A Novel MeV Ion Microbeam Technique for Measuring Diffusion of Small Molecules in Polymeric & Biological Matrices

by

D.W.Drew

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Department of Physics
University of Surrey
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Abstract

This thesis describes initially the development of novel MeV ion micro-beam techniques. It then discusses their application to the measurement of the diffusion of small molecules in polymeric and biological matrices which hitherto were not possible. The matrices studied were skin tissue, human hair, polymeric cable insulation and hydrophilic polymers.

The important novel aspects of the techniques are:

- Use of $^3$He scanning ion microbeam.
- Use of dual uncollimated charged particle detectors to measure induced nuclear reaction products.
- Use of a very thin window detector capable of detecting X-rays from elements heavier than beryllium.
- Fast freezing of samples with liquid nitrogen to freeze diffusion profiles and eliminate sample deformation.
- Use of a liquid nitrogen cooled target stage to both retain water and effectively eliminate beam heating effects when exposing samples to vacuum and the ion microbeam respectively.
A Dedication

This is dedicated to all those people whose help has culminated in this work. The dedication is not restricted to those who have assisted my research. It is for all the people, friends and institutions who over the years have given me the encouragement and opportunity to pursue the education I missed first time around.
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Chapter 1

Introduction

This work describes the development and applications of the target chamber and scanning ion microbeam at the EPSRC 2 MeV Ion Beam facility at the University of Surrey. The use of this combination to investigate the diffusion of small molecules and water in biological and polymeric matrices is then described. The ion microbeam analysis techniques used include; Rutherford BackScattering (RBS), Nuclear Reaction Analysis (NRA) and Particle Induced X-ray Emissions (PIXE).

Ion beams have been used for several years at Surrey [1] to measure interdiffusion of polymers using an energy loss technique. Beams of millimetre dimensions are used, one of the polymers is deuterated and either a nuclear reaction technique [2] [3] or forward elastic scattering [4] is used to profile the deuterated polymer depth distribution.

In general, with ion beams of a few MeV, these techniques can only measure diffusion in the top few microns [1]. As ions pass through matter they lose energy. The rate of energy loss is dependent on the mass and energy of the ions coupled with the composition of the target sample [5]. This defines the maximum depth the ion beam can reach in a sample with the ion beam impinging on the surface. However the maximum depth which can be analysed is dependent on other factors such as the effective threshold energy below which the reaction will not occur, or the resultant particles being of insufficient energy to reach the detector.
CHAPTER 1. INTRODUCTION

During work undertaken in collaboration with Unilever plc – an investigation of the feasibility of monitoring the diffusion of cosmetics in the biological polymers skin and hair – a need was revealed for the measurement of diffusion profiles in samples to much greater depth, in some cases of the order of millimetres. This prompted development of scanning microbeam techniques at Surrey which would enable measurement depths required.

There are problems inherent in the study of biological samples in an evacuated scattering chamber. For example, exposure of skin at room temperature to a vacuum leads to dehydration. Many conventional methods of fixing biological specimens for use in a vacuum such as freeze drying, staining or setting in resin also rely on dehydration of the sample. The removal of water must inevitably remove or redistribute many of the substances we wish to profile [6]. This is especially true if the substance we wish to profile is water! Also, even if water desorption is not a problem – as in the case of hair – bombardment by an ion beam at room temperature rapidly leads to destruction of the hair due to beam heating.

Environmental chambers and external beams are alternatives to using vacuum chambers. In environmental chambers the sample is housed within either a helium or nitrogen cell. The ion beam enters through a thin foil window [7]. An external beam can be created by either allowing the beam to exit the vacuum into air through a thin foil or small aperture [8] [9]. Both these alternatives have some advantages, such as ease of sample changing and heat dissipation. Beam current measurement is however difficult. Also the method of scanning the sample has to be mechanical and hence slow, otherwise the scanning beam would require a window slightly larger than the dimensions of the scan – requiring a thick window to ensure vacuum integrity. There is then the likelihood of beam spot “blowup”.

The decision was made to explore an in-vacuo solution at the Surrey Van de Graaff. This would allow use of the ion microbeam transputer driven raster scan being developed in tandem by the Department of Electrical Engineering at Surrey. This allows data to be correlated with beam position giving 2-dimensional areal den-
sity maps [10]. It would of course need to be combined with a liquid nitrogen cooled target stage to prevent water desorption. This would also simultaneously nullify beam heating effects and if insulated provide a pathway for current measurement.

In the following thesis I will initially describe the ion microprobe beam line at Surrey – the procedure developed for optimising beam spot size and current is given in Appendix A. I will then describe the target chamber and the developments introduced – the incorporation of the liquid nitrogen-cooled target stage, twin charged particle detectors capable of high energy proton detection and a state-of-the-art ultra-thin window X-ray detector.

This is then followed by a section demonstrating qualitatively the applicability of the system in a biological matrix (skin tissue) and a beam-sensitive polymer using a proton microbeam. To conclude, the use of a $^3$He microbeam, unique in the world, to measure the diffusion of deuterated surfactant in hair and heavy water in polymer is described. The latter has been the subject of a paper which has been accepted for publication.
Chapter 2

The Surrey Microprobe

2.1 Introduction

All ion beam experimentation was undertaken at the EPSRC/University of Surrey Ion Beam Facility in the Department of Electrical Engineering Accelerator Laboratory. The facility comprises three accelerators, only one of which – the 2 MeV Van de Graaff positive ion accelerator – is routinely employed for analysis. The 2 MeV Van de Graaff can supply $^1$H, $^3$He and $^4$He ions to any one of four lines (figure 2.1). Only lines 2, 4 and 5 are routinely used; line No.2 for RBS and NRA analysis of inter-polymer diffusion, line No.4 for RBS analysis of samples ion implanted by the Electrical Engineering Implantation group and line No.5 (microprobe) for RBS, NRA and PIXE analysis of diffusion of small molecules in thick samples and bulk analysis of biological samples.

This report will only consider the description and operation of the Surrey microbeam. This naturally splits into three distinct areas: the Van de Graaff, the beamline and the target chamber. Section 2.2 will consider the generation and acceleration of positively charged particles from the Van de Graaff. Section 2.3 will consider the collimation, focusing and scanning hardware of the ion microprobe. The target chamber will be dealt with separately in chapter 3 due to the specific modifications made to this part of the apparatus during the course of this work.
CHAPTER 2. THE SURREY MICROPROBE

Concrete shielding

Van de Graaff

'The Cave'

Momentum Selecting Magnet

Line 1

Line 2

Line 4

Line 5

Target Chambers

Figure 2.1: Schematic layout of Van de Graaff and beam lines.

The multi-component nature of the three areas of the microprobe beamline require a step-wise setup procedure to produce a perfectly focused microprobe. Previously, information about this has been verbally passed among users, and as with any knowledge delivered in such a manner, has been subject to a certain amount of inaccuracy. To this end, Appendix A is included to provide a stepwise guide to the optimal set up of the microprobe.

2.2 Van de Graaff

The 2 MeV Van de Graaff Ion Particle Accelerator (figure 2.2) is of the type AK manufactured by the High Voltage Engineering Corporation, Massachusetts U.S.A.[11]. It is situated in a 600mm thick concrete block walled reentrant 'CAVE'. The ion beam line enters the laboratory through an aperture in one wall, entering the momentum/direction selection magnet, where it is diverted down the required beam line.

Essentially, the Van de Graaff ion accelerator consists of a moving belt, a belt charging unit, a high voltage terminal, a positive ion source and an accelerator tube all contained within a pressure vessel and an exit portal.

The belt (made of an insulating material) runs between two pulleys – a drive
pulley mounted on the generator base and a terminal pulley mounted on the high voltage terminal. The drive pulley is maintained at a negative voltage. Positive charges are sprayed onto the belt. The belt then carries the positive charges to the terminal where they are removed from the belt and deposited on the terminal shell. As the positive charge accumulates on the terminal, the potential increases to a value limited both by the insulation of the terminal and the balance between the charge supplied on the belt and the charge drawn away by the beam. Positive ions are produced by the ionisation of gas at low pressure in the ion source bottle. The gas is stored in a cylinder and allowed to flow slowly into the bottle where it is ionised by rf excitation. The positive ions thus formed are withdrawn from the ion source bottle into the accelerator tube. The positive ions flow through the accelerator tube, accelerated by the generator voltage that corresponds to the voltage of the terminal shell. These positive ions are sent through a tube extension to the exit portal.

2.3 Microprobe Beamline

This section describes the components of the beam line. The ordering follows the ion beam from where it exits the Van de Graaff to where it enters the target chamber.
A schematic diagram of microbeam line is shown in both side and plan view in figure 2.3.

2.3.1 Up Stream X–Y Steering Plates

Vertical and horizontal electric field plates are situated upstream of the momentum selection magnets. These are used to align the ion beam, directing it into the momentum selection magnet. Prior to my beginning work on microbeam development these did not exist. There was no control over either the height or horizontal position of entry to the magnet. Thus a particular magnet current setting could correspond to various beam energies. The beam height could also vary from day to day. Together with my supervisor, I wrote a case for their purchase to the University Foundation Fund. It was accepted and the Electronic Engineering department enabled their inclusion.

2.3.2 Viewer No.1

The viewer consists of a quartz plate mounted at 45° on a retractable plunger, and a glass window for viewing the fluorescence on the quartz plate. In operation the plate is moved into the path of the ion beam manually, allowing the size, shape and alignment of the beam to be observed, figure 2.4.

2.3.3 Momentum Selecting Magnet

Ions are charged particles and as such can be deviated by a magnetic field. As the force \( q(B \wedge y) \) is perpendicular to the ion velocity, circular motion is induced. The radius of curvature in metres is given by:

\[
300r = \frac{\sqrt{2mE}}{Bq}
\]  

(2.1)

where

\( E = \) energy of ion (ie beam energy in MeV)

\( m = \) mass of ion (MeV/c\(^2\))
Figure 2.3: Side and plan views of microprobe beamline from the Van de Graaff to the vacuum chamber showing relative positions of major components.
CHAPTER 2. THE SURREY MICROPROBE

Figure 2.4: Schematic diagram of viewer in position for observing beam.

\( B = \) magnetic field (tesla)
\( q = \) Number of charges on ion

The choice of \( B \) selects an ion of a given charge, mass and energy and also steers the ion beam down a given beam line.

2.3.4 Energy Feedback Slit

The energy of the ion beam is held constant using a pair of vertical plates forming a slit. A vernier above each plate allows the slit position and width to be adjusted. Small energy changes within the accelerator will alter the deflection in the momentum selecting magnet, causing an imbalance in the current intercepted by the left and right edges of the slit. The difference signal is fed back to the Van de Graaff indicating a compensating energy change. With the beam energy, \( B \) and the feedback slit position set, only the upstream horizontal steering plate need be adjusted to provide consistent day-to-day energy stability.

2.3.5 Viewer No.2

This has the same specification as viewer No.1. Immediately down stream of the Energy Feedback Slit, it shows the position and width of the slit.
2.3.6 Down Stream X–Y Steering Plates

These consist of vertical and horizontal electric field plates and are used to align the ion beam on to the target area in the target chamber.

