Optimisation and application of AP MeV SIMS

by

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A dissertation submitted in partial fulfilment of the requirement
for the degree of

Doctor of Philosophy

at the

Ion Beam Centre
Department of Electronic Engineering
Faculty of Engineering and Physical Sciences
University of Surrey

March 2018
Abstract

Ion beam analysis comprises of a group of analytical techniques tackling the elemental composition of thin films by probing them with MeV ions. These techniques exploit information from photons and particles that come from the interaction of the MeV ions with the sample surface. Secondary ions, yet another species ensuing from such interactions can also be analysed providing information on molecular composition. The only ion beam analysis technique addressing the molecular composition is MeV SIMS, enabling detection and imaging of organic matter. The molecular detection and imaging of organic material is dominated by other surface sensitive techniques, such as TOF SIMS, providing a strong competition to MeV SIMS. In a pursuit to fully exploit the advantages of MeV SIMS in the field, the possibility to extract MeV ions into the air can also be utilised, thus offering the potential for application of ambient based MeV SIMS.

In this work, a fully ambient MeV SIMS setup is introduced and commissioned at the University of Surrey Ion Beam Centre, and termed “Ambient Pressure MeV SIMS”. The aims of this thesis are to optimise AP MeV SIMS for detection and imaging of organic species, as well as to explore potential applications for the technique. The complex optimisation of AP MeV SIMS described in this work encounters many parameters influencing either the electronic sputtering or gas dynamic of secondary ions. A great volume of the optimisation process has addressed the issue of an immense background contribution by investigation of its identity and origin. Moreover, the atmosphere encompassing the sampling area was investigated and the effect of different angles and types of a sheath gas directing the sample was tested.

The following work of this thesis demonstrates the application assessment of AP MeV SIMS. Here results of analysis of amino acids, explosives and synthetic organic pigments are
presented. Finally, a description of a feasibility study on merging of AP MeV SIMS and HIPIXE with a purpose of simultaneous molecular and elemental imaging under ambient conditions is given.
Acknowledgement

Many thanks to all who have helped me to achieve results in this ambitious project. Most of all I would like to extend my gratitude to the supervisors, Prof Roger Webb and Dr Vladimir Palitsin, firstly for giving me the opportunity to work in this field of research, and secondly for their valuable advices and guidance during the progress of the SPRITE project and over the course of my PhD.

Much appreciation is felt for technical help and theoretical insight given to me by Dr Julien Demarche in the first two years of the project.

I would like to acknowledge the Marie Curie Initial Training Network for the funding during the project.

I would like to express my thanks to Dr Kiron Prabha Rajeev for the support during the course of this PhD.

I dedicate this thesis to my Mother, who has always been there for me.
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1. Introduction

1.1 MeV SIMS

MeV SIMS is the mass spectrometry of secondary ions sputtered via interaction of a solid target with a beam of heavy ions. The secondary ion mass spectrometry using MeV ion beams is a surface sensitive technique as it sputters ions from the uppermost layers of a surface. Generally, mass spectrometry (MS) is an analytical technique based on separation and analysis of ions according to their mass to charge (m/z) ratio. Mass spectrometry is used in many different fields and is applied to pure samples as well as the complex mixtures. A mass spectrum is a plot of the ion signal as a function of m/z ratio and can be used to obtain information on the elemental or isotopic signature of a sample, the masses of particles and molecules and to elucidate chemical structures of molecules such as the lipids, proteins, nucleic acids and polymers. Samples in all three states of aggregation can be analysed in a typical MS experiment. There are many different sources used to ionise molecules in order to be detected by a mass analyser. Some of them will give molecular ions whereas others may cause some of the molecules to break into the charged fragments. The amount and the mechanism of the energy deposited into the molecular system determine whether a molecular ion or fragmented molecular ions will be the final outcome of an ionisation process. Following this criteria, a MS technique can be characterised as the soft ionisation technique invoking little fragmentation and the hard ionisation technique invoking high degrees of fragmentation. The generated ions are then subjected to an electric or magnetic field and separated according to their m/z ratio. Ions with the same m/z ratio will undergo the same amount of deflection. Lastly, the ions are detected by an ion detector. The choice of detector depends on the instrumental design and nature of the experiment each instrument was designed to perform. Most of the detectors used in MS are the particle detectors which will detect signal from incident ions by generating
secondary electrons which are then multiplied further. Others will detect signal from incident ions by inducing a current generated by a moving charge.

Whatever a specific configuration of a mass spectrometer technique may be, it will always comprise an ionisation source and a mass analyser. Considering different types of the ionisation sources, the ionisation processes in MS can be divided into the gas phase ionisation, field desorption and ionisation, atmospheric pressure ionisation, laser desorption and particle bombardment[1]. The main representatives of the gas phase ionisation group of techniques are Electron Ionisation (EI), Chemical Ionisation (CI) including the Desorption Chemical Ionisation (DCI) and Negative-Ion Chemical Ionisation (NCI). The field desorption and ionisation group of techniques are represented by the Field Desorption (FD) and Field Ionisation (FI) techniques, accordingly. There are many different MS techniques based on the atmospheric pressure ionisation such as Electrospray Ionisation (ESI) and Atmospheric Pressure Chemical Ionisation (APCI). The well-known representative of the laser desorption group of ionisation MS is Matrix Assisted Laser Desorption Ionisation (MALDI). Finally, MS techniques based on the particle bombardment are Secondary Ion Mass Spectrometry (SIMS) and Fast Atom Bombardment (FAB). Traditionally, primary ion beams in keV energy range were used in SIMS analysis. Nowadays, MeV primary ions are also employed for the SIMS analysis in a technique known as MeV SIMS. Heavy ions were already used in the 1970s to sputter molecules from insulators in a technique known as Plasma Desorption Mass Spectrometry (PDMS). The historical overview on the MeV SIMS will be given in the following section.
1.2 Evolution of MeV SIMS

MeV SIMS is a surface sensitive technique based on the analysis of emitted ions from the uppermost layers of a surface with a beam of heavy ions. The technique finds its background in PDMS technique invented in first half of 1970s by MacFarlane’s group at Texas A&M University[2]. In PDMS ejection of the analyte deposited as a solid film on a thin aluminium foil was achieved by bombardment with high energy fission fragments from $^{252}$Cf source such as 110 MeV $^{100}$Sr$^{20+}$ and 75 MeV $^{150}$Ba$^{20+}$, placed behind the foil. The mass determination was obtained with a simple linear time-of-flight mass analyser. Until the invention of the PDMS technique, protein and peptide analysis was performed with an Electron Impact (EI) technique, having a requirement for extensive derivatisation of the analyte which would modify it and give a complex spectrum followed by numerous fragmentation and rearrangement reactions. The available mass range and sensitivity was also considered to be a big disadvantage of the EI technique[3]. The MacFarlane group demonstrated the possibility of obtaining mass spectra of peptides of up to a molecular weight of approximately 3.5kDa and nucleic acids of more than 6 kDa[4]. Already a few years after, the scientific community recognised the significance of using heavy ions to desorb secondary species from the surface of multi-layered organic material. Tandem accelerators were used by groups at Darmstadt, Orsay, Erlangen and Uppsala in addition to $^{252}$Cf source in order to study various aspects of the basic mechanisms involved in PDMS. At the Uppsala University the first spectrum of insulin was obtained by bombardment with 80 MeV $^{127}$I ions from a tandem accelerator[5]. The Uppsala group also worked on a prototype $^{252}$Cf PDMS which they launched on the market in 1984 marketed by Bio-Ion Nordic AB[6]. Some of the important early experiments on analysis of biomolecules were carried out with these instruments by the Odense and John Hopkins groups demonstrating the significance of PDMS[7], [8]. Overall, more than 50 PDMS spectrometers had been used around the world[6]. However, in the second half of 1980s some new techniques for the
analysis of proteins and peptides were introduced which had a negative impact on the further development of the PDMS technique. These techniques were MALDI [9], [10] and Electrospray Ionisation[11] (ESI). In comparison to PDMS, both MALDI and ESI have demonstrated a better ability to produce gas-phase ions from proteins. On the other hand, mass spectrometry of the secondary ions, SIMS, had been introduced at the beginning of the twentieth century, after the experiments performed by J.J. Thomson where positive secondary ions produced by the bombardment of a metal surface in a discharge tube with a primary ion, were observed and identified[12]. Traditionally, SIMS was used to depth profile the elemental composition of inorganic materials and semiconductors. The real breakthrough in material characterisation with SIMS happened in 1970s when Benninghoven demonstrated that SIMS doesn’t necessarily need to be a destructive technique, and that so-called “soft” ionisation can also occur, if an ion dose does not exceed $10^{13}$ ions cm$^{-2}$[13]. In this mode, the characteristic secondary molecular ions can be generated from a surface or near surface region. The birth of Static SIMS presented a significant advancement for wider scientific community where magnetic sector and quadrupole mass analysers got replaced by time-of-flight mass analysers in a technique called TOF SIM, which is still one of the leading surface sensitive characterisation techniques. So where does the MeV SIMS belong among all these above mentioned techniques? To categorise MeV SIMS is not an easy task. Firstly, one should consider the underlying mechanism of MeV SIMS which is electronic sputtering, the same as in PDMS. Although, the development of PDMS has stopped, the unsolved problems in understanding the mechanisms of sputtering of large molecules from the surface via electronic energy loss has left the area open to further study by MeV SIMS. Secondly, from the point of view of the primary ion generation MeV SIMS can be considered as one of the set of IBA techniques. The major difference between MeV SIMS and other IBA techniques such as Proton Induced X-ray Emission (PIXE), Proton Induced Gamma-ray Emission (PIGE) or Elastic
Recoil Detection (ERD) is that MeV SIMS is used for the molecular analysis of organic molecules whereas all the other IBA techniques provide mostly elemental information and, perhaps, the chemical state. Lastly, MeV SIMS is a surface sensitive technique which can be utilised for molecular analysis; it has strong similarities with TOF SIMS and XPS. In terms of the applications, MeV SIMS is undoubtedly most similar to the conventional TOF SIMS technique, at least at first glance. Indeed, both of these SIMS techniques can be applied to numerous areas such as art, organic and biological materials, environmental analysis and forensics[14]–[18]. In art, for example, the application of SIMS can be used to study paintings authenticity by analysing pigment, binders and additives simultaneously, which is considered impossible to do with any other technique currently used such as Raman, UV-VIS spectroscopy and FTIR-ATR[19]. In material analysis, SIMS has been used for many different systems such as: nanomaterials, photovoltaics, polymer surface modification, catalysis, corrosion, adhesion, semiconductor devices and packaging, magnetic media, display technology and thin film coatings. Together with the applications, MeV SIMS and keV SIMS share other similarities such as mass resolution, sensitivity and potentially high spatial resolution. Yet, there are some substantial differences between MeV SIMS and keV SIMS which originate from the difference in the primary ion beam energy. MeV SIMS uses the same equipment as IBA and can be combined, even simultaneously, with other ion beam analysis methods such as PIXE to provide quantitative elemental and chemical composition together with the molecular one. Potentially most importantly, MeV SIMS can be performed in air under full ambient conditions, which opens the possibility for realising Ambient Pressure MeV SIMS (AP MeV SIMS). The era of the ambient mass spectrometry started over a decade ago with aim to explore new ways to analyse samples relevant to more “real life” applications with little or no sample preparation[20]. Since AP MeV SIMS widens the scope of vacuum MeV SIMS analysis and makes its applicable to areas of interested which were so far unreachable, it might be considered
as the next step on the evolutionary chart of MeV SIMS (Figure 1). Nowadays, there are several laboratories across the world exploiting MeV SIMS technique with most of them using the vacuum setup. Among the MeV SIMS laboratories only Kyoto University and University of Surrey Ion Beam Centre have developed fully ambient systems. The two ambient setups differ in ways how the sampling is being performed. Whilst in the Ion Beam Centre the beam nozzle, a sample, the mass spectrometry and the sheath gas capillaries are all placed in the open air, in the Kyoto University a target chamber with $10^{-1}$ atm pressure is used which is beneficial for the transport of secondary ions and suppression of the ambient background but limiting for the size and shape of the samples[21]. It is also worth mentioning the existence of a Coordinated Research Project, run by the IAEA, “Development of molecular concentration mapping techniques using MeV ion beams” which commenced in 2014. The aim of this project is to bring together all the MeV SIMS laboratories in order to organise a systematic set of experiments and simulations for better comprehension of the electronic sputtering, as well as promotion of MeV SIMS technique. Besides laboratories that are exploring the MeV SIMS technique for molecular concentration mapping, others using MeV ions for PIXE, known as HIPIXE, are also employed in the project[22]. Once more, the importance of merging IBA techniques has been recognised, and endeavours to strengthen each of them individually and make them more able to compete with other non IBA techniques such as EDX, XPS, TOF SIMS, etc. Obviously, there are numerous other techniques which also rival with IBA techniques. In order to be able to compete with them and develop new application areas new technical improvements and upgrades which could enable this should be considered. Of course, not every technique opens the possibility to be extended such as MeV SIMS. The versatility of MeV SIMS in the above overview illustrates its great potential, justifying the growing interested and emergence of MeV SIMS.
1. Evolutionary line of AP MeV SIMS. The birth of SIMS started in 1910 with J.J. Thomson’s bombardment of a metal surface in a discharge tube with a primary ion. Static SIMS emerged in the end of 1960’s. Soon after, the MacFarlane group presented generation of secondary ions from a peptide film via electronic sputtering using the $^{252}$Cf source, known as the birth of PDMS. PDMS will soon get replaced by MALDI and ESI developed by Hillenkamp and Fenn groups. In 2008, the Kyoto group starts to investigate the mass analysis of organic molecules in a technique known as the MeV SIMS. Currently, there are 6 laboratories, placed mainly in Europe, which are utilising the MeV SIMS. The Surrey Ion Beam Centre had commissioned the fully ambient application of MeV SIMS, known as the AP MeV SIMS.

1.3 Advantages of using MeV over keV primary ions in SIMS

The use of MeV ions in SIMS can be beneficial when compared to keV ions in several features. When lighter MeV ions are employed such as the $^{16}$O ions, MeV SIMS can be combined simultaneously with some other ion beam analysis techniques, such as the RBS and PIXE. The
concept of the merging of MeV SIMS and HIPIXE for simultaneous molecular and elemental mapping in the air will be explored later in this thesis. When heavy ions in MeV energy range are used in SIMS, higher secondary yields can be obtained. In this work, we measured secondary ion yields and damage cross sections for the leucine molecular ions using 4 MeV O\(^{4+}\), 5 MeV Si\(^{4+}\) and 25 kV Bi\(_{3}\)\(^{+}\) primary ions. The given results will show the highest secondary ions yield and the lowest damage cross sections were achieved with the 5 MeV Si\(^{4+}\) ions.

Employing MeV over keV ions in SIMS can also result in higher mass range. The higher secondary ion yields and the mass range obtained with MeV ions can be compared with keV cluster ions due to the non-linear secondary yield enhancement\(^{[23]}\) observed for the keV cluster ion beams such as gold, bismuth and argon clusters. The energy deposition for MeV and keV cluster ions will be addressed in the following chapter.

The most significant advantage of MeV ions over the keV ions is the ability of MeV ions to be extracted into the air. The concept of applying of MeV SIMS as an ambient mass spectrometry technique is the main objective of this thesis. AP MeV SIMS can be used for detection and mapping under fully ambient conditions with spatial resolving power potentially <5\(\mu\)m and, as such, can be very competitive to all the other ambient mass spectrometry techniques such as DESI and MALDI, which are usually achieving spatial resolutions of few tens of microns, even after being subjected to certain technical improvements. Moreover, a sample used in AP MeV SIMS analysis does not require to be dissolved or mixed inside of a matrix, thus showing a potential to be applied for molecules with a wide range of molecular structures. The comparison between AP MeV SIMS and some other mass spectrometry techniques such as DESI, DAPCI, LA-ICP, LAESI, MALDI and TOF SIMS will be drawn in chapter 3 where possible benefits of using AP MeV SIMS for detection and mapping of organic molecules over these techniques
will be described more into detail. Having an ambient mass spectrometry technique based on the analysis of secondary ions through sputtering with heavy ions capable to achieve spatial resolutions of few microns and to be combined simultaneously with other IBA techniques in order to support elemental composition and maps in addition to molecular composition and maps would be a very powerful analytical tool which could probably mainly be used for the cultural heritage analysis. However, in order to achieve it a great challenge of transporting of secondary ions into the mass analyser has to be overcome. The eternal battle of detecting signal over an immense ambient background is present in every ambient mass spectrometry technique. In our case, we are expecting the background to be very intense, as in SIMS only a few sputtered secondary species will get ionised and will need to compete with numerous molecular species present in the surrounding ambient which will get ionised through interaction with heavy ions.

1.4 Thesis Aims and Objectives

The research conducted in this work aims to explore the potential of MeV SIMS technique as an ambient mass spectrometry imaging technique. The Ambient Pressure MeV SIMS setup had been commissioned at the Surrey Ion Beam Centre in 2012. An extensive optimisation of the system which had been carried out through this project had modified it to the current state which can now be utilised for the mass detection and molecular imaging. The overall work of this thesis has several objectives addressed as following: exploring AP MeV SIMS as a special application of MeV SIMS and a new ambient mass spectrometry technique, optimisation of various parameters related to secondary ion yield and secondary ion transport, and possible application areas of AP MeV SIMS. As an extension to the applications, the feasibility of
merging AP MeV SIMS and HIPIXE for simultaneous molecular and elemental imaging under ambient conditions was investigated, which was the first attempt ever applied on a complex sample containing more than one organic and metallic component. Additionally, MeV SIMS and TOF SIMS measurements were performed in order to compare analytical performances and contribute to general understanding of material damaging with MeV and keV ion beams.

1.5 Thesis Overview

Chapter 1 begins with a definition of MeV SIMS. The general concept of mass spectrometry will be explained and a distinction between different groups of the mass spectrometry techniques based on the ionisation source will be drawn. In Chapter 1 the origin of MeV SIMS and AP MeV SIMS is presented with a scope of demonstrating the complexity and capabilities of the MeV SIMS technique. Finally, advantages of using MeV over keV ions in SIMS are outlined in this chapter. This thesis explores the potential of one of this advantages which is the application of MeV SIMS under ambient conditions for molecular detection and imaging.

In the following chapter, we review previous work upon which our research draws. In chapter 2 we survey energy loss of swift ions traversing matter which results in the ejection of secondary species through electronic sputtering. We will also discuss two basic approaches used to describe the electronic sputtering: Thermal Spike and Hydrodynamic Models. Next, experimental data on secondary yields and damage cross sections for 4 MeV O$^{4+}$, 5 MeV Si$^{4+}$ and 25 keV Bi$^{3+}$ primary ion beams will be presented. These measurements were conducted to compare efficiencies between primary ions in keV and MeV range. Lastly, we focus on
ionisation of the secondary species together with some effects that can alter the process of ionisation.

Chapter 3 is also a theoretical survey aiming to compare AP MeV SIMS with other imaging mass spectrometry techniques. Here, we developed an approach for choosing various parameters which will determine advantages and disadvantages of AP MeV SIMS over DESI, DAPCI, LA-ICP MS, LAESI, MALDI and TOF SIMS.

In subsequent chapters, an overview of the experimental work obtained in this research is given. In chapter 4 the challenges of AP MeV SIMS will be presented. This involves the effect of the atmosphere and transmission of secondary ions into the mass spectrometer capillary. The latter consists of heating and biasing of the mass spectrometer capillary, positioning of the mass spectrometer capillary with respect to the beam axis and angle of He flow capillary with respect to the sample. In chapter 4 we will then describe interaction of an external beam and target. Finally, we will discuss IBA under ambient conditions and merging of MeV SIMS and other IBA techniques.

Chapter 5 is an overview of the AP MeV SIMS setup at the Surrey Ion Beam Centre.

In chapter 6 optimisation of AP MeV SIMS is described. At the beginning, samples used in AP MeV SIMS will be presented and influence of the vapour pressure of samples on the mass detection introduced. The process of mass calibration following with determination of limit of detection will then described in chapter 6. Next, molecular detection of samples introduced at the beginning of this chapter will be shown. After the molecular detection, our focus will be directed into describing the background and memory effect found in AP MeV SIMS spectra. The optimisation process comprised of secondary yield comprised investigation of ion beam species and energies, primary ion fluence and an attempt of post-ionisation.
In chapter 7, a feasibility study of merging of AP MeV SIMS and HIPIXE for simultaneous molecular and elemental imaging in air will be presented.

Finally, a conclusion is given as a closure of the thesis.
2. Theoretical background of MeV SIMS

2.1 Introduction

This chapter tackles the theory behind the MeV SIMS technique. It starts with a brief description of the physical parameters which are secondary yield, damage cross section and efficiency. These parameters are the working functions of the technique. The following sections will explain the underlying theory of MeV SIMS which is the origin of these parameters. The interaction of MeV ions with matter will give an insight into the consequence of such interactions which will lead to the generation of secondary ions as a starting point of analysis using the MeV SIMS technique. Next subsection which will be depicted in this chapter is the energy loss of MeV ions in matter through nuclear and electronic stopping. This chapter also deals with some of the existing theoretical models covering the process of electronic excitation, which should give a better perception on how the secondary ions get emitted and ionised from the target. This is important due to the poor understanding in this area. In the following subsection, results on secondary yields and damage cross section and efficiencies for 4 MeV O^{4+}, 5 MeV Si^{4+} and 25 keV Bi_{3}^{+} primary ion beams for the leucine molecular ion will be presented. The next subsection considers the changes a molecular system undergoes when receiving external energy through the interaction with MeV ions and its causality with fragmentation, radicalisation and ionisation of molecules. At the end of the second chapter, an interpretation of potential changes in sputtering yield is mentioned, known as the matrix effect.
2.2 Physical parameters in MeV SIMS

2.2.1 Secondary yield

Secondary or sputtering yield is the ratio of the number of atoms sputtered to the number of impinging primary ions. Secondary yield depends on ion velocity, stopping force, charge state and angle of incidence [24]. Moreover, the chemistry of the target and ion beam species can significantly alter the secondary yield with a non-linear dependence. This is known as the matrix effect—see section 2.3.3.1.

2.2.2 Disappearance (Damage) Cross Section (DCS)

Damaging as a consequence of bombardment of the sample with a primary ion can be characterised by the damage cross section, \( \sigma \). This parameter determines the average size of the surface area damaged by one single primary ion bombardment. To avoid measurement of areas affected by previous probe ions the ion fluence has to be kept below what is termed “the static limit”. The static limit is defined as the ion fluence at which 10% of the surface atoms have been displaced by interaction with the primary ion beam. Also, we can rephrase this in a way that any of the signals should not change by more than 10% from their values at the beginning of the measurements. If we assume the proportionality of the time differentiation of the secondary ion yield, \( Y \) to the product of \( Y \) and flux, \( f \) then:

\[
- \frac{dY}{dt} = \sigma Yf
\]

Equation 1

where \( \sigma \) is a constant of proportionality. Therefore,
\[ \int_{0}^{t} \frac{1}{Y} \text{d}Y = \int_{0}^{t} -\sigma \text{f} \text{d}t \]

\[ \ln \frac{Y_t}{Y_0} = -\sigma \text{f}t, \]

and

\[ Y = Y_0 \exp(-\sigma \text{f}t) \quad \text{Equation 2} \]

where \( Y \) is the secondary ion yield after the irradiation and \( Y_0 \) the initial yield from the pristine sample[25]. The product of ion flux, \( f \) and time, \( t \) is ion fluence and it represents the number of primary ions hitting the sample area per cm\(^2\).

