Novel Applications of Ion Beam Analysis Techniques

by

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Abstract

Ion beam analysis (IBA) has been used as a powerful tool for studying materials for many years. Depending on the specific experimental design, IBA techniques can provide a non-destructive means of analysing samples to obtain such information as the elements or isotopes present and diffusion or depth profiles. Ion beam analysis has the ability to keep up with the rapid progress in new materials both as technology improves and as scientists have the creativity to develop existing and new techniques.

Many different types of IBA exist. The experiments reported in this thesis were carried out using backscattering of the beam ions, ion induced X-ray emission, and ion induced nuclear reactions. The two experimental projects involved the use of modern cadmium-telluride detectors, including a unique array of CdZnTe detectors.

The subsidiary project investigated using nuclear reaction measurements to study moisture diffusing into epoxy resin bonded with aluminium. Current standard techniques cannot measure diffusion profiles directly, resulting predictions rely on assumptions as to the particular mode of moisture migration. I have shown that the ion beam analysis technique can be applied to directly study moisture diffusion profiles parallel and perpendicular to the interfacial region whilst the bond remains intact. Further use of the technique would be of importance in studying the effect of moisture on bond integrity in automotive and aerospace industries - this would result in better predictions of the longevity of adhesive joints.

For the main experiment, novel ion beam methods were developed to characterise, for the first time non-destructively, gold flecks dispersed within low density foam cylinders. The techniques allow the measurement of both the mass of gold in the cylinders and the average size of the individual gold flecks. Several different problems not previously encountered in ion beam analyses have been addressed and understood.
Declaration of Originality

"This thesis and the work to which it refers are the results of my own efforts. Any ideas, data, images or text resulting from the work of others (whether published or unpublished) are fully identified as such within the work and attributed to their originator in the text, bibliography or in footnotes. This thesis has not been submitted in whole or in part for any other academic degree or professional qualification. I agree that the University has the right to submit my work to the plagiarism detection service TurnitinUK for originality checks. Whether or not drafts have been so-assessed, the University reserves the right to require an electronic version of the final document (as submitted) for assessment as above."

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The subsidiary experimental project reported in Chapter 4 was collaborative work. The samples were prepared by collaborators for research as part of 'Modelling the Interfacial Degradation in Adhesively Bonded Joints' C.D.M.Liljedahl 2006 PhD Thesis University of Surrey. The experimental techniques were designed and applied by me. The data was collected by me. The experimental data was initially shown in the C.D.M. Liljedahl thesis with some preliminary analysis, however I personally reanalysed all the data myself, and the more correct and detailed results are presented in my thesis in Chapter 4. I initially presented the experimental techniques in the conference proceedings for 'XVII International Conference on Ion Beam Analysis': 'Using a Scanning Microbeam and a CdZnTe Array for Nuclear Reaction Measurements of Water Diffusion into an Adhesive Resin' Nuel.Instr.Meth.B, 2006, 249:406-408. The data and experimental techniques were subsequently presented in 'Characterising Moisture Ingress in Adhesively Bonded Joints Using Nuclear Reaction Analysis' Int.Jour.Adhesion& Adhesives, 2009, 29(4):p356-360. The analyses presented in my thesis are more accurate and have experimental uncertainties assigned to values.
"I take each thing as it is, without prior rules about what it should be."

Bob Dylan
Dedication

I dedicate this work to my parents, who have supported me throughout my protracted education; they now face the challenge of finding a new topic of conversation to hold with their friends.
I would like to thank Professor Tony Clough for introducing me to interesting experimental projects and for all his help in bringing them to fruition. I am very grateful for his continued dedication even after retirement and promotion to Professor Emeritus status.

I also wish to express my appreciation to EPSRC for funding part of my PhD, to my good friend Dr. M. Salah Rihawy, formerly my student colleague, for his unfailingly sanguine disposition and calming presence in any situation, to my official supervisor, Dr. Paul Sellin, for ‘adopting’ me following Tony’s retirement and to electronic technician Eric Worpe for bringing to life my designs for the new modified CZT array.

Special thanks must go to everyone at the Surrey Ion Beam Centre, in particular the following people: Mark Browton, who expertly made or altered just about anything we needed to modify experimental set-ups in the microbeam chamber; Adrian Gansell, who assisted us with his truly unparalleled Jedi-level control of the beam; Dr. Chris Jeynes, who took the time to give me an initial tutorial on running the accelerator and for his infectious enthusiasm on all things ion beam; Dr. Geoff Grime, who helped me with the continually updated versions of OM_Daq; and finally Dr. Inma Gomez-Morilla, a colleague and friend who no longer works at Surrey, but who assisted me, while here, during many late night accelerator laboratory sessions. I enjoyed collaborating with Dr. Andrew Comley, Dr. C. David Liljedahl and Professor Andrew Crocombe.

Last, but by no means least, I would like to thank both Dr. Annika Lohstroh and Dr. Walter Gilboy, who have provided many inspirational insights during discussions about a wide range of topics on experimental physics during my time as a PhD student. I also really appreciate the encouragement they have provided throughout.
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Chapter One: Introduction

Associated with the study of inter-polymer diffusion in thin films, the use of the nuclear reaction $\text{D}(^3\text{He},p)^\alpha$ was pioneered at Surrey in 1989 [1]. Initially, the characteristic features of the reaction:

- its Q-value (+18.352 MeV) leading to the production of $\sim 14$ MeV protons, and
- inverse kinematics – the energy of a proton produced at backward angles increases as the incident $^3\text{He}$ energy decreases,

were exploited to measure deuterated polymer profiles in thin films (a few microns) as a function of depth. Subsequently, with the availability of a 2D scanning microbeam the reaction was used to measure profiles of deuterated water diffusing in polymeric materials to depths of several millimetres [2]. The proton detectors used in all this work were 1500µm thick silicon surface barrier detectors, thick enough to detect the full energy of the protons from the reaction.

For applications in which either very low concentrations of deuterated material need to be measured or a very small beam spot size or beam current is required, a different sort of detector is needed, with a large surface area, maximising the solid angle subtended.

Detectors of a material with the required characteristics:

- high stopping power
- good energy resolution
- large surface areas

became available in the last few years: Cadmium Zinc Telluride (CZT) detectors. These have been characterised at Surrey [3, 4]. Part of this thesis records the first use of a multi-detector array of CZT detectors in the measurement of water diffusing into a structural adhesive epoxy resin. How moisture progresses into structural adhesives is an important problem, providing the means for accurate predictions of longevity of bonds. This is traditionally studied by destructive techniques, relying on assumptions rather than directly measuring the position of moisture relative to the bulk adhesive and the interfacial region.
between the adhesive and metal substrate. Using the nuclear reaction \( \text{D}(\text{He},p)\alpha \) and the novel CZT array provides the means for the measurement of diffusion profiles directly along the join, without first separating the layers.

Another materials problem where no reliable non-destructive analysis technique exists is the quantification of gold distributed in flecks in foam cylinders. To address this, ion beam techniques for measuring both the mass of gold and also the average size of the gold flecks needed to be developed; this is the main project reported in this thesis.

Two techniques which I thought may be useful are Particle Induced X-ray Emission (PIXE) and Rutherford Backscattering Spectrometry (RBS). PIXE and RBS have been used in materials analysis at the Surrey Ion Beam Centre for many years - recent work has involved the measurement of heavy elements in concrete [5].

The detailed size of the gold flecks in the foam cylinders is unknown but is certainly of the order of several microns diameter. Crucially in gold flecks of this size gold L X-rays (energies <20keV) are strongly attenuated. Hence detecting gold L X-rays cannot lead to a measure of the gold mass in the absence of detailed knowledge of the fleck size. Gold K X-rays (energies between 65 and 85keV) however are minimally attenuated in such flecks and, if they can be detected in sufficient quantity, do offer a means of measuring the gold mass unambiguously.

PIXE historically has been carried out primarily with the use of Si(Li) detectors. These are efficient for X-ray energies up to ~20keV, but above this energy the efficiency falls off rapidly. As Si(Li) detectors are very inefficient in the Gold K X-ray region this provided the challenges of both

- selecting detectors which are efficient, and
- developing an ion beam technique which would allow the measurement of not only the mass of gold but also the average size of the flecks.

At the time, newly developed thermoelectrically cooled CdTe detectors manufactured by Amptek® became available in a form which would allow them to be inserted in a vacuum chamber.
These are efficient for the detection of X-rays over the full energy range needed, encompassing both gold K and L X-rays and I decided to base the technique around them. Their usage for gold X-ray measurement does however introduce challenges not present in the detection of X-rays from lighter atoms using Si(Li) detectors and these challenges – of different backgrounds and different apparatus geometry - had to be understood and corrected for.

Another technique I also thought may be applicable to the gold mass determination was the use of Rutherford Backscattering of the incident proton beam by gold. As proton backscatter detectors were already incorporated in the technique as monitors of the proton beam fluence it was straightforward to also record backscatter spectra from the gold at the same time as the X-ray spectra were measured, as a complementary technique. In the main part of this thesis I describe the development and outcome of the application of these joint techniques to the determination of the mass and size of the gold flecks.

These two projects are introduced and described in full detail in separate self-contained chapters. These follow sections on background theory and an overview of the experimental systems available. Overall conclusions and recommendations for further work follow the two experimental chapters.
Chapter Two: Theory

2.1 Ion Beam Analysis

2.1.1 General Overview

Ion Beam Analysis (IBA) is a term encompassing a range of materials analysis techniques. Generally, a beam of energetic ions (ionised atoms) from an accelerator is directed onto a target and the effects of the interaction of the ions with the target studied. My interest is in the concentration profiles of particular elements/molecules and these can be studied given prior knowledge of the type of ion and its kinetic energy, together with detection of both scattered ions and induced atomic or nuclear reaction products. It is often beneficial to use more than one technique simultaneously to gain complementary information.

Such analysis techniques were pioneered in the middle of the last century, as suitable accelerators became available, and continue to progress with the continual development of both accelerator technologies and detection systems. Many IBA techniques exist and a non-exhaustive glossary is tabulated below, in table 2.1.

<table>
<thead>
<tr>
<th>Initials</th>
<th>Technique Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ERD</td>
<td>Elastic Recoil Detection (also ‘Forward Recoil Spectrometry’): detection of light ions scattered in the forward direction.</td>
</tr>
<tr>
<td>IBIC</td>
<td>Ion Beam Induced Current: direct observation of carrier mobility in electronic devices (resolved in space and time).</td>
</tr>
<tr>
<td>NRA</td>
<td>Nuclear Reaction Analysis: detection of reaction products following an ion induced nuclear reaction.</td>
</tr>
<tr>
<td>PIXE</td>
<td>Particle Induced X-ray Emission: detection of characteristic X-rays emitted with transition of atomic electrons re-aligning following ejection from ion bombardment.</td>
</tr>
<tr>
<td>PIGE</td>
<td>Particle Induced Gamma Emission: a particular type of NRA.</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Backscattering Spectrometry: detection of ions backscattered due to Coulomb repulsion by target nuclei.</td>
</tr>
<tr>
<td>NRBS</td>
<td>Non-Rutherford Backscattering Spectrometry: detection of ions backscattered not just by Coulomb repulsion, but also by strong interaction with the target nuclei. Important for energetic light ions incident on light nuclei.</td>
</tr>
</tbody>
</table>

Table 2-1 - Some IBA techniques.
IBA can be performed with heavy or light ions, depending on the experimental needs. Typically, non-destructive analysis is performed with MeV energies of light ions \((Z < 8)\). Both broad beams and scanning micro-beams of ions are used.

### 2.1.2 Terminology, Units and Dimensions

The number of ion charges passing a point per unit time, the beam current, is a very important quantity measured in the appropriate SI unit - the Ampère (amp, A). Associated with this is the measurement of the integrated current \(Q\), in Coulombs (C); from this the number of ions, \(I\), incident on a target can be calculated from equation 2.1.1 below:

\[
I = \frac{Q}{Ze}
\]

**Equation 2.1-1**

where \(e\) is the magnitude of the charge on the electron, \(1.602 \times 10^{-19} \text{C}\), and \(z\) is the ionisation state of the ion (e.g. \(z=1\), singly ionised, \(z=2\), doubly ionised).

Two other quantities are defined in terms of \(I\): the fluence is the number of ions passing through unit area; the flux is the number of ions passing through unit area per unit time.

Energies used in ion beam analysis are not quoted in SI units (Joules, J). Instead, the base unit of the electron-volt, \(eV\), is used. An electron-volt is the energy gained by a charge of magnitude \(e\) accelerated through a potential difference of one Volt; this relationship is shown in equation 2.1.2:

\[
eV = 1.602 \times 10^{-19} \text{C} \times 1\text{V} = 1.602 \times 10^{-19} \text{J}
\]

**Equation 2.1-2**

The electron-volt is clearly a more natural unit for energy measurement in atomic and nuclear physics than the Joule. At accelerators with terminal voltages of a few MV beam energies of the order of a few MeV are generated for ions in a low charge state. Increasingly higher energies are generated of course for ions in higher charge states.
the number of nuclei or atoms per unit area is given by equation 2.1-3, where Avagadro’s number \( N_A \) (6.022 \( \times \) 10\(^{23} \)) will be present in \( A \) grams of atoms of atomic mass \( A \), \( \rho \) is the density of the material and \( t \) is the thickness.

\[
N = \frac{N_A \cdot \rho \cdot t}{A}
\]  

Equation 2.1-3

The ‘cross-section’ of a reaction (e.g., a reaction with a nucleus producing other ions or \( \gamma \) rays or a reaction with atomic electrons producing X-rays) or elastic scattering is a measure of the probability that it will occur. If \( I \) ions are incident on an area \( a \) of a ‘thin’ target (i.e., one sufficiently thin that the particular reaction probability varies little with beam energy loss in the target an ion interacts with at most one constituent nucleus or atom) then the number of reaction products generated (at all scattering angles) from a particular reaction, \( R \), is given by equation 2.1-4.

\[
R = I \times [N \cdot a] \times \frac{\sigma}{a}
\]  

Equation 2.1-4

where the reaction cross-section, \( \sigma \), has the dimensions of area and is measured in units of barns (10\(^{-28} \) m\(^2 \), b) and sub-units millibarns (10\(^{-3} \) barns, mb), microbarns (10\(^{-6} \) barns, \( \mu b \)) etc.

In principle \( \sigma \) can be determined using the relationship in equation 2.1-5:

\[
\sigma = \frac{R}{IN}
\]  

Equation 2.1-5

The magnitude of the reaction cross-section is dependent on the energy of the incident ions. At a particular energy the yield of scattering products of a particular reaction can be very angular dependent. The ‘differential cross-section’ \( d\sigma/d\Omega(\theta,\phi) \) is the fraction of the cross-section proportional to the probability of scattering into unit solid angle (the variable
(\Omega) at an angle - in cylindrical polar co-ordinates - \((\theta, \phi)\) to the incident beam. The cross-section is then given by equation 2.1.6:

\[
\sigma = \int_0^{2\pi} \frac{d\sigma}{d\Omega}(\theta, \phi) \cdot d\Omega
\]

Equation 2.1.6

\(d\sigma/d\Omega(\theta, \phi)\) has units of barn/sr or subunits millibarn/sr, microbarn/sr.

For non-polarised ion beams and targets where \(d\sigma/d\Omega(\theta, \phi)\) is independent of \(\phi\), the following relationships given in equation 2.1.7 and 2.1.8 apply:

\[
\frac{d\sigma}{d\Omega}(\theta, \phi) = \frac{d\sigma}{d\Omega}(\theta)
\]

Equation 2.1.7

\[
d\Omega = 2\pi \cdot \sin \theta \cdot d\theta
\]

Equation 2.1.8

Measured reaction cross-sections and differential cross sections for a wide range of incident ions and target nuclei atoms are available as tabulations and graphs plotted against incident ion energy, with the differential cross sections plotted for specific angles [6, 7]. These enable the ion beam analysis experimenter to determine (for instance) both the beam energy and detection angle necessary in order to maximise a particular reaction rate and product yield.

2.1.3 Particle Induced X-ray Emission (PIXE) Analysis

In Particle Induced X-ray Emission (PIXE) analysis, an energy spectrum of X-rays, originating in the beam particles' interactions with atoms, is detected. The occurrence of
peaks at energies characteristic of particular elements and the ratios of their intensities can be used as a very reliable way of determining the elemental composition of a given sample material.

In an atom, negatively charged electrons are bound in energy shells around the nucleus. Following the convention started by Charles Barkla who first identified that different elements produce different characteristic X-rays [8], the innermost shell is labelled the K shell, the next layers are the L shell, the M shell, and so on. Excluding the K shell, shells are split into subshells with configurations defined by quantum numbers. The electrons are attracted to the positive nucleus, so energy must be given to an electron to remove it from the atom or to move it to a higher energy state (further from the nucleus). Conversely, when an electron falls from a higher to a lower shell, when a vacancy presents itself, an amount of energy corresponding to the energy difference between the two shells is released.

In PIXE, a beam of ions, usually protons (hence this IBA technique is sometimes referred to as Proton Induced X-ray Emission), is directed onto a sample. The ions interact with and remove bound electrons from target atoms. As electrons in higher levels fall in cascade to fill vacancies, the energy lost by each electron – the energy difference between two atomic energy levels of the target atom – is released in the form of ‘characteristic’ X-rays.

The level to which electrons fall determines the principal nomenclature of the characteristic X-rays; for example electrons falling to the ‘K shell’ produce the K series of X-rays. Each Barkla shell label is given a subscript determined by the level from which the electron falls – originally according to the number of shells traversed by the electron – $\alpha$ (1 shell), $\beta$ (2 shells), $\gamma$ (3 shells). However, this spectroscopic notation was defined before electron transitions were well understood. Electrons falling from the L to the K-shell produce $K_{\alpha}$ X-rays, M – L produce $L_{\alpha}$ X-rays. However, $K_{\beta}$ X-rays can be produced by electrons travelling from M – K or N – K or making even larger transitions as the combinations become more complex. A second, numerical subscript denotes the exact transition from subshell to subshell such as $K_{\alpha_1}$ and $K_{\alpha_2}$ (and historical names such as $L_1$ and $L_0$), which can then be identified by looking up reference tables and figures. This nomenclature is called Siegbahn notation. In 1991 the International Union of Pure and Applied Chemistry recommended a more logical system [9]; however, it has not been adopted in favour of the traditional notation. Some principal transitions are shown below in figure 2.1.3-2.
Figure 2.1.3-1: Principal energy transitions giving rise to characteristic X-rays, reproduced from [10]. Approximate relative intensities between L and K lines are shown; they vary with proton beam energy.

Because X-rays originate within the atom, as a secondary effect of ions knocking out electrons, the distribution of characteristic X-ray intensities with detection angle is essentially isotropic. The differential cross-section depends only on the energy of the ion beam, $E$, and this is expressed in equation 2.1-9:

$$\frac{d\sigma(\theta)}{d\Omega} = \frac{\sigma(E)}{4\pi}$$

Equation 2.1-9

2.1.4 Backscattering Spectrometry (BS) Analysis

2.1.4.1 Rutherford Backscattering Spectrometry (RBS)

Rutherford Backscattering Spectrometry (RBS) refers to the elastic backscattering (angles near 180°) of charged particles by atomic nuclei in a target solely by the Coulomb force. Its
name is derived from Sir Ernest Rutherford’s analysis of the scattering of alpha particles by a gold foil [11] resulting in the following formula in equation 2.1.10 for the differential cross-section for Rutherford Scattering (in units of mb/sr):

\[ \frac{d\sigma}{d\Omega} = 1.296 \left( \frac{zZ}{E} \right)^2 \cos \theta \left( \frac{\theta}{2} \right) \]

Equation 2.1-10

where \( z \) is the number of charges +e on the incident ion, \( Z \) is the number of charges on the target nucleus, the incident ion energy is \( E \) (in MeV) and the backscatter angle of the detector is relative to the incident beam direction \( \theta \).

2.1.4.2 Non-Rutherford Backscattering Spectrometry (non-RBS)

Non-Rutherford Backscattering occurs primarily for light ions elastically scattering from light elements when they approach a nucleus sufficiently closely for the scattering to be affected by the strong interaction. The same kinematics as for RBS govern the scattering but the angular and backscatter-energy dependence of the differential cross-section is no longer given by the Rutherford Scattering formula.

2.1.4.3 Kinematics

For a proton of mass \( M_1 \) backscattering from a target atom of mass \( M_2 \), the ratio between the maximum energy of the proton after backscatter, \( E_{bs} \), and incident the energy of the proton, \( E_{inc} \), is known as the kinematic factor, \( K \), see equation 2.1-11.

\[ K = \frac{E_{bs}}{E_{inc}} \]

Equation 2.1-11

A schematic of backscattering is shown below in figure 2.1.4-1:
Figure 2.1.4-1: Schematic diagram showing the backscatter of a projectile from a target nucleus.

The recoil energy of the target nucleus is equal to the difference between the incident and backscatter energies: \( E_{\text{rec}} = E_{\text{inc}} - E_{\text{BS}} \). By conserving energy and momentum, the following expression for the kinematic factor can be obtained, equation 2.1-12:

\[
K = \left[ 1 - x^2 \sin^2 \theta + x \cos \theta \right] / \left( 1 + x \right)^2 \quad \text{where} \quad x = \frac{M_1}{M_2}
\]

Equation 2.1-12

Figure 2.1.4-2: A graph of the kinematic factor, reproduced from [12].
Figure 2.1.4.2 is a graphical representation of the kinematic formula (equation 2.1.12), from [12]. This shows that clearly shows that at larger backscatter angles, as a function of the ratio $M_2/M_1$, $K$ tends to the simplified version given in equation 2.1.13.

$$K \to \left(\frac{1-x}{1+x}\right)^2 \quad \text{where} \quad x = \frac{M_1}{M_2}$$

Equation 2.1-13

Combining equations 2.1.11 and 2.1.12 it follows that for large backscatter angles, the maximum backscatter energy of the proton can be approximated to equation 2.1.14:

$$E_{bs} = E_{inc} \times \left[\frac{M_2 - M_1}{M_2 + M_1}\right]^2$$

Equation 2.1-14

Using equation 2.1.14, considering a proton backscattering from

- a high $Z$ material, gold ($Z=79$), the maximum backscatter energy of the proton will be approximately equal to the incident energy: $E_{bs} \sim E_{inc}$ or
- a low $Z$ material, oxygen ($Z=8$), the maximum backscatter energy of the proton will be less than and proportional to the incident energy: $E_{bs} \propto E_{inc}$.

Knowing the rate of energy deposition, $dE/dx$ (see §2.2), of the ions in the sample material, the energy of detected backscattered ions can be used to determine not only the intrinsic charge of atomic nuclei within a sample but also their depth concentration profile. Ions backscattered from nuclei nearest the surface exposed to the incident beam have the highest energy - hence a thick layer of an element produces a broad range of backscatter energies.

2.1.4.4 Other Uses for Backscattering

Backscatter measurements can also be very useful in determining the relative beam fluence in different scans, and this is detailed later in §3.3.3.
2.1.5 Nuclear Reaction Analysis (NRA)

2.1.5.1 General

In Nuclear Reaction Analysis (NRA), products of nuclear reactions between the incident ions and target nuclei are analysed to allow identification of specific nuclei present in the target. The differential cross-section (probability) of the specific reaction occurring is, in general, dependent on both the energy of the incident ion and the angle of emission of the reaction product. Nuclear reaction cross sections are small compared with those of RBS or PIXE. Compensatory measures need to be taken to increase the reaction product yield: high currents are useful to increase the reaction rate, and beam energies should be chosen to maximise the probability of the reaction occurring. Consideration must also be given to the target-detector geometry in order to optimise the proportion of reaction products detected.