2.3.7 Aperture

The aperture intercepts the beam providing a circular source for subsequent focusing. There are apertures of four fixed diameters; 1mm, 200μm, 50μm and 25μm located in a stainless steel plate figure 2.5. The steel plate is placed in the ion beam path by means of a vertical vernier, a smaller vernier provides lateral movement by means of a pivot located at the base of the vertical vernier. The aperture plate can be retracted to allow the entire ion beam through.

On moving the aperture plate down into the ion beam, the first aperture encountered is of 1mm diameter followed by the 25μm, 50μm and the 200μm diameter apertures respectively. The vernier is graduated in millimetres with one revolution corresponding to one millimetre of vertical travel. There is no absolute scale on the
2.3.8 Viewer No.3

This has the same specification as viewer No.1. Immediately down stream of the aperture, this viewer can be used for locating and fine tuning the optimum aperture position.

2.3.9 Viewer No.4

This has the same specification as viewer No.1. Equidistant between the aperture and the Raster Scanner, this viewer can be used for focusing the Van de Graaff before insertion of the aperture plate.

2.3.10 Transputer Controlled Raster Scanner

This is an X- and Y- beam raster scanner, using transputer controlled vertical and horizontal electric field plates [10]. It allows areal scans on target with dimensions from the order of millimetres to the order of microns. The raster scanner is controlled and operated via a Sparc workstation in a nearby computer room. The operation of this software will be explained in greater detail in section 4.5.

2.3.11 Magnetic Focusing System

A Harwell Russian quadruplet focusing lens system[12], will optimally reduce and focus the apertured beam diameter by a factor of five. Beam focusing is achieved both by varying the magnet's fields one by one and physically moving them (figure 2.6). The magnets are suspended on a ball-bearing float table allowing lateral movement. Each corner of the table can be adjusted for height. The magnets can also move parallel to the ion beam for aligning the focal point. Each magnet will rotate about the ion beam for fine focusing. Since the addition of the upstream X-Y steering plates (section 2.3.1) the movement required for focusing is minimal.
Figure 2.6: Harwell Russian quadruplet focusing lens system: side and axial view showing directions of movement used during focusing of the microbeam. Magnets 1 & 3 control vertical position of the focused microbeam and magnets 2 & 4 control horizontal position of the focused microbeam. Axial rotation of magnet 1 allows fine turning of the focused microbeam.
Chapter 3

Target Chamber and Data Acquisition

3.1 Introduction

The microprobe target chamber has evolved over the years in response to varying demands of different users. At the outset of this research, systematic investigations clearly demonstrated the limitations of the existing target chamber setup. It was obvious that a logical stepwise optimisation of the target chamber was required, to provide a more precise analytical tool for our studies.

This chapter describes the existing chamber and all the subsequent modifications which enhanced its operation. Owing to the different requirements of the users of the microprobe facility, all modifications needed to be as transparent as possible – where these developments have directly affected other work they have been effected only after consultation. To this end utmost efforts have been made to ensure that most changes are reversible.

Accordingly the aim of this chapter is two fold;

• to describe the general layout of the target chamber, sample holding assembly, particle and X-ray detectors, cold finger assembly, peripheral equipment and access.
• to explain the modifications to the target chamber undertaken during the course of this work and the motives behind them.

To explain the motives behind the modifications we will need to understand both the internal arrangement of the chamber at the commencement of this work and the original chamber construction. The next section will give an overview of the original construction; many of the features mentioned there will be discussed in greater detail later in the chapter.

All modifications unless otherwise stated have been undertaken in the mechanical workshops of the Department of Physics.

3.2 Description of Target Chamber

Prior to Modification

One of the main limitations on the original construction of a target chamber at the end of the microbeam was the working length of the Harwell Russian quadruplet—the distance from the magnets to the focal plane of the microbeam (i.e., the plane in which the target sample needs to be positioned). All other criteria including detector positioning and chamber access have in some way been dictated by this parameter. The working length of 210 mm [13] not only limits the amount of room within the target chamber but restricts access to the upstream side of the chamber. Plates here support vacuum feedthroughs for the detectors and the optical microscope used for sample location and focusing purposes (figure 3.1). Since the focal plane is fixed the target samples have to be placed within this plane; this is achieved by a translatable target stage.

The original target stage was made of two platforms: The outer platform was in the form of a sleeve which slid in the direction of the ion beam allowing the target sample to be manually placed in the focal plane. The inner platform contained the target holder which could be translated horizontally and rotated around both the vertical and horizontal axis. Each of these movements was activated by a linear
electric motor. The inner platform also hinged backwards to allow targets to be changed by removing the rear of the chamber. However, due to the location of the linear motors on the rear of the inner platform the angle at which it could swing backwards was at most $\sim 60^\circ$. Hence access to the target holder was somewhat restricted. The plate containing the samples was attached to the target holder with a screw located in each corner. The inner platform was kept in position under normal operations by means of a retaining screw.

Previous work undertaken in this chamber consisted of routine surface analysis of semiconductor, metal and dry organic samples at room temperature. Consequently, the method of target changing did not pose a problem. A complete day's samples could be placed on a single target plate and inserted prior to the initial pump down. The work done during the course of this thesis however required several rapid sample changes in a day and cooling to liquid nitrogen temperatures. A further detail which slowed sample changing, was that the inner platform was hinged on the righthand side (looking into the rear of the vacuum chamber). This required many of the actions in the chamber being undertaken by the left hand—awkward for a right-handed operator such as myself.

The target chamber contained two detectors: an Oxford Instruments detector for PIXE measurements with a thin Beryllium window allowing detection of X-rays from all elements heavier than Sodium, and a 100 $\mu$m thick 50mm$^2$ surface area silicon surface detector for RBS at an angle of 165°. Additionally I discovered that the X-ray detector was not aligned with the beam's focal point — causing a serious loss of efficiency.
To allow the study of diffusion of light elements into polymers and biological matrices the chamber needed:

- A new target stage assembly with a target holder which was:
  - Precision translatable
  - Liquid nitrogen cooled
  - Electrically and thermally insulated
  - Capable of rapid sample changes

- An X-ray detector capable of detecting all elements down to Carbon.

- Multiple particle detectors to enhance low count rates from low cross-section nuclear reactions.

- Repositioning of both X-ray and particle detectors to maximise efficiency.

### 3.3 Vacuum Chamber

A schematic layout of the present vacuum chamber is shown in figure 3.1; the target staging and detector array have been omitted for clarity of presentation and will be discussed in sections 3.3.1 and 3.3.3. The rear of the chamber can be removed for general access to allow the changing of target assemblies, detectors and samples.

#### 3.3.1 Target Stage Assembly

The target stage assembly now consists of movable platforms allowing the sample to be translated in two directions; along the axis of the beam and secondly, horizontally with respect to the beam. Moving the sample in the axial direction allows the surface of interest to be placed in the focal plane of the ion beam. The horizontal movement of the target stage allows placement at the focal point. With an appropriately sized sample plate, multiple samples can be analysed or alternatively, very wide samples traversed in steps. The platforms sit one within the other, the traversing stage inside the axial stage. The platform allowing axial movement is located on runners in the
CHAPTER 3. TARGET CHAMBER AND DATA ACQUISITION

Axial view looking up the Beamline

Figure 3.1: Schematic diagram of vacuum Chamber showing external side and axial view, the target staging and detector array have been omitted for clarity – the feedthrough plates on the upstream side of the chamber are colour coded for reference. The scale is approximate and for guidance only.
vacuum chamber and is driven manually via a rack and pinion accessed externally. Inside this sits a second platform, hinged, to allow it to be swung backwards to permit access to the sample plate. The platform is hinged on the left (looking in from the rear of the vacuum chamber) and it swings outwards by 90°—further movement is restricted by a stopper. Within this hinged platform the target plate sits on a pair of horizontal slides. Horizontal translation (in increments of 25μm) is by means of a micro stepping motor. These platforms can be seen in the photographs in figure 3.2 with the target stage in place showing the stepping motor and with the horizontal platform swung backwards showing the target plate. The stepping motor assembly consists a Stepping Linear Actuator (RS 318-711) and stepper motor driver board (RS 217-3611), the power supply and control box was designed and built in the electronic workshops of the Physics Department.

The placement of the screw holes for mounting the sample plate is the same as the old assembly, although two of the diagonally opposing corners contain locating lugs. The sample plate is pushed onto these and secured with two hexagonal headed bolts. The advantage of this type of bolt is they can be placed on the end of an Allen Key, inserted and tightened rapidly with one hand if necessary.

### 3.3.2 Cold Finger Assembly

The cold finger assembly consists of a ITL¹ liquid nitrogen reservoir cold finger assembly entering the top of the chamber through a nylon flange. The bottom of the cold finger is attached to the translatable copper target stage via a copper braid, so as not to restrict the movement of the target stage. The cold finger and the target plate are electrically and thermally insulated from the chamber; the cold finger by the nylon flange (figure 3.3) and the sample holding plate by four small teflon washers and nylon screws which attach it to the backing plate of the horizontal platform. This allows the beam current to be monitored via an external pick up on the cold finger assembly. It is necessary to minimise the contact area of the teflon spacers

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¹ITL Instrument Technology Limited
Figure 3.2: Photographs of the target chamber: the upper photograph showing the rear of the target staging and the lower photograph showing the target staging in position for sample loading. In the chamber can be seen the particle detectors and microscope.
and nylon screws between the sample plate holder and the backing plate to reduce thermal transfer. During preliminary work on the target staging a teflon plate was used in place of the washers. The thermal transfer was such that the stepping motor was achieving similar temperatures to that of the sample holding plate – \( \sim 100^\circ \text{K} \) (measured using a thermocouple) during the course of an experiment. This caused the stepping motor to malfunction. Since exchanging the teflon plate for the teflon washers the temperature of the backing plate and stepping motor do not drop more than a few degrees below ambient temperature over the period of a full working day.

The apparent over-engineering of the nylon flange became necessary after observations of the methods employed by users when exchanging the target staging for one which does not allow the cold finger to be used. When the cold finger is replaced, the bottom must be aligned so it does not touch the target staging. This was normally achieved by the "over tightening" of one or more of the bolts fixing the cold finger to the flange, causing the threads in the flange to fail. The present design, shown in figure 3.3, has had extensive testing and appears to be successful.
3.3.3 Detector Arrays

3.3.3.1 PIXE Detector

By chance, as I was designing the target stage assembly the original X-ray detector's beryllium window fractured. In consultation with my supervisor and Dr Chris Jeynes the EPSRC Liaison Officer, it was agreed that it should be upgraded to an Oxford Instruments state-of-the-art ATW1\(^2\) window X-ray detector for PIXE measurements allowing detection of X-rays from all elements heavier than Lithium. A removable filter can be placed in front of the detector to increase its sensitivity to heavy trace elements by stopping the majority of X-rays from lighter elements. A repair time of 3 weeks was given by Oxford Instruments. In fact it took of the order 3 months. However it has performed precisely to specification (~ 130 eV resolution at the \(^{55}\text{Fe}\) line). Its resistance to pressure change is however questionable. In roughly 18 months the ATW window has fractured twice, although in the second instance some inadvertent abuse by another accelerator user was very likely responsible. Access to the chamber has now been restricted to users aware of the sensitive nature of the window.

To align the new detector so that it points at the beam focal point I designed a new feedthrough flange and detector support. These were rapidly constructed in the accelerator facility workshops. The detector realignment has allowed data acquisition time to be significantly reduced.

