THE DEVELOPMENT AND APPLICATION OF A TRANSMISSION X-RAY PHOTOELECTRON SPECTROMETER (TXPS)

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Thesis Submitted to the University of Surrey for the Degree of Doctor of Philosophy

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Though patience be a tired mare, yet she will plod.

William Shakespeare

How often have I said to you that when you have eliminated the impossible, what ever remains, however improbable, must be the truth?

Sir Arthur Conan-Doyle

Nothing in the world is so powerful as an idea whose time has come.

Victor Hugo

This thesis is dedicated to Patricia for her patience and support.
ABSTRACT

There is a growing demand to obtain XPS analyses from increasingly smaller sample areas. The development of a Transmission X-Ray Photoelectron Spectrometer (TXPS) will allow spectrum acquisition and imaging with a lateral resolution approaching $1\mu m^2$. The principle is based on back-foil excitation where thin samples are placed on an aluminium foil or have an evaporated source backing. Electron irradiation of the foil produces characteristic X-rays locally and this, in turn, gives rise to a small source of photoelectrons from the opposite side of the sample. Rastering the electron beam scans the X-ray interaction volume which allows imaging. Photoelectron lateral resolution is dependent on the sample and foil thicknesses and is determined by the width of the X-ray excitation envelope and on the electron beam diameter.

In this work a VG Scientific MA500 is modified to give the ideal 180° geometry for TXPS. A hemispherical analyser with an extended high magnification transfer lens ensures a large solid angle of photoelectron collection, and the hemispherical analyser gives the (previously unobtainable) energy resolution necessary to obtain chemical state information. Aspects unique to TXPS spectral and image interpretation are described. The analysis conditions where sample damage is likely are investigated. Photon induced damage is manageable, but is shown to be far more of a technique drawback than Joule heating. Specimen charging presents no particular problems, although it can be both positive and negative in TXPS.

It is believed that TXPS is the ideal way of examining ultramicrotomed sections through interfaces and soft composite materials. Harder materials, such as ceramics and metals, require ion beam thinning in a similar way to TEM specimens. Specimen production needs are addressed as well as the problem of making the TXPS technique far more routine to the analyst. A magnesium/aluminium alloy is ion beam thinned to demonstrate TXPS from a harder material. The interlayer between a chlorine containing latex and mild steel is also analysed by TXPS, following the removal of the bulk substrate and ultramicrotomy. Data are examined and an iron valence state change across the interface allows conclusions to be drawn about the continued growth of the protective interphase under environmental exposure.
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- My industrial supervisors Dr. Dave Barnes (ICI) and Dr. Peter Moreland (Zeneca) for many useful discussions and the use of their laboratory facilities. Colin Gould and Joe McMahon for their electron microscopy work at ICI.
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Stephen N. Jenkins
(November, 1993)
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ACRONYMS

AES Auger Electron Spectroscopy.
B Spectral Background Channel Height (on the Low Kinetic Energy Side of the Peak) Used in Mapping.
BE Binding Energy (eV).
BOC British Oxygen Company plc.
BTMA500 Manufacturer's name for the instrument modified in this thesis (British Telecommunications 500Å specification microanalyser).
CAE Constant Analyser Energy.
CCD Charge Coupled Device.
CHA Concentric Hemispherical Analyser.
CSLM Confocal Scanning Laser Microscope.
CMA Cylindrical Mirror Analyser.
CRR Constant Retard Ratio.
DVM Digital Voltmeter.
e^-AES Electron Induced Auger Electron Spectroscopy.
EDX Energy Dispersive X-Ray.
EMA Electron Microprobe Analysis.
ESCA Electron Spectroscopy for Chemical Analysis.
FWHM Full Width at Half Maximum.
G/L Gaussian to Lorentzian Ratio.
ICI Imperial Chemical Industries plc.
IXPS Imaging X-Ray Photoelectron Spectroscopy.
IBPF Image Band Pass Filter.
KE Kinetic Energy (eV).
P Spectral Peak Channel Height Used in Mapping.
PE Poly(ethylene).
PET Poly(ethylene terephthalate).
PESM Photoelectron Spectromicroscope.
PMMA Poly(methyl methacrylate).
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>PVC</td>
<td>Poly(vinyl chloride).</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Backscattering Spectroscopy.</td>
</tr>
<tr>
<td>RS</td>
<td>Rapid Solidification.</td>
</tr>
<tr>
<td>SAXPS</td>
<td>Small Area X-Ray Photoelectron Spectroscopy.</td>
</tr>
<tr>
<td>S/B</td>
<td>Signal to Background Ratio.</td>
</tr>
<tr>
<td>S/N</td>
<td>Signal to Noise Ratio.</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy.</td>
</tr>
<tr>
<td>SXR</td>
<td>Scanning X-Ray Radiography.</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy.</td>
</tr>
<tr>
<td>TXPS</td>
<td>Transmission X-Ray Photoelectron Spectroscopy.</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra-High Vacuum.</td>
</tr>
<tr>
<td>VG</td>
<td>Vacuum Generators.</td>
</tr>
<tr>
<td>XAES</td>
<td>X-Ray Induced Auger Electron Spectroscopy.</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy.</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction.</td>
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INTRODUCTION

The aim of this project was to develop a small area XPS technique, to obtain spectra from areas of the order of 1 µm² and ultimately to analyse an interface with a primer material. This was considered to be possible using Transmission XPS (TXPS), which uses an electron beam to cause back-foil photoelectron excitation via an attached aluminium source foil. As samples had to be thin, they would need to be prepared by ion beam thinning or ultramicrotomy.

Previous workers examined the theoretical performance of the technique and experimentally showed that back-foil analysis was possible. However, their work neither explored the possibilities for materials analysis nor the practicalities of spectral interpretation. Most notably no attempt was made to consider and develop sample preparation procedures. The specialised specimen needs of TXPS have subsequently been a key argument against the further development of the technique.

In this thesis the development, building and commissioning of the TXPS instrument is detailed together with the prospects for useful materials analysis. The theoretical history of TXPS performance is examined with respect to actual data. The drawbacks of the technique and the ways in which these problems can be minimized or eliminated are discussed. TXPS sample preparation needs are explored, together with the various imaging requirements, which all make the technique far more routine. The aspects of image and spectral interpretation unique to TXPS are considered along with experimental demonstrations. The first chemical state resolution data using the technique are also shown. Comparison is made to early and presently commercial small spot and imaging XPS instruments.

The applications of the TXPS technique are given a high priority. A magnesium alloy is examined to explore the possibility of ion beam thinning as a TXPS sample preparation procedure for harder materials. Of particular interest, however, is the interface between an ICI primer coating ('Haloflex') and mild steel. Previous work had shown that there was dissolution of the steel substrate during drying. It precipitated as an insoluble oxide or more complex mineral and iron oxidation state information is helpful in the discussion of the basic mechanism. Haloflex was the original catalyst for this work, which was financially supported by a grant from the Royal Society Paul
Instrument Fund and ICI Chemicals and Polymers Ltd. in the form of a SERC CASE Award.
1.0 SMALL AREA XPS TECHNIQUES AND IMAGING XPS

Conventional XPS is an area integrating technique. It collects signals from a large area (10mm$^2$) thereby removing any problems of representative analysis of the sample. However, in material science and metallurgy, there is often a need for more spatially localised chemical and chemical state surface analysis. Apart from a few exceptional cases in AES, chemical state analysis is only obtainable by XPS. The difficulty in obtaining small area XPS is that X-rays are extremely hard to focus. However, there are four main routes to small area XPS:

i) **Defined Collection System:** where the whole sample area is irradiated and a portion of the signal is selectively sampled and analysed.

ii) **Defined Source System:** where the area of X-ray irradiation is reduced and the maximum solid angle of photoelectrons is analysed.

iii) **Hemispherical analyser Imaging:** using the double focusing properties of the analyser.

iv) **PESM:** a novel route to imaging XPS allowing parallel detection.

1.1 Defined Collection System

The first attempt to perform a small area XPS technique was by Keast and Downing [1]. They used a collimating tube through a steel plate, positioned between the sample and analyser. See fig.1. The plate was at 45° to the horizontal and polished to a mirror finish on the underside. This allowed the sample area to be correctly positioned over the area of interest. The tube did not interfere with sample X-ray irradiation. Experimental results gave 700μm spatial resolution (this was the internal diameter of the collimator). It would, in principle, have been possible to reduce the area of analysis by further reducing the tube internal diameter but the technique would have suffered badly from lack of photoelectron counts. Image acquisition simply required sample rastering, but this was never put into practice.
Fig. 1
Photoelectron Collimation [1].

Fig. 2
Apparatus used by: (a) Yates and West [2] (b) Seah and Smith [3].
Yates and West [2] used an ESCALAB II to show that an electron transfer lens could be used to obtain small area analysis. The ratio of the aperture area to lens magnification described the analysed area. To maximize resolution, electron optical aberrations had to be minimised or compensated for. Even with the latest ESCALAB the best spatial resolution obtainable is 100μm. Pre-lens scanning of the virtual image of the input aperture on the specimen surface allowed Seah and Smith [3] to build up images. This became the basis of the Kratos Axis machine.

1.2 Defined Source System

<table>
<thead>
<tr>
<th>METHOD</th>
<th>AREA (mm x mm)</th>
<th>RELATIVE INTENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>5x10</td>
<td>1000000</td>
</tr>
<tr>
<td>Single Aperture Collimator</td>
<td>0.1x0.1</td>
<td>200</td>
</tr>
<tr>
<td>Double Aperture Collimator</td>
<td>0.1x0.1</td>
<td>2</td>
</tr>
<tr>
<td>Reflection Focused X-Rays</td>
<td>0.1x0.1</td>
<td>200</td>
</tr>
<tr>
<td>Zone Plate Focused X-Rays</td>
<td>0.1x0.1</td>
<td>5000</td>
</tr>
<tr>
<td>Monochromator Focused X-Rays</td>
<td>0.1x0.1</td>
<td>&gt;2500</td>
</tr>
</tbody>
</table>

Table 1
Comparison of Defined Source System X-Ray Intensities.
This involves methods of producing fine X-ray spots on sample surfaces and collecting as much of the resultant photoelectron signal as possible. Since X-ray electrostatic focusing to a fine spot is impossible, collimation, reflecting optics, zone plates and crystal monochromators are used. For a comparison of these methods see table 1.

![Diagram of X-ray illumination methods](image)

**Fig. 3**

*Fig. 3: X-Ray Illumination of a Small Area of Sample [3]: (a) Single Aperture, (b) Double Apertures, (c) Reflecting Optics, (d) Zone Plate.*

1.2.1 **Collimation of the X-Ray Beam**

One or two apertures are placed between the sample and analyser to collimate the beam. If a single aperture (fig.3a) is used to obtain 100μm resolution, it must be within 2mm of the sample. This reduces the X-ray spot intensity by a factor of 5000. The short sample/aperture distance limits the practical obtainable resolution [3]. With
a double slit system (fig.3b) the final aperture can be further from the sample, since the beam is diverging to a lesser extent at the final aperture. Although the obtainable spot areas are much smaller, the relative intensity is now reduced by a factor of 500,000 relative to ordinary XPS. Thus, intense synchrotron sources are needed to provide sufficient count rates. Using conventional X-ray sources this method is virtually unworkable. Overheating limits the use of conventional sources at higher powers.

The refractive index of materials at X-ray wavelengths is more or less constant. Conventional lenses, therefore, are hopeless for focusing X-rays. However, reflection of X-rays at grazing incidence and diffraction are possible.

1.2.2 Focusing of the X-Ray Source Using Reflecting Optics

The high reflection efficiency of some materials at grazing incidence allows total internal reflection to be used to focus X-rays onto the sample as shown in fig.3c. The solid angle of X-rays accepted by the device depends on the maximum grazing angle at which total internal reflection can operate. To attain a 100μm spot the relative intensity is lower than conventional XPS by a factor of 5000.

1.2.3 Zone Plate Focusing of X-Rays

Zone plates can be used to focus X-rays. They are used in a similar way to conventional lenses for light, except zone plates work by diffraction back to a focus on the sample. See fig.3d. The two stops in the diagram remove zero and second order diffraction beams. A 100μm spot has a relative intensity reduction factor of 200, which is considerably better than the previous X-ray spot size reduction methods.
1.2.4 **X-Ray Focusing Using a Crystal Monochromator**

An X-ray point source is created at the impact point of a finely focused electron beam on the anode (e.g. aluminium). The X-rays from the focused source strike the monochromator crystal and undergo Bragg diffraction. The type of crystal is chosen so that the lattice spacing diffracts the desired x-radiation off a known plane (e.g. (1010) plane of α quartz for Alkα radiation). The crystal is bent during growth to cause all the diffracted beams to converge on a single point. This is the position of the sample. See fig.4. The X-ray point source, crystal and sample all are positioned on a Rowland circle.

100μm spots are achievable, but the power of conventional X-ray guns has to be reduced to avoid overheating of the anode. This cooling problem can be overcome by rotating the anode. Conventional sources give count rate reductions of 400 relative to ordinary XPS, but monochromatisation leads to better spectral energy resolution and improved signal/background ratios by the removal of Bremsstrahlung.

![Diagram](image)

**Fig.4**
Small Area XPS by X-Ray Monochromatisation.

All of the previous methods could be turned into imaging techniques simply by moving the specimen by stepper motors or piezoelectric stages.
1.2.5 **Transmission XPS**

TXPS is also a defined source system technique, where a focused electron beam creates a point source of X-rays on a foil placed immediately on top of a thin sample. Some transmitted X-rays excite photoelectrons from the top few atomic layers of the back of the sample. These electrons are then analysed. This is the principle behind this project and so will be described later.

1.3 **Imaging Through the Hemispherical Analyser**

1.3.1 **Using the Double Focusing Properties of the Hemispherical Analyser**

Small area analysis and imaging is possible using the double focusing properties of the hemispherical analyser; it gives positional information in the non-dispersive plane of the analyser and energy information in the dispersive. The kinetic energy of an electron will define its degree of deflection in the dispersive plane, whilst positional information is maintained in the non-dispersive. This determines the image point. Double focusing means that a mono-energetic point source of photoelectrons will be focused on a certain point by the analyser.

A mono-energetic photoelectron entering the analyser will produce a 1:1 magnification inverted image at the analyser exit plane. A one-dimensional image, or line scan, is produced at the position usually occupied by the electron detector, so it is replaced by a two-dimensional position sensitive detector [4]. A fluorescent screen can be used as a detector, but a channel plate needs to be used for quantification. The channel plate is a resistive anode which gives electron positions accurately. Gurker et al. first discussed this principle [4] and the idea was then realised using a GCA Mc. Pherson ESCA 36 [5].

The analysed area must be a strip perpendicular to the dispersive plane of the analyser. Therefore, a narrow strip of sample surface must be illuminated. Alternatively, a narrow region of X-ray flooded surface can be selected. Gurker used
a double slit system at the analyser entrance. This produces a map of energy versus position along a line, the so called E:X plot. See fig.5.

Fig.5

The Double Focusing Properties of the Hemispherical Analyser Used to Produce E:X Plots.

At the time of his work the lateral resolution of the technique was controlled by improvements in the quality of the channel plate. Ultimately, though, it will be determined by the illuminated area. Gurker obtained 100μm resolution, both in his computer simulation and in the experimental realisation. The maximum and minimum energies detected on the channel plate are determined by the analyser pass energy. Gurker did not have a retarding field and so had poor energy resolution.
Using a multi-position specimen holder, it is possible to construct a chemical map of a particular photoline from a series of line scans. The specimen only needs one direction of movement during analysis.

The use of a channel plate with parallel detection reduces the time required for spectrum acquisition. However, channel plate positioning is difficult.

Magnification of the signal before entering the analyser improves the lateral resolution of the technique. Scienta (ESCA300) based their imaging system on Gurker's
principle, whilst seeking to maximize photoelectron count rates [6]. Normally X-ray gun power is severely limited by over-heating. To achieve high count rates they have used a new high power source. The anode is rotated while being water cooled. Monochromatisation ensures good energy resolution in the final analysis. The apparatus, shown in fig.6, also features a 300mm radius hemispherical analyser. The ESCA300 can operate in two modes, either giving high energy resolution or high lateral resolution; achieving 25μm in the latter mode. The disadvantage of this method is the loss of energy and spatial information in the analyser dispersive plane.

1.3.2 Using the Retention of Angular Information in the Hemispherical Analyser

Fig.7
ESCASCOPE Electron Optics.
VG Scientific (Fisons) have developed a machine (ESCASCOPE) based on the idea that if spatial information is converted into angular information at the input slit of the analyser, it is retained at the exit aperture [7]. See fig.7.

The system is based on a conventional spectrometer with two lenses left unchanged. Lenses 3 and 5 have been added. These are quasi-Fourier transform lenses. The object plane of the analyser corresponds to the diffraction plane of lens 3. Thus, electrons from different sample positions enter the hemispheres at different angles. The hemispherical analyser not only introduces energy dispersion but also produces an image of the diffraction plane at its own output plane. Spectrum detector 1 (channeltrons) can be used to obtain standard spectra or by allowing the photoelectrons to pass through lens 5 an image is projected at the imaging detector 2. Lens 5 recovers the spatial information stored as angular information.

In latest upgrade of the instrument 2μm lateral resolution is reported for imaging, although point analyses are still restricted to 15μm [8,9].

1.4 Photoelectron Spectromicroscope (PESM)

The photoelectron spectromicroscope (PESM) is a revolutionary approach to imaging XPS, allowing analysis to be carried out at the micrometer level. It has a near 180° acceptance angle and collects images in parallel. Thus, almost all of the electrons that are emitted, within a certain band of energy, are collected. The original work was performed by Turner et al [10-13] and is now under development with Kratos Analytical Ltd.

The sample is positioned in between a 7 Tesla superconducting cryomagnet as shown in fig.8. An X-ray monochromator source is used to irradiate the sample. The superconducting coils produce a diverging magnetic field which projects a magnified image onto the detector. The magnetic field reduces along the axis of the apparatus. The original angular distribution of electrons emitted from the specimen is increasingly collimated so that their velocity vectors tend to follow the field lines. Electron
momentum is conserved as well as their total energy. Any initial radial momentum tends to reappear as axial motion, so, electrons emitted at nearly 90° to the machine axis can be collected.

![Diagram of Photoelectron Spectromicroscope (PESM)](image)

**Fig.8**

Schematic of Photoelectron Spectromicroscope (PESM).

In the lower magnetic field regions electrons are filtered using an analysis technique developed specifically for the PESM: Image band pass filter (IBPF). Surrounding this are coils which give the required uniform magnetic field. Only electrons of selected kinetic energies pass through the IBPF to be magnified by the trim coils and finally reach the detector. The detector is a twin channel plate which illuminates a phosphor screen. The image magnification is directly proportional to the square root of the ratio of the magnetic field at the sample to the field at the detector. Since the sample field is set at 7T, the magnification is varied from 15x to 300x by changing the trim coil field.

The PESM imaging is in real time and analysis is fast due to the huge transmission of electrons from the sample to the detector. The image may be projected at any distance from the filter since the beam is parallel and always in focus. Samples can be rough without causing depth of field problems. There are no electrostatic lenses which means there are no chromatic aberration limitations.
The original electron filter used simple retarding grids. They only have 1eV to 10eV resolving power, which is unsuitable for XPS. They also left dark regions on the images from grid shadows. However, the realisation of the IBPF allowed both high energy and lateral resolution to be obtained.

1.4.1 Image Band Pass Filter (IBPF)

The IBPF in fig.9 removes electrons above and below the required energy threshold levels, leaving the image comprising of electrons of certain kinetic energies. Adjusting the IBPF allows the recording of a whole spectrum over a period of time. Even now analysis times are short by virtue of the high transmission of analysed electrons.

![Fig.9](image)

Schematic of the Image Band Pass Filter [14].

The IBPF allows continuous image filtering, over the required energy range, using both retardation and deflection. It is comprised of an arrangement of both high and low energy filters. On entering the filter the image is deflected towards a low energy filter. Electrons are retarded to the kinetic energy lower limit. Only electrons of sufficiently low kinetic energy will be stopped by this field and reflected (this is an electron mirror). The remainder will be lost to the system. The image is guided by a
cross field and then reflected off a second low energy mirror before entering a high energy filter. Electrons of too low energy will be repelled and lost to the system. The second half of the analyser is a mirror image of the first half and any image shearing and energy-dependent dispersion introduced by the first half is removed. The second half deflects the image back on axis within the instrument and towards the detector.

By reducing the angle of collection of the IBPF, both the energy and lateral resolution of the PESM can be improved. It is, therefore, anticipated that photoelectron maps with resolutions of a few micrometers will be possible up to 1500eV. At present, predictions suggest the instrument can reach 5µm at 30eV and 30µm at 1000eV with no angle definition. See table 2 [14].

The PESM works very well with Ultra-Violet radiation Sources. However, both energy and lateral resolution are degraded at higher electron kinetic energies making it less suitable for use with conventional X-ray sources. A tuneable X-ray source obtainable from a synchrotron would produce the best XPS results, but the cost would be high.

<table>
<thead>
<tr>
<th>E (PHOTO-ELECTRON ENERGY)</th>
<th>SPECIMEN SEMI-COLLECTION ANGLE</th>
<th>ΘC</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°</td>
<td>30°</td>
<td>10°</td>
</tr>
<tr>
<td></td>
<td>ΔE</td>
<td>5</td>
</tr>
<tr>
<td>0.3</td>
<td>0.3meV</td>
<td>0.5µm</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0meV</td>
<td>1.0µm</td>
</tr>
<tr>
<td>3.0</td>
<td>3.0meV</td>
<td>3µm</td>
</tr>
<tr>
<td>10.0</td>
<td>11meV</td>
<td>3µm</td>
</tr>
<tr>
<td>30.0</td>
<td>32meV</td>
<td>5µm</td>
</tr>
<tr>
<td>100.0</td>
<td>0.1eV</td>
<td>17µm</td>
</tr>
<tr>
<td>300.0</td>
<td>0.2eV</td>
<td>17µm</td>
</tr>
<tr>
<td>1000.0</td>
<td>1.1eV</td>
<td>30µm</td>
</tr>
<tr>
<td>COSINE LAW DIST.</td>
<td>100%</td>
<td>25%</td>
</tr>
</tbody>
</table>

Table 2

Theoretical PESM Performance at Various Collection Semi-Collection Angles.
2.0 TRANSMISSION X-RAY PHOTOELECTRON SPECTROSCOPY (TXPS)

2.1 Principle of Transmission X-Ray Photoelectron Spectroscopy

In conventional XPS, samples are flooded by X-rays causing their atoms to be ionized. Measurement of the kinetic energies (KE) of these electrons allows binding energies (BE) to be calculated from

$$BE = hv - KE$$

where $hv$ is the energy of the X-radiation. These characteristic binding energies allow recognition of the elements and their chemical state. It is this elemental bonding information together with the simple XPS quantification procedures based on elemental sensitivity factors that make XPS stand out as a surface science technique.

X-rays are produced in flood guns by accelerating electrons at a target material (normally aluminium or magnesium) which emits photons of a known line width. Some of these non-monochromatised photons leave the gun via a thin window to irradiate the sample. The aluminium window itself removes some Bremsstrahlung and ensures no stray electrons can reach the sample.
There are many different approaches to obtaining small area XPS. These were discussed earlier. X-rays simply cannot be focused. This makes XPS of small areas difficult as the signal strength is often too small. One approach is TXPS.

The principle of TXPS is very similar to that of an X-ray gun. Electrons are accelerated at a target which produces characteristic photons. However, an electron gun replaces the X-ray flood gun and the effective anode is a foil or coating in intimate contact with a thin sample surface. A focused electron beam produces characteristic X-rays and Bremsstrahlung locally from the foil, which in turn excites photoelectrons and Auger electrons from a small area in the top few atomic layers of the back side of the sample. See fig.11. As in conventional XPS, inelastically scattered electrons will give rise to the background in spectra.

The accelerating voltage must be sufficient to efficiently excite X-rays. The size of the photoelectron spot is dependent on many factors. The size of the initial X-ray excitation volume is determined by the accelerating voltage and the electron beam diameter. There is spreading of the X-ray beam in the source foil and sample. Sample and target thickness are, therefore, important in determining TXPS lateral resolution. Realistically sample thicknesses are between 100nm and 1μm.

![The Principle behind TXPS.](image)
2.2 Review of Previous TXPS Work

2.2.1 J. Cazaux

J. Cazaux first proposed the principle of TXPS in the mid 70's and backed up his ideas by theoretical calculations [16]. Although C.T. Hovland published the first spectra, Cazaux produced the majority of results during the early 80's. Cazaux used a modified Auger spectrometer [17] with a single cylindrical mirror analyser (CMA) shown in fig.12.

![Cazaux's Single Pass CMA TXPS Apparatus.](image)

To perform TXPS, a scannable electron gun was placed opposite a CMA; the sample and source foil were located between the two. Inside the CMA an additional electron gun could be used to perform conventional electron induced Auger electron spectroscopy (e’AES). The electron guns typically ran at beam currents of a few µA at 10kV. The electron spot diameter was normally 15-20µm although 10µm was obtained in later work. Two secondary electron detectors, one on each side of the sample, allowed sample positioning. Spectra were obtained in a pulse counting mode and first and second order derivatives could be obtained using a lock-in amplifier. Line analyses and images were obtained by rastering the electron beam. Cazaux used two mechanisms for obtaining his X-ray source: Either (i) placing a 5µm or 3µm aluminium foil in
contact with the sample or (ii) actually using the sample itself as a source.

By setting the analyser for a particular characteristic photoline and scanning the electron beam over the source foil, Cazaux obtained images of sample surface elements.

The apparatus gave predictable count rates of $2 \times 10^4$ photoelectrons/s. Conventional XPS at the time of Cazaux’s experimental work gave similar count rates. $10^{11}-10^{12}$ photons/s/mm$^2$ were obtained [18], which compared adequately with the flux obtained by synchrotron radiation after monochromatisation. Cazaux obtained spatial resolutions of 10μm [19], but required a smaller electron probe size to allow further improvements, predicting 1μm ultimately.

2.2.1.1 Results

The first spectrum obtained by Cazaux’s laboratory was of 25nm of gold sputtered onto a 5μm aluminium source foil. The analysis time was 200s and the lateral resolution was 30μm. Signal to background ratios (S/B) were similar to those obtained by conventional XPS.

![Gold sputtered onto an Aluminium Source Foil.](image-url)
The arrangement of the apparatus allowed direct comparison between e'AES and TXPS of magnesium oxide deposited on 5μm of aluminium. Both photoelectron and Auger peaks were observed in the TXPS spectrum with good S/B ratios.

Fig. 14
Comparison of e'AES and TXPS.

Fig. 15
Influence of Accelerating Voltage on Photoelectron Intensity (Au/Al).
Fig. 15 illustrated that as the accelerating voltage was increased, the gold photoelectron peaks became more intense relative to the background [17].

Deposition of potassium iodide onto an aluminium source foil showed that insulators could be easily analysed by TXPS, as in conventional XPS. See fig. 16. Electron induced AES of insulators suffered from charging, which caused peak shifting with time. Auger peaks were therefore broadened. Broadening presented problems in long term Auger analysis (mapping). By inducing the Auger electrons by X-ray excitation in the transmission mode, these problems were avoided.

![TXPS of an Insulator (Potassium Iodide)](image1)

Fig. 16

TXPS of an Insulator (Potassium Iodide).

![Ferritin Analysed by TXPS](image2)

Fig. 17

Ferritin Analysed by TXPS.
Unavoidably thick biological specimens such as ferritin (15μm) were also analysed successfully.

Images obtained of gold deposited on 3μm magnesium were recorded (fig.18): (a) is an XPS image and (b) an is electron induced AES image, although Bremsstrahlung would have made a major contribution. (c) is a Bremsstrahlung induced Auger electron image of carbon deposited on a silver source. They show approximately 30μm resolution and were recorded in 4 minutes.

![Fig. 18](image)

Images obtained of Samples Deposited on Magnesium: (a), (b) and Silver: (c) [17].

The most recent example of TXPS imaging is fig.19, where sodium chloride crystals were dispersed on an aluminium foil [19]. Topography would still be dominant.
in these images because background had not been subtracted. Specimen thickness was important in determining the registered intensities. Assuming the sample was already thick enough to saturate photoemission, any further thickness increase simply added to the degree of X-ray absorption and, therefore, photoelectron intensities were lowered. This was an important difference from conventional XPS, which only shows changes in background shapes with specimen thickness.

Fig. 19
9kV Images of Small Sodium Chloride Crystallites on 5μm Aluminium Foils [17]. (a) Na 1 s, (b) Cl 2 p, (c) Na(KLL), (d) C 1 s, (e) O 1 s, (f) Point Spectrum on a Crystallite.

By clever use of source foils and photoelectron converters, Cazaux's equipment became multipurpose [17]. See the acronym index for further details. It allowed:

1) TXPS by back-foil excitation.
2) e⁻ AES using the standard electron gun inside the CMA.
3) XAES by back-foil excitation.
4) SXR (Scanning X-Ray Radiography or X-Ray Fluorescence) is the analysis, using
a converter material, of emerging bulk X-rays excited by X-rays from a source foil (fig.20a).

5) EMA (electron microprobe analysis) using a converter without a source foil so that the electron beam directly excited the sample (fig.20b).

As XAES does not need small X-ray line widths, silver and gold sources could be used. This allowed thinner foils because of their lower electron stopping distances. Higher spatial resolutions then became attainable.

(4) and (5) used converters on the back of the samples to convert emerging X-rays into photoelectrons to be detected by the CMA. Knowing the binding energy of the converter surface atoms allowed the deduction of the photon energy from the kinetic energy of the emerging photoelectrons. Lateral spatial resolution was independent of the sample to converter distance. It only depended on the source and sample...
thickneses in all the 5 cases. X-ray analyses by electron spectroscopy was interesting for light element analysis due to the highly resolved photoelectron peaks. Heavy element analysis required the choice of a converter whose binding energy would give measurable kinetic energies (50-2000eV).

2.2.1.2 Comments

1) Cazaux's apparatus was versatile. It could still perform many different techniques whilst still functioning as a normal Auger electron spectrometer. Few modifications needed to be made to a standard CMA arrangement. The major disadvantage of the technique at the time was the need to have thin samples, although they could still be thicker than those used in TEM today. Cazaux failed to show images or spectra where different chemical state information was resolved.

2) EMA can now be done on small areas in conventional TEM equipment using an EDX detector.

3) SXR can be performed on the BTMA500 instrument in its present arrangement using an EDX detector.

4) Using natural surface coatings on samples, as sources or converters, causes difficulties in spectral interpretation.

2.2.2 C.T. Hovland

Hovland [20-23] was the first person to produce a TXPS spectrum following the theoretical predictions made by Cazaux. The basic set up and geometry of the apparatus was similar to that used by Cazaux except that Hovland used a double pass CMA with retard grids to analyse the photoelectrons. This type of analyser was designed to obtain the energy resolutions desired for XPS chemical shift information. A single pass CMA failed to reach this level. He used a lanthanum hexaboride filament in his high resolution electron gun. The gun ran over a range of 0.1 - 10kV and 10^{-10} -
$3 \times 10^{-5}$A to give a minimum beam diameter of 0.5µm. Sample positioning was critical when CMAs were used. Hovland's three degrees of freedom allowed careful alignment of the sample at the CMA's focal point.

Fig. 21
TXPS Using a Double Pass CMA.

2.2.2.1 Results

![Graph showing results]

Fig. 22
Effect of X-ray Source Thickness on Photoelectron Count Rates and S/B Ratios.
Hovland discussed some simple considerations when using TXPS. The thickness of the aluminium foil determined the photoelectron source area due to X-ray dissipation. He considered that the limits on the minimum thickness were electron beam heat dissipation, sufficient filtering of the continuous background radiation (which would increase the background in photoelectron spectra), and prevention of penetration of the electron beam through the thin foil. Experiments with three thicknesses of aluminium foil (fig.22 [21]) revealed that the highest signal intensity was from the 2μm foil with comparable S/B ratios to thicker foils. The background was numerically higher due to less filtration of the Bremsstrahlung. From experiments with nickel grids, 6μm foils gave photoelectron source spot diameters of 20μm (fig.23 [20]) and 2μm foils 12μm [22].

![Image of nickel grid on a 6μm aluminium foil.](image)

**Fig.23**

Nickel Grid on a 6μm Aluminium Foil.

![Image of lilypollen Cls image and spectra on and off the grain.](image)

**Fig.24**

Lily Pollen Cls Image and Spectra on and off the grain (Dark=High Intensity).
Transmission X-Ray Photoelectron Spectroscopy (TXPS)

Images (fig.24) of lily pollen using the carbon photoline showed decreased intensity on the grain from an increased Alkα path length (bright regions correspond to reduced intensity). The mass absorption effect had the result of decreasing the overall sample photoelectron signal by a factor of 10. This was used only to locate areas for point analyses. No significant background corrections were made. Both on and off the pollen carbon and oxygen were observed. The off pollen analysis is of a thin formvar plastic material used to stick the sample down to the aluminium foil.

Fig.25

Calcified Coating on Trachelomonas On and Off the Sample (Image, Line-scan and Spectra On/Off sample).

Imaging to locate the area for point analysis was also used in the examination of a calcified outer coating on an algae called trachelomonas. Spectra on and off the particles showed the chemical composition of the coating. The point analysis on the coating had aluminium signal from poor positioning of the point.
2.2.2.2 Comments

Once again there is not any presentation of results showing chemical state resolution. Although the double pass CMA has good energy resolution, it has a far worse transmission function than its single pass predecessor. This means that photoelectron peak intensities will be much lower and this can lead to an inability to achieve peak resolution (unless very long analysis times are used). The hemispherical analyser now can have a higher transmission and it does not have similar problems with critical sample positioning.

