SURFACE SCIENCE AND ANALYSIS

Surface science is the study of the chemical and physical properties and processes that take place at surfaces. Surfaces, or more generally interfaces, are the boundaries between two phases such as betwen a solid and a gas or between a solid and a liquid. It is at these interfaces that many of the important characteristics of the material are decided. Some examples are: appearance (e.g. colour), reflectivity, corrosion resistance, chemical reactivity (e.g. catalysis), abrasian resistance, and adhesion. Surface forces are also very important in determining the properties of many technologically important mixtures or processes.

Often the surface composition of a substance is very different from the bulk composition. As the surface dictates many important properties of a material it is the surface composition rather than the bulk composition whichn is often most important.

Most surface analysis techniques require expensive items of equipment, which in New Zealand are housed in Universities or Crown Research Institutes. This article discusses the techniques of X-ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Scanning Probe Microscopy (SPM) and Ion Beam Analysis (IBA).

INTRODUCTION

Surfaces, or more generally interfaces, are the boundaries between two phases such as between a solid and a gas, or between a solid and a liquid. It is at these interfaces that many of the important characteristics of the material are decided. Some examples are: appearance (eg. colour), reflectivity, corrosion resistance, chemical reactivity (eg. catalysis), abrasion resistance, and adhesion. Surface forces are also very important in determining the properties of many technologically important mixtures or processes. Examples of these include forces between solid particles in suspension, between emulsions, or between filter membranes and solids.

Often the surface composition of a substance is very different from the bulk composition. As the surface dictates many important properties of a material it is the surface composition rather than the bulk composition which is often the most important. With this realisation the analysis of surfaces and the study of surfaces are areas of science that have grown rapidly over the last twenty years.

How much of the surface are we really interested in? In some case this might mean only the first atomic layer, but for most practical applications we are interested in several layers or more. The various techniques that are available also vary in the depth that is analysed so that “surface analysis” has a different meaning depending on the technique used.

There is now a wide range of techniques that are available to study surfaces. This article will concentrate on some of those that are available in New Zealand.

The techniques available

Most surface analysis techniques require expensive items of equipment, which in New Zealand are housed in Universities or Crown Research Institutes. Some instruments are widely available, such as scanning electron microscopy (SEM) and Energy dispersive spectroscopy (EDS). Others are found only at one location such as X-ray photoelectron

spectroscopy (XPS), Auger electron spectroscopy (AES), Scanning probe microscopy (SPM) all at the University of Auckland and Ion Beam Analysis (IBA) at the Institute of Geological and Nuclear Sciences, Gracefield. This article discusses the most surface sensitive of these techniques: XPS, AES, SPM and IBA.

X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

The technique

XPS is also known as ESCA (Electron Spectroscopy for Chemical Analysis). There is currently only one instrument for this technique in New Zealand that is based at Auckland University. It is a Kratos XSAM800 dual technique instrument for XPS and Auger analysis.

In XPS a sample is irradiated with X-rays that excite photoelectrons which escape from the surface. Two general types of information can be obtained. The photoelectron kinetic energy relates directly to the energy which binds it to the material. This binding is dependent on the precise chemical configuration of the surface atoms so that chemical shifts (changes in the binding energy) are produced in the peaks of the XPS spectrum. We can therefore obtain information on the elemental composition of the surface and also on the chemical state of these elements.

Quantification

XPS gives relative concentrations of elements and of chemical species. It is not a precise technique but is still extremely useful for determining the difference between surface and bulk compositions or between two samples. A detection limit of about 0.1 - 1% is possible, depending on the element and analysis conditions. All elements except H and He can be detected. An XPS spectrum of the surface of teflon, -**Error!**-CF_2-CF_2-$)_n$-, is shown in **Figure 1**.

Chemical information

The real strength of XPS is that it is capable of supplying chemical state information on surface species. Few other techniques are capable of this. This is possible by measuring the slight shift in the energy of the photoelectron peaks (the "chemical shift").

