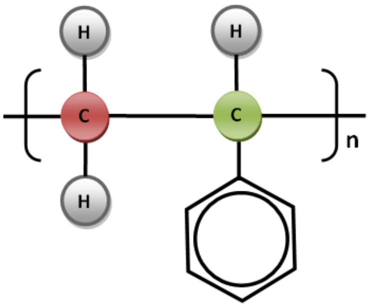


Figure 19: **Empirical formula for PS.**

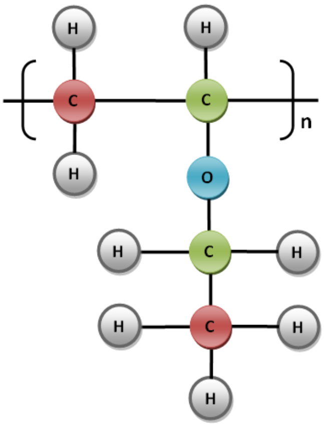


Figure 20: **Empirical formula for PVEE**

In an ideal world, the quantification tables in Figure 18 should be interpreted in the context of the chemical information in Figure 19 and Figure 20. These empirical formulae imply the relative proportions of carbon to oxygen for PS and PVEE in these XPS measurements. There is a third element, namely hydrogen, but sadly XPS cannot measure hydrogen. In terms of elements measureable by XPS, Figure 20 implies PVEE includes four carbon atoms for each oxygen atom. Thus the expectation is quantification from PVEE would yield atomic concentrations for oxygen and carbon with values 20% oxygen and 80% carbon. PS is formed from only carbon and hydrogen. The results in Figure 18 obtained from these survey data suggest for the surface these samples are predominantly PVEE and by tilting the sample differing proportions of PS signal are produced. These survey spectra are therefore providing insight into the composition of these samples, however the world is not ideal and there could be reasons why oxygen is at the surface unrelated to the expected PS and PVEE materials. Nevertheless, even from these survey spectra alone, the samples are shown to be potentially PS and PVEE, and more importantly these survey spectra suggest the only contamination possible to these surfaces might be compounds of oxygen and carbon. For example no significant amount of fluorine or sodium is evident in these spectra. Conclusions similar to these are at times sufficient reason to perform XPS on a sample using survey modes only.

Narrow Scan Spectra

XPS offers the possibility of identifying chemical state for an atom in a molecule. The binding energy for a transition from a given element, such as a C 1s electron, differs depending on the element to which carbon is bonded and the type of bond formed (single bond, double bond etc.). These shifts in binding energy vary in magnitude and direction. For example, poly(styrene) contains two bonding environments for carbon, but the shift is small and difficult to resolve , in practical terms resulting a single asymmetric C 1s peak shape. Poly(vinyl ethyl ether) on the other hand results in two C 1s peaks shifted in binding energy to the extent two resolvable peaks of nominally equal intensity are formed. A blend of these two polymers results in high resolution spectra from a C 1s energy interval containing both well resolved PVEE peaks overlapping with PS peaks. To obtain a better understanding for these PS/PVEE materials a peak model is typically used to partition the intensity within a C 1s data envelope. An example of a PS/PVEE blend C 1s spectrum is shown in Figure 21.

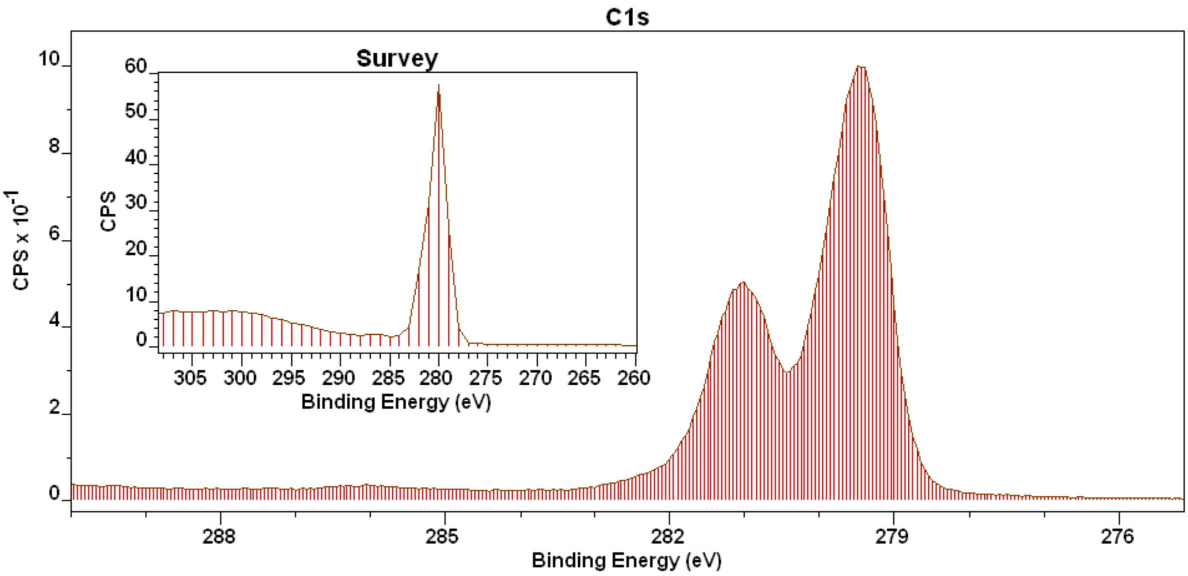


Figure 21: High resolution C 1s data collected from a PS/PVEE layered material. The insert represents the same sample measured using a lower resolution survey mode. Note how the C 1s peak in the survey spectrum hints at but does not reveal the same peak structure offered by the high resolution spectrum.

A comparison between the C 1s data measured using a survey mode and one selected for resolving the PVEE peaks shown in Figure 21 illustrates the essential difference between these types of measurements. The survey mode shown in the inset tile in Figure 21 is designed to permit a larger step size allowing a shorter acquisition time for a given transition accommodated by smearing the signal from potentially narrow peaks so not to miss these peaks when using large energy steps. High resolution spectra are acquired following a survey measurement to reveal the structure hidden by the survey mode. The acquisition time in high resolution data is focused on more limited energy ranges so finer energy steps can be used to match the instrumental energy resolution, thus revealing detail not available in survey data.