2.2.3 Efficiency

Another parameter that can be calculated if we know the value of damage cross section is the efficiency \( E_{\text{eff}} \) which is defined as the secondary ion yield, \( Y_0 \) divided by the damage cross section, \( \sigma \). The efficiency, \( E_{\text{eff}} \) can be described as the number of detected secondary ions when the outermost layer of the surface gets completely sputtered and provides a figure of merit for the technique.

2.3 Interaction of MeV primary ions with solid matter

MeV SIMS is the mass spectrometry of secondary ions created as a consequence of the interaction of a heavy ion beam and a solid target.
Formation of secondary ions from the surface or near surface regions is just one of the many events occurring when a MeV ion beam interacts with the material. Many other IBA techniques investigate other features such as the generation of X-rays, $\gamma$-rays, recoiled atoms or the backscattering of the beam (Figure 2).

![Diagram of IBA techniques](image.png)

Figure 2. Various events occurring as a result of the interaction of a MeV ion beam with solid with the common acronym of the IBA technique associated with each event.

Material ejection from a solid by, among others, an ion beam can be induced by several processes which can either act individually or simultaneously. These processes are beam-induced evaporation, nuclear (collisional, elastic, knock-on) sputtering, electronic (non-elastic) sputtering and desorption of thin layers[26]. The electronic sputtering is the underlying mechanism in MeV SIMS which is responsible for the production of secondary species. In contrast to evaporation where the material erosion is caused by many particles through a beam-induced heating, sputtering is described as the single-particle induced erosion of material. Desorption can be described as the removal of a part of a monolayer or full monolayers which are deposited on a different substrate [26]. Secondary species which will get sputtered via elastic or non-elastic collisions will mostly be in the form of neutral species such as atoms, clusters or molecules. It has been estimated that only one in thousand emitted species will be ionised [27]. Secondary ions can be the molecular species and their fragments. Fragments of
target molecules normally originate from a different radial region (infratrack) than intact molecular ions which are emitted in a region known as the ultratrack (Figure 3)[25]. All the emitted ion species can be extracted into a mass spectrometer where they can be detected by a mass analyser.

Figure 3. Interaction of a MeV ion beam with a solid surface where two different regions below surface are created. Infratrack is a cylindrical region of high density characterised by intense ionisations and excitations due to direct Coulomb forces. More remote regions are known as the ultratrack, where new generations of secondary ions are produced by high energy electrons (δ rays). Fragment ions are ejected from the infratrack while the molecular ions are ejected from the ultratrack[28].

2.3.1 Energy loss, $dE/dx$

Emission of material through the interaction with a MeV ion beam can be considered as an outcome of a chain of collisions with the nuclei and electrons in the target material. The incident particle beam will travel inside the target to a certain depth until it comes to rest. The
interaction of the ion beam and solid will cause energy and momentum transfer from the particle beam. The energy transfer followed by deflection of the ion trajectory is known as the term scattering[29]. The impinging ion will transfer energy to both the nucleus and electronic system of the constituent atoms of the target material. Hence, the ion scattering event can be characterised by the nuclear and electronic stopping. The term stopping force is used for the effectiveness of the target material in causing energy loss of the ion and determines the rate at which an ion slows down and comes to rest. Stopping force is the force that the medium exerts on the penetrating particle [26]:

\[
\frac{dE}{dx} \equiv NS(E)
\]

where \( N \) is the number density of atoms in the medium and \( S(E) \) the stopping cross section. Stopping force has the dimension [energy/length], whereas the stopping cross section has the dimension [energy x area]. The bombardment of a solid target and an ion beam will initiate collisions with the nuclei and the electrons. The former events will cause a large-angle scattering, whereas for the later events any significant deflection of the primary particle will be excluded. In parallel to the division of the collision processes, the stopping force can also be split up into the nuclear component, \((dE/dx)_n\), and the electronic component, \((dE/dx)_e\). The total stopping force is the sum of both of these components. The energy loss of an ion inside of the media is described by the four regimes characterised by different ratios between nuclear and electronic stopping forces caused by the projectile velocity (Figure 3). These regimes are the low energy (I), intermediate energy(II), high energy (III) and ultrarelativistic (IV) regime (regimes III and IV are not shown in Figure 4)[26]. The nuclear stopping is dominant in regime I but decreases gradually, which is inversely proportional to the electronic stopping. In regime II the electronic stopping follows the sharp rise and the nuclear stopping contribution to the
sputtering decreases significantly. The threshold value at which the nuclear stopping is much more effectively engaged into the sputtering process is when the ion’s velocity is below a velocity at \( v_B Z_{\frac{1}{2}} \), where \( v_B \) is the Bohr velocity and the \( Z_f \) is the atomic number[26].

At velocities higher than the threshold velocity the electronic stopping will prevail and become dominant[30]. Total energy loss for ion velocities below the threshold velocity can be estimated with the Lindhard-Scharff theory. The nuclear stopping can be expressed as[26]:

\[
N_{S_n}(E) = \frac{\pi a_s^2 \gamma N_s}{(E/\epsilon)} S_{n}(\epsilon)
\]

Figure 4. SRIM calculation showing nuclear stopping (red) and electronic stopping (black) as a function of primary ion energy for leucine target bombarded with chlorine ion beam. The nuclear stopping is higher up to energies at 1 MeV after which the electronic stopping starts to increase and becomes completely dominant. Nuclear stopping stagnates after 1 MeV.
where

\[ \gamma = \frac{4M_1 M_2}{(M_1 + M_2)^2}, \]

with \( M_1 \) and \( M_2 \) being the masses of the primary ion and the atom,

\[ a_L = \text{Lindhard's screening parameter}, \]

\[ a_L = 0.8853 a_B (Z_1^{2/3} + Z_2^{2/3})^{-1/2} \]

\[ \varepsilon = \text{Lindhard's reduced energy}, \]

\[ \varepsilon = \frac{(32.53M_2E)}{Z_1Z_2(M_1 + M_2)(Z_1^{2/3} + Z_2^{2/3})^{1/2}} \]

\( E = \text{energy in keV}, \)

\( S_n = \text{nuclear stopping cross section}. \)

The electronic stopping can be expressed as [26];

\[ S_e(\varepsilon) = k_L \varepsilon^{1/2} \]  

Equation 5

where \( k_L \) is a proportionality constant depending on the atomic number, the mass of the ion beam and the target atom.

At velocities higher than the threshold velocity the electronic stopping can be estimated with the Bethe-Bloch equation which describes the energy loss of swift particles by a distance of charged particles travelled of charged particles traversing matter[31].

\[ -\frac{dE}{dx} = \frac{4\pi e^4 Z^2}{m_0 v^2} NB \]  

Equation 6

where \( B \) is the “stopping number”, the atomic number adjusted depending upon the speed of the projectile.
\[
B \equiv Z \left[ \ln \left( \frac{2m_0v^2}{I} \right) - \ln \left( 1 - \frac{v^2}{c^2} \right) - \frac{v^2}{c^2} \right]
\]

and

\[
v = \text{velocity of the charged particle}
\]

\[
z = \text{charge of the charged particle}
\]

\[
c = \text{speed of light}
\]

\[
N = \text{number density of absorber atoms per unit area}
\]

\[
Z = \text{atomic number of absorber atoms}
\]

\[
m_0 = \text{electron rest mass}
\]

\[
e = \text{electron charge}
\]

\[
I = \text{A parameter, treated as experimentally determined, representing average excitation and ionisation potential}
\]

An important feature of the Bethe-Bloch approximation is the quadratic energy loss dependence on the charge and velocity of the incoming particle, \(z^2v^2\). Energy loss is independent of the mass of the incoming particle and relatively independent of the absorber material. It has been calculated that energy loss for the particles with same velocities is similar for different materials, with exception of the hydrogen\([32]\). According to Bohr’s estimation\([33]\), the average ion charge state of heavy ions is defined as:

\[
Z^* = Z_1^{1/3} \frac{v}{v_B}
\]

for the velocity range where \(1 < Z^* < Z_1/2\).
The average ion charge state increases with the ion velocity. An ion beam will reach a charge state equilibrium after having penetrated a few layers from the surface, regardless of the initial charge state [26]. However, energy transfer by electron pick-up can be substantially close to surface hence some charge effects might occur. Electronic stopping inside of the material is a simple function of the energy S(E), without taking into account the individual incoming ion and electron events due to a large number of such interactions and the frequent charge state changes the incident ions can undergo while traversing the medium.

2.3.1.1 Linear Energy Transfer (LET)

Linear Energy Transfer or LET is defined as the energy dissipated by an ionising particle per unit length of the track and is usually expressed as electron kilovolt per micron[34]. The ionising particle loses energy through excitation and ionisation of molecules along its track but also close to the track and in subsidiary short tracks called δ tracks. The δ tracks occur when an electron receives a sufficient amount of energy from the ionising particle and will then form a track of its own. When the total energy loss per unit length of the track is being considered, without taking into consideration any energy distribution to the neighbour of the track, LET is denoted as the \( \text{LET}_\infty \) and its value equals to the stopping force. The “local” LET describes the energy dissipated per unit length of track that is confined to the locality of the track. Generally, LET is used in radiotherapy to express the radiation quality. In order to describe the radiation, more than a single LET value needs to be employed due to change in LET value as the particle slows down. The LET values will be higher within the last few microns of the path when compared to the initial energy. When heavy particles are used to irradiate a target, LET is termed as the “high” LET in contrary to the “low” LET involving photons and protons. Heavy ions have the higher density of ionisation events over the photons and protons[35]. It is found
that the increase in the density of energy release by the ionising particle has an effect on molecular ions. The dependence of radical and molecular yields of papain enzyme on high LET presented in figure 5 showed that the radical yield reduced whereas the molecular yield increased[36].

Figure 5. The effect of \(^4\)He\(^{2+}\) LET on the Gibbs free energy of formation for • -Gr. N\(_2\)O saturated, ○ -Gr. N\(_2\) saturated, ■ -Gn.r. N\(_2\)O saturated, □ -Gn.r. N\(_2\) saturated.

The molecular and radical ion yields are represented by the Gibbs free energy of formation, \(G[37]\). The molecular ions are denoted as the reparable species, \(Gr\). whereas the radical ions are denoted as the non-reparable species, \(Gr.n\). both of these present in solutions saturated by either \(N_2O\) or \(N_2\). The Gibbs free energy of formation of the reparable molecular ions will increase with LET, whereas the Gibbs free energy of formation of the non-reparable radical ions will decrease with LET. In both cases, the Gibbs free energy of formation is higher for the solutions saturated by \(N_2O\) which can be due to reactive nature of \(N_2O\) stimulating the oxidation
reactions. The above-described effect of high LET on the molecular yields can be applicable for MeV SIMS as it is expected that for the heavy particles bombardments the concentration of secondary ions along the track will become higher when compared with the low LET.

2.3.2 Models of electronic excitation

Nuclear energy loss can be described as an elastic collision between the impinging ion and the target nuclei which can induce atomic displacements and phonons. Displacements occur when the energy transfer of the ion hitting the target exceeds the threshold energy, $E_d$, for its displacement, i.e. enough energy to break the binding forces and move the atom out of its original position[38]. For keV primary ions, sputtering is dominated by these nuclear collisions, and the ensuing cascade of moving particles can further induce desorption and ionisation of surface molecules. It can be described by Sigmund’s linear cascade model[13], where knock-on target atoms will induce a series of collision cascades of atom displacements within 30Å of the surface, in a billiard ball like movement. Some of the atoms participating in the collision cascade are directed towards the surface, causing the emission of sputtered particles. For MeV-primary ions, sputtering can also occur by transfer of the ion energy deposited into the electronic system to the kinetic energy of the nuclear system. The precise way in which this sputtering process happens is very much material dependent and has been studied mainly for frozen gases and inorganic molecules[39].
2.3.2.1 Thermal Spike Models

These models describe the ejection process as evaporation resulting from energy deposited in the vicinity of the surface, which subsequently becomes melted. The energy deposited by the ion into the electronic system is transferred to the host atoms via electron-phonon interactions which produce a high-temperature region formed along the ion trajectory. The electron-phonon coupling is based on the scattering of electrons by lattice vibrations. The energy of the lattice vibrations is characterised by the set of the numbers of phonons in the normal modes. The electron-phonon coupling is described by an interaction parameter, $G$ which represents the energy transferred between the electrons and ions. The parameter $G$ is estimated by the two temperature model (2T) which distinguishes temperatures for the electrons and ions. Besides the temperature dependence, $G$ is also influenced by the material structure [40], [41]. The energy transfer from the electrons to the atomic structure by the electron-phonon cooling will cause the production of tracks, surface hillocks and material modifications which is addressed in thermal spike models[42]. The ion track of ionised and excited species will be created in a time of around $10^{-15}$ s after a MeV ion hits the surface[43]. It should be noted that the track length can vary even for ions that have the same stopping force if they have different ion velocities[44]. Material defects and structure modifications appear after the material cooling and lattice recrystallisation[40]. Thermal spike models have many different variations mainly due to the difference in form of solid materials. In the amorphous materials the electron mobility is lower than that of the crystalline phase and hence the model needs some modification[45]. Electronic excitation can also induce a transition from the crystal to the amorphous phase. In the case of large thermally labile molecules, such as proteins, it is most likely that desorption of intact molecules comes from outside of the high energy density infratrack region[46]. It is more likely that large, molecular ions are ejected from the lower
energy density ultratrack region (Figure 3). In order to eject large intact molecules the coupling
between the excitation energy and the internal modes of the organic molecules must be weak,
otherwise, they will break. The process of sputtering from a surface which has been excited
with a MeV heavy ion through the creation of a thermal spike can be described by the time-
dependent temperature profile as suggested by Mozumber[47] :

\[ T_s = T_0 \left( 1 + \frac{4\delta t}{r_0^2} \right) - 1 \exp \left[ -\frac{-r^2}{r_0^2 + 4\delta t} \right] \] \hspace{1cm} \text{Equation 8}

where \( r_0 \) is the radius of a cylindrical track whose axis is normal to the surface with a distance
of \( r \) from the centre of the track, \( \delta \) is the thermal diffusivity and \( T_0 \) is the initial temperature.
This model uses a temperature profile which is appropriate for the ion solid interactions with
high linear energy transfer (LET)[48].

\[ T_0 = \frac{1}{\pi p C_v r_0^2} \frac{dE}{dx} \] \hspace{1cm} \text{Equation 9}

where \( p \) is the pressure and \( C_v \) is the heat capacity at constant volume.

The initial temperature \( T_0 \) is estimated through LET of the exciting ion, \( dE/dx \) using the
equation 9.
2.3.2.2 Hydrodynamic Models

Unlike the thermal spike model above, the hydrodynamic models, such as pressure pulse and shock wave, consider desorption of material as an ejection of the part of the track volume caused by high pressure. In the pressure pulse and shock wave models the momentum gives rise to the sputtering whereas the uniform energy diffusion in all directions is assumed different to the thermal spike which is random in its magnitude and direction[49]. In order to be ejected without a significant dissociation, the large molecules must reach a sufficient momentum without obtaining internal energy needed to dissociate. Both of these hydrodynamic models give rise to an expression for the sputtering yield as $Y \propto \left(\frac{dE}{dx}\right)_{eff}^3$. The sputtering is considered to be anisotropic with respect to the surface normal and results in a crater[50], [51]. A variety of craters shapes and depths will results as a consequence of the material ejection. The appearance of the crater has been investigated for many bio- and organic materials like L-valine, Langmuir-Blodgett (LB) films and immunoglobulin[52], [53]. For L-valine, different forms of craters and combination of craters and tails have been observed, whilst LB films craters are narrower and longer, with the appearance of some hillocks. In the case of immunoglobulin, craters were also narrow but surrounded with rims[52]. Hydrodynamic processes are used to explain ejection of intact, large bio-organic molecules. However, thermal spikes models cannot be fully excluded, especially in case of the volatile molecules[52]. All of these ejection processes are involved in some forms of deterioration, although occurring on different timescales[54]–[56]. It has been found that the incident angle has a profound influence on the form and depth of craters. Crater formation is also noticed when a keV cluster ion like C$_{60}^+$ or Au$_3^+$ strikes a surface. The combined energy dispersion for each the atoms in the cluster enhances the sputtering yield due to the increased energy density deposited in the surface of the material compared to a keV single atomic ion. The cluster creates a crater and sputters a
larger number of molecules[57]. In a cluster beam, the energy is distributed equally among all the constituent atoms and overall damage can be reduced. In the case of a 15 keV C\textsubscript{60}\textsuperscript{+} cluster instead of a single ion impacting the surface, there will be 60 separate collisions of 250 eV each[58], whereas a 15 keV Au\textsubscript{3}\textsuperscript{+} cluster will give 3 separate collisions of 5 keV each. Therefore, the projectile does not penetrate as far into the sample and a greater amount of energy is deposited in the surface region increasing the sputtering yield substantially. The fact that most of the energy is deposited close to the surface means that there will be less chemical damage left deeper in the target. When a cluster primary beam is used, the sputtering process can be characterised as a non-linear effect increasing sputtering and secondary ions yield[59].

A hypothesis used to explain how the increased ion yields are achieved by the cluster ions is describing producing of protons via a bond breaking mechanisms in the compressed region directly underneath the penetrating cluster[57]. These protons are then attached to neutral molecules, with preference to higher mass molecules which move slower, and form the quasimolecular ions. The non-linear sputtering effect could be utilised for getting a better insight on the energy deposition for the MeV ions due to the similarities with keV cluster ions. In comparison to keV ions, the clusters cause more “shallow” penetration, inducing so called soft ionisation just like the one observed when the MeV ions are used (Figure 6)[60]. A Molecular Dynamics simulation shows ejection of benzene molecular ions (red) and fragment ions (green) caused by bombardment with a 10 keV fullerene and a 6 MeV oxygen ion. In both of these processes, material is being ejected from a conical region with the fragmentation placed inside of a cylindrical region surrounding the ion track. The energised ion track caused by an MeV ion will be substantially longer which will cause more fragmenting of molecules and increase the volume and length of the cylindrical region. The longer ion track in case of the MeV primary ions will most likely make depth profiling unamenable since there will be a substantial volume of fragments along the ion path which will leave only lower mass fragments
observable. The comparison of the energy deposition path of MeV ions with that produced by cluster ions still provides valuable information in understanding the electronic sputtering process better. A similarity in the fragmentation patterns and yields between clusters and MeV ions indicates the similarities in the mechanisms of desorption between them.

2.3.3 Comparison of secondary yields, damage cross sections and efficiencies for 4 MeV O\(^{4+}\), 5 MeV Si\(^{4+}\) and 25 keV Bi\(_{3}^{+}\) primary ion beams

Measurements of secondary yields were performed using leucine thin film samples (100 nm) evaporated on Si wafer. The experiments were performed at the University of Surrey and at the Ruđer Bošković Institute in Croatia. In Croatia, only MeV SIMS was utilised, whereas in Surrey two different methods were used, MeV SIMS in the Ion Beam Centre and TOF SIMS.
in the Centre for Engineering Materials. At the Ruder Bošković Institute, a 5 MeV Si$^{4+}$ beam was accelerated from a 1 MV Tandetron and in the Ion Beam Centre, a 4 MeV O$^{4+}$ beam was accelerated from a 2 MV Tandentron. TOF SIMS measurements were performed with a TOF.SIMS 5 instrument using a 25 kV Bi$_3^+$ cluster beam.

Figure 7. Relative molecular yield for the leucine molecular ion, (M+H)$^+$ as a function of primary ion fluence, $f_t$ following an exponential decay (left) and the damage cross section, $\sigma$ calculated as the slope (right). Measurements were performed using the 4 MeV O$^{4+}$ beam.

Secondary yield follows an exponential decay as a function of primary ion fluence, $f_t$ with the slope, $\sigma$ representing the damage cross section (Figure 7). MeV SIMS measurements were performed with pulsed beam only. The ion fluence of impinging ions was determined from the beam current measured in a Faraday cup (Surrey) and from semi-direct measurement with a diode (Croatia)[61]. Uncertainty was estimated to be around 10%. Ion yield was determined as the integrated area of the corresponding peak divided by the number of impinging ions during the measurement. Hence, the error on impinging ion and the statistical error were both taken into account. The calculated values for yields, damage cross sections (DCS) and efficiencies
for 4 MeV O\(^{4+}\), 5 MeV Si\(^{4+}\) and 25 kV Bi\(^{3+}\) primary beam are presented in Table 1. The 4 MeV O\(^{4+}\) ions sputtered the least ions, whereas the 5 MeV Si\(^{4+}\) sputtered the most secondary ions.

<table>
<thead>
<tr>
<th>Ion Beam</th>
<th>Secondary Yield ((Y_0))</th>
<th>DCS ((\sigma/cm^2))</th>
<th>Efficiency ((E_{\eta}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>4MeV O(^{4+})</td>
<td>8.95E-05</td>
<td>8.60E-14</td>
<td>1.04E+09</td>
</tr>
<tr>
<td>5MeV Si(^{4+})</td>
<td>3.70E-02</td>
<td>8.69E-14</td>
<td>4.30E+11</td>
</tr>
<tr>
<td>25kV Bi(^{3+})</td>
<td>2.71E-03</td>
<td>4.06E-13</td>
<td>6.68E+09</td>
</tr>
</tbody>
</table>

Table 1. Calculated values for secondary yields \((Y_0)\), damage cross sections \((DCS, \sigma)\) and efficiencies \((E_{\eta})\) for the leucine molecular ion, \((M+H)^+\).

The highest secondary yield achieved by the 5 MeV Si\(^{4+}\) is in an agreement with the previous studies which have shown higher secondary yields when higher primary beam energies and masses were used[62]. The damage produced by 4 MeV O\(^{4+}\) and 5 MeV Si\(^{4+}\) beams is very similar but the 25 kV Bi\(^{3+}\) created one order of magnitude greater damage. Interestingly, the 5 MeV Si\(^{4+}\) ions are two orders of magnitude more efficient than cluster TOF SIMS with 25 kV Bi\(^{3+}\) beams showing six fold better efficiency than the 4 MeV O\(^{4+}\) ions. The damage cross sections for amino acids on metal substrates under the bombardment of a 2.5 keV Ar\(^+\) beam had been previously determined by Benninghoven et at all at approximately \(\sigma = 10^{-14}\) cm\(^2\).