Chemical shifts in the XPS peak positions may be very large, as for example in case of sulfur where the position of the S 2p peak for the following compounds is as indicated: FeS 161.6 eV, S 164.0 eV, $(CH_3)_2SO$ 166.5 eV, K_2SO_3 167.5 eV, $CuSO_4$ 169.3 eV. The resolution in the peak position is usually about 0.1 eV. These energies represent the energy with which the electron is bound to the atom. It is possible to get relative concentrations of the different chemical species when several components are present in one sample.

For carbon compounds, which are frequently studied, we observe quite large shifts in peak position. For example the following peak positions are found: Fe_3C 283.9 eV, graphite 284.5 eV, cellulose 286.2 eV, CH_3C*OONa 288.2 eV, polycarbonate -OCO_2- 290.4 eV and Teflon 292.2 eV. **Figure 2** shows a narrow scan spectrum of a polymer.

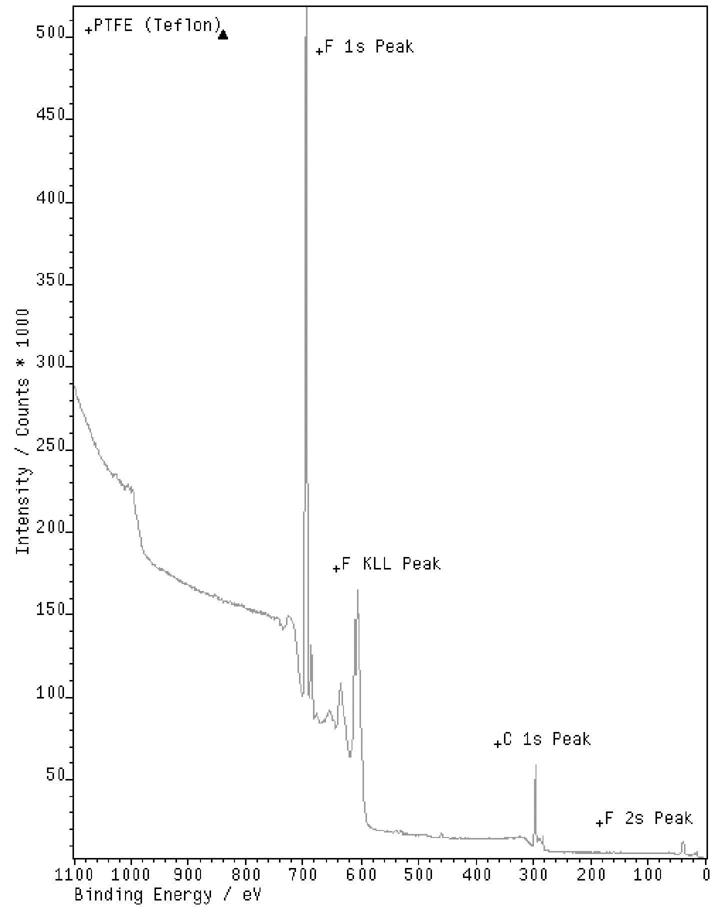

Figure 1 - XPS spectrum of the surface of teflon

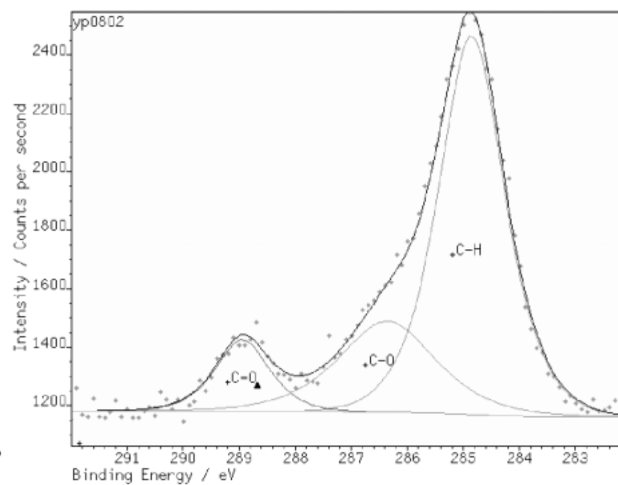

Figure 2 - Narrow scan spectrum of a polymer

On the other hand there are some cases of compounds that have similar chemical shifts, such as Si 2p for silicates (mica 102.4 eV) and for silicone (p-methylsilane 102.4 eV) making it impossible to distinguish between the two materials using XPS alone.

