Application Note: 31067

Unattended Analysis of Multiple Insulating Samples

Key Words

- Surface Analysis
- Automation
- Insulating Samples
- Theta Probe

Introduction

The purchase of a modern XPS spectrometer is a major investment for any organization. It is therefore essential that the spectrometer is producing results for a high proportion of the time. This means that overnight and weekend operation, in the absence of the analyst, is essential. It must be possible to define a long and complex series of measurements and then leave the instrument to acquire the data without any further intervention.

To achieve this goal the instrument must:

- Have a reliable and accurate sample stage so that the right point on the right sample is analyzed
- Have a large sample stage, capable of accommodating a large number of samples of differing type, size and thickness
- Have a microscope accurately aligned with the sample position. This allows the analysis positions to be defined without exposing the samples to X-rays.
- Have all the analytical components of the instrument controlled by the data system
- Have a high quality charge compensation system to cater for insulating samples without the need to adjust the conditions
- Have a focusing monochromator so that only the analysis area of delicate samples is exposed to X-rays during analysis
- Have a comprehensive and versatile data system to allow, if necessary, a different experiment to be performed on each sample or a complex series of analyses to be performed on the same sample.

The Thermo Scientific Theta Probe satisfies all of these requirements.

Sample Handling

All Theta Probes are fitted with a stage capable of moving 75 mm in the X and Y directions and 25 mm in the Z direction. A simple clip arrangement means that samples can be rapidly and securely attached to the sample holder.

Figure 1 shows a photograph of a sample holder loaded with insulating samples for unattended operation.

The stage can be positioned with a resolution of 1 µm, which means that small area analysis can be included in a series of unattended analyses.

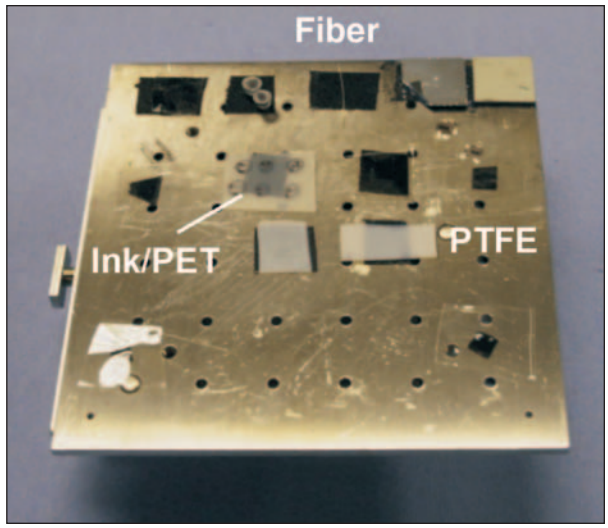

Figure 1: Sample holder loaded with a variety of insulating samples in preparation for overnight analysis

Data System Control

The *Avantage* data system has control of all of the analytical functions of the instrument. For the analyzer, this allows the user to select the energy range for each measurement, the pass energy, number of scans, dwell time per point, energy step size, snapshot or scanned mode of operation, and angle resolved or angle integrated mode. Each of these can be different depending upon the analysis being performed.

The ion gun is under full control from the data system. This allows sputtering to be part of the sequence of measurements. The sputtering can be either for sample cleaning prior to analysis or a full depth profile acquisition. Beam energy, current and scanned area can all be controlled.

The charge compensation system can be switched off and on by the data system, as required, allowing insulating samples to be included in the sequence of analyses.

Charge Compensation

Charge compensation is such that the user only needs to turn it on or off. The pre-set conditions will cope with a wide range of samples and analysis conditions. It is unnecessary to adjust the conditions between measurements. This is true whether the X-ray spot size is changed between measurements or whether the sample topography changes markedly from one sample to another. It is possible to move from a flat smooth sample to a fiber or to change the X-ray spot size from 400 µm to 15 µm without adjusting the conditions. Full details of the charge compensation method can be found in document AN31022.

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Microfocusing Monochromator

The monochromator technology in Theta Probe allows the user to select the spot size of the X-rays for each analysis under computer control. This allows the analysis of small features even during unattended operation of the instrument.

Use of a microfocusing monochromator also means that samples are only exposed to X-rays during analysis, delicate samples are not subjected to potentially damaging X-ray flux prior to analysis.