2.3.4 Ionisation probability

The secondary species emitted from the surface will have a range of kinetic energies which depends on the choice of primary atom species as well as its energy and the angle of incidence. Moreover, the type and number of bonds of the targeted sample will influence significantly the
formation of secondary species, both neutral and ionic. In order to understand the process of molecules fragmentation, the bond cleavage energy should be calculated. First of all, we need to define the enthalpy \( (H) \) of a system. Enthalpy is contributing to the total energy of a system together with its kinetic and potential energy and it comprises of internal energy \((U)\) and the product of the pressure of the system and volume \((pV)\). We can describe enthalpy as a function of heat and work energy. For an ideal gas, the \( pV \) will equal \( RT \), whereas at \( T=0 \) the enthalpy will only be determined by the internal energy of the system. Internal energy comprises of electronic \( (E_{elec}) \), vibrational \( (E_{vib}) \), rotational \( (E_{rot}) \) and translational \( (E_{tran}) \) energy. The whole molecule is under a constant translational and rotational motion. At \( T=0 \) a molecule is in its ground state and each of these four parameters is in so called eigenstate\([63]\). In the interaction of an ion beam and molecules, discrete energy packages will be absorbed by molecules which will shift them into excited eigenstates. Fragmentation will occur if the internal energy overcomes the dissociation energy or at least equals its value, but not for values below the dissociation energy\([64]\)–\([66]\). The dissociation energy is inversely proportional to the bond length meaning that dissociation energy will be lower for single bond molecules than for double bond ones. Double bond molecules will have lower dissociation energy than triple bond molecules. Is it important to note that breaking of a bond is just an initial step in the complex process of creating ions which require an additional energy. In MeV SIMS the ionisation of molecules will occur in several ways. Unlike MALDI where multiple charged ions can occur, in MeV SIMS only single charged ions are found to be present. The polarity of these ions is generally a matter of the molecule structure rather than the beam properties although the beam atomicity and charge can stimulate the creation of ions with a certain polarity in a process known as a chemical enhancement. The principal fragments called the molecular secondary ions are mainly generated by protonation which will give cations whilst deprotonation will give negative ions or anions. The situation of creating cations and anions in SIMS is far from being
straightforward and in some cases, the protonation will give anion instead of cation and vice versa. These species are known as quasi-molecular ions and have been observed in Heavy Ion Induced Desorption (HIID) and keV SIMS[67], [68]. The formation of molecular radicals is also a common occurrence in keV SIMS[13]. Such molecular species could probably appear in MeV SIMS as well. Since the molecular parent ions are energetically unstable they will form daughter ions, the fragments. The simplest way is the formation of two fragments from a parent ion but most often, especially for the molecules with higher molecular weight, the parent ion will give multiple fragments which won’t be easily identified as the species originating from the principal fragment, especially for the analysis under ambient conditions. Besides principal molecular fragments, a molecular cluster can also be created in reactions of building adducts with either another molecule or a specific fragment[69]. To determine the fragmentation patterns of molecules is a very challenging task especially for the MeV SIMS community which is lacking on a spectral library which is a useful aid for spectral analysis. Each mass spectrometry technique induces different ways of fragmentation and therefore the spectral libraries from other technique can often only give information of fragmentation possibilities for a specific molecule but in most cases, it isn’t well reflected in the MeV SIMS analysis.

2.3.4.1 Matrix effect and chemical enhancement

The interpretation of secondary ion mass spectra is a complex task due to number and variety of different fragments organic molecules are likely to generate and the influence of surrounding environment for the targeted molecules, i.e. the matrix effect which will cause the discrepancy in sputtering yield[70]. The interferences in the sputtering yields due to the matrix effect make quantification of SIMS very difficult. The matrix effect originates from the ionization efficiency and the sputtering yield and is a function of the electronic (and vibrational) states of
both the sputtered species and the surface as well as the chemical bonding of the species to the surface and has mainly been exploited by desorption mass spectrometry techniques, FAB and MALDI[71],[72]. The main sources of the matrix effect are ion beam and species present in the sample. Primary ion beam effect on the secondary ion yield is being reflected as an enhancement of positive or negative secondary ions which can range up to the four orders of magnitude. An oxygen beam, showing great electron affinity, helps create more positive secondary ions, whilst a cesium beam excites more electrons over the surface potential barrier, being an electropositive atom[73]. In order to achieve the best detection sensitivity the choice of primary ion beam should be taken into consideration. The chemical environment also alters the yield of sputtered ions in a way that some surrounding species can attract or lose electrons or protons and suppress the signal from the original species[74]. The quantification has been developed for the elements and inorganic molecules with the aid of relative sensitivity factors, RSF[75]. The concentration of an element of interest can be derived from the impurity element and the reference element. The RSF are generally derived from the measurement of ion implanted standards or other calibrated standards[76]. The matrix effect presents an obstacle in the quantification of the secondary ion mass spectrometry techniques, but can also cause the misinterpretation of a presence of a certain species. In TOF SIMS characterisation of a rat brain section with haloperidol solution spun cast on the surface, the images of haloperidol showed its localization albeit it was spread homogeneously over the whole surface of the sample. The haloperidol was chemically enhanced with molecules of cholesterol and it appeared that is was present partially in the rat section[77]. The proposed solution for trying to reduce the matrix effect is the use of MetA-SIMS. This approach has been firstly introduced for the ubiquitous plasticiser, PDMS and later used for some other polymers like Irganox 1010[78]. The results showed not only the detection of the metal-cationised quasi-molecular ion but also the increased intensities of positive and negative ion species originally present in the sample. The
MetA-SIMS works on a principle of matrix exchange whereas the metals, mostly silver and gold, added into substrate caused a new matrix effect which suppressed the original matrix effect[79], [80]. Besides the MetA-SIMS another approach which is already well known from some other techniques like PDMS and MALDI is Matrix-enhanced (ME-SIMS). ME-SIMS is the most popular sample preparation technique leading to a secondary ion yield improvement[81]. This approach of ion yield enhancement employs a sample pretreatment by mixing it with an organic matrix which is chemically selective for a molecule whose ion yield we would want to alter. Unlike the MetA-SIMS, the ME-SIMS is unsuitable for imaging due to potential changes in the sample a matrix can cause[82].
3. AP MeV SIMS as an imaging atmospheric mass spectrometry technique

3.1 Introduction

In the third chapter of this thesis, the background of AP MeV SIMS together with its position amidst other IBA and MS techniques was described. Furthermore, the emphasis was put on the interaction of MeV ion beam with solid matter. This chapter heads away from the MeV SIMS part of AP MeV SIMS and concentrates on the similarities between AP MeV SIMS and other imaging mass spectrometry techniques, especially ambient ones. Ambient mass spectrometry techniques, like AP MeV SIMS, encounter all the challenges originating from the transport of ions into the analyser, and the impact of the surrounding ambient surrounding on sensitivity. Hence, as a starting point of this third chapter, atmospheric mass spectrometry techniques will be defined, and their applicability in this area summarised. After their general description, a comparison between atmospheric mass spectrometry techniques and AP MeV SIMS will be drawn. Considering the differences between ionisation sources and ionisation processes, atmospheric mass spectrometry techniques can be divided into three mains groups: spray, plasma and laser based ambient mass spectrometry techniques. Specific representatives of each group will be discussed, and a brief summary of their performance given in order to demonstrate the extensiveness, in terms of possibilities for modification these techniques can offer, according to the analytical demands. Not many techniques show this type of “flexibility”, hence it has to be outlined. A direct comparison between other ambient mass spectrometry techniques and AP MeV SIMS should consider seven points, which could be employed as useful criteria when it comes to choice of the most suitable technique. These points are: (i) the underlying mechanism: (ii) surface damage: (iii) change of physical state of the sample surface: (iv) geometry: (v) fragmentation: (vi) resolving power and LOD: and (vii) possibility to
implement chemical reactions. In the following section, we will compare MALDI and TOF SIMS. Both of these two techniques dominate in some means of analytical performance that is not possible by the others. They also share historical ties with (AP) MeV SIMS and much more, in comparison to TOF SIMS. To close this chapter, common analytical performances (the seven points mentioned above) of all the technique described are presented in a table and commented on accordingly.
3.2 Development of Atmospheric Mass Spectrometry Techniques

The rise of new atmospheric mass spectrometry techniques over the last decade has been enormous; there are currently over 30 acronyms for such techniques. Ambient pressure mass spectrometry (APMS) is defined as a technique that requires minimum or no sample preparation, with ionisation occurring at atmospheric pressure. According to this definition, MALDI and ESI could be excluded from this group since they both require certain sample preparation. In the case of MALDI, samples have to be co-crystallised with a suitable matrix, whereas in ESI samples have to be dissolved in an appropriate solvent such as acetonitrile, methanol or water. MALDI, ESI as well as Electron Impact ionisation (EI) and Chemical Ionisation (CI) techniques require enclosed ionisation such as in a capillary (for ESI), or a specially designed vacuum chamber (for MALDI, EI, CI). Another common feature of APMS techniques is the speed of analysis, with little or no sample or equipment preparation the analysis time can be as short as seconds. Thus, the demand for sample preparation present in MALDI definitely acts as a constraint in the application spectrum of these two techniques, as it is very hard to develop a suitable matrix for every sample being analysed or match its solubility unless a standard matrix can be used. The broad application spectrum is exactly what makes APMS techniques attractive to the scientific community, and is what creates the need for their further development and coupling to each other. An example of applying APMS techniques includes the trace analysis of food products, such as the controversial case of melamine in milk powder originally analysed by Desorption Electrospray Ionisation (DESI), and also analysed by employing other atmospheric mass spectrometry techniques, such as Direct Analysis in Real Time (DART)[83], [84]. Other examples include environmental analysis, such as the analysis of organic aerosols using Aerosol Flowing Atmospheric-Pressure Afterglow Mass Spectrometry (AeroFAPA-MS), or monitoring of pesticides in groundwater analysed with a combination of liquid chromatography and atmospheric pressure chemical
ionisation mass spectrometry[85], [86]. Together with food quality and environmental analysis, APMS techniques find their application in pharmaceutical and biochemical fields, such as drug quality assurance and metabolomics research[86]–[88]. A particularly interesting biochemical application is in vivo analysis. Considering two features of APMS techniques, which are that they are non-invasive and rapid, these techniques can be utilised for analysing living organisms at a molecular level for various purposes, such as studies of chemical mechanisms that would benefit clinical diagnostics and pharmaceutical therapy. An example of a rapid ambient analysis which could be applied for the in vivo analysis is the detection and quantification of complex viscous samples based on Neutral Desorption Extractive Electrospray Ionisation Mass Spectrometry (ND–EESI-MS)[89]. Further to the aforementioned uses of APMS techniques, some of them are also capable of obtaining molecular images. Direct mass spectrometry imaging is of great importance for biomedical analysis. The most popular atmospheric mass spectrometry technique for imaging is DESI. The first image obtained using DESI was a 2D image of rat brain tissue where specific lipid molecules were distinguished from sub-anatomical brain structure[90]. Ambient mass spectrometry imaging has also been demonstrated with other techniques such as LAESI (Laser Ablation Electrospray Ionisation) and Desorption Atmospheric Pressure Chemical Ionisation (DAPCI) in several examples of imaging biological tissue as well as document identification[91], [92].

The development of ambient mass spectrometric techniques also resulted in the development of small field-portable ambient mass spectrometers. Although the larger counterparts are still dominant in terms of the sensitivity and mass resolution, the need for portable mass spectrometers pushes their development strongly forward. Utilisation of portable mass spectrometers is particularly useful for purposes of homeland security, terrorism and forensics where rapid analysis is required at the scene rather than the laboratory.

The aim of ambient mass spectrometry is to detect organic entities in their natural environment,
which always involves complex matrices. The chemical effects of such matrices can cause misinterpretation of molecular species present in the sample or miscalculation of their quantity[93]. Hence, quantification is not a simple process, and often requires a number of standards of known concentration. However, most of the analyses lack a full understanding of the sample matrix, presenting a certain disadvantage for the analysis.

Furthermore, in contrast to exploiting the numerous applications of APMS techniques, significantly less effort has been applied to investigations of underlying ionisation mechanisms. It is also worth mentioning that although, from a theoretical point of view, there are no limitations in the size and shape that samples could take in ambient analysis, that might not be the case from a practical point of view as in most cases the size of the sample is determined by the size of ionisation source, unless there is the option to employ scanning. Finally, significant background originating mainly from the surrounding ambient atmosphere makes the APMS spectra difficult to understand and interpret.

### 3.3 Comparison of AP MeV SIMS with other ambient imaging mass spectrometry techniques

AP MeV SIMS has all the features of an APMS technique; it enables direct and rapid analysis with minimum or no sample preparation. Additionally, it can be used for molecular imaging just like DESI, DAPCI or LAESI. The ionisation source in case of AP MeV SIMS is a MeV ion beam which employs an accelerator, making it more complex from a technical perspective than the rest of the ambient mass spectrometry techniques. Thus, the overall performance of an AP MeV SIMS experiment is technically more demanding than any other APMS technique. Generally, APMS techniques differ in mechanisms of generation of ions from the target. One of the criteria for examining APMS techniques is the distinction of ionisation and ejection
processes. In AP MeV SIMS, DESI and MALDI, both of these processes are caused by a single agent. In all the other APMS techniques described here, these processes are usually divided into two steps.

3.3.1 Desorption Electrospray Ionisation (DESI)

DESI is a spray based technique used for the analysis of gas-phase ions originating from secondary micro-droplets. The DESI process, known as the ‘droplet pick-up’ mechanism, is complex in nature as it consists of multiple events[94]. The surface of a material firstly gets wetted in order to dissolve its constituents. A micron thick wet film is then removed from the surface and the dissolved molecules will become ionised by primarily charged droplets, which generate secondary micro-droplets. The formation of both primary and secondary droplets has been explored using Phase Doppler Anemometry (PDA) and numerical simulations[95]. The primary droplets have an average diameter of 2-4 µm, and speed of 120 m/s under a typical DESI experiment. The secondary droplets vary between 0.5 and 10 µm in diameter and have a range of velocities dependable on the size of the primary droplet, the take-off angle, and the distance from the impact point[95], [96]. Numerous factors have an impact on the performance of a DESI experiment, such as polarity, the electrical conductivity of surface, the choice of solvent, and geometry[97], [98].

3.3.2 Desorption Ambient Pressure Chemical Ionisation (DAPCI)

DAPCI was developed in order to extend DESI to the analysis of molecules with low polarity since DESI can only be used for the highly polar molecules. The ionisation mechanism
involved in DAPCI is different compared to that of spray based techniques. The charged solvent mist used in DESI is replaced by a solvent vapour created by corona discharge. The DAPCI setup involves a capillary with a tapered tip, stainless-steel electrode directed towards the sample surface. An inert sheath gas passes through the capillary and flows to the emitter at high velocity. A high DC voltage (3 to 6 kV) is applied to the electrode inducing a corona discharge at the tip of the electrode, which will ionise the solvent vapour. In some cases, the sheath gas may be heated[99], as well. The process of ionisation occurs after the desorption of neutral species from the surface into the gas phase, which is very similar to the one in APCI consisting of proton/electron reactions or some other ion-molecule reactions[100]. The desorption process employed in DAPCI is unclear, unless a heated sheath gas is employed, which then includes thermo-desorption.

3.3.3 Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP) and Laser Ablation Electrospray Ionisation (LAESI)

Coupling of mass spectrometry techniques with other mass spectrometry as well as some non-mass spectrometry techniques has always been driven by the need to enhance the analytical capabilities of an individual technique. Examples of such coupled techniques are LA-ICP MS and LAESI. Laser desorption/ablation based mass spectrometry techniques have been widely used to examine large molecules like peptides, although they are also suitable for analysis of organic dyes, porphyrins, organic salts and UV-light absorbing synthetic polymers. Laser ablation creates a great number of neutrals, similarly to electronic and nuclear sputtering in SIMS, which makes them suitable to be combined with post-ionisation techniques. The most established atmospheric pressure laser ablation mass spectrometry technique is LA-ICP, where the ablated material from the surface gets atomised and ionised in the high-pressure plasma.
LA-ICP has been widely used for chemical imaging of biological tissues, with a spatial resolution of a few micrometres achieved in recent years[101]. In LAESI a solid surface is first ablated by a pulsed infrared laser at atmospheric pressure followed by secondary ionisation of ablated material with an ESI source. The advantage of using the IR laser is that biological samples do not require drying prior to analysis since the resonant frequency of water is in the IR part of the spectra.

3.3.4 Comparison of AP MeV SIMS with DESI, DAPCI, LA-ICP MS and LAESI

The comparison of AP MeV SIMS with DESI, DAPCI, LA-ICP MS and LAESI is covered by the following points:

- **Underlying mechanism**
  MeV primary ions cause desorption and ionisation of secondary ions via electronic stopping. One of the possible explanations of the mechanism is based on shock wave and pressure pulse models described in section 2.3.2. In DESI, sputtering through momentum transfer during collision or ionisation by other electronic processes is excluded since the kinetic energy of primary droplets is less than 0.6 meV[95]. In LA assisted techniques, three thermal processes are responsible for the material removal; vaporisation, normal (equilibrium) boiling, and explosive boiling (phase explosion)[102]. Which one of these mechanisms will prevail is dependent mainly on the laser properties.

- **Surface damage**
  In SIMS, only the uppermost layers get sputtered making it a surface technique.
Conversely, DESI causes damage depth on a macroscopic depth[103]. The material depletion in DESI is dependent on the solvent, for example, typical aqueous combinations of solvents used in DESI (such as MeOH:H$_2$O and ACN:H$_2$O) are more damaging for biological tissues than non-aqueous solvents (such as ACN:DMF and EtOH:DMF (1:1)), which are considered to be morphologically friendly[103], [104]. In AP MeV SIMS a parameter which can cause visible surface damage is the beam current, which, in our experience, would have to be greater than a few hundreds of pA. LA-ICP MS and LAESI leave visible morphological changes on surface samples known as ripples and craters.

- **Change of physical state of the sample surface**

In DESI the investigated material gets wetted by the solvent, which makes this technique (together with damaging of the surface) unpropriate to be applied in analyses focused on cultural heritage investigations. DAPCI and LA-ICP will not change the physical state of the sample but might leave visible damage that pose limitations to the type of sample that can undergo analysis. Hence, AP MeV SIMS is the only one amongst these techniques which could be a suitable tool for cultural heritage analysis.

- **Geometry**

Numerous parameters related to geometry play important roles for AP MeV SIMS and DESI. In AP MeV SIMS the mass spectrometer capillary is directly connected with the analyser, yet its distance and angle with respect to the beam might be influential on the molecular signal. In DESI, the signal coming from the target is dependent on distances and angles of the solvent tip to the sample
and inlet of the analyser. The influence of geometry on secondary ion yields in DAPCI, LA-ICP and LAESI is less pronounced than in DESI and AP MeV SIMS.

- **Fragmentation**

DESI, LA-ICP and LAESI induce minimal fragmentation resulting in the generation of a molecular ion, in either positive or negative polarity modes. AP MeV SIMS will generate more fragments besides the molecular ion, which can be useful for confirming the identity of a certain molecule. This becomes more important for molecules with higher molecular weights. The use of plasma in DAPCI can cause unwanted fragmentation.

- **Spatial resolving power and LOD**

DESI, DAPCI, LA-ICP and LAESI typically achieve lateral resolutions around 200 microns. In AP MeV SIMS, the preliminary results showed lateral resolution of 50 microns. Hence, AP MeV SIMS can be considered advantageously competitive to other APMS imaging techniques. The limit of detection (LOD) for DESI, DAPCI, LA-ICP and LAESI is in order of few ppm to a few ppb[105]–[107].

- **Possibility to implement chemical reactions**

In situ reactions, which can improve sensitivity and selectivity, can be implemented in all of these techniques. In DESI, for example, a chemical agent can be added to the solvent of choice and cause the formation of adducts with the analyte. Although these types of implementations can’t be used in AP MeV
SIMS, there are still possibilities to introduce certain agents that could enhance the creation of specific secondary ions, such as a polar sheath gas. One of the potential candidates for such a sheath gas would be nitrous oxide, N$_2$O. Additionally, generation of either positive or negative secondary ions can be enhanced with the choice of the ion beam species as has already been described in section 2.3.4.

3.4 Imaging mass spectrometry techniques – MALDI and TOF SIMS

Two main methods used for chemical mapping of various samples, especially tissues, under vacuum conditions are MALDI and TOF SIMS. In the 1980s MALDI and ESI became dominant over gas chromatography in the field of lipid analysis as they overcame the need for saponification and alkylation[108]. However, chemical modification of samples still occurs with MALDI due to the use of a matrix. In TOF SIMS a sample is directly targeted by a focused ion beam. Since ESI is used for the analysis of liquid samples, the focus here will remain on MALDI and TOF SIMS, which are both known as soft ionisation techniques. Initial phases of MALDI analysis consist of merging the sample with a suitable matrix and applying such a mixture onto a solid surface. This step is known as a formation of a ‘solid solution’ where the matrix has to be present in a great excess so it can isolate the molecules of analyte from each other, which aids the desorption process. The matrix-analyte mixture is then exposed to a focused laser beam, usually a N$_2$ ($\lambda=337$ nm) or tripled frequency Nd/YAG ($\lambda=355$ nm) laser focused on $\sim 50$ µm of the sample surface. The matrix usually absorbs the wavelengths of laser irradiation that cause vibrational excitation, and thus disintegrate the solid solution[9]. The emitted clusters comprise of matrix, analyte and salt ions. The matrix will evaporate and leave the analyte in the gas phase. This event is known as matrix excitation and is the first part of a
two-step ionisation model, the most accepted model in MALDI[109], [110]. This primary photoreaction is followed by ion-molecule reactions similar to chemical ionisation, giving mostly single charged ions[111]. Another model suggests the production of ions directly from the clusters forming multiple charged species[112]. Sample preparation is a critical step in MALDI, not just for determining the sensitivity of the technique, but also for validating the spatial localisation information of images[113], [114]. The MALDI process usually causes less fragmentation than AP MeV SIMS, leaving the analyte almost intact, which makes this technique very suitable for large biomolecules (up to 150 kDa) even in complex mixtures. The fragmentation rigidity, on the other hand, hinders determination of molecular structure. However, this could be overcome by employing tandem analysers that would enable the MS/MS function. In TOF SIMS the fragmentation is more pronounced than in MALDI and AP MeV SIMS, which would imply that structural analysis is more achievable. However, the high rate fragmentation characteristic of TOF SIMS can be a drawback in tackling the structure. Nowadays, large Ar clusters are found to cause less fragmentation compared to C60[115]. Quantification in both MALDI and TOF SIMS would be only achievable with the use of internal standards, due to the induced or naturally occurring matrix effects. In terms of sensitivity, MALDI is dominant over TOF SIMS[108], nevertheless TOF SIMS is considered the superior imaging technique as it has a spatial resolving power of only a few hundred nanometers, whereas the lateral resolution of MALDI is between 50-500 μm. Another advantage that TOF SIMS offers is the possibility for imaging both organics and inorganics, as well as conductive and non-conductive samples. Moreover, both elemental and molecular analysis can be achieved with this technique. TOF SIMS instruments such as the IONTOF.5 can be used in dynamic and static mode[116]; such instruments combine pulsed metal ion liquid guns with the TOF mass analyser. The liquid metal ion sources can be focused to spot sizes as small as 10 nm. The TOF analyser allows the efficient transmission and simultaneous
detection of all ions that come into the mass spectrometer[117]–[119]. The need for the beam to be pulsed compromises the time required for the acquisition since the beam is effectively “on” only $10^{-4}$ of total time, it can also affect the spatial resolution of the measurement[113]. Another disadvantage of TOF SIMS is the requirement for ultra-high vacuum (UHV) conditions preventing in vitro or ambient analysis. Additionally, sample preparation is often needed for TOF SIMS and this can be complex for biological samples as the vacuum system will remove all volatile components including water. Another limitation presenting a constraint to the analysis of large biomolecules[120] is the mass range, which is up to 2 kDa – it is almost impossible to sputter larger molecules using even large cluster ions[120]. These limitations are mostly significant for bioanalysis; however, the biggest drawback of TOF SIMS, when compared with MeV SIMS, is its inability to be applied in air, which would also prevents other applications, such as cultural heritage.