Sample requirements
X-rays are relatively non-destructive so that even delicate materials such as polymers and organic coatings can be analysed. The first requirement for samples is that they can be placed in a vacuum (which of course excludes solutions and oils). The second requirement is that the sample is a suitable size - preferably 15 mm x 15 mm (but they may be a powder or a sample as small as only 1 mm^2 but no larger than about 20 x 20 x 5 mm). Recent developments in XPS have resulted in instruments that are capable of small spot analysis and imaging but this is not yet available in New Zealand.

Depth of analysis
Depth distributions of elements and chemical compounds can be obtained from by two methods. One method is to simply rotate the sample from normal to the electron energy analyser to an acute angle. The escape depth of the photoelectrons determines the depth of analysis. This is generally 1-5 nm. The escape depth of the electrons is defined by their energy and, to a lesser extent, the composition of the sample. Therefore the thickness of the surface layer from which electrons are collected will vary as $1/\cos\theta$ where θ is the angle of departure from the plane normal to the analyser. This method is useful for probing the surface to less than the escape depth of the electrons (1 - 5 nm).

For depth analysis greater than 1-5 nm (and up to 0.1 μm) is is necessary to etch the surface with an ion beam and record successive XPS spectra between etches. For this purpose the XSAM800 is fitted with an argon ion gun.

XPS imaging
Recently advances in instrumentation have enabled the XPS images to be collected. The instruments rely on one of two mechanisms to achieve this. One is to have a lens system that has a very tightly defined photoelectron collection area and can scan the sample. This is done with a lens system where the sample effectively sits between two lens elements. The second method is to use the normal lens system but to focus the X-rays and scan the sample with the X-ray beam. This has been made possible by recent developments in X-ray sources. XPS imaging enables mapping of the distribution of particular elements or functional groups on a surface.

AUGER ELECTRON SPECTROSCOPY (AES)

The technique
In AES a beam of electrons is used to excite Auger electrons from the surface. Since an electron beam can be focused into a fine spot this technique can be used to collect an image of the region under analysis. When used in conjunction with a photodetector it is possible to get both an image of the sample similar to that from a scanning electron microscope and also an image (usually referred to as a map) representing the distribution of a particular element.

Sample requirements
Similar constraints apply to AES as to XPS. An additional restriction is that the sample is preferably electrically conducting otherwise the surface may charge which results in a shift in Auger electron energies. This is particularly important when making elemental maps.

Quantification, depth of analysis and chemical information

Similar considerations for quantification and depth analysis apply as for XPS. It is also possible to gain chemical information from AES although this is not quite as easy or precise as with XPS.

Related techniques
It is also possible to use the Auger setup to record EELS spectra and maps (Electron Energy Loss Spectroscopy). The basis of this technique is that a low energy electron beam is used (500 eV compared with 3-5keV for Auger) and the inelastic portion of the spectrum is recorded (those electrons that have energies from just under 500eV to perhaps 450eV). This part of the spectrum reflects on the valence orbital bonding of the surface species.

Applications of XPS and AES
The range of possible applications of XPS and AES is very wide. In New Zealand these techniques have been applied to studies ranging from quick sample analyses through more complex industrial problem solving to research of a longer term or more pure science applications. Just a few of the types of studies that have been carried out recently have been selected below.

The Research Centre for Surface and Materials Science at the University of Auckland carries out analyses for a wide range of New Zealand Industries. Examples of this work include identification of the cause of discolouration of silver-plated light fittings in new houses; identifying deposits and corrosion products on aluminium components; finding the source of black marks on steel; and analysing deposits on printed circuit boards.

Forest Research in Rotorua has carried out a large number of surface chemical studies of wood and wood fibres using XPS for composition affects on colour and other properties.

The University of Auckland and Massey University have been looking at the effects of surface chemistry on fouling in industrial environments including the chemical and dairy industries. Previous studies of fouling have generally neglected surface chemical effects that we now have the ability to investigate.

At the Department of Chemistry of the University of Auckland, studies have been performed into gas/solid absorption process in catalysis and emission controls, including investigating novel routes to surface modification for specialty applications.

