Case study – plasma oxidation of polystyrene

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"Surely you were aware when you accepted the position, Professor, that it was publish or perish."

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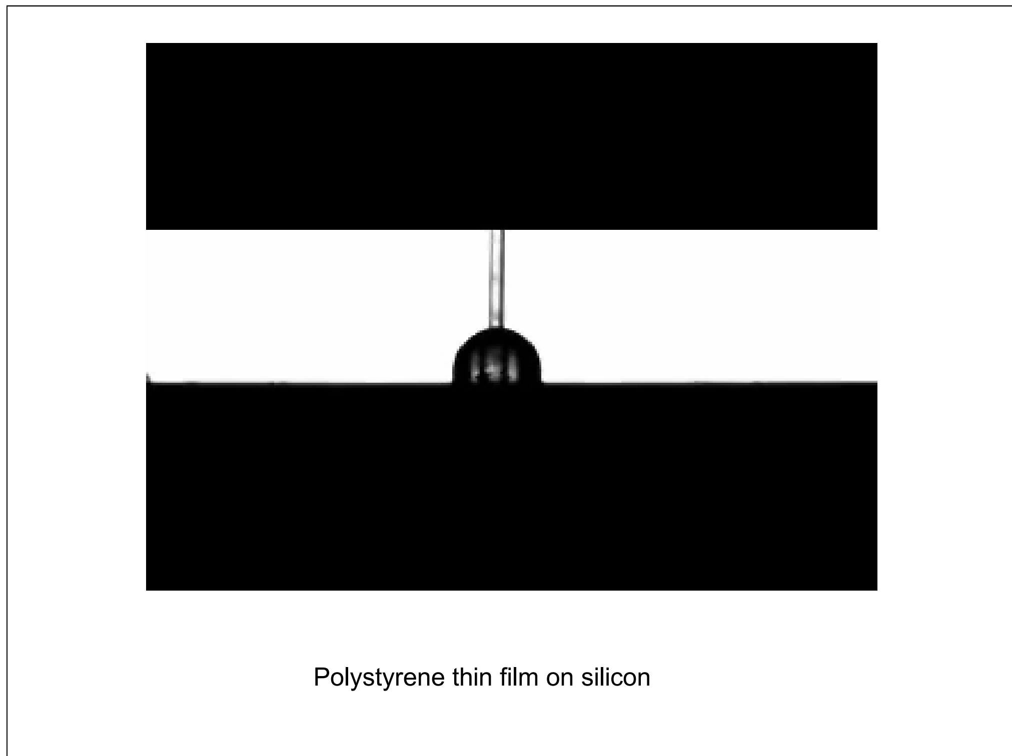
ARXPS web site:
http://goliath.inrs-emt.uquebec.ca/surfsci/arxps/index.html

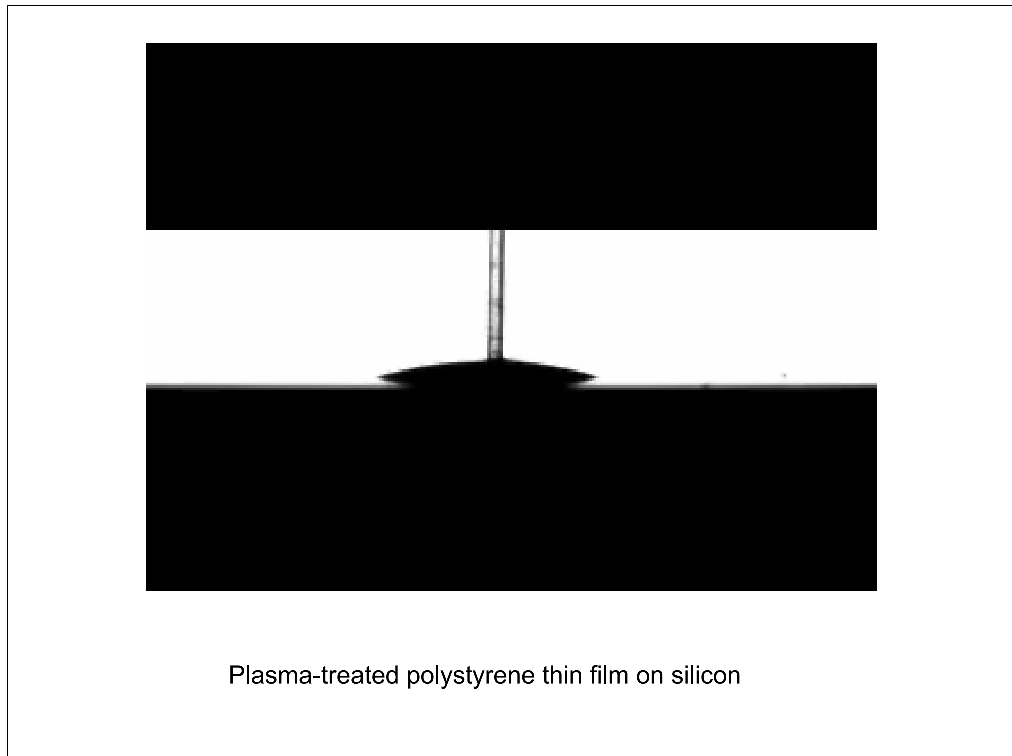


Polystyrene thin film on silicon

I propose to talk about a case close to my heart – the use of XPS to study the modification of polymer surfaces by radio frequency plasmas.

Polymers are cool materials with some excellent bulk properties but their surface properties leave something to be desired for certain applications. For example, if one wants to print on them with water-based inks, the water has to properly wet the surface in order for the printed image not to bead up. Surface wettability is also an issue in other applications, such as the use of adhesives on polymers and in polymeric biomaterials.

Here we see a water droplet deposited onto a polystyrene thin film, spin-coated onto a clean silicon wafer. The wettability of the surface can be assessed from the angle that the surface of the water droplet makes with the polymer at the point of contact, which is about 95º here. On polystyrene, water tends therefore to bead up rather than to spread out, and we can say that the polystyrene surface is naturally hydrophobic.



Plasma-treated polystyrene thin film on silicon

This is the behaviour of a water droplet following the exposure of the polystyrene surface to a plasma for one minute. For those interested the plasma parameters in this case were

Plasma gas : 10% oxygen / 90% helium mixture

Gas flow rate : 100 sccm

Gas pressure : 100 mtorr

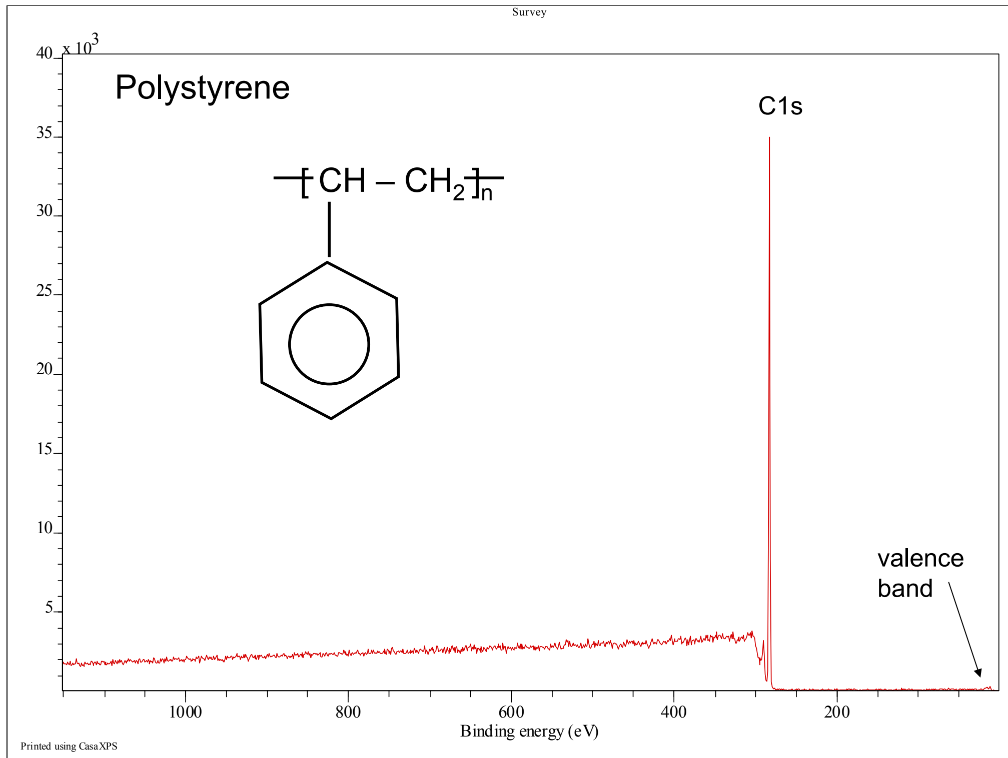
RF frequency : 13.56 MHz

RF power : 15 W

Sample suspended 5 cm above the powered antenna plate, outside the visible glow region.

The contact angle following plasma treatment is about 15º, so the polystyrene surface has been rendered significantly more hydrophilic.

Plasma treatments are widely used in industry for the modification of the wettability of polymer surfaces. But what is happening? What can XPS tell us?



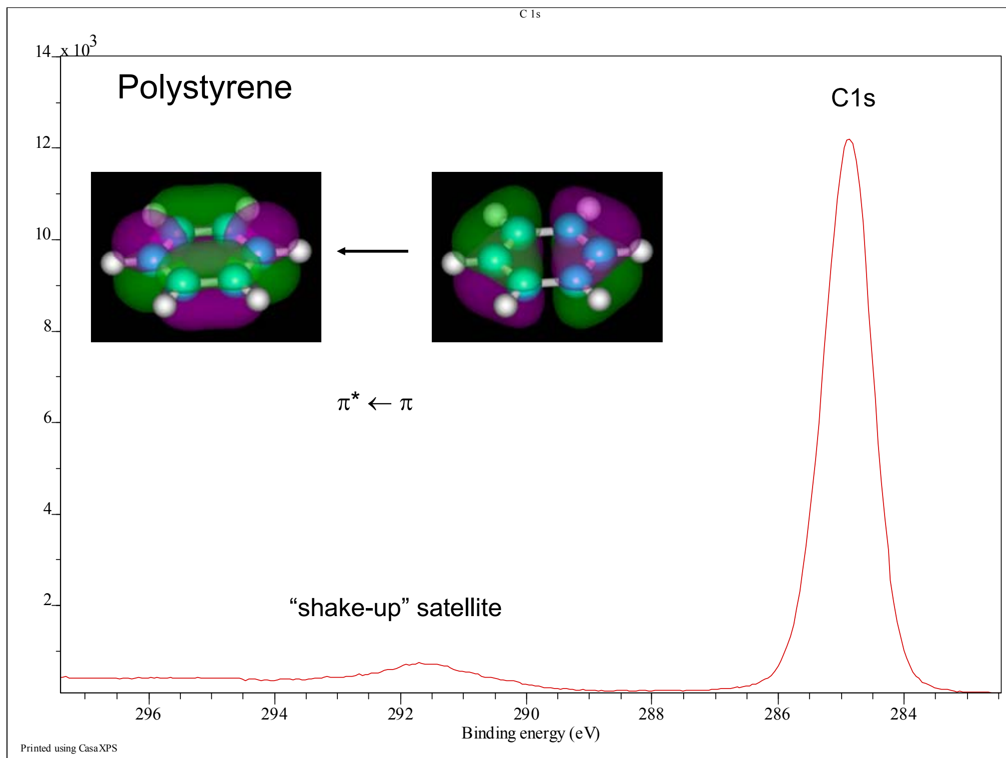
We will use this example, the investigation by XPS of the modification of a polystyrene surface by a helium / oxygen plasma, to illustrate some practical aspects in the analysis of XPS data.