MALDI is most frequently used as a vacuum based technique, although it can easily be applied under atmospheric pressure[121], [122]. The sensitivity in AP MALDI is lower than under vacuum conditions, but there are new approaches trying to overcome this, such as placing the sample on top of the matrix and applying the laser beam from the back of the sample. This derived MALDI is known as laser sprayed ionisation (LSI), or field free transmission geometry atmospheric pressure (FF-TG-AP MALDI)[111], [123].
3.5 Summary

The description and comparison of the imaging mass spectrometry techniques in this chapter are summarised based on their characteristic analytical performances (shown in Table 2). All of these techniques are powerful tools for certain fields of applications, with DESI, MALDI and TOF SIMS having the most distinct roles among all of them. AP MeV SIMS is yet to prove its establishment in the field. DESI is the most developed technique from the series of APMS techniques and shares many similarities with AP MeV SIMS regarding the influence of the geometry of sampling on the ion yield. Ion transport mechanisms and impact of the environment on the detectability of analytes are challenges for all of the APMS techniques. Nonetheless, their importance has been growing constantly proportional to the need for rapid and preparation free analysis. In terms of the imaging, the APMS techniques might never compete with the well-established vacuum based techniques such as MALDI and TOF SIMS. However, MALDI requires the use of a matrix, and its great sensitivity depends mainly on knowledge of the molecules to be measured in order to choose the most appropriate matrix. Hence, the technique is best employed for already known compositions and their chemical properties. Nevertheless, this does not diminish the importance of MALDI for chemical mapping of large biomolecules, even when they are bonded with some other media such as tissue, as it has a mass range that no other technique can attain. Among all the techniques described, TOF SIMS and LAESI achieve the lowest mass range, but, TOF SIMS is the only technique with nanometre resolution. Evidently, all of these techniques have certain advantages and disadvantages. Depth profiling can be performed with TOF SIMS, LA-ICP and LAESI and is being explored for MALDI and DESI. In AP MeV SIMS, depth profiling might be difficult due to the energy deposition, but it would be worth exploring.
Table 2. Summary of analytical capabilities amongst different imaging mass spectrometry techniques.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Probe</th>
<th>Detection</th>
<th>Environment</th>
<th>Information obtained</th>
<th>Typical</th>
<th>Best</th>
<th>Depth profiling</th>
</tr>
</thead>
<tbody>
<tr>
<td>MALDI</td>
<td>UV laser photons</td>
<td>Ions</td>
<td>HV &amp; atmoph. pressure</td>
<td>Molecules up to 150kDa</td>
<td>50-500µm</td>
<td>10µm</td>
<td>maybe</td>
</tr>
<tr>
<td>TOF SIMS</td>
<td>keV ions</td>
<td>Secondary ions</td>
<td>UHV vacuum</td>
<td>Elements, molecules up to 2kDa</td>
<td>50nm for elements, 200nm</td>
<td>Yes</td>
<td></td>
</tr>
<tr>
<td>AP MeV SIMS</td>
<td>MeV ions</td>
<td>Secondary ions</td>
<td>UHV vacuum &amp; atmospheric pressure</td>
<td>Molecules up to 10kDa</td>
<td>50µm</td>
<td>1µm</td>
<td>Maybe</td>
</tr>
<tr>
<td>DESI</td>
<td>Charged solvent droplets</td>
<td>Ions</td>
<td>Atmospheric pressure</td>
<td>Molecules up to 66kDa</td>
<td>400µm</td>
<td>200µm</td>
<td>maybe</td>
</tr>
<tr>
<td>DAPCI</td>
<td>Electrical discharge</td>
<td>Ions</td>
<td>Atmospheric pressure</td>
<td>Molecules up to 5kDa</td>
<td>250µm</td>
<td>150µm</td>
<td>no</td>
</tr>
<tr>
<td>LA-ICP</td>
<td>UV laser photons</td>
<td>Ions</td>
<td>Atmospheric pressure</td>
<td>Elements</td>
<td>10µm</td>
<td>100µm</td>
<td>yes</td>
</tr>
<tr>
<td>LAESI</td>
<td>IR laser photons</td>
<td>Ions</td>
<td>Atmospheric pressure</td>
<td>Molecules up to 2kDa</td>
<td>350µm</td>
<td></td>
<td>yes</td>
</tr>
</tbody>
</table>
The low ion yield which is in range of $10^{-3}$ and $10^{-4}$ is a common feature of all these techniques, therefore, the opportunity to apply post-ionisation, which AP MeV SIMS and laser-based techniques offer, could be a very important approach in overcoming the low secondary ion yield. AP MeV SIMS is comparable in many features with other APMS techniques, with the potential of achieving lateral resolutions of several tens of micrometres, which is already more advanced than the lateral resolution achieved by some other imaging techniques, even though they have undergone numerous technical improvements. The final thought of this chapter will be a quote from Vickermann - “DESI can be thought of as an atmospheric version of SIMS” - indicating that the idea of having an ambient counterpart of SIMS has been recognised[113].
4. The challenges of AP MeV SIMS

4.1 Introduction

Chapter 4 presents the challenges of AP MeV SIMS technique. Considering that AP MeV SIMS is an ambient technique, most of the challenges are related to the transport of secondary ions from the sampling site into the mass spectrometer. Thus, the effect of the atmosphere has to be investigated as much as possible to be able to understand and optimise the transport process. In section 4.3 the effect of the atmosphere is described together with ways of manipulating the ambient atmosphere by introducing He and N₂O gasses and setting an environmental chamber on the beam nozzle.

The following section describes the transmission of secondary ions into the mass spectrometer capillary by the means of heating and biasing the mass spectrometer capillary, positioning of mass spectrometer and He flow capillaries in respect to the beam axis and adjusting an angle of the He flow capillary in respect to the sample.

In section 3, interaction of the external ion beam and target will be presented describing how secondary ions are getting desorbed in AP MeV SIMS. This will be followed by a section on IBA under ambient conditions describing advantages and disadvantages of using external beams in IBA.

Lastly, merging IBA techniques will be described, with focus on pairing MeV SIMS and PIXE.
4.2 The effect of the atmosphere

In AP MeV SIMS, the secondary ions desorbed from the target have to be transported in the most efficient manner from the site of the interaction of ion beams and target into the mass spectrometer capillary and, finally, into the mass spectrometer. Having the interaction site between ion beams and target under ambient conditions makes all the constituents of ambient prone to become ionised through the interaction with ionising radiation. These ambient peaks compete with the secondary ions in their transport into the mass spectrometer capillary hence the influence and effect of the surrounding atmosphere on the secondary yield has to investigate. The role of the sheath gas is primarily in the transmission of the secondary ions into the mass spectrometer capillary. However, by introducing the He sheath gas we also manipulate with the surrounding atmosphere around the interaction site between ion beams and target. In order to test the effect of the He flow on the secondary yield, spectra acquired under the same experimental conditions such as the beam species and current, the mass spectrometer capillary temperature and the acquisition time but altering the presence of both the He sheath gas and the ambient were compared. The sample used for the measurements was the yellow pigment PY3 first dissolved in acetone and then placed on a glass slide with a brush. The same sample was used through the whole course of the acquisition, with a change of a spot for every following spectrum. The results were very similar with the presence of He gas and without any sheath gas present (Figure 8). The only change occurring as a variation of He flow was in the background peaks. The spectra taken with the presence of the He flow were “cleaner” than
their counterparts which showed the more abundant mass region in the interval from m/z 199 to 250 with the peaks at m/z 199, 220, 233 and 241 present with the absence of a sheath gas. All the spectra collected were in negative ion mode using 6.5 MeV Cl$^{3+}$. The comparison of an ambient background with and without He flow was then obtained for the positive ion mode where no change was noticed in comparison with spectra of air. As it will be shown in section 6.7, the PEG and PPG peaks are dominant background peaks in the positive spectra. Since their presence and intensity isn’t correlated with the type of atmosphere we assume their source to be inside of the mass analyser.

Next, the He sheath gas was replaced with nitrous oxide, N$_2$O. By replacing highly inert He with N$_2$O which is a weak oxidising agent, we wanted to explore the effect N$_2$O has on the generation of ionised species. For this purpose, samples of TNT were used.
Figure 8. Comparison of spectra of the PY3 in the negative ion mode with the presence of the He gas and without a sheath gas (top diagram). The presence of the He flow suppressed some of the background peaks such as the m/z 199, 220, 233 and 241 (bottom diagram).

The outcome of utilising N₂O was the same as with He as the spectra of TNT showed the same peaks with the intensity variation noticeable for the TNT related peaks at m/z 197, 226 and 227
which were more intense when the He gas was supplied (Figure 9). The reactivity of N\textsubscript{2}O was not sufficient enough to induce chemical reactions in the sample. All the spectra were acquired using the 6.5 MeV Cl\textsuperscript{3+} ion beam.

![Figure 9. Comparison of spectra of TNT in the negative ion mode (top) and Leu in the positive ion mode (bottom) acquired with the presence of the He and the N\textsubscript{2}O sheath gas. All the spectra were obtained with the 6.5 MeV Cl\textsuperscript{3+} ion beam.](image)

The last step in assessing the impact of the atmosphere on secondary yield is to use an environmental chamber which encloses the space around the beam nozzle. The environmental
chamber is a 3D-printed cone made of plastic material with a designated area for samples and inputs for gas and mass spectrometer capillaries (Figure 10.)

Figure 10. Environmental chamber placed onto the beam nozzle. The chamber comprises of the gas and MS capillary outputs. The number of samples placed inside the chamber depends on their size and shape. Samples are exchanged manually using the sample rotator.

The first series of experiments included a blank Si wafer which was placed inside of the chamber. The chamber was evacuated using a Membrane pump. The spectra which include the environmental chamber were acquired with the presence of N₂O gas as well as without a gas. These spectra were compared with a spectrum of blank Si wafer taken before placing the atmospheric chamber with the presence of N₂O as seen in Figure 11.
Figure 11. Comparison of spectra of blank Si wafer taken without the use of the atmospheric chamber, inside the evacuated environmental chamber with the presence of N₂O sheath gas and inside the evacuated environmental chamber without the presence of a sheath gas. For the spectra taken inside the chamber the polydimethylsiloxane peak at m/z 221 is the most intense peak. The polydimethylsiloxane peak is more intense when no sheath gas was used.

Both spectra of the blank Si wafer in the positive ion mode taken inside of the chamber showed a dominant peak at m/z 221 which can be identified as polydimethylsiloxane originating from the body of the atmospheric chamber. The polydimethylsiloxane peak shows a higher intensity without a presence of the gas inside of the atmospheric chamber. We found the polydimethylsiloxane peak in the spectra taken with the atmospheric chamber suppressed the peaks that usually dominate the positive background, the PEG and PPG related peaks. A similar
comparison was also performed for the negative ion mode. Spectra of the blank Si were obtained with the presence of the atmospheric chamber with He gas as well as without a sheath gas. These two spectra were then compared with the spectrum of the Si blank taken without the atmospheric chamber and with the presence of He gas. The spectra taken inside of the chamber showed to be very similar as the m/z 212 dominates for both of the cases. However, the spectrum with the presence of He shows the much higher intensity of the m/z 212 peak. When compared to the spectrum acquired without the atmospheric chamber where the m/z 220 dominates the spectrum, it seems that the spectra taken inside of the chamber are less saturated. Nevertheless, the number of counts in their case is so increased that more peaks became visible at first glance when compared to the spectrum collected without the atmospheric chamber. The conclusion we can draw from the comparison of the spectra taken with and without the atmospheric chamber for both of the polarities indicates that the peaks which completely dominate the spectra taken with the atmospheric chamber are due to contamination coming from the chamber itself. In the case of the positive mode, it is straightforward to identify the polydimethylsiloxane peak at m/z 221, but we could not do the same for the m/z 212 in negative mode. Future experiments considering the effect of the controlled atmosphere on the background would involve a chamber composed of a different material, preferably metal in order to avoid possible interferences with the organics.
4.3 Transmission of the secondary ions into the mass spectrometer capillary

4.3.1 Heating of the mass spectrometer capillary

A critical point of AP MeV SIMS technique is the efficient secondary ion transport and preservation during the course of transport. A key factor for that is to successfully bring the desorbed ions from the interaction site of ion beams and target which is at atmospheric pressure to the first differentially pumped region of Q-TOF where keeping the mass spectrometer capillary heated plays an important role. The nature of the setup for AP MeV SIMS at Surrey Ion Beam Centre requires use of an inlet capillary with the length of \( l = 50 \text{cm} \). If the capillary is not kept heated, chemical species originating both from sample and atmosphere would accumulate on its walls which would cause an instant memory effect and could also induce a set of chemical reactions which might potentially neutralise the sputtered ions. In order to assess the optimal working temperature of the mass spectrometer capillary, a set of measurements was performed on TNT sample using the 8 MeV O\(^{4+}\) primary beam. We used a range of temperatures starting at 25\(^{\circ}\) C and finishing at 150\(^{\circ}\) C. The effect of applied temperature on TNT principal fragment at m/z 226 was observed (Figure 12). The dependence of relative molecular yield shows that optimum temperature range is between 60-100 \(^{\circ}\)C with a peak value at 72 \(^{\circ}\)C. The diagram in figure 12 also shows that at 105 \(^{\circ}\)C relative yield for TNT principal fragment has the same value as at 25 \(^{\circ}\)C but drops significantly after the mass spectrometer capillary temperature rose to 125 \(^{\circ}\)C, 135 \(^{\circ}\)C and 150 \(^{\circ}\)C. The reason for the significant yield drop at temperatures higher than 95.5 \(^{\circ}\)C is related to the thermal degradation of TNT molecule since the melting temperature of TNT is at 80.8 \(^{\circ}\)C.
Figure 12. Temperature dependence of principal fragment m/z 226 of TNT molecule. Spectra were acquired in negative ionisation mode.

Thus the optimal working temperature of the mass spectrometer capillary should ideally be assessed for every sample considering its thermal stability.

In our previous experiments, we determined the optimal temperature of the mass spectrometer capillary for analysing Scotch tape (the non-sticky side) and leucine. These results can be found in the internal presentation of Work Package 4 (WP4) of the SPRITE project[124]. The Scotch tape showed a similar trend as TNT, with optimal value at 95.5 °C for peaks at m/z 147 and 178, with a significant decline in molecular yield for both peaks after the optimal temperature.

In the case of the leucine thin film, the mass spectrometer capillary heated at 70 °C gave the highest value of molecular yield for the peak at m/z 86. When assessing the effect of heating of the mass spectrometer capillary on secondary yield, we have to look into its performance. The heating was achieved by wrapping a filament around the body of the mass spectrometer
capillary. The filament is spread almost across the whole length of the mass spectrometer capillary. However, the tip of the capillary is not heated due to its proximity to the Si$_3$N$_4$ window which might induce thermal stress. Another reason is that the mass spectrometer capillary has to pass through a manipulator which gives a spatial limitation for insertion of something bigger than the capillary on its own. Not heating the mass spectrometer capillary across the whole length, especially at the tip of the capillary which is exactly at the sampling spot is definitely a disadvantage and thus the heating design and maybe the manipulator must be reassessed. Finally, it is also worth to mention a limitation in the temperature applied to the capillary due to the O-ring present in the inlet of the mass spectrometer. Usually, polymer O-rings should withstand temperatures up to 200 ºC before they begin to degrade. If degraded, O-rings can act as an additional source of polypropylenes and poly(tetrafluoroethylene)s and also degrade the vacuum seal.

4.3.2 Biasing the mass spectrometer capillary

Another parameter which might influence ion transport through the mass spectrometer capillary is the bias potential applied to the capillary with a purpose of both bringing the ions towards the capillary and preventing them from interacting with the capillary walls. Besides applying the bias potential on the mass spectrometer capillary a voltage can also be applied to the cone of the mass spectrometer which will affect the overall fragmentation of the analysed molecules and this is used for a different purpose[125]. The effect of the bias potential on the ion yield was investigated for a thin film of leucine deposited on Si wafer. The first daughter fragment at m/z 86 was measured (Figure 13).
The ion yield for this fragment was normalised to the number of total secondary ion counts. A small rise in yield was observed when 5V was applied but yield fell when a potential higher than 5V was used (Figure 14). According to these results applying a bias potential will be excluded from the subsequent experiments.
4.3.3 Position of the capillaries with respect to the beam axis

The demand for achieving the most efficient ion transport also requires obtaining of the optimal position of both of the capillaries, mass spectrometer and He flow one with respect to the beam axis. The beam exit is positioned through the centre of the Si₃N₄ window (Figure 15). The Si₃N₄ is a square with dimensions of 1mm x 1mm placed in the centre of the beam nozzle which is a circle with a diameter of 3mm. The distance of the mass spectrometer capillary from the beam axis is labelled as the d₁ and the distance of the He flow capillary in respect to the beam axis is labelled as the d₂. The distances d₁ and d₂ are describing how far the mass spectrometer and He flow capillaries are retracted from the beam axis.
Figure 15. Distances of the mass spectrometer ($d_1$) and He flow ($d_2$) capillaries with respect to the beam axis. The beam axis is positioned at the centre of the Si$_3$N$_4$ window which is positioned at the centre of the beam nozzle. The beam nozzle has a diameter of 3 mm.

In the following measurements, optimal values of $d_1$ and $d_2$ were assessed. The optimisation of the distances of the mass spectrometer and He flow capillaries comprised of two steps. Firstly, a dependence of the number of total ion count for a sample of TNT drop case on filter paper for three different values of $d_1$ was assessed, 1.5mm, 0.75 mm and 2.5mm (Figure 16). The highest number of total ion counts was achieved at $d_1=1.5$mm. Next step was to assess the optimal value of $d_2$ for the $d_1=1.5$mm. Two different distances of the He capillary from the beam axis were tested, 3.5mm and 5mm. At $d_2=3.5$mm the number of total ions counts was 3.99x$10^4$, whereas at $d_2=5$mm the number of total ions counts was 4.21x$10^4$. The difference in number of total ions counts for the two different positions of the He flow capillary in respect to the beam axis was not significant hence manipulating the distance of the He flow capillary
in respect to the beam axis does not have the same impact on the number of total ion counts for
the sample of TNT as the distance of the mass spectrometer capillary in respect to the beam

Figure 16. The dependence of a number of total ion counts (TIC) for the sample of TNT for
different distances of the mass spectrometer capillary from the beam axis, \(d_1\) as defined in
Figure 8. The measurements were performed with the 6.5MeV O\(^{3+}\) primary beam.

axis. The number of total ion counts for the sample of TNT for the values of \(d_1 = 0.75\text{mm}\) and
\(d_1 = 2.5\text{mm}\) decreases to 87% and 79% when compared to the number of total ion counts at
\(d_1 = 1.5\text{mm}\). For the case of the assessment of the dependence of the distances of the He flow
capillary in respect to the beam axis on the number of the total ion counts for the sample of
TNT, at the \(d_2 = 5\text{mm}\) the number of total ion counts decreased to 95% of its value at
\(d_2 = 3.5\text{mm}\). After the investigation of the influence of different positions of the mass
spectrometer and He flow capillaries in respect to the beam axis on the number of total ion
counts for the sample of TNT was performed, the assessment of the dependence of molecular yields of the molecular ion at m/z 226 and first daughter ion at m/z 197, both relative to the number of total ion counts, on the distances of the mass spectrometer capillary in respect to the beam axis was done (Figure 17).

Figure 17. Dependence of the relative molecular yields for the TNT molecular and first daughter ions on different distances of the mass spectrometer capillary in respect to the beam axis, $d_1$. The relative molecular yields are constant with a value of $0.015 \pm 0.002$.

The relative molecular yields for both the molecular and first daughter ion are the highest when the mass spectrometer capillary was 1.5mm retracted from the beam axis. When the mass spectrometer capillary was brought closer to the beam axis at the distance of 0.75mm the relative molecular yield for the molecular ion decreased to the 86% and the relative molecular...
yield for the first daughter fragment decreased to the 73% of their value when the mass spectrometer was at 1.5mm distance to the beam axis. Furthermore, when the mass spectrometer capillary was retracted at the distance of 2.5mm from the beam axis, the relative molecular yield for the molecular ion decreased to the 77% and the relative molecular yield for the first daughter fragment decreased to the 75% of their value when compared to the relative molecular yields for the mass spectrometer capillary being 1.5mm retracted to the beam axis.

The results on the dependence of the number of total ion counts and relative molecular yields for the molecular and first daughter ion for the sample of TNT on distances of the mass spectrometer capillary in respect to the beam axis were in contrary to expectations, as the smallest distance of the mass spectrometer capillary to the beam axis did not give the highest number of the total ion counts nor the highest relative molecular yields for the molecular and first daughter ions. The reason for this could be the better alignment of the secondary ions flow towards the inlet of the mass spectrometry capillary when the distance of the mass spectrometer capillary in respect to the beam axis is 1.5mm, rather than 0.75mm and 2.5mm when the secondary ions diverge around the inlet of the mass spectrometer capillary and thus fail to enter it. The results showing the insignificant dependence of the molecular yields to the distances of the He flow capillary in respect to beam axis are in agreement with the concept of the more efficient collection of secondary ions by the mass spectrometer after modifying the vacuum backing system by adding an additional rotary pump to the Q-TOF as described in section
5.4.1. As a consequence of such modification, the influence of the He flow on the transport of secondary ions decreased.

In order to complete the assessment of the dependence of the number of total ion counts and molecular yields on the distances of the mass spectrometer and He flow capillaries, the measurements on such distances in respect to the sample should be performed as well. In our case, such precise measurements could not be conducted due to the limitations in our setup.

