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MATERIAL SPECIFIC INFORMATION FROM OBJECTS IN
ABSCONDITUS

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Material Specific Information from Objects in *Absconditus* for
Warhead Dismantlement Verification

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Abstract

A long-standing problem within nuclear disarmament is that there are no established methods to verify that a nuclear weapon (NW) has been dismantled according to the treaties in place. The Nuclear Non-proliferation Treaty (NPT), the treaty that aims to reduce the stockpiles of nuclear weapons, also encourages research into technologies to verify the dismantlement without compromising sensitive information.

During the dismantlement process, inspectors have limited access to the nuclear weapon under dismantlement and similarly there are also restrictions on the containers the weapon components are stored in once separated. This project examines the development of a verification method to attest the presence, or indeed absence, of the high explosive component of a nuclear weapon. Various bulk detection methods have been reviewed and X-ray diffraction (XRD) was found to be a promising method that would, at high energies, permit the penetration of metal containers and have the sensitivity needed to identify the explosive.

Conventional pencil beam geometry of XRD was used to demonstrate the feasibility of the technique. One of the fundamental requirements to identify a material via XRD is to have knowledge of the location of the scattering source. Several novel techniques were established and considered to enable depth perception with angular dispersive XRD (ADXRD) along the primary axis including an analytical method, novel post-sample encoders (linear wire and Archimedean spiral) and the successful development and introduction of an algorithm by which the diffraction data is compared to a set database of materials to produce a likelihood of materials at specific locations.

Focal construct geometry (FCG) - which uses a hollow conical incident beam - was introduced as a method to increase the number of photons available and hence offer enhanced diffraction data with improved intensity.

Although useful in situations where the high penetration is not required, ADXRD is limited by the characteristic peak, meaning it cannot penetrate through highly

absorbing materials such as metals. Higher energy photons can be utilised if energy dispersive XRD (EDXRD) is considered.

The use of higher energy sources was evaluated in terms of their efficiency at generating photons contributing to EDXRD than of the characteristic peaks, ADXRD. It was found that, the higher the voltage of the source, the higher the proportion of photons contributed to EDXRD than that of the characteristic peaks.

As with the conventional pencil beam geometry, post-sample encoders were introduced to enable depth perception along the primary axis. This post-sample pin hole encoder allowed for the first time the explosive diffraction signature to be separated from the concealments' diffraction, a limitation of the pencil beam techniques introduced here. The depth resolution of the technique was evaluated analytically to indicate possible improvements to increase detectability of concealed objects. Simulations were conducted enabling a comparison with experimental data and then extended to higher energy via simulation, to provide an indication of the potential use and any limitations that may arise.

Overall, this project is the first to demonstrate that XRD is a potentially viable technique for material phase identification behind highly absorbing metal barriers and has introduced several novel techniques for depth perception including post-sample encoders and a new algorithm for ADXRD diffraction profiles. Furthermore, this thesis is the first instance of FCG XRD being identified and applied to the problem of nuclear weapon dismantlement verification with the capability to identify and locate concealed explosives inside highly absorbing containers, advancing the possibility to aid the verification of nuclear warhead dismantlement.

Keywords:

X-ray Diffraction, Focal construct geometry, High Energy, *McXtrace*, Encoders, Explosives, Nuclear Weapons, Verification, Dismantlement, Beam Geometry, Annular Beam

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List of Abbreviations

AD	Angular dispersive
AD-FCG	Angular dispersive - Focal construct geometry
ADXRD	Angular dispersive X-ray diffraction
API	Associated particle imaging
CACSSI	Coded aperture coherent scatter spectral imaging
CAI	Coded aperture imaging
CCD	Charge Coupled device
CT	Computerised tomography
CW	Chemical Weapon
CTBT	Comprehensive Test Ban Treaty
ED	Energy dispersive
EDXRD	Energy dispersive X-ray diffraction
ED-FCG	Energy dispersive - Focal construct geometry
FCG	Focal construct geometry
FNA	Fast Neutron Analysis
FWHM	Full width at half maximum
GADDS	General Area Detector Diffraction System
HE	High explosive
IAEA	International Atomic Energy Agency
ICAN	International Campaign to Abolish Nuclear Weapons
KDEX	Kinetic Depth Effect Imaging
LTBT	Limited Test Ban Treaty
NES	Neutron elastic scatter
NIST	National Institute of Standards and Technology
NGO	Non-government Organisation

NPT	Nuclear Non-proliferation Treaty
NQR	Nuclear quadrupole resonance
NRA	Nuclear Resonance Absorption
NW	Nuclear weapon
NWS	Nuclear-weapon states
PET	Positron emitting tomography
PB	Pencil/pin-hole beam
PFNA	Pulsed Fast Neutron Analysis
PFNTS	(Pulsed) Fast neutron transmission spectroscopy
PFTNA	Pulsed fast-thermal neutron analysis
PGNAA	Prompt Gamma-ray Neutron Activation Analysis
PDF	Powder diffraction file
PINS	Portable Isotopic Neutron Spectroscopy
PNET	Peaceful Nuclear Explosions Treaty
PTBT	Partial Test Ban Treaty
SNR	Signal-to-noise ratio
TAI	Treaty Accountable Item
TNA	Thermal Neutron Analysis
TPNW	Prohibition of Nuclear Weapons Treaty
TTBT	Threshold Test Ban Treaty
UV	Ultraviolet
VNIITF	All-Russian Scientific Institute of Technical Physics
WMD	Weapon of mass destruction
XDI	X-ray diffraction imaging
XRD	X-ray diffraction

List of Symbols

λ	Wavelength, Å
d	d -spacing, Å
2θ	Diffraction angle
χ	Momentum transfer
D	Source-to-detector distance
D_S	Source-to-sample distance
D_{SD}	Sample-to-detector distance
r	Radius in the detector plane
r_s	Radius in the sample plane
φ_m	Mean opening angle of annular beam
φ_{min}	Minimum opening angle of annular beam
φ_{max}	Maximum opening angle of annular beam
D_{LE}	Source-to-linear encoder distance
D_{SE}	Source-to-spiral encoder distance
$D_{S:LE}$	Sample-to-linear encoder distance
$D_{S:AS}$	Sample-to-spiral encoder distance
$D_{LE:D}$	Linear encoder-to-detector distance
$D_{AS:D}$	Spiral encoder-to-detector distance
D_A	Source-to-aperture (pin-hole) distance
E	Energy, keV

h	Plank's constant, $6.629 \times 10^{-34}\text{Js}$ (1J = $6.242 \times 10^{18}\text{eV}$, $h = 4.136 \times 10^{-15}\text{eVs}$)
c	Speed of visible light, $2.998 \times 10^8\text{ms}^{-1}$
t	Thickness of sample
b	Thickness of pin-hole aperture
a	Radius of pin-hole aperture
D_i	Source-to-sample distance
D_j	Aperture-to-source distance
ζ	Intersection angle
α_{LE}	Off-centre distance of linear encoder in encoder plane
α_D	Off-centre distance of linear encoder in detector plane
r_{LE}	Radius of Debye cone within linear encoder plane
ψ	Polar angle for Archimedean spiral
r_{AS}	Radius of Debye cone
r_1	Inner radius of annular collimator
r_2	Outer radius of annular collimator
W_a	Width of opening in annular collimator aperture. i.e. $r_2 - r_1$
r	Mean radius of the annular collimator gap
a_c	Diameter of pencil beam collimator
Z_{eff}	Effective atomic number

“Somewhere inside all of us is the power to change the world”

Roald Dahl

Preface

A long-standing problem within nuclear disarmament is that there are no standard methods to verify that a nuclear weapon (NW) has been dismantled according to international law without revealing sensitive information about the weapons design. This research aims to discover a potentially viable technology to aid the identification of the high explosive component within a nuclear warhead container and evaluate its use.

Under the Non-Proliferation Treaty (NPT), it is the UK's obligation to develop methodologies and technologies to verify possible nuclear disarmament agreements.¹ Nuclear disarmament is the process by which stockpiles of NWs are reduced and eliminated. The biggest challenge within nuclear disarmament is the absence of an established technique for verifying that a NW has been dismantled without compromising sensitive information.^{1,2} An ideal verification technique would involve an agreed upon set of measurements and procedures that would prove the dismantlement of an authenticated warhead has occurred as required, without also the need to measure any parameter which could be interpreted to provide details of the design of the warhead.³

Verified dismantlement of nuclear warheads potentially requires confirmation without directly witnessing the process. During the process in which a nuclear warhead is dismantled a country, or organisation, verifies that the weapon has been dismantled correctly according to the agreed upon conditions. Physical access to weapons, and the components arising from their dismantlement, may also be denied. Contained within the body of the warhead will be fissile, explosive, and non-nuclear components. Following dismantlement, the components may be placed in separate containers. Verification can be achieved by first confirming the presence of the explosive and fissile components within the body of the warhead (before dismantlement), and then confirming the separation of the explosive component from the fissile component (after dismantlement).

Chapter 1

Nuclear Weapons: Treaties and Dismantlement

“If only I had known, I should have become a watchmaker”

Einstein, 1945

In this chapter, the application of this work - specifically verification of weapon dismantlement - is discussed, outlining the current treaties surrounding the non-proliferation of nuclear weapons and the requirement for a technique with the capability to determine contents of highly absorbing containers.

Dismantlement scenarios are detailed, outlining the possible stages in the dismantlement process at which measurements could be taken to verify the weapon is suitably disarmed according to the treaties in place.

1.1 Nuclear Weapons

Nuclear weapons differ from conventional shells by containing nuclear material in addition to a high explosive (HE) such as TNT.⁴ Their destructive power can equal hundreds if not thousands of conventional bombs purely using HE material. Discovered by French scientists in 1939, nuclear material can be used to cause a

nuclear chain reaction by which atoms of uranium-235 or plutonium-239 can be made to spilt into two smaller fragments by bombarding the nucleus of an atom with a neutron.⁴ During this splitting process, called fission, a large amount of energy, known as binding energy, is released causing a much more powerful explosion than an ordinary bomb.⁵ Later developments to nuclear weapons included smaller but higher yielding devices known as hydrogen bombs. These weapons use a process called nuclear fusion, which involves the making of a larger atom from two smaller ones, usually deuterium and tritium. Fusion produces a much higher yield than a fission reaction.

Advancements in nuclear weapons technology, since the Cold War where the US built high-yield weapons several feet long, has meant systems have reduced in size from being atomic demolition munitions capable of being carried to more compact weapons capable of being projected.⁶

1.1.1 Treaties

By 1954 both the US and the Soviet Union had both successfully tested hydrogen bombs and were developing larger, more powerful weapons. In the years that followed, the UK, France and China all developed and tested nuclear weapons.

The first of many multilateral agreements, all of which can be seen in Table 1.1, used to ideally curb the production and proliferation of NWs was the Partial Test Ban Treaty (PTBT) also known as the Limited Test Ban Treaty (LTBT). The PTBT was brought into effect when talks for a comprehensive test ban treaty failed due to a lack of established technology that could monitor and verify underground nuclear tests.⁷ The PTBT limits the testing of NWs, restricting the environment in which explosions can be conducted. The atmosphere, outer space, under water, and in any other environment where the explosion would cause radioactive debris to be present outside the territory of the responsible state, was prohibited. The PTBT was employed not just to stop the proliferation of NWs but to protect the environment as the nuclear fallout and consequent environmental damage from the explosions was causing public concern.

Table 1.1 Multilateral treaties to limit the testing, storage and proliferation of NWs.

	Treaty	Effective from
Testing	Partial (or Limited) Test Ban Treaty (PTBT/LTBT)	10 th October 1963
	Threshold Test Ban Treaty (TTBT)	11 th December 1990
	Peaceful Nuclear Explosions Treaty (PNET)	11 th December 1990
	Comprehensive Nuclear Test-Ban Treaty (CTBT)	Not in force
Storage	Outer Space Treaty	10 th October 1967
	Seabed	18 th May 1972
Non-proliferation	Non-Proliferation Treaty (NPT)	March 1970
Prohibition	Treaty on the Prohibition of Nuclear Weapons (TPNW)	Not in force

As can be seen from Figure 1.1, the PTBT did not control the proliferation of NWs but did reduce the amount of radioactive material in the atmosphere.⁸ The PTBT was the foundation of many other multilateral treaties. The Outer Space Treaty, prohibits the storage of nuclear arms or other weapons of mass destruction (WMD) in outer space or on any celestial body. The Seabed Treaty, similar to the Outer Space Treaty, prohibits the storage of NWs and WMD's on the seabed or ocean floor in an attempt to prevent the introduction of international conflict and nuclear weapons in areas already free of them.

The Peaceful Nuclear Explosions Treaty (PNET) allows nuclear explosions for non-military purposes on the basis it complies with the other treaties and a single explosion does not exceed 150 kilotons*, along with grouped explosions not

* The yield of a nuclear weapon is the amount of energy released during an explosion and is measured in terms of its TNT equivalent, so a kiloton is equivalent to a thousand tons of TNT.

exceeding the 1500 kiloton limit with the individual explosions verified to be less than 150 kilotons.

Much like the PNET, the Threshold Test Ban Treaty (TTBT) prohibits the testing of a nuclear device with a yield greater than 150 kilotons. This threshold was set to stop the testing of new or existing NWs which have a yield in the megaton range which could cause serious environmental damage. The restrictions imposed by the treaty have reduced the yield of new warheads which could be used for military purposes. Along with limiting the size of nuclear explosions, the treaty also forces all parties to share data about the test conducted, allowing for the blast to be verified. However, this also means the data collected is available to any other party.

The Comprehensive Test Ban Treaty (CTBT), not yet in force due to it not being ratified by several key states such as the US, will supersede the PTBT when it comes into force, banning all nuclear testing globally. Unlike when the PTBT was agreed upon, established technology to differentiate between earthquakes and nuclear tests now exists thus verifying violations of the treaty is now possible.⁸

The Non-Proliferation Treaty (NPT) was a result of United States and the Soviet Union negotiating an international agreement prohibiting the further spread of nuclear weapons. The nuclear-weapon states (NWS), UK, France and China along with the United States and Russia, are officially recognised countries that possess nuclear weapons by the NPT. The NPT, opened for signature in 1968, is an international treaty which currently (as of July 2018) has 191 state parties with 93 signatory states all agreeing to limit the distribution of nuclear weapons by non-proliferation and disarmament.^{9,10} Along with aiming to reduce the nuclear threat the treaty also states the right to peacefully use nuclear technology and bans the transfer of weapons or weapon technology to non-nuclear states.^{5,11} Although the NPT has grossly limited global production of nuclear weapons, some countries have not signed the treaty and are suspected of developing or possessing the devices.⁵

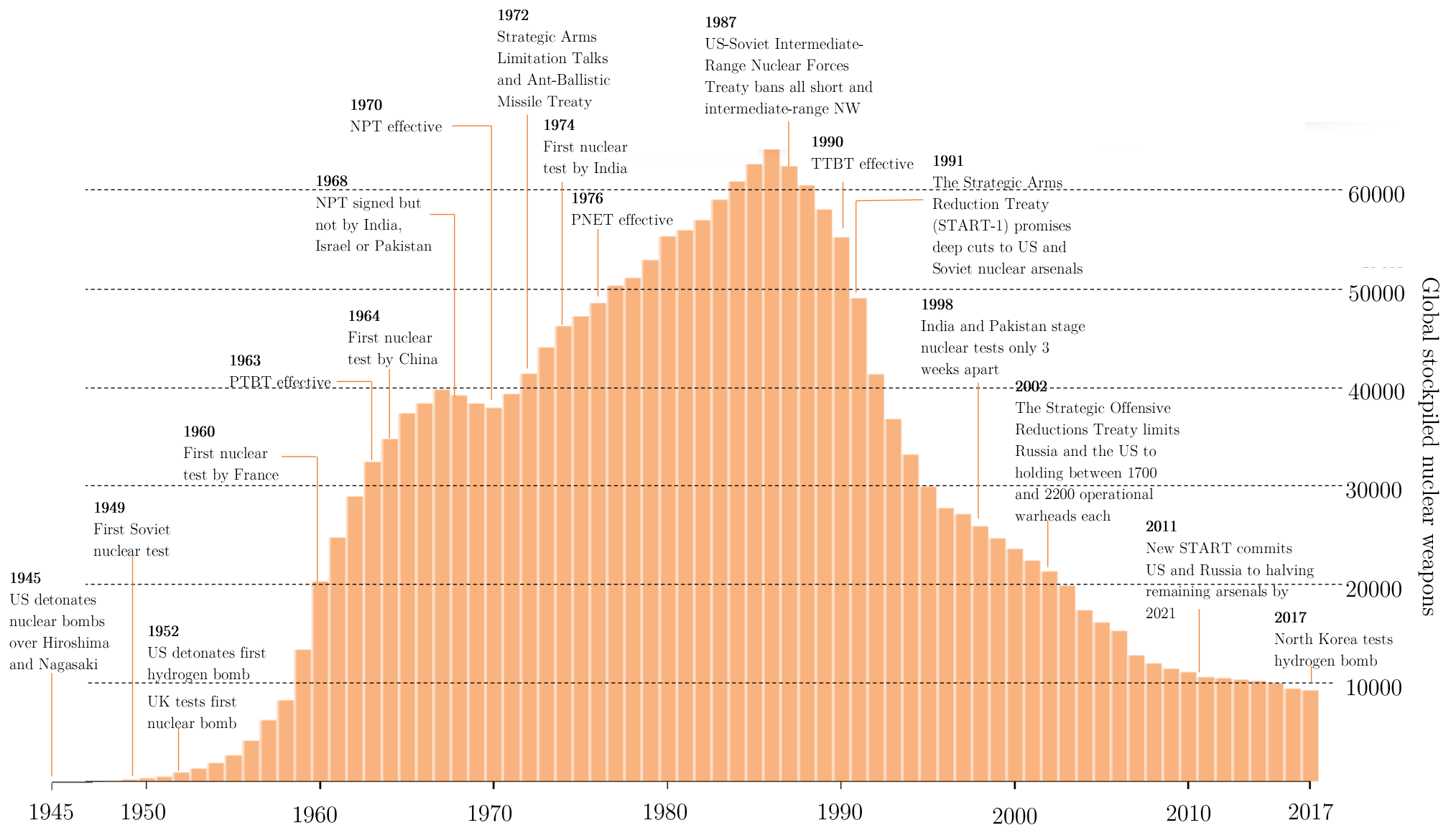


Figure 1.1 Total global nuclear stockpile from 1945 to 2017 alongside a brief timeline of production and disarmament. Modelled on an image in New Scientist using data from Bulletin of the Atomic Scientists Nuclear Notebook.

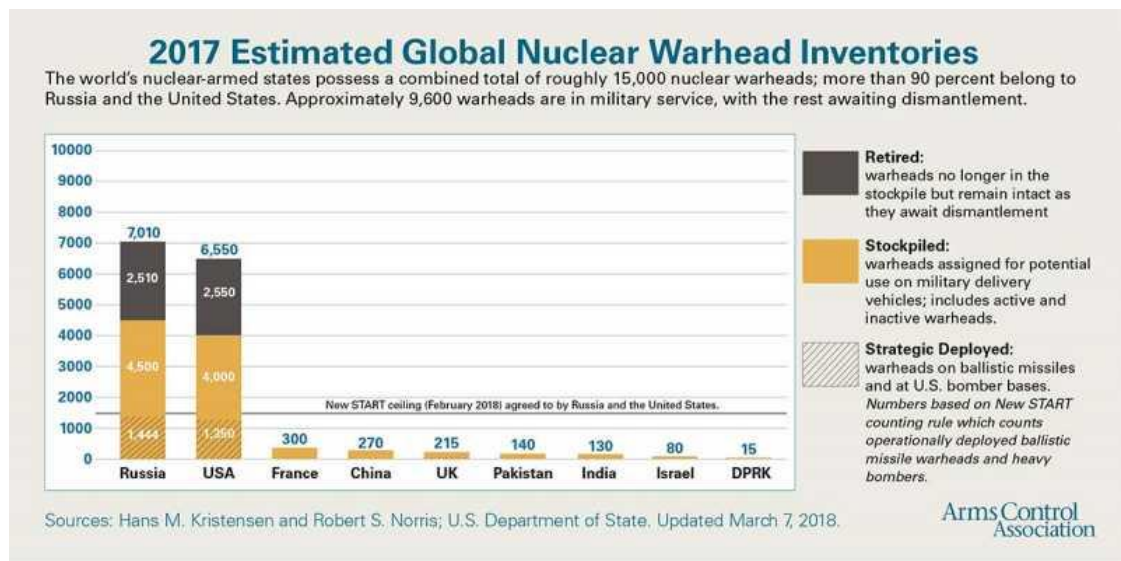


Figure 1.2 Diagram from the Arm's Control Association showing the global stockpile of Nuclear Weapons as of March 2018.

The global total of nuclear weapons reached its peak in the 1980s with the US and Russia possessing 23000 and 40000 nuclear weapons respectively (Figure 1.1). The current estimates of nuclear arsenals, including strategic warheads and lower-yield devices stockpiled around the world, are shown in Figure 1.2.

Made famous by the 2017 Nobel Peace Prize winners, the International Campaign to Abolish Nuclear Weapons (ICAN), is a coalition of non-governmental organizations encouraging adherence to and implementation of the treaty. The Treaty on the Prohibition of Nuclear Weapons (TPNW) forbids the use, threat of use, development, production, manufacturing, acquisition, possession, stockpiling, transfer, stationing and instalment of nuclear weapons or assistance with any prohibited activities and will supersede all the other treaties discussed. On the 7th July 2017, countries around the world voted for the implementation of the TPNW and it will be entered into effect once 50 countries have signed and ratified it. A NWS may ratify the treaty if it agreed to dismantle all its NWs.¹²

Although many treaties both bilateral and multilateral exist surrounding the testing, distribution and storage of nuclear weapons, verification of such activities has been one of the factors disabling the countries from signing the treaty such as

with the CTBT. Currently there is no established method to verify the dismantlement of a NW which would confirm the disarmament of NWS.

1.1.2 Dismantling and verification of NWs

During an inspection to verify NWs are being dismantled according to the treaty in place, a host country demonstrates to the inspectors that they are compliant with the regulations. To do this the host country may provide the inspector with a list of possible explosives contained within the NW (the exact explosive depends on weapon design and yield) so as not to compromise design of the weapon. It may be the inspectors' duty to verify that not only is the HE present, and is one of the possibilities discussed, but also that the material present at the start of the dismantlement process is the same material present at the end.

1.1.2.1 Explosive Detection Scenarios

A general process for a typical dismantlement procedure for a treaty accountable item (TAI), is illustrated in Figure 1.3. The various scenarios presented here have been identified as potential opportunities to gain confidence in the dismantlement regime.

- (i) Scenario one: Item declared as NW arrives at high security area

When the TAI, declared as a nuclear weapon, arrives at the high security area, it is then presented to the inspectors either as a complete weapon or concealed inside an additional container (Figure 1.3). In either situation, the inspectors are prohibited to view the inside of the item presented and must obtain measurements from the exterior of the TAI, by the agreed upon methods with the consent of the host country. At this time, it would be beneficial to be able to obtain measurements that would not only confirm that the TAI is a NW, but also measurements that would allow for comparison after dismantlement. This would increase confidence that the components resulting from the dismantlement process, originated from the TAI that was presented at the start of the procedure.

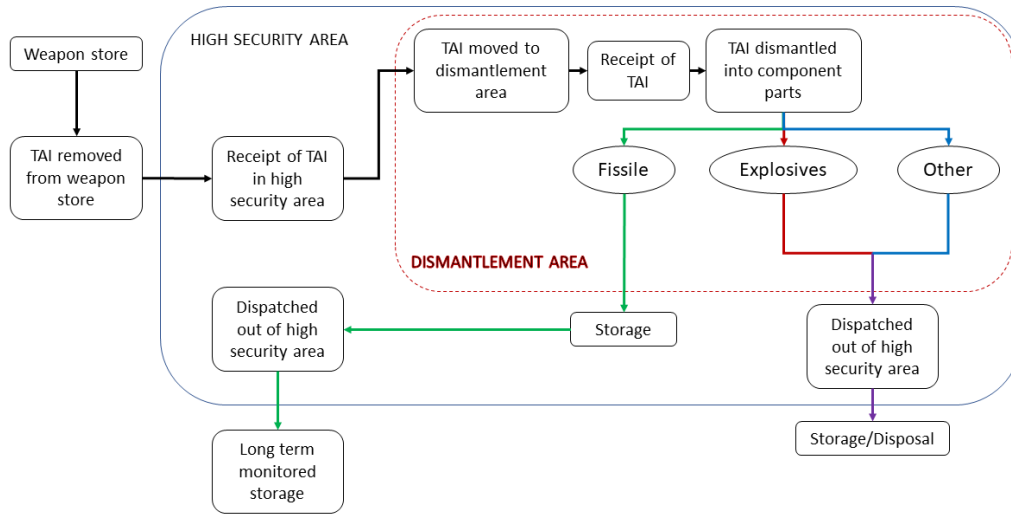


Figure 1.3 Simplified dismantlement procedure.

The primary question that needs to be addressed is whether the explosive can be identified. A technique is needed that not only identifies the presence of the key elements or properties of explosives but can distinguish between the different types of explosive and materials of similar elemental composition.

However, at this stage it would also be beneficial to confirm the authenticity of the TAI. To achieve this, it is necessary to gain some spatial understanding of what is presented. The configuration of the weapons, specifically the position of the fissile material in relation to that of the explosive, would increase the confidence of the inspectors. If the host country allows such measurements to be taken, the depth resolution of such a technique would need to be fully assessed to prevent the release of sensitive information.

The class and mass of the explosive used would also be a strong indicator of the power of the weapon and its capability as a NW. These parameters are however, considered to be sensitive information, so a compromise needs to be met. The identity of the explosive remains anonymous if the explosive can be classified, i.e. the explosive needs to be able to be classed as a military grade high explosive, as opposed to a low-grade explosive that would not be capable of initiating a nuclear reaction. The mass of the explosive, also sensitive information, can be narrowed

down to a possible range and then confirmed to be within this range, limiting the amount of information shared.

(ii) Scenario two: Inspectors presented with fissile container

Upon leaving the dismantlement area, the weapon would have been dismantled into its component parts, the fissile component of which would have been placed in a container ready for transportation to a permanent storage facility. Without access to the container, the inspectors need to verify that no explosives are left inside this container with the fissile material. This would ensure that the weapon has been suitably dismantled. A technology would be required that could detect explosives to confirm their presence or absence.

(iii) Scenario three: Inspectors presented with explosive container

Once separated from the main body of the warhead, explosives will be placed in a suitable container ready for transportation for either storage or disposal. The inside of the container will not be accessible to the inspectors so a similar technique to the above scenarios is required to identify what is inside the container.

At this stage, it is important to not only confirm the explosive material is concealed inside the container but to confirm that no fissile material is present, increasing confidence that the weapon has been sufficiently dismantled.

1.1.3 Previous Research and Techniques

The UK, US, Russia, Norway, the International Atomic Energy Agency (IAEA) and the Non-Government Organisations (NGOs) have all collaborated to develop methods to verify disarmament, in accordance to Article VI of the NPT, the majority of research focusing on confirming dismantlement.¹³

Much of the research previously conducted within verification has focused on confirming the authenticity of NWs, looking at the presence and proximity of the fissile material and the HE, as well as identifying the presence of nuclear material.⁶ There are very few examples, at least in public knowledge, that outline current methods of verification for dismantlement purposes, specifically for the identification of HE's.

The Portable Isotopic Neutron Spectroscopy (PINS) system is a technology with the ability to non-intrusively evaluate suspected chemical warfare munitions in sealed containers.¹⁴⁻¹⁶ It is used routinely by the U.S. Army, the Defense Threat Reduction Agency, and other military units to identify chemical filler within a weapon.¹⁷ Before PINS was developed, chemical weapons (CW) and storage containers were inspected and identified by direct sampling. This involves drilling a hole in the munition or container wall and a small sample of the contents extracted for chemical analysis. This is not just dangerous, as whatever compound is stored inside could be lethal, but also time-consuming and costly.

Today, PINS is used to identify CW and to distinguish them from high explosive (HE) munitions. The characteristic elements chlorine, fluorine, phosphorus (VX or sarin) and sulphur (mustard gas)¹⁵ which are present in unique combinations within chemical warfare agents and are not present in HEs, which are composed predominantly of nitrogen, oxygen, hydrogen and carbon allowing for discrimination. The presence of a HE is determined by the detection of nitrogen and the absence of chlorine, phosphorus and sulphur.¹⁵

PINS is based upon a technique called Prompt Gamma-ray Neutron Activation Analysis (PGNAA) which works by employing neutron radiation from a radioisotopic ^{252}Cf source (californium-252) or electronic neutron generator which penetrate the container wall and then are captured or scattered by the nucleus of the chemical elements present inside. As described in §2.1.1.2, capture reactions and inelastic scattering occur in the nuclei of the atom. The nuclei emit high energy gamma rays which are characteristic of the chemical element. The energetic gamma rays can easily escape the container and are detected by a high purity germanium (HPGe) gamma-ray detector.^{14,15} The relative abundance of different chemical elements in the material are determined by the relative peak intensities associated with each gamma-peak, and thus reveal the components of the scanned object.

PINS, although has the ability to identify smoke fills (the component within smoke grenades used to conceal the location or movements of military personnel, usually made up of white phosphorous) and chemical weapons, is not very sensitive to explosives due to the relatively low neutron cross section of nitrogen.¹⁴ Seabury and

Caffrey at the Idaho National laboratory have modified the technique, adapting the currently used system in order to improve the detection and identification of explosives.^{16,17} The modifications include using a DT (deuterium and tritium) electronic neutron generator to improve the characterisation ability of the system by providing data on the abundance of carbon and oxygen as well as the previously measurable nitrogen and hydrogen.¹⁶ The system whilst improved - having the ability to discriminate between some types of explosives - still has a relatively low sensitivity not having the ability to identify a material leading to high false positives. The adaptations mean an increased amount of tungsten shielding is required making the technique bulkier, less portable and more costly.

The development of a non-destructive *in situ* technology with a high specificity needed to discriminate between various different explosives, would simplify and greatly improve the inspection ability not just for the dismantlement of NWs, but also for CW inventories.

1.1.4 Concluding remarks

Currently there is no established method to verify the dismantlement of a NW without compromising the weapons design. The NPT whilst restricting the testing, storage and distribution of NWs also encourages the dismantlement and research into the verification techniques.

The development of a technology with the capability to detect and identify the high explosive component of a nuclear weapon under dismantlement, would greatly improve the ability of the inspectors to verify the disarmament of the weapon. The required technology needs to be material specific, have the capability to penetrate the metal container whilst also restricting the information obtained to keep any design features undisclosed.

Chapter 2

Verification Technologies

The development of a high sensitivity, portable, non-destructive technology to identify the high explosive component of a NW without the need for excessive, expensive shielding would improve the implementation of the NPT by increasing the inspector's confidence that the monitored item is a warhead and thus verify dismantlement has occurred.

Conventional explosive identification methods stem from the forensic and environmental sciences, where the collection and analysis of vapours or particles is key to detection.^{18,19} Here, the application requires detection and identification to occur through a highly absorbing barrier so focus on possible detection technologies has derived from the security industry where detection of concealed objects is required.

2.1 Explosive Detection Technologies

There are two types of explosive detection methods; 'trace' methods which rely on collection and analysis of explosive vapours or particles and radiation methods which irradiate an object, such as a package or container, to detect a characteristic signature of a specified material.

Trace detection methods are non-invasive and measure traces of characteristic volatile compounds that evaporate from the explosive or present on the container surface.¹⁹ However, the sensitivity of such techniques largely depends on the vapour pressure of the compounds of interest and the collection, transport and trapping efficiency of the vapour.¹⁹

Research conducted for the purpose of warhead verification by the All-Russian Scientific Institute of Technical Physics (VNIITF) in Chelyabinsk-70 observed that techniques based on collecting vapours for analysis, were less effective when employed to detect HMX-type explosives (nitroamine high explosives), which are employed in modern NWs, thought to be due to their very low vapour pressure.¹⁸ Vapour analysing methods have proved particularly ineffective when detecting explosives in a sealed NW or HE container.^{18,20}

Radiation methods, based on irradiating a container with a form of radiation to detect a characteristic signal emitted, are more suited for explosive detection when the explosive is concealed inside a container (e.g. warhead) due to access restrictions.¹⁸ High energy X-ray transmission imaging is currently employed to image the contents of chemical weapons to indicate the fill (whether solid or liquid) and deduce the configuration of the explosive system, before further inspection by neutron techniques to identify the chemical component. A ^{252}Cf source is used, obtaining and analysing the resulting thermal neutrons and/or gamma rays, but this system isn't sensitive enough to identify the explosive, discussed in §1.1.3, detailing the PINS system.¹⁸

Due to their clear advantages over vapour detection methods, and current use in the chemical weapons dismantlement industry, a radiation detection method was sought. The advantages and limitations of radiation technologies, currently used in the security industries, have been reviewed for the purpose of finding a new method for the detection of HEs inside metal containers. Most radiation explosive detection research, within public knowledge, has been conducted in the aviation security industry, the techniques widely used have been reviewed here in terms of use within nuclear dismantlement applications.

2.1.1 Radiation Methods

Radiation techniques generally work by directing a form of radiation at an object and from interpreting the resulting radiation emanating from the object, determine whether or not it contains a target material, such as an explosive.²¹

Radiation methods employed in the aviation security industry focus on identifying the morphology of weapons or detecting the presence of illicit substances, by imaging the internal structure of objects being examined, such as luggage.²²⁻²⁴ But with the potential to identify or characterise the compound composition, they have the advantage of gathering spatial and quantitative information.²⁰

In order to confirm the presence of a specific explosive substance, the technique utilised needs to be able to identify explosives i.e. be material specific, as discussed in §1.1.2. Radiation systems use the characteristic emissions produced from incident particles or rays interacting with a material to identify the structure of a compound.²⁰ There are many different radiation methods that possess high selectivity allowing for compound differentiation, such as Terahertz imaging, but which are not able to penetrate a metal barrier.^{25,26} Nuclear Quadrupole Resonance (NQR), employs an externally applied radio frequency magnetic field pulse at a characteristic frequency which results in the production of a coherent signal that can be detected with a RF detection coil. NQR has shown promise for the detection and identification of landmines, particularly involving RDX due to unique NQR absorption frequency of ^{14}N . The signal is however disrupted by metal casing, obscuring the quadrupole resonance signal by remnant magnetisation of the metal.^{19,27}

A summary of radiation detection techniques can be seen in Figure 2.1 and an indication is given of the techniques which have demonstrated capability of explosive detection through a metal barrier.^{28,29} The benefits and limitations of the techniques seen as potentially viable are discussed in the next section. Since imaging techniques would reveal details about the morphology of the weapon therefore compromising sensitive material, discussed in §1.1.2, they have not been reviewed in detail as they are not applicable to this research.

2.1.1.1 Electromagnetic Radiation Techniques

Low energy electromagnetic radiation, which would allow for the differentiation of explosives, such as infrared and UV radiation cannot be used here due to their poor penetration ability. X-rays and gamma rays also offer material specific interactions and are high energy forms of electromagnetic radiation with short wavelengths meaning they possess high penetrative capability.^{28,30-32} X-ray photons and gamma ray photons of the same energy are identical, however the way in which they are generated is different.⁶ X-rays originate from interactions with an atom's electrons, and are produced by the bombardment of a metal target with electrons, exciting the electrons within the target. When the electrons drop back into the stable ground state a quantum of energy is released as a photon. Gamma rays on the other hand,

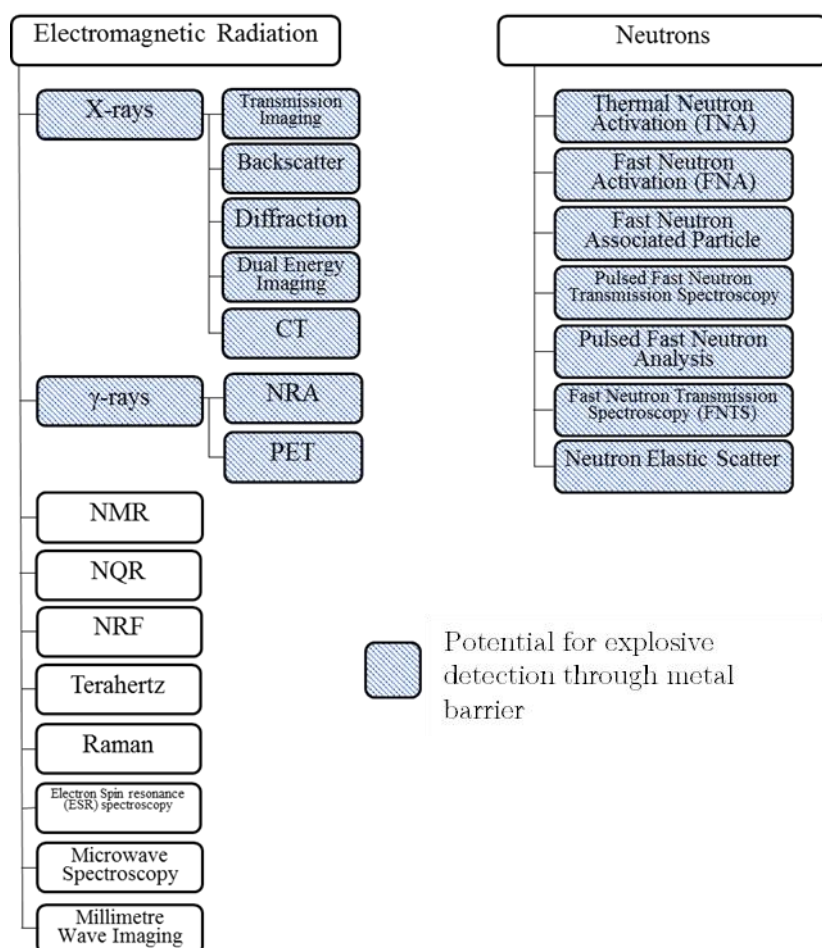


Figure 2.1 Summary of radiation techniques.

are produced by the nucleus of a radioactive source when the nucleus falls from an excited state, releasing excess energy as gamma rays and discrete energies.²⁸

These differing production methods result in differing spectra, whilst gamma ray radiation is in very discrete energies, X-ray radiation has discrete peaks overlaid onto a continuum of radiation named Bremsstrahlung radiation up to the applied voltage across an X-tube during production, discussed more in §3.2.2.1.

X-rays

X-rays were first discovered in 1895 by Wilhelm Röntgen^{30,33,34} observing the transparency of black cardboard under radiation whilst using a cathode ray tube.^{20,35} Röntgen noted that crystals, although shielded by the black cardboard, were glowing from radiation produced from the cathode ray tube. In the years that followed the imaging properties of X-rays were quickly realised resulting in the first Nobel prize for physics in 1901. From the initial discovery three primary branches of science have developed. The first is X-ray radiography, an imaging technique to observe the internal morphology of an object. Radiography takes advantage of the relatively low absorption of X-rays, which varies between materials as it is dependent on both the atomic number and density of the material.³⁰ The attenuation properties of X-rays proved to be very useful, first being used medically in World War One and since then through development of X-ray generation, detection and data acquisition it is a commonly used technology in both the medical and security industries today.

X-ray crystallography, mainly concerned with structure analysis, was the next major technique developed, stemming from the single crystal research by Max von Laue in 1912 who confirmed the dual nature of X-rays i.e. their particle and wave nature.^{30,36} X-ray crystallography is the study of crystalline materials by diffraction of a monochromatic beam of X-rays.

The final branch of science developed from the discovery of X-rays is X-ray spectroscopy, the characterisation of materials by X-ray excitation employing a polychromatic beam of radiation.

The utility of X-ray imaging systems stems from their capacity to investigate non-destructively the internal structure of an object.³⁷ Conventional transmission X-ray imaging systems, based on radiography, are deployed in airports around the world to detect weapons and find areas within luggage which could conceal explosives.^{21,38} Some modifications have been made since the original technology, adopted in the early 1970's, but to this day X-ray imaging systems are still the state of the art for weapons detection and are the most commonly used inspection system within the aviation security industry which is where the majority of research, and therefore most developments, have occurred in radiation explosive detection technologies.^{21,39}

A high energy X-ray transmission imaging system has previously been proposed for the authentication of nuclear weapons to detect nuclear material.^{6,40} The system is based on the standard X-ray transmission imaging system employed within aviation security. It utilises a high energy polychromatic fan beam of X-rays (to penetrate nuclear weapons it is suggested to use > 450 keV X-ray source⁴⁰) with a linear set of detectors on the opposite side of the object, which collects X-rays that have transmitted through the object.⁴¹ The object is then scanned through the beam so the whole volume is interrogated. The intensity of the detected beam depends on the energy of the incident beam, the atomic number, density and thickness of the object.⁴² High atomic number materials absorb more photons, attenuating the beam, reducing its intensity thus appearing darker on the greyscale image, as shown in Figure 2.2. The X-ray beam is also greatly attenuated when the object is dense or thick. The primary mechanisms responsible for X-ray attenuation are Compton scattering and photoelectric absorption, discussed in more detail in §3.2.



Figure 2.2 Conventional X-ray transmission image of an 81 mm mortar shell with a tube of Al_2O_3 through the centre. Image taken at 180 kV, 55 μA with 1415 ms exposure.

These 2D greyscale images provide information on the morphology of concealed objects and when imaging a single material, can provide information on its density by measurement of the attenuation of the beam.³⁸ Analysing images, such as Figure 2.2, weapons (i.e. knives and guns) can easily be found due to their recognisable structures but using this technique for identifying illicit materials has its limitations as explosives and drugs have no defined shape. In an aviation security environment, some information could be gained from analysing images of wires and detonators which could lead to further investigation of the object under inspection. However, the concealed compounds cannot be identified either from their morphology or their density due to all objects present superimposing in the image resulting in a summation of densities, therefore explosives can be hidden behind highly attenuating materials such as metals.^{21,38,43} Thus, conventional transmission X-ray radiographic imaging does not have the capability to distinguish between a thin sheet of highly dense material or a thick slab of low density material, both of these situations would attenuate the beam of photons equally if superimosed.^{28,44}

Although this method is very effective at detecting weapons by observing the shape of the dense material it does not allow for the identification of the explosive material and would reveal sensitive information regarding the weapons design.

More recent X-ray imaging, proposed within aviation security for the detection of explosives, utilises backscattering of X-ray photons where both the detector and transmitter are placed on the same side of the object under inspection.^{22,38,45}

Backscatter imaging describes photons which have undergone Compton scattering where the energy of the incident photon is reduced by the recoil energy of the struck electron, see §3.2. The backscattered image appears bright for low density organic materials since incident photons penetrate deep into the organic materials, where there is a lower electron density, compared to materials like metals which comprise a high electron density.^{22,46} Although backscattering reduces the superimposition of objects, whilst also allowing the detection of concealed objects when the far side is inaccessible, the intensity of the Compton backscatter decreases with increasing energy, limiting the penetration capability. Thus, materials at the centre of the inspection volume are not as easy to distinguish compared to materials near the surface of the volume.

Combining the image created from backscattered photons with the transmission image, measuring the number of reflected and transmitted photons, can separate the effects of density and atomic number. This would allow the system to indicate high density, low atomic number materials i.e. explosives.^{41,44}

A further advancement in detection of explosives is transmission dual-energy X-ray systems, introduced in the 1980's, and currently employed in most European airports for checking cabin baggage.⁴⁷ Dual-energy X-ray systems compare the images resulting from two different beam energies (e.g. 60/100 keV).^{28,48,49} Lower energy X-rays are more easily absorbed by the photoelectric effect but whether or not they are absorbed depends on the thickness and atomic number of the material. At higher energies the X-ray photons suffer less absorption, as Compton scattering dominates at higher energies so while areas of heavy metals are dark in both images, areas of light elements are darker in the low energy images. Like the transmission system, the dual-energy method applied to individual objects can give a measure of

density and thickness.⁴⁴ The problem distinguishing a thin sheet of high atomic number material and a thick sheet of low atomic number material, when using the conventional transmission detection, no longer occurs when using dual-energy technology due to the greater discrimination ability.⁴⁸

The ratio between the two mass attenuation coefficients (discussed in §3.2) determined from the two energy exposures in conjunction with the measured density, indicate the materials' effective atomic number, Z_{eff} (an equivalent atomic number for a combination of different materials), which is compared to an existing database for classification.^{21,49} Based on each pixels' calculated Z_{eff} , the 2D image is annotated by approximately classifying each pixel and allocating a colour; based on that classification organic ($Z_{\text{eff}} < 10$) is orange, inorganic ($10 < Z_{\text{eff}} < 18$) is green and metallic ($Z_{\text{eff}} > 18$) is blue, Figure 2.3.³³

Although dual-energy improves the discrimination ability between benign substance and explosives, the concealed explosives are still difficult to distinguish due to superimposition.⁴⁴ To overcome the superimposition of objects, a volumetric imaging system could be used, enabling a 3D view from which objects thicknesses, position, hence mass densities could be determined.^{49,50}



Figure 2.3 Dual-energy X-ray transmission images (a) petri dishes filled with various powder samples and a lead block at the top (b) explosive container with sample of NH_4NO_3 in centre and (c) and 81 mm mortar shell composed of iron.