We start with the analysis of the untreated polystyrene surface. This survey spectrum comes from a standard database of polymer spectra

http://www.surfacespectra.com/xps/index.html

http://mmrc.caltech.edu/mmrc_html/polymer_HR-XPS/

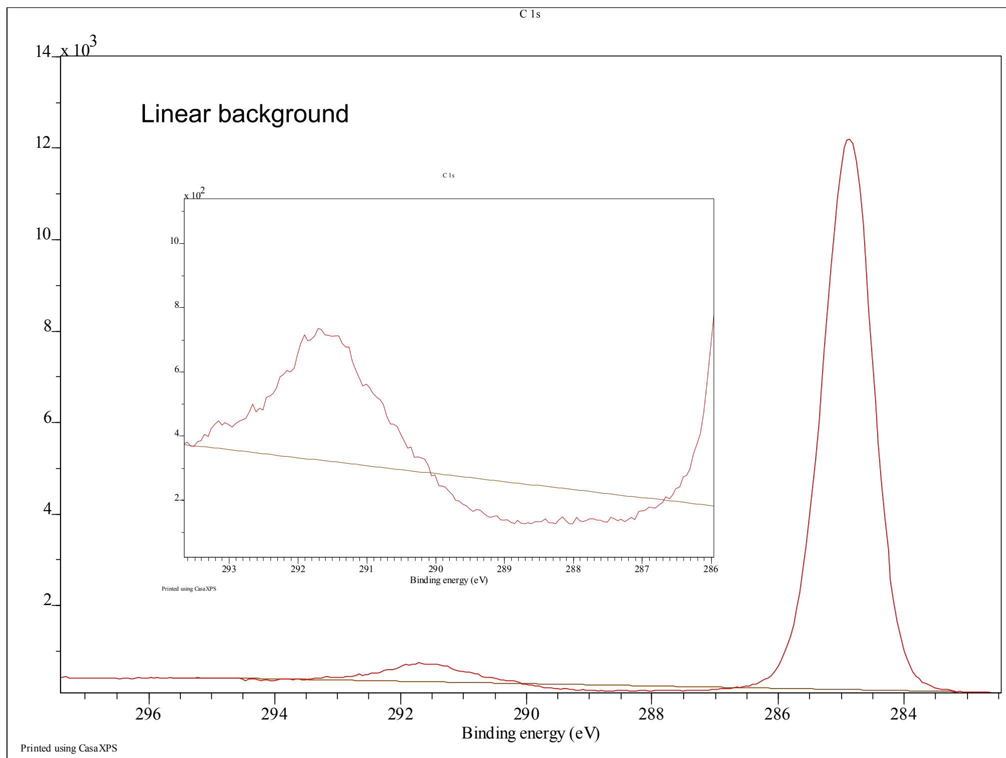
The spectrum, consistent with the nominal structure for polystyrene, shows only carbon.



The high-resolution scan of the C1s peak shows two features. The first, at around 284.9 eV, is the familiar peak due to simple photoemission from the C1s orbital. It can be decomposed into two peaks separated by 0.24 eV, a peak at higher binding energy corresponding to sp^3 hybridized carbon in the polymer backbone and a peak at lower binding energy, three times as intense, corresponding to sp^2 hybridized carbon in the benzene rings.

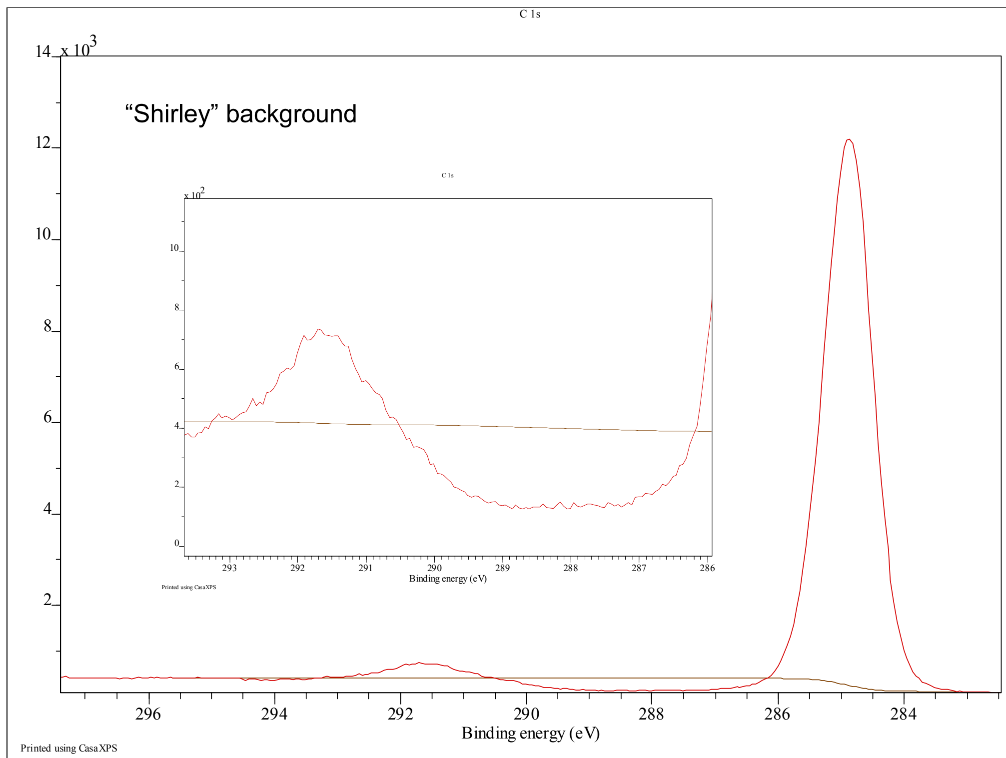
Separated by about +6.7 eV from this peak we see a satellite peak. This peak is due to "shake-up" excitations taking place in the π orbitals on the benzene rings. Simultaneous to the ejection of the photoelectron from the 1s orbital, an electron is promoted from an occupied π bonding orbital on the benzene ring to an unoccupied π^* antibonding orbital. The energy of this excitation is deducted from the kinetic energy of the photoelectron, which emerges with a slightly lower kinetic energy and therefore an apparently higher binding energy.

The shake-up satellite, then, is characteristic of the presence of intact benzene rings in the polymer surface and therefore represents a handy diagnostic for the estimation of structural damage in the polymer due to the exposure to plasma.



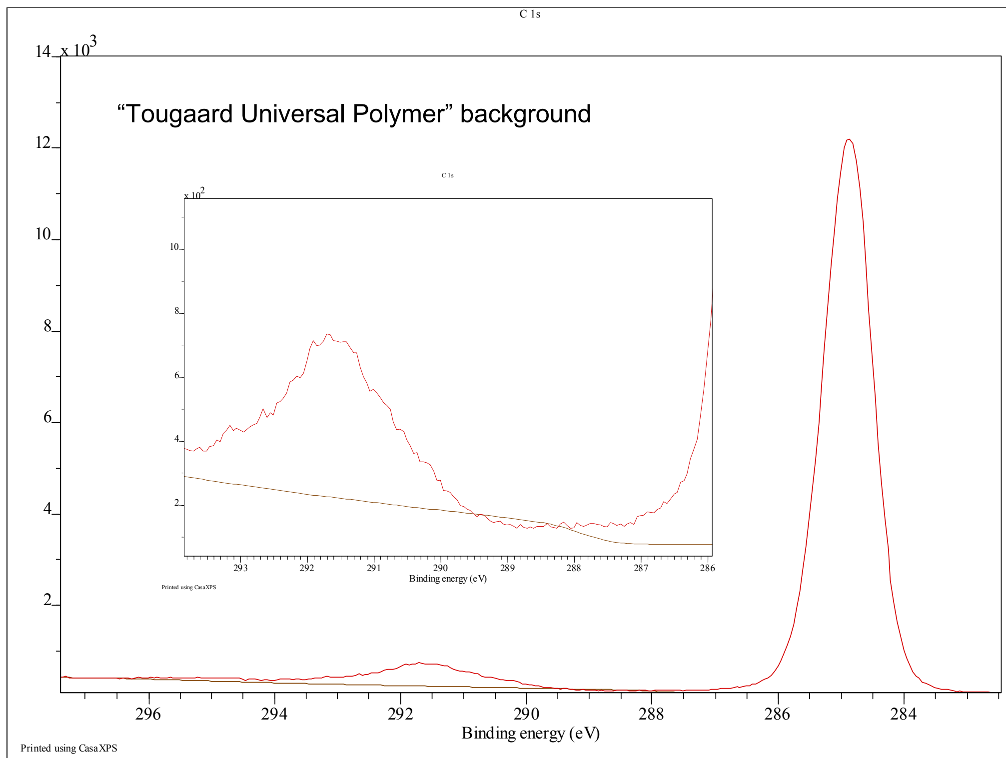
In order to treat XPS in a quantitative manner, we need to subtract the background from the peaks. A number of background shapes have been proposed for this purpose. The most simple is a straight line drawn between two points chosen by the person doing the analysis, the “linear” background. It is a reasonable choice for wide band-gap materials, especially polymers, that exhibit symmetrical peaks.

However, in the case of polystyrene, this background cuts through the spectrum in the region between the main photoelectron peak and the shake-up satellite.