2.2.3 W. Brünger

Cazaux's technique of back foil excitation was adapted to an unmodified commercial Auger microscope (VG Auger Microlab) by Brünger in 1988 [24]. A field emission source was used in the geometry shown in fig.26. Photoelectrons were collected using a hemispherical analyser.

Fig.26
Brünger's TXPS Apparatus Arrangement.
The composite X-ray source and sample was an X-ray lithography mask with a silicon membrane. The 2μm thick silicon acted as the X-ray source. A wide scan at 10kV is shown in fig.27. The silicon nitride structures are shown in the image using the N1s photoline. Spectral resolution was 2.3eV and lateral resolution was 4μm.

![TXPS Spectrum of Si₃N₄ Structure on a Silicon Substrate.](image)

Fig.27
TXPS Spectrum of Si₃N₄ Structure on a Silicon Substrate.

![N1s TXPS Line-scan Across 5μm Wide Si₃N₄ Lines with 10μm Spaces.](image)

Fig.28
N1s TXPS Line-scan Across 5μm Wide Si₃N₄ Lines with 10μm Spaces.
Fig.29

Images of Lithography Mask.
(a) SEM, (b) TXPS: N1s Photoline (high intensity = black).

2.2.3.1 Comments

This latest attempt to perform TXPS showed the best lateral resolution ever obtained using a high brightness field emission gun. Brünger's work showed the potential of TXPS using a perfectly flat compound X-ray source with silicon-based samples.
3.0 INTRODUCTION TO THE CONSTRUCTION AND X-RAY SOURCE NEEDS OF THE TXPS INSTRUMENT

3.1 Repairing and Building of a Transmission X-Ray Spectrometer From an Auger Spectrometer

The machine used in this research project was a Vacuum Generators Scientific MA500, originally received as a gift from British Telecom. The machine itself had not been used for some time and required extensive repairs to the vacuum system. On the MA500 the heavy electron gun was below the analysis chamber. This design gave mechanical stability and provided an ideal geometry for TXPS, as samples then rested flat in a horizontal plane. In order to collect in a reflection manner the Clam II hemispherical analyser and photomultiplier were orientated below the horizontal, as shown in fig.30.

Initially the photomultiplier was moved into a position where transmitted electrons could be detected and an EDX detector was added. Roughing and diffusion pumping lines were required for the X-ray detector as it had to be removed during bake-out. An extra bakeable beryllium window was introduced between the sample and the detector to avoid contamination of the specimens from any unbaked assembly.
Temporary Dexion supports held the detector in position until a permanent support was made.

After suitable top flange modifications the hemispherical analyser and transfer lens, normally used in AES in the MA500, were placed on top of the chamber held up by a Dexion support frame. This allowed the examination of electron spectra in transmission. However, this situation was far from ideal. There was a 150mm gap between the transfer lens nose and the top of the sample. The solid angle of electron collection was consequently very poor and remained so until money was found to finance the design and manufacture of a longer lens.

Fig. 31
Schematic of TXPS in the BTMA500 Corresponding to the Photographs in fig. 32.

To perform efficient TXPS a long transfer lens was required to carry photoelectrons from the sample to the entrance aperture of a second VG Microtech Clam II hemispherical analyser. The Royal Society Paul Instrument Fund paid for the necessary equipment to build the final instrument. A schematic and photographs of the
The instrument in its final state are given in fig.31 and fig.32 respectively. By varying double-sided flanges used as spacers at the top of the analyser chamber it was possible to perform analyses at various working distances from 38mm to 10mm which allowed greater flexibility when initially setting up the instrument. Further details of lens design and necessary modifications to ensure efficient collection of photoelectrons are given in section 4.2. The lens itself was of high magnification and was powered by the existing MA500 lens supply. With this equipment and its ideal 180° geometry, efficient TXPS was performable. Modification of the electron gun scan unit using a donated system gave the possibility of digital mapping controlled by the Link 860 computer. Spectral processing, such as peak fitting, was not possible on this computer system and it was incompatible with IBM PCs. Data had to be manually added to the PC based software packages.
Fig. 32
Photographs to Show Geometry and Port Positions on the BTMA500

3.2 Sample Holding

Fig. 33
Stub Design.
A stub suitable for TXPS had not only to hold thin foils in position, but also allow exposure to the primary beam from one side and collection of the maximum solid angle of photoelectrons from the other. The design that was chosen is shown in fig.33. The stub sat in the manipulator and gripped the thin foil samples using a washer and threaded clamp. The stub had a 2.5mm diameter hole bored through the centre. The washer itself originally had a lip to allow easy positioning when screwing the clamp down. This had to be removed to avoid X-ray shadowing problems and so a washer with a 25° taper towards the centre was made. The X-ray detector was orientated at 30° to the horizontal.

The transmission secondary electron image in fig.34 was of a copper grid, taken before the hemispherical analyser was added, to ensure the beam would pass through the stub. The rastered 10kV primary beam was totally absorbed by the 11µm thick grid to give the dark regions. The bright areas in between were caused by the high energy primaries passing through the grid holes and exciting secondary electrons from the analysis chamber roof. Some of these secondaries were attracted in by the positive bias applied on the photomultiplier to give the apparent shadow image. The probability of secondary electron collection from the chamber roof was obviously higher than from the underside of the grid bars.

Fig.34
Secondary Electron Shadow Image (Transmission) a of Copper Grid.
Once the hemispherical analyser was placed on top of the MA500 it was possible to collect an electron spectrum caused directly by a 0.4keV primary beam passing up the chamber, through a sample-less stub and into the transfer lens (distance from lens to sample: 150mm). See fig.35. This showed the satisfactory geometry of the system.

![Fig.35](image)

400eV Primary Beam Directly Entering the Hemispherical Analyser (working distance 150mm).

3.3 Thin Foils as X-Ray Sources for TXPS

Electron bombardment of a target material, providing the excitation voltage exceeds the ionization potential, causes emission of X-rays on electron orbital relaxation (or Auger electron emission). In TXPS it is necessary to maximize the X-rays transmitted through the foil. Again this is in contrast to conventional XPS where the X-rays from the source material are maximized in the reflection direction. In the BTMA500 the X-rays were monitored with an EDX detector as shown in fig.31.

The choice of TXPS target material suffers the same constraints as conventional XPS in that the natural line widths must be narrow and the source must have sufficient
energy to excite all elements that may be of interest. In TXPS there is also no opportunity for monochromatisation which limits the targets to a few of the elements in table 3. Dense materials, such as silver, would be advisable to minimize the interaction volume size and allow the use of thinner foils. Unfortunately, denser elements generally have broader X-ray lines together with many other X-ray peaks which would complicate photoelectron spectral interpretation. Realistically, targets for TXPS are limited to aluminium, magnesium and perhaps silicon. These elements satisfy the criteria previously discussed.

<table>
<thead>
<tr>
<th>Line</th>
<th>Energy, eV</th>
<th>Width, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y M\textalpha</td>
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<td>0.47</td>
</tr>
<tr>
<td>Zr M\textalpha</td>
<td>151.4</td>
<td>0.77</td>
</tr>
<tr>
<td>Nb M\textalpha</td>
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</tr>
<tr>
<td>Mo M\textalpha</td>
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<td>Ti L\alpha</td>
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<tr>
<td>Cr L\alpha</td>
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<td>Mg K\alpha</td>
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<td>Al K\alpha</td>
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<tr>
<td>Cu K\alpha</td>
<td>8048.0</td>
<td>2.6</td>
</tr>
</tbody>
</table>

Table 3
Energies and Widths of Some Characteristic Soft X-Ray Lines [15].

![Fig.36](image)

Transmission EDX Spectrum of a 5\textmu m Thick Aluminium X-Ray Window.
Irradiation of a 5μm aluminium X-ray window by a 10kV electron beam gave the transmitted EDX spectrum in fig.36. The spectrum shows the typical AlKα peak and Bremsstrahlung shapes observed from conventional X-ray sources. Indeed, the AlKα intensity was so intense that the EDX spectrum showed a sum peak. TXPS spectra could, therefore, be efficiently excited using thin foil sources as indicated by Cazaux [17] and Hovland [21].

3.4 To Produce the Aluminium Source for Samples

To excite sufficient numbers of X-rays for TXPS, an electron accelerating voltage of approximately 10kV is necessary. There is an ideal aluminium source thickness required at such a potential. The entire primary electron beam must be attenuated within the source to avoid any direct interaction with the thin film samples. This sets a constraint on the minimum aluminium thickness. If the entire interaction volume is within the target, then the production of X-rays is maximized. Beyond the ideal thickness AlKα intensity is self absorbed, and the intensity emerging from the opposite side of the source drops again. The ideal thickness must be found to give the maximum possible intensity of photons and, therefore, the maximum intensity of photoelectrons from the backside of the aluminium.

Cazaux and Hovland both used aluminium foils (2,3,4,5,6 and 8μm) as their X-ray sources in their work on TXPS. In order to obtain the maximum possible XPS spatial resolution, the sample must be in intimate contact with the source of X-rays, and the target must be as thin as possible.

In conventional SEM EDX analysis the significance of X-ray absorption increases with depth from the electron beam entrance plane. The exact depth distribution of characteristic radiation is shown in the top left of fig.37 and in the Bishop and Poole paper [25]. In fig.37 X-ray emission dominates close to the surface, but further into the bulk absorption increases and the X-ray yield drops. In TXPS, however, the X-rays created deeper in the target (or nearer the sample plane) are quantitatively more important as in the transmission mode they will be absorbed to a lesser extent. An
integral, modified from Bishop and Poole [25], describes the situation which gives the maximum X-ray intensity.

\[ I_0 = \int_0^t \phi(z) e^{-\chi (0-z)} \, dz \]  

(2)

\( z \) is the depth (in units of mass thickness) below the target surface, \( t \) is the source thickness, \( \chi \) the absorption parameter and \( \phi \) is the distribution with depth of characteristic ionizations produced within the target by the electron beam. In the expression \( I_0 \) is a maximum when the mass thickness of the source material, \( t \), just contains the X-ray interaction volume.

The aluminium source thickness affects the intensity of X-rays beyond this ideal thickness maximum according to equation 3.

\[ I = I_0 e^{-\mu \rho x \sec \theta} \]  

(3)

\( \mu \) is the X-ray absorption coefficient, \( \rho \) is the density of aluminium, \( x \) is the distance between the X-ray source and the specimen and \( \theta \) is the angle of emission relative to the target normal.

<table>
<thead>
<tr>
<th>MA500 evaporated 1.32μm Al (Specimen Current)</th>
<th>Cazaux (Foil Thicknesses) at 1μA</th>
</tr>
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<tr>
<td>400nA</td>
<td>1μA</td>
</tr>
<tr>
<td>X-Ray Spot Diameter (μm)</td>
<td>4.3</td>
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<tr>
<td>Absorption in Al: ( I/I_0 )</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 4

Calculated X-Ray Spot Sizes Emerging from the Back Side of the Target and the Effect of X-Ray Self Absorption Through Different Source Thicknesses. 1.32μm of Aluminium is the Ideal Target Thickness.
The evaluation of the effect of absorption on X-ray intensities for various thicknesses of source is shown in table 4. It shows that the aluminium thickness has a marked effect on the emerging AlKα intensity even though the self-absorption coefficient is low. This calculation assumes that all the X-rays are created at the ideal thickness (at the chosen accelerating voltage) and pass through the remaining foil thickness perpendicular to the surface, which is clearly not the case. In reality, they will be created somewhere within the target, as demonstrated by the shape of the X-ray excitation envelope in fig.37 obtained by φ(pz) Monte-Carlo simulations [26] and the X-ray intensity will be distributed radially. The points on the plot represent individual X-ray excitation events. The overall X-ray source is concentrated below the surface within a few tenths of a micrometer laterally from the electron beam at 10kV. X-rays created close to the exit plane will not be as likely to be absorbed as those created further from the sample. The overall distribution of X-rays in the effective source is a complex combination of X-ray creation depth and lateral position relative to the central electron beam. The mathematics describing this distribution and calculation of lateral resolution of the TXPS technique is given in [16,19]. Cazaux's results are used later in the text. Table 4 illustrates the importance of aluminium thickness. It has a marked effect on the X-ray spot size and, therefore, on spatial resolution. Thinner foils than those used by Cazaux need to be used to obtain the ultimate spatial resolution.

Fig.37
Alkα Excitation Envelope from Monte-Carlo Simulations (10kV, 10000 Trajectories) [26].
There are several possible routes to making sources for TXPS. A single foil can be used, but this gives problems of transmitted primary electrons if pinholes exist in the aluminium. Two coincident foils eliminates this problem as it is unlikely that two holes will line up. In most TXPS work two 0.8μm foils were used. The final method of producing a source is by coating the back of the sample. Such a covering needs to be deposited in a chemically clean manner, avoiding any contamination. This leads to the suggestion of sputtering or evaporation. Neither will damage the sample. Bishop and Poole's [25] calculations suggest that in order to allow 98% of the primary beam to interact with the sample, a thickness of 0.77μm is needed. Such a thickness of film is only obtainable using evaporation.

The ideal thickness of source material can be thought of in two ways. If only production of characteristic X-rays is considered, an interaction volume similar to fig.37 defines the necessary thickness. However, it is shown later in section 5.2 that if any primary electrons emerge from the back of the source and sample they radically increase the TXPS spectral background. It is more important to consider the maximum electron interaction volume depth (or Bethe range) at 10kV rather than the size of the X-ray excitation envelope, where the difference in size is the range of an electron with an energy just below the X-ray excitation threshold. The Bethe range of 10kV electrons in aluminium is 1.32μm [26].

A method was developed to calibrate the thickness of aluminium deposition in order to evaporate 1.32μm. Graphite discs were first produced using an accurate cutting machine, then polished, cleaned and dried. Aluminium was evaporated onto the 0.5mm thick, 3mm diameter graphite discs. Using Bishop and Poole curves [25], predictions of the aluminium thicknesses were made with reflection EDX measurements. The thick carbon substrate meant that no fluorescence corrections needed to be made to measured AlKα intensities.

3.4.1 Evaporation Methods

A preliminary experiment used a six turn single tungsten filament (0.5mm diameter) surrounding a known mass of aluminium wire. The filament was suspended
at a known height above the graphite discs. All of the aluminium was evaporated once the diffusion pumped vacuum in the bell jar reached $10^{-4}$ Torr. Eight samples were used. Once one coating was complete, one disc was removed or masked and then the filament and aluminium replaced. Evaporating and repeating the operation gave a distribution of aluminium coating thicknesses for reflection EDX measurements. The quantities of aluminium used failed to reach the ideal thickness plateau as can be seen from the X-ray intensity / mass evaporated plot, fig.38.

To reach the ideal thickness the process would have been tedious. It was better to increase the aluminium mass evaporated. However, when larger amounts of aluminium were used the filaments began failing before full evaporation.

![Fig.38](image)
Preliminary Evaporation Results.

3.4.2 To Determine a Reliable Method for Evaporation of Large Amounts of Aluminium

It is clear that any evaporation method must be reliable if a definite quantity of aluminium is to be consistently evaporated onto already prepared thin foil samples. The original single tungsten filament method was extremely unreliable, failing 80% of the
time at larger aluminium masses. Many other techniques were attempted before finally succeeding in producing a reliable aluminium coverage.

Molybdenum sheet was bent into boat shapes to form the filaments. Many of these boats were found to have holes in them, and some actually cracked in two, well before full evaporation. The reason for failure was that molybdenum and aluminium formed an intermetallic at elevated temperatures. The intermetallic had a melting point below the boiling point of aluminium.

Failure of tungsten coil and v-shaped filaments were due to the formation of an Al/W intermetallic where the tungsten met the molten aluminium. These intermetallics had higher resistivities than the bulk tungsten [27] and so the current density (and consequently the temperature) rose between these reacted regions. This caused accelerated aluminium diffusion into the tungsten and an even greater local temperature, which ultimately led to melting or creep failure. See fig.39.

![Fig.39](image)

**Mechanism of Tungsten Wire failure.**

In theory, if the aluminium and tungsten were kept separate the reaction could not have occurred. Protective oxide filament coatings failed to separate the molten aluminium from the tungsten long enough to avoid critical amounts of intermetallic formation, so the next logical step was to try alumina crucibles. These were also found
unsuitable because of poor crucible thermal conductivity and creep of the tungsten wire under the mass of the crucible, at elevated temperatures, which led to shorting out of windings and aluminium settling in cold spots.

On heating the aluminium and melting it, several molten blobs were normally formed on tungsten coils. They moved around the coil under the influence of surface tension and gravity. Inevitably, they ended up in one large blob and led to failure close-by. Clearly, it would have been an advantage to attempt to hold the aluminium in small droplets to try to avoid concentration of the effect. This was achieved by winding several wires around each other. The wire was now also effectively thicker, and so it would have also taken longer for the tungsten to reach critical intermetallic formation and fail. Large masses up to 0.19g of aluminium were successfully evaporated by turning 3 twisted wires into 3 turn coils and using aluminium wire folded between the coils. There was a small amount of residual aluminium on the filament. Providing this and the intermetallic formation was relatively constant from one experiment to the next, it was anticipated that there would not be any problems using the technique regularly.

![3 Winding 3 Coil Tungsten Coils Used in Successful Evaporation.](image)

**Fig. 40**

3 Winding 3 Coil Tungsten Coils Used in Successful Evaporation.
3.4.3 Cleaning Tungsten Filaments Prior to Evaporation of Aluminium

Whilst experimenting with the alumina crucibles, residual black marks from the tungsten wires were noticed. Tungsten oxide from the wire is black and is volatile between 400° and 500°C. This, if not cleaned off, would have been evaporated onto the sample prior to the aluminium. This layer of tungsten oxide between the aluminium source and sample would, because of its large X-ray absorption coefficient, have absorbed some of the AlKα radiation when performing TXPS.

The black oxide was removed by an electrolytic method. By making the wound tungsten filament the anode in a 0.1M sodium hydroxide solution and passing 8V for approximately 10 minutes, the metallic appearance of tungsten was recovered. Distilled water and acetone were then used to remove the alkali and dry the filament. After this treatment, there was no longer an increase in vacuum pressure during the filament heating up cycle prior to aluminium evaporation.

Fig. 41
Filament Cleaning Apparatus.
3.4.4 The Results Used To Predict the Necessary Coating Conditions to Obtain the Ideal Aluminium Thickness

The final method involved the use of sodium hydroxide electrosealed tungsten filaments. These filaments comprised three 0.5mm diameter, 10cm long wires twisted around each other and wound around a former to give 3 interwoven coils. The aluminium wire was placed into the centre of the windings. It was folded to avoid loss of material from dripping. This entire assembly was held in the electrodes 6cm from the surface of the intended substrate (6cm was the distance from the coil centre to the substrate centre). The actual height above the sample plane was less. The substrate was not immediately below the coil as dripping was most likely to occur here if the apparatus was poorly set up.

![Filament Containing 1mm Diameter Aluminium Wire](Image)

Evaporation Distance (6cm)

[Stub and Sample Holder]

Fig.42
Evaporation Apparatus Arrangement.

The EDX measurements of AlKα intensities are shown in table 5. These results were normalized using a standard. This was a graphite stub with several evaporations carried out on it; it was a better comparison than the EDX standard. Fig.44 graphs 1 and 2 show that an X-ray intensity plateau occurred as the thickness of aluminium corresponding to the outermost regions of the X-ray excitation envelope was reached.
Table 5
Results of Evaporation Experiments (*graphical prediction).

<table>
<thead>
<tr>
<th>Mass in Evaporator (g)</th>
<th>Intensity of AlKα (l)</th>
<th>Normalized Intensity (l/I_{std})</th>
<th>Thickness x Density (z: mg cm^{-2})</th>
<th>Aluminium Coating Thickness (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (C std)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0.0419</td>
<td>12349</td>
<td>0.29492</td>
<td>0.051</td>
<td>0.189</td>
</tr>
<tr>
<td>0.0690</td>
<td>23349</td>
<td>0.55762</td>
<td>0.091</td>
<td>0.335</td>
</tr>
<tr>
<td>0.0818</td>
<td>31665</td>
<td>0.75620</td>
<td>0.128</td>
<td>0.473</td>
</tr>
<tr>
<td>0.0983</td>
<td>34092</td>
<td>0.81417</td>
<td>0.142</td>
<td>0.525</td>
</tr>
<tr>
<td>0.1149</td>
<td>38605</td>
<td>0.92193</td>
<td>0.177</td>
<td>0.657</td>
</tr>
<tr>
<td>0.1228</td>
<td>39203</td>
<td>0.93005</td>
<td>0.182</td>
<td>0.674</td>
</tr>
<tr>
<td>0.1364</td>
<td>39092</td>
<td>0.9336</td>
<td>0.184</td>
<td>0.682</td>
</tr>
<tr>
<td>0.1477</td>
<td>40434</td>
<td>0.9656</td>
<td>0.206</td>
<td>0.761</td>
</tr>
<tr>
<td>0.1671</td>
<td>40863</td>
<td>0.9759</td>
<td>0.208</td>
<td>0.769</td>
</tr>
<tr>
<td>0.1841</td>
<td>41967</td>
<td>1.0022</td>
<td>-</td>
<td>0.945*</td>
</tr>
<tr>
<td>0.6353 (Al std)</td>
<td>41873</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Bishop and Poole’s [25] calculations allow the thickness of surface coatings to be calculated from intensity ratios for cases where absorption corrections are unnecessary. The two series of graphs in the paper evolve from Monte-Carlo calculations and the ones of significance to this work are given in fig.43. The first graph allows the derivation of a Bethe range from the incident beam energy. The second plot uses the
reciprocal of the overvoltage, $E_o/E$ (where $E_o$ is the energy required to initiate the X-ray emission electron transition), and the integral ionization function ($\rho$) contours (from comparison of X-ray count rates to a standard sample) to determine thicknesses of coatings as a function of the Bethe range.

Graph 2 was converted into the aluminium coating thickness graph 3 using Bishop and Poole's calculations. Their curves do not extend above $\rho=0.98$, so the final point was lost from graph 2. The data collected in the evaporation experiment only explored the size of the X-ray excitation envelope rather than the size of the 10kV electron interaction volume. In section 5.2 the importance of complete attenuation of the primary beam is demonstrated. So, in TXPS, evaporation of a thickness of aluminium corresponding to the Bethe range is required. The 10kV figure of 1.32\(\mu\)m comes from the computer data of Joy [26] and extrapolation of graph 3 yields 0.26g of aluminium wire being required in the evaporator.
The coating relationship can, of course, be written as a simple equation linking the aluminium mass placed in the evaporator $m$ (in g) at 6cm distance and the coating thickness $t$.

$$t = 5.134 m \mu m$$ (4)

Such a relationship would have been helpful if larger accelerating voltages were required, where larger ideal thicknesses would have been needed to stop the primary
beam. Evaporation of aluminium beyond the ideal thickness would have caused the loss of spatial resolution in a similar way to was observed when Cazaux's 5µm and 3µm thick foils were compared to the evaporated ideal thickness of 1.32µm in table 4.

3.4.5 Evaporation Model

A model would be useful to predict evaporation thickness including evaporation distances for practical production of aluminium sources. Assume the aluminium mass m, is spread over the entire surface of a sphere of radius r, where r is the distance from a point source of aluminium at the centre of the three wire tungsten coil to the substrate.

\[
\text{mass/cm}^2 = \frac{m}{4 \pi r^2} \quad (5)
\]

If the value z (Al thickness x density) from Bishop and Poole calculations is plotted against the mass of aluminium in the evaporator, the gradient is given by \(1/4\pi r^2\). See fig.44 graph 4. Thus, the expected value of r from the measured sample coverage is given by

\[
\frac{1}{4 \pi r^2} = 1.4 \times 10^{-3} \quad (6)
\]

\[
\therefore r = 7.6\text{cm}
\]

This is 26% larger than the expected 6cm, so there is less aluminium on the sample than is predicted by the simple model. This lost aluminium is left on the filaments. Crystalline residual deposits were observed; probably oxidised intermetallic. Equation 6 must take into account this overestimate due to aluminium loss. This requires the insertion of a correction term to give equation 8.
\[
\frac{z}{m} = \frac{1}{4 \pi r^2} = \frac{\rho t}{m}
\]

(7)

\[
\frac{\rho t}{m} = \frac{1}{4 \pi \left(\frac{7.6 r^2}{6}\right)} = \frac{1}{20 r^2}
\]

(8)

\[
\therefore t = \left(\frac{m}{20 \rho r^2}\right)
\]

Where \(r\) is in cm, \(\rho\) is in g/cm\(^3\), \(m\) is in g and \(t\) is in cm. For TXPS the thickness \(t\) is chosen as the Bethe range in aluminium at the required accelerating voltage.

Summarising, a method was developed to evaporate a known thickness of aluminium onto the samples for later examination by TXPS as an alternative to foil sources. Cleaning of the tungsten coils ensured minimum absorbence of X-rays after production. Equations to predict the coating thickness were evaluated for various evaporation conditions, taking into account residual aluminium left on the tungsten coils. The evaporation source was never routinely applied to TXPS samples, but section 8.4 shows an example where its use would have been vital to successfully perform materials analysis on a microtomed section. Section 4.5.1 shows the only experimental use of a coated X-ray target.
4.0 PERFORMANCE CALCULATIONS AND COMMISSIONING OF TXPS IN THE MA500

4.1 Spatial Resolution

The drawback of ordinary XPS is its lack of spatial resolution. It is essentially a surface composition averaging technique. TXPS should give consistently good spatial resolution over electron energies up to 2000eV, unlike some other competing techniques (e.g., PESM).

Spatial resolution in TXPS is dependent on several factors: The electron beam diameter, the accelerating voltage, the thickness of the source foil and its atomic number together with the sample thickness and material. To obtain the best resolution, the electron beam spot must be as small as possible and the source and sample should be very thin, minimising the divergence of the X-rays and X-ray self-absorption. Estimates of the electron, X-ray and photoelectron diameters can be made.

Cazaux used a crude electron gun which was only able to give, at best, a beam diameter of 10µm. This restricted the resolution of his apparatus. The diameter of the MA500 electron beam depends on the beam current used, according to the relationship

\[ d = 66 \left( \frac{i}{q} \right)^{1/2} \tag{9} \]

where \( d \) is in nm and \( i \) is in nA [28]. At equivalent beam currents to those used by Cazaux (1µA) \( d \) is 2.1µm and at 20nA it is 0.3µm.

The photon flux from a target can be obtained from the number of electrons in the primary beam using equations 10 and 11.

\[ q \times = i \times t \tag{10} \]

\( x \) is the number of electrons arriving at the source foil in time \( t \) and \( q \) is the charge on an electron. The Green and Cosslett [29] equation 11 is used to predict the number of X-rays produced per primary electron for an aluminium target.
\[ N = N \left( \frac{E_2}{E_1} - 1 \right)^{1.63} \] (11)

The \( N \) constants are listed in the paper. Here at 10kV \( N = 1.4 \times 10^{-5} \), so, for a primary beam of 1\( \mu \)A, \( 6.2 \times 10^{12} \) electrons/s excite \( 1.5 \times 10^9 \) photons/s (\( \Phi \)).

For the sake of simplicity in further calculations, aluminium self absorption at low angles has been assumed to be negligible. Earlier absorption calculations cannot be used here (table 4). The values show the effect of X-rays passing through the full foil thickness. They illustrate the importance of aluminium thickness in obtaining the maximum number of photons from the source. Cazaux would have suffered more from photon absorption. Correction of data to allow for absorption would only require division by a factor of approximately two, even in the worst case.

\[ \text{Fig.45} \]
Cazaux's Simple Derivation of TXPS Lateral Resolution.

Cazaux predicted the lateral resolution in TXPS to be given by equation 12 [19]. This equation was an approximation to his original theoretical work detailed in [16]. It was assumed that the sample was infinitely thin and all the X-ray spreading was in the
source foil. This was not unreasonable, since the microtomed samples used in this thesis were only about one fifth of the total source and sample thickness. The expression assumed that the X-ray source was located on the irradiated surface of the target and its dimensions were that of the electron beam. This expression was valid when the incident electron spot diameter was greater than the diffusion length, or Bethe range, of the electrons [30]. For the MA500 this is only true down to specimen currents of 400nA at 10kV. Cazaux treated the uncertainties as aberrations and combined them in

\[
d_R \approx \left( 4 \frac{z^2}{d_e^2} \right)^{1/6}
\]

z was the distance from the X-ray source to the exit surface of the sample and \(d_e\) was the diameter of the electron beam. See fig.45. Cazaux assumed, for simplicity, that the cone of effective X-rays had a semi-apex angle of 45°, above which target self-absorption was dominant. The signal contribution of high angle X-rays could be ignored.

<table>
<thead>
<tr>
<th>MA500 Specimen Currents (1.32μm Evaporated Al)</th>
<th>Cazaux at 1μA (Foil Thicknesses)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1μA</td>
<td>400nA</td>
</tr>
<tr>
<td>X-Ray Spot Diameters (μm)</td>
<td>3μm</td>
</tr>
<tr>
<td>X-Ray Spot Diameters (μm)</td>
<td>5μm</td>
</tr>
<tr>
<td>5.0</td>
<td>4.3</td>
</tr>
<tr>
<td>17</td>
<td>21</td>
</tr>
<tr>
<td>Photon Densities (Photons/s/mm²)</td>
<td>Photon Densities (Photons/s/mm²)</td>
</tr>
<tr>
<td>9.7x10^{12}</td>
<td>8.1x10^{11}</td>
</tr>
<tr>
<td>5.1x10^{12}</td>
<td>5.5x10^{11}</td>
</tr>
</tbody>
</table>

Table 6
Calculated X-Ray Spot Diameters (μm) and Resultant Photon Densities (Alkα photons/sec/mm²).

The lateral resolution is normally defined to one standard deviation each side of the mean. It is obtained by scanning the probe across an edge. Thus, the calculated resolutions can be converted into X-ray probe diameters knowing the resolution is
defined between 16% an 84% of the difference between the maximum and minimum intensities. Values are shown in table 6. The 45° semi-apex angle means that in terms of solid angle from all of the emitted X-rays, only ⅛ actually interacts with the analysis area. Photon densities can then be calculated for comparison between TXPS on the MA500 and Cazaux’s apparatus.

Cazaux managed to obtain images with these photon densities. The above table indicates that higher resolutions could have been obtained with the MA500. Higher photon intensities, for equivalent resolutions, gives higher signal to noise (S/N) ratios. Cazaux claimed that to achieve 10% contrast in images $10^{12}$-$10^{13}$ photons/sec/mm² were required [17]. All MA500 intensities satisfy this criterion.

Table 7 lists values of lateral resolution derived directly from the simple relationship given in equation 12. These figures reflect the approximate 10μm resolution obtained by Cazaux. The MA500 has the potential of obtaining far better resolutions even at high beam currents using the LEG500 electron gun. As with other surface analysis techniques, lateral resolution is balanced against signal intensity. Here lower currents improve resolution but S/N ratios suffers.

<table>
<thead>
<tr>
<th>Cazaux:</th>
<th>MA500: 1.32μm of evaporated Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>3μm Al Foil</td>
<td>1μA</td>
</tr>
<tr>
<td>10μm electron beam diameter (1μA)</td>
<td>12μm</td>
</tr>
</tbody>
</table>

Table 7
Predicted Lateral Resolution of Instruments.
4.2 **Comparison of the Transmission of Analyser and Lens Design**

The transmission of an analyser determines the amount of signal that the analyser will detect relative to the total produced. The greater this value, the better the signal to noise ratios in the spectra. The analyser entrance slit was separated from the sample in the MA500, as is true in all modern spectrometers based on a hemispherical analyser. A transfer lens was necessary to carry electrons over this distance and refocus them on the slit system ready for energy filtering.

The large distance from the sample to the top port of the analyser chamber meant that a long transfer lens was required to perform TXPS in the MA500. VG Microtech redesigned the standard Clam II lens design to carry the electrons over the long distance and to give the opportunity for high magnification at relatively low working distances. Design modifications were restricted by the 10kV lens power supply available on the MA500. The lens magnification needed to be as high as possible to collect the maximum solid angle of photoelectrons. This is shown in fig.46. The nose of the lens could be brought closer to the sample than the standard 38mm working distance. The original VG 38mm value arises from the need to get a primary beam onto the top of the sample as well as signal out; a problem which does not arise in TXPS. The only physical restrictions on the reduction of the working distance in the MA500 were sample rotation for ion etching and stub removal. Beyond a certain solid angle of acceptance (30° [31]), some photoelectrons would not be refocused on the hemisphere entrance aperture. This was the important instrumental limitation to working distance changes. Working distances from 10 to 16mm were achievable by careful choice of spacer flanges, which increased the solid angle of collection by one order of magnitude relative to 38mm.

By modification of the long-nosed transfer lens delivered by VG, 6x magnification was achieved. The higher magnification lens required higher lens gains. Changes were made to the lens programming boards including the addition of a potentiometer to allow stable focusing of the lens and a lens gain limiting potentiometer to prevent accidental application of voltages above 10kV. The lens was always focused using a high kinetic energy peak, after working distance modifications, as these required the higher lens gains. The high energy peaks were used for reasons of lens safety and
because these were the most difficult to converge on the analyser entrance aperture.

The lens working distance (and hence the transmission) was altered several times during the course of TXPS work. In very early work with the original MA500 lens system, the working distance was 150mm which, as anticipated, proved almost completely unworkable. 38mm with the LEG61 electron gun yielded spectra as shown in section 4.5.2, but it was not until the acquisition of the long-nosed system that the minimum working distance was reduced to 10-16mm.