Avantage Data System

The *Avantage* data system is described in detail in application note AN31005. For unattended operation, the key feature in the *Avantage* data system is the experiment tree and so this aspect of the data system will be reviewed here.

All of the experimental parameters can be controlled in a single experiment, in any combination, using the concept of the experiment "tree", illustrated in Figure 2.

The various parts of an experiment are defined as "objects" on the tree. As the experiment continues, the instructions contained within each object are performed. If there is a branch at any given object the instructions contained within the branch are performed before moving on to the next object at the same level in the hierarchy.

In the example shown in Figure 2, the first action is to set the X-ray source to 15 kV, at a power of 150 watts and a spot size of 400 µm.

The next object moves the sample so that the PTFE sample is coincident with the focused X-ray beam. C 1s and F 1s spectra are then acquired. The X-ray spot size is then changed from 400 µm to 200 µm and acquisition of spectra is repeated. This process is performed again for spot sizes of 100 µm and 50 µm. At 20 µm the acquisition includes a survey spectrum.

The following step is to change the X-ray spot size to 200 µm, and move the analysis position to the fiber sample where a line scan experiment is performed. At each point in the line scan, C 1s, N 1s, Si 2p and O 1s spectra are recorded.

When the line scan is completed the analysis shifts to the 'Ink on PET' sample where C 1s and O 1s maps are recorded.

This is just part of the experiment tree that was required for the analysis of all of the samples shown in Figure 1. Other objects, not shown in this example, would control the ion gun, electron gun etc. A very useful object allows a section of the tree to be repeated a defined number of times. This would be used for creating sputter profiles or line scans.

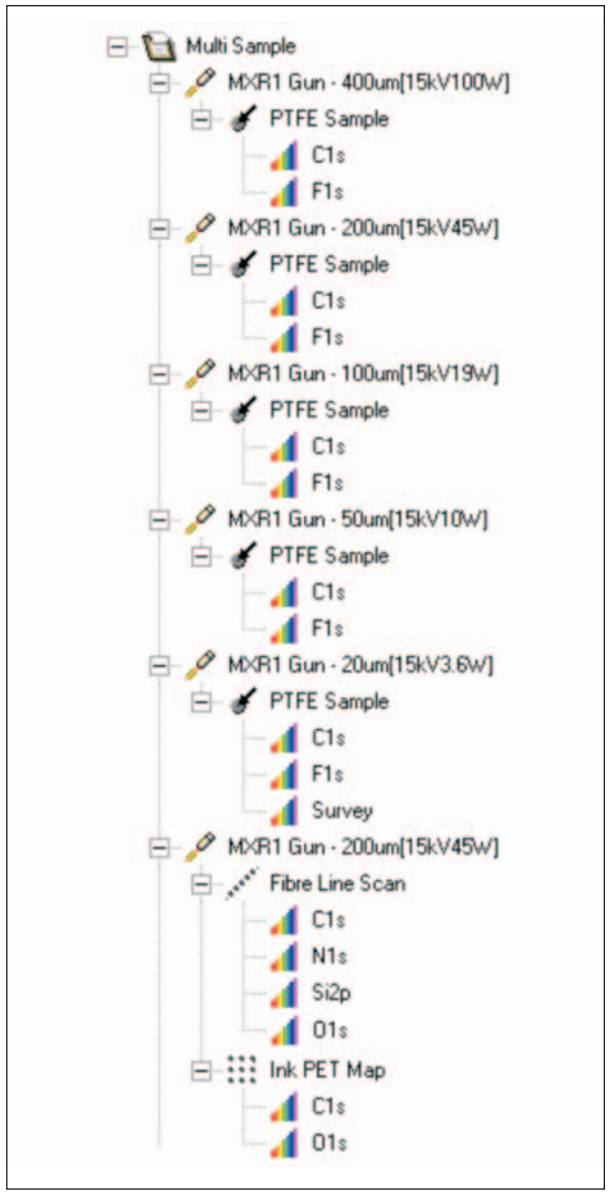

Figure 2: An example of an experiment tree in the *Avantage* data system

Each of the objects on the tree has its own set of user defined properties (e.g. the energy range for spectrum acquisition or scanned area for the ion beam).