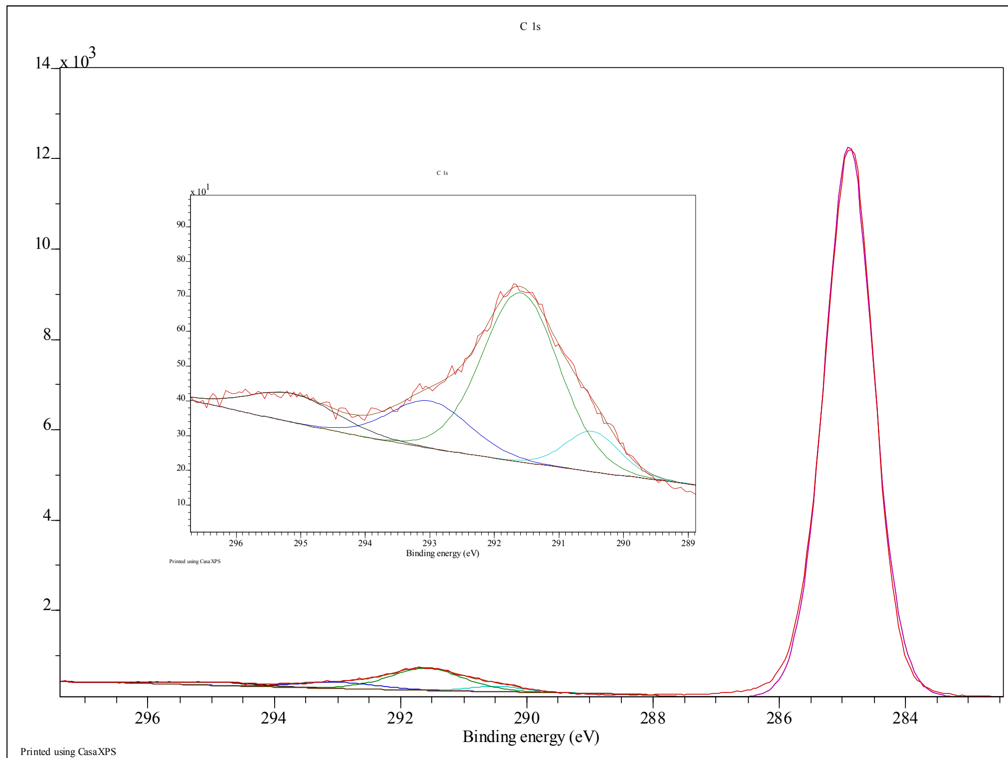
A more sophisticated background shape is the so-called “Shirley” background, whose height is proportional to the integrated peak intensity up to that point on the energy scale, going from lower to higher binding energy. This somewhat arbitrary mathematical form is a step forward from the linear background for those materials exhibiting small or zero band gaps and asymmetric peak shapes, and can be considered to factor out “intrinsic” energy loss mechanisms to some extent.

However, in the case of polystyrene, the “Shirley” background is even worse than the linear background between the main photoemission and satellite peaks.



Tougaard has spent many years studying and modelling the various energy loss mechanisms for photoelectrons in solids and has produced formulae for background shapes in a number of types of material which are based on the real physics of electron transport. The disadvantage of a Tougaard background is that it is necessary to acquire a spectrum going some 30 eV beyond the peak in order to obtain a proper fit, however, it can be seen above that even in a 20 eV window the "Tougaard Universal Polymer" background behaves much better in the problem region than either the linear or Shirley backgrounds.

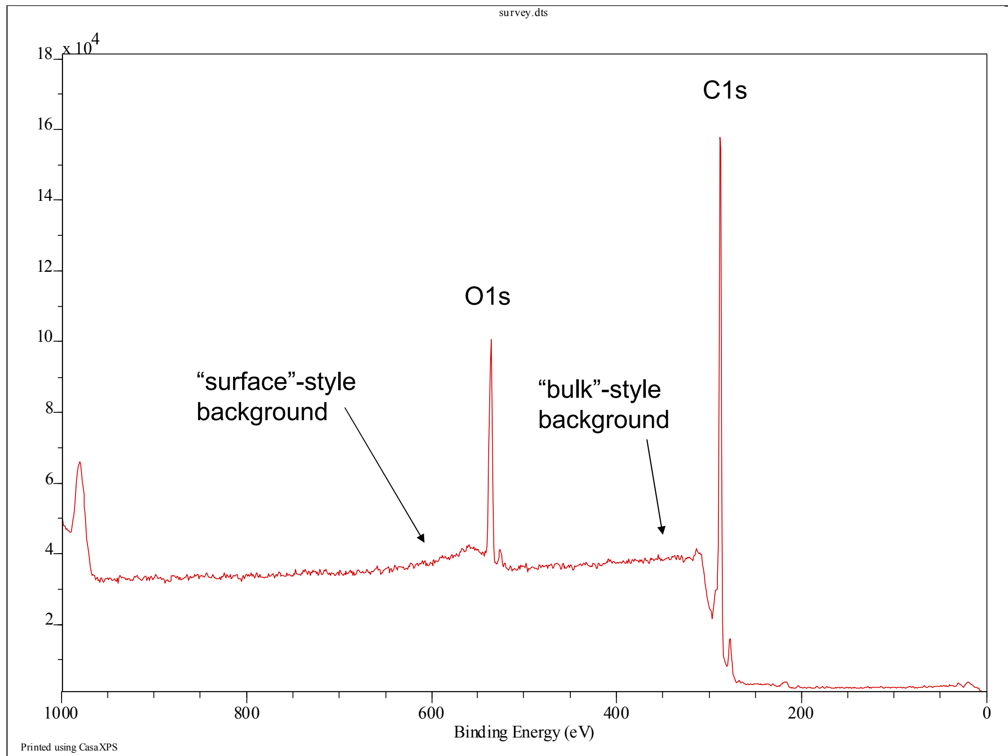
We will therefore use the Tougaard Universal Polymer background in the analysis of the data to be presented here.



Having decided upon the best shape for the background, the next step is to characterize the shape of the polystyrene spectrum in terms of symmetrical component peaks. The analysis software allows us to position component peaks in the spectrum and then to optimize the peak positions, intensities and widths by minimizing the sum of the squared differences between the experimental data and the synthesized spectrum given by the sum of the component peaks.

In this case we will fit the main peak at 284.9 eV with a single component, and use 4 components to reproduce the shape of the shake-up satellite. By noting the relative positions, widths and intensities of the component peaks in this spectrum, an equivalent polystyrene spectrum can be inserted into a more complex envelope obtained from a plasma-treated sample, in order to identify new peaks, or in order to monitor changes in the intensity of the shake-up components.

Here is the plasma reactor. We'll pop the polystyrene film sample inside and expose it to the plasma for one minute.

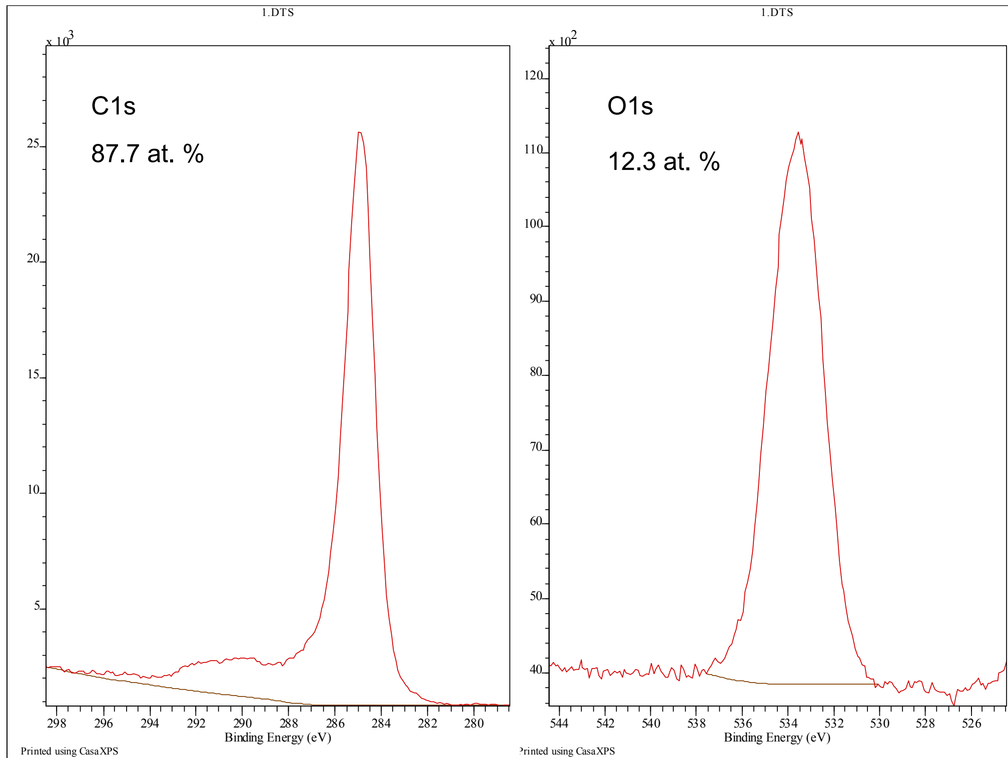


When we take the plasma-treated sample out and rush it to the X-ray photoelectron spectrometer for analysis, we get this survey spectrum.

Compared with the spectrum for untreated polystyrene, we note the presence of the O1s peak. Exposure to the oxygen / helium plasma, apparently, has led to the incorporation of oxygen into the polystyrene surface.

