

Positron Annihilation Lifetime Studies of Inorganic Materials Using A New Positron Beamline

Jason Roberts

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Australian
National
University

For my father,
who sparked my interest in science.

DECLARATION

I declare that this thesis is an account of research undertaken between March 2008 and June 2012 at The Research School of Physics and Engineering under the supervision of Dr James Sullivan and Professor Steve Buckman. Except where acknowledged in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or part for a degree in any university.

Jason Roberts

Friday 29th June, 2012

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The development of such an apparatus was made possible by the input and support of many individuals. I would like to acknowledge their contribution here.

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ABSTRACT

In recent years, effects caused by the nanoscale structure of a material have become increasingly important for technological progress. With improvements in fabrication techniques, nanoscale structures can now be produced with growing control. As a result, techniques to characterise these properties have been developed and are also becoming increasingly important. One such collection of non-destructive techniques, which can provide unique information about a target sample, is Positron Annihilation Spectroscopy (PAS).

The initial aim of the research presented here was the development and characterisation of a positron beamline for materials studies. This beamline, now operational, has been developed to measure the positron lifetime in a target material. This technique, referred to as Positron Annihilation Lifetime Spectroscopy (PALS), allows the size of open volume type defects (or voids) up to ~ 10 nm to be determined. In addition, as the technique is implemented using a variable energy positron beam, thin film samples can be characterised and measurements can be performed in a depth sensitive manner. The beamline uses a Surko trap to isolate and cool positrons from a moderated radioactive source. Positrons are released from the trap using a timed potential ramp, though hardware restrictions limit the effectiveness of this technique. This arrangement results in a pulsed positron beam of up to two thousand pulses per second with a temporal Full Width at Half Maximum (FWHM) of 800 ps. Typical spectra, which contain $\sim 10^6$ counts, can be recorded in two hours; although to resolve shorter lifetime components (< 600 ps) longer measurement times are required.

Due to consequences from the unusual operating regime of the Surko trap, a new analysis program was developed for the analysis of the resulting PALS spectra. This software, dubbed CAMSFIT, is specifically designed to account for the temporal distribution of positron pulses in beam based systems. This is achieved by analysing the PALS spectrum of the target material relative to the

spectrum of a well characterised sample which contains only very short positron lifetimes. This analysis technique allows lifetimes greater than ~ 300 ps to be resolved when using pulses of 800 ps.

With these tools, two studies of inorganic materials have been performed. The first study focused on investigating nanometre sized voids in natural zircon crystals. Such voids are the result of self-irradiation from radioactive substitutional impurities such as uranium. Samples which had suffered a range of radiation doses were investigated and such voids were observed, though not universally. The second study focused on characterising zeolite sheets prepared using a papermaking technique. Several sheets were prepared and the concentrations of the starting reagents were varied. While only a preliminary study, it has been found that it may be possible to tailor the properties of the sheets to specific applications.

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LIST OF ACRONYMS

ACAR	Angular Correlation of Annihilation Radiation
AMO	Atomic and Molecular
AMOC	Age-Momentum Correlation
ANSTO	Australian Nuclear Science Technology Organisation
ANU	The Australian National University
A-PAM	Anionic Polyacrylamide
AWG	Arbitrary Waveform Generator
BGV	Beamline Gate Valve
CAMS	Centre for Antimatter-Matter Studies
CFD	Constant Fraction Discriminator
CSF	Canadian Standard Freeness
DBS	Doppler Broadening Spectroscopy
DLL	Dynamic Link Library
ESG	Exponential-Sided Gaussian
FPSI	First Point Scientific Incorporation
FT-Raman	Fourier Transform Raman Spectroscopy
FWHM	Full Width at Half Maximum
GUI	Graphical User Interface
ILC	International Linear Collider
MCP	Micro-Channel Plate
MELT	Maximum Entropy Lifetime Analysis

NIRS	Near-Infrared Spectroscopy
NMR	Nuclear Magnetic Resonance
<i>o</i>-Ps	orthopositronium
PALS	Positron Annihilation Lifetime Spectroscopy
PAS	Positron Annihilation Spectroscopy
PDADMAC	Poly Diallyl Dimethyl Ammonium Chloride
PEEK	Polyetheretherketone
PENELOPE	Penetration and Energy Loss of Positrons and Electrons
PET	Positron Emission Tomography
<i>p</i>-Ps	parapositronium
Ps-TOF	Positronium Time Of Flight
RGA	Residual Gas Analyser
ROI	Region Of Interest
RTE	Rectangular Tao-Eldrup
SAXS	Small-Angle X-ray Scattering
SCGV	Sample Chamber Gate Valve
SCLLV	Sample Chamber Load Lock Valve
SCRV	Sample Chamber Roughing Valve
SEM	Scanning Electron Microscope
SLAC	Stanford Linear Accelerator Center
SRS	Stanford Research Systems
TE	Tao-Eldrup
TEM	Transmission Electron Microscopy
UCSD	University of California San Diego
UWA	University of Western Australia

CHAPTER 1

INTRODUCTION

With the discovery of the positron in the 1930s and the development of positron sources soon after, a new tool became available for the characterisation of materials. Due to its antimatter nature, the positron can be used in unique ways to provide insight into materials. However, techniques utilising these properties were not developed until the 1950s, with several remaining experimentally inaccessible until decades later.

With improvements in understanding and hardware, many of these techniques can now be implemented using positrons emitted directly from radioisotopes and relatively simple detection systems. However, these arrangements limit the techniques' capabilities to probing the whole sample with no selectivity. To probe more specific regions of the target material, for example the surface, these techniques must be implemented in a beam-based manner. Due to the low intensity of positron beams, when compared to the electron equivalent, new approaches were required before sufficiently intense beams could be achieved. In the last twenty years, several developments have resulted in significant increases in the intensity of positron beams. These developments have allowed positron beams to become more readily available for a range of applications, including the study of materials.

This thesis describes the development of a new positron beam apparatus, including a customised approach to the analysis of the resulting data. It contains six chapters including this introductory chapter which provides a brief overview of the topic and the document's layout.

In the second chapter, background knowledge about the positron and its applications is presented. Firstly, a brief history of the positron is given before discussing its properties, the formation of positronium, the process of annihila-

tion and finally positron sources. This is followed by a discussion of the processes a positron undergoes following its implantation into a solid material. Finally, the applications which utilise the properties and processes of the positron for determining information about materials are discussed.

The third chapter focuses solely on the experimental apparatus developed as part of the research presented here. This apparatus employs recently developed techniques to produce a pulsed positron beam; these techniques have been implemented here to produce a temporally narrow pulse which is used to study the positron lifetime in materials. Both the technique and apparatus are discussed in detail as well as the software developed for the operation of the latter.

Within the fourth chapter the analysis of positron lifetime spectra is discussed. This includes a brief overview of existing software, detailing the approaches used and why they are not applicable to the newly developed apparatus. This leads into an in-depth discussion of a newly developed analysis program specifically designed by the author for the challenges encountered. The analysis of a variety of simulated spectra is presented to show the capabilities of the new software.

The fifth chapter presents positron lifetime data collected from two different types of inorganic materials. The first series of samples are naturally occurring zircon crystals which have suffered varying amounts of radiation damage, rendering them partly amorphous. This study aims to observe the presence of open volume type defects. The second series of samples investigated are zeolite sheets which have been prepared in-house; the technique used to produce these sheets is also discussed. In this study, the porosity of sheets produced with differing concentrations of starting reagents is compared to a control sample.

In the sixth and final chapter, a summary of the work presented within this thesis is given. In addition, possible future modifications of the apparatus and analysis software are discussed.

CHAPTER 2

BACKGROUND

The properties of the positron are exploited by several techniques to provide information about various biological processes, atomic scale interactions and the properties of materials; the latter of these is the focus of the work presented in this document.

The most widely known use for positrons is Positron Emission Tomography (PET), a medical imaging technique first proposed in the 1950s. Today, this technique is used to produce three-dimensional images of functional processes in the body.

In addition, a large amount of our understanding of fundamental quantum interactions has arisen from theoretical modelling of collision based systems. While electron collisions have long been studied, the positron presents a new projectile with the ability to access unique fundamental interactions. Using experimental data from positron interactions for guidance and verification, existing theoretical models can be improved to further develop this understanding.

Finally, positrons can be injected into a material to provide insight about its nanoscale properties. In this chapter, the properties of the positron will be introduced followed by the techniques developed to investigate materials. In particular, the lifetime of the positron inside a material, and its application to material studies, will be discussed.

2.1 The Positron

The positron is the electron's antiparticle and was the first example of antimatter to be discovered. It has the same mass m_e ($\sim 9.109 \times 10^{-31}$ kg) and intrinsic spin quantum number ($s = \frac{1}{2}$); however, it has a charge of $+e$ ($+1.602 \times 10^{-19}$ C)

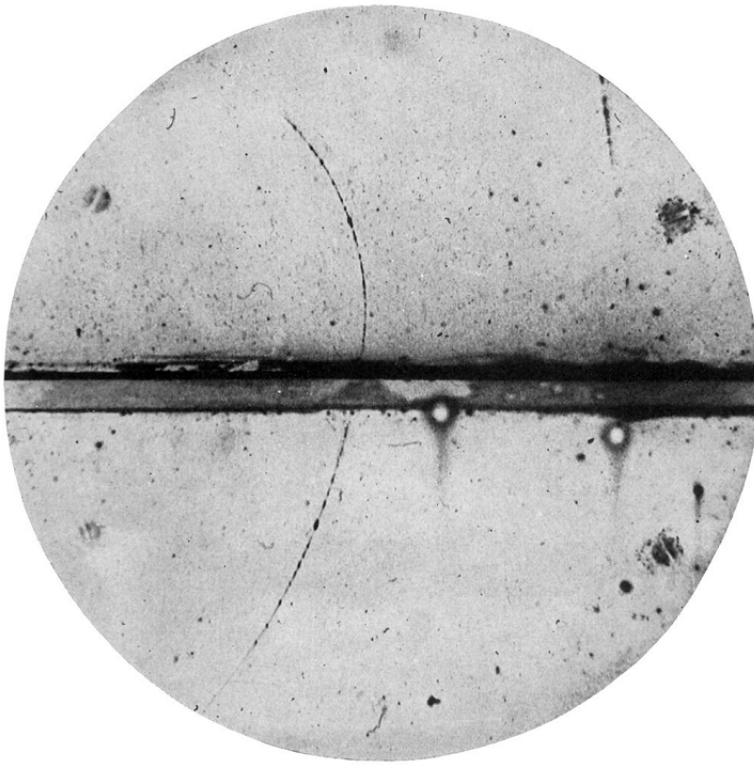


Figure 2.1: Shown here is a well known image taken during the 1932 experiment revealing the positron. A 6 mm lead plate separates the two halves of the chamber, which sits inside a magnetic field of 15 kG. The track indicates that a light, positively charged particle passed, from bottom to top, through the lead plate (reproduced from Anderson, 1933).

rather than $-e$. Due to their antimatter nature, positrons are able to undergo the process of annihilation with an electron.

2.1.1 Prediction and Discovery

In the late 1920s, Paul Dirac developed a relativistic quantum mechanical equation for the electron which allowed both positive and negative energy solutions (Dirac, 1928). The full implications were initially misunderstood by Dirac (1930b) and it wasn't until three years later that he proposed this negative energy solution represented a new particle, the antielectron (Dirac, 1931). For this work, he was jointly awarded the 1933 Nobel prize with Erwin Schrödinger for their contribution to atomic theory.

This new particle was discovered the following year by Anderson (1932, 1933), who dubbed the particle the positron. The discovery was made while photographing cosmic ray tracks in a vertical Wilson chamber (commonly known as a cloud chamber) which showed evidence of light, no more than twenty electron masses, positively charged particles. An image from the experiment is shown in figure 2.1.

2.1.2 Properties of the Positron

The positron and electron have equal mass, spin states and magnitude of charge, only differing in the sign of the charge. However, this minor difference has far reaching ramifications. There are two interactions which can occur between an electron and a positron that are of interest here. These are the formation of positronium and the process of annihilation. As positronium will almost always undergo self-annihilation after a brief period, its properties will be discussed prior to the annihilation process.

Positronium

Positronium is a short lived, bound electron-positron pair. Its existence was first proposed by Mohorovičić (1934) who referred to it as *electrum*. However, the name did not become widespread and instead Ruark (1945) coined the term *positronium*, with the chemical symbol *Ps*. It wasn't until much later that Deutsch (1951) not only discovered positronium, but proceeded to investigate its properties through the study of positron annihilation in gaseous targets.

Where a free positron is available, positronium can form with a free or a bound electron (and vice-versa, however, due to the apparent imbalance between matter and antimatter this possibility will not be considered). In quantum mechanics (and classical mechanics) the motion of two particles, with masses m_1 and m_2 , acting under the influence of a central force can be described by the motion of a fictitious particle with a reduced mass $\mu = \frac{m_1 m_2}{m_1 + m_2}$ moving relative to the centre of mass. This is known as the centre of mass coordinate system and allows positronium to be considered as a hydrogen-like system.

In the hydrogen atom the mass of the proton, m_p , is $\sim 1836m_e$ and hence the reduced mass of the system, μ , is $\sim m_e$. However in positronium, where the masses of the two particles are equal, the reduced mass is $\mu = \frac{m_e}{2}$. Since the energy levels of hydrogen and positronium are proportional to their reduced mass, the energy levels of positronium lie at half the corresponding level in hydrogen. Furthermore, the interaction of the spins between the electron and positron in positronium gives rise to two distinct spectral series, a singlet and a triplet series (this will be discussed in more detail below). In hydrogen, the interaction of the electron spin with the nuclear (proton) spin is much weaker and, to a high degree of accuracy, can be ignored. Thus, the hydrogen atomic spectrum has only doublet series.

As a result, positronium has a binding energy of 6.80 eV. This allows it to form with bound electrons from an atomic or molecular system at collision energies of 6.80 eV below the ionisation threshold (or higher). In atomic systems, this interaction is usually the first inelastic process which may occur. The energy range between the threshold for positronium formation and the threshold for the first excited state of an atom is referred to as the Ore Gap (which is of interest for positronium formation).

Initially, research into the formation of positronium was mainly focussed around the production of positronium beams to allow the study of its interactions with various targets. Typically this is done by passing a positron beam through a target gas at an energy within the Ore gap of the target. This method of positronium formation is referred to as the Ore Model.

This mechanism also results in the formation of positronium when positrons are implanted into insulating materials. Within picoseconds of being injected into a material, high energy positrons thermalise to electronvolt energies (this process is discussed in section 2.2). At these energies, a large fraction will capture a bound electron and form positronium prior to annihilating. However, if the positron

slows past the point at which it may capture a bound electron, positronium may still form via the Spur Model (Mogensen, 1982). This involves the positron combining with a spur electron; an electron which has been ejected as the positron has deposited energy into the material. While this may also occur within gaseous targets, it is more pronounced in condensed matter.

A third model, the Blob Model, was developed by Byakov and Stepanov (1996) and can be considered as an extension of the spur model, adding functionality through a more complex consideration of the environment just prior to the formation of positronium. During the final stages of thermalisation, between 500 eV and the ionisation threshold, approximately thirty electron-ion pairs are generated within a spherical volume called the blob. These electrons are assumed to have a Gaussian distribution around the blob centre and as recombination occurs at an exponentially decaying rate, this Gaussian is assumed to be maintained. Total recombination is expected to occur after 20–30 ps. The positron, which now has insufficient energy to cause further ionisation, will fully thermalise and may travel away from the centre of the blob. Its density function can be described by a spherical volume typically slightly larger than the blob radius. Following this, the positron may annihilate directly or form positronium with an electron from the blob. The probability of the latter will be governed by the overlap of the blob and the positron density function.

As noted above, positronium can exist in two states depending on the relative spins of the positron and electron. The singlet state ($S = 0$), where the two spins are antiparallel, is referred to as parapositronium (p -Ps). The triplet state ($S = 1$) has parallel spins and is referred to as orthopositronium (o -Ps). The self-annihilation rates of these two states differ greatly and will be discussed in the following section.

Annihilation

Annihilation is the process that occurs when a subatomic particle collides with its respective antiparticle. This results in the conversion of the two annihilating particles to force carrier particles, such as the photon. In the case of a collision between an electron and a positron, their total energy is almost always converted into several γ -rays. With the exception of re-emitted positrons, all positrons injected into a material will undergo annihilation. This can occur directly, with

an electron bound within an atomic or molecular system, or after the formation of positronium.

Direct annihilation can occur through a number of different mechanisms. While radiationless and single photon annihilation are possible, they require the interaction of a third body to conserve momentum and energy and will not be discussed here. Three γ -ray direct annihilation was first calculated by Ore and Powell (1949) who determined this process to be approximately 370 times less likely than the two γ -ray process. Annihilation events emitting additional γ -rays are expected to be suppressed at a similar rate and therefore only direct annihilation through two or three γ -rays will be considered; annihilation via two γ -rays will be discussed in detail.

Two γ -ray annihilation is most likely to occur when the positron and electron are in a spin singlet state ($S = 0$), though this is not a restriction. This results in the emission of two 511 keV γ -rays 180° apart with respect to the reference frame of the positron-electron system. The likelihood of this process, denoted by $\sigma_a(2\gamma)$, was determined by Dirac (1930a) and is

$$\sigma_a(2\gamma) = \frac{4\pi r_0^2}{\gamma + 1} \left(\frac{\gamma^2 + 4\gamma + 1}{\gamma^2 - 1} \ln \left[\gamma + \sqrt{\gamma^2 - 1} \right] - \frac{\gamma + 3}{\sqrt{\gamma^2 - 1}} \right), \quad (2.1)$$

where r_0 is the classical electron radius and γ is the Lorentz factor. For non-relativistic speeds, $v \ll c$ and therefore $\gamma \rightarrow 1$, this simplifies significantly to

$$\sigma_a(2\gamma) = 4\pi r_0^2 \frac{c}{v}. \quad (2.2)$$

Annihilation with a bound electron takes a similar form, but includes a term, $\frac{Z_{eff}}{4}$, to represent the effective number of electrons, per atom within the target material, which are in a singlet spin state relative to the positron, resulting in

$$\sigma_a(2\gamma) = Z_{eff} \pi r_0^2 \frac{c}{v}. \quad (2.3)$$

It can be seen that the annihilation cross section increases as the energy of the system decreases, however, it should be noted that the cross section does not become infinite as $v \rightarrow 0$. The annihilation rate for a two photon decay in a substance, $\lambda(2\gamma)$, is then given by the expression

$$\lambda(2\gamma) = N Z_{eff} \sigma_a(2\gamma) v, \quad (2.4)$$

where N is the number of atoms per unit volume.

Annihilation will also take place after the formation of positronium. In order to conserve the total angular momentum of the system, a restriction can be placed on the number of photons emitted during annihilation, n_γ . This was first expressed by Yang (1950); Wolfenstein and Ravenhall (1952) as

$$(-1)^{n_\gamma} = (-1)^{L+S}, \quad (2.5)$$

where L and S are the orbital angular momentum and spin quantum numbers of the system respectively. However, this may be better expressed (McEachran, 2011; Rich, 1981) as

$$(-1)^{n_\gamma} = (-1)^J, \quad (2.6)$$

where J is the total angular momentum quantum number, taking integer values from the range $|L - S| \leq J \leq L + S$.

Regardless of the form used, for p -Ps ($S = 0$) in the ground state ($L = 0$), annihilation must occur via an even number of photons. For o -Ps ($S = 1$) in the equivalent state, annihilation must occur via an odd number of photons with the exception of a single photon, which is forbidden in free space. While it is possible for p -Ps and o -Ps to decay with more than two and three photons respectively, it is unlikely and hence will not be considered here. The decay rates of p -Ps can be approximated by replacing the NZ_{eff} term in equation 2.4 with one representing the density of the electron at the position of the positron. This can be obtained from the equivalent hydrogen wavefunction by replacing a_0 with $2a_0$. The decay rate can then be approximated by

$$\lambda_{p\text{-Ps}}(2\gamma) = \frac{r_0^2 c}{2(na_0)^3} \quad (2.7)$$

$$= \frac{\alpha^5}{2n^3} \left(\frac{mc^2}{\hbar} \right). \quad (2.8)$$

The corresponding annihilation rate for o -Ps was derived by Ore and Powell (1949) and is given by

$$\lambda_{o\text{-Ps}}(3\gamma) = \frac{2(\pi^2 - 9)}{9\pi} \frac{\alpha^6}{n^3} \left(\frac{mc^2}{\hbar} \right). \quad (2.9)$$

While these approximations allow the lifetimes ($\tau = \frac{1}{\lambda}$) of p -Ps, $\tau_{p\text{-Ps}}$, and o -Ps, $\tau_{o\text{-Ps}}$, to be reasonably well calculated, the inclusion of quantum electrodynamic radiative corrections is required for agreement with experimental measurements. Table 2.1 shows the results from this method in comparison to more sophisticated calculations which include radiative corrections as well as recent experimental measurements.

State	Without corrections	With corrections	Experimental
p -Ps	124.49 ps	125.164(3) ps ^a	125.14(2) ps ^b
o -Ps	138.67 ns	142.0458(2) ns ^c	142.03(2) ns ^d

Table 2.1: Shown here are the lifetime values for the two different states of positronium. The method outlined previously yields close approximations which are compared to more complex theories, which include quantum electrodynamic radiative corrections, and recent experimental measurements.

^aAdkins et al. (2001); Czarnecki et al. (2000)

^bAl-Ramadhan and Gidley (1994)

^cAdkins et al. (2001, 2002)

^dVallery et al. (2003)

2.1.3 Positron Sources

Following Anderson's discovery of the positron, an artificial source of positrons was soon unearthed by Joliot and Curie (1934) in the form of irradiated boron. Over the next few decades many more sources were proposed and discovered.

There are two basic processes which can be used to produce positrons, nuclear decay and pair production. As yet, the ability to store and transport large numbers of positrons has not been developed, requiring each laboratory wishing to use positrons to have one of these source types. With the exception of the radioisotope ^{22}Na , which will be covered in some detail, these sources will only be briefly discussed.

Nuclear Decay Sources

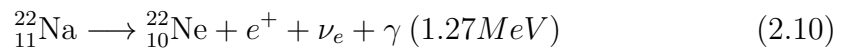
Nuclear decay sources may be further divided into longer lived radioisotopes, which can be created and transported, and short lived radioisotopes which are typically created *in-situ*. Table 2.2 shows a selection of radioisotopes which undergo decay through the emission of a positron (β^+ decay).

Element	Halflife ($\tau_{\frac{1}{2}}$)	β^+ Energy	β^+ %
^{11}C	20 mins	960 keV	99.8
^{18}F	1.8 hrs	633 keV	96.7
^{22}Na	2.6 yrs	540 keV	90.3
^{26}Al	7×10^5 yrs	1.17 MeV	81.7
^{56}Co	77 days	1.46 MeV	18.4
^{58}Co	71 days	475 keV	14.9
^{64}Cu	12.7 hrs	653 keV	17.6

Table 2.2: Shown here are a selection of radioisotopes which undergo β^+ decay. Shown are the maximum energy and the percentage of nuclear decays which proceed through β^+ decay.

Long lived radioisotope sources are the most common sources in use today. Of the available radioisotopes, ^{22}Na is the most widely used due to its favourable decay properties, the ease of handling and manipulating its various salt solutions and its short biological halflife of only a few days. It is also utilised by the apparatus which is the subject of this thesis and as such, its decay will be discussed in some detail.

^{22}Na can decay to ^{22}Ne via three different processes, two of which result in the emission of a positron while the third decay route is through electron capture (Allen et al., 1955). The possible processes are depicted in figure 2.2 with the dominant process shown in equation 2.10.



It can be seen in figure 2.2 that 90.3% of the radioisotope will undergo β^+ decay, emitting a positron. With the exception of a very small percentage, these are accompanied by a 1.27 MeV photon. The remaining 9.6% of decays undergo electron capture, resulting in no positron. However, this process is still accompanied by a 1.27 MeV photon as the newly formed ^{22}Ne decays to its ground state. Equation 2.10 shows the most common decay process which results in ^{22}Na decaying to ^{22}Ne through the emission of a positron, an electron neutrino and a 1.27 MeV photon.

Short lived radioisotopes ($\tau_{\frac{1}{2}} \lesssim 1$ day) are usually created through the capture of a thermal neutron, such as $^{64}_{29}\text{Cu}$, or through proton bombardment, such as

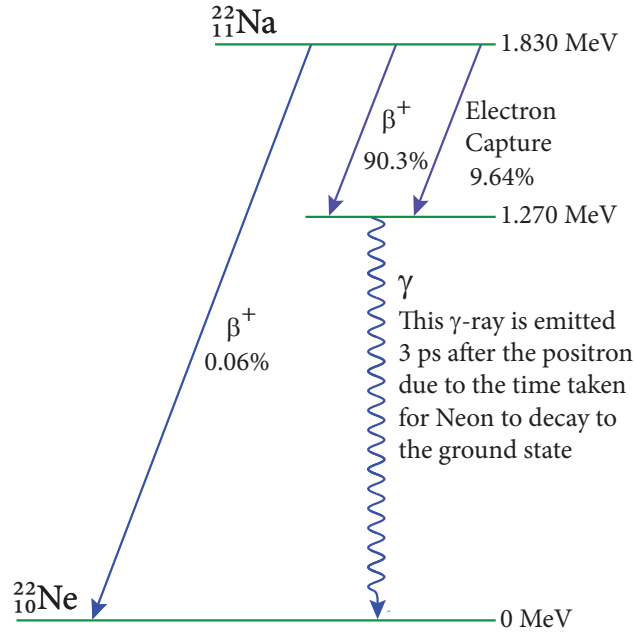
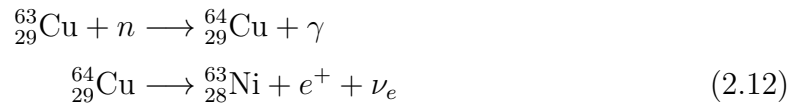
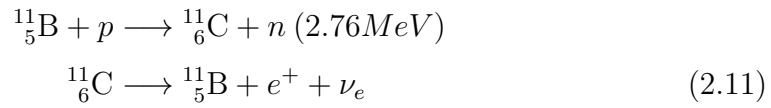


Figure 2.2: Shown here are the three decay processes of ^{22}Na to ^{22}Ne . Approximately 90% of the decays result in the emission of a positron, while ~10% undergo electron capture.

$^{11}_6\text{C}$. For the two examples given, the creation and subsequent decay processes are shown in equations 2.11 and 2.12 respectively. These radioisotopes are generally used where a nuclear reactor or particle accelerator is available to drive the initial creation.



Pair Production Sources

There are three main types of pair production sources, high intensity laser pulses, electron beams and nuclear sources, which all produce a positron-electron pair. This process requires at least twice the rest energy of the electron ($2m_e = 1.022\text{ MeV}$), which is referred to as the pair production threshold.

Using high intensity laser pulses as a positron source was first proposed by Bhabha (1935). This type of source operates by accelerating electrons at the focal point to relativistic energies. These fast electrons can produce an electron-positron pair by scattering in the Coulomb field of a nucleus, referred to as the Trident process. More recent calculations have been carried out by Shearer et al. (1973), who determined that energy densities of $\sim 10^{19} \text{ W cm}^{-1}$ would be needed to produce a significant number of positrons. Recently, Chen et al. (2009) used this method to produce 2×10^{10} unmoderated (moderation will be discussed in the following section) positrons per steradian using a gold target, achieving the highest recorded positron density of $\sim 10^{16} \text{ e}^+/\text{cm}^3$.

Electron beam sources operate by directing an electron beam onto a target material with a high atomic number. In these sources, electrons can be injected with energies from tens of MeV up to several GeV. These electrons rapidly lose energy through two main processes: Bremsstrahlung radiation which dominates at energies $>10 \text{ MeV}$ and collision processes. Under these conditions, Bremsstrahlung radiation is produced at energies exceeding the pair production threshold. These high energy photons then interact with a nucleus and undergo materialisation, resulting in the production of an electron and a positron. In the early stages, these particles are born with sufficient energy to repeat the process, resulting in a cascade effect. However, this method results in large amounts of damage to the target material at higher electron beam intensities. An alternate method by Balakin and Mikhailichenko (1979) involves using radiation produced by passing the electron beam through a series of undulators. This type of source was recently demonstrated at the Stanford Linear Accelerator Center (SLAC) by Alexander et al. (2008) and is planned to be used in the International Linear Collider (ILC) (Scott et al., 2011).

Currently the most intense moderated positron source is at the Munich research reactor, FRMII, which can produce $\sim 10^8 \text{ e}^+\text{s}^{-1}$ at a beam energy of 1 keV (Hugenschmidt et al., 2004, 2006). This technique uses thermal neutrons from the reactor to excite the $^{113}\text{Cd}(n,\gamma)^{114}\text{Cd}$ reaction. ^{114}Cd is produced in an excited state and decays through the emission of several γ -rays totalling 9.05 MeV . On average, 2.3γ -rays are emitted with no less than 1.5 MeV each. These γ -rays then undergo the process of pair production, outlined previously, in a platinum target.

2.1.4 Moderation of Positron Sources

Regardless of the process used, all known positron sources produce high energy positrons with a broad energy distribution; for ^{22}Na , Wright (1953) observed this to extend up to 540 keV. While there are several applications for positrons at these energies, the ability to produce low energy positron beams extends the range to studies of low energy interactions, surface studies, probing materials in a selective manner and many more.

The first recorded observation of low energy positrons was made by Cherry (1958), who noted their emission from chromium covered mica. However, this effect was only investigated in detail after Madey (1969) observed re-emission of low energy positrons, ~ 20 eV, from polyethylene. This process, the diffusion and re-emission of low energy positrons from materials, became known as positron moderation.

Currently, there are two main types of moderators in use: metallic and solid rare-gas moderators. These operate under two different models, the negative work function model and the hot positron model respectively. Both moderator types require very high purity materials as even a small percentage of contaminants will result in a significant reduction in the efficiency of the moderator. The reasons for this will be discussed further in section 2.2.

Metallic Moderators

Metallic moderators can be operated in several distinct geometries, from reflection (Mills Jr., 1979) and transmission (Chen et al., 1985; Lynn et al., 1985) to more complex mesh (Fornari et al., 1983) and vane (Dale et al., 1980) type arrangements. However, the mechanism behind these various geometries is the same and will be the focus of the discussion here.

Upon implantation into metallic materials, high energy positrons will thermalise within a few picoseconds. This is achieved through various inelastic processes, dominated by ionising collisions, before positrons diffuse through the material (these processes will be discussed more in section 2.2.2). Here it is sufficient to say that in defect free metallic materials, the diffusion distance, L_+ , is governed by

$$L_+ = (D_+ \tau)^{\frac{1}{2}}, \quad (2.13)$$

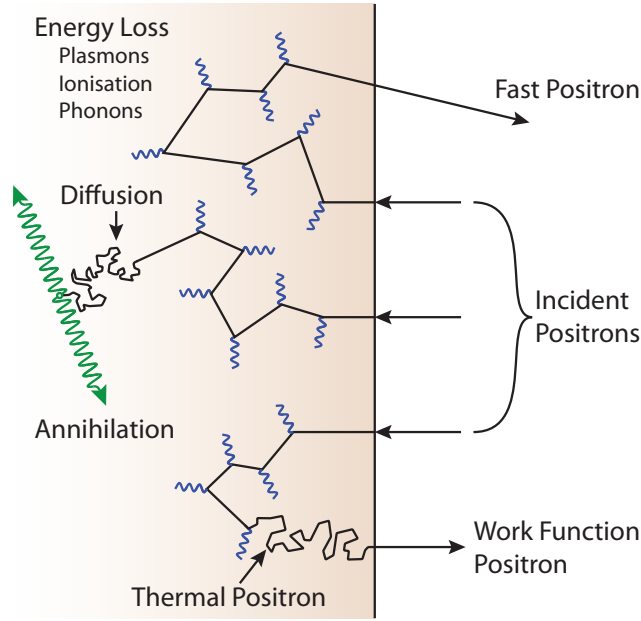


Figure 2.3: Shown here are three of the processes which can take place following the implantation of a positron. The processes shown here are of interest for moderation techniques (reproduced from Charlton and Humberston, 2001).

where D_+ represents the diffusion coefficient and τ represents the free lifetime of the material. In these materials, positrons typically have a lifetime between 100 ps and 500 ps (Charlton and Humberston, 2001).

For defect free metallic materials at 300 K, the positron lifetime is ~ 100 ps while D_+ is on the order of $1 \text{ cm}^2\text{s}^{-1}$ (Schultz and Lynn, 1988). This allows the positron to diffuse on the order of 100 nm. However, even a small concentration of defects drastically reduces this diffusion length due to trapping, as will be discussed in section 2.2.2. Thermal positrons which encounter a surface during diffusion may be emitted as a free positron if the surface has a negative work function for positrons, ϕ_+ (Mills Jr. et al., 1978). Such surfaces were predicted by Tong (1972), who first reported the significance of a dipole potential at the surface, D . This negative work function is possible due to the electron distribution extending out into the vacuum a short distance, typically on the order of 0.1 nm. The work function is determined by two potentials: the chemical potential, μ_+ , experienced in the bulk and the surface dipole potential, D , experienced at the surface as shown below.

$$\phi_+ = -D - \mu_+ \quad (2.14)$$

Later work by Hodges and Stott (1973) accounted for positron-electron screening to provide a more complete theory.

The most common metallic moderators are polycrystalline tungsten, in a transmission geometry, and single crystal tungsten, either W(100) in a reflection geometry or W(110) in a transmission geometry. Vehanen et al. (1983) showed that these moderators can reach an efficiency of 0.3%, producing low energy positrons with an energy width of 0.7 eV; however, typical efficiencies are an order of magnitude worse. When these clean single crystal materials are employed as a second moderation stage, referred to as remoderators, the energy width is almost always ~ 75 meV at room temperature (Schultz and Lynn, 1988). A smaller energy width of 32 meV was achieved by Gullikson et al. (1985) using a Ni(100) remoderator; this was later improved to 27 meV, with an efficiency of $\sim 12\%$, by cooling the Ni(100) to 77 K (Gullikson and Mills Jr., 1987).

Solid Rare Gas Moderators

Following the discovery of the single crystal metallic moderators, Mills Jr. and Gullikson (1986) observed numerous positrons re-emitted from solid noble gases. In contrast to the metallic moderators, there are no free electrons near the surface of these solids. This results in little dipole contribution and therefore a positive work function inhibiting the emission of thermal positrons which diffuse to the surface (Gullikson and Mills Jr., 1986). However, in these materials the energy loss mechanisms at low energies are very inefficient (discussed further in section 2.2.1), preventing the positrons from fully thermalising. In this case, positrons typically encounter a surface with much more energy which allows them to overcome the positive work function of these materials and escape into the vacuum. These rare gas moderators increase in efficiency as one travels from xenon to neon in the periodic table, reaching efficiencies of almost 1% (Mills Jr. and Gullikson, 1986; Khatri et al., 1990; Greaves and Surko, 1996). However, the emitted positrons have a larger energy width, on the order of eV, and typically this type of moderator is employed with a secondary cooling method.

2.2 Positrons in Materials

Upon implantation into a sample, a positron will undergo several processes before annihilating with an electron. These processes will be discussed here in a chronological order starting with thermalisation, then the subsequent diffusion before, finally, the trapping of the positron.

2.2.1 Implantation and Thermalisation

Following the implantation of positrons into a sample, they will rapidly thermalise, typically within a few picoseconds. The implantation profile is a probability distribution which represents the depth at which a positron will thermalise. This is of particular interest if information about the sample is to be collected in a depth sensitive manner. However to control this profile, positrons of a discrete, controllable energy must be used. Positrons implanted directly from a source possess a large distribution of energies, in the example of ^{22}Na the energy spectrum extends up to 540 keV, as shown in figure 2.4. This results in a correspondingly broad implantation distribution which can extend up to the order of millimetres, providing information about the sample without any depth selectivity.

With the development of low energy positron beams, the ability to control the implantation depth and probe the sample in a depth controlled manner was developed. This also allowed the thermalisation processes, which were alluded

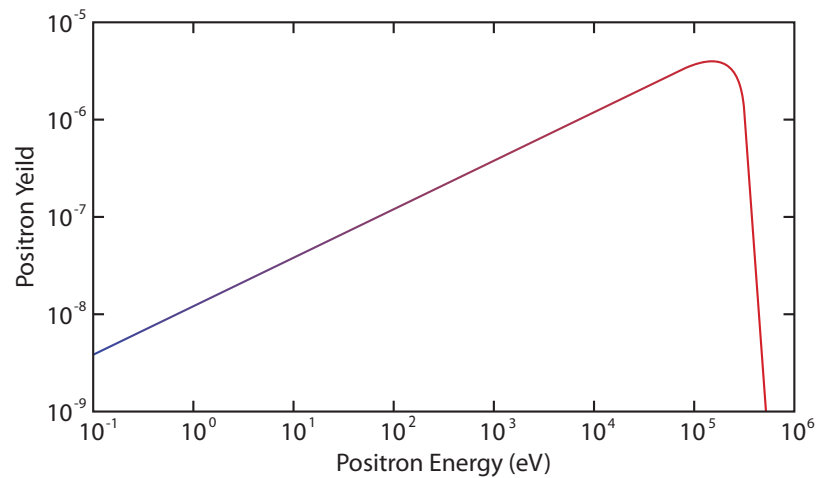


Figure 2.4: Shown here is energy distribution of positrons emitted from ^{22}Na (reproduced from Charlton and Humberston, 2001).

to in the discussion of moderation, to be studied. At energies above 100 eV, the thermalisation process is almost identical for positrons and electrons. For particles with energy above ~ 10 MeV, the initial thermalisation process is dominated by the emission of Bremsstrahlung radiation. Once below this level, inelastic scattering from the nuclei within the material plays a larger role until ~ 100 keV. At these energies, thermalisation takes place through ionising collisions or excitation of core electrons. Once energies approach the Fermi level in metals, or the band-gap in semiconductors and insulators, the thermalisation process proceeds differently for each material.

Near the Fermi energy in metals, Perkins and Carbotte (1970) showed inelastic interactions with conduction electrons, namely plasmon excitation and electron-hole pair formation, dominate the thermalisation process. These energy loss mechanisms reduce the energy of the positron to much less than the Fermi energy. Once at these low energies, thermalisation proceeds more slowly through phonon excitation.

Thermalisation in semiconductors proceeds via the same mechanisms. However, the introduction of the band gap prevents energy loss through electron excitation once the energy of the positron is less than the band gap. Thermalisation is then restricted to phonon scattering, resulting in an increase in the thermalisation time. Thermalisation in insulators proceeds at a slower rate again due to the increased band gap. Rather than phonon excitations, these materials usually result in the formation of positronium through the capture of a bound electron (Ore model) or, once slowed further, an electron previously liberated (Spur and Blob models). This is possible due to the small amount of energy lost to each phonon excitation, resulting in a slow energy loss rate. In the case of a neon moderator, the average energy loss due to phonon excitation is 6 meV (Gullikson and Mills Jr., 1986). The implantation profile, $P(z, E)$, varies with the positrons' implantation energy, E , and the material's density, ρ . For simple materials, Makhov (1961) developed the Makhov implantation profile through electron implantation experiments, given by

$$P(z, E) = \frac{mz^{m-1}}{z_0^m} \exp \left[- \left(\frac{z}{z_0} \right)^m \right] \quad (2.15)$$

$$z_0 = \frac{AE^n}{\rho \Gamma \left(1 + \frac{1}{m} \right)}.$$

However, this can be equally applied to positrons under these conditions. The parameters of this profile, m, n and A can be obtained theoretically from Monte Carlo simulations (Valkealahti and Nieminen, 1983, 1984), however, Ghosh (1995), also using a Monte Carlo approach, showed that these parameters are material dependent. These parameters have also been experimentally determined in a range of samples which can be seen in table 2.3.

Widely used empirical values are $m = 2, n = 1.6$ (Vehanen et al., 1987) and $A = 4.0 \mu\text{cm}^{-2}\text{keV}^{-n}$. An example using these values is shown in figure 2.5 which demonstrates different implantation energies for a material of density 5 gcm^{-3} . More simply, the mean implantation depth, $\bar{z}$, can be calculated using

$$\bar{z} = \frac{AE^n}{\rho} \quad (2.16)$$

with the experimentally determined values for A and n shown in table 2.3.

Sample Composition	$A (\mu\text{cm}^{-2}\text{keV}^{-n})$	n	Determined by
Al	3.32	1.60	Mills Jr. and Wilson (1982)
<i>a</i> -Si	2.58	1.7	Gebauer et al. (1997)
Cu	-	1.43	Mills Jr. and Wilson (1982)
Au	8.31	1.42	Baker et al. (1991)
ZnS & Al ₂ O ₃	3.8	1.62	Vehanen et al. (1987)
Ge & GaAs	3.5	1.60	Soininen et al. (1992)
<i>a</i> -polymers	2.81	1.71	Algers et al. (2003)

Table 2.3: Shown here are a range of experimentally determined values for the A and n parameters of the Makhov implantation profile.

However, for more complex materials, such as layered materials or materials containing interfaces, a full Monte Carlo simulation is required to accurately predict the implantation profile. In order to accomplish this, an existing computer program, Penetration and Energy Loss of Positrons and Electrons (PENELOPE), developed by Baró et al. (1995) is used. PENELOPE is designed to use scattering theory and cross section measurements to simulate the effect of four different processes: elastic scattering, inelastic scattering, Bremsstrahlung radiation and annihilation. PENELOPE successfully simulates the implantation of positrons with

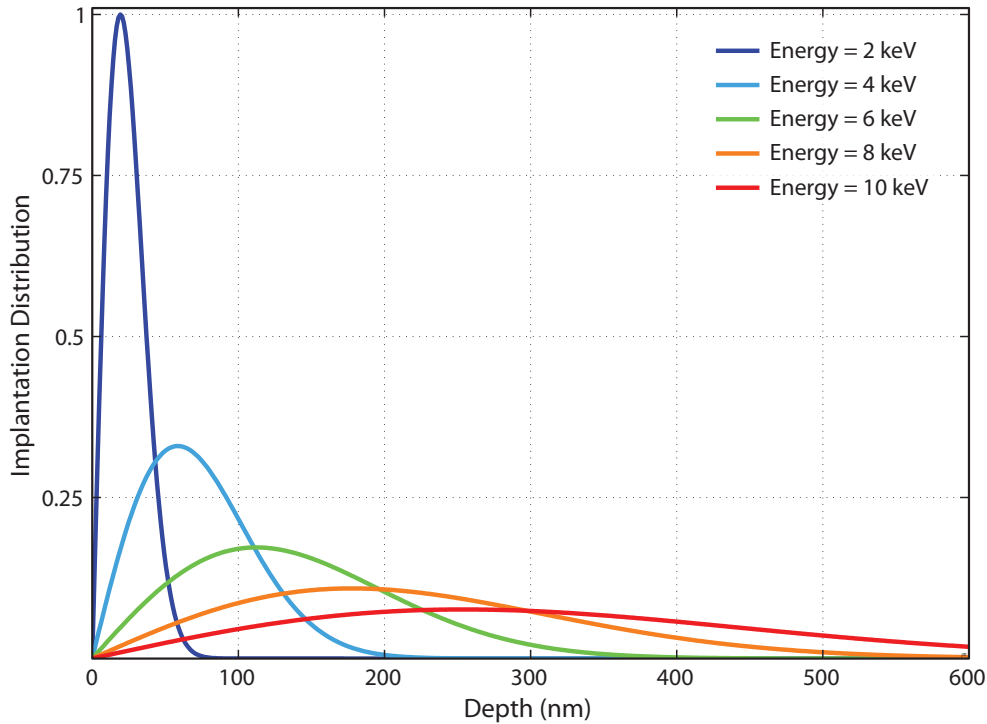


Figure 2.5: This image demonstrates how the implantation profile varies for different positron energies. Here, a density of 5 gcm^{-3} was used with the parameters set to $m = 2$, $A = 4.0 \text{ } \mu\text{cm}^{-2}\text{keV}^{-n}$ and $n = 1.6$.

up to $\sim 1 \text{ GeV}$ in energy, showing good agreement with experimental measurements and the Makhov implantation profile where applicable.