One such volumetric imaging technique is Computed Tomography (CT). CT is mainly used for medical imaging but has found use in security scanning within US airports.^{21,44} CT uses the same transmission technology but instead of solely collecting data in one direction, CT collects data from multiple angles around the object, essentially creating a ‘sliced’ image of the object.^{21,44} Practically this is achieved by a rotating gantry with the X-ray source and detector placed on opposite sides of the object.²¹ Instead of the detector capturing images it accumulates the energy of the transmitted photons. The data from all different angles is then computer processed to reconstruct the image. Collecting many of these ‘slices’ throughout the length of an object creates a 3D image which overcomes the ambiguity associated with the previous techniques providing a greater understanding of the internal structure of an object offering information of shape, thickness, density and texture of objects allowing voxel by voxel imaging.³⁷ CT systems, as well as providing better understanding of the structure of an object, when used in conjunction with dual-energy technology provides Z_{eff} data along with density information which isn’t affected by superimposition.^{38,42,44,49-51}

These imaging techniques have limitations regarding their discrimination capability. Harding *et al.*(2012) and Yinon (1999) have demonstrated that the range of densities for innocuous materials significantly overlaps with that of illicit materials, which complicates the practicality of the techniques. CT scanners have other drawbacks as well which includes their high cost associated with maintenance of their instrumental and mechanical mechanisms throughout their lifespan. CT, whilst overcoming many of the problems presented by conventional transmission imaging and dual-energy technology, it is still not material specific, making the technology redundant for identifying explosives.³⁸

A technique with the high sensitivity[†] capable of identifying explosives is X-ray diffraction (XRD).^{52,53} XRD is a commonly used analytical technique within crystallography for material identification with applications in many fields

[†] Sensitivity is the ability to correctly identify a threat material known to be present.

including material science, pharmaceuticals, geology, diagnostics and forensic science.^{54–56} Harding (2009)⁵⁷ and Speller (2001)⁵⁸ have previously demonstrated the capability of XRD for detection of concealed explosives. Recently it has been used in a variety of novel diagnostic systems and is one of the most promising emerging techniques for bulk detection of concealed explosives.^{52,59,60} XRD employs the interference of elastically scattered photons (Rayleigh scattering) to produce characteristic signatures of the material under investigation. In order to identify the signature, the data collected is compared to standard signatures of known polycrystalline materials, thus a database of characteristic signatures from known possible explosives is required. Rather than determining Z_{eff} and the density of objects, as with dual-energy and CT systems, XRD provides information on the atomic structure of the material under investigation. The fundamental principles of XRD are discussed in greater depth in §3.2.

There are two different types of XRD; angular dispersive XRD (ADXRD) and energy dispersive XRD (EDXRD) both of which have been applied to the detection of explosives, detailed more in §3.3^{23,28,53,61–66} ADXRD employs a tightly collimated incident beam of monochromatic radiation, where the angle, 2θ , subtended by the trajectory of the diffracted photons, with respect to the primary beam, is measured to enable the calculation of the atomic spacings within the crystalline material. In contrast EDXRD utilises a polychromatic beam to obtain diffracted flux from the sample at a fixed 2θ angle. An energy sensitive detector is used to collect the diffracted photons which measures their wavelength and thus enabling the d -spacings to be calculated.⁶⁷

The relatively low intensity of diffracted X-rays compared with the principal X-ray beam has been a significant limiting factor, limiting the use of XRD for screening systems requiring high throughput.⁶⁸ But advancements in the field, discussed more in §4.1, has seen prototype XRD screening systems developing, some of which are already employed within airports as secondary detection systems.^{53,69}

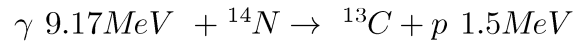
Gamma Rays

French chemist and physicist, Paul Villard, is credited with the discovery of gamma radiation in 1900, while studying radiation emitted from radium. Gamma rays have

found many applications within the food industry killing bacteria, medical industry, sterilising equipment and industrial application detecting defects in metal castings. More recently dual-energy imaging gamma ray technologies have been developed for screening cargo containers for detection of nuclear material similar to that used within X-ray dual-energy imaging.^{6,70} Material specific gamma ray techniques are Positron emitting tomography and Nuclear resonance absorption.

Positron emitting tomography (PET) uses high energy photons, from a gamma ray source, to interrogate the nitrogen content within an inspection volume.⁷¹ Due to this high energy, the penetrating ability of the gamma rays makes it ideal for working with metal containers.²⁸ The technique works by a gamma ray of energy 9.17 MeV, activating an atom of the stable nitrogen isotope ^{14}N , removing a neutron to become ^{13}N , an unstable isotope of nitrogen. This unstable isotope then decays into ^{13}C , releasing a positron-electron pair which immediately annihilates, producing two 511 keV photons propelled in opposite directions, this process is called pair production. These are detected and counted to give a measure of the nitrogen concentration within the volume.⁷²

Nuclear Resonance Absorption (NRA), also known as Gamma Resonance Absorption (GRA) also uses high energy gamma-rays but instead of exciting an atom of nitrogen to make it unstable, the gamma ray is absorbed via resonance absorption:



The protons produced are counted alongside the electrons resulting from Compton scattering, as with X-rays. The number of protons measured indicates the total attenuation (resonant and non-resonant) whereas the electron signal determines the non-resonant attenuation, so using both measurements together allows determination of the net resonant attenuation.²⁸ Using this information a nitrogen radiograph is constructed, and along with a 9.17 MeV radiograph, the distribution of nitrogen within the inspection volume can be observed. This technique is useful for when only small amounts of nitrogen are present due to there being a large absorption cross section.

Both gamma ray techniques discussed have the great penetration ability needed to pass through the metal containers required to identify the explosives. However, the technique will only detect the nitrogen content of the explosives and the initial system, linear accelerator, used to produce gamma rays of 9.17 MeV is very large, heavy and required lot of radiation shielding for the health and safety of the operators.⁷¹

2.1.1.2 Neutron techniques

Like gamma rays, neutron based detection methods involve probing the nucleus of an atom in order to generate detectable, characteristic signatures allowing the presence or absence of explosives to be determined.^{20,73-75} Neutrons, being uncharged particles are not affected by electromagnetic forces and thus have a high penetration capability, making them an attractive probe for munitions and storage containers since they can easily penetrate thick steel walls.^{15,75} Neutrons are not only sensitive to the elemental structure of materials but due to interaction with the nucleus, as opposed to the electrons, isotopic mixtures can also be recognised.²⁸

When neutrons interact with a material, the emitted gamma rays or neutrons are measured to give an indication of the elements present. Different chemical elements found in explosives like nitrogen, carbon and oxygen, emit characteristic gamma rays following scattering or absorption of neutrons. Analysing the spectrum emitted from a material can give an indication of the elemental composition and thus determine the presence of an explosive. There are many different neutron based methods, summarised in Table 2.1.^{19,28,73-77}

Thermal Neutron Analysis (TNA) was one of the first technologies proposed for explosive detection and is therefore one of the most researched.⁷¹ TNA involves the irradiation of the object by thermalised neutrons and subsequent detection of gamma rays from neutron capture.^{19,20,78} A thermalised neutron is produced by moderating high energy neutrons thus having low kinetic energy (<0.025 eV), which equates to the energy of the neighbouring particles within the material. Due to their low energy and slow speed they have large cross section in reactions such as fission which makes them desirable for chain reactions. Compared to other elements such as carbon or oxygen, that would also be found in explosives, nitrogen and hydrogen

have a large thermal capture cross section. The thermal capture reaction with nitrogen results in the production of distinctive 10.8292 MeV gamma rays thus the amount of nitrogen present can be measured using a gamma ray detector.⁷¹ Arrays of gamma detectors can be used to tomographically determine the density distribution of nitrogen and hydrogen.^{44,75}

Although TNA doesn't require an accelerator as it doesn't need a monoenergetic beam of neutrons, it does use a neutron emitting radioactive source. For this application that requires the end device to be portable, the safety precautions necessary to store and transport a neutron source would make this technique impractical. Although this technique has a high penetrating ability the transporting, heavy shielding and collimation of thermal neutrons means this technique quickly becomes unfeasible along with a high cost.⁴¹

An alternative to using thermal neutrons is to use fast neutrons. The use of fast neutrons, i.e. neutrons with a high kinetic energy (>0.1 MeV) produced by nuclear fission, is popular amongst the nuclear technologies, as can be seen in Table 2.1, due to their relative ease to be produced compared to thermal neutrons.

Fast Neutron Analysis (FNA) was developed as an attempt to gain more information, about other elements, mainly C and O, from an object. FNA uses a collimated beam of high energy (14 MeV) fast neutrons to initiate inelastic scattering. The gamma rays released from nuclei by inelastic scattering events have distinctive energies that are detected by an array of detectors surrounding the object and can be quantified to indicate the relative concentrations of elements.²⁸ Although the technique provides the ability to detect a greater number of the fast high energy neutrons, a significant background is created making it difficult to extract the signal from the gamma ray detectors.

A monoenergetic beam of neutrons, generated by an accelerator, is required due to the high energy needed to excite nuclei as part of the inelastic reactions. Production of neutrons by an accelerator is one of the major drawbacks of this technology as the weight, volume and operating costs along with installation and lack of portability means it is unsuitable. Other smaller sealed tube accelerators are available but produce a low neutron yield, have a short tube life, stability problems

Table 2.1 Summary of neutron based explosive detection techniques adapted from *Yinon*,²⁸ *Buffler*⁷⁵ and *Gozani*^{73,74}

Technique	Probing Radiation	Detected radiation	Measures
Thermal neutron analysis (TNA)	Thermalised neutrons	Gamma rays	H, N
Fast neutron analysis (FNA)	Fast neutrons	Gamma rays	C, N, O
Pulsed fast neutron analysis (PFNA)	Nanosecond pulses of fast neutrons	Gamma rays	C, N, O
Associated particle imaging (API)	14 MeV neutrons and α particles	Gamma rays in coincidence with α particles	All elements except H and He
Pulsed fast-thermal neutron analysis (PFTNA)	Fast and thermalised neutrons	Gamma rays	H, C, N, O
(Pulsed) Fast neutron transmission spectroscopy (PFNTS)	Nanosecond pulses or continuous fast neutrons	Neutrons	C, N, O
Prompt-gamma neutron activation analysis (PGNAA)	Thermalised neutrons	Gamma rays	H, C, N, O
Neutron elastic scatter (NES)	Fast neutrons	Scattered neutrons	H, C, N, O

and the same shielding issues of volume, weight and cost as a conventional accelerator.^{46,71,79}

Combined with the previously mentioned disadvantages, FNA also has a relatively poor image quality, having very low resolution and a poor signal-to-noise ratio of its 2D images, leading to long detection times.²⁸ A way to reduce the background noise is to use Pulsed Fast Neutron Analysis (PFNA) which still uses the same

technology as FNA but irradiates the object with lower energy fast neutrons in fixed time windows determined by pulse operation of the neutron source. Time of flight information can be used to gain a 3D image of the irradiated object allowing the location of illicit substances to be identified by measuring the time between the creation of the neutron in the target and the detection of the gamma ray thus this technology would be useful for spatial information.⁷⁵ PFNA is one of the best technologies for material identification and can even be used on large containers, with the ability to penetrate through metal barriers but an accelerator is required to generate the neutrons.⁴¹ It provides much more information than X-ray CT or magnetic resonance but sadly still has the disadvantages of being expensive, bulky and heavy.^{28,78}

Similar to FNA and PFNA, Associated Particle Imaging (API) detects gamma rays from inelastic scattering events. Unlike PFNA, API can determine the position of the scattering source without a need for a pulsed source. The source for API tags the neutrons when they are created, recording the time and direction by detecting the α particles which are simultaneously released 180 degrees from each other using a position sensitive detector.^{75,79} As with PFNA, API uses time of flight data, allowing calculation of the distance travelled by a neutron meaning a 3D image can be created.^{28,41} The need to have an α -particle detector built into the system impedes the use of API outside of the laboratory, once again being bulky and expensive.⁴¹

Pulsed Fast-Thermal Neutron Analysis (PFTNA) is a combination of TNA and PFNA. The microsecond pulses of 14.1 MeV neutrons produce gamma rays, as previously described, by inelastic scattering interactions allowing the detection of oxygen and carbon, whilst the thermalized neutrons produced by the neutron generator, create neutron capture reactions allowing nitrogen and hydrogen to be detected.^{71,75} This technique negates the previous high background problem with FNA improving the signal-to-noise ratio. Whilst this technique solves some of the detection issues presented by the other techniques it still has the disadvantages of weight, size, expense and relatively low signal-to-noise.

Pulsed fast neutron transmission spectroscopy (PFNTS) utilises the unique resonance structures produced by nuclei when bombarded with a fan beam of

intense “white” neutrons produced from a nanosecond pulsed accelerator. The beam is transmitted through the object and the measured transmission spectra provides information on the densities of the elements present by evaluating the total cross section of the desired elements. The disadvantages of this technique are much the same as for the previously mentioned methods of which the high costs and maintenance of a heavy nanosecond pulse accelerator-based system results in it being impractical.

In contrast to many of the nuclear techniques mentioned, neutron elastic scattering (NES) measures scattered neutrons. It incorporates neutron resonant scatter and neutron elastic backscatter. Using this method, illicit materials are distinguished from common materials via the concentrations of HCNO and the relative ratios of carbon, hydrogen and oxygen with nitrogen. These ratios for illicit materials are generally lower than that of common materials whilst having a higher concentration of nitrogen. Fast neutrons are used for elastic scattering due to exhibiting a large cross section with light nuclei. Elastic collisions cause no structural change in the target nuclei but, as with elastic scattering in X-ray diffraction, the neutron is scattered in a specific direction with a reduced, unique energy. Comparing the energy and intensity of the incident neutrons to that of the backscattered neutrons along with the ratios of the various signals from individual elements, allows the elemental composition to be estimated.²⁸

The other part of the NES system involves the use of neutron resonant scatter. Here, individual elements exhibit unique changes in cross section, at various incident energies, due to their morphology. At resonance energies, the nuclei are no longer spherical meaning the direction in which the neutrons are scattered differs.²⁸ Combining the data from neutron backscatter and the resonant scatter allows the target material to be identified. Like many of the other neutron techniques presented, NES has the disadvantage of requiring fast neutrons which comes with all the other shortcomings previously discussed.

Overall, neutron-based detection techniques possess a high level of sensitivity and high specificity[‡], with the ability to provide elemental composition even behind thick metal barriers due to their sought after, high penetration capability. All these factors make the technology highly desirable for detection of explosives within metal containers. However, the problems with neutron use still outweigh the advantages. Field deployment of neutrons sources, or radioactive materials, is not only problematic due to the shielding requirements and general bulky, heavy nature of the generators but would also produce high expenses incurred from licensing and intensified security along with the transportation of heavy goods. Advantages have been made within the field, such as portable neutron generators, which would allow easy transportation along with the ability to be switched off while in transit, but the shielding required when the device is in use would still cause portability and cost issues.

Further reading regarding X-ray and neutron techniques for explosive detection can be found in Wells (2012)³⁸, Yinon (2007)⁸⁰ and Whetstone (2014)⁸¹.

2.2 Concluding remarks

In this chapter, primary techniques currently being explored for the detection and identification of explosives with the potential to penetrate through metal barriers have been reviewed. A summary of the advantages and limitations of the most promising non-imaging techniques is given in Table 2.2.

X-ray transmission imaging doesn't allow for the discrimination needed to identify explosives. Advancements in the field such as backscatter imaging and dual-energy technology providing a slightly higher level of discrimination, allowing materials to be characterised broadly into organic and inorganic but suffers from geometric restrictions, superimposing objects under investigation. Whilst removing the limitation caused by superimposition of objects, CT does not provide the high level of specificity needed to identify explosives. XRD provides a high level of specificity by providing information on the atomic structure of the material and thus is the

[‡] Specificity is the ability to label benign object as nil-threats.³⁸

most encouraging X-ray technique reviewed, with the potential to not disclose the weapons design.

The high penetration capabilities make the neutron technology highly desirable for detection of explosives within metal containers. However, the disadvantages associated with neutron techniques; high cost, large size, shielding requirement outweigh the advantage of penetration capability.

Due to its high specificity and advantages over the nuclear techniques, XRD was chosen to investigate the possibility of identifying explosives inside metal containers for weapons dismantlement verification. The fundamental principles of XRD are discussed in Chapter 4.

Table 2.2 Summary of non-imaging bulk detection techniques reviewed.^{20,41,46,77,78,80}

Bulk Detection Technique	Advantages	Limitations
X-ray diffraction	Non-destructive High sensitivity Portable Source Cost Effective	Weak signal
Gamma rays	High Penetration ability	Sensitivity - detects only nitrogen containing explosives Operational safety – health hazard, requires shielding Requires very advanced high current accelerator - large/heavy/requires radiation shielding High cost
Neutrons	High sensitivity High penetration ability	Detects only nitrogen containing explosives and non-nitrogen explosive peroxides High cost Operational safety – health hazard, requires shielding Needs neutron source/accelerator – large/heavy/need radiation shielding thus not very portable

Chapter 3

X-ray Diffraction

X-ray diffraction involves the identification and characterisation of unknown compounds, typically polycrystalline materials, by obtaining structural, chemical and physical information.³⁰

This chapter outlines the key principles involved in powder X-ray diffraction along with the fundamental interactions involved, focusing on coherent scattering as this is the only interaction employed in XRD. A qualitative comparison is given of both ADXRD and EDXRD for the purpose of weapons dismantlement. Traditional transmission pencil beam geometry is presented alongside the more recent focal construct geometry technique, introduced in §4.1.4, used to increase the number of photons incident on the sample.

3.1 X-ray Interactions with Matter

When photons interact with matter a number of different processes may occur, illustrated in Figure 3.1.³⁷ Absorption of a photon occurs either by photoelectric absorption at low energy or pair production at high energy, in both instances the photons undergo a total loss of energy. On the other hand, a photon which is transmitted has no energy loss, penetrating the material without any interaction.^{20,30}

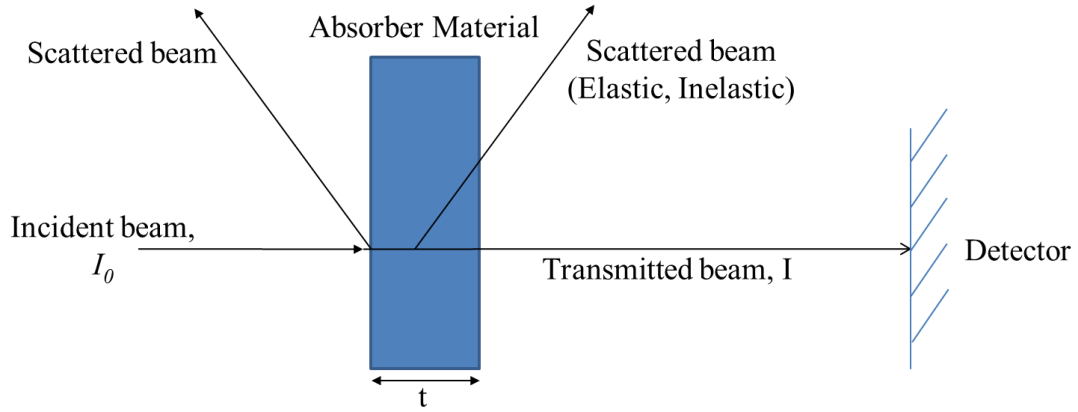


Figure 3.1 Illustration of the possible occurrences when a photon is incident of a material.

When a beam of X-ray photons with initial intensity, I_0 , is incident on a material of thickness, t , a proportion of the photons will be absorbed as the beam interacts with the material, Figure 3.1. As a result of this interaction the intensity of the beam will decrease according to the Beer-Lambert law^{21,33,34,82}, Equation (3.1), where I is the proportion of the incident beam which has been transmitted.

$$I = I_0 e^{-\frac{\mu}{\rho} \rho t} \quad (3.1)$$

As can be seen from Equation (3.1), reduction of the beam intensity is dependent on thickness of the sample, t , together with the density of the material, ρ , the mass attenuation coefficient (μ/ρ) (where μ is the linear attenuation coefficient, cm^{-1}) both of which are material specific. Transmission X-ray imaging is based on this interaction, discussed in §2.1.1.1.

The other named interaction, scattering, occurs when any of the incident radiation is deflected or reradiated. Scattering occurs by two different processes; coherent scattering, also known as elastic scattering or Rayleigh scattering, and incoherent scattering also known as inelastic scattering or Compton scattering.

Elastic scatter, so called due to the elastic collision between the incident photon and an electron within the sample volume, results in a photon being emitted at a different direction from the sample with the same energy and wavelength as the

incident photon. It leads to diffraction effects where the resultant peak positions and relative intensity, provide information on atomic number and density.

Inelastic scattering (or incoherent scattering) of a photon results in the photon losing part of its energy when colliding with an electron. The energy of the incident photon ionises the electron within the sample volume and is reemitted as a Compton photon with a lower energy. Since Compton photons are emitted in arbitrary directions very few reach the detector window.³⁰ Within the scattering region of 3-10° from the primary beam axis, coherent scatter dominates whereas at larger angles incoherent scatter is more prevalent. Compton scattering is independent of atomic number and provides a direct measure of density.⁴⁴

3.2 Introduction to XRD

X-ray diffraction techniques are based on the coherent scattering of X-ray photons from matter. Materials with long range order, arranged in an ordered, periodic lattice i.e. crystalline materials, exhibit X-ray diffraction when interrogated by X-ray radiation.^{53,59,61–66,83–86} When diffraction occurs, characteristic interference peaks are formed, unique to each individual material, offering atomic structural information.⁵³

When an incident X-ray beam interacts with an atom, the electrons within the atom oscillate with the same frequency as the incident X-ray beam, generating X-rays of the same wavelength as the incident beam, scattered in all directions. These spherical scattering waves, produced at adjacent points throughout the crystal, expand in space until they interact with each other. Depending on the angle of incidence, wavelength of the incident X-ray beam and the distance between the crystallographic planes of the crystal, known as *d*-spacing, the expanding waves produce constructive interference when in-phase and destructive interference when out-of-phase.^{30,31,34} Constructive and destructive interference effects result in X-rays only detected at characteristic angles.⁸⁷

The phase of any two waves corresponds to their path difference. When the path difference is coincident ($n\lambda$, n being an integer) the waves are said to be in-phase and combine to form one synthesized wave with double the amplitude. The path

difference depends on the direction of the X-ray with respect to the crystal. Deconstructive interference occurs when the path difference is $\lambda/2$.³¹

Constructive interference is commonly understood by Braggs law:

$$\lambda = 2d \sin \theta \quad (3.2)$$

Where λ is the wavelength of the incident wave, d is the atomic d -spacing of the crystal and θ is the diffraction angle at which constructive interference occurs. Braggs' Law is a simplified model considering X-ray scattering as a reflection from planes of atoms, Figure 3.2.

Diffraction is often seen as a reflection as it appears that the atoms act as mirrors. The two phenomena however do differ. Diffraction occurs between all atoms of a crystal which lie in the path of the incident beam in contrast to reflection, which takes place at the surface of the material. As discussed, diffraction only occurs when particular angles of incidence satisfy Braggs Law whereas reflection occurs at all angles of incidence. The efficiency of both phenomena also vary greatly; reflection is almost 100% efficient whereas diffraction is only about 1% of the incident beam.³¹

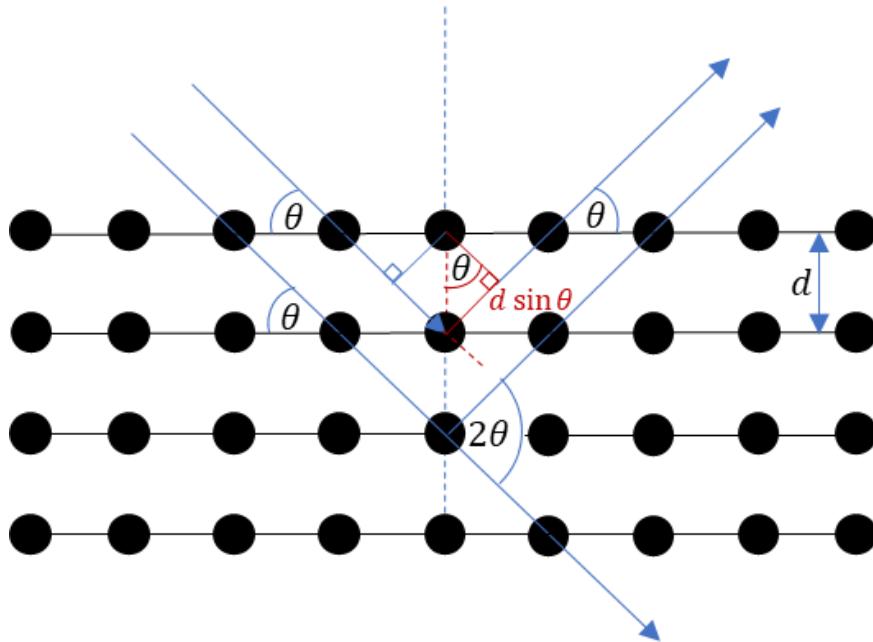


Figure 3.2 Diagrammatical representation of Braggs' Law illustrating the reflection of X-rays from two atomic planes.

3.2.1 Basics of Crystals and their Structures

Crystals are made up of identical small infinitely repeating units of atoms termed unit cells.^{31,34} Parallel planes of atoms intersecting a unit cell are used to define direction and distances within the crystal. The crystallographic planes are identified by Miller indices. Miller indices are defined as the reciprocals of the fractional intercepts which the plane (hkl) makes with the crystallographic axis.

Polycrystalline materials consist of randomly orientated crystalline domains, a few to more than a million of which will be in the path of the incident beam. A high proportion of the crystalline domains will have planes simultaneously fulfilling Bragg's Law. When using a single crystal not all planes satisfy Bragg's Law at a fixed incident angle, so a partial diffraction pattern is formed. It is therefore customary to rotate single crystals during data collection, so Bragg's Law is satisfied at multiple orientations; simulating a polycrystalline sample.

Constructive interference within an ideal polycrystalline sample will result in the appearance of cones with enhanced intensity, known as Debye cones, illustrated in Figure 3.3. A polycrystalline material with randomly orientated individual small crystal grains generates scattering maxima in the Debye cones with a smooth, continuous and uniform intensity around their circumference, Figure 3.4 (left).

The diffraction angle (2θ) of the Debye cone can be determined by measurement of the Debye cone radius within the detector plane and applied to Bragg's law, assuming knowledge of sample position. Applying Bragg's Law to experimental data, allows the interplanar distances between centres of atoms or ions to be

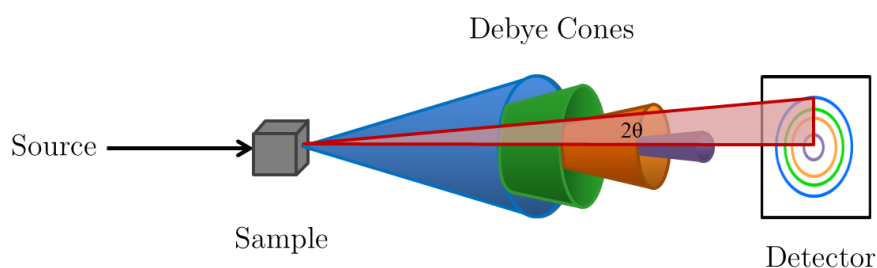


Figure 3.3 Schematic diagram of X-ray diffraction

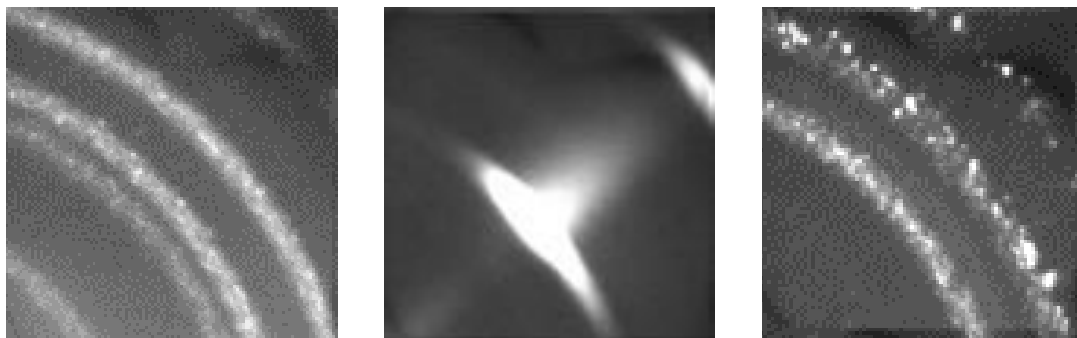


Figure 3.4 Scattering patterns obtained with offset area detector from relatively randomly orientated crystals with small grain size, Al_2O_3 (left), a sample with preferred orientation, Al (middle) and a sample with large grain size, Cu (right).

calculated, providing distinctive structural information on the material being analysed. The calculated d -spacings, in order of 10^{-10} m are comparable to the X-ray region of the electromagnetic spectrum and are used to identify unknown materials through comparison with a library of materials with their corresponding d -spacings. This provides the basis of angular dispersive XRD.

Material identification studies are typically carried out either using ideal powders or single crystals. Powders exhibiting large grain size or preferred orientation, common in real world problems, are usually avoided because relative intensities deviate from theoretical calculations or standard diffraction database, such as Powder Diffraction FilesTM (PDFTM) files.³⁴

Preferred orientation occurs when there is a bias towards one direction in the crystalline domains in the path of the incident beam. Depending on the degree of preferred orientation within the section of sample, resultant Debye cones tend to be smooth but with a non-uniform intensity around the circumference, Figure 3.4 (middle). In extreme cases, with a high degree of preferred orientation, Debye cones appear discontinuous presenting as arc segments due to the absence of certain orientations. When there is a small bias towards one direction, i.e. preferred orientation is low, the Debye rings have areas of low intensity.

Diffraction patterns appearing as spots, as opposed to rings indicate the presence of a crystal with large grain size, thus acting similar to a single crystal producing

Laue spots. A large grain size results in the incident beam passing through a limited number of crystalline domains.⁸⁸ When the effect of grain size is minor, the Debye cones appear spotted, as in Figure 3.4 (right), but can become discontinuous in extreme cases.

Diffraction profiles are calculated from transmission ADXRD images by integrating a selected 2θ range (selected by detector position) along the Debye rings. Integrated data obtained from a 2-dimensional area detector provides better intensity and statistics for samples with preferred orientation or large grain size compared to a translating point or line detector.

3.2.1.1 Explosives

There are many different varieties of explosives, but the majority consist of the same four elements carbon, hydrogen, oxygen and nitrogen in differing ratios. The major exceptions being the chlorine bearing explosives, LX-17 and PBX-9502, and the non-nitrogenous explosive TATP (from study by Seabury).¹⁷

A general rule currently used to distinguish between explosives and inert materials is that explosives contain a high proportion of nitrogen and oxygen and low proportions of hydrogen and carbon. Together with the relatively high density of $1.2\text{--}2.0\text{ g cm}^{-3}$, for HCNO materials, the presence of an explosive can be determined but this method is not specific enough for this application where the explosives' identity needs to be realised.^{51,75}

As explosives are polycrystalline materials, XRD can be used not just to characterise but to identify each individual explosive, as they each produce a unique diffraction pattern, some examples of which are shown in Figure 3.5. Explosives, as discussed in Chapter 4, have previously been analysed with XRD for security screening applications.^{65,88,89} These studies demonstrated that explosives possess non-ideal properties that makes them difficult to detect using conventional XRD techniques. O'Flynn has worked with explosives such as hexamine and Semtex (mixture of RDX and PETN) which showed preferred orientation and large grain size when analysed.^{65,88-90}

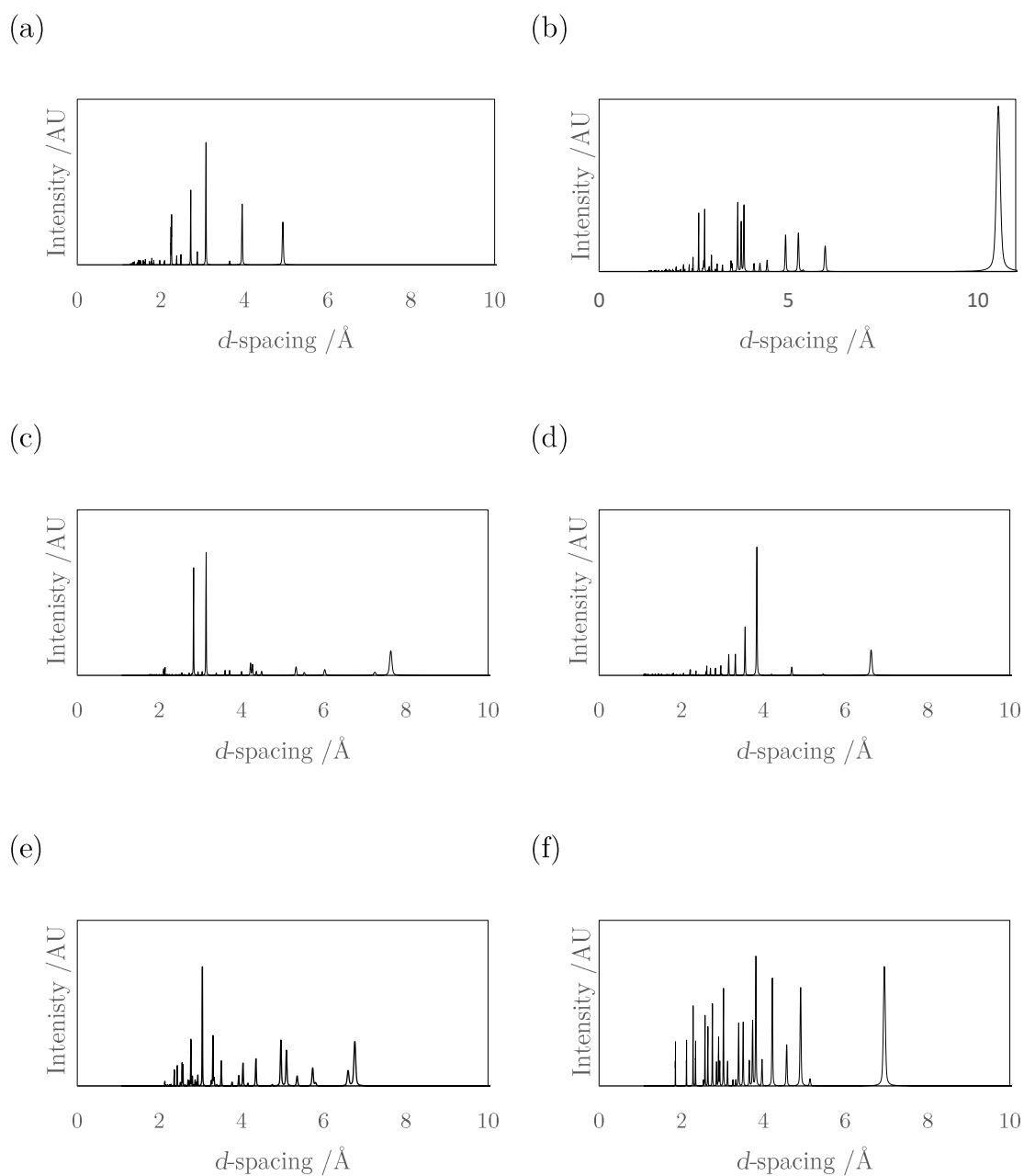


Figure 3.5 Diffraction profiles of explosives a) AN b) HNS c) TATB d) PETN e) RDX f) TNT

3.2.2 Principles of XRD

As previously noted, the intensity of a diffracted beam is approximately 1% of that of the incident beam. Both the position and the intensity of the peaks combine to

be a unique characteristic profile that can be used to identify the substance.⁹¹ The integrated intensity of peaks from a polycrystalline sample can be calculated by:

$$I_{hkl} = k_1 \frac{p_{hkl}}{v^2} LPA F_{hkl}^2 e^{-2M_t-2M_s} \quad (3.3)$$

Where k_1 is a scaling factor between experimental and calculated intensities, F_{hkl}^2 is the structure factor, p_{hkl} is the multiplicity factor, v is the volume of the unit cell, $e^{-2M_t-2M_s}$ is the temperature factor, also known as the attenuation factor which arises due to thermal lattice vibrations and weak static displacements. LPA represents the Lorentz, polarisation and absorption factors, all detailed in Woolfson (1997)⁹², He (2009)³⁴ and Cullity (2001)⁸⁷.

The structure factor, F_{hkl}^2 , is significant when determining crystal structures as the relative intensity of the beam depends on the atoms position within the unit cell. The structure factor includes atomic positions and is directly related to the intensity of the diffracted beam of the associated plane (hkl).

$$F_{hkl} = \sum_{j=1}^m f_j e^{2\pi i(hx_j+ky_j+lz_j)}$$

Where m is the number of j atoms, f_j is the atomic scattering factor, x, y, z refer to the fractional coordinate of the atoms within the unit cell and h, k and l define the reflection. If an hkl reflection produces a structure factor equal to zero, the intensity of that hkl reflection will be zero.

The intensity of the diffracted beam, when using X-ray transmission diffraction, is dependent of the thickness of the sample. The optimal thickness to gain the maximum intensity, at a specific energy, can be determined by:

$$t = \frac{\cos 2\theta \ln \cos 2\theta}{\mu \cos 2\theta - 1}$$

where 2θ is the diffraction angle and μ is the linear absorption coefficient (cm^{-1}).³⁴

3.2.2.1 X-ray Spectra

A variety of X-ray sources, from sealed X-ray tubes to rotating anode generators to synchrotron radiation are used in XRD. X-ray tubes are the most common and

economical means for generating X-rays. The electric potential is generated between a heated filament (cathode) and a heavy metal target material (anode) typically tungsten, rhenium or molybdenum fixed to a copper base to aid the dissipation of heat.^{31,93} The heating of the cathode results in a release of electrons into the vacuum surrounding the filament. The high voltage maintained attracts the electrons to the target which strike at high velocity. The high velocity electron rapidly decelerates when it strikes the target resulting the in the release of X-rays in all directions. Not every electron decelerates via the same interaction, some instantly lose all energy whilst others lose fractions of their energy deflecting off many different atoms within the target. This creates a continuous spectrum of various X-ray energies and is called Bremsstrahlung radiation, Figure 3.6.⁸⁷ The total intensity of Bremsstrahlung radiation is related to the atomic number of the target, the tube current and the accelerating voltage. To produce a high intensity of Bremsstrahlung radiation a target with high atomic number such as tungsten with a high accelerating voltage, combined with a high tube current is employed. Once the voltage of the source is

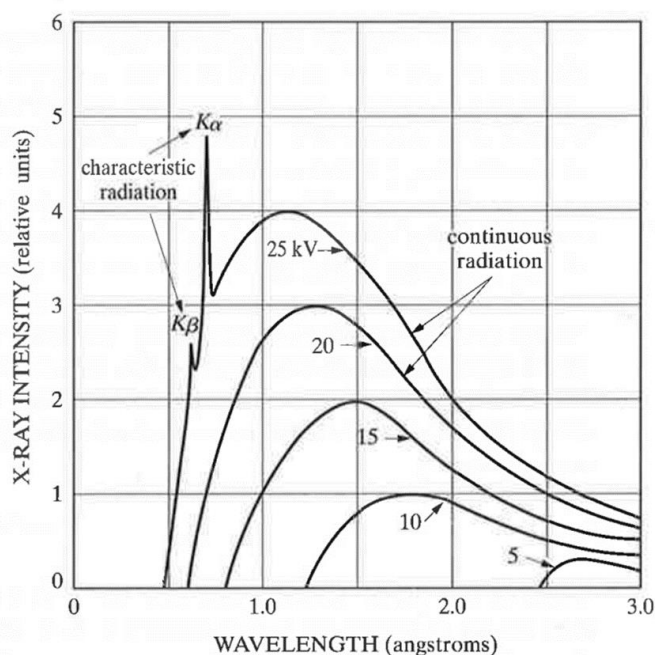


Figure 3.6 X-ray spectra of molybdenum generated at different voltages modified from Elements of X-ray Diffraction, B.D.Cullity, Addison-Wesley Publishing, Third Edition, 1967.⁸⁷

increased past a certain point sharp peaks at certain energies superimpose on the continuous spectrum. These sharp peaks are known as characteristic lines since their wavelengths are unique for each target element.³⁰ These characteristic lines are produced when the electrons striking the target have sufficient kinetic energy to remove an electron from the inner shell of the atom. With the hole in the inner shell of the atom, the atom becomes excited. An electron from an outer shell fills the hole, replacing the previous electron, regaining the atoms stable state, releasing energy. The X-ray produced has energy equal to the difference in energy shells, which is specific to the target metal and related electron shell.³¹ Producing X-rays in this way, via an electron tube is limited to 450 kVp, to gain higher energies an accelerator is used.^{33,93}

High Energy X-ray diffraction

High energy photons are required to penetrate a metal container, but the coherent scattering cross section decreases with increasing photon energy, as shown in Figure 3.7, obtained from NIST[§] (National Institute of Standards and Technology).⁶⁷ However, it has been confirmed both analytically and experimentally that the intensity of the coherent scatter within the Debye cone is independent of the photon energy.⁹⁴

Another practical aspect to consider is the production of high energy X-rays capable of being transported for utility in other countries for weapons verification. As described in §3.2.2.1 X-ray tubes are limited to producing X-rays up to 450 kVp.^{33,93} The rate at which the anode can be cooled plays a significant part in this limit.³⁰ At the higher voltages a pulsed X-ray source can be used, operating for only small fraction of a second, negating the need for cooling. This is achieved by slowly charging a series of capacitors and then abruptly discharging them across an X-ray tube.

[§] <https://physics.nist.gov/PhysRefData/Xcom/html/xcom1.html>

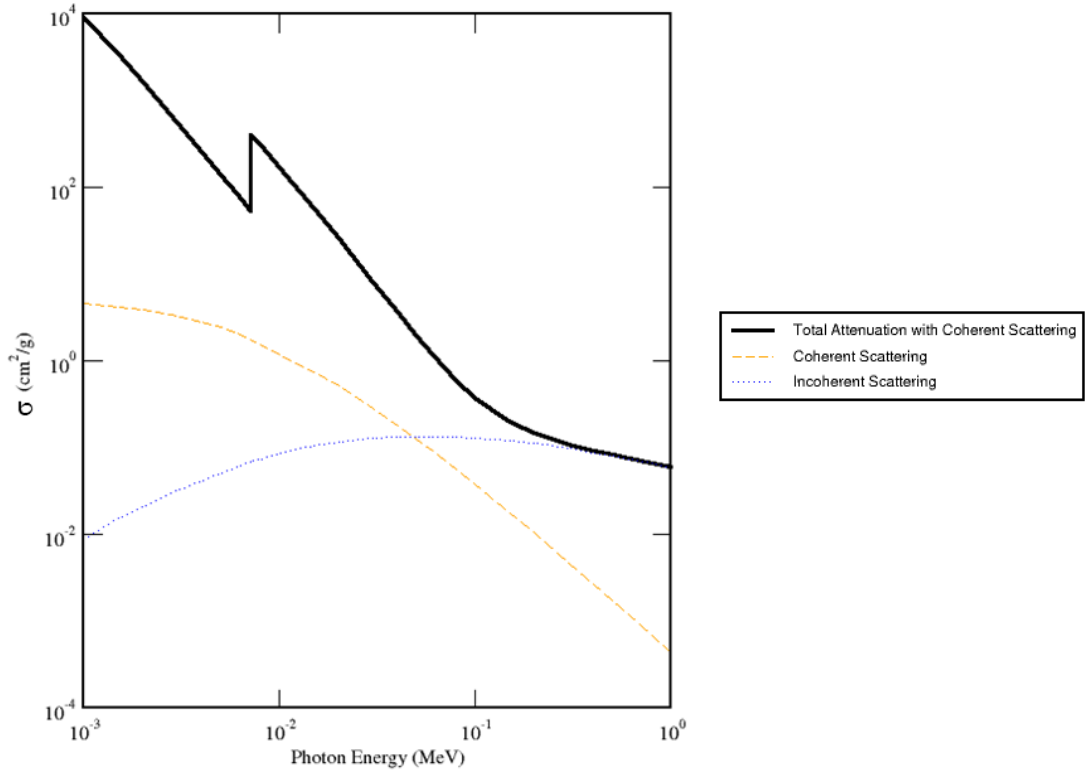


Figure 3.7 Total photon cross section σ_{tot} in Fe, as a function of energy, showing the contributions of different processes: coherent scattering and incoherent scattering up to 1 MeV. Obtained from NIST.