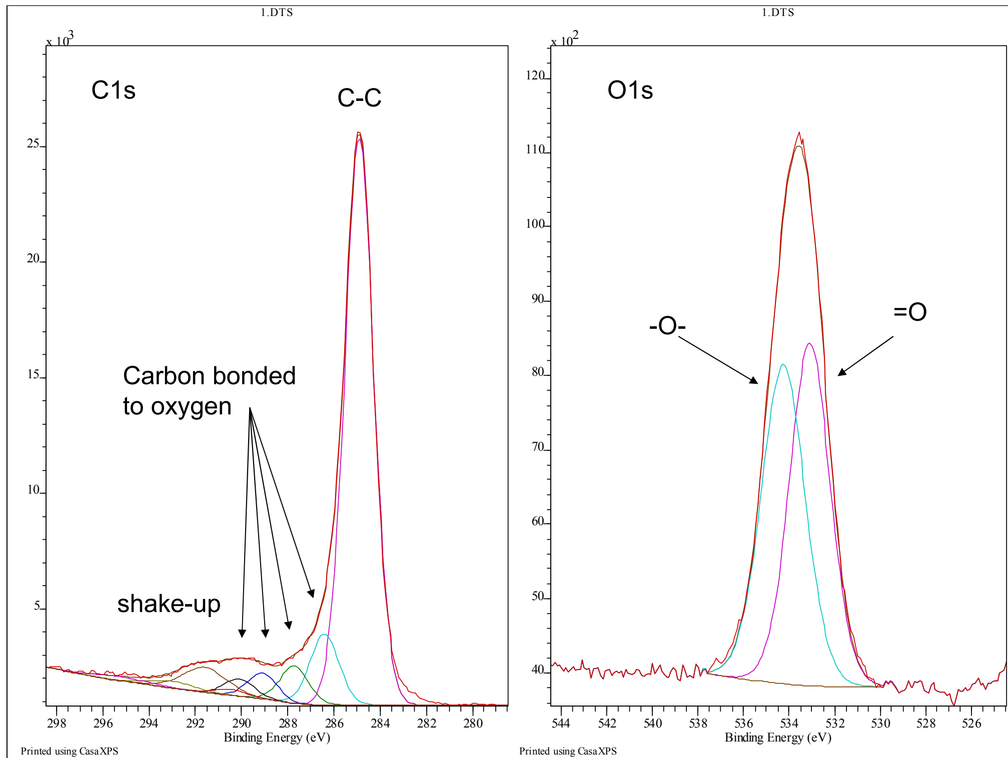
Eyeballing the behaviour of the background on the high binding energy side of the carbon and oxygen peaks, we notice a difference. The background on the left of the carbon peak is essentially flat (as it is in the spectrum of the untreated polystyrene), characteristic of a uniform carbon atom distribution with respect to depth. The background to the right of the oxygen peak, however, exhibits a rapid decline and then an essentially flat background that appears to be a continuation of the background associated with the carbon peak. This is characteristic of the case in which the oxygen atoms are concentrated at the very surface of the sample and absent in the subsurface bulk.

It would appear that the exposure to plasma has oxidized the polystyrene, but that the "oxide" is confined to a thin surface layer.



From the high-resolution scans of the C1s and O1s peaks, subtracting a "Tougaard U Poly" background and correcting for the transmission function, photoemission cross section and photoelectron attenuation lengths, the apparent composition of the sample (on a hydrogen-free basis of course) is 12.3 atom % oxygen, 87.7 at. % carbon. According to this stoichiometry, on average there is one oxygen atom for every styrene unit in the analyzed volume.

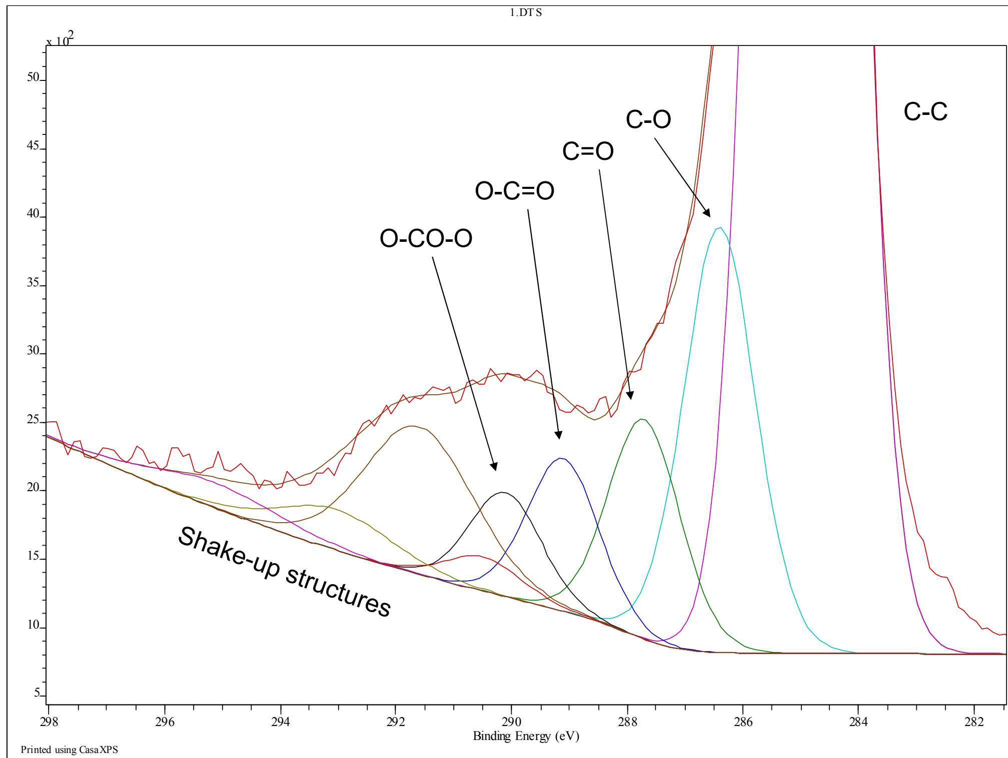
The O1s peak is new and there is also new intensity in the C1s peak



Inserting the components for untreated polystyrene into the C1s envelope, and adjusting the intensities of the shake-up components to fit (maintaining the relative proportions between them), it is found that additional components are needed to reproduce the experimental peak shape. The new intensity in the C1s envelope is observed between the "carbon-bound-to-carbon" and shake-up components, corresponding to the formation of carbon-oxygen bonds.

Peak-fitting is not "peak deconvolution" in the proper sense of the term but rather "peak synthesis", the construction of an identical envelope from a number of components that will hopefully have some physical meaning in the context of the experiment. It is not unreasonable to suppose that the new intensity observed in this experiment is due to the presence of a finite number of distinct chemical groups formed due to the exposure to plasma. Surveying the literature for XPS C1s peaks obtained from various polymers, it is reasonable to suppose that the new components will have the same shape and width as the principal "C-C" component, and that they will exhibit chemical shifts consistent with that shown in the standard spectra. For example, the peak associated with "C-O-C" carbon in various polymers shows an average peak shift of +1.45 eV from the C-C component.

The O1s peak can be decomposed, with some difficulty because of its apparent symmetry, into components corresponding to -O- and =O oxygen peaks observed in polymers.



Looking closer at the region of new intensity, we see that four components, in addition to those present in untreated polystyrene, have been added to reproduce the experimental C1s peak shape. The width of these components has been fixed by hypothesis at the width of the principal C-C peak, and the positions of the new components has been fixed relative to that of the C-C peak by reference to the chemical shits of specific carbon-oxygen groups reported in the standard database referenced on page 3. The synthetic peak shape produced in this manner corresponds closely to the experimental C1s envelope. It should be admitted, nonetheless, that the choice of chemical groups used in the peak fitting represents the imposition of the prejudices of the experimenter onto the experimental data. In this case the formation of the following chemical groups by the plasma exposure is used to explain the new intensity in the C1s envelope:

+1.5 eV : C-O-C or C-OH : ether or hydroxyl

+2.9 eV : C=O : carbonyl

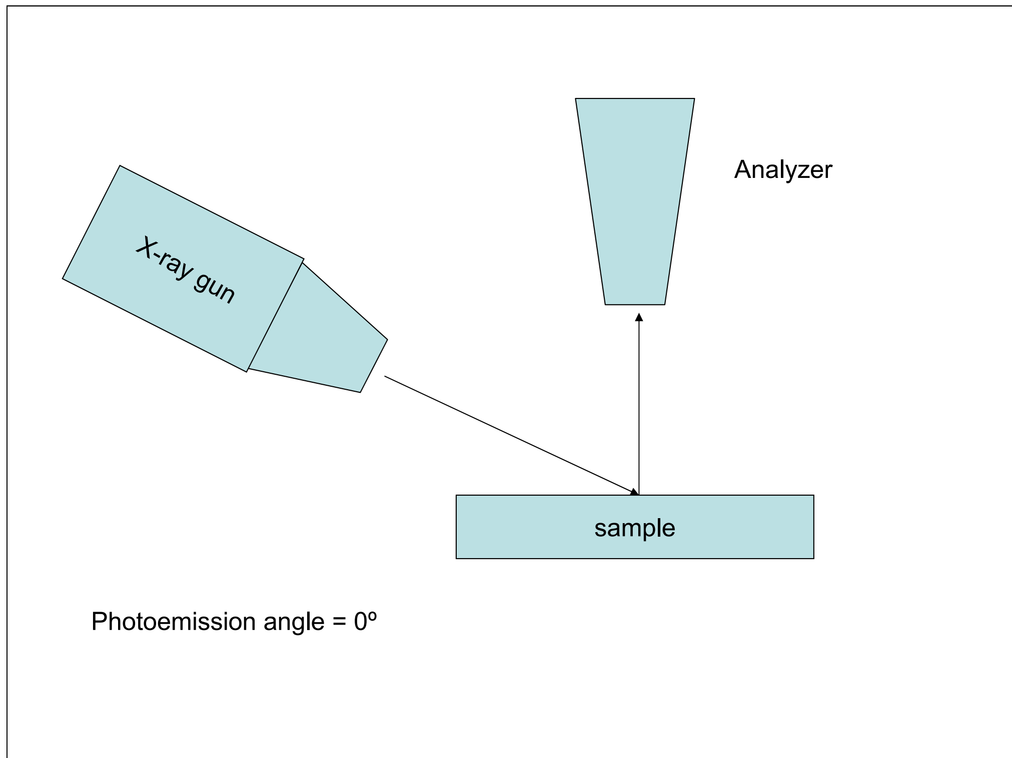
+4.2 eV : -O-C=O or COOH : ester or organic acid