Assuming a point source of photoelectrons are all refocussed into the analyser, an expression can be derived to calculate transmission from elementary geometry. The transmission, expressed as a percentage of excitation over 4\(\pi\) steradians, is given in equation 13 where \(d\) is the working distance from the sample to the nose of the lens, and \(a\) is the radius of the entrance aperture. See fig.47.

\[
T = \frac{1}{2} \left[ 1 - \frac{d}{(d^2 + a^2)^{1/2}} \right] \times 100\% \tag{13}
\]
The instrument transmission is shown to be improved by decreasing the working distance whilst necessarily increasing the lens magnification. When $d$ is 38mm the transmission is 0.43%, but at 10mm it is dramatically increased to 5.28%. Only the more recent work benefitted from this high transmission. The CMA used by Cazaux only had a 2% transmission from the $4\pi$ steradians [17], showing the improvement in collection efficiency using the MA500. This may be used advantageously in reducing the specimen current or the analysis time.

4.3 Photoelectron Count Rates

In conventional photoelectron spectrometers X-rays are created by electron bombardment of a metallic anode under the influence of an accelerating voltage. The resultant X-rays flood the sample surface over an area of the order of 10mm$^2$ exciting photoelectrons. The photoelectron flux collected (photoelectrons/s) is given by
\[ I_{PE} = \Phi \beta_x(A_i, \hbar \nu) T \]  

(14)

where \( \Phi \) is the number of incident photons/sec, \( T \) is the efficiency of collection of the spectrometer and detector (Transmission) and \( \beta_x \) is the quantum yield for production of photoelectrons from the surface layer of thickness \( \lambda \) (escape depth of the material).

\[ \beta_x(A_i, \hbar \nu) = N_A \sigma_i(A_i, \hbar \nu) \lambda \]  

(15)

Here \( N_A \) is the atomic concentration of atoms analysed (for a pure element \( N_A = 5 \times 10^{22} \) at.cm\(^{-3} \)) and \( \sigma_i(A_i, \hbar \nu) \) is the photoelectron cross-section for the sub-shell \( i \) of atom \( A \) using the exciting radiation \( \hbar \nu \).

This law has been applied to TXPS by Cazaux [17] and allows predictions of the MA500 performance. The photon flux and analyser transmission have already been calculated for the modified MA500. Transmission calculations assumed that all of the photoelectrons which entered the transfer lens passed the analyser entrance slit and were collected.

\[ \beta_x (Au_{4f_{7/2}} Alk\alpha) = 3 \times 10^{-3} \]

This value is for a thin pure gold sample mounted on an aluminium source. Photoelectron intensities are thus:

<table>
<thead>
<tr>
<th>Cazaux: (1( \mu )A beam Current) 2% Transmission</th>
<th>Modified MA500: 0.945( \mu )m of Evaporated Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>3( \mu )m Al Foil 5( \mu )m Al Foil</td>
<td>5.28% Transmission 2.08( \mu )m Beam Diameter (1( \mu )A)</td>
</tr>
<tr>
<td>( 5 \times 10^7 )</td>
<td>( 8 \times 10^8 )</td>
</tr>
<tr>
<td>5( \mu )m Al Foil</td>
<td>0.43% Transmission 1.32( \mu )m Beam Diameter (400nA)</td>
</tr>
<tr>
<td>( 3 \times 10^7 )</td>
<td>( 2 \times 10^8 )</td>
</tr>
</tbody>
</table>

Table 8

Transmission XPS Expected Photoelectron Densities (Au4f photoelectrons/mm\(^2\)/s).
The table shows that the modified MA500 will give higher photoelectron count rates/mm², even with its lower transmission at equivalent beam currents. Cazaux's high electron spot diameter was his equipment limiting factor. His X-ray spot diameter was also increased by the larger thicknesses of aluminium foils used.

The modified MA500 working distance (lens to sample), and hence transmission, has a pronounced effect on the count rates. This was an important factor in the design of the long-nosed transfer lens to carry the photoelectrons into the hemispherical analyser.

The table also shows the balancing effect between the need to attain ultimate spatial resolution and obtaining maximum count rates. To increase the spatial resolution, the electron beam diameter has to be reduced. This can be done by reducing the beam current. This reduces the number of photons excited and thus the number of photoelectrons. However, the intensities at the low currents are still comparable to those from Cazaux's single pass CMA apparatus. These calculations could not be extended below 400nA because of the limiting applicability of the equations. Specimen currents down to a 1nA are possible in the BTMA500 to produce a 66nm electron spot size but the count rates would be impractically low.

Finally, it should be noted that the calculated photon densities at the 5.28% transmission level are comparable to the count rates later obtained for gold TXPS on the MA500. Count rates were approximately 150 counts/s on the Au4f peak at 200eV pass energy (100nA). The validity of the simple theory has been confirmed to a certain extent.

4.4 Comparison of Count Rates in the ESCALAB Mk.II with TXPS on the MA500

Photoelectron count rates in the TXPS apparatus must be compared to a standard modern apparatus (eg. ESCALAB II). Higher count rates in TXPS mean spectra with good signal to background ratios can be obtained faster. Dwell times used to build up images can also be lower. In TXPS, the power required to generate the same count
rates per unit solid angle as conventional XPS is given by

\[ P = 300 \left( \frac{d_i}{d_c} \right)^2 \left( \frac{A_c}{A_t} \right) \]  \hspace{1cm} (16)

where \( d \) is the distance from the X-ray source to the sample and \( A \) is the area from which photoelectron signal is generated. The subscripts refer to the transmission and conventional instruments. The equation assumes that the conventional X-ray source runs at 300W at 10mm distance from the sample. The instrument accepts photoelectrons generated over an area of 10mm\(^2\). It is assumed that the transmission source can be approximated by a point source 1μm from the sample. If it generates electrons over an area of 1μm\(^2\) then the power required, from equation 16, is 30W.

The actual power generated in TXPS running at 10kV and a beam current of 100nA is 0.001W. The photoelectron flux is a factor of 30000 less than the ESCALAB II. The ESCALAB II has 3 channeltrons and so collects 3 times as many photoelectrons. TXPS count rates are therefore lower by a factor of 90000.

Analyser transmission in the modified MA500 is 5.28% instead of 0.5% in the ESCALAB II. This reduces the count rate factor down to 8500.

The lower count rates mean that analysis times (or the specimen current) have to be increased during TXPS. All small area XPS techniques require long analysis times and such sacrifices are necessary to obtain a high degree of spatial resolution.

4.5 Early Attempts to Obtain TXPS Spectra

In order to present a case to the Royal Society Paul Instrument Fund to finance the final TXPS apparatus, the potential of the technique had to be demonstrated. Attempts were therefore made to obtain a TXPS spectrum using the available equipment.
4.5.1 Original Analyser System

By temporarily constructing a Dexion support system and with the appropriate flange modifications, the original BTMA500 Clam II analyser was placed on top of the system. This allowed the primary beam to be detected by the analyser, as previously shown in fig.35. It also made the collection of some TXPS spectra possible although they are somewhat noisy as a result of the 150mm working distance. The transmission was extremely poor in this arrangement and count rates were very low. Spectra were obtained in approximately 6 minutes.

The spectrum in fig.48 was observed by collecting photoelectrons emitted from the back of the aluminium X-ray source foil. The secondary electron peak can be seen at low kinetic energy and the oxygen Auger peak at 510eV. The Fermi shoulder is also seen at 1486eV, above which are Bremsstrahlung induced interactions only. The spectrum was collected in CRR mode.

![TXPS of 5μm Aluminium X-Ray Window.](image)

Fig.48

TXPS of 5μm Aluminium X-Ray Window.
0.945µm of aluminium was evaporated onto a steel TEM sample and analysed by the temporary TXPS arrangement. The sample was heavily oxidized and dirty from the original preparation procedure. The result was the observation of only the secondary peak and oxygen and carbon Auger and photoelectron peaks. See fig.49.

The signal/noise ratios in this work were very poor and it would be fair to comment that there are many other 'bumps' in the previous two spectra which could be interpreted as peaks. An alternative arrangement of the apparatus was necessary to collect more convincing spectra.
4.5.2 Addition of an External Electron Gun

The long working distance attempt at TXPS had revealed very little in the way of convincing spectra, and it became clear this had to be the next goal whilst still awaiting the final apparatus. The geometry of the BTMA500 was such that the LEG500 electron gun could not be used with the Clam II hemispherical analyser in its standard Auger position (working distance 38mm to the rear of the analyser chamber). An external electron gun needed to be added to excite the TXPS X-rays.

The electron gun used was a LEG61 with a 1μm spot diameter running up to 5kV. It produced specimen currents typically of the order of 1μA. Beam rastering to produce secondary electron images required the use of the physical imaging unit used by the AG61 ion gun. Scan voltages were obtained by slaving off the LEG500 scan unit.

When the first image appeared at 4.1kV, only 30 Volts on the photomultiplier was required as a result of the high specimen current of 1μA. The image itself showed virtually the whole top of a window stub. The electron gun had a large working distance giving this large field of view. A diagram of the window stub is shown in fig.50.

Saturating the filament current caused burn out of 0.8μm aluminium foils which were silver dagged to the window stub. Lower filament currents meant that higher magnifications could be set to concentrate the rastered beam on the target. After
initial problems with the spectrometer control unit and having to stabilize the LEG61 power supply, a satisfactory Auger electron spectrum was obtained.

By focusing the beam on the 0.8μm aluminium foil (5x Magnification) and rastering at the maximum permitted accelerating voltage of the gun (5kV), it was hoped to obtain a TXPS spectrum having now obtained a satisfactory transmission geometry. Unfortunately only Auger peaks were observed even though at very high count rates. Transmitted EDX spectra showed a huge AlKα peak and subsequent sum peak. Only slight signs of photoelectron peaks were seen, even after evaporating copper on top of an aluminium foil despite the high photoelectron cross section of the Cu2p3/2 peak.

It was proving very difficult to align the sample to produce the highest count rate, as the sample not only had three degrees of freedom as well as rotation, but also the position of the electron gun raster could be moved electrostatically. The gun itself had to be moved from port 1 to port 2 to reduce the working distance. See fig.32a and for the schematic fig.51.

Now TXPS spectra only showed C(KLL) peaks with no photoelectrons. This was probably due to direct excitation from stray electrons from the stub; perhaps a problem of poor alignment. Increasing the accelerating voltage up to 4.4kV as well as altering the filament current, gun magnification and sample position and orientation did not improve the situation although O(KLL) also appeared. See fig.52.

![Diagram](image-url)

Fig.51
Schematic of the Successful Equipment Geometry Used in the LEG61 Experiments.
Use of the dual anode X-ray source in the reflection mode (fig.51) demonstrated that the analyser was working correctly. Normal XPS spectra of the surface could be obtained, if only with a low take-off angle.

The most encouraging spectrum that was collected (fig.53) showed the 'beginnings' of the photoelectron background shape. Auger peaks seemed to have
appeared and perhaps the Cu\textsubscript{2p} doublet. The difficulties in obtaining even this spectrum suggested that sample positioning was vital, as indeed it is in many spectrometers. It soon became clear that a method needed to be devised to ensure correct sample positioning prior to TXPS analysis. This seemed to be the only way to obtain convincing spectra.

### 4.5.2.1 X-Ray Gun Excited TXPS and Successful TXPS Spectra Acquisition

![Graph of X-Ray Gun Induced Transmitted XPS Spectrum of Copper Evaporated onto an Aluminium Foil (10kV, 10mA, 1000s, CRR=2).](image)

With the X-ray source on port 3 in fig.32a it was possible to irradiate the rear side of the sample and analyse the front (this geometry is again shown in fig.51). Thus, by holding the thin foil sample in a window stub, it was possible to supply externally the exciting AlK\textalpha radiation rather than trying to induce it from electrons. The spectra were collected in CRR mode. Fig.54 shows a spectrum induced in a copper coated aluminium foil (0.8\mu m) with 10kV exciting radiation (X-ray power is 100W). The sample
position was indeed found to be critical to successfully collect a spectrum as had been anticipated. Having set the optimum sample position it was possible to collect a spectrum at with a 4kV electron beam.

A sputtered layer of gold also gave a transmitted X-ray gun excited spectrum at 10kV and 4.5kV (power 45W) (fig.55a). The sample was carefully aligned for maximum counts using the manipulator. The excitation source was then changed. Now the sample was lined up correctly for the lens and analyser. With the electron gun at port 2 (fig.32a) the electron beam only had to be aligned on the sample using the quadrupoles controlled by the physical imaging unit.

The image of the sample foil is shown in fig.55b at the lowest magnification. The electron beam was focused on the sample foil and magnified before collecting spectra. A true TXPS spectrum obtained at 4.2kV is shown in fig.55c showing all the expected gold peaks and carbon peaks from sample contamination. The count rate remained independent of magnification since the current (and hence photon flux) was the same and the sample was correctly aligned so that at a low magnification all of the electron beam hit the sample.
Performance Calculations and Commissioning of TXPS in the MA500

(b) 2mm

(c)

4000

Counts

2816

Kinetic Energy (eV)

Au4p3/2, Au4p1/2, Au4d3/2, Au4d5/2, C1s
Fig. 55

Gold Sputtered onto an Aluminium Foil.

(a) X-ray Gun Transmitted XPS Spectrum (4.5kV, 10mA, 800s, CAE=50eV).
(b) Low Magnification SEM Image of the Sample and Stub to Allow Beam Alignment.
(c) First TXPS Spectrum Induced by Back-Foil Excitation (4.2kV, 120nA, 800s, CAE=50eV).
(d) Au4f_{5/2} and Au4f_{7/2} Peaks Resolved (20eV Pass Energy) by Transmitted XPS Showing Incorrect Relative Intensities (4.2kV, 120nA, 1500s, CAE=20eV).

Fig. 55d shows the Au4f peak from TXPS. This peak is a standard energy resolution test. It was resolved satisfactorily into its 4f_{5/2} and 4f_{7/2} components with the correct relative intensities at 5eV using X-ray gun TXPS. At 20eV the spectrum shows evidence of a double imaging fault with the transfer lens. At higher pass energies two electron paths to the analyser entrance slit were possible. The spectral effect was that at higher pass energies the peak height ratios were reversed, and one extra shoulder peak added by the superposition of two pairs of peaks slightly shifted in kinetic energy. The effect swamped the spectra but as the slit width was reduced, or the pass energy decreased, one of these paths was removed.

A similar transmitted X-ray gun alignment procedure was carried out using an aluminium foil with an evaporated copper coating. The TXPS spectrum is given in fig. 56. The pass energy was set at 100eV. The copper coating was considerably thicker than the gold. This demonstrated the first signs of the applicability of the technique to thicker specimens.
This section demonstrated that TXPS could be achieved in the modified MA500. Even with the LEG61, the raster area of analysis was measured as having already reached 0.25mm². The work highlighted the potential for easier analysis with a purpose-built TXPS instrument.

4.6 Construction and Commissioning of the Final Design of the Transmission X-Ray Photoelectron Spectrometer

Having received the Paul Instrument Fund money and purchased the necessary hardware for TXPS as shown in figs.31 and 32, some time was spent reconditioning and upgrading the hemispherical analyser to a Clam II from its original VG ESCA III usage. A channel electron multiplier was aligned and set to the correct distance from the
analyser exit slit. The separation between the entrance slits and the back end of the lens also had to be set before screwing it to the bell jar. To obtain a working distance of 38mm, two 64mm diameter double-sided flanges were used with annealed copper gaskets. Initial light bolting of the lens and chamber through these flanges allowed the lens to be accurately aligned with the nose of the electron gun below. A dentist's mirror was used to look straight down the lens at the electron gun nose. The bolts were tightened to swing the lens around until the best alignment was achieved. The analyser and finally the channeltron assembly were added. Alignment was not perfect at the first working distance chosen (38mm). The electron gun was approximately 1mm from the centre of the transfer lens.

Once again at UHV, with the manipulator out of the way, a 1kV electron beam was aimed at the analyser up the long nosed transfer lens. The electrons were detected by the channeltron as shown in fig.57. Fig.58 was a secondary electron image of the view up the transfer lens showing the field break-through grid on the back of the lens, the entrance slits and the retard grids on the analyser. This showed the analyser was only slightly out of alignment. The dark marks were dents in the retard grid foil. Contrast was poor due to the large distance between the photomultiplier and the grids. The opening and closing of the slits was also checked by this method. Each of the two grids could be focused on individually.

![Graph](image)

**Fig.57**

1kV Primary Electron Beam Detected by the Analyser.
Having modified the lens gain resistors on the lens programming board in the spectrometer control unit (362), it was possible to increase the lens gain to 10kV. The higher magnification lens (6:1) required a higher voltage than the 3:1 lens, but the exact voltage was determined by setting the hemisphere voltages on the primary beam and maximizing the count rate.

The first spectra to be obtained were in constant retard ratio mode of an aluminium foil with a copper grid on top. C(KLL) was observed together with a broad O(KLL) background. Argon ion etching showed that the oxygen was buried and the aluminium Auger peaks appeared at higher kinetic energy (see fig.59). The O(KLL) peak intensity decreased relative to carbon when the sample was tilted. This was to be expected when there was surface contamination over an oxide. There appeared to be no sign of the photoelectron peaks. The reason for this became understood when the influence of accelerating voltage was investigated.
Carbon Contamination on an Aluminium Oxide Covered 0.8μm Foil (10kV, CRR=4) (Poor Spectral Calibration).

TXPS Aluminium Spectrum from Two Aluminium Foils (1.6μm, 10kV, 1.8μA 300s, CRR=2).
The first photoelectron peak was observed from two coincident 0.8μm aluminium foils at a CRR of 2. Broad Al(KLL), O(KLL) and O1s peaks were observed. See fig.60. A double thickness of aluminium greatly reduced the huge background problem associated with transmitted primaries and its induced secondaries and allowed the photoelectron peak to emerge from the spectral noise. This observation is clarified in section 5.2.

The analyser and lens appeared to be working correctly at this point, although spectral shape and background varied greatly under different analysis conditions. Understanding of these effects was necessary before real samples could be tackled and spectra usefully interpreted.
5.0 TXPS SPECTRAL ACQUISITION

5.1 Energy Resolution

5.1.1 Analyser Energy Resolution

The importance of XPS relates to its surface chemical state information. Auger spectroscopy yields good spatial resolution (0.1μm routinely), but has the potential of giving very little chemical state data apart from a few cases such as aluminium where exceptionally large shifts are seen on the Al(KLL) line. It is, therefore, a surface specific elemental technique only. Auger peaks are very broad because they involve several electron transitions including the outer and valence band of atoms, which have poorly defined energy. XPS peaks are narrow and so chemical shifts are resolvable. An analyser must be capable of resolving this information.

The cylindrical mirror analyser (CMA) used in the early TXPS experiments [17,20] was designed for Auger electron spectroscopy. Auger line widths are often of the order of 10eV and thus energy resolution was not an important consideration. Typical resolving powers ΔE/E are 5%, giving line widths of 5eV on a 100eV electron. The hemispherical analyser was designed for XPS analysis, taking advantage of the possibility for chemical state resolution in the highly resolved photoelectron line. Typical resolving powers are 0.5%, giving line widths of 0.5eV on a 100eV electron. In fact, in XPS, resolution is limited by the natural line width of the x-radiation. For AlKα this is 0.85eV.

A hemispherical analyser is a natural choice in TXPS. Previous work by Cazaux, using a single pass CMA, was not capable of resolving chemical states. Hovland's use of a double pass CMA, although greatly improved the analyser's resolution, meant that the high signal transmission of the single pass analyser and the consequent high count rates were lost. The hemispherical analyser now has the signal intensity advantage.
5.1.2 TXPS Analyser Energy Resolution at Different Pass Energies

To give some idea of the performance of the analyser at various pass energies the full width at half maximum (FWHM) of O1s peaks from a 6µm thick silicon single crystal were measured. It was thought that because the lens had a high magnification it could produce a pencil photoelectron beam, giving a small virtual slit at the hemispherical analyser, reducing the need for use of the low pass energies. The results in fig.61, however, showed a significant improvement in resolution between 50 and 20eV pass energies so it had to be concluded that the pencil photoelectron beam effect did not avoid the low pass energies. Fig.61 also shows the FWHM of the O1s peak collected from a silicon single crystal film using Alkα radiation in an ESCALAB II and Sikα from the crystal itself in the TXP spectrometer. Peak widths were comparable at low pass energies but at high pass energies the ESCALAB showed a better FWHM. These results demonstrated the TXPS analyser to be behaving satisfactorily.

![Graph](image)

Fig.61

FWHM of O1s Peaks from a 6µm Silicon Wafer in the ESCALAB II using the Alkα Source and from a 6µm Silicon Wafer Acting as Both a Source and Sample in the TXP Spectrometer (mag. 200x).

5.1.3 Standard Energy Resolution Test

Manufacturers of instrumentation always analyse a clean silver stub to
demonstrate spectrometer energy resolution. They use the Ag3d_{3/2} and Ag3d_{5/2} peak separation which should be 6eV. Such a test was undertaken in TXPS, but the silver was evaporated onto 1.6μm (two 0.8μm) of aluminium foils from a cleaned tungsten filament wound with silver wire. Of course, bulk specimen silver analysis was not possible using TXPS. The instrument proved capable of resolving the two peaks in the 100eV pass energy wide scan and gave the 6eV separation in the 20eV pass energy narrow scan (fig.62). The analysis time for each scan was 600s and these results permitted confidence in later spectral analysis.

![Fig.62](image)

Silver 3d TXPS Analyser Resolution Test (9.5kV, 560nA, 38mm working distance).

5.1.4 NaFion Analysis by TXPS

The heavily fluorinated ion exchange polymer NaFion 117 (see fig.63) was extensively analysed by TXPS. The polymer contained only C/F, C/O, S/O bonds and Na. The idea was to be able to distinguish between true sample signal and contamination which would have shown up as a C/C,H peak component in the C1s
narrow scan. The difficulty in obtaining NaFion spectra had already been highlighted by virtually fruitless attempts to perform X-ray gun TXPS, simply because of the sample's 17μm thickness. Consequently, some NaFion was thinned using ultrasonic agitation in a petri-dish containing acetone. Some water splashes were seen on the inside of the dish suggesting water contamination may have been present in analysis. The polymer was severely swollen by the solvent. It was mounted on two 0.8μm aluminium thin foils prior to extensive exposure to the roughing vacuum and then diffusion pumping.

Wide scans at a CRR of 4 were performed at various accelerating voltages to determine the ideal analysis conditions. The sharpest peaks were obtained at 9kV. Above 11kV the massive increase in background due to a emerging interaction volume was observed.

The spectra in fig.64 were preliminary scans used to obtain peak separations to determine the nature of the surface. There should have been very little oxygen in NaFion relative to fluorine. The large oxygen peak shown was likely to have been associated with contamination or residual acetone. The shape of the C1s peak itself was unlike that expected from NaFion conventional XPS data [32], and the separation from the F1s peak (used as its internal standard at 400.5eV) suggested it was mainly

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fig.63

NaFion Repeat Unit.
from overlayer contamination rather than NaFion. Fluorine 1s has a high photoelectron cross section and so was still observed in spectra even with its intensity being attenuated by the partial overlayer.

Fig. 64
Spectra from Unetched NaFion (Working distance 38mm, 9kV, 1.7μA).
(a) Wide Scan (600s, CAE=100eV), (b) C1s (1000s), (c) O1s (1600s), (d) F1s (750s) (b, c and d CAE=20eV).

To reveal the fluorinated polymer, argon ion etching was required. This was known to defluorinate NaFion, but this was unimportant as quantification at this stage of TXPS work was not necessary. The goal was to achieve peak resolution.
A series of three ion etches (5kV, 0.1mA) were carried out interspersed with analyses. The first etch increased the intensity of fluorine and decreased the intensity of both oxygen and carbon peaks. The carbon narrow scan showed broadening on the low kinetic energy side, consistent with incomplete overlayer removal. The FWHM of F1s was also decreased. Further etching reduced the oxygen intensity nearer to that expected for NaFion and the fluorinated polymer signal started to appear. A third etch finally gave a more convincing carbon spectrum. Ion etching, totalling 2 minutes, reduced the O1s intensity down to a level more expected for NaFion and brought out the F1s signal. C1s chemical state information was now resolvable, shown in fig.65: Although signal to noise levels are very poor in this narrow scan, comparison with standard XPS data coupled with the wide scan data left little doubt that this was the first chemical state data to ever be obtained by TXPS. Comparison of peak positions to standard XPS of the NaFion sample can be seen in table 9. The sample still had carbon contamination shown by the C-H/C-C peak, but the narrow scan also had three peaks shifted to lower kinetic energy from C-FO, CF$_2$ and CF$_3$. A simple hand fit revealed:-
Table 9
Comparison of TXPS NaFion Peak Positions with Standard XPS.

The shifts were fairly consistent with those from conventional XPS and there was not any C-F, as expected from the NaFion repeat unit diagram in fig.63. The main discrepancy was the CF₃ peak, which, although shown to be broad in conventional XPS, in TXPS showed what could have been judged a fourth peak. Knowing the source to have a FWHM of 0.85eV, the other peak widths seemed reasonable.

After completion of this experimental work the NaFion sample was examined in both an optical microscope and then the Confocal Scanning Laser Microscope (CSLM) (see section 8.3 for more details on the CSLM). The sample appeared slightly discoloured from an uncertain combination of photon and ion etch damage together with electron beam Joule heating conducted from the target foil. The low level of damage was surprising considering the extensive analysis time. The CSLM was used to accurately determine the specimen thickness by the difference in focal length between the polymer and source foil below. It revealed the thickness of the NaFion as being 4µm which explained the poor counting statistics. Later polymer experimentation used microtomed samples no thicker than 1µm. This appears to be the practical limit to specimen thickness, a view which was concurrent with that of Cazaux himself [30].
The NaFion sample showed the first evidence that the TXPS apparatus had sufficient energy resolution to perform chemical state analysis on polymeric materials. However, there are several examples throughout this thesis showing clearer energy resolution performance on the C1s peak. Good energy resolution was vital for future work studying the interface between Haloflex and mild steel for ICI.

5.2 The Ideal Analysis Voltage

Evidence for a critical spectroscopy accelerating voltage was gathering from a number of experimental sources. It was clear it not only affected the background level in spectra, but also the ease with which Transmission SEM imaging could performed. See section 6.1. Establishment of routine analysis conditions demanded an understanding of the role of accelerating voltage on the shape of the spectra.

Fig. 66 shows a montage of spectra collected at various accelerating voltages, in point analysis mode, of copper evaporated onto two 0.8μm aluminium foils. This was the normal source combination that was used in TXPS applications work. See section 8.0. The copper was argon ion cleaned and the spectra were acquired at 200nA specimen current in 900s. At 3.5kV there was early evidence of the photoelectron and Auger peaks. The signal to noise ratio (S/N) in the analysis was very poor, but had the acquisition time been extended these peaks would have improved. The count rate approximately doubled by 5kV, but it was not until 7kV that the S/N improvement became very apparent. This improvement was echoed at 8.5kV and 9kV, where the background on the low kinetic energy side of the Cu2p peak was lower in relative magnitude. Although the count rate increased between 9 and 9.5kV, there was also an increase in overall background that the whole spectrum rested on, suggesting a degree of primary electron transmission. At 10.5kV this background increase was much more apparent and by 11.8kV the Cu(KLL)/Cu2p ratio had drastically increased. The photopeaks had almost disappeared into the background. At 14kV all that remained were the Auger peaks.
The Effect of Accelerating Voltage on Copper Spectral Shape (Copper Evaporated onto Two 0.8μm Aluminium Foils) (200nA, 900s, CAE=200eV)

The results demonstrated the ideal analysis voltage was approximately 8.5kV. The higher the accelerating voltage, the further the penetration of both the primary
beam and its induced secondaries. Below 8.5kV, the number of X-rays produced reduced with accelerating voltage according to fig.67. Efficient production of Alkα X-rays ideally required the electron exciting voltage to be an order of magnitude greater than the threshold for excitation [15]. The lower the energy, the further the average X-ray production sites were from the sample and so they were self-absorbed by the source foil to a greater extent. Photoelectron count rates were, therefore, lower at smaller accelerating voltages. A similar effect illustrating Green and Cosslett's law [29] was seen by Cazaux [17] in section 2.2.1.1. He was analysing far below the ideal voltage for his target foil.

Fig.67
Dependence of Efficiency of Alkα X-Ray Production with the Energy of Bombarding Electrons [15].

Above the 9kV value, primary electrons and their induced secondaries were transmitted through the target and sample causing the overall background increase
shown in fig.68a. These electrons could excite Auger peaks directly and so they began to dominate the spectrum as the accelerating voltage was increased. The photopeaks were still excited, and when the spectrum scale was expanded, they could be seen (even though they were a little masked by shot noise). Photoelectron signal was insignificant on the scale shown in fig.66 and so effectively disappeared. Routine TXPS at such a voltage would have been impractical as a result of the signal to background ratios (S/B). Electron beam damage, of course, would have needed consideration too. The dominance of electron induced effects was a consequence of the low probability of photoelectron excitation. The probability of Alkα X-ray excitation by a 10kV electron beam is only about 1 in 4000 [29] and these X-rays are emitted radially, which further diminishes the effective X-ray intensity. Thus even if only a small proportion of the electron interaction volume protruded from the back of the source, it would have severely affected the collected spectral shape, swamping the photoelectron signal.

The spectra in fig.66 were used to study S/N and S/B ratios at various accelerating voltages. This gave a clearer understanding of the constraints to TXPS analysis conditions and demonstrated a balance between achieving ultimate S/N and minimizing electron beam damage.

When there were no primary electrons transmitted in TXPS, the high energy end of the clean copper spectrum showed little background. As the first few electrons from the interaction volume emerged, the background at 1000eV (KE) increased sharply with accelerating voltage as shown in fig.68a. The power increased with accelerating voltage, contributing slightly to the rise, but it was dominated by the transmission effect. The increase began at 9.5kV so, in terms of background and possible electron beam damage, 9kV would be the ideal voltage.

As far as S/B just beyond the Cu2p3/2 peak was concerned the ideal voltage was, once more, approximately 9kV. See fig.68b. Both peak and background increased proportionately with accelerating voltage below the ideal voltage, as a result of more efficient excitation of the characteristic lines and the copper Auger inelastic tail. The sharp drop was caused by the emerging primaries and its induced secondaries rapidly increasing the entire spectral background.

The S/B, when the background was taken at 1000eV, told a slightly different story. The ideal voltage in fig.68c was approximately 8.5kV. This particular ratio was
far more sensitive to background changes and provided a safer indication of whether primary electrons were being transmitted.

Fig.68
The Effect of Accelerating Voltage on Background, S/N and S/B for the Cu2p_{3/2} Peak. (a) Background at 1000eV (KE), (b) S/B Just Beyond the Cu2p_{3/2} Peak, (c) S/B at 1000eV (KE), (d) S/N.

Fig.68d shows the improvement in S/N with accelerating voltage, where the noise was measured as the difference between the highest and lowest channel heights just beyond the Cu2p peaks. Initially S/N increased with accelerating voltage as a consequence of more efficient X-ray excitation and the mean excitation depth having been pushed nearer the sample. The peak in the data represented an ideal voltage, at about 9.5kV, above which the S/N dropped away. The overall count rate and shot noise
increased rapidly when the Bethe range exceeded the foil thickness, as shown in fig.68a. Photoelectron P-B increases were swamped by the noise increase at high accelerating voltages. In effect fig.68d is a combination of two curves: The left hand side was dominated by signal increases and the right hand side by noise increases.

From fig.68 it was clear that there was indeed some discrepancy in exactly how to define the ideal analysis voltage. S/N considerations estimated the value to be higher than S/B methods. To routinely set up TXPS, S/B at high kinetic energy was the most reliable estimate when analysing electron sensitive materials such as polymers, otherwise S/N would have yielded the most efficient spectroscopy conditions.

![Fig.69](image.png)

The Effect of Accelerating Voltage on the Bethe Range for Aluminium.

The stopping power of a solid target is defined as the rate at which an electron loses energy [33]. The loss of energy from the original accelerating voltage down to rest occurs by a wide variety of mechanisms including inelastic, phonon and plasmon scattering and the emission of secondary electrons as well as various types of radiation.
The electrons' path can be described by Monte-Carlo simulations. Consideration of a large number of electron trajectories produces an interaction volume. The true path length of a electron, as opposed to the mean free path, is found by integration of the Bethe expression which allows the development of Bethe ranges. The effect of accelerating voltage on TXPS spectral shape corresponds well to the Bethe range data from Joy [26]. These data are presented in fig.69. Comparison may be made between these data and fig.66. Under ideal analysis conditions, primary electrons should not be able to penetrate the target as any emergent electrons will not only cause the background increase but may damage the sample. The source foil thickness must be larger than the Bethe range. Fig.69 suggests that for a 1.6μm aluminium source foil there will be no danger until just above 11kV. Fig.66 put this figure between 9kV and 9.5kV. The discrepancy was explained by the non-uniformity of the target. It suffered from the roughness of two 0.8μm foils (about 100nm roughness on each aluminium foil surface) and so it was possible to conceive the ideal voltage was 1.5kV less than would have be expected for a 'perfectly' flat source.

5.3 The Effect of Specimen Current and Magnification on Spectrum Quality

A series of wide scans of a copper sample, at 38mm lens working distance, were collected using decreasing specimen currents at the ideal voltage. As the current was dropped, the count rate reduced and noise became more significant simply because fewer characteristic X-rays were being created. Below 500nA, the noise became too significant within the set analysis time. Thus, unless analysis times were extended above 600s, the electron beam size would have been limited to approximately 1.5μm putting restrictions on the optimum resolution obtainable by TXPS. The lower specimen currents were much more acceptable with an improved lens transmission which, as pointed out earlier, was achieved by reducing the working distance to 10mm.