3.3 Comparison between ADXRD and EDXRD

As introduced in the literature review, presented in Chapter 3, there are two ways XRD can be implemented. Analysing Braggs' Law, it is apparent that the atomic structure can be interrogated by fixing the wavelength λ and measuring the diffraction angle, θ , or fixing the angle of measurement and employing a broad energy polychromatic source.⁸⁶ The former of these two techniques is angular dispersive XRD (ADXRD) and is the conventional laboratory arrangement employed for XRD. It measures the intensity of coherent scatter from a sample over an operational angular range. Used in material analysis to provide high resolution crystallographic data, it is considered to be the “gold standard” for material specificity.^{30,67,95,96} The latter is energy dispersive XRD (EDXRD), a more

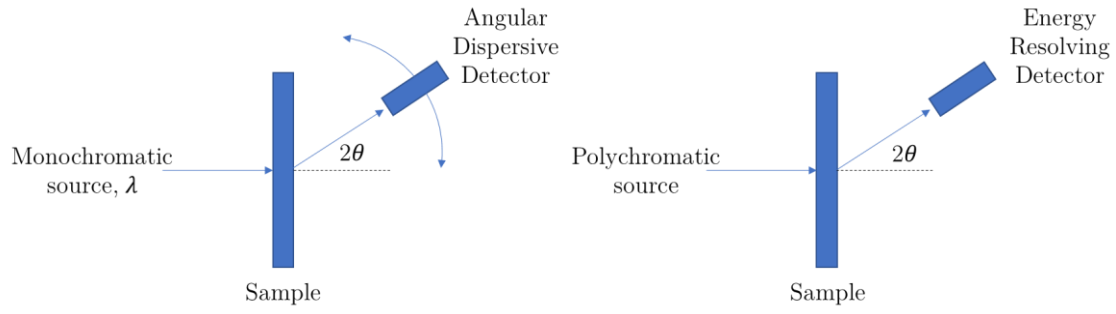


Figure 3.8 Diagrams of ADXRD (left) and EDXRD (right) geometries.

recent technique first reported for use in the medical industry by Johns and Yaffe (1983) but has more recently been employed as a highly effective tool in identification of explosives and illicit materials.^{55,91,97–99}

ADXRD diffractometers irradiate samples with a monochromatic, well collimated beam of X-rays. Traditionally, a point detector attached to a moving arm rotated around the sample with constant radius collecting scattered radiation, illustrated in Figure 3.8. More recently the scatter has been viewed simultaneously by employing a line or area detector negating the need for mechanical movement, a previous drawback in the technique, whilst also reducing the acquisition time. Although a higher resolution than EDXRD, ADXRD suffers from limiting factors such as preferred orientation that can adversely affect data interpretation leading to false alarms. This has been mitigated by sample rotation.⁶⁸ EDXRD has a higher throughput than ADXRD due to shorter acquisition times required for statistically significant data but requires a well-defined 2θ , with narrow collimation optics, which considerably reduces the beam flux. A compromise between the high energies needed for high penetration and high resolution is needed in EDXRD.

EDXRD utilises an energy resolving detector at a small fixed angle (2θ), typically $<10^\circ$, Figure 3.8, as it has previously been demonstrated that at these low angles, coherent X-ray scatter dominates over incoherent scattering; thus greater diffraction maxima are obtained at low scattering angles.^{86,91,97,100} At lower incident energies, 2θ increases with a decreasing peak intensity due to increased attenuation effects.^{91,100} Demonstrated by the momentum transfer equation, Equation (3.4), at low energies 2θ is inversely proportional to the energy, E .

$$\chi = \frac{E}{hc} \sin \theta \quad (3.4)$$

where χ is the momentum transfer. At high 2θ angles the momentum space is increased, thus more information is contained in a limited energy window therefore an increased energy resolution is acquired at high 2θ .⁸⁴ This results in a compromise between the high penetration required with high energy, at low 2θ and the high energy resolution acquired at low energy, high 2θ .⁸⁴

EDXRD has the capability to be performed at high energy due to its polychromatic incident beam, more so than ADXRD which is limited by the need for a narrow energy window without using a synchrotron. It is difficult to realise such a narrow energy range, so there is a trade-off between energy and X-ray flux when using spectral filtration methods. EDXRD suffers from signal blurring (broad diffraction peaks) which is introduced due to the angular range covered by the detector, meaning strict requirements are placed upon collimation optics to define scattering geometry.⁹⁰ Such collimation means the vast majority of the diffracted signal is not used.

ADXRD is limited by the relatively long acquisition times as the probability of generating diffracted photons is restricted by the monochromatic beam. ADXRD also relies on the collimation optics to produce a small footprint impinging on the sample to ensure the high angular resolution. This small gauge volume is beneficial when locating the source of scatter but also limits the quality of the diffraction produced if the sample has unideal structural conditions such as large grain size or preferred orientation which forms discontinuous Debye rings within the detector plane.^{67,101–103}

EDXRD increases the probability of generating diffracted flux from the sample by utilising a polychromatic source. As with ADXRD, a high level of collimation is required to reduce the acceptance angle for the collimated photons, in turn enabling the origin of scatter to be located. This high level of collimation can mean that as much as 99% of the diffracted flux is lost. EDXRD is also limited by the energy resolving capability of the detector.^{65,84,98}

Harding *et al.*(1999)³⁶ compared the throughput of scatter photons between the two techniques. It was concluded that EDXRD had a greater throughput of scatter photons and thus is the technique of choice for coherent X-ray scattering when high resolution isn't required.

While both EDXRD and ADXRD should yield good results, each requires that one substantially filter the X-rays spatially, spectrally or both, affecting the counting statistics.^{88,104} The effectiveness of both approaches vary; ADXRD producing higher resolution data thus lower false alarms and EDXRD having a high throughput due to its speed advantage resulting from the static equipment setup and higher flux density. But when diffraction patterns of the highest quality are required, the angular sensitive technique is the method of choice.³⁶

Most developing technologies to detect and identify concealed illicit materials focus on the use of EDXRD due to the speed advantage over classical ADXRD methods, which is highly desirable in security screening environments. The major limitation of EDXRD, compared to ADXRD, is the energy resolution making the technique less specific.¹⁰¹ Both ADXRD and EDXRD suffer from weak diffraction signals compared to the principle X-ray beam which can be easily masked by other structures within the weapon restricting the sensitivity and specificity.¹⁰¹

More recent developments involve the combining of ADXRD and EDXRD for greater system specificity and speed, as discussed in Chapter 4.

3.4 XRD Geometries

XRD systems have a wide variety of configurations and component options to fulfil requirements of different samples and applications. XRD systems usually consist of an X-ray source, X-ray optics (to condition the primary beam to the required wavelength, focal spot, beam profile or divergence), a sample stage (to establish the geometric relationship between the primary beam, sample and detector) and a detector (to intercept and record the scattered photons).^{31,34}

Diffraction is regularly used in reflection mode to analyse the surface of materials. However, transmission diffraction is preferred when compounds are concealed, as at high energy, coherent scattering is confined to the forwards direction due to its

short wavelength.^{38,69} Transmission is also beneficial for its lack of air scattering from the incident beam, as the scatter produced by the air is absorbed by the sample, blocking it from the detector. Reflection mode is frequently employed at low energy in place of transmission due to the limited capability of transmission to penetrate thick samples.

The shape of the primary beam is defined by the shape and size of the focal spot and the X-ray optics used. The profile of the incident beam is of great importance in XRD in order to acquire high quality and resolution data. A non-collimated incident X-ray beam would cause scattering in all directions and thus the diffraction pattern would not be recoverable, as the origin of scatter is unknown.

Primary beam optics are employed to shape and direct incident X-rays, to limit the possible origins of scatter. Consequently, collimation optics can influence the intensity and angular resolution of diffraction data. Different combinations of these result in either a line focus beam, a divergent beam, a highly parallel beam (employing Soller slits or parallel polycapillaries) or a point beam.³⁴

3.4.1 Pencil beam

A pin-hole collimator is frequently employed to control divergence and size of the incident beam. The size of the collimator employed is a compromise between intensity and resolution, illuminating only a small area of the sample. The smaller the collimator, the lower the photon flux striking the sample and the longer the acquisition time required for statistically significant data.³⁴

The pin-hole collimator allows analysis of scattering elements from different voxels^{**}, seen in both ADXRD and EDXRD where the beam collimation is highly important for phase identification.^{23,53,62,84,98}

^{**} A voxel represents a value on a regular grid in three-dimensional space i.e. a 3D pixel.

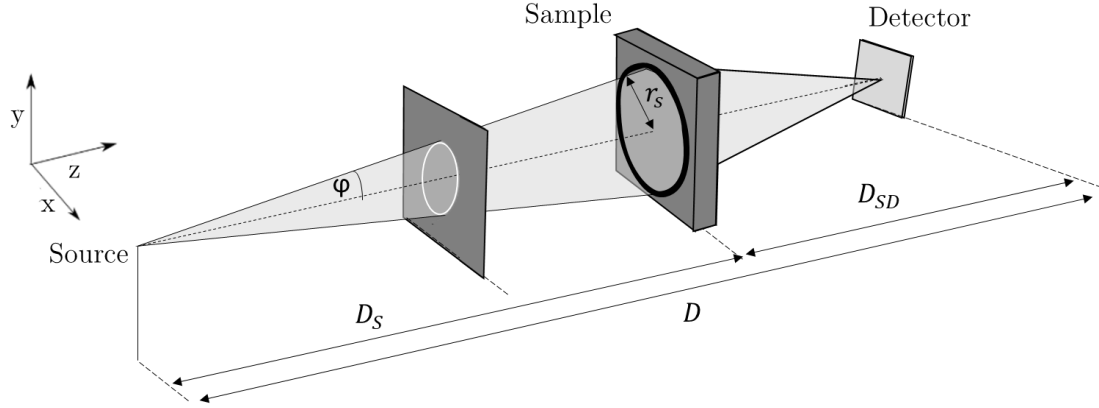


Figure 3.9 Illustration of FCG arrangement.

3.4.2 Focal construct geometry

Focal construct geometry, FCG, is an evolving novel geometry for powder XRD that uses an annular beam collimator in place of the conventional pin-hole collimator for the traditional pencil beam arrangement, Figure 3.9. Previous research has demonstrated the capability of FCG to enhance the resultant diffraction profiles compared to pencil beam XRD, increasing the intensity of the scattering maxima.^{101,105,106} A brief literature summary of the novel technique is provided in Chapter 4.

FCG, the fundamental parameters of which are described by Rogers *et al.* (2012)¹⁰⁷, describes a hollow conical beam incident on the sample formed by an annular collimator. Figure 3.9 illustrates the typical FCG transmission mode angular dispersive arrangement where the collimator, sample and detector are all normal to the primary axis (z -axis). The annular collimator shapes the primary beam into the hollow conical topology, projecting a circular ring footprint within the sample plane, Figure 3.11 (a).

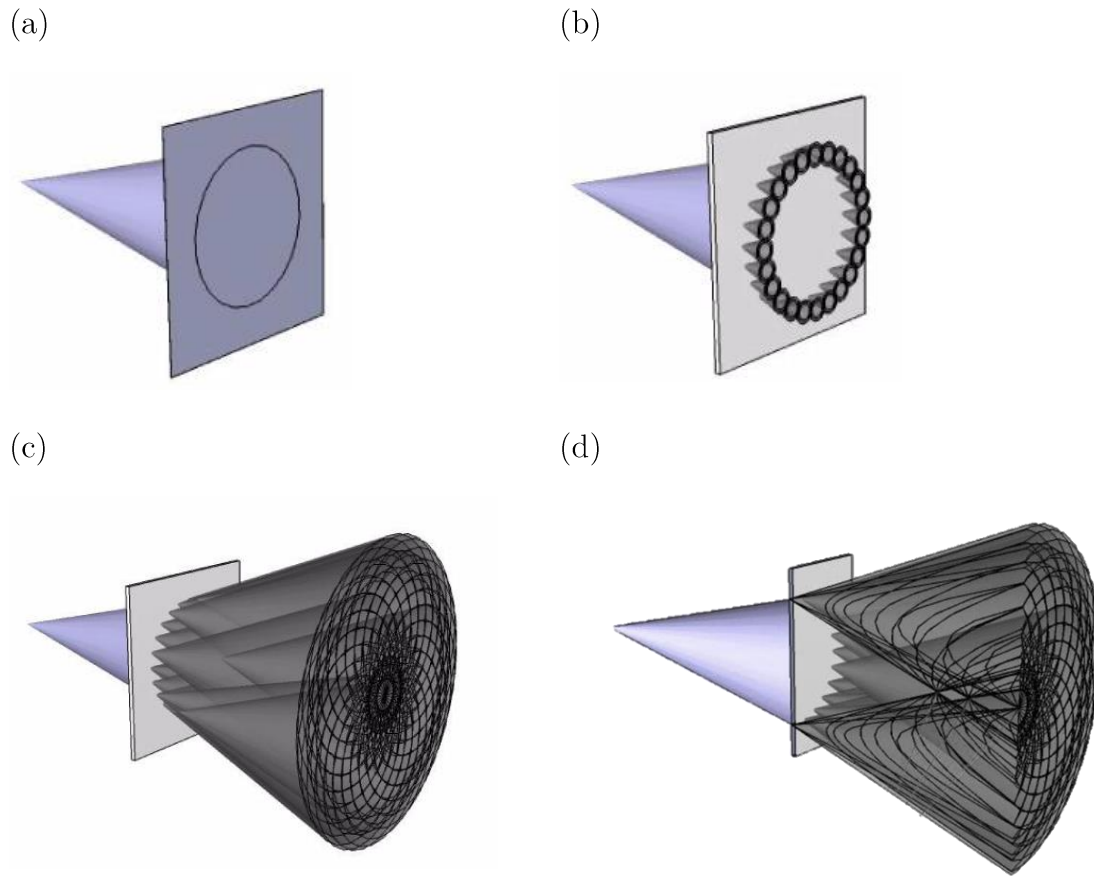


Figure 3.10 Illustrations of FCG geometry (a) shows circular footprint of primary beam on the sample (b) shows infinite number of Debye cones forming around circular footprint (c) Debye cones converge (d) Cross-section through centre of (c) to show hot spot formation.

The circumference of the circular footprint can be seen as an infinite number of pencil beams, each generating a Debye cone, Figure 3.10 (b), §4.1.4. Each of the generated Debye cones expand to eventually converge to a focus before diverging, Figure 3.11. The convergence point arises due to the Debye cones all sharing the same radius, emanating from the same sample, Figure 3.12. A cross section of Figure 3.10 (c) can be seen in Figure 3.10 (d) where the convergence points, termed ‘condensation foci’ form along the primary axis.

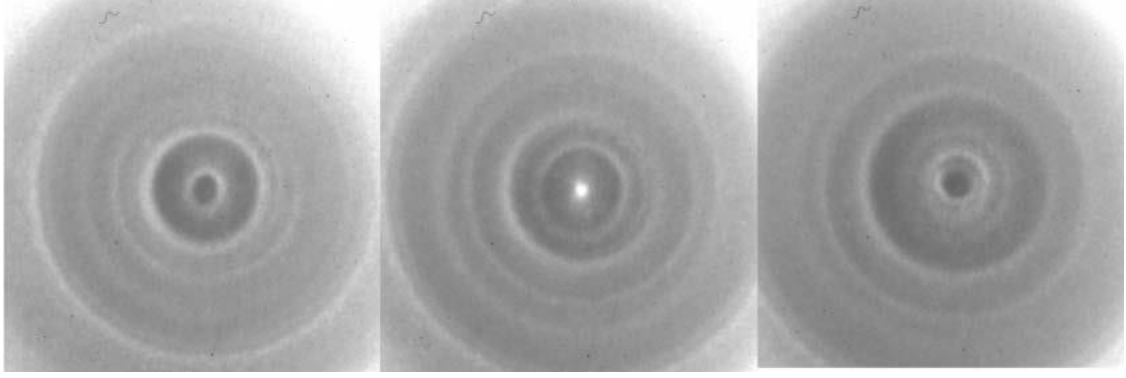


Figure 3.11 Sequence of diffraction images from Al_2O_3 obtained from different detector positions along the primary axis with an area detector. The left image shows converging condensation rings prior to their condensation into a focal spot observed in the middle image obtained slightly further along the primary axis, followed by the right image showing the diverging condensation ring. Images from Rogers *et al.* (2010).¹⁰⁶

Overlapping Debye cones form bright circular patterns, known as condensation rings, shown in orange in Figure 3.12. In the detector plane, these can be seen as the bright converging and diverging rings, Figure 3.11.

As condensation foci are created using multiple Debye cones, they have an enhanced intensity, compared to the corresponding peak in a diffraction pattern created from a pencil beam geometry. By translating an area detector along the primary axis, the location of these condensation foci can be determined and can be used to calculate 2θ diffraction angles Equation (3.5).

$$2\theta = \varphi_m + \tan^{-1} \frac{r_s}{D_{SD}} \quad (3.5)$$

where φ_m is the mean angular divergence of the incident beam, r_s is the radius of the circular footprint and D_{SD} is the sample-to-detector distance, illustrated in Figure 3.9.

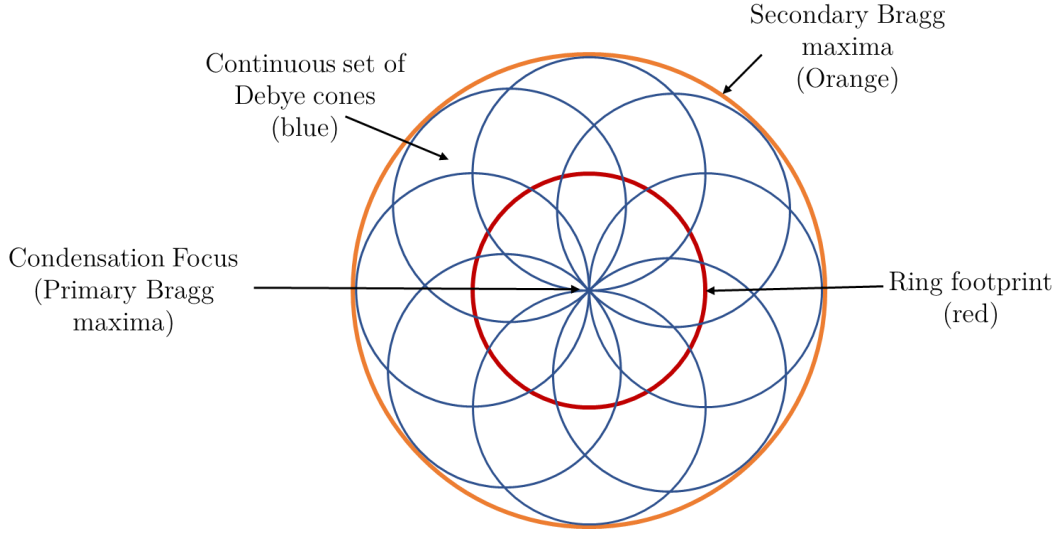


Figure 3.12 Detector view of the formation of a condensation focus including primary beam (red), the continuous Debye rings produced by the Bragg reflection (blue) the focus spot at the centre and the secondary Bragg maxima (orange).

FCG can also be conducted in energy dispersive mode, ED-FCG, employing a polychromatic energy source. A polychromatic annular incident beam incident on a sample, modelled as a sample comprising of a single d -spacing, generates diffracted flux of multiple wavelengths, as with pencil beam geometry. In FCG this creates focal spots along the primary axis, extended in spectral energy and distributed along the z -axis. Thus, a focal spot exhibiting a narrow spectral range can be measured by a finite detector at a given position along the primary axis. Therefore, when a number of d -spacings are considered, multiple spots from different d -spacings can converge upon the same stationary point along the z -axis.

To translate the obtained energy spectra into d -space as conducted in pencil beam geometry, Equation (3.5) can be substituted for the diffraction angle in Braggs Law to construct Equation (3.6).

$$d = \frac{\lambda}{2 \sin \left(\frac{1}{2} \left(\tan^{-1} \left[\frac{D_S \tan \varphi_m}{D - D_S} \right] \right) \right)} \quad (3.6)$$

where D is the source to detector distance, shown in Figure 3.9. FCG has been shown to improve the effects of grain size and preferred orientations which impede the pencil beam geometry, inhibiting identification due to absent peak maxima.^{101,107}

The effects of sample orientation have also been evaluated by Prokopiou *et al.*(2014)¹⁰³ to demonstrate that the ability of FCG to produce high-resolution, enhanced intensity, diffraction data was not influenced by the orientation of the sample.

The theory behind the technology has been established by Rogers *et al.*(2010)¹⁰⁶ and has since been adopted for potential use within the security industry.^{102,105,107}

Chapter 4

Recent Advancements in XRD

This chapter introduces some of the latest developments within the field of X-ray diffraction, focusing on developments which aid the identification of concealed materials.

4.1 X-ray diffraction and Explosive Detection

XRD technologies are currently one of the most promising emerging material identification techniques for explosive detection and identification, as discussed in Chapter 2.^{23,61-64,84,85,108,109} Numerous researchers have thus explored the use of XRD for many different applications.^{26,36,38,97}

Notable developments with the field are 3D X-ray Diffraction (3DXRD)^{110,111}, Tomographic Energy Dispersive Diffraction Imaging (TEDDI)^{112,113} and X-ray Diffraction Imaging (XDI)^{38,57} all using XRD tomography for structural imaging as it offers simultaneous crystallographic data from various compounds within an inspection volume.¹¹⁴ Unusually, 3DXRD employs ADXRD via a synchrotron source, taking advantage of the high fidelity structural measurements the technique offers. Systems using XRD are almost exclusively based on energy-dispersive approaches due to the increase in diffraction flux, thus possessing the speed advantage required for industrial applications. EDXRD systems usually involve

high collimation of the incident and diffracted beam, restricting the measurable diffracted flux, discussed more in §3.3.^{68,115}. This has resulted in research focusing on increasing the diffracted flux by implementing brighter sources^{††} or longer scan times.

Some of the more the recent systems are briefly reviewed here.

4.1.1 Developments Employing ADXRD

Dicken *et al.*(2011) combined XRD with kinetic depth effect imaging (KDEX) to generate 3-dimensional images with the material discrimination abilities of XRD.⁹⁵ KDEX, an imaging technique similar to CT mentioned in Chapter 3, requires views from various angles to generate a 3D image. Unlike CT, KDEX doesn't require reconstruction and also requires fewer viewpoints to construct the final image.¹¹⁶ KDEX, involves the rotation of either the sample or the source and detector combined to gain the various viewpoints of the inspection volume. An X-ray fan beam is utilised to obtain images at each angle increment allowing for the 3D visualisation using motion parallax, Figure 4.1(a). Dicken *et al.*⁹⁵ additionally used angular dispersive XRD to obtain diffraction patterns from a single viewpoint at various positions through the inspection volume using a monochromatic pencil beam geometry. Figure 4.1(c) illustrates the position at which the inspection volume was interrogated with the pencil beam geometry.

Unlike other XRD techniques that use a scattering collimator to pinpoint a voxel where the diffraction originates, Dicken *et al.* (2011) increases the scattering flux by removing the need for scattering collimation, instead using four detector positions at different distances along the primary axis away from the scattering volume. These four detector positions enable the use of a peak tracking algorithm discussed in Dicken *et al.*(2010)¹¹⁵ to locate the origin of scatter and hence determine the diffraction angle, thus identify the scattering material.

^{††} Brightness is defined as the total number of X-ray photons passing through a surface having unit solid angle. It is the measure of strength from a point source used to compare sources with the same spot size.

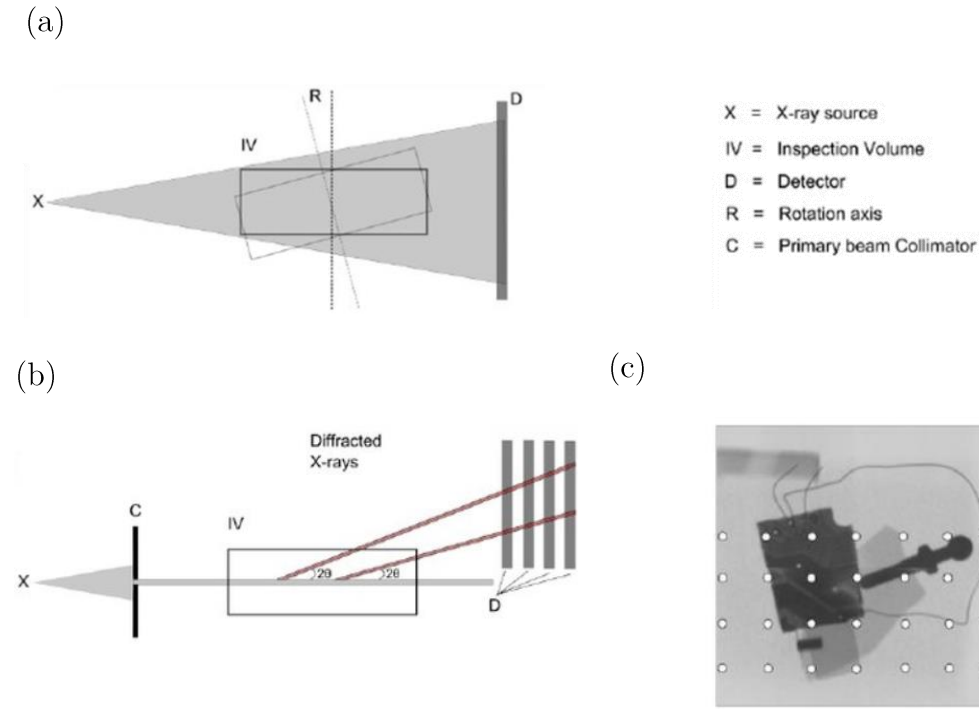


Figure 4.1 (a) Geometry of KDEX with rotating sample (b) Geometry of XRD system with four area detector positions and (c) Transmission image obtained from area detector in (a) with points indicating where XRD was obtained from. Images from Dicken *et al.*(2011)⁹⁵

KDEX offers increased morphology recognition in the presence of complicated structures compared to traditional 2-dimensional transmission imaging but due to the addition of XRD this combined technique also offer chemically specific spatially resolved information.⁹⁵ The technique has currently only been implemented with a relatively low energy X-ray source (Mo ~ 17.5 keV). Requirements for higher energy X-ray source for applications where a higher penetration ability is needed such as security screening or indeed weapons verification require further investigation due to the decrease in angular resolution at high energy. This could be overcome by increasing the sample to detector distance, but these extended dimensions are unfavourable combined with the decrease in sensitivity the extended distance would cause, given additional air absorption and the inverse square law.⁹⁵

A more recent approach to utilising ADXRD to gain depth perception without the need for transmission imaging, employs coded aperture masks as encoders.⁶⁰ The coded aperture X-ray scatter imaging system, also known as CAXSI, introduced by

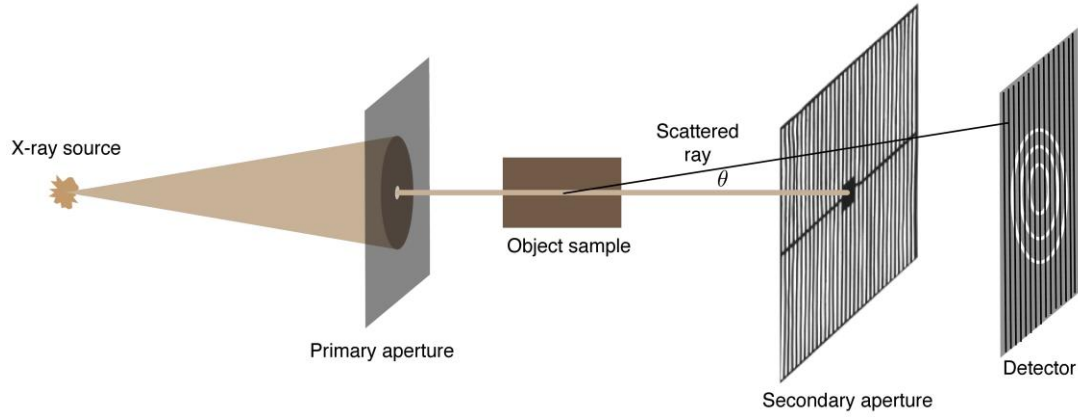


Figure 4.2 Pencil beam geometry with encoder placed between the sample and the area detector. Image from MacCabe *et al.* (2012).

MacCabe *et al.* (2012) uses a post sample secondary aperture, the coded aperture mask, to encode diffracted scatter with its point of origin to aid the identification of the sample. CAXSI, the geometry of which is depicted in Figure 4.2, employs a pencil beam, created by a pin-hole primary aperture, to focus the incident beam along the primary axis. A secondary aperture consisting a periodic array of lead bars constructed in a comb like structure is placed between the sample and the 2-dimensional area detector to encode the resulting diffraction maxima.

The comb like aperture is placed such that it blocks the primary beam and intersects the emanating Debye cones from the sample. The aperture absorbs a proportion of the diffraction scatter, leaving a “shadow” in the transmitted diffraction pattern. Since the position of the coded aperture mask is known in relation to the detector, it acts as a reference structure, unambiguously modulating the diffraction.⁶⁰

MacCabe *et al.* (2012) designed and implemented an analytical decoding procedure to interpret the encoded image obtained by the 2-dimensional area detector, to determine the position of the sample along the primary axis. Knowledge of the samples location thus allows the radial positions of the Bragg maxima to be interpreted for material identification.

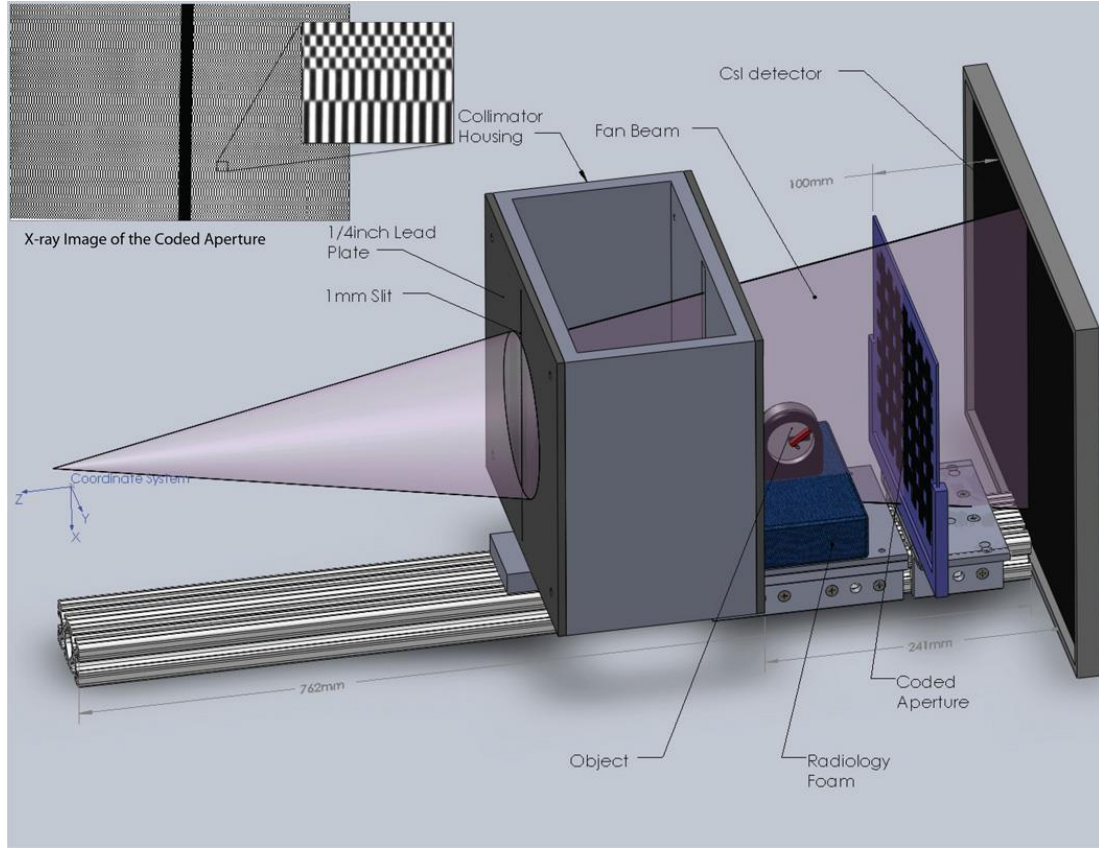


Figure 4.3 Diagram of fan beam geometry using post-sample coded aperture mask.¹¹⁷

MacCabe *et al.* (2012) repeated the study, increasing the number of samples spatially separated along the primary beam. The two powder samples' respective positions were successfully recovered, hence material phase was also determined using a single snapshot.

In later work, the pencil beam was replaced by a pulsed fan beam and the coded aperture mask with a finer structure to improve the spatial resolution and momentum transfer resolution.¹¹⁷ The coded aperture consisted of a lead strip, to block the primary fan beam from the detector, and a sequence of alternating opaque and transparent line blocks of variable widths, shown in the top left of Figure 4.3.

The spatial resolving capabilities of the system design were demonstrated by recovery of the word 'DUKE' from 3D plastic printed letters aligned parallel to the fan beam. To demonstrate the effectiveness of the snapshot method, the second

hand of a clock was placed in the beam path, Figure 4.3, with a single exposure obtained at 0.5 s intervals. In the reconstructed images of the clock face, the second can be seen to rotate in each 2D slice demonstrating time-resolved imaging capabilities that allows for new insight in time-dependent processes.^{37,117}

4.1.2 Developments Employing EDXRD

Kazantsev *et al.* presents a novel multichannel reconstruction method for spectral tomography in order to provide an additional spectral dimension to conventional X-ray greyscale imaging. This additional data can be used to distinguish individual materials by characteristic absorption peaks.^{118,119}

The new method takes advantage of the rapid developments within photon counting and energy discrimination detectors. Energy discriminating detectors enable the acquisition of the chemical composition of the materials. The newest hyperspectral detectors to be developed achieve an energy resolution of less than 1 keV resulting in hundreds of energy channels. Although these hyperspectral detectors have previously been used to acquire energy data, the results suffered from low signal-to-noise ratio, acquisition artefacts and angular under-sampled datasets. To overcome these effects, primarily due to operation at low count rates, longer exposure times have been used but this still results in noisy, angular under-sampled results.¹¹⁸

The new regularised iterative reconstruction method, presented by Kazantsev *et al.* is shown to produce higher intensity images than existing reconstructive methods, whilst also exploiting the additional information enabled by mutually correlated energy channels.¹¹⁸ Kazantsev *et al.* use multichannel reconstruction, meaning data is reconstructed directly without any special rearranging steps, which would be classed as material-decomposed reconstruction. Furthermore, the parallel level sets framework proposed by Kazantsev *et al.* has previously been employed to other imaging applications, so is already well defined.¹²⁰

The presented paper demonstrates the novel reconstruction method by performing realistic numerical experiments on a phantom consisting of quartz, pyrite, galena and gold, and compares to the classical channel-wise variation regularization

method in order to demonstrate its advantages. The technique shows that structural correlation embedded into the regularization term can result in significant improvements in the image quality also noting that the information obtained from the neighbouring energy channels is not always reliable for multichannel problems, causing severe noise distortion. The iterative reconstruction method presented was demonstrated to be more efficient than the method used as a comparison, simple to implement and can be parallelized in the future to optimise performance.¹¹⁸

The multichannel X-ray tomography system - known as the Manchester “Colour Bay” - has been realised by Manchester University and is currently operating at Warwick University.

4.1.3 Combining ADXRD and EDXRD

Current developments for illicit substance detection and identification primarily focus on combining EDXRD with ADXRD for depth resolved imaging, thus a greater system specificity and speed.^{89,90,99,121}

Moss *et al.* (2017) recently reported the development of a portable analysis system combining transmission X-ray imaging with XRD.¹²² The method used for the XRD system stems from work reported by Christodoulou *et al.* (2011)⁹⁹ employing a pencil beam polychromatic source and a pixelated cadmium telluride (CdTe) based detector, the HEXITEC, Christodoulou *et al.* (2011) demonstrated the benefit of using multiple scattering angles in a partial least squares analysis^{‡‡} and prediction model, predicting the various concentrations of caffeine samples using one, two and four angles. The HEXITEC having a large angular window offers the simultaneous acquisition of spatially and energy resolved data, unlike standard EDXRD systems where the scatter beam is usually highly collimated to obtain scatter from a fixed angle. When multiple angles were used, the prediction abilities employing multivariate partial least squares (PLS) regression test, were more accurate indicating that measurements from multiple diffraction angles optimise specificity.⁹⁹

^{‡‡} A statistical method used for constructing predictive models when factors are many and highly colinear by finding a linear regression between the variables.

O’Flynn *et al.* (2012)⁹⁰ and O’Flynn *et al.* (2013)^{65,109} advanced on Christodoulou *et al.* (2011) work using a greater number of diffraction angles to analyse explosive materials.⁸⁹ O’Flynn examined the acquisition times of the technique, previously requiring 25-30 minutes for sufficient resolution.^{90,99} The pixelated detector offered the opportunity to sum the energy spectra obtained at each pixel to compute a single momentum transfer spectrum. Although the data collected in 1 second demonstrated significant noise, the diffraction peaks were still apparent.^{65,109}

The effects of large grain size have also been examined using a sample of hexamine powder, resulting in slight variations in the momentum transfer spectrum when observing different sections of the same sample.^{65,88} The analysis of thick samples also proved to adversely affect the angular resolution of the system due to peak broadening thus reducing the specificity.

O’Flynn *et al.*^{65,89} comments on the small size of the primary beam employed, suggesting it would be impractical for security applications having to scan an entire sample with a highly collimated incident pencil beam. It is suggested that a practical solution is to combine the XRD technique with transmission X-ray imaging to isolate a region of interest for the XRD analysis.

This idea formed the basis of the *miniPixD* which combines transmission X-ray imaging with XRD to demonstrate image guided X-ray diffraction (IGXRD).⁸⁹ A compact table-top source, evaluated in O’Flynn *et al.* (2016)⁸⁸, is collimated using a lead mask, Figure 4.4 (right), to provide two independent sources of radiation; a slot to produce an incident fan beam for the transmission imaging and a pin-hole for XRD measurements.

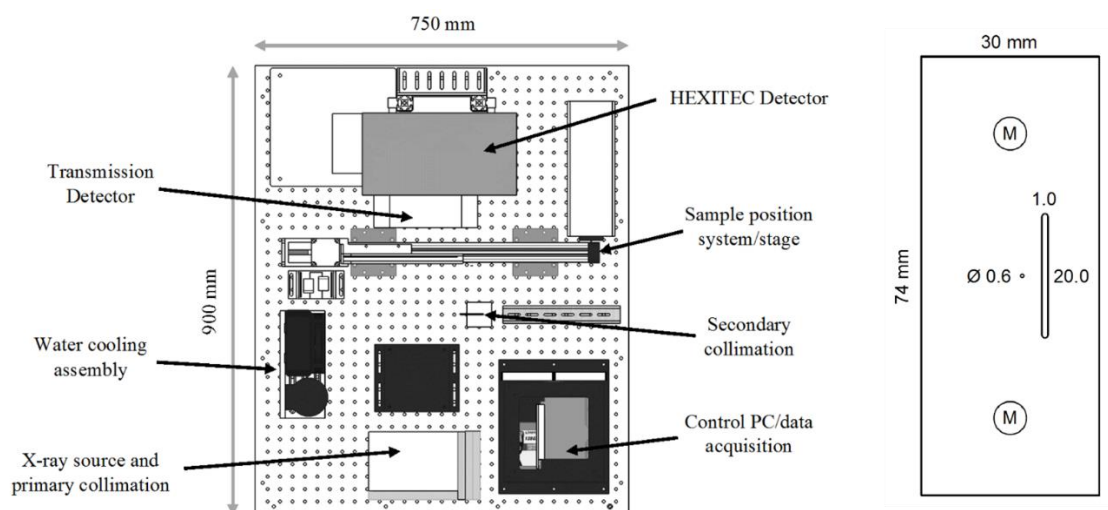


Figure 4.4 Left: Schematic of *miniPixD* Right: Schematic of split X-ray source collimator. Both diagrams from O’Flynn *et al.* (2017).⁸⁹

Figure 4.4 (left) depicts arrangements of all the components used including the two detectors used. A line array detector was used to obtain the transmission image, chosen over an area detector for a compact system, restricting the obtainable image quality and increasing the acquisition time, and a HEXITEC detector, offset to obtain a quarter of the diffraction pattern to avoid the primary beam.

For the technique to be implemented successfully, the distance between the sample and the detector must be known *a priori*, limiting the utility within the security industry to small items such as envelopes, wallets or blister packs.⁸⁹ The PixD method, is restricted by the sample thickness, as the thicker sample results in each pixel within the HEXITEC being open to a wider range of scattering angles, reducing the angular resolution of the diffraction pattern. Furthermore, real world applications would involve more than one material, usually with the target material concealed behind a barrier. The overlapping materials would have a negative effect on the reliability of the diffraction pattern measured.

Another technique that combines both EDXRD and ADXRD by using an energy sensitive detector is ‘coded aperture coherent scatter spectral imaging’, also known as CACSSI, introduced by Greenberg *et al.* (2013).^{37,104} CACSSI employs the ADXRD coded aperture approach, detailed in §4.1.1, by MacCabe *et al.*^{60,117} to resolve depth and material characteristic information of unknown samples at

unknown locations. The advantage of the Greenberg *et al.* technique, over the previous mentioned system by O’Flynn *et al.*, sees that the object’s location needn’t be known *a priori*.

A coded aperture mask replaces the scattering collimator, the conventional method of gaining depth perception for EDXRD techniques.⁵⁷ This allows a greater proportion of the scatter to reach the energy sensitive pixelated detector as the coded aperture mask has an open fraction of $\sim 50\%$.¹²³ Initial papers reporting the technique used the same comb like coded aperture mask employed by MacCabe *et al.* (2012) with the addition of an energy sensitive detector to record the position and wavelength of the diffracted photons.³⁷ The system has since developed into using a coded aperture mask composed of random opaque and transparent blocks

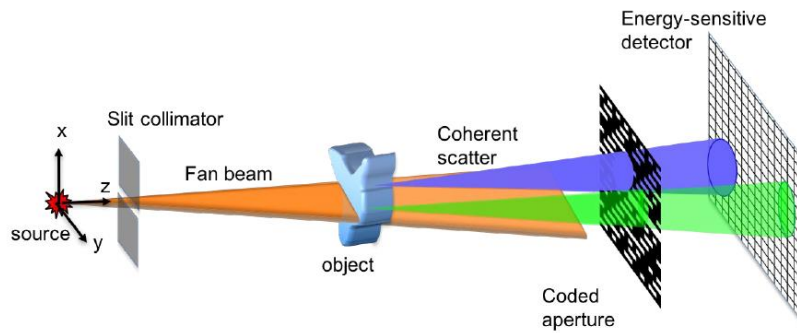


Figure 4.5 Geometric arrangement of CACSSI. Figure from Greenberg *et al.* (2017)¹²⁴

in a 2-dimensional array, to minimise the ambiguity of the projected mask providing a better localised image, illustrated in Figure 4.5.¹²⁵

The technique has been adapted to use a pencil beam, fan beam and a cone beam, to image the full-volume of an object.^{125,126} The reconstruction, in all three beam geometries, involves an iterative, model-based reconstruction algorithm to separate the signal from each sample and thus recover the scatter spectrum associated with each voxel independently.^{123,125} The pencil and fan beam techniques involve a raster scan of the objects to cover the full volume of the object.^{125,127} The fan beam, capable of volumetrically imaging whole planes at a time, has been developed into a prototype for a secondary airport screening system, a fan beam coded aperture XRDT, based on the CACSSI system in Figure 4.5.^{124,128} The system appears like a standard X-

ray transmission airport scanner, with luggage being passed through a tunnel with the fan beam scanning each plane line by line to identify location and identification of potential threats.

The prototype XRDT system can either record multi-energy transmission images or use the XRD capability to identify the compounds present. As well as powdered samples, the system has shown promise for the detection and identification of threat liquids but the long scanning times of the system still currently renders the system unsuitable for the field work.^{104,124,128} The implications of non-ideal powdered samples have also been evaluated with a pencil beam, modelling powdered samples with large grain size and preferred orientation resulted in the technique having poor imaging quality however this could be minimised by measuring a larger fraction of the overall scatter.¹²⁹

4.1.4 Focal construct geometry

Due to the weak signal of XRD many researchers have concentrated on increasing the flux density of the interrogating beam to in turn increase the signal generated from the object under inspection. This has been done by using expensive collimator optics such as multilayer mirrors, polycapillary collimators and zone plates, requiring a complex set up. Synchrotron radiation has also been used, as mentioned in previous examples of developing technology, but cost and lack of portability limit its utility.

Focal construct geometry, a novel configuration of an annular collimator to create a hollow conical incident beam, introduced by Rogers *et al.*(2010)^{106,130} aims to increase the diffraction intensity of diffractogram without the need for brighter sources or expensive beam optics.¹⁰¹ This bespoke arrangement, discussed more in greater depth in §3.4.2, impinges a ring footprint of the object, Figure 3.10 (a), to increase the interrogated volume (compared to pencil beam), resulting in each point acting as a new source of diffraction photons, Figure 3.10 (b).