The Q-value of a nuclear reaction is the difference in rest mass energies of the initial and final reaction products. Reactions with positive Q-values release energy, and are known as exothermic reactions. Reactions with negative Q-values can only be initiated with incident ion energies above a kinematic threshold and are known as endothermic reactions.

A nuclear reaction of X(a,b)Y is shown diagrammatically in figure 2.1.5-1:

Figure 2.1.5-1: Schematic diagram of nuclear reaction, initiated with projectile, a, onto target nucleus X.
Energy and momentum conservation laws can be used to determine the energy of the ejectile (b) emitted at specific angles, see equation 2.1-15:

\[
\sqrt{E_b} = \sqrt{m_e m_b E_a \cos \theta \pm \sqrt{m_e m_b E_a \cos^2 \theta + (m_f + m_b) [m_f Q + (m_f - m_b) E_a]}} \over m_f + m_b
\]

Equation 2.1-15

2.1.5.2 Specific Nuclear Reaction used for Detecting Deuterium

The following reaction is used:

\[ ^3\text{He} + \text{D} \rightarrow \text{p} + \alpha \]

The differential cross-section of this reaction is nearly isotropic in the laboratory reference frame and the cross-section is very large, ~800mb at maximum (\(^3\text{He}\) beam energy ~0.7MeV) [13]. Because of the high Q-value +18.352MeV and the lightness of the deuteron, the higher the incident \(^3\text{He}\) beam energy, the lower the proton energy at backward angles (in the laboratory frame of reference) [14]. This reaction is very suitable for tracing water (or other hydrogenous solutions) diffusion in materials. The proton is detected in preference to the alpha owing to its much higher kinetic energy (~14MeV rather than ~2MeV, detected at backward angles). For this reaction the solution of equation 2.1-15 is single valued, only the positive sign is used.

2.1.5.3 PIGE

Particle Induced Gamma Emission (PIGE) is a type of NRA where nuclear reactions are induced leaving the target nucleus in an excited nuclear state which subsequently de-excites via emission of gamma photons. These signature gamma photons can then be used to identify a particular nuclide. As for PIXE (§2.2.7), the gammas are produced as a secondary effect of the reaction, this time internally in the nucleus, so the differential cross-section for PIGE is also essentially isotropic.
2.1.5.4 Specific PIGE Reaction used $^{19}$F$(p, p'\gamma)^{19}$F

\[ p + ^{19}\text{F} \rightarrow p' + ^{19}\text{F}^+ \rightarrow p' + ^{19}\text{F} + \gamma \]

In this reaction the first excited state ($^{19}\text{F}^+$) of fluorine is formed, subsequently decaying to the ground state of fluorine emitting a gamma-ray of energy $110\text{keV}$. This reaction can be used as a high energy photon calibration point for X-ray spectra.

2.2 Ion Beam Energy Loss

Within any atom, the nucleus is known to occupy an extremely small proportion of its volume. When an ion travels through matter it is far more likely to interact with electrons.

As discussed above this may lead to the ejection of electrons from ions and consequent X-ray emission from the atoms. In addition the ion itself loses energy, through interactions predominantly with the electrons, but also with the nuclei. How the rate will vary with depth as the beam loses energy in a thick sample can be estimated using ion energy loss with depth, $dE/dX \text{MeV/mm}$, data.

For light ions with energies of MeV this is given by the Bethe-Bloch equation, a simplified version of which is shown below in equation 2.2-1:

\[ \frac{dE}{dx} \propto \left( \frac{Z^2 \rho}{A\beta^2} \right) \times \ln \left( \frac{2\gamma^2 \beta^2 m_e c^2}{I_0} \right) \]

Equation 2.2-1

where $\beta = v/c$ the velocity of the ion relative to the speed of light $c$, $\rho$ is the density of the material, $m_e$ is the electron mass, $z$ the number of charges $e$ on the incident ion, $Z$ the number of electrons in the target atoms and $I_0$ the average ionisation energy of target atoms.
At very low energies and very high energies different formulations hold, all of which are taken into account in programs such as The Stopping and Ranges of Ions in Matter, SRIM, a computer program that uses iterative Monte-Carlo simulation methods to calculate the expected penetration of particles into target media [15, 16]. It considers inter-atomic Coulomb potentials with respect to collision scattering and produces data in terms of penetration depth and energy deposition. Contributions from energy loss due to different elements are also summed together to give the energy loss by the molecular constituents of samples.

This program also tabulates ranges, $R$ for ions where (see equation 2.2-2):

$$R = \int_0^E \frac{dx}{dE} (E) \, dE$$

**Equation 2.2-2**

Range difference is often the most accurate way of working out a depth versus energy scale for a sample.

### 2.3 Bremsstrahlung

Bremsstrahlung, literally 'braking radiation' in German, is the name for photons emitted by slowing charged particles; these photons are a source of background radiation which underlie PIXE spectra. For ion beam analysis using a proton beam, bremsstrahlung can be produced by the projectile protons, the displaced electrons and excited target atoms. The main types are described below.

Secondary electron bremsstrahlung (SEB) occurs when a proton hits an electron and ejects it from the target atom. Such electrons will slow down travelling through the target material largely due to the positively charged nuclei. There are a great many electrons available for collision, however the proton is 1836 times more massive than the electron so the proton cannot lose much energy in any such interaction: secondary electron bremsstrahlung can dominate PIXE spectra but only at low energies. The maximum energy which can be imparted to the electron, $E_e$, from the energy of the proton of energy $E_p$, will be in the
case of a head-on collision: this upper limit is given by equation 2.3-1, where masses of the electron and proton are \( M_e \) and \( M_p \) respectively.

\[
E_e = 4 \cdot \frac{M_e}{M_p} \cdot E_p
\]

Equation 2.3-1

Proton bremsstrahlung (PB), also referred to as nuclear bremsstrahlung (NB), is caused by photons emitted directly as the proton decelerates via Coulomb interactions with multiple target nuclei. The PB background profile extends across the full energy range of PIXE spectra: it is insignificant compared with the SEB at the low energy end of PIXE spectra (\(< \sim \text{8keV, depending on beam energy} \)), but decreases slowly with increasing photon energy and is significant at higher X-ray energies when the PIXE yield is low.

Atomic bremsstrahlung (AB) is caused by protons elevating inner electrons to a higher continuum state from which they de-excite. This is significant for heavy atoms such as gold in the L X-ray region. Uniquely a lot of work has been done in understanding this particular phenomenon by Ishii and his co-workers [17] which also references his previous papers.

2.4 Transmission

There are various processes by which photons are attenuated in different media, depending on photon energy and the atomic number of the elements present. For low energy photons incident on low to medium \( Z \) materials, the photo-electric effect and Compton scattering will dominate. The linear attenuation coefficient (\( \mu \text{ cm}^{-1} \)) and the more frequently used mass attenuation coefficient, \( (\mu/\rho) \text{ cm}^2\text{g}^{-1} \) incorporate all possible photon attenuation mechanisms in the overall attenuation for each element. Reference tables and graphs plotting mass attenuation coefficients against photon energy are available from sources such as NIST [18].

Transmission, \( T \), is the probability of photons with energy \( E \), passing through a material, and is defined as the fraction of those emerging, \( I_{\text{out}} \), out of those incident \( I_{\text{in}} \). The
transmission of photons for a material of thickness \( t \) cm, of density \( \rho \) g cm\(^{-3}\) with (energy dependent) mass attenuation coefficient \((\mu/\rho)\) cm\(^2\)g\(^{-1}\) is given by equation 2.4.1.

\[
T = \frac{I_{\text{out}}}{I_{\text{in}}} = e^{-\frac{\mu}{\rho}t}
\]

Equation 2.4-1

### 2.5 Diffusion

When the spatial distribution of a substance is inhomogeneous in a medium, there is a general tendency for the molecules to travel in the direction of lower concentration (assuming negligible intermolecular forces). Such transport is known as diffusion. In 1855 Adolf Fick quantified diffusion in space and time by equation 2.5.1, known as Fick's second law [19]:

\[
\frac{\partial \phi}{\partial t} = -D \frac{\partial^2 \phi}{\partial x^2}
\]

Equation 2.5-1

where \( \phi \) is the concentration of the diffusant - the number of molecules per unit volume at distance \( x \) and time \( t \). \( D \) is the diffusion coefficient, particular to the diffusant and the substance into which it is diffusing. The minus sign is indicative of the diffusion travelling towards the direction of lower concentration. There are different types of diffusion, classified by the rate at which the concentration of diffusing molecules varies with time:

When \( \phi \) is proportional to the square root of time, see equation 2.5.2,

\[
\phi = \frac{1}{kt^2}
\]

Equation 2.5-2

the diffusion is classed as Fickian.
For the boundary conditions such that the concentration is a constant, \( \phi_0 \), at \( x=0 \) (surface) (from constant exposure to penetrant) and zero at \( x=\infty \) (unaffected due to being so far away), at \( t>0 \), the general solution is equation 2.5.3:

\[
\phi = \phi_0 \cdot \text{erfc} \left( \frac{x}{\sqrt{4Dt}} \right)
\]

Equation 2.5-3

For the diffusion of liquids into polymers where swelling is involved, the time dependence of the moving front is linear i.e. the front moves with constant velocity, \( V \). Equation 2.5-2 then becomes equation 2.5.4:

\[
\phi = kt
\]

Equation 2.5-4

This is called Case II diffusion (chapter 11 in [20]). The front is preceded by a precursor which has an exponential form. According to Peterlin [21], the diffusion coefficient, \( D \) \( \text{cm}^2 \text{s}^{-1} \) for Case II diffusion where a liquid ingresses into a polymer inducing some swelling can be derived from equation 2.5.5 describing the concentration of the precursor:

\[
\phi = \phi_0 \times e^{-\left( \frac{Vx}{D} \right)}
\]

Equation 2.5-5

where \( \phi_0 \) is the yield at the start of the exponential decay curve, \( x \) is the horizontal distance from the start of the exponential decay curve, and \( V \) and \( D \) are defined above. \( \phi_0 \) is the average yield of the flat region at infinite time. This is shown in figure 2.5.1, reproduced from [22].
Figure 2.5-1: Components of a Case II diffusion profile reproduced from [22].

\[ \phi = \phi_0 \exp(-tx/D) \]
Chapter Three: Experimental Systems

3.1 The Ion Beam Facility

Ion Beam Analysis (IBA) at Surrey is performed using a 2MV Tandetron from High Voltage Engineering Europe. It was installed in Summer 2001 in the Surrey Ion Beam Centre (IBC), a national facility funded by the Engineering and Physical Sciences Research Council (EPSRC) for both academic and industrial research. It was commissioned in Easter 2002 with two beamlines:

- an in-vacuo microbeamline -30° to the right of the beam direction [23];
- a millibeamline at +10° with a Rutherford Backscattering Spectrometry (RBS) chamber. This latter beamline has been extended to enable an external microbeamline. The external beamline allows a beam of scanning ions out to air through a Kapton® foil window [24].

This set-up of the facility is shown in figure 3.1.1.

![Diagram of the ion beam analysis facility](image)

Figure 3.1-1: The ion beam analysis facility in 2006, with key features labelled; in 2007 the in-situ scanning microbeamline was relocated to the -10° position.
3.1.1 Ion Source

The ion source of the analysis accelerator at the Surrey IBC is a duoplasmatron (model 358 [25]). The filament is heated to produce electrons by thermionic emission and accelerated to the anode. The electrical arc through the gas generates plasma which is constrained geometrically and magnetically by the arrangement shown in figure 3.1.1-1.

![Diagram of a duoplasmatron ion source](image)

**Figure 3.1.1-1: Duoplasmatron ion source.**

Tandem accelerators require an input of negative ions, dictated by their design of the high voltage at the centre. The charge polarity of the extractor is selected depending on the ions produced for the beam: negative ions can be formed from a hydrogen plasma but not from helium, due to a negative electron affinity. Hence positive helium ions are extracted from the source; before injection into the Tandetron they must therefore be converted to negative ions.
### 3.1.2 Einzel Lenses

Einzel lenses focus the ion beam after leaving the source and before reaching the multipurpose injector. The potential applied to the centre plates, see figure 3.1.2-1, determines the amount of focus caused by the electric field lines deflecting the ions.

![Electric Field Lines](image)

**Figure 3.1.2-1:** An einzel lens focussing a positively-charged ion beam (direction of ions left to right).

### 3.1.3 Charge Exchange Canal

After exiting the source and an einzel lens, ions continue through the charge exchange canal. In this a reservoir of lithium can be heated to very high temperatures, typically 550°C (the melting point of lithium is 180.54°C [26]). The associated lithium vapour collects at the top of the canal and electrons are donated to the positive helium ions, converting a small fraction of them to negative ions. When hydrogen is used the lithium is not heated, and the ions pass through the charge exchange canal unaffected.

Charge transfer can occur when a positive ion collides with a neutral particle. Alkali metals have one electron in the valence band, therefore are good electron donors and are often used as such neutral particles in charge exchange canals. Lithium has the lowest mass and is the least active of all the alkali metals, and was selected by HVEE because of its easy handling and safety characteristics [27]. Negative helium ions can be formed in a metastable excited state through charge exchange with the positive helium ions, with lifetime long enough to allow acceleration in the Tandetron.
3.1.4 Multi Purpose Injector – the Low Energy Analysing Magnet

Following the charge exchange canal, after further focusing with a second Einzel lens, the multi purpose injector (MPI) directs the desired ions into the accelerator. The strength of the magnetic field determines which ions, of mass, $M$, and charge, $q$, will have the correct curvature radius, $r$, to enter the accelerator, see equation 3.1-3. Ions that fail to meet these criteria are prevented from entering the accelerator by exit slits about the aperture.

The magnitude of force $F$ exerted on a particle of charge $qe$, moving with velocity $v$, in a magnetic field $B$, is given by equation 3.1-1:

$$F = qevB$$

Equation 3.1-1

Centripetal force is defined by equation 3.1-2:

$$F = m\left( \frac{v^2}{r} \right)$$

Equation 3.1-2

To obtain an equation for the radius of curvature, equations 3.1-1 and 3.1-2 can be combined to make equation 3.1-3:

$$r = \frac{mv}{qeB}$$

Equation 3.1-3

If the momentum term, $mv$, is rewritten in terms of kinetic energy equation 3.1-4:

$$E = \frac{1}{2}mv^2$$

Equation 3.1-4

then equation 3.1-5 can be obtained:

$$r = \frac{\sqrt{2mE}}{qeB}$$

Equation 3.1-5
3.1.5 Accelerator

The accelerator is a Tandetron model from High Voltage Engineering Europa BV. It is known as a tandem accelerator because the ions are accelerated twice. Negative ions gain energy as they are accelerated towards a terminal maintained at a positive potential. At this point, the geometric centre of the accelerator tube, electrons are removed by interaction with a 'stripper gas'. The ions, now positive, are then accelerated a second time, away from the terminal. In this way the singly charged ions (H\(^+\), He\(^+\), He\(^++\)) emerge with approximately twice their energy at the terminal voltage, doubly charged ions (He\(^{++}\), He\(^{+++}\)) thrice the energy. The beam energy can be found using the equation 3.1-6:

\[ E_{beam} = eV_{extraction} + (q+1)eV_{terminal} \]

Equation 3.1-6

where \( eV_{extraction} \) is the energy of the ions extracted from the source (20keV).

The high voltage at the terminal is achieved using a Cockcroft-Walton type generator stack, connected perpendicular to the direction of ion travel so the accelerator is 'T'-shaped, and the basic design is shown in figure 3.1.5-1, reproduced from [28]. The ions travel through a highly evacuated accelerator tube which is suspended within a pressure vessel. Electrical isolation is an important consideration with the high voltages generated. Sulphur hexafluoride, SF\(_6\), is used as a dielectric gas in the vessel and sharp points have been avoided in the design. These factors minimise electrical arcing, or 'sparking', which limits the achievable terminal voltage.

Figure 3.1.5-1: Tandetron high voltage diode stack. Diagram reproduced from [28].
Collisions with nitrogen stripper gas atoms remove electrons, converting the ions from negative to positive. The stripper gas is kept at low pressure and is within an outer cell, which pumps out extraneous gas that would otherwise leak into the beamline. Fine holes allow the beam to pass through.

The main advantages of the Tandetron over the traditional Van de Graaff design are that a lower terminal voltage is required for the same beam energy and potentials at both ends of the accelerator are close to ground. The Tandetron design is also easier to service with the ion source separate from the pressure vessel and at ground potential. The diode stack high voltage generator eliminates the need for moving parts inside the accelerator, such as the charging belt in a Van de Graaff or a Pelletron Tandem, reducing the opportunity for mechanical failure.

3.1.6 Switching Magnet: the High Energy Analysing Magnet

The switching magnet deflects the beam after exiting the accelerator, into the desired beamline. It works on the same basic principle as the MPI (§3.1.4), and can be considered to be the high energy analysing magnet.

3.1.7 Scanning

For an area of interest larger than microns, focussing down to this size is still advantageous. The beam can be scanned over the area of interest (this area is beam energy dependent, typically up to 2mm x 2mm). The beam is raster scanned using magnetic deflection by two perpendicular dipole magnets upstream of the focussing quadrupoles: the amount of deflection is proportional to both the magnetic field strength and the ion momentum. Such scanning can help obviate beam heating effects (as the beam spot is constantly moving). It also allows the position association of detected events via data acquisition software.

Figure 3.1.7-1: Scanning magnets.
3.1.8 Quadrupole Magnets

A minimum of two magnetic quadrupoles is necessary to achieve a point focus - a singlet can only focus the beam in one plane [29]. This is shown below in figure 3.1.8-1 reproduced from [30].

Figure 3.1.8-1: Quadrupole focussing magnets, reproduced from [30]:
(a) Quadrupole lens cross section, (b) nett focussing effect of two quadrupole lenses, (c) the optical analogy ('lenses').
3.1.9 Microbeamline

The accelerated ions are focussed at the end stage of the microbeam line using an "Oxford" triplet configuration \([10, 31]\) of three magnetic quadrupole lenses. Two controls are used to finely adjust the focus to obtain the smallest beam spot allowed by the beam conditions (at best ~1\(\mu\)m diameter).

![End of microbeamline showing 'Oxford Triplet' configuration of three quadrupoles.](image)

Figure 3.1.9-1: End of microbeamline showing 'Oxford Triplet' configuration of three quadrupoles.

3.1.10 In Vacuo Microbeam Target Chamber

The target chamber is 17cm in diameter and can house several detectors, depending on the requirements of each particular experimental run. The whole lid is removed when replacing or altering the detectors inside the chamber. Samples are attached to a stage, which is lowered through a small port in the centre of the chamber lid to place the target in-line with the beam. The sample position can be adjusted vertically and horizontally using finely gauged micrometers. The chamber is evacuated with a roughing pump and a turbo pump, so that the beam line may be opened. Keeping the chamber under vacuum minimises the ion and reaction product energy losses in air.
3.1.11 External Beamline

The external (i.e. in-air) beam set-up is suitable for samples which cannot stand vacuum conditions or are too large for the chamber, however straggling through the beam line exit foil and particle collisions with air atoms leads to a larger beam spot size and limitations on the reactions which can be used. The loss in focus from this is significant enough to warrant having only two quadrupoles on the beamline. Figure 3.1.11-1 shows the external beamline and microbeamline, in the positions from figure 3.1-1.

Figure 3.1.11-1: The ends of both the beamlines.

In experiments described in thesis only the microbeam was used but I also made significant contributions to experiments using the external beam [32].
3.2 Radiation Detection and Data Acquisition Systems

Solid state detectors are based on p-n junction diodes, which are reverse biased and on the point of conducting. Incident radiation produces electron hole pairs in the semiconductor material, which undergo net migration in the applied electric field. The pulses of current produced represent the incident radiation. Some semiconductor detectors require cooling to reduce leakage current to acceptable levels; for example silicon and germanium detectors traditionally used in gamma-ray spectroscopy are cooled to liquid nitrogen (LN$_2$) temperature (77K; -196°C) which often require relatively large LN$_2$ dewars.

3.2.1 Silicon Charged Particle Detectors

The backscatter detector normally housed in the microbeamline target chamber is a silicon surface barrier (SiSB). SiSBs are made from n-type silicon with localised etching and treatment to form a thin p-type silicon layer, and a gold deposited contact. The original backscatter detector had a surface area of 50mm$^2$ and a depletion depth of 300μm, and was replaced with a SiSB of area 150mm$^2$. It is used routinely for the detection of backscattered ions from the beam. It is held at an adjustable angle, typically at 165° from the beam axis. It is replaced by SiSBs of different dimensions depending of the requirements of ‘non-routine’ analysis experiments. For example, for the purposes of $^3$He–D nuclear reaction analysis experiments, it is sometimes replaced with a thicker SiSB of area 100mm$^2$ and having a 1500μm thick depletion depth, capable of detecting the full energy of 15MeV protons. Silicon surface barrier detectors, used since 1960s, are being superseded by Ion Implanted Silicon (IIS) detectors. These are manufactured by accelerating p-type ions and implanting them directly into the silicon. This makes them slightly less fragile than their predecessors.

3.2.2 CdTe and CZT Detectors

CdTe is a II-VI semiconductor. Improvements in crystal growth techniques in the 1990s saw this material developed for X-ray and gamma photon spectroscopy, as an alternative to silicon and germanium detectors. As it has a relatively large band gap, CdTe is in principle capable of room temperature operation. The higher atomic numbers of cadmium and tellurium (48, 52 respectively) result in superior photon detection efficiency, particularly at photon energies higher than 20keV [33].
The addition of zinc, typically 10-20 percent, to the cadmium substrate to produce CdZnTe (CZT), was expected to increase the overall resistance so reduce leakage current by increasing the band gap. This initially resulted in better resolution when detecting low energy photons, however the benefits of zinc rely on uniform distribution across the crystal and led to an increase in manufacturing difficulty; the decision between using CdTe and CZT for photon spectroscopy was not easy [34].

CdTe photon detectors suitable for inserting directly into the target chamber are available commercially from Amptek Inc. Quoting from the Amptek® website [35], recent developments in CdTe detectors have shown significant advantages over comparable CZT detectors in photon spectroscopy:

"The use of Schottky contacts in CdTe detectors reduces the leakage current far below that of CZT. This permits the use of a much higher bias voltage than in a standard detector. Since the charge transport properties of the CdTe detector are much higher than CZT, the net result is a vast improvement in the usable depth (sensitivity). Additionally, because hole tailing and electronic noise are reduced, not only is the sensitivity improved but resolution is much better."[35]

3.2.2.1 CdTe Photon Detector

In the main experimental project of this thesis, it was necessary to detect high energy gold K characteristic X-rays (~65keV-85keV) in addition to gold L X-rays (~9keV-13keV). The Amptek® photon detectors chosen for this project have CdTe chips of 25mm², 1mm thick. Each detector is mounted on a two-stage thermoelectric cooler, which also cools input FET feedback components to the charge sensitive preamplifier; these components are kept at approximately -30°C to further reduce thermal noise. The photon detection efficiency is close to 100% from photon energies of 10keV-60keV, at 70keV 91%, 80keV 82% and at 90keV 72%. A full table of values with corresponding graph are available at [36].
3.2.2.2 CZT Charged Particle Detector Array

Although originally developed for photon detection, CZT detectors are ideally suited as room temperature charged particle detectors for use as large area arrays in nuclear reaction analysis.

A large solid angle detector is extremely useful for nuclear reaction analysis, reaction cross-sections being typically very small. This is especially significant when running at the low currents associated with using a microbeam, reaction rates then being very low.