On a copper coated 1.6μm aluminium source, increasing the scan unit magnification, at a constant specimen current, did not compromise the TXPS spectrum quality. In fact the peaks appeared to improve in definition. Compared to analysing
with a stationary point, low magnification rastering of the electron beam (100x) appeared to broaden the Cu2p peaks. The explanation lay in the focusing properties of the lens. Electrons from different areas of the sample had different focusing conditions in the lens and analyser. Thus, electrons of slightly different energy were collected and counted from different sample areas. Rastered spectroscopy from a large sample area had an overall effect similar to opening up the analyser entrance slits or increasing the pass energy.

The count rates were stable with magnification because the electron, and hence photon, flux remained constant. This was an advantage over many of the other XPS imaging techniques in section 1.0 which suffer from poorer count rates at higher magnifications as, unlike TXPS, they are unable to increase their photon density.

Point analysis also reduced the noise levels. This was actually attributable to feedback from the scan unit in the raster mode.

5.4 TXPS Photoelectron Peak Shape

5.4.1 TXPS Peak / Background Ratios

Peak shapes were an interesting feature of TXPS. Peaks exhibited high backgrounds on the low kinetic energy side with respect to conventional XPS. This related to the characteristic X-ray intensity being higher just below the surface than at the immediate surface. The inelastic component of the peak was, therefore, emphasized in TXPS. Such an effect was compounded by the occurrence of two plasmon loss peaks on the low kinetic energy side of both the Si2s and Si2p peaks. This is shown later in fig.94b collected from the back of a silicon source. TXPS peaks were less sharp than electron spectroscopists are normally used to, but were still adequate for quantitative analysis. The larger loss features could complicate spectral interpretation, but there would be cases where they can be useful, for example in deciding whether a diamond film contains graphite at crystallite boundaries. In EELS [34] diamond and graphite plasmon peaks are shifted by different amounts relative to the core peak and, from the above reasoning, would be resolvable in TXPS.
5.4.2 The Effect of Sample Thickness on Inelastic Background Gradient

In later work on microtomed PMMA/PVC films the thickness of the film had an effect on spectral shape. In XPS Tougaard [35] explained that the extent of the inelastic tail was proportional to the thickness of overlayers. Relatively speaking, TXPS sample films were thick overlayers, never thicker than 1μm, and so the gradient behind the peak must have been related to film thickness. Later spectra (figs.93 and 96b) show different extents of Cls inelastic tails from similar materials, consistent with this idea. Both depth and concentration of the element of interest also would have affected this gradient, but the samples here had a uniform concentration mainly being made up of mounting resin with a small localised area of buried polymer blend.

![Graph](image)

Fig.70 Sample Thickness Effects on the Inelastic Background Gradient of the Cls Peak.

A series of samples, microtomed to different thicknesses, were prepared from a polymer to specifically investigate the effect of thickness on the gradient of the Cls inelastic background beyond any characteristic loss features. The data were normalised to the height of the Cls peak above background. This avoided any problems of transmitted primary electrons which would have increased the background to different extents from sample to sample. The background variation also prevented the use of normalisation to total counts. Fig.70 shows the gradient decreased with increased film
thickness. Abnormally low gradients were occasionally noted with the thinner films where the chosen analysis area scrutinised two overlapping films, effectively giving one of twice as thick. These points were moved on the plot to double thicknesses. No problems were observed with thicker films as they were much easier to handle during copper grid mounting. The data confirmed that thicker samples gave a greater opportunity for inelastic interaction which spread the inelastic component over a larger range of kinetic energies behind the peak.

5.5 Spectra from a Silicon Single Crystal X-Ray Source

A silicon X-ray source had shown its worth in conventional XPS [36] producing X-rays with an energy of 1739.6eV with a respectable line width of 1eV. SiKα has the advantage of being able to ionise deeper core levels than AlKα or MgKα, most notably the Al1s and Al(KLL) peaks. Unlike the Al2s and Al2p peaks, Al1s has a high photoelectron cross-section.

5.5.1 Spectra from the Back of the Silicon Target

A 6μm thick silicon single crystal was analysed in transmission. The source produced radiation at 1739.6eV, so the O1s peak was seen at roughly 1208eV and the O(KLL) at 510eV. A spectrum was collected at 12kV and 2μA in 300s (CRR=4) and is shown in fig.71a. The lens was at 38mm working distance.

The lens was then moved to a working distance of approximately 10-16mm and a problem of the outer hemisphere being earthed through one analyser leg was solved. This accounted for the poor count rates and energy resolution in earlier spectra. Fig.71b shows a spectrum acquired in 300s from the silicon wafer demonstrating this improvement.
Fig. 71
Spectra Collected from a Silicon Single Crystal (12kV, 300s).
(a) 2μA at 38mm Working Distance (CRR=4).
(b) 1μA at 10mm Working Distance (CAE=100eV).

5.5.2 The Search for the Al 1s Peak Using Sika

The Al 1s core level is too deep to be obtained with conventional sources, but should be obtainable at Sika. The Al(KLL) peak is also easier to resolve and it shows a larger chemical shift between aluminium metal and aluminium oxide than the one observed for aluminium photopeaks. The sample used for TXPS here was a 0.8μm aluminium foil on top of a silicon single crystal source. Problems were found in sensitivity of the high kinetic energy peaks and so the Auger peaks allowed transfer lens refocussing. A loss of sensitivity at low kinetic energies was not a problem since the count rates were high here. Sample foils were ion etched to remove the contamination overlayer. A narrow scan of the aluminium Auger peak is shown in fig.72, with the
oxide and metal components clearly separated. The occurrence of an Al1s peak in the wide scan confirmed the Auger peak to be X-ray induced. 11kV would not have penetrated the 6μm silicon wafer and so direct electron excitation was not a possibility. The relative components of the Auger peak changed when tilting the specimen, as expected when analysing an oxide coating on aluminium in conventional XPS. Al1s S/N was very poor because SiKα is very strongly absorbed by aluminium. This effect was very apparent with a sample thickness of 800nm. The limited supply of single crystal prevented the possibility of evaporation of aluminium onto the source to obtain a more convincing analysis.

![Graph of Al(KLL) Peak Excitation by a Silicon Single Crystal Source](image)

Fig.72
Al(KLL) Peak Excitation by a Silicon Single Crystal Source (11kV, 3μA, 300s, CAE=50eV).

5.5.3 Conclusions on the Use of a Silicon Wafer Source

The silicon wafer performed satisfactorily as a X-ray source, although its thickness inhibited the use of low specimen currents. This is of significance to later comments on Joule heating where sample damage of polymers could be caused.
The thickness of aluminium samples was found to be very important in order to get an Al1s peak of a reasonable magnitude. This was a result of the strong absorption of SiKα in aluminium. Aluminium samples should have been no larger than a few hundred nanometres thick.

The successful use of a silicon source foil here and Brünger's results in section 2.2.3 highlighted the potential for use of TXPS on semiconductor materials placed on specially thin silicon wafers. The wafers would have acted as compound X-ray sources.
6.0 MAPPING AND IMAGING CAPABILITIES IN TXPS

In the previous chapter the ability to acquire a spectrum in TXPS was demonstrated together with the ideal conditions under which it had to be collected. The possibility of forming a local source of X-rays from a focused electron beam also gave the opportunity for rastering and performing TXPS chemical mapping in a similar manner to AES.

Finding the way around specimens in most small area XPS techniques is difficult. Often methods rely on UHV microscopes or CCD cameras carefully aligned so that a known area in the sample is analysed. This method can be troublesome. When the actual XPS map is used for alignment, it is frequently difficult to quickly establish how this relates to the specimen. To make TXPS a relatively routine technique a specimen alignment procedure needed to be found. It had to be possible to find the way around quickly at low magnification and then focus on a particular area of interest, especially if the sample was susceptible to analysis damage. Random point analysis was clumsy and TXPS mapping was too slow. The final solution was transmission secondary electron microscopy (TSEM). Both TXPS mapping and TSEM will now be discussed in detail.

6.1 Transmission Secondary Electron Microscopy (TSEM)

By rastering the electron beam and increasing the accelerating voltage beyond the ideal voltage, so that the interaction volume penetrated the target, it was possible to obtain a transmitted secondary electron image using the photomultiplier in transmission shown in fig.32a. Clarity of Transmission SEM images showed a dependency on accelerating voltage. At or below the ideal spectroscopy voltage there was no real contrast in images, due to the secondary electron excitation only being caused indirectly from the relatively improbable X-ray production. To obtain any contrast in the image higher accelerating voltages were necessary; as demonstrated in fig.73, where a copper grid was placed on top of two 0.8μm aluminium foils. At 8.5kV all that could be seen was a bright spot attributable to a pinhole in one foil. At 9kV
very slight contrast had appeared, which was far more evident at 9.5kV. At 10kV the entire grid was resolvable and at a considerably reduced specimen current. As the accelerating voltage was increased the required currents became less and image clarity improved. By 13kV the image quality no longer required the full photomultiplier voltage but at 16kV the glare from the foil regions was too great. The current at 16kV was higher because of instrumental constraints.
The TSEM image was caused by transmitted primary electrons and its induced secondaries. The image contrast was caused by combined sample and foil local thickness variations. Whilst the aluminium foil showed brighter areas from non-uniformity, the copper grid totally absorbed any emergent electrons. At voltages at and below the ideal analysis voltage there was no TSEM contrast, except if there were pinholes in the foil as in fig.73a. It seemed that a reasonable voltage above the ideal voltage was required to provide enough secondaries to give a clear image. The transmitted images were poor in quality compared to conventional reflection SEM images because the imaging probe was the full diameter of the interaction volume (approximately 1µm at 12kV plus the beam diameter [37]) and the foil topography also caused a lot of distortion.

TSEM imaging was possible with many different samples at about 11kV with specimen currents of about 5nA. See section 8.0. Necessary currents increased rapidly
with the reduction of accelerating voltage and the contrast deteriorated. These observations could be explained by consideration of the Bethe range. No contrast was observed below the ideal voltage where the Bethe range was less than any part of the foil thickness. The image partially appeared at 9-9.5kV when local foil topography meant that the thickness sometimes fell below the Bethe range. At 10kV and above, the foil was always thinner than the Bethe range and so there was transmission uniformly across the exposed source.

Fig.74
Images of 88μm x 88μm Gold Squares on an Aluminium Source (a) 10kV, (b) 8kV.
Experiments examining gold squares sputtered onto 1.6µm of aluminium revealed contrast in the transmitted secondary electron image. At 10kV gold regions appeared darker. Reduction of the accelerating voltage reversed the contrast, suggesting that at 10kV the primary beam was penetrating the aluminium, and to a lesser extent the gold. At 8kV the beam was unable to penetrate and the image was X-ray excitation dominated. Here the Auger and photoelectron cross-sections of gold were higher than for aluminium or oxygen, so the gold region appeared brighter. See fig.74.

6.1.1 The Backscattered Electron Contribution to TSEM Images

(a) Copper Grid, Al/PET Arrangement on the TXPS Stub.
(b) Apparent Transmission SEM Image from Backscattering Phenomenon (5kV).
TSEM images, particularly at low accelerating voltages, included a significant contribution from the electron gun side of the target foil. This was shown by placing a copper grid on the underside of the X-ray source as shown in fig.75a. The sample was 7μm of PET covered with a convenient 1μm thick coating of aluminium. The SEM image, supposedly in transmission, is shown in fig.75b. It was clear that the image was from the underside of the source. In this case the specimen absorbed all of the primary electrons in the forward direction. Backscattered electrons hit the top of the electron gun chamber where they created secondary electrons. See fig.76. These were collected by the bias on the photomultiplier and so appeared to be transmitted. Copper has a higher backscattering coefficient than aluminium and so appeared brightest.

![Diagram](https://example.com/diagram.png)

Fig.76
The Origins of the Backscattered Contribution to TSEM Imaging.

Normally, during specimen alignment the backscattered electrons did not cause confusion in TSEM imaging because the samples were much thinner and the accelerating voltages were higher. The long and narrow path back down the stub required for a backscattered contribution resulted in only a relatively small effect on the overall image and real TSEM image domination.
Mapping and Imaging Capabilities in TXPS

6.2 Mapping in TXPS

Mapping in TXPS only requires rastering of the primary electron beam. This in turn moves the X-ray source and, likewise, the region of photoelectron excitation. This section includes the acquisition of some TXPS maps and a discussion of aspects of their interpretation. Lateral resolutions are measured from various images and linescans and an attempt is made to obtain an ultimate technique lateral performance. Accelerating voltage and source thickness effects are thereby investigated. Lateral resolution with respect to source crystallinity is also explored.

The intensity colour code used in the maps throughout this thesis is given in appendix 2, together with the normal procedure used for setting pixel intensities. Image figures are generally divided into four separate quadrants.

6.2.1 Comparison of a Single Crystal and Polycrystal X-Ray Source

TXPS imaging was used to compare lateral resolutions from aluminium polycrystal and silicon single crystal X-ray sources and results served as a guide to whether it was worthwhile pursuing the use of a single crystal source.

A 125μm pitch copper grid was placed on top of two 0.8μm aluminium foils and mapped in O1s at 9.5kV and 520nA over a 5.5 hour period. The target surface oxide was mapped. As in AES mapping, a single channel was collected on the peak and also one on the high kinetic energy side in order to monitor the background. This side of the peak was used to avoid the inelastic tail. Fig.77a shows the peak (P), background (B) and peak minus background (P-B) attained from the image. The algorithm (P-B)/B reversed the image contrast as a result of the very low intensities of background in the grid regions relative to the source regions. However, although the image was dominated by thickness, it was still suitable for estimation of lateral resolution.
Fig. 77
TXPS O1s Maps (5.5Hrs, CAE=100eV) of a 125μm Pitch Copper Grid on
(a) 1.6μm of Aluminium Foils (9.5kV, 520nA)
(b) 6μm Silicon Single Crystal (21kV, 520nA)
(The colours in these images were chosen only to reflect the distribution of intensity within an individual map, rather than for comparison of absolute intensities between the different algorithms.)
A similar grid was placed on a 6μm thick silicon single crystal (100) and mapped, again in O1s, at the same specimen current for 5.5 hours, but the target extra thickness required the use of 21kV. The ideal voltage to obtain a good signal to noise ratio in the O1s peak was far less critical than with the aluminium polycrystal. The silicon produced respectable S/N right down to 10kV, although there was an eight-fold increase in count rates at 21kV with respect to those at 10kV. The images are arranged as before in fig.77b showing the oxide that was present on the source.

Both of the sets of images apparently showed oxide on the copper grid surfaces, but the characteristic radiation would have been unable to penetrate the 11μm thick copper grids. Characteristic X-rays emitted at high angles to the sample normal, when the electron beam and interaction volume were under a grid bar, could have excited detectable photoelectrons from nearby exposed regions.

Fig.78
Comparison of the Silicon Single Crystal and Aluminium Polycrystal O1s Maps Using Similar Colour Schemes.
Lateral resolutions were obtained from the images in two ways:

i) Directly from the map measuring the thickness of the 'uncertainty' region across the edge of the grid bar, knowing a grid bar to be 37μm across.

ii) By using pixel intensities across the grid edge to build up a map line scan.

Table 10 shows that similar lateral resolutions were obtained using the single crystal and the aluminium foils, despite a degree of disagreement between the two calculation methods. The silicon was approximately four times as thick as the aluminium foil source. Additionally, the accelerating voltage was twice as large, which would have been expected to result in a larger interaction volume and consequently a larger X-ray spot size. Both electron beam diameters were approximately 1.5μm which, of course, caused a degradation in measured lateral resolutions. Despite all of these restrictions the single crystal resolution was still comparable and the remarkably good performance will now be explained.

<table>
<thead>
<tr>
<th></th>
<th>Aluminium Source &amp; Copper Grid (Mag. 500x)</th>
<th>Silicon Source &amp; Copper Grid (Mag. 500x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time to Acquire Map</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>(Hours)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Accelerating Voltage</td>
<td>9.9</td>
<td>21</td>
</tr>
<tr>
<td>(kV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specimen Current</td>
<td>0.52</td>
<td>0.52</td>
</tr>
<tr>
<td>(μA)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Power</td>
<td>5.15</td>
<td>10.92</td>
</tr>
<tr>
<td>(mW)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lateral Resolution</td>
<td>7.0</td>
<td>9.1</td>
</tr>
<tr>
<td>from Line Scan (μm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lateral Resolution</td>
<td>7.7</td>
<td>7.0</td>
</tr>
<tr>
<td>from Map (μm)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 10
Comparison of Resolutions Obtained from the Aluminium Polycrystal and Silicon Single Crystal Maps in fig.78.
The use of a single crystal suggested possible effects from electron channelling or forward scattering phenomena. Sika X-ray diffraction definitely did not play an important role because the wavelength was too long (7.25Å). This meant the radiation was only diffracted off high order planes; an event which was improbable and consequently of little importance. All the single crystal did was effectively stretch the interaction volume in the beam direction by electron channelling [31]. Although the electron penetration into the source increased, the electrons were subsequently scattered out of the channelling direction, to undergo similar scattering and energy loss events as normally were expected in a polycrystal interaction volume. The width of the X-ray excitation envelope was unchanged and so lateral resolution enhancement was not possible.

The fact that the corners of the silicon image grid bars were much less rounded in fig.78 was evidence for photoelectron forward scattering [38] having contributed largely to the yield of photoelectrons in the analyser direction. Under aluminium polycrystalline source conditions, the count rates were poor close to the grid edges where many of the emerging photoelectrons collided with the protruding edges and were lost. This effect degraded the apparent edge resolution, in these highly topographical images, most severely of all at the corners causing the rounding. With forward scattered photoelectrons contributing significantly to the photoelectron signal, the results of the grid edge resolution tests were distorted. The resolution on the silicon image was not as degraded by the grid edges and so was apparently improved relative to aluminium. This satisfactorily explained the single crystal resolution enhancement in table 10. Single crystals offered no opportunity for improved lateral resolution once a sample was placed on top of the source as photoelectron forward scattering would no longer have contributed to the image.

There was some scepticism with the resolutions quoted in table 10. The map estimations were, to some extent, dependent on the colour schemes and thresholds chosen. In the linescans, pixel intensities varied greatly even across a grid bar or gap. These variations caused the setting of the upper and lower thresholds on the linescan to become slightly unreliable and required a certain extent of experimentalist judgement. Such subjective judgement was necessary in map resolution measurements too. More reliable lateral resolution assessments are given in section 6.2.3 for flat gold images.
6.2.2 The Effect of Accelerating Voltage and Source Thickness on the Lateral Resolution in TXPS

The photoelectron lateral resolution and photon density calculations performed earlier used an equation derived by Cazaux [19] assuming the semi-apex angle of effective X-rays was 45°. A second group of similar expressions were also derived by Cazaux in [17] which yielded slightly different measures for the lateral resolution of TXPS in the MA500. The 45° semi-apex angle led to a resolution $d$

$$d = \left( h^2 + \frac{r_x^2}{2} \right)^{\frac{1}{2}}$$

(17)

where $h$ was the distance from the focus of the X-ray source to the object plane and $r_x$ was the radius of the X-ray source. This radius includes the radius of the electron beam and a measure of the range of incident electrons in the target material.

$$r_x \approx \left( r_e^2 + r^2 \right)^{\frac{1}{2}}$$

(18)

$r$ was measured by Monte-Carlo simulation as shown in table 11 [26]. This was the radius of the X-ray excitation envelope and was a better approximation than the Bethe range used by Cazaux. The mean depth of X-ray excitation was also given as this was the effective source depth ignoring preferential absorption of X-rays produced further from the sample plane.

<table>
<thead>
<tr>
<th>Accelerating Voltage (kV)</th>
<th>Bethe Range (μm)</th>
<th>Radius of X-Ray Excitation Envelope (μm)</th>
<th>Mean Depth of X-Ray Excitation (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.41</td>
<td>0.28</td>
<td>0.11</td>
</tr>
<tr>
<td>10</td>
<td>1.32</td>
<td>1.01</td>
<td>0.36</td>
</tr>
</tbody>
</table>

Table 11
Data from the Monte-Carlo Simulation [26] for Aluminium.
The effects of the accelerating voltage and specimen current on the lateral resolution, for a given source thickness, were considered using these equations. It was assumed that the sample was infinitely thin and that all of the X-ray spreading was within the target. For this calculation the source thickness was chosen as the Bethe Range at 10kV (1.32μm [26]) to prevent any primary electron transmission. Table 12 highlighted the importance of specimen current on the obtainable lateral resolution. The size of the interaction volume was dominated by the beam diameter in MA500 TXPS, although a greater accelerating voltage did degrade the resolution slightly.

<table>
<thead>
<tr>
<th>ACCELERATING VOLTAGE (FOIL THICKNESS)</th>
<th>LATERAL RESOLUTION (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Infinitely Small Electron Beam Diameter</td>
</tr>
<tr>
<td>5kV (1.32μm)</td>
<td>1.2</td>
</tr>
<tr>
<td>10kV (1.32μm)</td>
<td>1.4</td>
</tr>
<tr>
<td>5kV (0.41μm)</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 12

The Effect of Accelerating Voltage and Specimen Current on the Predicted Lateral Resolutions in the BTMA500. (1.32μm and 0.41μm were the Bethe Ranges of 10kV and 5kV Electrons in Aluminium Respectively.)

Reducing the thickness of the source to 0.41μm and the corresponding ideal voltage down to 5kV improved the predicted lateral resolution in table 12 and values almost reached the 1μm level. Here the interaction volume was smaller and the degree of X-ray spreading was reduced. An experimental proof of the value of thinner targets is given in the following section.
6.2.3 TXPS Lateral Resolution Measurements

The calculated lateral resolution that should have been obtainable by TXPS has been derived in two earlier sections of this thesis. Resolution has been shown to be dependent on electron beam diameter, the accelerating voltage and the target and sample thicknesses. Often attempts to measure the resolution were hampered by various sample irregularities. It was felt that the large extent of thickness contrast in the copper grid images degraded the measured resolution by a partial transmission masking effect near the grid edges (see section 6.2.1) and polymeric samples shown later did not show any features for dimensional reference. Samples were, therefore, made specifically to measure resolution. A thin coating of gold was evaporated onto various source foils using a copper grid mask. The mask was subsequently removed, before TXPS mapping, to reveal an array of gold squares of a known size. Gold was coated onto both a single 0.8μm and two 0.8μm foils to demonstrate the improvement of lateral resolution using thinner sources.

Fig.81 shows a gold image from the double foil case and a lateral resolution of 12.2μm measured by pixel intensities across a square edge. A line scan revealed a 14.6μm lateral resolution. These figures were considerably poorer than the values derived from the Cazaux equations. The single 0.8μm aluminium foil demanded the use of a lower accelerating voltage in order to still contain the entire interaction volume, and so the width of the excitation envelope was smaller. Fig.79 shows TXPS images of the sample at 3.8kV. The maps show that the grid mask did not shield the aluminium target particularly well and permitted gold to be evaporated under the grid wires to a significant extent. The grid must have been lifted away from the mask slightly for this to occur. Nonetheless, grid cross regions were still sufficiently shielded to allow resolution measurements, giving a value of approximately 2.6μm from the pixel line scan in fig.80. This resolution was much closer to the theoretical values calculated in section 6.2.2, although it was still disappointing considering the low accelerating voltage used. This performance was, to some extent, blamed on the roughness of the aluminium source, meaning low accelerating voltages were again used with respect to the Bethe Range (0.26μm at 3.8kV). It ensured the interaction volume was totally within the foil, but permitted additional X-ray spreading.
The experimental count rates were notably similar to those from later ultramicrotomed sections. Thus, although the accelerating voltage had been radically reduced, the count rates were still workable. The reduction of the X-ray self absorption and the mean source to sample distance must have compensated significantly for the loss of X-ray excitation efficiency for this to have been achieved.

Fig. 79
TXPS Au4f Images of Gold Squares Evaporated onto one 0.8 µm Aluminium Source (3.8 kV, 60 nA, CAE=200 eV, 3.9 hrs.).

Fig. 80
Pixel Line Scan Across a Grid Cross of Fig. 79.
6.2.4 The Effects of Specimen Thickness on TXPS Imaging

In view of the possibilities for quantitative mapping using XPS, unlike in AES, it is worth discussing its prospects in TXPS. Quantitative mapping in XPS was performed in the VG 220i instrument [39] by normalising all point intensities to an atomic percentage using the standard fluorine based sensitivity factors. This normalisation procedure removed the topography problem of AES and the sensitivity factors alleviated the need for scatter diagrams [40].

In TXPS, the detected intensity of a given element depended not only on its atomic concentration, but also the X-ray dose at that point. Roughness within the source led to a distribution in the penetration of the electron interaction volume and a variability in the extent of X-ray absorption before reaching the sample surface. In locally thicker target areas a lower intensity arose from a combination of the mean X-ray excitation distance from the surface of interest being larger, and the extent of X-ray self-absorption being greater. This effect was shown with a combination of statistical noise in the source regions of fig. 101. TSEM also showed the target thickness variations.

Topographic effects were noticeable when the image compared relative intensities between the source and a microtomed section on top. The sample absorbed a large proportion of the X-ray intensity before surface photoelectron signal could be created, as is shown in the polymer samples of fig. 101. This made image interpretation tricky. The Al2p and O1s (P-B) maps complimented one and other well, but the Cls (P-B) made little sense. The extra 600nm of sample thickness clearly could not simply be compared with the source. A topography removal algorithm such as (P-B)/B was necessary to produce the correct relative contrast. This algorithm scrambled the contrast of the O1s and Al2p images. The extreme thickness variations of the source/film comparison was an exceptional case. Under normal specimen imaging circumstances relative intensity differences were only required between points on the same sample surface.

In ultramicrotomed sections the samples have a uniform thickness and therefore contrast will have a real quantitative meaning. The images may need a small normalisation process to take into account the local thickness variations. The reliability
of point to point relative intensities in TXPS imaging was gauged by looking at gold squares evaporated directly onto an aluminium source. A copper grid was used as a mask for the deliberately very thin gold coating (a few atomic layers). The layer thickness made an insignificant local increase in thickness with respect to the roughness variations in the foils themselves. Fig.81 shows both O1s and Au4f images with the (P-B) images showing the correct relative contrast. The Au4f (P-B) intensity is highest in the gold square regions and in the O1s (P-B) image the intensity is greatest in the original grid bar areas. The effect of background is also notable in the images. The Au4f peak has little background on the high kinetic energy side of the peak, so the background image is relatively dark, with the highest intensity in the gold squares. The O1s peak is at a lower kinetic energy and is situated in an area where the background will be very high from the inelastic components of the various gold peaks. The O1s (B) image is, thus, dominated by gold features, but the unnaturally high gold regions were reduced to the correct contrast by the P-B algorithm. The Au4f peaks suffered little problems from the inelastic tail of the Al2p peak because of its poor photoelectron cross-section.

![Fig. 81](image-url)

**fig.81**

**TXPS Mapping of Gold Squares Evaporated onto an Aluminium Foil Source** (8kV, 100nA, CAE=200eV, O1s 10hrs, Au4f 6.4hrs).
Grid corners produced a semi-masking effect during the gold evaporation. This is the cause of the rounding of the gold square edges in the images. The other important feature of the images are the non-abruptness of the changes in contrast. At the centre of both grids and squares are areas of fairly uniform intensity. However, as an interface is crossed the intensity changes gradually. This reflects the lateral resolution of the TXPS technique and the importance of high angle scattered X-rays. This image shows a lateral resolution of 12.2μm. The correctness of the relative contrast in the image suggests that TXPS of micrometred sections and other flat samples will also yield the correct relative intensities, consistent with atomic concentrations. TXPS quantitative mapping will therefore be possible.

The validity of the previous conclusion can be explored by examining images collected from the Haloflex paint and mounting resin in fig.105. These images show a micrometred section with a stripe of chlorinated paint from corner to corner. This is surrounded by mounting resin on both sides. The copper grid predictably shows up as being dark and totally absorbing. The Cl2p (P-B) map clearly shows the paint stripe with respect to the resin. Bright spots can also be seen in several places in the paint background maps corresponding to holes, but these points are removed by Cl2p (P-B). Fig.109 shows the iron at the interface between the mounting resin and the paint. The Cls (P-B) image shows a continuous carbon signal across the field of view, but the Fe2p (P-B) picks out the iron rich areas unambiguously.

Mapping in XPS using just the peak alone, without considering background, was suggested by Kirschner [41] on grounds of only requiring background acquisition in AES because of the large extent of the background. He claimed XPS would not require background subtraction because of a vastly improved S/B ratio. This method is ill-advised and may lead to incorrect image interpretation. It would have led, for example, to the conclusion that the O1s intensity is highest on the gold squares in fig.81!

Ion beam thinned tapered samples will of course present a problem to P-B TXPS mapping. The intensity will vary across the image, decreasing in the thicker sections. Maps normalised to atomic percent will still be possible, with only counting statistics variation across the sample.
6.2.4.1 The Applicability of (P-B)/B for Thickness Contrast Removal in TXPS

Algorithms such as (P-B)/B and (P-B)/(P+B) have traditionally been used in AES imaging in an attempt to remove topographic effects on relative intensities, a problem which becomes acute in examination of metallic in-situ fracture surfaces. The principle behind the (P-B)/B algorithm is very simple. In conventional AES imaging, the electron collection efficiency depends on the local angle that a plane containing the point of interest makes with respect to the analyser transfer lens direction. Both peak and background reduce with this angle. In fig.82a point 'A' will have more elastic, inelastic and uncharacteristically ionized electrons in the spectrum than point 'B'. (P-B)/B normalises this effect in an image because peak scales with background intensity.

![Diagram](attachment:image.png)

**Fig. 82**
(a) The Effect of Specimen Topography on Spectral Shape in AES.
(b) The Effect of Sample Thickness on Peak and Background in TXPS.
The difference in terms of image manipulation needs between TXPS and AES lies in the origin of the majority of background. In AES it is largely made up of uncharacteristically ionized electrons, but in TXPS it is totally inelastically scattered electrons. In AES the background is consequently a good measure of the magnitude of signal from a given point and satisfactory for normalization procedures. The effect does not hold true for TXPS. An extra local sample thickness attenuates more X-rays before they reach the sample surface. This, whilst reducing the number of possible photoelectrons in the peak, increases the magnitude of the inelastic events and hence the background height. The fact that peak and background do not scale in TXPS makes \((P-B)/B\) impractical for TXPS and accounts for the scrambling of the Al2p and O1s images previously mentioned. Even with a background taken on the high kinetic energy side, there will still be effects from inelastically scattered electrons of peaks at higher kinetic energies (should they exist). See fig.82b.
7.0 TXPS SAMPLE AND ANALYSIS STABILITY

7.1 Sample Damage

Sample damage is of major concern to electron spectroscopists. Sample degradation is frequently observed in XPS analysis, particularly of polymers. This photon damage is especially important in TXPS where the dose/mm² is so much higher. Electron beam heating must also be considered for TXPS since X-ray guns require a considerable amount of water cooling. Although the powers involved in TXPS are considerably lower than those in X-ray guns, the power densities are high (up to 10000W/mm²). This must be conducted away by the target material to avoid thin film damage.

7.1.1 The Extent of Photon Damage in TXPS

With respect to AES, XPS has traditionally been considered a non-destructive technique as a consequence of its low photon densities. However, since there has been a demand for improvements in lateral resolution, higher X-ray doses per mm² are necessary to achieve a given signal to noise ratio in spectra within a reasonable time. Cazaux [42,43] considers the doses required to obtain certain surface concentration sensitivities and the practicalities of both the selected area and the defined source system to achieve higher spatial resolutions. He says the photon densities achievable in TXPS are comparable to those from a synchrotron source at that time. However, improvements in X-ray focusing elements such as zone plates will eventually allow synchrotrons to go below the 1μm level in XPS.

Photon damage in conventional XPS using Alkα and Mgkα sources is found to be less damaging than AES [41]. Primarily this is a result of the flux being $10^{12}$ photons/s spread over an area of about 10mm². The relative sample stability under conventional XPS analysis can not be confidently applied to samples when equivalent photon and electron spot sizes are used. When damage is considered per particle, the difference is far less marked. Equal fluxes of photons (to electrons) were found to degrade protein
and chemisorbed species on metals were desorbed, as it was only dependent on the production of core holes and not on the mechanism by which they were produced. In organic polymers [44,45], 1.5keV photons have been found to be 3 times as damaging as 10keV electrons [44,46]. It is thus expected that electrons and photons are generally similarly damaging, with a slight advantage to the photons on the basis that they have a lower excitation energy (1.5kV instead of 10kV) and will thereby produce less secondary electrons. Kirschner [41] suggests a difference of a factor of 2 or 3.

Photoionisation cross sections for MgKα lie between $10^{-19}$ and $10^{-18}$ cm$^2$. The energy dependence of ionisation cross sections is different for photons and electrons and cannot be compared. The maximum cross section for electrons occurs at about four times the binding energy, decreasing slowly above this energy, typically $10^{-18}$ cm$^2$. This small advantage for AES is spread generally over several broad peaks giving comparable intensities between AES and XPS at the same pass energy, within a factor of three [41].

The final, and most significant consideration is the extent of background using the two techniques. Until now Kirschner has suggested that there is little to choose between using a fine focus X-ray or electron beam. However, the Auger peaks lie on a considerable background which is significantly larger than the peak. This is a result of the abundance of secondary electrons to give the core hole and the inelastically backscattered primaries. In XPS the photoelectrons are directly excited by the X-rays and so the photoelectron peaks are of similar magnitude to the Auger peaks, but without the secondary electron background. The S/B ratio for AES is about 0.1 up to 1 for some cases, whereas for XPS it is 10 to 100. This two orders of magnitude difference in signal to background is the factor that divides the techniques on the basis of statistical uncertainty from noise. This means 100 times more primary electrons in AES are needed than X-rays in XPS to generate equivalent statistical uncertainties. Thus, at equivalent lateral resolutions and doses, radiation damage using photons rather than electrons can be reduced by up to two orders of magnitude.