+5.2 eV : -O-CO-O- : carbonate

Component intensity as % of total intensity in C1s envelope

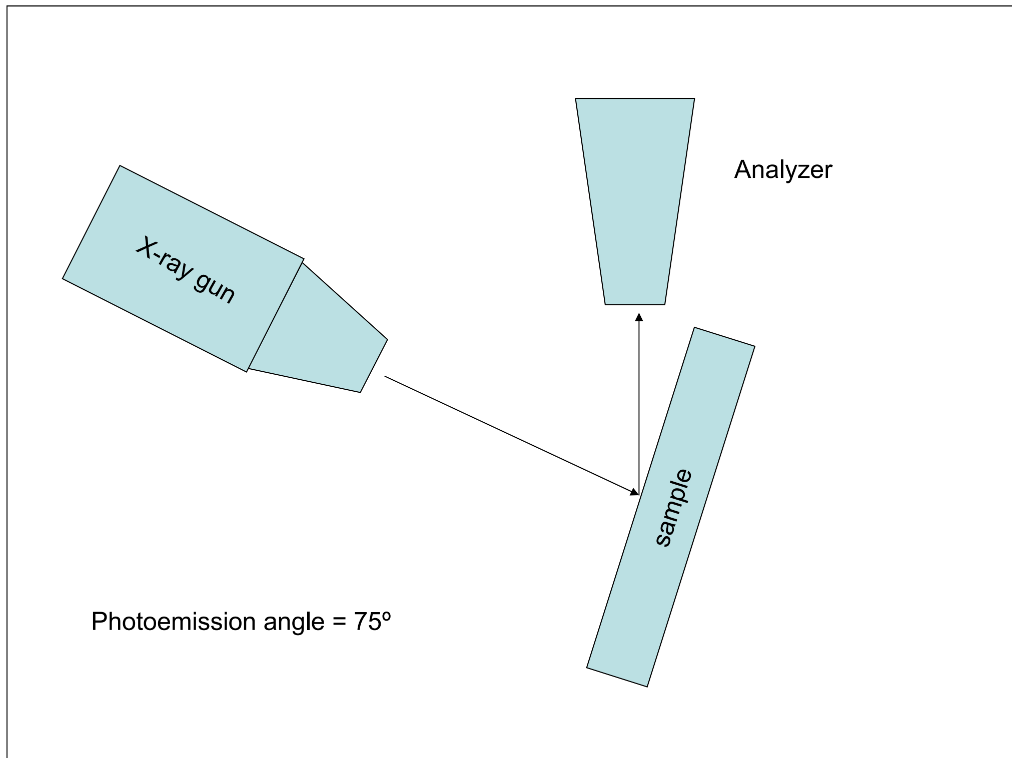
	Untreated PS	Treated PS
C-O		9.2
C=O		4.7
O-C=O		3.3
O-CO-O		2.3
shake-up	9.3	8.1

According to the peak fitting (and the assumptions about the origins of the new intensity) 9% of the carbon atoms contributing to the signal are singly bonded to one oxygen atom, 5% are doubly bonded to one oxygen atom, 3% are singly bonded to one oxygen atom and doubly bonded to another, and 2% are in organic carbonate groups somehow. We also observe a slight decrease in the intensity of the shake-up peak, an indication of some damage done to the benzene rings in the polymer structure.

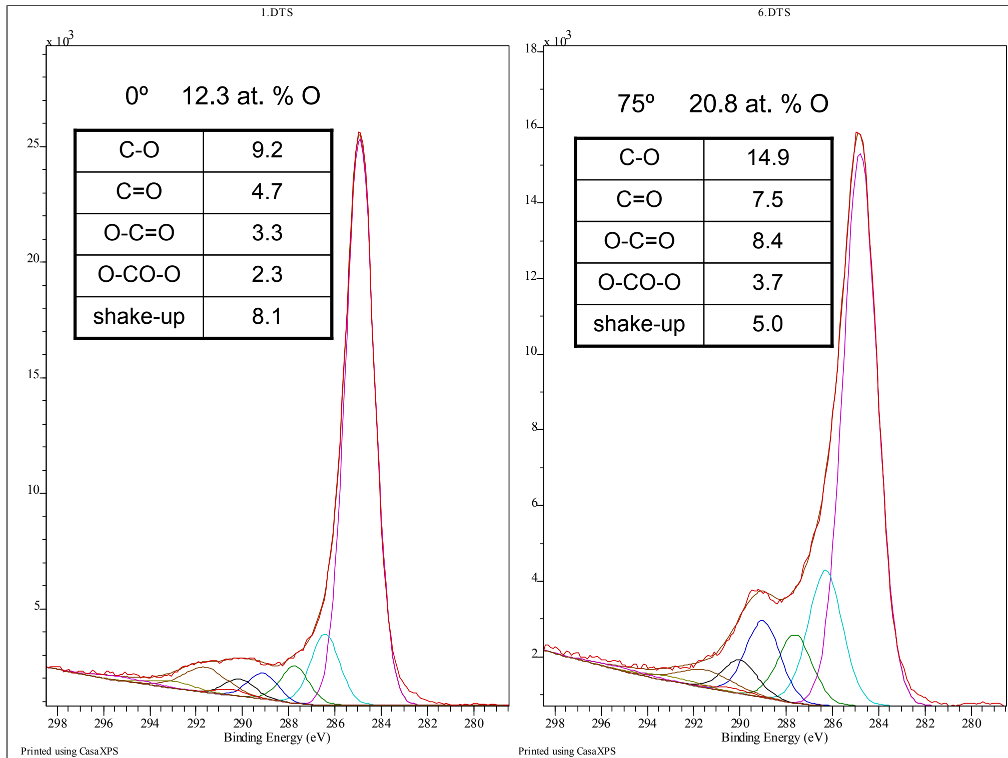


This spectrum was taken with the sample oriented thusly: the photoelectrons entering the analyzer left the sample making an angle of zero degrees with respect to the normal to the sample surface, i.e. a photoemission angle of 0º.

The angle between the X-ray beam and the direction of entry into the detector is 54.7º.

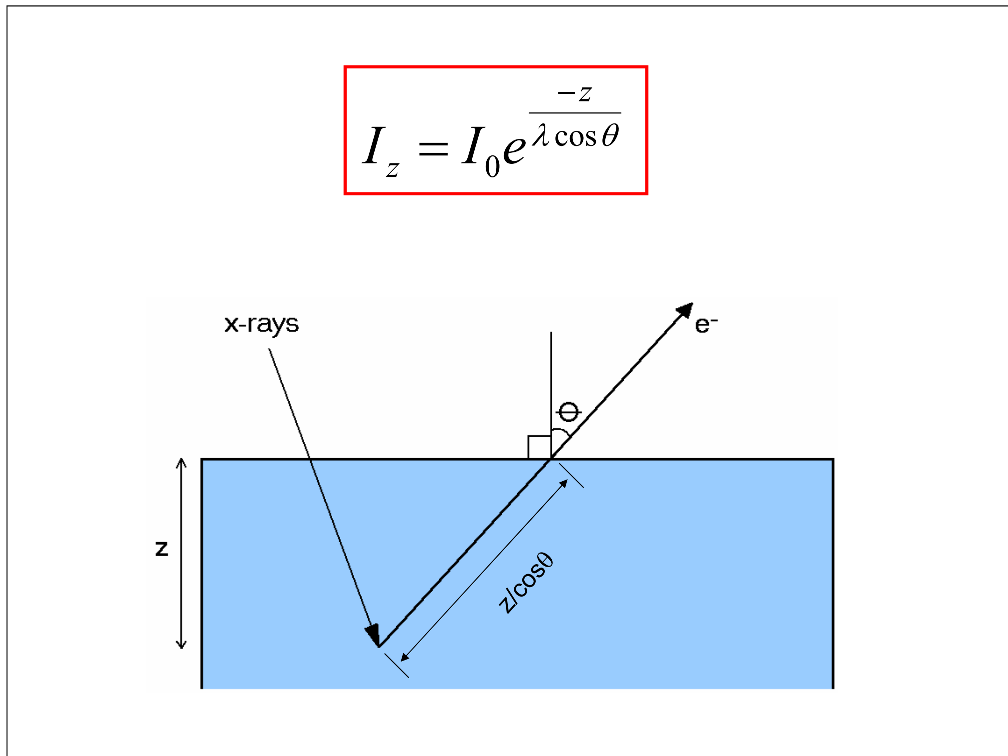


But we are not confined to making XPS measurements at a photoemission angle of 0º. Suppose we make a measurement on the same sample at a photoemission angle of 75º, (a “take-off” angle of 15º).



We get a different result!

When the measurement is made at a 75º photoemission angle, there appears to be 20.8 at. % oxygen in the surface, and the intensities of the carbon-bonded-to-oxygen components in the C1s envelope increase in intensity relative to the C-C peak. The intensity of the shake-up satellite decreases at the grazing angle.



This is because at grazing angles, the XPS measurement is more surface sensitive. The real distance a photoelectron originating at a depth z must travel through the sample in order to escape into the vacuum is z/cosθ, where θ is the photoemission angle. Therefore, a photoelectron originating from an atom 3 nm deep, and having to travel 3 nm through the sample at a photoemission angle of 0º, has to travel 11.6 nm when the photoemission angle is 75º. At 75º, many more of the photoelectrons originating from deep atoms will suffer inelastic collisions before emerging from the sample, and will contribute to the spectral background rather than to the characteristic XPS peak. At the grazing angle, those atoms closer to the surface stand a better chance of emitting photoelectrons that emerge from the sample unscathed, and hence, the peaks in the spectrum will be more representative of them, rather than those atoms deeper down.

The Beer-Lambert law, assumed to describe this phenomenon in the case in which elastic collisions can be ignored, relates the intensity of the signal I_z arising from an atom layer at depth z, to the intensity of the signal I_0 arising from the same atom layer but at the surface, through the photoelectron inelastic mean free path λ and the photoemission angle θ.

$$I(\theta) = kF\sigma \int_0^{\infty} c(z) e^{\frac{-z}{\lambda_e \cos\theta}} dz$$

Setting p = $(\lambda \cos\theta)^{-1}$

$$I(p) = kF\sigma \int_0^{\infty} c(z) e^{-pz} dz = kF\sigma\, L[c(z); p]$$

We see that the observed peak intensity is related to the Laplace transform of the concentration depth profile.

Unless c(z) = constant for each element measured, the apparent composition of the sample will depend upon the photoemission angle.

