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XPS ANALYSIS OF BIOMATERIALS USING A NEW METHOD OF INTEGRATED CHARGE COMPENSATION

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The major problem in X–ray photoelectron spectroscopy of polymeric and other insulating materials is that of "charge neutralisation" or " charge compensation". Due to variable potentials on the surface of the investigated specimen broadening of peaks, or even multiple peaks, are observed. Various methods are applied to achieve the charge compensation. The AXIS series of instruments provide a secure and reliable charge compensation method, which uses the characteristic properties of the magnetic lens. The system enables confident determination and use of small binding energy shifts in both spectroscopy and imaging.

1. Introduction

Recent advances in X–ray Photoelectron Spectroscopy (XPS) instrumentation have resulted in large increases in basic instrument sensitivity and also brought easy access to imaging and point analysis capabilities. In particular, scanning lens systems [1] are important in that they provide both high resolution mapping and "microprobe" style analysis, whilst maintaining facilities for familiar and well characterised spectroscopic methods. Instruments based on magnetic lenses provide maximum acceptance angle for collection and transport of photoelectrons and so enable high speed analysis with minimal sample damage. Application of these new capabilities to the analysis of polymeric and other insulating materials [2] is only useful if a stable, routine, and easy to use means of "charge neutralisation" is available. Only then it is possible to acquire reliable, repeatable XPS data from insulators, irrespective of their physical form and without special sample mounting requirements.

In recent years, analysis of polymers and biomaterials using XPS has become quite common, due to its ability to provide quantitative elemental and chemical state information. When analysing polymers and biomaterials with XPS, two issues have to be considered. Samples of this kind are normally very good insulators and, therefore, liable to suffer from severe charging problems. This effect is enhanced by the micro–roughness of their surfaces which can lead to differential charging on the surface of one single sample.

Conventional charge compensation methods involve putting low energy electrons back onto the surface of the sample. This can be achieved by using a flood source and generating other low energy electrons close to the sample, e.g., using a UV (or other X-ray source). The disadvantage of this method may be chemical decomposition of the sample, e.g., due to polymer cross linking. This decomposition could be even more rapid than the primary X-ray degradation where the sample has strong UV absorbing bonds, e.g., phenyl rings or $> \mathrm{C} = \mathrm{C} <$.

The more usual method is a low energy (1 - 14 eV) focussed electron source. This source is usually incident at some angle to the surface with the X-ray source incident at a different angle. Trying to match both foci can be difficult. If the flux is not matched then the surface will have different surface potentials and the kinetic energies of the photoelectrons will be different. This can be seen in spectra as distorted peak shapes with tails and even multiple peaks, where actually only one peak is present. When a spectrum from an unknown sample or chemically treated sample is obtained, then it may be difficult to determine if multiple peaks represent different chemical states or charging artefacts. Adjusting the charge neutralisation conditions until the most intense and narrowest peaks are obtained can be done, but in this potentially time-consuming procedure, the sample may be already degrading.

Another method described is a grid in close proximity to the sample [3] with an additional electron source. Though it is possible to achieve reasonable results with this method, there are also some drawbacks. The transmission is reduced and it is possible to measure signal from the grid. Angle resolved XPS is also not easily possible.

Changing the X-ray flux, e.g. by changing the power or spot size, may require different charge neutralisation conditions. Different materials may also require different neutralisation conditions. In the case of rough samples or samples with complex topography, such as powders, fibres or woven meshes, even different areas of the same sample can require different neutralisation conditions. The AXIS charge compensation method overcomes many of these problems.

XPS is only a relatively non–destructive method of analysis. It is known that many bio-important, especially biological materials, are degraded by electromagnetic radiation, particularly by ultraviolet and X-rays. In the case of XPS, X-ray irradiation cannot be avoided, so the exposure time or more precisely the overall dose should be minimised. Decreasing the X-ray intensity reduces the degradation, but the acquisition time must be increased to achieve the same signal to noise ratio. The total dose for a particular signal to noise ratio is the same. One means of reducing degradation is to increase the collection efficiency of the spectrometer, resulting in a higher signal and hence signal to noise ratio for a given X-ray dose. Conventional hemispherical analysers have only a small analyser acceptance angle to collect the emitted photoelectrons. Use of a magnetic immersion lens, introduced on the AXIS XPS spectrometer, enables the use of increased acceptance angles.