In the Departments of Chemical and Materials Engineering Department and Chemistry at the University of Auckland, engineering design and surface treatments for wear minimisation have been investigated. These range from production of coatings for performance enhancement in the process industry, including carbon/ceramic composites, to improving wear resistance of artificial hip joints using ceramic coatings. Studies of oxides on aluminium to improve adhesion to foils have been investigated.

SCANNING PROBE MICROSCOPY (SPM)

The range of techniques available
Scanning probe microscopy is the generic name for a wide range of techniques each with their own acronym. Most people have heard of scanning tunnelling microscopy (STM) which was developed in 1981 by Binnig and Rohrer (for which they received the Nobel Prize in 1986). However there have been major developments since then. The best known of these is

probably atomic force microscopy (AFM) developed in 1986 by Binnig, Quate and Gerber. Now there is a range of variations on these basic methods, with labels such as TMAFM, LFM, CFM, some of which are described below.

Atomic force microscopy (AFM)

Atomic force microscopy is a form of microscopy where a morphological image is obtained of a surface. This image shows the topographic features on the surface. But what is really amazing about the technique is the resolution that can be achieved - under certain conditions it is possible to see individual atoms!

The AFM works a bit like an old record player (before the advent of CD's). In the record player a stylus was dragged along a groove in the record and bounced up and down with the bumps in the groove generating a voltage in the pick-up. As shown in **Figure 3** in the AFM the principle is similar although there are some major refinements. The sample goes back and forth and scans from top to bottom (rather than rotating like the record). The tip (in place of the record player stylus) is very sharp and small and is mounted on a microscopic force sensor. A laser reflecting off the back of the cantilever to a photodiode array senses the deflection of the cantilever. In most AFM systems the cantilever holding the tip isn't allowed to bend very much but rather the sample (or cantilever holder) moves up and down attempting to keep the force (the atomic repulsion) of the tip on the sample constant. A feedback system is used to maintain this constant force as the sample is scanned.

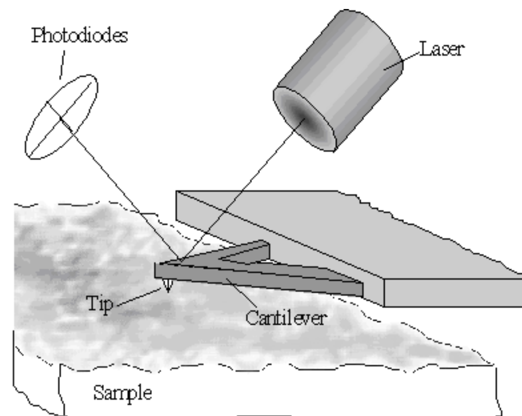

Figure 3 - Schematic of atomic force microscope operation

As a tip approaches a surface it is initially attracted towards the surface largely due to capillary forces. This attraction is non-localised. However as the tip approaches closer it experiences a repulsive force which is very localised.

To get very high magnification images needs two factors: a sharp tip and a way of very accurately controlling the movement of the sample (or tip). The control of movement is achieved with a piezoelectric tube, on which the sample (or tip) sits, that can be controlled in three dimensions by applying voltages to it. Applying a voltage to a piezoelectric material causes it to expand or contract just as applying pressure to a piezoelectric material causes a voltage to be generated. The accuracy with which motion can be controlled by these piezoelectric devices is quite incredible; it can be as good as 0.1Å.

So the AFM is just a microscope that has amazing resolution? Yes but not "just". Even if only using the device as a topographic microscope there is the major advantage that the sample does not have to be in a vacuum but may be examined in air or under a liquid. There are many other uses to which the instrument may be put. Scanning electron microscopy, with which many people will be familiar, requires that the sample is placed in a vacuum and normally requires the sample to be electrically conductive (therefore a coating of carbon or gold is often applied to the sample). With AFM the sample does not have to be conductive

and the sample may be imaged in air or in a fluid! Special fluid cells are available to look at samples under the fluid of your choice. Typically this will be water or an electrolyte solution.