Going back to a simplified form of the equation describing the "no-loss" peak intensity, we see that the signal is a convolution of the concentration depth profile for the element in question with the the Beer-Lambert term describing the attenuation of the emerging photoelectrons, integrated over the thickness of the sample. In the equations above

$I(\theta)$ is the signal intensity at the photoemission angle θ

k is a scaling constant

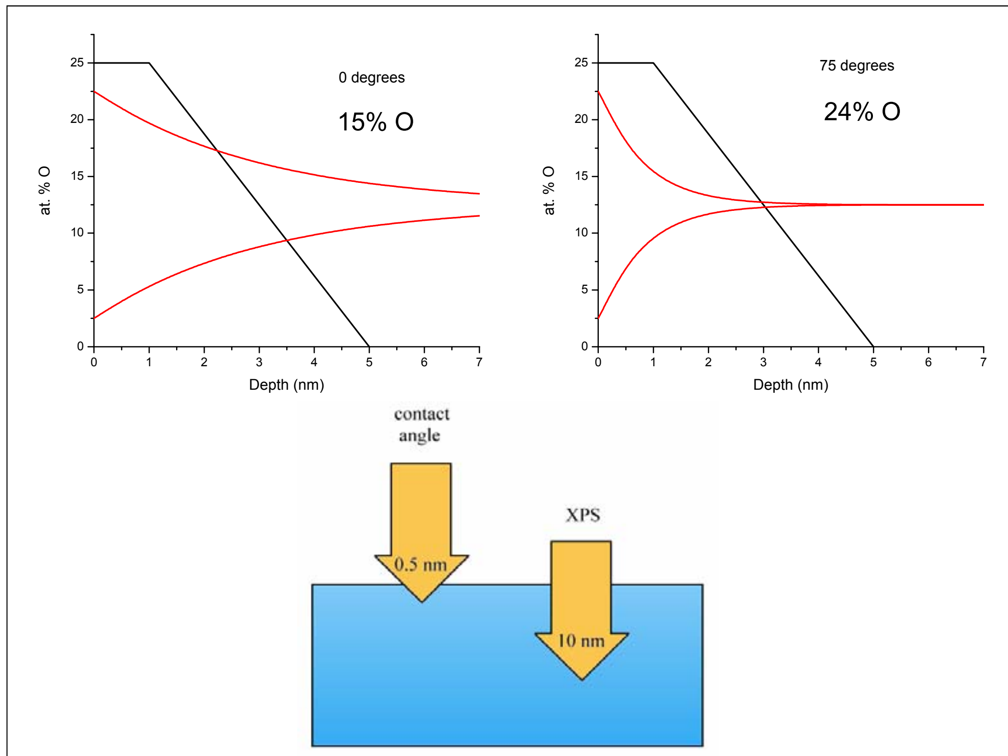
F is the analyzer transmission function

σ is the photoemission cross-section

c(z) is the concentration depth of the element in question at depth z

λ_e is the photoelectron inelastic mean free path

So the signal intensity in the no-loss peak is related to the Laplace transform of the concentration depth profile



Why do we care about this stuff? Because we are attempting to elucidate the behaviour of the water contact angle, in terms of the compositional information we obtain from XPS. But are the two techniques sampling the same material?

The contact angle measurement has a “sampling depth” of about 0.5 nm, according to measurements performed on Langmuir-Blodgett layers. The “sampling depth” of XPS will depend upon the photoemission angle.

The red cones in the figures above illustrate how the relative contribution to the peak intensity varies with depth, the height of the cone being proportional to the relative contribution to the integrated signal.

The concern is that for a non-uniform concentration depth profile, such as that shown in black in the figures above, the apparent composition of the sample will vary depending upon the photoemission angle. In order to determine the composition at depths relevant to the contact angle measurement, the measurement must be made at grazing angle.

Better yet, can we determine the form of the entire depth profile?

$$I(p) = kF\sigma \int_0^\infty c(z) e^{-pz} dz = kF\sigma \, L[c(z); p]$$

Can we calculate c(z) from I(p)?

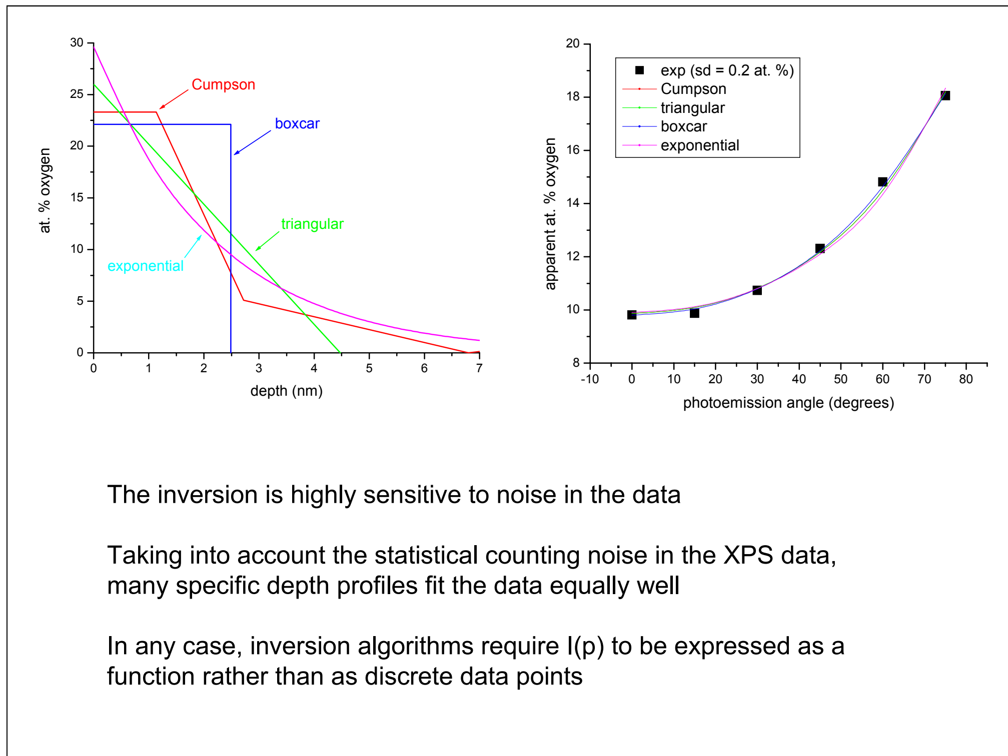
$$c(z) = L^{-1}\left[\frac{I(p)}{kF\sigma}; p\right]$$

$p = (\lambda \cos\theta)^{-1}$

The inversion of the Laplace transform is an “ill-conditioned” problem …

The logical thing to do would be to take experimental data at a series of photoemission angles and perform an inverse Laplace transform on them to recover the depth profile. This is the essential goal of Angle-Resolved X-ray Photoelectron Spectroscopy, ARXPS.

However, methods for the inversion of the Laplace transform require a function as an input, rather than discrete data. Worse, the inversion of the Laplace transform is an “ill-conditioned” problem, meaning that the result is highly sensitive to noise in the data.



Essentially, given a finite level of noise in the data, there is no unique depth profile that can be derived from them. The example above shows four depth profiles on the left, and the data to which they were fitted (symbols) on the right. As can be seen (lines at right) the four profiles all fit the data within the experimental error on the data points (standard deviation 0.2 at. %).

The depth resolution $\Delta z/z$ of ARXPS is coupled to the uncertainty in the concentration in the depth profile, and even for a relative uncertainty in the concentration of 50%, the depth resolution is only 0.8

So why bother? Because, the standard technique for acquiring an XPS depth profile, ion bombardment, is not appropriate in the case of polymers.

Our approach:

Take XPS data at six photoemission angles (0º, 15º, 30º, 45º, 60º, 75º)

Correct the experimental data for F, σ; calculate apparent composition (at. %) at each angle

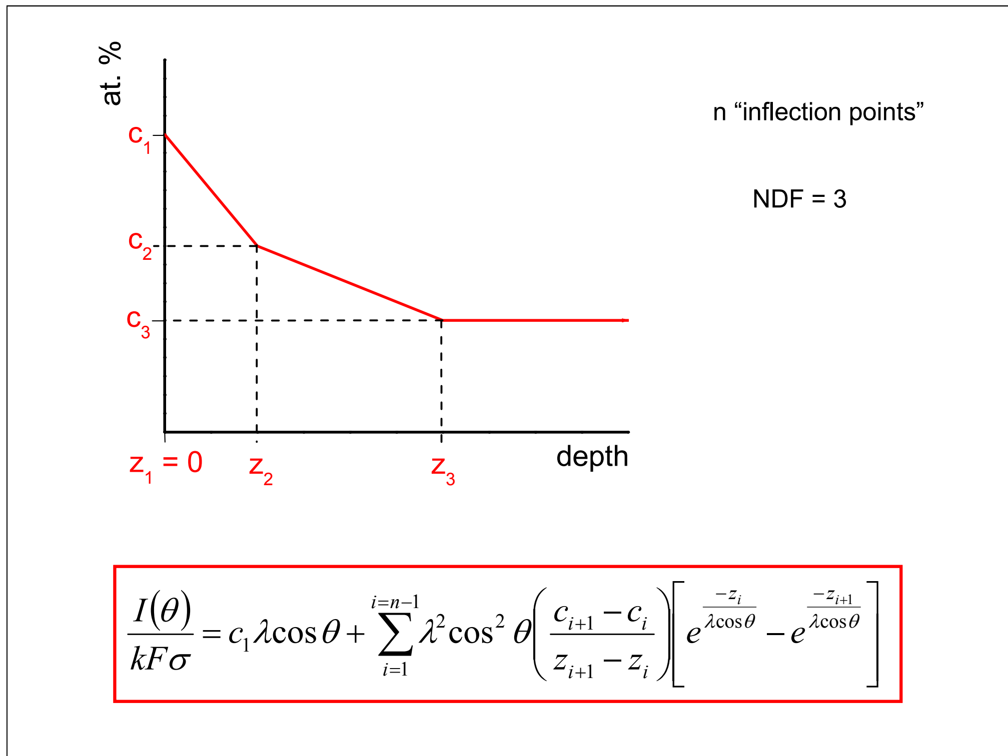
Propose a depth profile for each element measured

Calculate an apparent composition at each angle from the Laplace transform of the proposed depth profiles

Compare the experimental apparent compositions with those calculated from the proposed depth profiles and calculate the sum of the squared differences

Minimize the sum of the squared differences by optimizing the depth profile shapes

The so-called “Paynter’s method”.



$$\frac{I(\theta)}{kF\sigma} = c_1 \lambda \cos\theta + \sum_{i=1}^{i=n-1} \lambda^2 \cos^2\theta \left(\frac{c_{i+1} - c_i}{z_{i+1} - z_i} \right) \left[e^{\frac{-z_i}{\lambda \cos\theta}} - e^{\frac{-z_{i+1}}{\lambda \cos\theta}} \right]$$

Shown at bottom is the Laplace transform of a generalized concentration depth profile shown above. The profile consists of linear segments joining n “inflection points”, each defined by a concentration parameter c_i and a depth parameter z_i. The profile is assumed to plateau after the last inflection point.

With enough parameter pairs c_i,z_i any desired profile shape can be simulated. However, an analysis of the information content of ARXPS data shows that the number of degrees of freedom (which translates to the number of adjustable parameters in the profile shape), for realistic levels of noise in the data, is just three, compared to 10^4 for an MRI. This limits the profile shapes that can be legitimately fitted to ARXPS data to a few rather simple shapes or mathematical forms.

$$\frac{I(\theta)}{kF\sigma} = c_1\lambda\cos\theta + \sum_{i=1}^{i=n-1}\lambda^2\cos^2\theta\left(\frac{c_{i+1}-c_i}{z_{i+1}-z_i}\right)\left[e^{\frac{-z_i}{\lambda\cos\theta}} - e^{\frac{-z_{i+1}}{\lambda\cos\theta}}\right]$$

Experimental peak intensities $I(\theta)$ are corrected for F and σ

Eliminate k by calculating

$$at.\%\,(i,\theta) = \frac{I(i,\theta) \big/ F(E_i)\sigma(i)}{\sum I(i,\theta) \big/ F(E_i)\sigma(i)}$$

$\lambda(E_i)$ values come from experiment or from theory

In contrast to regular practice, the ARXPS peak intensities are not corrected for the photoelectron inelastic mean free path, because it is included in the calculation.