2. *Magnetic lens and charge compensation*

Figure 1 shows a schematic diagram of the AXIS instrument. The magnetic lens is located below the sample. X-ray induced photoelectrons are constrained to enter the transfer lens by the magnetic field. Even electrons emitted at low angles are similarly constrained and thus the acceptance angle is large, resulting in a high

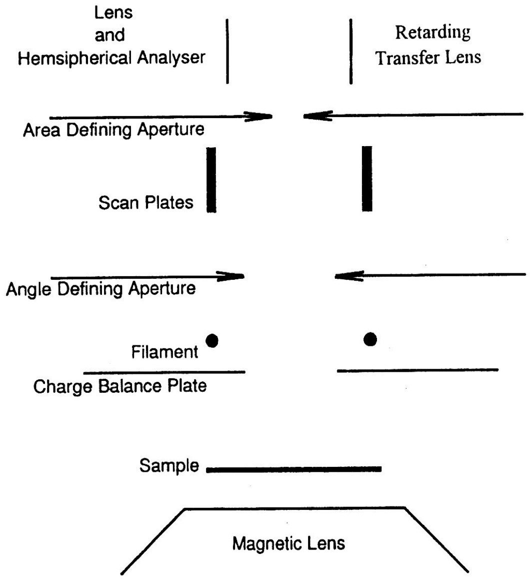


Figure 1. Schematic diagram of the AXIS magnetic lens and charge compensation system.

efficiency. The analysis area is defined by an aperture introduced at a crossover point on the electron trajectory, and a spatial resolution of better than 30 μm can be easily achieved. Scan plates below this aperture enable the analysis area to be scanned across the sample to produce chemical state images. Above the analysis area defining aperture, an electrostatic retarding lens and a hemispherical analyser are used to analyse energy of photoelectrons.

The AXIS patented charge compensation system [4] utilises the same magnetic field that is used to increase the collection efficiency of the analyser. The magnetic field lines, which are used to focus the photoelectrons into the lens/analyser, can also be used to transport very low energy electrons back onto the sample. Electrons are injected into the magnetic field from a filament which is coaxial with the transfer lens. This filament does not have a line of sight to the sample. Typically, the electrons have an energy of between two and three eV and, hence, the peak position is shifted to lower binding energies by this amount. The exact energy is determined by additional extraction optics. The combination of magnetic and electric fields also acts to select only a very narrow energy band of electrons. Thus, the neutralizing electrons are rather monoenergetic and do not contribute to the observed peak width.

Use of the same magnetic field ensures a good matching of the analysed area and the flux of neutralizing electrons without shadowing of the neutralizing electrons. This is true for a whole range of photoelectron take-off angles and ensures that all facets of a rough sample are neutralized.

3. *Results*

The charge compensation method of AXIS enables spectra with the highest energy resolution to be acquired routinely, without the need for special sample mounting. A factor limiting the energy resolution appears to be the surface cleanliness of the polymer, but a C 1s energy resolution (FWHM) of better than 0.8 eV can typically be obtained from polyethylene and polytetrafluoroethylene (PTFE). On polyethylene terephthalate (PET), a FWHM of less than 0.7 eV can be obtained for the carboxyl carbon bond [5].

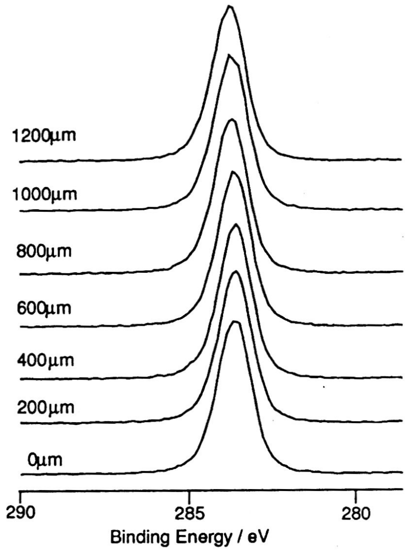
TABLE 1.