Scanning tunnelling microscopy (STM)
Because it is generally restricted to conducting samples, scanning tunnelling microscopy is now a lesser-used technique. It differs from AFM in that instead of measuring the force between the tip and the sample a tunnelling current is measured. This is done by applying an electric potential between the tip and the sample. The tunnelling current provides a feedback to control the piezoelectric tube. Typically an image records the sample (tip) displacement needed to maintain a constant current. Some types of atoms on the surface can show up as a depression rather than a protrusion. Although superior to the AFM in terms of resolution, the technique has fallen out of favour as a simple imaging tool but has gained favour with physicists studying surface electronic structure.

Tapping Mode (TMAFM)
Conventional AFM operates in contact mode, that is, the tip is dragged along the sample physically in contact with the surface (in the repulsive regime). Tapping Mode , which is a trademark of Digital Instruments, is a modification of AFM where a piezoelectric crystal in the cantilever assembly holder causes the cantilever to oscillate at or near the cantilever's resonant frequency. The tip is then brought in contact with the sample surface so that it just begins to touch or tap the surface. This enables sample damage to be reduced. In addition it has resulted in the powerful technique of phase imaging.

Phase Imaging
Phase imaging has been used for some time without the phenomenon being well understood. It was observed that surface detail not clearly visible in height images showed up with good contrast in phase images. In addition the elastic modulus of the surface can affect the image so that differences in surface hardness can be detected. Phase imaging works by detecting the phase shift of the cantilever oscillator when it interacts with the sample surface. The theoretical basis of the technique is now well understood. Where small local variations in height are of interest on a sample with larger height variations overall then phase imaging is also a very useful technique. An example of a phase image is shown in Figure 4.

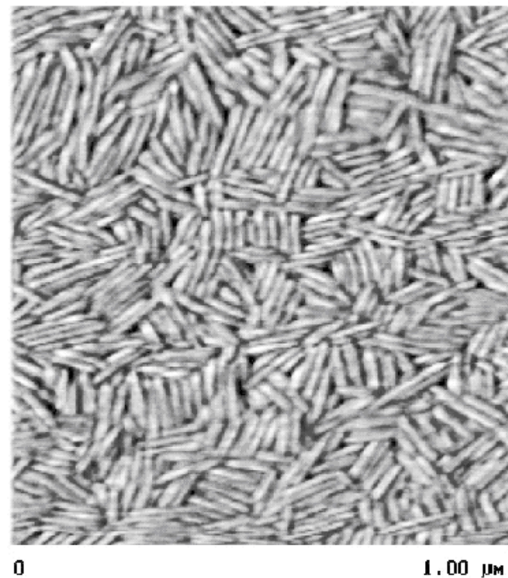

Figure 4 - AFM phase image of protein rodlets from *Neurospora crassa* on mica

Lateral Force
When a tip is dragged across a sample surface there will be a resistance to the movement of the tip. This resistance to the dragging of the tip, known as the lateral force, can be measured on an AFM. The tip is dragged at right angles to the long axis of the cantilever (in the "y" direction) so that the cantilever will twist as the tip encounters a lateral force. This twisting will cause the laser deflecting off the back of the cantilever to be deflected to one side and a

pair of photodiodes can measure this deflection. (We need four photodiodes then to measure height and lateral force simultaneously). This lateral force measurement can tell us about the frictional forces on a microscopic scale or can show up differences on a surface, especially compositional, that are not apparent in height images.

Force Curves

The AFM can also be used to measure the force between the tip and a sample as the tip is brought towards the sample and pulled away from the sample. In this way electrostatic forces between the tip and sample can be measured in air or in liquids. The force is proportional to the tip deflection to a first approximation and an example of a tip deflection verses distance curve is shown in **Figure 5**. Modifying the surfaces can result in changes to these attractive forces. In air there is often a strong attraction between, for example, a silicon nitride tip and a mica sample due to the capillary attraction from the surface layer of adsorbed water and other contaminants. Immersing the sample in water can reduce this interaction. Frequently the force between the tip and a surface in a liquid is strongly dependent on the pH of the liquid. Colloidal particles can be attached to AFM cantilevers. It is then possible to measure the force between the colloid and a surface of interest.