Once the tree has been defined, the analyst can start the experiment and the instrument performs each experiment object in the tree, in turn. Experiment trees can be saved so that the analyses can be repeated, if required, under identical conditions.

Example of Unattended Acquisition of Data

All of the samples shown in Figure 1 were analyzed in a single unattended experiment. Note that all of these samples are insulators and include an inorganic substance, mica, smooth flat polymers and a fiber. A variety of different experiments were performed including spectroscopy only, small area measurements, line-scans and mapping. All of the data to be shown here were obtained without the need to change the settings for the charge compensation system. Examples of the data obtained from some of the samples will now be given.

1. PTFE

A C 1s spectrum and an F 1s spectrum were acquired using each of five different X-ray spot sizes in the range 20 µm to 400 µm. A survey spectrum was acquired using the 20 µm spot size and is shown in Figure 3.

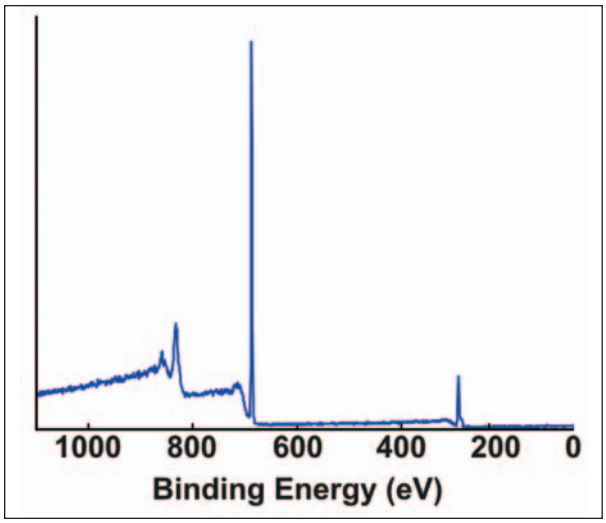

Figure 3: Survey spectrum using a 20 µm spot size during unattended operation of Theta Probe. This spectrum was acquired following the acquisition of spectra at 400 µm, 200 µm, 100 µm and 50 µm.

At each spot size narrow scans from the C 1s and F 1s regions were also acquired. Figure 4 shows the normalized C 1s spectra at each spot size. Note that the width of the peak is only slightly affected by the spot size. The same is also true of the F 1s spectra.

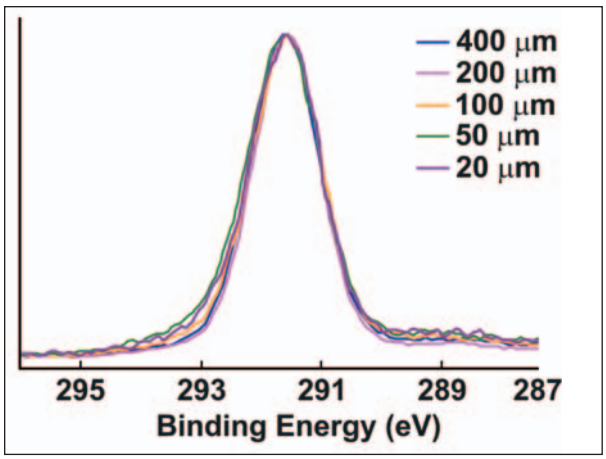

Figure 4: C 1s spectra from PTFE acquired with each of 5 different X-ray spot sizes. The same charge compensation conditions were used for each spectrum.

2. Polymer Fiber

One of the samples in this set was a polymer fiber, a line scan was acquired along part of its length. Such a measurement is a test of both the accuracy of the stage movement and the efficiency of the charge compensation system. Any errors would result in variable signals along the length of the fiber.

Figure 5 shows the optical image of the fiber, from the zoom microscope and camera directed at the analysis position. The position of the line scan is also indicated on this photograph.