3.3.3.2 Particle Detectors

Charged particle reaction products and elastically scattered beam ions are detected in two EG&G Ortec 1500\(\mu\)m thick 100mm\(^2\) surface area silicon surface barrier detectors. At the onset of this research a single detector could be placed at a backward angle of 165° in the horizontal plane 50mm distance from the target. The techniques to be outlined in chapter 4 will show that the energy resolution can be

\(^2\)ATW1 is a trade name.
sacrificed in favour of increased count rate. To that end another detector was added and both were relocated to improve efficiency. The detectors are located 20° below the horizontal plane at symmetric angles of 135° to the incident beam at a distance of 25mm from the target.

### 3.3.4 Optical Microscope

The target stage can be viewed optically both in large field and small field to facilitate location on the target sample and in focusing the beam during the setup procedure. The focal plane of the microscope coincides with the focal plane of the focused microbeam. In a similar manner to the X-ray detector the microscope was realigned and a cross-hair eyepiece added to aid in beam location. Looking into the eyepiece of the microscope from the down-stream side of the target chamber, the target is in the same orientation as the view down the beamline.

### 3.4 Development of Target Holder

This section concentrates on the development of suitable apparatus for holding the samples cut in cross-section within the vacuum chamber. It is no coincidence that the resultant device is also fundamental to the preparation of the samples prior to being sectioned. Experimentation on samples that require freezing in liquid nitrogen before preparation and transfer to the vacuum chamber showed that handling, and preparation time must be kept to a minimum. There are two reasons for this; to prevent the samples from warming up and to reduce the degree of burns to the user's fingers!

The device is basically a small vice, a schematic diagram is shown in figure 3.4 in which one jaw of the vice is securely mounted on the sample plate, the other jaw is free to move relative to this one. The sample to be cut in cross-section is placed between the copper jaws and with the use of two screws, further gripped within the vice.
Figure 3.4: Schematic diagram of the target holder "Copper Jaws". One jaw is fixed to the sample plate by two retaining screws, the position of the other jaw is dictated by the tightening of two screws through the fixed jaw, thus gently gripping the sample. The sample can be further held in position by insertion of the pointed screws.
Chapter 4

Ion Beam techniques and Data Acquisition

4.1 Introduction

The aim of this chapter is to examine the ion beam techniques used in this study – NRA and PIXE – and to show how the precise preparation of samples coupled with analysis by a scanning ion beam can be used in the depth profiling of thick samples. The latter part of this chapter will give an overview of the data acquisition system including examples of 2-dimensional density distribution maps obtained using the scanning Microprobe.

4.2 Nuclear Reaction Analysis

Nuclear Reaction Analysis (NRA) involves the detection of products from a two-body final state reaction:

\[ a + b \rightarrow C^* \rightarrow d + e + Q \]

Where \( a \) and \( b \) are the incident projectile and target nucleus, \( C^* \) is the compound nucleus, \( d \) and \( e \) are the products and \( Q \) is the energy equivalent of the mass difference between the initial particles and the resultant particles. If \( Q \) is positive the reaction
is exothermic. Nuclear reactions are isotope specific with no direct relationship between the mass of the target nucleus and the energy of the detected particles. One method of profiling the diffusion of water and organic molecules in polymers requires the exchange of deuterium atoms for hydrogen atoms in the diffusant. The deuterium nuclei can then be located using the reaction:

\[ ^{3}\text{He} + d \rightarrow ^{5}\text{Li}^{*} \rightarrow p + \alpha \quad Q=18.4 \text{ MeV} \]

A typical spectrum from this reaction is shown in figure 4.1, the result of a 1.5 MeV \(^{3}\text{He}\) ion beam impinging on a fully deuterated polystyrene sample. The reaction products are well separated from the backscattered particles in the spectrum. The incident \(^{3}\text{He}\) particle strikes the deuterium target resulting in the forward recoil of the compound nucleus. As the incident \(^{3}\text{He}\) ions travel through the sample they lose energy, any compound nucleus produced at depth will have a reduced forward momentum. This results in particles emitted at backward angles from the reaction having increased energy. The resultant detected high energy protons lose little of their energy travelling out of the sample compared with the alpha particles. This is reflected in a narrower alpha peak. The shape of the proton distribution illustrates the varying capture cross-section, which is smoothly varying above the Coulomb repulsion effective threshold (0.3 MeV \(^{3}\text{He}\) energy) and has a maximum cross-section at \(\sim 0.6 \text{ MeV} \(^{3}\text{He}\) energy\) (figure 4.2).

Other competing \(^{3}\text{He}\) induced reactions occurring in a polymeric target are listed below:

\[ ^{12}\text{C}(^{3}\text{He},p)^{14}\text{N} \quad Q = 4.7789 \text{ MeV} \]
\[ ^{13}\text{C}(^{3}\text{He},p)^{15}\text{N} \quad Q = 10.6650 \text{ MeV} \]
\[ ^{3}\text{He}(^{3}\text{He},p)^{5}\text{Li} \quad Q = 10.8940 \text{ MeV} \]

The spectrum of these reactions induced by a 2 MeV \(^{3}\text{He}\) beam impinging on a thick Carbon sample is shown in figure 4.3. The upper figure shows the \(^{3}\text{He}\) reaction on \(^{12}\text{C}\), the resultant proton peaks have lower energy side peaks which correspond to the 13.0 MeV \(^{15}\text{O}\) intermediate compound state excited at a \(^{3}\text{He}\) energy of 1.3 MeV [15] as the \(^{3}\text{He}\) ions lose energy in the target. The lower figure shows the resultant
Figure 4.1: Typical spectrum from a 1.5 MeV $^3$He ion beam impinging on a thick fully deuterated polystyrene sample, the collimated ($2\text{mm} \times 10\text{mm}$ slit) detector is at $165^\circ$ to the incident beam at a distance 50mm from the target, subtending a angle of 0.008sr. The Proton and alpha peaks are from the $d(^3\text{He},p)\alpha$ reaction. The low energy peaks are the backscatters from the carbon present in the polystyrene (see insert). The three small peaks in the center are from a triple-$\alpha$ source – Cm, Am and Pu – located near to the target.
Figure 4.2: Total cross-section for the $^3$He+D nuclear reaction as a function of $^3$He energy.

proton peaks from $^3$He reaction on $^{13}$C and the $^3$He reaction on itself. This latter reaction is a time dependent feature. Much of the $^3$He ion beam does not result in either a nuclear reaction or a backscatter but is retained within the target sample, hence the concentration of $^3$He within the target sample increases with time.

As can be seen there are no major peaks greater than ~5.5 MeV. Thus detection of protons from the d($^3$He,p)$^α$ reaction is the obvious means of characterising the presence of deuterium.

In the conventional energy loss technique only protons which lose their full energy in the detector (those with energy > 12 MeV in figure 4.1) are used. These dominate the spectrum due to the use of a collimator in front of the detector; this both prevents protons from hitting the edge of the detector and limits the angular spread accepted, essential for good energy resolution. The depth of the struck deuterium is determined by relating the proton energy using kinematics to the $^3$He energy at collision, then using the range difference between this energy and the beam energy to calculate the depth. Depth resolution is determined by the energy resolution. This technique is
Figure 4.3: Typical spectrum from a 2 MeV $^3$He ion beam impinging on a carbon block. The collimated detector (2mm x 10mm slit) at 20° below the horizontal plane at 135° to the incident beam and 25mm distance from the target. The lower graph has an expanded abscissa to show peaks of lower yield.
however limited to depths of a few microns.

To probe larger distances a scanning beam technique is required. After diffusion of deuterated molecules into a sample surface, the sample is cut perpendicular to the surface and this edge exposed to the $^3$He microbeam. Scanning the beam across this edge, the depth distribution of the deuterium can be profiled by simply counting the number of protons produced as a function of beam position. In this technique the depth resolution is determined by the size of $^3$He beam spot.

To maximise the number of protons detected, the detector is used without a collimator. Protons incident near the edge of the detector do not lose all their energy in the detector and this results in a long tail as shown in figure 4.4. It is evident from figure 4.3 that competing reaction products above 6 MeV are negligible. Counting the number of protons in the region 6 MeV to 12 MeV enhances the count rate by $\sim 30\%$.

### 4.3 Rutherford BackScattering

Rutherford BackScattering (RBS)[16] is the Coulomb elastic scattering of charged particles. Incident ions scatter elastically from target atoms with an energy characteristic of the mass of the struck nucleus.

\[
\text{Energy}_{\text{out}} = K_m \text{Energy}_{\text{in}} \quad (4.1)
\]

where $K_m$ is the kinematic factor

\[
K_m = \left( \frac{M_1 \cos \theta + \sqrt{M_2^2 - M_1^2 \sin^2 \theta}}{M_1 + M_2} \right)^2 \quad (4.2)
\]

$M_1, M_2$ are the nuclear masses of the incident and target atoms respectively and $\theta$ is the scattering angle in the laboratory system. The insert of figure 4.1 shows the RBS spectrum of $^3$He ions scattered from the carbon in deuterated polystyrene. The shape corresponds to the scatter cross-section which increases with the decrease of incident particle energy as it passes through the sample.
Figure 4.4: Typical spectrum from a 2 MeV $^3$He ion beam impinging on a thick fully deuterated polystyrene sample. The uncollimated detector of area 100mm$^2$ is 20° below the horizontal plane at 135° to the incident beam and 25mm distance from the target, subtending an angle of 0.16sr. There is a significant yield in the tail, the number of counts in the region 6 MeV to 12 MeV is 30% of the total counts in the full energy proton peak.
4.4 Particle Induced X-ray Emission

Particle Induced X-ray Emission (PIXE)[17] results from incident ions undergoing collisions with the electrons of target atoms in which inner-shell electrons are ejected. The resulting vacancies are filled by outer-shell electrons ($\sim 10^{-16}$ seconds) and characteristic X-rays whose energies identify the particular atom are emitted. The transitions filling vacancies in the innermost shell produce K-series X-rays, those filling the next shell produce L-series X-rays and those filling the next shell produce M-series X-rays. Within each series there are different X-ray energies resulting from transitions from different outer-shells (figure 4.5). This work mainly concentrates on the X-rays which result from transitions in the K series, namely $K_\alpha$ and $K_\beta$. However for heavier elements such as copper the $L_\alpha$ and $L_\beta$ lines are also observed. A typical PIXE spectrum resulting from a proton beam impinging on a copper TEM grid mounted on glass is shown in figure 4.6. The characteristic X-ray peaks are superimposed on a background continuum of bremsstrahlung X-rays caused by deceleration of the ejected electrons. In transitions which result in low energy X-rays the $\alpha$ and $\beta$ lines are not resolved. A possible complication in interpretation of the X-ray spectrum is the occurrence of sum peaks – these are the result of the detector not resolving in time the arrival of two separate X-rays, hence the resulting pulse height is the sum of the two energies. This feature is most pronounced when the event rate is high[18].

With ion beams in the MeV range the X-ray yield is due to the multiple collisions. In each collision the ion only gives up a small fraction of its energy. As we have seen, the energy of the X-ray is characteristic of the target atom not the energy of the incident ion. Therefore, unlike NRA and RBS analysis in which the spectrum can give depth information according to energy loss, the X-ray peaks in the spectrum give no information as to the depth within the sample at which the interaction took place. PIXE however, is ideally suited to the scanning microprobe technique, where the number of characteristic X-rays can be related to beam position – allowing the profiling of any element whose X-rays can be detected.
Figure 4.5: Simplified atomic level diagram showing some of the transitions resulting in characteristic X-rays.