Cazaux [47] agrees with such an idea on the basis of work in [42] which gives a better probability of causing signal than damage in XPS than AES. Cazaux discusses the resolution constraints in XPS and AES and the dose increases necessary to improve lateral resolutions in XPS. The dose has to be improved by six orders of magnitude to improve XPS from 1mm resolution down to 1μm, which can be achieved by increasing
the photon density or by narrowing the collection area whilst increasing the experiment
duration dramatically. The problem was how to obtain the full benefit of the Kirschner
two orders of magnitude damage advantage and to obtain a small dense source. Such
densities are achievable by rotating anode sources, synchrotrons and TXPS.

XPS at such lateral resolutions has lost its huge damage advantage over AES, but
still maintains a small one together with an easier charging effect to deal with.
Charging will be discussed later. Kirschner concludes much of the literature on beam
damage in AES can be applied to photon beams with the high flux densities.

As briefly mentioned earlier, the high photon densities involved in TXPS make
photon damage a prime concern. The ease with which polymers are darkened in
conventional XPS does nothing to alleviate any fears. Organic materials exhibit a wide
range of damage rates, with aromatic polymers such as polystyrene degrading incredibly
slowly whereas halogen containing polymers degrade relatively quickly. Beamson and
Briggs [48] have monitored polymer degradation under monochromated Alkα radiation
in a Scienta ESCA300 instrument. The instrument has a rotating anode source and a
seven quartz crystal monochromator, which means the technique not only benefits from
a high degree of energy resolution, but also boasts count rates similar to those achieved
in conventional XPS. It is for precisely these reasons that the instrument is so ideal for
photon damage studies. This work was carried out with the source set at 1400W (14kV,
100mA). In this study [48] it was pointed out that the same relative damage rates might
be expected from an unmonochromated source in conventional XPS at equivalent photon
densities. Wagner [49] said that only about 3% of photon damage comes from
Bremsstrahlung so this can be neglected. A monochromated source does not suffer from
much sample heating because of the large distance to the X-ray anode. In conventional
XPS heating effects can be the dominating damage mechanism.

Comparison of Scienta ESCA300 and TXPS analysis conditions, together with the
appropriate instrumental considerations, allows the Beamson data to be used for TXPS.
This gives a guide to the polymeric damage rates in TXPS. It is also useful for
optimizing acquisition times for minimum damage.

The photon density is dependent on the accelerating voltage, specimen current
and the irradiation area. The photon excitation efficiency is related to the accelerating
voltage, so it is not sufficient to just compare power densities from TXPS and the
ESCA300. TXPS is normally performed at 8kV whereas the polymer degradation data were collected at 14kV.

For TXPS the photon density $P_T$ is given by

$$ P_T \propto \frac{N_T i}{A} $$

where $N_T$ is the X-ray excitation efficiency for TXPS at 8kV and $i$ is the specimen current. For simplicity, if we assume the irradiation area $A$ is given by the electron beam diameter then using

$$ d = 66 \left(i^2\right)^{\frac{1}{2}} $$

and by converting into consistent units we obtain

$$ P_T \propto \frac{10^{-9} N_T i}{\pi \left(\frac{33}{10^6}\right)^2 \left(i^2\right)^2} = 0.292 N_T \tag{21} $$

The constant of proportionality in this expression relates to the solid angle of characteristic photons actually interacting with the surface of the sample producing photoelectron signal. Photon densities depend on the separation of the point source of X-rays and the irradiation area as is schematically shown in fig.83.

Fig.83
The Effect of the Source and Sample Separation on the Photon Density.
The approximate area of analysis is given by

$$\pi \left( \frac{66 \ (i^2)}{2} \right)^2$$ (22)

which is only a fraction of a sphere of radius $r$, where $r$ is the distance between the effective point source of X-rays in the target and the sample surface. Thus, the proportion of photon flux that hits the analysis area is

$$\frac{\pi \left( \frac{66 \ (i^2)}{2} \right)^2}{4 \pi r^2} = \left( \frac{33 \ (i^2)}{4 \ r^2} \right)^2$$ (23)

Substituting into equation (21) to remove the proportionality we obtain

$$P_T = 0.292 \ N_r \left( \frac{33 \ (i^2)}{4 \ r^2} \right)$$ (24)

where $r$ is in nm and $i$ in nA.

A similar photon density relationship can be deduced for the ESCA300.

$$P_S = \frac{N_s \ I \ S \ R}{A}$$ (25)

where $N_s$ is the X-ray excitation efficiency at the operating voltage, $I$ is the input current, $S$ is the total solid angle of acceptance of the seven monochromator crystals, $R$ is the crystal reflectivity for Alk$\alpha$ and $A$ is the area of the X-ray spot on the sample. From [6,48] $I=100 mA$, $S=0.076$, $R=0.10$ and the sample area is $0.5x6\text{mm} = 3\text{mm}^2$.

Making sure the units are consistent and dividing equation 24 by 25 we can obtain a damage power factor $F$. This factor allows the Beamson and Briggs polymer damage curves to be used for TXPS by simply dividing the time axis by $F$. An example Beamson and Briggs [48] plot is given in appendix 3.
The ratio \( N_T/N_S \) for Alk\( \alpha \) can be obtained, to a first approximation, from a curve produced by Dolby [50] by extrapolation to 14kV. Photon excitation efficiency curves are known to plateau out as the accelerating voltage is increased, because although more X-rays are produced, there is a greater contribution from self-absorption. This plateau effect is be assumed to be negligible over the accelerating voltages considered here together with the fact that the transmission and reflection emission modes are unwisely being directly compared. Applying the \( N_T/N_S \) value of 0.428 for TXPS at 8kV, equation 26 becomes

\[
F = 1.34 \times 10^5 \left( \frac{1}{r^2} \right) \tag{27}
\]

This equation gives a fairly reliable translation of the damage curves for application in TXPS (i in nA, r in nm). No attempt has been made to introduce the effects of heating as it is shown to be small under normal TXPS analysis conditions in section 7.1.2.

<table>
<thead>
<tr>
<th>Sample Geometry</th>
<th>Specimen Current</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact</td>
<td>1( \mu )A</td>
<td>134</td>
</tr>
<tr>
<td></td>
<td>100nA</td>
<td>13.4</td>
</tr>
<tr>
<td>Non-Contact</td>
<td>1( \mu )A</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>100nA</td>
<td>0.09</td>
</tr>
</tbody>
</table>

Table 13
The Effect of Specimen/Source Geometry on the Damage Power Factor F (8kV).
The values of $F$ will now be evaluated for the sample contact and non-contact cases, assuming the X-ray source depth is at the centre of a 1\,$\mu\text{m}$ thick target and the sample film is 0.5\,$\mu\text{m}$ thick. In the non-contact case, the source and sample are separated by an 11\,$\mu\text{m}$ thick copper grid so $r$ is 12\,$\mu\text{m}$, but in the contact case $r$ is only 1\,$\mu\text{m}$. Table 13 shows the effect of different TXPS specimen currents and sample geometries on $F$. The sample geometry dramatically effects $F$. PVC may be analysed for 430\,mins under ESCA300 analysis conditions before the chlorine content is reduced to 80\% of its initial intensity (see appendix 3). This time is extended to 460\,mins for non-contact TXPS at 1\,$\mu\text{A}$ (8\,kV). However, in the contact case, analysis does risk a more severe loss of chlorine signal. At 100\,nA (a typical current used in TXPS) the chlorine intensity will have reduced to 80\% of its start value in 32\,mins of point analysis. This is considered to be acceptable given that in a typical situation 160\,mins should be enough to obtain all the necessary wide and narrow scans from a single point. At 1\,$\mu\text{A}$ the rate of loss is completely unacceptable.

This derivation shows the inherent dangers of the high photon densities used in TXPS of polymers, and indeed any imaging XPS technique. TXPS does have the advantage of limiting photon damage to very local areas, unlike defined collection systems such as the ESCASCOPE. For equivalent photon densities, analysis by other techniques will destroy the entire sample, whereas TXPS analysis may simply be switched to another appropriate fresh area of the sample.

In TXPS care must be taken to monitor any elemental losses so that quantification data can be usefully interpreted. Beamson and Briggs suggest that their curves can be used to extrapolate back to the original pre-exposed concentration. To quantitatively apply equation 27 to the curves, $r$ should really be estimated more accurately. Experimentally the sample thickness will be known. The separation between the exit side of the target and the effective point source is better calculated from the mean depth of X-ray excitation by Monte-Carlo simulation [26]. The TXPS irradiation area would also be more accurately evaluated by taking into account X-ray spreading in a similar manor to the method used in earlier lateral resolution calculations.
7.1.1.1 TXPS Photon Damage of Haloflex

During TXPS experiments, care was always taken to minimize both electron and X-ray induced sample damage. In terms of electron damage, TSEM accelerating voltages and specimen currents were always kept to a minimum as was the time of exposure. A similar strategy was used for dealing with X-ray damage. The electron beam was blanked or rastered at low magnification when data were not being collected to minimize photon doses and dose densities. In this way damage was totally prevented or delocalised.

There were several opportunities to monitor X-ray damage during TXPS work, but the ideal case involved the chlorinated primer Haloflex. See section 8.5.1. The chlorine in the paint came from two sources: Firstly HCl and secondly the latex itself. Presumably the HCl was lost relatively quickly under the vacuum conditions which left the majority of chlorine signal from the latex. Two TXPS spectra were collected from the same point with a 5900s photon exposure in between. A 900s wide scan was performed on a fresh area of paint and then a narrow scan in the Cls region was

![Graph showing Cls and Cl2s Narrow Scan of Haloflex](image-url)
performed for 5000s. This was followed by another 900s wide scan. The narrow scan included the Cl2s peak and the C1s featured broadening on the low kinetic energy side consistent with C/Cl and C/O bonds within the polymer. See fig.84. The quantified intensities from the wide scans are given in table 14 and showed a loss of Cl2p signal with time. These data were put into context by comparing them to data from conventional XPS. Fig.85 shows the quantified atomic percentage data collected from a fully cured painted stub with the X-ray gun set at typical analysis conditions (10kV, 24mA) and fully pulled out to reduce the rate of damage and heating effects from the nose. The XPS sample was fairly brown in colour showing there was a reasonable amount of photon damage over the whole sample. Both atomic concentrations of chlorine and oxygen decreased with exposure to the X-ray source and the gradient of the chlorine curve was 0.027 at%/min. This signal loss compares to 0.053 at%/min for TXPS. TXPS damage was far more severe than conventional XPS once signal to noise considerations were made. This was not surprising when the photon densities were considered. Nonetheless, the chlorine still remained at 2/3 of its original measured TXPS concentration after over an hour of constant exposure to radiation.

<table>
<thead>
<tr>
<th>Mean X-Ray Exposure Time (s)</th>
<th>Quantified Atomic % of Element</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C1s</td>
</tr>
<tr>
<td>450</td>
<td>61.6</td>
</tr>
<tr>
<td>6350</td>
<td>65.6</td>
</tr>
</tbody>
</table>

Table 14.
Quantified Alkα X-Ray Damage of Haloflex by TXPS (8kV, 100nA).

Consistent TXPS point analyses within areas of approximately 2500μm² have led to complete loss of Cl2p signal from Haloflex. It was, however, noted that a 30s argon
ion etch had a much more drastic effect on chlorine intensity than extended periods of TXPS. More severe etch times completely removed the Cl2p signal. After several days of concentrated analysis in a single 125μm pitch grid region of the primer, and having totally removed any traces of the chlorine, point analyses of neighbouring grid squares showed the chlorine to be at a normal fresh sample analysis level. TXPS photon damage was thus very localised, which is a distinct advantage over many other imaging XPS techniques. The other techniques tend to irradiate the entire sample and use the collection system to determine the irradiation area. Thus, subsequent point analyses suffer from worsening amounts of photon damage, even if the points of interest are relatively far apart.

![Fig.85](image)

**Fig.85**

Plot of Changes in Atomic Percentage of Haloflex Constituents with Time under AlKα Irradiation in Conventional XPS (10kV, 24mA).

7.1.1.2 **Summary**

This section has examined the literature to compare photon and electron induced damage and shown XPS to still have an advantage over AES at high photon densities. It has also demonstrated that photon damage does occur in TXPS. Data from the Scienta ESCA300 Database [48] have been modified for TXPS using a derived equation
to achieve an estimate of the sample damage rate. The extent of degradation can be predicted for many polymers and collected data can be used to extrapolate back to the pre-analysis concentrations.

Following the failure to obtain a convincing spectral analysis of the PMMA/PVC blend (section 8.2.2), there was some doubt whether TXPS would ever show a reliable polymeric analysis stemming from the fears of excessively high photon densities. This section and the Haloflex work has shown conclusively that damage levels were manageable, providing a small degree of care was maintained during analysis.

TXPS offers a route to microfocused XPS which only damages the area of analysis, rather than large areas of the sample from which the data are not collected. This is a significant advantage of TXPS over other imaging XPS techniques.

7.1.2 Joule Heating

In AES, Joule heating under the analysed electron beam spot can cause interdiffusion, segregation and perhaps evaporation. The temperature rise in bulk samples is given by

$$\Delta T \approx \frac{2}{k \pi} \left( \frac{P}{d_e} \right)$$

(28)

where \( P \) is the power of the electron beam and \( k \) is the target thermal conductivity [51]. Electron beam heating is generally not a problem with ceramics as a result of adequate thermal conductivity with respect to glasses, but in glasses temperature rises can be extremely high. See table 15.

Electron beam stimulated desorption is also a major problem in AES of insulators giving rise to time dependent loss of oxygen, nitrogen, carbon and boron from ceramic materials [51]. This is obviously detrimental to any quantitative analysis. Knowledge of the time dependency criterion does allow extrapolation to the pre-analysed concentrations.
In TXPS heating of the thin foils by the electron beam is also of concern. In TEM, dislocations are given sufficient energy to glide. The temperature rises in TXPS are of course considerably lower than TEM because of the thicker targets and lower accelerating voltages, but they must be considered, particularly since polymers will provide a large proportion of analytical samples.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal Conductivity $k$ (Wm$^{-1}$K$^{-1}$)</th>
<th>Temperature Rise, $\Delta T$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>390</td>
<td>2</td>
</tr>
<tr>
<td>Al</td>
<td>221</td>
<td>3</td>
</tr>
<tr>
<td>SiC$_{3}$ALN</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>17</td>
<td>40</td>
</tr>
<tr>
<td>Glass</td>
<td>0.8</td>
<td>880</td>
</tr>
</tbody>
</table>

Table 15

Steady State Temperature Rise $\Delta T$ for Different Materials Analysed in Point Mode by AES (10kV, 10nA, $d_0=0.1 \mu m$) [51]

The maximum thin foil temperature rise $\Delta T_{\text{max}}$ has been predicted under electron beam excitation by an equation derived by Castaing [52]

$$\Delta T_{\text{max}} = \frac{W}{4 \pi k e} \left( 1 + 2 \ln \frac{R}{r_0} \right)$$

where $W$ is the electron probe power, $k$ is the source conductivity, $e$ its thickness, $r_0$ the electron beam radius and $R$ the radius to a circumferential heat sink. The equation can be applied to a target foil in TXPS to predict the temperature rise. If the X-ray source is in contact with a sample, because the sample is thin with respect to the target, this will be the maximum sample temperature rise (source 1.6 $\mu$m, sample 200nm). Such a
calculation applied to TXPS experiments yields the values given in table 16.

Examination of equation 29 reveals the linear dependence of temperature rise with accelerating voltage. The sample thickness and specimen current are important too. Doubling the specimen current does not quite double the temperature rise, since the electron beam diameter is increased according to

\[ d = 66 \left( \frac{1}{i} \right)^{\frac{1}{2}} \]  

which describes the electron beam characteristics of the MA500 (d is the beam diameter in nm and i is the specimen current in nA). Converting equation 30 into appropriate units for substitution (m and A) into equation 29

\[ r_0 = 1.044 \times 10^{-3} i^{\frac{1}{2}} \]

Thus

\[ \Delta T_{\text{max}} = \frac{Vi}{4\pi ke} \left( 1 + 2 \ln \frac{R}{1.044 \times 10^{-3} i^{\frac{1}{2}}} \right) \]

This equation applies for the specimen temperature rise in the MA500, where \( V \) is the accelerating voltage and \( i \) is the specimen current (\( R=10^3 \text{m} \)). It highlights the danger of sample overheating when increasing the specimen current. In terms of heat conduction away from the point source, it would be advantageous to increase the target thickness. However, this will reduce attainable lateral resolutions in TXPS by X-ray spreading and there will be a general loss of signal through X-ray self-absorption.

Table 16 shows that for most samples the temperature rise by Joule heating and subsequent energy transfer will not be a problem. TXPS results in this thesis seem to agree that \( \Delta T_{\text{max}} \) is small. No great signs of polymer damage have been found. Providing specimen currents do not exceed a 1µA at analysis voltages, Joule heating should not be a problem with polymeric samples. Quadrupole monitoring of gas emissions from Haloflex polymeric samples under analysis showed no change in vacuum level (5x10^{-9} Torr) throughout a period of specimen current increases up to 520nA at 9.5kV. A slight brown colouration on some polymeric samples was observed after
excessive periods of analysis. This colouration was certainly not any worse than is frequently observed in conventional XPS and was most likely from photon damage instead of Joule heating. Fluorine is an element notorious for loss under adverse analysis conditions, but it remained present in the TXPS sample right up until removal from the vacuum system. Neither a PMMA/PVC blend nor a Haloflex primer material showed any signs of degradation from Joule heating. The sample and target foil can always be separated by a copper grid to reduce any chance of overheating.

<table>
<thead>
<tr>
<th>Source &amp; Thickness (μm)</th>
<th>Accelerating Voltage (kV) at 1μA specimen Current</th>
<th>ΔT_{max} (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Two 0.8μm aluminium</td>
<td>10</td>
<td>30.9</td>
</tr>
<tr>
<td>3μm Silicon</td>
<td>20</td>
<td>55.3</td>
</tr>
</tbody>
</table>

Table 16
Sample Temperature Rises from Castaing's Equation (R_0=1mm).

7.2 Specimen Charging

7.2.1- Charging in AES

Sample analysis in AES of insulating materials is a difficult process. Unlike XPS, samples could charge both positive or negative, so charge compensation is far more difficult. These subjects are dealt with by Hofmann [51]. Whether a high resistance sample tries to charge positive or negative is dependent on the ratio of primary electrons to emitted secondaries.

\[ \delta = \frac{I_S}{I_p} \]  \hspace{1cm} (32)

When \( \delta = 1 \) there is no charging. When \( \delta > 1 \), the sample attempts to charge positive and
when $\delta<1$ negative charging occurs. In AES there is an abundance of low energy secondaries. Hofmann suggested that for samples where $\delta>1$, as the sample surface charges positive, the secondary electrons are attracted back lowering $I$, and reachieving ground potential. The surface charge thus vanishes. A high negative charge can build up in AES ($\delta<1$) which can deflect or indeed, in extreme cases, reflect [51] the beam. Negative charges cannot be as easily dealt with as positive charges; they can be a serious problem.

The charging effects are reduced by a variety of methods including the reduction of primary beam current density, improving the conduction paths by conducting grids or coatings and having only a thin insulating layer, lower than the range of the primary beam. Impurities, dopants or introduction of irradiation induced defects can be used to reduce the specimen resistivity. Heating can be used to increase conductivity but may lead to elemental surface enrichment by diffusion and segregation. Increasing the angle of incidence with respect to the normal increases the total secondary electron emission and will therefore increase $\delta$. Irradiation with low energy electrons can increase secondary emission and also reduce surface charging. This has been explained by positive charge trapping and production of defects. Ions, below the critical threshold for sputtering, can be used to supply surface positive charges to neutralise negative charging. Ultra-Violet photon radiation with energies just above the band gap also increases surface conductivity.

7.2.2 Charging in XPS

In conventional XPS, if the sample is sufficiently conducting, the positive charge that results from the loss of electrons from the photoionisation process is neutralised by electrons from the earthed specimen bulk. However, in insulators, this neutralisation can only be partial, leaving a positive surface potential. This value typically varies from a few Volts to several tens of Volts [53] and so electron kinetic energies are
reduced by the same factor. In XPS the degree of charging reaches an equilibrium level after a few seconds exposure to the X-ray beam. Charging of the sample in XPS is not as severe as would be expected for two reasons. Firstly, stray electrons from the sample chamber help the neutralisation. They are created by the characteristic X-rays and Bremsstrahlung from the X-ray window of the X-ray gun. Secondly, the positive charging prevents the low kinetic energy tail of the secondary electron peak escaping.

Differential charging is a problem in XPS. This is when separate areas of the sample surface have different resistivities and so reach different equilibrium potentials with respect to the spectrometer potential. This makes spectral calibration less reliable. The problem is evident when the sample matrix is a conductor and contains non-conducting clusters.

In XPS spectral charging problems are reduced or eliminated by the use of several procedures.
1) A thin insulating layer on a conducting substrate allows electrons from the substrate to tunnel to the surface and eliminate charging. This effect is apparent with layers from a few tens to several hundred Angstroms, dependent on the insulator properties.
2) Internal reference may be used which relies on a spectral peak being accurately assigned a kinetic energy. C-H/C-C of C1s on polymers may, for example, be used at 285eV (BE). Extraneous hydrocarbon contamination, which is always present on a sample surface from handling or diffusion pump oil can be accurately assigned a peak position and thus be used for calibration purposes.
3) A thin gold coating on the surface can also be used for calibration because of its inertness. Au4f7/2 is given the value 84eV (BE).
4) Cunning methods do not try to remove charging effects, but use relative peak positions to obtain chemical states of atoms by examining the difference in energy of two core levels. It allows acquisition of either chemical state or direct compound determination. Another procedure uses the modified Auger parameter [54]. Here the sum of the binding energy of the photoelectron and the kinetic energy of a core-core-core Auger peak of the same element is independent of charging. Both figures are charged by the same amount. Information is thereby directly available on the extent of extra-atomic screening of core holes.
Plasmon and interband transition losses on the low kinetic energy side of the peaks are also independent of charging.

5) Electron flooding can be used to neutralise the positive charge. This method is particularly useful when there is differential charging and is also necessary when monochromated X-ray sources are used.

7.2.3 Charging in TXPS

Cazaux [55] has recently studied sample charging using his multi-purpose TXPS instrument. His aim was to study the effect at high photon densities, rather than specifically TXPS. To eliminate any electron beam heating and electrical conduction via the source foil, 0.32mm thick mica was placed between the sample and the aluminium.

Fig.86
5µm Polycarbonate Film Studied by Cazaux [55].
(a) Radiation Damage Seen as an Increase in C/O Ratio with Time.
(b) Charge Shift Indicating a Time Dependency.
His first experiment used a 5μm polycarbonate film (C\textsubscript{10}H\textsubscript{14}O\textsubscript{3}), with the electron beam held stationary; monitoring the C\textsubscript{1s} and O\textsubscript{1s} peaks over one hour. Peaks were not only shifted by the film charging positive, but the O\textsubscript{1s} intensity decreased with time indicating a change in chemical composition. See fig.86a. The critical damaging dose was calculated to be 10\textsuperscript{12}-10\textsuperscript{13} Alkα photons/mm\textsuperscript{2} from Green and Cosslett [29]. This correlated with the optical observation of a brown colouration of a few micrometers diameter. When this experiment was repeated with a raster frame of 200μm, to reduce the photon density to 3x10\textsuperscript{9} photons/s/mm\textsuperscript{2}, the O\textsubscript{1s} intensity was stable. The brown colouration was no longer observed. Time dependency of C\textsubscript{1s} peak position was still observed, shown in fig.86b, with a maximum of +53V charge shift and a time constant of 19 minutes in

\[ V_s(t) = V_s(\infty) \left( 1 - e^{-\frac{t}{\tau}} \right) \] (33)

In this thesis, TXPS charging of thin samples was observed. Normally, it was less severe than seen in Cazaux's observations and stability was achieved in under ten seconds. Charging shifts were only a few electron volts in the positive direction; similar to those observed in conventional XPS. With Haloflex, for example, +3eV shifts were typical. Specimen films in contact with the source charged very little as charge compensation can occur via electrons from the source conduction band. The non-contact films charged to a greater extent because there was no conduction from the target and less emitted electrons reached the film.

Some negative charging was occasionally observed in TXPS. Initially this seemed somewhat surprising but the phenomenon was fairly easily explained. Up to 30eV of negative charging was sometimes recorded with unetched polymers on an aluminium sources. A narrow scan showing negative charging is given in fig.84. Both the targets and samples were found to be charging, although the shifts returned to positive values following short argon ion etches. Identical analysis conditions were used for both the etched and unetched samples. The TSEM images at the ideal voltage were very poor and the TXPS spectra had small high energy backgrounds, so the primary electron beam was not being transmitted. These observations led to the conclusion that it was principally the sources that were charging up and taking the samples with them. Poor
source to stub earths, coupled with the fact that the secondary electron emission function of aluminium is below unity (the number of emitted secondaries is lower than the electron beam input) [56] resulted in the negative potential drift. Ion etching cleaned the source surfaces sufficiently to remove the poor earth problem and permit normal positive TXPS charging, similar to XPS.
8.0 APPLICATION OF TXPS TO MATERIALS SCIENCE

An XPS technique which can give a high degree of spatial resolution would have many potential applications within materials science. In conventional XPS and small area techniques sample preparation is minimal, with only the requirement of careful handling to avoid surface contamination. In-situ fracture techniques largely avoid even these problems. Unfortunately TXPS requires thin samples, preferably sub-micrometer (100nm-1μm).

Sample preparation has always been the key argument against TXPS, but developments in ultramicrotomy mean thin film preparation is now routine in TEM for a wide range of problems in material science. Samples may also be ion beam thinned from the bulk side towards the surface of interest. Thus the difficulties in preparation of suitable soft X-ray transparent specimens has largely already been overcome by the electron microscopy community in their quest for electron transparency. Care must obviously be taken to ensure that the preparation procedure does not destroy or distort the very chemical information required. TXPS specimens are generally restricted to hard and soft materials. There are cases where hard materials in contact with soft materials could be analysed. Further sample preparation is required as discussed for Haloflex/mild steel in section 8.5. Table 17 shows some of the possible uses for TXPS, some of which are discussed in this chapter. The table demonstrates the contribution TXPS can make to each field, with its improved lateral resolution, relative to other small area XPS techniques.

The following chapter shows how the TXPS technique was taken from an experimental instrument to a real analytical tool capable of collecting XPS data useful to the materials scientist. The problem of dealing real samples were tackled, overcoming problems such as specimen alignment at low magnification and exact methods of TXPS sample preparation. Examples of samples made from hard, soft and mixed materials are given together with the resulting data. Interpretation of the information is attempted along with discussions of various TXPS data limitations.
## Application of TXPS to Materials Science

<table>
<thead>
<tr>
<th></th>
<th>XPS</th>
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<th>iXPS</th>
<th>TXPS</th>
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<td>$10^4$</td>
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<td>Pull-out &amp; Inter-lamina Pathways</td>
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<td>Etch Profiles</td>
<td>Surface Blemish</td>
<td>Etch Bevel Analysis</td>
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<td>Tapered Sections</td>
<td>Locus of Failure in Peel Tests</td>
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<td>Surface Blemish</td>
<td>Large Pit Electro-Chemistry</td>
<td>Correlation of Potential &amp; Composition in Pits</td>
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<td>BIOCOMPATIBILITY</td>
<td>Implant Surfaces</td>
<td>Tablet Homogeneity</td>
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<td>Diatom Surfaces</td>
<td>Cell Adhesion</td>
<td>Tissue Sections</td>
</tr>
</tbody>
</table>

Table 17

The Uses of TXPS and Various Other Small Area XPS Techniques in Material Science at Different Attainable Lateral Resolutions.
8.1 **Ultramicrotomy**

Ultramicrotomy is a technique developed for directly slicing tissue sections for biological light microscopy. Firmly mounted samples (1mm x 1mm) on a pivot arm are moved past a sharpened diamond knife or freshly prepared glass knife. The slices are collected in a liquid filled trough.

The sample is advanced by the desired thickness by thermal or mechanical means after each cut. Glass knives are prepared from freshly broken glass which will become blunt after a few cuts of harder samples. Thus with glass knives, much time is spent preparing them. Diamond knives are more generally used for the harder samples but these are, of course, expensive.

There are now many examples where ultramicrotomy has been used for preparation of films in material science; most of which require the diamond knife [57]. Copper and aluminium, both ductile materials, can be successfully microtomed as well as brittle ceramics such as mullite, silica glass and alumina [58]. Soft materials undergo a progressive slicing but with hard materials it is a controlled fracture. Cutting is known to introduce damage in the metal in the form of high dislocation densities and perhaps twinning [59]. Ultramicrotomy may also be used for preparing foils from materials where there would be great difficulty by other techniques. Porous materials such as bone, two phased materials, crystals in difficult orientations, oxides on metals and metal powders may all be sectioned under the correct conditions [60].

Where only small samples are available, for example powders or thin polymers, the samples can be set in a resin. This gives the sample sufficient rigidity to mount in the grips. Rapidly solidified aluminium alloy powders (0.5–50μm diameter) have been sectioned in this manner to thicknesses between 30 and 100nm [57]. They did, unfortunately, have a tendency to curl up. Although dislocations were introduced by sectioning there was no evidence of elemental redistribution.

Carbon fibre/epoxy resin systems have also been successfully thinned by ultramicrotomy despite the obvious difficulty of the difference in mechanical properties between fibre and matrix [61]. A difficulty with maintaining the fibre in the cross section was observed.

Polymers and polymer blends may be cut by ultramicrotomy with control of the
cutting temperature. Above the glass transition temperature ($T_g$) there is considerable distortion of the cut section. Circular sections are made elliptical and stretch lines are caused perpendicular to the knife cutting direction. Temperature can be controlled down to liquid nitrogen temperatures (+/- 2K) using specially designed cryomicrotomes. However, too far below $T_g$ the specimen may shatter during slicing. Polymer blends are often difficult to cut because of differences in $T_g$. Polymers are swollen by many solvents normally used in the collection trough and for this reason polymers are often microtomed dry, with no collection fluid. This problem is particularly important in cryomicrotomy, where there are few suitable solvents to begin with. Where polymers are embedded in resins there is a danger of swelling when mounting. There is a reasonable selection of resins to choose from so that such a problem can be avoided.

Porous structures such as crazed polymers will collapse under cutting conditions, so, for satisfactory ultramicrotoming, it is necessary to use a reinforcing impregnant. The impregnant must be liquid below $T_g$ to allow voids to fill, and solid at the sectioning temperature. Sulphur, for example, can be used for glassy polymers as it sublimes under high vacuum. If the impregnant cannot be easily removed, it must be distinguishable from the sample. This, in the case of TEM, means having a different electron density, but in TXPS it will be more complicated. For TXPS imaging, elemental differences between the film and impregnant will be sufficient but TSEM imaging will show no topographical contrast. Their use also will be ill-advised on grounds of chemical state and surface interference.

Crystalline polymers are difficult to section as a result of the toughness of spherulites which locally change mechanical properties. Hard fillers or pigment particles in paints also can cause local tearing of the film. In this thesis primer samples were prepared by ultramicrotomy. The sample shown in fig.87a was made by painting mild steel with ICI Haloflex and allowing it to dry. The steel was then dissolved off, using an iodine/methanol stripping rig [62], leaving the primer and an interfacial interaction region intact. Ultramicrotomy permitted 100nm sections to be cut by floating onto water and, apart from a small amount of tearing and filler/pigment loss, there was little damage to the sample. Particles were lost simply because of their size and hardness relative to the cross-section (see appendix 4). The interfacial interaction region, about 4μm across, remained undamaged. See fig.87b.
Fig. 87

High and Low Magnification TEM Images of Microtomed Haloflex with an Interfacial Darkening Corresponding to a Surface Reaction Region, all Set in a Polystyrene Based Mounting Resin.
8.2 PMMA/PVC Sample Analysis

A PMMA/PVC 50/50 blend was the first sample material to be analysed by TXPS. The polymer blend was imaged using ToFSIMS [63] and the two components were observed as separate phases, in a chlorine map, with irregularly shaped domains of PVC approximately 50 to 150 μm in size. Courtaulds supplied the material as a test sample to explore the capabilities of TXPS, with a view to supplying samples for analysis studying polymer interdiffusion.

The polymer blend samples were prepared by Courtaulds. They were embedded in a resin and then cryomicrotomed to thicknesses between 100 nm and 1 μm in 100 nm steps. Samples were placed onto coarse TEM copper grids. The samples were used to investigate sample preparation and handling procedures required for TXPS of polymers.

8.2.1 Sample Alignment Prior to Analysis

Once a polymer sample on a grid was mounted on a source foil in the spectrometer, the film was too small to see. The films on the target looked transparent in reflected light microscopy and could not be seen by transmitted light microscopy. Tilting the light source in a low magnification microscope made the films appear like oil on a puddle. Unfortunately, stretching of the thinner films between the coarse grid bars meant the whole film could not be observed at once. Some parts of films appeared transparent to light at certain orientations but not at others. Rough film shapes had to be sketched, rather than photographed, because of the tilting needs to see all the film. Optical microscopy, prior to mounting, identified the best areas of the sample for analysis with respect to the grid. The film was much more visible than after mounting. Tilting, when no source was present, even revealed film overlaps where it was effectively twice as thick. Grid coverages were less than 50%, being worse with thinner films. Film edges normally could be seen, but it sometimes proved difficult to distinguish between thin polymer stringers and the true film edge. As expected, the thickest films were found to have the best coverages and were the most stable on handling.
In later Haloflex work the confocal laser scanning microscope (CSLM) was used to produce quick reference images of the grid and sample prior to source mounting. CSLM did not suffer from film stretching effects. The CSLM was also used to image the mounted films. The images were not as clear, but were more reliable than sketches!