Acquisition time is important when measuring certain materials. A sample may change within the sample chamber when exposed to the vacuum, x-ray source and charge compensation mechanism, to name but three possible causes for surface modification. It is therefore important to measure spectra with regard to temporal effects. Matching acquisition time to the desired information should be part of experimental design, hence the conservative use of time implied by the survey mode.

High resolution data is typically achieved by the use of lower pass energies for the hemispherical analyser. Interestingly, these data in Figure 21 were both acquired using the same pass energy on a Scienta 300 XPS instrument at Daresbury Laboratories. Reducing the energy resolution for the survey data is achieved by altering apertures widths used to control the spread of electron trajectories accepted by the HSA. One should therefore be aware energy resolution is not determined by the energy step-size but a combination of instrumental settings. Further, changes observed in these spectra are achieved by altering the electrons leaving the sample selected for analysis. The consequence of such selection mechanisms is adjustments to the collection efficiency for an instrument depending on operating mode selected. Such changes in the response of the instrument are generally accounted for by, so called, transmission correction. The response of an instrument to a given number of electrons generated by a sample varies as a function of kinetic energy for these electrons.

A discussion of high resolution spectra necessarily requires a discussion of instrument characteristics embodied in transmission correction.

The reason a transmission correction is important is as follows. If the raw intensity for a peak is used to measure the composition of a sample, the resulting composition will also include instrumental differences rather than being only sample-dependent. Transmission correction therefore requires energy dependent correction factors to scale peak intensities for changes in intensity which are instrumental in nature. Photoelectron transition probabilities, examples of which are Scofield cross-sections, are independent of instrumental factors, so logically these two corrections are applied separately. However, empirically determined sensitivity factors necessarily include instrumental influences, and as a result not all RSFs require absolute transmission correction.

Not all instruments and not all data are presented with well characterised transmission functions. Nevertheless, quantification without transmission correction from high resolution spectra is possible and will be illustrated. The survey mode is typically the best characterised operating mode for an instrument and generally atomic concentration tables are generated from these survey modes. The objective in transmission correction is to obtain equivalent atomic concentration results from high resolution data to that obtained from these survey modes. In CasaXPS, quantification using TAGS is the method for combining chemical state information from high resolution spectra with the elemental information obtained from the survey spectra. Quantification using TAGS requires only that the survey mode is well characterised.

Backgrounds and Lineshape used in Peak Models

To make use of high resolution spectra, data envelopes such as the C 1s spectrum in Figure 21 must be explained in terms of a set of well defined component peaks above a background signal. For the data shown in Figure 21, the objective is to measure the relative proportions of PS to PVEE in the sample. To proceed towards a peak model one must decide on the algorithm for estimating the background signal, the lineshape best suited to describing the transitions and the number of such transitions the sum of which is responsible for the data envelope.

Historically relatively simple algorithms were used to remove a background from a set of peaks. Backgrounds typically used are a linear interpolation between the intensities at the limits of a defined energy interval and the, so called, Shirley background. The Shirley algorithm computes the background contribution using a weighted average based on peak intensity to the left and right of the current energy under consideration. Simply from the physical origin of a background signal, one might feel uncomfortable with an algorithm using information which cannot contribute to a background signal, namely intensity from electrons with lower kinetic energy, so apart from simplicity the merit of using these backgrounds must lie in practical convenience. To address these concerns Tougaard suggested alternative procedures for computing a background contribution to XPS peaks.

A Tougaard 2-parameter universal background is based on the existence of an energy loss cross section $F(x)$ representing the probability an electron at energy offset x undergoes a loss event and therefore appears as a contribution to the background. The background is computed from the measured spectrum $S(E)$ using the integral:

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

where

$$F(x) = \frac{Bx}{(C + x^2)^2}$$

For a user defined C parameter the B parameter is adjusted in CasaXPS 2.3.17 to ensure the computed background meets the data at the limits of an energy interval over which the background is computed. The merits of the Tougaard background include the concept of calculating the background signal for spectral data representing electrons with higher kinetic energy and still involve a relatively simple computational procedure. Further the Tougaard 2-parameter universal cross-section allows the background to be adjusted to reduce the influence of peak structure on the background. The greatest flaw in the Shirley approach is the non-physical shapes which can appear in the background. A Tougaard algorithm effectively is a smoothing kernel adjusted for differing circumstances. There are dangers introduced by allowing variations in a background shape, so the advantages in using an adjustable background must be paid for by discipline when applying these backgrounds.

The selection of lineshape is of great importance when constructing a peak model. Again, traditionally lineshapes based on product and linear combination of Gaussian and Lorentzian functions is used to model photoelectron peaks. Underlying the use of these lineshapes is simplicity rather than applicability. Photoelectron lineshapes rarely conform to these mathematical forms and optimisation based on a least squares principle is compromised when fitting data with poor approximations to the true line profile. For these reasons the lineshape considered is a more flexible functional form based on a Lorentzian shape modified and numerically convoluted with a Gaussian. This LF lineshape derives from ideas introduced by Doniach-Sunjic asymmetric lineshapes, but altered to force functional forms with finite area. Infinite lineshapes are of limited practical use as intensity measurements are arbitrary and ill defined.

A Lorentzian lineshape with FWHM *f* and position (in kinetic energy) *e* is given by

$$L(x\colon f,e) = \frac{1}{1 + 4\left(\frac{x-e}{f}\right)^2}$$

The basis for both the LA and LF lineshapes in CasaXPS is

$$LA(x\colon \alpha,\beta,f,e) = \begin{cases} [L(x\colon f,e)]^{\alpha} & x \le e \\ [L(x\colon f,e)]^{\beta} & x > e \end{cases}$$

The lineshape parameter entered on the Components property page for the asymmetric Lorentzian is LA(α, β, *m*), where *m* is an integer between 0 and 499 defining the width of the Gaussian used to convolute the *LA* functional form.

Depending on the values chosen for the parameters α and β, the LA lineshape can define functional forms with infinite area. For this reason the LA definition is modified by an additional parameter to ensure the LF lineshape corresponds to a finite area.