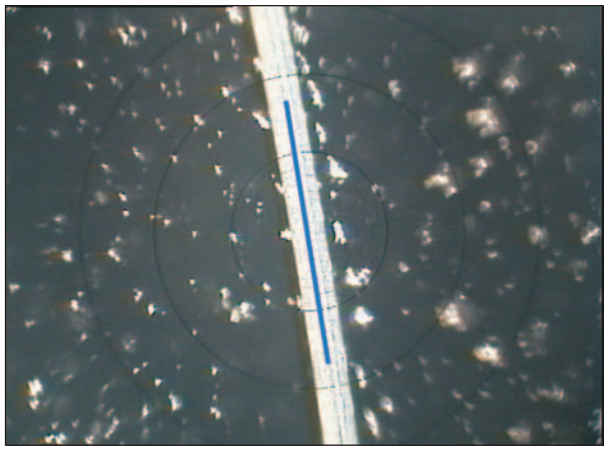

Figure 5: Optical image of the fiber in the analysis position. The blue line (1.7 mm long) indicates the position of the line scan.

A 200 µm spot was used to acquire the line scan, which consisted of 9 measurements. At each point on the line C 1s, O 1s, N 1s and Si 2p spectra were acquired.

Figure 6 shows the set of C 1s spectra, normalized to show the consistency of peak position and peak shape.

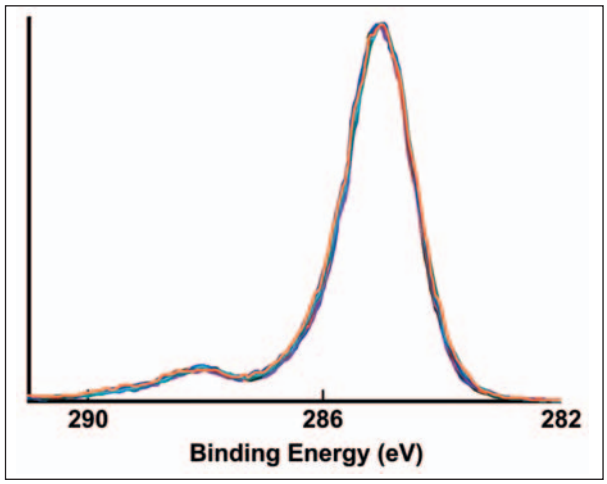

Figure 6: Normalized C 1s spectra from each point on the line scan

Quantification can also be applied to the data forming the line scan in order to judge its consistency, this is shown in Figure 7.

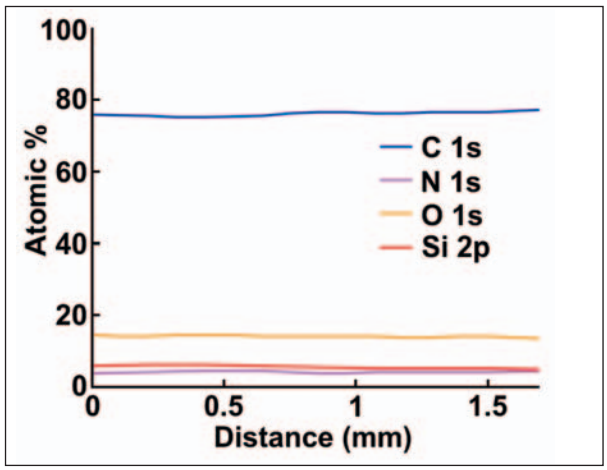

Figure 7: Quantified line scan along the 1.7 mm length of the fiber

3. Chemical State Mapping

A sample was prepared by drawing a 'θ' symbol on a polyethylene terephthalate (PET) substrate using a fiber tipped pen. Figure 8 shows the optical view of this sample in the analysis position and the area from which the map was taken is marked in green.

Snapshot spectra were then collected at each of the mapping points for the C 1s and O 1s regions. Snapshot mode was used to significantly reduce the data acquisition time (see application note AN31009 for details on snapshot acquisition). A 200 µm X-ray spot size was used to acquire the data. The area mapped covers ~ 3 x 3 mm. A total of 400 (20 x 20) mapping points were used.