Figure 4.6: This figure shows a typical X-ray spectrum resulting from a proton beam impinging on a target, in this instant a copper TEM grid mounted on glass. Notice that at low energies the $\alpha$ and $\beta$ peaks are not resolved.
4.5 Data Acquisition

The method of acquiring data with a scanning microbeam was achieved by the development of a transputer controlled raster scanner designed and built by the Department of Electrical Engineering at Surrey[10]. Data is correlated with beam position allowing up to four 2-dimensional areal density maps and associated spectra to be recorded. The raster scanner is operated and controlled via a work station on which the 2-d density distribution maps and spectra are displayed in real time. Figure 4.7 shows a schematic diagram of the electronics relating the particle and X-ray detector signals with the raster scanning control box and work station. This section will give an overview of its capability – a more detailed description of the software operation is given in Appendix B.

The microbeam is raster scanned across the sample (in the X- and Y- axes) through a fixed number of pixels, 128×128, dwelling of the order $\mu$s at each position. The software allows this fixed number of pixels to be evenly distributed over a coordinate system of 4096×4096. Thus for the maximum area to be scanned there can be up to 32 possible intervals between dwell points. The number of intervals between the dwell points is referred to as the 'step size' of the raster scan. Reducing the step size and defining the starting point within the coordinate system allows areas of differing size and position to be mapped without moving the target. The maximum area of the target that can be analysed by the scanning microbeam is primarily dependent on the mass and energy of the incident ions. Typically for a 2 MeV microbeam this is in the region 2mm×2mm. The diameter of the microbeam spot can be chosen such that entire area is exposed to the microbeam.

The 2-d density distribution maps are obtained by selecting an energy window around a chosen peak in the spectrum. Only the data within this window is correlated with beam position. An example of a 2-d density map is seen in figure 4.8. It was obtained by placing a 'window' around the Cu-Kα X-ray peak in figure 4.6 (2 MeV proton microbeam impinging on a TEM grid mounted on glass), the diameter of the microbeam was nominally 8$\mu$m.
Figure 4.7: Schematic diagram showing the detector configurations; the two particle detectors or the X-ray detector.
Figure 4.8: 2-d density map of the Cu-Kα X-ray distribution from a TEM copper grid mounted on glass. The figure was obtained by ‘windowing’ the Cu-Kα X-ray peak in figure 4.6. The distance between the centre of the wires is 127μm. Note: the grid wires are of two diameters; the thick wire has a diameter of 30μm and the thinner of the two is the same as the letter K in the centre of the map, 23μm diameter. The beam size is nominally 8μm diameter.
CHAPTER 4. ION BEAM TECHNIQUES AND DATA ACQUISITION

4.6 Summary

For ion beams impinging on a single spot on a sample surface only bulk analysis of elements is possible using PIXE, only the top few microns can be examined using NRA. However by preparing samples in cross-section and using a scanning micro-probe in which the data and beam position are correlated to give a 2-d density distribution map both techniques can be used to profile diffusion to a greater depth. The maximum depth achievable is not constrained by the width of the scan as thicker samples can be analysed by traversing the sample a measured distance between consecutive runs. The advantages for viewing the diffusion profile of light molecules in cross-section in polymers are many: PIXE can be used for all elements heavier than beryllium, NRA for light elements (particularly deuterium). Energy resolution which is all important for depth resolution in energy loss spectra from NRA can be forgone. This allows detectors subtending greater solid angle to be used. As a consequence of optimising detector solid angles data acquisition times can be reduced. Many of the experiments undertaken during the course of this thesis could not have been attempted without this significant reduction in the time taken to process each sample. A similar motivation was present for the relocation of the X-ray detector (section 3.2). The next two chapters show examples of diffusion in a variety of biological and polymeric matrices using the techniques and methods outlined in this chapter.
Chapter 5

The Scanning Proton Microprobe

5.1 Introduction

In chapter 3 the microbeam cryo-target chamber was described, together with the modifications which were realised during the course of the research outlined in the present chapter and the following chapter. This chapter concentrates on the methodology and analysis using protons as the probing ions to monitor diffusants in biological and polymeric matrices – skin tissue and medium voltage cables.

With the proton microbeam the primary method of detection is of the X-rays from particle induced X-ray emission (PIXE). The cross-section for X-ray production is greater for protons than α-particles for elements heavier than carbon[19]. Also, protons have greater depth penetration than heavier particles of the same energy. For example, in a light polymer or skin tissue, a 2 MeV helium beam has a penetration of a few microns, a 2 MeV proton penetrates an order of magnitude deeper[5].

Two experiments will be discussed:

1. Characterising skin tissue treated with a silicone shower gel.

2. Characterising ‘Bow-Tie’ trees in medium voltage polymer cable insulation.
This study was undertaken during a period when the Van de Graaff reliability was uncertain. Ideally the microbeam energy is chosen to obtain optimum results. However the Van de Graaff underwent a period in which the pressure vessel had to be removed on a regular basis. Immediately subsequent to each removal the maximum energy achievable was approximately 1 MeV – the energy being increased incrementally over a period of days, to the maximum of 2 MeV. During this period there arose a backlog of users who required the higher energies. Therefore it was decided to undertake some of the experiments – investigating the feasibility of the scanning microbeam for the detection of substances in thick samples – during some of these low energy periods. During this development stage, for the reasons described here, the beam energy of each experiment represents the maximum available on the day.

5.2 Silicone Shower Gel in Skin Tissue

5.2.1 Introduction

For responsible manufactures of cosmetic products it is important to ascertain the extent to which creams and gels applied to the skin diffuse into the skin. Few techniques have the spatial resolution or elemental concentration sensitivity to measure such profiles. Nuclear Magnetic Resonance of hydrogen in the product has been the preferred technique to date[20].

Scanning ion beam analysis has in principle the advantage of improved spatial resolution and the capability of simultaneous detection of several elements labelling the product molecule. Measuring the profiles of two or more of these would give enhanced confidence that the profile represented that of the whole molecule. In this initial study silicon in a silicone-based shower gel is profiled in skin tissue.
5.2.2 Sample Preparation

All samples were supplied as part of a collaborative study by Dr P. Doyle at Unilever plc. The samples consisted of sections of pig skin comprising the dermis and epidermis. The surface area of the dermis was approximately 15mm x 20mm, the samples were approximately 3mm in thickness. The dermis had been washed and then treated with shower gel containing encapsulated silicone oil. The surface hairs were still in position. Each sample was sealed in a separate polythene bag.

To prevent the samples dehydrating during evacuation of the target chamber they were fast frozen in liquid nitrogen prior to loading in the chamber. A section of pig skin was clamped vertically in the copper vice bolted to a copper sample mounting plate as described in section 3.4. It was plunged into liquid nitrogen to fast freeze the skin. This rapid cooling has the effect of preventing the formation of large ice crystals and consequent swelling[21]. The sample was then removed and cut in cross-section with a scalpel level with the copper jaws. The sample was loaded into the target chamber which was then evacuated; at the same time the cold finger reservoir was filled with liquid nitrogen.

Great care must be taken in mounting sample such as skin tissues, compared to say, a section of polymer. Skin is non-uniform in its dimensions, it does not have parallel smooth surfaces to align with the copper jaws. Figure 5.1 shows a schematic diagram of a sample mounted in cross-section with a sloping dermis presented to the detector. The dermis is indicated by the thick dark line. Assuming a thin uniform layer of diffusant in the surface of the sample, the scanning microbeam will see not just the diffusion profile but part of the dermis surface giving a greatly enhanced X-ray yield, thus distorting the resulting spectra. This illustrates the importance of correlating the 2-d density maps with physical shape and orientation of the sample with respect to the scanning microbeam and the detector. This is achieved by recording a 2-d carbon X-ray scan and observing the sample under a microscope directly after removal from the vacuum chamber.

Skin tissue is soft and easily deformed when compressed between the copper
Figure 5.1: Schematic diagram of a tissue sample mounted in cross-section with the dermis on the same side as the detector but not flush with the sample holder - the dermis is indicated by the thick dark line.

jaws. A method of adjusting the orientation of the sample within the copper jaws was required. Modifications were made to the copper jaws resulting in pointed grip screws (section 3.4). These can be individually inserted to grip and gently push the tissue without undue deformation, aligning the dermis with the jaws.

5.2.3 Experiment

The 200μm diameter aperture was used giving a nominal microbeam diameter of 40μm. The beam energy was 1.5 MeV (the maximum achievable, section 5.1) with a beam current of 1nA. The X-ray detector was used without a filter, consequently all X-rays from elements heavier than beryllium were detected. Using the optical microscope the area of interest was located and placed in the focal plane of the microscope (section 3.3.4). The scanning microbeam was then used to locate the edges of the copper jaws. It was found that high X-ray yield from the copper L-series X-rays resulted in a sum peak (section 4.4) at energy 1.89 keV, very close to the characteristic silicon X-ray energy of 1.74 keV. The X-ray yield from silicon could easily be masked by the copper sum peak, so the scanning microbeam was aligned
to scan just inside the copper jaws for subsequent experiments to remove the sum peak.

5.2.4 Results and Discussion

To obtain the 2-d density maps (section 4.5) – an energy window is placed around a chosen peak in the spectrum, and the data within this window is correlated with beam position. This method cannot distinguish between the characteristic X-ray from the chosen element and a signal from the background continuum. Figure 5.2 shows an X-ray spectrum from a cross-section of pig skin in which the dermis was treated with shower gel containing silicone oil. The energy window for silicon, in which the data is correlated with beam position, is also shown. It can be seen that there is substantial background signal which requires interpretation in the silicon map.

The resulting 2-d density maps obtained in the initial measurement by windowing the silicon and carbon X-ray peaks are shown in figure 5.3. The carbon map shows the extent of the sample, the dermis is on the extreme left and the epidermis extends to the right. The sample is in the orientation as that depicted in figure 5.1, hence the enhanced yield from the dermis in both the carbon and silicon maps.

From the energy spectrum the silicon X-ray yield can be calculated by subtracting the background in the relevant window. This figure is in agreement with the yield from the enhanced areas of the 2-d density map, – including the areas of high intensity corresponding to the bottom of the epidermis, which are thought to arise through cross contamination whilst the samples were in the polythene bags. From this we conclude that the yield in the 2-d density map from the area of the epidermis is due to background signal. Obviously the spatial resolution obtainable from the 2-d density map depends on the orientation of the sample, ignoring beam diameter for the moment. Even so this initial experiment suggests that the silicone oil has remained on top of, or within the dermis. As a side remark, it is believed that the 2-d carbon map is the first micro-PIXE scan of carbon ever obtained.
Figure 5.2: X-ray spectrum of skin tissue mounted in cross-section with the dermis on the same side as the detector. The lower graph has an expanded ordinate to show the background continuum under the lower energy peaks and the position of the window around the silicon X-ray peak which is correlated with beam position to produce the 2-d density map.
Figure 5.3: 2-d density maps showing the distribution of data from the carbon peak (upper map) and data from the silicon peak (lower map) in figure 5.2. The tissue is in cross-section with the dermis to the left, the same side as the detector. The enhanced yield from the dermis is described in the text. The silicon yield from the back of the epidermis is thought to have been from cross-contamination whilst in the polythene bag. The nominal beam diameter was $40 \mu m$. 
The next experiment was designed to improve the spatial resolution by mounting another tissue sample the other way around, so that the dermis is both on the opposite side to the detector and flush with the copper jaw. In this way it was intended to reduce the enhanced yield due to the sample geometry. The sample plate was positioned using the stepping motor in 25µm increments, until the X-ray yield from the copper jaws, just to the right of the scan, disappeared.