LF(α, β, *w*, *m*) is identical to the LA lineshape with the exception that the specified values of α and β are force to increase to a constant value via a smooth function determined by the width parameter *w*. The examples in the workshop videos use the LF lineshape as the preferred lineshape where asymmetry is necessary for obtaining a good fit to a data envelope.

Definition of LF Lineshape

$$L(\alpha,\beta) = \begin{cases} \left(\frac{1}{1+4\left(\frac{x-E}{f}\right)^2}\right)^{\alpha} & x \le E \\ \left(\frac{1}{1+4\left(\frac{x-E}{f}\right)^2}\right)^{\beta} & x > E \end{cases}$$

A function LD is defined in terms of the function $L(\alpha,\beta)$ where α and β approach a common value A as follows.

$$LD(\alpha,\beta,\omega)\ \rightarrow L(A,A)\ as\ x \rightarrow E \pm \omega$$

Voigt function v is the convolution of a Lorentzian l with a Gaussian g defined by the following function shape.

$$v(t) = l * g \equiv \int_{-\infty}^{\infty} l(\tau)g(t-\tau)d\tau$$

Generalized Voigt function:

$$LF(\alpha,\beta,\omega,n,m) = \left(\left(\left(LD(\alpha,\beta,\omega) * G(n)\right) * G(n)\right) * G(n) * \underset{m-1\ times}{\cdots}\right) * G(n)$$

where $G(n)$ is a Gaussian of width characterised by the parameter value n.

While synthetic lineshapes are essential for general applications, there are circumstances where the preferred option is to create lineshapes from data. These lineshapes can be defined directly in terms of spectral data, for example, given C 1s spectra from PS and PVEE, the hope might be these two spectral shapes can be used to fit the blended layer data in Figure 21. The alternative is to process lineshapes from data by combining spectra via the calculator options in CasaXPS. A spectrum apparently from a pure metal sample potentially includes minor oxide contributions. Data treatments may allow a more realistic metal peak to be synthesised for use when modelling a metallic contribution to an unknown spectrum.

Notes on Atomic Concentration and XPS

In general, XPS atomic concentrations should be viewed as a means to remove measurement-dependent signal variations from XPS peak intensities. If the values reported for the atomic concentrations are the expected elemental proportions for a material then, 1) the instrument has been fully characterised, 2) the sample is free from surface contamination, 3) the relative sensitivity for emission peaks are known, 4) the sample is fully homogenous and uniform in composition and 5) escape depth variations are properly corrected for the emission signal used in the calculation. The follow discussion is aimed at explaining the reasons behind these five statements.

The atomic concentration B_i for an element is computed from n corrected peak areas $\{A_k\colon k = 1, n\}$ using the formula

$$B_i = 100\times\frac{A_i}{\sum_{j=1}^{n} A_j}$$

Provided the raw peak areas are accurately adjusted to account for escape depth, sensitivity and other instrumental factors, for ***homogeneous*** materials the values B_i provides an estimate for the amount of substance within the surface layer of a sample.

For ***inhomogeneous*** samples, the atomic concentration reported by XPS is ***not*** a true atomic concentration of the materials at the surface. For homogeneous materials there is the potential for obtaining accurate atomic concentrations. However, nominally homogeneous materials are not necessarily homogeneous from the perspective of XPS. For example, a surface contamination is sufficient to move a homogeneous material such as SiO_2 to an inhomogeneous sample, and so the expected ratio for oxygen to silicon from SiO_2 should not necessarily be expected. The reason for anomalous atomic concentrations is any overlayer alters the relative intensity for emission peaks as a consequence of signal attenuation from scattering of electrons en route to the vacuum, and attenuation of signal varies as a function of kinetic energy for emitted electrons. Emission peaks used when computing an atomic concentration typical vary in kinetic energy as exemplified by Si 2p and O 1s electrons for SiO_2 samples. Attenuation by an overlayer for O 1s signal will be greater than signal from Si 2p simply due to the difference in kinetic energy for these two sources of elections.

The following simplistic analysis is intended to illustrate how depth distributions influence XPS atomic concentrations. The example of a carbon overlayer to a SiO_2 substrate is used to illustrate the consequences of an overlayer to the reported atomic concentration for a substrate, and how a correction based on film thickness can be applied to recover the expected composition for the substrate.

Attenuation of XPS Signal

XPS is surface sensitive precisely because photoelectrons are scattered within the surface layers of the sample.

Inelastic scattering of electrons passing through the surface material en route to the vacuum result in energy loss for these scattered electrons. For electrons emanating from a given depth x nm within the surface the number of electrons arriving at the vacuum is modelled by an exponential relationship where the initial number of electrons is reduced by a factor of $e^{-x/a}$. Scattered electrons appear within an XPS spectrum as background signal and only electrons emitted without inelastic scattering events appear with the characteristic energy of a photoelectron emission peak.

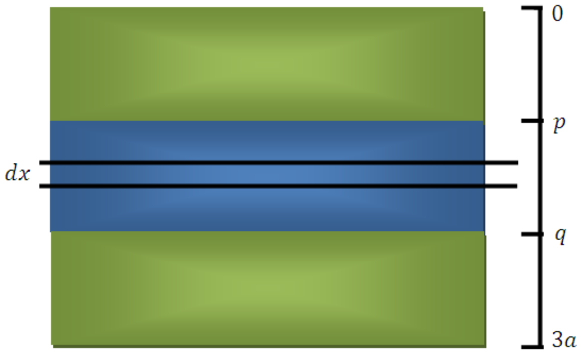


Figure 22: Intensity for electrons emerging from a layer within the surface is obtained by integrating the signal over the interval [p,q] using the exponential attenuation model $e^{-x/a}$.

The intensity emitted at the surface I from a layer of material between the depths of p and q (Figure 22) is proportional to the integral:

$$I \propto \int_p^q e^{-x/a}\,dx = a\left[e^{-p/a} - e^{-q/a}\right]$$

The main message to receive from these equations is the intensity for an emission peak within a spectrum is strongly dependent on the location of the material within the surface region.