The fabrication of SiSB detectors thick enough to detect the full energy of 14MeV protons (~1400μm) is also difficult and consequently expensive. Per unit of active area, they are an order of magnitude more expensive than CZT crystals. When using them in an array a considerable amount of area is wasted due to the bulky housing around the active area of the silicon wafer and fitting them into the limited space in a microbeam chamber is difficult due to their bulky rear connectors. CZT detectors have no surround, are typically only a few millimetres thick and have only two thin pins (earth and signal) protruding from them.

As an example figure 3.2.2-1 shows front and side views of a SiSB detector and a CZT detector. The SiSB detector, manufactured by Ortec®, has been used for detecting the high energy protons from the \(^3\)He–D nuclear reaction by myself and others previously in the same research group [37, 38]. The CZT detector, manufactured by eV Products Limited, has dimensions of 15mm × 15mm × 3mm and is capable of stopping protons of energies of up to more than 15MeV [4]. The mount on the SiSB detector takes up a lot of space; the active detection region is 1.5mm thick and the total detector thickness is almost ten times greater (13.8mm). In contrast to this, most of the CZT detector is the active detection region (see below, figure 3.2.2.1).
Figure 3.2.2-1: Front and side view of silicon surface barrier detector and CZT detector, both capable of fully stopping the high energy protons from the $^3$He-D nuclear reaction. The SiSB side view diagram was reproduced and modified from [39]. The photograph of the front view of the CZT detector is reproduced from [40].

A prototype detector array has been designed and constructed [41] at Surrey for in vacuo charged particle NRA, and is shown below in figure 3.2.2-2. It comprises twelve CZT detectors as described above and shown in figure 3.2.2-1. They are arranged in a square about a 3cm x 3cm hole. The detectors all have equal gain. The detector outputs are hard-wired together in groups of four— the top and bottom rows horizontally and the remaining four side detectors - and sent to three separate preamplifiers. Each preamplifier output is sent to its corresponding amplifier. In use, the array is located 1cm upstream of the target and subtends a useful solid angle of $\sim \pi/2$ sr.
3.2.3 Data Acquisition Software

The ion beam analysis accelerator at Surrey uses scanning and focussing hardware from Oxford Microbeams Ltd and Oxford Microbeams Data Acquisition software ‘OM_Daq’ [43]. The software is run on a PC, which is connected to a multi-ADC, and can record events for up to eight different detector amplifier outputs simultaneously, generating on-screen multi-channel analyser spectra. Element identification markers are available for PIXE and RBS spectra. The software correlates the 2D position of the scanning beam with detected events in user-defined energy regions of the spectra. Thus maps can be generated to represent the position of detected events within the scan area. An extremely useful feature is that data can be recorded in event-by-event or ‘List Mode’ so that the experimental results may be rerun offline. A mask can be drawn to cover an area of particular interest and derivative spectra generated using counts detected from within the masked region of the scan area.
3.3 General Experimental Methods

There are several procedures and considerations that are common to different experiments.

3.3.1 Sample Preparation

Ideally, owing to the sensitivity of ion beam analysis techniques, a perfectly flat, smooth front face, exactly perpendicular to the beam direction would provide the least unambiguous results. Non-uniformity, especially dents, holes and fissures increase the surface area or edge exposed to the beam. On the 2D elemental maps (PIXE, reaction product or backscatters) dense regions of high counts can be indicative of such artefacts, the effects however can be more subtle.

It is of course not always possible to have 'perfect' samples. They are mounted with the surface to be analysed as perpendicular to the beam line as possible and careful inspection is performed before and after analyses, to identify any regions which might adversely influence the results.

Specially designed copper or carbon blocks are used to clamp the samples in position facing the beam. Copper blocks are sanded with a very fine gauge emery paper then washed with butyl alcohol to expose a clean and shiny, flat surface; carbon blocks are cleaned with a damp filter paper.

3.3.2 Sample Preservation

Before exposure to the ion beam, consideration is given to the integrity of the sample. Samples which are usually unsuitable for vacuum conditions include both those which are very thin and brittle and any samples which are, and need to remain, 'wet' during analysis. These must be analysed with an external beam. If samples contain some form of moisture diffusion profile obtained over a specific time frame, they can be analysed with an in vacuo microbeam by flash freezing (immersion in liquid nitrogen) the samples at the relevant time - also preventing ice crystals from forming and cracking samples. These must also be maintained at low temperatures during ion beam analysis by attachment to a cold stage.
Operational settings, such as the source filament current, control the amount of current which can be directed through the system. Retractable Faraday cups (also used as beam stops) measure the current before injection to the accelerator and in the beamline. Magnets and collimating slits affect the available current as it travels en route to the target. The current can be increased to partly compensate for low cross section reactions; it can be reduced when targets are fragile or particularly susceptible to charging or heating. Obtaining an absolute measure of beam current at the point of incidence on a sample is difficult.

In order to monitor fluctuations in beam current during experimental runs and to enable the experimenters to provide similar beam conditions for samples of the same type, the sample holder arm has been designed to allow the conduction of current from the sample to an electrically isolated connector on the external (top) part of the sample holder. This is connected to an ammeter. However this measure of beam current cannot be used as an absolute measurement as it is extremely dependent on the sample material, how the sample is connected to the holder and the area over which the beam is directed.

A Faraday cup in alignment with the beam can be inserted at the back of the microbeamline sample chamber. However for the thick samples used in measurements described in the following chapters this would have served no useful purpose - the beam was completely stopped by the sample/sample holder.

There is an alternative to measuring the absolute beam current both for inter-sample data normalisation and for absolute normalisation, if a standard is available. A scanning beam is used, which scans both the sample and part of the holder. Together with scattering data from the sample, the number of ions backscattered from the sample holder per unit area is measured in each scan. The number of ions backscattered from the sample holder per unit area is proportional to the number of ions incident on the sample. Measuring these allows data from experimental runs to be inter-normalised. As each set of data is recorded in the same data acquisition system, this can obviate the numerical effects of detection dead-time and even different data acquisition run times (this is investigated in detail in the main experiment in §5.8.7.2).
4.1 Introduction

Joints are bonded with structural adhesives in the aerospace industry. Depending on the specific performance demands on a joint, adhesives can offer a variety of advantages over more traditional joining techniques. Adhesive bonds can provide more efficient load transfer than rivets and bolts, preventing localised areas of high stress concentration. They can also save weight, reduce aerodynamic drag and are more resistant to corrosion, unprotected holes and welds may promote corrosion [44].

The inspection of adhesive bonds, using X-ray and ultrasound, can reveal breaks in a joint, but cannot discern whether or not a fully intact bond will fail. So, for safety reasons, components of primary aircraft structures are still predominantly mechanically fastened [45], though adhesives have been used in primary structures to some extent for over sixty years [46].

Bond integrity is therefore an important area to study. As newer formulations of adhesives are continually developed, long-term in situ ageing data can be difficult to obtain. Aircraft frequently encounter humidity, condensation and rain; moisture is known to have a detrimental effect on the durability of adhesive joints.

4.2 Standard Techniques

Gravimetric methods determine total moisture uptake in bulk samples of adhesive resin; diffusion coefficients are calculated, assuming Fickian diffusion. The worth of this approach in the prediction of service life and strength of adhesive bonds has two major limitations: the application to bulk specimens rather than bonded joints, and the inability to measure ingress profiles directly (they can only be inferred) [47, 48].

A comparison of moisture diffusion in bulk epoxy resin and adhesive joints was carried out by Zanni-Deffarges and Shanahan [49]. In this study, moisture diffusion was derived from

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1 This chapter contains the products of joint research between myself and collaborators as detailed in the main text and clearly stated under the 'Declaration of Originality' on page ii.
specially developed mechanical stress tests performed on both bulk and joint samples, and compared with standard gravimetric measurements on bulk specimens. Their results suggest that diffusion was faster in the bonded sample than the bulk alone.

4.3 Previous Studies

Direct measures of moisture diffusion profiles in adhesive bonds have been attempted using various techniques, including Fourier Transform Infra Red (FTIR) Transmission Microscopy and Time of Flight Secondary Ions Mass Spectrometry (ToF-SIMS).

FTIR-transmission-microscopy was used to study the diffusion of heavy water, D$_2$O, through epoxy resin bonding two silicon wafers [50]. Heavy water was used to distinguish between absorbed moisture and hydrogen present in the epoxy. The IR beam was directed through all three layers, along the length of the sandwiched substrate/adhesive joint. This technique was successful in obtaining diffusion profiles along the sample, however provided no spatial information on moisture diffusion specifically in the bulk and towards the interfacial regions. It is necessary for the bonded substrates to be IR transparent for this technique.

ToF-SIMS, a destructive ion beam technique, was used to study D$_2$O diffusing into an epoxy resin [51] bonding aluminium plates. The moisture diffusion analysis was performed after separating the two layers at the interfacial region of interest; this allows the massive sputter source ions to interact with the fracture surfaces along the full depth, however the joint cannot be studied directly. Additional osmotic effects were circumvented by careful treatment of the sample before immersion in D$_2$O. There is no mention of measures taken to preserve the diffusion profiles after immersion, when separating the two layers or during the sputtering analysis. Such oversight could lead to contamination between the two surfaces and migration of moisture during analysis if performed under vacuum conditions. Information regarding total diffusion from the exposed edges was obtained, all from within the interfacial region; the exact location of D$_2$O from the initial immersion within either side could not be reliably determined. The spatial resolution was 69µm at best, also inhibiting detailed inspection.

Nuclear reaction analysis seems ideally suited to measuring moisture diffusion. The ingress of heavy water (as a substitute for water) can be directly measured on bonded joints using
the D(He,p)α reaction (§2.2.2). Unlike ToF-SIMS (with bombarding ions of considerably higher masses such as Cs and Ga), it is a non-destructive technique.

Its only previous use seems to have been in 1980, when Schulte and Deiasi applied NRA to measure moisture ingress in epoxy resin [52]. The equipment used was not capable of raster scanning. A broad (~15μm x 200μm) rectangular ³He⁺ beam was directed over a large sample area and the sample moved systematically across the static beam. By summing the proton yield from each position, horizontal ingress profiles were obtained, in steps of the width of the beam spot. The protons were detected in a thin surface barrier detector, covered with a 150μm thick Mylar® stopping foil both to reduce the energy of protons sufficiently to allow them to be fully stopped within the depletion depth of the detector and to prevent backscatters and alpha particles being detected.

4.4 Present Study

This study was undertaken to measure, using NRA, moisture diffusion into epoxy resin bonding two aluminium plates. It was part of a project set up by collaborators in the School of Engineering at the University of Surrey; the results of preliminary data analysis are presented in [53]. I designed the experiment to significantly improve upon the previous NRA technique [52], and presented this in [54]. Compared with the previous technique, the beam could be focussed down to a smaller beam spot and raster scanned across the sample, providing more detailed position information of the detected products over a selected area on the surface. This is useful for distinguishing between the moisture concentration at the interfacial region and in the bulk adhesive. The charged particle detector used for detecting the reaction products was a novel, large solid angle CZT array, described in §3.2.2.2; easily capable of detecting the full energy of the high energy protons (unattenuated by stopping foil). This allowed the use of lower beam currents minimising localised beam heating, further reduced by scanning and the use of a cold stage which also preserved the moisture profiles.

4.5 Description of Samples (Prepared by Collaborators in the Department of Mechanical Engineering)

Long strips of 3M DP490 epoxy resin [55] 1.5mm thick, sandwiched between two plates of aluminium (0.25mm thick) were exposed to heavy water, D₂O, along one side for two different immersion times. Diffusion profiles were preserved by subsequently storing the
samples at low temperatures. The samples were sectioned in a plane orthogonal to the axis of ingress, at a distance along the strips so that there are no contributions of D$_2$O from the two far ends. Sectioning using a saw alone would leave extremely coarse surfaces, compromising the integrity of experimentally obtainable information. To rectify this, each exposed surface was smoothed using a diamond knife in a cryo-ultra-microtome system. The mode of exposure to a solution and the technique for cutting subsequently a sample for ion beam analysis are two of the most critical considerations for a successful measurement of diffusion in a sample; in this instance these stages were carried out by collaborators. Another procedure of vital importance is the technique for keeping the sample frozen in vacuo so liquid diffused over a specific length of time cannot migrate during analysis.

The samples (housed in the copper block sample holders) are shown below in figures 4.5-4(a) and 4.5-4(b). The resin in both samples contains bubbles throughout. The 96 hour sample is deformed on the left hand side, the side exposed to heavy water. Close inspection, see figure 4.5-2 concluded that the extent to which microtoming had been performed was insufficient for this sample so that some coarse ridged cut area remained.

![Image of sectioned samples]

Figure 4.5-1: The sectioned faces to be analysed by the beam of (a) the 43 hour sample and (b) 96 hour sample.
Figure 4.5-2: Photograph of the left hand side of the 96 hour sample to show the coarse region in detail. Lighting was positioned such to emphasise the rough area, demonstrating that it lies in a plane which falls behind the bulk of the front surface.

4.6 Experimental Arrangements and Techniques

The samples were clamped between two copper blocks on a sample plate with the sectioned plane upwards, as shown below in figure 4.6-1.

Figure 4.6-1: Full view of copper block sample holder (clamping the 96 hour immersed sample).

A cold stage, capable of maintaining any sample at sub-zero temperatures in vacuo, was previously designed and constructed: this is shown below in figure 4.6-2. The copper sample mount was held by a flexible, tensional aluminium strip attached to an aluminium back-plate. The back-plate is permanently linked by copper braid to another substantial copper block attached to a vertical metal tube which is fed by a narrow pipe from the liquid nitrogen reservoir. The sample holder end itself is suspended on a Teflon® rod, parallel to the tube.
A 1560keV, 150pA $^3$He microbeam (10μm in diameter) was raster scanned in the sectioned plane over an area of 1mm × 1mm. The CZT array (§4.2.2.2) was mounted 10mm upstream of the sample to detect protons from the D($^3$He, p)α reaction. To detect aluminium and copper backscatters, a 50mm², 300μm thick silicon surface barrier detector was also situated 78mm from the target at an angle of 160° to the beam axis. This set-up is shown below in figure 4.6.3. A block diagram of the signal processing system is shown in figure 4.6.4. The calibrated spectrum from the SiSB detector is shown in figure 4.6.5.
Figure 4.6-4: Signal processing schematic diagram.

Figure 4.6-5: Charged particle spectrum from SiSB, energy calibration points were taken from the backscatter edges of carbon, oxygen and aluminium, and also the protons from the nuclear reaction analysis. (Alpha particles are also detected from the reaction). Note the different axis used for proton yield, in order to best display backscatter edges and protons on the same spectrum, preserving the backscatter edges with a linear rather than logarithmic vertical scale.
A proton spectrum from the CZT array is shown in figure 4.6-6.

![Proton spectrum from CZT array](image)

**Figure 4.6-6: Proton spectrum from CZT array.**

In order to reduce the system dead-time, the backscattered helium-3 ions and the $\alpha$-particles from the reaction were discriminated out of the spectra from the CZT array. Protons in the full energy peak from symmetric sets of four detectors in the CZT array and helium-3 backscatters from the surface barrier detector (see figure 4.6.5) were associated with the raster scan position using the data acquisition software to create proton and backscatter maps - shown in §4.7 below.

Starting from the side of heavy water ingress - left side for the 96 hour sample, right side for the 43 hour sample - each sample was moved systematically along horizontally, scanning areas near to the aluminium plates to build up a series of water profiles along the sample.
4.7 Experimental Results and Discussion

Profiles of heavy water were obtained by the following stages. First, the proton scan maps were rotated individually so that the aluminium plate was exactly horizontal, best judged by looking at the backscatter maps (as the location of the aluminium is very clear). Any angular deviation was mostly from pivoting of the sample holder arm about the neck of the chamber, when loading the sample and from filling the liquid nitrogen reservoir (as discussed above). There is also always the possibility of a very small deviation from normal from the orientations of both the sample relative to the copper blocks and the copper blocks relative to the end of the cold stage. Following rotation, maximum vertical and horizontal limits were defined. For the horizontal profiles the experimental run with the least amount of resin incorporated in the vertical scan was chosen to define the vertical limits for the others; the proton yield was summed from the aluminium to this vertical limit at each point along the horizontal length. These yields were normalised for varying beam conditions by comparing $^3$He ions backscatters from the aluminium substrate per unit area. The profiles were matched according to overlapped position. The vertical profiles were obtained by following the same procedures but summing across the same fixed horizontal width for each scan map along a vertical length from the interfacial region into the bulk of the resin; the centres of the fixed horizontal widths were defined with reference to the exposed edge.

4.7.1 96 Hour Data

Scan maps are shown in figures 4.7.1.4(a) and 4.7.1.4(b), positioned to demonstrate the relative locations along the sample. The 96 hour sample was analysed along the bottom from left (side exposed to heavy water) to the right in steps overlapping each scan by half the scan width. This was to maximise the detail of information obtainable. Then the sample, suspended at the end of the cold stage, was moved down so that the scan area was at the top interfacial region, and scans were carried out from right to left. I have outlined the edges of the scan maps with borders, to clearly show overlaps.

Care was taken to minimise disturbance to the cold stage (described in §4.6), however some disturbance was inevitable. Liquid nitrogen was topped up in the reservoir (shown in figure 4.6.2) between scans; this led to small movements in the position of the sample. This is why the location of the top right scan is further right than the bottom right scan.
(The amount of overlap across the top interfacial region was reduced to compensate for the distance).

Figure 4.7.1-1: Scan maps for (a) protons detected by the CZT array from reaction with heavy water; and (b) backscattered $^3$He ions detected by SiSB, from a region in the backscatter spectrum from the carbon edge to the copper edge.

As shown in figure 4.5.2, the left hand side of the 96 hour sample was rough and did not reach the front flat surface, as a result of too little microtoming (not machining far back enough for a completely flat area over the full cross sectioned area). Therefore the true edge of ingress, starts at the far left of the first scan maps, but the flat surface begins 0.6mm along the bottom half, and up to 1.5mm along the top. Vibrations, from liquid nitrogen boiling in the top of the cold stage, were found to have significantly distorted the 2D maps of detected products in the third scanned area along the bottom interfacial edge (in the direction of $D_2O$ ingress), shown below in figure 4.7.1-2 where (c) is clearly distorted compared with (b); this is most noticeable at the three dense patches (at the centre of (b) and the left side of (c)).
Figure 4.7.1-2: Three proton maps of overlapping scanned areas from the bottom row of the 96 hour sample (a), (b), (c) from the left edge moving right.

Taking these factors into consideration means that unambiguous diffusion profiles could only be deduced from the first two scans along the bottom interfacial region, excluding more than half of the first.

The CZT array detected high proton yields from heavy water present in bubble craters along the bottom of the sample, however these are not visible in the backscatter maps for the same scan areas, see figure 4.7.1-1. The backscatter energy range associated with the backscatter map was from the carbon edge to the end of the backscatter spectrum. Alpha particles from the nuclear reaction are included but their detected yield is very low compared with backscatters from aluminium (the cross-section for an interaction of the beam resulting in backscatters is far higher than for nuclear reaction, see §2.4.5).

A low yield of backscatter counts are present across the entire resin surface due to oxygen in the resin and the heavy water. Oxygen from heavy water is not observed in the backscatter map from the ice underneath the aluminium (identified in the proton maps in figure 4.7.1-2) due to geometrical shadowing of the SiSB detector by the aluminium substrate.
The craters do not show enhanced yields in the backscatter maps from greater surface area as the heavy water has filled them making a new flat surface of heavy water ice, which contains oxygen as does the resin.

Figure 4.7.1-3: Horizontal profile.

As mentioned above, useful profile information was unobtainable from the first part of the sample. The horizontal profile of the yield of protons from the rest of the sample (normalised to Aluminium Backscatters/Unit Area), shown above in figure 4.7.1-3, has a flat top before decreasing, indicative of Case II diffusion. It can therefore be assumed that this can be extrapolated back to the beginning of the sample to compensate for the excluded section. There are fluctuations in the profile due to the statistical variation in yield, however a two peaks feature from 1.1mm to 1.2mm, corresponding with the three dense patches, clearly shown in figure 4.7.1-2(b) the larger peak occurring where the two dense patches are vertically aligned.
Vertical moisture profiles (again normalised to Aluminium Backscatters/Unit Area) are shown in figure 4.7.1-4, mapping the heavy water from the interfacial region into the bulk resin. They were obtained for various distances from 0.88mm to 1.61mm (as mid-points along the summed widths), from the edge of ingress. The three densely populated regions of the second scan are prominent in the vertical profile summed at the distance of 1.19mm. The dense regions correspond to bubbles in the resin filled with water as the front progressed through the sample; these were also observed in the horizontal profile. More profiles were obtained by overlapping the horizontal widths of the sums, shown below in figure 4.7.1-5 to better demonstrate the horizontal position dependence of variation most likely due to bubbles. Excluding such localised distortions, the further along the sample the profile was obtained, the lower the moisture content of the bulk. There is more moisture towards the interfacial region than towards the bulk.

Figure 4.7.1-4: Vertical profiles from in the resin to the interfacial region.
Learning from the 96 hour immersed experimental runs, steps were taken to minimise the information lost: the cold stage was better secured by modifying a foam insulation tube and using that to support the weight of the nitrogen receptacle. For the 43 hour immersed sample the scanned areas were not selected to overlap but to join exactly to the edge of the adjoining scan area (by using the fine adjust micrometer control) to significantly reduce any uncertainty in matching the profiles onto one another.

For the 43 hour sample, the ingress of D$_2$O was from the right hand side. The long sides (the depth thickness of the sample as viewed by the beam) are not perfectly parallel but diverge at the site of cut, so in this case part of the length of the side was incorporated into the scan. The proton maps and corresponding backscatter maps, shown below in figures 4.7.2-1(a) and 4.7.2-1(b) respectively were compared with sample photographs to determine the end of the surface, hence it was possible to exclude products detected from along the side when plotting profiles.
Figure 4.7.2-1: 43 hour sample Scan maps for (a) protons detected by the CZT array from reaction with heavy water; and (b) backscattered helium-3 ions detected by SiSB, from a region in the backscatter spectrum from the carbon edge to the copper edge.

The backscatter maps in 4.7.2-1(b) show bubble craters predominantly along the top half. The bubbles on the right hand side are faint as they are filled by heavy water, seen in 4.7.2 1(a). Away from the edge of ingress the crater regions appear denser from higher yields, reflecting the larger surface area viewed by the beam. The following horizontal profiles were reversed so that the increasing distance from the exposed edge is from left to right, for consistency with the profile from the other sample.

Figure 4.7.2-2: Horizontal profiles for both interfacial regions.
The horizontal profiles for the 43 hour sample, shown above in figure 4.7.2-2, contain some breaks. Some of the scan maps needed to be rotated (through very small angles) for the sample to be perfectly square on, due to the sample holder arm deviating from the vertical. This is due to the position of the flexible neck leading to the chamber which moves as the sample is moved into focus. Also the liquid nitrogen feed is lowered into the sample stage then filled with liquid nitrogen after the chamber has been evacuated and how it settles down affects the position of the sample holder arm.

The profile obtained for the bottom interfacial region of the 43 hour sample is flat from the edge of ingress which is in agreement with the 96 hour bottom profile. The profile obtained for the top interfacial region matches the bottom profile, however the flat section is distorted from water in clusters of small bubbles near the edge of ingress, visible in the photographs. For this reason the bottom profile was used in the main data analysis and compared with the 96 hour bottom profile (to follow in §4.8).

![Graph showing vertical profiles](image)

Figure 4.7.2-3: Vertical profiles from in the resin to the interfacial region.
The vertical moisture profiles at three different distances away from the edge exposed to the heavy water, towards the bottom interfacial region, show flat profiles except for that closest to the edge see figure 4.7.2.3. This profile has a raised yield in regions corresponding with clusters of small bubbles. There is more moisture towards the exposed edge, which is intuitive and correlates with the horizontal profiles.