Figure 5.4 shows the 2-d density maps for the carbon and silicon peaks thus obtained. Inspection of the sample showed it had been sectioned through the root of a hair, the indent on the right of the maps corresponds to the hair follicle. The hot spot in the silicon map coincides with the base of the root which is seen protruding in the carbon map. Similar calculations to those described above suggest that all of the silicon is located around the hair root, with little or no silicon in the epidermis.

The samples were inspected with a microscope upon removal from the vacuum chamber for signs of damage or deterioration. The sample's visual appearance showed no signs of dehydration and there was no damage from the ion microbeam.
Figure 5.4: 2-d density maps showing the distribution of data from the carbon peak (upper map) and data from the silicon peak (lower map). The tissue is in cross-section with the dermis to the right, on the opposite side to the detector. The copper jaw is ~50μm to the right of the map. The sample was sectioned through the root of a hair, the indent on the right of the maps corresponds to the hair follicle. The hot spot in the silicon map coincides with the base of the hair which is seen protruding in the carbon map (indicated by the arrow). The nominal beam diameter was 40μm.
5.2.5 Summary

These measurements on silicone-containing shower gel on pig skin are, to my knowledge, the only ones ever performed in this general field – cosmetics applied to skin – using scanning micro-PIXE. They were intended only to demonstrate the feasibility of the overall technique and were not continued. The following points summarise the measurements:

- Fast freezing with liquid nitrogen allows sample preparation without sample deformation.
- The liquid nitrogen cold finger allows successful exposure of biological samples to both vacuum and ion microbeam.
- Scanning microbeam analysis of skin tissue to determine the extent of diffusion is possible without tissue deformation.
- Analysis of the extent of diffusion from spectra with the present method of sample preparation requires detailed knowledge of the sample topography.
  - This is given by:
    a) the detection and areal scan of characteristic X-rays from carbon – the first time this has ever been done using a proton beam.
    b) optical microscopy.
5.3 Water Trees in Medium Voltage Cables

5.3.1 Introduction

The degradation of the insulation in underground electrical cables due to the phenomenon of ‘water treeing’ is well documented[22]. It is the name given to defects arising in the cable insulation. Their physical appearance range from, as the name suggests, tree like structures emanating from the interface between an outer protective carbon-black screen the ‘semi-con’ and the polymer insulator, to areas radiating out from a point defect within the polymer insulator each with the appearance of a bow-tie. Bow-tie structures from Hydro-Québec high voltage cables have been studied with a PIXE scanning microbeam elsewhere[23].

A UK cable manufacturer was keen to investigate the feasibility of location and characterisation of water trees and bow-tie trees in medium voltage underground cables with the ion microbeam. Their interest was directed towards heavy elements in the insulation.

5.3.2 Sample Preparation

The samples were in the form of radial slices cut from a field aged medium voltage cable, from which the central copper conductor had been removed, – a cable is field aged by simulated use whilst submerged in a tank of water. The cable sections had been stained, a treatment which aids the visual location of normally invisible bow-tie trees. A sample of the powdered dye and a section of undyed cable were produced on request. Figure 5.5 shows a diagram of a section of medium voltage cable.

All samples were inspected under a microscope to locate any visual structures indicating the presence of water trees or bow-tie trees. The sites of visual structures near the surface of the cables were noted for closer inspection with the microbeam. The samples were then carbon coated in a vacuum deposition chamber to form a conducting layer (∼200Å). A pellet of the powdered dye was made using a stainless steel hydraulic press, the pellet also being carbon coated.
Figure 5.5: Diagram illustrating a section of laterally cut medium voltage cable as supplied. The inner copper core was removed prior to sectioning, the outer and inner semi-con were in place. Radial dimensions: outer semi-con ~1mm wide, inner semi-con ~1.5mm wide and the insulator ~4.5mm wide, each section was ~2mm thick.

5.3.3 Sample Loading

This procedure was identical for all samples including the dye pellet. The samples were attached to a aluminium sample plate with copper clips screwed to the sample plate. The clips were placed at the top and bottom of the samples so as to not interfere with the microbeam. The clips also facilitate the removal of charge from the carbon coated surface of the sample. The sample plate was fixed to the target assembly in the vacuum chamber, which was subsequently evacuated and the cold finger reservoir filled with liquid nitrogen. Using the optical microscope, the area of interest was located and placed in the focal plane of the microscope (section 3.3.4). When the vacuum was $10^{-5}$Torr (or better), the gate valve to the beamline was opened to expose the sample to the scanning microbeam. The gate valve was not opened until the microbeam was in scanning mode due to possibility of the sample sustaining beam damage from a continuous localised microbeam.
5.3.4 Experimental

The proton beam energy was 1.5 MeV (the maximum achievable, section 5.1) For the initial scans the 200μm aperture was used giving a nominal microbeam diameter of 40μm. The 50μm aperture giving a nominal microbeam diameter of 10μm was used for later work. Initial work used a filter in front of the detector to reduce the intensity of the low energy X-rays thereby increasing the sensitivity to the X-rays from the heavier elements. The filter was then removed to map in addition the distribution of carbon and oxygen X-rays in the vicinity of a visible surface structure.

5.3.5 Results and Discussion

Figure 5.6 shows the X-ray spectrum obtained from the dye pellet. The main constituents are carbon, oxygen, sulphur and chlorine. Figure 5.7 shows the X-ray spectrum from an undyed section of cable, showing the cable contains little sulphur or chlorine. This suggests that location of the visible water trees (which have taken up the dye) using the microbeam will be indicated by the sulphur and chlorine X-rays. A sample of the dyed cable which had visible structures near the surface was then analysed.

Figure 5.8 shows a typical X-ray spectrum from a section of dyed cable containing a structure thought to be a bow-tie tree. Figure 5.9 shows the 2-d density map of the distribution of data from the chlorine peak obtained from an area of dyed insulator and outer semi-con. (For interpretation of X-ray spectra and 2-d maps see section 5.2.4). The 2-d density map indicates a number of hot spots in the semi-con as well as the insulator. Later observations showed that the hot spots in the semi-con were due to small dry flakes of dye on the surface which were easily removed by dabbing with a damp cotton bud. The yield on the outside of the semi-con (left side of map) is enhanced due to the sample detector geometry (figure 5.1).

The scan was redefined to the area just inside the outer semi-con around the chlorine hot spot in the insulator and a series of maps obtained. Figures 5.10 to 5.14 show the 2-d density maps of the distribution of data from the respective X-ray
Figure 5.6: Characteristic X-ray spectrum of dye pellet showing the element composition of carbon, oxygen, sulphur and chlorine.
Figure 5.7: Characteristic X-ray spectrum of undyed section of cable, the filter is in front of the detector consequently all X-rays below 2 keV are substantially attenuated. The scan is of the insulator adjacent to the inner semi-con showing the significant peak is from silicon. The series of peaks marked by the arrows are believed to be a combination of potassium, calcium and tin X-rays resulting from a hot spot (possible bow-tie tree) at the interface with the insulator and the inner semi-con.
peaks: Cl, S, Fe, Cu and Zn. Two of the higher yield L-series X-ray peaks from Sn are not resolved from the X-ray peaks of K and Ca, figure 5.15 shows the 2-d density map of the distribution of the sum of these peaks.

Following this series of maps the 50μm aperture was inserted giving a nominal 10μm beam spot diameter, the filter was removed from the X-ray detector facilitating the 2-d density mapping of the carbon and oxygen X-ray peaks. The X-ray spectrum is shown in figure 5.16 and the corresponding 2-d density maps in figures 5.17 and 5.18.

Initial analysis of the 2-d density maps and corresponding X-ray spectra was by the method described in section 5.2.4, in which the 2-d density maps are interpreted in terms of the level of background X-rays under the each respective peak. The maps of Cu, Fe and Zn need no such interpretation as there is no background continuum under these peaks. All of the 2-d density maps except the carbon map (figure 5.17) show a correlation of increased intensity with the visible structure in the surface of the dyed insulator. The carbon map however shows a reduction of intensity in the area of the structure. This reduction in intensity is consistent with a volume within the insulator filled to some extent with the other elements detected. Increased intensity of oxygen X-rays may be due to oxidation. The overall shape of the structure suggests the location of a bow-tie.

It is interesting to note that most of the 2-d density maps show a correlation of intensity in the top left corner, however no visible structure was observed upon subsequent inspection of the sample under the microscope.
Figure 5.8: Typical spectrum of characteristic X-rays from a section of dyed cable containing a visible structure — X-ray detector was used with a filter, hence the reduced yield below ~2 keV. The lower graph has an expanded ordinate to show peaks of lower yield. All X-rays are from the K-series unless stated.
Figure 5.9: 2-d density map showing the distribution of data from the chlorine peak in the X-ray spectrum of a section of dyed cable and outer semi-con. The semi-con is the vertical region on the left and insulator on the right, both show evidence of hot spots. The nominal beam diameter was 40μm.

Figure 5.10: 2-d density map showing the distribution of data from the Chlorine peak in the X-ray spectrum of a section of dyed cable containing a visible structure. The nominal beam diameter was 40μm.
Figure 5.11: 2-d density map showing the distribution of data from the Sulphur peak in the X-ray spectrum of a section of dyed cable containing a visible structure. The nominal beam diameter was 40μm.

Figure 5.12: 2-d density map showing the distribution of data from the Iron peak in the X-ray spectrum of a section of dyed cable containing a visible structure. The nominal beam diameter was 40μm.
CHAPTER 5. THE SCANNING PROTON MICROPROBE

Figure 5.13: 2-d density map showing the distribution of data from the Copper peak in the X-ray spectrum of a section of dyed cable containing a visible structure. The nominal beam diameter was 40\(\mu\)m.

Figure 5.14: 2-d density map showing the distribution of data from the Zinc peak in the X-ray spectrum of a section of dyed cable containing a visible structure. The nominal beam diameter was 40\(\mu\)m.
Figure 5.15: 2-d density map showing the distribution of data from summing the peaks of Calcium, Potassium and Tin in the X-ray spectrum of a section of dyed cable containing a visible structure. The nominal beam diameter was 40μm.

Figure 5.16: Typical spectrum of characteristic X-rays from a section of dyed cable containing a visible structure. X-ray detector without a filter, consequently all X-rays from elements heavier than beryllium are detected.
Figure 5.17: 2-d density map showing the distribution of data from the Carbon peak in the X-ray spectrum of a section of dyed cable containing a visible structure. The nominal beam diameter was 10μm.

Figure 5.18: 2-d density map showing the distribution of data from the Oxygen peak in the X-ray spectrum of a section of dyed cable containing a visible structure. The nominal beam diameter was 10μm.
CHAPTER 5. THE SCANNING PROTON MICROPROBE

5.3.6 Summary

As in the case of shower gel diffusing into skin, this study of 'trees' in polymeric cable insulation was intended as a demonstration of the capability of the overall technique I have developed. It is clear that the distribution of elements in structures with the dimensions of typical bow-tie trees can be determined with high sensitivity.