A spectrum such as the one in Figure 23 is a combination of several factors as illustrated by analyser response to the energy of the collected electrons and a plot of signal variations as a result of transfer lens characteristics. The response of the electron analyser and the relative efficiency of the transfer lens system alter the relative intensity of emission peaks as a function of kinetic energy. Elemental composition is presented as atomic concentrations calculated from peak intensities corrected for instrumental response and relative sensitivity between emission peaks. Nevertheless, even if data are correctly adjusted for instrumental response and relative sensitivity for different emission peaks, the in depth distribution of materials can greatly alter the values reported for an atomic concentration of a surface for the following reasons.

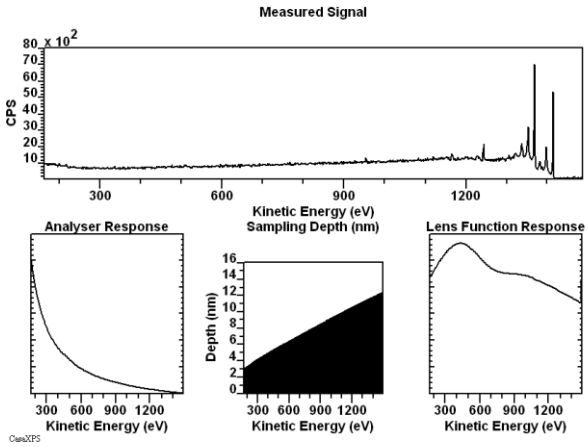


Figure 23: A survey spectrum from ion gun cleaned Al metal. The three plots below the spectrum illustrate the types of adjustments to a spectrum which should be expected over and above material composition influences on the measured intensities.

By way of example, consider the following thought experiment.

The consequence of inhomogeneous depth distributions with very simple layer structure is illustrated by two scenarios for two materials measured using emission electrons with similar kinetic energy. Carbon and ruthenium measured using C 1s and Ru 3d emission peaks are two such materials.

Ru 3d and C 1s are emitted with the same kinetic energy. Assuming the same effective attenuation length a for both materials (which is not necessarily true), applying the exponential attenuation model then the following statements are true:

a) 95% of signal originates from $3a$ depth.
b) 63% of signal originates from a depth.
c) 86.5% of signal originates from $2a$ depth.
d) Only 8.5% of the signal originates from between $2a$ and $3a$ depths.

The following two depth distributions for carbon and ruthenium would result in very different atomic concentration values obtained by XPS.

Scenario 1: A layer of carbon of thickness a nm on top of a layer of ruthenium of depth $2a$ nm measured using Al anode x-rays.

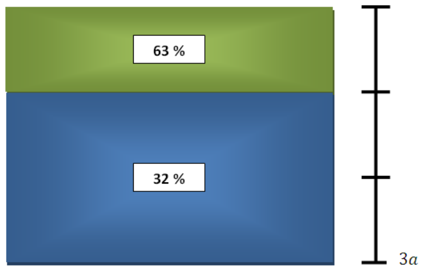


Figure 24: Scenario 1 a layer of carbon over a ruthenium layer of twice the thickness as carbon.

Given a model with ratio Ru:C = 2:1 shown in Figure 24, XPS RSF corrected intensity ratio 32:63 approximately 1:2. Thus the ratio is the exact opposite of the true value for the amount of Ru to C.

Scenario 2: A layer of carbon of thickness a nm below a layer of ruthenium of depth $2a$ nm measured using Al anode x-rays.

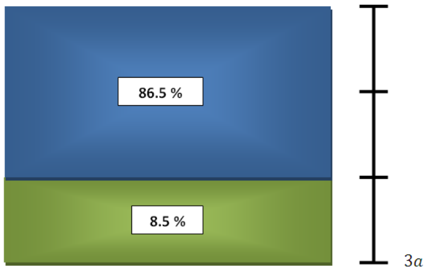


Figure 25: Scenario 2 has identical amounts of C to Ru in the top $3a$ nm as Scenario 1.

Given a model with Ru:C in the ratio 2:1 within the first $3a$ nm as shown in Figure 25, measured by XPS the RSF corrected intensity ratio would be 86.5:8.5 approximately 10:1.

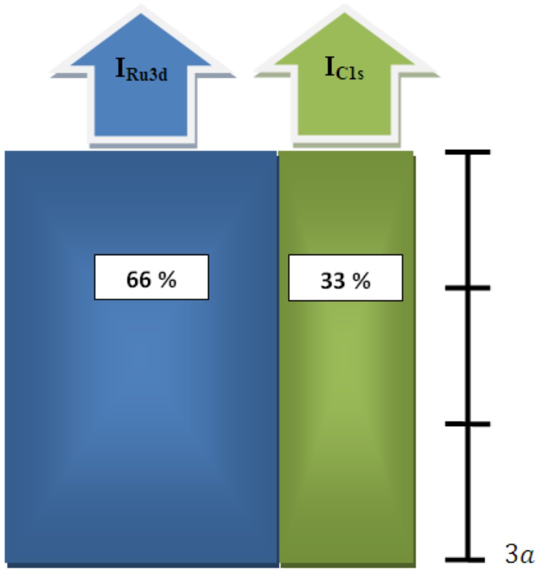


Figure 26: A Scenario in which the correct 2:1 ratio for Ru to C might be possible.

The surface sensitivity of XPS provides remarkable information about the top 10 nm of material, but unless a sample is prepared to be homogeneous in depth (Figure 26) and without contamination, the atomic concentration reported by XPS is not a representation of the sample composition in terms of proportions of elements. The following, however, demonstrates how a substrate material measured by XPS can return representative atomic composition.

XPS Experiments for ppHex films on SiO_2Substrate

An overlayer of ppHEX on SiO2 illustrates how the relationship between substrate materials is altered by different depths for an overlayer. The substrate is SiO_2 and therefore the ratio for oxygen to silicon should be 2:1. The experimental peak intensities are scaled using Scofield cross-sections for O 1s and Si 2p transitions to obtain estimates for the amount of oxygen to silicon. Deviation from the expected ratio of 2:1 is expected when using Scofield cross-sections due to limitations in library RSFs. The point to observe is not the absolute experimental ratio but the consistency of the ratio calculated from the peak areas determined from the uncorrected and corrected data. Corrected spectra are obtained by applying the adjustment to the intensity as follows:

$$I_{corrected} = I_{raw} e^{\left({}^{d}/_{a(E)} \right)}$$

where the raw intensity I_{raw} is corrected using the film depth d divided by the effective attenuation length $a(E)$. The effective attenuation length varies as a function of kinetic energy E.