4.8 Main Data Analysis

The horizontal profiles demonstrate Case II diffusion; they comprise a flat component and an exponential decay curve.

![Graph of Case II diffusion profile for 43 hours.](image)

**Figure 4.8-1: The Case II diffusion profile for 43 hours.**

The 43 hour horizontal profile above, figure 4.8-1, was procured from the full width of 3 scanned areas, providing many data points. The profile data were thus able to be averaged in order to achieve a smoother curve for a more reliable fit.
The velocity of the advancing flat front, a distance of $(0.62\pm0.01)$ mm travelled in 43 hours $(154,800s)$, $V=(4.01\pm0.06)\times10^{-6}$ mm.s$^{-1}$. By fitting a curve through the exponential precursor (to obtain $V/D$) using equation 2.5.5,

$$
\phi = \phi_0 \times e^{-\frac{Vx}{D}}
$$

Equation 2.5-5

the diffusion coefficient, $D$, was found to be $(1.3\pm0.1)\times10^{-6}$ mm$^2$.s$^{-1}$ and using a straight line fit plotting the natural logarithm of the yield (removing a baseline) a value of $(1.1\pm0.1)\times10^{-6}$ mm$^2$.s$^{-1}$.

Trying to accurately fit the 96 hour data is a lot more difficult, see figure 4.8.2. Extrapolating the exponential decay curve backwards to reach the average height of the flat part, the curve intersects with the flat average at ~1.36 mm. This is taken as the end-point of the flat-top, giving a velocity, $V=(4.1\pm0.3)\times10^{-6}$ mm.s$^{-1}$ – in excellent agreement with the 43 hour result.

![Graph showing the Case II diffusion profile for 96 hours.](image)

Figure 4.8-2: The Case II diffusion profile for 96 hours.
The high peak and low dip at ~1.17mm and ~1.26mm do not appear to be part of the exponential, but part of the flat section of the profile - these high and low deviations are due to bubble crater contours in the surface.

Another difficulty is that the curve does not apparently fall completely, that is the scans did not go far enough into the sample to measure the full exponential precursor. For this soaking length of time, it would be useful for the sample to be wider; this would allow analysis of a longer distance from the exposed edge.

The diffusion coefficient should be the same for the 96 hour immersed sample as the 43 hour sample. As for the 43 hour data, fitting using the exponential curve gives a diffusion coefficient of \((1.1\pm0.8)\times10^{-6}\text{mm}^2\text{s}^{-1}\) and fitting a straight line through the natural logarithm provides a diffusion coefficient of \((0.8\pm0.6)\times10^{-6}\text{mm}^2\text{s}^{-1}\). These values have much larger associated errors, for reasons given above, but are compatible with those obtained from the 43 hour data.
4.9 Conclusions

An array of CZT detectors has been used to measure a water (D_2O) diffusion profile in a resin sandwiched between two plates of aluminium, using a scanning in vacuo ^3He microbeam. This is the first time that a CZT array has been used in an NRA measurement. The technique is ideal for use with low ^3He beam currents (~150pA). To test the technique, pure D_2O was used as a first approximation to water diffusing into epoxy resin, as in the study by Schulte and Deiasi [52].

The vertical profiles were not fitted to obtain diffusion coefficients; the profiles for the 43 hour sample were flat, and for the 96 hour sample, the limited results available show an increase towards the resin/aluminium bond, but profiles were distorted by large bubble craters.

The horizontal profiles show that heavy water travelled into the epoxy resin by Case II diffusion. This is in contrast to the reported findings of Schulte and Deiasi [52] as mentioned above. However, reviewing their paper I note that the first of the two horizontal profiles they reported was fitted to a Fickian diffusion curve, whilst the data points follow a Case II shape.

The results of the measurements have been published [56], with preliminary assumptions about the end-point of the flat top of the Case II diffusion profile, and the fitting of the exponential precursor.
Chapter Five: The Development of Techniques to Measure the Mass and Size of Gold Flecks in a Foam Matrix

5.1 Introduction

At the Omega high power laser facility in Rochester, NY research has been initiated by AWE, Lawrence Livermore and Los Alamos National Laboratory on X-ray transmission through 'clumpy plasmas' encountered in models of the early universe. The experimental work requires a small sample of foam seeded with gold flecks which, in vacuo, is vaporised by the laser via a hohlraum, forming a 'clumpy plasma'. The penetration of X-rays through this plasma is recorded using X-ray flash photography [57].

The aim of our investigation at Surrey was to characterise foam samples, using MeV scanning ion micro-beam analysis, in order to measure the quantity of gold dispersed therein. They are cylindrical, 1mm in diameter and 1mm long, encased within a polyimide (Kapton®) sleeve, see figure 5.1-1. The foam is a triacrylate polymer (C₉₅H₂₀O₂) of density 57.8mg.cm⁻³. The size of flecks and the overall mass of gold contained within each foam sample was to be determined; preliminary information provided was a mass estimate of up to a possible maximum of 15% of the weight of the foam and an average fleck size of order several microns.

Figure 5.1-1: Foam cylinder encased in polyimide sleeve. (Fine wires were attached for sample mounting purposes.)
Samples were fabricated by Wigen Nazarov of the University of St. Andrews under contract to AWE. Several have been provided throughout this investigation, as the project developed. For the main part of the investigation, the gold was distributed throughout each sample in flecks, estimated to be approximately 5μm in size and unknown shape. Some comparison samples had submicron sized flecks.

To determine the size, location and mass of the gold particles, ion beam techniques have been specially developed and applied; the investigation has developed by learning from, and modifying methods as the project progressed. Therefore background information and considerations relevant to the entire study are detailed together, followed by the individual experimental methods, results and analyses organised in a chronological, integrated manner.

5.2 Previous Studies

In the only previous ion beam analysis study of heavy particles distributed in foam, found in published literature, Antolak et al [58] describe the characterisation of low density cylindrical targets containing a distribution of micron-scale molybdenum particles. The cylinders were of diameters ranging from 4-8mm, of length approximately a quarter of the diameter, and two different types of low density polymer foam.

PIXE analysis was used to quantify the weight of molybdenum loading distribution, revealing a lower mass content than anticipated. RBS provided confirmation of this. The step on the RBS spectra corresponding to the molybdenum was not square but curved down to the highest energy. The study attributed this to non-uniform loading of the particles, specifically less molybdenum towards the front surface.
5.3 Experimental Design and Ratiocination

5.3.1 Ion Beam Techniques: PIXE

PIXE can be used to measure physical characteristics of the gold flecks. Characteristic X-rays of gold are of relatively high energies compared with elements of lower mass, so in routine PIXE analysis of gold using Si(Li) X-ray detectors L X-rays (~9-12keV) are detected. The Si(Li) detector efficiency starts to fall above 20keV and is negligible by 50keV [33, 59].

Depending on fleck size, a proportion of gold L characteristic X-rays may suffer attenuation within the flecks from which they originate. Hence L X-rays alone cannot determine both the mass and the average size of the gold flecks. Gold K X-rays, being of much higher energy (between ~65keV and ~85keV), are relatively unaffected by self-attenuation. This means that measuring the number of K X-rays produced would provide a truer representation of the amount of gold contained within the foam. The number of L X-rays produced could then be used to determine the average attenuation of the gold flecks – and hence their average size.

However the cross-sections for K X-ray production are, for beam energies attainable with the Surrey accelerator, far lower than those for L X-rays. Special consideration was therefore given to the efficiency of detector to be used, at X-ray energies of up to ~90keV. For this reason, Amptek® CdTe detectors were purchased; these are almost 100% efficient in the 10-60 keV X-ray range and 72% efficient at 90keV (see §3.2.2.1). Hence, they are an ideal choice for detection of both gold characteristic K and L X-rays.

The K X-ray production cross section, whilst extremely low at the beam energies employed throughout these experimental runs, increases with incident beam energy. Hence the statistical error on mass determination will be lowest at the highest attainable beam energy.
5.3.2 Ion Beam Techniques: Backscattering Spectrometry

The foam is of a low density, with high density flecks dispersed throughout. Useful information could clearly be gained from backscattering spectrometry, considering the energy losses of both the incident protons in the beam and protons backscattered from, respectively, the carbon and oxygen constituent elements of the foam and the gold flecks at various depths. The maximum backscatter depth at which gold can be located is limited by the position of the oxygen backscatter energy edge, see §2.1.4.3. This limiting depth will be referred to as $D_L$.

Using equation 2.1.14, the maximum energy of a proton backscattered from gold is approximately equal to the incident energy of the proton, and the energy difference between the gold and oxygen edge is proportional to the incident energy. The range of protons in foam is also proportional to the incident energy. Thus, the higher the energy of incident protons, the greater is the depth (the limiting depth $D_L$) at which backscatters from gold flecks emerge from the foam with energies greater than the oxygen backscatter edge.

Considering gold flecks of several microns diameter, the energy of protons backscattered from the gold will be at a maximum when incident protons backscatter from the front of a gold fleck at the front surface of the foam cylinder. Conversely, the minimum proton energy will correspond to backscatters from the back of a gold fleck (after penetration through the full depth) at the back surface of the sample. Many of the lower energy counts in the gold backscatter spectrum occur at energies below the oxygen edge.

Backscatter measurements can also be very useful in determining the relative amount of beam passing through each sample, particularly if a scanning microbeam is available; this can scan over both the sample and a part of the sample holder (in our case, carbon blocks). The number of backscatters from a specific block area are proportional to the beam fluence.

If a standard is used (in this case a gold foil) the ratios of PIXE K and L X-ray yields from each sample can be compared to the respective PIXE K and L X-ray yields from the standard, using backscatters from the carbon block to inter-calibrate the yields.
5.4 Preliminary Experiments

5.4.1 Aims

Preliminary experiments were carried out in order to confirm the suitability of ion beam analysis for this study.

5.4.2 Mounting the Sample for Ion Beam Analysis

As detailed in §5.1 the sample is a foam cylinder encased in a polyimide sleeve. Gold flecks, of unknown size, are distributed throughout.

Copper K X-rays have similar energies to gold L X-rays and larger production cross sections at proton energies achievable [60, 61] making it sensible to minimise the amount of copper present within the scan area. Carbon blocks were designed and made as a replacement for the standard copper blocks designed for use in other experiments (including the experimental project described in Chapter 4). These would still prevent charge build up and could be used to provide an accurate relative measure of the integrated beam charge - by dividing the number of protons backscattered by carbon per unit area for each experimental run.

The smooth rounded sleeve was unsuitable for clamping directly between the two blocks (the usual sample mounting procedure) because of its delicate construction. Instead, a fine wire was attached to either side of each cylinder sleeve, parallel to the length, glued halfway down the thickness and length, extending beyond the back of the cylinder (see figure 5.1.1). This method was designed at Surrey and realised in-house at AWE. They found that the most suitable wires were in fact copper. However, as they are at known positions relative to the sample and a scanning beam was used, the K X-rays they produced did not interfere with the L X-rays from the gold. An additional benefit of this design was that it would ensure the sample face was normal to the incident beam. It was preferable that the foam be viewed directly by the beam, rather than through the sleeve in order to:

- maximise the energy of protons leading to interaction, hence maximise the information obtainable,
- ensure symmetry about the beam axis, to simplify analysis.
In practice, a wire became detached from the polyimide sleeve, during the sample mounting process. This left one remaining wire to use, but this was sufficient. (In the latter stages of the project, the arrangement was adjusted such that one wide wire was glued underneath, providing a larger surface area, improving the strength of the join).

As a comparator, an accurately measured 2µm thick gold foil was used, secured by clamping beneath the heads of screws securing the carbon blocks to a base plate, shown below in figure 3.4.2.1.

Figure 5.4.2.1: Sample in holder (wire clamped in carbon blocks); the gold foil standard is on the left.

### 5.4.3 Experimental Arrangements

The initial proton beam energy (achieved with a 1250kV terminal voltage) was 2.585MeV. This was selected as the highest energy usable with the existing beamline design without creating a large neutron background in the laboratory. The beam of protons entered the foam sample with 2.585MeV and would exit at the back with ~1.6MeV, assuming no gold collisions. This means that gold K and L X-rays could be generated from gold flecks throughout the entire sample length. The energy of protons backscattered from the gold is at a maximum when incident protons backscatter from the front of a gold fleck at the front surface of the foam cylinder, and the minimum proton energy corresponds to backscatters from the back of a gold fleck at the back surface of the sample. The uniquely gold energy region of the backscatter spectrum has its lower limit at the oxygen edge, and at a beam energy of 2.585MeV this means that only gold flecks to a limiting depth $D_L$ of order ~0.3mm in the foam cylinder will contribute to this region.
Figures 5.4.3-4(a) and 5.4.3-4(b) show the experimental set up from two different views. The detection region \(25\text{mm}^2 \times 1\text{mm}\) of the CdTe X-ray detector, an AmpTek® XR-400T, was situated 23mm from the target at a backward angle of 135°; the charged particle detector was situated 78mm from the target at a backscatter angle of 165° - an Ortec® SiSB detector of small active detection area \(100\text{mm}^2 \times 400\mu\text{m}\) was used to minimise broadening effects on backscatter measurements.

The signals from these detectors were processed as shown schematically in figure 5.4.3-4(c). They were transmitted to pre-amplifiers (pre-amps) (an integral part of the CdTe detector, an individual Ortec® preamp in the case of the SiSB detector). After these the signals passed through amplifiers to individual Analogue-to-Digital Converters which were read by the OM_DAQ hardware/software installed in the controlling PC. This, when associated with scanning signals received from the Oxford Microbeam scanning system, correlates data from up to eight X-ray or particle detectors to generate on-line energy spectra and on-line 2D maps.

![Figure 5.4.3-4: Target and detector arrangement (a) side view; (b) over-head view; (c) signal processing diagram.](image-url)
A photograph of the set-up from the outside the chamber is shown in figure 5.4.3-2. The relative positions of the beam line and CdTe X-ray detector are marked. As in the case of the resin analysis experiment (Chapter 4), the sample is suspended in the beam on a vertical rod.

Figure 5.4.3-2: Photograph showing position of the X-ray detector relative to the beam and target (sample size not to scale).

As described above, a CdTe X-ray detector and a SiSB detector were used. The 2.585MeV protons were raster scanned over an area including the sample and surrounding carbon blocks with a beam current of 600pA for 30 minutes. The gold foil was exposed to 300pA of protons for 15 minutes. The scan area size was 2000µm x 2000µm, with beam spot size of 3µm. The software correlates the 2D position of the raster scan with a detected event (see §3.2.3). Data was recorded in 'event-by-event' (List) mode so that the experimental results could be rerun in order to investigate and identify particular events of interest.
5.4.4 Energy Calibration Methods

Each detector/amplifier/ADC data acquisition system was calibrated to convert multichannel analyser channels to energy.

5.4.4.1 PIXE Spectra Calibration

The energy axis of the X-ray spectra was calibrated primarily using a Variable Energy X-ray source (from Amersham International Plc). Six different metal foils are bombarded by alpha particles from $^{241}$Am. The alphas eject electrons from the foil atoms causing the emission of characteristic X-rays. The six foils and their X-ray energies are listed below in Table 5.4-1:

<table>
<thead>
<tr>
<th>Foil</th>
<th>$K_{\alpha}$ X-ray Energy, keV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>8.04</td>
</tr>
<tr>
<td>Rb</td>
<td>13.37</td>
</tr>
<tr>
<td>Mo</td>
<td>17.44</td>
</tr>
<tr>
<td>Ag</td>
<td>22.10</td>
</tr>
<tr>
<td>Ba</td>
<td>32.06</td>
</tr>
<tr>
<td>Tb</td>
<td>44.23</td>
</tr>
</tbody>
</table>

Table 5.4-1: Calibration energies for X-ray spectra.

A higher energy calibration point was obtained by inducing the reaction $^{19}$F(p,p$\gamma$)$^{19}$F: gamma photons are emitted with 110keV energy. A 2.585MeV proton beam was used with thick PTFE tape containing 75% fluorine as the target.

A calibration graph is shown below in figure 5.4.1. The corresponding spectrum is shown in figure 5.4.2: the characteristic $K_\alpha$ X-ray peaks and $^{19}$F(p,p$\gamma$)$^{19}$F gamma peak are labelled. (A peak is also present at 59.5keV from the $^{241}$Am).
Figure 5.4.4-1: Calibration graph of energy against channel.

Figure 5.4.4-2: Calibration peaks - characteristic $K_{\alpha}$ X-rays produced from the six targets within the variable X-ray source, and a gamma from $^{19}F(p,p'\gamma)^{19}F$. 
5.4.4.2 Backscatter Spectrum Calibration

The backscatter spectrum was calibrated using the high energy edges of the sample (C, O, Au) and gold foil standard (calculated from equations 2.1-11 and 2.1-12) in each case; these beam energy dependent values are listed below in table 5.4-2.

<table>
<thead>
<tr>
<th>Backscatter Edge</th>
<th>Backscatter Energy of 2585keV Protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1857 keV</td>
</tr>
<tr>
<td>O</td>
<td>2018 keV</td>
</tr>
<tr>
<td>Au</td>
<td>2534 keV</td>
</tr>
</tbody>
</table>

Table 5.4-2: Calibration energies for backscatter spectra.

A calibration graph (performed after the experimental run) at 2.585MeV beam energy is shown below in figure 5.4.4-3 and corresponding spectrum is shown in figure 5.4.4-4.
Energy = Channel x 2.0678 - 52.308

Figure 5.4.4-3: Calibration graph for backscatter energies.

Figure 5.4.4-4: Backscatter spectra of the sample and foil standard, overlaid – as stated in the text, backscatter calibrations were performed using taking data, using C, O and Au edges.
5.4.5 Preliminary Results and Discussion

The results shown are divided into two sections: those for the gold standard and for the first foam cylinder sample. 2D maps are shown for full scan areas corresponding with selected features from the spectra, and conversely, maps are shown for small regions of interest to study corresponding spectra.

5.4.5.1 Gold Standard

5.4.5.1.1 PIXE

![X-ray spectrum](image)

Figure 5.4.5-1: X-ray spectrum.

The X-ray spectrum produced from the 15 minute long 300pA experimental run on the gold foil standard is shown in figure 5.4.5-1. Over the full energy range many counts are observed towards the lower energy end of the spectrum.
The low energy end of the PIXE spectrum, shown in figure 5.4.5.2, contains well-resolved gold L X-ray peaks, from 8.5\,keV-13.4\,keV: \( L_\alpha, L_\alpha', L_\beta, L_\gamma \).

There is a continuum at the low energy end of the spectrum, most likely due to secondary electron bremsstrahlung: the continuum extends up to 5.6\,keV, the maximum energy imparted to a stationary electron during a collision with an incident proton of 2585\,keV. The peak at 3.3\,keV is possibly due to contamination or a characteristic X-ray from the cadmium in the detector being detected - the \( L_\beta \) X-ray of cadmium has an energy of 3.3\,keV.

Figure 5.4.5-2: Low energy end of X-ray spectrum.

Figure 5.4.5-3: Map of gold L X-rays.

Figure 5.4.5-4: Map of bremsstrahlung photons.
Associating the counts in two regions of figure 5.4.5.2 with the 2D scan position to create 2D maps, the gold L X-ray map clearly shows the gold foil, and the region devoid of counts is that of the exposed carbon block, see figure 5.4.5.3. Figure 5.4.5.4 shows that the bremsstrahlung originated from the entire scan area. More of these photons were detected from the (higher Z) gold than the exposed carbon block.

Within the area representing the foil in both scans, there is an unexpected decrease in the X-ray yield along the right edge. Further investigation found that this anomaly was not present in the backscatter gold map (shown later), eliminating imperfections in the foil as a cause; the PIXE maps of the sample (shown later) also did not show this feature. The drop in yield was confined to the PIXE detector set-up only when scanning over that area on the foil. Care had been taken when selecting the part of foil to scan, however it was concluded that the location was too close to the screw head and washer securing the foil which were preventing some of the X-rays from reaching the detector.

In the fifteen minutes of the experimental run, at this energy, very few gold K X-rays were generated, as would be expected. The high energy end of the X-ray spectrum is shown above in figure 5.4.5.5, and figure 5.4.5.6 below is the corresponding 2D map of gold K X-rays.

![Figure 5.4.5-5: High energy end of X-ray spectrum.](image-url)
5.4.5.1.2 Backscattering Spectrometry

The backscatter spectrum for the gold foil standard, figure 5.4.5.7 has a prominent gold region, from 2000keV-2570keV, and a carbon region from 140keV-1900keV. The gold region has a flat top and has near-vertical sides, consistent with a material of uniform thickness and density, with no significant non-Rutherford cross sections at that energy. A 2D map of backscatters from gold is shown below as figure 5.4.5.8:
The carbon region in the backscatter spectrum, figure 5.4.5.7, slopes downwards from the high energy end due to non-Rutherford cross-sections. However, there is a step down, towards the higher end, occurring at 1570keV. To investigate this feature, maps were generated for the carbon at energies above this discontinuity (figure 5.4.5.9) and below it (figure 5.4.5.10).

Figure 5.4.5.9: Proton backscatter map generated from carbon in the high energy step.

Figure 5.4.5.10: Proton backscatter map generated from the main continuum of carbon.

Figure 5.4.5.9 shows that the detected protons with high energy, backscattered from the carbon, came from the region where no gold foil was present. Figure 5.4.5.10 shows that protons backscattered from the carbon detected with low energy came from all regions of the scan, including from behind the gold foil. After backscattering at depth or through gold foil the protons would have lower energy than if backscattered from the exposed near surface (without gold foil).
5.4.5.2.1 PIXE

Figure 5.4.5-11: Low energy end of the X-ray spectrum, from the full scan area.

The X-ray spectrum, the low energy end of which is shown in figure 5.4.5-11 contains gold L X-ray peaks, however the main feature is the suspected secondary electron bremsstrahlung. The bremsstrahlung identified for the experimental run on the gold foil standard was confirmed by once again generating a 2D map from this energy window, figure 5.4.5-12. (The high energy end showed no features when viewed over a full energy scale as in the X-ray spectrum for the foil standard, figure 5.4.5-1; a separate spectrum at the high energy region will be shown after the low energy region discussion).

Figure 5.4.5-12: Secondary electron bremsstrahlung.
As before, in the case of the gold foil standard, these low energy photons were produced from the entirety of the scan area. There is a region of high counts towards the bottom right of the scan area which may be responsible for the extra peak(s) in the original spectrum, figure 5.4.5-11.

![Graph showing X-ray spectrum](image)

**Figure 5.4.5-13**: Low energy end of the X-ray spectrum, from the full scan area, including gold L and lower energy X-rays.

Figure 5.4.5-13, the PIXE spectrum contains the gold L X-rays as anticipated, but also copper K X-rays, to their immediate left, which have a high energy tail beneath the gold L\(_x\) peak. These copper peaks are due to the copper wire being included in the area scanned. There is also a peak to the left of the copper, possibly a copper escape peak, or other contamination such as characteristic X-rays from residue left by iron present in emery cloth used to ‘clean’ the carbon block areas immediately above the sample (this region can be seen in figure 5.4.2-I). A large bremsstrahlung continuum is present with a more prominent extra peak than that found in the spectrum of the gold foil standard, figure 5.4.5-2.
Maps below are those corresponding to gold L X-rays - figure 5.4.5.14, copper K X-rays - figure 5.4.5.15 and the lower energy peak - figure 5.4.5.16.

Figure 5.4.5-14: Gold L X-rays.  Figure 5.4.5-15: Copper K X-rays.