2.2.2 Diffusion and Trapping

Once the positrons have thermalised they do not immediately annihilate, instead they remain mobile and can travel through the material. This process is referred to as diffusion and, depending on the material, can significantly alter the final annihilation profile from the implantation profile. In insulating materials, positronium formation primarily occurs through the spur or blob model during the final stages of thermalisation. However, positronium will also thermalise and diffuse through the material in a similar manner (Kubica and Stewart, 1975).

During the diffusion process, positrons are repelled by the nuclei and tend to occupy the interstitial regions of the material. Positrons will diffuse until they either annihilate in the bulk, arrive at a surface at which they are trapped and subsequently annihilate, or are emitted from the surface (moderation). Here a brief overview of the diffusion process will be given.

For defect free metallic materials, the diffusion length has already been discussed in section 2.1.4. However, the majority of materials studied do not meet this criteria and require a more complex approach due to the presence of defect sites. Brandt and Arista (1979) showed that the energy distribution of a diffusing positron ensemble will not be Maxwellian due to the presence of energy dependent trapping rates. This requires the application of the Boltzmann equation to describe the subsequent motion of the ensemble through the material. This assumes that positrons may only be trapped following thermalisation, which is a reasonable assumption and significantly simplifies the problem at hand. However, Lynn et al. (1987) have shown that some trapping may occur prior to thermalisation.

The Boltzmann equation for the motion of positrons through a material is

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = D_+ \nabla^2 n(\mathbf{r}, t) - \lambda_{eff} n(\mathbf{r}, t) - \frac{\partial}{\partial \mathbf{r}} \left(v_d n(\mathbf{r}, t) \right), \quad (2.17)$$

where $n(\mathbf{r}, t)$ is the positron density as a function of position and time, λ_{eff} is the effective annihilation rate and v_d is the field dependent drift velocity.

The effective annihilation rate, λ_{eff} , includes both the bulk annihilation rate, λ_b , as well as a trapped annihilation rate, $\kappa_t C(z)$, as shown below. The trapping term represents a depth dependent concentration of defect sites, $C(z)$, which have a trapping rate, κ_t .

$$\lambda_{eff} = \lambda_b + \kappa_t C(z) \quad (2.18)$$

Solutions for the diffusion length have been found by Lynn (1981) for metals, where $v_d = 0$ due to the absence of internal fields. Complementary to this, solutions have also been found by Mills Jr. and Murray (1980) which included the drift term, through experimental investigations of positrons which diffused to the surface.

Upon encountering a trapping site, a positron can make the transition from a delocalised state to a localised state. The trapping rate, κ_t , of thermalised positrons is normally proportional to the trapping site concentration, C , and the specific trapping rate for the trapping site, μ , as shown below.

$$\kappa_t = \mu C \quad (2.19)$$

The specific trapping rate varies with the type of trapping site as well as the temperature.

Here, vacancy clusters of radius r (discussed in section 2.2.3) will be considered. The specific trapping rate is governed by two processes, the diffusion of the positron and the likelihood of transition into the trap. An approximate expression for this was derived by Seeger (1974), and is

$$\mu = \mu_{\infty} \left(1 + \frac{\mu_{\infty}}{\mu_D} \frac{r}{\sqrt{\pi D_+ t}} \right) \quad (2.20)$$

$$\mu_{\infty} = \left(\frac{1}{\mu_D} + \frac{1}{\mu_{tr}} \right)^{-1} \quad (2.21)$$

$$\mu_D = \frac{4\pi D_+(T)r}{\Omega} \quad (2.22)$$

$$\mu_{tr} = B(T)r^2, \quad (2.23)$$

where t is time, Ω is the atomic volume and $B(T)$ is a constant which may vary with temperature.

Equation 2.20 shows that μ approaches μ_{∞} after long times. Contained within equation 2.21 are the diffusion limited trapping rate, μ_D , and the transition limited trapping rate, μ_{tr} . In materials which contain a large concentration of trapping sites, typically in the form of shallow traps, diffusion to a trapping site will occur rapidly. Under these conditions, trapping will proceed at a rate governed by the site's ability to transfer energy to the surrounding material, resulting in $\mu_{\infty} = \mu_{tr}$. The rate at which this happens can be described by Fermi's Golden Rule (Hodges, 1970, 1974). Similarly, for materials which contain few trapping sites, or deep traps, the specific trapping rate is limited by the diffusion of the positrons, $\mu_{\infty} = \mu_D$.

Determining the final annihilation profile due to the diffusion of the positrons is a non-trivial process which requires an in-depth understanding of the material, including the trapping sites it may possess.

2.2.3 Trapping Sites

The discussion here will focus on common trapping sites encountered in a material. These sites are normally divided into three different categories: bulk sites, which exist within the bulk structure of the material; interface sites, which can occur when two different materials or crystal structures meet; and surface states, which exist at the surface of a material. Each of them will be discussed separately in the following section.

Bulk Sites

Within the bulk, trapping sites are created by defects in the material due to impurities or structural anomalies. Here, the examples given will use a simple cubic lattice to clearly illustrate the defects. The first type of defect considered will be vacancy and open volume type defects which are of particular interest to positron trapping. Vacancy type defects are highly localised, affecting only a few unit cells of the material. The simplest case is a monovacancy, with just a single atom missing from the lattice, as shown in figure 2.6. Vacancy type defects generally result in an attractive potential due to the absence of a positive ion core. However, in semiconductors and insulators these vacancy defects can also be charged. Such defects have been studied by Puska et al. (1990), including the consideration of various charged states, using Fermi's Golden Rule to determine the trapping rates. The formation of larger vacancies is also possible, with a collection of these forming a void, also depicted in figure 2.6. However, once these voids become sufficiently large (≥ 50 atoms), they begin to act as surfaces rather than open volumes within the material. This then introduces the possibility of the positron becoming trapped within a surface state. This type of trap will be discussed briefly later in this section.

The second bulk site which will be discussed is a dislocation within the crystal structure. There are two main types of dislocations: an edge dislocation which is confined to a single plane of atoms and a screw dislocation which involve bonds between planes. Edge dislocations are the simplest type of dislocation defect; an example of these is illustrated in figure 2.7. These defects are generally caused by the termination of a plane of atoms in the middle of a crystal. In such a case, the surrounding planes are distorted by the termination. The second type of dislocation defect, a screw dislocation, is more complex and not confined to

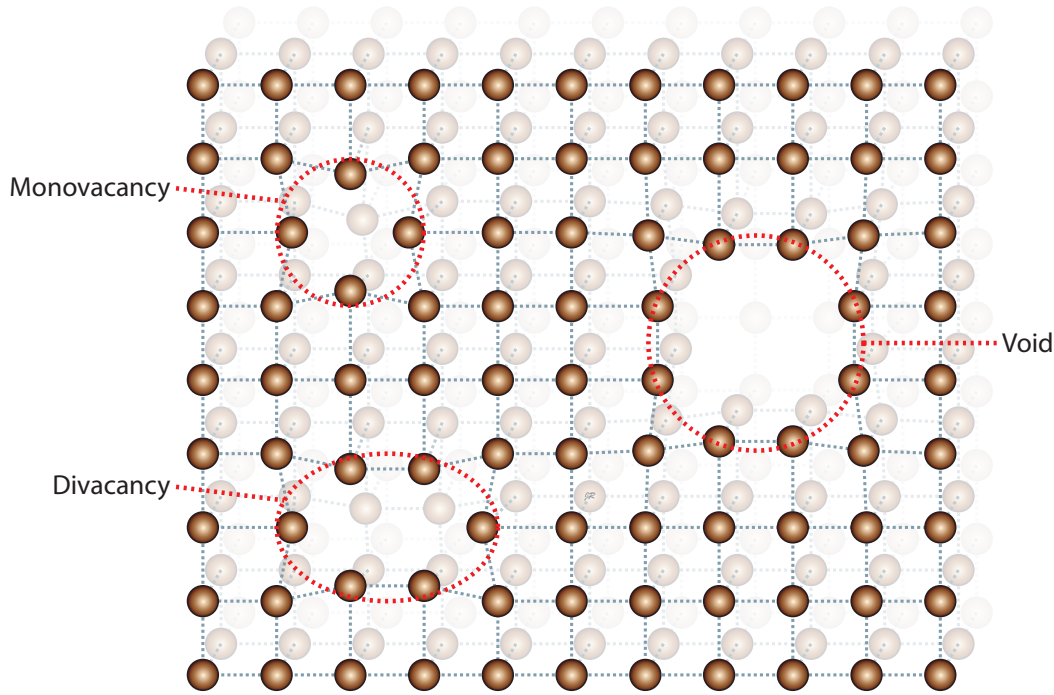


Figure 2.6: Shown here in the left part of the lattice structure are a monovacancy and a divacancy, while on the right is an example of an open volume type defect, or void.

a single lattice plane. This occurs when part of a lattice plane is shifted and bonds in place of the adjacent atomic plane. Often this type of dislocation can affect many atomic planes, resulting in a helical path along the dislocation line. Both types of dislocation defects have been modelled using a variety of different techniques, from considering the dislocations as a continuous shallow trap (Brandt and Paulin, 1972), to a collection of linearly arranged vacancies within a shallow trap (Smedskjaer et al., 1980).

Finally, impurities within the material can introduce trapping sites. While self-interstitial atoms are point defects, like monovacancies, these will not trap positrons due to the resulting repulsive potential. However, foreign atoms of a lower-valence element, whether interstitial or substitutional, can attract and weakly trap positrons. Figure 2.8 shows these types of defects, including a precipitate of impurity atoms. The effects of these impurities is of particular interest due to their presence in doped materials. The effect on the positron lifetime was first studied by Vehanen et al. (1982) who investigated iron samples doped with carbon. This study showed the formation of carbon-vacancy pairs which triggered

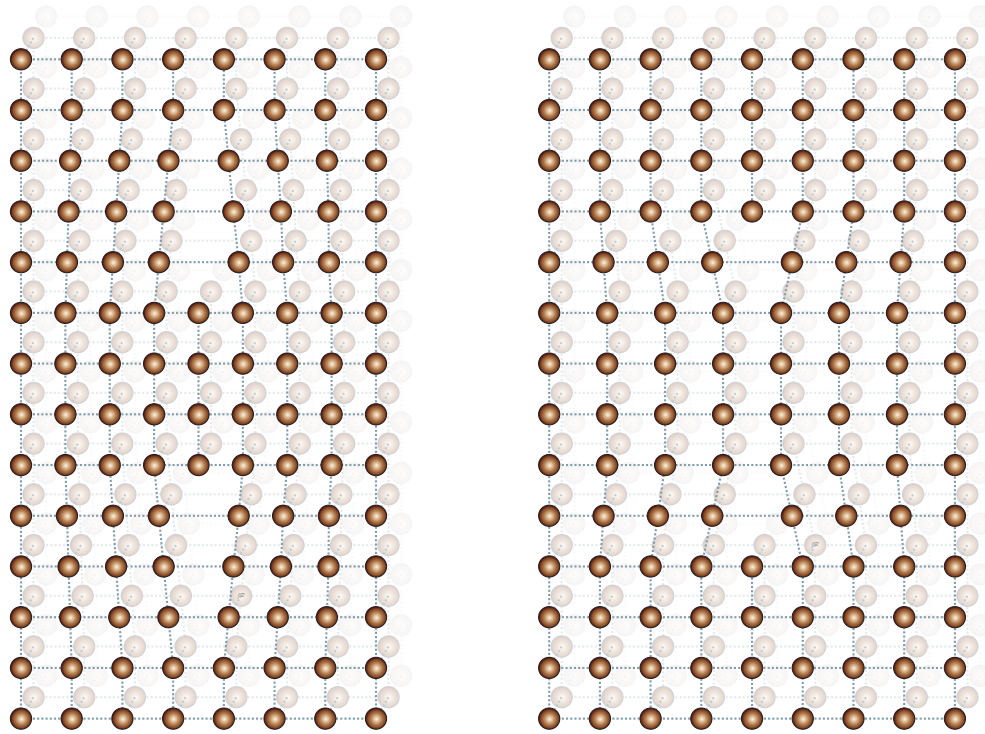


Figure 2.7: Shown are two situations which can introduce an edge style dislocation. Both structures contain a dislocation loop which results in two edge dislocations in each structure. The left structure containing an interstitial plane, an extra plane within the structure, while the right structure contains a series of vacancies.

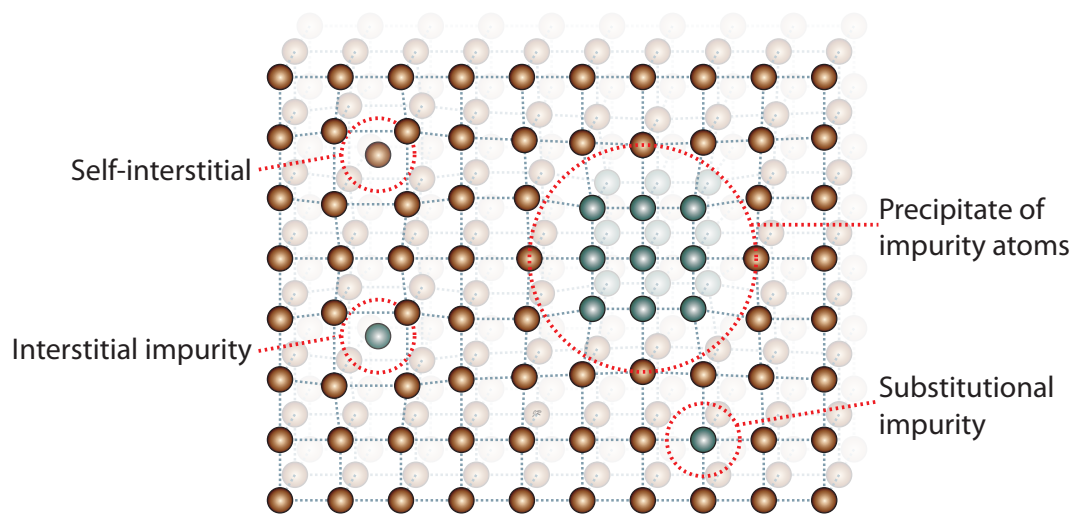


Figure 2.8: Defects introduced by impurities, both foreign to the material and self interstitial.

a series of different studies into these impurity-vacancy structures. The annihilation characteristics of these bulk defects were modelled by Puska and Nieminen (1983) to aid the analysis of experimental data. For light interstitial impurities in metallic materials this was later updated by Puska and Nieminen (1984).

Interfaces

Interface type defects can occur at the boundary between two different crystal orientations, as shown in figure 2.9, or at an interface between layers of different compositions within a material. When either of these occur, defects can exist in the form of dislocation type defects or small open volumes due to the mismatch in crystal orientation or the lattice constant. Due to the effect of the interface, these defects often result in the formation of a two dimensional trap. This type of defect is of particular interest in silicon devices due to the interface between silicon and silicon dioxide. This interface has a direct influence on device performance due to its effect on charge transport properties.

Surface States

As a positron travels through a material the surrounding electrons are attracted, increasing the average electron density near the positron. While inside the material this effect can be considered to be isotropic. However, when a positron encounters a surface this effect results in an image potential (Puska and Nieminen, 1994).

This attractive image potential, combined with the repulsive atom cores, can create a potential well within which the positron can become trapped. This model was proposed by Hodges and Stott (1973) after observing lifetimes of ~ 400 ps in neutron induced voids in Al. Positrons trapped in these surface states may form positronium which can then escape from the surface potential due to the more negative work function.

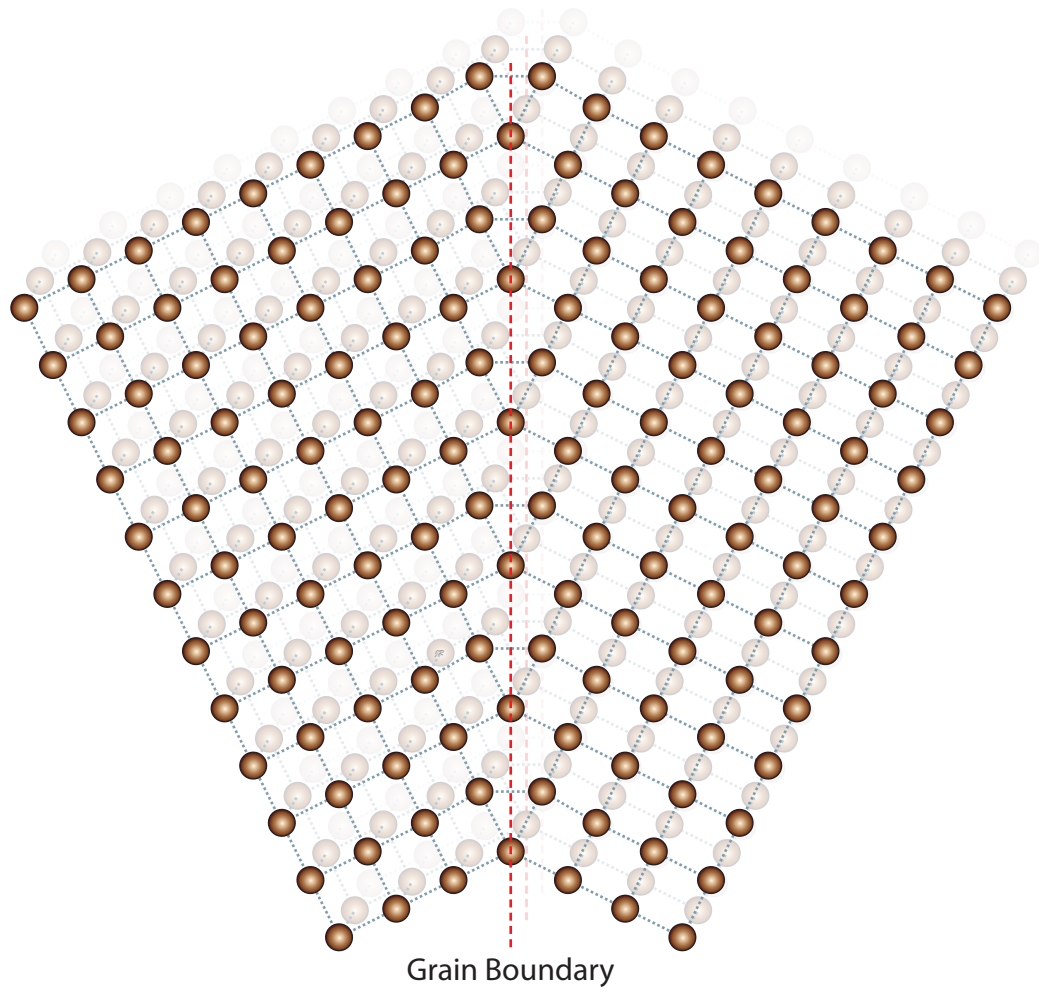


Figure 2.9: The defect shown here is introduced due to the mismatch in the crystal orientation. This figure shows a 53° grain boundary along the $[001]$ direction.

2.3 Characterising Materials with Positrons

A wide range of the known particles, as well as photons from the entire electromagnetic spectrum, are employed to characterise materials. The positron is no exception to this. As soon as positrons were able to be generated in sufficiently large numbers, techniques utilising the positron's unique properties were developed to investigate the nanoscale properties of materials.

As stated in section 2.1.2, for annihilation via two γ -rays, the γ -rays are emitted with 511 keV of energy, 180° apart with respect to the reference frame of the positron-electron system to conserve momentum. However, in the laboratory frame of reference, these γ -rays can have a slight deviation from both 511 keV and 180° . Typically, this can be attributed solely to the momentum of the electron, as the positron is considered to reach thermal temperatures prior to annihilation. The angular shift was first noted by DeBenedetti et al. (1949) and can be considered the birth of Positron Annihilation Spectroscopy (PAS). The technique of measuring the angular spread of the annihilation γ -rays became known as Angular Correlation of Annihilation Radiation (ACAR). The slight Doppler shift away from 511 keV in the annihilation γ -rays was not experimentally accessible until the late 1970's (Lynn et al., 1977). This technique is referred to as Doppler Broadening Spectroscopy (DBS). A brief discussion of these techniques, as well as some other PAS techniques, will be given here. As it is the technique upon which the experimental work in this thesis is based, a more in depth discussion of the Positron Annihilation Lifetime Spectroscopy (PALS) technique will given in the next section.

2.3.1 ACAR

Angular Correlation of Annihilation Radiation (ACAR) is the study of the angular spread of the annihilation radiation for two γ -ray annihilation events. This angular deviation, θ , can be given in terms of the momentum of the annihilating particles, ρ , and the rest mass of the electron, m_0 , by

$$\theta = \frac{\rho}{m_0 c}. \quad (2.24)$$

Typically this deviation is very small ($<0.5^\circ$), requiring the coincidence detectors to be a large distance from the source of the annihilation event to achieve

the required angular resolution. Initially ACAR spectra were collected using two scintillator detectors 180° apart, one of which could be rotated about the sample position allowing access to the angular information. This single dimension technique has been improved by the development of Anger cameras which consist of multiple detectors arranged in a honeycomb pattern. This allows the angular deviation of the γ -rays to be determined in two dimensions, resulting in a much improved count rate while maintaining the same angular resolution.

Annihilation within voids typically decreases the deviation from 180° as the probability of positrons annihilating with high momentum, typically core, electrons is reduced.

One of the early applications of this technique was the investigation of the Fermi surfaces of various metals. Initial measurements performed by Lang and Hien (1958), who studied single crystal cadmium, and later by Berko and Plaskett (1958), who studied single crystal aluminium and copper, focused on determining the shape of the Fermi surface. The technique was later expanded by Krivoglaz and Smirnov (1959) to determine the magnitude of the Fermi energy, demonstrated by Dekhtyar and Mikhalekov (1960, 1961) with single crystal bismuth and zinc. With improvements in detector technology, allowing access to the energy of the annihilation γ -rays, other PAS techniques are now typically preferred over ACAR. However, recently Manuel et al. (1995) successfully used 2D-ACAR, in conjunction with lifetime measurements to determine the annihilation fraction of *o*-Ps, to resolve charged and neutral arsenic vacancies in gallium arsenide.

2.3.2 DBS

Doppler Broadening Spectroscopy (DBS) is a technique which measures the energy spectrum of the annihilation γ -rays. As discussed, due to the total momentum of the annihilating particles, these γ -rays can be Doppler shifted by as much as 5 keV when annihilation occurs with high momentum electrons. Detection of this shift is typically performed with a high purity germanium detector, which are able to resolve these energy differences. The technique was expanded by MacDonald et al. (1978) who used two collinear detectors in coincidence; this allows the total energy of the annihilating particles to be determined. This method improved the resolution and signal to noise ratio of the measurements. This technique is referred to as ‘two dimensional DBS’, as the Doppler shift can be determined as a function of the total annihilation energy.

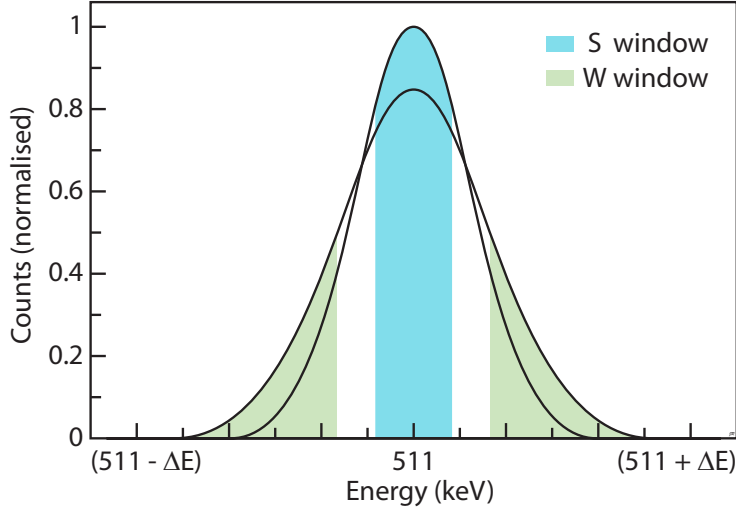


Figure 2.10: Shown here are two representative DBS spectra with typical windows for the S and W parameter shown. The S and W parameters are the ratio of the counts within the respective windowed regions to the total number of counts. Typically, ΔE is ~ 5 keV.

DBS spectra contain detailed information about the momentum distribution of the annihilation electrons. However, accessing this information requires the detector resolution function and background spectrum, both non-trivial, to be deconvoluted. DBS measurements are instead typically analysed using the S- and W-parameters as depicted in figure 2.10.

The S parameter is the ratio of the number of γ -rays detected in a window centred about 511 keV to the total number of γ -rays detected. This represents the relative fraction of annihilations which occur with low momentum electrons. Conversely, the W parameter is the relative number of counts which have undergone a significant Doppler shift due to annihilation with high momentum electrons. These windows are shown in figure 2.10 with narrow and broad energy spectra to demonstrate how these parameters can change. The absolute value of these parameters is of little significance as the window is chosen to give S parameters near 0.5 in order to achieve maximum sensitivity against small variations. Instead, these parameters are typically measured in a relative manner across a series of samples or as a function of temperature or implantation energy to provide insight into the physical characteristics of the samples.

These parameters are most useful when the ratios are plotted in the SW plane. This is demonstrated in figure 2.11, which has been constructed to show this effect for a sample with a thin film. When the implantation energy is low,

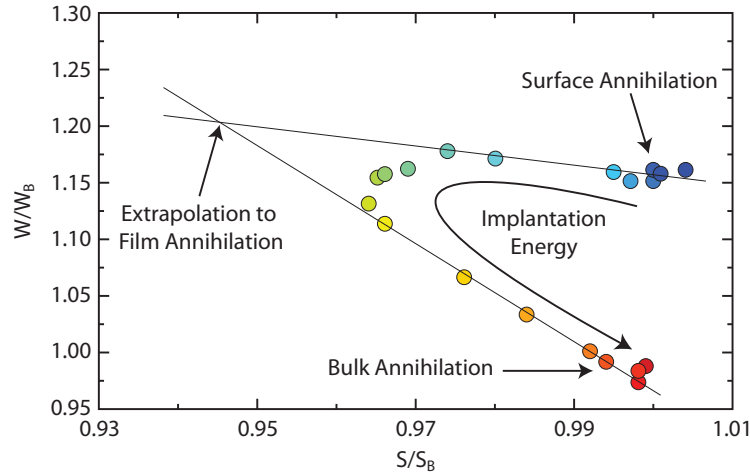


Figure 2.11: This image is to demonstrate the effect when plotted in the SW plane (based on Dull, 2009).

the positrons annihilate primarily at the surface. As the implantation energy is increased annihilations begins to take place in the film before progressing to the bulk. The parameters for annihilation within the film can be extracted through extrapolation.

Much like ACAR, within voids there is a reduced probability of annihilation occurring with high momentum electrons. This results in a relative increase in the S parameter, and a corresponding decrease in the W parameter.

2.3.3 AMOC

This powerful technique involves combining DBS in coincidence with lifetime measurements, referred to as Age-Momentum Correlation (AMOC). Studies of the lifetime of the positron within the sample will be discussed in section 2.4, however, here it is sufficient to say that the lifetime of the positron within a material will be increased in most trapping sites due to the decreased electron density. In the same manner that depth profiling allows information to be collected in a depth sensitive manner, AMOC allows the DBS parameters to be determined for each lifetime within the sample, and vice versa. As each lifetime within the sample represents a specific trapping site, the DBS parameters can be determined for each site, providing information about the local environment. These results can be displayed as a contour plot showing the γ -ray signal as a function of the positron lifetime and the energy of the annihilation γ -ray, as shown in figure 2.12.

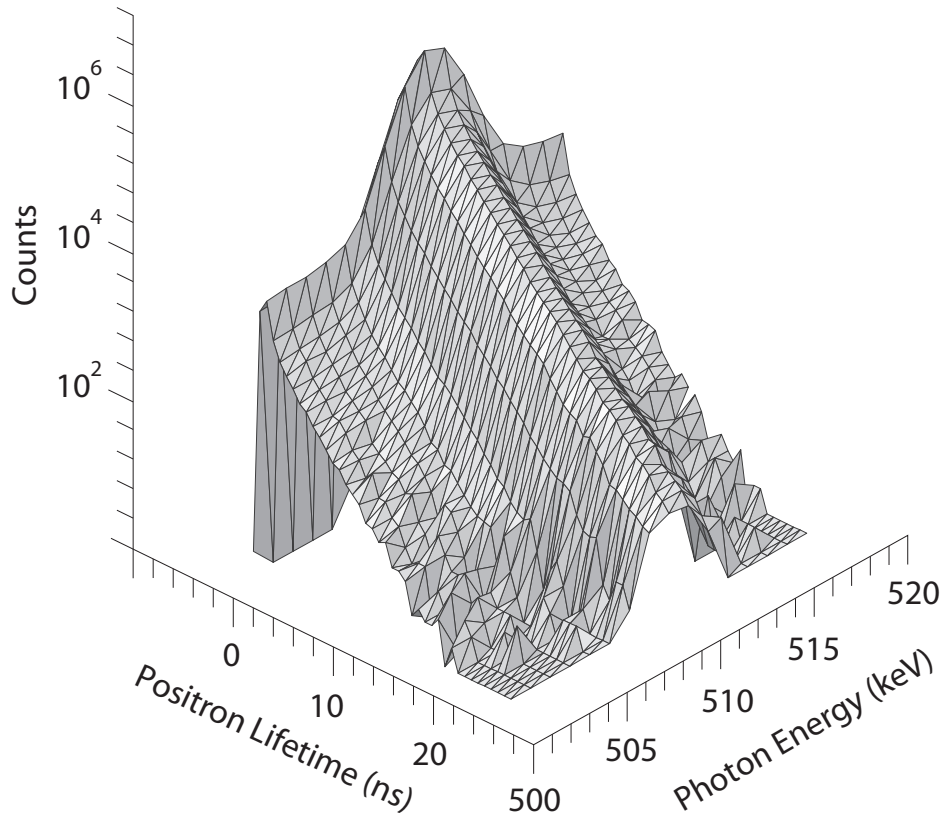


Figure 2.12: This image shows the data collected from the AMOC technique (reproduced from Castellaz et al., 2002).

2.3.4 3γ Annihilation Spectroscopy

This technique, developed by Petkov et al. (2001) and also referred to as ‘ 3γ branching ratio’ or ‘ $3\gamma/2\gamma$ ’, investigates the ratio of 3γ decay events to 2γ decay events. As outlined in section 2.1.2, annihilation almost always proceeds via two γ -rays for direct annihilation and p -Ps, while o -Ps undergoes annihilation via three γ -rays. Within a porous material, o -Ps can undergo pick off annihilation (which will be further discussed in section 2.4) on the pore wall, resulting in a two γ -ray decay event. Due to this process, in a material containing larger pores, more positrons will undergo decay through the emission of three γ -rays. Much like DBS, the decay process is determined through a measurement of the decay energy of the γ -rays emitted, although a high resolution detector is not required. As discussed, 2γ decay events result in the emission of two ~ 511 keV γ -rays. However, in a 3γ decay event the energy distribution of the annihilation γ -rays linearly increases over the range 0–511 keV. Through comparison to a sample which produces only 2γ events, the fraction of 3γ events can be derived

and information regarding the sample porosity determined. This technique has successfully been applied to the study of thin films by Xu et al. (2002); Brusa et al. (2004).

2.3.5 Ps-TOF

Positronium Time Of Flight (Ps-TOF) is another technique which can be used to determine information about the porosity and pore interconnectivity of the sample, though this is a surface sensitive technique and requires a pulsed low energy positron beam; such an apparatus was constructed by Mondal et al. (1999). The positron beam is used to produce positronium near the surface of the sample. This may then diffuse to pores which, if connected to the surface, can result in the emission of positronium from the sample. A scintillator detector is arranged to detect annihilation from positronium which drifts sufficiently far from the sample. The time for the positronium to reach this window and annihilate is recorded, allowing its energy to be determined. This allows information about the connectivity of the pores and the diffusion of positronium to be determined as demonstrated by Yu et al. (2003).

2.4 Positron Annihilation Lifetime Spectroscopy

The PALS technique, upon which the experimental work in this thesis is based, focusses on the lifetime of the positron within the material, rather than the energy or angular distribution of the annihilation γ -rays. This technique is particularly suited to study open volumes in dielectric materials, such as polymers. In these materials, positronium will readily form and preferentially localises within open volumes. While the lifetime of *p*-Ps (125 ps) is too short to allow this level of interaction, *o*-Ps has a much longer lifetime (142 ns) and will become trapped within open volumes and interact with molecular electrons. Of particular interest is the process of pickoff annihilation, where the electron within *o*-Ps is exchanged with a molecular electron to form *p*-Ps, which rapidly annihilates. This allows the *o*-Ps lifetime within the material to be related to the size of the open volume, through the Tao-Eldrup (TE) model (discussed section 2.4.3).

The lifetime was first noted to vary in different amorphous materials by Bell and Graham (1953); an extract from this research is shown in figure 2.13. These

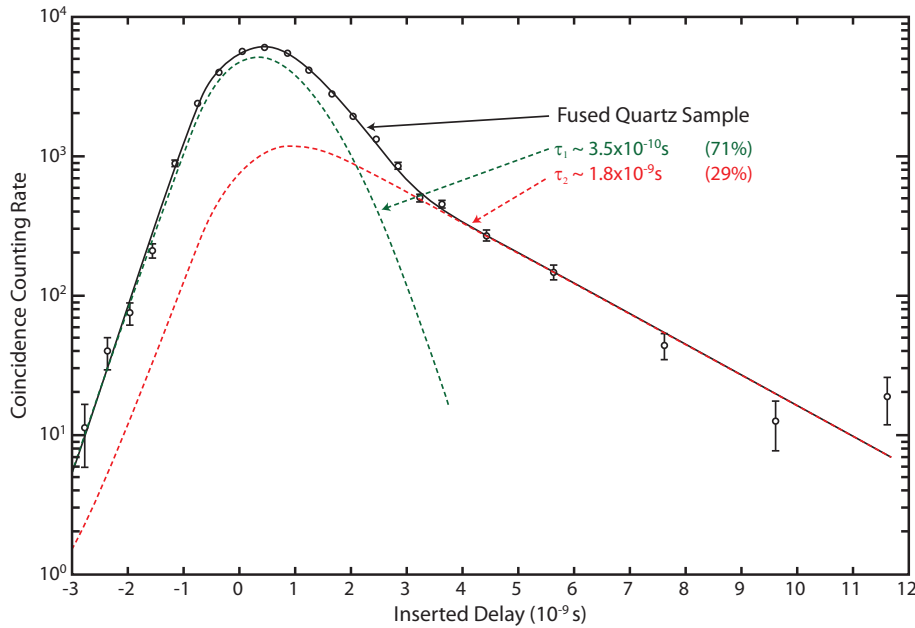


Figure 2.13: This image shows the data collected from the PALS arrangement of Bell and Graham (1953), which allowed two lifetime components to be determined for fused quartz (reproduced from Bell and Graham, 1953).

measurements were performed using a pair of focussing coils and two apertures to select positrons of 220 keV. Upon exiting the source, positrons passed through a thin stilbene crystal which provided a ‘start’ signal for the timing circuitry. The subsequent ‘stop’ signal was provided by detection of one of the annihilation γ -rays. Following this, Stump and Talley (1954) performed PALS measurements on lead and tin at superconducting temperatures. This was performed by coating the inside of a lead or tin cylinder with ^{22}Na and submersing it within liquid helium. The ‘start’ signal was then provided by the high energy (1.27 MeV) γ -ray emitted shortly after the positron is born (shown in figure 2.2). This second method, where positrons are implanted into the sample directly from a radioactive source, has become known as conventional (or benchtop) PALS.

As moderating materials were developed, the ability to implement PAS techniques in a depth sensitive manner became possible. This requires the production of a pulsed positron beam and is referred to as beam-based PALS. Much like conventional PALS, the stop signal arises from the detection of an annihilation γ -ray. However, the start signal can be derived from several different systems, depending on the arrangement. Both PALS configurations will be discussed within this section.

2.4.1 Conventional PALS

The standard arrangement for conventional PALS was first detailed by Berko and Hereford (1956) who investigated positron lifetimes, among other things, in liquids. In this arrangement the ^{22}Na positron source, typically in a salt solution, is mounted between two or more identical sample pieces. Timing information is collected using two scintillation detectors, in the same fashion as Stump and Talley (1954). Under this arrangement, high energy positrons are implanted from the source directly into the sample. This results in a broad implantation distribution, yielding information for the bulk of the material only. Analysis of the resulting spectrum also requires annihilation from within the source material to be taken into account.

2.4.2 Beam based PALS

Using the techniques for moderation discussed in section 2.1.4, low energy positrons can be produced allowing the implantation depth and spatial area probed to be controlled. However, the implementation of a moderation technique temporally disconnects the implantation of the positron from its birth in a radioisotope or pair production source. This requires PALS measurements to be performed using a pulsed beam to allow synchronisation between the implantation of the positron and the detection of an annihilation γ -ray. Methods for generating an appropriate ‘start’ signal can be achieved using a number of different methods, depending on the bunching technique. Typically, the method used to pulse the positron beam can also be used to provide the required synchronising start signal. However, it is also possible to determine the implantation time of the positrons through detection of secondary electrons emitted from the surface of the sample (Gidley et al., 2006). There are several methods which have been employed to produce a pulsed positron beam and these will be discussed in the following section.

While controlling the implantation depth can easily be achieved through manipulation of the positrons’ energy, producing a spatially resolved positron pulse is more complex. This was first demonstrated by Zecca et al. (1995) who developed a pulsed positron beam with a spot size of $20\text{ }\mu\text{m}$, referred to as a scanning positron microscope. This allows PALS, as well as other techniques, to be conducted in a spatially sensitive manner which is particularly useful for probing

fatigue in materials. This was also recently demonstrated by Oshima et al. (2011) using an independently developed scanning positron microscope.

Bunching Techniques

A pulsed beam can be produced using two concepts, chopping or bunching, which were both initially developed for ion beams. Chopping involves using an electric field to periodically deflect the continuous beam across an aperture. While this results in almost zero beam intensity outside the pulses, the average beam intensity is significantly reduced. Contrary to this, bunching techniques can maintain a much higher average beam intensity, though there is always a finite background intensity outside the pulses. These two techniques are however not mutually exclusive and are often applied in series.

The most common method of bunching positrons for beam-based PALS is through the application of a radio frequency cavity buncher as positrons are transported to the sample (Schödlbauer et al., 1988; Suzuki et al., 1995). Compression is achieved through the application of a sinusoidal potential on the cavity; particles at the head of the bunch are slowed while particles at the tail are sped up. Using this method, Schödlbauer et al. (1988) achieved a timing resolution <200 ps.

Two alternative methods were proposed by Mills Jr. (1980). The first is the application of a quadratic potential along the length of a positron cloud. This method was first implemented by Chu and Mills Jr. (1982) and then later by Cassidy et al. (2006) who used a Surko trap (which will be discussed in section 3.3) based system rather than a chopper to form the initial pulses. The latter of these successfully compressed positron bunches of 20 ns to ~ 1 ns. This method can be implemented through accelerator rings connected in series using specific value resistors to produce the desired effect.

The second method proposed requires more sophisticated hardware due to the shape of the potential applied to the positron cloud. This is referred to as the ‘timed potential technique’, with the applied potential, $V(t)$, taking the form

$$V(t) = -\frac{m_e F_L^2}{2et^2} + E_0. \quad (2.25)$$

In this bunching technique, the positron pulse arrives at the sample at $t = 0$ after traversing a distance F_L , which is referred to as the focal length.

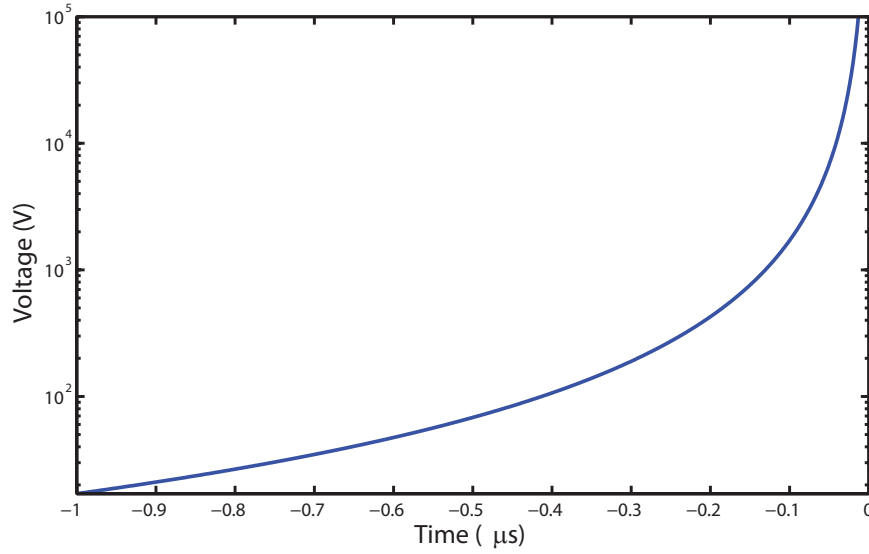


Figure 2.14: This plot shows the functional form of the timed potential technique, described in equation 2.25, with $F_L = 2.45$ m and $E_0 = 0$ V. When implemented on a positron cloud this results in a temporally compressed pulse being incident on a sample at $t = 0$.

This method was successfully implemented by Mills Jr. and Pfeiffer (1979) to produce pulses of tens of nanoseconds and later by Greaves and Moxom (2003) who, using a trap based apparatus, compressed 18 ns pulses to ~ 4 ns. The experimental apparatus used in the research presented in this thesis (discussed in chapter 3), also implements this timed potential technique as shown in figure 2.14. The difficulties of implementing this method, due to the rapidly increasing voltage as $t \rightarrow 0$, are discussed in section 3.4.1.

2.4.3 Interpreting the Lifetime

The analysis of PALS data will be discussed in more detail in chapter 4. However, the models which can be used to relate the lifetime to a pore size will be discussed here. The TE model is a simple quantum mechanical model developed by Tao (1972) and refined by Eldrup et al. (1981). In the model, *o*-Ps is trapped inside a spherical volume within an infinitely deep potential well. It is assumed that annihilation only occurs within a small region, ΔR , of the pore edge, either spontaneously through an odd number of γ -rays or through pickoff annihilation. ΔR has been empirically determined to be 0.16–0.17 nm through the study of materials which contain small, well characterised pores (such as zeolites). Within

this region, o -Ps is assumed to have a spin averaged annihilation rate, λ_A , given by

$$\lambda_A = \frac{1}{4}\lambda_{p\text{-Ps}} + \frac{3}{4}\lambda_{o\text{-Ps}}. \quad (2.26)$$

The rate of pickoff annihilation can be expressed in terms of the pore radius, R , and the spin averaged annihilation rate, λ_A , as

$$\lambda_{\text{pickoff}} = \lambda_A \left[1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \left(\frac{2\pi R}{R + \Delta R} \right) \right]. \quad (2.27)$$

The total annihilation rate, λ_T , can then be given by the sum of the vacuum and pickoff rates, $\lambda_{o\text{-Ps}}$ and λ_{pickoff} respectively, as

$$\lambda_T = \lambda_{o\text{-Ps}} + \lambda_{\text{pickoff}}. \quad (2.28)$$

The TE model can be successfully used for small pores where the assumptions made by the model are reasonable. First, within small pores the pickoff annihilation rate reduces the lifetime of o -Ps to ~ 2 ns, allowing the much longer self annihilation lifetime of 142 ns to be reasonably ignored. Second, as the first excited state is 100–200 meV above the ground state, it can also be reasonably assumed that only the ground state is populated at room temperature.