A set of six spectra (Figure 27) with ppHex thickness ranging from 1.58 nm to 15.4 nm show the ratio for oxygen to silicon ranges from 1.5 to 0.6 (Table 4). However, following correcting the spectra (Figure 28) to account for attenuation of the O 1s and Si 2p peaks as a result of the ppHEX overlayer, the O:Si ratio ranges from 1.7 to 2.4, with three film thickness corrected spectra returning a ratio of 1.9 (Table 5).

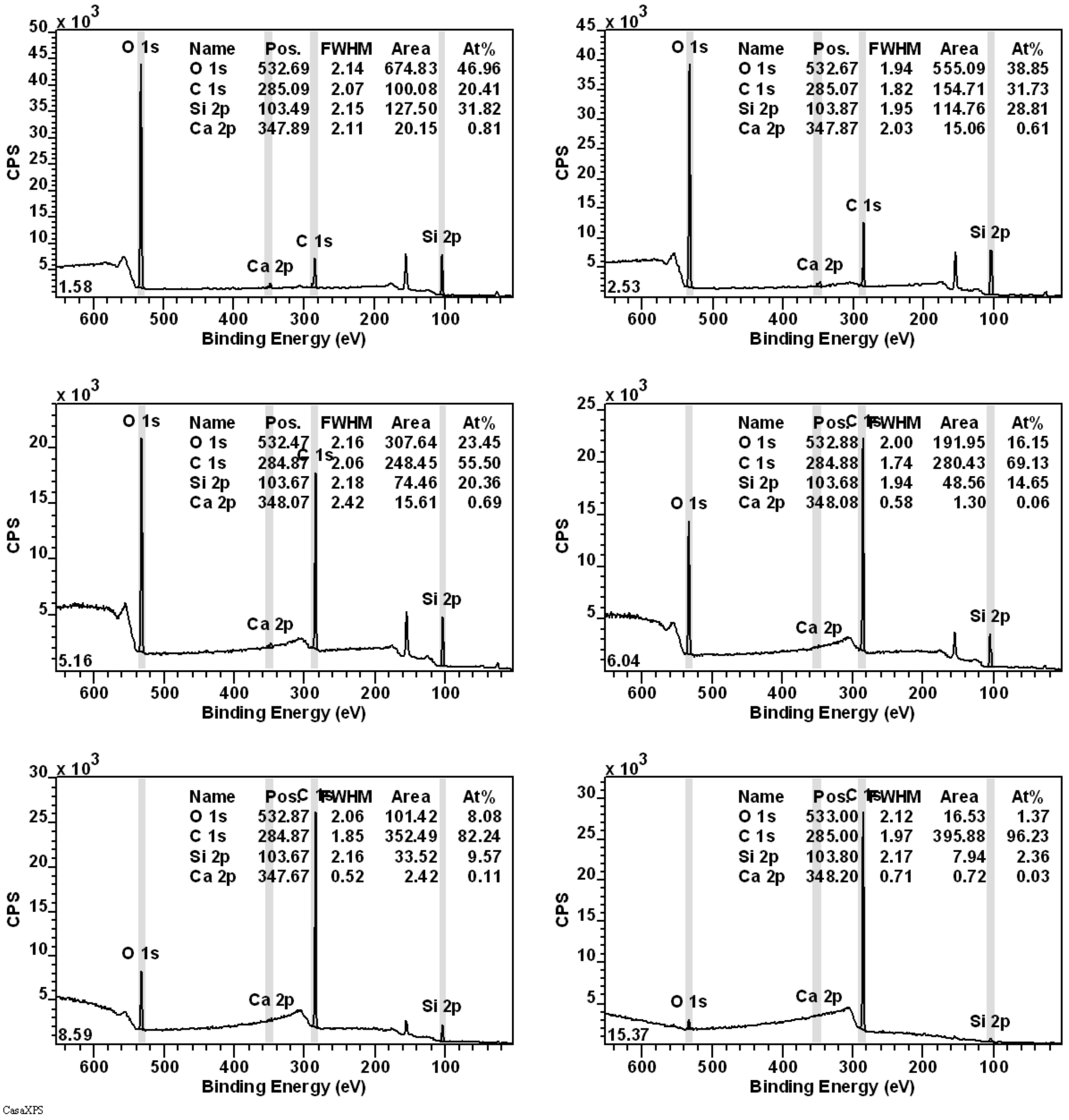
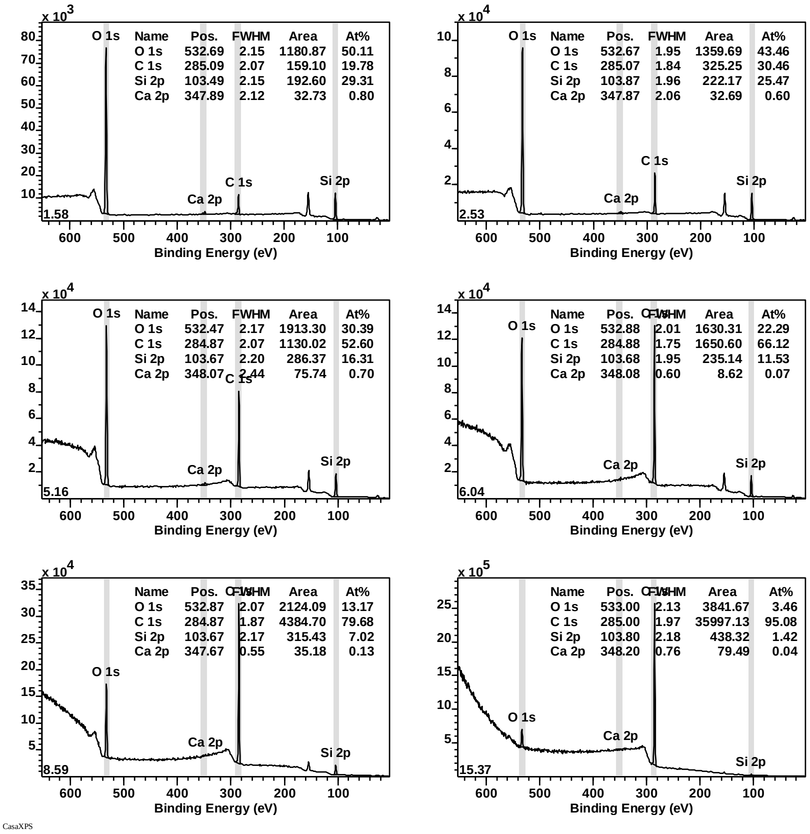


Figure 27: ppHEX on SiO_2 samples with a range of ppHEX overlayer depths demonstrate the attenuation of both O 1s and Si 2p emission peaks. Film thickness values correspond to depths determined by means of Ellipsometry.