As stated above in this section, a small overlap with the copper Kβ peak occurred when selecting the energy range for the gold L X-ray elemental scan map. As a result, the gold L X-ray map, figure 5.4.5.14, highlights the copper wire (towards the bottom of the map), as well as gold flecks. It shows a higher concentration of gold L X-rays emanating from the bottom left of the sample (as viewed). The position of the copper wire is confirmed by the copper K X-ray map, figure 5.4.5.15.

Figure 5.4.5-16: Low energy peak: Iron? Emery residue?

In the X-ray spectrum, figure 5.4.5.17, a peak is present to the left of the copper Kα; this was initially suspected to be either a copper escape peak or some kind of contamination. The map generated for this peak, figure 5.4.5.16, contains a high concentration of counts from the location of the end of the wire, but counts also from the gap between the carbon blocks. It is not sample-related so this has not been investigated any further.
The high energy region of the PIXE spectrum, figure 5.4.5-17, contains very few counts. The counts do not originate uniquely within the area of the sample within the scan. There may be gold K X-rays present, however there are not enough counts for any reliable measure. Gold L X-rays are present (shown in figure 5.4.5-17), however, the production cross section for K X-rays is much lower.
5.4.5.2.2 Backscattering Spectrometry

In the backscatter spectrum, shown in figure 5.4.5.18, the carbon region is not flat, but is sloping downwards towards lower energies. This is due to a sloping non-Rutherford cross-section. There is a raised step at around 900 keV (this is investigated below). The oxygen step is enhanced at the high energy edge from surface oxygen contamination on the carbon blocks. There is a small amount of nitrogen present in the polyimide sleeve, and this might be contributing to the slight increase in yield of the oxygen step immediately next to the carbon edge – there is a much greater amount of oxygen present within the scan area, and masks are used to exclude the sleeve for calculations. The gold step falls in magnitude towards the highest energy, as in the study by Antolak et al [58] of molybdenum in foam – possibly due to an uneven gold loading.

Maps were generated corresponding to the energy regions in the proton backscatter spectrum corresponding to backscatters from carbon (predominantly), oxygen, and gold (figures 5.4.5.19, 5.4.5.20 and 5.4.5.21 respectively).
Figure 5.4.5-19: Protons backscattered from carbon.

Figure 5.4.5-20: Protons backscattered from oxygen.

The carbon backscatter map, figure 5.4.5-19, shows dark regions which appear to be in shadow. This is probably due to protons losing energy in the sample cylinder en route to the detector. This can be confirmed by masking these areas in the map and observing the spectra generated. The bright regions can also be investigated.

Figure 5.4.5-21: Protons backscattered from gold.

The oxygen in the foam, figure 5.4.5-20, appears mostly uniform, whereas the gold observed is predominantly to the lower left hand side of the sample, figure 5.4.5-21. (The map of gold L X-rays, figure 5.4.5-21 also shows a greater distribution of gold to the lower left of the sample.)
5.4.5.2.3 Further Investigation of Spectrum Features in the Vicinity of the Sample

The following results are from maps regenerated offline after selecting a specific region within the scan area – these ‘masked’ regions are displayed for each relevant detection event, followed by spectra associated with the specific region.

5.4.5.2.3.1 Foam

Within the foam area, the new masked area shown in figure 5.4.5-22, gold L X-rays are generated from the flecks. The copper K X-rays from the wire are absent and a large amount of secondary electron bremsstrahlung is present, shown in the corresponding spectrum below in figure 5.4.5-23.

![Figure 5.4.5-22: Gold L X-rays produced from mask around foam.](image)

![Figure 5.4.5-23: X-ray spectrum produced from within the masked area.](image)
The spectrum below, figure 5.4.5.24, contains protons backscattered from gold, oxygen and carbon. The yield of carbon is much lower than that from the entire scan area because the masked area excluded the sleeve and surrounding carbon block. The discontinuity in the slope at ~950 keV is no longer present. The oxygen and gold steps are as before. The unevenness in the oxygen step is still present.

![Backscatter spectrum generated from within masked region.](image)

Figure 5.4.5.24: Backscatter spectrum generated from within masked region.

5.4.5.2.3.2 Sleeve
Along the edge of the sleeve, a bright region was present in the carbon backscatter map see figure 5.4.5.19; immediately below this bright region a dark shadow with very few counts was present. Masks were drawn to cover these two regions separately, see figure 5.4.5.25 and figure 5.4.5.26; corresponding spectra were generated shown below in figure 5.4.5.27 and figure 5.4.5.28.
Figure 5.4.5-25: Map of protons backscattered from carbon in the 'bright' region of high counts.

Figure 5.4.5-26: Map of masked region of dark area of the carbon backscatters.

Figure 5.4.5-27: Backscatter spectrum produced from masked area of the bright region of carbon backscatters.
Both backscatter spectra have a carbon edge at the same energy as before, and nitrogen is present. The carbon yield falls and drops off at around 1000 keV. In the spectrum from the 'bright' region map (figure 5.4.5-25, the end edge of the sleeve) figure 5.4.5-27, the yield rises to a maximum at approximately 900 keV, then falls off with decreasing energy. The spectrum from the 'dark region' map, (figure 5.4.5-26, below the sleeve), figure 5.4.5-28, does not contain this lower energy component - the yield reduces to background levels at around 1000 keV.

SRIM was used to calculate the energy loss of protons (through the polyimide sleeve and foam) backscattered from different depths within the sleeve and through the foam adjacent to the sleeve, considering the angle and path to the detector. This showed that protons incident on the end of the sleeve have a range of less than a tenth of a millimetre, (the length of the sleeve is 1 mm). Backscattering from carbon at the very front of the edge of the sleeve will produce protons of energy at the carbon edge. As the protons are scattered from further into the sleeve length (until fully stopped) they will lose energy before
backscatter and also after backscatter with a diagonal path through part of the sleeve (depending where in the thickness of the sleeve the proton was backscattered). There is a strong C(p,p)C elastic scatter resonance peak at ~1740keV (incident energy) [62-65]. The peak resonance on the backscatter spectrum occurs mainly at ~950keV. Protons can reach the backscatter detector with this energy by travelling a horizontal length of 89μm to reduce 2585keV to 1740keV, backscattering with this energy leaves the protons with backscattered energy ~1250keV, then losing energy travelling along a diagonal path back through the sleeve 11μm at a vertical height 2.85μm into the thickness of the sleeve.

Protons backscattering at this horizontal distance but smaller vertical depths into the sleeve will be detected with higher energy, and those backscattering at greater vertical depths into the sleeve will be detected with lower energy. Protons scattering at smaller horizontal distances into the length of the sleeve can reach the 1740keV resonance energy on the diagonal path back through the sleeve after scatter. Such contributions are the reason for the broad tail of the detected peak (figure 5.4.5.27) from the narrow resonance.

The region immediately below the top edge of the sleeve is in shadow, as viewed by the charged-particle detector. Protons backscattered at the front of the foam will travel to the detector but those backscattered at depth will be attenuated by the polyimide sleeve, hence are missing from the spectrum (see figure 5.4.5.28).

5.4.6 Conclusions from Preliminary Data

The preliminary experiments were successful: the delicate sample seemed unaffected by the beam and the vacuum. The data obtained demonstrates that a lot of information can be gained using backscatter and PIXE analysis together with a scanning microbeam. Of particular importance for the understanding of spectra is the ability of the scan-controlling, data taking software list mode data, the off-line selection of both:

- parts of the scan associated with particular features of the BS or PIXE spectra and
- regions of BS and PIXE spectra associated with a selected area of the full scan.

The elemental maps generated by gold L-shell PIXE and BS appear to show that the gold loading is not uniformly distributed but has an areal concentration which is higher towards
one side. There is an inbuilt bias in the BS map caused by some proton backscatters from gold losing energy through the sleeve en route to the SiSB detector. These would be detected with lower energy outside the region selected for the elemental map. L X-rays, however, have no such bias and their map shows a slightly higher concentration to one side. This could be due to the heavy particulates sinking slightly through the foam during sample fabrication or to some asymmetry in the measurement technique.

If the sloping continuum of gold in the backscatter spectrum reflects non-uniform gold loading, it would mean there is more gold at depth than at the surface, (not left-right as demonstrated by the 2D L X-ray maps). This might be due to gold sinking towards one end of the foam cylinder during the sample fabrication process.

If the same sloping continuum of the gold in the backscatter spectrum is produced in further experimental runs, if the gold is assumed to be simply a low density continuous distribution, it would mean one of the following:

- the sample has been analysed with the end of less gold facing the beam in both cases (and also in the separate experiment of [58])
- there could be less gold at both ends with a dense distribution of gold at the centre of the cylinder samples.

However the gold is distributed in substantial flecks of order 5 micron diameter - i.e. at the flecks the density is 19.3 g/cm³, between the flecks it is very low. Proton scattering in this case needs to be specially modelled before any conclusions can be drawn.

K X-rays from gold have been detected for both the foil (and possibly the sample) but the yield is very low. Increasing the beam energy would have the effect of increasing the yield of both K and L X-rays from gold. It would also increase the range of energies between the highest energy oxygen backscatter and the high-energy edge of the gold peak, thus improving the depth information retrievable from backscatters in gold flecks distributed through the foam tube (i.e. increasing $D_L$). The small gold pieces are of unknown shape and size, so assumptions would be necessary to calculate path lengths through foam and gold prior to and following backscatter.
5.5 Main Experiment

5.5.1 Aims

The success of the preliminary experiments confirmed the viability of the main experiments - to create a useful technique for measuring the total mass loading and average fleck size of gold loaded into such foam cylinders.

Modifications made to the accelerator laboratory after the preliminary experiments included:

- replacing the previous beam slits with highly polished tungsten carbide, and
- moving the accelerator control desk further away from the zero port, onto a purpose built mezzanine.

Following these improvements, higher beam energies were achievable without producing radiation background hazardous to the user, specifically reduced neutron doses than would have previously been experienced. The main experiment was designed to use a higher beam energy to improve the K X-ray yield and also to maximise the depth at which information was obtainable from proton backscatters.

Understanding the main features of the spectra derived from the initial experiment allowed us to perform subsequent experiments at higher energy in an improved manner. The secondary electron bremsstrahlung identified at the low energy end of the spectra was discriminated out.

The results of the preliminary experiments showed more gold X-rays detected towards the single CdTe detector, on the left hand side (beam facing sample). To investigate any experimental detection asymmetry which might obfuscate the true gold areal distribution, an additional CdTe detector was mounted on the right hand side, at the same angle to the beam.

For backscatters from the foam samples into the single backscatter detector, those emerging through the foam cylinder and the upper portion of the polyimide sleeve had considerably less energy than those emerging only through the foam. To identify a central
region of the cylinder, a second backscatter detector was also incorporated below the beam axis.

3.5.2 Samples

For this experiment, in addition to ~5μm gold flecks in foam cylinders, samples were provided (comparison samples) with similar overall gold mass but with the gold in the form of submicron flecks. These should allow a cross-check on the determination of gold mass by using K X-rays by using also:

- L X-rays – as attenuation in the flecks will be minimal - and
- backscattering – as the gold distribution should give rise to a spectrum characteristic of a low density foil.

The samples were mounted in the carbon blocks and labelled in-house at AWE. Six samples were provided. Initially samples had been glued to two narrow copper wires which were clamped between blocks, as described in §2.4.2. Being narrow, the surface area available for adhesion to the polymer sleeve was limited, and as a consequence problems had been encountered with wires detaching from the sample. To eliminate this difficulty, broader wires were used, one per sample, glued to the underside of each polymer sleeve. None of the samples were perfectly cylindrical or identical: the sleeve wrappings, amount of foam within the cylinder and the circularity of the cylinders varied greatly, testament to the difficulty of manufacture and the fragility of the samples. They were inspected visually before analysis but photographed in detail afterwards through a microscope. This was to prevent potential heat damage to the samples caused by the lamp of the microscope.

They were labelled on white polymer sheet attached below the samples to the carbon blocks with 1-6 marks. Samples 1-2 were standard samples and 3-6 were submicron-loaded comparison samples.
Figure 5.5.2-1: Foam samples mounted in carbon blocks, below gold foil standard.

The samples are shown above in figure 5.5.2-1. These are shown in greater close-up below in figure 5.5.2-2 to demonstrate the differences between the samples.

Figure 5.5.2-2: Close-up of samples mounted in carbon blocks. (a) samples 1 and 2; (b) samples 3 and 4; (c) samples 5 and 6.
Obvious flaws were observed in the last two samples, numbered 5 and 6 (figure 5.5.2.2/c). The front surfaces were not flat, instead were pitted and creased respectively. There were also some gaps between the foam and sleeve. For these reasons samples 5 and 6 were excluded from ion beam analysis, leaving two standard and two comparison samples remaining. From this initial end-on inspection, samples 2 and 4 (figure 5.5.2.2/a) and figure 5.5.2.2/b) appeared to be most uniform so data taking was prioritised on these – experimental runs of duration two hours compared with one hour runs for samples 1 and 3. For the experiments to characterise cylinders containing standard sized gold flecks, sample 2 is hereinafter referred to as the primary sample, sample 1 is hereinafter referred to as the secondary sample.

Detailed photographs were taken using a camera mounted on a microscope following the experiments (for reasons explained above in this section), shown below in figure 5.5.2.3. Although samples 1-4 had appeared to be useable, this detailed inspection revealed large amounts of foam missing in sample 4. Data analysis was therefore prioritised on samples 1-3, sample 3 being the only useful comparison sample is from hereinafter referred to as the validation sample.

Figure 5.5.2-3: Photographs taken with camera mounted on a microscope.
5.5.3 Experimental Arrangements

Following modifications to the accelerator facilities, a terminal voltage of 2000kV was applied, generating a proton beam energy of 4.128MeV. The protons were scanned over an area of 1500μm × 1500μm, with a beam current of 50pA over the samples and 20pA over the gold foil (the lower beam current was selected for scanning over the higher density foil standard in order to prevent extremely high L X-ray yields which would raise the dead-time). The beam spot size was 2μm. The experimental run time on the primary sample was 2 hours; an experimental run time of 1 hour was used for the secondary sample, the validation sample and the foil standard. (Sample 4 was analysed for 2 hours but rejected from the main analysis subsequently for reasons discussed above in §5.5.2).

At a proton energy of ~4MeV, gold L X-rays, ~9-15keV are produced in abundance but they are attenuated by up to 35% in 5μm of gold. Gold K X-rays have energies of 66-78keV, so they are only attenuated by ~1%. Even with the increased proton energy, however, their yield is still very low – there is an approximately four-fold increase in K X-ray production cross-section as the proton energy increases from 2.585MeV to 4.128MeV [60]. Both K X-rays - to determine the overall quantity of gold present - and L X-rays - to determine from the attenuation the average size of the flecks – needed to be detected.

Two Amptek® CdTe X-ray detectors (detection region 25mm² × 1mm) - for the PIXE measurements - and two Ion Implanted Silicon (IIS) Ortec® charged particle detectors (100mm² × 300μm) - for the backscattered protons - were selected to be set up symmetrically about the target, shown below in figure 5.5.3-2(a) and 5.5.3-2(b). The signal processing schematic is shown in figure 5.5.3-2(c). The experimental arrangements are also shown in photographs - figures 5.5.3.2 and 5.5.3.3.
Figure 5.5.3-1: Target and detector arrangement (a) side view; (b) over-head view; (c) signal processing. The ADCs connected to the detectors are labelled with their numbers for reference: X-ray detectors connected to ADC 1 and 4 are to the left and right of the sample respectively, $P_L$ and $P_R$; charged particle detectors connected to ADC 3 and 2 are above and below the sample respectively, $B_T$ and $B_B$. 
Figure 5.5.3-2: Set-up as viewed through side window in chamber.

Figure 5.5.3-3: Set-up as viewed from above looking into chamber.
5.5.4 Energy Calibration Methods

The two PIXE detectors were energy calibrated in the same manner as in the preliminary experiment. The two backscatter detectors were energy calibrated also as before, but this time for the higher beam energy of 4.128MeV. The new calibration energies are listed below in table 5.5.1. The calibration graph for $B_B$ and corresponding overlaid spectra are shown as examples in figures 5.5.4-1 and 5.5.4-2.

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<thead>
<tr>
<th>Backscatter Edge</th>
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<td>C</td>
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</tr>
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<td>O</td>
<td>3222keV</td>
</tr>
<tr>
<td>Au</td>
<td>4046keV</td>
</tr>
</tbody>
</table>

Table 5.5-1: Calibration energies for backscatter spectra, for the new higher beam energy.

![Graph of backscatter calibration for $B_B$.](image)

Figure 5.5.4-1: Graph of backscatter calibration for $B_B$. 

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Figure 5.5.4-2: Backscatter spectra of the validation sample and foil standard overlaid, from detector B$_n$ — as stated in the text, backscatter calibrations were performed using taking data, using C, O and Au edges.
5.5.5 Experimental Results and Discussion (1)

5.5.5.1 Gold Foil

5.5.5.1.1 PIXE Data

Figure 5.5.5-1: X-ray spectrum from P_L; the K X-rays at higher energy are featured as an insert owing to low yield.

Figure 5.5.5-2: X-ray spectrum from P_R; the K X-rays at higher energy are featured as an insert owing to low yield.
The gold L X-ray peaks, in the X-ray spectra in figures S.5.5.1 and S.5.5.2, were in different ratios to those measured in the preliminary experiments at 2.585MeV (see figure S.4.5.2 spectrum) when adjusting for the change in beam energy. The extra change in ratio is attributed to M X-rays of energy 2.123keV [66] (detected but discriminated out of the spectra) detected in coincidence with the L X-rays (and the K X-rays) expected from the preliminary experiments. These have the effect of moving some counts which would normally be in the:

- $\text{L}_\alpha$ peak to the $\text{L}_\beta$ peak
- $\text{L}_\beta$ peak to the $\text{L}_\gamma$ peak
- $\text{L}_\gamma$ peak to an extra peak.

For the K X-rays some counts will be moved to energies 2.123keV above the $\text{K}_\alpha$ and the $\text{K}_\beta$ peak.

The resolution from $P_R$ is considerably poorer than $P_L$, possibly due to it being a first-generation detector. This will be addressed later.

![Figure 5.5.5-3: Gold L X-rays from $P_L$ - the LHS detector.](image1)

![Figure 5.5.5-4: Gold L X-rays from $P_R$ - the RHS detector.](image2)

The gold L X-ray maps from the two detectors are different. The CdTe in the X-ray detectors were arranged to be at a distance of 23mm from the target, as close as possible to avoid interference from any potential beam halo on the detector entrance windows. Being
this close, a small variation in solid angle over the scan area is inevitable. Hence, for a perfectly flat gold foil held perpendicular to the direction of the beam, the left hand side detector would see an increased yield of counts on the left and decreased yield on the right of the foil, and vice versa for the right hand detector. The variation in solid angle would be small (less than ±5%), and with two detectors at equal opposite positions about the sample any such bias could be negated by summing the signals from both. The L X-ray maps do not appear to show equal and opposite yields: a bigger change in yield across the horizontal length of the foil from the detector on the left (P_L) can be seen in figure 5.5.5.3, compared with the detector on the right (P_R), figure 5.5.5.4. At the left-hand edge of these maps there is also an unexpected yield decrease from P_L and corresponding yield increase from P_R. This will be investigated in more detail.

![Figure 5.5.5-5: K X-rays (P_L).](image1)

![Figure 5.5.5-6: K X-rays (P_R).](image2)

The gold K X-ray maps are shown in figure 5.5.5.5 and figure 5.5.5.6. The right hand side detector (P_R) shows the foil with the edge less well defined, with more counts outside of the foil region, compared with the left. This is because of a poorer signal-to-noise ratio: higher background is visible in the K X-ray region of the spectrum from P_R (figure 5.5.5.2), than the spectrum from P_L (figure 5.5.5.1) and will be investigated further.
5.5.5.1.2 Backscatter Data

The spectra from each of the two IIS detectors are shown below in figures 5.5.5-7 and 5.5.5-8.

Figure 5.5.5-7: Backscatter spectrum from scan over gold foil, from $B_T$.

Figure 5.5.5-8: Backscatter spectrum from scan over gold foil, from $B_B$.
The main features within the backscatter spectra, figures 5.5.5-7 and 5.5.5-8, were also present in the preliminary experiments (see figure 5.5.5-1). The step at the higher energy end of the carbon continuum represents protons backscattered from the region of the carbon block exposed directly to the beam, not covered by the foil. The gold band is from the gold foil. A new feature, an oxygen step, was not seen previously. Maps were generated for the carbon, oxygen and gold.

The carbon backscatter maps, figures 5.5.5-9 and 5.5.5-10, show contours within the area of the foil.

The oxygen was present in a distinct area on the left hand side of the scan, between the foil and carbon, see figures 5.5.5-11 and 5.5.5-12.
5.5.5.1.3 Further Investigation and Discussion

The original aim was for the gold foil to lie as flat as possible against the carbon block, held in place by the two washers. This was investigated, and it was found that foil had been removed and glued onto the carbon block in-house at AWE, shown in figure 5.5.5-15.
The oxygen detected is from exposed glue. Glue underneath the foil does not contribute to the oxygen step in the spectra as the backscattered protons lose energy through the gold before being detected so are underneath the carbon region of the spectra - the oxygen map was generated from the oxygen region on the spectra above the carbon edge. The unevenness in the carbon map within the gold foil region shows where the foil was pressed against the carbon into the glue. The effect of adding glue caused the carbon backscatters to be attenuated to differing extents, however the gold foil was on top, as seen in the carbon and gold maps in figures X.X.X-9, X.X.X-10, X.X.X-13 and X.X.X-14 respectively.

To quantify any change in yield across the scan maps, seen in figures X.X.X-9 and X.X.X-4 profiles were obtained for all four detectors: the PIXE detectors are situated in a plane horizontal to the sample (which produced the maps with unexpected features) and the backscatter detectors in a vertical plane to assess horizontal uniformity as viewed from above and below which could substantiate whether any features are a function of the detector or position figure X.X.X-16 below shows the region within the foil selected: counts were summed vertically as a function of horizontal position of scan.

Figure 5.5.5-16: Diagram to show summed area for profiles.
Figure 5.5.5-17: Profiles of gold summed vertically along the horizontal distance across the scan from both PIXE and BS detectors.

The profiles are shown above in figure 5.5.5-17. Overall gold backscatter yields are less than those from PIXE. However, despite lower statistical accuracy, the protons backscattered from gold clearly show a flat profile from each detector. There appears to be no significant contour feature across the foil as viewed from above and below.

The higher yield of gold L X-rays could provide a more accurate reflection of an uneven gold surface as a result of gluing, this may explain the feature from pixel 20-125 with an arch (extra counts) in the $P_L$ profile and a dip (fewer counts) in the $P_R$ profile. It might also indicate that the feature is not significant in the vertical plane but is in the horizontal plane.

However, a far more important effect can be seen: the $P_L$ profile has an obvious gradient relating to change in detection solid angle, which is not matched equally in the $P_R$ profile. (The $P_R$ profile might have a slight gradient, depending on the correct identification of the feature from pixels 20-125.) As mentioned earlier in §3.5.5.17 $P_L$ and $P_R$ were situated close to the sample, in the horizontal plane, causing a slight variation in solid angle from left-right. The two PIXE
detectors were placed symmetrically about the sample (shown in figures 5.5.3.1 and 5.5.3.2), so the effect of an increase and decrease in yield should be equal and opposite.