These assumptions were addressed by Dull et al. (2001) who extended the TE model, resulting in a new model known as the Rectangular Tao-Eldrup (RTE) model. In this model, a rectangular potential well is assumed, allowing the excited states of o -Ps to be accounted for. The probability of these states is assumed to be given by a Maxwell-Boltzman distribution. As a rectangular potential is used, the pore size can be solved for a single dimension trap (sheets), two dimensional traps (channels) and three dimensional traps (pores). Figure 2.15 shows this model for room temperature pores, comparing it to the TE model.

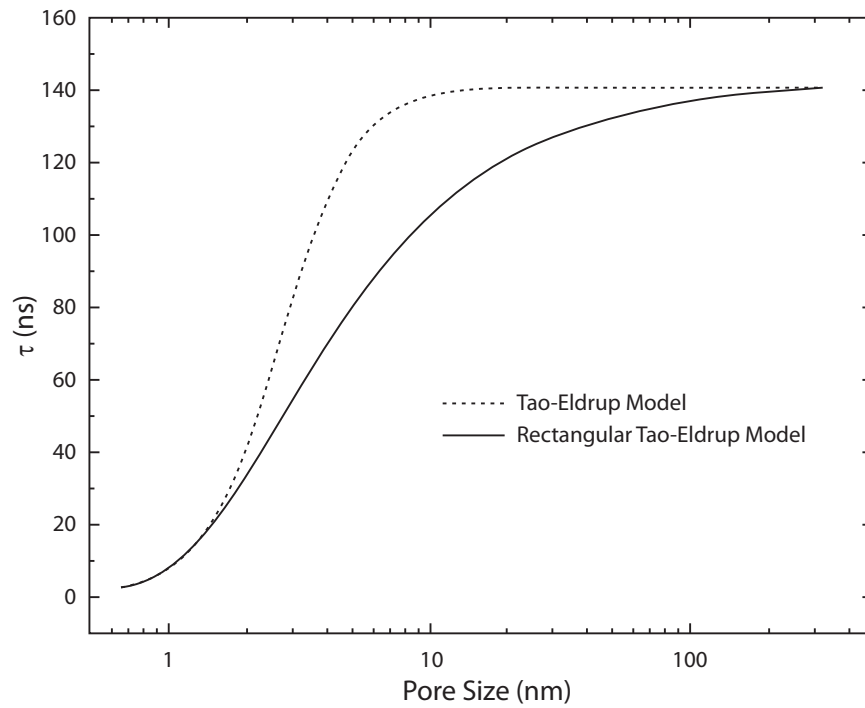


Figure 2.15: This plot shows a comparison of the TE model and the RTE model. Here, the RTE model is shown for three dimensional traps at room temperature to allow for a comparison to the TE model. Different temperatures or trap geometries would result in changes to the relationship between the pore size and the lifetime.

CHAPTER 3

THE CAMS MATERIALS BEAMLINE

Located at the The Australian National University (ANU), the Centre for Anti-matter-Matter Studies (CAMS) materials beamline is the second of two positron beamlines to be developed. The first beamline constructed by Sullivan et al. (2008) is dedicated to studying low energy positron interactions with vapour Atomic and Molecular (AMO) targets. Both beamlines expand on the techniques developed by Murphy and Surko (1992) and Gilbert et al. (1997) at the University of California San Diego (UCSD). The technique is a two-stage process involving moderation, followed by trapping and cooling to produce a pulsed, low energy positron beam. The beamline can be considered in four separate stages functionally named the source, trap, transport and sample stages. The source stage is where the initial beam is produced through the moderation of positrons from a radioactive source. These moderated positrons then enter the trap stage where they are trapped, cooled and released to generate a pulsed beam. The pulses traverse the transport stage before entering the sample stage which contains the sample(s) to be studied, a load-lock system and the detector. Each stage, as shown in figure 3.1, will be discussed in detail within this chapter.

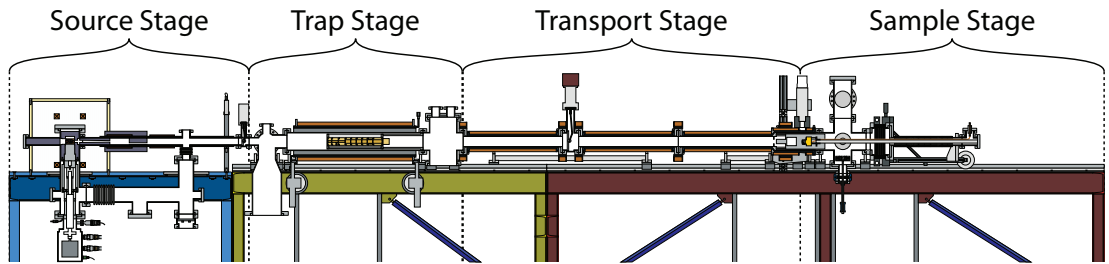


Figure 3.1: Shown here is a schematic diagram of the entire beamline.

3.1 The Source Stage Hardware

The source stage assembly, shown in figure 3.2, was manufactured by First Point Scientific Incorporation (FPSI). The primary role of the source stage is to house the beamline's radioactive positron source, ^{22}Na , and moderate it to produce a continuous beam of low energy positrons. Moderation, as discussed in section 2.1.4, is achieved using a solid neon moderator. The moderator is maintained at 6.8 K using a cryogenic coldhead unit described in section 3.1.3, and may be easily regrown using an automated procedure detailed in section 3.2.2. Moderated positrons are radially confined by a magnetic field of ~ 300 G, generated by solenoids, and electrostatically accelerated away from the moderator using a 25–30 V potential discussed in section 3.1.4. Figure 3.2 shows a cross section view of the source stage with the major components labelled. Each of these components will be discussed in the following sections, followed by their operation.

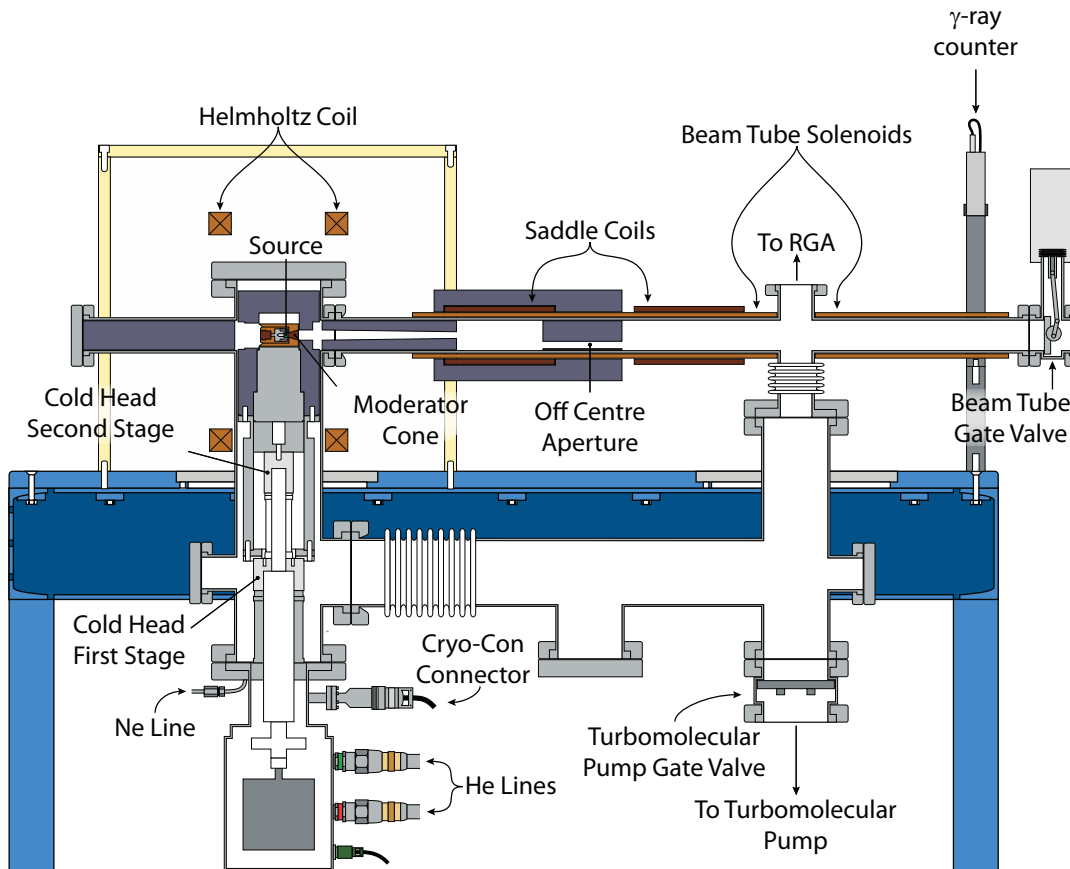


Figure 3.2: Shown here is a schematic diagram of the source stage with the major components labelled.

3.1.1 Vacuum & Shielding Arrangement

The chamber housing the radioactive source is pumped by a single turbomolecular pump, Pfeiffer TMU 262P, capable of pumping at 210 L/s¹. This is controlled by a DCU 100 control unit and backed by a mechanical roughing pump, Pfeiffer DUO 10. Additional pumping is also provided by the cryogenic coldhead unit as background gases are frozen onto the cryogenetically cooled surfaces. Due to the negative impact of contaminants, such as N₂, on the moderator's efficiency, as discussed in section 2.1.4, a great deal of care is taken to ensure this system is kept clean. Raising the chamber to atmospheric pressure is achieved using dry nitrogen through the vent valve on the turbomolecular pump. On evacuation of the chamber, it is baked and pumped thoroughly to achieve the cleanest system practicable. The pressure in the source chamber is monitored with a hot cathode ion gauge (Pfeiffer PBR260) and is typically 5×10^{-9} mbar with a moderator present, though pressures lower than 1×10^{-9} mbar are achievable. The backing pressure is monitored with a Pirani gauge (Pfeiffer TPR265). The source chamber is also fitted with a burst disk, the purpose of which will be discussed in section 3.2.3. The turbomolecular pump can be isolated from the chamber by a Thermionics Laboratory Inc. 6" gate valve. At the end of the source stage is located a $2\frac{3}{4}$ " gate valve, referred to as the beam tube valve. This serves to isolate the source chamber from the rest of the beamline while growing a moderator, discussed in section 3.2.2, as well as to allow any necessary maintenance to be carried out without affecting other stages of the beamline, or vice-versa. Also fitted is a Residual Gas Analyser (RGA), from Stanford Research Systems (SRS), model SRS RGA 200. This is controlled using software specific to the hardware through a COM port connection. Although not used during normal operation, it proves extremely useful when any problems, for example leaks, are encountered with the vacuum system.

Due to the high activity of the ²²Na source, a considerable amount of shielding is required to prevent exposure to the high energy γ -rays emitted during the decay process. Shielding is provided by Elkonite², a tungsten (70% $\pm$ 20%) copper (30% $\mp$ 20%) alloy, and a considerable amount of lead shot. The Elkonite shielding resides within the vacuum chamber as close to the source as practicable.

¹This is the rated pumping speed for N₂. All pumping speeds will be presented using this standard.

²A group of tungsten copper alloys developed by CMW Incorporation.

Its high density makes it very effective at shielding the high energy, ionising γ -radiation produced during the radioactive decay of the ^{22}Na source. In addition, the vacuum chamber is housed within a 400 mm diameter cylinder filled with ~ 250 kg of lead shot. Due to the experimental requirements, radiation emitted along the direction of the beamline is not effectively shielded by this arrangement. This angle is limited as much as possible using a cylindrical block of lead, mounted to the outside of the vacuum chamber, and additional internal shielding through which the moderated positrons are guided (discussed in section 3.1.4). This shielding arrangement reduces the radiation levels within a few metres of the source to those comparable with background levels. While radiation shielding is the primary concern, the hardware must still be easily accessed. This can be achieved, after removal of the source, by simply draining lead shot through a ball valve located beneath the experiment.

3.1.2 The Positron Source

The beamline described here uses a radioactive sodium-22 (^{22}Na) source which has a half life of 2.6 years. A discussion of the decay of ^{22}Na can be found in section 2.1.3.

The ^{22}Na source was obtained from iThemba labs in February of 2007 with an activity of 54.4 mCi (~ 2.01 GBq) and is contained within a Halle-b type capsule (Krause-Rehberg et al., 2004). The majority of the capsule is titanium, with the exception of the cup holding the radioactive material. Rather than titanium, the cup is made from tantalum, a much denser material, to reflect as many backwards emitted positrons as possible. The opening to the cup is covered by a $5\text{ }\mu\text{m}$ titanium window, through which the positrons are emitted, which serves to secure the source. This capsule is then screwed into a customised holder. This holder allows the capsule to clip into a copper block, which has a conical opening onto which the moderator is grown, mounted on a Cryogenic Coldhead. This conical shape is more than twice as efficient as using flat layer of neon covering the source (Mills Jr. and Gullikson, 1986).

3.1.3 Moderator System

Due to the high energy with which the positrons are born, moderation is used to reduce their energy. Here, only the hardware will be discussed, however, a more

in-depth discussion of the process can be found in section 2.1.4. The Moderator System can be split into two distinct parts, the Cryogenic Coldhead and the neon Gas System. The system has been designed to allow moderators to be re-grown using an automated, computer controlled process.

The beamline uses a solid neon moderator (Mills Jr. and Gullikson, 1986) which, due to the temperatures involved, requires a cryogenic coldhead unit to produce and maintain. The unit consists of a DE204 expander and an ARS-4HW compressor, both purchased from Advanced Research Systems. The expander is a gas refrigeration unit which operates on the compression/decompression cycle of ultra high purity helium. Helium is circulated by the compressor at an operational pressure of ~ 1900 kPa (~ 270 psi). The expander operates in two stages, as labelled in figure 3.2. The first stage achieves a temperature of ~ 30 K, while the second stage is capable of reaching ~ 5 K under ideal operating conditions. However, due to the large thermal mass mounted on the second stage, which includes a significant amount of Elkonite shielding, the lowest possible temperature when operated in this apparatus is ~ 6 K. This temperature is sufficiently low for a neon moderator, which is typically stored at 6.8 K once successfully grown. If left unchecked, the expander will drive the temperature to this minimum; precise control is achieved using a Cryo-con 34 Temperature Controller. The controller monitors the temperature using a diode installed on the source capsule mounting stage and controls the temperature using a heating element located inside the source mount arrangement. An additional diode is also mounted on the second stage of the expander to allow the observation of any temperature differences. This arrangement allows the temperature in the region of the source and moderator to be maintained within 0.1 K of the set point.

Neon for this system is sourced from a ultra high purity (99.999%), high pressure lecture sized gas cylinder located beneath the experiment. This is regulated to ~ 70 kPa (10 psi) to provide a stable, super-atmospheric source. Gas is admitted into the vacuum chamber through a MKS Instruments mass flow controller, model 1179A. This is a thermal-based mass flow controller which measures the flow rate through a heated tube by monitoring the amount of heat transferred to the flowing gas. The 1179A model also has elastomer-seals to maintain a clean system.

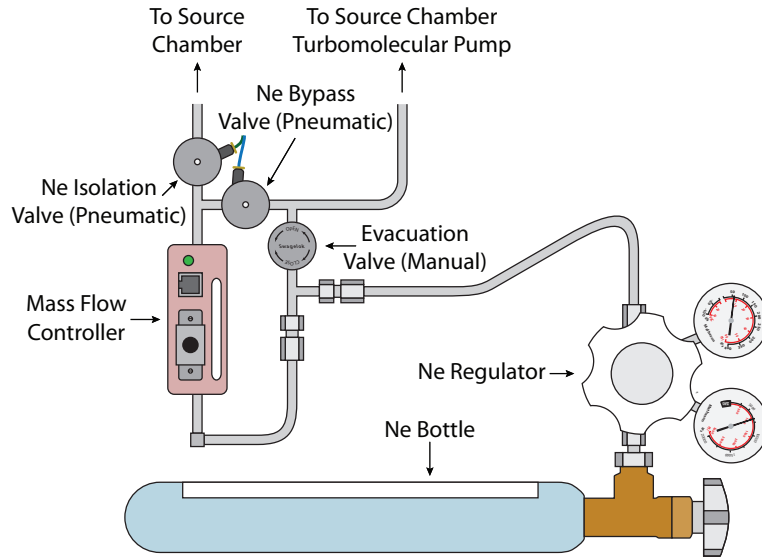


Figure 3.3: Shown here is a schematic diagram of the neon gas handling system for moderators in the source stage. As indicated, both the regulator and evacuation valve are manually operated, while the bypass and isolation valves are operated pneumatically through a computer interface.

3.1.4 Confinement & Guidance

Moderated positrons are radially confined using a strong axial magnetic field. This field is generated along the length of the beamline using several different solenoids; these will be discussed in section 3.5. In the region of the source and moderator, this field is generated using a pair of coils in a Helmholtz configuration, depicted in figure 3.2. The coils have a radius of ~ 230 mm and are separated by the same distance; the positron source is centrally located within this pair. Typically these are operated at a current of 3.9 A, generating an axial field of ~ 85 G at the source. This field strength is maintained up to the trap stage by two beam tube solenoids, which have been wound onto water-cooled coil formers and slid onto the vacuum chamber prior to welding the flanges on. These two solenoids have a total combined length of ~ 715 mm, and are separated by a gap of ~ 50 mm. These coils generate a field of ~ 295 G when 13.9 A is passed through them (Greaves, 2011). The final set of solenoids in the source stage are the saddle coils. These differ from all other coils on the beamline and are used to generate an off axis component, or kink, in the axial magnetic field. This kink guides moderated positrons through an off centre aperture as shown in figure 3.2. Due to their higher energy, unmoderated positrons are relatively unaffected and annihilate on

the aperture. It should be noted that this aperture also provides shielding from the γ -radiation emitted in the same direction. These coils are typically operated at a current of 1.0 A and generate a field of approximately 25 G.

The solenoids outlined here are all connected in series with their equivalent partner. The currents are controlled through software which is interfaced with three Xantrex power supplies. An XFR 60-20 powers the beam tube coils while two XDL 56-4Ps power both the Helmholtz and saddle coils.

Moderated positrons are electrostatically guided towards the trap stage through the application of a small positive potential to the source mount; typically this is 29 V. This potential is controlled by the same system which controls the trap electrodes, discussed in section 3.3.2.

3.2 Operation of the Source Stage

Other than the periodic growing of a moderator, the source stage requires minimal attention to produce a moderated beam. Figure 3.4 shows an image of the resulting annulus shaped beam, which arises due to the conical shape of the moderator. This was captured during the development of the beamline using a double stack Micro-Channel Plate (MCP) assembly with a phosphor screen and a CCD camera. The MCP was located in a low field region (~ 150 G) in the trap stage.

Control of the source stage hardware, with the exception of the turbomolecular pump, helium compressor and moderator potential, is achieved through Labview software developed by FPSI. Customisation of this software was carried out to meet the specific needs of the apparatus. The software operates on a standard PC with a National Instruments PCI-6221 card. This computer interfaces with the hardware of the source stage, through the National Instruments card and six RS-232 ports, and operates as an isolated system. There are two exceptions to this; the first is the status of the beam tube gate valve, which can be read by another system through a separate hardware connection. However, control of the valve is retained solely by the source stage computer. The second is the moderator potential, which is controlled by a separate system, discussed in section 3.3.2.

The purpose of the controlling software can be broken down into two main tasks; monitoring the source stage and controlling the growth sequence of moderators. For the majority of the time, the software only operates in a passive

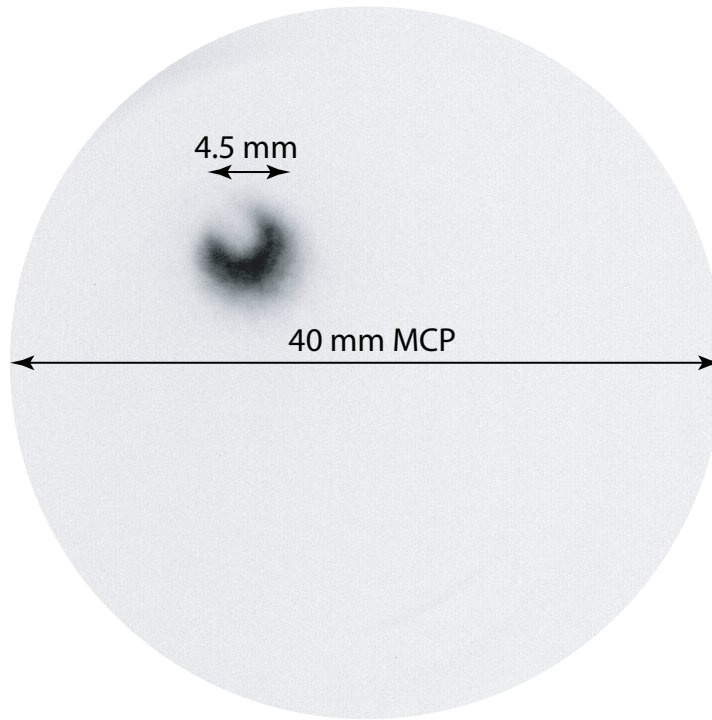


Figure 3.4: Shown here is an image of the moderated beam captured using a CCD camera during the development of the beamline. The beam was incident upon a double stack MCP assembly with a diameter of 40 mm.

manner. In addition, there are a number of safety interlocks to prevent hardware damage should any anomalous conditions be encountered.

3.2.1 Monitoring Systems

At all times, the software monitors five detectors on the source stage and records the values. These include the two Pfeiffer pressure gauges previously mentioned (for the main chamber and backing pressure), the two temperature diodes associated with the expander and a Scionix Holland CsI(Tl) scintillation detector located near the beam tube gate valve as depicted in figure 3.2. The raw count rate from this detector, due to annihilation on the closed beam tube gate valve, is logged and a conversion to the positron beam current is performed. Calibration of this detector to determine the moderated beam current was carried out prior to the installation of the other stages. This was performed using a SRS Low-noise current pre-amplifier, model SR570, and a Keithley 197 Autoranging Microvolt DMM. Absolute measurements of the beam current can still be carried out using retractable beamflags in the trap stage.

The values from the detectors are recorded periodically at a frequency set by the user, typically every ten seconds. These logs are reset during the moderator grow sequence resulting in the time scale, shown in minutes, being equivalent to the age of the moderator.

3.2.2 Moderator Growth Sequence

Due to deterioration from the absorption of contaminants, such as the buffer gases of the trap, a new moderator must be grown approximately once a week. In order to ensure consistent moderator performance, an automated system is used. This can be broken into a four step process which will be explained here. The various set points and delays mentioned in this explanation can be easily varied. The values given here are currently considered to be the optimised values, determined through empirical tuning, to maximise slow positron output. It should be noted that while the process is designed to begin with an existing moderator, it is not a requirement.

The first stage is to allow the source mount to warm to 20 K, resulting in the existing moderator boiling off and being pumped away. Warming is achieved by simply halting the operation of the expander, no active heating is necessary. Once the set point has been reached, 100 s is allowed for the neon, now gaseous, to be pumped away.

The second stage reactivates the expander to cool the moderator surface to 7.3 K. Once this is achieved, the set point is slightly increased to 7.4 K to ensure that during the grow phase the temperature is stable. Once again, 100 s is allowed to pass for stability.

Once the desired temperature has been achieved the growing phase is entered and the logs from the various detectors are reset. First the gate valve above the turbomolecular pump is closed, isolating the source chamber. Then, neon is admitted through the neon isolation valve and mass flow controller (both depicted in figure 3.3) for 1000 s (~ 17 mins). Under these conditions, the source chamber reaches an equilibrium pressure of $\sim 1 \times 10^{-4}$ mbar. As the neon moderator forms, the γ -ray signal from annihilation on the closed beam tube gate valve increases before stabilising as the optimum thickness is reached.

Once 1000 s has passed, the admission of neon is shut off and the gate valve above the turbomolecular pump is opened. For the next 600 s (10 mins), the

moderator remains at 7.4 K, allowing any gaseous neon to be pumped away. Following this, the set point is lowered to 6.8 K which has been found to provide the longest moderator lifetime. The γ count rate, pressure and temperature logs for this process are shown in figure 3.5. For a ~ 0.74 GBq (~ 20 mCi) source this process results in a moderated beam current of ~ 0.2 pA.

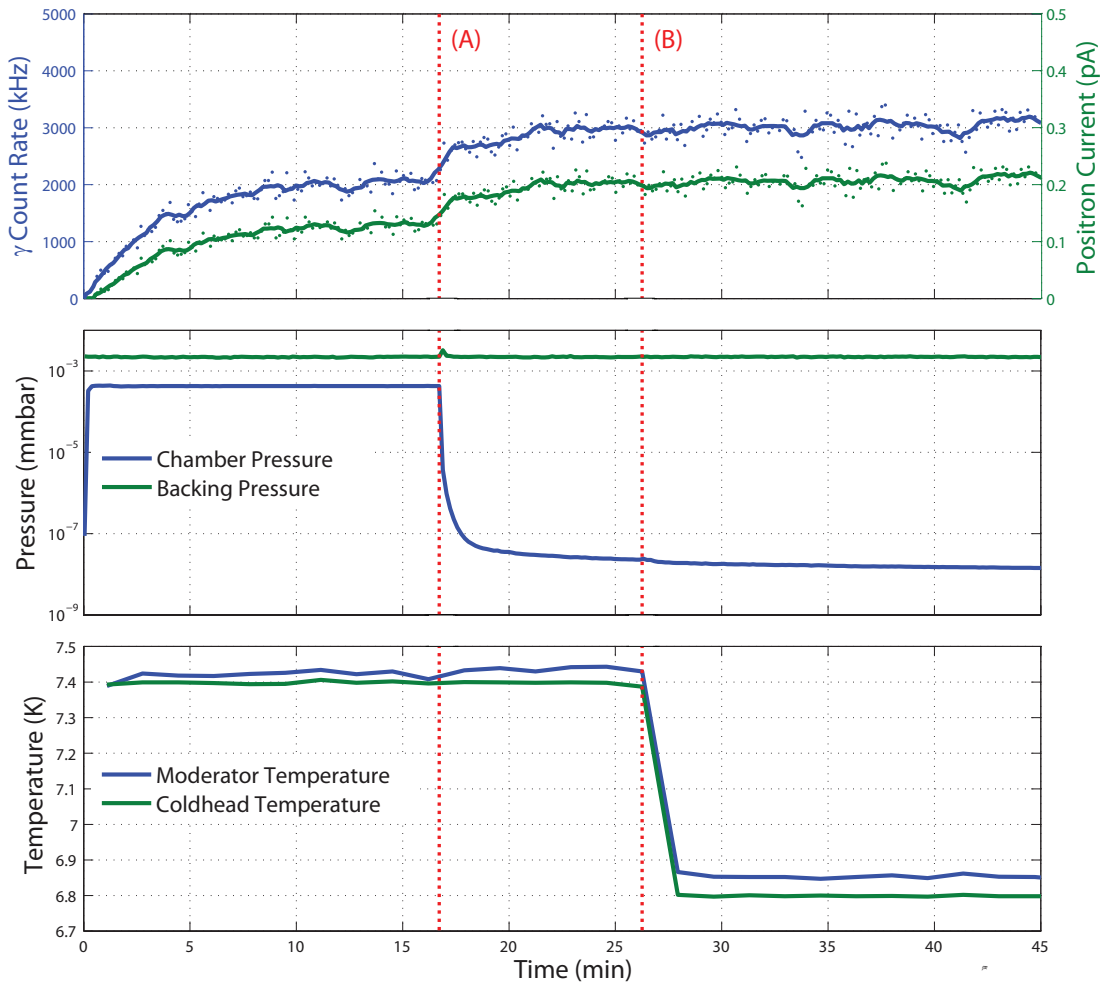


Figure 3.5: Shown here are the first 45 mins of the source stage logs. At 0 mins neon is admitted into the isolated chamber, causing the pressure to rise. As the moderator is formed the γ -ray signal can be seen to increase. At ~ 17 mins the neon is shut off, indicated by (A), and the pressure begins to decrease. The temperature remains at 7.4 K for another 10 mins, indicated by (B), during which the remaining gaseous neon is evacuated from the chamber. Following this, the temperature is reduced to 6.8 K and the moderator growth sequence is complete.

3.2.3 Safety Interlocks

Due to the substantial cost, both financial and in lost experimental time, involved in either replacing or repairing many components of the source stage, a number of interlocks are present to prevent or limit damage. These systems range from the protocols of the DCU 100, which will not be discussed, to systems which actively monitor various sensors.

The simplest safety interlock is a burst disk fitted to the vacuum chamber. This is a thin, stainless steel disk which is pierced when the pressure in the source chamber approaches twice atmospheric pressure. This prevents the source stage from over pressurisation which may occur in the event of a power failure. This situation results in cessation of pumping and coldhead operation, as well as isolating the source chamber due to both gate valves returning to their normal, closed, state. If a moderator is present at this time, it quickly begins to boil off and build up pressure in the sealed chamber.

In addition to the five detectors logged by the monitoring system, the temperature of each solenoid is tracked. This is done by calculating its resistance from the driving current and voltage supplied by the power supply. In the event that the resistance of the solenoid exceeds the equivalent temperature set point, the Labview software shuts down power to the solenoid. This prevents overheating from burning out the solenoids.

The final interlock in this stage of the apparatus controls power to the helium compressor. While the compressor contains a built in temperature cutoff, an interlock has been included to provide redundancy. This takes the form of a small inline turbine fitted in the cooling water supply line to the compressor. When the flow drops to an insufficient level, the voltage output by the turbine falls below a threshold and causes the power to the compressor to cut off. This prevents the compressor from ever operating with insufficient cooling.

All the safety interlocks discussed here do not automatically reset once the cause has been rectified; instead, the user must manually reset each interlock.

3.3 The Trap Stage Hardware

The positron trap is based on a similar apparatus at the UCSD, the design of which was conceived by Murphy and Surko (1992). The evolution of the trap system started with Dehmelt et al. (1978) modifying a Penning discharge tube to store electrons. This was further modified by Malmberg and Driscoll (1980) and developed into a series of cylindrical electrodes which became known as a ‘Penning-Malmberg trap’. Surko et al. (1989) then proposed using a Penning-Malmberg trap with a buffer gas system to accumulate moderated positrons. The design, albeit modified somewhat in the following years, has become known as a ‘Surko trap’.

The design involves trapping moderated positrons through the combination of a potential well structure and inelastic interactions with a buffer gas. Once trapped, cooling to room temperature is possible through repeated inelastic collisions. The trap stage can be broken down into several sections: the vacuum arrangement and trap solenoid, the trap assembly and the buffer gas system. Each section will be discussed in detail.

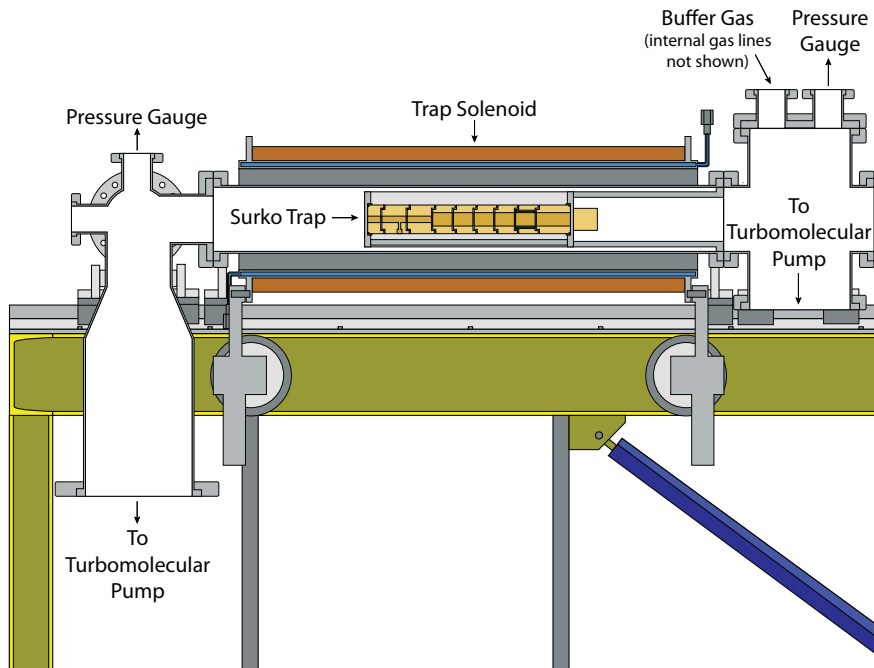


Figure 3.6: Shown here is a schematic diagram of the trap stage with the major components labelled.

3.3.1 Vacuum Arrangement & Trap Solenoid

The trap is housed within a straight 800 mm long, 6" diameter stainless steel vacuum chamber. At each end of the vacuum chamber are located multiported vacuum chambers. These are referred to as endstations and are distinguished as the entrance endstation, which is closest to the source, and the exit endstation, which is closest to the sample. Originally, both endstations were fitted with hot cathode ion gauges (Pfeiffer PBR260). However, due to their short lifespan and high repair cost, these were replaced with inverted magnetron type cold cathode gauges (Pfeiffer PKR251).

The entrance endstation is fitted with a Pfeiffer TPU 1201P turbomolecular pump capable of pumping at 1250 L/s. This is controlled through a DCU600 control unit and backed with a Pfeiffer DUO 35 mechanical rotary pump. Also located in this endstation is a retractable gold-plated copper disk, 60 mm in diameter, referred to as the entrance beamflag. This can be extended into the path of the moderated beam, using an MDC rack and pinion linear feedthrough, to measure the moderated positron beam current entering the trap.

Initially, the exit endstation was only fitted with a single turbomolecular pump, a Pfeiffer TMU 521P capable of pumping at 520 L/s. This pump, which is still present, is controlled through a DCU100 control unit and backed by a Pfeiffer DUO 20M. An additional turbomolecular pump, a 210 L/s TMU 262P backed by a DUO10, was fitted to reduce the effect of the buffer gases on the positron pulse (this will be discussed further in section 3.4.3). In this configuration, the total pumping speed of the exit endstation is 730 L/s (~40% of the entrance). Due to the high pressures of the buffer gases, when compared to other Surko trap configurations, the additional pumping at the entrance endstation is required to reduce the effect of the buffer gases on the lifetime of the moderator.

Each of these turbomolecular pumps can be isolated from its backing pump using a pneumatic angle valve controlled through a TTL interface (discussed in section 3.7.2). The roughing pressure is monitored using Pirani gauges which are controlled, along with the inverted magnetron gauges, through a Pfeiffer Maxigauge controller (type TPG 256A). This pumping arrangement allows a base pressure better than 3×10^{-9} mbar to be achieved. However, operational pressures measured at the endstations are typically $\sim 1 \times 10^{-6}$ mbar due to the buffer gases used in the trap.

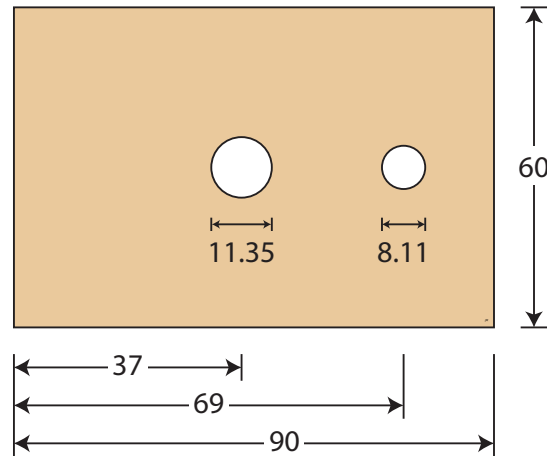


Figure 3.7: Shown here is a schematic diagram of the exit beamflag with the dimensions given in millimetres. The 11.35 mm and 8.11 mm apertures reduce the beam spot size at the target to ~ 6 mm and ~ 4.3 mm respectively.

The exit endstation is also fitted with a beamflag, allowing measurements of the trapped beam. Initially this beamflag was identical to the entrance beamflag, however, its design and purpose were altered. The beamflag is now a flat copper rectangle with two apertures as well as a blank section for beam current measurements, the dimensions are given in figure 3.7. This modification also required the addition of a vertical manipulator, model LDM100/64-H. The apertures on this beam flag are used to physically reduce the spot size of the beam at the sample. The ratio of the aperture size to beam spot size at the sample is equivalent to the square root of the ratio of the magnetic field at the two locations. The latter of these fields can be adjusted to provide fine control of the spot size at the sample, if necessary.

Between these endstations the vacuum chamber is surrounded by the trap solenoid. This solenoid is wound onto a separately mounted water-cooled cylindrical frame allowing the guiding magnetic field to be tuned and hence aligned with the trap electrodes. The solenoid is 660 mm in length and has an inner and outer diameter of 90 mm and 112 mm respectively. It has 1551 turns over 10 layers allowing a current of 20 A, supplied by a TKD-Lambda GEN80-19 power supply, to generate a field just over 550 G. These details are also repeated in tables 3.1 and 3.2 for easy reference.

3.3.2 The Trap

The trap is designed to collect positrons from the moderator, cool them and then re-emit them in a temporally narrow, sub-nanosecond, pulse. Here, the physical properties of the trap will be discussed in detail, as well as the hardware associated with its control.

The trap consists of nine gold-plated, copper electrodes as shown in figure 3.8. The first three electrodes have internal diameters of 10 mm and lengths of 20 mm, 40 mm and 40 mm, respectively. These electrodes are electrically isolated by PEEK spacers which also provide a gas seal. At three quarters (30 mm) of the way down the second electrode and central to these three electrodes, lies a port through which N_2 is introduced; this can be seen in figure 3.8. Electrodes four through eight all have an internal diameter of 20 mm and length 30 mm. One of these electrodes contains a segmented interior, shown in green, to allow the implementation of a ‘rotating wall’ to radially compress the trapped positron cloud. This phenomena was first demonstrated for positrons by Greaves and Surko (2000) and recently modelled by Isaac et al. (2011). While depicted at electrode position eight, this electrode is at present physically located in position seven in preparation for implementation. Unlike the first three electrodes, these larger inner diameter electrodes are electrically isolated using ruby ball spacers.

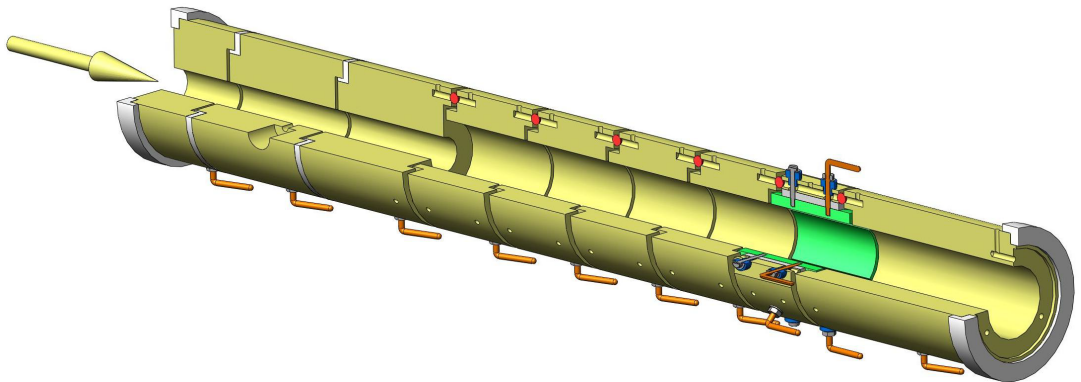


Figure 3.8: Shown here is a rendered image of the trap electrodes. The direction of the positrons is indicated by the arrow in the top left hand corner. The PEEK spacers can be seen between the first three electrodes, while electrodes four through nine are separated by ruby ball spacers. The segmented electrode is shown in green at the eighth electrode position and the N_2 inlet port can be seen in the second electrode.

The ninth, and final, electrode also has an inner diameter of 20 mm but is 60 mm in length.

This assembly is housed within a sealed cylindrical stainless steel canister 330 mm in length. Inside the canister, electrical connections to each of the electrodes are made using Accu-Glass Kapton³ shielded coaxial wires. The electrical connections are made using push-on style connectors for their vacuum compatibility and ease of removal; these are electrically isolated using ceramic spacers. By using identical electrical connectors on the outside of the canister, the electrodes are connected through to several Positronic Industries hermetic D-subminiature connectors located at the exit endstation. Each connector has five coaxial feedthroughs, with a total of three connectors being utilised; these are internally connected using crimp-style connections. This arrangement allows the shielding of the cable to be grounded externally at the amplifiers, rather than at the body of the experiment.

These electrodes are controlled through a National Instruments computer comprising a PXI-1042Q chassis with a PXI-8196 embedded controller. With the exception of the trapping well (this will be discussed in section 3.4.2, however, it is normally electrode eight), the electrode potentials are driven by a single 16-bit National Instruments PXI-6733 card. Connections to the eight output channels are made through a SB-68 breakout box. The trapping well is driven by a 14-bit, 100 MS/s National Instruments PXI-5412 Arbitrary Waveform Generator (AWG). The AWG also has an associated trigger-line output, PFI0, which is used to initiate the detection system at the appropriate point of each trap cycle. This will be described in greater detail in section 3.9.5. It should be noted here that the same computer is used to interface with the hardware of all subsequent stages of the beamline, though additional National Instruments cards. A schematic diagram depicting the full computer can be seen in figure 3.31.

The outputs from the National Instrument cards are input into Elbatech T506 HV amplifiers using double shielded coaxial cables. These cables are double shielded to reduce noise pickup prior to amplification. Two amplifier racks, each containing six channels, are utilised by the beamline giving a total of twelve channels. Each channel has two gain settings, $\times 10$ or $\times 20$, which are accessed through separate inputs. The unused input is capped to also reduce noise pickup, to which the trapping and cooling mechanisms are sensitive. The amplifiers are limited to

³A polyimide film developed by DuPont.

a maximum input of 10 V, regardless of the channel or gain setting, allowing a maximum of 200 V to be output. The maximum slew rate of the amplifiers is slightly higher than $400 \text{ V}/\mu\text{s}$ with the capacitive load of the trap electrodes in place. The restrictions this causes will be discussed in section 3.4.1. The outputs of the amplifiers are connected to the D-subminiature connectors with coaxial cable. The length between the connectors and the amplifiers is minimised, keeping the capacitance low to allow the highest possible slew rate.

The setup outlined here allows the operation of the trap to be computer controlled and the software will be discussed in section 3.9.1.

3.3.3 The Buffer Gas System

The buffer gas system is used to introduce N_2 , for trapping moderated positrons, and CF_4 , for cooling trapped positrons, into the trap. The gases are sourced from ultra high purity cylinders stored on a gas balcony outside the laboratory. They are regulated to $\sim 70 \text{ kPa}$ (10 psi), before being supplied to the beamline through quarter inch stainless steel gas lines.