Consequently, the coherent scattered photons arising from specific objects around the ring footprint will focus to a point along the symmetry axis, Figure 3.10 (d). As this point is a summation of the diffraction from multiple interrogation positions

around the ring its intensity is greatly increased by several orders of magnitude compared to a corresponding pencil beam geometry.¹⁰¹

FCG allows the simultaneous formation of several high intensity points along the symmetry axis. These high intensity points correspond to specific crystallographic planes within a polycrystalline material, formed from the on-axis intersection of the Debye cones from the scattering material.

FCG negates the need to integrate the intensity data as with an extended detector in pencil beam geometry. By contrast in FCG the centrally positioned detector is linearly translated along the primary axis (alternatively the sample could be translated) to allow the direct measurement of the high intensity foci with their corresponding sample-detector distances.⁶⁷ The sample-detector distance is used, like in conventional ADXRD to calculate the diffraction angle, 2θ , and hence the d -spacings, detailed more in §3.4.2.

FCG has been shown to mitigate the effects of structural complexities such as grain size or preferred orientation that effect the traditional pencil beam geometry.^{101,107} The effects of sample orientation have also been evaluated by Prokopiou *et al.*(2014)¹⁰³ to demonstrate that the ability of FCG to produce high-resolution, enhanced intensity diffraction data was not influenced by the orientation of the sample.

FCG has also been used for XRD tomography by raster scanning a sample through an annular beam of X-rays.¹³¹ Evans *et al.*(2015)¹³¹ uses a single detector plane to capture the diffraction at each position. Evans *et al.* (2015) shows that the Bragg maxima, which form the high intensity spots, are encoded with the shape and location of the crystalline features along the annular beam. Spatial distribution of the high intensity points was recovered and unlike conventional absorption imaging the comparison of optical sections, each comprised of a different Bragg maximum, enables the computation of a material's lattice spacings.¹³¹

FCG has also been extended to higher energies using a tungsten X-ray source so the technique is more favourable in applications where highly penetrating radiation is required.⁶⁷ Dicken *et al.*(2015) used the same angular dispersive arrangement,

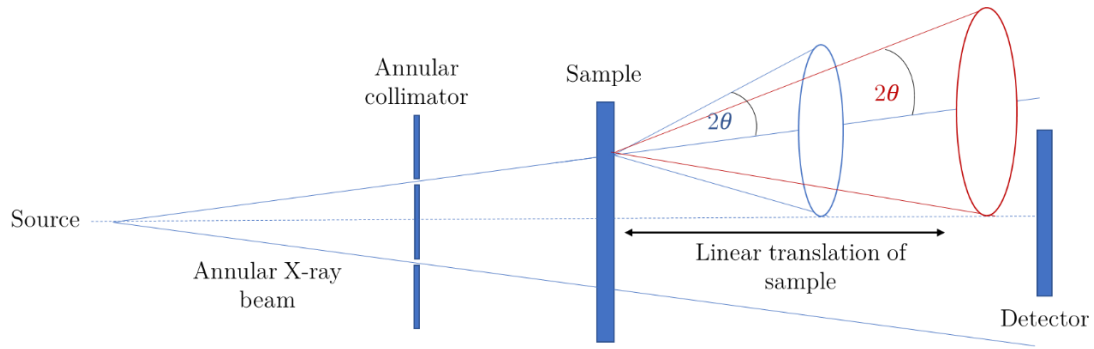


Figure 4.6 Schematic diagram of FCG geometry demonstrating Debye cones emanating from an angular gauge volume. The blue Debye cone indicates the low energy beam path, the high energy beam path is depicted by the red Debye cone.

with a high energy tungsten source, collimated to a conical beam impinging on a sample. A 2-dimensional area detector was used to collect the diffracted photons. Like with the lower energy Cu source, high energy FCG was shown capable of obtaining complete diffractograms from samples with large grain size and preferred orientation.

The high energy X-ray monochromatic incident beam causes a decrease in diffraction angles, 2θ , increasing the angular range. Figure 4.6 illustrates this by depicting the beam paths of two Debye cones, one from a low energy source, shown in blue and one from a high energy source, shown in red. This means that for highly penetrating radiation, hence higher energy, the sample-detector distance needs to increase for measurements of the high intensity spots.

Initially produced to enhance the diffraction intensity at a measured point when using ADXRD, more recent applications of FCG have evolved to using EDXRD to take advantage of the increase in flux afforded by the broadband spectrum.¹³² Dicken *et al.*(2015)¹³² employs a polychromatic X-ray source and an energy sensitive point detector. As with conventional EDXRD, there is no requirement to take multiple measurements along the primary axis as with the angular dispersive FCG system. Unlike traditional EDXRD, the system presented by Dicken *et al.* (2015) doesn't employ a scattering collimator. Dicken *et al.* also investigated the effect of large grain size on the resultant diffractogram, a common problem within EDXRD.

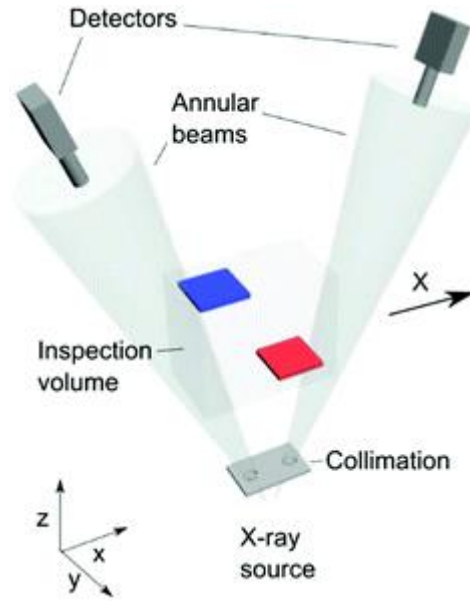


Figure 4.7 System employed by Dicken *et al.* (2018) using pair of hollow conical incident beams in conjunction with two energy dispersive detectors. Image from Dicken *et al.* (2018)¹¹⁴

The number of grains orientated such that Bragg's condition is satisfied influences the integrated intensity of the X-ray diffraction peaks in the diffractogram.¹⁰⁰ Hence, the relative peak intensity may change between various gauge volumes within the same sample, increasing the risk of losing peaks, and thus false alarms. FCG, having a larger, annular gauge volume employs a greater number of grains for a single diffractogram, enhancing the particle size statistics and hence minimises the effect of large grain size.

The geometric broadening of the ED-FCG system was investigated by Dicken *et al.* (2015) and found that the finite size of the energy-sensitive detector to be the largest contributing factor to the d -spacing resolution. Other parameters effecting the peak widths were the thickness of the sample and the width of the opening angle of the annular collimator. It is suggested that the peak broadening can be reduced with the use of high aspect ratio collimation of the diffracted flux to restrict the solid angle subtended by the detector, increasing the d -spacing resolution of the system.

The energy dispersive system was developed further to enable the identification of material phase when the sample position is unknown.¹¹⁴ This has been demonstrated by employing two simultaneous hollow conical beams from a single X-ray source, Figure 4.7.

Each hollow conical shell is optically coupled with an energy-dispersive detector to capture the diffracted flux. The conceptual geometry was modelled using a single conical shell beam with the sample tilted between two separate scans.

A systematic algorithmic approach is implemented to determine the presence of a specified material. Using the detector energy bins and possible locations of the sample in relation to the detector, a range of possible d -spacings are computed. These are compared to the obtained diffractogram enabling the axial location and d -spacing of the material to be deduced.¹¹⁴

This technique offers uncollimated high flux diffraction data without the need for *a priori* knowledge of the sample location.

Dicken *et al.* (2017)¹³³ has also implemented a technique to identify the materials location and phase employing a post-sample pin-hole collimator and an pixelated energy-resolving detector. Three different samples were used, spatially separated along the primary axis, which each generate a circular conic section projected onto the detector plane. From the single snapshot projection, the ADXRD image on the pixelated energy-sensitive detector enables the location of the sample to be determined, whilst the EDXRD data corresponding to each pixel allow the material phase to be deduced.¹³³

4.2 Concluding Remarks

Due to the growing need for a non-invasive materials characterisation technique not just within aviation security but fields such as medicine and forensic science, there has been several recent developments within XRD which have reduced exposure times and enabled depth awareness.

Depth resolution within the inspection volume has been studied employing specially designed encoding patterns both pre-sample¹³¹ and post-sample⁶⁰. Coded apertures

have been a notable development within the field, capable of increasing SNR, compared to conventional pin-hole arrangement and producing a good angular range. Recent developments within coded aperture masks, acting as post-sample encoders, modulate the scattered X-rays in a position dependent manner in order to determine the origin of the scatter to enable material identification without a *priori* knowledge of material location.⁶⁰ The benefit of the coded aperture mask approach by Greenberg *et al.* is that the objects voxels are all measured in parallel, while leaving the signal sufficiently well-conditioned for the recovery of the material phase from a single measurement.³⁷

Pencil beam limits the inspection volume being analysed at once requiring long acquisition times for raster scanning the whole sample. Focal construct geometry is a collimation system designed to increasing the flux density of the diffraction, whilst also interrogating a larger volume of the sample, decreasing the acquisition time necessary to produce a sufficient SNR.^{67,103}

The development of energy sensitive pixelated detectors for multispectral high energy X-ray detection has advanced the field of XRD imaging with the capability of simultaneously measuring ADXRD and EDXRD.^{134–136} The HEXITEC detector, introduced by Seller *et al.* (2011)¹³⁵ is one of those advancements and it is being employed in many applications.^{109,136,137,119,138,139} The ability to simultaneously employ ADXRD and EDXRD means the high resolution of ADXRD can be used while the high flux of the EDXRD can be used to enhance the throughput of a system without compromising the system performance.¹⁰⁴

Chapter 5

Aims and Objectives

The aim of this project is to identify and explore the potential use of a technology to be a tool used as part of a verification regime. X-ray diffraction has been chosen as a promising bulk detection technology for the detection and identification of explosives, as detailed in §2.2.

5.1 Aims and Objectives

This project has been split into two distinct parts; the first involves the use of pencil beam ADXRD to locate and identify the material inside a given volume; the second investigates improving the intensity of the signal by using focal construct geometry (FCG), evaluating the constraints, such as the resolution of the system, that could restrict the use of the technique.

The objectives of this research are as listed below:

- Ascertain a technology that has the potential to identify an explosive within a highly absorbing metal container without revealing sensitive information and investigate its utility.
- Interpret the radiation signal to identify the material inside a metal container by using a variety of techniques before comparing their

effectiveness. Previous research has not worked backwards to locate sample, new methodology shown in §6.4.2 for all techniques used.

- Use an analytical method to determine the source of the radiation, i.e. the sample location, in order to interpret the diffraction pattern and identify the material.
- Evaluate use of novel encoders to obtain depth perception within an inspection volume, to locate and subsequently identify the concealed material.
- Use an algorithm-based technique that searches through the diffraction profile to determine the presence, or absence, of specific illicit materials held in a database.
- Evaluate use of focal construct geometry (FCG) and advance FCG to look inside metal containers.
 - Demonstrate the enhanced intensity gained from using FCG compared to pencil beam geometry.
 - Explore the efficiency of ED technique as opposed to AD, at the high energies needed to penetrate metal containers.
 - Employ ED-FCG to identify a sample concealed within metal container.
 - Combine AD-FCG and ED-FCG by introducing the HEXITEC detector.
 - Utilise and evaluate use of novel pin-hole encoder to enable depth perception within inspection volume.
 - Evaluate effectiveness of the depth perception technique at high energy via simulation.

Chapter 6

Materials and Methods

This chapter introduces the instruments, geometries and methods used during the experimental research undertaken. Experimental work was conducted and compared to simulated results obtained using *McXtrace*, a Monte Carlo based simulation software.

6.1 Approach

Low energy conventional pencil beam ADXRD was employed for a comparative study against *McXtrace* to validate the use of the software. Once validated, experimental work was conducted to demonstrate the feasibility of using ADXRD to identify a sample contained within a given volume.

One fundamental requirement in conventional ADXRD, as discussed in §3.2, is to have knowledge of the origin of scatter i.e. the sample, which allows calculation of atomic d -spacings. Several techniques - analytical, post-sample encoders and algorithmic - are explored to enable depth perception when using a pencil beam geometry without greatly reducing the scattering flux impinging on the detector as previously discussed techniques introduced in Chapter 4.

Focal construct geometry was introduced to increase the diffraction flux and to mitigate effects of preferred orientation and large grain size, characteristics of

explosive powders.^{65,88,90} This was achieved by employing an annular collimator in place of the pin-hole collimator in conventional pencil beam ADXRD to shape the incident beam, altering the footprint impinging on the sample, thus increasing the volume interrogated simultaneously. This was explored, analytically and experimentally, by comparing the intensities resulting from employing an annular collimator and a pin-hole collimator.

Angular dispersive FCG was investigated, before ED-FCG was considered due to the increased penetration capability offered, due to the higher energy photons obtainable by using the Bremsstrahlung portion of the X-ray spectrum. The efficiency of the two techniques were compared by analysing the X-ray source spectra generated by increasing the source voltage. Tungsten sources were analysed due to being the highest energy portable sources commercially available.^{93,140}

ED-FCG was demonstrated employing the high energy W source, with the effect of increasing the thickness of iron investigated. The use of an energy sensitive pixelated detector to combine AD and ED techniques, was evaluated initially conducting some angular dispersive experiments in both pencil and FCG geometries to assess its capabilities.

A post-sample pin-hole encoder, in conjunction with the HEXITEC detector, were employed to introduce depth awareness. This offers the capability to isolate scatter originating from select positions along the primary axis. The depth resolution of the technique was evaluated, before simulations were conducted to extend the method beyond the laboratory using higher energy X-ray sources.

6.2 Instrumentation

6.2.1 Experimental

A variety of sources, detectors and optics were used in various instrumental set-ups conducted at the different energies. The individual components are listed below and described later in terms of the geometries in which they were used for.

6.2.1.1 Sources

Copper (Cu) - 1.5406 Å

The Cu target source is a sealed glass X-ray tube with a single Goebel instant mirror, which acts as a monochromator, to increase the intensity of the primary beam operating at 40 kV and 40 mA.³⁴ The beam is collimated into a pencil beam using a pin-hole aperture of radius $a_c = 0.25$ mm. Used for angular dispersive diffraction in conjunction with the General Area Detector Diffraction System (GADDS) detector housed within a D8 Bruker Discovery. This system will be referred to as D8-GADDS.

Molybdenum (Mo) - 0.7093 Å

The Mo source used was a Panalalytical XRD glass tube powered by a Philips PW1830 generator surrounded by a PW1927 radiation cabinet and used a standard watercooled sealed glass tube (40 kV, 30 mA). The take-off angle of the X-ray source was set to 6 ° with a line of focus 0.4 mm wide and 12 mm long. When a monochromatic source was needed a zirconium (Zr) filter was used.

Tungsten (W) - 0.20899 Å

The high energy tungsten source employed within this work was a VJ Technology IXS1680 with an output of 40-160 kVp and 0.5-10 mA. Focal spot size 1.2 mm with 20 ° half cone beam.

6.2.1.2 Optics

The optics comprised both pre-sample collimators and post-sample encoders. When employing the Cu source, within the Bruker D8-GADDS, the pencil beam optics detailed in §6.2.1.1 were employed. Bespoke collimation optics were designed for both a pencil beam and conical beam geometries when using Mo and W sources. At low energy (<20 keV) - Mo - the collimators used were made from brass (chemical formula Cu_3Zn_2 , density 8.73 g/cm³ - sufficiently dense to inhibit the path of the X-rays; see Appendix B) and at the higher energy W X-ray source, the collimators were made from tungsten. The dimensions of the collimators used are displayed in Table 6.1. A diagram of both the (a) pencil beam and (b) annular beam optics can be seen in Figure 6.1.

Table 6.1 Dimensions of collimators employed.

Source	Collimator type	Material	Density /g/cm ³	Thickness /mm	Radius /mm
Mo	Pencil beam	Brass	8.73	2.2	0.125
	Pencil beam	Brass	8.73	2.2	0.25
	Annular	Brass	8.73	1	Inner: 6.25 Outer: 6.5
	Annular	Brass	8.73	2.2	Inner: 7.75 Outer: 8.0
	Annular	Brass	8.73	2.2	Inner: 7.75 Outer: 8.0
W	Annular	Tungsten	19.3	Proprietary	Proprietary

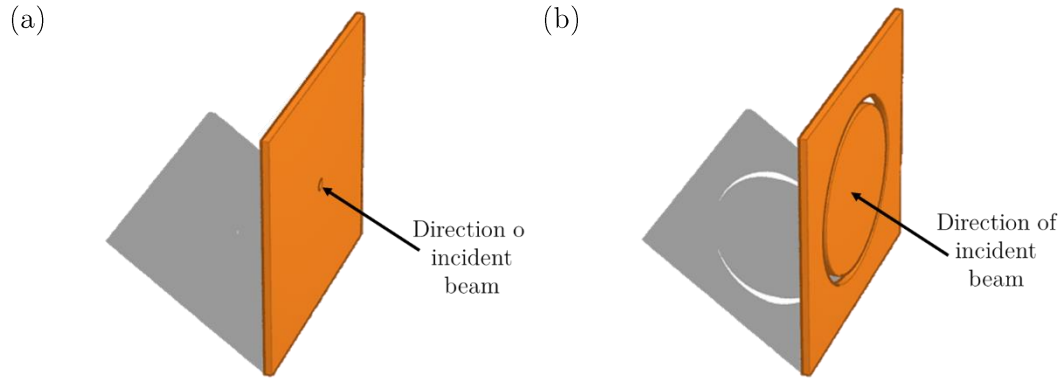


Figure 6.1 Diagram of a) pencil beam collimator b) annular collimator.

Post-sample encoders were used for depth perception, detailed in §6.4.2.2, with a low energy (Mo) source. Linear and spiral encoders - constructed of a 0.5 mm tungsten wire - were used for depth perception. The linear encoder was a single straight wire placed off-centre. The spiral encoder was a single turn of an Archimedean spiral as to avoid ambiguity arising from multiple encoding, centred in the primary beam. At high energy (W source) a post-sample pin-hole aperture was used to offer depth awareness.

Table 6.2 Metals used in the construction of post-sample optics.

Material	Density /g/cm ³	Type	Geometry
Tungsten, W	19.3	Linear Encoder	0.5 mm wire
		Archimedean Spiral Encoder	0.5 mm, single turn wire
Lead, Pb	11.34	Pin-hole Aperture	4 mm thick, radius=0.75 mm

6.2.1.3 Detectors

Angular Dispersive Detectors:

Bruker D8-GADDS 8 keV

The GADDS comprises of a 1024 x 1024 pixel, 100 mm diameter area detector (each pixel is ~100 μm), which is optimised for the detection of X-rays at 8 keV, iron.

Princeton Instrument PIXIS 1024

The Princeton Instruments PIXIS is a 13.3 x 13.3 mm area detector with 1024 x 1024 pixels (each pixel 13 μm x 13 μm) CCD which is thermoelectrically cooled to ~233 K. The detector provides low flux imaging for energies ranging from 3 keV to 20 keV.

Energy Dispersive Detector - X-123CdTe

The X-123CdTe is an energy dispersive detector for the detection of X-ray or gamma rays in the range of 5-150 keV. The active area is 25 mm² with an energy resolution of 1.5 keV FWHM at 122 keV.

Energy sensitive pixelated detector - HEXITEC

The HEXITEC detector features both ADXRD and EDXRD simultaneously combined.^{65,109} The pixelated detector bonded to a CdTe crystal allows the simultaneous measurement of the energy of the individual incident X-ray photons and the position of every photon in the 4-200 keV range, providing spatial resolution

needed for angular dispersive measurements.^{109,134,141,142} The 20 x 20 mm active area of the detector is composed of 80 x 80 250 μm pixels which provide a complete energy spectrum with an average energy resolution of 800 eV FWHM at 60 keV.^{99,134}

6.2.2 Simulations: *McXtrace*

McXtrace is a free, open source, Monte Carlo based software package used for simulating X-ray instrumentation and performing virtual X-ray tracing experiments for data analysis¹⁴³⁻¹⁴⁵. Other X-ray simulation packages exist, most notably *SHADOW*¹⁴⁶, others include *RAY*¹⁴⁷, *PENLOPE*¹⁴⁸, *Phase* and *SRW* (*Synchrotron Radiation Workshop*), but have not been used here for a variety of reasons.¹⁴⁹ The latter two simulation packages mentioned, based on the physical optics and wavefront propagation, only have limited availability due to the licenses being proprietary but are very popular amongst X-ray scientists.¹⁵⁰ Unlike *SRW*, *SHADOW* and *RAY* both use Monte Carlo methods and are based on geometry optics and ray-tracing and both provide accurate reliable results when modelling the particle nature of X-rays. *SHADOW* is very popular due to being built under an open source license but lacks a user-friendly interface. *McXtrace* was chosen for this work due to being openly available, highly versatile and user-friendly without any requirement to have in depth knowledge of programming or access to any proprietary software for its operation.¹⁵⁰

McXtrace software package is based on *McStas*, a tool used for simulating neutron scattering instruments and experiments which has been used for over a decade.¹⁵¹ The software has an open modular structure allowing users to tailor the program for their specific requirements.

Usually, X-ray beamlines are made up of a series of different components, beginning with the source emitting photons incident on optics and samples, concluding with a detector. Each one of these elements modifies the beam characteristics - divergence, position, wavelength and time - which introduces intercorrelations between them, forming a complex system which is difficult to model analytically, such as phase-space theory which loses validity when describing the resulting effects.^{149,152} Individually, the devices themselves often have analytical models. A

way to connect all these single discrete models together, modelling a complex beamline, is to use the Monte Carlo method.¹⁴⁴

The Monte Carlo method was founded by the Manhattan Project scientists who developed the first atomic weapon.¹⁵³ Challenged with only a limited supply of uranium, they used simulation to calculate reliable probabilities of what would happen in a chain reaction, thus reducing the amount of raw material needed for testing.

Monte Carlo is based on replacing a deterministic system, a system in which no randomness is involved in determining the potential states of the system, with probabilities. Within the field of XRD this is done by assigning probabilities to each of the possible reflection planes from which diffraction can occur and generating numerous random events. Integrating over these events, measurable features of the X-ray beam can be estimated.

McXtrace is used here as a comparison to experimental measurements and later to extend the research beyond the capability of the laboratory.

6.2.2.1 Components

McXtrace is split into three levels of code; Instrument file, components and kernel. The user describes the devices and geometry of the system in the instrument file using the component library. Components within the pre-existing database can be added to the instrument file and tailored to the specific needs of the beamline. The kernel, unseen by the user, links all the independent components together, managing the propagation of the photons between the specified components.¹⁴³

An X-ray tube may be modelled using the source component *Source_flat*, which represents a flat rectangular or circular surface uniformly emitting numerical photons around 4π steradians. The spectrum emitted may either be Gaussian or uniform around a central wavelength or energy. Spectrum data can also be read in from an external file, a feature that has been used throughout this research to simulate the laboratory source. A modified version of this source was later used to model the annular beam, incorporating the annulus aperture within the component,

but this could have easily been simulated using a separate aperture component. Slits and apertures are modelled as either rectangular or circular apertures in an infinitely thin sheet of perfectly absorbing material.

The sample is modelled by the *PowderN* component where a relative probability of scatter from a reflection is calculated from a set of partial scattering cross sections. Cross sections for individual Debye cones are governed by:

$$\sigma_{coh,r} = f e^{-2W} \frac{N}{V_0} \frac{4x^3}{k^2} \frac{j_\tau |F_\tau|^2}{\tau}$$

Where W is the Debye-Waller factor (describes attenuation of scattering X-rays), V_0 , the unit cell volume, j_τ , the multiplicity of reflection, $|F_\tau|^2$, the structure factor, N , number of unit cells in the sample volume, k , the wavevector of the photon and f is the packing factor of the powder. These are all part of the material input file or component file constructed by the user to create the instrument file.¹⁴⁴

Simulated detector components include the position sensitive detector, *PSD_monitor*, used to model the ADXRD detectors, an energy dispersive detector *E_monitor* and *EPSD_detectors* to model the HEXITEC detector. Like the physical detector, the *PSD_monitor* records the position of the incident photon within a plane, the *E_monitor* simply records the energy of the photons incident on the detector window and the *EPSD_monitor* is a combination of both, recording the position and energy of each pixel. The size and number of pixels of each detector can be tailored to the detector being modelled in all components.

6.3 Materials

The materials used within the study were chosen to model the warhead container and the concealed explosives. The polycrystalline materials were chosen for the initial work due to their similar density to explosives. The container was modelled using sheets of metal; aluminium and steel.

6.3.1 Polycrystalline Materials - Explosive Simulants

Calcium carbonate (CaCO_3) and aluminium oxide (Al_2O_3) were selected as suitable test materials due to having similar densities to explosives (military explosives have

Table 6.3 Polycrystalline sheet samples used for low energy - Cu - experimental work.

Material		Density /g/cm ³	Thickness /mm
Al ₂ O ₃ (plate)	Aluminium oxide	3.95	0.17
CaCO ₃ (sheet)	Calcium carbonate	2.71	0.05
CaCO ₃ (sheet)	Calcium carbonate	2.71	0.10
Al (sheet)	Aluminium	2.70	0.016

Table 6.4 Polycrystalline sheet samples used at low energy - Mo - experimental work.

Material		Density /g/cm ³	Thickness /mm
Al ₂ O ₃ (plate)	Aluminium oxide	3.95	0.24
Al ₂ O ₃ (plate)	Aluminium oxide	3.95	1.53
Al (sheet)	Aluminium	2.70	1.30
CaCO ₃ (plate)	Calcium carbonate	2.71	0.10

a density greater than 1.6 g/cm³)²⁰, they are self-supporting, readily available, easily manipulated and their diffraction profiles have relatively few peaks allowing for easy demonstration of the techniques.

Calcium carbonate, when in the form of sheets (i.e. paper - a mixture of cellulose and CaCO₃), can be easily multiplied to model a thicker sample.

During the 17.5 keV Mo-K α experiments, the Al₂O₃ sample used was a pure NIST (National Institute of Standards and Technology) standard SRM 1976 of 0.24 mm thickness as shown in Table 6.4, made with low preferred orientation and small grain size.

Powdered samples were used in the high energy experiments as simulants for explosives. The powders were placed in standard 90 mm petri dishes, height 15 mm, illustrated in Figure 6.2. To minimise effects of preferred orientation and a large grain size, that can produce incomplete diffraction patterns, fine powders were used.

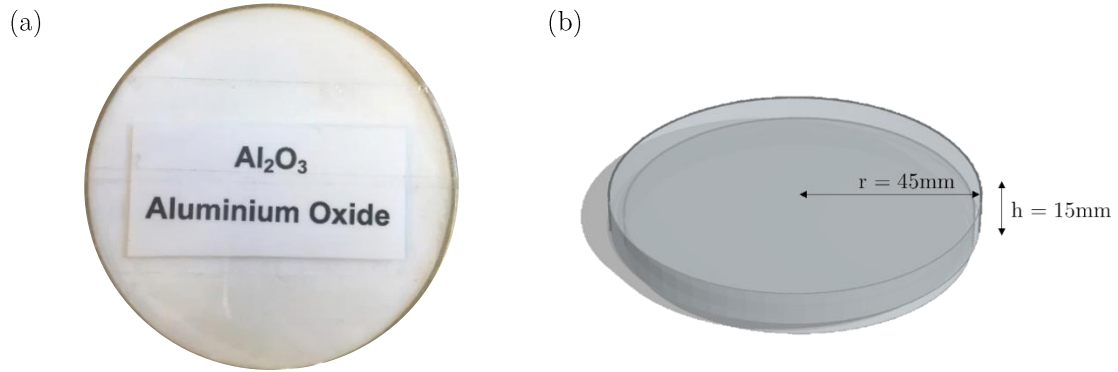


Figure 6.2 (a) Photograph and (b) diagram of standard 90 mm petri dish used to contain powder XRD samples for the high energy experimental studies.

Table 6.5 Powdered samples used in the high energy FCG experimental work.

Material		Density /g/cm ³
Al_2O_3	Aluminium oxide	3.95
CaCO_3	Calcium carbonate	2.71
NaCl	Sodium chloride	2.16

6.3.2 Metals

Aluminium and iron (experimentally steel was used in place of pure iron; steel is an alloy of iron and carbon) were selected due to being standard materials used in metal storage containers. Initially, thin sheets were used and slowly increased in number to model a thicker container wall. Table 6.6 gives the dimensions of the sheets used in the tungsten (W) geometry; the table gives the thinnest sample used.

Table 6.6 Metals used in experimental tests to model the warhead container.

Material	Density /g/cm ³	Dimensions /mm	Thickness /mm
Steel	7.86	11 x 11	0.3 (Mo) / 0.5 (W)
Aluminium	2.70	10 x 10	0.016 (Cu) / 1.3 (Mo) / 0.5 (W)

6.4 Methodology

This section describes the process by which the work was carried out and the geometries involved at the various stages of the project.

6.4.1 Viability of *McXtrace*

McXtrace was initially assessed as a viable simulation software to reproduce experimental data. Fundamental abilities of the software were compared to ADXRD low energy experimental data. All data was obtained using the D8-GADDS system, detailed in §6.2.1, pictured in Figure 6.3.

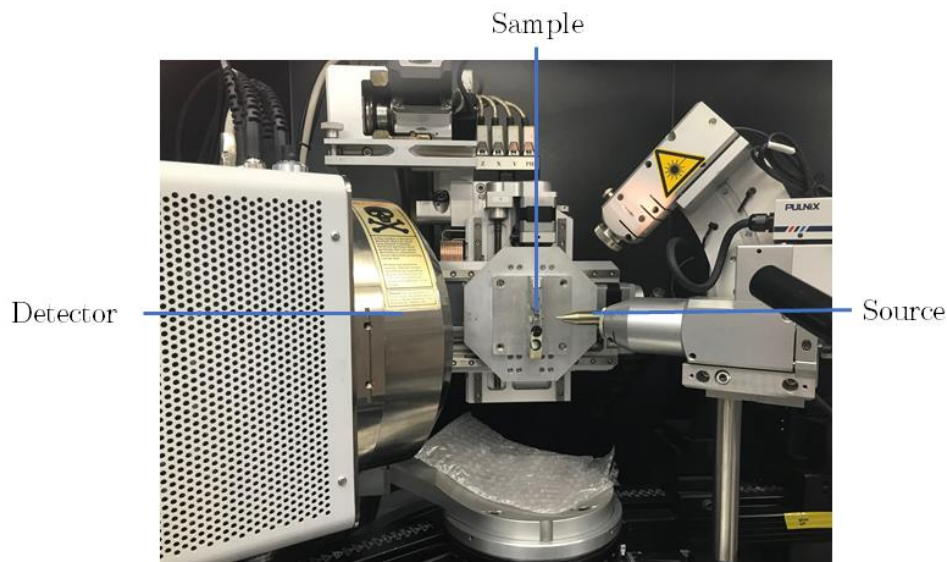


Figure 6.3 Photograph of the D8-GADDS employed for the low energy ADXRD experimental work. The source, sample stage and detector are labelled.

As with all pencil beam experiments the detector is offset from the primary axis, so as to avoid the primary beam, which would flood the detector, reducing the ability of the diffraction to be detected, shown in Figure 6.4. Additionally, the primary beam has the potential to damage the detector.

The geometry illustrated in Figure 6.4 was setup experimentally and modelled in the simulation software. An ADXRD image was obtained from 0.17 mm Al_2O_3 and compared to the simulation results. The consideration of geometry by the software was evaluated by translating a sample of 0.1 mm CaCO_3 along the primary axis in 2 mm increments and compared to simulated data.

The interactions of the sample were then evaluated by altering the sample thickness. Here, the resulting intensity of the scattering beam was compared against analytical data obtained from the NIST database along with experimental data from 0.016 mm sheets of Al which were multiplied to model a thicker sample.

As various energies were required for this research and the main role of *McXtrace* is to extend the capabilities of the laboratory, the energy of the source was also altered to test the response against analytical models.

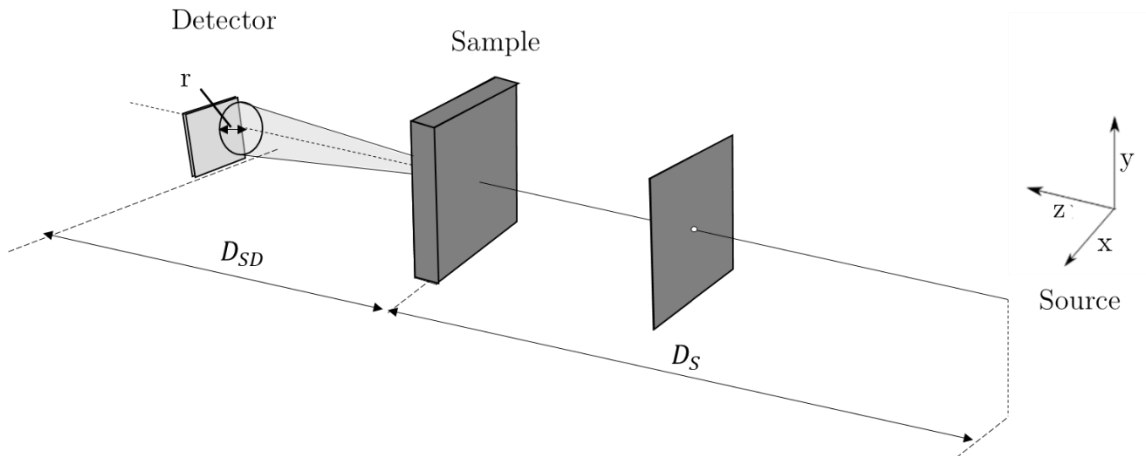


Figure 6.4 Schematic of the geometry of the D8-GADDS low energy XRD.

6.4.2 Interpretation of scatter: depth perception

As discussed in §3.3, EDXRD systems are currently the focus of many techniques to detect concealed illicit materials due to its speed advantage over ADXRD methods. Fast throughput however is not a primary requirement of this application, so attention focussed on using ADXRD with its superior material specificity and spatial awareness capability.⁹⁶

In classical ADXRD the geometry of the whole system is very important, and the sample position in relation to the detector is crucial to know the origin of the scatter to thus determine the diffraction angle. Techniques introduced here allow an unknown sample to be identified when the position is unknown via ADXRD methods.

Firstly, the analytical method employs an angular dispersive detector to obtain two images from two different positions along the primary, z -axis. Having knowledge of the distance between the two measurements enables the distance between the sample and the detector to be calculated using geometry and simultaneous equations. The encoder technique is a similar geometry dependent method but introduces a post-sample reference structure to ‘encode’ the scatter originating from the sample. The algorithmic method introduces an algorithm by which the diffraction data is compared to a set database of materials to produce a likelihood of materials at specific locations.

All three techniques are evaluated, testing their accuracy and reliability before being compared to one another.

6.4.2.1 Analytical

Based on a technique introduced by Dicken *et al.*¹¹⁵, by altering the distance between the unknown scattering source and the detector (D_{SD}) through known increments, several diffraction patterns can be obtained from various positions. Due to the linear relationship of the peak maxima positions and the detector positions, the equivalent peak maxima at each detector position can be identified. Using trigonometry and Bragg’s Law a series of simultaneous equations be constructed and used to calculate the unknown sample-to-detector distance, D_{SD} .

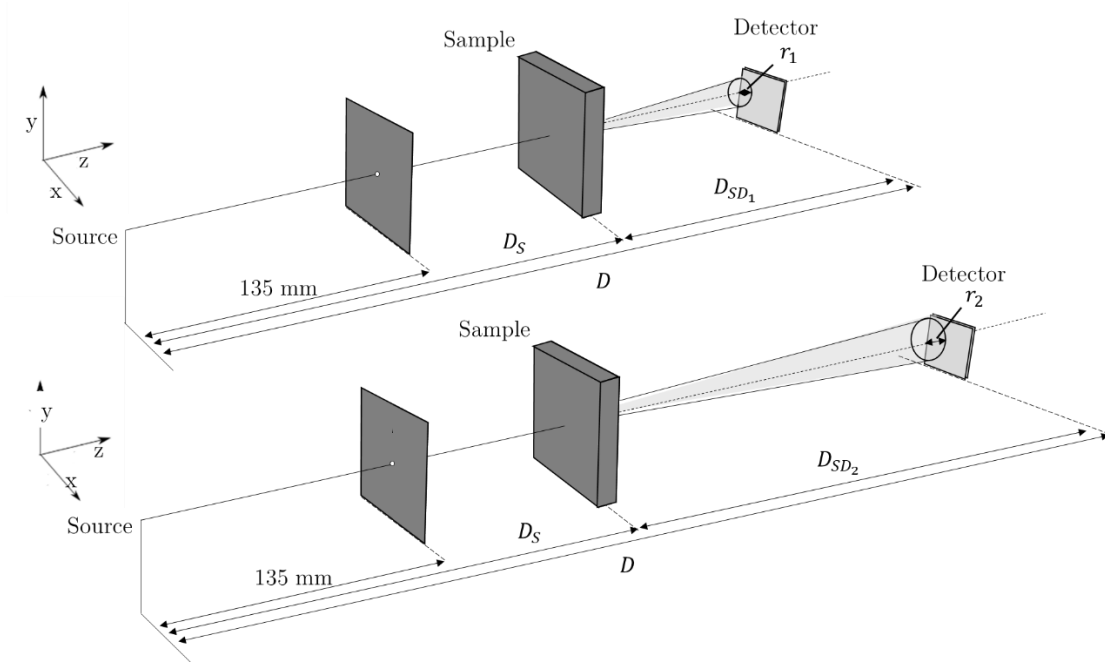


Figure 6.5 Diagram demonstrating two different detector positions for use of the analytical method when determining the origin of scatter.

This method relies on having a minimum of two D_{SD} positions, each with a diffraction pattern. The distance between the two detector positions, $\Delta D_{SD}(= D_{SD_2} - D_{SD_1})$, can be measured and using the geometry labelling in Figure 6.5, simultaneous equations can be constructed, shown below, and solved to find the initial D_{SD} i.e. D_{SD_1} , Equation (6.1).

$$(1) \quad \tan 2\theta = \frac{r_1}{D_{SD_1}} \qquad (2) \quad \tan 2\theta = \frac{r_2}{D_{SD_2}} = \frac{r_2}{D_{SD_1} + \Delta D_{SD}}$$

Equated and rearranged,

$$D_{SD_1} = \frac{\Delta D_{SD} r_1}{r_2 - r_1} \tag{6.1}$$

The simultaneous equations can also be solved for the diffraction angle, resulting in Equation (6.2). This equation is independent of the location of the sample, only the distance travelled by the detector and the measured radii are needed meaning the material can be identified without identifying the location. This feature is useful

in the context of weapons dismantlement as it allows sensitive information, such as the design of the weapon, to stay unknown.

$$2\theta = \tan^{-1} \left(\frac{r_2 - r_1}{\Delta D_{SD}} \right) \quad (6.2)$$

The analytical technique was demonstrated using the Mo Zr-filtered source in conjunction with the PIXIS detector. The pin-hole aperture of radius, $a_c = 0.25$ mm was employed to generate the pencil beam incident on the 1.53 mm Al_2O_3 sample, fixed in place. The PIXIS detector was translated $\Delta D_{SD} = 10$ mm between the two required ADXRD measurements.

6.4.2.2 Encoders

Post-sample encoders were employed as a reference structure to determine the origin of scatter. As discussed in §4.1.1, coded apertures such as the ‘comb’ harmonic encoder, presented by MacCabe *et al.*(2012)⁶⁰, offer depth awareness along the primary axis, identifying the location of samples contained within the inspection volume and hence allow material identification. Encoding of the Debye cones at the detector plane occurs from the absorption of the scatter by the encoder, appearing as intersection points on the Debye ring.

Two post-sample encoders are introduced here for the encoding of pencil beam diffraction data. As with MacCabe *et al.*(2012)⁶⁰ the encoder is placed between the sample and the detector. They were chosen due to their simple geometry, offering unambiguous interpretation and a large open fraction, allowing most of the scattered X-rays to reach the detector unlike the comb-like encoder which only having a ~50% open fraction, removes half the scattered X-rays.

Firstly, the linear encoder, shown in Figure 6.6, is a linear tungsten wire placed off-centre to the primary axis, shown in Figure 6.7. The off-centre position, distance α_{LE} (measured from the centre of the Debye ring and the central axis of the encoder), generates unique polar angles, ζ , between the x -axis and the intersection of the Debye rings. r_{LE} , the radius of the Debye ring, is measured from the central axis of the encoder and the centre of the Debye ring, shown in Figure 6.7.

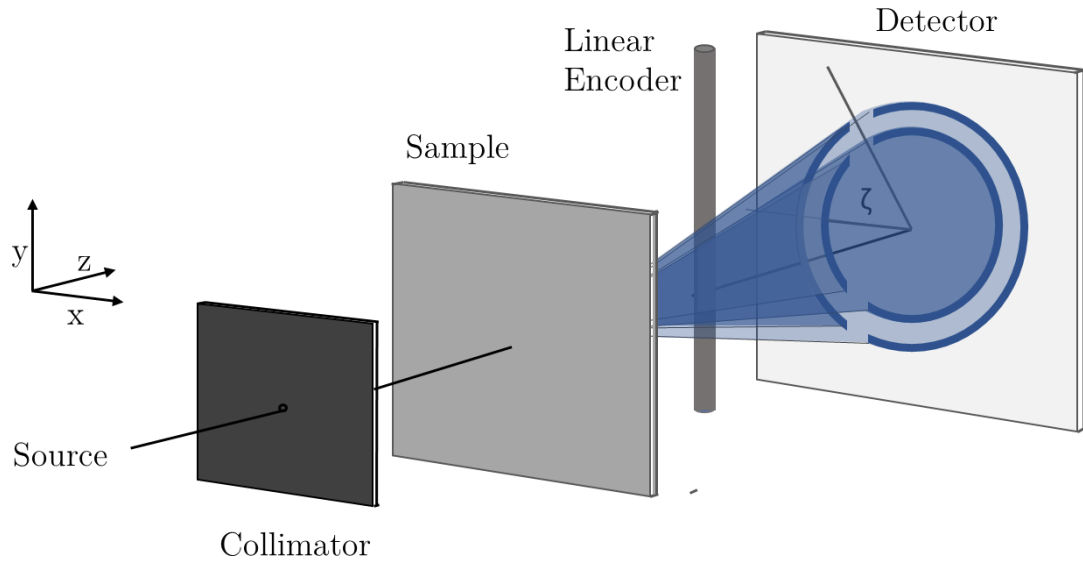


Figure 6.6 Illustration of linear encoder geometry in a pencil beam system.

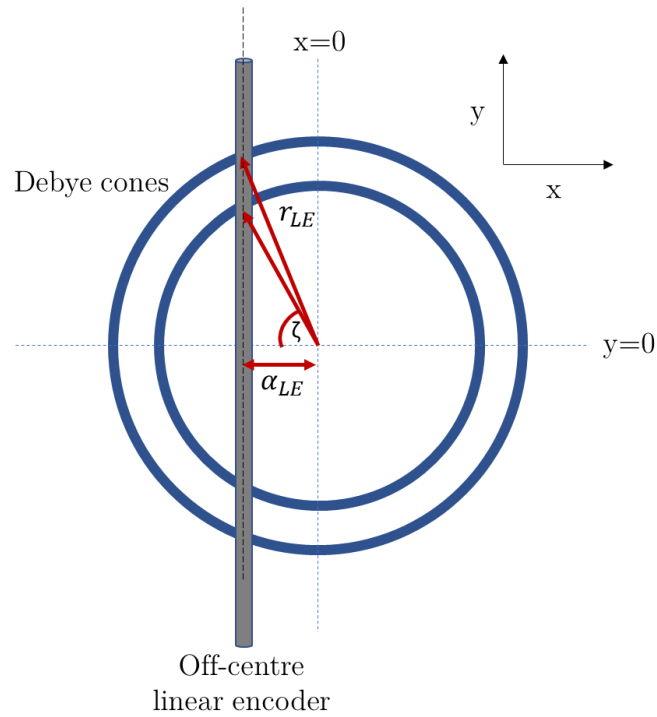


Figure 6.7 Diagram of placement of the linear encoder, with intersection angle, ζ , and offset distance α_{LE} , within the encoder plane.

Within the same sample, and therefore the same origin of scatter, each individual Debye ring will generate a unique intersection angle with the linear encoder. When more than one sample is involved the shadow of the linear encoder moves along the x -axis.

As with the analytical method, it is necessary to know the radii of the Debye cones at a minimum of two positions. The reference structure offers this possibility. Equation (6.3) is used to calculate the radius of the Debye cone within the encoder plane, r_{LE} .

$$r_{LE} = \frac{\alpha_{LE}}{\cos \zeta} \quad (6.3)$$

From Figure 6.8, which shows the geometric arrangement of the linear encoder pencil beam system, a relationship can also be determined for the offset distance in the detector plane, α_D . The offset distance is different in the two planes due to the expanding nature of the Debye cone.