The Pr profile is significantly lower than that from Pt. This, along with the mismatched gradients, provided strong evidence that the Pr detector was further away from the sample than Pt. Contacting the manufacturers confirmed this; the active detection site, the CdTe chip, had been positioned closer to the entrance window following improvements to the design of their detector. The CdTe of Pt was 20mm from the sample, and that of Pr 23mm away. The implications are that summing signals from the two detectors cannot obviate bias due to this asymmetry. The older detector, Pr, also had older electronics which led to a poorer resolution and larger electronic noise background, most noticeable at higher X-ray energies, where the gold K X-ray yield is low. This is evident in 5.5.5.2.

The backscatter detectors are sufficiently far away from the sample to prevent any noticeable gradient from variation in solid angle, however this would be in the vertical plane, and consequently be absent from the horizontal profiles.

5.5.5.2 Validation Sample

This validation sample was at an angle to the beam, that is the cylinder length was not perpendicular to the front surface of the carbon block. This can be seen below in the carbon backscatter maps of the full scan area, figures 5.5.5.18 and 5.5.5.19.

![Figure 5.5.5-18: Validation sample carbon backscatter map from B_T.](image)

![Figure 5.5.5-19: Validation sample carbon backscatter map from B_R.](image)

The shadows under the top sleeve in figure 5.5.5.18 and above the bottom sleeve in figure 5.5.5.19 reflect the position of the backscatter detectors, as described before in §5.4.5.2.2
and §5.4.5.2.3. As demonstrated in figure 5.5.5-20, the bottom-right regions of a mask drawn over the front face of the cylinder would not cover gold-loaded foam for the full length of the sample. This would therefore not accurately reflect gold loading throughout the cylinder.

![Diagram of beam penetration of sample at an angle.](image.png)

**Figure 5.5.5-20:** Diagram to show beam penetration of sample at an angle.

This is also clear from the gold L X-ray maps below, figure 5.5.5-21 and figure 5.5.5-22, of the full scan area (excluding copper wire so that low counts are visible on the same colour scale).

![Gold L X-ray map from P_L.](image1.png)

![Gold L X-ray map from P_R.](image2.png)

**Figure 5.5.5-21:** Gold L X-ray map from $P_L$.

**Figure 5.5.5-22:** Gold L X-ray map from $P_R$.

A smaller mask was drawn to encompass the shaded region labelled in figure 5.5.5-20, where protons can interact with gold flecks from the full length of the sample. The gold L X-ray maps suggest a uniform loading throughout, therefore the smaller face area of the mask can be used and mass results can be scaled up to represent the full volume of the cylinder.
5.5.5.2.1 PIXE Data

Figure 5.5.5-23: Validation sample PIXE spectrum from a masked region within the sleeve, from \( P_L \).

Figure 5.5.5-24: Validation sample PIXE spectrum from a masked region within the sleeve, from \( P_R \).
For the validation sample the P_L PIXE spectra, figure 5.5.5.25, displays gold L X-ray peaks with much better resolution than the corresponding spectrum from the P_R detector figure 5.5.5.27. Also, the background noise is worse from the P_R detector, which is particularly significant at higher energies with the low yield of K X-rays.

The masked L X-ray maps, figure 5.5.5.25 and figure 5.5.5.26, show that the gold is loaded uniformly (as explained before with figure 5.5.5.21 and figure 5.5.5.22). Being submicron in diameter, the gold is not observably clumped into flecks, but rather diffused throughout the entire foam matrix.

The masked gold K X-ray maps, figures 5.5.5.27 and 5.5.5.28, have far fewer counts compared with the gold L X-ray maps, as would be expected. The P_L map has a slightly higher concentration of gold K X-ray counts towards the top right, however there are so few counts it does not seem significant. There are more counts in the P_R map, this reflects the larger electronic noise in the spectrum.
5.5.5.2.2 Backscatter Data

As seen in §5.4.5.2.2 and investigated in §5.4.5.2.3.2, unlike the X-rays, backscattered protons suffer energy loss when passing through the polyimide sleeve before detection. The depth in the cylinder at which the gold is situated will limit the energy of backscattered protons, and variations in path lengths through foam and gold will occur according to the size of the gold pieces. Protons suffer reduced energy when travelling through the sleeve before reaching the detector. This effect was most noticeable in the carbon backscatters, creating shadows in the carbon maps where backscattered protons were shifted to energies below that selected to represent carbon on the spectra (which included low energies). When protons backscattered from gold travel through the sleeve before detection, they will lose energy and may be shifted to energies below the oxygen edge, and hence are not usable for a gold mass measurement, whereas other protons backscattered from gold at the same depth in the cylinder would be usable. The effect is less pronounced for gold backscatters than for carbon backscatters due to their higher energies (and hence lower energy loss in the sleeve). This means that the very top of the gold map from the $B_r$ detector, and the very bottom of the map from the $B_n$ detector, may be less reliable.

Two maps were used for backscatter measurements:

- a larger map within the sleeve, similar to that used in the PIXE section, selected to encompass what appeared to be a roughly uniform concentration of gold throughout, and
- a smaller map, excluding carbon shadows which would definitely reject areas where useful backscatters could be lost from the effect of energy loss in the sleeve.
Figure 5.5.5-29: Validation sample backscatter spectrum from the larger masked region within the sleeve, $B_T$.

Figure 5.5.5-30: Validation sample backscatter spectrum from the larger masked region within the sleeve, from $B_R$. 
The backscatter spectra, figures 5.5.5-29 and 5.5.5-30, show the same shape as in the preliminary experiments, with the exception of the gold region. Previously the gold region had been curved and sloping, however now it resembles a more normal backscatter step, typically representative of a low density foil with gold distributed throughout. The difference between the preliminary sample and this validation, submicron loaded sample may be due to the gold flecks in the preliminary sample being distributed non-uniformly, or possibly the size of gold flecks plays an important role. This will be investigated with the two standard samples in the main experiment. For this validation sample it means that backscatter measurements can be used to obtain a measure of mass. The maps for this mask show gold dispersed throughout, figures 5.5.5-31 and 5.5.5-32.
Figure 5.5.5-33: $B_T$ spectrum from the smaller mask.

Figure 5.5.5-34: $B_R$ spectrum the smaller mask.
The backscatter spectra from the smaller mask, figures 5.5.5.35 and 5.5.5.36 show the same shape as for those generated by the larger mask, but with considerably lower backscatter yields, as would be expected. The backscatter maps, figures 5.5.5.35 and 5.5.5.36, show the mask area and the gold dispersed throughout.

5.5.5.3 Discussion of Data

5.5.5.3.1 Gold Foil Standard

For the detection of backscatter events from gold there is no variation in solid angle over the scan.

For the detection of X-ray events:

1. the CdTe chips in the detectors for $P_L$ and $P_R$ are at different distances from the sample
2. the signals from $P_R$ are much noisier than for $P_L$ and by association the resolution is worse
3. there is a variation in solid angle across the scan

As the number of K X-rays needs to be measured as accurately as possible, (2) precludes the use of $P_R$. (1) also precludes the use of $P_L$ and $P_R$ as a matched pair able by addition to annul the solid angle variation with horizontal scan position. Hence in mass determinations of gold in the samples to be studied, results from $P_L$ shall be used and corrected for the
solid angle variation by averaging over scan position. Results from L X-rays in $P_L$ and $P_R$ maps can be used to provide information on the areal distribution of gold in the samples.

5.5.5.3.2 Validation Sample

The backscatter data shows a gold step, typical of a low density gold foil, rather than the slope obtained in the preliminary experiments. This means that it should be possible to calculate the mass of gold from backscatters with energies above the oxygen edge.

The gold L X-rays will not suffer self-attenuation as the gold pieces are so small. Thus both L X-rays and K X-rays may be used to measure the gold mass in the sample. Comparing the spectra from the two detectors at energies above the L X-ray region (shown clearly as inserts from 50keV - 90keV), the spectrum from $P_R$ figure 5.5.5.2v is much noisier than that from $P_L$ figure 5.5.5.2v - as was found for the foil standard data. $P_R$ was one of the earliest detectors of this kind that Amptek® developed, whilst $P_L$ was an improved design - with a much lower noise profile. Hence for quantitative measurements of the gold mass only data from the newer detector was used. Another detector of the same design as this has since been purchased and it will replace the older one in subsequent measurements. The CdTe in the newer detector is nearer to the entrance window, making a larger difference in solid angle across the scan area.
5.5.6 Data Analysis of Validation Sample

5.5.6.1 Terms Required for Analysis

5.5.6.1.1 X-ray Analysis

In order to calculate the gold mass and average size of gold flecks in the samples several factors are required.

The number of gold-related events detected during an experimental run in a scan mask area determined off-line will be proportional to:

- the number of protons striking the target within the scan-mask area (the beam fluence)
- the number of gold nuclei, \( n \), available for scatter within the scan mask area
- the probability of a proton-gold interaction resulting in a detectable particle or photon
- particle or photon attenuation before reaching the detector
- the solid angle subtended by the detector at the sample
- detection efficiency.

The number of events detected, \( N \), is obtained from the sum of counts between energy limits defined on the relevant spectrum. In the case of PIXE, there is substantial underlying background which must be removed in order to obtain the nett number of counts in the corresponding peak(s).

As stated in §3.3.7, a relative measure of beam fluence, the number of incident ions in unit area, can be obtained from the number of protons backscattered from the carbon block sample holder, \( C_{BS} \), within a mask of measured area, \( a_C \), see equation

\[
Q = k_C \times \left[ \frac{C_{BS}}{a_C} \right]
\]

Equation 5.5-1

where the constant \( k_C \) is the same for the carbon blocks associated with both the sample and foil data. The quantity \( C_{BS} / a_C \) is proportional to \( Q \), and so henceforth will be written as \( q \).
If the fluence per unit area is multiplied by the area of the scan mask, \( a_s \) or \( a_F \) for the sample and foil respectively, this is a relative measure of number of protons incident on the scan mask area. So for the validation sample and foil, respectively (see equation §5.5.2 and §5.5.3):

\[
Q_s = k_C \times q_s \times a_s
\]

**Equation 5.5-2**

\[
Q_F = k_C \times q_F \times a_F
\]

**Equation 5.5-3**

The number of gold nuclei available for scatter can be found from Avagadro's Constant, \( N_{Av} \), divided by atomic number, \( A \) (giving the number of gold atoms per unit weight of gold), multiplied by the mass thickness, \( \rho t \), multiplied by the area of the sample, \( a_s \) (see §2.1.2 equation 2.1.3).

So the gold in the validation sample is given by equation §5.5.4:

\[
n_s = \left[ \frac{N_{Av} \cdot \rho_{Au} \cdot t_s \cdot a_s}{A_{Au}} \right]
\]

**Equation 5.5-4**

where \( \rho_{Au} \) is the density of gold in the foam and \( t_s \) is the length of the foam cylinder (1mm).

For the foil standard, equation §5.5.5:

\[
n_F = \left[ \frac{N_{Av} \cdot \rho_{Au} \cdot t_F \cdot a_F}{A_{Au}} \right]
\]

**Equation 5.5-5**

where \( \rho_{Au} \) is the density of gold, 19.3 g.cm\(^{-3}\) and \( t_F \) is the thickness of the foil standard, 2\( \mu \)m.
The differential cross-section of a proton-gold interaction resulting in X-ray production at the scattering angle of a PIXE detector is determined from the proton-energy dependent production cross-sections, $\sigma(E)$ [61]. As these are isotropic the differential cross-section is the published cross section divided by 4\pi (see equation 2.1.9), evaluated at the average energy of protons in the sample or the foil.

For the foil the average energy of a proton inducing an interaction is the energy $E_F$ at the mid-point of the foil. For the submicron loaded validation sample it is the energy, $E_S$, halfway along the cylinder, assuming a uniform loading of gold throughout.

The differential cross-section of a proton-gold interaction at a particular depth in the sample or the foil standard resulting in a Rutherford Backscatter, for a particular detection angle, $\theta$, is inversely proportional to the square of the energy of the incident proton (see equation 2.1.10).

These energies, $E_S$ and $E_F$ are found using SRIM to obtain proton energy loss through paths of materials. The differential cross-section is then divided by the area of the scan mask, $a_S$ or $a_F$, to obtain the probability of scattering into unit solid angle.

For X-rays, the transmission, is the probability of X-rays passing through a material of thickness $t$ cm, of density $\rho$ g.cm$^{-3}$ with mass attenuation coefficient $(\mu/\rho)$ cm$^2$.g$^{-1}$.

Thus transmission, $T$, can be expressed as equation 2.4-1 (shown earlier in §2.4):

$$T = \frac{I_{out}}{I_{in}} = e^{-\rho \frac{\mu}{\rho} t}$$

Equation 2.4-1

Where $I_{out}$ and $I_{in}$ are the exit and input X-ray fluxes respectively. The mass attenuation coefficient $(\mu/\rho)$ is dependent on the energy of the X-rays. Therefore the proportion of photons transmitted will depend on both the photon attenuation properties of the material...
and the energy of the incident photons. Therefore gold Lα, Lβ, and Lγ, Kα, and Kβ X-rays need to be considered separately.

When characteristic gold X-rays are generated in the cylindrical samples, they may be subjected to attenuation prior to detection, by the following materials:

- Gold – considered as a low density foil
- Foam – a low density polymer C13H22O6
- Sleeve – a polyimide

Considering L X-rays in the sleeve and the foam initially, the density and size of both the foam and sleeve are known. The total transmission, $T_{FoamSleeve}$, is found by multiplying individual contributions from the foam and the sleeve, equation 5.5-6:

$$T_{FoamSleeve} = T_{Foam} \times T_{Sleeve}$$

Equation 5.5-6

As the X-ray detectors are at angles of 45° to the sample, some of the X-rays emitted from some gold flecks (a) pass only through the foam on their way to the detector, X-rays emitted from others (b) pass through both the foam and the polyimide sleeve. This is shown below in figure 5.5.6-1:

Figure 5.5.6-1: View from the middle of the sample showing the two routes for photons exiting the foam in the direction of the detector (a) passing through foam only and (b) passing through foam and sleeve.
Assuming that only X-rays emitted at 45° in the horizontal plane will intercept a detector, then in a cylindrical sample, the ratio of (a) to (b) will vary depending on the horizontal plane from which the X-rays are emitted.

For instance, for the median plane, the ratio, given by $\frac{A}{B}$ will be unity, as the areas from which they originate $A$ and $B$ are the same:

![Diagram](image)

Figure 5.5.6-2: A diagram to demonstrate that the ratio between areas A and B vary at different horizontal planes through the sample (front view of cylindrical sample is in the middle with the two horizontal planes marked).

For a plane at a height $r \sin \theta$, where $r$ is the cylinder radius and $\theta$ is indicated on the diagram above, figure 5.5.6-2, the ratio will not be unity.

To calculate the ratio and to derive the overall attenuation of X-rays in the foam and the polyimide sleeve a simple BASIC program was written. This program works out:
1. a sum of path lengths passing only through foam for a large number of points in triangular areas (A) in horizontal planes from the median plane to the tangential plane.
2. a sum of the corresponding number of points – proportional to the areas (A).
3. a sum of path lengths passing only through the foam to the sleeve for a large number of points in the areas (B) in horizontal planes from the median plane to the tangential plane.
4. a sum of the corresponding number of points – proportional to the areas (B).
5. a sum of paths at 45° in the sleeve for each of the points in (B) in each plane.

From these the following are then calculated:

- the mean path length in the foam missing the sleeve \((1)/(2) = 0.41\) mm
- the mean path length in foam towards the sleeve \((3)/(4) = 0.41\) mm
- the mean path length in the sleeve \((5)/(4) = 59.4\) microns
- the ratio of the points in the foam with path lengths missing the sleeve to the points in the foam with path lengths towards the sleeve \((2)/(4) = 40/60\).

Data from Lawrence Berkeley Laboratory [67, 68] is then used to calculate the mean attenuation of L X-rays (in the ratio \(L_x/ L_\beta/ L_\gamma = 1/0.685/0.1\) at a beam energy of 4MeV [69]) in the foam and polyimide sleeve – the Foam-Sleeve Attenuation:

\[ T_{\text{FoamSleeve}} = 0.9800 \]

The solid angle subtended by the detector at the sample is \(\Omega\) sr and the X-ray detection efficiency is \(\varepsilon_X\).

Thus for the number of L X-rays detected from the low density gold in a foam cylinder, \(N_S\), can be calculated from equation 5.5.7.
\[ N_s = k_C \times \left[ q_s \times a_s \right] \times \left[ \frac{N_{\text{Au}} \cdot \rho_{\text{Au}} \cdot t_s \cdot a_s}{A_{\text{Au}}} \right] \times \frac{\frac{d\sigma}{d\Omega}}{a_s} \times \frac{E_s}{a_s} \times T_{\text{transfoam}} \times T_{\text{AuS}} \times \Omega \times \varepsilon_X \]

Equation 5.5-7

where \( T_{\text{AuS}} \) is the average transmission of L X-rays through the gold in the foam.

To obviate the need to calculate \( k_C \) the gold foil standard is used as a comparator for calculating absolute values of gold mass and average fleck size. Detecting a number of characteristic X-rays from the known amount of gold in the foil with the same experimental set-up as used for the samples also eliminates the need for information on X-ray detection efficacy such as solid angle \( \Omega \) and energy dependent detection efficiency \( \varepsilon_X \).

The number of L X-rays detected from the gold foil, \( N_F \), can be calculated from equation 5.5-8:

\[ N_F = k_C \times \left[ q_f \times a_f \right] \times \left[ \frac{N_{\text{Au}} \cdot \rho_{\text{Au}} \cdot t_f \cdot a_f}{A_{\text{Au}}} \right] \times \frac{\frac{d\sigma}{d\Omega}}{a_f} \times \frac{E_f}{a_f} \times T_{\text{foil}} \times \Omega \times \varepsilon_X \]

Equation 5.5-8

where \( T_{\text{foil}} \) is the average transmission of L X-rays in the foil.

Dividing the equation for the number of L X-rays detected from the sample by those detected from the foil standard, equation 5.5-7 by 5.5-8, cancels and removes the following factors:

- the backscatter beam-current proportionality constant, \( k_C \)
- Avagadro's Constant, \( N_{\text{Av}} \)
- the atomic mass of gold, \( A_{\text{Au}} \)
- the solid angle subtended by the detector, \( \Omega \)
- the efficiency of the X-ray detector, \( \varepsilon_X \).
The new expression is given as equation 5.5-9. Defining the mass, $M_{AuS}$ as the mass thickness, $\rho_{AuS} \cdot t_S$, multiplied by scan mask area from the sample scan $a_S$. Defining the mass, $M_{AuF}$ as the mass thickness, $\rho_{Au} \cdot t_F$, multiplied by scan mask area from the foil scan $a_F$. All the other symbols are as defined above.

\[
\frac{N_S}{N_F} = \left[ \frac{q_S}{q_F} \right] \times \left[ \frac{M_{AuS}}{M_{AuF}} \right] \times \left[ \frac{\frac{d\sigma}{d\Omega}}{E_S} \right] \times \left[ \frac{T_{FoamSleeve} \times T_{AuS}}{T_{Foil}} \right]
\]

Equation 5.5-9

This can be arranged and written in terms of the mass of gold in the sample incorporating the gold L X-ray transmission as equation 5.5-10.

\[
M_{AuS} \times T_{AuS} = \left[ \frac{N_S}{N_F} \right] \times \left[ \frac{q_F}{q_S} \right] \times \left[ \frac{M_{AuF}}{M_{AuS}} \right] \times \left[ \frac{\frac{d\sigma}{d\Omega}}{E_F} \right] \times \left[ \frac{T_{Foil}}{T_{FoamSleeve}} \right]
\]

Equation 5.5-10

The L X-ray transmission through the gold in the sample $T_{AuS}$ is the average of transmissions of $L_\alpha$, $L_\beta$ and $L_\gamma$ X-rays weighted in the ratio $L_\alpha/L_\beta/L_\gamma = 1/0.685/0.1$ [69].

The $L_\alpha$ X-ray transmission through the gold in the sample is given by equation 5.5-11:

\[
T_{\alpha} = e^{-\left( \frac{\mu}{\rho} \right)_{\alpha} \cdot \rho_{AuS} \cdot t}
\]

Equation 5.5-11

where $(\mu/\rho)_\alpha = 130.77 cm^2 g^{-1}$, $\rho_{AuS} = M_{AuS}/(a_S \times t_S) = M_{AuS}/(0.00404 cm^3 \times 0.1 cm)$ and $t$ is the average path length of L X-rays exiting the gold in the foam, $t=0.041 cm$. 

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Thus $T_\alpha$ is given by the expression below in equation 5.5.12:

$$T_\alpha = e^{-(0.0138 \times M_{AuS})}$$

Equation 5.5-12

where $M_{AuS}$ is in µg.

Similarly for $L_\beta$ and $L_\gamma$ X-rays respectively, $T_\beta$ and $T_\gamma$ are given by equations 5.5.13 and 5.5.14 below:

$$T_\beta = e^{-(0.0091 \times M_{AuS})}$$

Equation 5.5-13

$$T_\gamma = e^{-(0.0146 \times M_{AuS})}$$

Equation 5.5-14

Therefore, by combining equations 5.5.12, 5.5.13 and 5.5.14, weighted with their ratios, $T_{AuS}$ can be expressed as equation 5.5.15 below:

$$T_{AuS} = \frac{e^{(-0.0138 \times M_{AuS})} + 0.685e^{(-0.0091 \times M_{AuS})} + 0.1e^{(-0.0146 \times M_{AuS})}}{1.785}$$

Equation 5.5-15

Equation 5.5.15 can be solved to find $M_{AuS}$ and from this the mass of gold in the foam cylinder can be obtained from equation 5.5.16, scaling the result from the masked area to that for a complete cylinder, with a circular front face.

$$M = \frac{(M_{AuS} \times 0.7854)}{a_s}$$

Equation 5.5-16
For K X-rays the same equations apply - with the substitution of average differential cross-sections for K X-ray production. The transmissions of K X-rays in both the foil and the sample are essentially unity (0.990 for the foil and 0.999 for the sample).

5.5.6.1.2 Backscatter Analysis

For Rutherford backscattering, again, the same equations apply - this time with the substitution of average differential cross-sections for Rutherford backscattering from gold. Using equation 2.2.10, from the theory section, §2.1.4.1, equation 5.5.17 shows the relationship between the differential cross-section and incident ion energy:

$$\frac{d\sigma}{d\Omega} = \frac{k}{E^2}$$

Equation 5.5-17

where \(k\) is a constant, for protons incident on gold nuclei and a detector at a particular backscatter angle, \(\theta\). The average differential cross-section as the proton beam loses energy in the sample is given by equation 5.5-18:

$$\left(\frac{d\sigma}{d\Omega}\right)_E = \frac{\int_{E_1}^{E_0} \frac{k}{E^2} dE}{\int_{E_1}^{E_0} dE} = \frac{k}{E_0 E_1}$$

Equation 5.5-18

where \(E_1\) is the incident beam energy and \(E_0\) is the beam energy at a depth in the sample.