8.2.1.1 Scanning Electron Microscopy for Film Imaging

Low accelerating voltages and low specimen currents were used to image the sample immediately after introduction into the analysis chamber. An example image is shown in fig.88 with a copper grid on top of a polymer film and an aluminium source underneath. The image showed the micromached specimen as not being flat. The instrument magnification would not go low enough to image the entire grid and sample and so a montage had to be made from several images. The SEM image did not suffer from any polymer stringer problems and unambiguously disclosed the shape of the target film to be analysed by TXPS. Obviously, the polymer blend could not be distinguished from its mounting resin.

When the sample was rotated into its analysis position, imaging became far more difficult. At the ideal voltage, very few secondaries were available from the top of the sample, being only created by X-ray excitation. This would not produce an image which will be quick and useful for sample alignment. By increasing the accelerating voltage slightly to 11 or 12kV (at 10nA), imaging was possible as the interaction volume extended beyond the aluminium target.

Higher accelerating voltage images were by no means clear and straightforward to interpret. They were disguised by foil thickness contrast and artifacts of specimen and grid orientation. PMMA/PVC samples were placed both in contact with the target and separated by a grid. The advantages and drawbacks of each system will now be discussed for analysis and imaging.
8.2.1.2 Sample and Source Contact

The arrangement with the aluminium source and polymer film in contact is shown in fig.89a. Binocular optical microscopy, with careful control of the illumination direction, allowed the side of the grid that the film was placed on to be determined. The film could not be removed from the support grid onto the aluminium alone. This in fact proved more an aid to analysis than a hindrance. The grid squares acted as a useful guide around the specimen and help with orientation.

The first thought when considering the contact arrangement is Joule heating of the sample which has been discussed previously and appears not to be too serious. X-ray spreading is minimised and so will ultimately produce the highest TXPS lateral resolutions. Transmitted secondary electron imaging proved easier in this case as can
be seen in fig.89b, which corresponds to the earlier reflection SEM image in fig.88. The 600nm film absorbed the transmitted electrons from the projecting interaction volume and so appeared dark with respect to the target. Grid bars could not easily be seen in the images as a result of their fineness and separation from the Source. However, they could be picked up by careful observation. Contact of the polymer and the aluminium ensured a reasonable degree of image sharpness; a quality which was not matched in the non-contact geometry.

Fig.89
(a) Sample Contact Schematic, (b) 12kV Transmitted SEM Image of a 600nm PMMA/PVC Sample on 1.6μm of Aluminium Foils (15nA).
At 9.9kV, close to the ideal voltage for aluminium alone, an image could be seen at 100nA or more. It was far from clear. It did in fact show the same shadow image as at 12kV, but poorly. The aluminium surface showed up as bright spots where there were local thin regions in the foils and, in occasional cases, pinholes. See fig.90. The interaction volume protruded in these thin areas. The X-rays were unable to contribute to the image with any great effect.

Fig.90
9.9kV Transmitted SEM Image of 600nm PMMA/PVC Sample on 1.6μm of Aluminium Foils (400nA).
8.2.1.3 Sample and Source Non-Contact

In the non-contact geometry the X-ray source and sample were separated by the copper supporting grid, as shown in fig.91a. Thus the film would only suffer from photon damage and would avoid Joule heating. TXPS lateral resolution would be degraded by X-ray spreading in the gap between the aluminium and sample. Transmitted SEM images mainly showed the grid, which was 11μm thick. This totally absorbed imaging electrons and so appeared dark. The sample was far less clearly defined than in the contact case, and it appeared as a general darkening in the image. See fig.91b. Escape of a proportion of electrons, emerging from the back of the target around the sample to reach the photomultiplier and the remainder being absorbed by the film, gave a combination of two images: One of the aluminium topography and the other a shadow of the film. This was proved by increasing the accelerating voltage so the electrons were also transmitted through the film. This image appeared to be a totally aluminium surface with no local darkening. This film/grid orientation was definitely much harder to work with than the contact case and was not so effective as a low magnification specimen alignment procedure.

Transmission SEM imaging of 100nm thick microtomed films proved almost impossible in the non-contact case. The only guide to sample orientation appeared to be the lack of bright spots in polymeric regions. The image seemed totally dominated by aluminium topography. The extra thickness of sample made little difference to the total thickness and so samples could not be resolved.
Fig. 91

(a) Non-Contact Schematic, (b) Transmitted SEM Image 400nm PMMA/PVC Sample on 1.6μm of Aluminium Foils (12kV, 15nA).
8.2.1.4 **Effect of Bent Grids on TSEM**

![Image](image_url)

**Fig. 92**

(a) 12kV Transmitted SEM Image of the Non-Contact 400nm Sample on a Bent Grid (15nA).

(b) Schematic Explaining the Image Appearance in Terms of Proportions of Secondary Electron Escape.
These observations were noted when attempting TSEM imaging of the PMMA/PVC film in the non-contact mode. The transmitted image of the copper grid apparently faded and disappeared on traversing the specimen leaving only aluminium source roughness effects. See fig.92a. Changing the accelerating voltage and specimen currents did not improve the situation. The results were only explained after analysis by optical microscopy. The grid was partially lifted off the aluminium as a result of the central bend in the grid. The washer was not clamped down hard onto the stub which normally avoided foil tearing during sample preparation procedures. Therefore, as the electron beam was moved further away from the region where the aluminium and grid were in contact, less of the transmitted electrons were lost to the grid and the image became fuzzier. It eventually disappeared when significant proportions escaped around the grid. This effect is clearly shown in the schematic fig.92b.

8.2.2 TXPS of PMMA/PVC Blend

This work was carried out on polymer blends set in resin poorly prepared by Courtaulds. Over the entire analysis period no convincing PMMA or PVC spectra were obtained. ToFSIMS showed precious little evidence of chlorine in the samples after considerable gallium ion etching, except one small region of chlorine which appeared to be associated with the grid rather than the polymer film. Nevertheless, the samples produced some promising results showing the prospects of analysis by TXPS and the polymers seemed to be able to withstand excessive analysis times and power densities. The accumulated results shall now be examined together with their use in making TXPS of polymers far more routine.
8.2.2.1 Initial Work

This work used a silicon source in non-contact with the sample films. The possibility of reliable TSEM imaging had not been realised at this point for fear of specimen damage, and so spectroscopy was based very much on random point analysis. The analysis did provide some useful early results and is shown in fig.93. It showed sharp C1s and O1s peaks and broadening on the low kinetic energy side of the C1s 20eV narrow scan, which demonstrated convincing chemical state energy resolution. The spectra bore little similarity to those expected from PMMA or PVC and it was initially suggested that it was a carbon overlayer [30]; an idea which was unfounded on the basis of the large inelastic C1s background.

Fig.93
200nm Thick Microtomed Resin Contaminated PMMA/PVC Wide and Narrow Scans showing Chemical Shift on the C1s Peak (20kV, 2.2μA, 600s (100eV ,CAE=20eV Respectively)).
In this blind point analysis work evidence of a charge shifted Cl2p peak was found (shifted by 20eV) and is shown in fig.94a. Regrettably, the silicon source was clean enough to have several plasmon peaks as shown in fig.94b and so it was likely that the suspect Cl2p peak was in fact a second plasmon from Si2s. The second plasmon and Cl2p overlap since the second plasmon should be at 1540.2eV (KE) and the Cl2p peaks are at 1538 and 1540eV. Plasmon shift data were found from EELS [34], giving $E_p=22.9eV$ for SiO$_2$. This is given as Appendix 1. A digital map was taken of the suspect PVC containing regions but, for the reasons detailed above, it was in fact a silicon map rather than a chlorine map. Silicon source work was discontinued with the Courtaulds material, and aluminium was used as a replacement.
8.2.2.2 **Continued Work with the Resin Contaminated PMMA/PVC**

Initial spectral analysis of the 400nm non-contact PMMA/PVC sample revealed a contaminated overlayer across the sample and source surface. Thus the sample was lightly ion etched. As a result of the TSEM images showing little convincing contrast between the target and film regions, 9.5kV point analyses were used to try to determine the orientation of the specimen. It should be noted that the orientation confusion was a result of the bent copper grid's strange imaging effects. The points from the bent grid region gave both high and low count rates and the relative peak intensities varied slightly. The spectra could be generally categorised into three sets as listed below:

<table>
<thead>
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<th>Signal</th>
<th>Count Rate</th>
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<tr>
<td>Al &amp; O, little C</td>
<td>good*</td>
</tr>
<tr>
<td>O &gt; C</td>
<td>good</td>
</tr>
<tr>
<td>O &gt; C</td>
<td>poor</td>
</tr>
</tbody>
</table>

These results were consistent with the analysis of an aluminium surface. Some background intensities were high which suggested that analysis was performed over the ideal voltage. Spectra were similar to fig.95*.

![Fig.95](image)

**Fig.95**

Typical Contaminated Aluminium Source Spectrum (9.5kV, 1µA, 300s CAE=200eV) (Corresponds to the Previous List).
After analysis of several regions and imaging at 12kV, some point spectra showing the sample were taken (see fig.96a). At and around point 3 in the image, aluminium was found, but at points 1, 2 and 4 polymer was seen. A typical polymeric spectrum from these points is shown in fig.96b with carbon and oxygen peaks. Note that the C1s inelastic background is stretched relative to the 200nm sample in the initial work (fig.93).

The SEM image of the sample is given in fig.97 which can be compared to corresponding bent grid transmission image (fig.92a. The 'W' shape in fig.92a corresponds to the 'U' shape in fig.97. Grid distortion made the images different. The micrographs were effectively rotated about a central axis by the geometry of imaging. The light film tear region just above and left of centre in the SEM micrograph was analysed in transmission and point analyses were able to unambiguously distinguish between the film and source. Further TXPS of this sample concentrated on the bottom left dark region of fig.96a, where it was clear only polymer was being analysed. TSEM contrast in other areas gave little useful indication of whether the film and target foil was under investigation.
It became clear from spectra that there was uneven levels of contamination over the sample, and it required further ion etching. A procedure of etching and analyses of the dark region was carried out to try to remove a smeared resin layer. It was known that PVC was highly susceptible to chlorine loss but, at the time, finding the polymer blend in the resin was only of concern. Intermediate reflection SEM images showed no curling of the polymer film edges or any other obvious signs of degradation throughout the period of analysis. The vacuum level was stationary at 10^{-8} Torr but quadrupole residual gas monitoring would have been the most reliable confirmation of no degradation. Point analysis revealed nothing that resembled PVC throughout the extensive analysis period and the Cls/Ols ratio remained stable. Five ion etches were performed in total and it was not until the final etch that a substantial change in ratio was noted. The fifth etch was prolonged relative to other etches (2 mins. at 6 kV relative to 30 s or less for earlier ones). Reflected light microscopy later revealed the whole film to have taken on a brown colouration.
To examine sample degradation, C/O peak ratios from similar analysed points were compared. See table 18. No doses or accurate etch times could be assigned to these data, although the ion gun (Ion Tech source producing an elongated and diverging argon etched footprint from an aperture 1 x 5mm) did maintain a constant power. The samples were waved in front of the ion beam in an attempt to get a homogeneous etch independent of sample contours (from the grid, etc.). The unetched specimen showed a carbon overlayer which was quickly removed. The C/O peak ratio then remained stable, at least within point analysis area error, until the final etch. The fifth etch appeared to have degraded the specimen rather than removed the smeared mounting resin. Again no sign of PVC was seen, or indeed PMMA. It was comforting, however, to see the ion beam was causing more degradation than the high photon density X-ray beam coupled with the transmitted electrons at 9.5kV.
<table>
<thead>
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<th>Number of Ion Etches</th>
<th>C1s/O1s Ratio</th>
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<tr>
<td>1</td>
<td>4.0</td>
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<tr>
<td>2</td>
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<td>5</td>
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Table 18  
Argon Ion Etching Effect of the C1s/O1s Ratio in Wide Scans.

8.2.2.3 TXPS Analysis and Mapping of a Contact PMMA/PVC Sample

In this sample the two films were 600nm thick, which was a substantial proportion of the source thickness. They can be clearly seen underneath the grid in fig.88 and in the corresponding transmission image in fig.89b. The films appeared folded which could have introduced distortion into film TXPS images and degraded lateral resolution.

Point analysis at 9.5kV of the unetched sample showed significant differences between a film and source region. The high transmitted electron background (fig.98a) demonstrated this region to be the target surface. The source was contaminated as was the polymer region in fig.98b. Neither spectra gave any chlorine and so ion etching had once again to be employed. It should be noted that the shifts to higher kinetic energy (negative) were caused by the DVM mistakenly being left on the μA setting. This applied a bias to the specimen to read the specimen current and gave the peak shift. The apparent charging here should be ignored.
The first light ion etch revealed copper 2p and LMM peaks in the spectra apparently independent of whether analysis was on or off the grid! See fig.100a. The copper signal was related not to the contact geometry, but to the high rim on the particular stub clamping washer used. Transmitted X-rays, through the aluminium or film could strike the inner edges of the rim to excite copper spectra. Photoelectron peak shapes were expected to be the same as those in conventional XPS because the X-ray intensity was greatest at the sample surface. Peaks would not contain the emphasised inelastic components of TXPS. Copper signal distribution across the whole exposed source revealed something about the divergence of the X-rays. For a reasonably high copper intensity at the source centre the X-rays must have been fairly divergent. The P-B map in fig.99 displays the grid bars and stub edge as dark blue and black respectively. The Cu2p intensity was fairly uniform within one grid hole no matter how near the point was to the grid bars or where analysis was on the sample.
This was manageable in terms of removal of stub contributions to, for example, the O1s signal, but not very encouraging in terms of confidence in spatial resolution. Divergence was at least 45°.

Fig. 99
Cu2p3/2 Map to Demonstrate Alkα Divergence (9.5kV, 700nA, 2.7hrs., CAE=200eV).

Fig.100a shows a typical point analysis from this first etch. The squareness of the background had given way to a more typical TXPS spectral shape largely showing carbon with no evidence of chlorine. A second light etch brought out the copper still further. An example spectrum is fig.100b.

Having chosen a general area of interest at 12kV (see fig.89b), the accelerating voltage was reduced whilst maintaining focus to ensure no loss of lateral resolution. At this point TXPS mapping was performed to try to find the PVC in the sample. C1s, O1s, Al2p and Cl2p were mapped at 200eV pass energy. This took nearly 10.5 hours. The Link 860 computer was only capable of handling two peak and background windows simultaneously, and so this experiment was performed over two days.
Both Al2p and Ols displayed similar maps, with bright spots in locally thin areas of the aluminium. See fig.101. The P-B algorithm coped well with differentiating between the sample film and the source, but there was aluminium noise in the film regions. P-B did not bring out the required information in the C1s image but it was clear using the (P-B)/B algorithm. The stub edge appeared white here and the source black with some noise. It was true to say that (P-B)/B was not a good indication of absolute intensity, but it was useful in this specific case. The film surface regions suffered from an attenuated X-ray intensity because of the extra 600nm thickness. It will be shown in section 8.5.1 that the concentration differences across an individual film can be considered in TXPS without need for (P-B)/B.

The C12p map appeared to show a high intensity region just above centre in both P-B and (P-B)/B images. This could not be confirmed by later point analyses.
Fig. 101
TXPS Images of Double Etched Sample (9.5kV, 400nA, CAE=200eV) (O1s, Al2p & Cl1s: 2.7hrs., Cl2p: 2.5hrs.,)
8.2.3 Conclusions

The previous work, although not being particularly useful as analytical results for the Courtaulds specimens, began to demonstrate the potential of TXPS as a high lateral resolution XPS tool. The technique had successfully performed both local analyses and mapping on a specially prepared sample. Sample preparation procedures and microtoming seemed adequate and Transmission SEM helped in sample alignment; something which is frequently difficult in imaging XPS techniques. Sample thermal stability appeared to be good, although more work was required in this area such as quadrupole monitoring of emitted species during analysis.

The results highlighted the importance of attention to detail in sample preparation. Careful preparation of sources and grid choice promised to make analysis a far more routine practice and yield data useful to the materials scientist.

8.3 Imaging Using the Confocal Scanning Laser Microscope (CSLM)

This instrument is essentially a transmission and reflection light microscope, but it uses a laser as a light source. It has both a red and blue laser. A laser has the ability to be focused through the surface enabling the subsurface to be examined. The subsurface cracks may be traced in a glassy ceramic reinforced by silicon carbide, or reinforcing fibres may be imaged whilst still in their polymeric matrix. Such depth profiling is possible because the bulk of the sample is transparent to the laser wavelengths used. When the laser is focused on a plane at a given distance it appears bright. Thus, by focusing on a polymer film followed by the aluminium source support the difference in focal lengths yielded the film thickness. This technique was used for NaFion in section 5.1.4.

The main use of the technique in TXPS work was the imaging of microtomed sections on TEM grids. It was pointed out in section 8.2.1 how difficult the films were to image to discover sample geometry. Slight curvature in the films meant that the light source in reflected light microscopy had to be moved into several different
orientations to disclose the true shape of a microtomed section. This made optical microscopy impractical so sketches had to be drawn. The CSLM allowed quick acquisition of reference images, because although the grid bends did not allow all areas to be totally in focus at once, the image quality was still good. Across an individual film the image was very clear. An example Haloflex film is shown in fig.102 with the primer surrounded by mounting resin. The interfacial interaction region is just visible to the right hand side of the paint layer.

TEM imaging of the films after preparation was unadvisable because of the tendency for deposition of carbon under the electron beam, as well as obvious risks of chemical state interference from electron beam damage. The field of view of the TEM was also too small at its lowest magnification to image the entire grid. As a consequence of poor transmission SEM images in TXPS it was often necessary not only to be able to know how far the film was from the central 'A', but also its position with respect to the grid edges. These reference points all made the position of the sample easier to ascertain.

Fig.102
An Ultramicrotomed Haloflex Primer Sample and its Mounting Resin on a Copper Grid (Pitch 125μm)
8.4 Use of Evaporation Sources

The TSEM and TXPS lateral resolution requirements for specimen and X-ray source contact produces a viable case for the use of the source evaporation methods in section 3.4. Ultramicrotomed sections (approximately 400nm thick) mounted on copper grids are generally fairly rigid and, therefore, do not need any further support if the area of specific interest is set in the bulk cross-section. A problem arises when the area of interest is close to the film edges. Here cross-sections tend to curl up, so to allow surface analysis they must be mounted on grids and carbon support films [57]. These are normally 5-20nm thick and so the sample and source foil cannot then be in contact in TXPS unless an evaporation source is used. See fig.103. The carbon films provide a perfect all-over backing substrate for the aluminium. The complete coating means that the sample will not suffer from any transmitted primary electrons or its induced secondaries.

![fig.103](Evaporation Source for TXPS when the Ultramicrotomed Section Needs to be Kept Flat to the Analyse Film Edges.)
8.5 **An Interfacial Interaction Region Between Mild Steel and Haloflex Primer**

To form a continuous film many paints are polymeric. Most anti-corrosive binders (binders make up the body of a paint) used for primers on steel substrates are solvent based and generally exhibit better barrier properties than water-based systems. Water soluble polymers, derived from vinyl alcohols, acrylic acids and acrylonitriles, have poor protective properties as a result of their permeability to water vapour and oxygen, both requirements for the cathodic reaction in steel corrosion. Solvent-borne paints are based upon xylene, ethylene glycol, etc. The reason there is still interest in water-borne coatings is a result of the United States "atmospheric release of pollution laws" coupled with the rising cost of oil-based derivatives.

ICI have investigated the failures of water-borne systems [64] and classified them into two principal categories. The first suggested the emulsion did not provide a sufficient barrier to water and oxygen diffusion. The second blamed the requirement of large quantities of surfactants which could react with the monomer to give graft copolymers. These inhibited full particle coalescence during film formation which ultimately prevented the film achieving the required barrier properties.

ICI overcame these failings using a polymer based on chlorinated rubber technology. The Haloflex (Appendix 4) latex had a low permeability to water and oxygen coupled to a good resistance to a wide range of chemicals despite being water-borne. Its chlorine content was suggested the reason for the good barrier properties. This was achieved by copolymerising vinyl chloride with vinylidene chloride with additions of acrylic acids to control the film forming characteristics as well as introducing thermal stability. Haloflex had been seen to slowly dehydrochlorinate in alkaline formulations and systems. It was for this reason that the Haloflex paints were designed to end with a final pH of 4 to 5. This negated the dehydrochlorination. Pigments such as zinc phosphate were chosen which buffer the paint in this range and surfactants and thickeners were chosen to be effective at these pHs. It was unusual to have an acidic primer.

Both accelerated tests and standard exterior exposure on steel showed improvements over conventional copolymer water-borne systems. Padget and Moreland [65] showed the Haloflex paints had a 100 times lower permeability to water compared
to other water-borne paints. This work was complemented by a.c. impedance work which demonstrated the water uptake to be a lot lower for Haloflex [66]. The lower water sensitivity yielded lower corrosion rates in standard salt spray tests (ASTM B117-75).

The improvement in steel protection properties was related, to a significant extent, to the observed presence of an interfacial darkening effect or film between the primer and a steel substrate [65,67]. There was an interfacial reaction which lead to an extended interface zone between the two. The protection offered by this film was demonstrated by a.c. impedance techniques and X-Ray Diffraction (XRD) suggested the layer to be a member of the pyroaurite group of compounds which has the general formula:

\[ M_x R_y (OH)_{2x+3y-2z} (A^{2-})_z \cdot 2H_2O \]

where M is a divalent cation, R is a trivalent cation and A is an anion.

Haloflex is now established in the water-borne coatings market, so new formulations must be discovered for diversification into areas which require specialised coatings. Such areas would be galvanised and top coats. For such growth the protection mechanisms must be understood and, especially, the interlayer chemistry and conditions under which it will readily form.

Pyroaurite itself is a naturally occurring mineral, \( Mg_6 Fe_2(OH)_{16} CO_3 \cdot 4H_2O \), which has hexagonal plate-like crystals. Layers of trivalent hydroxides are introduced between brucite-like layers, \( Me(II)(OH)_2 \), which achieves a double hydroxide ionic structure of the general form \( [Me(II)]_{1-x} Me(III)_x (OH)_2 ]^{x+} \) and to retain electrical neutrality, and hence stability, \( X^- \) anions are required. This is achieved by forming hydrogen bonds directly with the anion or by involvement with an associated water molecule (O-H-X or O-H-OH-X). The water, or anions, form an interlayer between the layers of mixed hydroxide giving an overall double layer structure. Allman [68] said this layer was weakly bonded and hence showed mobility. Taylor [69] pointed out that the sites could be empty producing a means of accepting anions into empty sites or allowing anion exchange to occur with the weakly bound interlayers.

Pyroaurite structures have been recognised as exhibiting low rates of corrosion under conditions of limited oxygen supply, notably aluminium heat exchangers in
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desalination plants [70], aluminium/brass condenser tubes at seaside power stations [71], and cast irons in domestic central heating systems [72-74]. More examples and further details can be found in [62].

The composition of the scales observed in heating systems showed a mixed oxide structure dependent on the concentration of oxygen and the pH, where the pyroaurite or 'green rust' like structure was found under conditions of pH>6 and low oxygen concentration. This is important in contrast with the acidic nature of the Haloflex formulation. A relatively protective green rust was also observed on mild steel under conditions of boiling concentrated MgCl₂ [75].

Green rusts related to iron structures is of particular interest for comparison with the interlayer between Haloflex and mild steel. These rusts form in varied pH and concentration of oxygen conditions and so differ in structure slightly, with a general formula [76] similar to

\[
\text{Fe(II)}_6 \text{Fe(III)}_2 (\text{OH})_{16} \text{CO}_3 \cdot 4\text{H}_2\text{O}
\]

The term green rust I are given to those compounds formed in the presence of chlorine containing solutions with a rhombohedral crystallography and green rust II, which is hexagonal, to those formed in the presence of sulphate ions. The green rusts are considered as intermediates [62] in the formation of corrosion products (goethite (α-FeOOH) and Fe₃O₄).

In fig.104 Misawa [77] summarised the conditions and hence the mechanisms under which green rust formed considering the various iron oxides and hydroxides that could form. He differentiated between green rusts and green rust complexes formed in solution. The complex was identified elsewhere [78] as having formed under neutral or slight alkaline conditions, when final green rust formation was determined by the ferrous ion concentration of the solution and coexisting anions. Concentrated solutions coupled with the presence of chloride ions resulted in subsequent green rust I formation.

Work on the Haloflex/mild steel paint system by MacInnes [62] using electron diffraction in the TEM had showed green rust I and α-FeOOH to be present on the metal surface prior to exposure of the coated surface to an oxidising electrolyte such as aerated NaCl. Padget and Moreland [65] had shown, by a.c. impedance, that a 9 day exposure time to such an aggressive environment was required for formation of the
protective anion exchange layer. In [62] it was suggested that a discontinuous layer of green rust I resulted from initial primer application, which over the 9 days of environmental exposure grew to form a continuous protective layer. A simple model of this behaviour based on the Misawa mechanisms [78] and the reactions of Goto et al. [79] was developed by MacInnes [62]. The model relied on oxygen diffusion to the reaction site being the rate controlling step. This was valid knowing the exposure conditions to be under water and a 100μm paint coating, where oxygen availability would be limited. The model agreed well with the 9 day formation of the continuous protective film.

![Diagram of Oxides, Hydroxides and Intermediates of Iron in Aqueous Solutions at Room Temperature][1]

Fig. 104
Formation of Oxides, Hydroxides and Intermediates of Iron in Aqueous Solutions at Room Temperature [62,77].

The initial discontinuous pyroaurite type compound coating was explained by the paints initial acidity and dissolved oxygen in the aqueous phase. These produced Fe$^{2+}$
and OH⁻ ions. The Fe²⁺ hydrolysed in alkaline cathodic areas to form green rust in the presence of chloride anions available in the Haloflex paint formulation. The reactions continued until the acidity and available dissolved oxygen were used up. The green rust thus formed only in the cathodic areas.

EDX dot maps in the TEM of microtomed samples prepared in a similar manner to those for TXPS pointed out the elemental distribution throughout the paint coating including iron at the paint surface. A vigorous etching of the mild steel occurred on paint application breaking up the metal's oxide/hydroxide coating. The effect has been imaged in TEM both in [62] and in fig.87 of this work. However, the only conclusive evidence for the interlayer being the green rust mixed hydroxide came from XRD and some convergent beam electron diffraction in the TEM. MacInnes pointed out that the d-spacing of 7.10Å 'unambiguously identified the presence of green rust', but admitted that the measurement of d-spacings 'contained a number of inherent inaccuracies'. The number of coincident reflections was high between different iron compounds. Powder diffraction data were, however, obtained from scrape-removed surface material [67]. It was indisputable evidence of the pyroaurite type compound at the interface but to obtain more corroborating results an XPS study was undertaken [62] which involved iodine-methanol stripping of the mild steel and then argon ion depth profiling to reveal the interlayer chemistry. Argon ion etching is known to cause reduction of metallic species [15]. Such an effect was observed in the Haloflex analysis where Fe³⁺ was reduced to Fe²⁺ and eventually Fe⁰. It was, therefore, suggested that TXPS could be employed to shed more light on chemical state changes in the Haloflex coating.

8.5.1 TXPS of Haloflex

A considerable proportion of TXPS real sample work concentrated on the study of Haloflex to try to obtain some indications of the chemical state of the material at the mild steel interface. The analysis was stretching the TXPS technique to its limits, requiring chemical state energy resolution for polymer based iron spectra from an
interfacial darkening region of less than 4\(\mu\)m thickness and an extended interface of dissolved iron.

Samples were prepared at ICI Runcorn by painting grit blasted steel with a 20% pigment volume Haloflex based primer (PCP3). PCP3 was a non-commercial green \(\text{H}_2\text{O}_2\) doped paint (pH 5) which had undergone 1000hrs of hot salt spray exposure. The term 'green' referred to a 6% PVC content. The primer was doped with \(\text{H}_2\text{O}_2\), a high oxidizing agent, which produced a more extensive interlayer formation than normal. A complete list of formulation details are given in appendix 4. Salt spray ensured a complete interlayer formation, following partial conversion during drying. The final interlayer thickness was about 4\(\mu\)m. The bulk steel substrate was then dissolved away using the iodine/methanol stripping technique under a nitrogen atmosphere [62,80]. This was presumed to leave the iron interlayer intact on the paint with an unmodified chemical state. The films were then set in a polyester based mounting resin (styrene solvent) and finally diamond blade ultramicrotomed. Sample films were caught in a small trough containing distilled water and picked up on 125\(\mu\)m pitch copper grids. Care was taken to place the films close, but not quite on top of the central 'A' grid marker to permit easy orientation of the sample in the spectrometer.

Preliminary TXPS work with Haloflex samples proved very difficult. The samples were only 100nm thick and so TSEM did not help in alignment. Point analysis was the only method to orientate samples but this was tiresome and clumsy. For this reason, little useful progress was made with these samples and later films were cut to 400nm thickness allowing TSEM.

400nm samples proved far more successful, basically because of the simpler alignment procedures. A schematic of the microtomed section is given in fig.105a with the mounting resin surrounding the paint on two sides. The iron interlayer was situated at one of the paint/resin boundaries. In most sections it was not possible to readily see the iron layer by optical microscopy, although a brown colouration was clearer in the microtome bullets.

Having loaded the samples into the spectrometer on two 0.8\(\mu\)m aluminium source foils and performed TSEM at approximately 1nA, TXPS mapping was carried out. Fig.105b shows O1s and Cl2p low magnification maps. The maps show the sample partially obscured by a totally absorbing copper grid. For source and sample thickness
reasons the sample film appeared dark with respect to the surrounding foil in the O1s (P-B) map. The Cl2p (P-B) image plainly shows the diagonal stripe of heavily chlorinated paint across the film. The O1s (P-B) and both of the background maps have bright spots within the Haloflex. These were small tears from ultramicrotomy, as observed by TEM in fig.87a, revealing the underlying source foil. Despite these problems TXPS produced a clear and interpretable image of the paint in its mounting resin. The image was simple to collect following TSEM alignment.

Fig. 105
(a) Schematic of the Microtomed Haloflex Sample in the Polyester-Based Mounting Resin All Sat on a Copper Grid. (b) TXPS O1s and Cl2p Low Magnification Maps of the Sample and 125µm Pitch Copper Grid on an Aluminium Source (8kV, 100nA, CAE=200eV, 2.5hrs./element).
fig. 106
Wide Scan of: (a) Bulk Haloflex (900s). (b) Polyester-Based Mounting resin (900s). (c) Ion Etched Haloflex Showing the Presence of Barium in the Spectrum from the Barytes Filler (4000s) (8kV, 100nA, CAE=200eV).
Following imaging, TXPS point spectra of Haloflex were collected as shown in fig.106a. There was a marked difference in spectral shape between this analysis and that collected from the polyester-based mounting resin, which only exhibited carbon and oxygen peaks, given in fig.106b. Fig.106a demonstrated the extent of chlorine within the latex, although point analyses found that the chlorine was lost after long periods of analysis from the same point. This analysis damage was discussed in section 7.1.1.1 and was a combination of polymer degradation and loss of HCl left over from coating. The rate of chlorine loss was not found to be excessive, but certainly more severe than observed by conventional XPS. Fig.84 gives a narrow scan of the Cls and Cl2s peaks. The Cls peak shows broadening on the low kinetic energy side which corresponded, at least in part, to C-Cl bonds.

In some point analyses a very slight argon ion etch uncovered barium signal from barytes (BaSO₄), which was used as a filler in the primer at 1.6at%. Fig.106c shows a localised analysis from a heavily photon-exposed area. The Ba3d and Auger peaks have very high cross-sections, whereas for sulphur they are low, hence sulphur was not observed. By virtue of its particle size (up to 7μm in diameter), much of this filler fell out during ultramicrotomy so its observation demonstrated the potential sensitivity enhancements by increasing the localisation of XPS analysis. Zinc phosphate was not detected by TXPS as, from EDX in the TEM, the vast majority of these particles fell out too. Aluminium is also shown from the local tear holes in the latex.

Having successfully analysed and mapped the paint in its mounting resin, it was then necessary to find the iron interlayer itself. TSEM was little help at higher magnifications, except for focusing purposes and seeing grid bar outlines. Point analyses had to be used to determine which resin/paint boundary contained the iron interlayer. The iron photoelectron peaks themselves could not be found with the sample in an unetched state. However, a rising background on the low kinetic energy side of the Fe2p peak positions, corresponding to buried photoelectron and Auger signal, could be found and was sufficient to determine the interface of interest. Argon ion cleaning brought out the iron signal, as shown in the wide scan of fig.107, and was effective enough to give both the Fe2p₁/₂ and Fe2p₃/₂ peaks clearly in the narrow scan. The more of an overlayer that exists on top of the iron signal, the steeper the gradient behind the Fe2p₃/₂ peak. This had the effect of merging the Fe2p₁/₂ peak into the noise as shown.
later. The buried nature of the iron was presumably hydrated layers from the ultramicrotomy floating of the films onto the grids. The high surface energy oxide surfaces would readily pick up water whilst the low energy polymer remained uncovered. The pick-up of water casts a degree of doubt on any iron chemical state data collected by TXPS although after the considerable environmental exposure that the specimens had undergone prior to preparation; it is perhaps unlikely that any stable compounds will change any further. The data would have also been modified slightly by ion beam reduction.