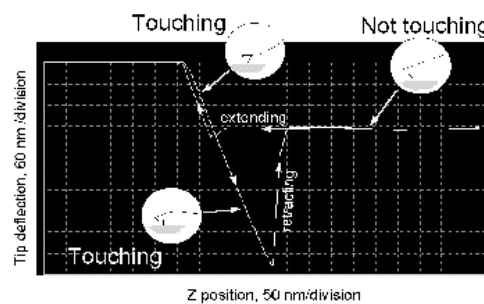

Figure 5 - Deflection vs tip-sample distance for a silicon nitride tip on silicon in air

Magnetic Force (MFM)

If a tip is coated with a magnetic material and a sample is scanned which contains magnetic regions then there will be a magnetic force acting on the tip in addition to the atomic repulsion. But to be able to distinguish between the sample topography and the magnetism of the sample we need to be able to separate these two effects. The atomic forces are very short range and the magnetic forces are longer range so there is an easy way to do this. The tip is scanned across the sample in contact with the surface to get the height data on the first scan and this data stored. On the next scan the tip is scanned over the same area but is lifted so that it follows a path with a fixed height above the surface as determined by the previous scan. In this way any variation in force felt by the tip will be due only to the magnetic forces.

Other Techniques

New techniques are continually being developed and many more can be expected over the next few years. For example some of the recently reported techniques include scanning capacitance microscopy, scanning near-field optical microscopy, scanning thermal microscopy, surface enhanced Raman spectroscopy using scanning near-field optical microscopy and chemical identification by STM photoemission.

Sample Requirements

There are two main sample requirements for AFM for the Digital Instruments Nanoscope IIIA at the University Auckland. They are limitations on size and surface roughness. Height variations (z movement) as low as 0.1 Å can be detected but the limit on the maximum height

variation of the surface is about 1μm. Samples must be small - about 12 mm maximum diameter and about 5 mm maximum thickness. Other instruments are available overseas that handle larger samples.

Applications of SPM and AFM

The SPM and AFM has been used in New Zealand for a range of applications. Just a few of the types of studies that have been carried out recently have been selected below.

The Department of Chemistry at the University of Auckland has looked at the nucleation and growth of diamond films from oxyacetylene flames using SPM and AES. These have practical applications in forming insulating coatings, high quality cutting and polishing surfaces and wear-resistant films.

Hort Research and Massey University have studied fungal hydrophobin proteins which self assemble into rodlets on surfaces and change the wetting properties of the surface.

The School of Biological Sciences at the University of Auckland has used AFM to investigate the structure of amylase proteins.

The Department of Chemical and Materials Engineering at the University of Auckland has looked at superconducting crystal structures and fouling on membrane filters.

ION BEAM ANALYSIS (IBA)

The Technique

Ion Beam Analysis (IBA) covers a range of techniques where a high-energetic ion beam hits a target producing a variety of emitted particles. IBA can determine the variation in the elemental composition in the surface of a material. This composition strongly influences the properties of the material being developed. The IBA method uses a particle accelerator to inject the nuclei of light atoms such as hydrogen or helium into the surface particles (at 0.75 – 3 MeV), resulting in emitted nuclei, gamma rays or X-rays.

A typical experimental arrangement is shown schematically in **Figure 6** with four types of Ion Beam Analysis which are carried out at the Institute of Geological and Nuclear Sciences (IGNS) in Gracefield listed in **Table 1**.

Table 1. Four types of Ion Beam Analysis carried out at IGNS, Gracefield.

Name of interaction	*Abbreviation*	*Description*
Rutherford Backscattering	RBS	Elastic scattering of the particle beam from the target nuclei.
Particle Induced X-ray Emission	PIXE	electrons are ionised and elemental specific X-rays are generated
Particle Induced Gamma-ray Emission	PIGME	nuclei are excited and gamma-rays are generated
Nuclear Reaction Analysis	NRA	a nuclear reaction occurs with the particle beam & target nuclei