With \(D_l\) (the limiting depth at which a backscattered proton from gold emerges from the sample with the same energy as a backscatter from oxygen at the surface of the sample) and using equation 5.5-18, the number of detected backscatters is given by equation 5.5-19.
\[ N_s = k_c \times [q_s \times a_s] \times \left[ \frac{N_{Au} \cdot \rho_{Au} \cdot D_L}{A_{Au}} \right] \times \frac{k}{E_o E_i} \times \Omega \times \varepsilon_x \]

Equation 5.5-19

For the foil standard, the lower energy limit is the energy the beam has at the back of the foil, \( E_b \); for the foil the number of detected backscatters is given by equation 5.5-20:

\[ N_F = k_c \times [q_F \times a_F] \times \left[ \frac{N_{Au} \cdot \rho_{Au} \cdot F_x}{A_{Au}} \right] \times \frac{k}{E_o E_i} \times \Omega \times \varepsilon_x \]

Equation 5.5-20

As before with equation 5.5-9 for the L X-rays, the relationships can be simplified by dividing the expression for obtaining the number of backscattered ions from the sample by those from the foil, equations 5.5-19 and 5.5-20 respectively, produce equation 5.5-21.

\[ \frac{N_s}{N_F} = \left[ \frac{q_s}{q_F} \right] \times \left[ \frac{M_{AuS}}{M_{AuF}} \right] \times \left[ \frac{E_o}{E_i} \right] \]

Equation 5.5-21

This can be rearranged and written in terms of \( M_{AuS} \), the mass of gold in a cylinder with the cross-sectional area of the scan mask used to obtain the data and length \( D_L \), equation 5.5-22.

\[ M_{AuS} = \left[ \frac{N_s}{N_F} \right] \times \left[ \frac{q_F}{q_s} \right] \times \left[ \frac{E_o}{E_i} \right] \times M_{AuF} \]

Equation 5.5-22
The mass of gold in the sample can then be obtained by equation 5.5-23, scaling the masked area and limiting depth (from which measurements were available) with the full volume of the cylinder.

\[
M = M_{Au} \times \frac{0.7854}{a_s} \times \frac{t_s}{D_L}
\]

Equation 5.5-23

So the factors needed in order to obtain the mass from the L and K X-ray and backscatter measurements are:

- Net counts detected
- Carbon backscatters per unit area
- Mass of gold in foil scanned
- Mean proton energy leading to interaction
- Probability of interaction occurring
- Attenuation properties of materials
5.5.6.2 Determining the Nett Number of L X-ray and K X-rays from PIXE Data

To get an accurate representation the number of L and K X-rays for comparison calculations it is necessary to define energy limits which will encompass the X-rays of interest (considering summation peaks of L and K X-rays detected in coincidence with M X-rays) and also to remove the underlying background.

In the gold L X-ray region there is a significant contribution from 'atomic' bremsstrahlung, see §2.3. Only one group [17] have attempted to quantify this effect. Using their calculation, the bremsstrahlung under the data in the L X-ray region was fitted with a standard exponential, see below in equation 5.5.23.

\[ y = e^{-(a+b \cdot E)} \]

Equation 5.5-23

determining the parameters \( a, b \) from the data points at 7.5 and 25 keV. The exponential was subtracted from the X-ray data and sum up the contributions from the \( L_\alpha, L_\beta \) and \( L_\gamma \) peaks, \( N_{LF} \).

Figure 5.5.6-3: PIXE spectrum for gold foil standard (from P1), with atomic X-ray L X-ray background fit superimposed.
Figure 5.5.6-3 shows the subtraction technique for the X-ray spectrum of the gold foil standard, with the background exponential plotted along with the L X-ray region of the spectrum. Parameters \( a \) and \( b \) were identified to be -10.3739 and 0.3595 respectively.

The proton or 'nuclear' bremsstrahlung extends to a maximum of the total energy of incident proton, so is present under the K X-rays, as a linear background. The efficiency of the CdTe X-ray detector is very good, however it begins to fall slightly above 60keV (§5.2.2.7). The linear bremsstrahlung contribution was obtained by taking an average yield in an otherwise featureless region from 46keV - 55keV, of lower energy than the K X-rays. From 60keV a line was fitted to follow the efficiency decrease, from using [36]. This background is shown below for the experimental run on the gold foil, figure 5.5.6-4. The mean yield from 45.97keV - 54.47keV was 0.507.

![Graph showing the calculated background under the gold K X-rays for the experimental run on the gold foil](image)

**Figure 5.5.6-4:** The calculated background under the gold K X-rays for the experimental run on the gold foil, from P1.

The following spectra show the gold L and K X-ray regions with backgrounds subtracted for the gold foil, figure 5.5.6-5, and the validation sample, figure 5.5.6-6.
Figure 5.5.6-5: PIXE spectrum for the gold foil standard, with background subtracted from gold L and K X-ray regions.

Figure 5.5.6-6: PIXE spectrum for the validation sample, with background subtracted from gold L and K X-ray regions.
5.5.6.3 Determining the Number of Protons Backscattered from Gold

Unlike the X-rays, there is no significant background under gold backscatters; no other elements more massive than oxygen are present. On the foil standard the gold backscatters are in a well-defined band, shown in figures 5.5.7 and 5.5.8. For the sample, backscattered counts were summed above the oxygen edge to the maximum backscatter energy 5.5.29 and 5.5.30.

5.5.6.4 Determining $g$, a Relative Measure of Beam Current

As viewed from both backscatter detectors, a uniform region from the carbon blocks was selected: an area without contamination such as flecks from emery cleaning, or any obstruction, such as being in the shadow of the sample cylinder. A mask was drawn to encompass this selected region, and backscatter spectra were generated.

The number of backscatters from carbon was summed for both detectors. The area of the masks were measured by summing the number of pixels (and converting them to appropriate units as necessary).

The example below is for the experimental run on the gold foil standard. Figure 5.5.7 is a superimposed image of the gold, oxygen and carbon backscatter maps (detailed maps for each backscatter detector are shown previously in 8.5.5.12. The region chosen for the carbon backscatter beam current measurements, shown in figure 3.5.6.8 was selected such that protons backscattered had not lost energy passing through gold foil, identified by backscatters from gold, or glue, identified by backscatters from oxygen, before reaching the detector. The area selected did not contain any specks of contamination such as traces of emery.
Figure 5.5.6-7: Superimposed gold, oxygen and carbon regions from the backscatter spectra of the experimental run on the foil standard.

Figure 5.5.6-8: Area selected from the carbon block from the experimental run on the foil standard.

Backscatter spectra were generated for the two detectors from the mask area, and the counts were summed from 800keV-2900keV (chosen to encompass most of the carbon backscatters but avoid the slightly differing discriminator levels at low energy). Figure 5.5.6-9 the backscatter spectrum from detector Bg, with the yield between limits shaded, the total sum between these energy limits was summed for both detectors.

Figure 5.5.6-9: Backscatter spectrum from Bg, the shaded region shows the counts which were summed between the limits.
A small amount of oxygen is present across the masked area, due to carbon oxidation.

The backscatter sample inter-normalisation technique is limited. Counting the number of protons backscattered from a measured region of exposed carbon block within the run time will give an excellent indication of the rate at which protons are being directed to the target. The dead time of the detection system will be affected by the production rate of reaction products, hence as the beam is scanned over an area, the dead time of the system will vary depending on position.

In order to find a comparable carbon backscatter per unit area, which accurately incorporates dead-time, it would be necessary to measure backscatters which had first interacted with gold. If a proton backscatters from gold it would not continue on its path in the forwards direction to backscatter with carbon. If a proton generates characteristic K and or L X-rays it will be capable of going on to backscatter from carbon, if the gold flecks are small enough to only attenuate a small proportion of the proton energy. For these reasons the backscatter normalisation can be examined for the validation sample, containing submicron sized gold pieces. The amount of gold loaded in the foam for the validation sample will influence the energy of protons reaching the carbon for backscatter. Therefore an estimate of the mass is required; possible normalisation adjustments will be investigated after calculating (the unadjusted) masses.
5.5.7 Calculation Results (I)

The values in table 5.5-2 and 5.5-3 show the values extracted from the data, as explained in §5.5.6. The calculated mass values are given in table 5.5-5 and were calculated from equations 5.5-10 – 5.5-16 and 5.5-21 – 5.5-23, also from §5.5.6.

<table>
<thead>
<tr>
<th>Foil Standard</th>
<th>Validation Sample</th>
<th>Ratio Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{\text{total}}$</td>
<td>1,091,400 ± 1,000</td>
<td>234,890 ± 490</td>
</tr>
<tr>
<td>$L_{\text{background}}$</td>
<td>56,070 ± 240</td>
<td>13,590 ± 120</td>
</tr>
<tr>
<td>$L_{\text{net}} : N_L$</td>
<td>1,035,300 ± 1,100</td>
<td>221,300 ± 500</td>
</tr>
<tr>
<td>$N_{LS}/N_{LF}$</td>
<td>--</td>
<td>0.21374 ± 0.00053</td>
</tr>
<tr>
<td>$K_{\text{total}}$</td>
<td>567 ± 24</td>
<td>134 ± 12</td>
</tr>
<tr>
<td>$K_{\text{background}}$</td>
<td>142 ± 12</td>
<td>57 ± 8</td>
</tr>
<tr>
<td>$K_{\text{net}} : N_K$</td>
<td>425 ± 27</td>
<td>77 ± 14</td>
</tr>
<tr>
<td>$N_{KS}/N_{KF}$</td>
<td>--</td>
<td>0.181 ± 0.034</td>
</tr>
<tr>
<td>$a_F$ and $a_S$ (pixels)</td>
<td>34,569</td>
<td>11,767</td>
</tr>
<tr>
<td>$C_{\text{RS}}$</td>
<td>86,820 ± 300</td>
<td>198,290 ± 450</td>
</tr>
<tr>
<td>$a_C$ (pixels)</td>
<td>10,741</td>
<td>6,539</td>
</tr>
<tr>
<td>$q$ (pixels$^{-3}$)</td>
<td>8.083 ± 0.027</td>
<td>30.324 ± 0.068</td>
</tr>
<tr>
<td>$q_F/q_S$</td>
<td>--</td>
<td>0.2666 ± 0.0011</td>
</tr>
</tbody>
</table>

Table 5.5-2: Validation sample - Number of counts of gold X-rays and backscatter normalisation data, with statistical errors quoted to two significant figures and data rounded accordingly. The ratios required for the mass calculations are presented in the same way, but were obtained from unrounded numbers. The terms are explained in §5.5.6.

The nett yields for gold L and K X-rays from the gold foil are, as would be expected, much higher than those for the validation sample.
Table 5.5-3: Validation sample - Numbers of counts of gold and normalisation backscatter data, with statistical errors quoted to two significant figures and data rounded accordingly. The ratios required for the mass calculations are presented in the same way, but were obtained from unrounded numbers. The terms are explained in §5.5.6.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Mass (μg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K X-ray</td>
<td>5.1 ± 1.0</td>
</tr>
<tr>
<td>L X-ray</td>
<td>4.4 ± 0.6</td>
</tr>
<tr>
<td>BS - Large Mask</td>
<td>4.9 ± 0.1</td>
</tr>
<tr>
<td>BS - Small Mask</td>
<td>5.0 ± 0.2</td>
</tr>
</tbody>
</table>

Table 5.5-4: Mass values obtained from the values above in tables 5.5.2 and 5.5.3.

The uncertainties on the mass values were acquired by combining the errors on the terms from the mass equations, from §5.6.

The K and L X-ray production cross-sections (at the mean energies) were assigned uncertainties of 5% and 10% respectively. There is variation in cross-section figures quoted in literature, from fitting models and experimental data, particularly for L X-rays of gold, commented on in the conclusions of [70]. The L X-ray values used were extracted from a
fit from [61]. The values were within the quoted experimental error (of 8.7%) of [71]. It is worth mentioning that the ratios of L X-ray lines quoted in the same reference are very similar to those used, which were from a more recent publication, [69]. The K production cross-sections were from [60] which provides a comprehensive list of reference values from interpolating after normalising and averaging experimental values.

The ratio of production cross-sections at mean proton energies were the dominant uncertainty in the mass value calculated from L X-rays. The most significant uncertainty in the mass calculated from the K X-rays was in the statistical uncertainty from the low yield. An uncertainty of 0.1% was assigned to the mass thickness of the gold foil, from the unevenness in the surface and possible crumpling (as investigated in §5.5.5) and also the value of the density of gold - 19.30g.cm\(^{-3}\) was the value used, from the online database presented in [26] collated from 4 different references on the properties of materials. Some other publications present the density of gold as 19.32g.cm\(^{-3}\), a negligible difference compared with the statistical uncertainties of yields.

The dominating errors in the backscatter calculations are from the statistical error on the backscatter yields, with the slightly larger error due to the lower yield from the smaller masked area used to collect the data. The backscatter masses were obtained by summing the counts from the two detectors, \(B_r\) and \(B_n\), from within the same mask area, and using the combined value in the calculation.

### 5.5.7.1 Correction for Variation in PIXE Detection Solid Angle

As discovered and discussed in §5.5.5.3 and §5.5.5.4 there is significant variation in the solid angle subtended by the \(P_i\) PIXE detection system, because of the CdTe detector being so close to the scanned area (closer than measured due to unspecified modifications made by the detector manufacturer and which cannot be obviated by using the second detector). Therefore the number of X-rays detected, and hence the calculated mass, will reflect the horizontal position of the sample within the scan area.

The horizontal gold profile from the foil standard can be used to correct for this, by comparing the mean yield of counts in the profile for the width and position of the scan
mask area of the sample and foil. The profile has some features deviating from the slope however these are small and should cancel, particularly in the regions of interest (right of centre). The mask used to obtain the number of L X-rays from the gold foil covered the entire foil region. Another way of compensating for change in solid angle across the width of the scan area would be to use a scan mask area of the gold foil of the same position and width of the sample scan mask area, however this would reduce the number of gold foil L X-rays, hence reduce the statistical accuracy from the gold standard.

So the value of $N_F$ for X-rays must be multiplied by the mean yield for the sample/foam from the relevant widths on the foil profile. Since the mass in the sample is proportional to $N_S/N_F$, this solid angle correction can be applied directly, by dividing the X-ray masses by the mean yield ratio as described above. The masses corrected for this variation in solid angle are given in table 5.5-5.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Mass ($\mu g$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K X-ray</td>
<td>5.2 ± 1.0</td>
</tr>
<tr>
<td>L X-ray</td>
<td>4.5 ± 0.6</td>
</tr>
</tbody>
</table>

Table 5.5-5: New mass values corrected for solid angle.

5.5.7.2 Dead-time Adjustment of $q_F/q_S$

The number of X-rays and backscatters recorded depends not only on the number detected but also on the dead-time of the octal multi-channel analyser system – common to all the analysers. During a measurement the overall dead-time was always ≤5%. The dead-time at any time is dictated by the summed rate of all four detectors (two backscatter, two PIXE) and consequently is a function of scan position – gold L X-rays from scanning the sample or foil are produced at a much greater rate than proton backscatters from the exposed carbon blocks. For samples containing gold flecks of ~5μm an unknown fraction of the beam will be essentially stopped by the flecks, thus as an initial measure of the ratio of beam fluence during foil and sample measurements the ratio of proton backscatters per unit area from areas on exposed carbon blocks, $q_F/q_S$ is used. The availability of a validation
sample containing submicron gold flecks – essentially a low density gold foil – allows the use of backscatters per unit area from carbon block beneath the sample $q_{S'}$ (and the 2μm gold foil $q_F$) as a separate measure of the proton fluence ratio $q_F'/q_{S'}$. Backscatters from carbon from behind the sample are subject to the same dead-time as the gold K X-rays, L X-rays and backscatters, in the foam or the foil.

For the foil, a mask was defined within the gold foil area on the scan. For the foam sample, in order to accurately calculate the emerging energy of the carbon block backscatters, a mask needs to be defined such that the backscatters emerge only through the foam (not through the foam/sleeve). For detector B₉, this is possible (see figures 5.5.7.19 and 5.5.7.20) – there is a substantial useful area at the top half of the front face of the sample. For detector B₇, because of the angle between the sample axis and the beam direction there is no such suitable area (see figures 5.5.7.18 and 5.5.7.20). Hence backscatters for the foil and the sample are generated for detector B₉, masked areas and corresponding backscatter spectra are shown in figures 5.5.7.1 and 5.5.7.2.

Figure 5.5.7.1: Spectrum of protons backscattered from a region on the copper mounting blocks covered by gold foil (shown as an insert).
The next stage was to define appropriate energy limits within the carbon region of the spectra. Previously, for measuring $q$, carbon backscatters from scan masks on exposed carbon, that is not covered by foil or a sample, were used from both experimental runs (in §5.5.4). With the carbon exposed, backscattered protons for both runs are detected with the same energies from the same depths in the carbon blocks. Energy limits were defined such that most of the carbon continuum was incorporated and these limits were to be used for all runs.

Now, with the beam passing through the foil or sample, the energy of the protons would be decreased by different amounts before reaching the carbon blocks; there is a need to compare protons backscattered from the same beam energy limits in the carbon.

Initial calculations (using $q_\text{F}/q_\text{S}$) of the gold mass in the validation sample using the backscatters from exposed carbon for normalising came to approximately 5μg; SRIM was used to evaluate the energy loss in this, the foam and the separate foil sample. The upper energy limit is determined when protons travel through the full length of the foam cylinder,
reaching the front of the carbon blocks with an energy, $E_H$, and backscatter from the front of the carbon block through the sample. The lower energy limit is where the protons travel through the sample, to a depth in the carbon block such that the proton energy is $E_L$, backscatter and travel through the carbon block and through the foam cylinder to be detected with an energy above the lower level discriminator cut-off threshold. Comparable limits for the foil standard were obtained by finding the depth at which the protons travelled into the carbon blocks, after first passing through the foil, to reach an energy of $E_H$ and $E_L$, and working out, using SRIM, the corresponding detected energies following backscatter at 165° and travelling back through carbon and the gold foil. The detected backscatter energy from $E_H$ for the sample and foam were 1.604MeV and 1.639MeV, detected backscatter energies from $E_L$ for the sample and foam were 759keV and 823keV. These limits are shown on figures 6.3.7.1 and 6.3.7.2.

Using these limits from the new masked spectra gives $q_F/q_S = 0.240$ compared with the uncorrected $q_F/q_S = 0.267$: 10% lower, which would reduce the mass by this amount. Thus the mass of gold in the validation sample from gold K X-rays, L X-rays and backscatter measurements are (given below in table 5.5-6):

<table>
<thead>
<tr>
<th>Technique</th>
<th>Mass (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K X-ray</td>
<td>4.7 ± 1.0</td>
</tr>
<tr>
<td>L X-ray</td>
<td>4.0 ± 0.6</td>
</tr>
<tr>
<td>BS - Large Mask</td>
<td>4.4 ± 0.1</td>
</tr>
<tr>
<td>BS - Small Mask</td>
<td>4.5 ± 0.2</td>
</tr>
</tbody>
</table>

Table 5.5-6: Mass values adjusted for dead-time correction.
5.5.7.3 Validation Sample Conclusions

Using data from the different measurements of PIXE gold L X-rays and PIXE K X-rays, and backscatters, the calculated total gold mass values for the validation sample were all in good agreement. This validates the technique of using K X-ray measurements to measure the mass.

The validation sample was found to have gold distributed uniformly across the surface area, in contrast with the preliminary sample, suggesting that there is a difference in the gold areal distributions possibly because of the fleck size (or some random defect).

The validation sample was found to have a gold backscatter spectrum corresponding to a low density uniform gold film — again in contrast with the preliminary sample — suggesting that the gold distribution in the preliminary sample is different, either:

- because of the fleck size, or
- because there is less gold near the sample end, or
- both of these reasons.

These differences are addressed further in the next section when considering the primary and secondary samples.

The 10% dead-time correction measured demonstrated that a difference exists in the system dead-time when scanning on the exposed carbon blocks or on the sample.
5.5.8 Experimental Results and Discussion (2)

5.5.8.1.1 Standard Size Fleck Samples

5.5.8.1.1.1 PIXE Spectra and Maps

Figure 5.5.8-1: Primary sample PIXE spectrum from a masked region within the sleeve, from $P_L$.

Figure 5.5.8-2: Primary sample PIXE spectrum from a masked region within the sleeve, from detector $P_R$. 

- 139 -
Figure 5.5.8-3: Secondary sample PIXE spectrum from a masked region within the sleeve, from detector $P_L$.

Figure 5.5.8-4: Secondary sample PIXE spectrum from a masked region within the sleeve, from detector $P_R$. 
The PIXE spectra were generated offline, from masks including the gold-loaded foam within the polyimide sleeve and excluding all else. As in the analysis of the validation sample, the primary and secondary samples’ PIXE spectra from detector P₁ (figures 5.5.8.1 and 5.5.8.3) contain gold L X-ray peaks with far better resolution than the corresponding spectra from detector P₂ (figures 5.5.8.2 and 5.5.8.4). This is because the background noise is much worse in detector P₂, which is particularly significant at higher energies with the low yield of K X-rays.

Despite the mask within the sample area excluding the copper wire support, a small peak ~8keV immediately to the left of the gold L characteristic X-ray peak remained where a large copper Kα X-ray peak had been (identified for the preliminary experiments in the PIXE spectrum in figure 5.4.5.2). This feature was neither present in the spectra generated from analysis of the foil standard nor for the validation (submicron fleck loaded) sample. Further investigation demonstrated that the peak came from the copper wire (present along most of the length of the cylinder), as a consequence of secondary interactions. 2D maps generated from this peak show events were detected from all areas of the scan i.e. when the beam was directed at all areas: some of the protons backscattered from within the cylinder or the carbon block hit the copper wire and generated characteristic copper X-rays.

To demonstrate this, maps have been generated from the copper Kα X-ray peak for the full scan area showing the end position of the copper wire, figure 5.5.8.5 and the scan area excluding the copper wire, figure 5.5.8.6, both for the primary sample.

Figure 5.5.8-5: Copper K X-rays from the full scan area on primary sample.  
Figure 5.5.8-6: Copper K X-rays from the full scan area on primary sample, excluding copper wire.
The vast majority of copper $K_{\alpha}$ X-rays are from the wire directly. Once this is excluded from the scan area, and the map is regenerated offline, copper $K_{\alpha}$ X-rays are detected as protons are directed on to both the carbon blocks and the sample. The tail of the gold $L_\alpha$ characteristic X-ray peak is under the copper $K_{\alpha}$ X-ray peak, so the gold in the flecks are also shown in the map. The white background is to show the low counts. As only the $L_\alpha$, $L_\beta$ and $L_\gamma$ X-rays are summed, the L X-ray yield counted is unaffected by these events.

**Figure 5.5.8-7:** Gold L X-rays from the $P_L$ detector for the primary sample.

**Figure 5.5.8-8:** Gold L X-rays from the $P_R$ detector for the primary sample.

**Figure 5.5.8-9:** Gold K X-rays from the $P_L$ detector for the primary sample.

**Figure 5.5.8-10:** Gold K X-rays from the $P_R$ detector for the primary sample.

Figures 5.5.8-7, 5.5.8-8, 5.5.8-9 and 5.5.8-10 are maps of gold X-rays for the primary sample. All show a concentration of gold loading towards the bottom-left of the sample as viewed, except for the K X-rays from the $P_R$ detector, figure 5.5.8-10. This is due to a low K X-ray yield and a high level of electronic noise intrinsic to this detector, shown in figure 5.5.8-2 - counts therefore do not necessarily reflect the presence of gold.
Maps of gold characteristic L and K X-rays from both PIXE detectors are shown in figures 5.5.8.11, 5.5.8.12, 5.5.8.13 and 5.5.8.14 respectively. The same trend of gold loading concentrated towards the bottom-left of the sample is observed as in the maps for the primary sample, again with the exception of the K X-ray map from the Pr detector – for the same reasons as in the Pr K X-ray map for the primary sample, figure 5.5.8.10.
5.5.8.1.1.2 Backscatter Spectra and Maps

Figure 5.5.8-15: Backscatter spectrum of the primary sample from a masked region within the sleeve, from $B_T$.

Figure 5.5.8-16: Backscatter spectrum of the primary sample from a masked region within the sleeve, from $B_B$.
Figure 5.5.8-17: Backscatter spectrum of the secondary sample from a masked region within the sleeve, from $B_T$.

Figure 5.5.8-18: Backscatter spectrum of the secondary sample from a masked region within the sleeve, from $B_B$.