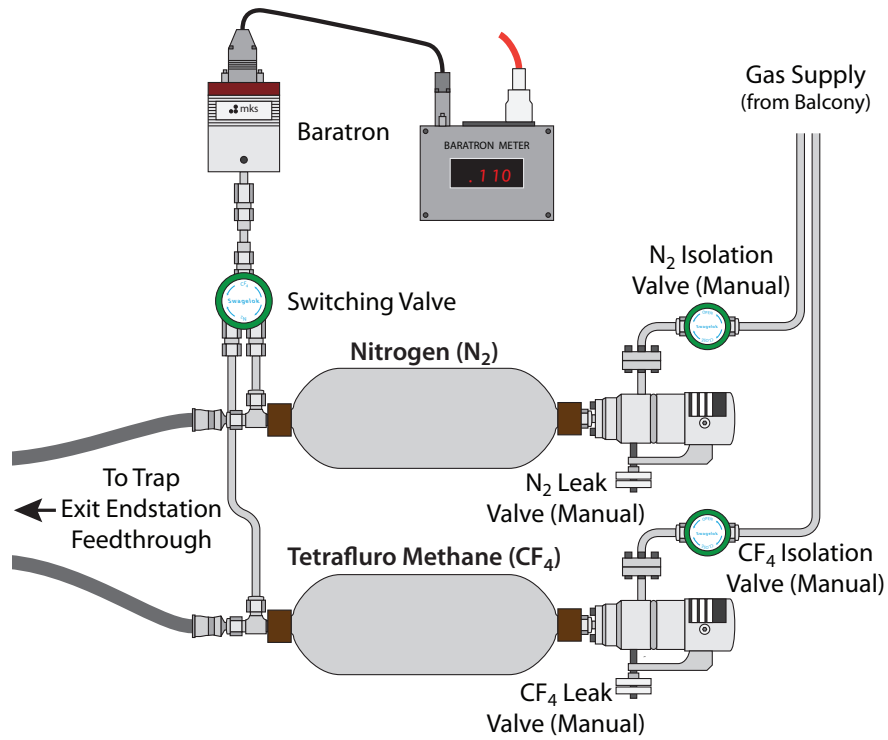


Figure 3.9: Shown here is a schematic diagram of the buffer gas handling system used to provide a stable source of N_2 and CF_4 to the trap, see text for details.

The gas handling system of the materials beamline is depicted in figure 3.9. Both gas supply lines have manual isolation valves before any of the subsequent handling system. The pressure of each gas supplied to the apparatus is controlled using a MDC leak valve, model ULV-075. After each leak valve a one litre cylindrical volume, connected in series, is used to dampen any pressure fluctuations. After these volumes the gas lines are teed off into a common switching bellows-sealed valve connected to a baratron pressure gauge, type 626B. This arrangement allows a single baratron to monitor both driving pressures, although not simultaneously.

Both buffer gases are supplied to the experiment at the exit endstation through braided gas lines. Internally, the gases are fed to the trap canister through teflon tubing. At this point the system differs for each gas. Inside the canister, N_2 is supplied, through teflon tubing, to the port in the second electrode (as outlined in section 3.3.2). This results in a partial pressure, with a triangular profile, of approximately 5×10^{-3} mbar (4 mTorr) at the centre of the first three electrodes and an order of magnitude lower in the larger diameter electrodes. Unlike N_2 , CF_4 is admitted into the canister and allowed to diffuse into the trap past the ruby ball spacers. This results in a CF_4 partial pressure of approximately 1×10^{-4} mbar (0.075 mTorr). However, these pressures are not directly measured and instead are only estimated (discussed in section 3.4.3) and adjusted empirically as required.

3.4 Operation of the Trap Stage

Unlike the source stage, the only hardware controlled through software in the trap stage are the electrode potentials and the power supply used to generate the confining magnetic field. The controlling software is described in section 3.9.1. Once again, the pumps of the trap stage are operated through their controllers and the buffer gas handling system is operated manually. The latter of these will be discussed here, including the effects of the driving pressure on the pulse characteristics. However, the operation of the trap electrodes and the implementation of the pulse compression method will be discussed in detail first.

The trap is operated in a cyclical manner to produce a well resolved, repeatable pulse of positrons from the moderated beam. Each iteration is referred to as one trap cycle and results in the emission of a single pulse of positrons from the

trap. Each trap cycle can be broken down into three distinct phases: loading, cooling and dumping. This cycle is typically repeated at ~ 1400 Hz although this can be increased up to 2000 Hz. The theory behind the operation of the trap will be discussed before presenting the electrode settings which, to date, have produced the best results.

3.4.1 Operational Theory of the Trap Electrodes

First, the magnetic confinement of the positrons will be discussed, including the implications this has for trapping. This will be followed by a discussion of the theory behind each phase of the trap cycle as well as the implementation of the timed potential technique.

Effects of the Magnetic Field

As discussed earlier, positrons are axially confined using a magnetic field of ~ 550 G. A brief review of the motion of a charged particle will be given here before discussing some of the more subtle effects. As shown in figure 3.10, the positron's path in a magnetic field follows a helical orbit. This can be described by two distinct motions, a linear velocity parallel to the magnetic field, $v_{\parallel}$, and the circular orbit perpendicular to the field. The radius of this orbit, known as the cyclotron radius R_c , is determined by the velocity perpendicular to the field, $v_{\perp}$, and the field strength, B , by the relationship

$$R_c = \frac{mv_{\perp}}{eB}. \quad (3.1)$$

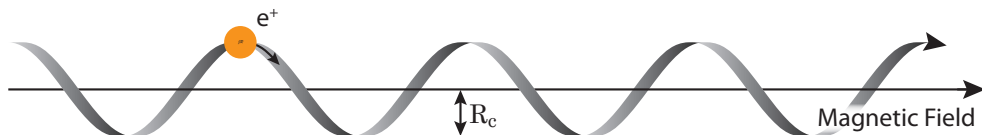


Figure 3.10: Shown here is the motion of the positron in a magnetic field. The radius of the path, R_c , has been exaggerated to clearly demonstrate the motion.

Under the experimental conditions presented here, this radius is on the order of μm . With the velocity divided in this manner it is also possible to consider the total energy, E_{Total} , in the same manner

$$E_{\text{Total}} = E_{\parallel} + E_{\perp}, \quad (3.2)$$

where $E_{\parallel}$ is the kinetic energy along the field and $E_{\perp}$ is the kinetic energy in the circular motion. Under these conditions, the potentials applied to the cylindrical electrodes of the trap only affect the positrons' parallel energy.

The magnetic field along the length of the beamline is generated using a series of varying solenoids and as such, it is not constant. The most rapidly changing region in the field lies between the two beamtube solenoids, shown in figure 3.11 (a plot of the full magnetic field of the beamline is shown in figure 3.24). However, even at this point the length over which the magnetic field varies is much greater than the cyclotron radius, R_c , of the positrons.

$$R_c \ll \left| \frac{\mathbf{B}}{\nabla \cdot \mathbf{B}} \right| \quad (3.3)$$

Under these conditions the magnetic moment, μ , is an adiabatic invariant resulting in

$$\mu = \frac{E_{\perp}}{B}. \quad (3.4)$$

In addition, unless there is an inelastic event, the total energy of the positron must be conserved.

The relationships shown in equations 3.2 and 3.4 result in the transference of energy between the parallel and perpendicular components as the positron moves between regions with different magnetic fields. Due to the dependence on the positron's parallel component to successfully trap them, this must be kept in mind when setting, or optimising, the electrode potentials. When moving from the lower magnetic field of the source region (~ 100 G), where the moderator potential is applied, into the higher magnetic field of the trap region (~ 550 G), a portion of $E_{\parallel}$ is converted into $E_{\perp}$; the effect this has on the moderated beam can be seen in figure 3.12.

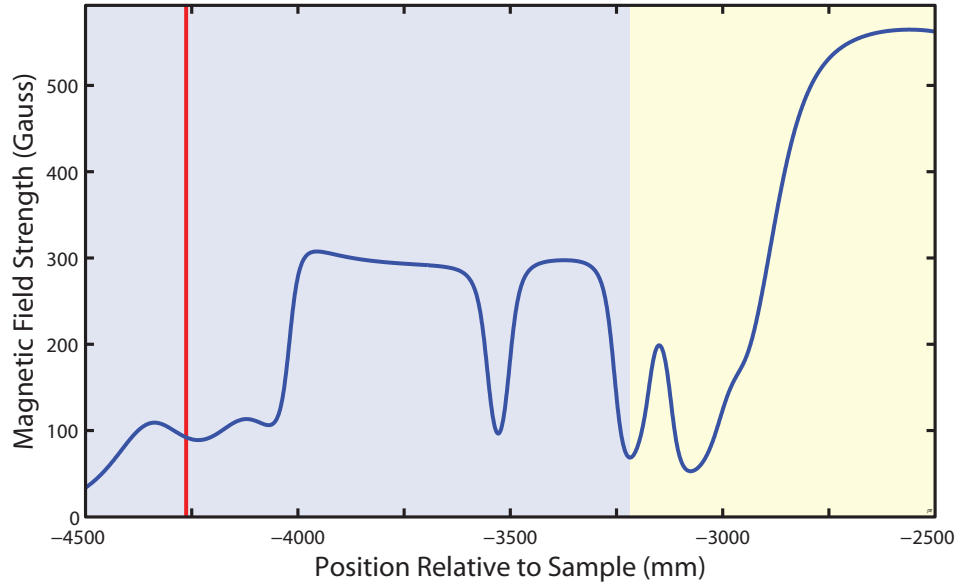


Figure 3.11: Shown here is the axial magnetic field in the source and trap region of the beamline. The shaded blue region indicates the source stage, while the yellow region indicates the first half of the trap stage. The vertical red line indicates the position of the ^{22}Na source (relative to the sample).

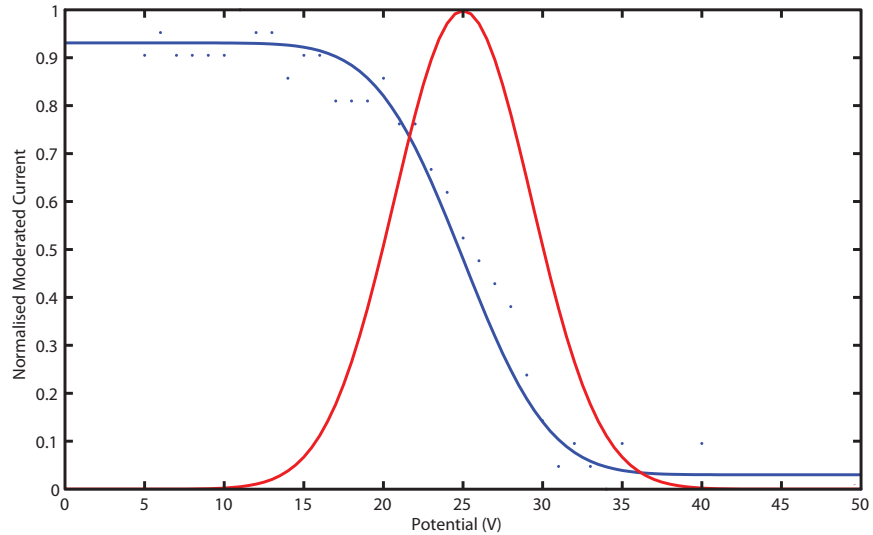


Figure 3.12: Shown here is a cutoff curve of the moderated beam, as it passes through the trap, showing the $E_{\parallel}$ energy distribution. The resulting Gaussian curve has been calculated and is shown in red. Here, the moderator potential was set to 29 V. The width of the Gaussian curve, which shows the energy distribution of the parallel component of the positron beam at the trap, is increased due to the adiabatic effects discussed.

Loading

The loading phase of the trap cycle is optimised to collect moderated positrons from the source stage. Primarily, this is accomplished as the positrons pass through the higher pressure region of N_2 within the first three electrodes. The desired process is an inelastic collision, where the positron will excite the N_2 molecule, and lose sufficient energy to become trapped within a potential well, as shown in figure 3.13.

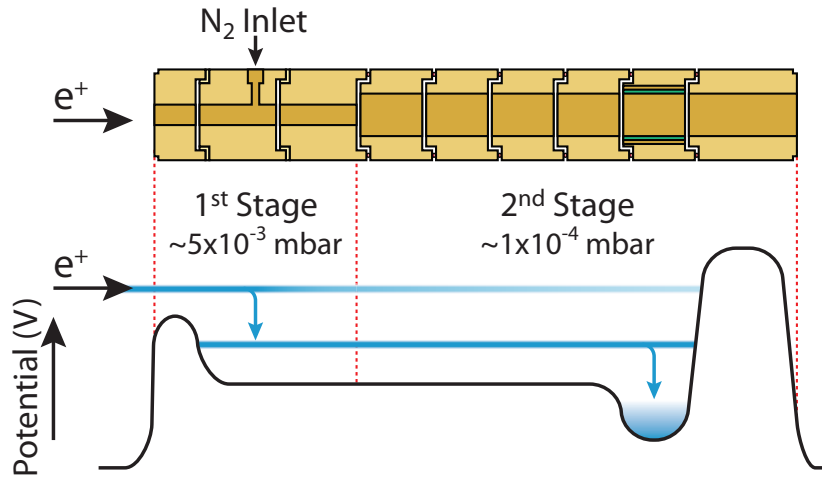


Figure 3.13: This figure demonstrates the basic principle behind the trapping mechanism. The initial trapping occurs inside the first stage which contains a higher pressure of N_2 . Loading into the second well is achieved through the same mechanism. However, as the positrons are already trapped they can pass over this well several times before undergoing an inelastic event.

This criterion is fulfilled by an electronic excitation of the N_2 molecule, which becomes possible at 8.40 eV (excitation of the $a'^1\Sigma_u^-$ state). However, the competing positronium formation channel opens only slightly at 8.78 eV, 6.80 eV below the first ionisation threshold. Excitation of this channel results in the loss of the positron from the trap as the resulting neutral is no longer magnetically confined and collides with the trap walls. Because of this, the collision energy must be carefully selected to maximise the trapping efficiency. The relevant cross sections for positrons incident on N_2 are shown in figure 3.14. There are three electronic excitation processes which are possible near this energy. These involve exciting an electron from the ground state, denoted $X^1\Sigma_g^+$, to either the $a^1\Pi_g$, $a'^1\Sigma_u^-$ or the $w^1\Delta_u$ state. These states, as well as their vibrational levels, are shown in figure 3.15. It can be seen that the $a^1\Pi_g$ excitation channel turns on

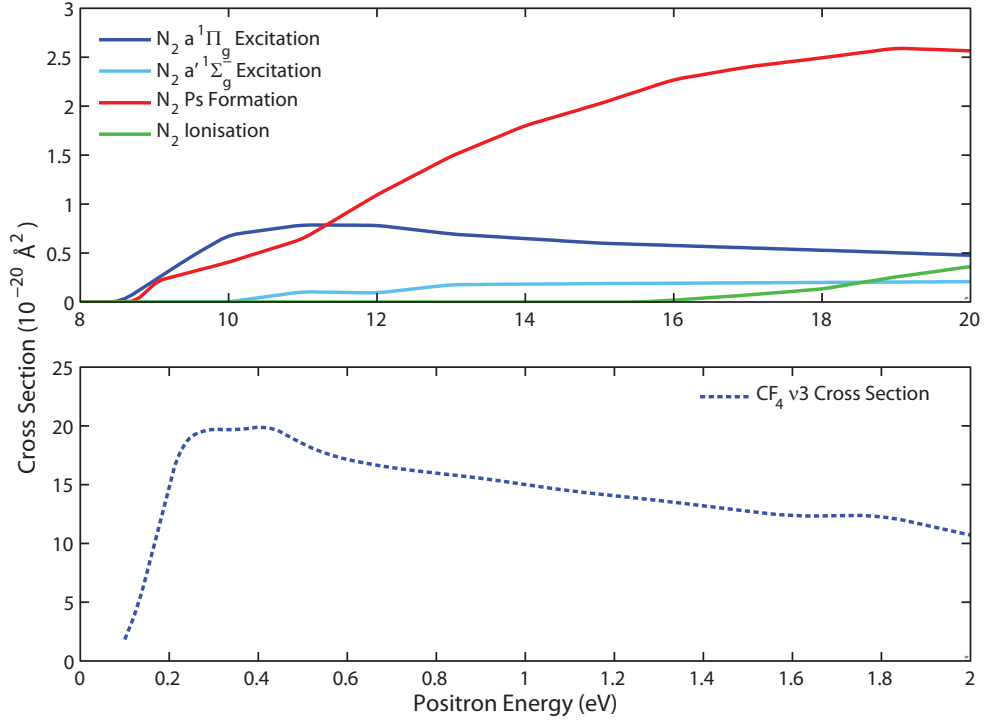


Figure 3.14: Shown are the cross sections for molecular nitrogen which are of interest during the trapping process (Sullivan et al., 2001; Marler and Surko, 2005a). The ν_3 vibrational cross section for tetra-fluoro methane, used for cooling, is also shown (Marler and Surko, 2005b).

strongly at 8.55 eV and until ~ 11 eV, is the dominant cross section. At an energy of ~ 10 eV the ratio between this channel and the positronium formation channel is maximised. At this energy the cross section for the $a'1\Pi_g$ excitation channel is approximately seven times larger than excitation to the $a'1\Sigma_u^-$ state (Sullivan et al., 2001). Excitation to the $w'1\Delta_u$ state is negligible and will be ignored.

At this collision energy it is possible to cause a simultaneous vibrational excitation. For the $a'1\Pi_g$ and $a'1\Sigma_u^-$ states it is possible to excite up to the sixth and eighth vibrational states respectively (Benesch et al., 1965). However, a distribution of states, which can be determined by the Franck-Condon Principle, will be populated. This results in the positrons successfully loaded into the trap having an energy distribution somewhat larger than that of the moderated beam.

As depicted in figure 3.13, trapped positrons then undergo a second inelastic collision to become trapped within a narrower potential well. The mechanism for this process is identical to the initial trapping. However, as the partial pressure of N_2 is considerably lower in this region the positrons may make numerous passes,

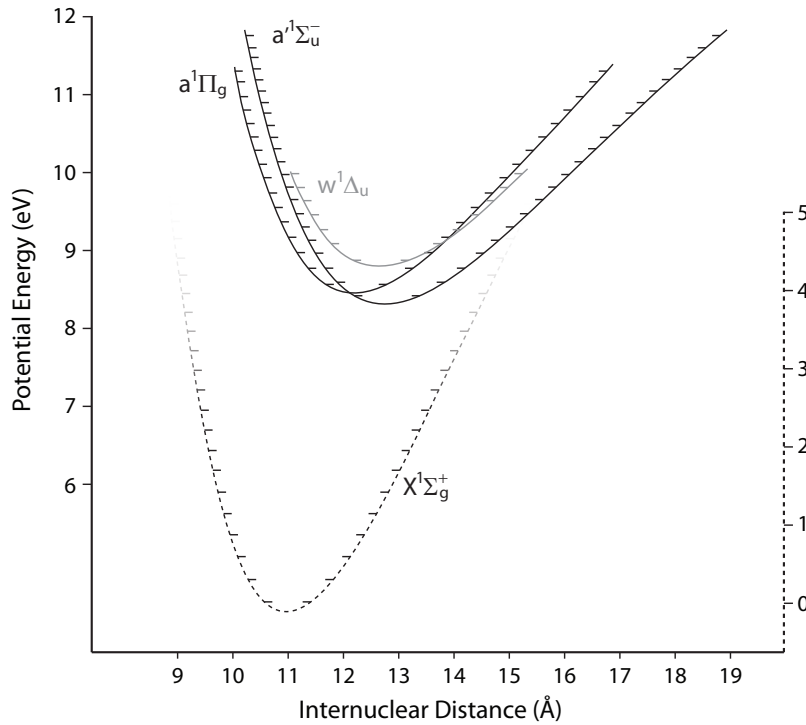


Figure 3.15: Shown are the energy levels of the three states of N_2 which are of interest for the trapping mechanism (reproduced from Benesch et al., 1965).

as they are confined within the trap, before undergoing this process. In addition to this loading mechanism, a recent simulation by Petrović (2011) has shown that positrons may be more effectively loaded into the trap through repeated vibrational excitations of CF_4 . Due to the different pressure ratios used by the system described here when compared to similar Surko traps (see section 3.4.3), a small percentage of positrons may be loaded into the second well through this mechanism.

Cooling

The cooling phase of the trap cycle involves isolating the majority of the loaded positrons, which will accumulate at the lowest potential in the trap as shown in figure 3.13, and allowing them to cool to the buffer gas temperature.

Once isolated, positrons continue to undergo inelastic events with the buffer gases. Initially, this is in the form of vibrational excitations of CF_4 , which has four vibrational modes, ν_1 , ν_2 , ν_3 and ν_4 , with energies 0.112 eV, 0.054 eV, 0.154 eV and 0.078 eV respectively (Raju, 2006). Cooling is primarily achieved with the asymmetric stretch mode, ν_3 , which has a large cross section at low energies, as

shown in figure 3.14. Contributions from ν_1 , ν_2 and ν_4 are negligible. Through this process the positron cloud is able to cool to a distribution of ~ 150 meV. As CF_4 has neither a dipole or quadrupole moment, its rotational excitation cross section is very small, preventing CF_4 from cooling the positrons further. Instead, cooling to the thermal temperature of the buffer gases, ~ 38 meV, is achieved through rotational excitations of N_2 , which has a quadrupole moment. These rotational levels are typically separated by a few meV, allowing complete thermalisation.

Dumping and Pulse Compression

The third, and final, phase of the trap cycle is to release the cooled cloud of positrons from the trap. This is achieved by ramping the potential of the eighth electrode above that of the final electrode, resulting in the release of the positron cloud as it is no longer confined by the electrode structure. As discussed in section 2.4.2, the method used to produce temporally narrow pulses was proposed by Mills Jr. (1980) and is referred to as the ‘timed potential technique’.

Prior to the beamline’s construction, a bunching simulation was created using Matlab. This is a 1-d stochastic simulation which assumes the parallel energy to have a Gaussian distribution with a Full Width at Half Maximum (FWHM) of 40 meV. In addition, an arbitrary number of positrons are confined to a trapped length, also with a Gaussian distribution, set by the user. The resulting temporal distribution, is then determined through the application of various ramping potentials at different beam energies (determined by the potential of the final electrode in the trap). The simulation indicated that the timed potential technique would produce the best temporal resolution, FWHM of ~ 220 ps, at lower dump energies (~ 10 eV).

Once the beamline was operational it was established through empirical tuning that, contrary to the simulation, higher dump energies produced a narrower pulse. Several different configurations have been trialled, however the best FWHM achieved to date has been ~ 800 ps ($\sim 4\times$ larger than the simulation). The timing jitter of the electronics have been investigated and eliminated as the limiting factor of the pulse compression. Instead, divergence from the timed potential, due to limitations of the Elbitech amplifier, is one possible cause. There are two limiting factors imposed by the amplifiers. First, the maximum output of 200 V places an upper limit on how much of the ideal timed potential curve can be reproduced. Second, the maximum slew rate of the amplifiers prevents the

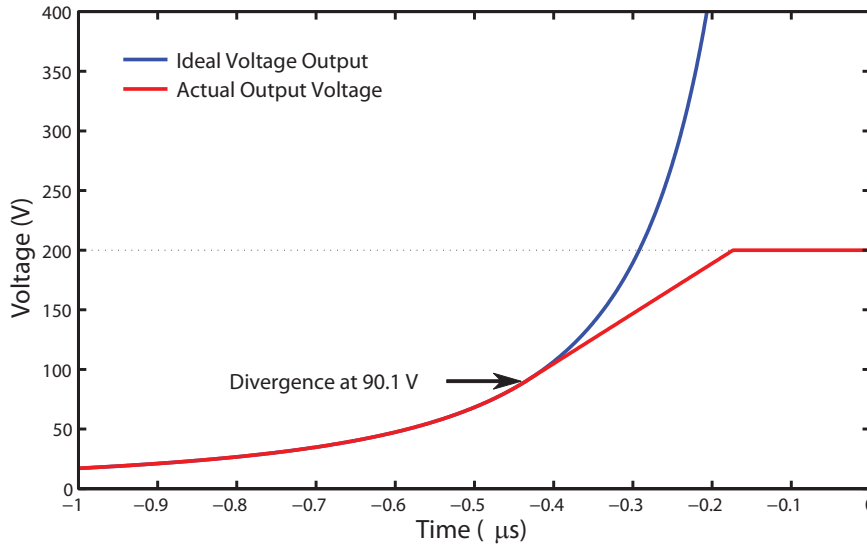


Figure 3.16: Shown here are the deviations from the ideal timed potential curve due to limitation in the electronic amplifiers used to generate the waveform. The maximum output voltage is limited to 200 V while the maximum slew rate ($420 \text{ V}/\mu\text{s}$) causes the output to diverge from the ideal curve at 90.1 V. A maximum slew rate of $1390 \text{ V}/\mu\text{s}$ would be needed to reproduce the timed potential function up to the maximum output voltage.

replication of the rapidly increasing parts of the ramp. Instead, in these regions the output ramps linearly at the maximum slew rate. This has been measured at $420 \text{ V}/\mu\text{s}$ with the capacitive load of the electrode and wiring (0.16 nF) in place. The effects of both these factors are shown in figure 3.16.

These restrictions were used in a Monte Carlo bunching simulation carried out using SIMION. This determines single particle trajectories in a three dimensional environment, determined by the physical arrangement of the electrodes and their potentials. This showed that at higher dump energies, the spatial extent of the trapped positron cloud was reduced due to field penetration effects altering the shape of the potential well. This effect has been approximated in figure 3.20. The simulation was initiated with 10^4 positrons at the minimum of the potential well. A Gaussian distribution was used for the spatial profile and the initial energy distribution was identical to the Matlab simulation. In addition, scattering from N_2 at 10^{-4} mbar was approximated both prior to, and during the release of the positron cloud. The temporal width of the resulting pulse, dumped with a potential ramp including the amplifier restrictions, was $\sim 1 \text{ ns}$. This result agrees well with the measured pulse which indicates that the amplifier restrictions, which

prevent the ideal timed potential from being reproduced, are limiting the pulse compression. In addition, the initial spatial distribution of the positron cloud significantly affects the temporal width of the pulse. This distribution is reduced by deeper well potentials, which then require higher dump energies.

3.4.2 Operation of the Trap Electrodes

Now that the processes which govern the trap operation have been discussed, the settings which have been found, through empirical tuning, to produce the best pulse will be outlined. The electrode potentials of each phase of the trap will be discussed in turn, with the minor addition of the experimental reset phase. As the duration of these phases must be tuned to the buffer gas pressures, these values will be given after the optimisation of the buffer gas system has been discussed.

Loading

Due to the non-zero response time of the detector, a high number of positrons per pulse is undesirable. If the number of positrons per pulse is too large, there may be several γ -rays incident on the detector within a short period, preventing the detection system from resolving two separate annihilation events. In order to avoid this, the operation of the trap can be tuned to produce more pulses per second which have fewer positrons. As this can be accomplished while maintaining trap throughput, the detection rate of suitable annihilation γ -rays increases; however, the ultimate count rate is fundamentally limited by the number of moderated positrons available and the trap efficiency.

Optimisation of the duration of the loading phase must be balanced with the N_2 pressure, which will be discussed in detail in section 3.4.3. The typical duration of the loading phase will be given after this discussion. Here it is sufficient to say that, for a fixed N_2 pressure, the duration of the loading phase must be sufficiently short to avoid overlapping events per trap cycle.

When the trap potentials are kept constant relative to the moderator potential, the number of moderated positrons successfully loaded into the trap broadly peaks at ~ 29 V, indicating the optimum moderator potential. While loading is not very sensitive to this potential, it is quite sensitive, as expected, to the difference between this potential and those of the trap. The parallel energy distribution of the moderated beam as it passes through the trap is shown in figure 3.12.

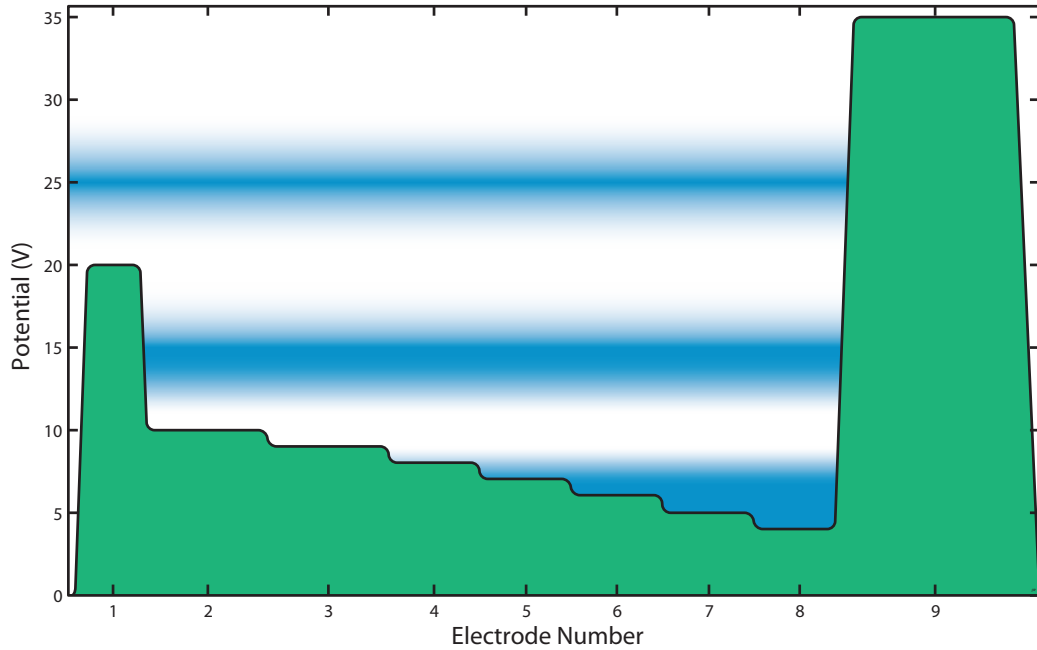


Figure 3.17: Shown here is a plot of the potentials of the trap during the loading phase of the trap cycle. The shaded blue regions show the moderated beam and an estimate of the distribution of positrons loaded into the trap.

The first three electrodes, which contain a higher partial pressure of N_2 , are set at 20 V, 10 V and 9 V respectively. Electrodes four through eight step down in 1 V steps from 8 V to 4 V. This stepped configuration has been found to increase the loading efficiency, though this configuration is different to what is expected, and found in other Surko trap systems. It is possible that this is due to the increased effect of trapped positrons loading into the final well through inelastic interactions with CF_4 . The ninth, and final electrode, is sufficiently high to prevent moderated positrons passing straight through the trap. For a moderator biased at 29 V, this is usually 35 V. These potentials are shown in figure 3.17.

Cooling

The goal of the cooling phase is to first form an isolated positron cloud and then allow it to cool to the buffer gas temperature, $\sim 38\text{meV}$ ($3/2K_B T$). An isolated cloud is formed by raising the potential of the seventh electrode to prevent additional positrons loading into the potential well at the eighth electrode, shown in figure 3.18. In addition, the spatial extent of the isolated positron cloud, along

the axis of the trap, is restricted by using a deep potential well. The deep well alters the shape of the potential well, creating a narrow region at the lowest potential due to field penetration from the adjacent electrodes. As the positrons thermalise, they accumulate at the bottom of this potential. These two effects are achieved by ramping electrodes seven and nine, in a three step ramp, from 5 V and 35 V to 181 V and 155V respectively. The resulting potentials are shown in figure 3.18. During the cooling phase, positrons continue to load into the first six electrodes of the trap. This allows the throughput of the trap to be maintained despite the long cooling time.

The duration of the cooling phase will depend on the combined pressure of CF_4 and N_2 as well as the ratio between the two gases. For a given setup, the duration must be sufficiently long to allow thermalisation to occur; higher combined pressure will require a shorter duration. However, excessively long cooling phases will result in the loss of a significant portion of the positron cloud through annihilation. As with N_2 , there are detrimental effects associated with higher CF_4 pressures and these will be discussed in section 3.4.3. Figure 3.19 shows the effect of the cooling time on the thermal distribution of the positron pulse for a fixed CF_4 and N_2 pressure.

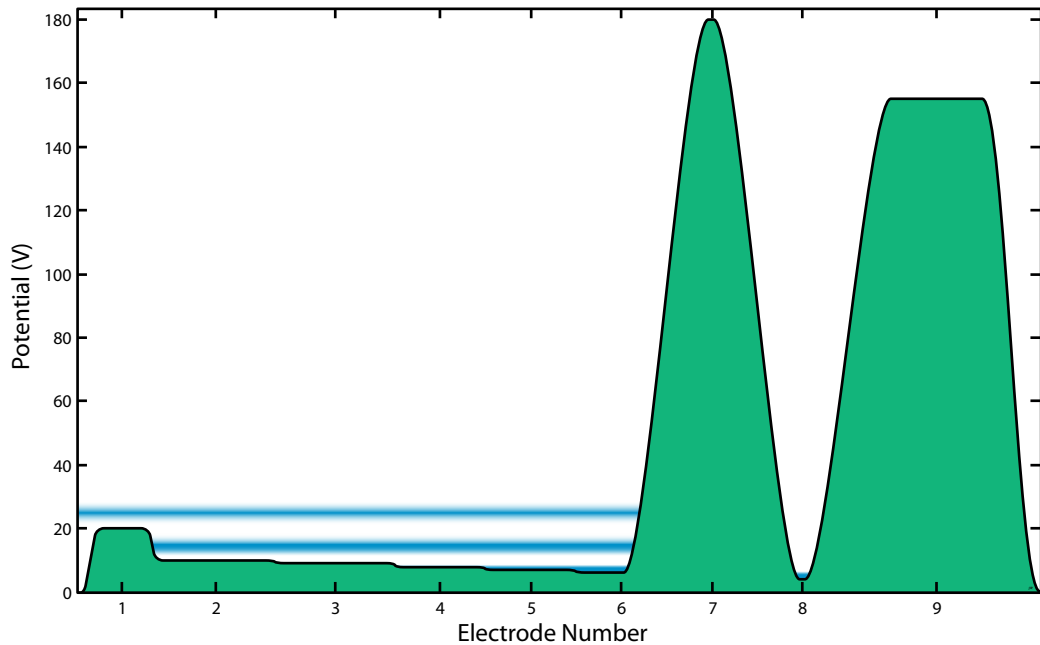


Figure 3.18: Shown here is a plot of the potentials of the trap during the cooling phase of the trap cycle. The positron cloud is isolated within a potential well which also spatially compresses the positron cloud as it cools.

When the duration of the cooling phase is sufficient for full thermalisation, the resulting temporal signal at the sample can be well described by a single Gaussian curve for $t < 0$ (the shape of the pulse for $t > 0$ will be discussed in section 3.4.3). When the duration is insufficient, the positron pulse contains two distinct temporal components which can be related to the energy distribution of the isolated positrons. The largest component represents positrons which have cooled to the thermal temperature of the buffer gases. However the second component, shown here to have a much larger temporal distribution, represents positrons which did not achieve thermal temperatures prior to being released from the trap (referred to as the partially cooled component). The decomposition of this is shown in figure 3.19 by fitting the sum of two distinguishable Gaussian curves.

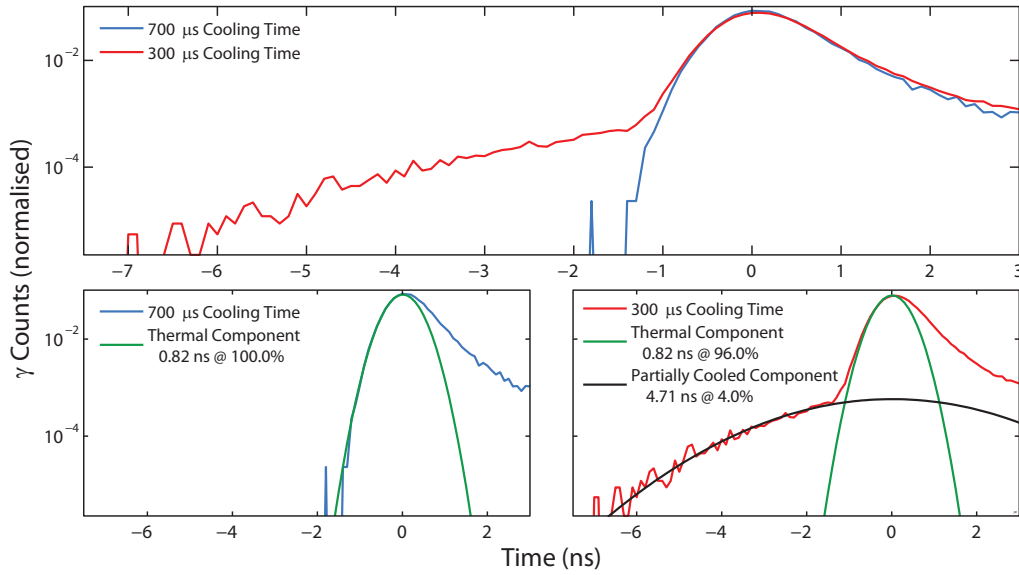


Figure 3.19: Shown here are two measurements conducted with different cooling times, the peaks of these spectra have been placed at $t = 0$. It can be seen that when the duration of the cooling phase is insufficient to fully cool the positron cloud, a two component positron pulse is formed. While these measurements represent the extremes of the tested range, the effect varies linearly with the duration of the cooling phase.

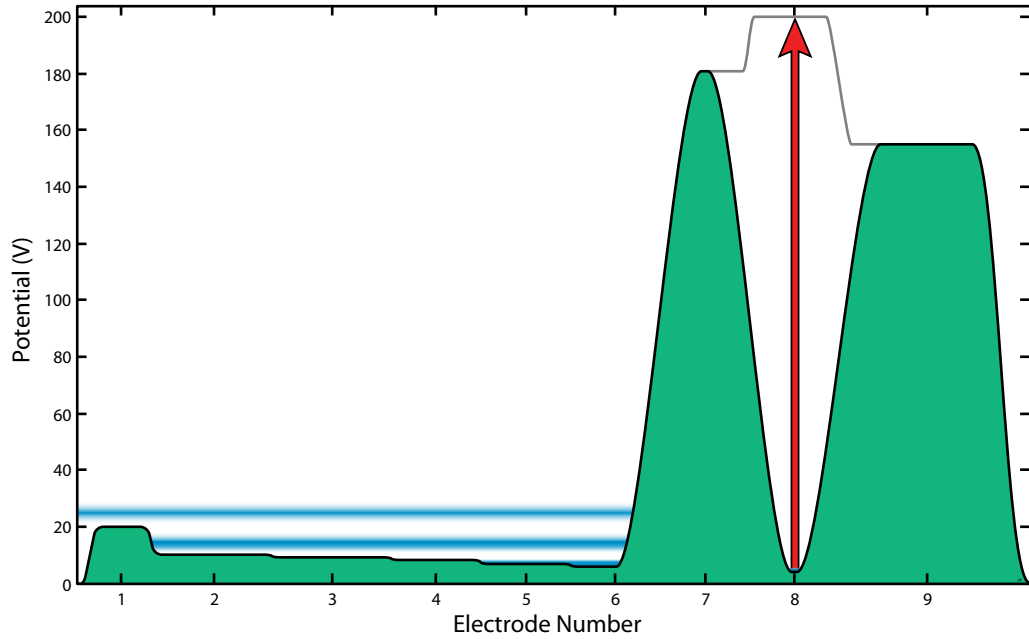


Figure 3.20: Shown here is a plot of the potentials of the trap during the dumping phase of the trap cycle. In addition, the ramping of the eighth electrode is indicated by the red arrow.

Dumping

The dumping phase uses the previously discussed timed potential technique to release the isolated positron cloud from the trap. Ideally this is done by ramping the eighth electrode, which is driven by the AWG, from 4 V to 200 V according to the timed potential technique. Over this voltage range the timed potential requires just under $2 \mu\text{s}$, as shown in figure 3.16. Figure 3.20 shows the electrode potentials while this ramp is performed. It can be seen that the positron cloud begins to exit the trap once the ramp passes 155 V. By this stage of the ramp, the maximum slew rate of the amplifiers has been exceeded and the positron cloud is effectively released with the fastest achievable linear ramp.

Experimental Reset

Following the dumping phase, there is an experimental reset time, typically $5 \mu\text{s}$ or less, to linearly ramp the electrodes back to the loading potentials. With the exception of the eighth electrode, these are ramped over the duration of the reset time. The eighth electrode is instead ramped near the maximum slew rate of the amplifier back to its loading potential, where it remains until the next trap cycle.

3.4.3 Operation of the Buffer Gas System

Operation of the buffer gas system revolves solely around control of the driving pressures of the buffer gases. However, the required pressures are intrinsically linked to the duration of the phases of the trap cycle. While the partial pressures of the buffer gases inside the trap are not monitored, knowledge of the vacuum configuration, pumping speeds and driving pressures allows them to be estimated using the flow equations. However, these values are of little interest here and the following discussion will instead only consider the driving pressures for simplicity. Optimisation of the buffer gas pressures is performed with the goal of maximising the count rate, while maintaining a desirable pulse shape with the shortest FWHM possible.

Due to the desire to cycle the trap quickly to keep the number of positrons per pulse low, moderated positrons must be trapped and cooled within 1 ms. This can be achieved by increasing the partial pressures of the buffer gases when compared to the operation of similar Surko traps. However, these pressures are limited by systematic effects on the pulse timing. These effects manifest as a tail in the timing spectra due to positrons lagging behind the pulse. This is parameterised by calculating the percentage of positrons which arrive after twice the FWHM has elapsed and is referred to here as the I_{tail} parameter.

It was quickly established through systematic testing that this parameter is proportional to the pressures of the buffer gas. Initially, this was thought to be due to the positron pulse undergoing scattering in the transport stage of the apparatus. This adversely affects the energy distribution of the pulse as positrons which undergo scattering will likely lose $v_{\parallel}$, delaying their arrival at the target. Simulations carried out in SIMION showed qualitative agreement and, as a result, an additional turbomolecular pump was installed in the transport region. This reduced the pressure in this region by an order of magnitude, however little effect was seen on the pulse shape. As a result, it is thought that the scattering is taking place as the positrons travel through the ninth (and final) electrode, or shortly after they exit the trap. In order to reduce the pressure in this region as much as possible, the additional pump was relocated to the trap exit endstation. Unfortunately, this only resulted in a minimal improvement (1–2% reduced scattering) in the I_{tail} parameter. However, it was found that the driving pressures could be increased further without the I_{tail} parameter increasing

as rapidly. This allowed the duration of the loading and cooling phases to be reduced, increasing the number of pulses per second. In order to eliminate this tail, a chopper may be implemented after the trap to truncate the pulse and discard any positrons which undergo scattering.

Optimisation of N_2

At larger N_2 pressures, the likelihood of a moderated positron undergoing an inelastic collision to become trapped within the potential well increases. However, this must be balanced against the I_{tail} parameter as well as the effect of reducing the lifetime of the positrons inside the trap due to the increased probability of positronium formation and direct annihilation. The later of these two considerations appears to have little effect on the resulting count rate due to the timing regime and, instead, the pressure is ultimately limited by the increase in the tail due to scattering. Once the optimal N_2 pressure is established, the duration of the trap phase is reduced to keep the number of positrons per trap cycle satisfactorily low.

Figure 3.21 shows the effects of increasing the driving pressure from 70 mTorr up to 375 mTorr for fixed trap cycle parameters. It can be seen that at higher N_2 pressures there is a corresponding increase in the count rate due to an increase in the number of positrons successfully loaded. For these measurements the duration of the loading phase remained constant; however it was sufficiently short that even at the higher pressures the effects of overlapping events per trap cycle were minimal. As discussed, the I_{tail} parameter shows a steady increase proportional to the driving pressure due to the increased probability of scattering upon release of the pulse. There is no significant effect on the FWHM of the pulse.