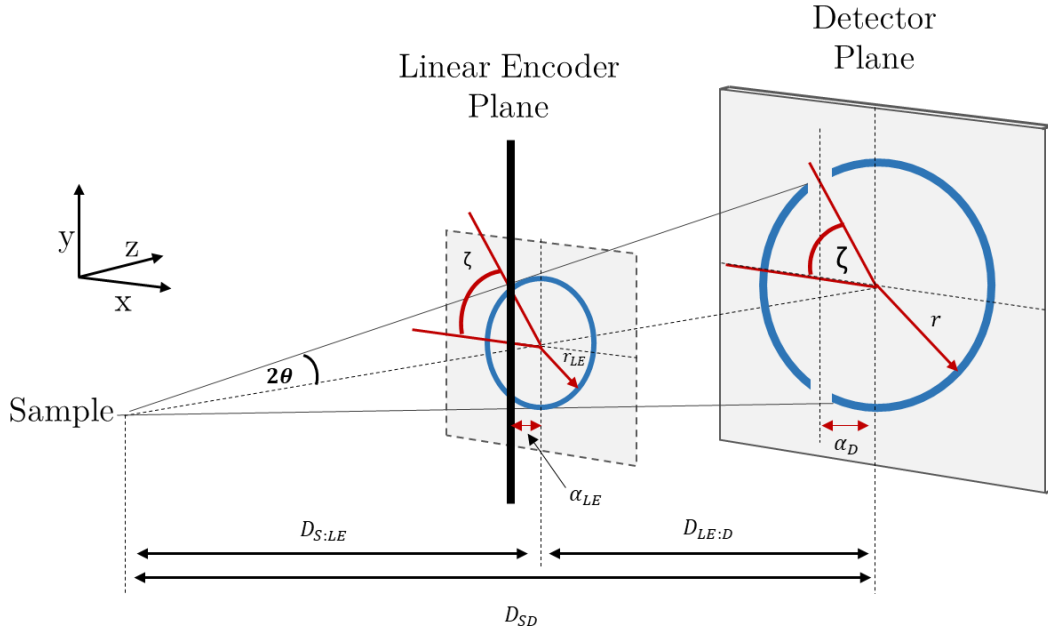


Figure 6.8 Schematic showing the geometric arrangement employed to encode pencil beam diffraction data with a linear encoder, represented with a single Debye ring (blue).

Using the same geometry as before but in the detector plane, the radius of the Debye cone in the encoder plane can also be determined by Equation (6.4).

$$r_{LE} = \frac{\alpha_{LE}r}{\alpha_D} \quad (6.4)$$

The diffraction angle, 2θ , labelled in Figure 6.8, can be used to determine Equation (6.5).

$$\tan 2\theta = \frac{r_{LE}}{D_{S:LE}} = \frac{r}{D_{SD}} \quad (6.5)$$

Where $D_{S:LE}$ and $D_{LE:D}$ refer to the distances from the sample to the linear encoder and the linear encoder to the detector respectively. The total distance from the sample to the detector is $D_{SD}(= D_{S:LE} + D_{LE:D})$. By combining Equations (6.4) and (6.5) an overall equation for D_{SD} can be established, Equation (6.6). Another equation for D_{SD} can be determined when combining Equations (6.3) and (6.5), shown by Equation (6.7).

$$\begin{aligned} D_{SD} &= \frac{r_{LE}D_{LE:D}}{r - r_{LE}} + D_{LE:D} \\ &= \frac{\alpha_{LE}D_{LE:D}}{\alpha_D - \alpha_{LE}} + D_{LE:D} \end{aligned} \quad (6.6)$$

$$= \frac{\alpha_{LE}D_{LE:D}}{r \cos \zeta - \alpha_{LE}} + D_{LE:D} \quad (6.7)$$

Equations (6.6) and (6.7) both contain variables which are either known or can be measured. The diffraction angle was also evaluated, producing Equations (6.8) and (6.9).

$$\begin{aligned} 2\theta &= \tan^{-1} \frac{r}{D_{LE:D} \left(1 + \left(\frac{\alpha_{LE}}{\alpha_D - \alpha_{LE}} \right) \right)} \\ &= \tan^{-1} \frac{r}{\frac{\alpha_{LE}D_{LE:D}}{r \cos \zeta - \alpha_{LE}} + D_{LE:D}} \end{aligned} \quad (6.8)$$

$$= \tan^{-1} \frac{r - \frac{\alpha_{LE}}{\cos \zeta}}{D_{LE:D}} \quad (6.9)$$

Similar to the analytical method, Equation (6.9) shows that the diffraction angle can be independently determined from the sample to detector distance, D_{SD} , revealing identity of the material without disclosing the location i.e. weapon design.

A simulation was initially conducted with a single 0.05 mm CaCO_3 sample and a linear encoder placed at $D_{LE:D} = 25$ mm, to demonstrate the technique, modelled on the D8-GADDS system, highlighting the unique polar angles created from varying the samples position along the primary beam.

The number of samples was increased to demonstrate the capabilities of the technique to distinguish multiple samples. Two spatially separated 0.05 mm CaCO_3 samples were observed in a single 60 s exposure and the position and phase data recovered using Equations (6.7) and (6.9). The same experiment is simulated, and the results compared. An error study is undertaken, evaluating the errors associated with determining the sample-to-detector distance, D_{SD} , and the diffraction angle, 2θ . This comprised of simulating numerous geometries, altering the position of the linear encoder (along the z -axis and the x -axis) and the samples position to obtain diffraction patterns from each geometry. Analysis of these images enabled the magnitude of error to be calculated via analytical propagation.

The second encoder to be introduced, as a method of encoding pencil beam diffraction data to identify the sample, i.e. recover 2θ information, is a single turn of an Archimedean spiral, Figure 6.9. An Archimedean spiral can be described by Equation (6.10);

$$r_{AS} = a_{AS} + b_{AS}\psi \quad (6.10)$$

where r_{AS} is the distance of the radius from the centre (illustrated in Figure 6.10), a_{AS} and b_{AS} are real numbers that are responsible for the shape and position of the spiral and ψ is the angular position of the radius. a_{AS} describes the tightness

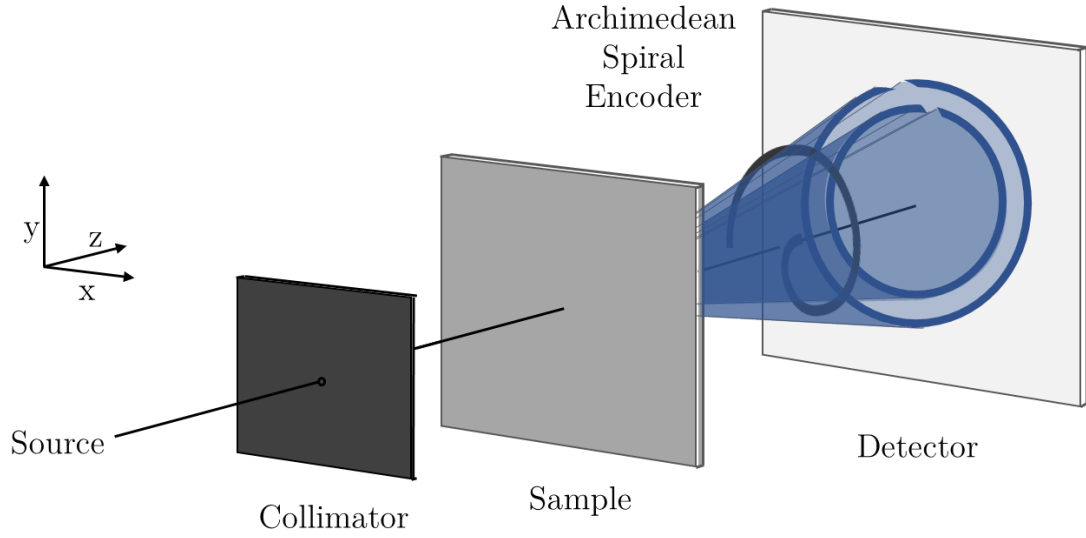


Figure 6.9 Illustration of Archimedean spiral encoder geometry in a pencil beam system.

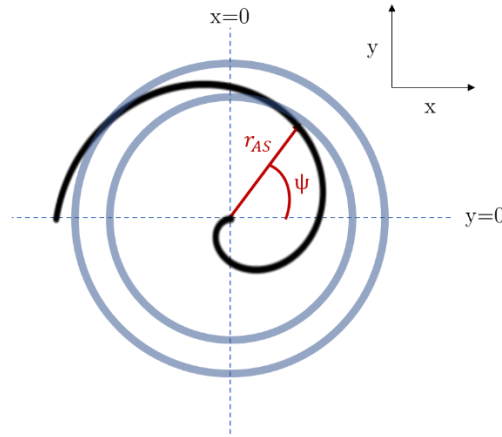


Figure 6.10 Diagram of an Archimedean spiral encoder, with radius, r_{AS} , and polar angle ψ .

of the spiral; an increase in a_{AS} will loosen the spiral as well as translate the centre along the x -axis. b_{AS} represents the distance between successive turns.

Utilising only a single turn of an Archimedean spiral reduces the ambiguity of the encoder; multiple turns would result in a single ψ corresponding to multiple radii. The encoder was also placed at (0,0) coordinate, as in Figure 6.10 and Figure 6.11, this not only makes the geometry easier to work with, allowing for accurate encoding, but also provides a beam stop for the primary beam.

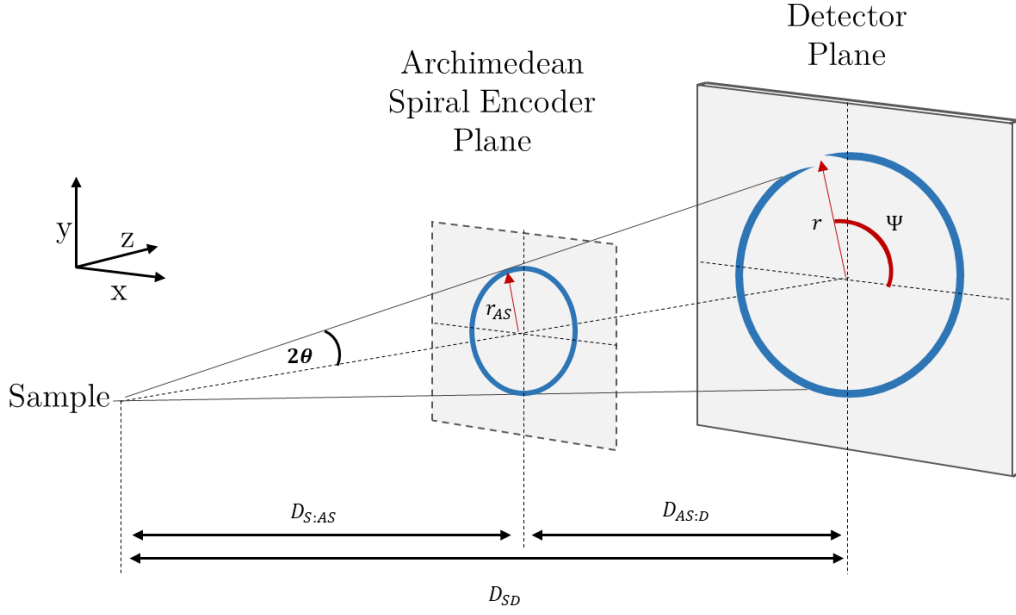


Figure 6.11 Schematic diagram of geometric arrangement employed to encode pencil beam diffraction data with an Archimedean spiral encoder, represented with a single Debye ring (blue).

As with the linear encoder, the spiral encoder blocks scatter it interacts with creating a shadow in the detected diffraction pattern. These characteristic discontinuities in the Debye cones occur at specific ψ ($\psi = r_{AS} - a/b$) relating to the encoder.

Using the same method as the linear encoder, and using Figure 6.11, the sample to detector distance, D_{SD} , can be calculated with Equation (6.11).

$$\begin{aligned}
 D_{SD} &= D_{S:AS} + D_{AS:D} \\
 &= \frac{D_{AS:D} \ a + b\psi}{r - (a + b\psi)} + D_{AS:D}
 \end{aligned} \tag{6.11}$$

where, as can be seen in Figure 6.11, $D_{S:AS}$ is the distance between the sample and the spiral encoder, $D_{AS:D}$ is the distance between the encoder and the detector and r is the radius of the Debye cone in the detector plane.

The diffraction angles can then be calculated by Equation (6.12).

$$\begin{aligned}
2\theta &= \tan^{-1} \frac{r - r_{AS}}{D_{AS:D}} \\
&= \tan^{-1} \frac{r - a - b\psi}{D_{AS:D}}
\end{aligned} \tag{6.12}$$

Once again, this means the diffraction angle can be determined without calculating the location of the sample.

The spiral encoders capability to distinguish spatially separated samples is demonstrated using two spatially separated 0.05 mm CaCO_3 samples, with the Bruker D8-GADDS system. The spiral encoder was placed a fixed distance $D_{AS:D} = 54$ mm from the detector with Sample 2, being fixed in place at $D_{SD_2} = 63$ mm and Sample 1 moving in increments of 2 mm between $D_{SD_1} = 69$ mm and $D_{SD_1} = 81$ mm. Angular diffraction images were obtained in 60 s exposures at each position and used to determine the position and material phase of each sample using Equations (6.11) and (6.12). The same geometry is simulated and a similar error analysis conducted as with the linear encoder to determine the errors associated with the positioning of the encoder when calculating the sample-to-detector distance, D_{SD} , and scattering angle, 2θ .

Both of these encoders were introduced as methods of recovering material phase data about an unknown sample in an unknown location within a volume. They are demonstrated experimentally and simulated to assess the accuracy and reliability of each technique.

6.4.2.3 Algorithmic Method

The algorithmic method presents a process by which angular dispersive experimental diffraction data is compared to a library of materials (d -spacings) to produce a likelihood of materials at specific locations. The method is loosely based on an algorithm historically devised by Hanawalt (1936) to identify a substance from its energy dispersive diffraction pattern by comparing between the main peak locations of the sample diffractogram and reference peaks in a library.⁶¹ The additional challenge to the present situation is not knowing the location of the

sample thus the atomic spacings for the angular dispersive experimental data are unknown.

It is a purely data driven method that involves no movement of any component or an additional reference structures to be added. The technique relies on the geometric considerations used within the analytical method. If the sample was placed closer to the detector (i.e. the sample-to-detector distance, D_{SD} , decreases) the radii of the resulting diffraction pattern within the detector plane will also decrease. The individual diffraction patterns from the library of known samples are transformed to how they would appear at a multitude of locations and compared to the experimental diffractogram to find the best-match.

MATLAB was employed to write the algorithm comparing positions of peaks within a diffractogram from a sample at a supposedly unknown position (i.e. a set of measured radii corresponding to Debye cone radii in the detector plane) to previously obtained data from a known sample at a known position. A set of Debye radii (within the detector plane) were computed for when the known sample was placed at specific increments inside the inspection volume. These calculated Debye radii are compared to the experimental diffractogram from the unknown sample and likelihood between each Debye radius can be calculated. When all materials and locations from the database have been compared to the unknown diffractogram, a Grid-based search (a Grid-search is a method of optimisation, parametrised by a grid of parameters) to obtain the best match or optimal combination of materials can be performed. The best-match displays the most likely combination of the database material at their determined location which best fits the experimental data.

6.4.3 Focal Construct Geometry

Focal construct geometry, FCG, discussed in §3.4.2, is introduced as a method of increasing the number of photons interacting with the sample. The aim of this was to improve the intensity of the resulting patterns but has the additional benefit of reducing effects of preferred orientation and large grain size.⁶⁸

6.4.3.1 Pencil Beam vs. FCG

A comparison between the intensity of the obtained scattering maxima of pencil beam and FCG geometries was conducted. Analytically, for an annular collimator of inner radius r_1 and outer radius r_2 , the area of the annulus is $\pi(r_2^2 - r_1^2)$. Similarly, for a pin-hole collimator with diameter a_c the area is $\pi \frac{a_c^2}{4}$. Thus the focal construct geometry:pencil beam (FCG:PB) area ratio is given by Equation (6.13).

$$I_{FCG:PB} = \frac{4 r_2^2 - r_1^2}{a_c^2} \quad (6.13)$$

If the pin-hole diameter is the same as the width of the annulus opening i.e. $a_c = r_2 - r_1$, then Equation (6.13) can be simplified to Equation (6.14).

$$I_{FCG:PB} = \frac{8r}{a_c} \quad (6.14)$$

where r is the mean radius of the annular collimator.

Data for the comparison was attained using the low energy Mo source (25 kV and 20 mA) in conjunction with the PIXIS detector, both pictured in Figure 6.12, to

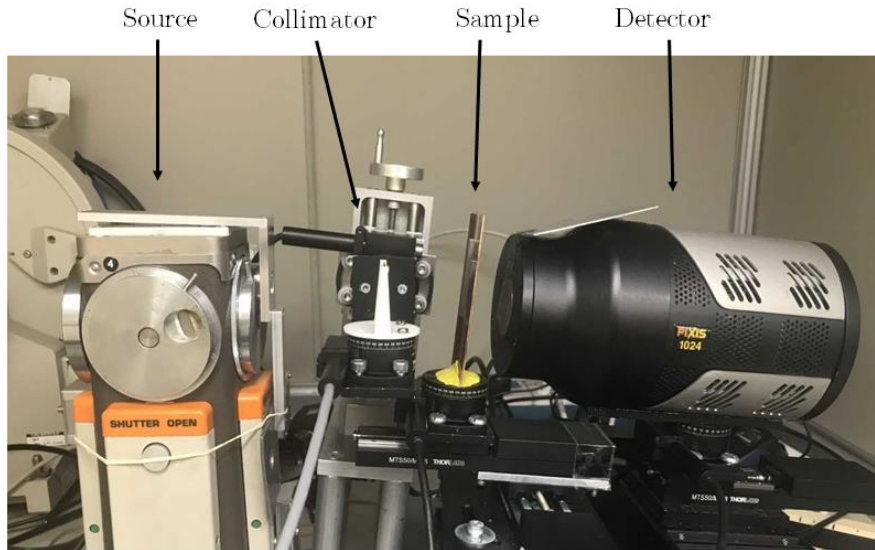


Figure 6.12 Experimental set up of the Mo Zr-filtered X-ray source showing use of the PIXIS angular dispersive detector.

compare the intensity produced by pencil beam geometry to FCG. As with the copper source, the detector was offset for the pencil beam experiments. Diagrams of the pencil beam and FCG arrangements can be seen in Figure 6.13.

The position of the sample was controlled electronically by a Thorlabs translation stage (MTS50/M-Z8 and L490MZ/M) with 50 mm movement and $\pm 4 \mu\text{m}$ positioning capability along each axis. The detector was mounted onto a motorised Thorlabs linear translation stage with 100 mm movement (NRT100/M) capability in the x -axis, and 50 mm translation capability on the y (L490MZ/M) and z (MTS50/M-Z8) axes with precision $\pm 4 \mu\text{m}$.

The collimator, sample and detector were all mounted onto individual CR1-Z7 Thorlabs motorised rotation stages, attached to the translation stages, allowing

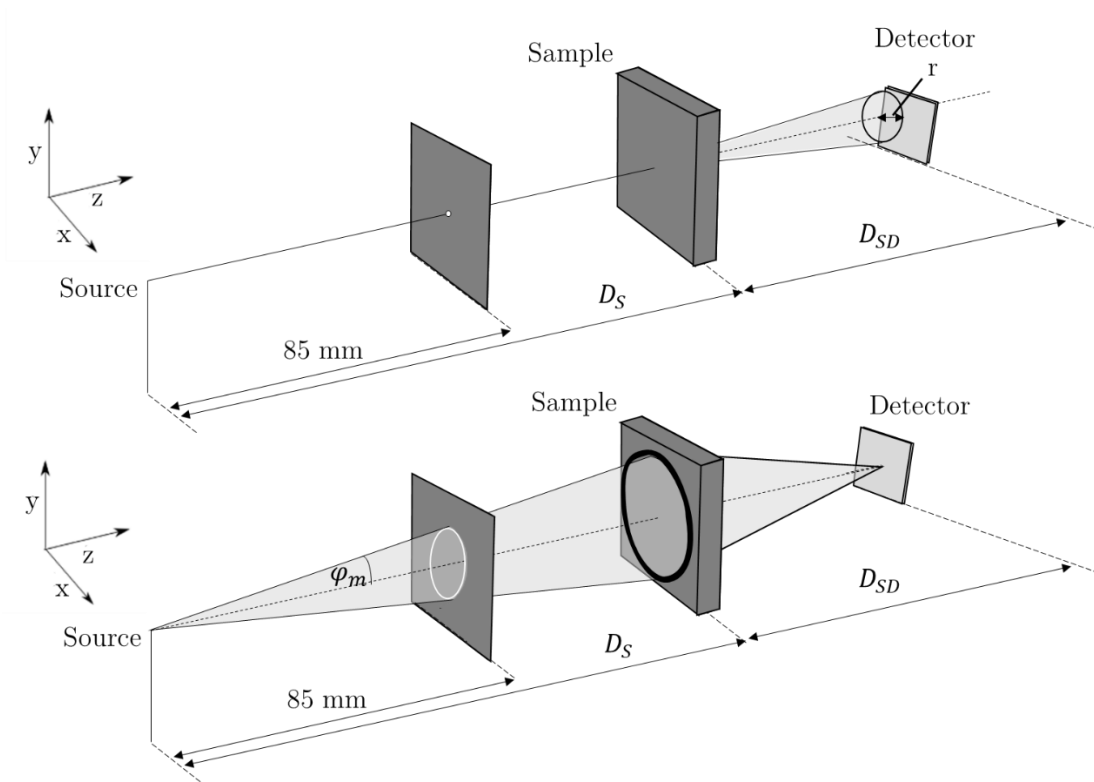


Figure 6.13 Geometric arrangement of both the pencil beam (top) and the annular beam (bottom) experiments conducted with Mo source.

360° rotation around the y -axis. The collimator had an additional rotation stage that allowed for rotation around the x axis with $\pm 0.02^\circ$ precision. A summary of all the translational and rotational capabilities of each component is illustrated in **Error! Reference source not found..** All the motorised stages were computer controlled for ease of operation during alignment.

For both geometries, the same 1.53 mm Al_2O_3 sample was used and placed $D_S = 135$ mm away from the source. To directly compare the intensity between the two geometries the $a_c = 0.25$ mm diameter pin-hole collimator was compared with the annular collimator with inner radius $r_1 = 6.25$ mm and outer radius $r_2 = 6.50$ mm giving an opening angle of $\varphi_m = 4.29^\circ$ when placed 85 mm away from source along the primary axis, Figure 6.13. The detector was placed $D_{SD} = 20$ mm away from the sample in the pencil beam geometry. To gain the full diffraction pattern for FCG, the PIXIS detector was translated along the primary axis to identify the condensation foci, comparable to the Debye cone radii obtained via the pencil beam geometry.

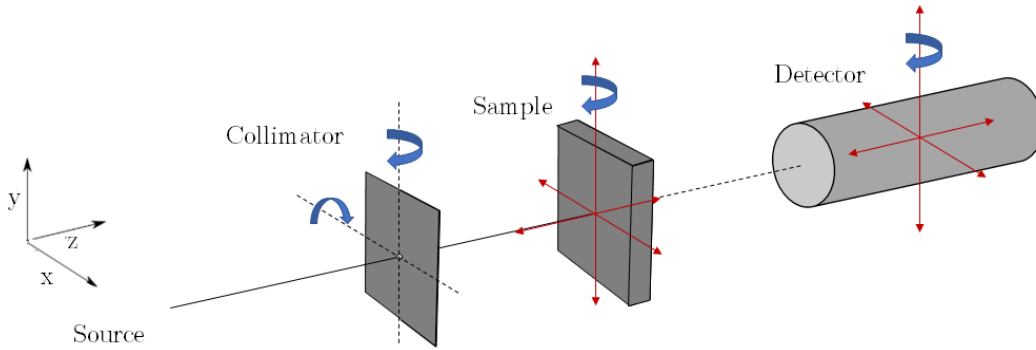


Figure 6.14 The translational and rotational capabilities of the instrumentation utilised for the Mo experimental data collection. The red arrows illustrate the translation capabilities along the respective axis and the blue arrows illustrate the rotation capabilities around corresponding axis.

6.4.3.2 AD-FCG

Simulations of the FCG setup employed in the previous section, §6.4.3.1, were conducted modelling the same 1.53 mm Al_2O_3 sample to demonstrate the capabilities of *McXtrace* to simulate FCG.

To demonstrate the capability of FCG to mitigate the effects of preferred orientation, which impedes the use of conventional pencil beam geometry due to missing d -spacings, a sample of 1.3 mm Al exhibiting preferred orientation was investigated. The same source, collimator and detector was employed to conduct the experiment as with the pencil beam experiment.

The Al sample was placed further away from the annular collimator, $D_S = 155$ mm than the previous geometry analysing Al_2O_3 , to enable observation of smaller d -spacings. The condensation foci resulting from smaller d -spacings form closer to the sample due to the corresponding large scattering angle. To enable observation, the detector needs to be placed closer to the scattering source however this results in the primary angular beam impinging on the detector window, flooding the detector. Moving the sample further away from the source increases the radius of the ring footprint on the sample, extending the condensation foci along the z -axis to avoid the primary beam flooding the detector window. The area dispersive detector linearly translated along the z -axis in 1 mm increments between $D = 185$ mm and $D = 215$ mm, with an image obtained at each position by the PIXIS detector, exposure time 30 s.

Simulations of the geometry, with an ideal 1.3 mm Al sample, were conducted to encompass a wider range of d -spacings, as the primary beam can be removed from the simulation prior to reaching the detector plane.

6.4.4 High energy AD vs. ED

As discussed in §3.3, angular dispersive (AD) methods employ the characteristic proportion of the X-ray source spectrum to investigate crystallographic structure of the material, as opposed to energy dispersive (ED) techniques which use the polychromatic Bremsstrahlung proportion of the incident beam. The two types of

radiation are produced simultaneously via an X-ray tube, as detailed in §3.2.2.1, but the proportions of each differ when generated at different voltages.

To evaluate the efficiency of each technique as the voltage of the X-ray tube is increased, X-ray source spectra for voltages up to 500 kVp were calculated and analysed, comparing the proportions of photons contributing to characteristic (AD) and Bremsstrahlung (ED) radiation.

Firstly, source spectra obtained from the VJ Technology W source were compared to source spectra calculated by *SpekCalc*, a program specifically designed for calculation of X-ray spectra from tungsten anode tubes. *SpekCalc* relies on deterministic equations for Bremsstrahlung emissions, combined with pre-calculated electron distributions.^{154–156} The model used by *SpekCalc*, which combines both semi-experimental models and Monte Carlo code, is described in both Poludniowski *et al.* (2009)¹⁵⁶ and Poludniowski and Evans (2007)¹⁵⁴. It has previously been thoroughly tested to show a strong agreement with experimental data.^{154,155} The advantages of *SpekCalc* over other pre-existing software programs is discussed by Poludniowski in previous papers.^{154–156}

SpekCalc was used to extend the voltage of the source beyond the capability of the lab to 500 kVp and the spectra evaluated. The higher the proportion of contributed photons, the higher the incident flux thus greater efficiency.

6.4.5 ED-FCG

In contrast to AD-FCG methods, ED-FCG employs the use of a stationary detector. An X-123CdTe Amptek energy dispersive detector was employed to measure a polychromatic focal spot of diffracted flux from the sample. The high energy tungsten source, VJ Technology IXS1680, in conjunction with an annular tungsten collimator was used to create the conical shell incident beam.

The technique is demonstrated by employing a 1 mm Fe sample, placed at $D_S = 150$ mm. Petri dish samples of Al_2O_3 and NaCl, detailed in §6.3.1, were individually placed in the beam and translated along the z -axis towards the detector. The Al_2O_3 sample was placed at $D_S = 143.0$ mm, $D_S = 160.8$ mm, $D_S = 174.5$ mm and

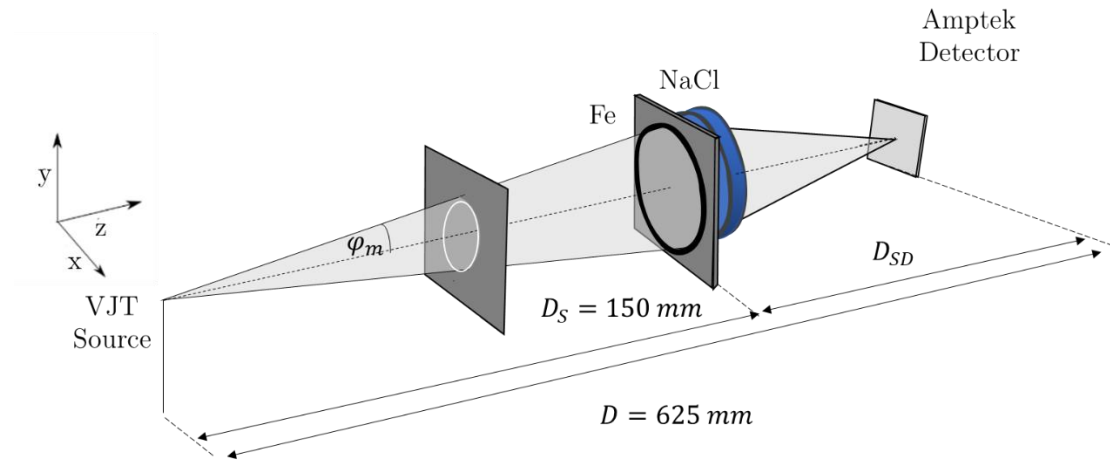


Figure 6.15 Diagram of high energy dispersive FCG geometry with samples modelling metal container.

$D_S = 194.0$ mm. Whereas the NaCl sample was placed at $D_S = 150.0$ mm, $D_S = 167.8$ mm, $D_S = 186.5$ mm and $D_S = 206.0$ mm.

The 15 mm sample of NaCl and the sheet of Fe were combined and arranged as illustrated in **Error! Reference source not found..** Individual 1 mm sheets of Fe were added, with a diffraction profile obtained after each addition to observe the effect of an increased thickness of Fe. This was done to model the effect of a thick metal container.

6.4.6 HEXITEC detector

A combination of both AD and ED techniques was sought as previous research detailed in §4.1.3, suggested this as a potential method to separate coherent scatter originating from different positions along the primary axis. The HEXITEC detector, offering simultaneous acquisition of AD and ED data through an array of 80 x 80 pixels each capable of measuring the scattered photons energy and corresponding scattering angle, was investigated.

The HEXITEC's capabilities are initially demonstrated employing pencil beam ADXRD geometry. The low energy Mo source was used in conjunction with the 0.125 mm radius pin-hole collimator, with the HEXTEC detector offset to avoid the pencil beam, as illustrated in Figure 6.13 (top). Samples of 1.30 mm Al and

1.53 mm Al_2O_3 were placed at $D_S = 135$ mm, with the detector at $D = 185$ mm. Images were obtained with 300 s exposure for each sample.

AD-FCG was demonstrated, employing an annular collimator, 85 mm from the source and centrally positioning the detector along the z -axis, Figure 6.13 (bottom). As the area of the detector window (20×20 mm) is greater than the previously employed PIXIS detector (13.3×13.3 mm), in the same Mo geometry, another annular collimator was introduced, with a greater radius, $r = 7.875$ mm, creating a larger opening angle, $\varphi_m = 5.29^\circ$, detailed in §6.2.1.2. This allowed the primary conical beam to propagate past the detector, without impinging on the detector window.

Samples of 1.53 mm Al_2O_3 and 0.10 mm CaCO_3 were individually observed using AD-FCG, with the detector incrementally translated along the z -axis, with 30 s exposures obtained after each 1 mm translation. For both samples the detector was translated between $D = 175$ mm and $D = 204$ mm.

Multiplex sampling was investigated, simultaneously observing the Al_2O_3 and CaCO_3 , spatially separated by 20 mm along the z -axis; Al_2O_3 placed at $D_S = 135$ mm and CaCO_3 at $D_S = 155$ mm. The detector was incrementally translated between $D = 180$ mm and $D = 214$ mm, with 30 s exposures taken at every 1 mm increment.

The ED functionality of the HEXITEC detector was examined using FCG geometry at high energy, employing the VJ Technology W source, placed at $D = 551.25$ mm. An annular collimator with $\varphi_m = 2.5^\circ$ was introduced as the higher energy results in smaller scattering angles. A 0.5 mm Fe sample was placed at $D_S = 138$ mm, and multiple exposures were obtained increasing the acquisition time by 120 s each time, up to 600 s.

6.4.6.1 Depth Perception

A method was sought to enable the origin of scatter along the z -axis. Similar to the encoders employed in pencil beam geometry, §6.4.2.2, a post-sample pin-hole aperture, in conjunction with the HEXITEC detector, was proposed to achieve depth awareness.

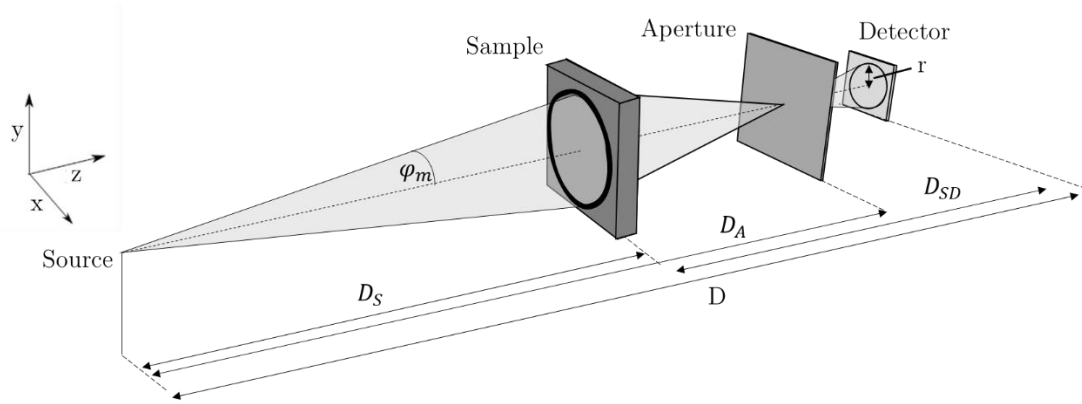


Figure 6.16 Schematic diagram of placement of pin-hole encoder in FCG geometry.

The pin-hole aperture is placed between the sample and the detector (Figure 6.16), as with the previously discussed post-sample encoders in §6.4.2.2, to modify the resultant scattering diffraction. The combined output of the HEXITEC detector allows the origin of the scatter to be determined, through interpretation of the angular dispersive output, whilst using the energy resolving pixels to identify the materials atomic spacings.

Contrasting the previously introduced pencil beam encoders, the pin-hole encoder in conjunction with the HEXITEC detector, has the capability of isolating scatter from different origins. This has the advantage of not just locating the sample but also the ability to detect scatter that would otherwise be overshadowed by strongly scattering materials.

The pin-hole aperture projects a ring of scatter, per sample, on to the detector. The radii of each of these rings is associated with a position along the primary axis. As can be seen in Figure 6.17, the closer the sample to the aperture, the larger the respective radii within the detector plane.

As the HEXITEC detector obtained not just the position of each of the scattered photons but also the energy, these rings can be individually selected to acquire material data from individual samples.

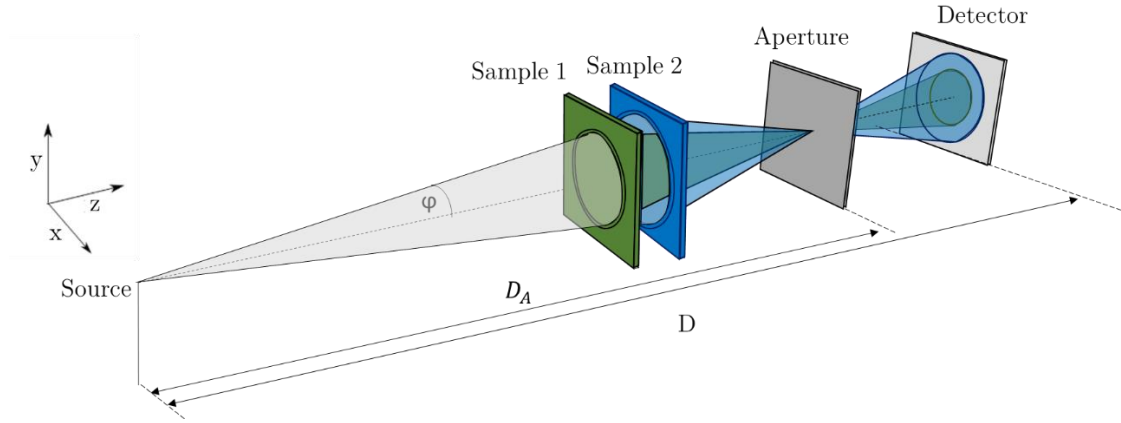


Figure 6.17 Diagram illustrating the geometry of FCG with two samples indicating how the use of the aperture induces depth perception.

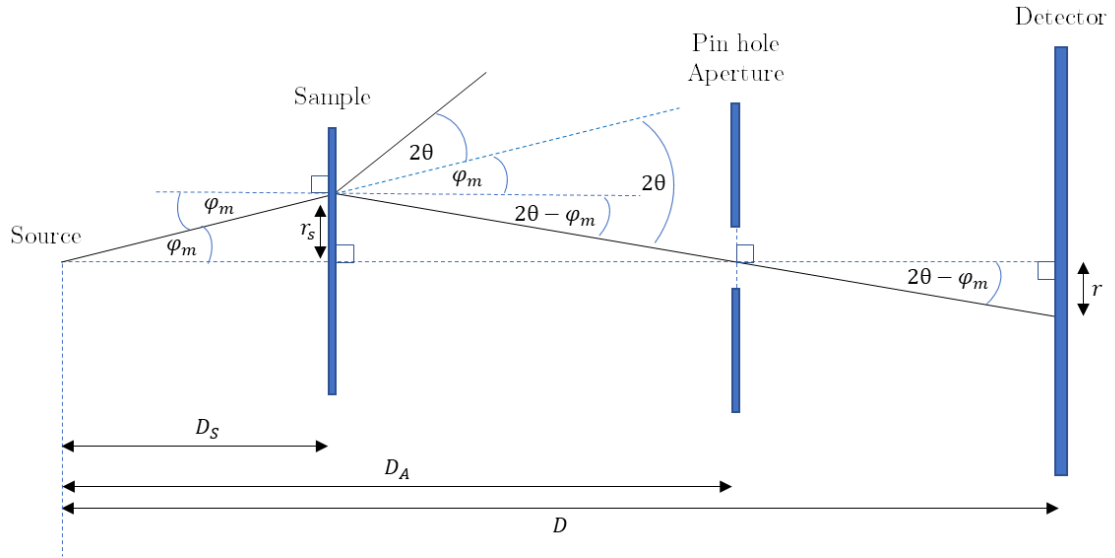


Figure 6.18 Schematic of beam path in FCG when pin-hole aperture placed between sample and detector.

Equations (1) and (2) are derived from the geometry of the system, shown in Figure 6.18, where D_S is the source to sample distance, r_s is the radius of the incident beam on the sample φ_m is the opening angle of the angular beam, created using the annular collimator, r is the radius in the detector plane, D is the source-to-sample distance and D_A is the source to pin-hole aperture distance.

$$(1) \quad D_S = \frac{r_s}{\tan \varphi_m} \quad (2) \quad \frac{r}{D - D_A} = \frac{r_s}{D_A - D_S}$$

From Equation (1) and (2) above, Equation (6.15) can be determined to enable calculation of the source-to-sample distance, locating the sample within the sample volume.

$$D_S = \frac{D_A r}{r + (D - D_A) \tan \varphi_m} \quad (6.15)$$

The schematic in Figure 6.18 can also be used to determine an Equation for 2θ .

$$\begin{aligned} 2\theta &= \tan^{-1} \left(\frac{r}{D - D_A} \right) + \varphi_m \\ &= \tan^{-1} \left(\frac{r_s}{D_A - D_S} \right) + \varphi_m \end{aligned} \quad (6.16)$$

Substituting Equation (6.16) into Braggs Law provides an equation for calculating the d -spacings of the material, Equation (6.17).

$$d = \frac{\lambda}{2 \sin \left\{ \frac{1}{2} \left(\tan^{-1} \left(\frac{r}{D - D_A} \right) + \varphi_m \right) \right\}} \quad (6.17)$$

This technique was demonstrated by analysing 15 mm Al_2O_3 and CaCO_3 samples (filled petri dish) employing the high energy W source. An annular collimator was designed resulting in an opening angle of $\varphi_m = 2.5 \pm 0.1^\circ$, with the HEXITEC detector placed at $D = 551.25$ mm. The pin-hole aperture was placed between the sample and the detector at $D_A = 376.66$ mm from the source, identified in Figure 6.17 and Figure 6.18. The samples were translated along the z -axis in increments of 9.6 mm to demonstrate the recovery of sample position from a single exposure. The technique was evaluated, analysing its precision to recover the sample position. This was conducted employing the same 15 mm Al_2O_3 and CaCO_3 samples and additionally a sample of 1 mm Fe.

Multiplex sampling was then investigated, placing a 15 mm CaCO_3 sample at $D_S = 180$ mm and a 1 mm Al sample at $D_S = 220$ mm. Conic sections of the AD-FCG image were selected to isolate scatter originating from positions along the z -axis, demonstrating the capability of the technique to extract individual diffraction profiles from a sample volume containing multiple samples.

The number of samples was increased to model a metal container, with two samples of 1 mm Fe placed either side of a 15 mm Al_2O_3 sample, placed at $D_S(\text{Fe}) = 140$ mm, $D_S(\text{Al}_2\text{O}_3) = 190$ mm and $D_S(\text{Fe}) = 240$ mm.

Using the same model, the effect of increasing the thickness of the container was evaluated by using a 0.5 mm Fe, either side of a 15 mm Al_2O_3 sample placed at $D_S(\text{Fe}) = 150$ mm, $D_S(\text{Al}_2\text{O}_3) = 190$ mm and $D_S(\text{Fe}) = 230$ mm. Additional 0.5 mm Fe samples were systematically added to either side of the Al_2O_3 with a 60 s exposure obtained after each addition, until 5 mm of Fe were placed either side of the Al_2O_3 sample.

The geometric limitations of the technique were explored examining the depth resolution along the z -axis axis. With a poor depth resolution, two spatially separated samples would appear as one in the recovered data, impeding the recovery of individual diffraction patterns. This was demonstrated using two 15 mm Al_2O_3 samples at a fixed 36 mm distance apart and translating them, together along the z -axis in increments of 12 mm from $D_S = 138$ mm to $D_S = 198$ mm.

The resolution of the system was analytically investigated before comparing to experimental results obtained by translating 15 mm samples of CaCO_3 and Al_2O_3 and 1 mm Fe along the z -axis. An infinitely thin sample was evaluated to, using the validated analytical methodology to indicate the depth resolution of the system. Multivariate analysis was conducted to consider the influence each parameter within the system has on the resulting depth resolution.

6.4.7 High Energy

Simulations were conducted to extend the technique to higher energy levels, which would be required to penetrate thicker containers. *McXtrace* was used to simulate the models used in experimental work and increase the voltage of the source

incident on the sample. A simple model was used comprising 1 mm Fe either side of 15 mm Al_2O_3 . The same model was used throughout each simulation, differing only in the energy of the source used.

As *McXtrace* doesn't have an inbuilt HEXITEC component, one was created by using multiple 1 keV position sensitive monitors of 80 x 80, 250 μm pixels. Each monitor was modelled to be in the same position along the z -axis and each simultaneously obtained an image of the scattered photons within the specified energy range. The images obtained were then transferred to ImageJ where a stack was created, examples of the images are shown in Figure 6.19, a montage created from a stack. As with the experimental method, an annulus selection was chosen to obtain data from individual positions along the z -axis. This enabled the acquisition of an energy spectrum by calculating the z -axis profile through the stack of images.

Simulations were conducted at higher energy levels to provide an indication of the performance at higher energy and indicate any limitation that might affect the use of the system.

6.5 Data Processing

MATLAB was employed for processing both simulated and experimental data.

6.5.1 Reference data

Reference data used to create diffraction profiles to attribute both simulated and experimental data was obtained from The Powder Diffraction File (PDF) maintained by the International Centre for Diffraction Data (ICDD) through Crystallographic Search-Match (version 2,1,1,1) software from which ¹⁵⁷ Reference data for Fe, Al etc., including calculated parameters such as 2θ values, can be found in Appendix A.