Table 4: Results from the uncorrected spectra in Figure 27 where the ratio of oxygen to silicon varies as a function of film thickness. These variations are entirely due to the attenuation of the lower kinetic energy O 1s electrons compared to the more energetic Si 2p electrons by the carbon overlayer and the change in sampling depth between O 1s and Si 2p peaks.

Overlayer Depth (nm)	C 1s : Si 2p	O 1s : Si 2p
1.58	0.641316	1.47582
2.53	1.10144	1.34879
5.16	2.72601	1.15201
6.04	4.71788	1.10212
8.59	8.5906	0.843573
15.37	40.7548	0.580616



Name	Pos.	FWHM	Area	At%
O 1s	532.69	2.15	1180.87	50.11
C 1s	285.09	2.07	159.10	19.78
Si 2p	103.49	2.15	192.60	29.31
Ca 2p	347.89	2.12	32.73	0.80

Name	Pos.	FWHM	Area	At%
O 1s	532.67	1.95	1359.69	43.46
C 1s	285.07	1.84	325.25	30.46
Si 2p	103.87	1.96	222.17	25.47
Ca 2p	347.87	2.06	32.69	0.60

Name	Pos.	FWHM	Area	At%
O 1s	532.47	2.17	1913.30	30.39
C 1s	284.87	2.07	1130.02	52.60
Si 2p	103.67	2.20	286.37	16.31
Ca 2p	348.07	2.44	75.74	0.70

Name	Pos.	FWHM	Area	At%
O 1s	532.88	2.01	1630.31	22.29
C 1s	284.88	1.75	1650.60	66.12
Si 2p	103.68	1.95	235.14	11.53
Ca 2p	348.08	0.60	8.62	0.07

Name	Pos.	FWHM	Area	At%
O 1s	532.87	2.07	2124.09	13.17
C 1s	284.87	1.87	4384.70	79.68
Si 2p	103.67	2.17	315.43	7.02
Ca 2p	347.67	0.55	35.18	0.13

Name	Pos.	FWHM	Area	At%
O 1s	533.00	2.13	3841.67	3.46
C 1s	285.00	1.97	35997.13	95.08
Si 2p	103.80	2.18	438.32	1.42
Ca 2p	348.20	0.76	79.49	0.04

Figure 28: Spectra corrected for ppHEX film thickness. Note the C 1s signal from the overlayer is not correctly adjusted as all signal for C 1s derives from the overlayer. A proportion of the O 1s signal may also derive from the overlayer due to contamination and therefore further corrections to the O:Si ratio may be necessary for a full treatment.

Table 5: Corrected spectra (Figure 28) identically analysed using quantification regions as the spectra in Figure 27 yield oxygen to silicon ratios from the substrate which are consistent and reasonably representative of the substrate composition.

Overlayer Depth (nm)	O 1s : Si 2p
1.58	1.70959
2.53	1.70647
5.16	1.86298
6.04	1.9333
8.59	1.87767
15.37	2.44389

Quantification of Homogenous Samples

The following statement is intended to summarise the essence of quantification by XPS.

An atomic concentration computed from a XPS spectrum involves isolating emission peaks, one per element (XPS spectra in general include multiple emission peaks for each element), then performing a sequence of corrections to these spectral intensities leading to values (normalised peak intensities) representative of the amount of substance sampled by at XPS measurement.

Rather than perform quantification of a compound material, single element samples are used for the following reasons. In restricting the discussion to homogenous sample of a single element the intension is to simplify XPS spectra to a set emission peaks from the same material. All peaks in these spectra, when properly corrected, should return the same value which could, in principle, be used to measure the amount of substance for these materials in other samples. In selecting copper, silver and gold spectra (Figure 29) a discussion of the quantification steps, typically used to quantify more involved samples, can be the focus of the discussion rather than the data itself. To this end, the three XPS spectra used throughout this section are from clean copper, silver and gold. By stating these samples are clean, the implication is the surface is free from any contamination by carbon and free from surface oxide formation.