XPS results obtained from the CIS line of polyethylene at various operating conditions. The X–ray source is either mono, which is the Alk_α *X–ray line energy selected by crystal diffraction, or* Mg *which is* Mgk_α *in the form of a flood source.*

Analysis area [μm]	X-ray source	X-ray power [W]	Binding energy [eV]	Peak width [eV]
700×300	Mono	65	283.42	0.86
700×300	Mono	150	283.44	0.89
700×300	Mono	450	283.44	0.89
700×300	Mg	65	283.40	1.20
120	Mono	300	283.42	0.86
60	Mono	300	283.42	0.86
30	Mono	300	283.43	0.85

Once adjusted, all other experimental parameters, such as X-ray power, size and position of analysis area and even a change of X-ray source, have little or no influence on the peak position or peak shape. Table 1 summarizes the peak positions and peak widths obtained from polyethylene, using a range of analysis areas and X-ray source conditions.

The stability of the peak position and peak shape is also important during mapping of elements and more particularly during mapping of chemical shifts. If charge neutralisation is not uniform, then the image may show unreal contrast, simply because the peak position has shifted. Figure 2 shows spectra (60 μm analysis spot) obtained along a 1.2 mm analysis line. They show the C 1s peak position and peak shape to be constant across the field of view.



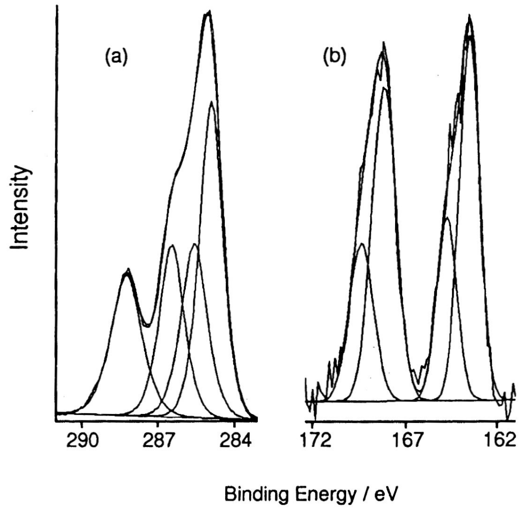


Fig. 2. C 1s spectra (60 μm analysis spot size) recorded at indicated positions across a polyethylene sample.

Fig. 3. (a) C 1s spectrum and (b) S 2p spectrum from crystalline β-casein (right).

β–casein is a protein extracted from milk which crystallises in very fine strands. The C 1s and S 2p spectra (Fig. 3) do not show any evidence of differential charging, despite the highly irregular surface of the crystals. Standard AXIS charge compensation conditions were used for this analysis. The curve–fitted components, representing different chemical states, each have a FWHM of around 1 eV. In the S 2p region, two different forms of sulphur are observed; a sulphide S=S bond and an oxidized S bond, possibly resulting from atmospheric oxidative cleavage of the S=S bond. Note that each of the peaks is asymmetric due to the spin orbit splitting of the S 2p line and these have been curve-fitted with linked components. No sample degradation was observed during the total analysis time of approximately 10 minutes.

4. Conclusions

A new method of self regulating charge compensation during the XPS analysis has been described. Experimental variables, such as sample form or topography, X-ray flux, analysis area and position of analysed area, have little or no influence on the performance of this method. Crystalline β-casein was analysed as an example of a biological material and high resolution XPS spectra were obtained.

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XPS ANALIZA BIOMATERIJALA PRIMJENOM NOVE METODE KOMPENZACIJE NABOJA

Važan problem rentgenske fotoelektronske spektroskopije polimera i drugih izolatora je neutralizacija naboja. Zbog promjenjivih potencijala na površini ispitivanog uzorka javlja se širenje vrhova pa i višestruki vrhovi. Niz uređaja AXIS pružaju sigurnu metodu kompenzacije naboja primjenom magnetske leće. Sustav omogućuje pouzdano određivanje malih energijskih pomaka u spektroskopiji i snimanju površina.