Unknown factors, such as the X-ray flux and the geometrical correction for the analysis area, are cancelled by calculating the composition in terms of atom percentages. The assumption inherent in this procedure is that the total atom density is constant as a function of depth.

Assumptions:

1) Sample is perfectly flat
2) Constant atom density wrt depth
3) Electron attenuation length independent of sample composition, photoemission angle, and depth
4) Analyzer acceptance angle is close to zero
5) Sample is amorphous and laterally homogeneous

But the assumptions don"t stop there! Here are a few more.

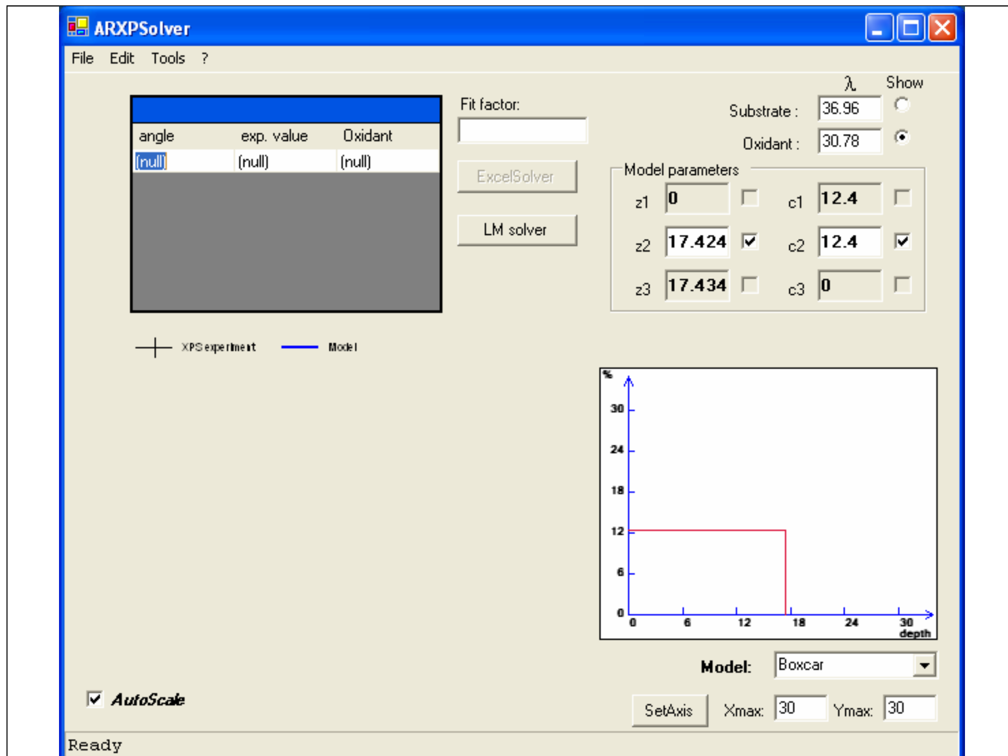
(1) Is not too much of a stretch if the polymer film is carefully prepared.

(2) Is debatable

(3) Is probably OK for polymer samples composed of light atoms of similar masses

(4) The acceptance angle is more like 12° so we close down the “acceptance angle” aperture to 6°

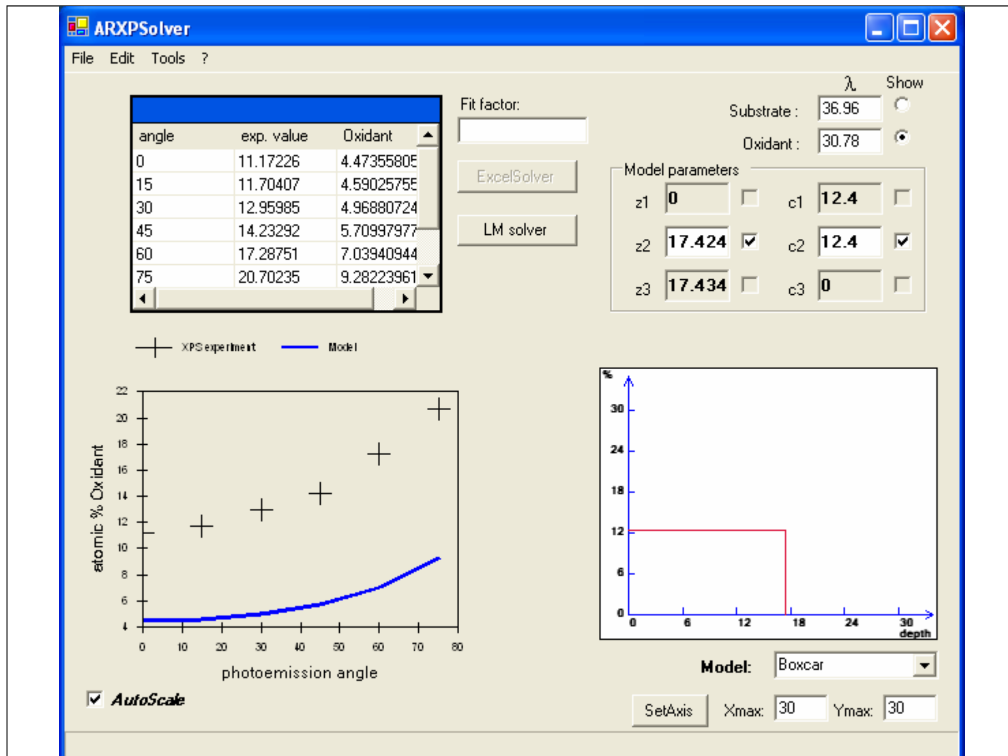
(5) OK for polystyrene!



We wrote a handy tool in visual basic, that runs under windows, to fit three basic profile shapes to ARXPS data. It assumes a binary system with one species exhibiting a concentration depth profile in a matrix composed of another species, let's say oxygen in carbon. It is called ARXPSolver and is available for free at

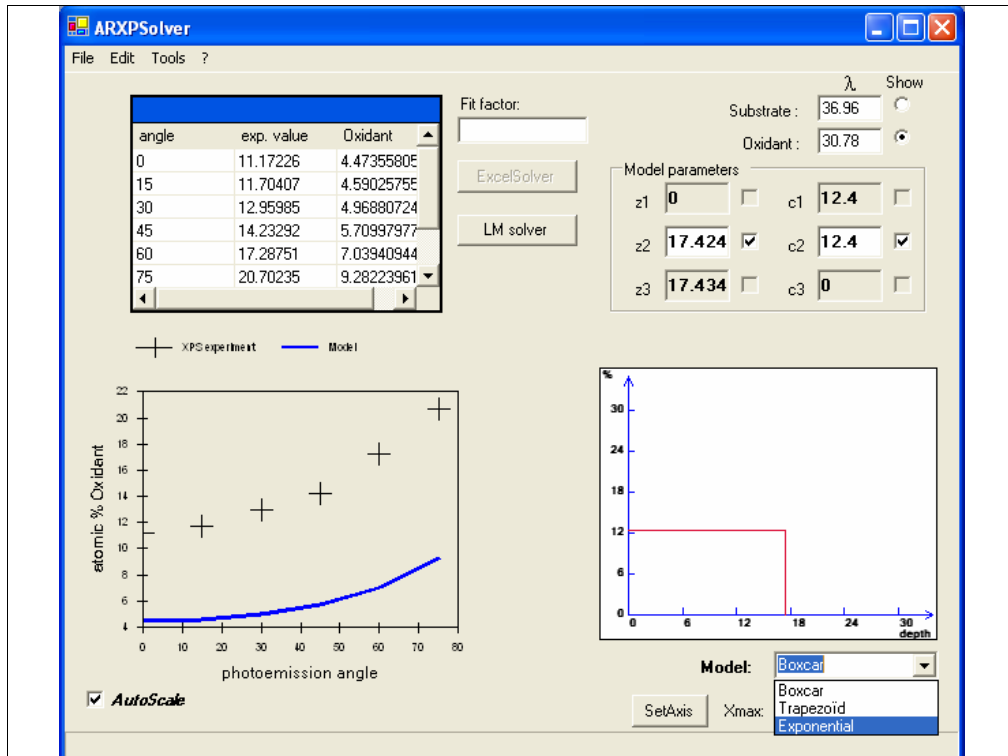
http://goliath.inrs-emt.uquebec.ca/surfsci/arxps/ARXPS.html

The user supplies inelastic mean free path values for photoelectrons originating from the "substrate" and "oxidant" species, entering them in the boxes at upper right.

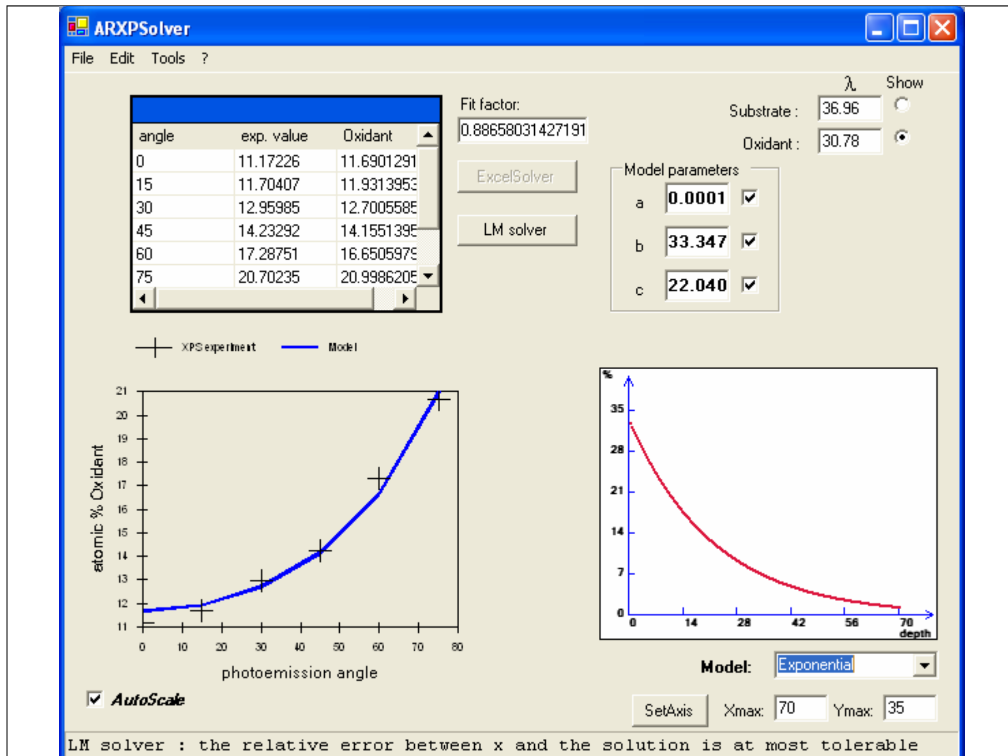


He then enters his ARXPS data into the table at upper left. The data can be transferred from a spreadsheet by a copy/paste operation. The model profile is defined by the parameters entered in the boxes at right, and displayed graphically below. The experimental data are displayed as crosses on the chart below the data table with the calculation based upon the model depth profile superimposed as a solid blue line. The graphical display of the model depth profile has “handles” on the red line that can be dragged with the mouse to change the shape of the depth profile, with the calculation (blue curve) being constantly updated in the window to the left. In this way, an approximate fit to the experimental data can be obtained.