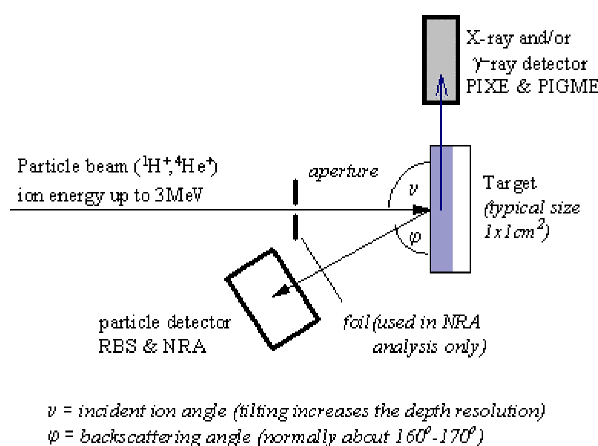

Figure 6 - Ion beam analysis experimental set-up

Sample requirements
It is possible to measure nearly any type of sample for almost any element with little or no preparation, provided that the sample is vacuum compatible. Besides solid state samples, examples include powders, rocks, air particulates on filters, chemical precipitates on filters, artefacts and biological samples such as bone, teeth and shells. Generally 10 milligrams of sample is required. However samples as small as 20 μm are often measured on the microprobe facility, the only one of its type in New Zealand. A maximum sample size of 5 cm x 10 cm is possible. IBA measurements are relatively non-destructive so that the sample is generally undamaged. Measurements usually take 1-20 minutes of beam time. Two classes of spectra are shown for sialon, a solid state ceramic material, in **figures 7 and 8**.

Quantification, depth profiles and imaging
In ion beam analysis the energies of the emitted species are characteristic of the material in the target so that elemental information can be obtained. The method is sensitive to light elements such as oxygen and nitrogen and can be quantified to an acuracy of better than 1%. The limit of detection ranges from 10-200 ppm, depending on the element and the composition of the sample.

The energies of the emitted species are modified by the depth from which they emanate, and thus they allow a depth profile of the composition to be obtained. The depth resolution at the