4.3.4 Angle of the He flow capillary with respect to the sample

Further investigation of the geometry has been directed into the assessment of the optimal position of the He flow capillary in respect to the sample/beam nozzle. The angle under which the sheath gas is directed onto a sample and takes the emitted species towards the analyser could also influence the secondary ion yield. Extensive simulations were performed in our group using ANSYS CFX, a high-performance computational fluid dynamics (CFD) software[126]. The modelled gas flow across the sample and into the MS in the configuration of the experimental system set-up show that more than 95% of the sputtered material should find its way into the capillary. Poor alignment of the capillaries, however, can lead to no secondary ions entering the Q-TOF2.
<table>
<thead>
<tr>
<th>Inclination of the He flow capillary with respect to the sample / °</th>
<th>Transmission of secondary ions into the mass spectrometer capillary / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>86</td>
</tr>
<tr>
<td>30</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>65</td>
</tr>
</tbody>
</table>

Table 3. Transmission of the secondary ions into the mass spectrometer capillary for the different inclinations of the He flow capillary with respect to the sample. The results were obtained by Dr Lucio Rosa using ANSYS CFX software.

In the simulations, three different inclinations of the He flow capillary in respect to the sample were used which showed significantly different transmission of secondary ions into the mass spectrometer (Table 3). The CFD simulations show 86% efficiency in secondary ion transmission for a 40º slope with respect to the sample (Figure 18). With 30º inclination, the He flow will fail to curve the secondary species into the MS capillary and rather bring them around it.

![Figure 18](image_url)

Figure 18. Computational Fluid Dynamics simulations on the efficiency of secondary ion yield for different angles of the He flow capillary with respect to the sample. For a 40º slope secondary ions will mostly follow trajectories going directly into the MS capillary with the
transmission efficiency of 86%. The transmission efficiency drops to 0% with 30° inclination and rises to 65% with 20° inclination.

If we move away from the 30° inclination, the secondary species will follow trajectories directed into the MS capillary, with 65% efficiency with a 20° inclination with respect to the sample.

The effect of various angles on the secondary ion yield was also tested experimentally using a goniometer (described in section 5.5) with an angle interval from 15-45°. For the experiments, TNT drop cast on Si wafer was used and each spectrum was taken from a new spot. The dependence of the change of angle on the secondary molecular yields of TNT principal fragment at m/z 226 and first daughter fragment at m/z 197 relative to the number of total ion counts is shown in figure 19. The trend of the relative yield variation similar for both the m/z 226 and 197 as is it showing a slight increase at 30°. The error was estimated to be at 10% for both cases. Considering the error, we could neglect the overall relative yield variation. In order to confirm the relative yield rise at 31° is likely to be an artefact, a set of independent measurements was performed using three different angles, 15°, 31° and 40°. The measurements were repeated three times and each time a pristine TNT sample was used. The results did not show any significant change in the relative molecular yield for m/z 226 and 197. Moreover, the influence of the angle of the He flow capillary in respect to the sample on the secondary yield is less pronounced as expected and can be considered negligible. This could demonstrate
that the improved differential pumping of the Q-TOF2 leads to the more efficient collection of the secondary ions into the mass analyser.

Figure 19. Dependence of secondary molecular yield of TNT principal fragment at m/z 226 and first daughter fragment at m/z 197 relative to the number of total ion counts for different angles of He flow capillary in respect to the sample. For the measurement, 6.5 MeV Cl$^{3+}$ primary beam was used. The relative molecular yields for the m/z 226 and m/z 197 are very similar when taking into consideration the error. The relative molecular yield increase for the both of the ions at 31° is likely to be an artefact.

The discrepancy between the simulation and experimental data can be explained by differences between the theoretical model used in simulations and the actual geometry. In the simulations, the different angles of the He flow capillary were achieved by moving the edge of the capillary, whereas in the experiments the He flow capillary was manipulated few millimetres away from
the edge causing the angles between the He flow capillary and sample to be different in the simulation when compared with the angles used in the experiments.

### 4.4 Interaction of the external ion beam and target

The external beam used in AP MeV SIMS is extracted through a 100nm thick Si$_3$N$_4$ window with size 1mm x 1mm supported by a Si frame placed at the end of the beam nozzle (Figure 20). The primary ion beam interacts with the sample at the surface normal. The desorbed secondary species will occupy the volume between the beam exit window and sample.

Figure 20. Interaction of the external ion beam and sample. The ion beam is extracted through a 100nm thin Si$_3$N$_4$ window. The desorbed secondary ions are then transmitted with a support of the He sheath gas into the mass spectrometer capillary to find their way into the mass spectrometer.
In the volume traversed by the beam from exit window to sample a He sheath gas is introduced through the designated plastic capillary. The He flow has several roles in AP MeV SIMS, with the most important one in supporting the transmission of the secondary ions from the sampling site into the mass spectrometer capillary. Other roles of the He sheath gas are connected with the beam degradation of external beams where the use of a light gas such as helium or hydrogen is beneficial to minimise the energy loss and straggling\[127\]. The latter will be more explored in the next section. Another role of the He sheath gas is to create a cleaner atmosphere around the sampling and, ideally to suppress the ambient background – see the following chapter. Consequently to all the above mention roles of the atmosphere in AP MeV SIMS, it is mandatory to explore all the impacts the atmosphere has in secondary ion transmission and mitigating background peaks in the mass spectra.

**4.5 IBA under ambient conditions**

The need to perform an analysis under ambient conditions comes from requirements for analysis of volatile or oxidable materials and preserving the original physical attributes of samples such as size and shape. The applications of IBA under ambient conditions require the use of an external ion beam. There are several advantages of performing IBA with external beams\[128\]: i) the in situ measurements can be performed on samples of any size and shape, ii) reduced risk of beam damage by removing the heat at the beam spot through convection by
air or the helium flow, iii) absence of the charge effects making it suitable for analysis of non-conductive materials without depositing a conductive surface layer or using an electron gun to neutralise the deposited charge, iv) possibility to draw molecular and elemental maps on areas up to several mm$^2$ by moving the sample stepwise under the fixed beam. The disadvantages of using external beams in IBA are related to the stopping power of ion beams in an external gas atmosphere and FWHM straggling[127]. The exit window induced straggling has restricted for a long time production of external beams to protons and limited the application of IBA under ambient conditions to PIXE. In PIXE, the induced beam energy straggling is not considered to be an issue due to the slow dependence of ionisation cross sections on beam energy. The beam energy loss is caused by the large stopping power in the external gas atmosphere and can also deteriorate the spatial resolution together with the straggling. The use of a light gas such as helium or hydrogen in the volume between the beam exit window and the target is beneficial for minimising the beam energy loss and straggling[127]. Another disadvantage of performing IBA with external beam related with the beam degradation is the beam current measurement which could be performed with the Faraday cup but the part of the charge created alongside the ion path in the atmosphere will get collected to the ground by the nearest conductors. One of the alternative solutions for the current measurement is to measure it from the RBS signal emitted from the window[129].

The most obvious field of application of IBA with external beams is art and archaeology. For this purpose, PIXE has been applied as an individual technique[130]–[133] as well as combined
simultaneously with RBS[134], [135] and ERD[136]. Having MeV SIMS applied with external beams gives us the possibility to explore new applications of IBA under ambient conditions and combinations of IBA techniques which were not explored so far.

4.5.1 The challenges of merging of MeV SIMS with other IBA techniques

The simultaneous use of multiple IBA techniques has already been reported. RBS can be used to provide matrix and charge correction to improve the quantitative accuracy of PIXE analysis[137], [138]. More recently RBS, PIXE, PIGE (and possibly ERD) have been combined to create what has become known as the Total IBA method[139]. The goal of Total-IBA is to provide a full elemental characterisation of a sample across the periodic table with the possibility of providing depth distributions (up to the range of the ions) and even three-dimensional information when a microbeam is used. Using several techniques simultaneously can be a significant challenge, both in collecting data from several disparate detectors and especially in combining the different software methods used to process the data to obtain the actual compositional information [140]. The data analysis for the combinations of IBA techniques requires a complex iterative procedure from each of the technique included in such combinations which prevented the full development of these combinations of IBA techniques[141]. Recently, DataFurnace software tool with the implementation of the largest array of the technique of any IBA code had been introduced[142]. DataFurnace that is capable
of simultaneous data analysis of different combinations of IBA techniques such as RBS, PIXE, ERD and PIGE.

The combination of the MeV SIMS and PIXE – preferably simultaneously with the same beam – provides useful complementary molecular and elemental information which can readily be combined. Moreover, PIXE could also be applied for the quantification in MeV SIMS, for certain types of samples such as the organometallic compounds. In such compounds calculation of the concentration of an organic part of the molecule would be obtained via the structural correlation with the element[143]. MeV SIMS relies upon electronic sputtering of the target material and this is much more efficient in insulating or organic targets, it is less efficient in conducting metallic materials. PIXE, on the other hand, is efficient at providing good signals from elemental metallic systems but does not readily provide molecular information from organics. Analysing different types of information i.e. organic and metallic content is advantageous as it prevents potential disagreements in qualitative and quantitative interpretation arising as a consequence of using different approaches for the same purpose. On the other hand, focusing on different information could be more demanding in terms of the working conditions fitting the requirements of both the techniques used in such experiments. The simultaneous use of MeV SIMS and PIXE presents a challenge in finding the optimal primary beam suitable to desorb secondary ions and emit X-rays. In MeV SIMS, energy deposition gets more efficient as the heavier primary ion is employed whereas in PIXE, where the particle energy loss passing through material excites the electrons in atoms, the maximum
ionisation cross sections are achieved with protons with an optimal energy for a proton beam between 1 and 4 MeV\[^{144}\]. Employing a heavy ion in PIXE is known as the HI PIXE. Another challenge in merging of MeV SIMS and PIXE is in finding an optimal beam current. Ideally, the requirement to obtain the static limit in MeV SIMS should be respected as described in section 2.2.2. However, such beam currents might not be sufficient enough for detection of X-rays. Thus, finding the most suitable beam species, energy and charge state is a prerequisite for the combination of MeV SIMS and PIXE.
5. The AP MeV SIMS setup at the Surrey Ion Beam Centre

5.1 Introduction

In this chapter, the concept of AP MeV SIMS will be presented from the technical point of view. To be able to apply the ion beam analysis techniques under ambient conditions, an external beam line had been commissioned in the University of Surrey Ion Beam Centre. Heavy ion beams used in the measurements are focused and extracted through an interface which can be either a nozzle or a cone, depending on the experimental needs. In most cases, the nozzle has been utilised. The external beam extraction nozzle, or cone, is mounted between two different capillaries. The first one provides a sheath gas for the secondary ion transport whereas the second one transports the ions into a mass analyser.

Molecular analysis is obtained with a Waters QTOF-2 mass spectrometer[145] which measures the time-of-flight of the secondary ions. The QTOF-2 mass spectrometer is a tandem comprising of a quadrupole analyser acting as a mass filter and a time of flight analyser acting as a detector.

In order to improve the collection of the secondary ions from the sampling site through the mass spectrometer capillary into the QTOF-2, the vacuum system comprising of one rotary pump and three turbo pumps was modified by inserting an additional rotary pump into the vacuum system. The modified QTOF-2 was then tuned for the optimal secondary ions transport by assessing the optimal values of the parameters related with the extraction of secondary ions from the mass spectrometer orifice into the first differentially pumped region and transmission and detection of secondary ions in TOF region.

The sampling of the secondary ions is performed by interaction of target and external ion beams extracted through the Si$_3$N$_4$ window. The sputtered secondary ions will be collected by the
mass spectrometer capillary with the support of the He sheath gas inserted through a separated capillary. Both of the capillaries are positioned and aligned using designated positioning stages.

The resulting mass spectra were acquired using the Waters MassLynx software supplied with the QTOF-2 instrument. In addition to the Waters MassLynx, mass information are also collected with OMDAQ-3[146] which enables collecting maps of molecular peaks.
5.2 The external beam line

The Ion Beam Centre at the University of Surrey houses a 2 MV Tandetron accelerator from High Voltage Engineering Europa (HVEE) commissioned in 2002. The accelerator unit can be divided into two parts, a central injector block, magnet orientated at 90º and tank housing a stripper gas and acceleration column. The central injector block energy side consist of Cs sputter and duoplasmatron sources, einzel lens, lithium charge exchange canal and beam steerers. The tandem acceleration is a two-step process. At the beginning, singly charged negative ions produced by one of the two sources enter a low energy acceleration tube. The ion optics will adjust the initial kinetic energy of ions to energies up to 80 keV. Negative ions are accelerated towards the positive electrode towards the middle of the machine, i.e. the positive high voltage terminal kept at terminal voltages up to two orders of magnitude higher than the at the beginning of the tube. At the high voltage terminal, negative ions become n-times positively charged by colliding with a stripper gas placed inside of special canal. The stripper gas used in this tandem accelerator was nitrogen. The positive ions are then accelerated towards the ground high energy tube base.

![Design of a beam line system of a 2MV HVEE Tandem Accelerator in Stephens’ laboratory of Surrey Ion Beam Centre.](image)

Figure 21. Design of a beam line system of a 2MV HVEE Tandem Accelerator in Stephens’ laboratory of Surrey Ion Beam Centre.
The quadrupole steerer will transport the ions into a switching magnet which will then direct them into one of the beam lines. The Tandetron comprises of four beam lines and five target stations; a nanobeam, a microbeam, a nano-focussed vertical beam, a broadbeam-milibeam, and a focused external beam line (Figure 21). The beam lines are orientated at different angles with respect to the switching magnet with a total interval of 40º. The external beam line is placed as an extension onto the milibeam line with additional end station positioned after the sample chamber used for the purpose of Rutherford Backscattering Spectrometry (RBS) measurements[147].

The focusing system is a quadrupole triplet lens system from Oxford Microbeams Ltd capable to focus a heavy ion beam down to a submicron spot size and allows a beam to be electrostatically scanned over an area of 2 mm x 2 mm. The beam exits the vacuum through a 100nm thin Si$_3$N$_4$ window placed at the end of the beam nozzle. The analysis is performed with an orthogonal quadrupole time of flight (QTOF-2) mass spectrometer by Waters (Figure 22). The setup enables the placing of up to four silicon drift detectors (SDD) for also measuring X-rays. The beam nozzle is flanked by two different capillaries. The first one is the mass

Figure 22. External beam line of 2MV Tandetron.
spectrometer inlet capillary which is connected to the QTOF-2 orifice. On the opposite side, a sheath gas capillary is introducing a gas which will assist in the transport of secondary ions and is referred as the “He flow capillary” since helium was utilised for this purpose unless stated otherwise (Figure 23).

Figure 23. The beam exit interface with the mass spectrometer capillary on the left and a sheath gas capillary on the right. The sheath gas is He.

5.3 Ion beam extraction

Ion beams require low pressure through the accelerator to minimise divergence and the external ion beams must be extracted into the atmospheric pressure or moderate vacuum either through a thin exit foil or a narrow orifice combined with differential pumping[148]. The introduction of 100 to 500nm thick Si₃N₄ windows in the 1990s presented a real breakthrough in the extraction of ion beams enabling the use of heavy external ion beams.
Figure 24. Schematic of the Si$_3$N$_4$ window with a top and cross (X) section view. The top view shows the membrane in the middle of the window frame. The cross section shows the backside cavity placed in between two silicon units surrounded by silicon nitride.

The Si$_3$N$_4$ windows are highly resistant to pressure and beam damage. The burst pressure or the maximum pressure a Si$_3$N$_4$ window can withstand depends on the thickness and size of the membrane (Figure 24). The burst pressure is much higher when applied on the top side of the membrane window (vacuum on the cavity side). The burst pressure for the 100nm thick Si$_3$N$_4$ with dimensions 1mm x 1mm measured by applying a positive pressure on the top side of the membrane window is 2.7 bar[149]. The use of Si$_3$N$_4$ windows combined with the strong focusing lenses (see the previous section in this chapter) has enabled to obtain external probes in the micron range.
5.4 Mass analyser

The Waters QTOF-2 is a hybrid quadrupole time of flight mass spectrometer with MS/MS capability designed specifically for high performance in the mass range from m/z 100-2000 although theoretically it can be used up to m/z 20 000. The QTOF-2 is characterised by high sensitivity, resolution and mass accuracy. Resolution defined as \( \frac{m}{\Delta m} \) at full width half height of a peak is 10 000\[150\]. In the original design samples are introduced through ESI, APCI or nanospray ionisation sources which were modified for AP MeV SIMS by introducing a 50 cm long stainless steel capillary into the inlet orifice (Figure 23). Once they have entered the mass analyser, secondary ions are introduced with a small velocity component in the axial direction into the set of four rods creating the quadrupole field. The field is generated by applying a RF voltage between one pair of opposing rods of the quadrupole. Next, a DC offset voltage is applied to the other pair of opposing rods. The ions with a certain m/z will have a stable flight path through the quadrupole in the resulting electric field whereas all the other ions will fail to reach the detector due to their unstable trajectories. The quadrupole has a twofold role acting as a mass filter or analyte-specific detector for ions of a particular m/z. Alternatively, the quadrupole can scan a range of m/z values by continuously varying the applied voltages. After passing through the quadrupole analyser the ions flow into the time of flight analyser. A reflectron time of flight analyser placed orthogradually to the quadrupole has the mass resolving role in both modes, MS and MS/MS. The tandem MS mode takes place in the hexapole collision cell – see Figure 25. The ions selected by the quadrupole analyser are fragmented by collision induced dissociation by introducing argon through the solenoid valve. A multicomponent ion lens comprised of the acceleration, focus, steer and tube lenses placed after the hexapole collision cell will firstly focus the ion beam of fragmented or unfragmented ions and send in onto the pusher where a section of the ion beam will be pulsed orthogonally for TOF analysis.
Figure 25. Schematics of the second generation of QTOF-2 instruments (Waters, U.K.) showing the capillary as a probe, ion optics and mechanical components.

The relectron will reflect ion beam towards the microchannel plate (MCP) detector using a constant electrostatic field. While travelling from pusher to MCP ions will be separated according to their mass to charge ratios (m/z) using time as a parameter directly correlated to a specific m/z value. Time is proportional to the square root of mass thus lighter species arrive at the detector earlier than heavier species. Repetition frequencies of the pusher are up to 20 kHz which will result in the recording of a full spectrum by the detector every 50 microseconds. Each spectrum will be summed in the histogram memory of the time to digital converter until it is transferred to a PC.
5.4.1 Modification of the QTOF-2 vacuum system

The mechanical components employed into the QTOF-2 concerning the vacuum system in original design comprise of one rotary pump and three turbo pumps (Figure 25). However, this has been modified for the purpose of AP MeV SIMS so that an additional rotary pump has been inserted to compensate for the increased gas load caused by the addition of the Helium pusher gas. The first rotary pump (RP1) is backing only the first turbo pump (TP1) whereas the second rotary pump (RP2) is backing both the second and third turbo pumps, TP2 and TP3. The vacuum alteration will increase the pressure differential between the QTOF-2 and the capillary-ambient interface, providing a greater flow from the target region into the mass spec capillary which should improve the transmission of the secondary ions. The disadvantage of this transformation is the rise in the collection of ions originating from ambient. The improved vacuum system should lower the flow resistance and enable utilisation of capillaries with larger inner diameter. Before the modification, the capillaries with internal diameters (ID) of 0.6 mm were used. The second capillary tested was the one with ID = 0.85 mm which didn’t cause any vacuum degradation. Hence, it was replaced with a capillary with ID = 1.2 mm which also resulted in a stable vacuum. Most likely, even capillaries with bigger inner diameters could be used. However, there is some other limitation which would prevent inserting bigger inner diameter capillaries. This is the diameter of a capillary holder attached on a goniometer located on the opposite end of the capillary than the mass spectrometer. The goniometers will be described in the following section as a part of a sampling setup. The mass spectrometer capillary used in most of the experiments composing the chapter 4 on the optimisation of AP MeV SIMS was the one with ID = 1.2 mm. The capillary with ID = 0.6 was used in sections 4.3.1 and 4.3.2 when applying heating and potential bias on the mass spectrometer capillary as well as section 9 when examining the post-ionisation.
5.4.2 Tuning of the QTOF-2 parameters for the optimal transport of secondary ions

Secondary ions emitted from a surface, as a consequence of interaction with an ion beam might not find their way into the mass analyser. To consider this behaviour in more details, different segments of the QTOF-2 need to be considered individually. Most likely, secondary ions which don’t get analysed will get “stopped” in the mass spectrometry capillary even before they enter the mass spectrometer.

<table>
<thead>
<tr>
<th>EXTRACTION OF THE SECONDARY IONS FROM THE MS ORIFICE INTO THE FIRST DIFFERENTIALLY PUMPED REGION</th>
<th>TRANSMISSION AND DETECTION OF SECONDARY IONS IN TOF REGION</th>
</tr>
</thead>
<tbody>
<tr>
<td>PARAMETER</td>
<td>TESTED RANGE</td>
</tr>
<tr>
<td>SOURCE TEMPERATURE</td>
<td>80 - 180 °C</td>
</tr>
<tr>
<td>CONE</td>
<td>25 - 40 eV</td>
</tr>
<tr>
<td>EXTRACTION</td>
<td>0 - 8 V</td>
</tr>
<tr>
<td>RF LENS</td>
<td>0.5 - 3 V</td>
</tr>
</tbody>
</table>

Table 4. Invested set of parameters for achieving optimal conditions for transport of the secondary ions from the mass spectrometer orifice into the first differentially pumped region and transmission and detection of secondary ions in TOF region.
Additionally, some other parts of the QTOF-2 can influence the signal strength. Dependable of the analyte, an optimal setup should be found which considers tuning of some of the numerous parameters of the instrument as illustrated in figure 26. Considering a specific region of the QTOF MS, tuning parameters can be grouped into three categories; source, analyser and MS2. Since the focus of this section is to find the optimal values for the guidance of the ions into TOF section, most of the investigated parameters considered here will be coming from the first two categories (Table 4).

Tuning of the QTOF-2 related parameters was assessed in this section. The selected parameters are related to the extraction of the secondary ions from the mass spectrometer orifice into the
first differentially pumped region and transmission and detection of secondary ions in the TOF region. The optimisation of these parameters was performed in negative ion mode using 6.5MeV Cl$_3^+$ ions on a sample of TNT drop cast on Si wafer. During the tuning of each parameter, the behaviour of chromatogram for TNT principal fragment at m/z 226, first daughter fragment at m/z 197 as well as a background ion at m/z 220 was observed. The optimal values were found as follows:

- **Source temperature in range of 100 - 140°C**
  The signal for both the TNT fragments and background peak remained unchanged outside of the optimal range. However, an additional background peak at m/z 678 appeared for temperatures higher than 140°C.

- **Cone energy in range of 36 – 40 eV**
  At values which were outside of the optimal range the signal decreased for both of the TNT peaks investigated.