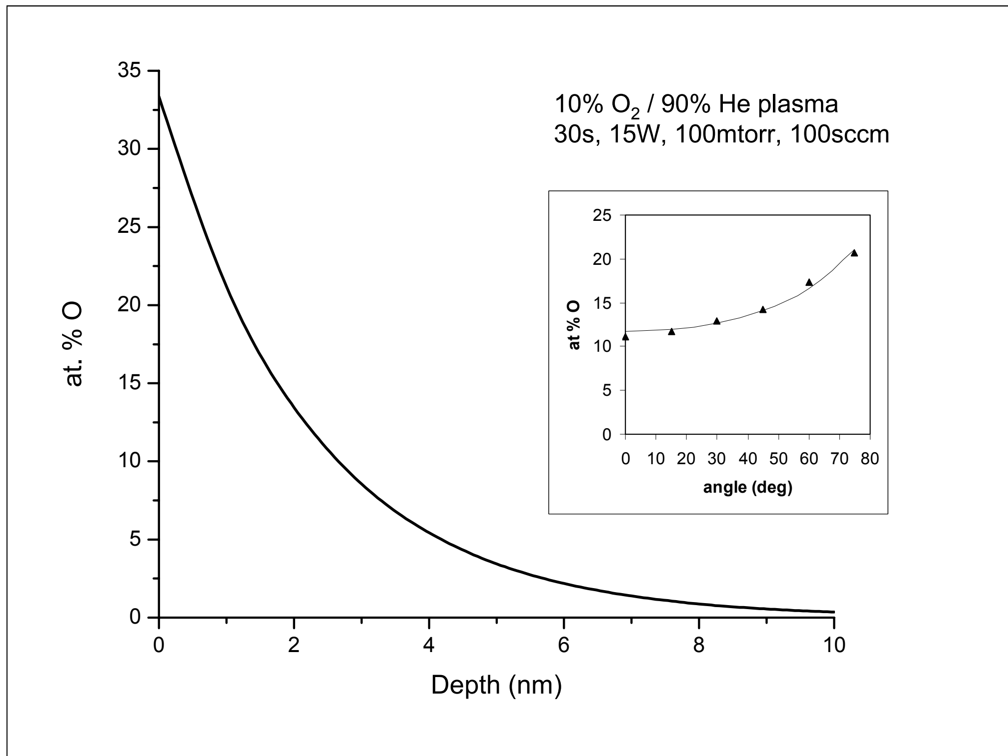
An integrated Levenberg-Marquardt non-linear least-squares optimization package can be invoked by pressing the “LM solver” button to complete the optimization of the depth profile.



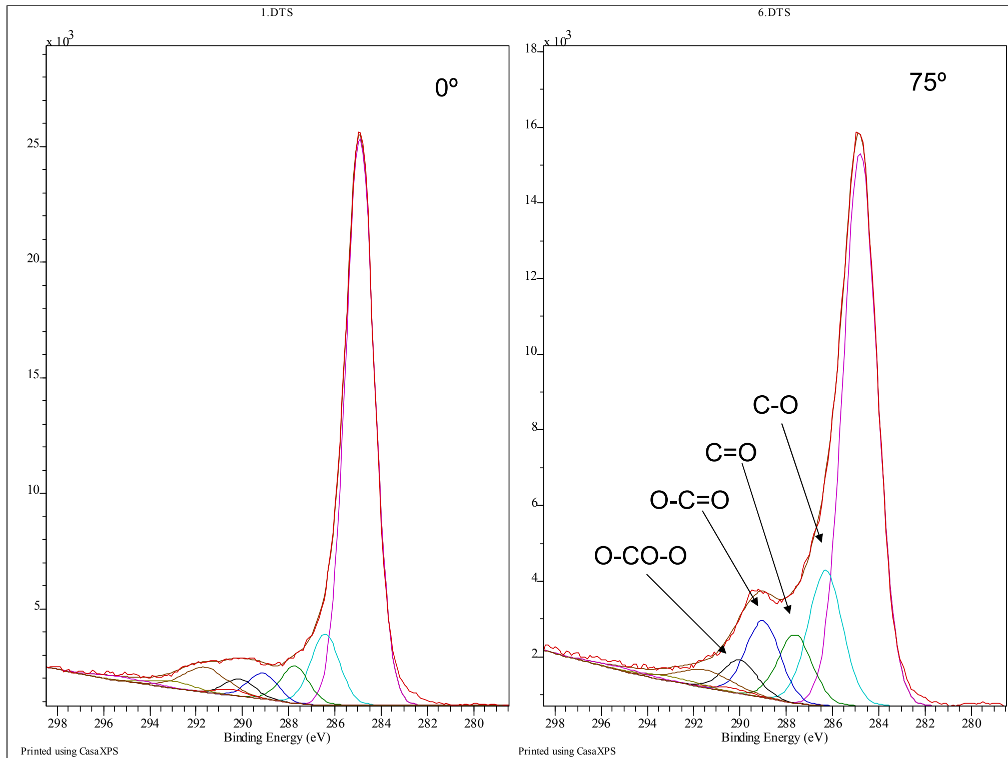
Three profile shapes are included. Let’s choose “exponential”.



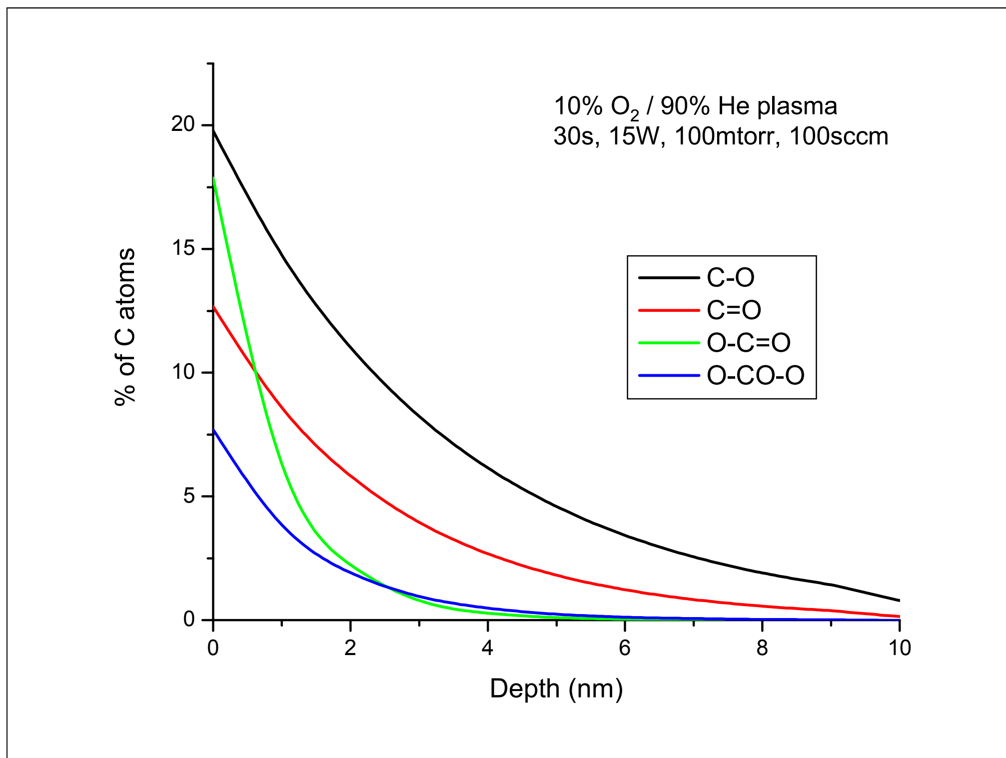
Choosing to optimise all three parameters in this model (by checking the boxes next to the parameter values) and hitting the solver button fits the profile to the ARXPS data.



From the apparent oxygen concentration (not corrected for the inelastic mean free path) measured at 15º intervals between photoemission angles of 0º and 75º, we fit the oxygen concentration depth profile (exponential model) shown above. The inset to the figure shows the experimental data (symbols) and a spline drawn through the calculations at the same angles, based upon the depth profile model. It can be seen that, according to this model, the oxygen concentration at the very surface of the sample is about 33%! This is the oxygen concentration “seen” by a water droplet.



How is the oxygen bonded to the carbon? We can perform the same exercise with the intensities of the component peaks in the C1s envelope as a function of the photoemission angle, assuming a constant carbon atom density with respect to depth.



We find a general trend for the C-O, C=O and O-CO-O components in which the more highly oxidized carbons are lower in concentration and more confined close to the sample surface. The O-C=O component stands apart from this trend in that it is more concentrated and confined at the sample surface than we would expect from the trend exhibited by the other components.

Other evidence, both in our data and in the literature, indicates that this component is actually representative of organic acid moieties, and it is the presence of these polar functional groups at the very surface of the plasma-treated polymer that probably has the greatest influence on the behaviour of water in contact with the material.

Summary

XPS is a surface sensitive technique, useful for studies of :

- Ultrathin films and surface layers
- Catalysis
- Oxidation and corrosion
- Adsorption at surfaces

XPS is an essentially non-destructive technique

XPS gives information on :

- Sample composition – periodic table except H, He – detection limit ~0.1%
- Chemical bonding – oxidation state
- Depth distribution – depth profile by ion bombardment or by ARXPS

References:

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