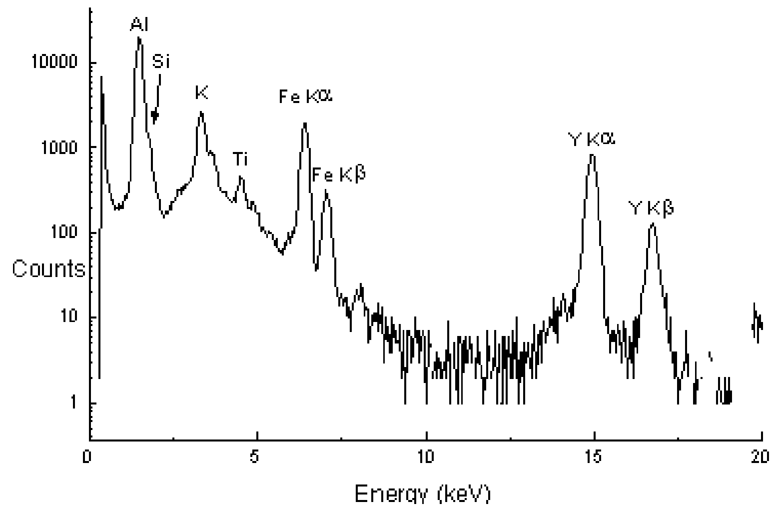

Figure 7 - PIXE spectrum of untreated sialon

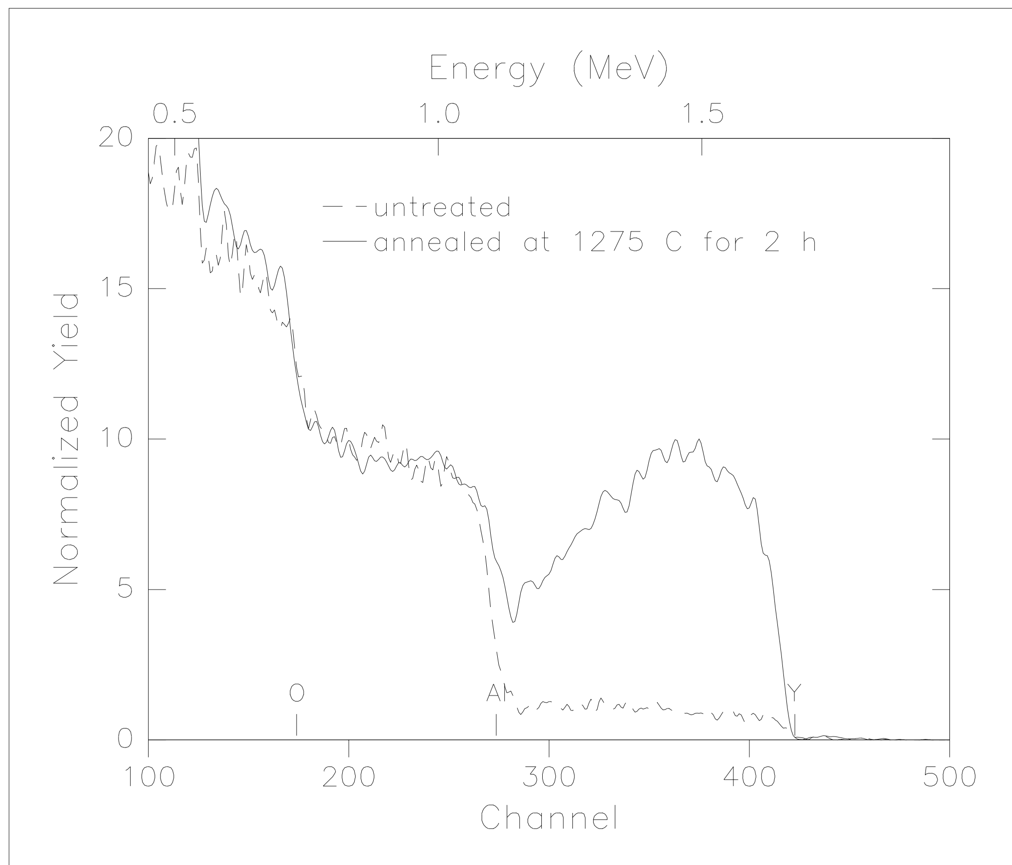

Figure 8 - RBS spectrum of sialon. Positions of O, Al and Y are shown

surface is better than 10 nanometers using standard RBS with $^4He^+$ 2.0 MeV ions. Depth profiles up to microns can be obtained.

Variations of elemental concentrations can be measured over the surface of a sample using the ion microprobe. This enables spot analyses of very small areas (20 µm). In addition, two- and even three-dimensional elemental maps of the specimen can be collected for an area as large as 5x5 mm. Up to 20 maps of light and heavy elements can be measured simultaneously.

Applications of IBA

A research programme to improve the properties of new materials being developed for New Zealand industry is being carried out by the Institute of Geological and Nuclear Sciences in collaboration with Industrial Research Ltd and Victoria University of Wellington. Three classes of material are under investigation - advanced ceramics, solar absorbers and highly cavitated surfaces. The programme provides a technical platform in specialist analytical techniques based on ion beam analysis. Two of these examples are detailed below.

Cavitated, or nanoporous, surfaces can be prepared on titanium alloys and these surfaces can be expected to differ markedly from unmodified surfaces in their physical and chemical properties. Since oxides make good catalysts and, in the case of titanium dioxide, a good biocompatible material, it is of interest to oxidise the nanoporous surface, and then characterise the structure and chemical properties of the resultant oxides. The results obtained by the Institute of Geological and Nuclear Sciences and Victoria University of Wellington show that a high-energy ^{4}He implantation (160 keV) affects the oxide phase formed at the surface, favouring the formation of the anatase phase of titanium dioxide rather than the rutile phase.

Solar absorbers, designed to absorb as much energy as possible from the sun and operate at elevated temperatures, are being made by at Industrial Research Ltd using films of titanium oxynitride. In perfecting these absorbers, the optimum amounts of oxygen, nitrogen and titanium have to determined, and the variation in film composition after operating at elevated temperatures measured. Ion beam analysis is ideal for this purpose. Similarly, advanced engineering ceramics, also being produced by Industrial Research Ltd, have to be tested for the rate of oxidation at their high operating temperatures. Ion beam analysis not only provides this but can also give detailed information which leads to improvements in the design of these materials. Advanced engineering ceramics are now being produced in New Zealand.

Written by Richard Haverkamp, Massey University, and Andreas Markwitz, Institute of Geological & Nuclear Sciences. Richard was the Technical Director of the Research Centre for Surface and Materials Science at the University of Auckland from 1995 till 1997.
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