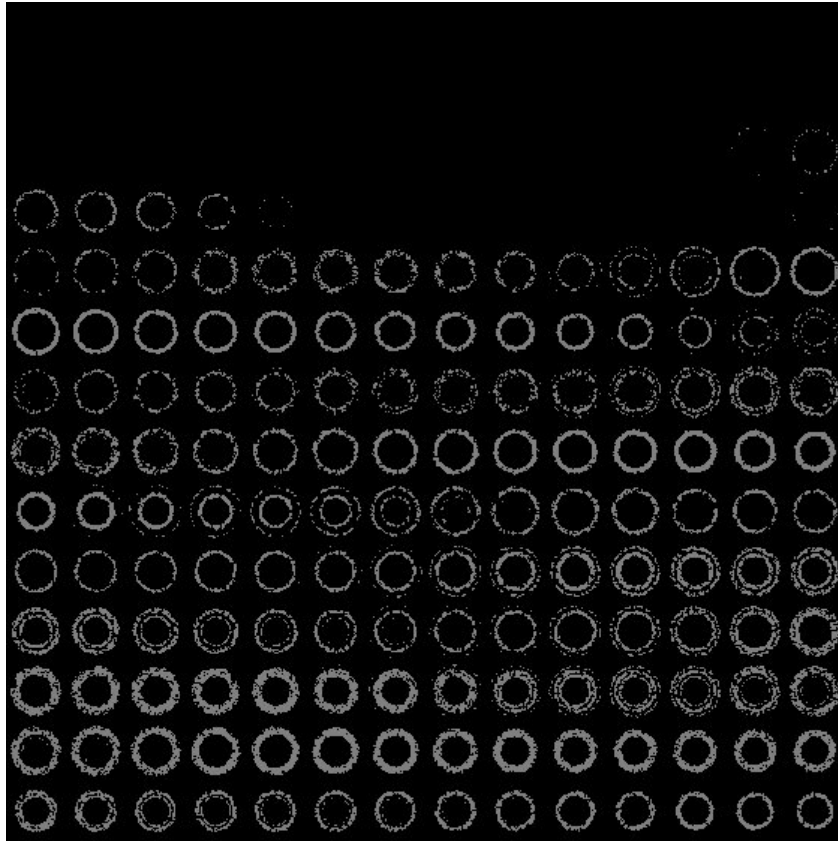


Figure 6.19 A montage created from a stack of images within ImageJ, each one relating a 1 keV energy range from 1 keV to 196 keV from a simulated FCG pin-hole geometry in *McXtrace*.

6.5.2 ImageJ

ImageJ was used for processing of ADXRD data from both the PIXIS and the HEXITEC from the Mo source. The program allows for azimuthal integration of acquired images to obtain diffraction profiles of the pencil beam data. For the FCG ADXRD data, where the detector is translated along the primary beam to observe the condensation foci converging and diverging, ImageJ allows processing through a stack of images to observe the intensity change over a specified area.

6.5.3 Measure of Noise

Several studies are conducted evaluating the signal (the coherent scatter) detectible when the obtained diffraction profile includes noise (other scatter). The noise or clutter within the diffraction profile originates from several factors including other

samples in close proximity (depth resolution), resolution of the detector and exposure time.

When analysing the effect exposure time has on the resulting diffraction pattern when using FCG with the HEXTEC detector, 0.5 mm Fe sheets were used. The minimum exposure time acquired was 60 s, increasing the exposure time up to 600 s in 120 s increments from 120 s exposure. Since the intensity of the resultant peaks within the diffraction profile are inconsistent with the reference profile (§8.4 and §0), a comparison noiseless profile was made by fitting a best fit model to the spectrum containing the least noise (600 s).

A best fit model was obtained using the *MATLAB* curve fitting function. The best fit obtained was a Gaussian model with 3 terms, in the format:

$$f(x) = a_1 e^{-\left[\frac{(x-b_1)}{c_1}\right]^2} + a_2 e^{-\left[\frac{(x-b_2)}{c_2}\right]^2} + a_3 e^{-\left[\frac{(x-b_3)}{c_3}\right]^2}$$

Where a is the amplitude, b is the position and c is related to the peak width. The best fit model was then subtracted from the normalised data to obtain the residuals from the best fit. The difference between the minimum and maximum residual for each exposure time was determined and used as the measure of the noise.

The same method was employed when analysing the effect of increasing the thickness of a container on the diffraction profile obtained from a concealed material when using the HEXITEC detector in conjunction with the pin-hole aperture to gain depth awareness and again when evaluating the effects of exposure time on the same model. The best fit model, once again obtained in *MATLAB*, was a Gaussian with 5 terms of the format:

$$f(x) = a_1 e^{-\left[\frac{(x-b_1)}{c_1}\right]^2} + a_2 e^{-\left[\frac{(x-b_2)}{c_2}\right]^2} + a_3 e^{-\left[\frac{(x-b_3)}{c_3}\right]^2} + a_4 e^{-\left[\frac{(x-b_4)}{c_4}\right]^2} + a_5 e^{-\left[\frac{(x-b_5)}{c_5}\right]^2}$$

This model is later used to evaluate the depth resolution of the HEXITEC - pin-hole system when the technique was extended beyond the capabilities of the laboratory with simulations.

Chapter 7

Pencil Beam Results

In this section the results obtained from the experimental tests, with corresponding simulations involving a pencil beam geometry, are presented. Firstly, *McXtrace* was evaluated as a viable simulation tool for the transmission XRD experiments conducted, §7.1. The results from the simulations are presented with a comparison between experimental results and/or empirical results where applicable.

Conventional pencil beam ADXRD was considered due to its high resolution and potential to identify the sample location without a sizable flux reduction.⁶⁰ A fundamental requirement to identify a material via XRD is to have knowledge of the origin of scatter. Three techniques were considered to enable depth perception with ADXRD along the primary axis; analytical, post-sample encoders (linear wire and Archimedean spiral) and algorithmic approach, discussed in §7.2.

7.1 Simulations: *McXtrace*

McXtrace was employed to facilitate the development of both pencil beam and FCG, initially by reproducing experimental data. *McXtrace* was later used to extend the techniques beyond the capabilities of the laboratory modelling X-ray sources with higher voltages. Initial work focused on confirming *McXtrace* as a viable simulation package for transmission X-ray diffraction research. Basic

capabilities of *McXtrace* were demonstrated and were compared to experimental results.

7.1.1 Comparison of diffraction profile

A comparison of simulated and experimental data for a conventional pencil beam using ADXRD geometry was completed with a 0.24 mm sample of aluminium oxide, Al_2O_3 illuminated with 8 keV ($\lambda=1.54 \text{ \AA}$) copper, monochromatic pencil beam source with the detector placed 20 mm away from the scattering object. Figure 7.1 illustrates the obtained radial plots, calculated by azimuthal integration of the obtained diffraction pattern, of both simulated and experimental data together with an Al_2O_3 reference diffraction profile, details of which can be found in Appendix A.

Data collected from both techniques is presented in Table 7.1 and confirms a high level of agreement as the peaks from the most prominent d -spacings, are within the experimental errors thus demonstrating the ability of the simulation package to model low energy simple angular XRD experiments.

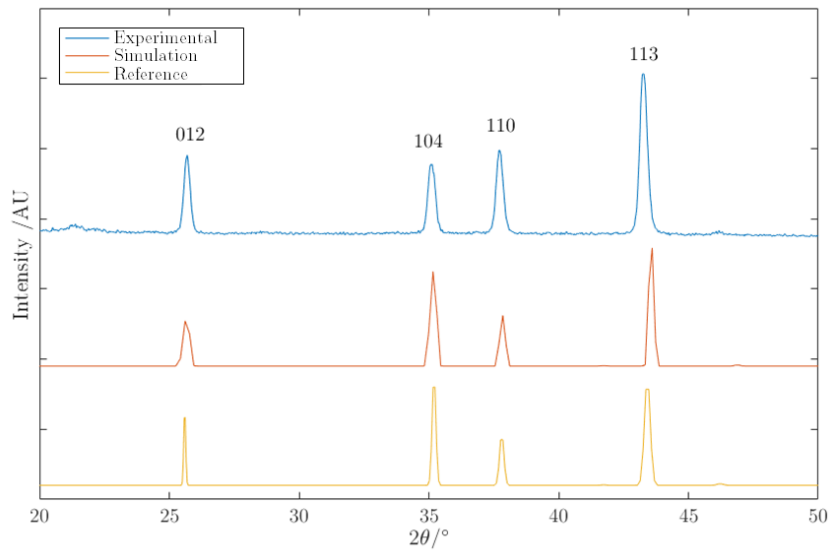


Figure 7.1 Radial plots obtained from experimental and simulated ADXRD data of a 0.24 mm thick Al_2O_3 plate together with an Al_2O_3 reference profile when $\lambda=1.54 \text{ \AA}$.

Table 7.1 Quantitative comparison of diffraction maxima positions from Figure 7.1.

Reflection	d -spacing /Å	2θ /°		
		Reference	Simulation	Experimental
012	3.48	25.55	25.61 ± 0.19	25.69 ± 0.28
104	2.55	35.11	35.16 ± 0.11	35.09 ± 0.14
110	2.38	37.73	37.75 ± 0.06	37.71 ± 0.09
113	2.09	43.30	43.32 ± 0.03	43.27 ± 0.06

7.1.2 Position of sample relative the detector

Using simple geometry, the diffraction angle, 2θ , can be calculated from the measured radius of scatter, r , at any distance from the scattering source, D_{SD} .

$$2\theta = \tan^{-1} \left(\frac{r}{D_{SD}} \right) \quad (7.1)$$

To test the relationship above, and the capabilities of *McXtrace*, the Bruker D8-GADDS diffractometer was arranged in pencil beam geometry with a 0.1 mm CaCO_3 sample. The same geometry was also generated within *McXtrace*. Experimental and simulated diffraction patterns for CaCO_3 are compared against a CaCO_3 reference pattern (Appendix A) in **Error! Reference source not found.** The sample was translated in 2 mm increments along the primary axis and diffraction patterns were obtained at each increment with 20 s exposure. The radial plots of the resulting angular dispersive diffraction patterns were measured experimentally and using simulations, displayed in **Error! Reference source not found.** and Figure 7.4, respectively.

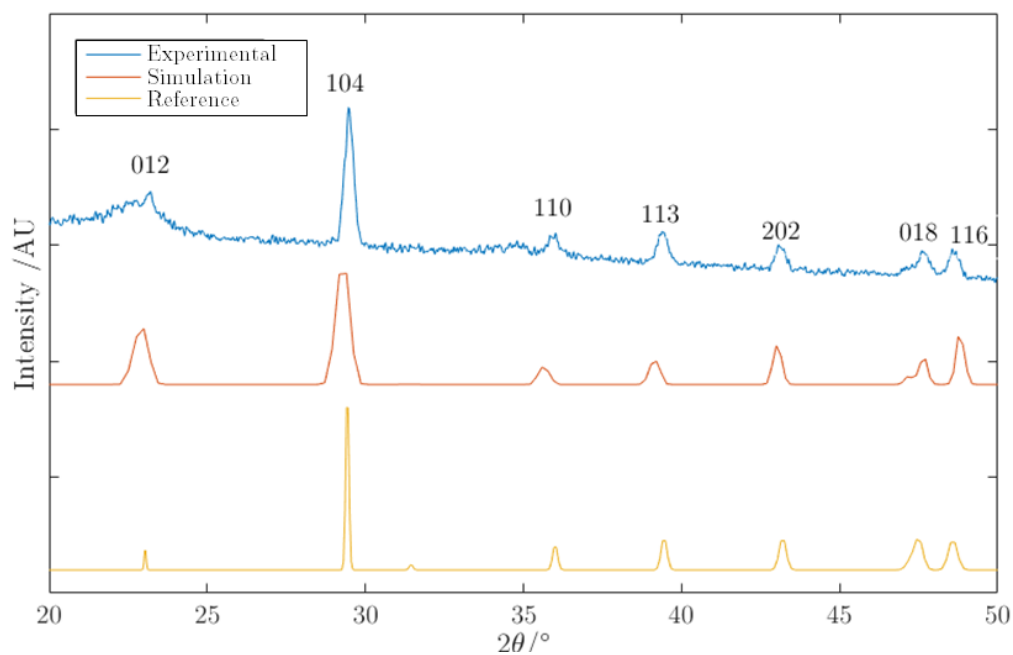


Figure 7.2 Experimental and simulated radial plots of ADXRD data against a CaCO_3 reference pattern.

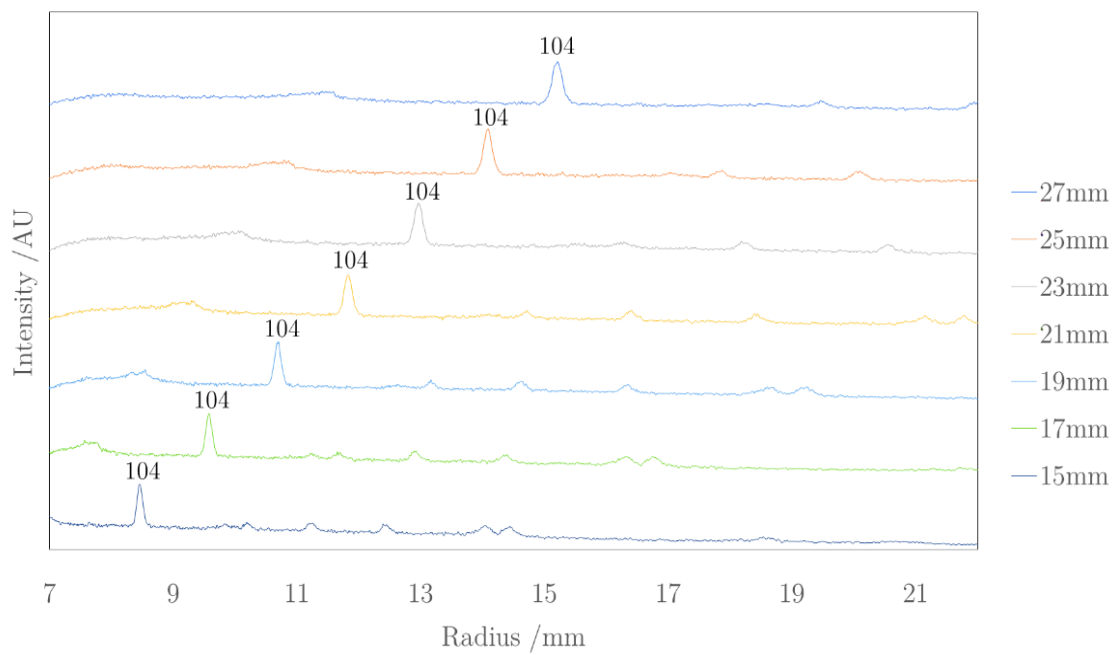


Figure 7.3 Radial plots obtained when translating a sample of CaCO_3 along the primary axis in increments of 2 mm. Distances shown correspond to sample to detector distance, D_{SD} .

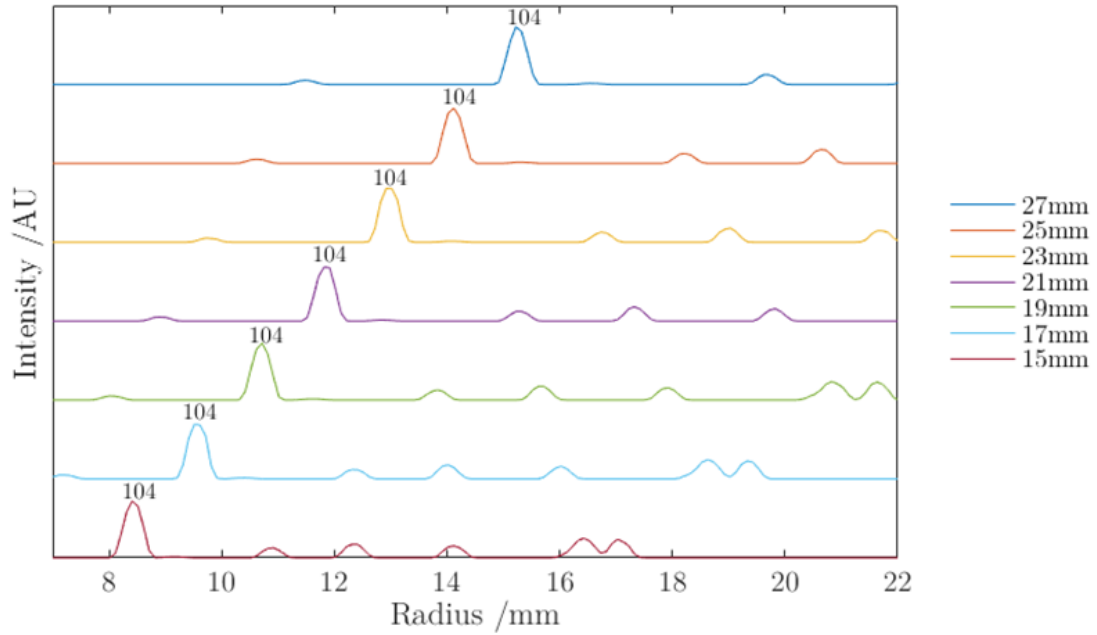


Figure 7.4 Radial plots from simulated ADXRD images of a CaCO_3 sample translated along the primary axis in 2 mm increments. Distances shown correspond to sample to detector distance, D_{SD} .

Radial measurements were taken from the 104 reflection, labelled in both **Error! Reference source not found.** and Figure 7.4, and listed in **Error! Reference source not found.**

Comparing the calculated d -spacing values from all detector positions with the CaCO_3 reference data shows a strong agreement at all sample-to-detector distances. This demonstrates that *McXtrace* not only models the physical processes well, but it also considers the overall geometry of the experimental set up with high accuracy.

7.1.3 Sample thickness

The thickness of a sample influences the amount of scatter in the resulting diffraction pattern. Taking a very thin sample of any material results in either photons passing straight through the sample without scattering or a small proportion of photons being scattered. As the thickness of the sample increases, the number of scattered photons is initially expected to increase due to a greater

electron density for the photons to interact with. There is a point where the sample becomes overly thick and absorption effects dominate.

Table 7.2 Measured radial distances from both the experimental and simulated data of a CaCO_3 sample translated along the primary axis.

D_{SD} /mm	Experimental			Simulated		
	Measured r /mm	Calculated $2\theta/^\circ$	Calculated d -spacing /Å	Measured r /mm	Calculated $2\theta/^\circ$	Calculated d -spacing /Å
15	8.42	29.3	3.04	8.45	29.4	3.04
17	9.56	29.4	3.04	9.58	29.4	3.04
19	10.68	29.3	3.04	10.71	29.4	3.04
21	11.82	29.4	3.04	11.83	29.4	3.04
23	12.92	29.3	3.04	12.96	29.4	3.04
25	14.06	29.4	3.04	14.09	29.4	3.04
27	15.21	29.4	3.04	15.21	29.4	3.04

Multiple sheets of 0.016 mm Al were used to model increasing thickness up to 0.128 mm (8 sheets in total). An example of the diffraction pattern obtained from the sheet of 0.016 mm Al using the Bruker D8-GADDS diffractometer, employed in 7.1.1 and 7.1.2, is shown in Figure 7.5. The image shows a high level of preferred orientation, identifiable by the inconsistent intensity around the Debye ring.

Analytical data obtained from the NIST database^{§§} in addition with simulated data, obtained at increments of 0.016 mm from 0.016 mm to 0.8 mm, were overlaid with experimental results, Figure 7.6. All three techniques resulted in maximum intensity being produced from Al of thickness ~0.065 mm.

^{§§} <http://physics.nist.gov/PhysRefData/FFast/html/form.html>

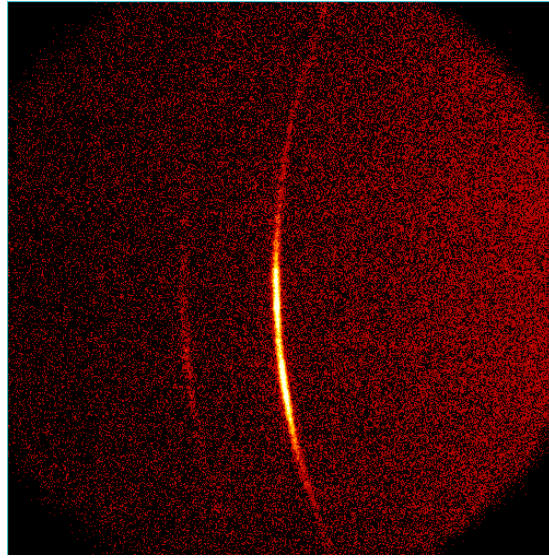


Figure 7.5 Diffraction pattern obtained from the Bruker D8-GADDS when observing a 0.016 mm sheet of aluminium foil.

This result demonstrates that *McXtrace* can successfully consider the thickness of the material, to identify the thickness at which absorption effects dominate over having a greater number over photons to interact with. This can be useful when determining the feasibility of X-ray diffraction to analyse the contents of metal containers as *McXtrace* will consider the absorption effects associated with the container.

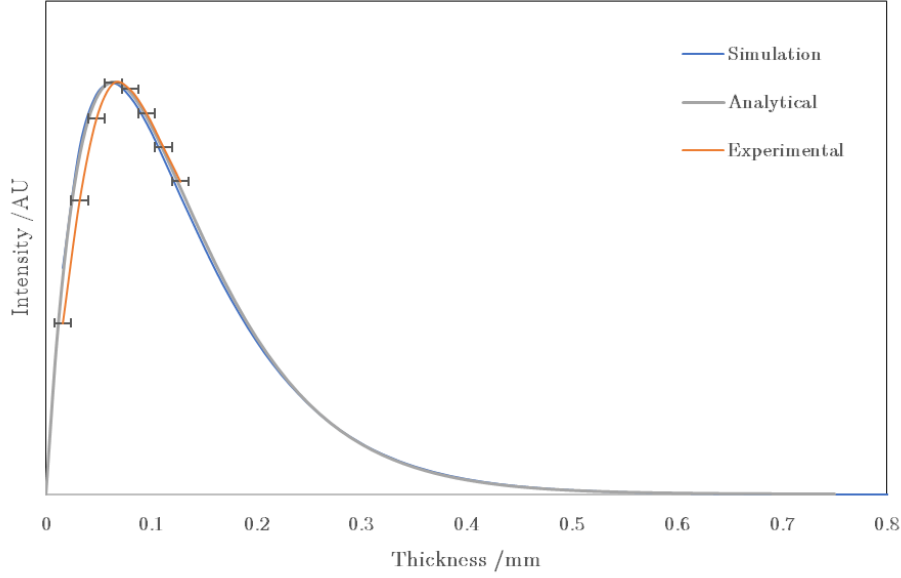


Figure 7.6 Normalized analytical, simulated and experimental data of total coherent scattering intensity resulting from samples of Al with increasing thickness.

7.1.4 Increasing the source energy

Each photon incident on the sample has energy, E (keV), proportional to the wavelength, λ (nm), of the X-ray source, demonstrated by the relationship shown below where h is Planck's constant ($\approx 6.6260 \times 10^{-34}$ Js) and c is the velocity of light in a vacuum ($\approx 2.998 \times 10^8$ ms $^{-1}$).

$$E = \frac{hc}{\lambda} = \frac{hc}{2d \sin \theta} \quad (7.2)$$

Equation (7.2) demonstrates that as the energy of the source increases the coherent diffraction angle, 2θ , decreases. A simulation was performed to observe this effect and test the response of *McXtrace* to energy variations.

The simulation was conducted with 0.1 mm thick CaCO_3 placed 30 mm away from a 100 x 100 mm angular dispersive detector along the primary axis. The energy of the source was varied from 10 keV to 50 keV in increments of 10 keV. Figure 7.7 shows the resulting diffraction patterns. Corresponding diffraction profiles, calculated by azimuthal integration of the respective image, are shown in Figure 7.8.

The intensity of the resulting diffraction pattern decreased as the energy was increased (shown in Figure 7.8). This is due to the proportion of coherently scattering radiation decreasing. A higher proportion of the incident photons will be transmitted through the sample at higher energies.

The highest intensity d -spacing, reflection 104, was considered to compare the simulated results to analytical calculation of diffraction angle θ at each energy. Analytically, θ was calculated by using Equation (7.2) with $d=3.035$ Å and the corresponding energy. The radius of the 104 reflection was measured using data from Figure 7.8 and utilised to calculate the simulated diffraction angle when $D_{SD} = 30$ mm, using $\tan 2\theta = r/D_{SD}$. There is high agreement between the simulated and the analytically calculated diffraction angles, as shown in Table 7.3, demonstrating that *McXtrace* is consistent with analytical values, fulfilling the requirement to be a viable simulation package to extend the conducted experiments into higher energy. The errors shown arose from the finite pixel size of the simulated CCD detector.

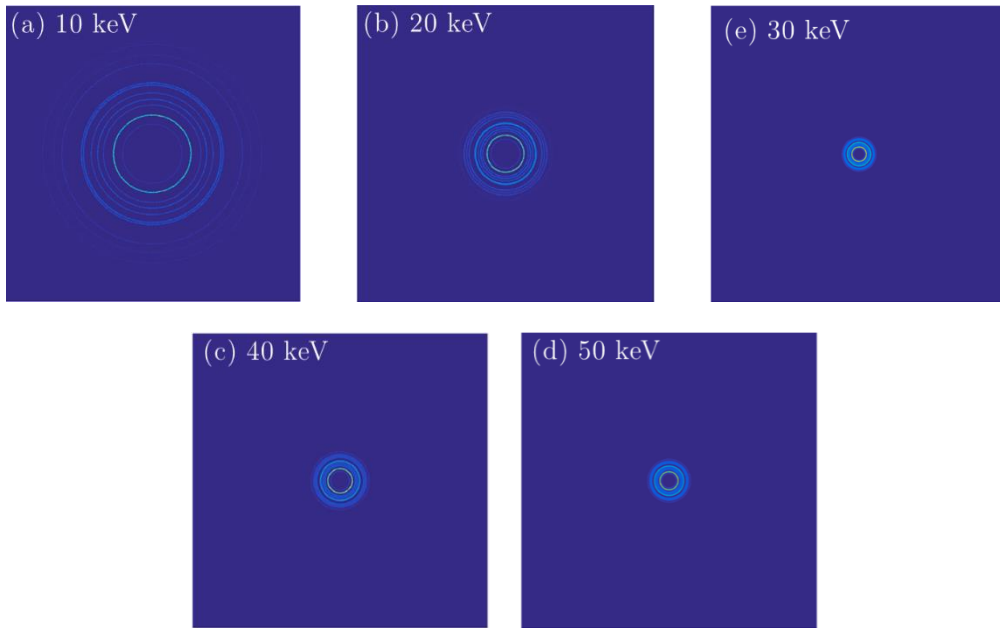


Figure 7.7 Simulated angular dispersive diffraction patterns from 0.1 mm sample of CaCO_3 . Each image represents a 100 mm x 100 mm CCD array.

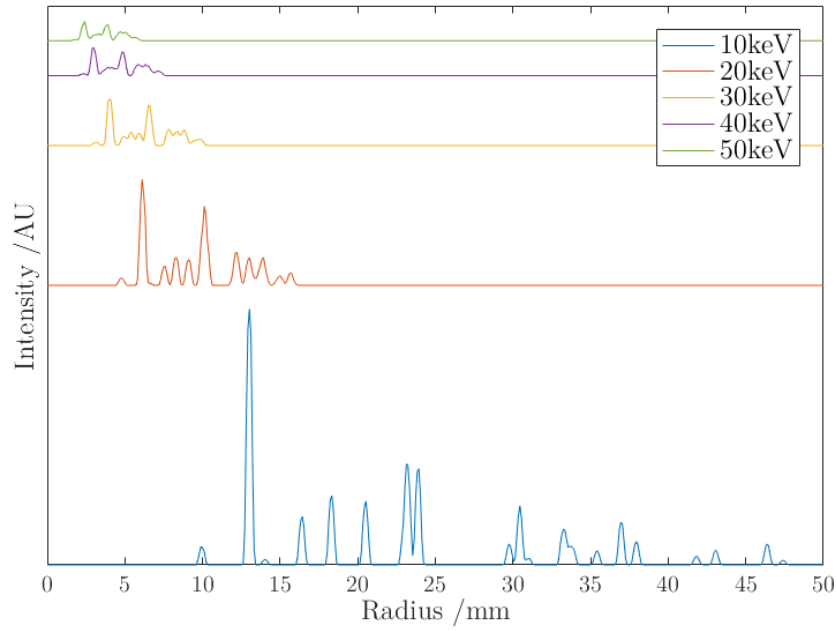


Figure 7.8 Intensity plots resulting from the azimuthal integration of diffraction patterns of CaCO_3 shown in Figure 7.7.

Table 7.3 Analytically calculated values of θ from CaCO_3 104 reflection ($d=3.035 \text{ \AA}$) and the values of θ from simulation of CaCO_3 .

Energy /keV	D_{SD} /mm	Calculated θ /°	Measured r /mm	Measured θ /°
10	30	11.79	13.02	11.73 ± 0.08
20	30	5.86	6.11	5.70 ± 0.10
30	30	3.90	4.01	3.80 ± 0.10
40	30	2.93	3.01	2.80 ± 0.09
50	30	2.34	2.40	2.20 ± 0.10

7.2 Interpretation of scatter: depth perception

As discussed in §6.4.2, in conventional ADXRD knowledge of the origin of scatter is crucial in determination of the diffraction angle and therefore identification of a sample. There are three techniques utilised within this research to aid the interpretation of scatter to ultimately determine the scattering angle and thus identify an unknown sample placed within a given volume; the results of all three

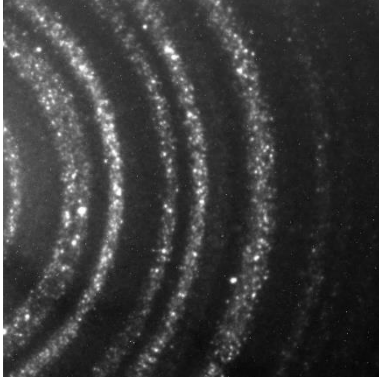
techniques; analytical, encoders and algorithmic, are presented here before being evaluated by consideration of their accuracy and reliability.

7.2.1 Analytical

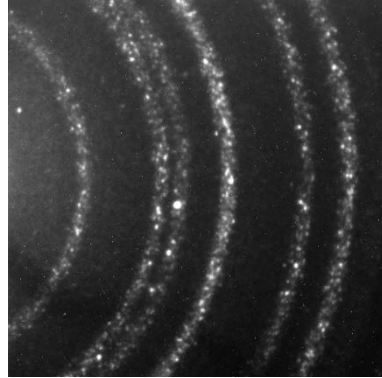
The analytical technique is based on acquiring a minimum of two diffraction patterns when the sample-to-detector distance, D_{SD} , is altered by a known amount, ΔD_{SD} . Here, a sample of 1.53 mm Al_2O_3 is placed an unknown distance from the source and both the location and the identity of the material are recovered independently. This technique is described in more detail in §6.4.2.1.

The Zr-filtered Mo source was set up in pencil beam geometry, using the $a_c=0.25$ mm radius collimator, with the 1.53 mm Al_2O_3 sample in conjunction with the PIXIS detector. The detector was translated 10 mm, initially placed at $D_{SD_1} = 20$ mm from the sample.

(a)



(b)



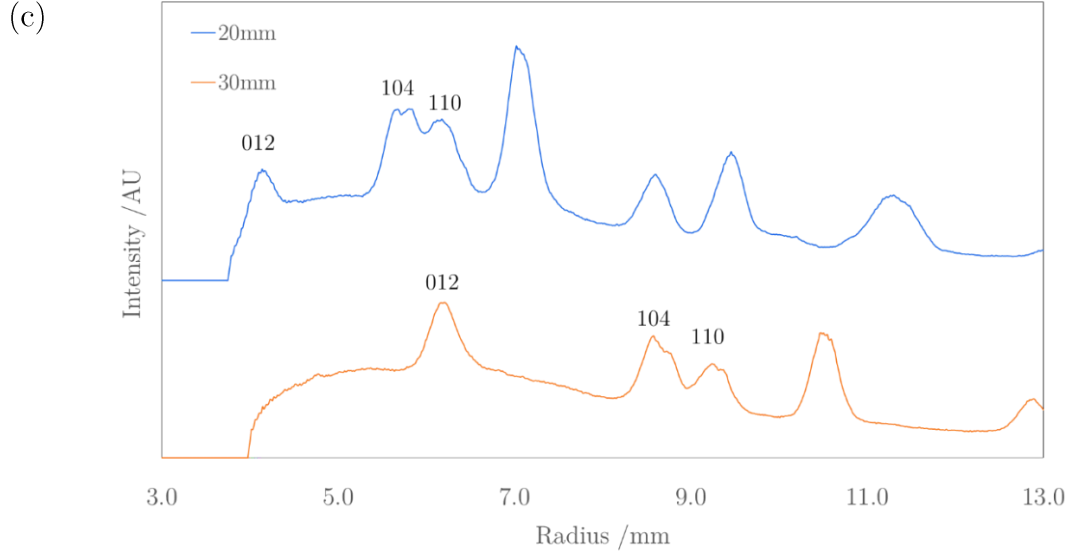


Figure 7.9 Diffraction patterns from PIXIS detector resulting from Mo Zr-filtered source incident on a sample of 1.53 mm Al_2O_3 (a) $D_{SD}=20$ mm (b) $D_{SD}=30$ mm (c) Diffraction profiles of (a) and (b).

The ADXRD images attained by the PIXIS detector can be seen in Figure 7.9(a) $D_{SD_1} = 20$ mm and (b) $D_{SD_2} = 30$ mm with their corresponding diffraction profiles, Figure 7.9(c), computed by performing azimuthal integration on the ADXRD image. *McXtrace*, with the same geometry, computed the ADXRD images in Figure 7.10(a) and (b) with the corresponding diffraction profiles in Figure 7.10(c).

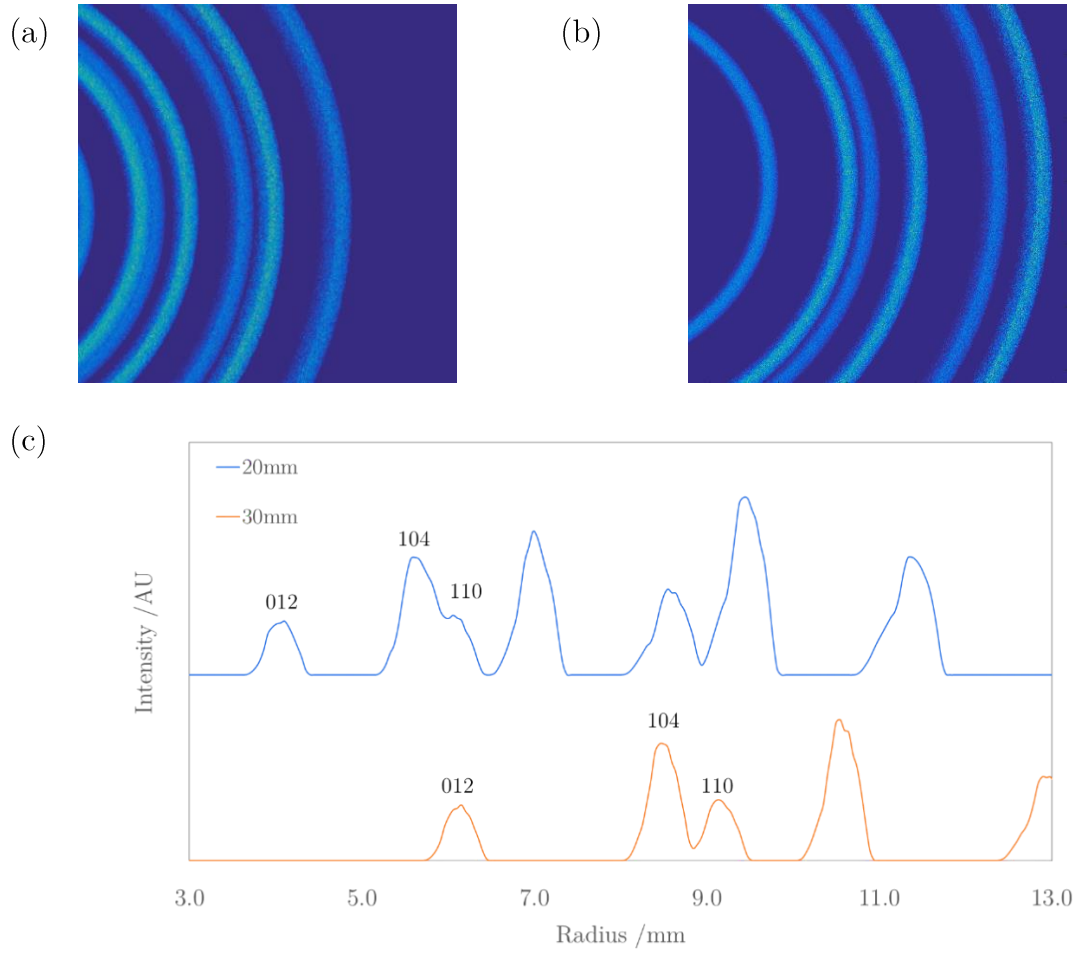


Figure 7.10 *McXtrace* simulated diffraction patterns of 1.53 mm Al_2O_3 from Mo Zr-filtered source when detector is positioned (a) $D_{SD_1}=20$ mm (b) $D_{SD_2}=30$ mm away from the sample. (c) diffraction profiles of (a) and (b).

The variable smoothness of the Debye cones between the experimental and simulated ADXRD images is due to the difference in grain size. An ideal sample would have a small grain size (or crystallite size) thus the Debye cones appear as smooth, continuous rings. If grain size is large, Debye cones become discontinuous or speckled, as with the experimental images, also demonstrated in Figure 3.4, §3.2.1. For very coarse grain size, only a small number of crystals will diffract resulting in a diffraction pattern consisting of only a few scattering maxima spots (Laue spots), similar to a single crystal.

Table 7.4 Calculated D_{SD_1} and 2θ values from experimental Al_2O_3 results when $\Delta D_{SD}=10$ mm.

Reflection	Known d -spacing /Å	Measured r /mm		Calculated D_{SD_1} /mm	Calculated $2\theta/^\circ$	Calculated d -spacing /Å
		r_1	r_2			
012	3.48	4.14	6.20	20.1 ± 1.01	11.6 ± 0.57	3.5 ± 0.37
104	2.55	5.70	8.59	19.7 ± 0.99	16.1 ± 0.77	2.5 ± 0.17
110	2.38	6.15	9.21	20.1 ± 1.01	17.0 ± 0.80	2.4 ± 0.16

The radial values for the first three reflections (012, 104, 110), labelled in Figure 7.9 (c) and Figure 7.10 (c) are measured and converted into respective D_{SD_1} and d -spacing values using Equations (6.1), (6.2) and Bragg's Law. The experimental results are shown in Table 7.4 and the results from the simulation are shown in Table 7.5.

Experimental errors were calculated via error propagation using the equations below with standard deviations $\sigma_{\Delta D_{SD}} = 0.5$ mm and $\sigma_{r_1} = \sigma_{r_2} = 6.5$ μm determined from the precision in which the variable could be measured, i.e. pixel size.

$$\begin{aligned}
\sigma_{D_{SD_1}}^2 &= \left[\frac{\partial D_{SD_1}}{\partial \Delta D_{SD}} \right]^2 \sigma_{D_{SD}}^2 + \left[\frac{\partial D_{SD_1}}{\partial r_1} \right]^2 \sigma_{r_1}^2 + \left[\frac{\partial D_{SD_1}}{\partial r_2} \right]^2 \sigma_{r_2}^2 \\
\sigma_{D_{SD_1}}^2 &= \left[\frac{r_1}{r_2 - r_1} \right]^2 \sigma_{D_{SD}}^2 + \left[\frac{r_2 \Delta D_{SD}}{r_2 - r_1} \right]^2 \sigma_{r_1}^2 + \left[-\frac{r_1 \Delta D_{SD}}{r_2 - r_1} \right]^2 \sigma_{r_2}^2 \\
\sigma_{2\theta}^2 &= \left[\frac{\partial 2\theta}{\partial \Delta D_{SD}} \right]^2 \sigma_{D_{SD}}^2 + \left[\frac{\partial 2\theta}{\partial r_1} \right]^2 \sigma_{r_1}^2 + \left[\frac{\partial 2\theta}{\partial r_2} \right]^2 \sigma_{r_2}^2 \\
\sigma_{2\theta}^2 &= \left[\frac{r_2 - r_1}{\Delta D_{SD}^2 + r_2 - r_1} \right]^2 \sigma_{D_{SD}}^2 + \left[-\frac{\Delta D_{SD}}{\Delta D_{SD}^2 + r_2 - r_1} \right]^2 \sigma_{r_1}^2 \\
&\quad + \left[\frac{\Delta D_{SD}}{\Delta D_{SD}^2 + r_2 - r_1} \right]^2 \sigma_{r_2}^2
\end{aligned}$$

Table 7.5 Calculated D_{SD_1} and 2θ values from simulated Al_2O_3 results when $\Delta D_{SD}=10$ mm.

Reflection	Defined d -spacing /Å	Measured r /mm		Calculated D_{SD_1} /mm	Calculated $2\theta/^\circ$	Calculated d -spacing /Å
		r_1	r_2			
012	3.48	4.14	6.21	20.0±0.13	11.7±0.05	3.5±0.02
104	2.55	5.73	8.58	20.0±0.10	15.9±0.05	2.6±0.01
110	2.38	6.16	9.24	20.0±0.09	17.1±0.05	2.4±0.01

$$\sigma_d^2 = \left[\frac{\partial d}{\partial \lambda} \right]^2 \sigma_\lambda^2 + \left[\frac{\partial d}{\partial \theta} \right]^2 \sigma_\theta^2$$

$$\sigma_d^2 = \left[\frac{\csc \theta}{2} \right]^2 \sigma_\lambda^2 + \left[-\frac{1}{2} \cot \theta \csc \theta \right]^2 \sigma_\theta^2$$

Errors were also calculated for the simulated results using error propagation as above with $\sigma_{\Delta D_{SD}} = 0.5 \times 10^{-15}$ mm and $\sigma_{r_1} = \sigma_{r_2} = 6.5 \mu\text{m}$. As the error from the measurement ΔD_{SD} is negligible in the simulated result, the significant error was from the radial integral performed manually. This error can be reduced by simulating a detector with smaller pixel size but here the simulation was modelled on the experimental detector.

7.2.2 Encoders

The encoder technique introduces two post-sample reference structures; a linear encoder and an Archimedean spiral described in detail in §6.4.2.2. The encoders were employed for recovery of sample position and material phase identification without the need for moving components. Simulations were conducted prior to experimentation to optimise positions of the components.

7.2.2.1 Linear Encoder

A linear wire was used as a post-sample encoder, the distinctive feature of which is its off-centre location, giving rise to unique polar angles with respect to the radius of the Debye cone. The geometry of the linear encoder is discussed in more detail in §6.4.2.2.

A 0.05 mm CaCO_3 sample was placed along the path of the primary beam at a known distance, D_{SD} , from the detector. The obtained scattering data was used to calibrate the system to identify encoder parameters such as the encoder-to-detector distance, $D_{LE:D}$, and the encoder's offset distance, α_{LE} , along the x -axis relative to the primary beam. These parameters are illustrated in Figure 6.8, §6.4.2.2.

A simple simulation was set up using a 0.05 mm thick CaCO_3 sheet, as with the calibration. The sample was traversed along the primary axis from $D_S = 1$ mm to $D_S = 10$ mm, in 2.25 mm increments, with a linear encoder placed after the sample, fixed in position at $D_{S:LE} = 25$ mm from the source and $\alpha_{LE} = 3$ mm. The detector was placed at $D = 50$ mm from the source and modelled on the low energy Cu, Bruker D8-GADDS system.

To demonstrate the technique a series of images obtained from a simulation are displayed in Figure 7.11. An overlay indicating the centre of the diffraction pattern and the angle used to determine the position and diffraction angle, 2θ , of the sample, specified by the intersection of the highest intensity maxima by the linear encoder is shown. The angle formed between the overlaid arrow and the horizontal x -axis can be seen to wane as the sample is moved further along the z -axis, towards the detector. This is the unique polar angle used to recover the location and phase of the sample.

A multiple sample experiment was conducted to demonstrate the capabilities of the technique to distinguish multiple samples with the low energy Cu source and D8-GADDS. A second 0.05 mm sample of CaCO_3 was placed along the z -axis, 32 mm away from the first sample, Figure 7.12. The sample thickness was chosen to allow sufficient transmission to observe diffraction from multiple samples simultaneously. The linear encoder was placed $D_{LE:D} = 39$ mm from the detector and offset by $\alpha_{LE} = 6$ mm.

A single image, acquired over 60 s, obtained from the multiple sampling experiment is shown within **Error! Reference source not found.**(a) alongside a simulated image, **Error! Reference source not found.**(c). As can be seen from the images, the scattering distribution contains diffraction patterns from both samples with the intersections from the linear encoder clearly visible as vertical shadows in the Debye

rings. Each shadow, one for each sample, corresponds to a different sample-to-detector distances, D_{SD} , indicating multiple samples.