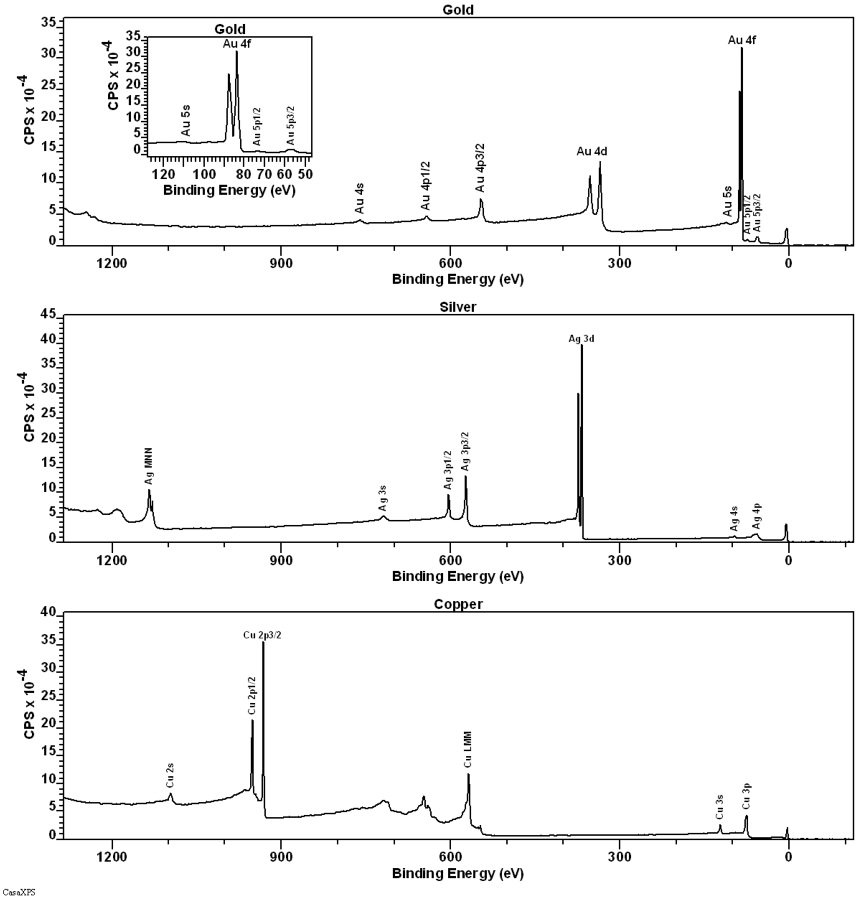


Figure 29: Survey spectra in the raw form measured from gold, silver and copper samples. The x-ray source is Al mono using hybrid lens mode, pass energy 80 on a Kratos Axis Ultra XPS instrument.

Relative Sensitivity Factors

Essentially, the probability of a scattering of a photon by an atom leaving the final electronic configuration with a hole in a specific core electronic shell is dependent on which core level is altered in the final state. The relative intensities for these photoemission peaks depends on these probabilities for the final state configuration and therefore the number of electrons detected are not uniformly distributed between the set of photoemission peaks in an XPS spectrum from a given element, but appear as a sequence of emission peaks with varying intensity.

The purpose of Relative Sensitivity Factors (RSF) is to correct peak intensities to account for differences resulting from the photoemission process.

Theoretical RSF, referred to as Scofield cross-sections, are used here to correct for peak intensity differences due to the photoemission process.

Transition probabilities calculated using Hartree-Slater approximations are tabulated by Scofield for photons of energy corresponding to Al and Mg x-ray sources. Scofield cross-sections do not account for angular distribution variation in the effective cross-section as a consequence of instruments detecting electrons in a specific direction relative to the photon source. Angular distribution correction to these Scofield cross-sections based on a given instrument geometry are applied resulting in RSF values appropriate for a given x-ray source and the angle between the x-ray source and the direction defined by the electron energy analyser.

For the data in Figure 29 the angle between the x-ray source and the direction of the electron analyser is assumed to be 60°. Scofield cross-sections are corrected for angular distribution using the factor $1-\frac{\beta}{4}(3\cos^2\theta-1)$ relative to spherically symmetric core electron configurations. The β value is computed for the element for which the Scofield cross-section is defined, and θ is the x-ray source to electron analyser angle.

Instrumental Transmission Correction

The number of electrons recorded by an instrument at a specific kinetic energy for the detected electrons deviate from the number of electrons emitted from the sample. The ratio of electrons leaving the sample to the number of electrons recorded at the detector varies as a function of the kinetic energy for the emitted electrons. To adjust for these variations in collection efficiency an instrument transmission function is measured.

Data in these examples are corrected for transmission using the National Physical Laboratory (NPL) transmission correction software. A transmission function is prepared for each operating mode for a given instrument. Differences in operating mode may include specific settings for the pass energy, electron optical lens modes, aperture settings and detector settings.

The examples presented here are measured using pass energy 80 and hybrid lens mode on a Kratos Axis Ultra. Figure 30 is a transmission function computed by the NPL software for these operating conditions of the instrument as stated and is used to correct the spectra in Figure 29.

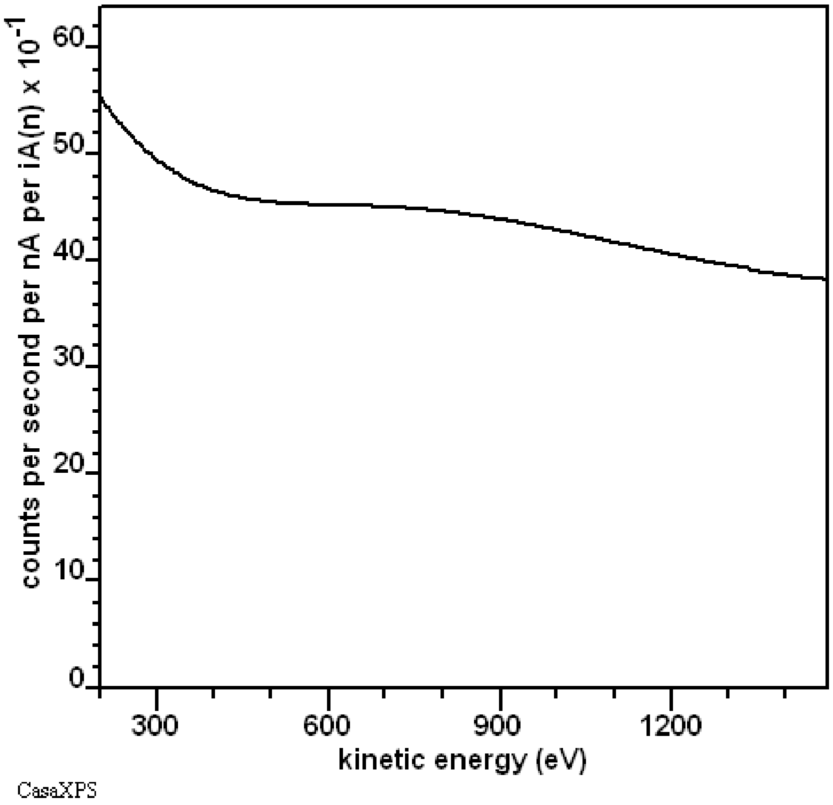


Figure 30: Transmission function calculated for a Kratos Axis Ultra pass energy 80 hybrid lens mode using the National Physical Laboratory transmission correction software.

Escape Depth Correction

Sampling depth, as illustrated in Figure 23, varies as a function of kinetic energy of the electrons detected. Even for a sample of uniform depth distribution such as gold, silver or copper, the number of electrons recorded for an emission peak reduces as the energy of the electrons decreases simply because the volume of material from which an electron can emerge without inelastic scattering reduces.