**fig. 107**
TXPS Wide and Narrow Scans of the Iron Interlayer Between Mild Steel and Haloflex (8kV, 100nA). (Wide: 4000s, CAE=200eV) (Narrow: 16008s, CAE=100eV).
The iron signal was found over a surprisingly large depth into the bulk of the paint. From TEM, PCP3 was seen to have a 4μm continuous interlayer. An Fe2p line scan was carried out across the interlayer by a series of point analyses to investigate the iron concentration with depth into the bulk paint from the resin interface. The Fe2p peaks were not always visible in the point spectra as a consequence of contamination build up. The areas under the peaks themselves were, therefore, not a good indication of concentration. However, even in the contaminated cases there was always an iron photoelectron and Auger inelastic background in the wide scans. The data were manipulated in two different ways to divulge a measure of iron concentrations. The gradient of the background is shown in fig.108a. There was no need to normalise the data because count rates were very similar across the area of interest. The integrated area under the Fe2p and Auger peaks was also used to give a measure of concentration having subtracted background from the higher energy peaks.
and normalised to the average channel intensity just beyond the Fe2p peaks. See fig.108b. Both plots apparently show the iron to be distributed over about a 50μm depth. Data interpretation were complicated by barium peaks and background on top of spectral noise. The data do show a sharper rise in iron on the resin side of the paint consistent with the presence of a heavily iron rich interlayer, but the effect was far less marked than expected.

The PCP3 interlayer was also imaged by TXPS as given in fig.109. The first map shows the iron to be distributed again over about 50μm, with the greatest signal density at the resin/primer interface. Unfortunately, the grid does obscure some of the information. The Cls map is of uniform intensity right across the map. This not only demonstrated the possibility of quantitative imaging by TXPS but also suggested the iron signal comes basically from polymeric areas rather than being a discrete layer of its own.

![Fe2p3/2 and Cls Images of the Iron Interlayer in Haloflex](image)

Fig.109

Fe2p_{3/2} and Cls Images of the Iron Interlayer in Haloflex. The Left Hand Side of each map is Resin and the Right Hand Side is Paint (8kV, 100nA, CAE=200eV, Fe2p_{3/2} 13.6hrs, Cls 2.5hrs).
To reliably interpret results it often proves vital to consider evidence from other analytical techniques. This argument has been shown to be true for TXPS iron depth distributions. Previous workers [62,81] have shown iron to be high at the interfacial darkening and also distributed over several micrometers into the bulk paint at the latex particle boundaries. The TXPS results in figs.108 and 109 appear to indicate that the iron is distributed over a much larger depth and so to investigate the credibility of the data similar samples were examined by backscattered electron microscopy, TEM and EDX analysis.

Fig.110

The residual microtome bullet containing the PCP3 sample was gold coated and silver dagged to an SEM stub. The distribution of the primer, interlayer and resin was
still the same as shown in fig.105a. The backscattered electron image in fig.110 shows the iron again at one interface but to only about 4μm depth. The bright areas in the bulk latex were fillers as listed in appendix 4. Various EDX linescans were performed across the interphase into the bulk latex to ascertain whether the iron could be found at comparable depths to those in TXPS. A typical linescan is shown in fig.111 with a sharp intensity rise as the interlayer was reached from the resin side. The chlorine intensity increased indicating the Haloflex was being analysed. The iron intensity dropped away over about 6μm in a similar manner to a diffusion profile. The results here disagree with TXPS not only in the size of the interphase but also in the sharpness of the rise, with TXPS indicating a blunt and broad increase from the resin side.

It became obvious that the discrepancy may have been related to TXPS surface sensitivity and smearing in the microtome, an effect which EDX bulk analysis would not have been particularly susceptible to. Artifacts of surface roughness were also a plausible explanation and so to further investigate the origin of the TXPS iron depth distribution, TEM was employed. The same batch of 400nm microtomed sections as those used in TXPS were examined.

![EDX Linescan](image)

**fig.111**

SEM EDX Linescan From the Resin Across the Interphase and into the Bulk Paint Showing the Iron and Chlorine Intensities.
The most noticeable difference between the backscattered electron and TEM images was the jagged nature of the interface. Whilst the surface of the bullet showed a relatively planar interphase, the microtomed sections were very angular similar to that shown in fig.87a. Fig.112 shows a typical small area of sample with a tortuous interlayer. Surface texture of the grit-blasted panels used originally for the samples showed the majority of surface roughness was below 8μm, but measurements up to 24μm were recorded [82]. The interphase formed clearly followed the angular metallic surface. The disagreement between the backscattered images and TEM was explained by the fact that many microtomed samples had been taken from the bullet before the residual piece was examined in the SEM. The TXPS samples could only be, at most, 3.2μm away from the TEM specimens and so were likely to be almost identical.

EDX of the TEM samples showed large concentrations of iron in the interphase region but much longer acquisition times were necessary to pick up iron signal from the bulk resin. Random point analyses found small quantities of iron 15μm and 35μm from...
the interphase. Intensities were an order of magnitude lower in the bulk than at the interphase. The results did not compare favourably with the TXPS interlayer data. TEM EDX also found occasional chunks of iron oxide in the mounting resin, as is shown in fig.112. These were residual pieces of loose material from the original bullet preparation.

EDX of particles in the bulk latex showed them to be pigment and filler materials such as chromium oxide and barytes. Holes in the primer were caused by tearing or falling out of the larger particles during ultramicrotomy, as debris analysis showed.

After the SEM data were examined surface smearing was considered a plausible explanation for iron TXPS observations. However, in low magnification TEM (fig.87a) knife stretch marks showed the direction of microtomy was almost parallel to the interfacial plane and in fact slightly towards the resin. The lines seen at higher magnification in fig.87b and fig.112 are knife scratch marks parallel to the cutting direction. No iron was found by EDX in the bulk of the resin and so smearing was finally ruled out. Film tear marks were not seen, so hard material was not dragged across the resin surface.

In section 6.2.4 the TXPS lateral resolution was measured as 12μm using two 0.8μm aluminium source foils. This estimate applied relatively well for the Haloflex sample as X-ray spreading would have been small within the 400nm section. The 12μm resolution compared to a 15kV SEM width of interaction volume capable of exciting FeKα X-rays from 8.3μm (for pure Fe₂O₃) to 26μm (for iron in a polymeric matrix) [26]. Lateral resolutions in EDX would have been less than half of these values, as X-ray excitation is most probable at the centre of the envelope. The lateral resolution in TXPS was, therefore, never better than SEM EDX. The best EDX resolution was when the electron beam was on the iron rich layer and the small envelope size here gave the sharp rise in intensity in the linescan. See Fig.111. The poorer TXPS lateral resolution was unable to achieve such a clearly defined line profile.

The evidence collected by TEM, backscattered electron imaging and corresponding EDX pointed to the TXPS enlarged interfacial region in the TXPS linescan to being an artefact of insufficient lateral resolution coupled with a jagged grit-blasted surface. The surface roughness varied up to 24μm and adding 12μm TXPS lateral
resolution, on each side of the interface, to a 6μm interphase gave a profile apparently more than 50μm wide. Care was taken in the TXPS work to align the interphase perpendicular to the linescan direction, but there may have been a minor increase in measured thickness from a few degrees of misalignment. From a closer reinspection of fig.109 it is possible that to imagine a rough interface, but realistically the data were a little too noisy for any conclusive comments.

TXPS linescan and image interpretation problems were a result of a number of analytical difficulties. Total analysis times were days long including alignment, cleaning and point analyses, so only one specimen was examined. Several areas of the sample should really have been examined to give a more representative result. Difficulty in finding the correct area for TXPS analysis was also a major problem. The imaging systems in the modified MA500 were insufficient to find the area for analysis with a non-jagged interphase. A UHV CCD zoom camera with a monitor was required. It would have needed the flexibility of X-Y adjustment so the area of interest can be chosen and matched to the TSEM image. A zoom camera would also have provided a useful visual monitor of sample damage. The conclusion of this section must also advocate the use of multi-techniques for meaningful materials analysis. Data interpretation with one technique is a hazardous route to take and can lead to the incorrect conclusions!

8.5.2 Study of the Chemical States of the Haloflex/Iron Interlayer

The area of most interest to ICI was the chemical state study of the Haloflex/mild steel interlayer. This was the original point of the TXPS work. MacInnes attempted to analyse the chemical state changes with distance away from the metal/paint interface into the bulk paint in two ways.

He first used argon ion etching to depth profile through a 40μm paint coating towards the interlayer. Whilst the data yielded a valuable elemental depth profile, Fe2p narrow scans suffered from high levels of ion beam reduction. This reduction was proved possible in Haloflex sections by removal of the bulk paint by solvent elution
using N methyl-pyrollidone and ion beam etching. The Fe2p chemical state changes were monitored. MacInnes observed a change from mainly trivalent iron prior to etching, to divalent and finally to mixed divalent and metallic states. He concluded that these results made the interlayer thickness appear more than an order of magnitude lower than observed in TEM micrographs and so the results were purely an artefact of ion beam reduction.

The second method used was a combination of UHV milling and small area XPS (SAXPS) in which a tapered section through the primer to the substrate was cut from the latex side. To minimize smearing of the paint over the newly exposed surface, the latex was cooled with liquid nitrogen to temperatures between -2°C and -10°C. Cutting of the tapered section spread the interface over a larger area and permitted local analysis using the small area facility on the ESCALAB II where the transfer lens iris produced a defined collection system (150µm area of analysis). A series of point analyses across the tapered section allowed an 80µm depth of Haloflex to be spread over a projected area. Depth analysis could be determined with 8µm error bars and each analysis was effectively 8µm apart [62]. Poor signal levels required 100eV pass energies in the narrow scans. The data were peak fitted rather unsatisfactorily. The low energy resolution really demanded wider peaks with FWHM of approximately 4.5eV [83] and the Gaussian to Lorentzian (G/L) ratio should have been set at 100% Gaussian, because spectrometer broadening was dominant at these levels [84]. The peak fitting program also limited fitting to 8 peaks. MacInnes' interpretation of his results suggested the Fe²⁺/Fe³⁺ ratio to be approximately unity at the metallic interface and to increase as analysis was carried out deeper into the bulk primer. This conclusion disagrees with a simple oxygen diffusion model and for this reason the SAXPS data were re-examined.

The Auger Parameters (α) in the form of Wagner plots [85] are frequently used to determine the chemical state and even the compound associated with the element. These plots rely on the fact that the combined photoelectron peak position and following Auger relaxation are very sensitive to chemical environment. The fact that the calculation only involves the difference in peak positions means that results are charge independent. Unfortunately, the iron peaks are very broad and the plot is notably unreliable except for iron organic compounds [86].
8.5.2.1 TXPS of the Haloflex Interlayer

To disclose the chemical state of the iron in a Haloflex/mild steel interlayer, Fe2p point narrow scans were collected at various distances from the mounting resin/H2O2 doped primer interface in an ultramicrotomed section. The specimens needed a short ion etch (less than 30s waving the specimen in and out of the divergent 6kV beam) to bring out the peaks clearly.

The data in the three spectra shown in fig.113 were probably the most reliable and adequately demonstrated the problems encountered during TXPS analysis. The data were certainly noisy and problems of carbon contamination were encountered. The bottom spectrum was collected on the bulk primer side of the interphase and the spectra above represent movement towards the resin interface first in a 5.5μm jump and
then 9.1μm. The jagged interphase would have quantitatively changed the relative ratios of iron chemical states, but the comparably poor lateral resolution of TXPS to the real interlayer size and the scale of the separations between each point scan meant that a swing in chemical state could still be validly interpreted as the interphase was crossed. The order in which the spectra were collected is shown to the left of fig.113. The Fe$_{2p_{1/2}}$ peak was seen to disappear into an increasing background on the low kinetic energy side of Fe$_{2p_{3/2}}$ peak as more carbon contamination was deposited in the general area of interest during analysis. The Fe$_{2p_{3/2}}$ inelastic tail became more significant and the Fe$_{2p_{1/2}}$ signal was submerged into the tail noise. This increasing background gradient was analogous to the effects on Cr$_{2p}$ spectral shape observed by Castle [87], where successive layers of titanium were evaporated onto a chromium substrate.

The noisy TXPS iron data given here could not be reliably peak fitted especially not to give any quantification information about relative peak heights. The quality of the data were, however, sufficient to match up with artificially produced curves to be used as templates based on fitting parameters used in the literature. Fe$_{2p}$ peaks were adequately fitted by Ke [88] and Brundle [83]. They not only produced standard spectra, but also suggested the correct parameters for fitting. Brundle suggested his fitting data compared satisfactorily with previous workers.

One further problem with the data from TXPS involved charge referencing. The Cl$_{1s}$ peak position could not be used as an adequate measure of charge shifts. Its kinetic energy demanded about a 5eV recalibration, which would have shifted all of the various iron chemical states out of the peak envelope. It meant that the peak positions had to be floated. The reasoning behind the shift had to be differential charging. The spectrometer calibration was good as was shown by the low and high energy barium peaks (Ba$_{4d}$ and Ba$_{3d}$) in fig.106c.

Discussions of an iron chemical state change across the interface would certainly be far more fruitful with the addition of other coincidental elemental concentration changes. This unfortunately was complicated by the contamination build up with time and the chlorine degradation. Carbon built up on the sample surface during analysis gradually reducing the O$_{1s}$ signal intensity and chlorine signal from the latex was both degraded by photon damage and buried.
Fig. 114 shows three templates placed on the top of the best set of TXPS experimental data (curve 1 of fig. 113). 100% Fe$^{2+}$, 100% Fe$^{3+}$ and a 50/50 mix are considered. Peak positions were essentially fixed to get the best fit using the Googly peak fitting routine [89] and widths were set at 4.5eV with 100% Gaussian. Both iron
spin doublets were 'fitted' and a Shirley background was used. The 2:1 Fe2p₃/₂/Fe2p₁/₂ peak height ratio could not be used as was found by Ke [88] and a 2:0.8 ratio was used, which was still within experimental error. Relative peak positions were set and two satellites were used as given in [88]. Relative main peak to satellite heights were also set from the literature. The Fe2p₃/₂ peak and its satellites were the most important peaks to consider for data/template comparisons as the noise was far less of a problem here. Appendix 4 lists the template fitting data.

The Fe³⁺ satellites are half of the size of those from Fe²⁺ and are further away from the Fe2p₃/₂ peak. Thus, the data appear more like the Fe³⁺ than Fe²⁺ because the larger Fe²⁺ satellites have a greater broadening effect on the shape of the low kinetic energy side of the Fe2p₃/₂ peak. The template fit predominately shows Fe³⁺, with a minor Fe²⁺ component.

The data in curve 2 of fig.113 are more noisy than curve 1. The template fitting regime was not carried out here for this reason, but comparison of the two spectra definitely shows that curve 2 has a larger Fe²⁺ component by virtue of the satellites again. The pronounced 'V'-shaped region between the iron spin doublets is characteristic of mixed valance states of iron [84]. Curve 3 does not show a particularly conclusive peak shape, although it does appear generally to be similar to 2, with even more contamination! The steep inelastic background gradient severely masks the extent of the Fe³⁺ satellite.

Comparison of the low kinetic energy side of the Fe2p₃/₂ peaks definitely suggested a chemical state change approaching the interface. The possibility that the iron could have been a combination of Fe⁰ and Fe²⁺ was dismissed. Fe⁰ would not have survived the coating procedures and could have only reappeared following ion etching by ion beam reduction. Even in the ion etch depth profiles performed by Maclnnnes Fe²⁺ and Fe³⁺ still featured predominately on the spectral narrow scans. To TXPS, ion etching was only a cleaning procedure so total ion doses were considerably lower than in the Maclnnnes work and so TXPS ion beam damage would not be anywhere as severe.
8.5.2.2 Re-Examination of MacInnes Milling SAXPS Data

The MacInnes SAXPS data were re-examined following suspicions of poor fitting. Some pitfalls of fitting iron spectra have already been discussed with regard to TXPS. Re-peak fitting of the SAXPS work was attempted but it was found to be too difficult. Both Fe$^{2+}$ and Fe$^{3+}$ each have two satellites. Adding the extra Fe$^0$ peak now present in the milling data and the fact that a pair of peaks needed to be fitted meant that ten peaks were strictly needed. Fitting could not be carried out with any confidence on such noisy and broad peaks even with a significant prior knowledge of many inter-peak relationships. Nevertheless, general SAXPS principal peak and satellite shapes may be safely discussed for comparison with TXPS data on a qualitative basis. The MacInnes data are replotted in fig.115, with the topmost spectrum from analysis depths closest to the interface.

[Diagram showing iron spectra with annotations]

Fig.115
Re-examined MacInnes SAXPS/Milled Haloflex Data (Alkα, 12kV, 20mA, 20040s, CAE=100eV).
In spectrum 'A' there is no obvious sign of a Fe$^{3+}$ satellite structure but there is evidence for the Fe$^{2+}$. An Fe$^0$ peak, which will possess a narrower FWHM, is also prominent on the low binding energy side of the Fe$^{2p_{3/2}}$ peak. In spectrum 'B' the 'V'-shape typical of mixed iron oxides is clear and the Fe$^0$ component to the left-hand side of the main peak has largely disappeared. The inelastic background is notably lower than in the other narrow scans, so there is no underlying metal. For this reason 'B' is most probably from swarf and so can be disregarded in the series of narrow scans except as perhaps clear evidence for mixed oxides within the extended interlayer. The 'V'-shape is also seen in 'C' with a larger Fe$^{3+}$ contribution than 'A'. The magnitude of the Fe$^{3+}$ satellite is partially increased because of some Fe$^0$ signal. There is a definite shoulder on the low binding energy side of the Fe$^{2p_{3/2}}$ and thus it is necessarily evident on the Fe$^{2p_{1/2}}$. The Fe$^{3+}$ satellite has grown even more in 'D' with respect to Fe$^{2+}$, once the reduction in Fe$^0$ component on the low binding energy side of Fe$^{2p_{1/2}}$ is remembered.

Summarising then, the Maclnnnes SAXPS data really show initial Fe$^0$ signal together with Fe$^{2+}$ close to the interface, which transforms to a Fe$^{2+/3+}$ mixed oxide in the bulk latex. The relative intensity of Fe$^{3+}$ with respect to Fe$^{2+}$ increases as analysis moves away from the metallic interface towards the primer surface.

8.5.2.3 Interpretation of the Chemical State Data from Haloflex

The re-interpreted Maclnnes data and the TXPS data had to be examined separately despite apparently having shown similar iron chemical state distributions. The Maclnnes data simply looked at the post-coating oxidation states of iron at various depths into the primer, whereas the TXPS work involved the H$_2$O$_2$ doped latex after hot salt spray exposure. The Haloflex interlayer was known to form not only under initial vigorous etching of the steel substrate during coating, but also it continued to develop slowly during drying and even subsequent environmental exposure [90]. The TXPS sample was originally chosen for its extensive interphase formation rather than its relevance to comparison studies. Nonetheless, simple models for both results were
developed and they will be discussed in turn, starting with the simpler MacInnes system.

In the re-interpreted MacInnes data the mean iron oxidation state increased in Fe\(^{3+}\) with respect to Fe\(^{2+}\) as analysis moved across the interphase toward the bulk primer. The large depth spread of the interphase was once again attributable to grit-blasting but the chemical state changes observed still required explanation.

At the interphase in the coating the actual chemical states that exist are dependent on the local availability of oxygen. It is suggested that the iron exists in a Fe\(^{2+}\) state under conditions of limited oxygen availability in a zone close to the interface upon application of the paint. The final iron chemical state is then influenced by the influx of oxygen from the air through the wet and drying primer film reacting with the iron effluxing from the corrosion process. Thus, it is expected that a chemical potential profile of oxygen exists in the coating. This has an effect on the local chemical state of iron throughout the thickness of the primer from the interface. It is then anticipated that a higher mean oxidation state of iron exists further from the interface. Areas of mixed oxidation state need to have the correct ratio of Fe\(^{2+}\) to Fe\(^{3+}\) ratio to form the pyroaurite type compound, but this does not rule out the production of this compound when one oxidation state is in excess. The remainder is merely present as an oxide, oxyhydroxide or even a basic chloride. The exact depth position of the pyroaurite type compound with respect to the mild steel substrate is dependent on the rate and extent of oxygen diffusion and of iron dissolution during coating.

The chemistry changes at the interface will now be discussed in a little more detail. The surface of steel before coating is covered in very thin films of iron hydroxides and oxides. On coating, at the immediate interface anodic dissolution occurs under limited oxygen supply following

\[
\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (34)
\]

and correspondingly in cathodic areas the cathodic reaction

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (35)
\]
takes place being accommodated under the pH 4-5 primer conditions. Hydrogen ions are consumed here too, by
leaving an excess of (OH'). The removal of hydrogen ions means there is a drift towards alkaline conditions, whereupon the pyroaurite type compound would form.

Further from the interface between the Haloflex and mild steel the oxygen availability is higher and so the oxidation reaction

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$  (37)

is more likely to occur with the related reduction reaction already given in equation 35.

On coating, under the limited oxygen concentrations available within the primer, Fe$^{2+}$ is the major initial oxidation state. The solubility product determines that Fe$^{3+}$ is soluble below pH 8.5 [91], rather than precipitated as Fe(OH)$_2$, simply because of the acidic conditions in the primer. Fe$^{2+}$ is, therefore, present as a soluble hydroxide and chloride in the damp/dry primer and offers no corrosion barrier. However, oxygen from the air diffuses into the drying paint around the coalescing latex particles and allows Fe$^{3+}$ ions to form by direct oxidation. Oxidation of Fe$^{2+}$ to Fe$^{3+}$ in Haloflex has been reported to speed up the more alkaline the pH becomes above pH 4 [92]. Fe(OH)$_3$ has a solubility product which allows precipitation above pH 5 [91] and this can happen in Haloflex under its formulation pH. In reality the oxygen concentration deep in the primer is probably insufficient to completely convert Fe$^{2+}$ to Fe$^{3+}$ and so the mixed Fe$^{2+}$ and Fe$^{3+}$ states can interact and precipitate a pyroaurite type compound. Such compounds have been cited as being stable in many low oxygen concentration aggressive environments as mentioned earlier. Pure Fe(OH)$_3$ is still attacked by chloride ions to form various complex compounds.

The reinterpreted SAXPS data did not disagree with the existence of the pyroaurite type compound in the interlayer. It gave a profile of oxidation states with depth rather than a fixed Fe$^{2+}$/Fe$^{3+}$ ratio. SAXPS identified that the chemical state environment was correct for the possible precipitation of the pyroaurite type compound within the profile. In XPS the data resolvable from the iron photoelectron peaks were relatively limited because of the peak broadness and the complex nature of the iron oxides and hydroxides. The distinct Fe$^{2+}$/Fe$^{3+}$ ratio of the pyroaurite type compound was lost in the distribution of other iron compounds at the interphase.
The chemical state distribution observed by TXPS point analyses across the interphase into the bulk latex showed a change of iron oxidation state from Fe\(^{2+}\) towards Fe\(^{3+}\). This pattern was similar to that seen in the reinterpreted Maclnnes data, but it was the result of a series of different mechanisms.

On initial coating, the wet primer corrodes the steel substrate to produce Fe\(^{2+}\). This ion is rapidly oxidized by the H\(_2\)O\(_2\) to Fe\(^{3+}\) and precipitates out as Fe(OH)\(_3\) [90]. Once several coats of primer were applied and allowed to dry, the specimen was then exposed to 1000hrs in hot salt spray (38°C). Padget and Moreland [65] proved that anodic dissolution continues in the Haloflex primer system during environmental exposure to eventually form a complete protective interlayer. Thus, the TXPS observation of Fe\(^{2+}\) closest to the substrate suggests that substrate dissolution was occurring, following the influx of water and oxygen from the atmosphere. Further from the interface Fe\(^{3+}\) would again be formed by Fe\(^{2+}\) oxidation, but in TXPS terms this was indistinguishable from the original Fe\(^{3+}\) formed during coating. In theory, the efflux of Fe\(^{2+}\) gives the opportunity for the pyroaurite type compound to precipitate during exposure.

8.5.3 General Conclusions and Comments

This section showed TXPS could provide useful chemical state data to complement previous work. It was possible to make specimens from an original sample comprising a hard substrate with a soft coating. The Haloflex data highlighted the technique’s possibilities for a comprehensive study of the primer system and its behaviour under a variety of exposure conditions. The need for input from other techniques was well established as well as the shortfalls of the present TXPS development instrument. Nonetheless, the present spectrometer proved the imaging capabilities of the technique and, more particularly, its ability to perform highly localised analysis. The noisy nature of spectra showed the need for longer acquisition times and better photoelectron collection efficiencies (for example an improved transfer lens system or more channeltrons), if ultimate elemental sensitivities are to be achieved, particularly at low pass energies.
8.6 Mixed Oxide Inclusions in a Rapidly Solidified Mg/Al Alloy

This section served as an important feasibility study for the preparation of TXPS samples from harder materials. Such samples required ion beam thinning. The resultant specimen had to have as large an area as possible below 1μm thickness, so the ion beam had to be set to the lowest incident angle that could be achieved in the sample preparation equipment. Ion beam thinned samples for TEM are normally thinned from both sides but, for TSEM specimen alignment purposes, samples for TXPS would have to be only thinned from one side. Thinning in this manner would have allowed the sample foil to be placed in direct contact with the X-ray foil to give a clear TSEM image. Etching from both sides would have given poorly defined TSEM, analogous to images collected for the non-contact polymeric samples in section 8.2.1.3.

The corrosion resistance of binary magnesium alloys in 3% NaCl solution saturated with Mg(OH)₂ were greatly improved by alloying with more than 10wt% aluminium. In the corrosive environment the surface formed a stable compound of the pyroaurite–sjögrenite family [93]. It was found that the spinel MgAl₂O₄ was important in forming the corrosion protective hydrotalcite [94].

In the quest for a more corrosion resistant alloy, a Mg-16wt%Al material was studied after different solidification routes; cast from ingot, splat quenched and made by extruding atomized powders [95]. Apart from the existence of the Mg₁₇Al₁₂ phase in the ingot, which was finely dispersed in the extruded powder, the powder-produced sample also contained stringers of oxides on the surfaces of the prior particle boundaries. XPS sputter depth profiling showed no change in oxygen levels with depth consistent with the existence of oxide stringers. RBS and XPS showed the splats and extruded powder to have a 10–50nm thick overall surface oxide/hydroxide coating compared to 100–200nm for the ingot.

XPS of the surface of the splat showed there was some Al³⁺ ions present, but on the ingot only Al⁰ was found. XPS of the extrusion looking for Al³⁺ was relatively inconclusive [96].

XRD looking for MgO and Mg(OH)₂ gave equivalent intensities for all three samples but the spinel (MgAl₂O₄) decreased in intensity from the splat through the extrusion to the ingot. This appeared to be the only difference between the three
samples and it was suggested there was a connection between the spinel concentration and the resistance to the 3% NaCl saturated in Mg(OH)$_2$ as it exhibited a similar trend [95]. Carbonate ions were also present on all alloys.

Baliga explained the existence of the spinel on the splat and in the extrusion very simply. The atomizing temperature and the high rate of quenching triggered a spinodal decomposition [96,97] producing spinel and MgO. This was a result of the high availability of aluminium and magnesium, from the alloy, and oxygen from the atomizing atmosphere [94]. The extrusion processing of the rapidly solidified (RS) powders led to the break-up of the oxide on individual particles, so on the surface of the extrusion there was a combination of high and low temperature oxides. The high temperature oxides were originally from the individual particle surfaces and the low temperature oxide formed by the oxidation of the freshly exposed alloy from extrusion broken-up powder. Less of the high temperature spinel on the extrusion surface would have meant less protective hydrotalcite would ultimately form in the saline environments compared to the splat.

To confirm the XRD observation of the spinel on the extrusion surface Al$^{3+}$ needed to be found. The fact that the RS processing route would have given rise to bulk oxide inclusions meant that it was equally applicable to analyse the main material. Argon ion etched and polished samples were originally analysed by XPS, but the fine distribution of spinel in the extrusion meant that XPS did not have sufficient sensitivity for conclusive detection [94].

Conventional XPS only has a few percent sensitivity for favourable photolines. Aluminium peaks excited by Al$\alpha$ do not have high photoelectron cross-sections. To detect the finely dispersed spinel (via Al$^{3+}$) and confirm the mechanisms of Baliga [95], a small spot XPS analysis technique such as TXPS was required. TEM foils for electron beam diffraction, which were electron transmitting, could not be made because the argon ion thinning technique knocked out the spinel inclusions [96]. The inclusions were 1µm or less in diameter. TXPS samples only have to be partially soft X-ray transparent. Thus, TXPS specimens would not suffer severely with the loss of spinel, because foils were up to 1µm thick rather than of the order of tens of nanometres in TEM. Although lateral resolution in TXPS is not good enough to analyse an individual spinel inclusion, the sensitivity of XPS is improved by a factor of $10^6$ over conventional
reflection XPS. This is a simple result of the increase in photon density. Point analysis at a distance from the ion etch hole should have allowed collection of aluminium and magnesium narrow scans, at low pass energies, giving the necessary $\text{Al}^{3+}$ signal to exclusively confirm the presence of the spinel inclusions in the extrusion material.

From backscattered electron microscopy, the extruded magnesium alloy was known to contain oxide stringers dispersed along the extrusion direction in a pseudo-layer structure [96]. The decision had to be made as to exactly what angle sectioning would be most beneficial for TXPS to pick up the sub-micrometer inclusions. Stringers were often highly separated and so cutting along the stringer direction was likely to have given a section which would not contain any oxide whatsoever. The oxide may have also fallen out, as it would not have been well supported by the underlying metal. Samples were sectioned at 60° to the extrusion direction in an attempt to spread the inclusions over a larger area, whilst still retaining the oxide in the specimen.

Samples were prepared by cutting 3mm diameter disks from the extrusion material and argon ion etching from one side (in a Gatan 600 Dual Ion Mill) at 15° to the rotating sample surface until a central hole appeared. This took approximately 36 hours. Liquid nitrogen cooling of the sample was necessary to prevent sample damage [94]. Optical micrographs were taken to find appropriate areas for analysis. An example photograph is shown in fig.116a. The areas of interest for TXPS were within 4µm of the hole. Only here was the sample of a sub-micrometer thickness which permitted sufficient characteristic X-ray transmission for TXPS.

The sample was mounted on two 0.8µm aluminium foils in a TXPS stub as shown in fig.116b. Optical microscopy, prior to sample loading, had shown the source to be separated from the sample in several places. Later TSEM blurring problems were avoided by blowing the aluminium into sample contact from the underside. The subsequent success of the blowing method highlighted the possibilities for TXPS analysis of relatively rough samples, but most particularly specimens thinned from the bulk towards a genuine surface of interest. This method would also eliminate worries of ion beam valence state reduction.
Fig. 116

(a) Optical Image of an Ion Beam Thinned Alloy Sample. (b) Schematic of the Ion Beam Thinned Magnesium Alloy Sample on the Aluminium Source. (c) TSEM of the Alloy Sample on the Aluminum Source (10.5kV).
Once in the spectrometer, TSEM was quickly performed on the sample to ensure clear images could be obtained. Fig.116c shows a typical TSEM image, with the aluminium source shown as a bright area and the alloy foil as dark. The boundary between these two regions was the area of interest to TXPS. The alloy was then in-situ argon ion etched to remove contamination collected from handling and transfer procedures. After a relatively short etch the samples were still heavily contaminated, with only C1s and O1s peaks visible. However, after several ion etches the contamination was completely removed and all that remained was the oxide. It was whilst subsequently trying to remove the natural oxide on the alloy that the dramatic effect of the impurities from the bottled argon was observed. Nitrogen peaks began appearing on spectra, most notably on source point analyses. Ionized nitrogen from air contamination was highly reactive and so readily combined with freshly exposed aluminium metal. Oxygen reacted in a similar fashion, although it was, of course, in a lower concentration in the air. See fig.117. These observations led to the addition of a BOC rare gas purifier. The nitrogen then disappeared from the analyses.

Fig.117
Aluminium Source Showing Nitrogen Pick-up from the Etch Gas Impurities (7.8kV, 100nA, CAE=200eV, 900s).
The approximate area to perform etched alloy analysis was fairly easy to ascertain by both TSEM and TXPS. TSEM allowed initial lining up, and in TXPS when the point was run over the sample edge, this gave a dramatic drop in count rate from X-ray absorption. The critical point for analysis was found to be just after this sudden drop region, where count rates were still sufficient but the edge of the interaction volume was far enough under the sample to negate X-rays emitted at high angles (with respect to the electron beam direction) contributing to the spectra. It was difficult to decide exactly when the aluminium signal from the source no longer made a contribution to the alloy spectra. It was obvious from the large Mg(KLL) structure in the wide scan in fig.118a that the interaction volume was basically under the sample. However, it became clear after comparison with a standard alloy XPS spectrum such as the one given in fig.118b [95], that the Mg2s/2p to Al2p/2s ratio was too low and that there was a definite source contribution to the signal. Tsakiropoulos [98] confirmed the alloy would have appeared to TXPS, with its several micrometers lateral resolution, to be single phase so the Mg/Al ratio would have been constant on the alloy regions and would only vary if appreciable amounts of high emission angle X-rays were interacting with the source. Fig.118c shows a spectrum with a correct ratio demonstrating that TXPS could be used to analyse ion beam thinned sections of harder materials.
The vacuum conditions in the spectrometer were not good enough to prevent reoxidation of the alloy immediately after ion etching. From private communications with Baliga [96] and from Ellingham diagrams [99], the reactivity of magnesium was so much higher than aluminium, that the oxide would primarily form on the magnesium in the freshly etched alloy. This meant the aluminium would remain in the metallic state, so any \( \text{Al}^{3+} \) component on aluminium peaks would unambiguously signify the presence
of the spinel. Oxygen in the 2+ oxidation state will not, of course, give a useful indication of the presence of oxide inclusions, being also associated with the freshly formed MgO.