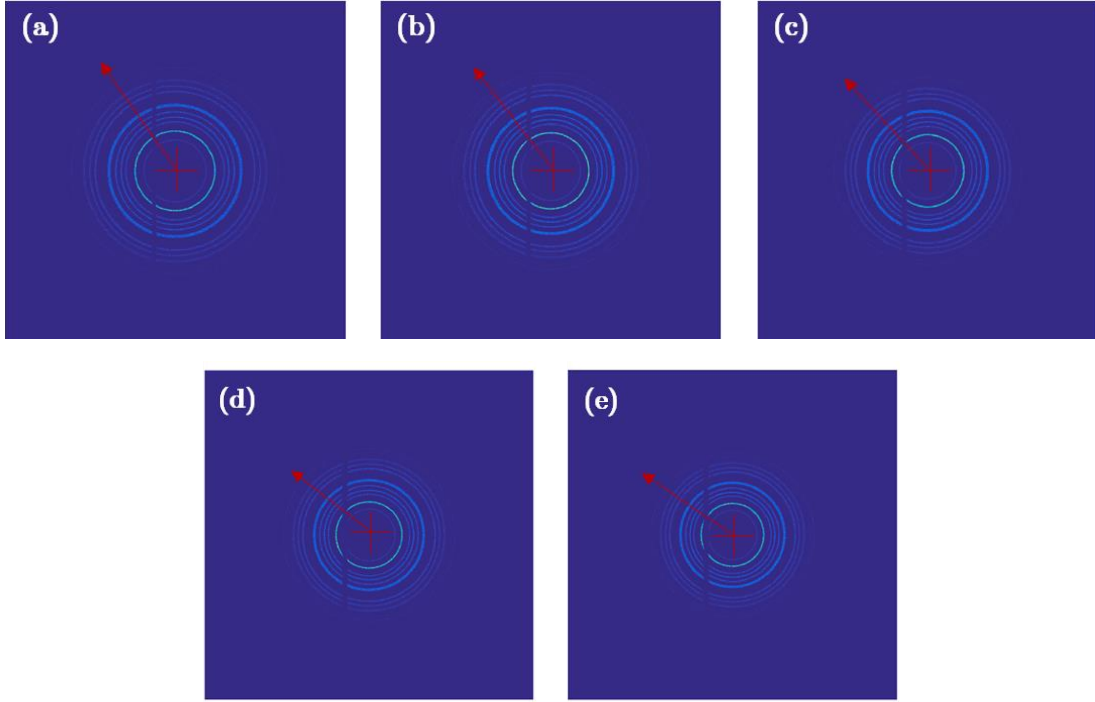


Figure 7.11 Resultant diffraction patterns from a sample of 0.05 mm CaCO_3 with linear encoder placed at $D_{LE:D} = 25$ mm, $\alpha_{LE} = 3$ mm when sample is placed at (a) $D_S = 1$ mm (b) $D_S = 3.25$ mm (c) $D_S = 5.5$ mm (d) $D_S = 7.75$ mm (e) $D_S = 10$ mm from the source. The detector was placed at $D = 50$ mm from the source.

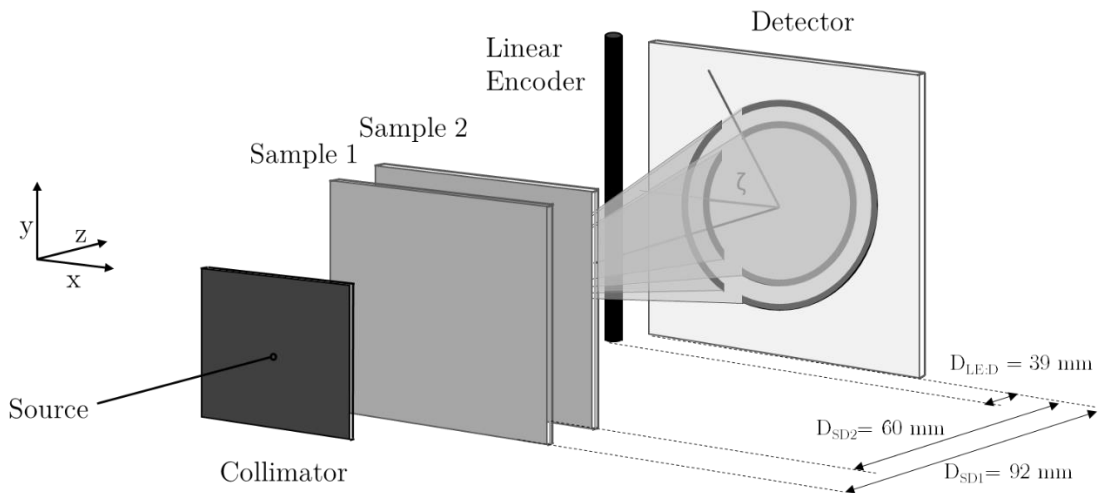


Figure 7.12 Schematic of set up (b) for linear encoder experimental work with two samples of

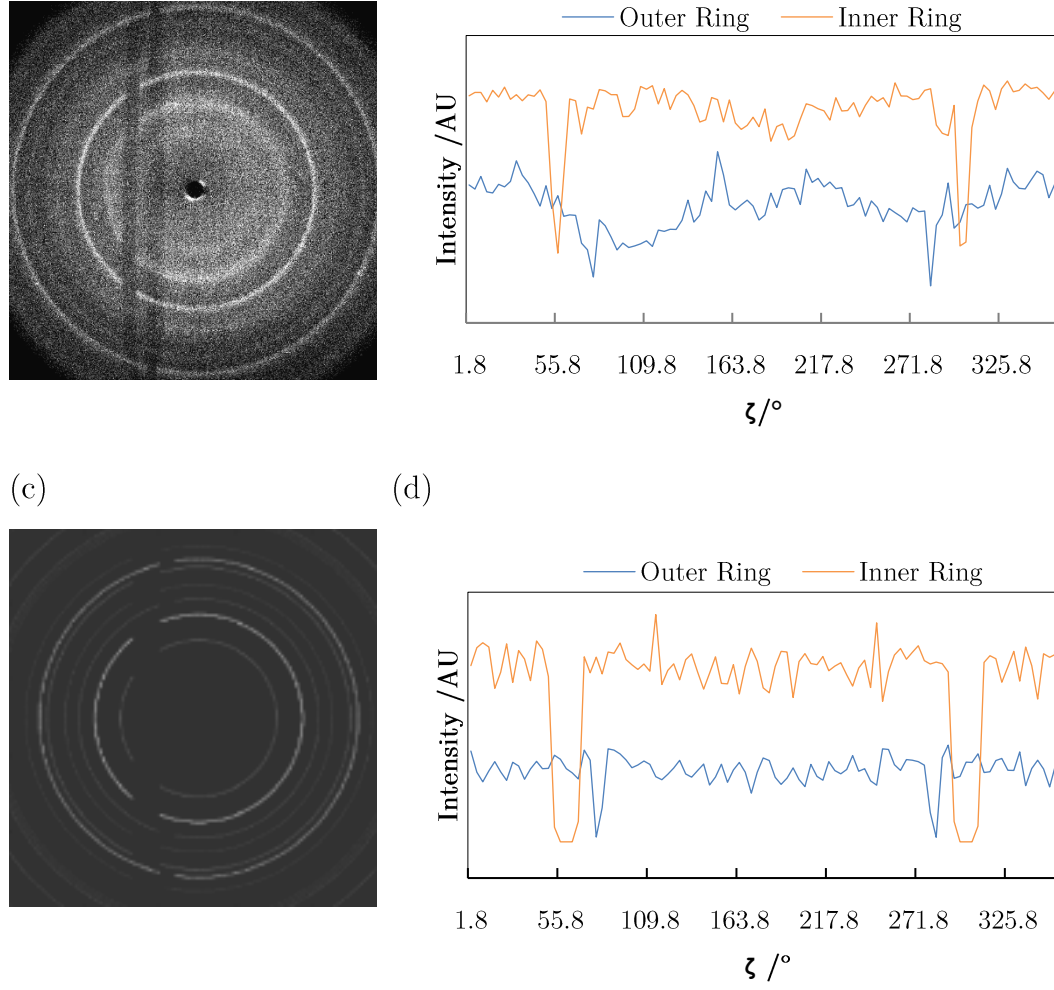


Figure 7.13 (a) Experimental diffraction pattern obtained with an off-centre linear encoder ($\alpha_{LE} = 6$ mm, $D_{LE:D} = 39$ mm) with two 0.05 mm thick CaCO_3 samples separated by 32 mm along the primary axis. (b) Azimuthal plots of experimental data in (a) allowing quantification of the intersection angle for each high intensity Debye ring. (c) Simulated diffraction pattern of geometry described in (a). (d) Azimuthal plots of simulated diffraction pattern, (c).

By analysing the Debye ring with the highest intensity from each sample, reflection 104, the encoded intersection angle, ζ , can be measured by radially integrating to form azimuthal plots, **Error! Reference source not found.**(b) and (d).

Using the measured simulated and experimental data and employing Equations (6.7) and (6.9) with Bragg's Law, the sample position relative to the detector (D_{SD}) and the d -spacing of the 104 CaCO_3 reflection can be recovered, Table 7.6.

Table 7.6 Calculated values of sample-to-detector distance, D_{SD} , and d -spacing from using the linear encoder. CaCO_3 Samples 1 and 2 were placed at 92 mm and 60 mm respectively from the detector. The corresponding d -spacing for CaCO_3 is 3.035 Å, (PDF 5-586, Appendix A).

Image	Sample	r /mm	ζ /°	Calculated D_{SD} /mm	Calculated 2θ /°	Calculated d -spacing /Å
Experimental	1	53.9	79.3	92.4 ± 3.67	30.3 ± 2.10	2.95 ± 0.20
	2	33.9	62.7	60.3 ± 1.76	29.4 ± 0.92	3.04 ± 0.09
Simulation	1	51.9	78.9	92.0 ± 1.39	29.3 ± 2.06	3.05 ± 0.20
	2	34.0	62.7	60.0 ± 0.02	29.4 ± 0.59	3.03 ± 0.06

Comparing the values calculated in Table 7.6 to the true values of Sample 1 placed at $D_{SD} = 92$ mm and Sample 2 at $D_{SD} = 60$ mm relative to the detector, indicates good agreement between the two. Additionally, the d -spacing of reflection 104, 3.035 Å, is within experimental errors determined by error propagation, explained below. This demonstrates that the linear encoder is a viable post-sample encoder to recover both spatial and phase information from an unknown sample. Experimental errors arose from measurement of $D_{LE:D}$, α_{LE} , r and ζ whereas in the simulation errors only arose from measurement of r and ζ accounting for the difference in magnitude. When conducting the error analysis for evaluation of the optimum encoder position the errors were treated experimentally.

As with the single sample, a series of simulated images demonstrating the movement of the intersection of the Debye cone was produced for the multiple sample experiment, Figure 7.14. Sample 1 was fixed in place at $D_{SD} = 92$ mm from the detector whilst Sample 2 moved along the primary axis towards the detector in 5 mm increments, with the linear encoder placed $D_{LE:D} = 39$ mm from the detector, Figure 7.12. These and others similar, with the position of the linear encoder varied along both the z -axis ($D_{LE:D}$) and the x -axis (α_{LE}), were used to consider the errors involved in the placement of the encoder.

The offset distance, α_{LE} , and the linear encoder-to-detector distance $D_{LE:D}$ were systematically altered via simulation and a diffraction pattern obtained at each

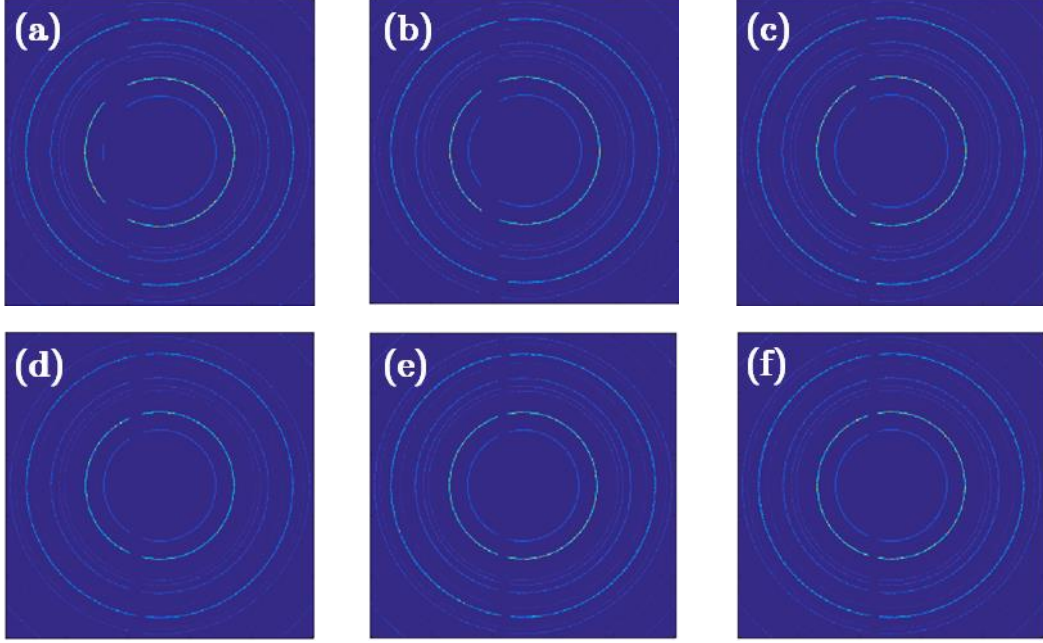


Figure 7.14 Simulated diffraction patterns of two spatially separated samples of CaCO_3 with a linear wire encoder placed in front of the detector, $D_{LE:D}=39$ mm at $\alpha_{LE}=6$ mm. Sample 1 was fixed at a distance $D_{SD} = 92$ mm from the detector, the Sample 2 placed at (a) $D_{SD} = 40$ mm (b) $D_{SD} = 45$ mm (c) $D_{SD} = 50$ mm (d) $D_{SD} = 55$ mm (e) $D_{SD} = 60$ mm and (f) $D_{SD} = 65$ mm from the detector.

position. The same simulation above was employed using the 104 reflection from the sample closest to the detector (Sample 2), to calculate the sample position and the diffraction angle.

Similar to the analytical method, the uncertainties associated with the position of each of the components were calculated using error propagation to determine the optimal geometry to gain the most accurate values for both D_{SD} and 2θ .

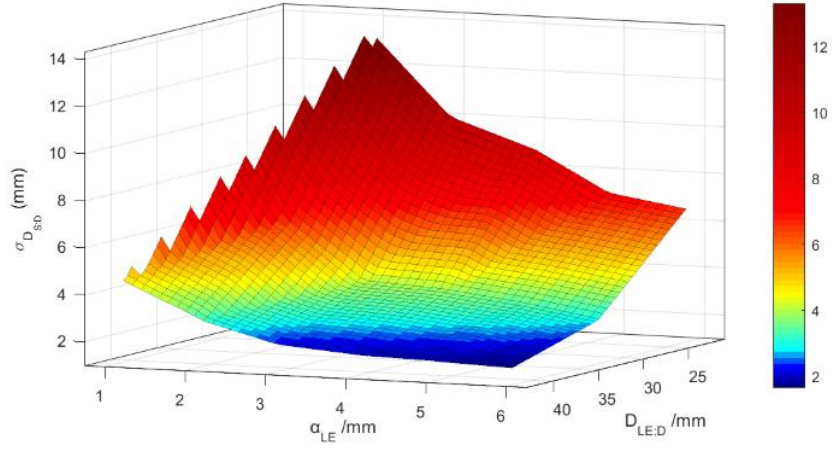
The errors associated with each variable when analysing the sample-to-detector distance, D_{SD} (Equation (6.7)), and the diffraction angle, 2θ (Equation (6.9)), can be calculated via Equations (7.3) and (7.4), respectively. Standard deviation errors

used were $\sigma_{D_{LE:D}} = \pm 1$ mm, $\sigma_{\alpha_{LE}} = \pm 0.1$ mm, $\sigma_{\zeta} = \pm 3^\circ$ and $\sigma_r = \pm 0.5$ mm. The results are shown in 3D surface plots, Figure 7.15.

$$\begin{aligned}
\sigma_{D_{SD}}^2 &= \left[\frac{\partial D_{SD}}{\partial D_{LE:D}} \right]^2 \sigma_{D_{LE:D}}^2 + \left[\frac{\partial D_{SD}}{\partial \alpha_{LE}} \right]^2 \sigma_{\alpha_{LE}}^2 + \left[\frac{\partial D_{SD}}{\partial \zeta} \right]^2 \sigma_{\zeta}^2 + \left[\frac{\partial D_{SD}}{\partial r} \right]^2 \sigma_r^2 \\
&= \left[\frac{r}{r - \alpha_{LE} \sec \zeta} \right]^2 \sigma_{D_{LE:D}}^2 + \left[\frac{r D_{LE:D} \sec \zeta}{r - \alpha_{LE} \sec \zeta} \right]^2 \sigma_{\alpha_{LE}}^2 \\
&\quad + \left[\frac{\alpha_{LE}^2 D_{LE:D} \tan \zeta \sec^2 \zeta}{r - \alpha_{LE} \sec \zeta} + \frac{\alpha_{LE} D_{LE:D} \tan \zeta \sec \zeta}{r - \alpha_{LE} \sec \zeta} \right]^2 \sigma_{\zeta}^2 \\
&\quad + \left[\frac{-\alpha_{LE} D_{LE:D}}{\alpha_D - \alpha_{LE}} \right]^2 \sigma_r^2
\end{aligned} \tag{7.3}$$

$$\begin{aligned}
\sigma_{2\theta}^2 &= \left[\frac{\partial 2\theta}{\partial r} \right]^2 \sigma_r^2 + \left[\frac{\partial 2\theta}{\partial \alpha_{LE}} \right]^2 \sigma_{\alpha_{LE}}^2 + \left[\frac{\partial 2\theta}{\partial \zeta} \right]^2 \sigma_{\zeta}^2 + \left[\frac{\partial 2\theta}{\partial D_{LE:D}} \right]^2 \sigma_{D_{LE:D}}^2 \\
&= \left[\frac{1}{D_{LE:D} \left(\frac{\left(r - \frac{\alpha_{LE}}{\cos \zeta} \right)^2}{D_{LE:D}^2} + 1 \right)} \right]^2 \sigma_r^2 \\
&+ \left[- \frac{1}{D_{LE:D} \cos \zeta \left(\frac{\left(r - \frac{\alpha_{LE}}{\cos \zeta} \right)^2}{D_{LE:D}^2} + 1 \right)} \right]^2 \sigma_{\alpha_{LE}}^2 \\
&+ \left[- \frac{\alpha_{LE} \tan \zeta}{D_{LE:D} \cos \zeta \left(\frac{\left(r - \frac{\alpha_{LE}}{\cos \zeta} \right)^2}{D_{LE:D}^2} + 1 \right)} \right]^2 \sigma_{\zeta}^2 \\
&+ \left[- \frac{r - \frac{\alpha_{LE}}{\cos \zeta}}{D_{LE:D}^2 \left(\frac{\left(r - \frac{\alpha_{LE}}{\cos \zeta} \right)^2}{D_{LE:D}^2} + 1 \right)} \right]^2 \sigma_{D_{LE:D}}^2
\end{aligned} \tag{7.4}$$

(a)



(b)

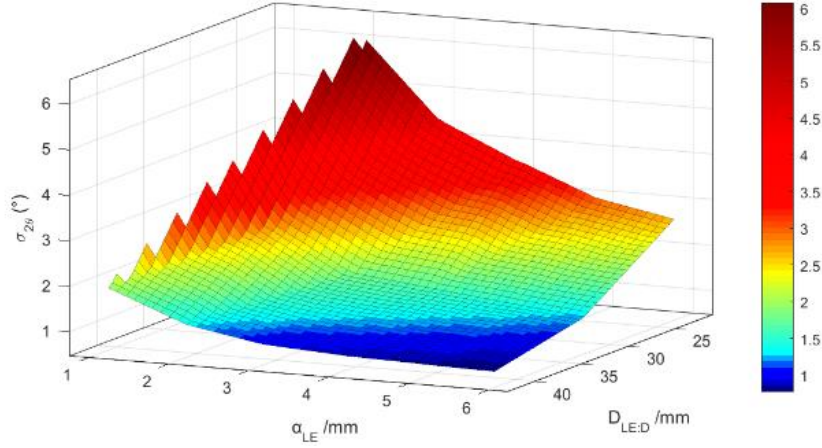


Figure 7.15 (a) 3D surface plot of the error associated with calculating the sample-to-detector distance (D_{SD}) and (b) 3D surface plot of error associated with measuring the diffraction angle (2θ) calculated using the 104 reflection from the sample closest to the detector (Sample 2) when using a linear encoder.

The greatest variation when calculating the D_{SD} distance arose from the encoder-to-detector distance, $D_{LE:D}$ whereas when calculating the diffraction angle, the highest contributing factor was the measured radius, r , in the detector plane.

The surface plots, Figure 7.15, demonstrate that the optimal position of the linear encoder for reducing the errors when calculating the sample-to-detector distance (D_{SD}) occurs when the offset position of the encoder is greatest (i.e. α_{LE} is large) and the encoder is placed close to the sample, i.e. large encoder-to-detector distance,

$D_{LE:D}$. The offset distance on the linear encoder at any point along the z -axis is limited by the size of the Debye cone, as it still must intersect the cone in order to encode. The same trend can be seen when evaluating Figure 7.15(b) when analysing the error associated with calculating the diffraction angle.

In summary, associated errors when calculating the sample position and diffraction angle are minimised when the offset distance and encoder-to-detector distance are maximised, limited by the radius of the Debye cone.

7.2.2.2 Spiral Encoder

The spiral encoder with $r_{AS} = 0.055\psi$, described in §6.4.2.2, was assessed in the same way as the linear encoder above with two samples of 0.05 mm thick CaCO_3 spatially separated along the z -axis, with one fixed in place at $D_{SD_2} = 63$ mm (Sample 2) and the other (Sample 1) translated in increments of 2 mm between $D_{SD_1} = 69$ mm to $D_{SD_1} = 83$ mm. The spiral encoder was placed at $D_{AS:D} = 54$ mm from the detector, illustrated in Figure 7.16.

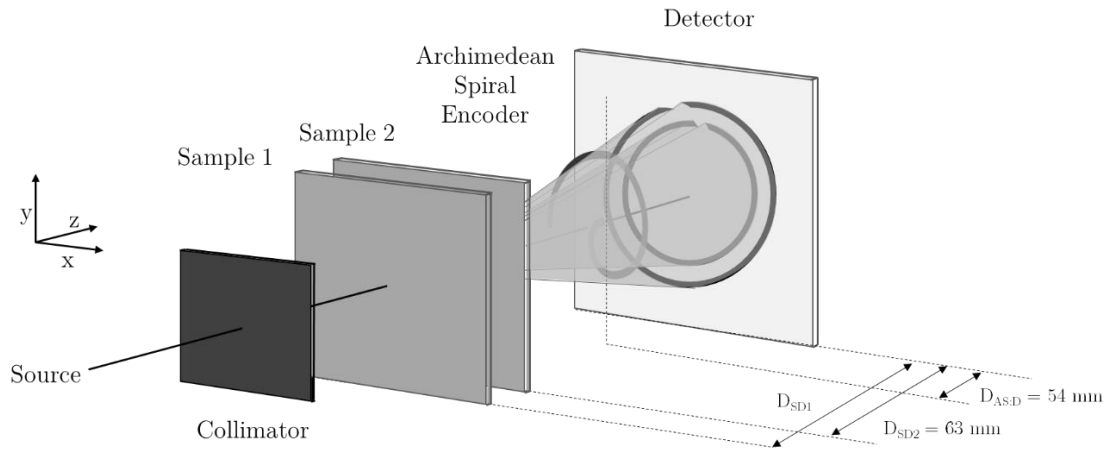


Figure 7.16 Schematic of set up used for spiral encoder experimental work with two samples of CaCO_3 spatially separated.

At each increment, a diffraction pattern was obtained. The corresponding simulated diffraction patterns are shown alongside the respective experimental diffraction

patterns in Figure 7.17. When observing just the 104 scattering maxima, the encoding region (the intersection) can be seen to rotate simultaneously with a decrease in the associated Debye ring radius. Data obtained from the translated CaCO_3 sample (Sample 1) is in Table 7.7.

As with the linear encoder, the radii of the Debye rings and their corresponding encoding angle, ζ , were measured by attaining azimuthal plots by radial integration.

Prior to the calculation of the diffraction angle and sample to detector distance, as in Table 7.7, the system was calibrated. The linear relationship predicted by Equation (6.10), $r_{AS} = a_{AS} + b_{AS}\psi$, was substituted for the polynomial relationship, $r_{AS} = 0.00009\psi^2 + 0.0166\psi + 1.324$, determined using known parameters for the location and phase of a sample of CaCO_3 , Appendix C. The simulation was set up with $r_{AS} = 0.055\psi$. The radii and measured encoding angles of reflection 104, as with the linear encoder, were then used to calculate the sample-to-detector distance via Equation (6.11) and diffraction angle via Equation (6.12) at each increment with the calibrated r_{AS} .

The errors associated with each variable when analysing the sample-to-detector distance, D_{SD_1} (Equation (6.11)), and the diffraction angle, 2θ (Equation (8.4)), can be calculated via Equations (7.5) and (7.6), respectively. Standard deviation errors used were $\sigma_{D_{AS:D}} = \pm 1$ mm, $\sigma_\psi = \pm 3^\circ$ and $\sigma_r = \pm 0.5$ mm, $\sigma_a = \pm 0.1$ mm, $\sigma_b = \pm 0.3$ mm determined by the possible precision of measurement. Experimental errors arose from measurement of $D_{AS:D}$, a , b , r and ψ whereas in the simulation errors only arose from measurement of r and ψ accounting for the difference in magnitude. When conducting the error analysis for evaluation of the optimum encoder position, the errors were treated as if the results were obtained experimentally. The results are shown in 3D surface plots, Figure 7.18.

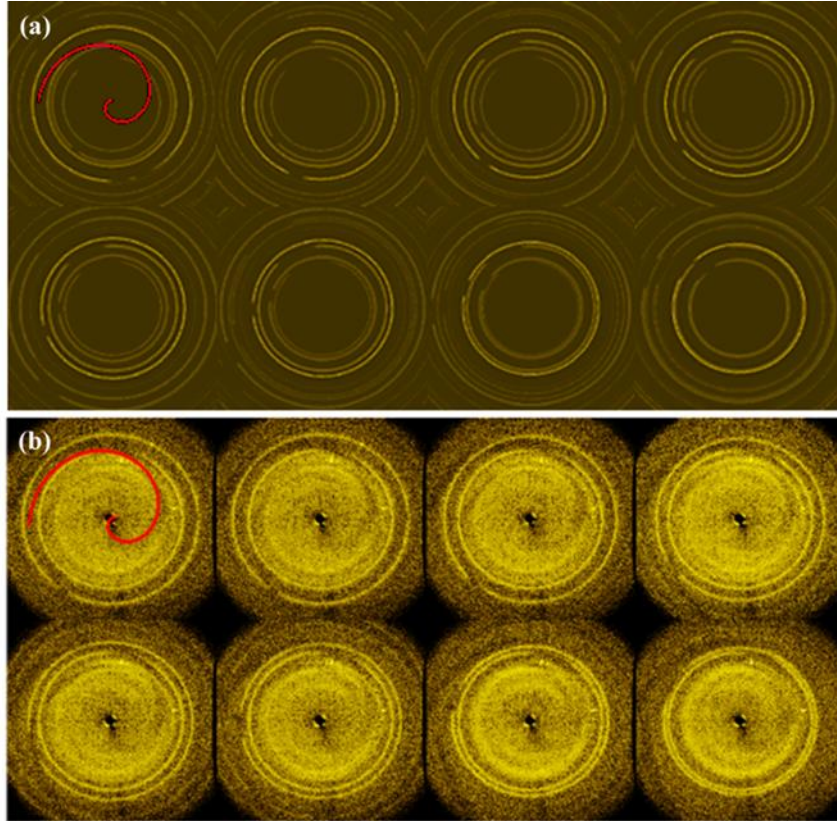


Figure 7.17 Angular dispersive diffraction patterns demonstrating the use of a spiral encoder (0.05ψ) obtained via (a) simulation and (b) experimental methods from two 0.05 mm CaCO_3 samples spatially separated along the primary axis. The sequence of patterns was collected when Sample 1 was incrementally translated along the primary axis, towards the detector by 2 mm.

Table 7.7 Results of the spiral encoding recovery from the translated sample, Sample 1. The sample-to-detector distance, D_{SD_1} , was incrementally increased by 2 mm. The corresponding d -spacing for the 104 reflection of CaCO_3 is 3.035 Å (ICDD database PDF 5-586, Appendix A).

	Sample to Detector Distance /mm	Measured r /mm	Measured encoding angle, ψ /°	Calculated 2θ /°	Calculated d -spacing /Å	Calculated Sample-to- Detector Distance /mm
Experimental	83	45.7	312.3	29.3 ± 0.82	3.04 ± 0.08	81.4 ± 1.66
	81	45.0	303.9	29.2 ± 0.81	3.05 ± 0.08	80.4 ± 1.63
	79	44.2	289.0	29.4 ± 0.80	3.03 ± 0.08	78.3 ± 1.58
	77	43.2	268.1	29.8 ± 0.78	3.00 ± 0.08	75.6 ± 1.50
	75	41.4	253.5	29.1 ± 0.76	3.07 ± 0.08	74.5 ± 1.48
	73	40.4	234.4	29.2 ± 0.75	3.06 ± 0.08	72.3 ± 1.42
	71	39.4	217.5	29.2 ± 0.73	3.06 ± 0.07	70.6 ± 1.38
	69	38.6	197.7	29.4 ± 0.72	3.04 ± 0.07	68.5 ± 1.33
Simulated	83	46.7	296.7	29.4 ± 0.3	3.04 ± 0.03	83.0 ± 0.004
	81	45.6	276.4	29.4 ± 0.3	3.04 ± 0.03	81.0 ± 0.004
	79	44.5	256.2	29.4 ± 0.3	3.04 ± 0.03	79.0 ± 0.004
	77	43.3	235.1	29.4 ± 0.3	3.04 ± 0.03	77.0 ± 0.004
	75	42.2	215	29.4 ± 0.3	3.04 ± 0.03	75.0 ± 0.004
	73	41.1	194.4	29.4 ± 0.3	3.04 ± 0.03	73.0 ± 0.005
	71	39.9	173.4	29.4 ± 0.3	3.04 ± 0.03	71.0 ± 0.005
	69	38.8	153.3	29.4 ± 0.3	3.04 ± 0.03	69.0 ± 0.005

$$\begin{aligned}
\sigma_{D_{SD}}^2 &= \left[\frac{\partial D_{SD}}{\partial D_{AS:D}} \right]^2 \sigma_{D_{AS:D}}^2 + \left[\frac{\partial D_{SD}}{\partial a} \right]^2 \sigma_a^2 + \left[\frac{\partial D_{SD}}{\partial b} \right]^2 \sigma_b^2 + \left[\frac{\partial D_{SD}}{\partial \psi} \right]^2 \sigma_\psi^2 + \left[\frac{\partial D_{SD}}{\partial r} \right]^2 \sigma_r^2 \\
&= \left[1 + \frac{r_{AS}}{r - r_{AS}} \right]^2 \sigma_{D_{AS:D}}^2 + \left[\frac{D_{AS:D}}{r - r_{AS}} + \frac{D_{AS:D} r_{AS}}{r - r_{AS}}^2 \right]^2 \sigma_a^2 + \left[\frac{\psi D_{AS:D}}{r - r_{AS}} + \frac{\psi D_{AS:D} r_{AS}}{r - r_{AS}}^2 \right]^2 \sigma_b^2 \\
&\quad + \left[\frac{b D_{AS:D}}{r - r_{AS}} + \frac{b D_{AS:D} r_{AS}}{r - r_{AS}}^2 \right]^2 \sigma_\psi^2 + \left[\frac{-D_{AS:D}}{r - r_{AS}}^2 \right]^2 \sigma_r^2
\end{aligned} \tag{7.5}$$

$$\begin{aligned}
\sigma_{2\theta}^2 &= \left[\frac{\partial 2\theta}{\partial D_{AS:D}} \right]^2 \sigma_{D_{AS:D}}^2 + \left[\frac{\partial 2\theta}{\partial a} \right]^2 \sigma_a^2 + \left[\frac{\partial 2\theta}{\partial b} \right]^2 \sigma_b^2 + \left[\frac{\partial 2\theta}{\partial \psi} \right]^2 \sigma_\psi^2 + \left[\frac{\partial 2\theta}{\partial r} \right]^2 \sigma_r^2 \\
&= \left[\frac{r_{AS} - r}{r - r_{AS}^2 + D_{AS:D}^2} \right]^2 \sigma_{D_{AS:D}}^2 \\
&\quad + \left[\frac{-D_{AS:D}}{r - r_{AS}^2 + D_{AS:D}^2} \right]^2 \sigma_a^2 + \left[\frac{-\psi D_{AS:D}}{r - r_{AS}^2 + D_{AS:D}^2} \right]^2 \sigma_b^2 \\
&\quad + \left[\frac{-b D_{AS:D}}{r - r_{AS}^2 + D_{AS:D}^2} \right]^2 \sigma_\psi^2 + \left[\frac{D_{AS:D}}{r - r_{AS}^2 + D_{AS:D}^2} \right]^2 \sigma_r^2
\end{aligned} \tag{7.6}$$

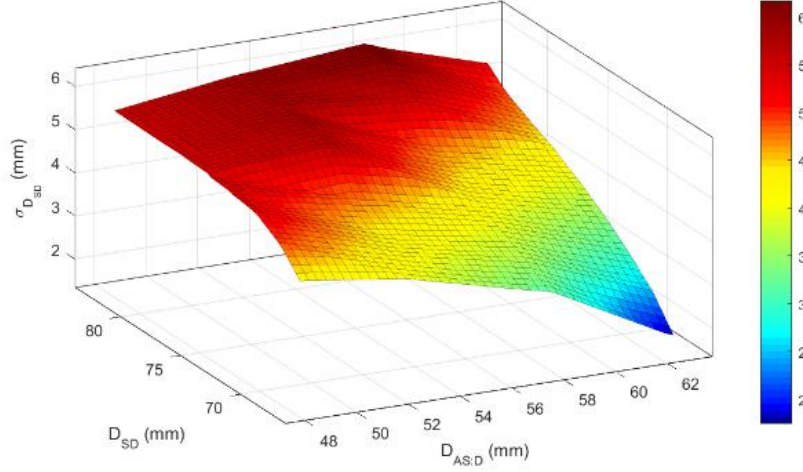
Repeating the same analysis as conducted for the linear encoder, it was determined that the optimum position of the spiral encoder (error is minimised) when the Archimedean spiral encoder is close to the sample, i.e. $D_{AS:D}$ is maximised. When calculating the sample-to-detector distance, D_{SD} , the most significant error arose from measuring the spiral-to-detector distance, $D_{AS:D}$. Considering the diffraction angle calculation, the most dominant errors were seen in the measurement of the radius in the detector plane, r .

7.2.3 Algorithmic

Unlike the previous two methods the algorithmic method has no additional experimental components. The method relies on an algorithm by which the obtained diffraction data (measured radii of Debye rings within detector plane) are compared to a set database of materials to produce a likelihood of materials at specific locations.

The algorithm relies on the geometric considerations utilised within the analytical method. When the position of the sample is unknown, the obtained diffraction pattern cannot be converted into meaningful scattering data. This is due to the variation in magnitude of the radii of the Debye cones within the detector plane, depending on the sample placement. As the sample moves towards the detector (i.e. the sample-to-detector distance, D_{SD} , decreases) the radii of the resulting

(a)



(b)

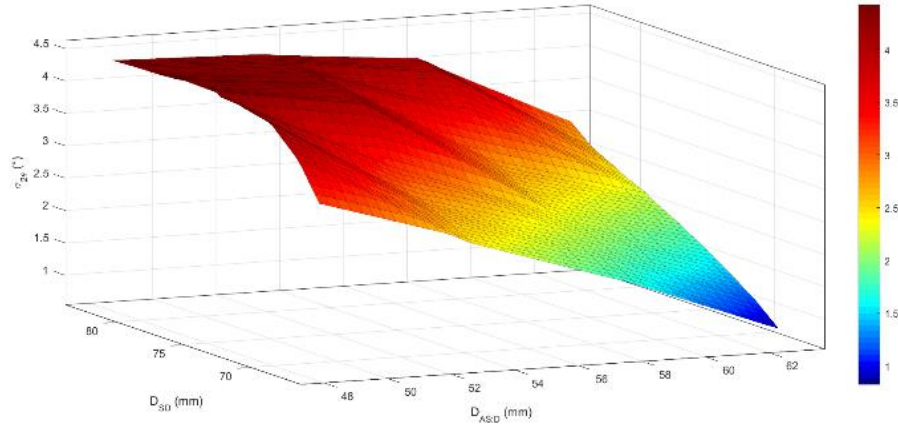


Figure 7.18 (a) 3D surface plot of the error associated with calculating the sample-to-detector distance and (b) 3D surface plot of the error associated with measuring the diffraction angle (2θ) calculated using the 104 reflection from the sample closest to the detector when using an Archimedean spiral encoder.

diffraction pattern within the detector plane will also decrease. This effect was demonstrated in §7.2.1, Figure 7.9.

The measured r values are converted into 2θ s, and thus d -spacings, at every possible sample position, D_{SD} . These calculated d -spacings are then compared to the known d -spacings of potential materials within the database and a likelihood can be calculated. When all materials and locations from the database have been compared

Table 7.8 Materials used in algorithmic technique with the four corresponding highest intensity d -spacings for each material.

Material	Material Reference Number	d -spacings /Å			
		d_1	d_2	d_3	d_4
Aluminium oxide, Al_2O_3	1	2.55	2.09	1.60	3.48
Iron, Fe	2	2.03	1.17	1.43	0.91
Aluminium, Al	3	2.34	2.02	1.22	1.43
Calcium carbonate, CaCO_3	4	3.04	2.29	2.10	1.88
Sodium chloride, NaCl	5	3.25	2.81	1.99	1.70
Ammonium nitrate, NH_4NO_3	6	2.73	3.96	4.96	2.26

to the unknown spectrum, a Grid-based search (a Grid-search is a method of optimisation, parametrised by a grid of parameters) is performed to obtain the best match.

For weapons dismantlement applications, the selection of potential materials previously established would be a list of potential explosives you would expect to find in a NW. Here, explosives have been substituted with benign materials to demonstrate the technique (Table 7.8), with their corresponding highest intensity d -spacings used within the algorithm. For each known material, a continuum of probability in d -space is calculated i.e. a spectrum indicating the probability of a peak existing at a particular d -spacing. This is achieved by including a Gaussian peak at each expected reflection, with a width of 0.02 Å. Limits are set on the range of possible d -spacings based on the d -spacings of the known materials. Consequently, from analysing Table 7.8 the minimum d -spacing used is Fe, $d_4=0.91$ Å and the maximum used is NH_4NO_3 , $d_4=4.96$ Å, thus the range set for possible d -spacings was limited to 0.60-5.00 Å.

The probability spectrum is normalised by dividing by the sum of the spectrum which provides a natural Occam factor, ensuring more complicated materials – i.e. those with more Bragg reflection peaks – are not favoured over those with fewer peaks. These types of materials are more likely to exhibit random matches.

Limits are set on possible values of distance D_{SD} according to the experimental setup (i.e. walls of the container), and a grid composed of D_{SD} -values against measured experimental r values. The grid is populated with d -spacings calculated from the respective experimental r values at the corresponding D_{SD} distances creating a probability spectrum, as with the theoretical data. An example of the probability spectra combining both theoretical and experimental data is shown in Figure 7.19 which displays the result when Al_2O_3 (Material 1) and Al (Material 3) are placed at $D_{SD}=21.24$ mm and $D_{SD}=37.15$ mm respectively.

The probability that the experimental data contains only one specific material (e.g. probability that the experimental data in Figure 7.19 contains Material 3), can be calculated by piecewise-multiplying the spectra together and summing the results. Summing together these individual probabilities for all possible D_{SD} s for a single material provides a combined posterior probability that the experimental data

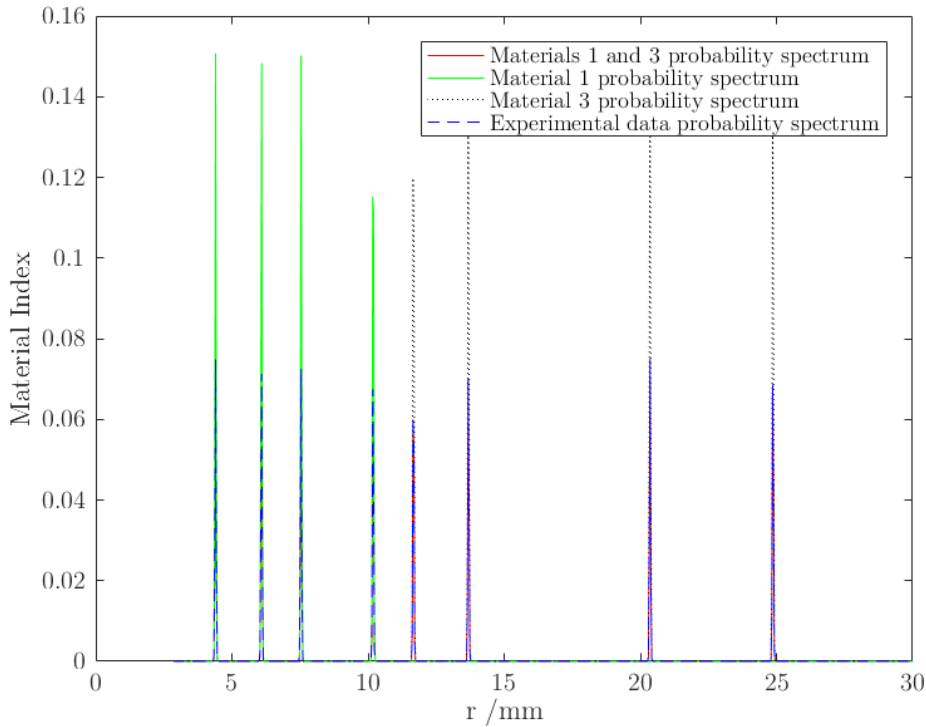


Figure 7.19 An example of overlaid theoretical and experimental probability spectra for experimental data containing both material 1 and material 3.

contains that material. This algorithm provides a working method to ascertain which materials the sample is most likely composed of.

Testing the algorithm with the 6 different potential materials, employing two materials at once, gives an output similar to that shown in Figure 7.20. In this case Materials 1 and 3 were placed at 35.95 and 25.35 mm respectively in a 20 mm box.

The most likely values appear bright yellow thus in this instance the algorithm has identified Materials 1 and 3 as the most likely materials at their respective positions. This demonstrates the use of the basic algorithm.

As with the other two techniques proposed for material identification the accuracy was evaluated for the algorithmic method. As the d -spacings are never actually calculated, the only error that can be associated with the technique is in the precision of locating the sample. The absolute precision error for determining the location of the sample, s , can be described by the standard deviation:

$$s = \sqrt{\sum (D_{SD} - \overline{D_{SD}})^2} \quad (7.7)$$

Where D_{SD} is the calculated sample-to-detector distance and $\overline{D_{SD}}$ is the actual sample-to-detector distance. The absolute precision errors for two samples placed within a 100 mm volume were determined by simulating the samples (Material 2 and Material 6) at 10 mm increments throughout the volume. Two ADXRD detectors, D1 and D2 were placed at $D = 500$ mm and $D = 800$ mm, respectively from the Mo, 17.5 keV source.

The radii were measured, and the algorithm used to retrieve the positions of the samples. They were then compared to the actual values and the absolute precision error calculated for each sample at every position used using Equation (7.7). The results are illustrated in Figure 7.21 where the yellow squares indicate a larger calculated absolute precision error. The error for Material 2 is more than that of Material 6, particularly in cases where Material 6 is in front of Material 2.

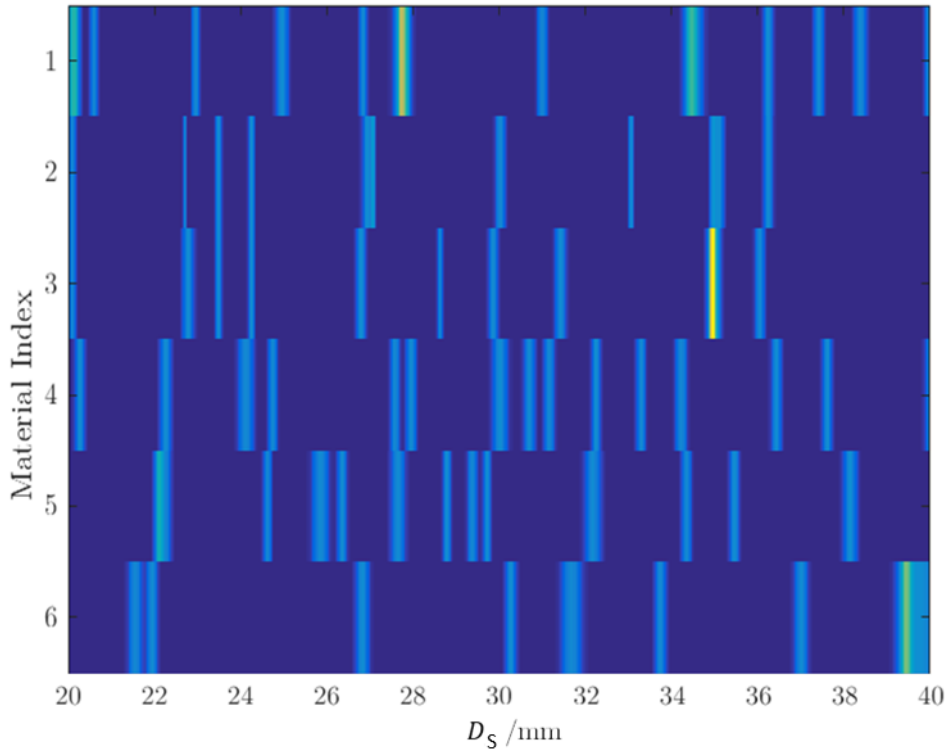


Figure 7.20 An example of the output showing the probability that a material is in the data at various positions from the source, D_S . In this example, a combination of Materials 1 and 3 at 35.93 mm and 25.34 mm respectively was simulated shown by the bright yellow bars indicating a good agreement with analytical calculations.