The backscatter spectra shown above in figures 5.5.8-15, 5.5.8-16, 5.5.8-17 and 5.5.8-18 are from the two detectors for the primary and secondary samples. In each spectrum the gold step is a sloping continuum, as in the case of the sample used in the preliminary
experiment. This strongly suggests that this backscatter spectrum feature is not due to a random defect in the sample as conjectured (§5.4.6). A uniform step would be needed to obtain a reliable measure of the mass of gold; there are too many unknown variables in this backscatter situation. Again however a preponderance of gold flecks are measured towards the bottom left in the gold backscatter maps, shown below for both the primary and secondary samples in figures 5.5.8-19, 5.5.8-20, 5.5.8-21 and 5.5.8-22. (The Bg gold maps, figures 5.5.8-20 and 5.5.8-22, show this effect to a lesser extent because backscatters from gold in this region are reduced in energy as they traverse the sleeve at the bottom of the sample, arriving at the detector with energies below the oxygen edge.)

Figure 5.5.8-19: Gold backscatters from the B\textsubscript{T} detector for the primary sample.

Figure 5.5.8-20: Gold backscatters from the B\textsubscript{B} detector for the primary sample.

Figure 5.5.8-21: Gold backscatters from the B\textsubscript{T} detector for the secondary sample.

Figure 5.5.8-22: Gold backscatters from the B\textsubscript{B} detector for the secondary sample.
5.5.9 Data Analysis of Primary and Secondary Samples

5.5.9.1 Terms for Determining the Overall Mass and Average Size of Gold Flecks

The terms are as defined previously in §5.5.6. For the primary and secondary foam samples, the mean proton energy used for the production cross section was selected as the energy \( E_S \) at the centre of a gold sphere halfway through the sample.

The transmission through foam and sleeve was found to be 0.98 for the validation sample, this will be the same for the primary and secondary samples. The transmission of L X-rays through the gold flecks in the primary and secondary samples will be lower than for the submicron sized flecks in the validation sample, because of larger attenuation. With the average transmission of L X-rays in gold through a path length of average chord length of a sphere, then this will allow an average size of gold fleck for the primary and secondary sample to be calculated. (It is unlikely that an X-ray will interact with a second gold fleck).

The average path length for an X-ray to escape from a specific gold atom randomly situated in the volume of the sphere in a specific direction will be the average chord length in that direction in a hemisphere. This has been worked out very neatly by Dirac [72] to be a third of the diameter of the sphere.
5.5.9.2 Determining $N$ from PIXE Spectra

Figure 5.5.9-1: PIXE $P_L$ spectrum for primary sample, with background subtracted from gold L and K X-ray regions.

Figure 5.5.9-2: PIXE $P_L$ spectrum for secondary sample, with background subtracted from gold L and K X-ray regions.
PIXE spectra from detector $P_z$ for the primary and secondary sample are shown in figures 5.5.9.1 and 5.5.9.2, with underlying backgrounds subtracted (using the method explained in §5.5.6.2). Gold L X-rays were summed from 9.0keV - 18.2keV to include $L_\alpha$, $L_\beta$, $L_\gamma$ and $L_\gamma$-M coincident X-rays. L$_\gamma$ X-rays were excluded to minimise any unrelated counts of a tail from the extraneous copper peak (investigated and discussed in §5.5.8.1.1.1). Gold K X-rays were summed from 62.0keV - 81.0keV to encompass the $K_\alpha$ and $K_\beta$ X-rays.

5.5.9.3 Gold Backscatter Analysis

For both the primary and secondary samples in the main experiments, the gold backscatter step is a sloping continuum as in the case of the sample used in the preliminary experiment §5.4.5.2.2. This is strong evidence against the phenomenon being due to a random defect in the preliminary sample. To investigate, this spectrum feature, counts above the oxygen edge were divided into three energy regions with maps generated for each, shown below as figure 5.5.9.3.

As the proton traverses the foam, gold backscatters with the same energy at the detector have originated at different points in different gold flecks at different depths. At the highest
backscatter detected energy only the front surface nuclei of the gold fleck(s) at the left-hand edge will contribute. At lower energies there will be contributions both from deeper lying nuclei within a surface gold fleck and from nuclei in gold flecks at increasingly greater depths, suggesting a gold backscatter profile which increases with decreasing energy. As mentioned in §5.3.2 there will be observable contributions to the backscatter spectrum at energies above the oxygen edge from flecks down to a limiting depth in the foam, $D_L$. Figure 5.5.9-4 shows how flecks at different depths into the foam can produce protons of the same backscattered energy (the example given shows flecks to the limiting depth).

Figure 5.5.9-4: Diagram indicating that different depths of gold can produce backscatters which are detected with the same energy, up to $D_L$.

In addition to this effect, if the actual density of gold flecks decreased towards an end of the sample, then the observed fall-off with increasing energy would be even faster.

The preponderance of gold flecks in the bottom left hand region of both samples is commented on above. The areal distribution matches that in the case of the sample analysed in the preliminary experiment (figure 5.4.5.21 shows the gold backscatter map, figure 5.4.5.22 shows the PIXE gold L X-ray map). In that measurement a single PIXE detector was used, and the possibility existed of an experimental horizontal asymmetry. For the two samples analysed here, at a higher beam energy, the possibility of experimental asymmetries was eliminated from the improved experimental set-up, by using two X-ray detectors and two charged-particle detectors. The fact that all three samples show this preponderance of gold flecks in the bottom left hand region indicates strongly that it is a true measure of the gold fleck distribution when the samples were being analysed (see
figures S.5.8.7, S.5.8.8, S.5.8.11 and S.5.8.12 for the gold L X-ray maps of the primary and secondary samples respectively). As the samples were mounted with random orientations about the beam axis, this indicates that the preponderance was not the initial distribution. It must have occurred between the mounting of the sample in the chamber and the measurement.

From figure S.5.9.3, it can be observed that this areal asymmetry is due to flecks very close to the analysed end of the sample - the 'Au High E' section. The 'Au Medium E' and 'Au Low E' show an areal distribution of flecks that becomes increasingly uniform with decreasing energy. The flecks closest to the analysed end are the ones most likely to be affected when the chamber is evacuated. Inspection of the chamber revealed that the roughing pump port is located below and left with respect to the sample front face. It seems likely that the roughing vacuum pump has affected the gold loading near the sample front face. This is not observed in the validation sample containing submicron gold flecks; presumably these are much more strongly bound to the foam lattice than the large flecks - which are of order $10^9$ more massive that the submicron flecks.
5.5.10 Calculation Results (2) - Gold Mass and Average Fleck Diameter

The gold mass for the primary and secondary samples can only be calculated from the gold K X-ray measurements. As shown earlier, the backscatter spectra cannot easily be used to obtain a mass value and the L X-rays are also unsuitable as within the large flecks in these samples there is considerable attenuation of the L X-rays - which is unknown (as the flecks’ sizes are unknown). However once a mass is available from the K X-ray data, the average attenuation of L X-rays in the gold flecks may be estimated and hence their average diameter inferred.

<table>
<thead>
<tr>
<th>Foil Standard</th>
<th>Primary Sample</th>
<th>Secondary Sample</th>
<th>Ratio Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_{\text{total}}$</td>
<td>1,091,400 ± 1,000</td>
<td>458,780 ± 680</td>
<td>220,600 ± 470</td>
</tr>
<tr>
<td>$L_{\text{background}}$</td>
<td>56,070 ± 240</td>
<td>38,010 ± 200</td>
<td>21,680 ± 150</td>
</tr>
<tr>
<td>$L_{\text{nett}} : N_L$</td>
<td>1,035,300 ± 1,100</td>
<td>420,770 ± 710</td>
<td>198,920 ± 490</td>
</tr>
<tr>
<td>$N_\text{LS}/N_\text{LF}$</td>
<td>--</td>
<td>0.40641 ± 0.00080</td>
<td>--</td>
</tr>
<tr>
<td>$N_\text{LS}/N_\text{LF}$</td>
<td>--</td>
<td>--</td>
<td>0.19213 ± 0.00052</td>
</tr>
<tr>
<td>$K_{\text{total}}$</td>
<td>567 ± 24</td>
<td>505 ± 22</td>
<td>272 ± 16</td>
</tr>
<tr>
<td>$K_{\text{background}}$</td>
<td>142 ± 12</td>
<td>360 ± 19</td>
<td>180 ± 13</td>
</tr>
<tr>
<td>$K_{\text{nett}} : N_K$</td>
<td>425 ± 27</td>
<td>145 ± 29</td>
<td>92 ± 21</td>
</tr>
<tr>
<td>$N_{\text{KS}}/N_{\text{KF}}$</td>
<td>--</td>
<td>0.342 ± 0.072</td>
<td>--</td>
</tr>
<tr>
<td>$N_{\text{KS}}/N_{\text{KF}}$</td>
<td>--</td>
<td>--</td>
<td>0.217 ± 0.051</td>
</tr>
<tr>
<td>$a_F$ and $a_S$ (pixels)</td>
<td>34,569</td>
<td>20,894</td>
<td>21,085</td>
</tr>
<tr>
<td>$C_{\text{BS}}$</td>
<td>86,820 ± 300</td>
<td>600280 ± 780</td>
<td>137860 ± 370</td>
</tr>
<tr>
<td>$a_C$ (pixels)</td>
<td>10,741</td>
<td>7,649</td>
<td>4,116</td>
</tr>
<tr>
<td>$q$ (pixels)</td>
<td>8.083 ± 0.027</td>
<td>78.48 ± 0.10</td>
<td>33.492 ± 0.090</td>
</tr>
<tr>
<td>$q_F/q_S$</td>
<td>--</td>
<td>0.10300 ± 0.00037</td>
<td>--</td>
</tr>
<tr>
<td>$q_F/q_S$</td>
<td>--</td>
<td>--</td>
<td>0.2414 ± 0.0010</td>
</tr>
</tbody>
</table>

Table 5.5-7: Primary and Secondary samples - Number of counts of gold X-rays and backscatter normalisation data, with statistical errors quoted to two significant figures and data rounded accordingly. The ratios required for the mass calculations.
are presented in the same way, but were obtained from unrounded numbers. The terms are explained in §5.5.6.

The net yields for gold L and K X-rays from the gold foil are, as would be expected, much higher than those for the samples, shown in table §5.5-7. The values reflect that the primary sample was analysed for twice as long as the secondary sample.

For the K X-rays, using equations §5.5-10 and §5.5-16 with attenuations of 0.99 for both the gold foil and the gold/foam/sleeve the masses of the two samples uncorrected for the dead-time can be obtained, these values are given in table §5.5-8.

<table>
<thead>
<tr>
<th></th>
<th>Primary Sample</th>
<th>Secondary Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass from K X-rays, µg</td>
<td>2.2 ± 0.5</td>
<td>3.2 ± 0.8</td>
</tr>
</tbody>
</table>

Table 5.5-8: Masses from the K X-ray data for the primary and secondary samples.

The dead-time correction, 10% for the validation sample, should be much smaller for these samples because:

- the gold L X-rays are strongly attenuated in the gold flecks
- there is less gold present (lower masses).

Hence, as the uncertainty in the mass values derived from the present experiment, due predominantly to the low yield of K X-rays is already ~25%, the dead-time correction would be insignificant.

The masses calculated for gold in the primary and secondary samples, shown in table §5.5-8 are both lower than the masses obtained from 4 different techniques on the validation sample, roughly by a factor of 2. It is postulated that this may be due to some gold being removed from the sample by the vacuum, as considered in §5.5.8.3.

The average diameters were obtained by first calculating $M \times T_{av}$ from equations §5.5-10 and §5.5-16 using the gold L X-ray data.
For the primary sample: $M \times T_{AuS} = 1.8497 \mu g$

Thus: $T_{AuS} = 1.8497 / (2.2 \pm 0.5) = 0.84 \pm 0.19$

as the predominant error is in the mass determined from the K X-rays, $M$.

Using the same method, for the secondary sample: $M \times T_{AuS} = 2.0304 \mu g$

gives $T_{AuS} = 0.63 \pm 0.16$.

Now, from equation §5.5.25 and the average path length through a spherical gold fleck by the relationship given by Dirac (§5.5.6.1):

$T_{AuS} = (e^{1.135.27.193} \cdot D^3 + 0.685e^{-86.3.193} \cdot D^3 + 0.1e^{-138.193} \cdot D^3) / 1.785$

Thus, solving for the primary sample,

the average fleck diameter:

$D = (2.4 \pm 2.4) \mu m$

and for the secondary sample:

$D = (6.4 \pm 4.0) \mu m$
Conclusions from and discussion of large flack data

Backscatter measurements on carbon in the retaining carbon blocks have been used to provide the relative beam fluence through the cylindrical foam/gold samples and the gold foil.

Backscatter measurements from the gold flecks in the samples do not show the spectrum one might expect from a low density distribution of gold in the foam but one that slopes down towards the highest backscatter energies (as seen in our preliminary measurements). This has been qualitatively modelled, taking into account the actual distribution of the gold - substantial flecks located at widely spread intervals in the foam. However it is still feasible that, in addition, the overall gold intensity near the end of the foam may be less. This would also give a sloping distribution (as hypothesised in the work of Antolak et al [58] for molybdenum distributed at low density in foam).

One result of detailed lack of quantitative knowledge as to the origin of the RBS spectrum shape is an inability to use backscatter data to estimate the average density of gold in the foam and hence its overall mass.

PIXE measurements, detecting gold K X-rays have been used successfully to estimate the mass of gold in the foam – after correction of the spectrum for underlying proton bremsstrahlung.

PIXE measurements, detecting L X-rays have been used in conjunction with the mass of gold determined from the K X-ray measurements, to determine, from the attenuation of the X-rays, the average effective diameter of the gold flecks – again after correction of the spectrum for underlying bremsstrahlung (in this case atomic bremsstrahlung). The L X-ray attenuation has been modelled for the cylinder, its polyimide sleeve and spherical gold flecks.

The L X-ray maps of gold flecks in three separate samples show a preponderance of flecks in the lower left region (with respect to the beam direction) of the samples. This has been attributed to the effect of the chamber roughing vacuum pump, the connecting port of which is below the sample on the left-hand side.
Removal of large near-surface flecks by the vacuum pump is consistent with the backscatter spectrum observed: in the 'Au Medium E' region on figure 3.2.9 there is a ridge - the higher energy end corresponds with surface gold flecks predominantly in the lower left region, the lower energy counts originated uniformly from all regions.

On further discussion with collaborators, it is likely that they have encountered the same problem, when using such samples for their experiments. The researchers noted results which implied non-uniform gold loading discovered during experiments at the Omega laser facility. The samples are held under vacuum conditions, the first stage of which using a roughing pump.
Chapter Six: Conclusions and Further Work

The experimental projects described in this thesis developed novel techniques of ion beam analysis. For measuring the diffusion of heavy water into resin, a CZT array was used to provide a large solid angle charged particle nuclear reaction detector; the high stopping power of the material meant that the individual detectors were compact enough for the array to be placed close to the target. For measuring gold flecks dispersed throughout foam cylinders, a gold X-ray PIXE technique was used with commercially available CdTe photon detectors measuring both gold K and L X-rays, in addition to a complementary backscattering technique. The CZT array was useful in the subsidiary project, but could be developed to benefit further work on the main experimental project.

6.1 Subsidiary project - The Development of a Technique for Measuring Water Diffusing Into an Adhesive Resin Using a Scanning Microbeam and a CZT Array for Nuclear Reaction Measurements

The resin study demonstrated the successful application of the technique to the measurement of heavy water diffusion. This is the first time such a technique involving a CZT array has ever been used in NRA.

Vertical moisture diffusion profiles were measured directly from the interfacial region into the resin without breaking the resin/aluminium bond. The measurements on the 43 hour sample show qualitatively a flat vertical profile, whilst the measurements on the 96 hour sample imply an increasing trend towards the resin/aluminium bond. However, the validity of the results is compromised by the highly cratered surface of the samples provided; the craters lead to enhanced regions of high and low counts which distort the profiles.

Quantitative information was obtained from the horizontal profiles for both samples, exposed to heavy water for 43 and 96 hours respectively. Case II diffusion was observed and values of the velocity of the front and the diffusion coefficient of the exponential precursor were derived. That the horizontal profiles followed the shape of Case II diffusion, rather than the normally assumed Fickian has implications for the interpretation of standard indirect moisture uptake measurements.
There is wide scope for further work. Sample preparation is always a critical factor in such ion beam analysis techniques. Future experiments would best be performed on bonded resins without bubble craters; the accuracy of the results was compromised by bubbles in the bonding resin (which would ultimately reduce the surface area available for adhesion on along the interfacial region). Further, a flat surface extending to the full width of the sample would allow useful information to be obtained by a scanning beam.

It would be beneficial to use wider samples to better encompass long horizontal diffusion profiles. Samples exposed to moisture for many different times would be necessary to provide a comprehensive study. Also, a mixture of $D_2O$ and $H_2O$ should ideally be used; $D_2O$ was used a first approximation. A ratio of 10%:90% would provide a better approximation to water, as shown in [73]. This would require longer analysis times to compensate for the lower concentration of marker isotopes. The large solid angle CZT array would be ideal for these measurements. At the time of experiment, network difficulties meant not being able to record in list mode, which would have made it possible to investigate individual features. Future work should be recorded in this event-by-event mode.

Further work could also analyse a variety of different adhesives to investigate whether or not trends are common to different compositions. It would provide extremely useful information on bond integrity to many industries.

6.2 The Development of Techniques to Measure the Mass and Size of Gold Flecks in a Foam Matrix

To the best of my knowledge, this is the first time that CdTe detectors have been used for high energy PIXE X-ray detection of gold. Two extra backgrounds have had to be considered - atomic bremsstrahlung, proton bremsstrahlung - in addition to secondary electron bremsstrahlung.

The samples being studied by ion beam analysis, ~5μm and submicron flecks of gold distributed in a foam lattice, are also completely novel. The only previous work found being studied using RBS was on molybdenum distributed in foam.
I have shown, for the validation foam sample containing submicron gold bits, consistency between the three techniques of RBS, L X-ray and K X-ray detection, using a scanning microbeam, in determining the mass of gold.

To compare yield events to beam current, monitor backscatters per unit area from the exposed carbon blocks were recorded for both the samples and the normalization gold foil. With the scanning beam, the dead time can change with scan position depending on the X-ray, RBS yields from elements present at each scan position, namely gold, carbon and oxygen in the sample - carbon in the mounting blocks. Hence data was taken with a low (~5%) average dead-time. To determine any effect of dead-time the backscatters per unit area from carbon block behind the sample and the gold foil are also recorded as a separate monitor of beam current. Using this monitor the mass of gold measured in the submicron gold sample is ~10% lower than when the backscatters per unit area from the exposed carbon blocks monitor is used.

I have shown, for the primary and secondary samples, containing gold flecks of the order of several microns, that only K X-rays can be used in determining the mass of gold. For both these, the foil standard and the validation sample, the main source of the dead-time is the high yield of gold L X-rays.

For future work, on samples containing gold flecks of the order of several microns, the L X-rays should be discriminated out. This will both obviate the dead-time correction and allow, if it can be achieved, the use of a more intense beam current to increase the K X-ray yield. This would lead to a more precise measure of gold mass and average fleck diameter. However this may result in an unacceptable neutron background, and it is more likely that exposure to the beam of ~10 hours per sample will be needed at our 4.128MeV maximum energy. Alternatives would be to use the following, singly or in combination:

- X-ray detectors subtending large solid angles (see §6.3 below),
- a high energy accelerator (~7MeV) where the K X-ray yield is substantially higher, or
- a 'closed laboratory' accelerator where higher beam currents can be tolerated.
I have also shown that, for the gold samples with the larger gold flecks, those distributed near the end of the sample exposed to the beam are moved by the suction of the roughing vacuum pump. This problem can be obviated by the use of a baffle to prevent direct suction on the sample face and a reduced pumping speed. For the submicron gold flecks no effect of the vacuum pump on the flecks was apparent, the distribution was uniform at all depths. Presumably the small flecks are more strongly bound to the foam lattice than are the large flecks. I understand that a similar vacuum system is in operation when the sample is being inserted into position at the high power laser facility and have recommended that this be inspected to obviate any similar problem there.

6.3 The CZT Array

Since the experiments I have redesigned the CZT array. Encountering difficulties obtaining new detectors I designed the new array to house eight detectors from the original array, leaving four from the original should spares be required in the future. Removing the four corner detectors from the previous arrangement of twelve made it possible to significantly reduce the vertical size of the centre hole by lowering the top two and raising the bottom two; moving four of the side detectors closer to the centre compensates for the removal of those farthest from the centre. I also designed a shield to protect the detectors from being struck by the sample holder arm and target when first lowering it in to the chamber and subsequently positioning the target. The shield is attached in front of the detectors. It covers the normally extremely vulnerable thin platinum contact wire, and leaves the CZT detection areas completely exposed. I also designed a mount to make it easy to attach the array securely inside the microbeam chamber, with an adjustable distance from the centreline (where the target is held). The new CZT array is shown below in figures 6.3-1(a) and 6.3-1(b), without and with the protective shield respectively.
Figure 6.3-1: The new CZT array (a) without the protective shield, (b) with the protective shield. The special mount is also shown.

The eight detectors are connected in two groups of four, according symmetrically about the centre point of the hole, the position of the beam: the four CZT detectors aligned vertically at the sides and the four aligned horizontally above and below the hole. This means that the output from the two groups will be from CZT detectors which subtend the same solid angle from the target. The outputs can be kept separate to generate two spectra, with minimal angular spread providing better resolution of spectral features if this is of importance. In addition to this, the two groups can be further divided into four groups of neighbouring pairs. This design would be particularly useful should any of the fragile detectors develop a problem and produce a noisy spectrum, the pair containing the problem can be disconnected leaving the opposite two functioning.

The original array and this new modified array were both built with the intention of use in charged particle detection from nuclear reaction measurements. The material CZT was initially developed for photon detection. If the new array is further modified it could be a useful large solid angle detector for use in future work on the gold in foam project (the main experimental work in this thesis, Chapter 5).

The following modifications would be necessary, to successfully collect the smaller signals associated with detecting photons.
The first stage of amplification of an electronic system has the most influence on the overall signal to noise ratio. The cable that connects the detector to the preamplifier is a major contributory factor in this stage; it is beneficial to minimise the distance from the detector to the preamplifier or to eliminate this connection cable completely could significantly improve the detection system. The ability to connect the CZT detector pins directly to a preamplifier would therefore be useful. A small hybrid preamplifier, by the detector manufacturers 'eV Products Ltd.', is designed for this purpose. Shown in figure 6.3-2, to the right hand side of a detector with 10mm x 10mm x 2mm CZT crystal.

Figure 6.3-2: A small eV hybrid preamplifier (right), shown with a 10mm x 10mm x 2mm CZT detector (left). Reproduced from [40].

The two pins protruding from the back of the CZT detector slot directly into the two holes at the top of the preamplifier. The output connections of the preamplifier are basic pins. Work would therefore need to be carried out to not only to attach the preamplifiers to the detectors on the circuit board, but also to connect the outputs to standard preamplifier cables to outside the microbeam chamber via a flange.

The CZT detectors are capable of room temperature operation in photon detection, as demonstrated in the α-γ coincidence measurements in [3], however thermoelectric Peltier cooling to ~30°C might improve resolution by reducing leakage current [74]. Fitting Peltier cooling devices to the detectors on the array for use in vivo would be a substantial task. Experiments should first be carried out with the spare CZT detectors, to verify whether or not cooling would benefit the detection of photons with these particular detectors - some recent studies have suggested that cooling can reduce detection properties in CZT [75, 76].


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