- **Extractor voltage at 3V**
  Although normally set in the range of 0-2V, in this case, the best signal for the TNT fragments was achieved at a higher voltage on the extraction lens.

- **RF Lens voltage at 1V**
  Presents the offset voltage on the hexapole and first differential pumping aperture.

- **Steering voltage at -0.5V**
This parameter directs the secondary ions into the pusher by adjusting the voltage difference between the bottom and top lens of the focus (steering) lens. The steering voltage should always be around zero. Voltages below and above -0.5V increase the intensity of the background peak together with the TNT peaks.

- **Entrance at range of 65-71 eV**

  By setting the voltage on the pusher entrance and exit, we define the axial speed of the ions through the TOF is set. At 65eV the beam should be central to the detector. Increased values of entrance up to 71eV didn’t cause any change to the signal of the TNT and background peaks.

- **MCP voltage at 2000V**

  The ToF voltage has to be chosen before starting with the acquisition. Additionally, four other MCP voltages were tested, two below and two above 2000V, in steps of 100V. It appears that at all the values the signal of all the investigated peaks did not change.

- **Transport voltage at 6V**

  This voltage sets the offset DC on the transport hexapole as well as the DC on the apertures of the gas cell. Although the optimal settings are usually found between 2 – 4 V, in our case 6V increased the signal of the TNT peaks.
5.5 Sampling setup and data acquisition

In AP MeV SIMS, samples are placed just in front of the beam exit window, at distances of a few millimetres. In order to enable an independent positioning of the capillaries, each of them was equipped with a 5-axis manual positioning stage. Each stage comprises an XYZ axis translator based on linear positioners and the α-axis goniometer attached to the rotating platform, all from OptoSigma (Santa Ana, California). The positioning stage will allow accurate orientation and alignment of the capillaries with respect to the sample/beam exit window and each other by providing three independent orthogonal translations (13 mm) and two rotations, full 360° on the rotation platform and additional ±15° on the high precision goniometer (Figure 27).

Figure 27. Positioning stages designated for each capillary enabling independent and accurate orientation and alignment.

The assessment of the optimal positions of the capillaries is described in section 4.3.3. The mass spectrometer capillary was heated during all the experiments and the He flow was kept
on during the measurements except for cases of testing the absence of He gas as well as the use of other sheath gasses – see section 4.2.

The data acquisition is obtained using the Waters MassLynx software supplied with the QTOF-2 [151]. Mass information from the QTOF-2 is recorded simultaneously in two parallel channels. First, the internal time-to-digital converter (TDC) was used with the Waters MassLynx software. The MassLynx software controls the QTOF-2 instrument, acquires and manipulates mass spectra [152], [153]. An additional 4GHz TDC (Kore Ltd, UK) was used simultaneously with an interface to OMDAQ-3. This allows OMDAQ-3 to create maps of mass peaks by correlating the recorded data with the instantaneous position of the sample stage. The data is stored in “list-mode” which allows post-processing of any mass and energy range. The advantage of using both channels is that the MassLynx software can be used to calibrate and identify the peaks observed in the OMDAQ-3 spectra.
6. Optimisation of AP MeV SIMS

6.1 Introduction

In this chapter, process of AP MeV SIMS optimisation will be presented. First, samples used in AP MeV SIMS will be described. The investigation of samples suitable for both the analysis and mapping has, in itself, been time-consuming. Nonetheless, several types of samples have proven to give suitable signals and were employed in the optimisation processes. All the tested samples were prepared “in-house” using different deposition techniques. Sample preparation involves certain standard procedures, such as substrate treatment to assure the surface is as clean as possible and minimise contamination. The same applies for sample handling and storage; see section 6.2.1 of this chapter.

Next, the influence of the vapour pressure on molecular detection of TNT and SOPs will be introduced as it can affect spectral interpretation and contribute to the memory effect.

Mass calibration procedure of the QTOF-2 instrument is described in section 6.4.

In the following section, the limit of detection for AP MeV SIMS will be determined using a TNT standard. The same set of measurements was also performed with the standard TOF SIMS in order to compare the capability of two of the techniques.

The molecular detection for samples of leucine, TNT and SOPs is presented in the following section. The spectra of leucine obtained with MeV SIMS in vacuum and air are quite different, making the leucine detection more achievable with MeV SIMS in a vacuum. Contrary to the general findings of the TNT analysis with various other techniques such as nuclear quadrupole resonance (NQR), TOF SIMS and other mass spectrometry-based methods, the detection of
TNT with AP MeV SIMS has been very successful. Although in this configuration, AP MeV SIMS can never become a portable technique which is a necessity for forensics, it can still be a very competitive technique offering information on TNT, or some other explosives. Preliminary analyses of the organic pigments with AP MeV SIMS showed the potential of this technique for the detection of the azo compounds. This can be applied to many different areas of interest, such as art forgery and document counterfeiting. Nowadays, organic polymers are causing environmental concerns which impose an additional requirement for the analysis of every day’s objects containing these molecules, such as cosmetic products and toys[154].

Ambient-based techniques create a rich background peaks composed of various molecular species present in the sampling surrounding volume. Here typical background spectra are presented in AP MeV SIMS for both of the ion polarities and try to identify their content. The following section will show how the data interpretation can be misleading as a consequence of a memory effect. The memory effect was thoroughly examined which helped establish the correct acquisition practice in order to avoid these artefacts in spectra.

Optimisation parameters which can enhance the ionisation process and help in the understanding of the electronic sputtering mechanism are the topic of chapter 6.9. These are mostly beamed related parameters such as beam species and current. Relative molecular yields of TNT principal fragment for two ion beam species, oxygen and chlorine with different energies will be compared. Another beam related parameter investigated in this section will be the beam current. The optimal ion current will be determined on TNT sample which shows the least bond breakage of the molecules examined here. The final section of this optimisation chapter will be an illustration of the principle of post-ionisation tested on AP MeV SIMS. The description of the setup used for this experiment on post-treatment of sputtered neutrals, results as well as the conclusions drawn from it will close the section and chapter.
6.2 Samples used in AP MeV SIMS

Samples used for optimisation of AP MeV SIMS can be roughly grouped into two categories according to their preparation. In the first category, we encounter various films prepared by one of the deposition techniques. These are leucine (Leu), arginine (Arg), polystyrene (PS) and poly(methylmethacrylate), (PMMA) which were all prepared in the class 1000 cleanroom in the Advanced Technology Institute (ATI) at the University of Surrey. The bio-films of leucine and arginine were evaporated onto a Si wafer using an organics evaporator. After the evaporation, the thickness of the films was measured using ellipsometry and was determined to be in the range of 120-200 nm for all the samples. The polymer films of PS and PMMA were spin coated onto a Si wafer. The other group of samples consisted of different explosives and paint pigments. The explosives used were trinitrotoluene (TNT), 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) and pentaerythritol tetranitrate (PETN) and were all dissolved in acetonitrile at concentrations of 500 ppm. Such solutions were dropped cast on a substrate which was a Si wafer, a glass slide or filter paper. Lastly, the pigments which were utilised in this work were pigments yellow 3 and 74 (PY3 and PY74), pigment orange 5 (PO5) and pigment red 112 (PR112). Each pigment is indicated by a pigment name and pigment number making it possible to ascertain which pigments are incorporated in certain colours and the chemical composition of those pigments together with their properties[155]. The pigments used in our experiments were dissolved in toluene and acetone and a thin layer was laid down using a brush onto a Si wafer or a glass slide. The most frequently used samples in this work were leucine, TNT, PY3, PO5 and PR112 since they gave the most representative and reproducible signal.
Amino acids are building blocks of proteins and as such play a vital role in their biosynthesis. Generally, amino acids are structured of at least one amino group (-NH₂), a carboxy group (-COOH) and a unique organic side chain[156]. The amino acid units will form a chemical bond amongst themselves via a chemical reaction between the carboxyl group of one unit and the amino group of another followed by releasing of a molecule of water. This type of a bond is known as a peptide bond and the chemical process as the condensation or dehydration.

Leucine is a branched molecule with an aliphatic group attached to an alpha carbon. It comes in forms of white crystals and is more soluble in alcohols than water[157]. Amino acids have been widely used in SIMS experiments due to their connectivity with proteins[158], [159]. In recent years, the importance of amino acids has been raised owing to their ubiquitous involvement in metabolic processes, and their capability to act as sensors and biosensors. Many different substrates for deposition of amino acid thin films have been investigated such as silicon, mica, dental titanium and cellulose, in order to understand the behaviour of biomolecules on various surfaces[160]–[162]. In MeV SIMS, thin films of amino acids deposited mainly on silicon are considered to be the reproducible type of samples for the purpose of examination of the fundamental theory of measuring ion yields and damage cross sections[163].

Figure 28. The structure of leucine with the chemical formula C₆H₁₃NO₂ and average molecular mass of 131.17 Da.
The amino acids most commonly used are leucine and arginine due to ease of their preparation. Leucine is a branched amino acid containing a hydrocarbon side chain with two methylene groups (Figure 28). The fragmentation patterns that occur during analysis depend on the structural sequence, internal energy absorption, the way of introducing the energy, ion beam charge state, etc. Most of the amino acids follow well-known fragmentation patterns[164], which can then be used to understand the fragmentation of peptides and proteins[165].

- **Explosives – TNT**

TNT is a derivate of toluene and comes in a form of yellow, odourless solid soluble in organic solvents such as acetone, benzene or acetonitrile (Figure 29). TNT explosive is used in military shells, bombs, grenades and the open air as well as for underwater mining[157]. In contrary to some of the commonly used explosives such as black powder or nitroglycerine, TNT is has a high activation energy and a melting temperature of 81 °C. It does not explode up to 240 °C and does not absorb or dissolve in water. All these features make TNT a suitable choice for rock-blasting and construction of railways and highways. Originally, TNT was developed as a yellow dye without the understanding of its explosive nature, even many years after it was synthetised[166], [167]. In forensics, explosives are generally divided into two groups according to their detonation velocities. TNT has a very high detonation velocity of 6 km/s, with an energy content of 4.6 megajoules per kilogram, and so is defined as a high explosive.
Figure 29. Chemical structure of TNT molecule. TNT is a nitrated benzene-derivate with a chemical structure of 2,4,6–trinitrotoluene.

The explosive detection considers the investigation of explosive residues, either post traces of materials that built up the explosive. The most common laboratory techniques for detection and analysis of explosives are gas and liquid chromatography, as well as various other mass spectrometry techniques. Portable detection methods based on ion mobility and surface acoustic waves are of great interest for counter-terrorism applications. Another technique employed for analysis of explosives is nuclear quadrupole resonance (NQR). The ion mobility spectrometry (IMS) has been widely used for screening of passengers and luggage for explosives and their by-products at airports. The IMS trace detection is measuring the mobility of charged particles and ions under ambient conditions. The molecular species can get ionised through several processes such as ionising radiation, electron attachment, field-, photo- or electrospray ionisation. The charged species are then being accelerated under a linear electrical drift field towards an ion collector electrode. As the last step of the analysis, molecules are being distinguished according to their characteristic arrival times at the collector electrode, which depends on the molecular size and/or cross-section[168]. Another mass spectrometry technique frequently utilised for the explosives analysis is DESI.
TNT is a derivative of toluene and comes in a form of yellow, odourless solid soluble in organic solvents such as acetone, benzene or acetonitrile. TNT explosive is used in military shells, bombs, grenades and the open air as well as for underwater mining[157].

- **Synthetic organic pigments (SOPs)—PY3, PO5 and PR112**

The synthetic organic pigments presented here are all synthesized from aromatic hydrocarbons. Unlike dyes, pigments are the insoluble colourants structured in a way that solubilizing groups are excluded from the chemical composition or by forming insoluble organic structure. The insolubility or in some cases partial solubility is responsible for important application properties of pigments such as tintorial strength, migration, recrystallization, heat stability, lightfastness and weatherability. The SOPs can be roughly classified into azo and non-azo (polycyclic) pigments. PY3 and PO5 belong to the monoazo yellow and orange groups whilst PR112 belongs to the disazo group[169]. The wide use of the synthetic organic pigments as colourants has turned them into a commercial success. Some of the conventional roles of the SOPs are in art, fashion, decoration, cosmetics. The decorative uses are manifested in car and machine industry, architecture, building, furniture etc. The most widespread use of organic pigments is in printing ink, paints and plastics[170]. The latest applications of SOPs are in high technology industries such as photo-reprographics, optoelectronic display, and optical data storage[170]. The high applicability of these compounds imposes a great demand for constant improvement of their functional properties, which are determined by the chemical structure. Pigments PY3, PO5 and PR112 belong to azo compounds, i.e. derivatives of diazene (diimide), HN=NH, with both hydrogens being substituted by hydrocarbyl groups, e.g. PhN=NPh azobenzene or diphenyldiazene[171]. Such polycyclic aromatics have usually planar structures.
stabilised by intramolecular hydrogen bonding (Figure 30). Analysis of SOPs is traditionally performed with mass spectrometry-based on gas chromatography (GC MS), including the Pyrolysis GC MS, Fourier Transform Infrared (FTIR) and Raman spectroscopies, and Nuclear Magnetic Resonance (NMR). The GC MS methods require substantial sample preparation, which involves the separation of mixtures and derivatisation if the compound is polar.

Figure 30. Structures of some azo pigments; a) PY3, b) PO5 and c) PR112.

Identification of SOPs using FTIR and Raman is challenging due to the overlapping bands in the spectra. Detection limits of these techniques are also considered problematic[19].
6.2.1 Sample preparation/ handling/storing precautions

(AP) MeV SIMS is a surface sensitive technique and thus requires a certain way of sample handling during the preparation and analysis in order to minimise possible contamination. As a first step, we would need to ensure that substrates used for the sample preparation are clean. The substrates used for all the samples above mentioned were cleaned in the cleanroom using a standard practice according to the type of a substrate[172], [173]. Next, the sample preparation has to be as controllable as possible in terms of the environment and conditions applied. Solvents of high purity should always be used if possible. Powder samples should be handled with a special care not to contaminate any parts of the equipment. Lastly, proper sample handling and storage should be employed such as wearing gloves, using clean utensils and appropriate choice of storage. The type of gloves is an important parameter in surface analysis. In TOF SIMS and XPS, it is strongly advised to avoid latex gloves and use polyethylene instead[174]. Latex gloves a potential source of silicones. In case of AP MeV SIMS, we can also expect some additional contaminants besides the silicones such as polyethylene- see section 6.7 hence only nitrile gloves will be used. The utensils used for sample handlings such as tweezers and spatula are exclusively metal. For sample storage plastic containers and bags were strictly avoided and glass containers and aluminium foil, both previously cleaned, have been used instead.

6.3 Influence of the vapour pressure of samples on the mass detection

The vapour pressure of a liquid or solid is the equilibrium pressure above its liquid or solid, that is the pressure exerted by its equilibrium in liquid or solid in a closed container at a given temperature[175]. Factors that influence the vapour pressure are temperature and types of
molecules that make up a solid or liquid. The vapour pressure is proportional to temperature and inversely proportional to intermolecular forces. In AP MeV SIMS, where sampling is performed in air, vapour molecules can also find their way into the mass spectrometer capillary together with desorbed molecules. If the vapours are originating from the sample, they can cause misinterpretation and memory effect. In case of detecting solely the vapours, the electronic sputtering is excluded as the mechanism responsible for desorption hence the presence of an ion beam is not needed. During analysis of TNT, the molecular ions originating from TNT were observed in mass spectra acquired even when the ion beam was not present on the sample of TNT. This was even more pronounced when the freshly prepared sample was used for analysis. Thus, freshly prepared samples should be avoided and they should be left to outgas at least a few hours prior to analysis. The occurrence of vapour molecules in AP MeV SIMS spectra was also noticed for the SOPs analysed in this work – PY3, PO5 and PR112. Once again, the intensity of the vapour molecules was higher for the freshly prepared samples. All the samples that showed the occurrence of the vapour in molecules had undergone similar sample preparation as the solids were dissolved or mixed in an appropriate organic solvent, acetonitrile in case of TNT and toluene or acetone in case of SOPs and such solution or mixture was deposited on Si wafer, glass slide and filter paper. AP MeV SIMS analysis of TNT and SOPs in solid phase did not show any signal from the samples hence the organic solvents had to be used. Although the vapour pressure for solids is low or extremely low in case of TNT, samples of SOPs and TNT used in AP MeV SIMS showed the influence of the vapour pressure on the mass detection. The interference of the TNT vapours on the molecular map of TNT will be shown in the following chapter.
6.4 Mass calibration

The mass spectrometer calibration obtained with the ESI source was performed prior the AP MeV SIMS experiments. As a calibration compound, a sodium caesium iodide mixture was used. Additionally, OMDAQ mass calibration of the spectra was obtained by assigning the peaks via visual correlation with the Q-TOF spectrum. In order to calibrate the Q-TOF instrument, a standard calibration procedure using the NaCsI calibration standard was obtained[153]. Once a stable spray was achieved, a set of spectra for one minute with a scan time of 1s, over the m/z range from 100 to 1000 was acquired (Figure 31). The acquired data should not have more than 500 counts/s, to prevent the deadtime distortion. After the acquisition, 30 scans were combined together into one spectrum.

<table>
<thead>
<tr>
<th>NaCsI reference values, m/z</th>
<th>NaCsI measured values, m/z</th>
</tr>
</thead>
<tbody>
<tr>
<td>132.9054</td>
<td>133.0342</td>
</tr>
<tr>
<td>172.884</td>
<td>173.012</td>
</tr>
<tr>
<td>322.7782</td>
<td>323.5680</td>
</tr>
<tr>
<td>472.6725</td>
<td>472.8024</td>
</tr>
<tr>
<td>622.5667</td>
<td>622.7036</td>
</tr>
<tr>
<td>772.461</td>
<td>772.6421</td>
</tr>
<tr>
<td>922.6552</td>
<td>922.8248</td>
</tr>
</tbody>
</table>

Table 5. Comparison between the reference values and measured values for the NaCsI related peaks. The reference values were taken from the Q-TOF calibration library.

If this spectrum agrees with the NaCsI reference masses from the spectrum library incorporated into the MassLynx software to a reasonable amount (around +/- .1 m/z value), then the
spectrum is saved (Table 5). The following step encounters selecting the TOF calibration type, which was a fifth order polynomial function to match the masses of the saved spectrum with the reference masses. Once the calibration was obtained and saved, it was applied to all subsequent acquisitions.

![Mass spectrum of NaCsI calibration standard obtained with ESI source in positive ion mode. The flow rate of the NaCsI solution was set at 3mL/h, with desolvation gas flow at 150 L/hr and temperature at 300°C.](image)

Figure 31. Mass spectrum of NaCsI calibration standard obtained with ESI source in positive ion mode. The flow rate of the NaCsI solution was set at 3mL/h, with desolvation gas flow at 150 L/hr and temperature at 300°C.

The accuracy of TOF measurements can be degraded due to changes in temperature by shifting mass values by many parts per million. In this case, an automatic correction procedure implemented in the MassLynx software was applied.
6.5 Limit of detection

The “limit of detection” (LOD) together with “limit of quantitation” (LOQ) are two parameters proving performance in method validation. These parameters are well-defined for applications using analytical techniques with well-established performance and procedure. Although AP MeV SIMS might still not be in such a phase of development where LOD or LOQ can be completely determined, it would be useful to have information on these parameters even in this early phase. Considering the fact that secondary ion mass spectroscopic techniques generally have an obstacle in obtaining the quantitative information due to the matrix effect (described earlier in section 2.3.4.1), determining of LOQ requires a very complex procedure[176]. Thus, only LOD will be dealt with in this work. There are several definitions for a limit of detection, depending on the association. According to IUPAC the limit of detection is the smallest amount of concentration of an analyte in the sample that can be reliably distinguished from zero[171]. LOD is expressed as $3s/m$, where “$s$” is the standard deviation of “$n$” replicates ($n \geq 7$) and “$m$” is the slope of the curve assuming the linear regression[177]. The experiments here on LOD were performed with AP MeV SIMS and conventional TOF SIMS. The AP MeV SIMS and TOF SIMS measurements were obtained on samples of TNT. Both sets of the samples were prepared in the same way, which was by drop casting of TNT solution on a clean Si wafer a few hours prior to the measurements being taken. The highest concentration of TNT crystals dissolved in acetonitrile was $c = 500$ ppm and the lowest $c = 5$ppm. Other concentrations used in the experiment were $c = 10$, 50 and 100 ppm. For each concentration, a set of three spectra from different sample areas were taken and their mean value was used for data interpretation. With AP MeV SIMS the signal from TNT principal and first daughter fragment was noticed at $c = 10$ ppm. Consequently, the dependence of molecular yield relative to the number of total ion counts on TNT concentration shows a linear trend for both of the fragments (Figure 32). However, this measurement cannot be fully reliable as the structure of the films was not
considered in the experiments. In order to properly describe the dependence of the relative molecular yield on TNT concentration, homogeneous films of TNT with same thicknesses have to be prepared. The best way to achieve the constant thickness is to prepare gel films with doped TNT.

In case of determining of LOD for TNT with TOF SIMS, no reliable results were obtained at any of used concentrations. The TOF SIMS experiments were carried out using a TOF.SIMS5 instrument at the University of Surrey Surface Analysis Laboratory. For the measurements the 25keV Bi$^{3+}$ ion beam and an incident angle of 45º to the surface normal. The pulsed current on target was kept at $I = 0.2 \text{ pA}$. Such working conditions ensured ion doses were kept below the static limit. The analysis of explosives, including TNT with TOF SIMS, was previously obtained by Mahoney et al using a TOF.SIMS4 instrument at the University of Münster. The working conditions were similar to the ones we used, including the same ion species, energy and incident angle. The only difference was in ion current which was in the case of the “Münster” experiments kept at $I = 0.3 \text{ pA}$. In terms of the samples, three different C4 samples comprising mostly of RDX, plasticisers and binders were used. In addition to RDX, HMX explosive was also found to be present in the samples.
Figure 32. LOD for TNT principal and first daughter fragment determined with AP MeV SIMS with current I = 1.7 nA. Relative molecular yield shows a linear dependence on the deposited concentrations of TNT on Si wafer. The film thickness was not considered in measurements.

HMX occurs as a by-product in the RDX synthesis. TNT may also be present in the sample which would be indicated by the m/z 226 in the negative ion mode. Considering the lack of publications on analysis of TNT with TOF SIMS in comparison to other explosives such as RDX, HMX and PETN, as well as our results of determining of the LOD with TNT we can draw a conclusion that the TOF SIMS analysis might not be the most suitable choice for TNT.