Optimisation of CF_4

Optimisation of the CF_4 pressure must be matched with the duration of the cooling phase to give the isolated positrons sufficient time to thermalise. As discussed in section 3.4.2, if the N_2 pressure, CF_4 pressure or the duration of the cooling phase are insufficient, the pulse broadens as the positron cloud hasn't thermalised to the buffer gas temperature. Increasing the CF_4 pressure allows a shorter cooling phase and, therefore, the trap to be cycled faster. However, as with N_2 , the pressure must be balanced against the I_{tail} parameter and the lifetime

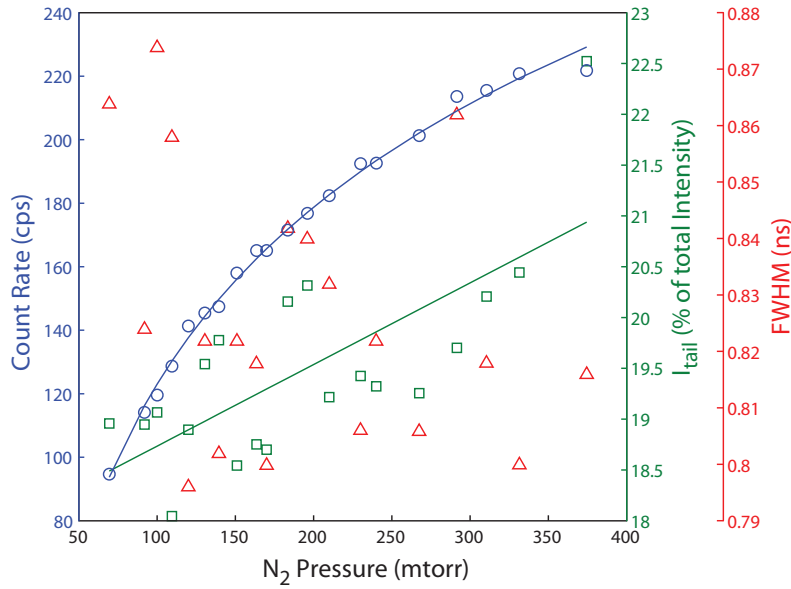


Figure 3.21: Shown are the effects of the N_2 pressure on the characteristics of the pulsed beam. During these measurements the CF_4 pressure was 100 mTorr. The lines show a logarithmic and linear fit to the count rate and I_{tail} characteristics respectively. No discernable systematic effect on the FWHM is observed.

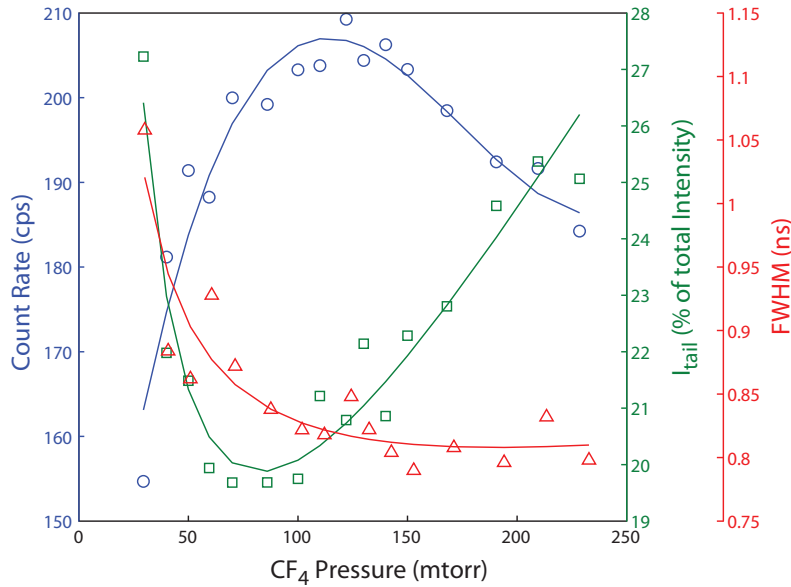


Figure 3.22: Shown are the effects of the CF_4 pressure on the characteristics of the pulsed beam. During these measurements the N_2 pressure was 240 mTorr. It can be seen that the count rate peaks slightly over 100 mTorr while a minimum in the I_{tail} parameter is achieved slightly under this pressure. The FWHM of the pulse approaches a minimum value of ~ 0.8 ns as the pulse achieves full thermalisation.

of the positrons inside the trap. Additionally, as CF_4 provides the majority of the cooling, the FWHM must also be kept in mind; this can be compensated for by adjusting the duration of the cooling phase. Unlike N_2 , the lifetime of the positrons begins to detrimentally affect the count rate at higher pressures as positrons are lost to direct annihilation. Due to its closer proximity to the exit of the trap, the effect on the I_{tail} parameter is much more pronounced.

Figure 3.22 shows the effects of increasing the driving pressure of CF_4 from 30 mTorr to 230 mTorr. It can be seen that the three characteristics discussed above are significantly affected. The count rate peaks around 125 mTorr, indicating there is a contribution from CF_4 to the loading of positrons into the well at the eighth electrode as discussed. Beyond this pressure the count rate decreases due to a reduction of the positron lifetime within the trap. At pressures lower than ~ 100 mTorr, both the FWHM and I_{tail} parameters are affected by insufficient cooling of the isolated positron cloud. As shown in figure 3.19, this results in a two component pulse, increasing both parameters. While the FWHM achieves a minimum value slightly over 100 mTorr, indicating that the positron pulse has been fully cooled, the I_{tail} parameter begins to increase sharply at ~ 90 mTorr. Much like the N_2 , this is due to positrons within the pulse scattering, either elastically or inelastically, upon release from the trap. During these measurements the duration of the cooling phase was held constant to allow the effects of the CF_4 pressure to be investigated.

3.4.4 Operational Parameters

Currently, the trap is operated at almost 1400 Hz with the driving pressures of the buffer gas system at 240 mTorr and 100 mTorr for N_2 and CF_4 respectively. With these driving pressures, and source activity, the duration of the loading phase is typically 250 μs . While this is just over a third of the total cycle time ($\sim 750 \mu\text{s}$), loading continues during the other phases of the trap cycle. The cooling phase is usually the longest part of the trap cycle and occupies almost all of the remaining cycle (500 μs); at these driving pressures this allows the isolated positron cloud to fully thermalise. The duration of both the dumping and experimental reset phases are very short ($\sim 3 \mu\text{s}$) and have no significant affect on the repetition rate.

3.5 The Transport Region Hardware

The transport region of the beamline is the ~ 1.7 m section between the end of the trap stage and the start of the sample chamber. The sole purpose of this region is to allow the pulse compression method to be implemented effectively. The region contains a series of solenoids and a Thermionics Laboratory Inc. 6" gate valve, referred to as the Beamline Gate Valve (BGV).

The 1.7 m span is comprised of two 0.5 m vacuum chambers, with a third 0.5 m chamber which has an additional flared section at the sample end. The hardware inside this flared section (within which a sample is positioned during measurements), which includes an electrical feedthrough, will be discussed in section 3.7. As previously discussed, an axial magnetic field is generated using a series of solenoids to confine the positron beam. Regardless of their physical location, the characteristic details of these solenoids are given in table 3.1.

The BGV is used to isolate the sample stage from the trap stage. This is used primarily when samples are being loaded, unloaded or swapped to limit potential damage in the event of any failures which result in a rapid loss of vacuum. This valve is computer controlled through the same processes as the valves in the sample stage (which will be outlined in section 3.7.2). The status of this valve is read separately by the beamline control computer (see section 3.9 for more detail).

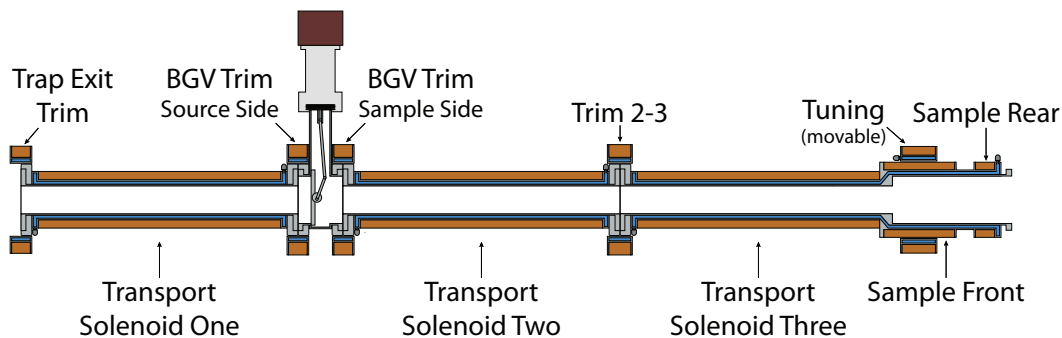


Figure 3.23: Shown here is a schematic diagram of the transport stage with the major components labelled.

Solenoid Name	Length (mm)	Radius (mm)	Turns	Layers	Wire Type
Helmholtz ^a	29	139.4	540	-	-
Beamtube ^a	467, 248	26.8	770, 420	-	-
Hand Wound 1	25	41	18	3	1.6 mm round
Hand Wound 2	35	25	38	3	1.6 mm round
Hand Wound 3	55	43	52	2	1.6 mm round
Trap Solenoid	660	105.0	1551	10	4×2 mm flat
Trap Exit Trim	32	99.6	207	12	1.6 mm round
Transport Solenoid 1	500	45.9	945	8	4×2 mm flat
BGV Trim Source Side	32	99.6	257	15	1.6 mm round
BGV Trim Sample Side	32	99.6	259	15	1.6 mm round
Transport Solenoid 2	500	45.9	947	8	4×2 mm flat
Trim 2-3	40	102.0	334	15	1.6 mm round
Transport Solenoid 3	500	45.9	939	8	4×2 mm flat
Sample Front	142	64.6	278	8	4×2 mm flat
Sample Rear	40	67.1	276	12	1.6 mm round
Tuning Coil	64	99.6	423	12	1.6 mm round

Table 3.1: Shown in this table are the physical details of the solenoids used to generate the confining magnetic field. The solenoids in the source and trap stage have been included in the tables for completeness. The radius is given for the centre of the solenoids.

^aValues for the radius and number of turns are estimated using information provided by Greaves (2011).

3.6 Operation of the Transport Region

Both the BGV and power supplies are computer controlled, which will be discussed in sections 3.9.3 and 3.9.4 respectively. The typical currents driven through each solenoid are given in table 3.2, with the resulting magnetic field at the centre of these solenoids plotted in figure 3.24. As previously discussed in section 3.4.1, due to the variations in the magnetic field there is the potential to cause energy to be exchanged between the parallel and perpendicular components. However, for the confining magnetic fields of the beamline this effect is adiabatic and does not affect the energy distribution.

The beamline described here is situated ~ 1.5 m from a second parallel beamline, which also uses a confining magnetic field, dedicated to the study of low energy positron scattering from gaseous AMO targets (Sullivan et al., 2008). It has been found that the confining magnetic field of this second beamline has an adverse effect on the count rate of the beamline discussed here (and vice versa) as well as influencing the position of the positron beam at the sample. The latter of these, a 1–2 mm shift, can be easily adjusted for through careful calibration of the sample position (discussed in section 3.8.2). While there is no perceivable effect on the quality of the positron pulse, the significant decrease in count rate ($\sim 40\%$) is highly undesirable. Investigations have shown that the largest effect of these stray fields ($\lesssim 0.5$ G) is on the operation of the trap. As a result, four 0.5 m^2 panels of 1 mm μ -metal were positioned, in a layered configuration, between the trap stages of the two beamlines. This arrangement ameliorated the interaction between the two beamlines and improves count rate detriment to $< 10\%$. More recently, small steering coils (10–50 AT) have been added to the entrance endstation to provide finer control of the position of the moderated beam upon entrance to the trap. These additions have removed the need for the μ -metal shielding and nullified the effect on the count rate.

Solenoid Name	Relative Position (mm)	Power Supply	Current (A)
Helmholtz	4348.0, 4118.0	XDL56-4P	3.9
Beamtube	3786.5, 3379.0	XFR60-20	13.9
Hand Wound 1	3169.0	ZUP10-20	13.0
Hand Wound 2	3136.0		
Hand Wound 3	2999.0	ZUP36-12	7.5
Trap Solenoid	2683.0	GEN80-19	19.95
Trap Exit Trim	2063.1	GEN30-25	8.00
Transport Solenoid 1	1777.9	GEN30-25	19.00
BGV Trim Coil Source Side	1492.7	ZUP36-12	8.99
BGV Trim Coil Sample Side	1284.2	ZUP36-12	9.03
Transport Solenoid 2	999.0	GEN30-25	19.00
Trim 2-3	714.0	ZUP36-12	8.03
Transport Solenoid 3	429.0	GEN30-25	19.00
Sample Front	94.6	GEN40-19	18.00
Sample Rear	-40.0	GEN40-19	11.00
Tuning Coil	119.5–59.0	ZUP36-12	0.00

Table 3.2: Shown in this table are the details pertaining to the operation of the solenoids. The relative position (given in mm) refers to the distance from the sample’s position during a measurement. With the exception of the Xantrex power supplies used in the source stage, the remaining power supplies are TKD-Lambda supplies.

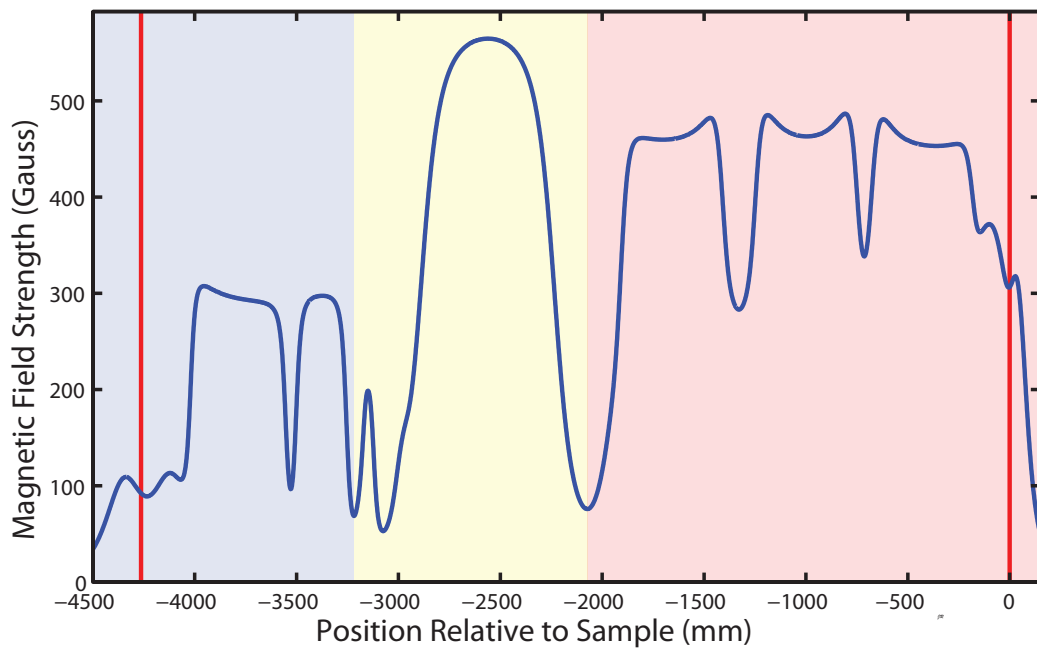


Figure 3.24: Shown here is the axial magnetic field of the beamline. The shaded blue region indicates the Source stage, the yellow region indicates the trap stage and the red indicates the transport and sample stage. The two vertical red lines indicate the position of the source (~ -4300) and the sample (0).

3.7 The Sample Stage Hardware

The sample stage lies at the end of the beamline and is used to house and manipulate the samples to be studied. This stage of the beamline can be further divided into three separate systems; the load-lock system, which is used for sample manipulation; the high voltage system, which is used to apply a bias to the sample; and the detection system, for detection of the annihilation γ -ray and determination of the subsequent timing information. Each of these areas will be discussed in-depth after the vacuum arrangement has been described. With the exception of the sample manipulation hardware, the sample stage is fully computer controlled. This allows processes to be automated to prevent damage to hardware or injuries to the user. The controlling software will be discussed in section 3.9.

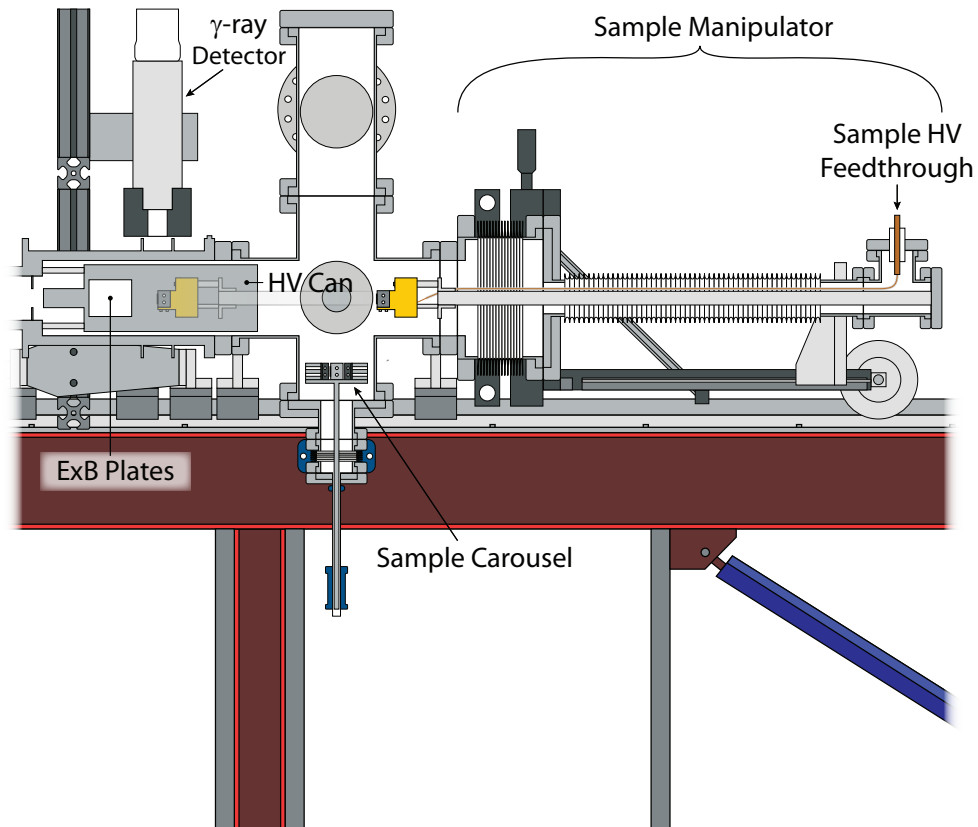


Figure 3.25: Shown here is a schematic diagram of the sample stage with the major components labelled.

3.7.1 The Vacuum Arrangement

The main vacuum chamber of the sample stage is a six way cross with four additional, smaller flanges protruding diagonally upwards. This gives a total of ten flanges and is referred to as the sample chamber. Of these flanges, two are used for vacuum hardware, six for sample manipulation hardware (including view ports), one electrical feedthrough and finally one flange to connect to the remainder of the beamline. In addition to these, there are two electrical feedthroughs located elsewhere in this stage.

The two vacuum hardware flanges are used for a turbomolecular pump, a Pfeiffer TMU 261P capable of pumping at 230 L/s which located on a tee above the sample chamber, and an inverted magnetron type cold cathode gauge, Pfeiffer PKR251. The pump is controlled using a DCU100 control unit and is backed by a Pfeiffer DUO 10 mechanical roughing pump; this pressure is monitored by a Pirani gauge, model TPR280. Both vacuum gauges described are controlled through a second Pfeiffer Maxigauge controller (type TPG 256A) which allows pressures to be read remotely.

A system of valves is in place to allow samples to be easily loaded into and removed from the sample chamber. This system will be discussed in the following section. The chamber typically achieves a base pressure of 8×10^{-9} mbar, though again operational pressures are typically 5×10^{-7} mbar due to the buffer gases from the trap.

3.7.2 Sample Manipulation

There are two requirements that the sample manipulation system, which controls the physical position of the sample, must fulfill. Firstly, due to the physical size of the sample chamber and the requirement for the measurements to be performed under a high magnetic field, the sample must be extended forward (into the flared section discussed in section 3.5) beyond the sample chamber. Also, fine control of the vertical and horizontal positions is also required and will be discussed further in section 3.8.2. Secondly, the process of loading and unloading samples into the sample chamber must be accomplished while maintaining high vacuum. This is commonly referred to as a load-lock system and involves the addition of a smaller vacuum chamber referred to as the load-lock chamber. The components of this system are shown in figure 3.26 and will be discussed in the following paragraphs.

The terminating flange of the beamline is fitted with a Thermionics Northwest Inc. xyz θ sample manipulator, model FM103-1.53-2-2-12/LM/HMP, which fulfils the first requirement of the sample manipulation system. This is a two stage piece of apparatus which allows the horizontal and vertical position to be adjusted ± 25 mm from the central position, while allowing 36" (914 mm) of travel along the axis of the beam. This is shown in the retracted position in figure 3.26, though the forward position is shown partly transparent. The θ stage, which allowed rotation of the sample, was removed to allow a wider tee to be fitted at the rear of the manipulator to alleviate problems encountered in the high voltage system. Inside the vacuum chamber, the end of the manipulator is fitted with a gold coated sample holder mounted using ceramic rods. This provides electrical isolation, allowing the sample to be biased. The design of the sample manipulator and holder includes the capability to add control of the sample temperature while the measurements are being conducted. However, hardware for this functionality has yet to be designed.

The load-lock chamber is mounted to one of the horizontal flanges of the sample chamber. This is a small four way cross chamber separated from the sample chamber by an MDC 2 $\frac{3}{4}$ " gate valve, referred to as the Sample Chamber Gate Valve (SCGV). Opposite this valve in the load-lock chamber is a Ferrovac magnetic transporter, model FD40, referred to as the load-lock arm. This is mounted using an MDC heavy duty, off axis port aligner, allowing the angle of the load-lock arm to be varied during sample manipulation. In order to allow access to the load-lock chamber a hinged door, aptly named the load-lock door, is fitted to the load-lock chamber. Due to the frequency with which this door is used, it seals with a rubber o-ring rather than a copper gasket. The final port in the load-lock chamber leads, through the Sample Chamber Load Lock Valve (SCLLV), to the sample chamber roughing pump detailed previously. The final valve in the system (not shown in figure 3.26) is the Sample Chamber Roughing Valve (SCRV) which can be used to isolate the low pressure side of the turbomolecular pump from the remainder of the roughing system. This prevents the turbomolecular pump from being exposed to high pressures when evacuating the load-lock chamber with the roughing pump. A discussion of the operation of the valves detailed here can be found in section 3.8.3. While figure 3.26 shows the components discussed here to scale, a simplified layout of the pumping arrangement can be seen in figure 3.30.

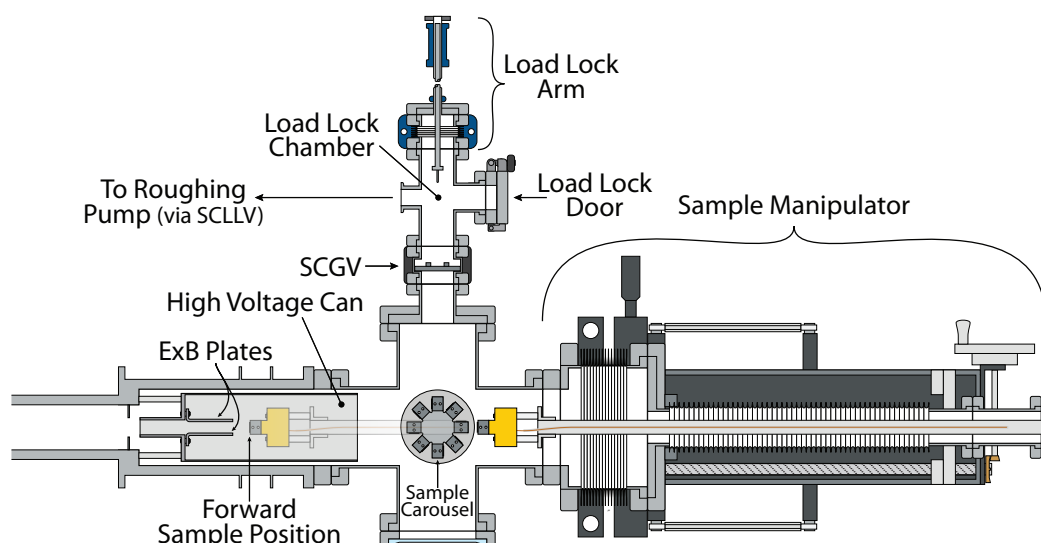


Figure 3.26: Shown here is a top view of the sample chamber with its components labelled. The details of the sample manipulation system can be seen as well as the internal components of the high voltage system.

In addition to the load-lock chamber, a sample carousel is mounted to the downward flange of the sample chamber. This is controlled using a second Ferrovac magnetic transporter and is capable of holding up to eight samples to streamline the loading or unloading process.

The three valves discussed here, as well as the BGV, are controlled by the beamline computer through a custom made TTL interface. This interface contains twelve channels, with channels one through four being used to control the valves discussed (more detail can be found in table 3.3). In addition, channel nine is utilised by the high voltage system (discussed in the following section) and channels ten through twelve are used to control the three roughing valves associated with the turbomolecular pumps of the trap stage.

Associated with the sample manipulation hardware already outlined, are five micro-switches; these allow the state of the system to be determined by the beamline computer. Of these switches, three are used to determine the location of the sample manipulator, one is used to identify when the load-lock arm is fully retracted and the final switch indicates when the load-lock door is closed. In addition to these micro-switches, the valve states are also determined by the beamline computer using magnetic reed switches. These states, in conjunction with access to the two pressure gauges of the sample stage, allow the operation of the load-lock chamber to be almost fully automated (with the exception being the manipulation of the sample blocks).

3.7.3 The High Voltage System

The high voltage system is used to apply a bias, up to -20 kV, to the sample. This bias controls the implantation depth of the positrons, allowing the sample to be studied in a depth sensitive manner (as discussed in section 2.2.1). In addition, the high voltage system also serves to prevent positrons reflected near the sample from interfering with the measurements. This is achieved by applying an electrical potential to four separate areas inside the vacuum chamber.

The first, and most obvious area to which the biasing potential is applied is the sample itself. This is done through the sample holder at the end of the sample manipulator. The remaining three areas all lie within the flared section at the end of the transport region which contains the high voltage can. This is a stainless steel cylinder with an inner diameter of 70 mm and length 200 mm with a narrow extension, 20 mm diameter and 50 mm long, at the entrance. It is mounted on ceramic rods allowing it to be biased at the same potential as the sample, ensuring the electric field at the sample is minimised. On the inside of the can, where the beam enters, are located two vertically oriented, parallel plates which are 57×45 mm (height by length) and separated by 16 mm, referred to as the E×B plates. Once again, these are mounted to the inside of the can using ceramics to provide electrical isolation. These components can be seen in figure 3.26.

The voltages to these four areas are provided by a two part system. The initial high voltage is provided by a Bertan 205B-20R high voltage supply. This supply is controlled through the beamline computer, which will be discussed in section 3.9.2. The potential output from this supply is used to float a custom made electrical system referred to as the E×B plates control box. This control box provides the four desired outputs. Two of the outputs, connected to the sample and high voltage can, are equal to the potential from the Bertan supply. The remaining two outputs are offset about this potential by an equal magnitude and connected to the E×B plates. The offset is manually controlled using a potentiometer as larger offsets are required at higher potentials. This arrangement is designed to induce a vertical drift in the trapped beam and eliminate reflected positrons from the spectra (this will be further discussed in section 3.8.1). While the offset is manually controlled, electrical power to the control box is automatically disabled, through channel nine of the TTL interface discussed previously,

whenever the Bertan supply is disabled. This prevents the users being exposed to high voltages when manipulating samples.

Located immediately in front of the high voltage can, inside the transport region, is a grounded mesh aperture with an inner diameter of 20 mm. This mesh limits the penetration of the electric field into the transport region, to ensure a near uniform electric field on approach to the high voltage can. This minimises the effect any stray fields may have on the transport and compression of the beam.

Also associated with the high voltage system is an interlock switch. This prevents the high voltage from being enabled, both the Bertan supply and the $E \times B$ control box, unless the sample manipulator is almost fully forward, where the potential can be applied safely. This interlock switch is separate from the position micro-switches discussed in the previous section.

3.7.4 The Detection System

The detection system is designed to measure and record the time elapsed between the release of the cooled positron cloud from the trap and the detection of an annihilation γ -ray.

This time is measured using a Comtech P7889 fast timing card, which features timing bins 100 ps in width. This card requires a PCI-X interface and as such is fitted into a computer containing a Supermicro PDSM4+ motherboard. This computer is referred to as the analysis computer. An internal clock on the fast timing card is started using a rising edge on the trigger line of the AWG. The jitter on this trigger is specified at <20 ps and allows synchronisation with the dump phase of the trap cycle.

Detection of one of the annihilation γ -rays can be achieved using a number of different scintillating materials. As the goal is to determine the lifetime of the positron in the sample, the total rise time of the detector must be short. This is best fulfilled by a BaF_2 crystal (1M1BAF2/2-X) coupled to an XP2020Q photomultiplier tube from Saint-Gobain Crystals. To this a VD124K/T voltage divider is fitted to provide a simple three-connection interface. A manually controlled Bertan 205B-05R high voltage supply, typically operated at 2.3 kV, is used to charge the photomultiplier tube. The signal from the anode is passed through two Telegartner attenuators of 10 dB and 6 dB (J01006A0836 and J01006A0835)

to protect the timing circuitry from excessively large voltages. This arrangement has a total rise time of 2.8 ns.

Pulses from the detector vary greatly in area, however, the pulse shape does not. This allows a software Constant Fraction Discriminator (CFD) to be implemented; this will be discussed in more detail in section 4.2.1.

3.8 Operation of the Sample Stage

There are three tasks which must be completed in preparation for a measurement. Firstly, the appropriate voltages for the high voltage system must be determined. Secondly, the beam position for the desired voltage is determined using a customised sample block. Finally, the sample to be studied is loaded onto the sample holder and extended forward into the target position where the measurement is performed. Each of these tasks is performed using a separate system of the sample stage, as previously described. The operation of each will be discussed here.

3.8.1 Control of the High Voltage System

The desired potentials of the high voltage system are determined by the properties of the sample. The potential at which the sample is biased controls the depth that the positrons are able to penetrate. As discussed in section 2.2.1, there are two methods used to do this. For samples of a single composition, the Makhov Implantation Profile can successfully be applied (Makhov, 1961) (examples of the profile are shown in figure 2.5). For more complex samples, such as layered materials, PENELOPE is used to model the thermalisation (Baró et al., 1995).

Once the implantation energy is determined, the potential difference of the $E \times B$ plates can be set. This potential difference creates an electric field within the confining magnetic field and induces a drift velocity, $\mathbf{u}$, given by

$$\mathbf{u} = \frac{\mathbf{E} \times \mathbf{B}}{B^2}. \quad (3.5)$$

This velocity is perpendicular to the electric field and independent of the axial direction of the positron. Without this drift velocity, backscattered (or reflected) positrons are seen in the lifetime spectra as a secondary pulse. This is because backscattered positrons are usually unable to exit the high voltage region. Instead, they reflect from the potential and are implanted after a delay governed

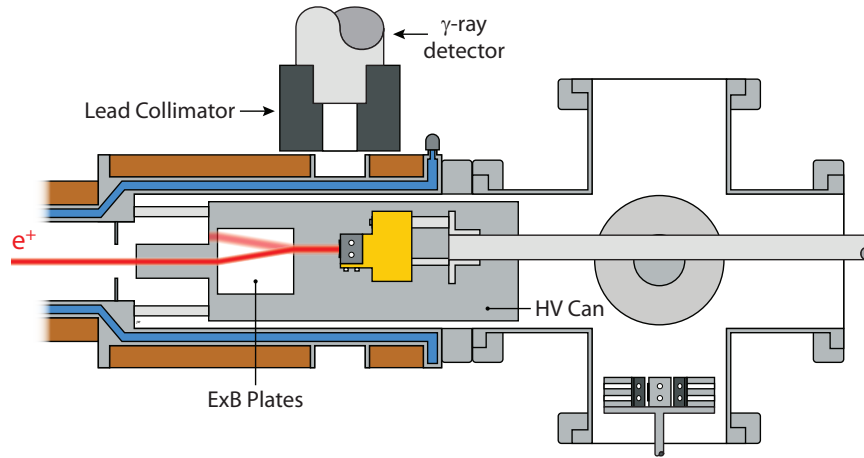


Figure 3.27: This figure shows the high voltage hardware in more detail and also illustrates the effect of the E×B plates. It can be seen that both the incoming and reflected positrons are deflected upwards. This also requires the sample to be raised. This upwards deflection is preferred, over a downwards deflection, as it also increases the solid angle of the detector and increases the count rate slightly.

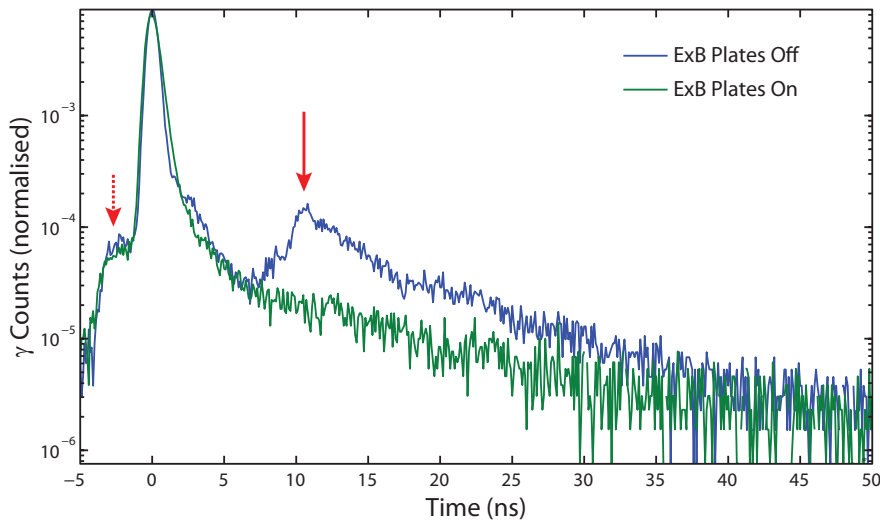


Figure 3.28: This figure shows two spectra, one with the E×B plates inactive and a second with a potential difference between the plates. The peak created by reflected positrons is indicated by the large red arrow at ~11 ns. The smaller dashed arrow on the far left (-3 ns) indicates a peak due to the beam clipping the entrance of the high voltage can. The second of these peaks can only be avoided by adjusting the beam position with the physical location of the trap solenoid.

by the implantation energy and the distance between the sample and the end of the high voltage region. Using this arrangement, an upwards drift velocity is induced in both the incoming positron beam and any backscattered positrons. This forces backscattered positrons to impact on the inside of the high voltage can, where the annihilation γ -rays are generally not seen in the lifetime spectra. This is demonstrated in figure 3.28.

For lower biases, this potential difference must be sufficiently low to prevent drifting the beam beyond the reach of the sample manipulator. However, at high biases (>10 kV) the potential difference is set to the maximum of the system.

If the sample chamber has been opened for an extended period, the high voltage system usually requires conditioning prior to operation. This is due to instability caused by surface contaminants which results in electrical discharges, or breakdown events. Conditioning is performed using a high voltage insulation tester, designed to withstand repeated high voltage breakdowns, and applying a gradually increasing voltage to remove contaminants with the discharges.

3.8.2 Calibration of the Sample Position

The beam position at the sample is influenced by several factors, with the most significant being the physical location of the exit of the trap solenoid and the potential difference applied to the $E \times B$ plates. With the exception of routine tuning, the position of the trap solenoid remains almost constant. However, calibration of the sample position is carried out when the implantation energy is altered or approximately weekly, whichever is shorter. Very little variation is seen in the horizontal position; however, due to the influence of the $E \times B$ plates, the vertical position can often change by up to 5 mm.

Calibration of the sample position is performed using a stainless steel sample block with a 6 mm hole drilled through the centre (this is often referred to as the holey block). When mounted onto the sample holder, the holder is exposed to the positron beam. The vertical and horizontal position of the sample block is then systematically adjusted. When the positron beam is aligned with the hole, a slight shift can be seen in the timing spectra due to the extra distance travelled through the thickness of the block (14 mm) before annihilating. Typically the shift in the timing spectra ranges from 200 ps up to 800 ps depending on the bias applied to the samples as demonstrated in figure 3.29.

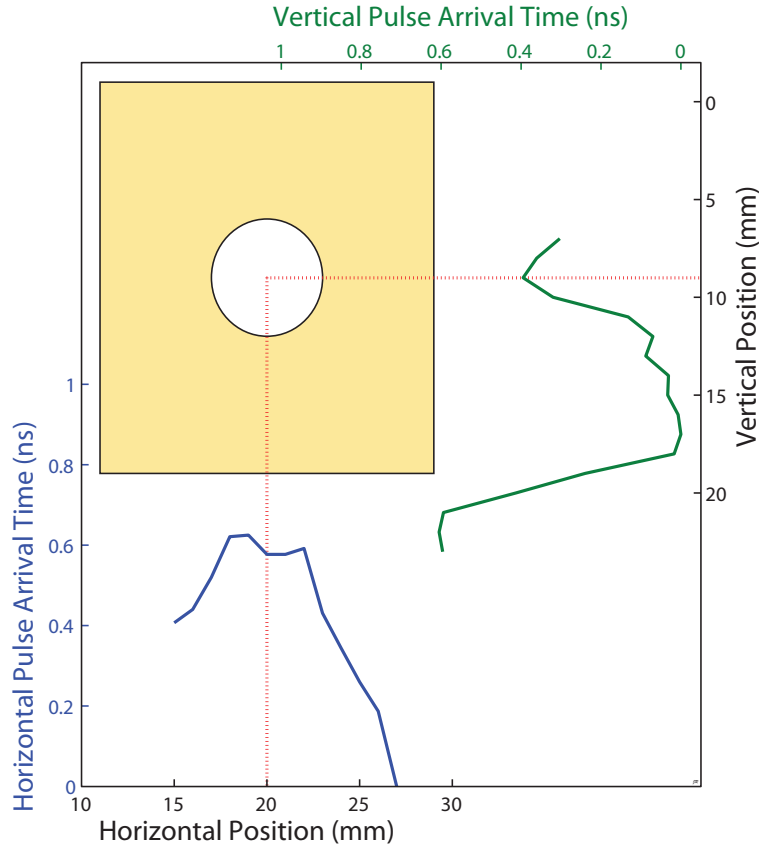


Figure 3.29: This figure shows the shift in the timing spectra as the beam passes through the hole in the block at 5 keV. From this it can be determined that the beam is located at (20,9). As the $E \times B$ plates are used to deflect the beam upwards, the vertical position is expected to be quite high. As a result of the physical size of the sample holder, the sample cannot be moved higher than a vertical position of 7 mm (with 0 mm being the limit of the sample manipulator and 25 mm being the central position). Due to this, the edge of the block is used to confirm the position. Here, the vertical calibration was carried out first with the horizontal position at 22 mm. The horizontal position was then performed (at a vertical position of 9 mm), giving rise to the much broader feature in the horizontal position.

3.8.3 Operation of the Load-Lock System

As outlined in section 3.7.2, the load-lock system revolves around four main pieces of hardware: the sample manipulator, the load-lock arm, the sample carousel and the load-lock chamber. This hardware is shown schematically in figure 3.26. Operation of the load-lock system is achieved using four valves: the BGV, the SCGV, the SCLLV and the SCRIV which are detailed in table 3.3 and shown in figure 3.30.

Acronym	Valve Name	Valve Type	TTL Channel
BGV	Beamline Gate Valve	6" gate valve	1
SCGV	Sample Chamber Gate Valve	2 $\frac{3}{4}$ " gate valve	2
SCLLV	Sample Chamber Load Lock Valve	Angle Valve	3
SCRIV	Sample Chamber Roughing Valve	Angle Valve	4

Table 3.3: Shown in this table are the details for the valves of the sample chamber.

The operation of the load-lock system is controlled through the beamline computer. This guides users who are unfamiliar with the system through the process and prevents damage to the hardware. While the procedures will be outlined here, a more in-depth discussion of the software can be found in section 3.9.3. There are three processes which can be performed, loading, unloading and swapping. Loading involves introducing a new sample into the sample chamber, while unloading refers to removing a sample from the sample chamber. The third process is swapping, which involves exchanging the sample on the manipulator with a sample on the carousel. In the following procedures there are two pressure thresholds, one for the sample chamber and one for the roughing line, which must be achieved before proceeding to the next step. These are currently set to 1×10^{-6} mbar and 6×10^{-3} mbar respectively, however, these can be overridden by the user.

Regardless of the process, the first step in all three processes is to disable the high voltage. The BGV is then closed to isolate the sample stage from the remainder of the beamline, thus limiting exposure to damaging conditions in the event of a malfunction or user error.

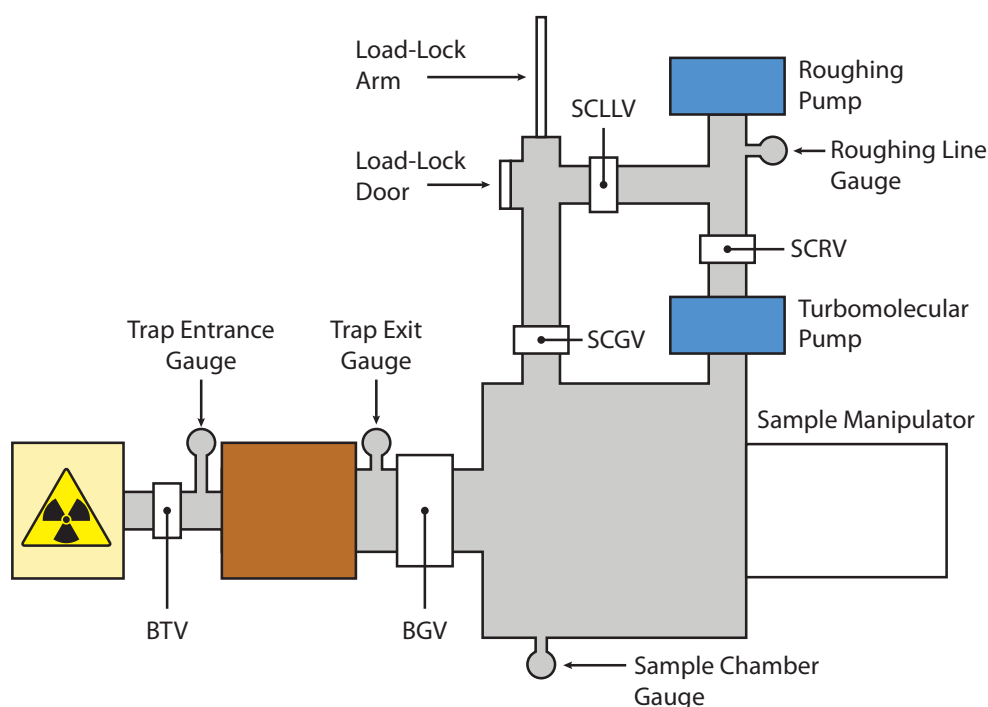


Figure 3.30: This figure shows a simplified layout of the pumping arrangement of the sample stage.