The possibility for confusion of the source and spinel aluminium chemical state meant that Al\(^{3+}\) data could not be meaningfully collected. The fact that the central hole in the sample foil was jagged increased experimental difficulties. The particular alloy under investigation had an annoying habit of curling up as it was ion beam thinned. It was also incredibly brittle and the thinnest areas were easily broken off during handling. The solution was to use a sample with a thicker outer wall, but time constraints prohibited further investigations.

To achieve a truly conclusive result it had to be possible to eliminate the source Al\(^{3+}\) signal totally from spectral analysis. A solution to the confusion would have been to use a different target material. Natural line width considerations, to obtain chemical state information, eliminated most elements from TXPS selection in section 3.3. Silicon would have been the obvious choice. Previous experience with this material showed that TSEM imaging was difficult through the 4-6\(\mu\)m of silicon single crystal, despite its perfect flatness which would have eliminated the roughness contributions to 'noise' in the image. The necessity for higher accelerating voltages also would have slightly reduced the obtainable lateral resolution and the sensitivity of the technique to pick up the oxide inclusions. However, observation of Al\(^{3+}\) would have left no doubt that the spinel existed in the extruded material, following XRD data, and contributed to alloy corrosion resistance.

8.6.1 Conclusions

This alloy work demonstrated the ability of the TXPS technique to analyse ion beam thinned hard materials. By the appropriate choice of source material it would have been possible to perform point analyses which uniquely separated the sample from stray target signal.

This section also has brought out other prospects for hard material sample preparation to add to the pseudo-bulk analysis. Following ion beam thinning of a
specimen from the bulk side, blowing the source into contact would have allowed true surface chemistry to be examined. Hard material samples in the form of a carefully polished tapered section would have behaved in a similar manner to the ion beam thinned specimens.

For reasons of confusion between the source and sample, the high degree of localisation of analysis in TXPS has yet to be able to demonstrate the existence of spinel inclusions within the bulk of the alloy. With the use of a silicon source, a result far beyond the sensitivity of conventional XPS would be achieved. This would have used the chemical state resolution available in TXPS, although the problem could have alternatively been solved in conventional AES because of the high degree of chemical shift between the oxide and metal peaks for Mg(KLL) and Al(KLL). In TXPS the shifts on these peaks would have served as a reliable cross-check for the photoelectron peaks as well as allowing the calculation of an Auger parameter ($\alpha$).

AES in the transmission mode would have been possible in the modified MA500, simply by increasing the accelerating voltage so that so that significant levels of the interaction volume penetrated the back of the sample and directly induced Auger electrons as shown in section 5.2. Count rates would have been considerably higher than TXPS.
9.0 COMPARISON OF TXPS TO A COMMERCIAL IMAGING XPS INSTRUMENT

To compare TXPS with a commercial imaging instrument microtomed samples of Haloflex PCP3 were examined in a Fisons Instruments 220iXL spectrometer. The system is the latest version of the ESCASCOPE and has commercially replaced the ESCALAB210 series, now being able to perform satisfactorily as a conventional area spectrometer as well as in the small spot and imaging mode.

The 220iXL has a large number of design improvements since the original launch of the ESCASCOPE whose design is detailed in section 1.3.2. The transfer lens now performs a magnification of 16 times prior to reaching the first imaging lens. The spectrometer now has six channeltrons spaced along the dispersion axis with the second imaging lens in the middle leading to a two-dimensional position sensitive detector. Thus, the instrument can be used in a parallel imaging mode or a spectroscopy mode. The 220iXL also has a magnetic lens system which allows the sample to be immersed in a magnetic field. The incoming X-rays are, of course, unaffected by this arrangement but the collection efficiency of the transfer lens is greatly improved. The spectrometer also features a high power focusing monochromator which allows spots as small as 80μm to be reached simply by focusing the primary electron beam on the anode and using a toroidally bent quartz crystal. A CCD zoom camera is also used to ease specimen alignment.

In a recent paper Forsyth and Coxon [100] showed a Cu2p3/2 image of a copper grid with 2μm lateral resolution acquired in 5 minutes without use of the magnetic lens. This represented a real achievement in imaging XPS, although in the 'point' analysis mode a spot of 15μm was only possible. On a gold grid sample in 15μm 'point' analysis mode the count rates were 1300ct/s on the Au4f peak which was approximately three times that achieved in TXPS in the modified MA500 at 8kV and 100nA. Considering the degree of optimisation in the commercial system compared to the TXPS instrument with its single channeltron, this was rather encouraging.

A Haloflex (PCP3) microtomed sample on a 125μm copper grid was silver dagged to the specimen transfer system in the 220iXL with the sample uppermost. The rough sample position was set using the zoom camera and then using the low energy flood gun (500eV) which normally provided charge neutralisation when the monochromator was
being used. The alignment image was formed using the secondary electrons emitted from the specimen as viewed by the transfer lens on the analyser CCD camera. This imaging was a particularly unambiguous method of sample alignment. Unfortunately, it did not lend itself particularly well to polymer sample alignment! The sample damage that this flood gun procedure caused is reflected in fig. 119, where the chlorine intensity was drastically reduced and even caused the sample to shrivel up. Nevertheless maps were acquired using the Alkα monochromator at magnifications to show the entire film as well as the iron interlayer.

![Graph with peaks labeled O1s, C1s, Cl2p, Cl2s]

Fig. 119

Two 1mm Diameter Monochromated Alkα XPS Spectra from the Haloflex/Resin Sample Showing the Extent of Chlorine Loss Before (Dotted) and After (Solid) Flood Gun Imaging. (10kV, 17mA, 1.1 mins, CAE=100eV).

Fig. 120 shows Cl2p, C1s and O1s maps of the Haloflex specimen in its mounting resin. A schematic of the sample is shown for TXPS samples in fig. 105a. The O1s images basically show the microtomed film on the grid, if a little noisily. The C1s (P-B) map more particularly picks out the film itself and the Cl2p (P-B) map clearly demonstrates the position of the chlorinated primer. Copper grids are notoriously contaminated with chlorine on the surface and this explains the appearance on the Cl2p
Comparison of TXPS to a Commercial Imaging XPS Instrument

maps. The Cls (B) map notably looks like the chlorine maps as a result of the background being dominated by the inelastic tail from the lower binding energy chlorine peaks especially the nearby Cl2s. The images were encouragingly similar to those obtained by TXPS, except the TXPS images had the drawback of being partially obscured by the support grid. The other major difference was the necessary acquisition times. The parallel imaging capability of the 220iXL meant that the three sets of maps were collected in 13mins. This compared to the sequential nature of TXPS which used 5 hours for just the Cl2p and O1s maps. The 220iXL's superior imaging power is, therefore, left in little doubt even if collection efficiencies are improved in a future TXPS instrument, say by use of multiple detectors or an improved lens transmission function. The 220iXL also has the added advantage of having a monochromated source, which improves spectral line widths and makes chemical state imaging easier. The first chemical state image ever recorded by a laboratory imaging XPS technique was also given in [100] and shows bettered than 5μm lateral resolution.
Comparison of TXPS to a Commercial Imaging XPS Instrument

(b) O1s

(c) Cl2p

Fig. 120
1mm Field of View 220iXL Images of a Haloflex Microtomed Section on a Copper Grid (10kV, 17mA). (a) Cls (4mins.), (b) O1s (4mins.) and (c) Cl2p (5mins.).
The same magnification was then used in the 220iXL in an attempt to find the iron interlayer. No signs of iron peaks were found until ion etching was used to clean off the first few atomic layers, as was demonstrated by TXPS of similarly prepared samples. Fig.121 shows the Fe2p$_{3/2}$ image following ion etching using the small spot Alk$_\alpha$ monochromator. The image only took 20mins to collect compared to 13.6hrs for TXPS in fig.109. In fig.121 the copper grid appeared to have a high intensity because of a clash of the charge shifted Fe2p$_{3/2}$ peak with a copper Auger peak. The iron interlayer was clearly visible and measured about 25µm across with respect to 50µm in TXPS. The apparent disagreement was most likely due to the shrinking of the film during low energy electron imaging.

Fig.121

1mm Field of View 220iXL Fe2p$_{3/2}$ Image of a Haloflex Microtomed Section on a Copper Grid (20mins).

Although the 220iXL work showed the TXPS results to be valid, it also showed that in terms of imaging acquisition times TXPS came a poor second. The 220iXL was
certainly an excellent laboratory XPS imaging instrument. There are of course other considerations to be made before final conclusions can be drawn about the relative merits of each technique. These shall now be discussed.

The second (and nonetheless important) comparison between the two techniques is their point analysis performance. Theoretically speaking, under the correct conditions, close to 1μm lateral resolution should have been achievable by TXPS. However, the best TXPS experimental value was 2.6μm (16% to 84% confidence limits) being to some extent limited by source foil roughness. This compared to a 15μm spot measured in the 220i which the authors said was equivalent to 7.5μm lateral resolution (20% to 80% confidence limits) [100]. This represented a result close to the aberration limit achievable under the 220i's transfer lens design. Point analysis requires the specimen to be moved in this instrument until the local area of interest is immediately under the focal point of the lens. Whilst this does not present a huge problem, it does make the transfer from mapping to local spectroscopy awkward. The effect of the low energy flood of electrons on polymers has already been shown and on flat specimens the zoom camera is of little help. Presumably in difficult cases the specimen has to be XPS mapped several times until the feature of interest is in the correct position. In TXPS, the XPS imaging step was the slowest but choice of point analysis only needed the raster marker to be moved. As explained in several other chapters, specimen alignment in TXPS was quickly performed using TSEM with an optical image as a useful reference. This reference would not have been needed if a zoom camera was added to the modified MA500 on the analyser side. A simple switching device would then have been advisable alternating between the light source and the photomultiplier to avoid scintillator disk damage.

The present TXPS instrument design and the 220i have similar count rates at high magnification (without the use of the XL lens). However, when features of interest do not demand high lateral resolution performance, the point spectroscopy signal levels on the 220iXL improve sharply. With these samples the point size in TXPS would remain fixed so the beam can be rastered or perhaps demagnified. TXPS count rates remain low unless the specimen current is increased. This of course is allowable as photon densities are reduced as shown by Cazaux [55].
TXPS photon damage is discussed in detail in section 7.1.1. Damage is intense but very localised in TXPS, being restricted to the area of current interest. The defined collection system of the 220iXL means that large areas of the sample are being irradiated whilst the signal is only being collected from a small area. Care must be taken when interpreting sequential 220iXL point analysis data from damage sensitive samples. This is a clear advantage of the TXPS technique in a materials area where samples would be the most common.

An area that must be mentioned in any comparison between the two techniques is sample preparation. Essentially there are no special sample preparation procedures necessary for the 220iXL unless cross-sections are of interest. Standard in-situ fracture techniques can be used for the 220i such as milling, liquid nitrogen fracturing and T-peeling. TXPS needs the production of soft X-ray transparent specimens from ion beam thinning or ultramicrotomy. This can only slow down the through-put of samples, but there are many examples where extensive sample preparation is a necessary evil prior to even conventional XPS analysis.

9.1 Conclusions

In an imaging mode the commercial instrument out-performs TXPS, especially in acquisition times. In terms of point analysis, TXPS has the edge, perhaps more so in any future developments of a specifically built spectrometer. TXPS does not have as many potential applications as the 220iXL, for sample preparation reasons, but it can offer local analysis in many spheres of materials science by the simple modification of a standard instrument.
10.0 CONCLUDING REMARKS

1) An electron beam held at a given position on a source foil allows acquisition of a TXPS spectrum from the opposite surface, with electron beam powers of the order of 0.001W. Thin specimen films may be placed on top of the target for analysis.

2) Rastering the electron beam allows TXPS elemental mapping to be carried out as the X-ray spot follows the electron beam. Maps have been successfully acquired and interpreted. Chemical state mapping has yet to be realised.

3) X-ray sources must be made from an element with a narrow natural X-ray line width such as aluminium, magnesium or silicon to achieve chemical state resolution because there is no opportunity for monochromatisation in TXPS.

The target metals may be thin foils or evaporated on the back of the sample. Foils suffer from pin-holes. Two foils are usually required to largely eliminate the damaging penetration of the electron beam. The foils are rough on the 100nm scale and so make TSEM imaging difficult.

Evaporated sources are flat compared to the foils and so it should not be difficult by TSEM to reveal the position of the sample. A continuous source would be ideal, such as one mounted on a grid and carbon support film. On a sample with a hole in the middle, like one from ion beam thinning, a carbon film could again act as a backing. Without the support film acting as an aluminium substrate covering the entire field of view, the primary beam glare would totally mask the TSEM image and swamp the photoelectron signal.

Silicon single crystals are totally flat and so in topographic terms they are ideal for TSEM imaging. The wafers are 6μm thick and so require uniform thinning to allow imaging at lower specimen currents and accelerating voltages.

4) An ideal spectroscopy accelerating voltage has been shown to exist for a given sample and source combination, where the electron interaction volume is just stopped within the target. Beyond this voltage primary electrons are transmitted which enhance the background and Auger peaks in the spectra. Prolonged exposure to such a voltage
at high specimen currents (μAs) risks sample damage. Below the ideal voltage, X-ray production is not optimum.

5) Energy resolution is improved using a hemispherical analyser rather than a cylindrical mirror analyser. The first TXPS chemical state resolution has been collected and usefully interpreted.

6) The count rate in TXPS is unaffected by magnification, providing the X-ray power remains constant, unlike other small area XPS techniques which suffer from loss of count rate with improvement in lateral resolution. Increasing scan unit magnifications or using point analysis in TXPS also improved the photoelectron peak energy resolution. This relates to priority selection of the axial beam through the transfer lens and analyser system.

7) The S/B in TXPS is worse than conventional XPS as the X-ray intensity is higher just below the surface than at the immediate surface. This means inelastically scattered electrons are emphasised with respect to elastically scattered electrons.

8) The shape of background in the vicinity of photopeaks is peculiar to TXPS. Peaks exhibit very strongly sloping backgrounds on the low kinetic energy side. This inelastic gradient has been seen to decrease with increasing specimen thickness.

9) Calculations and experimentation have shown TXPS in the BTMA500 to be able attain higher lateral resolutions than Cazaux's apparatus. The electron gun has a smaller spot size and the transmission of the system is better. Analysis currents are routinely lower too.

10) TXPS lateral resolutions of 1μm have yet to be demonstrated. A resolution of about 2.6μm is shown. The accelerating voltage affects the obtainable resolutions as does the specimen current and foil thickness. In the BTMA500 the ultimate resolution of TXPS can only be achieved by keeping all these at low levels.
11) Lateral resolutions calculated from each of Cazaux's two equations do not give quite the same result. A better approximation could be obtained using Monte-Carlo simulations ($\phi(pz)$) to calculate the exact positions which X-rays are generated, and then to evaluate their attenuation when leaving the back surface of the source at various angles. The emergent X-ray distribution will give the effective X-ray probe size and hence the lateral resolution in TXPS.

12) SEM at a few kV and less than 1nA produces a quick and simple reference image of the sample on top of the source.

13) At about 10nA, just above the ideal spectroscopy voltage (approximately 1-2kV), TSEM provides a useful tool for finding the samples on the source. TSEM relies on thickness contrast to show the sample. The sample film thickness has to be sufficient to dominate any topographical effects in the aluminium foil, otherwise TSEM images are unclear. Samples should be several hundred nanometres thick. Contact of the sample and target produces clearer images as a consequence of some electrons escaping around the sample to the photomultiplier in the non-contact case. Sample and foil flatness is also important.

14) Samples are easier to locate using reference points such as a copper grid or TSEM bright spots from holes in the source foil.

15) The CSLM provides a quick and effective method of producing reference images of the source mounted samples and the film on grid samples, avoiding any problems of carbon deposition from the TEM and electron beam reduction. The CSLM images do not suffer severely from the specimen curvature problems of reflected light microscopy. Addition of a CCD zoom camera to the TXPS instrument would negate the need for reference images.

16) There are many applications for TXPS encompassing all areas of material science. Specimens are limited by the need to be sub-micrometer in thickness, but this still leaves a large scope for technique use. An example of a sample made by ion beam
Concluding Remarks

Thin thinning demonstrated the applicability of TXPS to harder materials. Polymeric specimens showed soft materials could also be examined following ultramicrotomy. An interface between a mixed hard and soft material was also examined by chemical etching away the hard substrate.

17) Examination of an ion beam thinned RS magnesium/aluminium alloy extrusion gave the final TXPS route which would identify spinel inclusions. Conventional XPS had failed to show the existence of the spinel because of insufficient sensitivity and the unfavourable distribution of inclusions within the sample. The higher lateral resolutions in TXPS would identify Al$^{3+}$ ions by artificially increasing sensitivity after a number of random point analyses. Together with evidence from other techniques and samples from different processing conditions the TXPS results would conclusively explain the corrosion behaviour of the alloy.

18) The interlayer between mild steel and an ICI chlorinated primer (Haloflex) was successfully analysed by TXPS following ultramicrotomy. The ability to analyse a photon damage sensitive polymer was shown together with a lateral resolution sensitivity enhancement. The interfacial interaction region between the two materials was mapped and analysed and data showed an iron chemical state change across the interlayer in the hydrogen peroxide doped primer. The change in valence state was explained by iron and oxygen transport between the substrate, coating and environment which occurred during drying and subsequent saline exposure. Reinterpreted SAXPS data showed a similar chemical state change but the mechanism was explained by a slightly modified model. TXPS showed real possibilities for a comprehensive study of the primer system under a variety of environmental exposure conditions.

19) The TXPS work highlighted the need for data from several analytical techniques in complicated materials systems. TXPS results alone could have been misleading.

20) TXPS specimen damage by Joule heating is not a problem providing careful control of accelerating voltage and specimen current is maintained. Photon damage could be a problem, particularly with polymers. Indeed it is with many high resolution
Concluding Remarks

XPS techniques, including using synchrotron sources, but soft X-rays are still less damaging than electrons. Electron beam rastering can be used to reduce the local sample damage as well as beam blanking in between analyses. Photon damage of polymers has been correlated to degradation curves in the literature and successful analysis of sensitive materials has been experimentally shown.

21) Specimen charging has not presented any problems in TXPS. Generally, charging is stable and only a few eV in the positive direction, similar to conventional XPS. However, if there is a poor source earth negative charging can occur.

22) There is no conclusive evidence that the use of a silicon single crystal source improves the TXPS lateral resolution. It appears that the surprisingly high resolution attained in this work may have been an artefact of sample topography and photoelectron forward scattering.

23) The TXPS instrument built for this thesis was very much a development instrument. If a commercial system was developed there would be several hardware improvements. The count rates need to be improved in order to use lower pass energies and shorten acquisition times. Transfer lens transmission requires some improvements and a series of channeltrons should replace the single detector. A CCD zoom camera would also help in specimen alignment and monitoring of sample degradation.

24) In a comparison of TXPS on the MA500 to a commercial XPS spectrometer (VG 220iXL), TXPS could achieve higher lateral resolutions in a point analysis mode, but the acquisition times in the imaging mode were considerably longer. The commercial system did not require significant amounts of sample preparation either and boasted a larger variety of possible specimens.
11.0 FUTURE WORK

This thesis has shown that, in its present condition, TXPS in the BTMA500 suffers from a lack of photoelectron signal for fast spectral acquisition and also risks degradation of damage sensitive samples. The next generation of TXPS instrument will require an improvement in the photoelectron collection efficiency. This will be possible by increasing the number of channel electron multipliers or more significantly the transmission of the transfer lens. This could be achieved by shortening the distance between the first element of the lens and the sample. A stunted lens nose with a high transmission mesh over the end to prevent field break though will be necessary together with a power supply unit capable of achieving a voltage greater than 10kV. The recent XPS interest in immersion of the sample in a magnetic field may also have some impact on TXPS lens transmission, as the high energy primary electrons will be deflected far less than the emerging photoelectrons. The addition of a CCD UHV zoom camera would make the technique easier to use in terms of specimen alignment as well as allowing a visual inspection of the current condition of samples under investigation.

The applicability of the TXPS technique to a wider spectrum of materials samples is certainly an area where more research is necessary. The technique may then finally be in demand from instrument users, forcing manufacturers to offer an additional electron gun in the transmission geometry on an otherwise conventional instrument. TXPS does provide a relatively inexpensive route to XPS and imaging at the micrometer level.

The study of the Haloflex primer highlighted the possibilities for further TXPS investigations of the change in iron chemical state across interface both immediately after coating and following various degrees of environmental exposure.
To transform the BTMA500 Auger microscope into a Transmission X-Ray Photoelectron spectrometer, several pieces of equipment were required. A new vacuum bell jar to hold the hemispherical analyser, an electrostatic long-nosed transfer lens, a channeltron assembly and several vacuum flanges were all paid for by a grant of £17,038 from the Royal Society Paul Instrument Fund. The original proposal for SERC funding had failed despite a high assessment rating. The Royal Society assessor, Dr. Peter Duncumb, recommended the TXPS funding. Approximately £32,000 was applied for originally, which was not all accepted. The grant paid for the above equipment. The remainder of funding, for a digital scan unit, was to be reconsidered after TXPS had demonstrated adequate point analysis results. Fortunately the present scan unit was modified, using equipment donated by H. Bishop, so that TXPS mapping still could be carried out. P. Duncumb has continued to show considerable interest in the work.
Appendix 1

Plasmon Shifts

The table given in this appendix lists plasmon energies for some elements and compounds. It was taken from appendix 'C' of [34] where the data are used for EELS. $E_p$ is the measured energy and $\Delta E_p$ is the FWHM of the principle loss peak. The value in brackets is a free-electron plasmon energy calculated from equation 3.41 of [34].

Layer crystals, such as graphite and boron nitride, can show two possible plasmon peak energies. Bonding is weaker in the direction perpendicular to the basal plane giving 2 groups of valence electrons. Relative intensities of the peaks depends on the crystal geometry in EELS.

<table>
<thead>
<tr>
<th>Material</th>
<th>Eq. (3.41)</th>
<th>$E_p$ (eV)</th>
<th>$\Delta E_p$ (eV)</th>
<th>Material</th>
<th>Eq. (3.41)</th>
<th>$E_p$ (eV)</th>
<th>$\Delta E_p$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al (15.7)</td>
<td>15.0</td>
<td>0.5</td>
<td></td>
<td>K</td>
<td>(4.3)</td>
<td>3.7</td>
<td>0.3</td>
</tr>
<tr>
<td>AlAs (15.5)</td>
<td>16.1</td>
<td></td>
<td></td>
<td>KBr (12.4)</td>
<td>13.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$(am.)</td>
<td>26</td>
<td>10</td>
<td></td>
<td>Li (8.0)</td>
<td>7.1</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>As$_2$(cry.) (11.3)</td>
<td>18.7</td>
<td></td>
<td></td>
<td>KF (26.2)</td>
<td>25.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>As$_2$(anom.) (16.1)</td>
<td>16.7</td>
<td></td>
<td></td>
<td>Mg (10.9)</td>
<td>10.3</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>B$_2$(am.)</td>
<td>22.7</td>
<td>18</td>
<td></td>
<td>MgF$_2$</td>
<td>24.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BN(hex.) (9.2)</td>
<td>26</td>
<td></td>
<td></td>
<td>MgO</td>
<td>22.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BN(anom.) (24)</td>
<td></td>
<td></td>
<td></td>
<td>Mn (28.4)</td>
<td>71.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba (6.7)</td>
<td>7.2</td>
<td>2.7</td>
<td></td>
<td>Na (6.0)</td>
<td>5.7</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Be (10.4)</td>
<td>18.7</td>
<td>4.8</td>
<td></td>
<td>NaCl (15.7)</td>
<td>15.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi (14.0)</td>
<td>14.2</td>
<td>6.5</td>
<td></td>
<td>Ni</td>
<td>20.7</td>
<td></td>
<td></td>
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<tr>
<td>C(diam.) (31)</td>
<td>32.3</td>
<td>13</td>
<td></td>
<td>Pb (13.5)</td>
<td>13.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(grap.) (13; 21)</td>
<td>7.27</td>
<td></td>
<td></td>
<td>PbS (16.3)</td>
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<td></td>
</tr>
<tr>
<td>C(amor.) (24)</td>
<td>25</td>
<td>20</td>
<td></td>
<td>PbSe</td>
<td>15.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca (3.2)</td>
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<td>2.1</td>
<td></td>
<td>PbTe</td>
<td>14.2</td>
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<tr>
<td>Cd</td>
<td>19.2</td>
<td></td>
<td></td>
<td>Pt</td>
<td>35.0</td>
<td></td>
<td></td>
</tr>
<tr>
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<td></td>
<td></td>
<td>Pb</td>
<td>3.9</td>
<td>3.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Cr (26.8)</td>
<td>24.9</td>
<td></td>
<td></td>
<td>Sn</td>
<td>(15.1)</td>
<td>15.2</td>
<td>3.2</td>
</tr>
<tr>
<td>Cs (3.4)</td>
<td>2.9</td>
<td></td>
<td></td>
<td>Sr</td>
<td>(13.4)</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>Cu (16.9)</td>
<td>19.3</td>
<td></td>
<td></td>
<td>SrO</td>
<td>17.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Er</td>
<td>14.0</td>
<td></td>
<td></td>
<td>SrO$_2$</td>
<td>(17.4)</td>
<td>17.1</td>
<td>6.2</td>
</tr>
<tr>
<td>Er$_2$</td>
<td>16.8</td>
<td></td>
<td></td>
<td>Sr$_2$O$_3$</td>
<td>(16.4)</td>
<td>16.3</td>
<td>6.2</td>
</tr>
<tr>
<td>Fe (29.8)</td>
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<td></td>
<td></td>
<td>$\text{SiO}_2$</td>
<td>(16.6)</td>
<td>16.7</td>
<td>3.2</td>
</tr>
<tr>
<td>Ga (14.5)</td>
<td>13.8</td>
<td>0.6</td>
<td></td>
<td>$\text{SiO}_2$</td>
<td>(16.6)</td>
<td>16.7</td>
<td>3.2</td>
</tr>
<tr>
<td>GaAs(cr.) (15.2)</td>
<td>15.8</td>
<td></td>
<td></td>
<td>Si$_2$N$_4$</td>
<td>17.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaAs(anom.) (15.5)</td>
<td>15.5</td>
<td></td>
<td></td>
<td>Se</td>
<td>(14.3)</td>
<td>13.7</td>
<td>1.3</td>
</tr>
<tr>
<td>GaP(cr.) (16.5)</td>
<td>16.5</td>
<td></td>
<td></td>
<td>Se$I_{\text{cr}}$</td>
<td>(14.0)</td>
<td>13.4</td>
<td>1.6</td>
</tr>
<tr>
<td>GaSb (13.8)</td>
<td>13.3</td>
<td></td>
<td></td>
<td>Sr</td>
<td>(7.4)</td>
<td>8.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Ge (15.6)</td>
<td>16.2</td>
<td>3.3</td>
<td></td>
<td>Tb</td>
<td>13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge$_2$O (15.6)</td>
<td>15.7</td>
<td>3.8</td>
<td></td>
<td>Tb$_2$O$_3$</td>
<td>15.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg$\text{sol}$ (7.7)</td>
<td>6.3</td>
<td>1.5</td>
<td></td>
<td>Te$_2$O$_3$</td>
<td>(13.3)</td>
<td>15.3</td>
<td>6.2</td>
</tr>
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<td>Hg$\text{liq.}$ (7.5)</td>
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<td>1.0</td>
<td></td>
<td>Ti (17.8)</td>
<td>17.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In (12.5)</td>
<td>11.4</td>
<td>12</td>
<td></td>
<td>V (22.4)</td>
<td>21.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>InAs (13.8)</td>
<td>13.8</td>
<td></td>
<td></td>
<td>V</td>
<td>12.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>InSb (12.7)</td>
<td>12.9</td>
<td></td>
<td></td>
<td>Y</td>
<td>15.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>In$_2$Sb$_3$</td>
<td>(11.9)</td>
<td></td>
<td></td>
<td>$\text{Yb}_2$</td>
<td>17.2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Appendix 2

Map Acquisition

- The intensity colour code used in all of the maps within this thesis is as follows:
  
  White > Red > Yellow > Green > Blue > Purple > Black.

- The colour scheme in all of the maps reflects the pixel intensity for cross-map comparison (eg P-B and B) unless otherwise stated.

- A single channel was collected on the peak (P) and one on the high kinetic energy side to monitor the background (B).
Appendices

Appendix 3

Photon Induced Damage

This appendix gives the plot of $X_0/X_t \times 100$ against time for some chlorine containing polymers taken from the Scienta ESCA-300 Database [48]. It includes PVC used in section 7.1.1 to investigate the photon induced damage rates in TXPS. $X_0$ is the initial polymer Cl/C ratio, prior to exposure to the monochromated Alkα X-rays, and $X_t$ is the ratio after various exposure times. The time axis can be divided by F from equation 27 to convert the database plots for use with TXPS in the MA500. The degradation index quoted in the database, which gives the percentage damage of the polymer after 500min. exposure, can also be modified using the same F factor.

Scienta ESCA-300 acquisition details:-

Rotating anode Alkα monochromated X-ray source set at 14kV and 100mA. Other instrumental parameters and the X-ray spot size are given in section 7.1.1.
Appendix 4

Haloflex

Haloflex is a commercially available acidic water-borne latex primer and is a registered trade name of ICI plc.

The Haloflex formulation (buffered to pH 5-6) used in this study is as follows:-

<table>
<thead>
<tr>
<th>INGREDIENT</th>
<th>% W/W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haloflex 202</td>
<td>59.55</td>
</tr>
<tr>
<td>Synperonic PE 39/70 (30% soln.)</td>
<td>4.20</td>
</tr>
<tr>
<td>Stabiliser/ dispersant</td>
<td></td>
</tr>
<tr>
<td>Butyl 'Ethoxol' Coalescing Solvent</td>
<td>2.09</td>
</tr>
<tr>
<td>'Bevaloid' 642 Defoamer</td>
<td>0.20</td>
</tr>
<tr>
<td>Water</td>
<td>9.54</td>
</tr>
<tr>
<td>'Methocel' J12MS Thickener</td>
<td>0.20</td>
</tr>
<tr>
<td>Red Iron Oxide OR Green Chromium Oxide</td>
<td>2.57</td>
</tr>
<tr>
<td>Zinc Phosphate Anticorrosive Pigment</td>
<td>5.37</td>
</tr>
<tr>
<td>Barytes Extender</td>
<td>16.28</td>
</tr>
<tr>
<td>Hydrogen Peroxide*</td>
<td>1000 ppm</td>
</tr>
</tbody>
</table>

* Denotes only added for the TXPS study.
The diagram below shows the mean relative sizes of Haloflex components.

![Diagram of Haloflex components with sizes in microns](image)

**Haloflex Fe2p Template Peak Fitting Conditions**

The Haloflex iron interlayer did not contain any Fe⁰, as this was removed by iodine-methanol etching. Any fitting procedure only required the use of the Fe³⁺ and Fe²⁺ valence states. Each valence state had two satellites on the low kinetic energy side of the principle peaks. The Fe2p peaks were template fitted using the following data originally derived from iron fitting literature:-

<table>
<thead>
<tr>
<th>Peaks of Interest</th>
<th>Peak Separations (eV)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂p₃/₂ &amp; Fe₂p₃/₂</td>
<td>13.6</td>
<td>[85]</td>
</tr>
<tr>
<td>Fe³⁺ &amp; Fe²⁺</td>
<td>1.5</td>
<td>[83,88]</td>
</tr>
<tr>
<td>Fe³⁺ &amp; its Two Satellites</td>
<td>3.0 &amp; 8.4</td>
<td>[88]</td>
</tr>
<tr>
<td>Fe²⁺ &amp; its Two Satellites</td>
<td>2.4 &amp; 5.6</td>
<td>[88]</td>
</tr>
</tbody>
</table>
The area ratios of the principal peaks to their two satellites were fixed as follows [88]:—

\[
\begin{align*}
\text{Fe}^{3+} & : 1 : 0.1058 \\
\text{Fe}^{2+} & : 1 : 0.1980
\end{align*}
\]

The Fe\text{2p} doublet area ratios were set at 1 : 0.4 (Fe\text{2p}_{3/2} : Fe\text{2p}_{1/2}) to achieve the best fit. The noisy rising background, on the low kinetic energy side of the Fe\text{2p} peaks, led the ratio to depart from the theoretically predicted ratio of 1 : 0.5.

Brundle recommended the use of a FWHM of 4.5eV irrespective of the particular valence state of the oxide or hydroxide. In all of the TXPS template fitting, a value of 4.2eV appeared to more satisfactorily follow the peak shapes.

In the TXPS experiments the pass energy was set at 100eV to achieve a reasonable S/N. Analyser broadening governed the peak shape, so the template fitting used a 100% Gaussian line shape [87].
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TXPS PUBLICATIONS

This is a list publications produced by the Author in connection with this thesis, including written papers and oral/poster presentations at international conferences.


- Oral paper presented at the 'European Conference in Applications of Surface and Interface Analysis' (ECASIA-5), Catania, Sicily (October 1993).


- Poster paper presented at Quantitative Microbeam Analysis (NATO), Dundee (August 1992).