My initial study has led to further collaboration with industry. The characterisation of defects in the insulation of medium voltage underground cables and their correlation with ions diffusing into the insulation is being studied in detail in a one to two year investigation.
Chapter 6

The Scanning $^3$He Microprobe

6.1 Introduction

In chapter 5 a scanning proton microbeam was used to monitor diffusants in skin tissue and medium voltage cable. This chapter concentrates on the methodology and analysis using $^3$He ions to monitor deuterated diffusants in biological and polymeric matrices.

The primary objective was to investigate the feasibility of using a scanning microbeam of $^3$He ions for detection of deuterated substances in thick samples. To this end two experiments will be described, the second of which extends the method to obtain quantitative results.

1. Diffusion of deuterated solvents in human hair.

2. Diffusion of heavy water (D$_2$O) into the hydrophilic polymer THFM/PEM (tetrahydrofurfylmethacrylate/Poly(ethylmethacrylate)) for which the diffusion coefficient was obtained.

The experiments in this chapter were performed during the same period as the experiments using protons as the probing ions. Hence the liquid nitrogen cooled target stage and the scanning microbeam were in similar stages of development. The
beam energies used during these experiments represent the maximum obtainable on the day as explained in section 5.1.

6.2 Diffusion of Deuterated Solvents in Human Hair

6.2.1 Introduction

The diffusion of surfactants (the major component of shampoos) into human hair is of great importance to the cosmetics industry. The experiments below were carried out in collaboration with Dr P. Doyle at Unilever plc, who supplied samples of human hair pre-exposed to deuterated ethanolamine. The samples consisted of approximately 40 human hairs (~25mm in length) sealed in a small dry vial.

The objectives of the experiments were to:

1. Analyse the surface of the hair with a $^3$He microbeam (using the reaction described in section 4.2) to verify that the deuterated solvent were adhering to hair in detectable quantities.

2. Prepare the hair in both lateral and longitudinal cross-section to ascertain if (and the extent to which) diffusion had occurred.

Initial measurements carried out on hair at room temperature scanning a $^3$He microbeam (2pA) over the vicinity of a hair led to its almost immediate destruction. This led to the development of the liquid nitrogen cooled target stage.

6.2.2 Sample Preparation

6.2.2.1 Hair: Surface

The initial experiment was to investigate the distribution of deuterium on the hair surface. A number of hairs were attached to an aluminium sample plate; a narrow strip of double sided adhesive tape was fixed to the top and bottom of the sample
Figure 6.1: Schematic diagram of mounting block on which the hair is microtomed to expose a longitudinal cross-section, also showing the directions of sample movement during microtoming.

plate, over which hairs were pulled taut then firmly pressed into position. The hairs were finally (including the sample plate) carbon coated in a vacuum deposition chamber to form a conducting layer (~200Å).

6.2.2.2 Hair: Longitudinal Cross-Section

The thickest strand (~60µm in diameter) was selected for longitudinal sectioning. Figure 6.1 is a schematic representation of a microtome. A mounted resin block was microtomed to provide a surface parallel to the cutting edge. To facilitate attachment to the sample plate, the resin block was glued to an aluminium block prior to microtoming. Retraction of this block away from the cutting edge enabled a single hair to be glued to the cut surface. This provided a secure mounting for the hair, allowing accurate sectioning. The sample and resin block were then carbon coated in a vacuum deposition chamber to form a conducting layer (~200Å).

6.2.2.3 Hair: Lateral Cross-Section

A hair was cut in lateral cross-section with a scalpel. It was then clamped between the copper jaws (section 3.4), attached to the sample plate. To aid location of the hair
CHAPTER 6. **THE SCANNING $^3$HE MICROPROBE**

with the microbeam a short length of gold wire (50$\mu$m diameter) was attached with double sided tape horizontally approximately 100$\mu$m above the hair. Carbon coating was considered unnecessary due to the close proximity of conducting materials.

### 6.2.3 Sample Loading

This procedure was identical for all samples. The sample plate was fixed to the target assembly in the vacuum chamber, which was subsequently evacuated and the cold finger reservoir filled with liquid nitrogen. Using the optical microscope, the area of interest was located and placed in the focal plane of the microscope (section 3.3.4). When the vacuum was $10^{-5}$Torr (or better), the gate valve to the beamline was opened to expose the sample to the scanning microbeam. The gate valve was not opened until the microbeam was in scanning mode due to possibility of the sample sustaining beam damage from a continuous localised microbeam.

### 6.2.4 Results and Discussion

#### 6.2.4.1 Hair: Surface

The particle detectors are as described in section 3.3.3. However in this work only one detector had been repositioned within the chamber, 20° below the horizontal plane at an angle of 135° to the incident beam and a distance of 25mm from the target. The second detector remained in the original detector position at an angle of 165° to the incident beam in the horizontal plane 50mm distance from the target. Both detectors were uncollimated.

A 2 MeV $^3$He microbeam (200$\mu$m aperture with nominal beam diameter of 40$\mu$m, beam current 0.1nA) was used to scan the target area (1.8mm $\times$ 1.8mm) containing samples of hair treated with deuterated ethanolamine. The rate of proton detection is too low for efficient initial location of the hairs using the $d(^3$He,p)$\alpha$ reaction. Collecting data from the X-ray detector and correlating the characteristic X-rays from the aluminium in the sample plate with the beam position, the hairs were
located by the absence of X-rays from aluminium overlaid by the hair. The 2-d density map of X-rays from aluminium is shown in figure 6.2. Subsequent to locating the hairs, data was collected from the particle detectors. The area over which the microbeam was scanned was identical to give a spatial correlation between the X-ray and proton density maps. The spectrum collected from the particle detectors is shown in figure 6.4. Correlating the proton counts from the two peaks with the beam position gives the 2-d density map in figure 6.3. This clearly shows the uptake of deuterated ethanolamine on the surface or near surface of the hairs.

6.2.4.2 Hair: Longitudinal Cross-Section

The detector configuration is unchanged from the previous section. The $^3$He energy was 1.9 MeV (the maximum achievable, section 5.1). Using the 200μm aperture the nominal beam diameter was 40μm. Initial location of the hair was by use of the optical microscope. The scanning microbeam was then used to scan an area of approximately 2mm × 2mm, with a beam current of 0.1nA. As the orientation of the hair is known—vertical with respect to the beam—only a few counts are required to locate the position of the hair. This is achieved by mapping only the proton full energy peak from the d($^3$He,p)α reaction. Having located the hair, the scanning software was used to reduce the scan to 250μm × 250μm, the beam current was reduced to 2pA. The resulting 2-d density map is shown in figure 6.5. This clearly shows that there is diffusion of deuterated ethanolamine within the hair. The 40μm beam spot does not allow the diffusion profile to be resolved with confidence.

6.2.4.3 Hair: Lateral Cross-Section

The detector configuration is unchanged from the previous section. The $^3$He energy was 1.1 MeV (the maximum achievable, section 5.1). Using the 50μm aperture the nominal beam diameter was 10μm. Initial location of the hair was by optical microscope, or more correctly the gap between the copper jaws was located. The scanning microbeam was then used to scan an area, approximately 2mm × 2mm,
CHAPTER 6. THE SCANNING $^3$HE MICROPROBE

Figure 6.2: 2-d density map showing the distribution of characteristic X-rays from the aluminium sample plate. A 2 MeV $^3$He ion is completely stopped within 10$\mu$m in hair, consequently the position of the hairs are indicated by a lack of X-rays.

Figure 6.3: 2-d density map showing the distribution of protons from the d($^3$He,p)$\alpha$ reaction. The hairs are clearly visible and are in agreement with figure 6.2. The nominal beam diameter was 40$\mu$m.
Figure 6.4: Spectrum of a 2 MeV $^3$He ion beam impinging on the surface of hairs treated with deuterated ethanolamine. The spectrum was obtained from two un-collimated particle detectors. The near detector at 20° below the horizontal plane an angle of 135° to the incident beam at a distance of 25mm from the target, and the far detector at an angle of 165° to the incident beam in the horizontal plane 50mm distance from the target. The gain on the individual amplifiers was such that the peaks appear at different positions in the spectrum – the peak at channel 225 corresponds to the signal from the far detector and the peak at channel 170 to the near detector – so the yield from the two detectors can be compared. The ratio of the yields is in broad agreement with the solid angles – 0.16sr and 0.04sr.
Figure 6.5: 2-d density map showing the distribution of protons from the d(\(^3\)He, p)\(\alpha\) reaction. The hair (diameter 60\(\mu\)m) which is cut in longitudinal cross-section was treated with deuterated ethanolamine prior to sectioning. The nominal beam diameter was 40\(\mu\)m.
Figure 6.6: 2-d density map showing the distribution of protons from the d(³He,p)α reaction. The human hair (diameter 60μm) which is cut in lateral cross-section was treated with deuterated ethanolamine prior to sectioning. The nominal beam diameter was 10μm.

with a beam current of 6nA. The area of laterally sectioned hair is 0.003mm², with a beam diameter of 10μm and with such a large scan it is a time wasting exercise to use the d(³He,p)α reaction to locate the hair. Using the backscattered ³He from the copper to indicate the position between the copper jaws, the backscattered ³He from the gold wire indicated the horizontal position below which the hair is located. The scanning software was then used to define a reduced scan of 200μm × 200μm, the beam current was reduced to 2pA. The resulting 2-d density map is shown in figure 6.6

Subsequent visual inspection of the hair showed that the cut surface was not perpendicular to the axis of the hair – leading to an oval cross-section. There appears to be an area in the centre of the hair with reduced yield, suggesting that total diffusion has not occurred.
6.2.5 Summary

An objective of the work in this section has been to demonstrate the feasibility of using a scanning microbeam of $^3$He for the detection of deuterated substances in hair using the $d(^3\text{He},p)\alpha$ reaction. Not only has this been achieved, but the work also highlights the versatility of the microprobe target chamber which includes an X-ray detector as well as the particle detectors. The use of the complementary techniques of Particle Induced X-ray Emission (PIXE) and Rutherford Backscattering (RBS) proved vital in the location of samples.

Examining diffusion of deuterated ethanolamine in hair it is clear that the best technique is to use hair samples which have been laterally sectioned. A liquid nitrogen cooled target stage is also essential. From this study, which as far as I know is completely original, it is clear that deuterated ethanolamine does not fully penetrate the undamaged hair.
6.3 D$_2$O Diffusion in THFM/PEM

6.3.1 Introduction

The diffusion of water into polymers is of importance in the field of slow drug release systems[24]. The drug is incorporated in a polymer into which water diffuses from bodily fluids. It then slowly leaches out the drug by what may be complex mechanisms. Magnetic Resonance techniques have hitherto been used [25] to measure ingress of water into polymers but we describe here an MeV ion beam technique. This has the potential advantage that the profiles of egressing drugs can be monitored simultaneously using Particle Induced X-ray Emission[9] to identify the elements in the drug. In this section we describe only the technique for profiling the water ingress in one polymeric system, THFM/PEM (tetrahydrofurfylmethacrylate/Poly(ethylmethacrylate)).

These experiments were carried out in collaboration with P.Riggs of the Dental School, London Hospital Medical College, University of London.