Loading

In order to load a sample into the sample chamber, the load-lock chamber must first be isolated by closing the SCGV and the SCLLV. This allows the load-lock chamber to be accessed, through the load-lock door, to mount the sample on the load-lock arm. Once the load-lock door is closed, the load-lock chamber may then be evacuated by the roughing pump. First, the SCR is closed to isolate the turbomolecular pump and then the SCLLV is opened to pump the atmosphere from the load-lock chamber. The roughing pressure is monitored and once it reaches the desired level the SCLLV is closed and the SCR is opened. The pressure in the roughing line is checked once again to ensure that no pressure has built up while the turbomolecular pump was isolated.

The SCGV is then opened to allow the load-lock arm to be extended into the sample chamber. At this point the user may load the sample onto either the sample manipulator or the carousel. Once the load-lock arm is retracted, the SCGV is closed. The pressure in the sample chamber is then monitored until the threshold pressure is achieved, to allow the newly loaded sample to outgas, before another sample can be loaded or the BGV opened.

Unloading

While there are some similarities, unloading a sample is not simply the loading process in reverse. Firstly, the load-lock chamber is confirmed to be under vacuum by closing the SCR_V and then opening the SCLLV. Again, the roughing pressure is monitored until the threshold is achieved. The SCLLV is then closed and the SCR_V is opened. Once more, the pressure in the roughing line is checked before the SCGV is opened. The user may then extend the load-lock arm into the sample chamber and unload the sample from either the sample manipulator or the carousel. Once the load-lock arm is retracted, the SCGV is closed, isolating the load-lock chamber. The load-lock door may then be opened and the sample removed from the load-lock chamber. When the load-lock door is closed, the SCR_V is closed and the load-lock chamber is evacuated through the SCLLV. The roughing pressure is monitored and once the threshold is achieved, the process can be repeated. Alternatively, the pressure in the sample chamber is checked to be below the threshold before the BGV is opened.

Swapping

The swapping procedure is a much shorter process as the load-lock chamber is never exposed to atmospheric pressures. This process is identical to the unloading procedure until the opening of the load-lock door, which is not required. Once the samples have been swapped, the pressure in the sample chamber is confirmed to be below the threshold before the BGV is opened.

3.9 Computer Control of the Beamline

As has been mentioned throughout this chapter, the majority of the beamline is operated through various computer interfaces. This is achieved using three different computers, the source stage computer, the beamline computer and the analysis computer. The software of the source stage was provided by FPSI. This software is largely unchanged and has already been discussed in section 3.2. With the exception of the detection system, the remainder of the beamline's hardware is controlled using the beamline computer outlined in section 3.3.2; this is also shown schematically in figure 3.31. This software has been developed by the author in National Instruments Labview environment, which provides a simple interface

with the National Instruments hardware. Interfacing with other hardware is not as straightforward, though it is usually not problematic. During development, each system was operated through an individual control program. However, as the software continued to evolve these separate control programs were merged into a single program named ‘Beamline Control’. This was done to streamline the software, improve efficiency, allow the inclusion of more sophisticated features and to avoid hardware conflicts. However, Beamline Control can still be considered as four separate control systems, the trap electrodes, the high voltage system, the load-lock system and the confining magnetic field.

Here some of the functions of each control system will be discussed, including synchronisation and hardware protection measures.

3.9.1 Control of the Trap Electrodes

The most important requirement for the trap control software is to ensure that the driving potentials for the trap electrodes are all synchronised. While this can be easily accomplished for the analogue outputs of a single PXI-6733 card, the AWG (which drives the eighth electrode) must also be synchronised. This is further complicated by the difference in the output rates between the PXI-6733 and the AWG, 740 kHz (as eight analogue outputs are used) and 100 MHz respectively. Synchronisation is achieved through a two step process. Firstly, restrictions are placed on the values that the user may input for the durations of the different phases of the trap cycle. Secondly, the start of each trap cycle is initiated by the rising edge of a square wave, referred to as the pulse train, generated with the onboard clock. This ensures that over the duration of a measurement the electrodes remain synchronised, eliminating any potential timing creep between the PXI-6733 card and the AWG.

The pulse train is generated using one of the counter lines of the second PXI-6733 card and contains the same number of rising edges as the desired number of trap cycles. Synchronisation is achieved by passing this pulse train to the PXI-6733 and the AWG through the backplane of the PXI chassis. Each rising edge of the pulse is used to trigger the output of trap voltages. This output then continues at a constant rate, defined by the write frequency, until the supplied arrays have been executed. The frequency of the pulse train is equivalent to the trap cycle frequency.

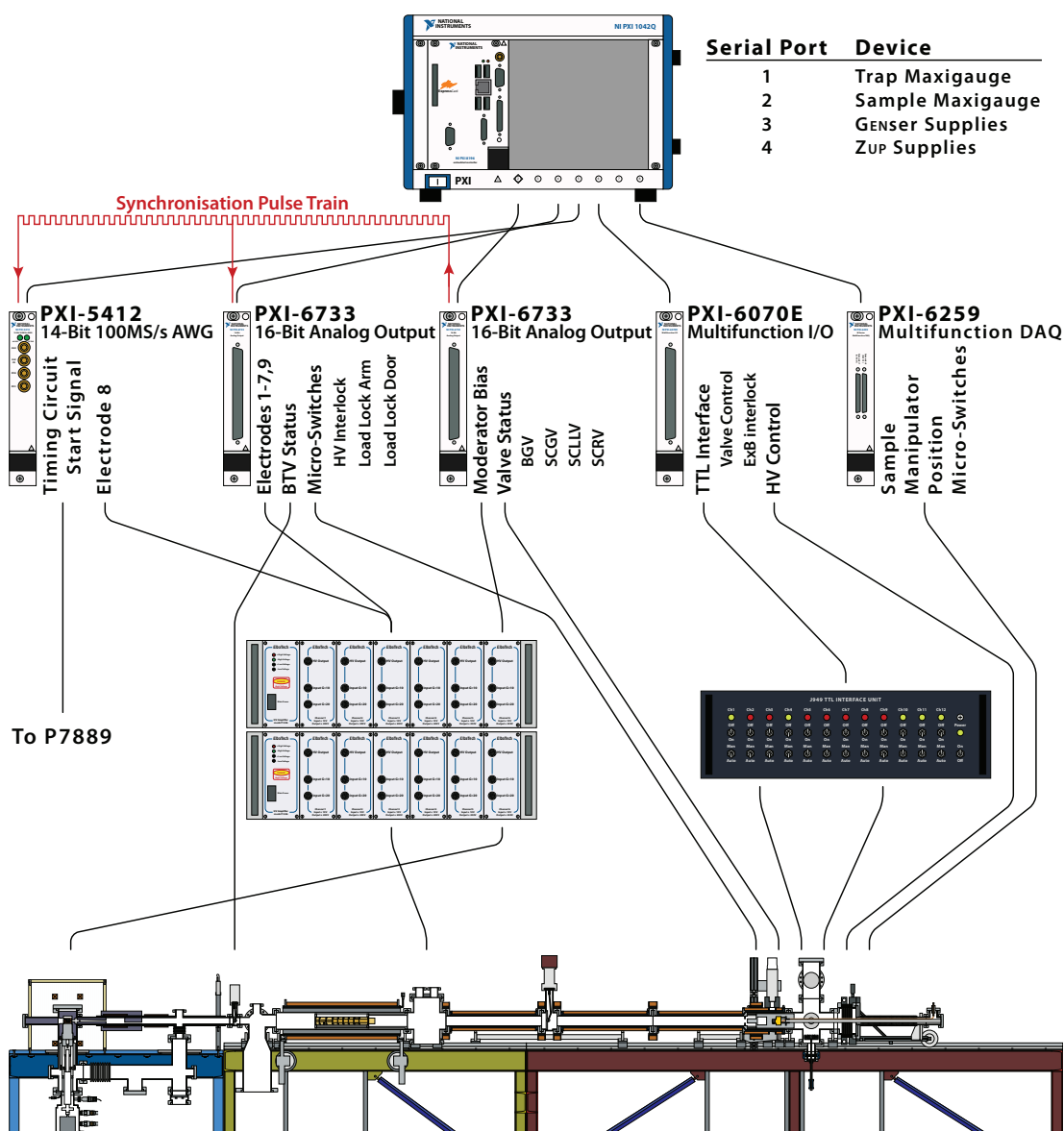


Figure 3.31: This figure shows a breakdown of the beamline computer and the various connections made.

The moderator potential is controlled using the same system as the trap electrodes, with the exception of the eighth electrode. However, this potential, prior to amplification, is output through the second PXI-6733 as depicted in figure 3.31. As this potential remains static during a measurement, no synchronisation is required.

The trap control software also prevents the user from inputting values which exceed the maximum voltage of the Elbatech amplifiers, though this requires knowledge of which input of the amplifier is in use. This has the effect of restricting the output from the 16-bit PXI-6733 card and the 14-bit AWG to $\pm 10\text{V}$, giving the step sizes shown in table 3.4, calculated with

$$\text{Step Size} = \frac{\text{Voltage Range}}{2^{\#\text{Bits}}} \times \text{Gain}. \quad (3.6)$$

In addition to the voltage limit, the user is warned when the maximum slew rate of the amplifiers is going to be exceeded.

Card	# Bits	$\times 10$ Channel	$\times 20$ Channel
PXI-6733	16	~ 3.05 mV	~ 6.10 mV
AWG	14	~ 12.21 mV	~ 24.41 mV

Table 3.4: Shown in this table are the minimum step sizes for both of the cards used to drive the trap electrodes.

3.9.2 Control of the High Voltage System

The high voltage system is computer controlled to protect users. As discussed in section 3.7.3, the high voltage system is comprised of two components: the Bertan high voltage supply and the E $\times$ B plates control box. The Bertan supply has been designed for remote operation and this interface will be discussed. However, the E $\times$ B plates control box cannot be remotely controlled and is instead simply powered off using a relay controlled through the TTL interface previously described.

Control of the Bertan supply revolves around two electrical connections. The first connection is binary (0 V or 5 V) to disable or enable the high voltage output. The second connection is a 0–5 V analogue signal which controls the magnitude of the high voltage output. The controlling analogue signal is ramped

to the desired value at a rate controlled through the user interface. In addition to ramping the magnitude of the output, whenever the high voltage output is disabled, the magnitude is first ramped back to zero. This ensures that when the output is enabled, it turns on at zero volts.

The monitoring of the output of the Bertan supply is done with two electrical connections, one for the voltage output and one for the current drawn. The second of these is monitored and if it exceeds a threshold (0.1 mA), a breakdown event is recorded. This allows the implementation of a breakdown interlock in addition to the safety interlock discussed in section 3.7.3. If ten breakdown events occur within three minutes, then the interlock is triggered and two things happen. Firstly, the trap is stopped to prevent triggering of the detection system. Secondly, the high voltage output is ramped to zero and then disabled. These actions prevent any damage to the Bertan supply and internal hardware due to sustained electrical breakdown.

3.9.3 Control of the Load-Lock System

The sequences discussed in section 3.8.3 are fully computer controlled. As discussed, this is achieved through interfacing with the Maxigauge controller, which operates the pressure gauges, and several microswitches.

Interfacing with the Maxigauge controller is achieved via RS-232 through a serial port and uses a communication protocol laid out in the Maxigauge manual. This allows the gauges connected to the controller to be remotely operated (switching on or off) and the pressure readings accessed. With the exception of the gauges in the source stage, which are interfaced with the source computer, all the gauges of the beamline can be accessed in this manner. However, only the gauges in the sample stage are logged as little extra information can be gained from logging those of the trap stage.

During operation of the load-lock chamber the turbomolecular pump is isolated from the roughing pump. While this is acceptable for short periods, extended periods will result in a buildup of pressure between the turbomolecular pump and the SCR. If this pressure becomes too large the controller shuts down the turbomolecular pump to prevent damage. In order to prevent this, isolation of the turbomolecular pump for longer than ten minutes results in the SCLV closing before the SCR is opened to pump away any pressure. During this time

the roughing line pressure is monitored and once sufficiently low, the software continues from where it was interrupted.

There are two microswitches which are of particular importance to the load-lock system. These are the switches which indicate the load-lock arm is fully retracted and the switch which indicates the load-lock door is closed. The first of these microswitches is used to prevent mechanical damage to either the load-lock arm or the SCGV due to the valve operating when the load-lock arm is not fully retracted. The second of these switches is used to determine when the load-lock door is closed. However, due to nature of the switch, a more complex check is done before the load-lock door is confirmed to be closed. After the computer receives the initial close state, ten seconds is allowed to pass before the state is rechecked. If the state remains closed then the door is considered closed. This prevents any accidental events from triggering valve operations and gives the user time to check that the door is closed.

3.9.4 Control of the Confining Magnetic Field

The power supplies which are used to generate the confining magnetic field, outlined in section 3.5, are controlled in the same manner as the Maxigauge controllers (RS-232 communication via a serial port). Both supply types are constructed to allow an initial connection from the computer to the first supply, and then subsequent supplies connected to the last (through RS-485), referred to as daisy-chaining. This requires each supply to be assigned its own unique address.

This allows the supplies to be controlled remotely as well as their current status to be interrogated. With this information, and knowledge of the physical properties of the solenoids (listed in tables 3.1 and 3.2), the resulting magnetic field can be calculated through the application of the Biot-Savart law. As only the field along the central axis of the beamline is of interest, this can be expressed as

$$\mathbf{B}(z) = \sum_{i=1}^n \frac{\mu_0 I_i N_i}{2L_i} \times \left(\frac{z + S_i + \frac{L_i}{2}}{\sqrt{\left(z + S_i + \frac{L_i}{2}\right)^2 + R_i^2}} - \frac{z + S_i - \frac{L_i}{2}}{\sqrt{\left(z + S_i - \frac{L_i}{2}\right)^2 + R_i^2}} \right), \quad (3.7)$$

where: n is the number of solenoids, I is the current through the solenoid, N is the number of turns of the solenoid, L is the length of the solenoid, S is the relative position of the centre of the solenoid and R is the radius of the solenoid. This allows the confining magnetic field to be calculated in real time.

Solenoid Name	Power Supply	Serial Port	Address
Trap Solenoid	GEN80-19	5	7
Trap Exit Trim	GEN30-25	5	3
Transport Solenoid 1	GEN30-25	5	4
BGV Trim Coil Source Side	ZUP36-12	6	2
BGV Trim Coil Sample Side	ZUP36-12	6	1
Transport Solenoid 2	GEN30-25	5	5
Trim 2-3	ZUP36-12	6	3
Transport Solenoid 3	GEN30-25	5	6
Sample Front	GEN40-19	5	1
Sample Rear	GEN40-19	5	2

Table 3.5: Shown in this table are the addresses for the various power supplies.

3.9.5 Computer Control of the Detection System

Interfacing with the Comtech fast timing card is achieved using software, Windows Server Program and MCDWIN, provided by Comtech. The server program enables full control of the fast timing card. In addition, through a Dynamic Link Library (DLL), all the functions, parameters and data of the card can be accessed. However, the server program does not contain any visual display of the data. While MCDWIN provides this and other features, it also interfaces directly with the server program to provide full control of the fast timing card and access to the card's parameters.

One of the most useful features of the MCDWIN software is the ability to quickly fit a Gaussian curve with a linear background to a desired region of the spectra. This can be performed during a measurement, without the need for any additional analysis. This feature is used to determine the arrival time of the positron pulse during the position calibration procedure discussed previously. It can also be used to provide an estimate of the FWHM of the pulse.

The software is configured to record the time stamps of both the falling and rising edges of the pulse from the detector. This allows the implementation of a software CFD, which will be discussed in section 4.2.1. While the software does contain the ability to perform a software CFD, this is only used to display the spectra in real time. Typically, the threshold for this is set to -0.12 V, though

values up to -0.15 V or even -0.2 V can be used to reject more of the annihilation γ -rays which don't deposit sufficient energy into the scintillator.

Much like the power supplies discussed previously, the fast timing card has the ability to be controlled, through the windows server program, using the same interface. While this would allow the timing circuitry to be initiated remotely, the cost of the required software (MCDLAN) outweighs the benefits.

CHAPTER 4

ANALYSIS OF PALS DATA

The problem of extracting PALS information, in the form of lifetimes and weights, from the resulting spectrum is nontrivial. Many different software approaches have been developed and these will be briefly discussed within this chapter. However, due to the unique characteristics of the experimental setup discussed in chapter 3 (herein referred to as the CAMS Materials Beamline), a new program was developed by the author as a part of the research described in this thesis. This software offers a unique analysis technique customised to the experimental output from this apparatus.

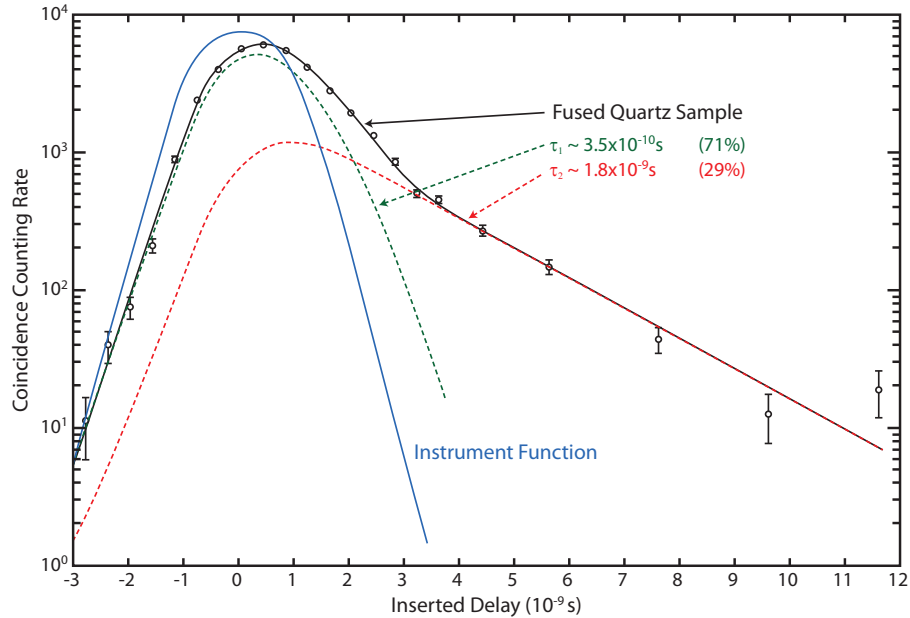


Figure 4.1: This image shows the PALS spectrum from Bell and Graham (1953) with the instrument function curve determined by allowing the positrons to impact the crystal of the detector (reproduced from Bell and Graham, 1953).

4.1 Data Analysis

A PALS spectrum is a histogram of measured annihilation times showing how long the positrons survive within the sample material. This spectrum is considered to take the form of an instrument function, $I_F(t)$, convoluted with a decay term, $D(t)$, with a constant background, B , as shown below.

$$F(t) = I_F(t) * D(t) + B \quad (4.1)$$

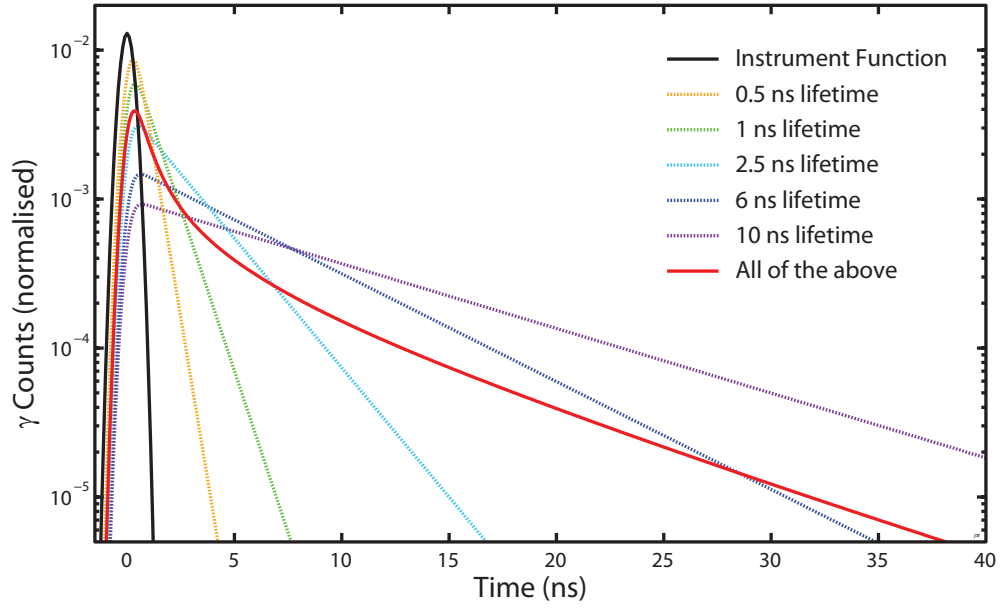
For conventional PALS, as discussed in section 2.4.1, the instrument function is typically taken to be the resolution of the detection system and timing circuitry. However, for beam-based systems this function also depends on the temporal distribution of the positron pulse. The decay term contains the desired information and is the summation of n exponential decay curves, each defined by an intensity, I_i , and lifetime, τ_i , given by

$$D(t) = \begin{cases} \sum_{i=1}^n I_i e^{\frac{-t}{\tau_i}} & t > 0 \\ 0 & t < 0. \end{cases} \quad (4.2)$$

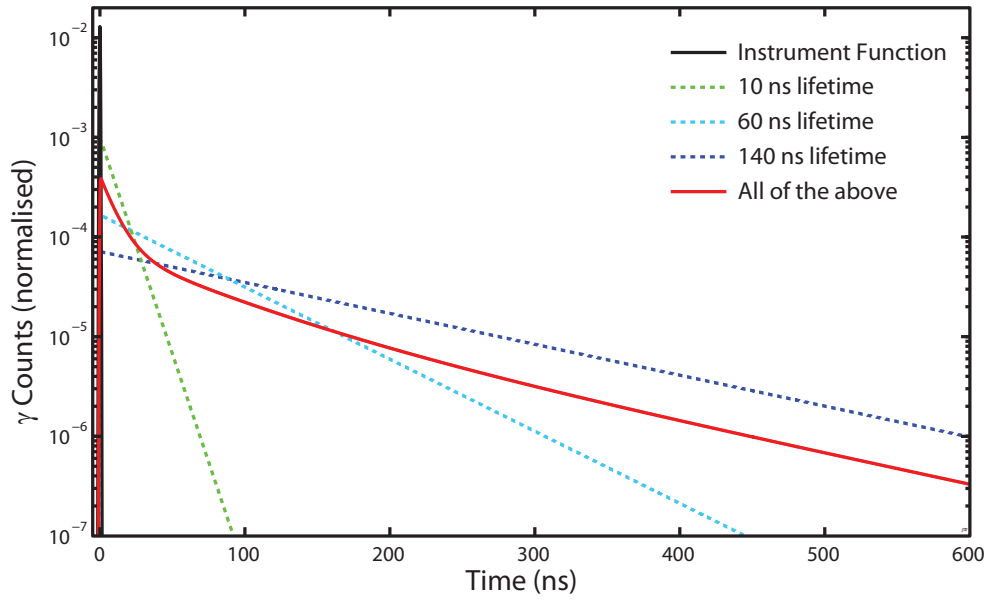
During the first PALS measurements performed by Bell and Graham (1953), the instrument function was determined by simply removing the sample and allowing the positrons to impact the detector directly. This was then compared to the spectrum collected with a sample in place; the example shown in chapter 2 (figure 2.13) is repeated in figure 4.1 with this instrument function spectrum included. It can be seen that for the setup used in these measurements the instrument function is well described by a Gaussian curve. While modern conventional PALS is performed with a different experimental arrangement, the same holds true and initially the analysis of PALS spectra assumed this, though more complex compositions are now used. An example of various lifetimes convoluted with a Gaussian instrument function is shown in figure 4.2.

4.1.1 Existing Software

The objective of any analysis program is to extract the desired information contained within the collected data; for PALS this requires solving the inverse prob-



(i) Shown here are the effects of short lifetime components.



(ii) Shown here are the effects of longer lifetime components.

Figure 4.2: Shown here is an example of a convolution of a 300 ps Gaussian instrument function with various lifetimes.

lem to determine the lifetimes, τ_i , and relative weights, I_i , of the components forming the spectrum. There are two methods of approach to this problem: either a direct deconvolution of the spectrum, or fitting a theoretical model to the experimental data. Existing PALS analysis software packages utilise both of these approaches; however, to date the second of these two methods has been the more successful.

PALSFit

PALSFit is a Windows-based PALS analysis package developed by Olsen et al. (2007) and is one of the most commonly used analysis tools for PALS data. PALSFit is a Graphical User Interface (GUI) version of the PATFIT software developed by Kirkegaard et al. (1981, 1989). The software contains two least-squares fitting modules: *Positronfit* and *Resolutionfit*. *Positronfit* is used to extract lifetime and intensity information from measured lifetime spectra, while *Resolutionfit* can be used to determine information about the instrument function of the apparatus used.

Positronfit was first developed by Kirkegaard and Eldrup (1972), using the FORTRAN programming language, and assumed the instrument function to be a single Gaussian curve. However, this was updated to ‘*Positronfit* extended’ only a few years later (Kirkegaard and Eldrup, 1974) to allow the instrument function to be comprised of up to seven Gaussian curves as described by

$$I_F(t) = \sum_{p=1}^p \omega_p \frac{1}{\sigma_p \sqrt{2\pi}} e^{-\frac{(t-\Delta t_p)^2}{2\sigma_p^2}}. \quad (4.3)$$

The total area of the instrument function is normalised to unity, as expressed by

$$\sum_{p=1}^p \omega_p = 1. \quad (4.4)$$

In this software the width, σ_p , and separation, Δt_p , of the Gaussian curves are fixed prior to the least-squares fitting routine.

Following this *Positronfit* was modified by Warburton (1978), with the resulting program referred to as ‘DBLCon’. This work aimed to allow short lifetime components, which are difficult to separate from the instrument function, to be better resolved. Rather than using the summation of several Gaussian curves to describe the instrument function, an Exponential-Sided Gaussian (ESG) is used.

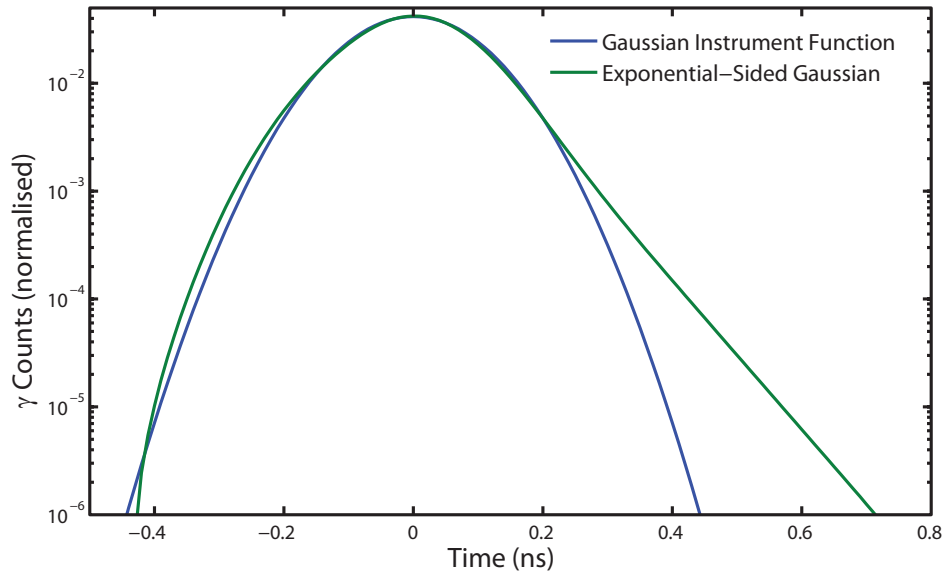


Figure 4.3: Shown here is the alteration Warburton (1978) made to the instrument function of *Positronfit*. The Gaussian instrument function (FWHM 153 ps) was replaced by an ESG, with $\tau_+ = 64$ ps, intensity 87% and $\tau_- = -42$ ps, intensity 13%.

This is a single Gaussian convoluted with two exponential lifetimes, $\tau_+ > 0$ for $t > 0$ and $\tau_- < 0$ for $t < 0$. Typical values for the parameters of the ESG were determined to be a Gaussian of FWHM 153 ps, $\tau_+ = 64$ ps with intensity 87% and $\tau_- = -42$ ps with intensity 13% (Sharma et al., 1976). Figure 4.3 shows the effect on the shape of the instrument function compared to a Gaussian curve.

In parallel to this, Virtue et al. (1978) also modified *Positronfit*, referred to as ‘Interactive *Positronfit*’. The main changes made here were to include the widths and intensities of the Gaussian curves making up the instrument function as parameters within the least-squares fitting routine. However, due to the inclusion of the additional variables, the number of Gaussian curves in the instrument function was restricted to two and the displacement between these removed.

Resolutionfit was first included in the PATFIT software package (Kirkegaard et al., 1981, 1989) to allow the resolution function to be better determined. *Resolutionfit* performs this using the same model as *Positronfit*, which is several Gaussian curves convoluted with exponential lifetimes. However, to prevent poor results the number of fitting parameters are limited by fixing the intensities of the Gaussian curves. In addition, it is advised to only include a single exponential lifetime. The results from this can then be used as the instrument function for *Positronfit*.

CONTIN

CONTIN is an analysis tool first developed by Provencher (1982) as a general tool for inverting observed data to access the desired information. This was applied to PALS data by Gregory and Zhu (1990). The method has the advantage that it avoids direct determination of the instrument function by utilising a reference material which has a single, well known lifetime. This allows CONTIN to employ a least-squares analysis to calculate a continuous distribution of lifetimes (rather than a single value) by solving the integral form of equation 4.2 as shown in equation 4.5.

$$D(t) = \int_0^{+\infty} I(\tau) e^{\frac{-t}{\tau}} d\tau \quad (4.5)$$

However, the problem is ill-posed and this often creates difficulty distinguishing between possible solutions, with each solution being equally valid based on the goodness-of-fit (Gregory, 1991).

MELT

The Maximum Entropy Lifetime Analysis (MELT) software was first developed by Shukla and Peter (1992), with subsequent updates described in a series of papers by Shukla et al. (1993, 1995, 1997). MELT uses the maximum entropy method, previously applied to ACAR by Hoffmann et al. (1991) and DBS by Kong and Lynn (1991), to analyse lifetime spectra. MELT takes the same approach as CONTIN and attempts to deconvolve the PALS spectra. This is performed using a probability distribution analysis and the application of Bayes' theorem. In order to extract a distribution of lifetimes, this requires a *likelihood* term which is determined from the data using a model function.

LTV9

LTV9 is an analysis program developed by Kansy (1996) which combines many of the techniques from preceding software. The analysis can be performed for continuous or discrete lifetimes, using the deconvolution and the fitting of a theoretical function method respectively. Deconvolution is carried out using an iterative four step process until the statistical noise within the data limits further analysis. Much like CONTIN, the solutions from the deconvolution routine are sensitive to the noise within the spectrum and often a set of equally valid solutions is obtained

rather than a unique solution. However, as the deconvolution method does not require information about the number of lifetimes contained within the spectrum, the results from this routine can be used as starting parameters for the fitting of a theoretical function. Analysis using the second method uses an instrument function similar to that described by Warburton (1978).

This software was recently updated by Kansy and Giebel (2011) to include positron trapping models within the analysis of the lifetime spectra.

Pascual

Pascual, recently developed by Pascual-Izarra et al. (2009), is an analysis program, written in the PYTHON computing language, which implements the fitting of a theoretical function to the measured data. This can be performed using two different optimisation routines: a local optimisation routine much like PALSFit or Ltv9, or a global non-linear optimisation routine. This second routine is based on the simulated annealing algorithm (Aarts and Korst, 1989) and utilises a Markov Chain Monte Carlo Bayesian Inference algorithm (Lee, 2004).

The local optimisation routine is much faster, however it is susceptible to becoming trapped within local minima rather than locating the global minima. The global optimisation routine is slower but does not suffer from this problem. However, during the final stages of optimisation, the routine converges slowly and often the results are less precise. In order to take advantage of the global optimisation routine, its results can be used as the starting parameters for the local optimisation routine. This allows solutions to be found when the local routine behaves erratically, removing the need for the user to select between possible solutions.

As the routines rely on fitting a theoretical function to the experimental data, an instrument function is used. This is described by the sum of an arbitrary number of individual functions; in most cases this takes the form of an ESG. While it is stated that an instrument function not conforming to this model can be added, support for this has not been included.

Other Software

There have been a number of other analysis techniques developed for the purpose of extracting the desired information from PALS spectra. While some have fol-

lowed the more conventional approach, such as LIFESPECFIT by Puska (1978) or POSIT by Unger (1992), attempts have also been made by Liu et al. (1995) using a stepwise regression analysis method. In addition, neural networks (Pázsit et al., 1999; Viterbo et al., 2001) and genetic algorithms (Lemes et al., 2005; Karbowski et al., 2008) have also been developed for the analysis of PALS spectra. However, the most commonly used technique remains the fitting of a theoretical model to the experimental data using an optimisation routine.

4.2 CamsFit

During the development stages of the CAMS Materials Beamline, a crude analysis program was established using the Mathworks' MATLAB environment. However, it was soon realised that the existing analysis software was unsuitable due to side-effects of the bunching method employed, discussed in section 3.4.3. Thus, another PALS analysis program, CAMSFIT, was developed by the author specifically to handle the problems encountered.

CAMSFIT carries out the analysis of PALS spectra using the method of fitting a function to the measured spectrum. As discussed, this requires the instrument function of the apparatus to be known; in other software this is described by the summation of a number of functions. An example of a Kapton measurement, performed using the CAMS Materials Beamline, is shown in figure 4.4. Kapton is a material which has been well studied due to its use for the deposition of a source solution in conventional PALS. Previously, Kapton was considered to contain only a single lifetime component of 386 ± 7 ps (Płotkowski et al., 1988); however, this has recently been resolved into two components of ~ 270 ps, with an intensity of $\sim 30\%$, and ~ 405 ps, with an intensity of $\sim 70\%$, by McGuire and Keeble (2006). As can be seen in figure 4.4, the resulting PALS spectrum is much more complex due to the influence of the temporal distribution of the positron pulse. The effect this has on resulting PALS spectra has been simulated and is shown in figure 4.5, with the same lifetime components as used in figure 4.2. This prevents the instrument function from being described by typical methods. While the *Resolutionfit* component of PALSFit is able to cope with more complex descriptions of the instrument function, the requirements here lie well outside its design parameters.

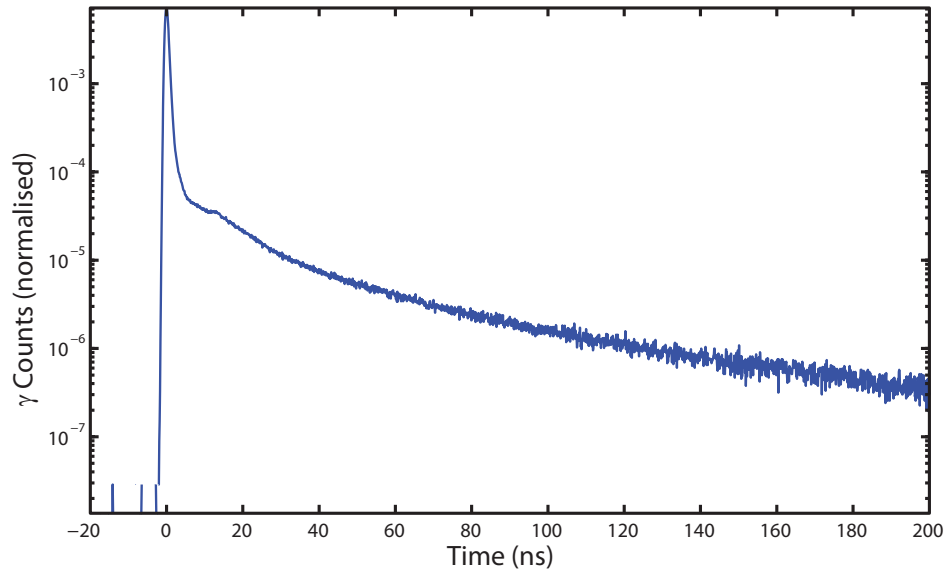


Figure 4.4: Shown here is a measurement performed on Kapton using the apparatus outlined in chapter 3. It can be seen that the spectra is heavily affected by the pulse shape.

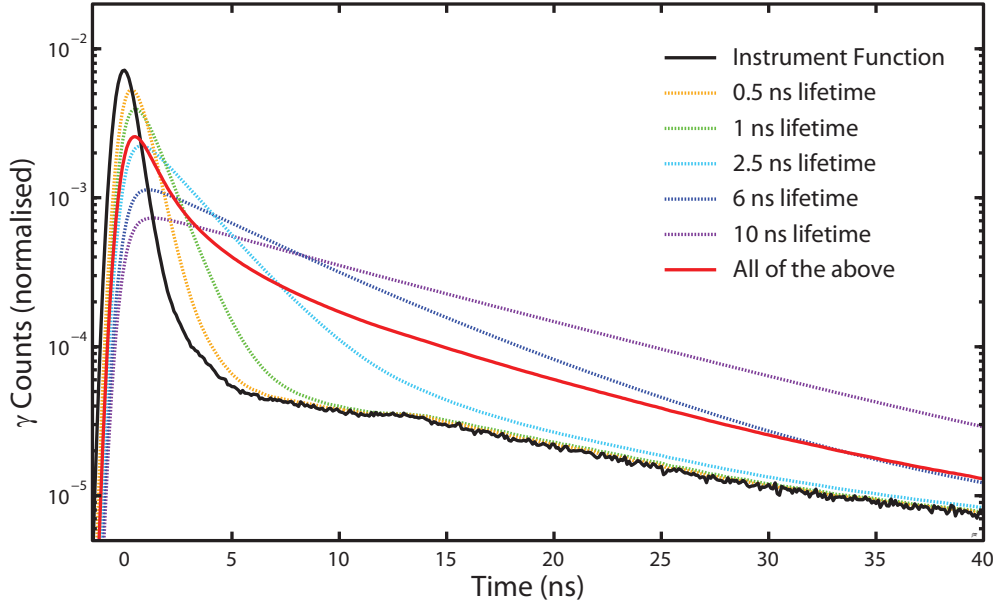
The primary aim of CAMSFIT is to provide a new technique for describing the instrument function, and carry out the analysis relative to this. This is achieved by allowing the instrument function to be described by a measurement and allowing this to be a component in the result. The operation of CAMSFIT will be described here in a chronological manner, beginning with the loading of data files before progressing to a discussion of the instrument and decay functions.

4.2.1 Loading of Data Files

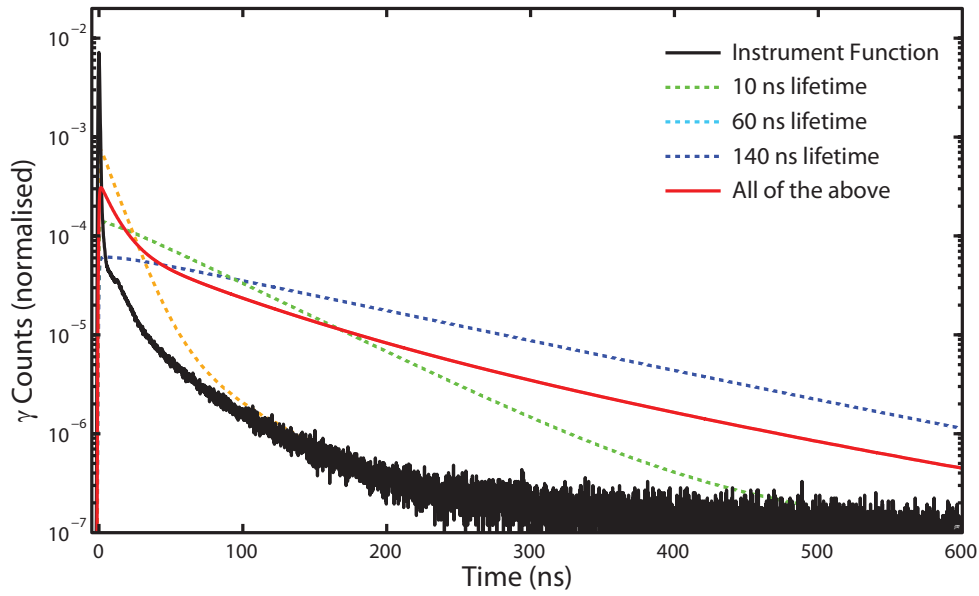
Due to the timing circuitry used, namely the Comtech fast timing card, data from the CAMS Materials Beamline is recorded in a non-standard fashion. While it would be straightforward to convert to a common format, these requirements are more easily met through the creation of a customised loading routine inside CAMSFIT. This involves the application of a sorting routine prior to the implementation of a software CFD.

Raw Data Format

Normally, PALS data is recorded as the number of annihilation events per bin, with each bin representing a known time range. However, data from the CAMS Materials Beamline is recorded in the format of timestamps, with two per annihi-



(i) Shown here are the effects of short lifetime components.



(ii) Shown here are the effects of longer lifetime components.

Figure 4.5: Shown here is an example of a convolution of a measured instrument function with various lifetimes. These examples are shown on the same scales as figure 4.2 to allow for direct comparison.

File header information (variable number of rows)	
[DATA]	
40000000	0
0	43536
40000000	43557
40000000	0
40000000	0
0	42936
40000000	42945
0	42985
40000000	42996
40000000	0

Table 4.1: Shown here is the format of the raw data as recorded by the timing system. Start signals, marking the release of the positron pulse from the trap, are recorded as ‘40000000 0’, with 40000000 indicating a rising edge and 0 the timestamp. There are three recorded events shown here, the first timestamp for each event represents the falling edge and is recorded as ‘0 *number*’, with 0 indicating a falling edge. The second time stamp, recorded as ‘40000000 *number*’, indicates the rising edge of the detection pulse. This allows the pulse width to be determined and a software CFD to be applied. The second and third events shown here have occurred within the same trap cycle.

lation γ -ray detected. These timestamps are relative to the start signal provided by the AWG (as described in section 3.7.4) and refer to the falling and rising edges of the pulse from the detector. Regardless of the detection of an annihilation γ -ray, each start signal is recorded in the raw data file. This results in the file taking the form shown in table 4.1. While this allows the resulting spectra to be chronologically reconstructed, it is of no interest for PALS measurements performed under constant conditions (as has been the case to-date).

This format results in raw data files of considerable size, with larger files exceeding 4 GB. Due to this, the files cannot be quickly read into the analysis software (without access to excessively large amounts of memory) and instead undergo a sorting routine.

Sorting Routine

As null events, trap cycles for which no annihilation γ -ray is detected, are of no interest they may be discarded from the raw data. This is achieved during the sorting routine which creates two additional files and is carried out once per raw data file. The first contains the header information from the raw data file with some additional parameters from the sorting process. The second file contains the data with null counts removed; typically this file is $<5\%$ of the size of the raw data file.

The sorting routine processes the raw data file line-by-line and, due to the large file size, usually takes several minutes to complete. Initially, the sorting routine was performed by a C++ program which completed the task faster than could be achieved within the Matlab environment. This was later updated to a PYTHON program which improved the performance further. In addition, the PYTHON program was modified to produce smaller files and impose the limitation of a single annihilation event per trap cycle. The latter of these two improvements allowed the threshold within MCDWIN, discussed within section 3.9.5, to be lowered without ringing from the detector affecting the PALS spectra. However, this also results in a small number of real events being discarded, though this effect is negligible.

Both these sorting routines are automatically called by CAMSFIT, if required, and the user can select which sorting routine to use.