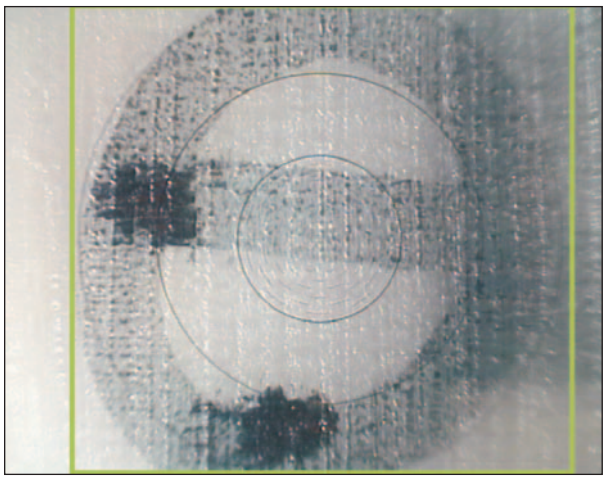

Figure 8. Optical view of the sample in the analysis position

One of the 400 C 1s spectra is shown in Figure 9, with peak fitting applied.

Target Factor Analysis (TFA) was used on the O 1s data from this image. It showed that there were two reference spectra, Figure 10. An image could then be constructed using non-linear least squares fitting using these two spectra as references. The images are shown in Figure 11. The images clearly indicate that one of the reference spectra was representative of the ink while the other was representative of the PET.

Conclusions

High quality data was produced from all of the samples shown in Figure 1. Once the measurement conditions had been defined using *Avantage*, there was no further intervention from the analyst until the whole set of data was acquired.

The ability to accomplish an analysis in this way increases the efficiency of the laboratory, allowing reliable data acquisition overnight and at weekends.

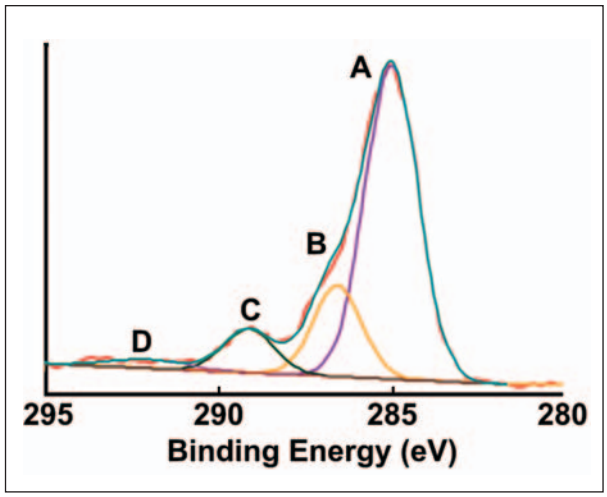

Figure 9: C 1s spectrum fitted with four peaks

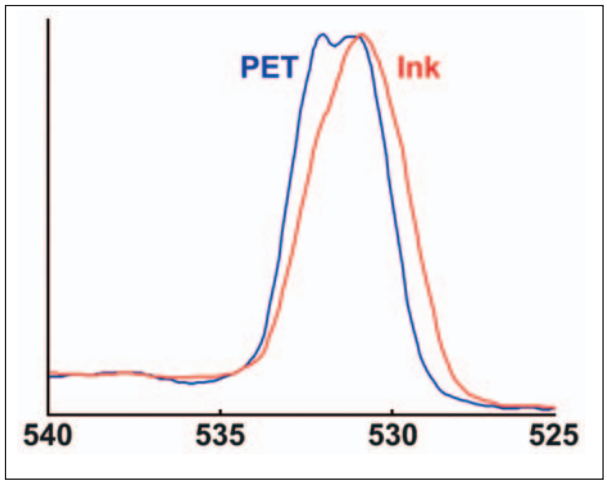

Figure 10: O 1s spectra from an area of the sample that shows both PET and ink. The components used to fit the peaks using NLLSF are also shown.

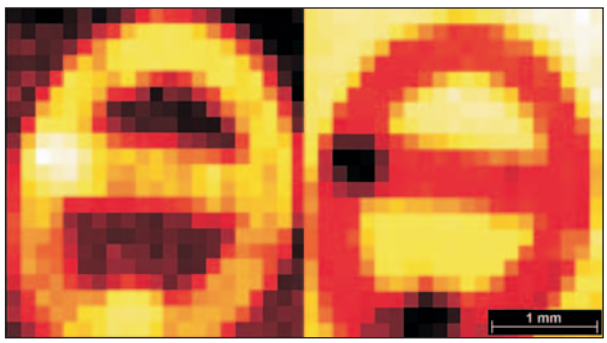

Figure 11: O 1s maps from (left) the ink component of the peak and (right) the PET component of the peak

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