With ion beam techniques it is difficult to profile water, containing hydrogen and oxygen, in polymers which contain both elements. Hence we use heavy water, D$_2$O and identify the deuterons using the reaction described in section 4.2:

\[ ^3\text{He} + \text{d} \rightarrow \text{p} + \alpha \quad Q=18.4 \text{ MeV} \]

Before describing the technique the question needs to be addressed – Is heavy water absorption a good model for normal water absorption? To check this a gravimetric study on the uptake of D$_2$O and H$_2$O in the hydrophilic system THFM/PEM was carried out by P.Riggs. A brief explanation of the study is reproduced here from a personal communication by him (section 6.3.2).

6.3.2 Gravimetric study

An initial study on the water uptake of materials from D$_2$O and H$_2$O was conducted on tetrahydrofurfylmethacrylate/poly(ethylmethacrylate) (THFM/PEM).
6.3.2.1 Sample Preparation

The THFM/PEM material was prepared by mixing poly(ethylmethacrylate) powder (10 grams) with 6 ml of tetrahydrofurfylmethacrylate containing 1% dimethylp-toluidine then allowing to gel for 30 minutes before moulding in a dental flask and curing at 100°C for 1 hour. The resultant gel was cured between two glass slides (separated by a 1 mm spacer) in a pressure cooker under a pressure of 2 bar at room temperature[26].

6.3.2.2 Experimental

The samples were prepared for immersion in D₂O and H₂O at 37°C. The samples were preconditioned in a dry atmosphere at 37°C for 1 week before immersion in the appropriate fluid. The samples were then removed from the fluid after 274 days and placed back in the dry atmosphere at 37°C. Gravimetric measurements were made on the samples at appropriate intervals throughout this process. Figure 6.7 shows the increase in wt% of the sample versus time.

6.3.2.3 Results and Discussion

Diffusion coefficients can be determined after a protracted period by studying desorption of D₂O & H₂O. However the molecular weight of D₂O (atomic mass 20) is ≈10% greater than H₂O (atomic mass 18) due to the extra neutron in the deuterium nucleus. We might therefore expect that the diffusion coefficient involved in the protracted absorption of D₂O should be 10% less than that for H₂O. These are displayed in table 6.1 and do indeed differ by ≈10%. Hence we conclude that D₂O is a good model for H₂O absorption in THFM/PEM. Their absorption characteristics appear to be the same and their diffusion coefficients for desorption after protracted absorption differ by ≈10% as expected. This shows the overall absorption characteristics of the materials did not alter drastically between the solutions. The diffusion
coefficient was obtained during desorption using the formula:

\[
\frac{M_t}{M_\infty} = 2\left(\frac{Dt}{\pi l^2}\right)^{\frac{1}{2}}
\]

as developed by Crank [27] for diffusion into a thin sheet at short times.

\(D = \) diffusion coefficient, \(t = \) time, \(l = \) thickness.

Table 6.1: Summary of diffusion coefficients from desorption of \(D_2O\) and \(H_2O\) from PMMA and THFM/PEM (samples immersed for 274 days at 37°C).

<table>
<thead>
<tr>
<th>Material</th>
<th>Solution</th>
<th>Diffusion coefficient cm(^2)s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>THFM/PEM</td>
<td>(H_2O)</td>
<td>(4.72 \times 10^{-8})</td>
</tr>
<tr>
<td>THFM/PEM</td>
<td>(D_2O)</td>
<td>(4.25 \times 10^{-8})</td>
</tr>
</tbody>
</table>

6.3.2.4 Summary

The use of \(D_2O\) as a model for the ingress of \(H_2O\) in to polymers is thought to be valid. Although there is a difference in the rates of absorption it does not appear
to alter the characteristics of absorption significantly. In order to evaluate the ion beam technique THFM/PEM was chosen as a test material, as obtaining a profile of the water in the sample could be valuable in characterising the absorption process.

6.3.3 Ion Beam Analysis

A number of THFM/PEM samples were made in the manner described in section 6.3.2.1 and supplied by P. Riggs, each sample measured 20mm × 40mm × 1mm. All samples were delivered vacuum packed in polythene bags to maintain a dry atmosphere.

6.3.3.1 Sample Preparation and Target Loading

For polymers used in drug release the appropriate temperature to study water diffusion is body temperature 37°C. A jar of heavy water is therefore warmed in a normal water bath to 37°C and a THFM/PEM sheet is suspended in the heavy water with its long side vertical for a measured time. It is then removed from the liquid, blown with dry nitrogen to remove surface water and then clamped vertically in the copper vice bolted to a copper sample mounting plate as described in section 3.4. It is then plunged into liquid nitrogen to freeze the profile. This rapid cooling has the effect of preventing the formation of ice crystals and the consequent swelling[21]. The sample is then scored horizontally along the sides at the height of the blocks and pressure applied perpendicular to the side to fracture it. This leaves a clean exposed edge (20mm × ~1mm) at the height of the copper blocks. The sample mounting plate is then transferred to the target chamber where it is attached to a copper block linked to a coldfinger fed by a liquid nitrogen reservoir. The timing of this procedure is critical to retain the low temperature of the sample. During sample changes the liquid nitrogen is blown off from the cold finger reservoir using a dry nitrogen supply. This dry nitrogen was then used to remove ice and moisture from the cold finger and target staging. During this time the sample was removed from its liquid nitrogen, sectioned as described and transferred to the target chamber.
The liquid nitrogen cold finger reservoir was then filled as the chamber was evacuated. Measurements have shown that the temperature of the sample holder does not rise above -50°C. Using the optical microscope, the area of interest was located and placed in the focal plane of the microscope (section 3.3.4). When the vacuum is $10^{-5}$ Torr (or better), the gate valve to the beamline is opened to expose the sample to the scanning microbeam. The gate valve is not opened until the microbeam is in scanning mode due to possibility of the sample sustaining beam damage from a continuous localised microbeam.

### 6.3.3.2 Ion Beam Measurement

The uncollimated particle detectors are as described in section 3.3.3.2. They are located 20° below the horizontal plane at symmetric angles of 135° to the incident beam each at a distance of 25mm from the target. The $^3$He beam energy was 2 MeV, beam size was 200μm diameter at the target surface and a beam current of 4nA was used initially. On the basis of this measurement it was realised it was feasible to reduce the beam size to 40μm and the beam current to 0.1nA for subsequent experiments.

### 6.3.3.3 Analysis

A typical pulse height spectrum is displayed in figure 6.8. This shows the backscattered ions, the two carbon-associated peaks and the high energy deuteron-associated peak. Figure 6.9 shows a pair of 2-d density maps from the initial study. The upper density map shows the correlation of the backscattered $^3$He ions with the raster scan. Scatters from the copper blocks are clearly evident at the sides, the exposed polymer edge is in the middle. This scan is used to locate the beam precisely on the polymer edge. The lower density map shows the correlation of the deuteron-associated proton peak and tail (≥ 6 MeV) with the raster scan. This includes insignificant contributions from both $^{13}$C($^3$He,p) and $^3$He($^3$He,p) interactions (<0.5%) from naturally occurring $^{13}$C in the polymer and adsorbed $^3$He. (Their relative contributions were
Figure 6.8: Typical pulse height spectrum showing the backscattered ions, the two carbon-associated peaks and the high energy deuteron-associated peak.
deduced from a separate measurement on Carbon). This particular sample of the polymer THFM/PEM had been exposed to heavy water for a period of 5 minutes at 37°C. The diffused D₂O is clearly visible in bands at either side.

6.3.3.4 Obtaining depth profiles

Diffusion depth profiles for the heavy water are obtained by summing the 2-d density map of protons from the d(^3He,p)α parallel to the sample surface. The 2-d density maps are an array of 128 × 128 pixels (section 4.5), it is a simple procedure to sum up in either the X or Y direction. For this procedure to be valid the sample surface must be parallel to one of the scanning axis. Figure 6.10 shows 2-d density distribution map ^3He backscatters from copper showing the fixed block of the copper jaws. This was used to align the fixed part of the sample holder, and hence the sample surface relative to the Y-axis of the scanning microbeam. The procedure for sample mounting does not allow the accurate alignment of the movable part of the copper jaws, hence only the aligned side is used for deducing the diffusion coefficient.

6.3.3.5 Results and Discussion

Spectra were taken for exposure times (in D₂O) of 10, 40 & 135 minutes. The 2-d density proton maps from the d(^3He,p)α reaction were summed in manner described above to obtain the depth profiles. These are shown for the different exposure times in figure 6.11. The profile corresponds to the solution of the diffusion equation for a semi-infinite medium, x > 0 where the boundary is kept at a constant concentration C₀, the initial concentration being zero throughout the medium [27]:

\[ C = C_0 \left( \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \right) \]  

(6.2)

By folding this with a Gaussian resolution function to incorporate both the radial intensity variations of the focused beam and imprecision in the scan/sample surface alignment and fitting the data in figure 6.11 we obtain the diffusion coefficients shown in table 6.2 together with the Gaussian standard deviations.
Figure 6.9: 2-d density maps: the upper shows the $^3$He backscatters from the copper blocks, the lower shows protons from the $d(^3He,p)\alpha$ reaction. The nominal beam diameter was 200$\mu$m.
It is believed that the resolution of 22μm for the 135 minute profile is due to sample geometry. Figure 6.12 shows a schematic diagram of a cross-section of THFM/PEM polymer in the copper jaws. The polymer is shown with the line of cleavage below the level of the copper jaws. From a position adjacent to the copper jaw, the resultant reaction products will only 'see' one detector as the particles destined for the other detector will be stopped in the copper jaw. The method of producing the 2-d density maps in which the counts from the two detectors are summed (figure 4.7) results in a reduced yield in this narrow region – the result is an apparent improved resolution. Within a few hundred microns of the copper jaw the reaction products are detected equally between the two detectors, hence the slope of the diffusion profile is unaltered.
CHAPTER 6. THE SCANNING $^3$HE MICROPROBE

Figure 6.11: $D_2O$ diffusion profiles in THFM/PEM for exposure times of 10, 40, & 135 minutes, the nominal beam diameter was 40$\mu$m.

Table 6.2: Summary of diffusion coefficients with the respective Gaussian standard deviations obtained by fitting Fickian diffusion profiles to the three sets of data for the absorption of $D_2O$ in THFM/PEM

<table>
<thead>
<tr>
<th>Immersion in $D_2O$ (minutes)</th>
<th>Diffusion coefficient cm$^2$s$^{-1}$</th>
<th>Gaussian standard deviation ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>$3.7 \times 10^{-7}$</td>
<td>40</td>
</tr>
<tr>
<td>40</td>
<td>$2.5 \times 10^{-7}$</td>
<td>40</td>
</tr>
<tr>
<td>135</td>
<td>$2.4 \times 10^{-7}$</td>
<td>22</td>
</tr>
</tbody>
</table>
Figure 6.12: Schematic diagram of a cross-section of THFM/PEM polymer in the copper jaws. The polymer is shown with the line of cleavage below the level of the copper jaws. From a position adjacent to the copper jaw, the resultant reaction products will only 'see' one detector as the particles destined for the other detector will be stopped in the copper jaw.
6.3.4 Summary

I have demonstrated the feasibility of using an ion beam scanning technique to measure heavy water diffusion coefficients in hydrophilic polymer. The important aspects of the technique are:

- Use of $^3$He scanning ion microbeam.
- Use of dual uncollimated particle detectors to both increase detection efficiency and eliminate any (small) angular dependence of yield.
- Fast freezing with liquid nitrogen to freeze heavy water diffusion profile in hydrophilic polymer.
- Use of a liquid nitrogen cold finger to both retain water and effectively eliminate beam heating effects when exposing polymeric samples to vacuum and the ion microbeam respectively.
Chapter 7

Conclusions

7.1 Summary

This thesis has described the development of novel MeV ion micro-beam techniques. It then discussed their application to the measurement of the diffusion of small molecules in polymeric and biological matrices which hitherto were not possible.