Software CFD

After performing the sorting process, the resulting data files can be loaded into CAMSFIT as a large array of timestamps. This format allows subsequent operations to be performed rapidly without any time consuming loops. However, this is still a very memory intensive operation and while it could be performed line-by-line, limiting the usefulness of the sorting routine, it would be prohibitively time consuming each time the file was loaded.

The signal pulses from the detector, described in section 3.7.4, vary greatly in size depending on the energy of the annihilation γ -ray and the amount of energy it deposits into the scintillation crystal. As the Comtech fast timing card is only able to record the point at which the signal crosses an arbitrary threshold, this can result in a large timing uncertainty. This is demonstrated in figure 4.6, which

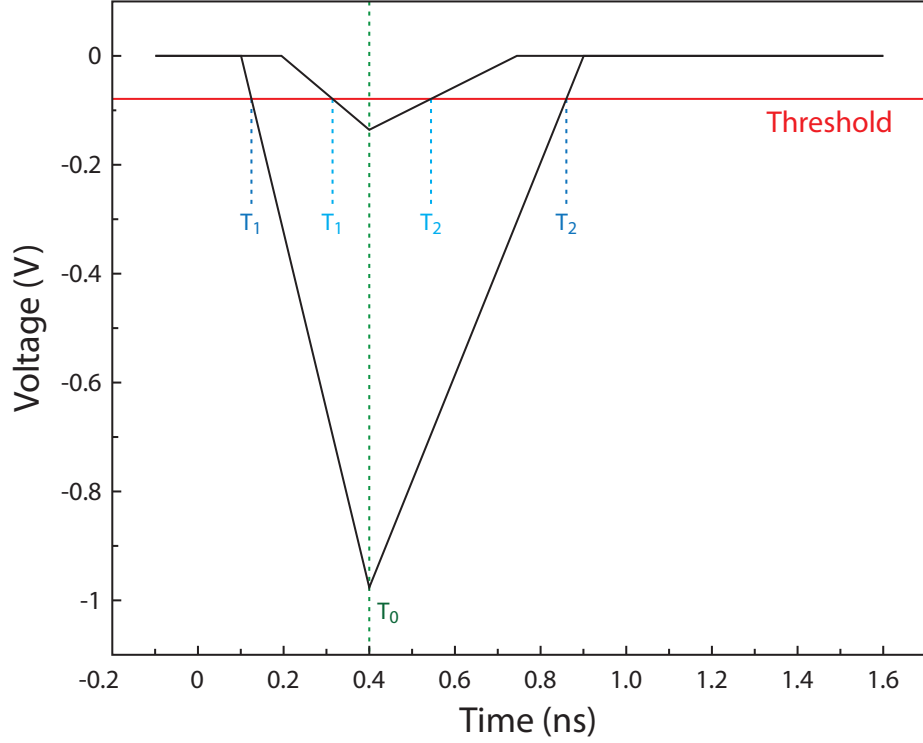


Figure 4.6: Due to the varying pulse size from the detector, the threshold crossings of the rising and falling edges are recorded to allow a software CFD to be performed. As the pulses are of a consistent shape, this allows the peak position, T_0 , to be determined using the parameters T_1 and T_2 .

shows two pulses of varying sizes which have peaks occurring at the same time. As the pulses are of consistent shape, this uncertainty can be avoided through the implementation of a CFD, which determines the peak position, T_0 . This is achieved using the timestamps at which the falling and rising edges of the signal cross the desired threshold and the fall and rise times, T_f and T_r respectively, of the detector. This is calculated using

$$T_0 = T_1 + (T_2 - T_1) \times \frac{T_r}{T_r + T_f}, \quad (4.6)$$

where T_1 and T_2 represent the timestamps of the falling and rising edges respectively.

During the software CFD process, the data is converted from the timestamp format output by the Comtech fast timing card to a more standard format of annihilation events per timing bin, with each bin spanning 100 ps (the resolution of the Comtech fast timing card). In addition to this, the data is normalised to an

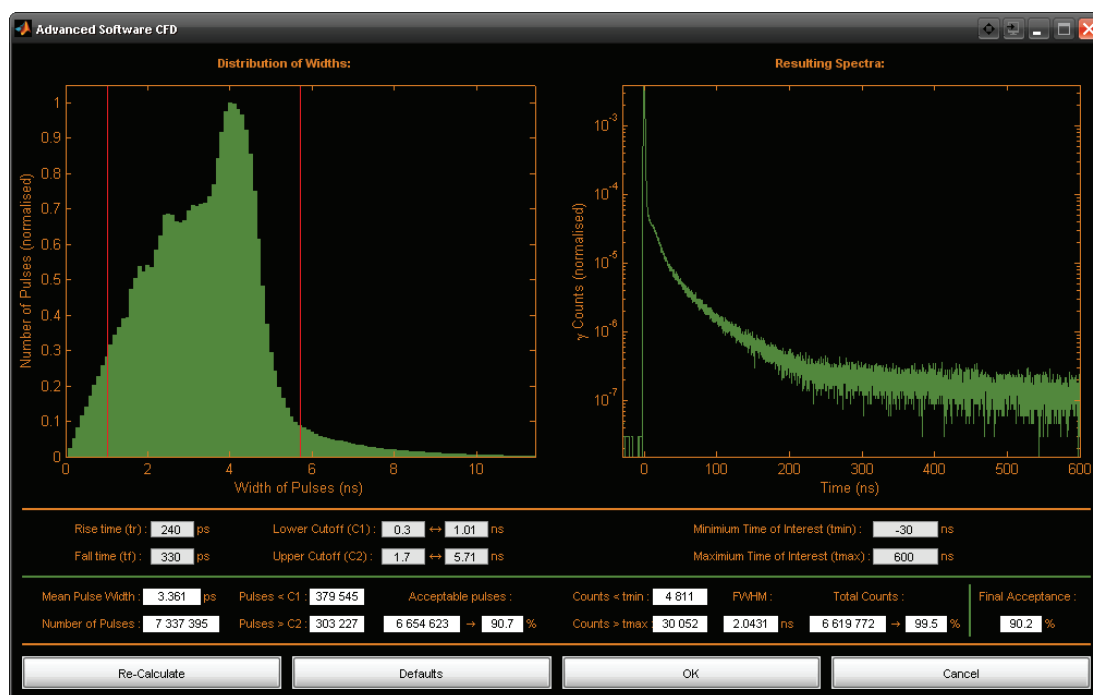


Figure 4.7: Shown here is the advanced software CFD interface with a standard data set loaded and the default parameters.

area of 0.1 counts; this is due to the bin size and all subsequent calculations being performed in nanoseconds. Under normal operation, this process is automatically implemented during the data loading process without any user input. During the process, pulses which are less than 30% or greater than 170% of the mean pulse width being discarded. Additionally, any events occurring outside the range of $-30 \text{ ns} < t < 600 \text{ ns}$ are also discarded. The effects of this range will be further discussed in section 4.2.5.

However, the user can select to use a more advanced interface, shown in figure 4.7. This interface displays the distribution of widths and allows the user access to the various parameters described above. This includes the fall and rise time of the detector, used to calculate the arrival time of the pulse. The interface allows the user to set the discrimination thresholds for the pulse width, either relative to the mean pulse width or in nanoseconds, and displays the number of pulses discarded. Access to the desired time range is provided in the same manner and the number of events discarded is also displayed. Finally, the overall acceptance rate is displayed. Because the software CFD has been developed to perform these calculations rapidly, the resulting spectrum is displayed almost immediately; for a large file these calculations take $\sim 2 \text{ s}$ on a standard computer.

4.2.2 User Options and Generation of $F(x, t)$

Much like other PALS analysis software, CAMSFIT has been designed to allow the user as much flexibility in determining the fitting parameters as possible. These parameters are typically in the form of Gaussian curves, which can be used for theoretical instrument functions, and lifetimes introduced into the decay function. In addition to these, there are three fitting parameters which are always present in the optimisation routine. These will be discussed prior to the user introduced parameters.

The first parameter, B , controls the background of $F(x, t)$ as previously introduced. CAMSFIT assumes the background to be constant; for the CAMS Materials Beamline this is true, with typical background levels of < 1 count per day. This parameter is estimated using the region prior to the arrival of the positron pulse and is typically limited to $< 1 \times 10^{-5}\%$ of the peak signal. However, the user is able to access these bounds and adjust them as required.

The second parameter, $\mathcal{S}$, controls the displacement of $F(x, t)$. As only the relative time is of interest, the peak signal is placed at $t = 0$ during the data loading procedure. However, the user is able to manually adjust this by whole bins, typically 100 ps increments, if needed. The $\mathcal{S}$ parameter allows the optimisation routine to introduce a smaller displacement. In the subsequent discussions, t will be replaced by t' , where $t' = t - \mathcal{S}$. By default, this parameter is limited to the width of a single bin, however, the user can alter these bounds.

The final parameter, $\mathcal{A}_a$, adjusts the total area of $F(x, t)$. This parameter will be discussed in more detail following an explanation of the decay function. By default, this parameter is limited to $\pm 1\%$, however once again, the user can adjust these bounds.

Instrument Function Options

Initially, CAMSFIT was a crude program, with no user interface and few options, designed to analyse the first few spectra collected by the CAMS Materials Beamline before the requirements were fully understood. During this time, CAMSFIT followed the basic format of a single Gaussian curve convoluted with a number of lifetimes. Although heavily modified, this functionality, referred to as a ‘Theoretical Function’, is still included in the current version. When using a theoretical

instrument function, the analysis performed is similar to existing software such as PALSFit, LTV9 or PASCUAL, though less sophisticated.

The instrument function takes the form of

$$I_F(x, t') = \sum_{i=1}^n I_i \frac{1}{\sigma_i \sqrt{2\pi}} e^{-\frac{(t'-T_i)^2}{2\sigma_i^2}}, \quad (4.7)$$

where $\sum_{i=1}^n I_i = 1$

and n represents the number of Gaussian curves with widths σ_i and displacements T_i . CAMSFIT allows the user to select between a single Gaussian curve ($n = 1$) or dual Gaussian curves ($n = 2$). However, an additional Gaussian curve can be introduced to account for reflections which occur in beam-based systems (as discussed in section 3.8.1). The width, relative intensity and displacement of each curve are all adjusted by the optimisation routine, allowing the user to introduce up to eight parameters within the instrument function. The user is also able to control the upper and lower bounds as well as the starting value of each curve individually. Unlike other PALS software, there is no functionality for including a source correction, required by conventional PALS to account for annihilation within the source material, as it is unnecessary for beam-based systems.

In order to account for the unusual pulse shape of the CAMS Materials Beamline, the author developed a new method for defining the instrument function. This is referred to as a ‘Measured Function’ and uses another PALS spectrum, measured under the same conditions, to define the instrument function. Initially, annealed nickel or Kapton was used as the positron lifetime within these materials is much shorter than the temporal width of the pulse. However, a variety of materials are now used depending on the samples of interest; for example, treated materials may be compared to virgin samples. While this prevents lifetimes inherent to the material from being identified, changes in the lifetime properties arising from the treatment of the sample can be. It may also be possible to determine the ‘true instrument function’ through the deconvolution of a PALS spectrum of a well characterised sample. This functionality is expected to be included in some form at a later date.

A measured instrument function can be implemented in two ways; these are referred to as a ‘Data Convolution’ and a ‘Function Convolution’. Both methods utilise a PALS measurement, rather than a theoretical function, to describe

the instrument function. The data convolution method uses a measurement to directly describe the instrument function. This method introduces no fitting parameters and doesn't have any further options. It is possible to include smoothing of the data, however, preliminary testing shows this to have little effect, if any, on the analysis.

The second method, a function convolution, is a more complicated technique which is comparable to the *Resolutionfit* component of PALSFit. Rather than using the measurement directly, a function is fitted. As the pulse shape closely resembles a typical PALS spectrum, this function takes the form $F(x, t')$ already discussed. The $I_F(x, t')$ component is described using a theoretical instrument function, as discussed in equation 4.7 above. In order to describe the measurement well, an additional Gaussian curve must be included to account for reflections from the sample. The decay function component, $D(t)$, is constructed using the same algorithm discussed in the following section.

Decay Function Options

Within CAMSFIT, the decay function takes the standard form as shown in equation 4.2. This can be expressed using the Heaviside function, $H(0)$, and a decay rate, where $d = \frac{1}{\tau}$, as

$$D(t) = \sum_{i=1}^n H(0) I_i d_i e^{-td_i}, \quad (4.8)$$

$$\text{where } \sum_{i=1}^n I_i = 1. \quad (4.9)$$

However, as mentioned previously the intensity of the lifetime components, T_i , is expressed relative to the instrument function. This is achieved by including a Dirac delta function, $\delta(t)$, in the decay function to allow the instrument function to appear as a component in the results. By including the $\mathcal{A}_a$ parameter, which allows the optimisation routine to adjust the total area of decay function, $D(t)$ then takes the form

$$D(t) = I_0 \delta(t) + \sum_{i=1}^n H(0) I_i d_i e^{-td_i} \quad (4.10)$$

$$\text{where } \sum_{i=0}^n I_i = 1 + \mathcal{A}_a. \quad (4.11)$$

As a result, for spectra which are indistinguishable from the instrument function no lifetime components are returned; instead $I_0 = 1$. To allow the optimisation

routine to displace the $F(x, t)$ function when t' is used, the $\delta(t)$ and $H(0)$ functions are replaced by a narrow Gaussian curve and an error function bounded between 0–1 respectively. $D(t')$ is then expressed as

$$D(t') = I_0 \frac{1}{\alpha\sqrt{2\pi}} e^{\frac{-t'^2}{2\alpha^2}} + \sum_{i=1}^n \frac{\text{erf}(\beta t') + 1}{2} I_i d_i e^{-t' d_i}. \quad (4.12)$$

The constants α and β control the width of the Gaussian curve and error function respectively. α can be accessed by the user, though it cannot be passed to the optimisation routine as a parameter. The second constant, β , is fixed within the program and cannot be adjusted by the user.

The number of lifetime components within the decay function, n , is controlled by the user, though with the restriction $n \in \mathbb{Z}^*$. Primarily, lifetime components are introduced by specifying the number of components and a range (in ns) over which to distribute them; a secondary method also exists and this will be discussed later. When using the primary method, the user can select to pass the decay rates of the lifetime components to the optimisation routine as parameters or fix them at a constant value. By using this functionality, it is possible to perform two types of analysis, a variable lifetime analysis and a fixed lifetime analysis. These will be discussed here including the default starting values and bounds of any parameters to be optimised.

A variable lifetime analysis typically includes no more than five lifetime components, though no upper limit is placed on this value within the program. Each component introduces two parameters to the optimisation routine, a decay rate and an intensity. By default, the starting value of the decay rates are evenly spaced across the range provided by the user. For all decay rates, the upper bound (minimum lifetime) is restricted to 100 ns^{-1} (10 ps) while the lower bound (maximum lifetime) is set using the range provided by the user. The starting value of the intensities default to 0.1% (0.001), with this parameter bounded between 0%–100% (0–1). The $D(t')$ function is constructed to preserve the condition expressed in equation 4.11. When performing this type of analysis, if more lifetime components exist within $D(t')$ than required to describe the experimental data, several decay parameters will converge to the same value. When this occurs, the intensity of this decay rate is divided among the matching components and displayed to the user in this format to avoid confusion.

A fixed lifetime analysis can include several hundred lifetime components, though once again no upper limit is placed on this value. Unlike the variable lifetime analysis, each component only introduces one parameter, the intensity, into the optimisation routine. The decay rates are instead fixed at values evenly spaced across the range specified by the user. The starting value and bounds of each intensity default to the same values as specified for a variable lifetime analysis.

Lifetime components can also be introduced into $D(t')$ using a secondary method, which is independent of the method detailed above. This method allows the user to introduce up to five components which have specific (fixed) decay rates. The intensity of each component can either be passed to the optimisation routine as a parameter or fixed at a specific value. Once again, when the intensities are included as parameters, the starting values and bounds default to the same values.

As discussed above, each parameter is passed to the optimisation routine with a starting value, an upper bound and a lower bound. While reasonable default values are generated as discussed, the user is able to alter these. For up to ten parameters (including B , $\mathcal{S}$ and $\mathcal{A}_a$) these values can be set for each parameter separately. If more than ten parameters exist, the lifetime components are grouped into three categories: decay rates, intensities of primary components and intensities of secondary components. This prevents the user from defining the starting value and bounds for each parameter individually, instead these parameters can only be specified for the group. However, due to the grouping, the starting value for any decay rates is no longer accessible.

4.2.3 Nonlinear Optimisation Routine

The optimisation is performed using Matlab's in-build *lsqcurvefit* function. This function is designed to solve nonlinear data-fitting problems using a least-squares approach using the same algorithm as the *lsqnonlin* routine. The algorithm attempts to find the values for the parameters, x , within the function $F(x, t)$ which best solve

$$\min_x \|F(x, t) - \text{Data}\|_2^2 = \min_x \sum_i (F(x_i, t_i) - \text{Data}_i)^2. \quad (4.13)$$

However, CAMSFIT is constructed to allow other optimisation routines, such as those developed by Pascual-Izarra et al. (2009), to be easily implemented. To date, the *lsqcurvefit* function has performed satisfactorily for almost all data sets and other routines have not been required.

4.2.4 Error Analysis

Upon completion of the optimisation routine, the errors of the returned values can be calculated. This is performed using the Jacobian from the optimisation function and the *nlparci* function from Matlab's Statistics tool. If the toolbox is installed, the user is queried if they wish to calculate errors. The error values are returned in the form of one standard deviation confidence intervals.

4.2.5 Region Of Interest

Typically, the raw data files contain information for events which extend from ~ -800 ns to ~ 1500 ns. During the software CFD this range is normally reduced to -30 ns to 600 ns, though these limits can be altered through the advanced software CFD interface. Even with this reduced data range, often the lifetime information is usually only contained within a small region near the peak of the spectrum. As such, computation time can be saved by only requiring the optimisation routine to fit to a Region Of Interest (ROI). By default, the function is fitted to the full range of the loaded data (-30 ns -600 ns). However, the user can reduce this range, either graphically or numerically without affecting the loaded data, to only include the region containing the lifetime information of interest. As altering the ROI doesn't alter the instrument function, $I_F(t)$, or the decay function, $D(t)$, the optimisation routine can be interrupted, the ROI altered, and then the routine resumed.

4.2.6 Conversion from Lifetimes to Poresizes

Under certain conditions, the positron lifetime can be converted to the size of an open volume within the material. This conversion is carried out using the TE or the RTE model as discussed in section 2.4.3. While the TE model can be easily solved, the RTE model requires a more complex approach. The method used in CAMSFIT follows the same approach developed by Pascual-Izarra et al. (2009) and uses MATLAB's *fsolve* function.

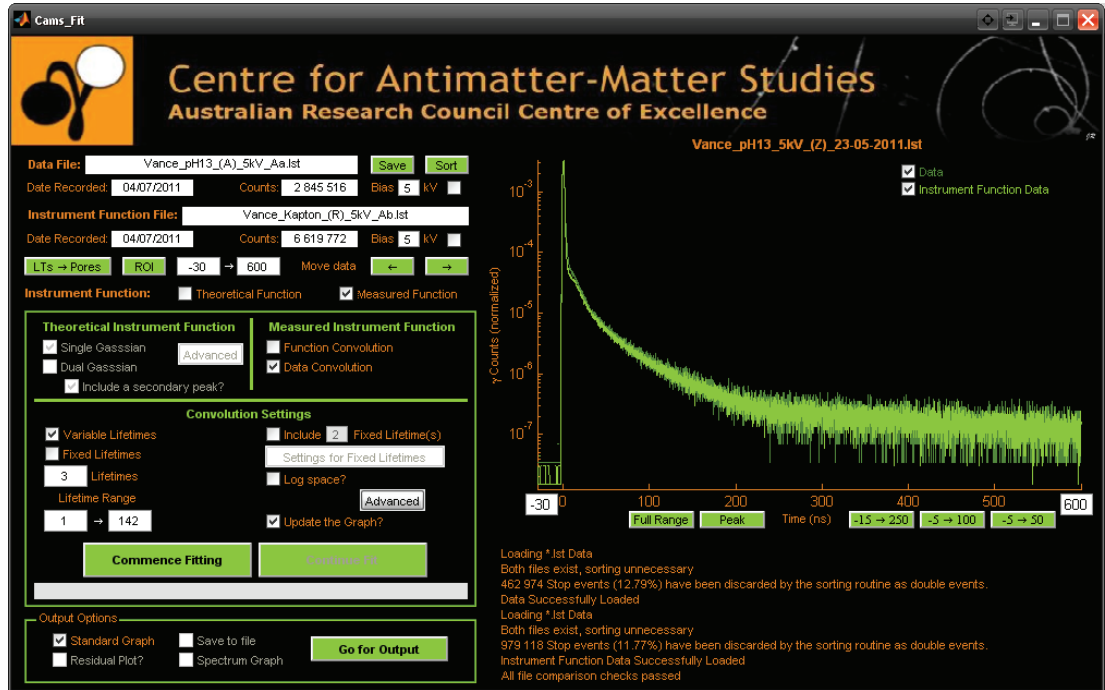


Figure 4.8: Shown here is the CAMSFIT GUI with an instrument function and a data file loaded.

4.2.7 The CamsFit GUI

CAMSFIT has been developed to provide a simple GUI. This allows the user to easily configure the desired analysis without a complete understanding of the underlying theory. All of the options discussed within this section can be accessed through simple user inputs or checkboxes on the GUI. During the optimisation routine, the convergence of the function is shown graphically at each iteration. This allows the user to observe the convergence and, if required, alter the starting conditions to improve the convergence or avoid local minima. This can also be disabled to accelerate the performance of the optimisation routine. A screen shot of the GUI is shown in figure 4.8.

4.2.8 Testing of CamsFit

The testing of PALS analysis software can be carried out using spectra with known lifetime components. Spectra meeting these requirements can be derived from the measurement of samples with known positron lifetimes. However, this also introduces experimental error, both from the determination of the positron lifetime within the sample material and from the measurement, into the spectra

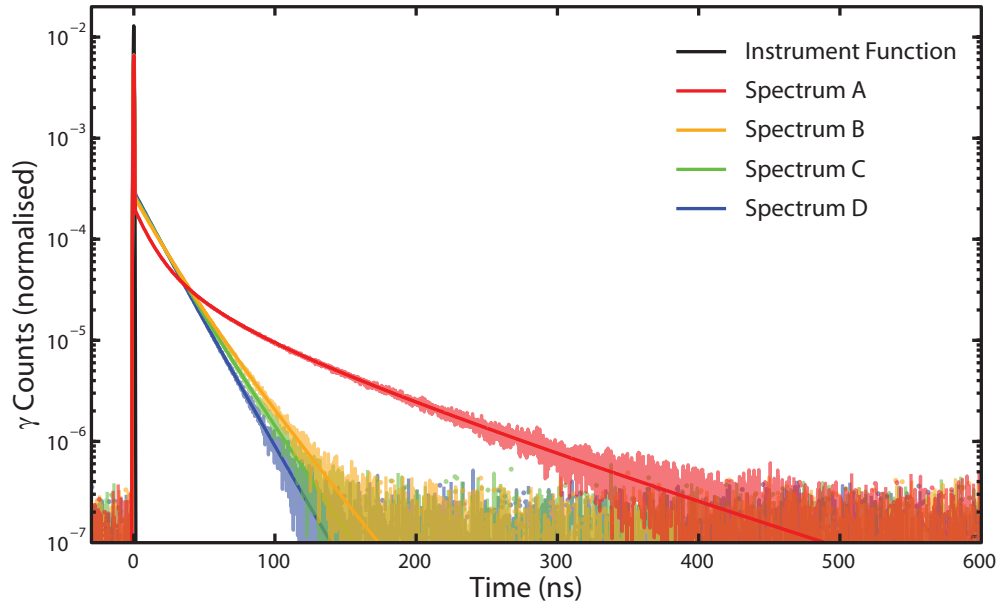
which complicates the analysis. In order to avoid these complications, testing can be performed through the analysis of simulated spectra which have known solutions. This allows the analysis program to be tested in a systematic manner to identify any problems or limitations of the software. Here, spectra have been simulated using a separate program before being loaded into CAMSFIT in the same manner, bypassing the sorting and software CFD processes, as other data files. Most existing PALS software has been tested using the method outlined by Shukla et al. (1993) for the testing of MELT. This same approach was also used by Kansy (1996) and Pascual-Izarra et al. (2009) for the testing of LTV9 and PASCUAL respectively. Initially, a similar approach is used here to test CAMSFIT before a wider range of spectra are used. While CAMSFIT has been tested over a wide variety of spectra, the scenarios included here are used to demonstrate the abilities and limitations of the software.

Due to the inclusion of a narrow Gaussian curve in $D(t')$, which as previously discussed allows the instrument function to be output as a component, CAMSFIT performs poorly for spectra generated with $I_0 = 0$. As PALS spectra from the CAMS Materials Beamline are always analysed with respect to the instrument function, simulated spectra will be comprised of 50% instrument function ($I_0 = 0.5$) and 50% lifetime components.

The first series of spectra generated employs a theoretical instrument function composed of a single Gaussian curve. This was convoluted with several lifetime components as detailed in table 4.2. After calculating the simulated spectrum, Gaussian noise was added to simulate spectra which contained 10^6 counts. The resulting analysis is also shown in table 4.2.

The same spectra can be simulated with a measured instrument function, rather than a Gaussian curve, to determine any effects this may have on the analysis. As shown in figure 4.3ii, due to the instrument function extending well past 100 ns the spectra with lifetime differences of 3 ns are more difficult to visually distinguish. However, the lifetime components can still be extracted from the spectra by CAMSFIT with similar precision as shown in table 4.3.

As expected, the shape of the instrument function affects the ability to resolve short lifetime components. This can be demonstrated through the simulation of spectra which contain a single short, <0.5 ns, lifetime component. Three such spectra have been simulated as outlined in table 4.5. The extraction of these short lifetimes is complicated by the existence of local minima to which the

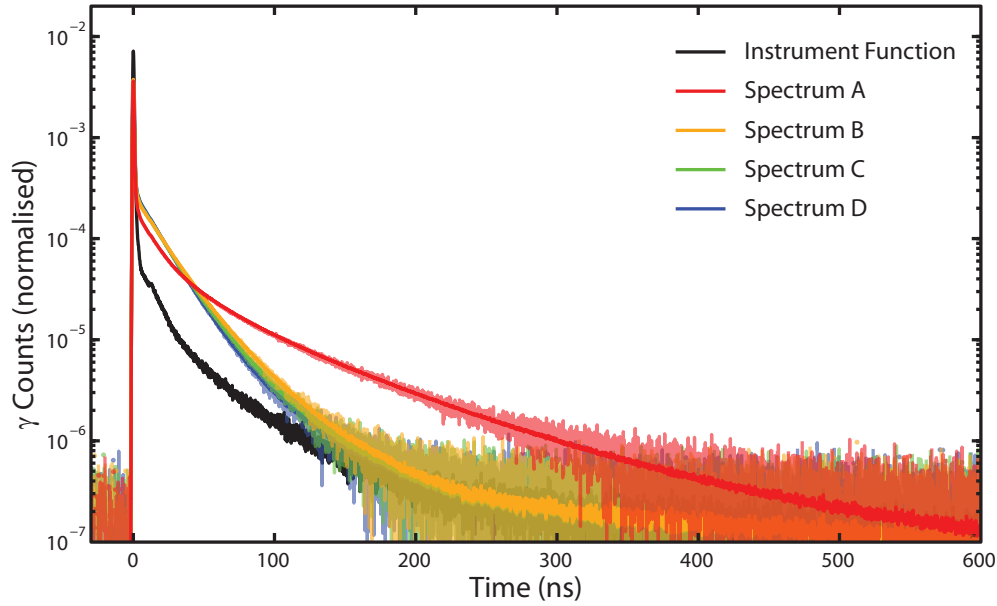


(i) Shown here are the spectra generated using a single Gaussian curve as the instrument function and the lifetime components shown in table 4.2.

Method	τ_1 (ns) I_1 (%)	τ_2 (ns) I_2 (%)	τ_3 (ns) I_3 (%)	τ_4 (ns) I_4 (%)
Simulation A	10 12.5	25 12.5	60 12.5	100 12.5
CAMSFIT	9.99 ± 0.03 12.4 ± 0.13	24.9 ± 0.66 12.7 ± 0.60	61.4 ± 7.65 12.2 ± 3.69	97.7 ± 7.11 12.6 ± 4.31
Simulation B	15 25	25 25		
CAMSFIT	15.0 ± 0.02 24.8 ± 0.16	24.9 ± 0.05 25.0 ± 0.16		
Simulation C	15 25	22 25		
CAMSFIT	15.0 ± 0.04 25.4 ± 0.35	22.1 ± 0.07 24.4 ± 0.35		
Simulation D	15 25	19 25		
CAMSFIT ^a	14.9 ± 0.10 23.6 ± 1.43	18.9 ± 0.13 26.2 ± 1.43		

Table 4.2: Shown here are the results from testing CAMSFIT with spectra generated using a theoretical instrument function. These spectra, shown in figure (i) above, include Gaussian noise at a level to represent a measurement of 10^6 counts.

^aThis reached the maximum number of iterations prior to converging and required the fitting procedure to be run a second time.



(ii) Shown here are spectra with the same lifetime components as table 4.2, generated using a measurement of Kapton as the instrument function.

Method	τ_1 (ns) I_1 (%)	τ_2 (ns) I_2 (%)	τ_3 (ns) I_3 (%)	τ_4 (ns) I_4 (%)
Simulation A	10 12.5	25 12.5	60 12.5	100 12.5
CAMSFIT	10.0 ± 0.03 12.4 ± 0.12	24.8 ± 0.65 12.2 ± 0.64	57.1 ± 6.15 10.6 ± 1.98	95.3 ± 4.0 14.4 ± 2.63
Simulation B	15 25	25 25		
CAMSFIT	15.0 ± 0.02 24.7 ± 0.15	25.0 ± 0.04 25.0 ± 0.15		
Simulation C	15 25	22 25		
CAMSFIT	15.1 ± 0.04 25.7 ± 0.34	22.2 ± 0.67 24.0 ± 0.34		
Simulation D	15 25	19 25		
CAMSFIT	14.9 ± 0.10 23.2 ± 1.38	18.9 ± 0.12 26.5 ± 1.38		

Table 4.3: Shown here are the results from testing CAMSFIT with spectra generated using a measured instrument function. Once again, the simulation included Gaussian noise (in addition to the noise in the instrument function) at a level to represent a measurement of 10^6 counts, these spectra are shown in figure (ii) above.

optimisation routine converges when the default starting parameters are used. When this occurs, a simple visual comparison of the fit can be used to determine that the optimal values have not been reached. The residual of the optimisation can also be used as an indicator, however, when experimental spectra are analysed often the visual comparison is more informative. When more reasonable starting parameters are used, as outlined in table 4.4, such solutions can be avoided.

With experimental spectra, these very short lifetime components are often unresolvable in spectra measured by the CAMS Materials Beamline. Under normal operating conditions, lifetimes less than 0.3 ns are difficult to distinguish due to effects caused by the drift in the experimental conditions. This drift causes very slight changes in the temporal distribution of the positron pulse which directly affects the PALS spectra. In addition, as no deconvolution of the instrument function is performed, and the materials used to determine the instrument function normally contain lifetimes similar to these values, little can be determined about the relative intensities of any resolved components. Also, if the target material contains only a single lifetime component of equal or less intensity and of greater or equal decay rate (shorter or equal lifetime) than the instrument function, CAMSFIT is unable to perform the analysis due to the restrictions previously described. Such samples have not yet been encountered; however, performing the analysis in reverse, analysing the instrument function spectrum with respect to the target material, should successfully extract the difference.

Parameters	Lifetime (ns)		Weight (%)	
	Initial Value	Range	Initial Value	Range
Default for a single component	71.5	0.01–142	0.1	0–100
For a single short component	0.5	0.01–1	25	0–100
Default for two components	1.0, 142	0.01–142	0.1	0–100
For two short components	0.1, 1	0.01–1	25	0–100

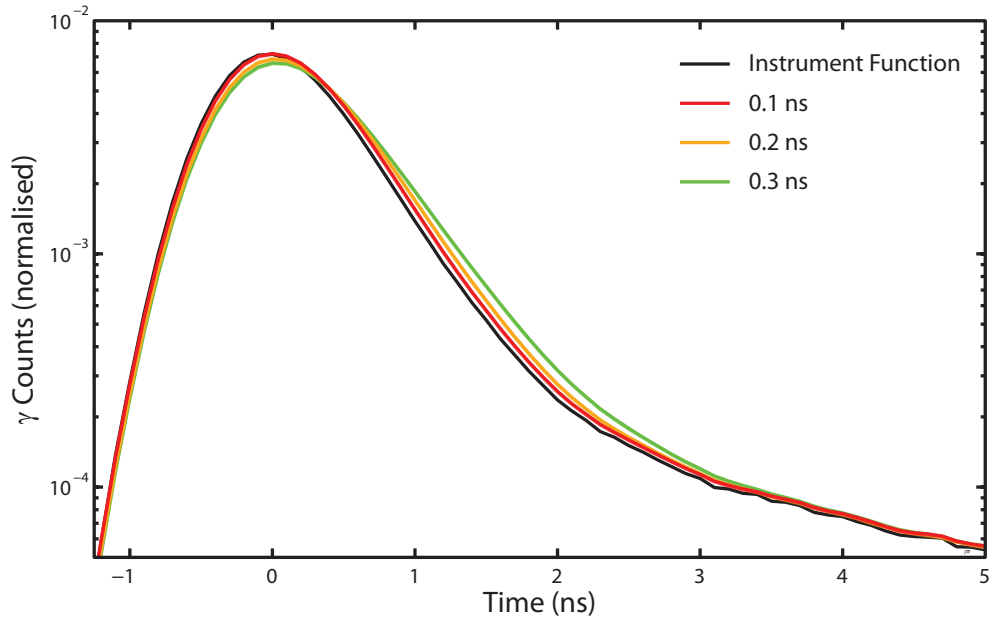
Table 4.4: Shown here are the default starting parameters when optimising with a single lifetime component. Also shown are the parameters used to resolve the short lifetime components simulated in table 4.5.

While CAMSFIT can successfully extract one short lifetime component, problems can be encountered when attempting to resolve two short components from the same spectrum when using a measured instrument function. This can be demonstrated using the two spectra detailed in table 4.6. The first spectrum can be successfully resolved into two lifetime components when using reasonable starting values. However, when the difference between the decay rates is reduced (as demonstrated in the second spectrum), CAMSFIT is unable to successfully resolve the components. With better starting values, this second spectrum can also be successfully resolved; however, for real spectra this becomes very subjective and often difficulties are encountered when distinguishing between several possible solutions. While this problem is still encountered when using an instrument function with a narrower FWHM, shorter lifetimes with smaller differences can be more easily resolved.

4.2.9 Summary of CamsFit

CAMSFIT employs a new analysis technique for extracting lifetime information from PALS spectra. While CAMSFIT provides no advantage for spectra collected using a conventional PALS arrangement, the influence of the pulse shape in beam-based spectra hinders the performance of existing analysis software. This problem is overcome by allowing the instrument function to be defined by a measurement rather than assuming a theoretical function. However, care must be taken selecting the material used. Presently, no deconvolution of the instrument is performed, though in the future this functionality is expected to be added to allow the instrument function to be determined more accurately. This will also allow short lifetime components to be determined with more confidence.

At this stage only a nonlinear optimisation routine is implemented; this can result in difficulties distinguishing between possible solutions for complex spectra. However, the program has been designed to allow other optimisation routines to be easily implemented in future updates, for example Pascual-Izarra et al. (2009). In addition, loading algorithms for data files of different formats can be added to allow spectra from a variety of systems to be loaded and analysed.



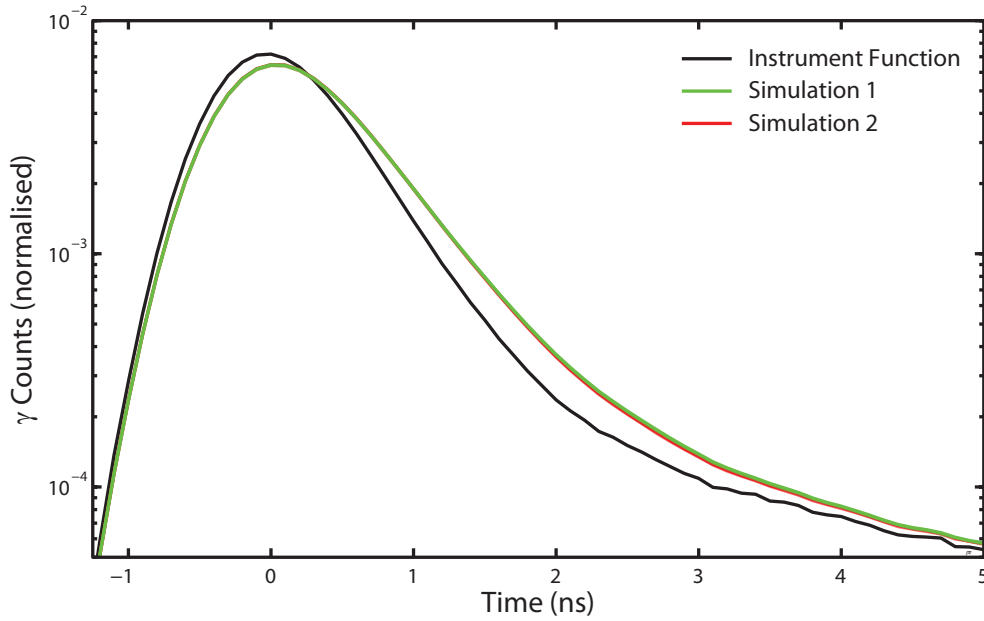
(iii) Shown here are the spectra generated using a measured instrument function and the lifetime components shown in table 4.5.

Method	τ_1 (ns)	I_1
Simulation	0.1	50
CAMSFIT ^a	0.195 ± 815	$1.3 \times 10^{-4} \pm 0.91$
CAMSFIT ^b	$0.1 \pm 2 \times 10^{-5}$	49.8 ± 0.01
Simulation	0.2	50
CAMSFIT ^a	0.293 ± 0.0014	21.3 ± 0.15
CAMSFIT ^b	$0.2 \pm 8 \times 10^{-6}$	49.8 ± 0.002
Simulation	0.3	50
CAMSFIT ^a	0.367 ± 0.001	32.7 ± 0.12
CAMSFIT ^b	$0.3 \pm 7 \times 10^{-6}$	$49.8 \pm 8 \times 10^{-4}$

Table 4.5: Shown here are simulated spectra, using a measured instrument function, with a single short (< 0.5 ns) lifetime component; these spectra are displayed in figure (iii) above. Once again, the simulation includes Gaussian noise at a level to represent a measurement of 10^6 counts, though due to the time displayed this is not visible. The ability of CAMSFIT to resolve these lifetime components is demonstrated, though the optimisation conditions must be adjusted.

^aUsing the default parameters as outlined in table 4.4.

^bUsing more reasonable starting parameters as outlined in table 4.4.



(iv) Shown here are two spectra which each contain two lifetime components <1 ns, generated using a measured instrument function.

Method	τ_1 (ns) I_1 (%)	τ_2 (ns) I_2 (%)
Simulation 1	0.260 25.0	0.640 10.0
CAMSFIT ^a	$0.297 \pm 5.7 \times 10^3$ 0 ± 3.01	0.434 ± 0.013 24.9 ± 2.62
CAMSFIT ^b	$0.260 \pm 4.5 \times 10^{-4}$ 24.7 ± 0.0473	0.639 ± 0.00139 9.93 ± 0.0542
Simulation 2	0.260 25.0	0.6 10.0
CAMSFIT ^a	0.424 ± 0.00697 24.8 ± 0.228	0.885 ± 0.0936 0 ± 0.359
CAMSFIT ^b	0.178 ± 0.015 11.7 ± 0.75	0.451 ± 0.0073 22.3 ± 0.931

Table 4.6: Shown here are the simulated spectra which contain two lifetime components, both <1 ns, and Gaussian noise at a level to represent 10^6 counts; the spectra are displayed in figure (iv) above. Spectra of this sort presents a challenge to CAMSFIT, particularly due to the effect of the broad instrument function (when compared to the resolutions achievable by conventional PALS apparatus).

^aUsing the default parameters as outlined in table 4.4.

^bUsing more reasonable starting parameters as outlined in table 4.4

CHAPTER 5

RESULTS

5.1 Zircon

In conjunction with: E. R. Vance, J. Davis, I. Karatchevtseva and R. B. Knott of the Australian Nuclear Science Technology Organisation (ANSTO), P. Gaugliardo from the CAMS node at the University of Western Australia and M. Hang of the University of Cambridge, an in-depth study of eight zircon samples was conducted. These were naturally occurring zircon crystals which were roughly elliptical in shape, with the smallest sample ~ 5 mm down the long axis. Samples were halved to produce a flat surface for examination; these surfaces were polished to a $1\text{ }\mu\text{m}$ diamond finish. In this study, PALS was used to determine the presence of any void type defects in radiation-damaged zircons that were also characterised by several other techniques.

During this study, four samples underwent annealing treatments at 700°C and 1200°C . At each stage, PALS and Raman spectroscopy were carried out to determine the effect on the crystal structure.

5.1.1 Background

Zirconium silicate, often referred to simply as zircon, is a ubiquitous trace mineral and the most frequently occurring form of the element zirconium. Zircon has a chemical composition of ZrSiO_4 and forms a tetragonal crystal, as depicted in figure 5.1, which decomposes to ZrO_2 and SiO_2 at $\sim 1600^{\circ}\text{C}$. Typically crystals are only small in size (< 1 mm), however they can grow to > 10 mm. Zircon crystals exist in a variety of colours, from various shades of yellow and red through to green and blue, and can also be colourless, referred to as ‘Matura diamonds’.

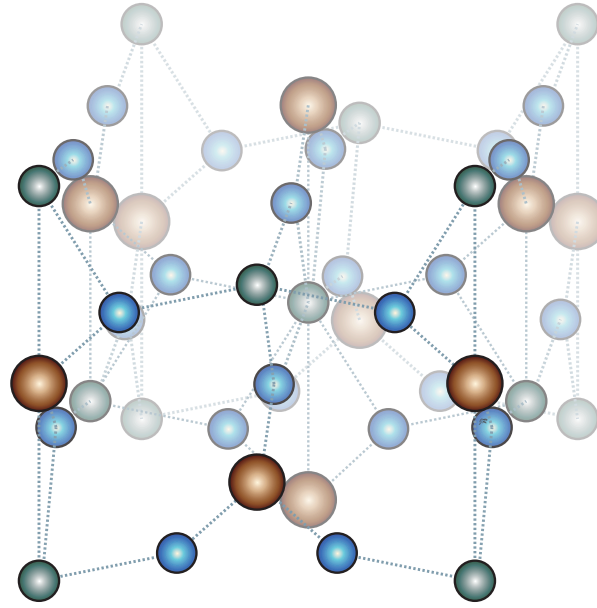


Figure 5.1: Shown here is the zircon unit cell with green representing zirconium, maroon representing silicon and blue representing oxygen.

While larger transparent specimens are typically used as gemstones, zircons are primarily used as an opacifier in decorative ceramics (Nielsen and Wilfing, 2010). However, due to their high resistance to mechanical and chemical disintegration, they also have a wide range of applications in industry. Zircons are of particular interest due to their ability to accept high-field-strength elements, such as hafnium, thorium or uranium, as substitutional impurities in place of zirconium. Because of this, natural zircons always contain small amounts of these elements which can be used for radiometric dating.