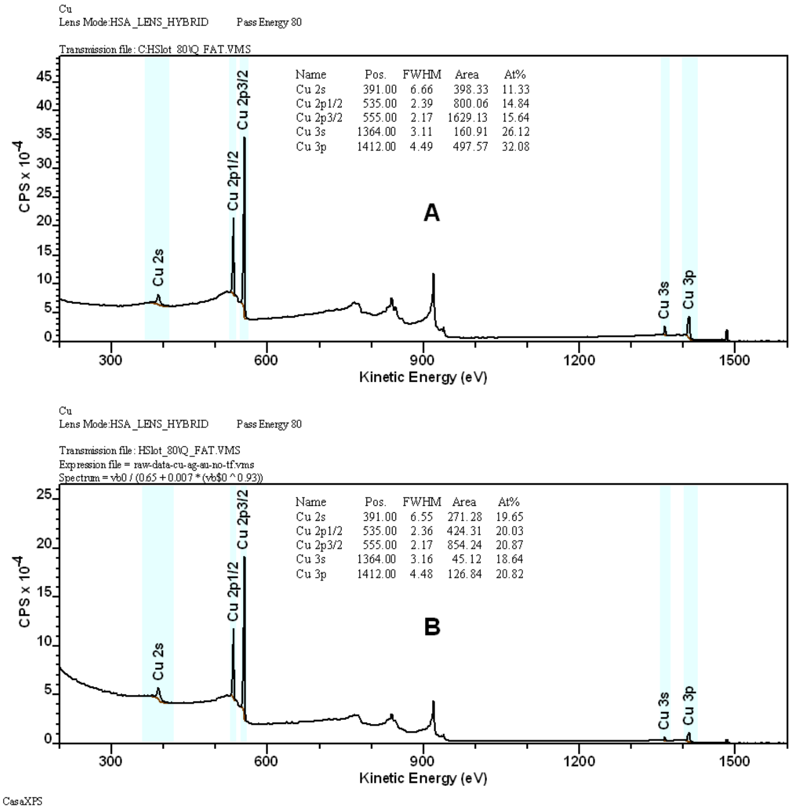
For a given analysis area, the volume of material sampled for a given kinetic energy for the emitted electrons can be modelled using the Inelastic Mean Free Path (IMFP) λ and Effective Attenuation Length (EAL)

Approximation (Seah) to IMPF (λ) and EAL

$$\lambda = \frac{(0.73 + 0.0095E^{0.872})}{Z^{0.3}} \quad (nm)$$

$$EAL = \frac{(0.65 + 0.007E^{0.93})}{Z^{0.38}} \quad (nm)$$

where E is the photoelectron kinetic energy and Z is the average atomic number provide a means of correcting for escape depth dependence on kinetic energy.



Cu
Lens Mode:HSA_LENS_HYBRID Pass Energy 80

Transmission file : C:HSlot 80\Q FAT.VMS

Name	Pos.	FWHM	Area	At%
Cu 2s	391.00	6.66	398.33	11.33
Cu 2p1/2	535.00	2.39	800.06	14.84
Cu 2p3/2	555.00	2.17	1629.13	15.64
Cu 3s	1364.00	3.11	160.91	26.12
Cu 3p	1412.00	4.49	497.57	32.08

Cu
Lens Mode:HSA_LENS_HYBRID Pass Energy 80

Transmission file : HSlot_80\Q_FAT.VMS
Expression file = raw-data-cu-ag-au-no-tf.vms
Spectrum = vb0 / (0.65 + 0.007 * (vb$0 ^ 0.93))

Name	Pos.	FWHM	Area	At%
Cu 2s	391.00	6.55	271.28	19.65
Cu 2p1/2	535.00	2.36	424.31	20.03
Cu 2p3/2	555.00	2.17	854.24	20.87
Cu 3s	1364.00	3.16	45.12	18.64
Cu 3p	1412.00	4.48	126.84	20.82

Figure 31: Clean copper Cu(0) before and after escape depth correction based on EAL. The quantification table in A includes transmission correction but not escape depth correction.

XPS data only offers the possibility for reporting the amount of substance when properly corrected emission peaks are used in the atomic concentration formula applied to truly homogeneous samples. Raw spectral intensities are subject to variations which are illustrated in Table 6 and Table 7 where Table 6 provides an example of %Area results calculated using the peaks shown in Figure 29 for copper, silver and gold which have been corrected for transmission, escape depth and emission variations, which should be compared against similar calculations in Table 7 where only emission variations are corrected.

Table 6: Percentage area calculated from transmission corrected and escape depth corrected spectra using angular distribution corrected Scofield cross-sections. Note the consistency of the %Area across a wide kinetic energy range for copper. These results should be compared against the results in Table 7.

Corrected % Area					
Cu 2s	Cu 2p1/2	Cu 2p3/2	Cu 3s	Cu 3p	
19.65	20.03	20.87	18.64	20.82	
Ag 3s	Ag 3p1/2	Ag 3p3/2	Ag 3d	Ag 4s	Ag 4p
17.28	16.61	17.04	17.74	15.1	16.23
Au 4s	Au 4p1/2	Ag 3p3/2	Au 4d	Au 4f	
19.33	19.92	20.3	20.64	19.81	

Table 7: Percentage area calculated from raw peak areas corrected for emission variation using angular distribution corrected Scofield cross-sections, but without any corrections applied to the spectral intensities to neither account for transmission nor escape depth corrections.

Raw % Area					
Cu 2s	Cu 2p1/2	Cu 2p3/2	Cu 3s	Cu 3p	
12.71	16.14	17	24.41	29.73	
Ag 3s	Ag 3p1/2	Ag 3p3/2	Ag 3d	Ag 4s	Ag 4p
13.25	14.82	16.15	20.25	16.12	19.41
Au 4s	Au 4p1/2	Ag 3p3/2	Au 4d	Au 4f	
16.98	17.4	20.7	21.81	23.12	

Note, these copper, silver and gold samples are ideal homogeneous samples for XPS analysis, which are seldom encountered in practical XPS measurements.