The important novel aspects of the techniques are:

- Use of $^3$He scanning ion microbeam.
- Use of dual uncollimated charged particle detectors to measure induced nuclear reaction products.
- Use of a very thin window detector capable of detecting X-rays from elements heavier than beryllium.
- Fast freezing of samples with liquid nitrogen to freeze diffusion profiles and eliminate sample deformation.
- Use of a liquid nitrogen cooled target stage to both retain water and effectively eliminate beam heating effects when exposing samples to vacuum and the ion microbeam respectively.
The matrices studied were:

- The diffusion of silicone-containing shower gel into skin tissue.
- The study of the elemental composition of structures in polymeric cable insulation.
- The diffusion of deuterated ethanolamine into human hair.
- The diffusion of heavy water into hydrophilic polymers.

In all cases the developed techniques were successful and it is clear that they can be applied to a wide variety of academic and industrial studies on diffusion in polymeric and biological matrices.

I have written up the work on diffusion of heavy water into hydrophilic polymer and it has been accepted for publication in Nucl. Instrum. Meths. B.

### 7.2 Further Work

Whilst doing this work I realised that several further improvements and developments of the techniques could be made but time did not allow their implementation.

For diffusion in hair – which has both radial and axial components – windowing the proton peak in the \( d(\text{^3He},p)\alpha \) reaction into sections will allow their simultaneous measurement. Such experiments would be as far as I know unique and the technique could be extended to, for example, the diffusion of water laterally and perpendicularly into latex films.

For diffusion in hydrophilic polymers the next development should be the simultaneous profiling of the water and the drugs – which are naturally labelled by specific elements – using NRA and PIXE. This requires further development of the software controlling data acquisition.

There needs be further development in the location of bow-tie trees in polymeric cable insulation. The trees are often buried down to 100µm below the surface of cable section. A cryo-microtoming technique needs to be involved to expose the
buried trees. Room temperature microtoming is undesirable owing to the need to embed the polymer in resin which can aggressively diffuse into the polymer.

Notes added in proof:
Using the technique I developed for studying diffusion in hair recent measurements on permed and undamaged hair have confirmed the immense usefulness of the technique for measuring the diffusion of cosmetic products in hair.
[P.M.Jenneson, D.W.Drew, A.Clough and J.Keddie – Surrey University Internal Report (Confidential)]

The technique I developed for studying diffusion into skin tissue has been used effectively to measure the diffusion of deodorant into rat skin, using Aluminium and Silicon as labels. Profiling more than one labelling element of a complex molecule gives much greater confidence that the whole molecule is diffusing in the same way as the elemental labels.
Appendix A

Microprobe Setup Procedure

A.1 Introduction

The microbeam line requires an exact setup procedure on each beam day. When the same ions and energy are used on consecutive days the procedure should still be followed – experience has shown there are no short cuts.

The Van de Graaff produces a beam of ions, the momentum selecting magnet then selects ions of a specific mass, charge and energy and steers them down the beamline (figure 2.3). The purpose of the beamline is to guide, collimate and focus the ion beam onto the target area in the target chamber. It should be clearly understood that unless the Van de Graaff is set up and focused correctly, no amount of subsequent effort in setting up the beamline will produce the optimum focused microbeam.

The initial procedure for setting up the beamline consists of starting at one end and proceeding down the beamline; however in reality it is more of an iterative process. The ion beam is required to strike the area in the target chamber which can be seen with the fixed small field optical microscope – otherwise it is not possible to focus the microbeam. To this end, each section of the beamline must be optimised with reference to this area. What follows is a stepwise guide to this setup procedure, with a check list for the initial startup.
A.1.1 Beamline Check List Prior to Startup

Beamline: (figure.2.3)
1. Retract all viewers
2. Wind out aperture plate (until the red line is observed on the vernier, any further damages the mechanism)
3. Scanning Plates:
   - Switch on power supply
   - Apply voltage to scanning plates (2.2 kvols).
   - Select setup on power supply – produces stationary beam, unaffected by scanning software, (select use when beam is focused)
4. Magnets:
   - Switch on power supply
   - Zero the magnet current
   - Select normal on both power supply and magnets
5. Down Stream X-Y Steering Plates:
   - Switch on power supplies
   - Set voltage to zero

A.1.2 Focusing the Van de Graaff

Observing the shape of the beam in the viewers down stream of the feedback slits and communicating with the technicians who operate the Van de Graaff – via a headset – allows the Van de Graaff to be focused. The width of the beam is dictated by feedback slits. (Note: only the technicians are permitted to alter the energy feedback slits). Ideally the beam should be of even intensity with the slit edges clearly defined. If the beam is not of even intensity there is a probability that when the aperture plate is inserted, the aperture itself may be intersecting a position of low intensity with the resulting loss of efficiency. It is good practise to check for uniformity in the viewers downstream of the aperture at this point.
A.1.3 Locating the Beam on Target Area

The ion beam may require deflection on to the target area within the target chamber using the down-stream X-Y steering plates. The method of locating and focusing the microbeam is by use of the optical microscope, and observation of the microbeam due to fluorescence on a section of quartz glass. It is a good idea to fix a copper TEM grid to the quartz glass to indicate the spatial dimensions and to calibrate the microbeam.

A.1.4 Insertion of Aperture

The aperture plate should be wound in whilst observing the ion beam in viewer No.3. The distance of travel can be calculated from the point at which aperture plate intersects the ion beam.

The aperture position can be finely tuned by maximising the ion beam current via the current monitor connected to the target staging.

A.1.5 Focusing the Magnets

There are two stages in focusing of magnets: Normal and Series mode. In Normal mode, each magnet is controlled by a separate current supply, this mode is used to align the four magnets individually in the target area. In Series mode all four magnets are used to produce a focused ion beam.
In **Normal** mode, focusing is achieved both by varying the individual magnetic fields one by one and moving them all with respect to the ion beam. The aim is to produce a line focus at the center of the target area (small field microscope) with each individual magnet.

Magnets 1 & 3 produce a horizontal line focus, and magnets 2 & 4 a vertical line focus.

When all are aligned, switch to **Series** on both the magnets and the current supply. Varying the controls of No's 1 & 2 produces a point focus. Magnet No.1 can be rotated for fine tuning.

### A.1.6 Verifying Scan Uniformity

After selecting **use** on the scanning power supply, the beamline is ready to operate the scanning software (Appendix B). Operating on the maximum scan area, observe the current monitor for a fluctuation. It may fluctuate as a function of beam position. The remedy is to gently adjust the position of the aperture until the current fluctuation ceases. One further verification is to use the scanning software. Take a maximum sized scan of a uniform target and plot in 3-dimensions and look for an even intensity. It is not sufficient to observe the maps produced on screen by the scanning software, the intensity color coding is limited. Routines have been written (Appendix C.1) to allow the acceptance of the **MAP** files by a commercial plotting...
routine UNIMAP. The maps displayed in UNIMAP have much greater variation of color coding. If the top on map is missing the aperture requires raising. Note: the maps as seen on the work station are upside down, the co-ordinate 0,0 is the top left corner. The software for extracting the data from the MAP file reverts the perspective to normal.
Appendix B

The use of data acquisition software

The development of the scanning software is still continuing, while being a powerful tool it must be used with knowledgeable caution. The uninitiated user can lose data. At best it can lock up and the data from that run is lost, at worst the user is unaware that the data has not been saved.

For brief overview see chapter 4 section 4.5. Login to Sparc work station in computer room. The scanning software is located in the directory `eepldm/ssd.g`. The startup command is xc. This produces three control windows and four map windows.

- **xcontrol** Main control for the scanning software, windowing for the maps and spectra information, all of which requires confirmation before software is enabled, saves to defaultfilename.set

- **spect** Displays the spectrum, saves to defaultfilename.spect

- **map** Saves the four maps windows to a single file, defaultfilename.map

The .spect file contains three spectra each of which can be defined for an area of the scan. The windows for generating the maps operate on the first spectra.
When running, the scanning software stores the data in buffers before periodically updating the map and spect windows, progress reports are continuously written to the screen. These progress reports include confirmation when saving the individual windows, occasionally the saving operation may fail in which no confirmation is given.
Appendix C

Data Manipulation Routines

C.1 Extracting the MAPS

Extracting the data from the MAP file: compile in C
Usage maptodat filename < filename.map

Four files in x,y,z:    filename0.dat
                     filename1.dat
                     filename2.dat
                     filename3.dat

#include <stdio.h>
#include <string.h>
#define WIDTH 128
#define FIRSTCHANNEL 0
char *malloc();
int main(argc, argv)
int argc;
char **argv;
{
int i, j, f;
FILE *fp[4];
char *buffer, *p;
if (argc != 2)
{fprintf(stderr, "Syntax:
	%s filename_prefix < input_file
", argv[0]); return(1);}
j = strlen(argv[1]);
buffer = malloc(j+6);
sprintf(buffer, "%s .dat", argv[1]);
p = buffer+j;
for(i=0; i<4; i++) {*p = '0' + i;
if ((fp[i] = fopen(buffer, "w")) == NULL) {
 perror(buffer); return(1); }
}
for(i=0; i< FIRSTCHANNEL; i++) (void) getchar();
for(i=0; i<128; i++)
for(f=0; f<4; f++)
for(j=0; j<128; j++)
if (j < WIDTH)
    fprintf(fp[f], "%d %d %d\n", j, i, getchar());
else (void) getchar();
for(f=0; f<4; f++)
close(fp[f]);
return(0);
}

Some of the .dat files contain spurious data in the first and last channel, to eliminate these channels redefine the variables WIDTH and FIRSTCHANNEL.

C.2 Extracting the Spectra

The spectra contained in filename.spect can be obtained by using an executable file located in the same directory as the scanning software call 'dkm2ssd'.

This produces three files in a format used by the Electrical Engineering Department in some related RBS sofware.

Usage dkm2ssd filename.spect

Three files in 'RBS' format: filename0.txt
                              filename1.txt
                              filename2.txt

These can then be reduced to x,y format by this command line in UNIX
awk 'flag == 1 {for(j=3;j<=NF;j++) printf "%d %d\n", i++, $j} /' filenamein > filenameout
APPENDIX C. DATA MANIPULATION ROUTINES

C.3 Summing up the 2-d density maps

These two routines for summing up the 2-d density maps are run in UNIX.

Summing across the maps (y=constant).

```
# Usage: projectac.com filename.dat > filename.out
sort -n +1 $1 | awk '
BEGIN { i = -1 }
$2 != i {if (i != -1) print i,n; i=$2; n=0}
{n += $3}
END {printf "%d %f\n", i,n}'
```

Summing up the maps (x=constant).

```
# Usage: projectup.com filename.dat > filename.out
sort -n $1 | awk 'BEGIN { i = -1 }
$1 != i {if (i != -1) print i,n; i=$1; n=0}
{n += $3}
END {printf "%d %f\n", i,n}''
```
Bibliography