One of the proposed methods to store nuclear waste (Ewing et al., 2004) and weapons-grade plutonium (Muller and Weber, 2001) is to immobilise it within crystal lattice structures, such as ceramics. However, the effects of the radioactive decay often lead to amorphisation of the crystalline material over geological periods of time (Ewing et al., 1988). This gradual restructuring leads to changes in the physical and chemical properties of the storage medium (Weber et al., 1988); for the immobilisation of radionuclides these changes are often undesirable. In minerals such as zircon, these processes have been present since the samples formation. Such samples provide an opportunity to study the effect of these processes over the long periods of time which the radioactive waste must be stored.

Low density, amorphous zircons were well known before the 1950s; however, it wasn't until research by Pellas (1954), and later Holland and Gottfried (1955), that the underlying process was realised. Their research showed that as natural, crystalline zircons suffer radiation damage from self-irradiation, they undergo amorphisation. This damage causes a decrease in the density, up to ~16%, and a broadening, and ultimately vanishing, of the X-ray diffraction peaks. This expansion, caused by the accumulation of damage, is undesirable as it can lead to micro-scale cracks and the subsequent release of immobilised radionuclides. In zircons, this damage has been investigated using Transmission Electron Microscopy (TEM) (Chakoumakos et al., 1987; Bursill and McLaren, 1966), solid state ^{29}Si Nuclear Magnetic Resonance (NMR) (Farnan et al., 2003, 2007), infrared and Raman spectroscopy (Wasilewski et al., 1973; Vance, 1975; Zhang et al., 2000), as well as other techniques. The consensus has been that the lattice damage is largely caused by the ~80 keV recoil α -nuclei, which have a range of ~20 nm, rather than the higher energy ~5 MeV α -nuclei. If enough radioactive impurities are present in the sample, the damage gradually aggregates until all traces of crystallinity vanish. However, this process is not completely understood and there is some debate regarding whether the damage occurs quasi-continuously or in stages (Chakoumakos et al., 1987; Wasilewski et al., 1973; Vance, 1975).

During the TEM studies performed by Chakoumakos et al. (1987), voids of 50–100 nm were observed in a severely damaged zircon. However, in the same study no voids were seen in a second sample which had received a similar α -dose. More recently a Small-Angle X-ray Scattering (SAXS) study by Radlinski et al. (2003); Rios and Salje (2004); Rios et al. (2005) investigated the properties of zircons which had received a range of α -doses through self-irradiation. Samples which had incurred in excess of half the α -dose required for full amorphisation, $\sim 10 \times 10^{18} \text{g}^{-1}$, showed evidence of regions ~1 nm in diameter which had a high-density contrast to the surrounding matrix. These regions have been attributed to voids which, due to general lattice damage, are unobservable using TEM.

5.1.2 SEM Microanalysis

In this study, Scanning Electron Microscope (SEM) microanalysis was carried out to determine the elemental composition of the zircon crystals. Samples were mounted in epoxy resin and ~5 nm of carbon was evaporated onto the surface

Sample	HfO ₂	ThO ₂	UO ₂	α -dose ($\times 10^{18}\text{g}^{-1}$)	Provenance
Zircon 10	0.91	<0.01	0.16	6.5	—
Zircon 11	1.64	<0.01	0.24	4.0	—
Zircon 19	0.94	<0.01	0.43	2.1	—
Zircon 26	0.90	<0.01	0.21	4.5	—
D23524	2.3	0.1	0.35	~ 3	Sri Lanka
D29620	0.44	0.2	<0.05	~ 1	Madagascar
Cam27 ^a	2.81	0.05	0.36	5.6	Sri Lanka
Cam27 ^b	2.6	0.1	0.35	—	
No.2 ^c	1.86	0.05	0.47	7.0	—
No.2 ^b	1.7	0.2	0.6	—	—

Table 5.1: Shown here is the sample information for the zircon samples studied. The concentrations of hafnium and uranium substitutional impurities, expressed as percentages, have been determined by SEM microanalysis. The α -dose has been determined by Raman scattering and estimates from X-ray diffraction; the α -dose required for complete amorphisation is $\sim 10 \times 10^{18}\text{g}^{-1}$.

^aDetermined by Zhang et al. (2000).

^bResults from this study; the data has been averaged over 5–6 points on polished samples.

^cDetermined as part of the study by Trachenko et al. (2007). Results provided by Zhang (2012).

(under vacuum) to prevent charging. The study was performed using a Zeiss Ultra Plus instrument with an attached Oxford Instruments X-Max 80 mm² SSD X-ray microanalysis system; an accelerating voltage of 15 keV was used.

The SEM study showed the samples to be quite homogeneous on the micrometre scale, with only hafnium, uranium and thorium impurities detected (these are detailed in table 5.1). Theoretical values for the concentrations of ZrO₂ and SiO₂ in pure zircon are 67.22 wt% and 32.78 wt% respectively. However, in this study the analysis showed all samples to have ZrO₂ and SiO₂ concentrations of 67.0 wt% and 31.5 wt% respectively. This corresponds to a stoichiometric silicon deficiency of ~ 5 atomic% relative to zirconium sites (which can contain hafnium, uranium or thorium as substitutional impurities). Similar measurements have been carried out by Vance and Mackey (1978) on a synthetic U-free zircon which did not show such a deficiency. Instead, it is expected that hydroxyl groups can substitute for silica during the formation of the sample; this alters the chemical composition

to $\text{Zr}(\text{SiO}_2)_{1-x}(\text{OH})_{4x}$ resulting in a deficiency of silicon relative to zirconium sites (Caruba et al., 1985). Samples Cam27 and No.2, previously studied by Zhang et al. (2000) and Trachenko et al. (2007) respectively, determined ZrO_2 concentrations of 63.3 wt% and 64.6 wt% respectively and SiO_2 concentrations of 33.4 wt% and 31.0 wt% respectively, thereby disagreeing with the measurements here. However, the uranium and thorium contents for these samples were found to be in fairly good agreement between the two studies.

5.1.3 Raman and Infrared Spectroscopy

In order to determine the α -dose each sample received through self-irradiation, Raman spectroscopy was performed from 150 cm^{-1} to 1150 cm^{-1} using a LabRam confocal micro-Raman spectrometer, coupled with a room-temperature CCD detector and a free-sample-space Olympus microscope. Samples were irradiated with a 632.8 nm neon-helium laser at a long working distance of 50 $\times$ -magnification; the resulting emissions were filtered using a diffraction grating of 1800 lines per mm.

In order to observe possible luminescence and fluorescence signals, Fourier Transform Raman Spectroscopy (FT-Raman) measurements were also conducted. These were performed at room temperature using a Bruker FRA 106 FT-Raman accessory attached to a Bruker IFS 66v spectrometer. For these measurements, an excitation radiation of 1064 nm from a Nd:YAG laser was used in conjunction with a silicon-coated calcium fluoride beam-splitter and a liquid-nitrogen-cooled high-sensitivity Ge-detector.

Near-Infrared Spectroscopy (NIRS) was carried out between $2500\text{--}11000\text{ cm}^{-1}$ to determine the presence of water, hydroxyl ions and uranium ions. This was performed using a Bruker IFS 66v spectrometer with a liquid-nitrogen cooled Mercury-Cadmium-Telluride detector coupled with a calcium fluoride beam-splitter and a tungsten lamp. The spectra, averaged from 521 scans, were collected under vacuum from unoriented crystals with an unpolarised source.

The Raman spectra from four of these samples, Zircon 10, Zircon 11, Zircon 19 and Zircon 26, are shown in figure 5.2. The width of the excitation bands in the spectra can be related to the α -dose that the sample has received, shown previously in table 5.1. The near infrared absorption spectra of these four samples are shown in figure 5.3. The absorption bands due to hydroxyl groups (OH^-) and

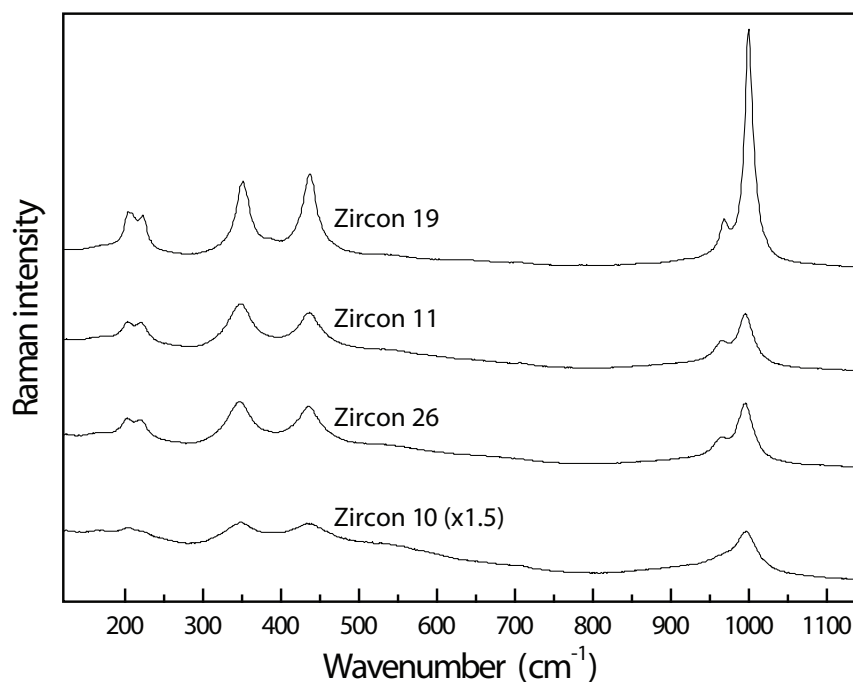


Figure 5.2: Shown here are the Raman spectra for four of the zircon samples. These samples later underwent annealing treatment and subsequent Raman spectroscopy.

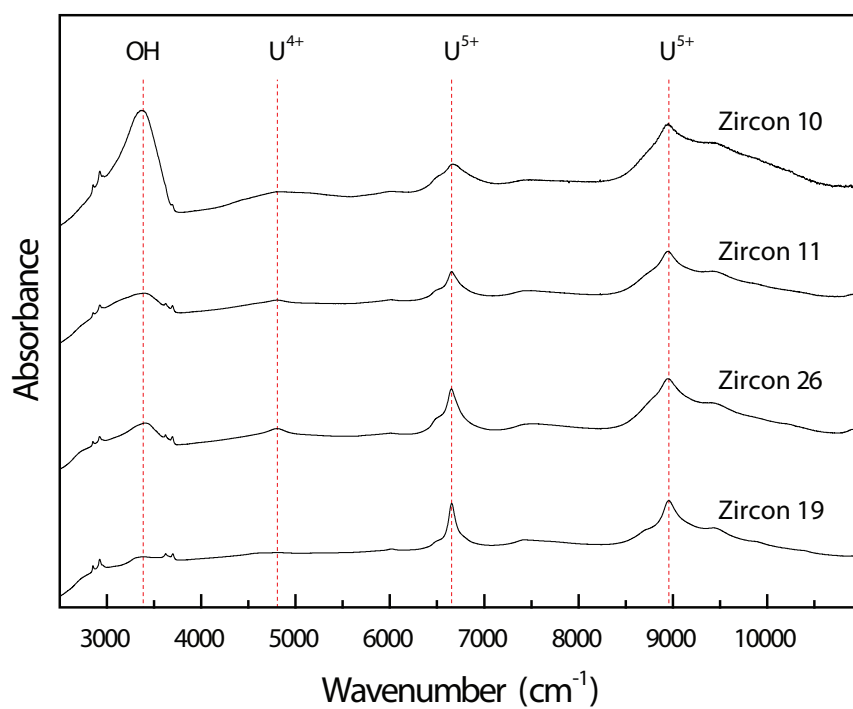


Figure 5.3: Shown here are the NIRS spectra of the four zircon samples showing the presence of water, hydroxyl ions and uranium ions.

water at $\sim 3400\text{ cm}^{-1}$ are indicated as well as the absorption bands due to U^{4+} and U^{5+} (Vance and Mackey, 1978). The remaining four samples underwent the same characterisation; however, their spectra are not shown here.

No correlation between the uranium content and radiation damage was found within the samples of this study. This indicates that the samples are of different geological ages; with the exception of D23524, D29620 and Cam27, the samples are of unknown provenances.

5.1.4 PALS Measurements

In order to determine the presence of void type defects caused by self-irradiation, PALS measurements were performed on the eight samples of this study using the apparatus detailed in chapter 3. However, some conventional PALS measurements were also attempted on two of the samples. With the exception of a study by Vance et al. (1980) which investigated a sample that had experienced very little damage with PALS, such studies have not been reported previously.

The beam-based measurements were performed at an implantation energy of 5 keV, giving the implantation distribution shown in figure 5.4. Higher implantation energies were tested however, as expected, no difference was seen. The measurements of zircon 19 and zircon 26 shown in table 5.2 were performed prior to the sample being cut, though this had a negligible effect on the result. These results show positron lifetimes corresponding to pores of 0.25–0.5 nm in size in some, but not all, samples which have incurred approximately half the α -dose required for full amorphisation. The previous PALS study by Vance et al. (1980), which used a conventional arrangement, showed three lifetime components in a sample which had suffered very little damage. The longest of these components, 1.63 ns, was initially attributed to annihilation within the source material as the lifetime remained unchanged after annealing at 1350°C. However, it is now thought that this lifetime is due to open volume defects, 0.57 nm in size, caused by gas pockets during the formation of the sample, rather than radiation damage (Vance, 2012). Such open volume defects would not necessarily be removed by annealing, even at high temperatures. Two short lifetime components of 0.18 ns and 0.40 ns were also resolved which, when compared to the conventional lifetime measurements presented in table 5.3, indicate the sample has received little radiation damage.

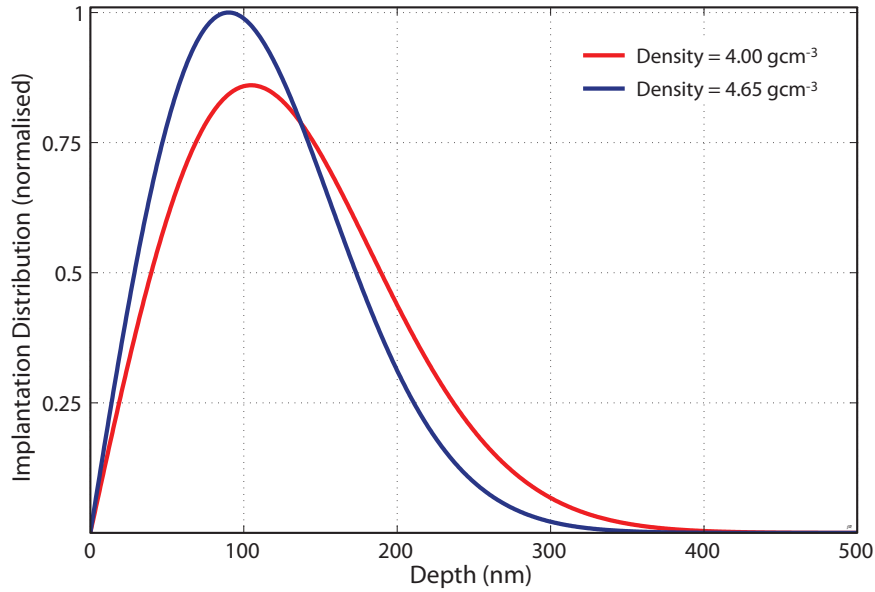


Figure 5.4: Shown here is the implantation profile for positrons into crystalline zircon (density = 4.65 gcm^{-3}) and amorphous zircon (density = 4.00 gcm^{-3}) calculated using the Makhov implantation profile (see section 2.2.1).

Sample	α -dose ($\times 10^{18} \text{ g}^{-1}$)	Lifetime (ns)	Intensity (%)	Pore diameter ^a (nm)
Zircon 10	6.5	0.73 ± 0.05	9.13 ± 0.06	0.29 ± 0.025
Zircon 11	4.0	1.46 ± 0.24	2.64 ± 0.22	0.53 ± 0.059
Zircon 19	2.1	No observed lifetimes	—	—
Zircon 26	4.5	0.66 ± 0.02	11.70 ± 0.30	0.25 ± 0.012
D23524	~ 3	No observed lifetimes	—	—
D29620	~ 1	No observed lifetimes	—	—
Cam27	5.6	0.36 ± 0.01	19.10 ± 0.40	—
No.2 ^b	7	0.41 ^b	37.0 ^b	—

Table 5.2: Shown here are the results of zircon measurements performed on the eight zircon samples. Where no lifetimes have been observed the measured spectrum is, within the limits of the noise, indistinguishable from the instrument function.

^aThis conversion has been carried out using the RTE model detailed in section 2.4.3.

^bThis measurement encountered experimental problems. As a result the lifetime components cannot be accurately determined; however, an upper limit of ~ 0.7 ns can be placed on the lifetime.

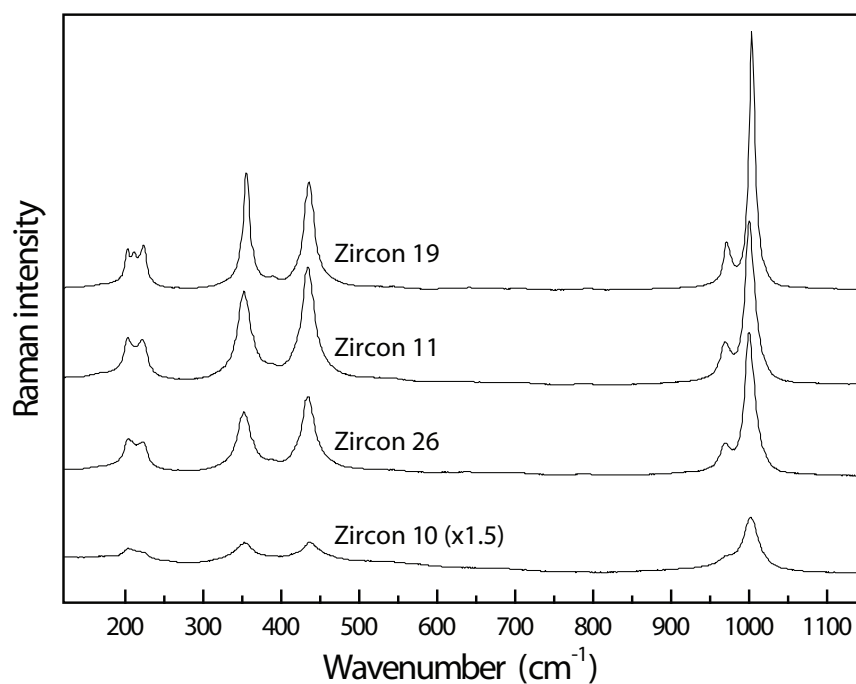
Sample	Beam based PALS		Conventional PALS	
	Lifetime (ns)	Intensity (%)	Lifetime (ns)	Intensity (%)
Zircon 10	0.73	9.13	0.347, 0.82	42.6, 1.2
Zircon 11	1.46	2.64	0.289, 0.82	42.9, 0.9

Table 5.3: Shown here is a comparison of the beam-based results and the conventional PALS results. The lifetime discrepancies are attributable to the difficulties encountered when performing conventional PALS on such small samples as well as the different regions probed between the two arrangements. The intensities of the lifetime components cannot be directly related to void concentrations.

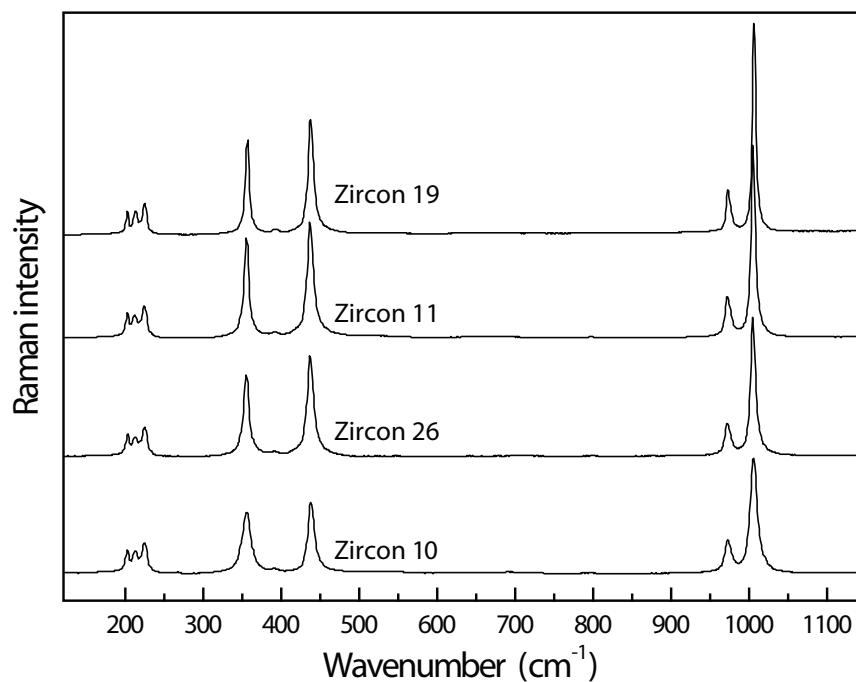
A preliminary study was made on the two largest samples, Zircon 10 and Zircon 11, using a conventional PALS arrangement. This was also performed within the CAMS collaboration using the apparatus at the University of Western Australia (UWA). The results from the conventional PALS apparatus are shown, in comparison to the beam-based measurements, in table 5.3. The very short lifetimes, due to free positron annihilation within the zircon structure, resolved by the conventional PALS measurements have not been observed in the two samples investigated with the beam based apparatus. This is due to the restrictions discussed in section 4.2.8. However, due to the difficulties in performing conventional PALS on such small samples, the beam based measurements are considered more accurate. In addition, due to the differing regions probed caused by the large disparity in implantation energies, 5 keV for the beam-based measurements verses up to 540 keV for the conventional arrangement, these results are not directly comparable. In order to allow a qualitative comparison, a systematic beam based study of varying implantation energies would be required to identify any possible surface or near-surface effects.

5.1.5 Annealing Treatment of Samples

Following the initial characterisation, four zircon samples (Zircon 10, Zircon 11, Zircon 19 and Zircon 26) were annealed first at 700°C and later at 1200°C. Both annealing treatments were carried out in air for two hours. After each treatment both Raman spectroscopy and PALS measurements were carried out to determine the effect this had on the sample.



(i) Shown here are the Raman spectra of the four zircon samples following heat treatment at 700°C. There is little difference between these spectra and those of the untreated samples (shown in figure 5.2).



(ii) Shown here are the Raman spectra of the four zircon samples following heat treatment at 1200°C.

Figure 5.5: Here are the Raman spectra for the zircon samples following annealing treatment at 700°C and 1200°C.

Sample	Treatment	Lifetime (ns)	Intensity (%)
Zircon 10	Unannealed	0.73 ± 0.05	9.13 ± 0.06
	700°C ^a	0.44 ± 0.01	30.70 ± 0.38
	700°C ^b	0.38 ± 0.10	25.20 ± 13.20
		0.71 ± 0.39	7.22 ± 14.70
	1200°C	No lifetimes observed	
Zircon 11	Unannealed	1.46 ± 0.24	2.64 ± 0.22
	700°C	0.29 ± 0.01	22.00 ± 1.15
	1200°C	No lifetimes observed	
Zircon 19	Unannealed	No lifetimes observed	
	700°C		
	1200°C		
Zircon 26	Unannealed	0.66 ± 0.03	11.70 ± 0.30
	700°C	0.49 ± 0.05	2.99 ± 0.30
	1200°C	No lifetimes observed	

Table 5.4: Shown here are the beam-based results for PALS measurements performed on zircon

^aWith normal constraints, area adjustment allowed to vary to 1%

^bWith relaxed constraints, area adjustment allowed to vary up to 5%

Shown in figure 5.5 are the Raman spectra for the four samples after annealing at 700°C (figure 5.5i) and annealing at 1200°C (figure 5.5ii). After the initial treatment at 700°C, a slight increase in general crystallinity of the samples is observed. However, following the annealing treatment at 1200°C, near-perfect restoration of the single crystal nature of the samples has occurred.

Following the annealing treatment at 700°C, the positron lifetimes have decreased in the three samples which lifetimes were initially observed (shown in table 5.4). For Zircon 10, the 0.73 ns lifetime has been reduced to 0.44 ns when normal constraints of the optimisation routine are used. However, when the constraints are relaxed this can be resolved into two components of 0.38 ns and 0.71 ns, indicating that the 0.38 ns component is dominant. By comparing to the untreated measurement, it can be seen that the lifetime component around 0.7 ns is still present and while the intensity appears slightly reduced, little can

be determined due to the large uncertainty. Zircon 11, which initially showed a lifetime component of 1.46 ns, only shows a single, very short lifetime component of 0.29 ns after the annealing treatment at 700°C. While the intensity of this component is much greater, which may indicate an increase in annihilation sites within the sample, a more in depth PALS study, performed over a range of temperatures, would be required to confirm such a hypothesis. Once again with Zircon 19, no lifetime components were observed. The positron lifetime in Zircon 26 has also decreased from 0.66 ns to 0.49 ns; this was accompanied by a decrease in the intensity of the lifetime component. Following the annealing treatment at 1200°C, no lifetime components are observable in any of the samples.

5.1.6 Conclusions

In some of the samples which had incurred approximately half the α -dose required to render them structurally amorphous, PALS showed evidence of nanometre sized voids. These results agree well with the results of the SAXS study reported by Radlinski et al. (2003); Rios and Salje (2004); Rios et al. (2005). However, some samples with similar, or higher, α -doses did not show evidence of such voids, indicating such features may not be universal in damaged zircons. It is proposed that such voids may form from radiation damage in conjunction with pre-existing hydrous material. As a result, SAXS studies are being carried out using the Australian Synchrotron to provide more insight into these samples.

In the four samples which underwent annealing, the positron lifetime components (and hence the size of open volume type defects in the material) were reduced in all samples by annealing at 700°C. The corresponding Raman spectra also showed improvement in the general crystallinity. Subsequent annealing at 1200°C reduced the positron lifetime to $\lesssim 300$ ps, the experimental limit of the apparatus, and restored the Raman spectra to those characteristic of unirradiated zircon.

5.2 Zeolites

Due to their nanoscale structure, zeolites are a material with a diverse range of industrial applications. In order to overcome some problems experienced when utilising zeolites in a pellet or bead form, Ichiura et al. (2001) recently described a new technique to produce zeolite sheets using a papermaking technique. The study presented here focused on utilising this technique and investigating the properties of the resulting sheets. The concentrations of the starting reagents was varied to alter the composition of the zeolite sheet produced; their porosity was then investigated using PALS.

5.2.1 Background

Zeolites are a family of highly porous crystalline aluminosilicate compounds; naturally formed examples were first identified by Cronstedt (1756). Zeolites form the aluminosilicate members of a family of microporous solids known as ‘molecular sieves’. These materials are able to selectively sort molecules based primarily on physical size due to their structure on the nanoscale. Zeolites have a three dimensional structure which results in uniformly sized open volumes of 0.3–2.0 nm (van Bekkum and Flanigen, 2001). These open volumes allow zeolites to preferentially absorb molecules of similar size and exclude molecules larger than the open volume.

Currently there are two hundred and one unique zeolite frameworks, referring to the corner-sharing networks of tetrahedrally coordinated atoms but not the extra-framework constituents, which have been identified; approximately forty of these occur naturally (Database of Zeolite Structures, 2012). The framework is primarily comprised of crystalline silica (SiO_2), with aluminium atoms (Al^{3+}) substituting for silicon atoms (Si^{4+}). This results in the framework possessing a small negative charge depending on the silicon aluminium ratio. This charge is counteracted by cations, such as sodium, potassium, calcium or magnesium, which are loosely bound within the structure. The exchangeability of such cations is affected by the silicon aluminium ratio, with exchange processes maximised by approximately equal numbers of each. Such zeolites are employed for ion exchange and absorption properties, particularly in detergents due to their ability to replace hard cations, such as calcium and magnesium, with soft ones, such as

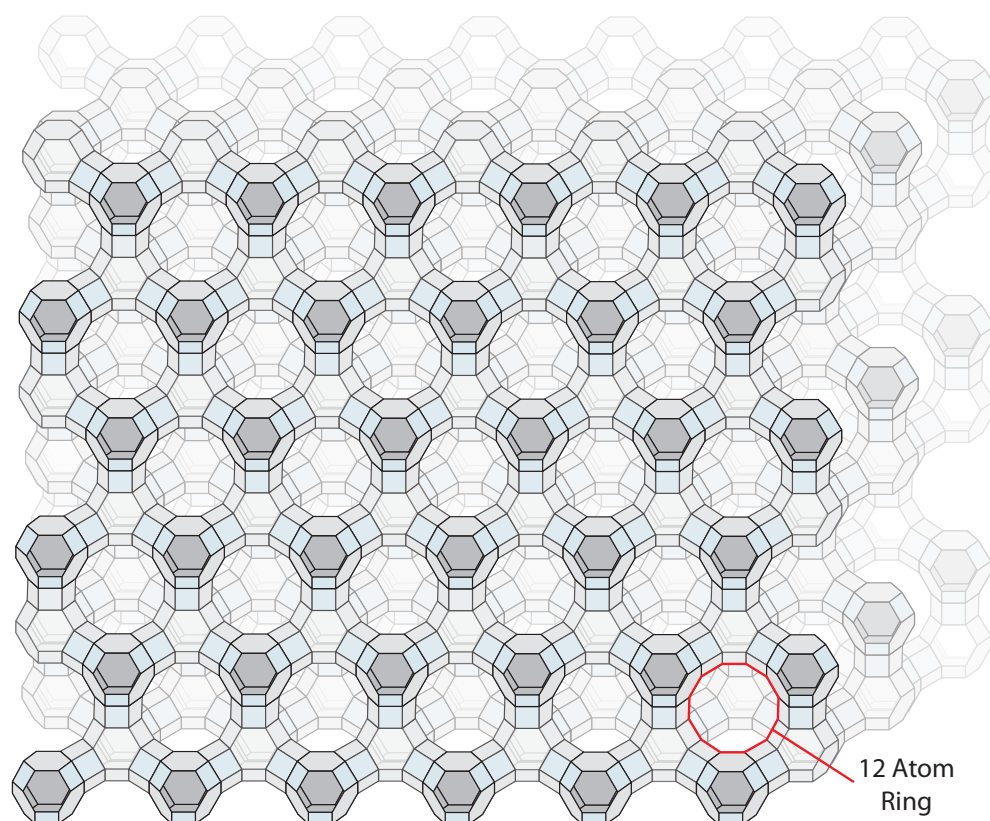


Figure 5.6: Shown here is the highly porous structure of a zeolite with a faujasite framework, such as zeolite X or Y.

sodium. However, zeolites comprised of more silicon are utilised as catalysts due to their resistance to the high temperature environments of the reactions and the regenerative processes.

In general, industry utilises zeolites in bead or pellet form which is suitable for many applications (Dyer, 1988); however, problems due to these forms are encountered. For example, physical contact can cause disintegration of the zeolite. Also, when deployed in a reaction tower, these forms result in a significant pressure loss due to the packing inefficiency. It has been proposed by Mitsuma et al. (1998) that a sheet form of zeolite would overcome these problems. Attempts have been made to produce such sheets using an extrusion method, however, the characteristic porous structure is destroyed by the high pressures required. More recently, Ichiura et al. (2001) proposed a papermaking technique to produce zeolite sheets; this method was employed during this study and will be discussed in the following section.

5.2.2 Fabrication Method

The method used here to fabricate zeolite sheets followed the technique outlined by Ichiura et al. (2001). In order to achieve this, a sheet maker was constructed, as depicted in figure 5.7, to produce the initial sheet. The sheet maker consists of a cylindrical volume of ~30 L which is comprised of two sections: an upper section which contains the majority of the capacity and a lower section which allows the volume to be drained through a ball valve. Situated between the two sections is a fine stainless steel mesh onto which the sheet forms; the two sections are sealed around the mesh using a rubber gasket. Upon successfully creating a sheet (which will be discussed shortly), the upper section is unbolted and removed to allow the sheet to be accessed for further processing.

Formation of the initial sheet is achieved through the addition of several solutions to the sheet maker before draining the liquid contents. Firstly, the sheet maker is approximately half filled with deionised water before a 0.2% pulp solution is added. This solution is prepared by adding 2.0 g of Tumut kraft fibre ¹ to 250 mL deionised water and blending until visibly dispersed. Following this, 55 mL of 0.1% Poly Diallyl Dimethyl Ammonium Chloride (PDADMAC) is added before 25 mL of 2.0% inorganic solution. The inorganic solution is comprised of zeolite, kaolin and glass fibre, with the control sample being prepared at a ratio of 5.5:1.5:1 by weight. Here, sodium Y type zeolite was used; this is a zeolite with a faujasite framework and a high silicon to aluminium ratio. This solution is also blended until visibly dispersed. The final component, 250 mL of 0.1% Anionic Polyacrylamide (A-PAM), is then added before the sheet maker is filled with deionised water to the 350 mm line. The solution is then agitated with a circular mesh stirrer of diameter 155 mm. The ball valve is then opened and the solution drains rapidly, forming the resulting sheet on the fine mesh.

After removing the fine mesh with the sheet from the apparatus, it is left to dry for 24 hrs under a fume hood before further processing. This differs from the Ichiura et al. (2001) method which specifies compression under 350 kPa for five minutes followed by 30 mins in a convection oven at 105°C. Instead, while drying ~20 kg is placed on the sheet to provide compression; increasing this weight up to

¹Supplied by Joel Young of Visy pulp and paper, Tumut. 30% of the mass of this pulp is water; it is rated at ~750 Canadian Standard Freeness (CSF).

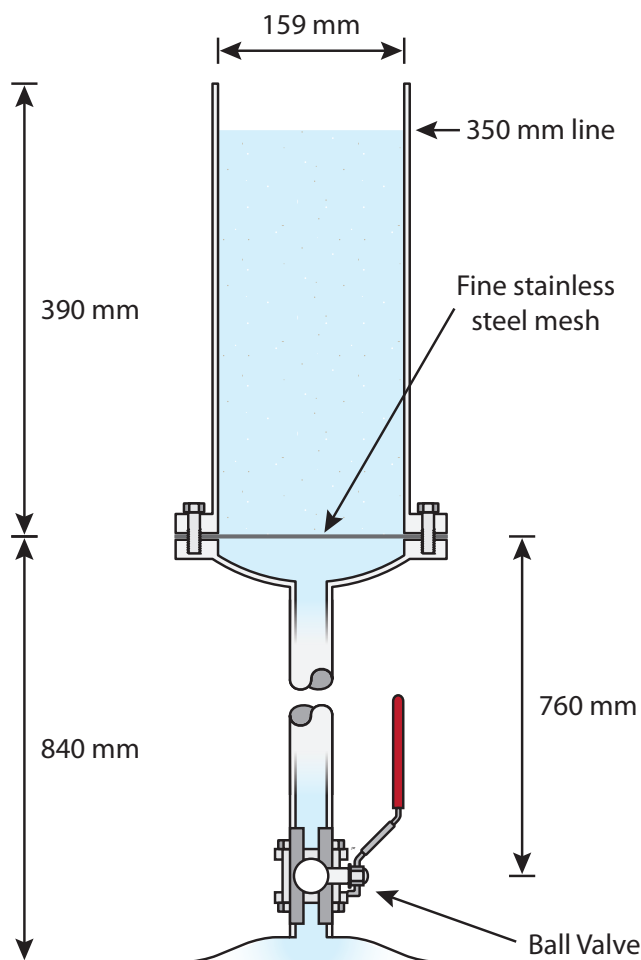


Figure 5.7: Shown here is the apparatus constructed to produce zeolite sheets according to the method outlined by Ichiura et al. (2001).

400 kg (just over half the compression specified by Ichiura et al. (2001)) showed no difference in the resulting sheet.

Once dried, the sheets (which have a texture much like coarse paper) were then sintered at 700°C for 20 mins ². This ignites the paper fibre and fuses the inorganic components together to form a rigid sheet. Due to the rigidity of the resulting sheet, samples were restricted to 30×30 mm to prevent cracking during the sintering process.

Using this method, three zeolite sheets were produced with differing glass fibre concentrations as shown in table 5.5. Zeolites with a faujasite framework

²This was carried out by Antia Smith from the Laser Physics Department of the Research School of Physics and Engineering at the ANU

have open volumes defined by 12 atom rings as depicted in figure 5.6. Typically these rings have a diameter of ~ 0.6 nm and define a slightly larger open volume, though this can vary depending on the composition of the zeolite (van Bekkum and Flanigen, 2001).

Sample	Zeolite content		Kaolin Content		Glass Fibre Content	
	Weight (g)	Relative %	Weight (g)	Relative %	Weight (g)	Relative %
Control	0.3714	100	0.1001	100	0.0608	100
Sheet 1	0.3701	99.66	0.0929	92.80	0.0820	134.87
Sheet 2	0.3721	99.80	0.1023	102.20	0.1056	173.68

Table 5.5: Shown here are the concentrations of the various components of the inorganic solution and the percentage change relative to the control sample.

5.2.3 Results

Following successful preparation of the three zeolite sheets, each underwent PALS measurements using the beamline described in chapter 3. Due to the highly porous nature of the sheets, a low implantation energy of 5 keV was used. The resulting lifetimes are shown in table 5.6.

Sample	Lifetime (ns)	Intensity (%)	Pore diameter (nm)
Control	0.28 ± 0.01	26.5 ± 1.63	—
	1.49 ± 0.03	10.1 ± 0.26	0.54 ± 0.007
Sheet 1	1.18 ± 0.01	13.2 ± 0.07	0.45 ± 0.003
	9.16 ± 1.16	1.46 ± 0.09	1.39 ± 0.081
Sheet 2	1.46 ± 0.02	10.9 ± 0.09	0.53 ± 0.005
	14.8 ± 4.56	1.01 ± 0.16	1.74 ± 0.262

Table 5.6: Shown here are the lifetimes observed in the three zeolite sheets.

Common to all the samples is a lifetime of 1–1.5 ns, corresponding to an open volume of ~ 0.5 nm. This lifetime can be attributed to annihilation within the open volumes of the zeolite material. In the control sample, no longer lifetimes are present; although a shorter component of 0.28 ns, due to free positron annihilation, can be deconvoluted. This short lifetime component has not been resolved

in the second or third sheet, though it can be assumed to be present. However, in the sheets which have an increased glass fibre content, longer lifetime components are present. When the glass fibre content is increased to 135%, a lifetime component of 9.16 ns is observed. This corresponds to a relatively large open volume of 1.4 nm. In the third sheet, which had a glass fibre content of 174% relative to the control, this lifetime increased to 14.8 ns, corresponding to an open volumes of 1.7 nm. It is expected that these larger open volumes are supported by the increased glass fibre content. These larger open volumes are also accompanied by an increase in the structural rigidity of the sheet due to the increased glass fibre content.

5.2.4 Conclusions

The results presented here show that the properties of the sheet may be tailored to the requirements of the application; however, an in-depth study is required. Through varying the glass fibre content, open volumes can be introduced into the resulting sheet in a controlled manner.

Following these preliminary samples, the preparation of zeolite sheets with a high zeolite content, as described by Ichiura et al. (2001), was initiated. This study is ongoing and intends to vary the zeolite and kaolin components in addition to the glass fibre content. With these increased concentrations the drainage time is significantly increased (>2 minutes). At this stage it is unclear if this will have adverse effects on the resulting sheet. In addition, these higher content sheets may require compression under 350 kPa (also described by Ichiura et al. (2001)) to aid in the drying and improve the structural performance of the resulting sheet.

CHAPTER 6

CONCLUSIONS

Within this thesis, the development of a unique apparatus has been described in chapter 3. This apparatus has been designed to utilise recently developed moderation and bunching techniques to produce a pulsed positron beam for materials studies. Currently, the pulses have a FWHM of 800 ps which can be used to resolve lifetimes of >300 ps for beam-based PALS studies.

Due to the techniques implemented to form the positron pulses, a new analysis method was developed specifically for the resulting data, as described in chapter 4. This software employs a new method for extracting lifetime components from PALS spectra collected using a positron beam. It uses a second spectrum to account for the temporal distribution of the positron pulse, enabling lifetime components to be extracted from the sample spectrum.

With this apparatus a study of natural zircon crystals was conducted. Recently published SAXS measurements have shown evidence of nanometre sized voids in samples which have suffered radiation damage through self-irradiation. Within chapter 5, PALS results are presented for eight zircon samples which have sustained a range of radiation damage. In some of the samples which had received approximately half the radiation dose to render them amorphous, such voids were observed. However, some samples which had received comparable or higher dose showed no evidence of such voids, casting doubt on their existence as a universal feature. As a result, further studies are being conducted on these eight samples using other techniques.

A study of zeolite sheets, prepared in-house using a paper making technique, has also been conducted. This recently developed technique aims to overcome the complications of using zeolites in pellet or bead form. Several sheets were prepared with varying concentrations of glass fibre to investigate their proper-

ties. It was found that at higher glass fibre concentrations, larger open volumes were formed in the resulting sheet. This would potentially allow sheets to be tailored to specific applications. An in-depth study has been initiated to investigate the effects of other starting reagents as well as attempting to form higher concentration zeolite sheets.

6.1 Future Modifications

The primary goals of developing the CAMS Materials Beamline, including a large suite of customised software for experimental control and data analysis, have been accomplished. However, there are numerous modifications and upgrades (both hardware and software) which can still be implemented to improve its operation and functionality. Some of these will be briefly discussed here.

The initial simulations suggested that a positron pulse with a FWHM of 200 ps would be achievable. However, to-date the best FWHM achieved has been ~ 800 ps. In order to reduce this further, the possibility of a secondary pulse compression method within the transport region (such as a radio frequency cavity buncher which would operate on the pulses formed by the positron trap) has been discussed and could be implemented in the future. In addition to this, a chopper may also be implemented to remove the tail caused by scattering from gases present in the system. While this would reduce the ultimate count rate, it would lead to a much more Gaussian pulse shape and improve the ability to resolve the lifetime data.

Presently, samples can only be measured at the ambient room temperature (296 K); however, the design of the apparatus includes the capability of a temperature controlled sample stage. With the necessary modifications, this feature will allow the characteristic lifetimes to be determined under a range of different temperatures, allowing the evolution of open volume type defects to be investigated as a function of temperature. In particular, this will allow the annealing of semiconductors and the glass transition in polymer type samples to be studied.

As the operation of the apparatus has been optimised during its development, leading to a noticeable increase in the ultimate count rate, the required measurement time has significantly decreased. Currently, measurement times are sufficiently long to negate automation of the sample manipulation system. However, if similar improvements in the signal rate are achieved in the future, this

system will require automation to avoid wasted experimental time. In order to use this improvement to its full capacity, automation of the data collection system would be required.

Another intended upgrade of the apparatus is the inclusion of a high-purity germanium detector. This will allow simultaneous DBS measurements to be performed, providing information about the chemical environment of the defect site. In addition, if these measurements are performed in coincidence, with the correct synchronisation and detector arrangement, AMOC measurements could be performed.

Further improvements are expected to be made to the analysis program CAMS-FIT, including added functionality and a more sophisticated analysis of the data. In particular, the capability to deconvolve the instrument function spectrum would allow the short lifetime components of the sample to be determined with more confidence. Also, a more complex optimisation algorithm would allow the analysis to be less dependent on the starting values. Finally, it has been proposed that rather than fitting discrete lifetime components, the spectra are analysed using Gaussian distributions of lifetime components. Preliminary investigations into this have been performed and indicate that this functionality can be readily included.

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