6.6 Molecular detection in AP MeV SIMS

It seems that it would be most appropriate to initially perform the mass spectrometry analysis in positive ion mode. This is because the numerous molecular spectral databases existing currently are almost exclusively for this mode[164], [178]. The situation gets even more conclusive for ambient based mass spectrometry techniques where the spectral data base for
the negative ion mode does not exist at all. The reason why the positive mode is preferential over the negative originates from the chemical structure of the vast majority of molecular species being prone to becoming positively charged. Positive ions i.e. cations are formed when an organic molecule either loses an electron or a hydroxyl group or gains a proton or some other positively charged element or molecule. Most common elements attaching to organic species are sodium and potassium ions, and the ammonium cation. It is normally more energetically favourable to attach a proton than to detach one. Electron loss is also energetically more favourable than electron gain. Whether a positive or negative mass spectrum will be more suitable for the interpretation of a specific organic molecule depends on the group of organic molecules the investigated sample belongs to. Most of them will undergo the protonation, as already mentioned. However, some of the groups of organic molecules will give rise to anions. Negative ionisation affinity is a normal characteristic of organic acids, carbohydrates, phenols and quinones. However, in some cases, there is no noticeable preference. This ambiguity is very often a characteristic of the more complex organic molecules, such as organic pigments. Thus, both ionisation modes should be examined for the analysis as they might give complementary information. In this work mainly spectra in negative ionisation mode will be mostly presented.

One of the first samples used for the molecular detection in AP MeV SIMS was leucine evaporated on Si wafer. Analysis of leucine with AP MeV SIMS using O^{3,4+} beams resulted in the m/z 86 peak (Figure 33). In some cases, a peak at m/z 157 was also observed which might correspond to a sodiated molecular ion of leucine. In negative ion mode, none of the leucine related peaks were found.
Figure 33. Positive ion mode spectrum of the leucine thin film on Si wafer obtained with O\(^{4+}\) primary beam taken in the air at the University of Surrey.

The vacuum analysis of leucine with MeV SIMS under static conditions showed the most intense peak to be at m/z 132, which is a protonated molecular peak (Figure 34). Besides the protonated molecular ion, we can notice a pattern of \([n^*M + H]^+\) up to 7n. This means that the leucine molecules build adducts, but do not bond via peptide bonds typical for peptides and proteins. A peptide bond is a bond between the amine group of one amino acid and the carboxyl group of another amino acid followed by a release of a water molecule.
Additionally, more leucine related peaks can occur in MeV SIMS spectra, which represent fragments of the molecular ion. The decarboxylated ion fragment found at m/z 86 is characterised as the immonium fragment. Although it was not present in figure 35, it did appear in the vacuum spectra of leucine acquired in the both University of Surrey and Ruđer Bošković Institute with 4MeV O<sup>4+</sup> and 5MeV Si<sup>4+</sup> primary beam. The m/z 86 is also observed in TOF SIMS measurements using 25 keV Bi<sup>3+</sup> primary beam, and is the most common leucine fragment described by other techniques such as ESI, APCI and LA ICP MS[165], [179]. Samples of leucine thin films used for measurements in the University of Kyoto, University of Surrey and Rudjer Bošković Institute were all prepared in the cleanroom of the Advanced
Technology Institute at the University of Surrey, following the same procedure. The difference in the spectra between University of Kyoto and others could be interpreted as the difference in primary ion species. The Cu$^{4+}$ primary ion is heavier than both Si$^{4+}$ and O$^{4+}$ ions and causes less fragmentation hence only molecular ions were observed.

The above-described example of leucine thin film analysis showed that the AP MeV SIMS analysis of leucine is not as conclusive as for the vacuum MeV SIMS analysis resulting with an intense molecular ion followed by gradually less intense molecular adducts.

The next sample of interest analysed in AP MeV SIMS was TNT. Most explosives give the best response in the negative mode as they contain nitro groups. TNT is prone to electron capture, which results with m/z 227 radical anion and is commonly detected by some other techniques used for detection of explosives such as DESI and IMS[180]. Besides the radical anion, several additional TNT related anions have been reported with IMS. These are the deprotonated molecular ion, m/z 226, multicomponent cluster ions such as [(M+NO$_3^-$)] and NO$_3^-$ fragment[181]. Both of these techniques are rapid with IMS also being highly sensitive. However, the exact nature of the analysed species can only be decisively determined after undergoing the MS/MS reaction. Moreover, the repeatability in IMS is still addressed as challenging. There are also concerns about the significant impact of the operational conditions such as drift tube temperature, drift gas and choice of ionisation method on the ion chemistry[182]. Although the TNT radical and deprotonated molecular ions are the only detected species by most of the techniques such as DESI, IMS, TOF SIMS, EESI (Extractive ESI) and LTP (Low-Temperature Plasma) analysis, they are not the only TNT related fragments[105], [183]. A nitroso (NO$^+$) group can also be detached from TNT molecule
resulting in the m/z 197 fragment, as seen in figure 35. Moreover, the deprotonated fragment can lose two nitroso groups which will give the m/z 166 peak.

Figure 35. Fragmentation pattern of TNT molecule.

In AP MeV SIMS, we have observed fragments at m/z 227, 226 and 197 regardless the primary ion species used (Figure 36 for the O^4+ primary beam). None of the other experimental conditions, such as beam current, sampling geometry, use of sheath gas or heating of MS capillary, could alter the presence of the TNT related fragments but they could manipulate with the ratio of the molecular ions with respect to the fragment ion. In addition to the four peaks mentioned above, the peak at m/z 210 was also found to relate to TNT. This peak is most likely created by detachment of the hydroxy group, (OH). Generally, it has been found that detecting of TNT is problematic due to low vapour pressure, which is 8 x 10^{-4} torr at 25 °C[157], [184]. The TNT by-products, 2,4-DNT and 1,3-DNT, have a much higher vapour pressure in
comparison with TNT. Thus, in some cases, TNT is more detectable from these two components, which are considered to be natural contaminants of TNT[185].

Figure 36. The spectrum of TNT obtained with AP MeV SIMS using the 8 MeV O$_4^+$ primary beam. The labelled peaks are TNT radical and molecular anions, at m/z 227 and 226 as well as the fragment anions at m/z 210 and 197.

These findings have implication for the stimulation of producing of the additional TNT vapours with the ion beam. This explains why AP MeV SIMS is extremely successful in detecting of TNT, without the need for performing the MS/MS operational mode as in IMS or DESI.

Finally, AP MeV SIMS was employed for the analysis of the PY3, PO5, and PR112, using the 6.5 MeV Cl$_3^+$ primary beam. Samples of pigments were prepared by mixing a small amount of the pure pigment with either toluene or acetone and applying it to a clean substrate. The substrates used for samples preparation were a glass slide, Si wafer, and filter paper. Such samples were left to dry for few hours prior the analysis. For the measurements, both
acquisition modes were used. In the positive mode, none of the pigment-related peaks were observed. In the negative mode, each one of the three pigments gave a different peak (Figure 37).

The occurrence of these specific peaks was constant, regardless of the type of the solvent or substrate or experimental conditions, such as the beam current used. The peak at m/z 220 can be related with the PY3, m/z 132 with the PO5, and m/z 153 with the PR 112 (Figure 30). The molecular weights of these pigments are; \( M_r(\text{PY3}) = 395.2 \ \text{g} \cdot \text{mol}^{-1} \), \( M_r(\text{PO5}) = 338.27 \ \text{g} \cdot \text{mol}^{-1} \) and \( M_r(\text{PR112}) = 484.76 \ \text{g} \cdot \text{mol}^{-1} \). Clearly, the peaks observed for each pigment can only correspond to fragments. The PY3 related fragment at m/z 220 is likely to be the \([\text{C}_{10}\text{H}_5\text{N}_2\text{O}_2\text{Cl}]^-\) anion. This structure would be achieved by detaching of the benzene ring which contains an amine group, (-NH\(_2\)) and a chlorine atom. In the case of the PO5 related...
fragment at m/z 132, an additional investigation into the fragmented structure has to be carried out, as there are several proposed structures likely to correspond to this m/z ratio such as the [C₉H₈O]⁺, [C₉H₁₁N] and [C₇H₇N₃]. Finally, the PR112 related fragment at m/z 153 might be formed from the naphthalene system with a nitrile (-CN) group. The structures of these pigments could not be confirmed due to lack of an existing database for the SOP’s, especially for the negative polarity.

6.7 Background in AP MeV SIMS

The positive ion mode (Figure 38) has a greater abundance of background peaks than negative ion mode (Figure 39) making the interpretation of negative AP MeV SIMS spectra easier than positive spectra. Besides being significantly more abundant, positive background peaks are also more intense than the ones in negative ion mode. On the other hand, the ambient background in positive ion mode is saturated with different polymers, with the most intense ones in m/z region from 400 and 600. Background peak identification was carried out for the positive ion mode as shown in table 6. The dominant peaks are the ones at m/z 404, 481 and 554. Each of these three peaks has satellite peaks which are the result of the subtraction by m/z 18. The m/z 18 would correspond to a molecule of water, H₂O⁺. Among the three most intense peaks, the m/z 481 is the highest one and is correlated with PEG polymer. PEG is a ubiquitous synthetic polymer with a repetition unit of m/z 44. It is present in mass spectrometer calibration standard solutions, organic solvents and acts as surfactants in many detergents including dish washing soaps. PEG is also used for coating Chem-wipes which are often used for wiping the glassware and working benches. The second most intense peak in the positive spectrum is the one at m/z 404, PPG which is also a ubiquitous polymer. PPG is more hydrophilic than PEG. The third most intense peak is at m/z 554 which hasn’t been identified.
Figure 38. Typical AP MeV SIMS ambient background spectrum in positive mode acquired with the 6.5 Cl$^{3+}$ beam.
Figure 39. Typical AP MeV SIMS ambient background spectrum in negative mode acquired with the 6.5 Cl^{3+} beam.

It might be connected to its predecessors, PEG and PPG since it follows the same pattern in terms of having the satellite peak as well as PEG and PPG. However, adding of the repetition units of these polymers does not match to the mass of m/z this peak. There is a possibility that this peak could be a copolymer between PEG and PPG. The PEG and PPG copolymers are well known for their unique moisture retention and wettability. Considering the presence of other background contamination, which is less intense than the ones just described, they mostly belong to a group of organic compounds known as phthalates and siloxanes. Interestingly, polydimethylsiloxane which is considered to be the main contaminant in conventional TOF SIMS as well as vacuum SIMS is suppressed by other contaminants in ambient analysis such as PEG and PPG.
Table 6. Identification of the most common background peaks for positive ion mode in AP MeV SIMS.

<table>
<thead>
<tr>
<th>m/z</th>
<th>Ion type</th>
<th>Formula for M or subunit or sequence</th>
<th>Compound ID or species</th>
<th>Possible origin and other comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>[A₁B+K]^+</td>
<td>[C₃H₆O]ₙH₂O</td>
<td>PPG</td>
<td>Polypropylene glycol, ubiquitous polyether</td>
</tr>
<tr>
<td>142</td>
<td>[M+CH₅CN+Na]^+</td>
<td>C₂H₅OS</td>
<td>DMSO</td>
<td>Dimethylsulfoxide, solvent</td>
</tr>
<tr>
<td>149</td>
<td>[f+H]^+</td>
<td>C₆H₄O₃</td>
<td>Phthalic Anhydride</td>
<td>fragment ion originating from phthalate esters</td>
</tr>
<tr>
<td>215</td>
<td>[A₃B+Na]^+</td>
<td>[C₃H₆O]ₙH₂O</td>
<td>PPG</td>
<td>Polypropylene glycol, ubiquitous polyether</td>
</tr>
<tr>
<td>225</td>
<td>[M+H]^+</td>
<td>C₁₃H₂₄N₂O</td>
<td>DCU</td>
<td>N,N’-Dicyclohexylurea</td>
</tr>
<tr>
<td>240</td>
<td>[A₃B+H]^+</td>
<td>[C₂H₄O]ₙH₂O</td>
<td>PEG</td>
<td>Polyethylene glycol, ubiquitous polyether</td>
</tr>
<tr>
<td>250</td>
<td>[A₃B+H]^+</td>
<td>[C₃H₆O]ₙH₂O</td>
<td>PPG</td>
<td>Polypropylene glycol, ubiquitous polyether</td>
</tr>
<tr>
<td>280</td>
<td>[M+H]^+</td>
<td>C₁₆H₂₂O₄</td>
<td>Dibutylphthalate</td>
<td>Plasticiser, phthalate ester</td>
</tr>
<tr>
<td>301</td>
<td>[M+Na]^+</td>
<td>C₁₆H₂₂O₄</td>
<td>Dibutylphthalate</td>
<td>Dibutylphthalate, plasticizer</td>
</tr>
<tr>
<td>331</td>
<td>[A₅B+Na]^+</td>
<td>[C₃H₆O]ₙH₂O</td>
<td>PPG</td>
<td>Polypropylene glycol, ubiquitous polyether</td>
</tr>
<tr>
<td>371</td>
<td>[M+H]^+</td>
<td>[C₂H₅SiO]₅</td>
<td>Polysiloxane</td>
<td>Polysiloxane, followed by m/z 388</td>
</tr>
<tr>
<td>388</td>
<td>[M+NH₄]^+</td>
<td>[C₂H₅SiO]₅</td>
<td>Polysiloxane</td>
<td>Polysiloxane, (see m/z 371)</td>
</tr>
<tr>
<td>404</td>
<td>[A₅B+K]^+</td>
<td>[C₁₃H₆O]ₙH₂O</td>
<td>PPG</td>
<td>Polypropylene glycol, ubiquitous polyether</td>
</tr>
<tr>
<td>445</td>
<td>[M+H]^+</td>
<td>[C₃H₆O]ₙH₂O</td>
<td>PPG</td>
<td>Polypropylene glycol, ubiquitous polyether</td>
</tr>
<tr>
<td>462</td>
<td>[M+NH₄]^+</td>
<td>[C₂H₅SiO]₆</td>
<td>Polysiloxane</td>
<td>Polysiloxane (see m/z 445)</td>
</tr>
<tr>
<td>481</td>
<td>[A₁₀B+Na]^+</td>
<td>[C₂H₄O]ₙH₂O</td>
<td>PEG</td>
<td>Polyethylene glycol, ubiquitous polyether</td>
</tr>
</tbody>
</table>
The polydimethylsiloxane peaks present in vacuum SIMS spectra are mostly present at lower masses and have a well-known signature in positive ion mode including a set of peaks at m/z 73, 147, 207, 221 and 281[186].

It is also worth mentioning that the QTOF-2 instrument used for the mass detection in AP MeV SIMS was shared with another group who was using it for pharmacological analysis. Sharing of the mass analyser increases the possibility for contamination of the instrument. It might also explain why the background in positive spectra in AP MeV SIMS changed after a certain time period with the aforementioned peaks in m/z region from 400 to 600 becoming more intense and masking all the other peaks.

### 6.8 Memory effect

The “memory effect” due to material adsorbing is a very well-known problem for the mass spectrometry techniques based both in a vacuum and air[187]–[190]. It is defined as the occurrence of a molecular species in a mass spectrum without its presence in the sample. The most common source of the memory effect in the experimental setup used here is the mass spectrometer capillary, which requires a careful and repeatable cleaning practice in order to avoid data misinterpretation. Here the memory effect was assessed on several different samples of explosives and organic pigments.
An example of the memory effect for a sample of TNT is shown in the following. The TNT principal fragment at m/z 226 and first daughter fragment at m/z 197 were observed in the spectrum of the blank (Figure 40a). We assumed that the origin of the memory effect is the mass spectrometer capillary. The tip of the capillary is a critical factor contributing to the memory effect, as it cannot achieve temperatures higher than approximately 60 °C. Although less intense, the TNT related peaks were still present even after cleaning the mass spectrometer capillary in an ultrasonic bath filled with water and left to dry in air. The beam exit window and the He flow capillary together with the sample stage are additional sources of the memory effect.
effect. During the sputtering event, most of the desorbed species are neutral, with less than 0.1% getting ionised[13]. In air, these clusters will move freely and may deposit on the beam nozzle and other surrounding parts of equipment. As the ion beam exits the window, it can ionise these previously adsorbed species. Experiments to investigate the memory effect were performed on TNT sample using a 6.5MeV Cl$^{3+}$ primary beam. Before the experiments commenced, a clean mass spectrometer capillary, using the abovementioned cleaning procedure, was placed into the mass spectrometer. A new beam exit window was mounted onto the nozzle and the sample stage together with the other mechanical parts of the setup which are surrounding the sampling area were cleaned by wiping with isopropyl alcohol. During the whole course of the experiment, the mass spectrometer capillary was kept heated at 110 ºC to prevent deposition of ambient desorbed material and molecules of water along its length. The temperature was chosen to be above the boiling point of water. First, a blank spectrum (Figure 40b) was obtained in order to ensure the absence of any other molecular species apart from those originating from the normal ambient. The blank spectrum was used as a starting point of a set of measurements with a TNT sample to obtain precise information on the time dependence of the memory effect. Then, a spectrum of TNT was acquired (Figure 40c). Immediately after acquiring a spectrum of the TNT sample, it was replaced by a clean Al stub and a spectrum of the blank was taken. The acquisition time of each spectrum was 5 minutes. This pattern was repeated until TNT related peaks appeared on the spectra of the blank Al stub demonstrating a memory effect. After the memory effect first appeared, the acquisition times for all of the TNT spectra taken before it appeared were summed and the measurement period before the occurrence of the memory effect (Figure 40a) was detected to be t=138min (Figure 41).
Figure 41. The calculated number of cycles of spectra acquisition of both the blank Al stub and the TNT sample prior to the occurrence of the memory effect. Each of the two samples was acquired 27 times until the TNT principal fragment was observed in the blank Al stub. A single acquisition time took 5 min.

When examining the spectra of the blank Al stub with the memory effect, we can notice the difference in the appearance of the TNT related peaks compared with the normal TNT spectrum. Unlike the normal TNT spectrum, where three different peaks corresponding to TNT can be observed (m/z 227, 226 and 197), in the spectra of the blank Al stub with memory effect, only peaks at m/z 226 and 197 were found. This is the molecular anion, [M-H] at m/z 226. The increase in intensity between the TNT principal fragment obtained with the TNT sample (Figure 40c) and the same peak without the TNT sample being present (Figure 40a) is more than tenfold for the case when the TNT sample is present. Nevertheless, the memory effect can still lead into the assignment of a molecular species even without its actual presence in analysed material and so care must be taken to avoid or reduce such memory effects.
6.9 Optimisation of the secondary ion yield

6.9.1 Ion beam species and energy

The secondary ion yield depends on the energy of the primary beam. Previous studies have shown a several times improvement in secondary ion yield with higher primary beam energies – section 2.3 and increased mass of the primary beam[62]. The difference in energy deposition for the heavier and more energetic primary ions, whereas more energy is being deposited into near surface area, suggests higher ionisation efficiency. The effect of heavier ions on secondary yield is known from previous research as the “velocity effect”. It considers an impact of higher energy density on the surface produced by heavier ions, which is caused by a shorter range of secondary electrons[191]. In this work, two different primary beam species, oxygen and chlorine will be used to investigate this effect. The stopping forces for both of these ions are shown in figure 42. Electronic stopping forces are dominant over nuclear stopping forces for both ions. Electronic stopping for the oxygen beam reaches a maximum value at around 5 MeV, whereas chlorine beam reaches a peak at around 20 MeV. In order to experimentally test the velocity effect a set of experiments on TNT drop cast on Si wafer was performed using oxygen and chlorine primary beams with several energies and charge states as shown in table 6. If we consider values for electronic stopping values for the energy range between 6.5 and 10MeV calculated by SRIM, electronic stopping for chlorine is 0.6 times higher at 6.5 MeV than that for oxygen. This difference increases gradually and reaches fivefold greater value for electronic stopping for chlorine at 10 MeV when compared to oxygen.
Figure 42. Electronic and nuclear stopping chlorine and oxygen primary beam in TNT calculated by SRIM-2013, the software on stopping and range of ions in matter.

<table>
<thead>
<tr>
<th>Primary beam</th>
<th>Oxygen</th>
<th>Oxygen</th>
<th>Chlorine</th>
<th>Chlorine</th>
<th>Chlorine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy/MeV</td>
<td>6.5</td>
<td>8</td>
<td>6.5</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Charge state</td>
<td>+++</td>
<td>++++</td>
<td>+++</td>
<td>+++</td>
<td>++++</td>
</tr>
<tr>
<td>*Range/mm</td>
<td>6.4</td>
<td>9.39</td>
<td>6.29</td>
<td>7.43</td>
<td>7.84</td>
</tr>
</tbody>
</table>

Table 7. Different primary beam species with a range of energies and charge states used in the experiments. *Values for projected ranges in air calculated by SRIM.

Using various energies and charge states for oxygen and chlorine primary beams shown in table 7, the molecular yields of the TNT principal fragment, [M-H] relative to the number of total ion counts were measured and compared (Figure 43). The highest value of relative molecular yield was achieved for the 9MeV Cl⁴⁺ and the lowest secondary ion yield for the
8MeV O\textsuperscript{3+} primary beam. The uncertainty was estimated to be 10\% which explains the higher value of relative ion yield for 9MeV Cl\textsuperscript{4+} instead of the 10 Cl\textsuperscript{5+} beam, as expected.

![Graph](image)

Figure 43. Comparison of measured relative molecular yields of TNT principal fragment as a function of electronic stopping for various energies of chlorine and oxygen primary beams.

Nevertheless, the experimental data on the dependence of relative molecular yield for TNT principal fragment on different ion beam species confirmed the increment of the relative molecular yield for the heavier primary beam species.

6.9.2 Primary ion fluence

The dependence of secondary ion signals on primary ion fluence is something worth exploring to ensure that the emitted material is coming from an undamaged area. The requirement for the static limit has to be respected in order not to radiate area that has been extensively damaged already by the beam. Therefore, the primary ion fluence has to be kept at 10\textsuperscript{12} to 10\textsuperscript{13} ions/cm\textsuperscript{2},

129
depending on the type of sample. For the purpose of obtaining the optimal signal to noise ratio, the measurements with a range of ion currents using the 6.5MeV Cl$^{3+}$ beam were carried out. The experiments started with an ion current of $I_{\text{total}} = 1600\text{pA}$ (electrical) which was gradually decreased to the lowest value of $I_{\text{total}} = 1\text{pA}$. The lowest three ion currents ($I_{\text{total}} = 10$, $5$ and $1\text{pA}$) were at the lowest range of the current integrator used in these experiments. In order to calculate values for primary ion fluence, the acquisition time ($t$), as well as the area of the damage ($A$), have to be known as shown in Equation 10:

$$N_{\text{ions}}/cm^2 = \frac{I(A)}{q(As)*A(cm^2)} * t(s), \quad \text{Eq. 10}$$

where $I$ is the current,

$q$ is the elementary charge with the value of $1.6 \times 10^{-19}$ C, expressed as ampere per second as the coulomb is the quantity of electricity carried in 1 second by a current of 1 ampere.

Each spectrum was collected for $t = 3\text{min}$ from a new spot. Since a broad beam ($1\text{mm}^2$) was used for the measurements, the damaged area ($A$) is estimated to be the same size as the beam. The sample used in the experiments was the standard TNT solution drop cast on paper. The relative ion yields for two TNT fragments, the principal at m/z 226 and first daughter fragment at m/z 197 were calculated for different values of the primary ion fluence (Figure 44). The dependence of relative secondary ion yield on primary ion fluence for the TNT fragments shows different trends for each of the two fragments observed. While the principal fragment achieves the highest value of relative ion yield at ion $2.99 \times 10^{14}$ ions/cm$^2$, the first daughter fragment achieves the highest value of relative ion yield at $4.49 \times 10^{15}$ ions/cm$^2$. The values for the relative ion yields can be used to calculate ratios of both the fragments. These ratios are used to interpret the impact of the primary beam on the molecular structure at different values.
of the ion fluence. The molecular structure remains almost intact when the principal ion is being produced through protonation or deprotonation. On the other hand, generation of daughter ions indicates a greater damage to the molecular system by breaking of intramolecular bonds.

![Graph](image)

**Figure 44.** Dependence of ion fluence on relative ion yield for the principal and first daughter fragment, m/z 226 and m/z 197 for the TNT sample. Measurements were performed using the 6.5 MeV $^{35}$Cl$^{3+}$ primary ion beam.

The results on the dependence of relative molecular yields for TNT molecular and first daughter ion on ion fluence showed the optimal values for the relative molecular yield occur at ion fluences at the order of magnitude $10^{14}$ ions/cm$^2$. The relative molecular yield for both of the ions becomes steady at fluence value of $2.25 \times 10^{14}$ ions/cm$^2$. At the fluence value of $9 \times 10^{14}$ ions/cm$^2$, the relative molecular yield for the molecular ions started to decline whereas the relative molecular yield for the first daughter ion started to rise. This can be explained by increased damage to the surface with more first daughter fragment ion being sputtered than the
molecular ion. For the last three points, the damage is even more increased and both of the molecular yields are dropping indicating. This would correspond to ion fluence values greater than the static limit.

6.9.3 Post-ionisation

Ionisation of the sputtered neutrals after they are already emitted from the surface is a well-established approach. Secondary (or sputtered) neutral mass spectrometry (SNMS) is based on this approach and is analogous to SIMS. The post-ionised mass spectrometric signal is expected not to be affected by the matrix effects. The post-ionisation has to be performed efficiently so that the post-ionised spectrometric signal becomes at least comparable with or preferably higher than the SIMS signal[192]. There are several ways to induce the post-ionisation based on electron impact, plasmas and lasers. We performed the post-ionisation using a plasma induced inside the mass spectrometer capillary by a 20kV high-frequency high voltage transformer coil which was placed around the mass spectrometer capillary (Figure 45).
The post-ionisation experiment was carried out with the 8MeV O\(^{4+}\) primary beam on a thin film of leucine evaporated on a Si wafer. Firstly, a spectrum of blank Si wafer was acquired with the ion beam only. After that, the plasma was applied, but without the beam being present. Lastly, both the beam and plasma were applied. The spectra of the Si blank for all the three cases are shown in figure 46. The spectra were normalised to the number of total ion counts. The background in the spectrum acquired with the beam only is significantly less abundant than backgrounds in spectra acquired with plasma as well as beam and plasma. Therefore, the background increment is due to the use of the coil. When analysing the background more carefully, a certain repetition pattern in steps of m/z 50 can be noticed. This pattern corresponds to the PTFE signature which would originate from the cap enclosing the coil.
Figure 46. Spectra of Si blank obtained using solely the 8MeV O$^{4+}$ ion beam, plasma and beam and plasma simultaneously. For the acquisition, positive ion mode was used.

Next, the same measurements were performed using a sample of leucine evaporated on a Si wafer. The spectra obtained from the samples of leucine and Si blank for all three conditions were compared in figure 47. A typical spectrum of leucine acquired with AP MeV SIMS using the 8MeV O$^{4+}$ contains two peaks associated with leucine. The peak at m/z 86 corresponds to the first daughter ion and is smaller another peak associated to leucine which is at m/z 157. This peak is believed to be associated with the sodiated molecular ion of leucine – see section 6.7. The m/z 86 can only be found in the spectrum acquired with the beam. There are some insinuations that the m/z 86 is also present with plasma and plasma and beam but the most likely this is not the leucine fragment ion as a peak with the similar intensity at m/z 86 can be found in any positive AP MeV SIMS spectrum. The second peak, the m/z 157 is still present with plasma as well as with plasma and beam but is dominated by other peaks.
Figure 47. Comparison of specific m/z regions for spectra of leucine and Si blank obtained with the 8 MeV O$^{4+}$ primary beam, plasma and beam and plasma simultaneously. In the first case where only the primary beam was employed, two peaks related to leucine were observed, m/z 86.6 and 157. In the second case, when only plasma was employed, only m/z 157 was observed. With beam and plasma both employed, only m/z 157 was observed. The peak at m/z 86 when only plasma and beam together with plasma were employed is most likely not assigned as leucine.

This is due to the intense background which consists mostly of PTFE peaks caused by oxidation by the ion beam and plasma. Additionally, a presence of the memory effect can also be responsible for the background saturation. Hence, the post-ionisation experiment can only be
considered as a trial. In order to differentiate and post-ionise the signal without increasing the background simultaneously, the experimental set up has to be designed differently.
7. Simultaneous molecular and elemental mapping in air by coupling AP MeV SIMS and HIPIXE

7.1 Introduction

In this chapter, the feasibility study of simultaneous external HIPIXE and AP MeV SIMS is presented. Employing a heavy ion in PIXE is known as the HIPIXE. Merging of IBA techniques has been desirable for the community in order to achieve complementary information which would make IBA techniques competitive with other, non-IBA techniques. So far, PIXE has been combined with RBS and applied for cultural heritage based analysis[141]. Having PIXE combined with MeV SIMS gives both the elemental and molecular information on the sample. This is unique when compared to any other combination of the IBA techniques. The challenges of merging MeV SIMS and PIXE will not be discussed here as they had already been described in section 4.5.1.

In our experiments, simultaneous analysis with HIPIXE in external conditions and AP MeV SIMS had been carried out using 6.5 MeV Cl$^{3+}$ and 8 MeV O$^{4+}$ primary beams. In this preliminary study, we used a test sample consisting of a thin film of trinitrotoluene (TNT) on a silicon wafer masked by strips of copper and an irregular spot of plastic explosive 4 (PE4). Besides the simultaneous elemental and molecular analysis under ambient conditions, we also performed mapping of each of the species of this test sample which was a combination of metals and organics. Here, maps of the TNT molecular ion and the ion associated with PE4, together with maps of the Si Kα and Cu Kα X-rays collected using a broad 8 MeV O$^{4+}$ primary beam (1mm$^2$) will be presented and reasons for choosing the 8 MeV O$^{4+}$ primary ion beam instead of 6.5 MeV Cl$^{3+}$ discussed.
7.2 Description of the experimental setup

AP MeV SIMS and HIPIXE spectra were collected simultaneously using the using both 6.5 MeV Cl\(^{3+}\) and 8 MeV O\(^{4+}\) ions with beam currents of 1nA and 100pA respectively extracted into the air as described in section 5.3. For the X-rays detection, two silicon drift detectors (SDD) (SGX Ltd, U.K) were placed at 45° from the surface normal. The active area of both detectors was 30mm\(^2\) and they were fitted with a 40µm thick Kapton filter to prevent backscattered ions entering the detector.

Secondary ions were detected and mass analysed using a Waters QTOF-2 mass spectrometer. The mass spectrometer capillary was heated to 80°C to minimize neutralisation of the ions. The ions were swept into the input capillary using a helium gas flow supplied by a second capillary. The two capillaries were placed opposite to each other and positioned independently using two 5-axis manual positioning stages. The mass spectrometer capillary was set at distance of 1.5mm from the beam axis. The configuration of the beam and detectors is shown schematically in figure 28- section 5.5.

![Test sample used for the simultaneous AP MeV SIMS and HIPIXE mapping in the air. A thin film of TNT on a silicon wafer was masked by strips of copper and an irregular spot of PE4. The scan size was determined to be 10mm x 10 mm as indicated by the blue rectangle.](image)

Figure 48.
Sample preparation consisted of drop casting a TNT standard solution at a concentration of 500ppm in acetonitrile onto a clean Si wafer surface. Two strips of copper tape were then fixed onto the TNT film, with a drop of PE4 between them as seen in figure 48. The sample was mounted on a motorized XYZ stage and positioned 2 – 3mm in front of the beam nozzle normal to the sample surface. Distribution maps were then created by scanning the stage in a meander pattern under the control of the OMDAQ-3 data acquisition software.

The X-ray signals from the SDDs were processed with a 4-channel digital signal processor (DT5724, Caen, Italy) using a newly developed interface to the OMDAQ-3 data acquisition and control software (Oxford Microbeams Ltd, U.K.)[146]. Mass information from the QTOF-2 was recorded simultaneously in two parallel channels – see section 5.5 for the description of data acquisition. Mass calibration of the QTOF-2 was carried out before the measurements using an electrospray source with a NaCsI standard. Energy calibration of the X-ray spectra was performed in OMDAQ-3 using the existing X-ray energy library. Point spectra were collected using both 8MeV O^{4+} and 6.5 MeV Cl^{3+}, but imaging was carried out using an 8MeV O^{4+} beam and 1nA beam current. The scan size was set at 10mm x 10mm with the beam size of 1mm x 1mm. The acquisition time for the imaging run was 8h.

### 7.3 Results

The 6.5 MeV Cl^{3+} beam was found to be efficient in desorption of secondary ions from both TNT and PE4 but had a very low cross section for exciting the Cu-K lines from the Cu stripes. In addition, an intense Cl Kα peak was observed which could interfere with signals from the sample. The Si Kα lines were observed in the spectrum. In contrast, the 8MeV O^{4+} ions, which are approximately 60% faster than the 6.5MeV Cl ions, also generated the TNT and PE4 secondary ions and Si Kα lines but have a much higher cross section for exciting Cu Kα X-
rays and did not have a contaminating signal from the primary ions. Hence, it was decided to proceed only with the 8MeV O\(^{4+}\) beam. Mass and X-ray spectra from the full 10mm x 10mm area are shown in figure 49(left). TNT is characterized by a molecular ion at m/z 226 and a first daughter ion fragment at m/z 197 ([M-H\(^+\)]\(^{-}\) and [M-NO\(^+\)]\(^{-}\) respectively, with M representing the TNT molecule). PE4 was detected by a peak at m/z 224, but in this case, it was not easy to determine the identity of the peak structure, due to the complexity of the PE4 compound which consists of two major constituents, RDX as the explosive ingredient and HTPB as the binder[193]. X-ray spectra with Si K\(\alpha\) and Cu K\(\alpha\) lines originating from the Si wafer and Cu tape strips are shown in figure 49 (right).

Figure 49. Mass spectrum overlay for TNT and PE4 marking the m/z 226 and m/z 224 which were chosen for mapping (left). The corresponding X-ray spectrum showing the Si K\(\alpha\) and Cu K\(\alpha\) lines (right). Spectra were collected simultaneously under ambient conditions using the 6.5Cl\(^{3+}\) ion beam.

The next step was to use a lower beam current which stays below the static limit in TOF SIMS[194]. In order to ensure that the sputtered material is coming from an undamaged area,
the ion fluence should be kept below $10^{12}$ ions/cm$^2$. Thus, the beam current was set at 100pA. At this current the count rate for Cu Kα was not sufficient to permit imaging, so a beam current of 1nA was utilized for the purpose of imaging although it exceeded the static limit for SIMS.

Molecular maps for the m/z 226 and m/z 224 ions can be seen in figure 50. The m/z 226 ion covers the whole scanning area indicating that TNT is observed in a gas phase at large distances from the sampling site. We believe that a heavy ion beam stimulates the transition of TNT into the gas phase which could explain the observed detectability of TNT with AP MeV SIMS. The TNT vapours are most likely migrating from a sample volume to surrounding areas as TNT can also be detected even when the ion beam is not hitting the sample surface. The m/z 226 TNT molecular ion is also present in the molecular map of the m/z 224 PE4 ion. However, the m/z 226 ion is mostly located away from the m/z 224 ion which makes the two secondary ion species easily distinguishable. In case of the TNT, we cannot be certain whether the signal originates from electronic sputtering of the solid phase material or if it is only detected from ionisation in the gas phase. Nevertheless, the PE4 related ion does appear to be localised to the original position of PE4 on the sample and is hence most likely a result of sputtering from the solid phase. Elemental maps of the Cu Kα and Si Kα are shown in figure 51. The Cu Kα lines originate from the two parallel Cu tape strips masking the Si wafer. The Si Kα lines are emerging from the Si wafer. The position of the Cu Kα corresponds to the location of the Cu tape strips and the position of the Si Kα correspond to the specific area of the Si wafer not masked by the copper. Finally, an overlay of a molecular map of the m/z 224 ion and elemental maps of the Cu Kα and Si Kα presented in figure 52 clearly distinguishes the three different species matching them to their original locations on the sample.
Figure 50. Molecular map of m/z 226 peak representing TNT (left) and m/z 224 peak representing PE4 (right). The m/z 226 peak is also found in the map of the m/z 224 peak. Unlike the m/z 226 peak being spread all over the area, the m/z 224 peak is well distinguished and it matches the exact location of PE4 on the sample.

Figure 51. Elemental map of Cu Kα lines (left) and Si Kα lines (right).
Merging of AP MeV SIMS and HIPIXE imposes a challenge for finding an optimal primary beam suitable to desorb secondary ions and emit X-rays. Although we managed to achieve both by using the 8MeV O$^{4+}$ primary beam, the requirement for preserving the static limit could not be achieved, as the beam current used for the mapping had to be sufficient for detection of the X-rays as well. In order to increase the cross sections of X-rays, the higher charge states of the oxygen beam should be considered in the future work. This could enable utilization of lower beam currents and improve later resolution by using focused beams. Additionally, we are considering placing the SDDs inside a vacuum to improve X-ray detection.
8. Conclusion

Analysis of proteins with PDMS, which started in 1974, can be considered as a milestone in the development of techniques amenable to detect molecules with molecular masses up to few tens of kDa. One of these techniques is MeV SIMS which shares the same mechanism responsible for desorption of secondary species with PDMS. Amongst the numerous IBA techniques, with each of them exploring a specific event caused by impingement of a heavy ion beam on matter, only MeV SIMS can provide information on molecular composition. Yet, only a few IBA laboratories are using MeV SIMS for purposes of exploiting the electronic sputtering for the analysis and molecular imaging of organic molecules. The biggest rival of MeV SIMS is the long-standing TOF SIMS, especially acknowledged for achieving the lateral resolution of a few hundreds of nanometres. The different energy deposition between MeV and keV ions results in longer ion range when MeV ions are employed, leading to a greater potential for sputtering of intact, non-fragmented molecules from the ultratrack region. Employing MeV over keV ions in SIMS will also result in higher secondary yield and mass range. Moreover, MeV ions retain focussed up to several millimetres in the air, making the application of MeV SIMS in ambient conditions feasible. In the University of Surrey Ion Beam Centre, the development of AP MeV SIMS instrument has been embarked upon.

Numerous atmospheric mass spectrometry (APMS) techniques, which have emerged in the last decade, are showing the great need for the analysis with minimum or no sample preparation with ionisation at atmospheric pressure. The ionisation source in AP MeV SIMS is unique when compared with other APMS techniques, and thus it can’t be placed into any of the already existing divisions of these techniques such as spray, plasma or laser ionisation based groups.
Comparison of AP MeV SIMS, DESI, DAPCI, LA-ICP and LAESI indicated mostly the differences but also some of the similarities between these techniques. AP MeV SIMS shows some of the advantages which could be utilised for the applications into areas such as the cultural heritage, where other APMS techniques might not be a good choice due to the surface damage issue. Another such parameter is the spatial resolving power, which is crucial for imaging. Both of these parameters are important when compared with other techniques such as MALDI. In this thesis, it has been shown that it is possible to obtain molecular maps with a lateral resolution of 10mm using AP MeV SIMS which gives a good starting point for this technique.

The challenges AP MeV SIMS is facing are mainly related with the impact of the ambient on transport and detection of secondary ions. The experiments where the atmosphere of the sampling area was controlled by applying N₂O instead of He, or excluding the sheath gas altogether, showed the suppression of PEG and PPG background peaks by polydimethylsiloxane ones originating from the environmental chamber. The mass spectrometer capillary is a key factor in transporting of the ions into the mass spectrometer. In our setup, the entrance of the mass spectrometer is distanced from the sampling site at around fifty centimetres, which causes additional difficulties in ion transportation. However, the size and mass of the instrument restrict the available position of the mass spectrometer in respect to the ion beam and the sample. The optimum distance of the mass spectrometer capillary with respect to the beam exit window for the relative yield of TNT principal fragment is found to match the position of the capillary at the frame of the window. It is important to keep the mass spectrometer capillary heated in order to ensure the cleanest pathway for the ions as possible, which would minimise the possibility of their neutralisation and memory effect. The optimum mass spectrometer capillary temperature is limited by thermal degradation of the vacuum O-
rings and the investigated sample. Applying a bias potential on the mass spectrometer capillary showed an insignificant rise in the relative molecular yield of the leucine first daughter fragment at five volts and a great decrease for the higher values. Correspondingly to the substantial background contribution, certain improvements of the AP MeV SIMS setup should be taken into considerations. Reducing the space between the sampling site and the mass spectrometer capillary would be beneficial for reducing the background and the memory effect. Such modification involves shortening the mass spectrometer capillary and bringing the mass spectrometer as close as possible to the ionisation source, i.e. the beam exit window reducing the ionisation region and shortening the secondary ions pathway from the ionisation site into the analyser. Thus, the overall number of surrounding molecules originating from the atmosphere that potentially get ionised by the ion beam would reduce and the deposition of desorbed material and molecules of water along the length of the mass spectrometer capillary would also decrease. Another modification being of a great importance in addressing the ion transportation and the memory effect is to ensure the mass spectrometer capillary is equally heated along its full length. Furthermore, electrostatic extraction of secondary ions should also be employed into the AP MeV SIMS setup, in order to improve their detection.

A parameter related to the He flow capillary explored in the optimisation process was the angle in respect to sample, which did not indicate the change of relative molecular yield for TNT for any of the angles tested indicating the He flow might not have an influence in the transport of secondary ions into mass spectrometer capillary. This was in contrast with the computational fluid dynamics simulations showing how poor alignments of the He flow and mass spectrometer capillary leads to no secondary ions entering the Q-TOF2. The best transmission efficiency i.e. 86% was achieved when the He flow capillary was at 40º with respect to the sample.
Samples investigated in AP MeV SIMS were leucine, TNT, PY3, PO5 and PR112 as representatives of different groups of organic compounds. The leucine related peaks occurring in AP MeV SIMS using the $O^{(3,4)+}$ primary beam can be considered as having an insufficient target signature when compared with the MeV SIMS analysis with the Cu$^{4+}$ ion beam. The analysis of TNT, on the other hand, proved to be very successful and repeatable, giving the fragmentation pattern which cannot be achieved by any of the other techniques conventionally used for this purpose. The ion beam is probably stimulating the rise of TNT vapours making it easily detectable in AP MeV SIMS showing its potential to be applied for explosive analysis. The obvious application of AP MeV SIMS would be an analysis of art objects such as paintings. PY3, PO5 and PR112 belong to SOP’s and can be found in contemporary art but also in optoelectronics, media storage, toys and cosmetics. Analysis of PY3, PO5 and PR112 with MeV SIMS resulted in a specific peak connected with each of the pigment. Anyhow, the chemical structure which would represent these peaks could not be given with great certainty. It would be worthwhile to investigate more into the analysis of SOPs as well as some other organic compounds used in art objects.

The extensive background contribution is associated with PEG, PPG and polydimethylsiloxane polymers, and what is believed to be their derivatives and copolymers. The main source of the organic contaminants has been shown to be the atmosphere, which surrounds the sampling site, as well as the mass spectrometer components. The Si$_3$N$_4$ window sealant and the He flow capillary were excluded as the background sources from this investigation. The background peaks make interpretation of spectra in the positive mode very difficult. Hence mainly the negative ion mode was mainly used for the optimisation in the work presented here. Another
obstacle which can cause misinterpretation of spectra is the memory effect of the instrument. The presence of the TNT molecular and first fragment peaks was observed even without the presence of the sample owing to the volatility of the TNT molecules. We found the main contributor to the memory effect to be the mass spectrometer capillary, due to inability to keep the capillary tip hot. The memory effect appeared after approximately two hours of the acquisition in the case of TNT.

Optimisation of AP MeV SIMS has proven to be an extremely complex process with many variables impacting the secondary ion yield. The optimisation parameters related to the primary beam investigated in this work were beam species and fluence. The relative molecular yield of TNT was higher for a chlorine ion beam, in comparison with an oxygen ion beam. The optimal primary ion fluence was tested with the 6.5 Cl\(^{3+}\) beam and was determined to be 2.99 x 10\(^{14}\) ions/cm\(^2\) for the principal TNT fragment, and 4.49 x 10\(^{15}\) ions/cm\(^2\) for the TNT first daughter fragment. Keeping the fluence at the optimal value for the principal fragment induces less damage to the molecular system. Besides the parameters that impact the production of secondary ions, the ones that might improve the secondary ion transport into the mass spectrometer and TOF analyser were explored as well. Tuning of the Q-TOF2 parameters, which is necessary in order to maximise a number of secondary ions reaching the analyser, was presented in detail. Lastly, the attempt of the post-ionisation resulted in the generation of PTFE peaks with very high intensity when plasma and/or beam were applied.

For the closure of this thesis, the feasibility study of simultaneous external HIPIXE and AP MeV SIMS was presented inspired by the concept of merging IBA techniques. We have demonstrated for the first time the simultaneous molecular and elemental mapping under ambient conditions on a thin film of TNT masked by strips of copper and an irregular spot of
PE4 by coupling AP MeV SIMS and HIPIXE. Combining of AP MeV SIMS and HIPIXE gives information about the molecular and elemental composition hence providing a unique viewpoint when compared to other combinations of IBA techniques which exclude MeV SIMS. Analysing different types of information i.e. organic and metallic content is advantageous as it prevents potential disagreements in qualitative and quantitative interpretation arising as a consequence of using different approaches for the same purpose. On the other hand, focusing on different information could be more demanding in terms of the working conditions fitting the demands of both the techniques used in such experiments.

In future work, improving lateral resolution should be considered as well as using the higher ion beam charge states and energy and lower current which should give higher cross sections of X-rays.

In this work, we showed AP MeV SIMS can be used for analysis of gases hence in future work this should be investigated further. AP MeV SIMS could be applied for the real-time gas flow samplings where fast chemical analysis is required, such as monitoring process transients and dynamic continuous reactions. Moreover, a fine tip capillary could be used for samples of surfaces for volatiles enabling micro imaging with AP MeV SIMS, and as such it could be even combined with Atomic Force Microscope.
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