The calculated absolute precision errors can be totalled for both samples in each different arrangement, the results of this is shown in Figure 7.22. The errors are greatly reduced by using a detector which is further away from the sample, D2. This is not surprising as the maxima, within the diffraction pattern, will be spaced further apart, due to the increased sample-to detector distance, and therefore easier to distinguish individual peak maxima.

The mean absolute error when using D1 is 15.6 mm, and for D2 is 0.6 mm. In this example it has been demonstrated that it more precise to use a detector which is further from the sample, D2, as the associated errors are reduced.

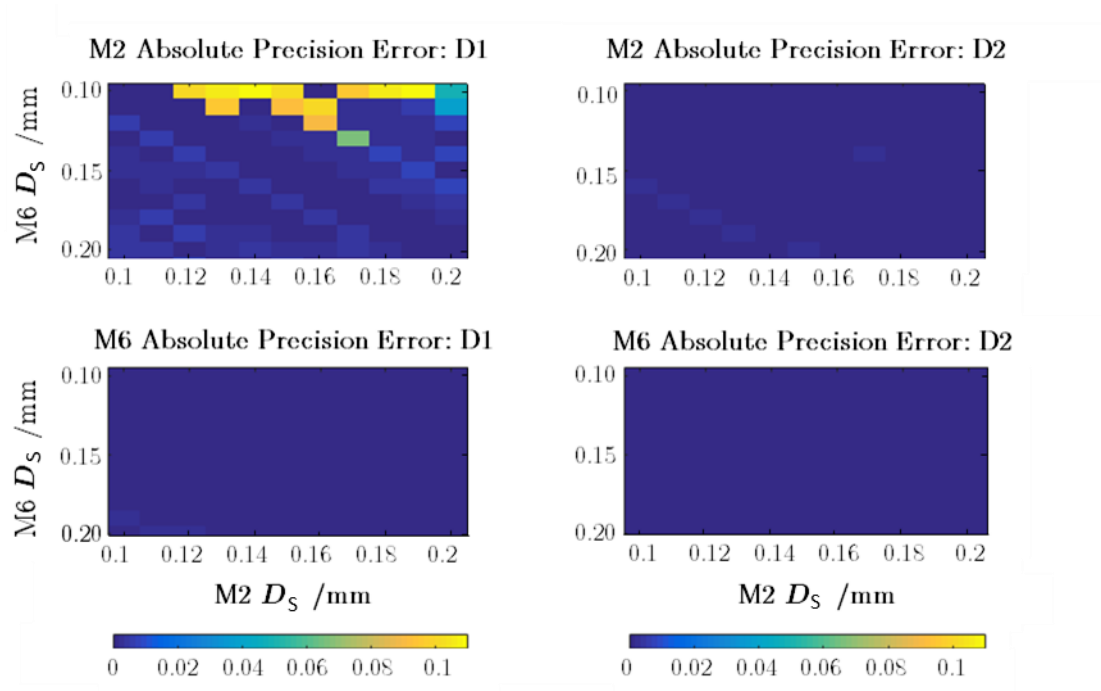


Figure 7.21 Absolute precision errors for simulations of Material 2 and Material 6 at varying positions within a 100 mm volume for the algorithmic search method.

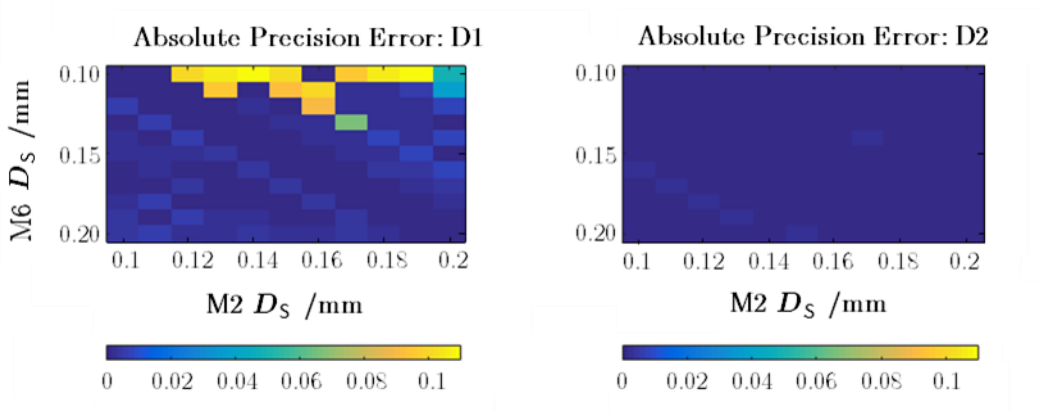


Figure 7.22 Illustration of absolute precision error calculated for Materials 2 and 6 combined.

7.2.4 Comparison of techniques

All the methods introduced here to interpret obtained coherent scattering patterns have successfully located and subsequently identified the material within the sample volume. However, a number of assumptions have been made: that i) angular

dispersive diffraction is employed ii) three Debye rings are always measurable on the detector and iii) intensities of peaks are irrelevant.

The analytical method, introduced first, is a simple method when there are two materials or less in the sample volume. With greater than two materials, the diffraction patterns become too overcomplicated to distinguish the peaks. The other limitation to this technique is the need for moving parts (i.e. translations along the z -axis) and thus a requirement for multiple measurements leading to greater imprecision.

The second strategy introduced in this study, the linear and Archimedean spiral post-sample encoders, was shown to be effective at providing geometric and structural information without the need for moving parts. Both encoders were shown to provide single axis positions with $\sim 1\%$ precision although accurate calibration of the encoder in relation to the detector was essential. Comparison of the induced errors from both encoders indicated that the Archimedean spiral yields a lower experimental error in the calculated D_{SD} distance than the linear encoder. Additionally, the Archimedean spiral encoder overcomes the primary limitation of the linear encoder; the requirement to be placed in close proximity to the primary axis - the space with the largest error - in order to intersect the Debye ring to thus encode the diffraction pattern. A spiral encoder emanating from the primary axis, encodes a beam of any size.

The algorithmic method involves no moving parts and no complicated calibration. It successfully identified the materials in every situation tested and has the smallest variation between the true location and the calculated location of every technique. This technique could be extended to identify more samples within the sample volume simultaneously on the condition that the maxima within the resulting diffraction pattern can be distinguished.

The reliability of each technique was evaluated by repeating the technique varying the geometries used, in the analytical and encoder techniques, and by varying both the samples and their corresponding positions in the **algorithmic approach**. The various set-ups were simulated each time with 2 samples present. The results are summarised in Table 7.9.

Table 7.9 Summary of errors associated with locating the sample in each technique presented.

Method	Percentage frequency technique identified location of samples /%	Average difference between calculated and known distance from detector /mm
Analytical	86.70	14.43
Linear encoder	91.64	5.72
Spiral Encoder	95.41	1.24
Algorithmic	100.00	0.6

Based on these results, the analytical method produces the greatest average variation from the true sample location and is also the least reliable, incorrectly determining the location 13.3 % of the time. The encoders both have less variation between the calculated and true value of the sample location and are also more reliable than the analytical technique. The spiral encoder demonstrated to be more reliable than the linear encoder, this was primarily due to the inability to determine the location in some linear encoder geometries due to the Debye cone bypassing the encoder. The algorithmic technique located the sample 100% of the time and additionally produced the least variation between the true sample position and the recovered sample location.

7.3 Concluding remarks

This chapter presents the results utilising a pencil beam geometry to interpret diffraction patterns when *no priori* information is known about the sample inside a gauge volume.

Using ADXRD, considered due to its superior resolution over EDXRD, initial simulations were undertaken to verify the simulation package chosen, *McXtrace*, modelled the parameters required; *d*-spacings, geometry, sample thickness and energy of the source.

After establishing the simulation package worked successfully, three methods of data interpretation were introduced. Previous research has not worked backwards when the sample location is unknown. All three methods - analytical, encoders and

algorithmic - were successfully demonstrated, being able to locate the sample to ultimately determine the scattering angle, thus determine the materials identity.

The analytical method demonstrated experimentally and with simulations, that by translating the detector along the primary axis, collecting images from two different positions the location of the scattering source could be determined, thus the scattering angle.

Novel post sample encoders, used as a reference structure in the collected diffraction pattern, were demonstrated both experimentally and via simulation to aid the interpretation of scatter without the need for moving parts. Two encoder types were introduced - linear and Archimedean spiral encoder - each shown to provide single axis position with 1% precision but each with their own limitations. They were chosen due to their simple geometry, offering unambiguous interpretation and a large open fraction, allowing a greater proportion of the scattered X-rays to reach the detector plane.

The linear encoder, whilst simple to implement, required a large off-centre location to reduced uncertainty. Implementing this coincidentally meant that Debye cones with small scattering angles bypassed the encoder, thus the obtained Debye ring didn't contain a reference point and therefore could not be interpreted. The spiral encoder overcame this limitation, but accurate calibration was required in order for it to be effective.

The final method of interpretation, algorithmic, successfully utilised a novel algorithm by which the obtained diffraction data (measured radii of Debye rings within detector plane) are compared to a set database of materials to produce a likelihood of the presence of the materials at specific locations.

The comparison of all techniques demonstrated that the algorithmic method was the most precise, identifying the samples location on average by within 0.6 mm, every time. Going forward, it is suggested to concentrate on the algorithmic method. One way to potentially improve these techniques would be to combine them; using an encoder to reduce the possible locations of the sample to then use the algorithmic method to match the diffraction pattern to a database of materials.

Chapter 8

FCG Results

Focal construct geometry (FCG) involves the use of a pre-sample annular collimator, in place of a pencil beam optic, to modify the morphology of the incident beam, increasing the number of photons incident on the sample, §3.4.2 discussed FCG in more detail. FCG was adopted in order to increase the diffraction intensity and mitigate the effects of preferred orientation and large grain size, characteristic of some explosive powders.⁹⁰ The intensity of the diffraction maxima obtained when using a pencil beam ADXRD was compared to using an annular collimator, presented in §8.1.

This chapter presents the results of the FCG portion of the research. Initially, FCG was compared, both analytically and through experimentation, to the pencil beam geometry to demonstrate the increased intensity. The FCG geometry was modelled in *McXtrace*, before introducing a sample with preferred orientation to demonstrate the enhanced capability of FCG.

ED systems are considered due to their efficiency and capability to access photons with higher energy, enabling a greater depth penetration. High energy simulated X-ray source spectra are analysed, comparing the proportions of photons contributing to characteristic (AD) and Bremsstrahlung (ED) radiation, to indicate the efficiency of the technique at higher energies, §8.3.

ED-FCG is demonstrated, employing the high energy W source. The results from demonstrating the ED-FCG technique at high energy are presented in §8.4.

The AD and ED functionalities of the HEXITEC detector were analysed before employing it in conjunction with a post-sample pin-hole aperture to enable depth perception, presented in §8.5.1. The depth resolution of the high energy FCG, pin-hole system is evaluated analytically and compared to experimental data, §8.5.1.1. Simulations were conducted to extend the system to higher energy, beyond the capabilities of the laboratory, to observe the affects and evaluate the potential restrictions, §8.5.2.

8.1 Pencil beam vs. FCG

As mentioned in §4.1.4, Rogers *et al.*⁶⁸ and Chan *et al.*¹⁰¹ have demonstrated, both analytically and experimentally, that FCG has an enhanced intensity when observing the condensation foci compared to Debye cones from a pencil beam.

A comparison between the intensity of the obtained scattering maxima of pencil beam and FCG geometries was conducted. Data for the comparison was attained using the Mo Zr-filtered X-ray source as it is easily interchangeable between the two geometries.

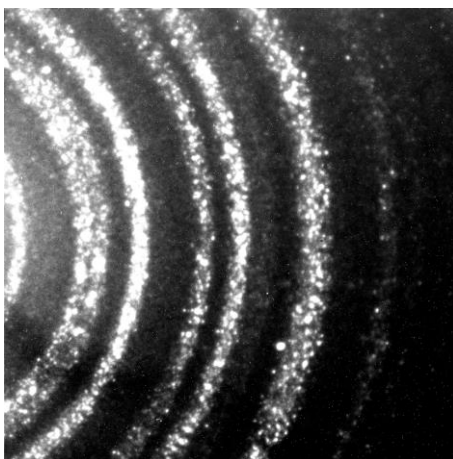


Figure 8.1 Diffraction pattern from Al_2O_3 obtained using the PIXIS detector 20 mm away from sample. Exposure time was 300 s and the detector was offset to avoid the primary beam.

For both geometries, the same 1.53 mm Al_2O_3 sample was used and placed 135 mm from the source. For the pencil beam a 0.25 mm diameter (radius 0.125 mm) collimator was fixed at a detector position of $D_{SD} = 20$ mm from the sample, offset to avoid the primary beam. The obtained diffraction pattern is shown in Figure 8.1. An azimuthal integration of the obtained image was performed using ImageJ to obtain the radii values of the maxima within the detector plane and converted into d -spacings. The result is shown in Figure 8.2 with the Al_2O_3 reference pattern overlaid (PDF 75-1862).

The same PIXIS detector was used in the FCG set up however, to collect the full pattern from a monochromatic source, the detector was translated along the z -axis. The annular collimator employed had dimensions $r_1 = 6.25$ mm and $r_2 = 6.50$ mm. A selection of the experimental data sequence obtained from Al_2O_3 as the detector was translated in increments of 1 mm along the z -axis is shown in Figure 8.3. Each image was taken with an exposure time of 30 s.

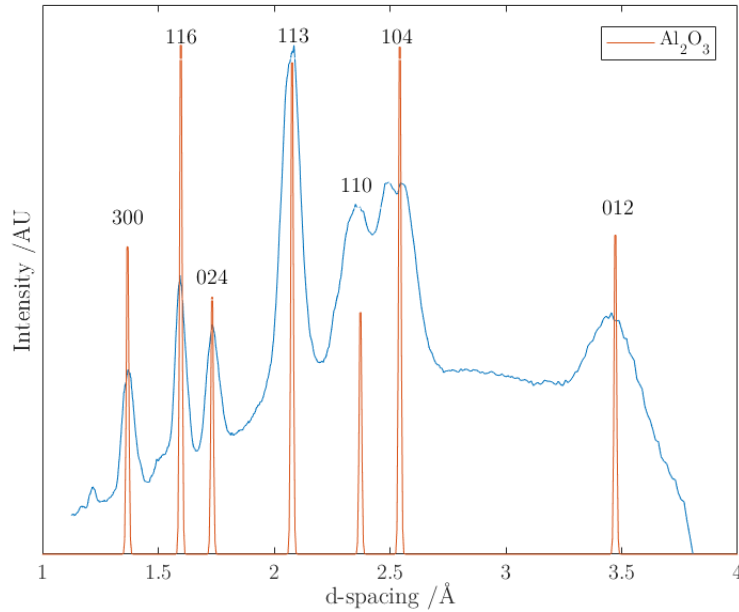


Figure 8.2 Diffraction profile of Al_2O_3 in pencil beam geometry obtained from azimuthal integral of Figure 8.1 overlaid with a reference profile of Al_2O_3 .

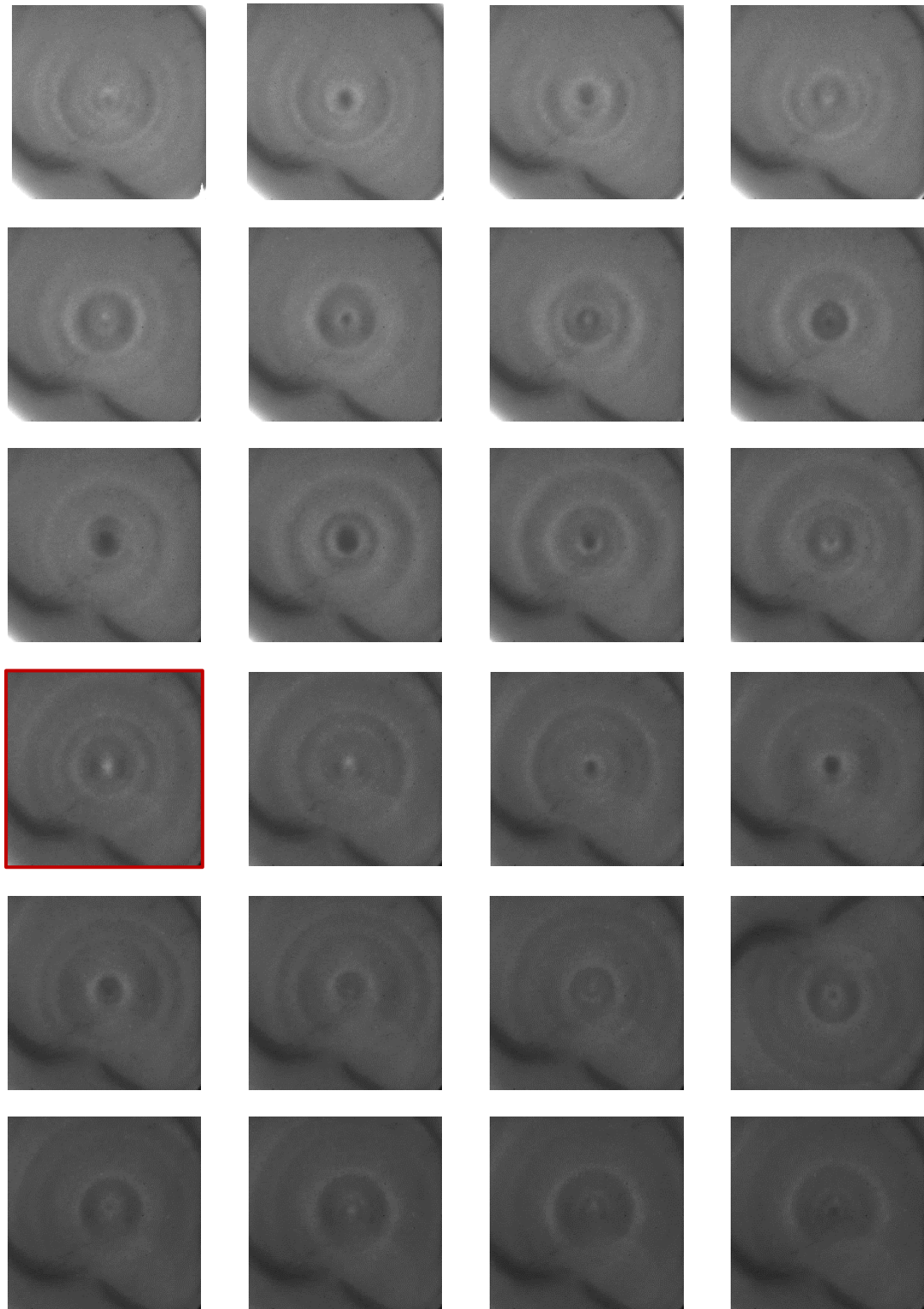


Figure 8.3 Selection of experimental FCG data sequence of Al_2O_3 , when the detector is translated in 1 mm increments along the z -axis.

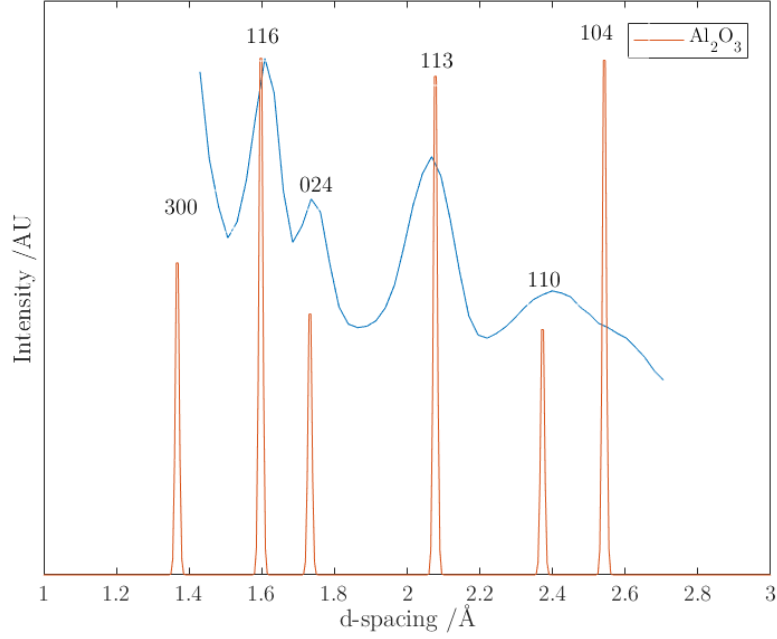


Figure 8.4 z -axis profile of mean intensity from central pixels corresponding with Al_2O_3 reference profile.

Highlighted by the red boxes in Figure 8.3 is the formation of a condensation foci discussed in §4.1.4. The enhanced condensation rings can be seen converging as they approach their condensation focus and subsequently diverging. The total intensity of the condensation rings around their circumference is equal to the intensity of their corresponding condensation foci.

Integration of the central area of each AD-FCG image, containing the condensation foci, through the sequence of images results in a diffraction profile, analogous to that of the pencil beam diffraction profile, Figure 8.4.

Applying the parameters employed here, the analytical ratio between FCG:PB was calculated using Equation (6.14), $I_{FCG:PB} = 204$. To view the diffraction patterns obtained from each geometry on a single plot the intensity of the obtained pencil beam data was multiplied by 408 ($= 204 \times 2$, the analytical value was multiplied by 2 as half of the pencil beam data was missing due to the detector being offset). The resulting diffraction profiles are displayed in Figure 8.5.

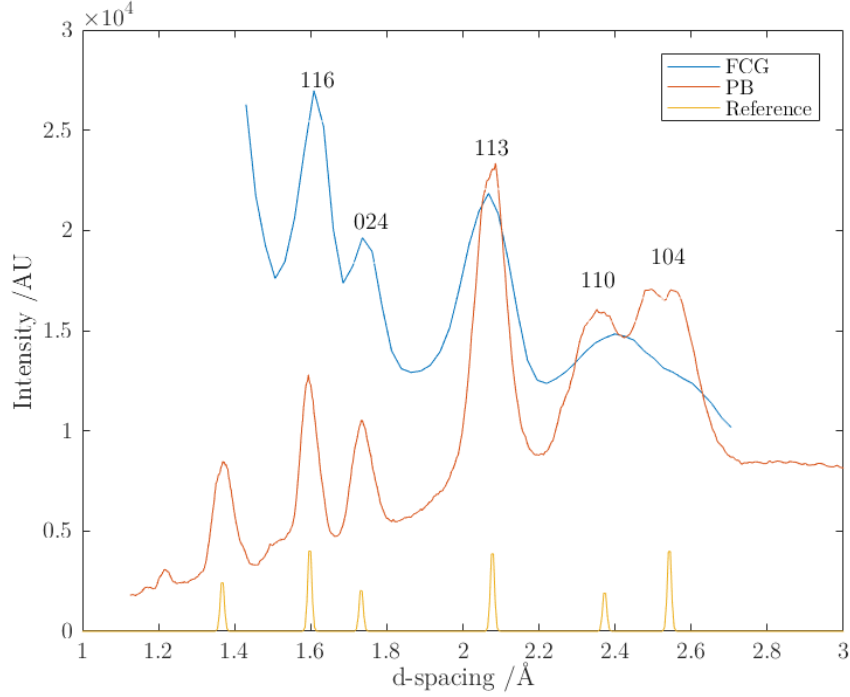


Figure 8.5 Overlay of FCG and PB diffraction data for Al_2O_3 . PB intensity was multiplied by 408.

The intensity of the main peaks, labelled in Figure 8.5 were measured and presented in Table 8.1. From these values, the experimental FCG:PB ratio was determined.

The measured FCG:PB ratio ranges from 382-1062, depending on the reflection used. The analytical FCG:PB value calculated, 408, lies within the experimental range. As noted by Rogers *et al.*(2010)¹⁰⁶ the differences between the intensities arising from the annular beam geometry and the pencil beam arrangement are primarily due to the Lorentz factor which varies with beam geometries. This could explain the inconsistencies in the FCG:PB ratio determined from experimental data.

Table 8.1 Intensity values of Al_2O_3 diffraction pattern in pencil beam and FCG geometry.

Reflection	Intensity PB	Intensity FCG	Ratio FCG:PB
116	25.4	2.698×10^4	1062
024	20.86	1.963×10^4	941
113	46.33	2.185×10^4	471
110	31.86	1.483×10^4	465
104	33.8	1.292×10^4	382

8.2 AD-FCG

The FCG geometry used in the previous section was simulated in *McXtrace*, modelling the Mo source ($\varphi_m = 4.29^\circ$), the 1.53 mm Al_2O_3 sample and the PIXIS detector to demonstrate the capability of the simulation software to simulate FCG. The detector was translated along the primary axis in 0.5 mm increments, with an image obtained from each position, shown in Figure 8.6. The condensation rings can be seen to converge and diverge as the detector translates through the condensation focus. Summing the intensity through the centre of each image (~ 50 -pixel diameter), generates a z -axis profile Figure 8.7, which correlates well with the overlaid reference profile.

To demonstrate the effects of preferred orientation, a 1.3 mm sample of Al was used. As discussed in Chapters 5 and 6, the use of FCG reduces the effects of preferred orientation and large grain size included in some explosive materials.^{65,88–90} The same Mo source, collimator and PIXIS detector, employed previously to analyse Al_2O_3 , were used again here. The Al sample was placed at $D_S = 155$ mm to enable the observation of smaller d -spacings, discussed in §6.4.3.2, with the detector translated in increments of 1 mm along the primary axis between $D = 185$ mm and $D = 215$ mm with an image obtained at each increment with exposure time 30 s; a selection of the images are shown in Figure 8.8.

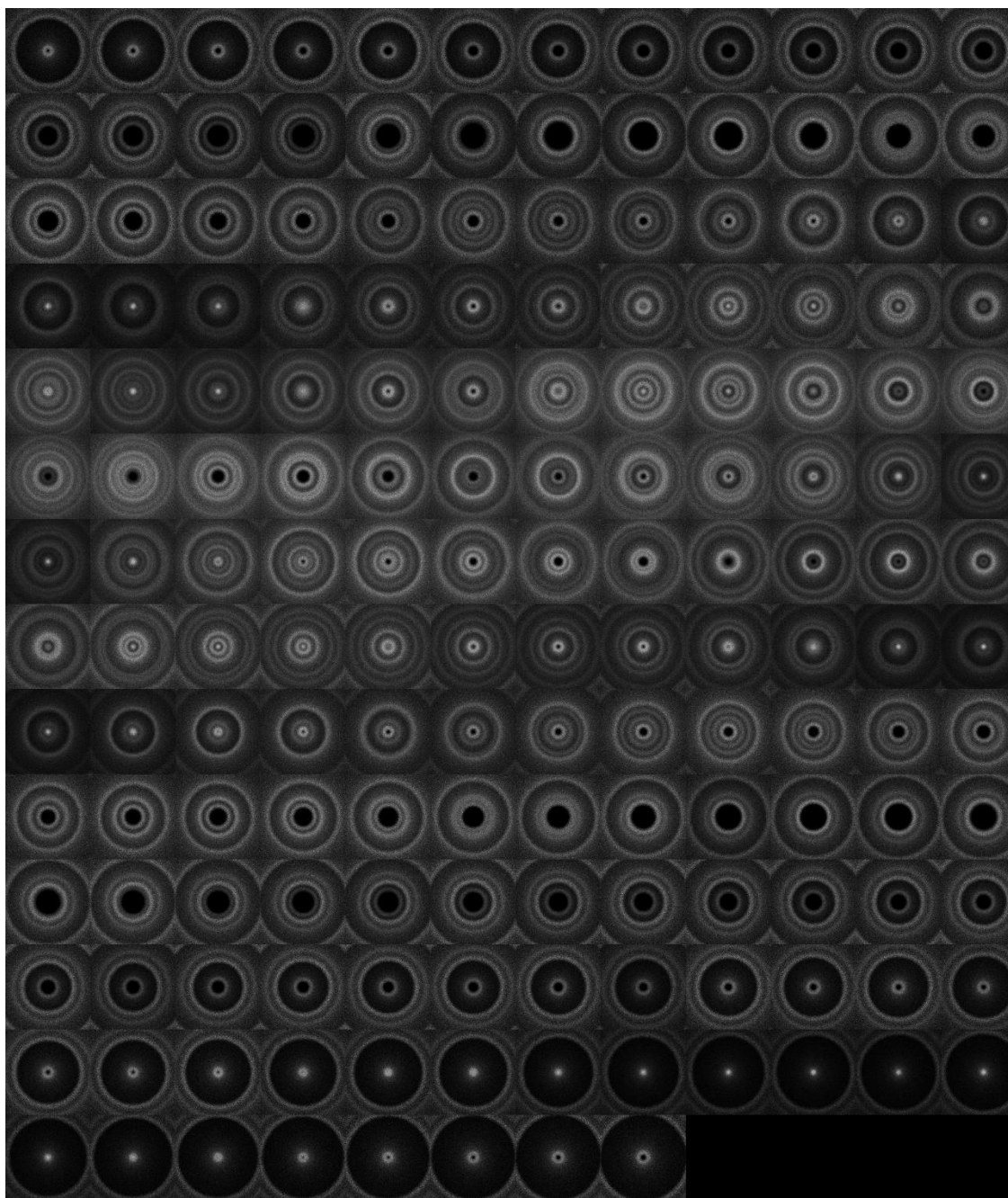


Figure 8.6 Montage of simulated AD-FCG images obtained with a 1.53 mm sample of Al_2O_3 employing the Mo annular collimated source translated in increments of 0.5 mm from $D = 168$ mm to $D = 250$ mm.

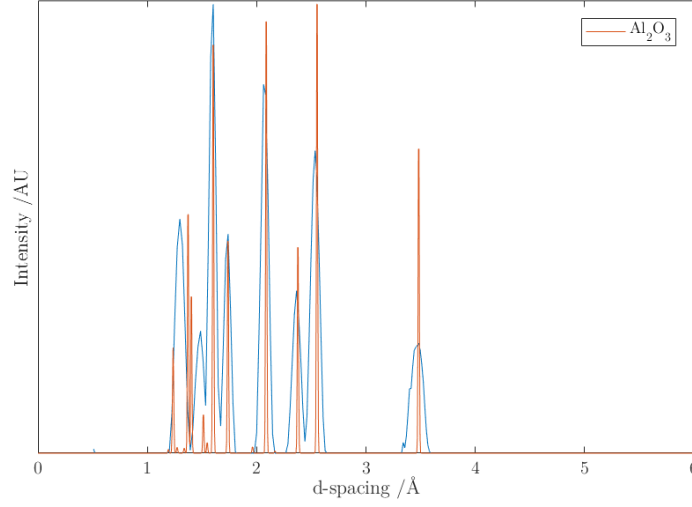


Figure 8.7 AD-FCG diffraction profile from integrating central regions of simulated FCG images collected from translating the detector along the z -axis in 0.5 mm increments.

Due to the preferred orientation, the images obtained from analysis of the 1.3 mm Al sample exhibit broken condensation rings. The broken condensation rings can still be seen converging as they approach their condensation foc, indicated by the red boxes around the images, and then diverging in opposite directions, Figure 8.8.

Integration of the central area (50 x 50 pixels) of each image, as conducted with the Al_2O_3 sample, results in the diffraction profile shown in Figure 8.9.

McXtrace was used to simulate Al as an ideal sample, i.e. without preferred orientation. The detector was translated in increments of 0.5 mm from $D = 140$ mm to $D = 210$ mm, with the 1.3 mm Al placed at $D_s = 135$ mm and the opening angle of $\varphi_m = 4.29^\circ$. The primary annular beam was removed from the simulation after diffraction, allowing acquisition of the lower d -spacings. The results are displayed in Figure 8.10.

The intensity of the middle 100 pixels of each image were summed and evaluated as for the experimental images. The resulting diffraction profile is displayed in Figure 8.11.

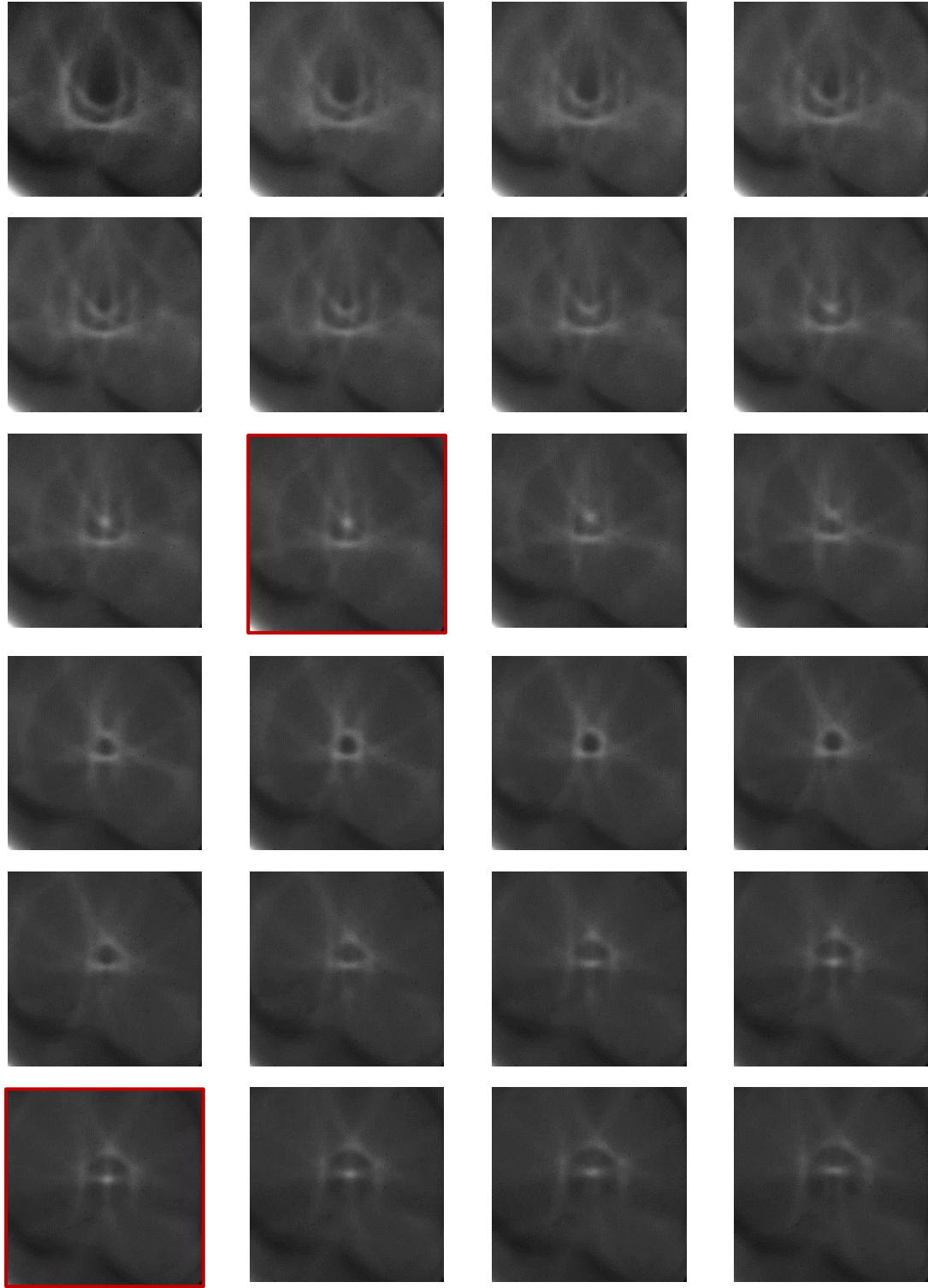


Figure 8.8 Sequence of FCG data obtained from sample of Al demonstrating preferred orientation. The detector was translated in 1 mm increments along the z -axis. The displayed images were obtained between $D = 185$ mm (top left) and $D = 208$ mm (bottom right). Red boxes around images indicate the formation of condensation foci.

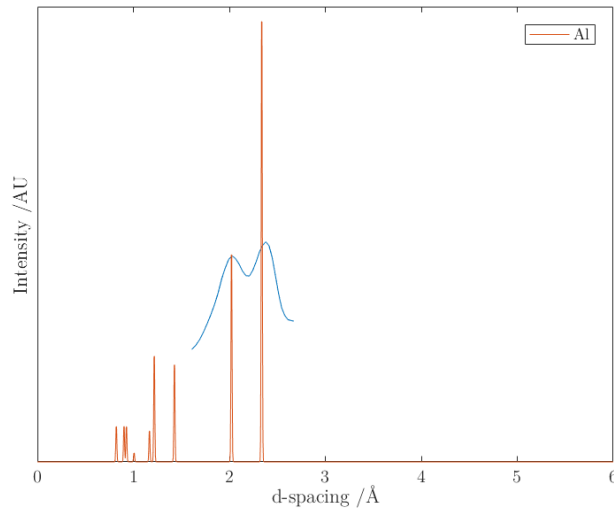


Figure 8.9 Diffraction profile of Al overlaid with reference profile.

8.3 High Energy: AD vs. ED

As discussed in §6.4.4, at high energy, AD techniques might not be the most efficient technique to use. ED systems are considered due to their efficiency and capability to access photons with higher energy, enabling a greater depth penetration. To evaluate this, X-ray source spectra were calculated and analysed, comparing the proportions of photons contributing to characteristic (AD) and Bremsstrahlung (ED) radiation.

In *SpekCalc*, the Bremsstrahlung cross section is treated using analytical theory, and the self-filtration within the anode, which allows modelling of specific experimental sources, is treated analogous to the experimental approaches. As with the *McXtrace* simulations, care was taken to use parameters that would be equivalent to the experimental source. There are a limited number of parameters and filters that can be used with the *SpekCalc* program, limiting the model which can be implemented. The experimental source has an anode angle of 35° along with a beam filtered by four different materials and thicknesses (beryllium - 0.8 mm,

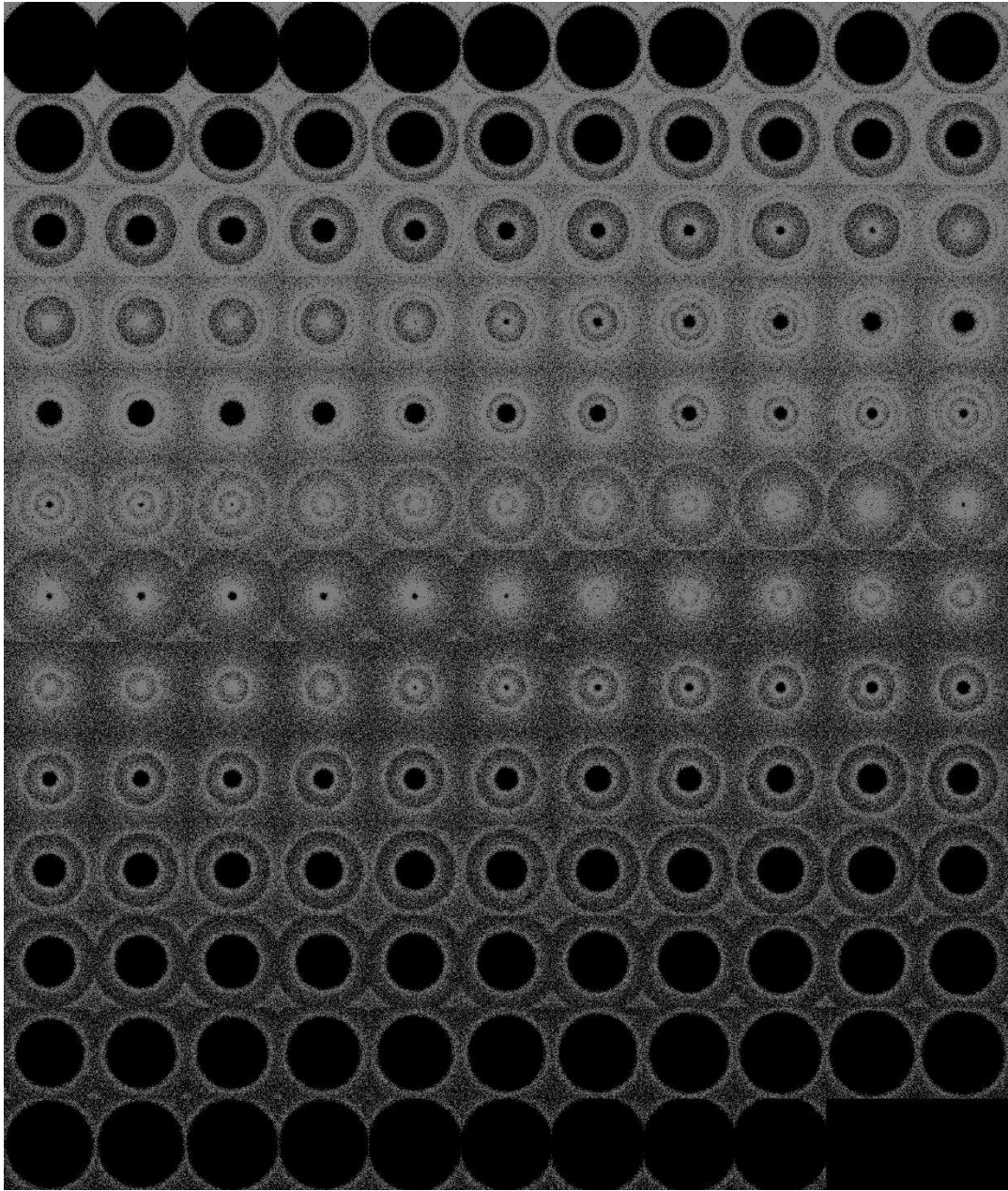


Figure 8.10 Image sequence of simulated Al in AD-FCG geometry with the detector translated from $D=140$ mm (top left) to $D = 210$ mm (bottom right).

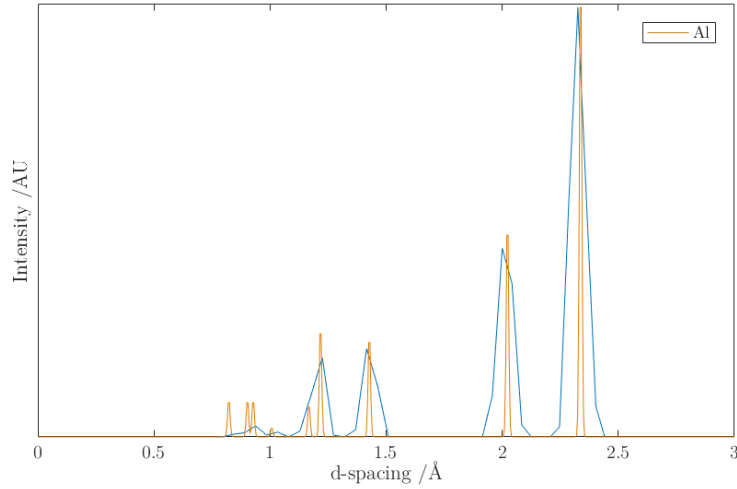


Figure 8.11 Obtained diffractogram from evaluating sequential images obtained from AD-FCG simulation of Al, using middle 100 pixels of each image, increments every 1 mm.

glass - 1.5 mm, transformer oil - 3 mm and Ultem 1000 - 1.5 mm). Out of these, only a beryllium filter can be applied within the *SpekCalc* software but using materials of similar density it was determined that using filters of 1.5 mm Al and 4.5 mm water would give a comparable filter, along with 0.8 mm beryllium. Using these parameters, a visual comparison was made with experimental source spectra to validate the use of the *SpekCalc* software. A good agreement between the two spectra at each voltage is observed, Figure 8.12.

SpekCalc was used to calculate the source spectra for X-ray tubes up to 500 kVp in increments of 10 kVp. The contribution of each radiation - Bremsstrahlung and characteristic - was measured and compared to experimental data collected by Tucker *et al.*¹⁵⁸, Figure 8.13. Figure 8.13 illustrates that the characteristic radiation only contributes to the source spectra after 80 kVp is applied. This is also demonstrated in Figure 8.12, 60 kVp, where no characteristic peaks are discernible. For characteristic peaks to be generated, photons above a certain energy are required to remove electrons from the inner shells of the atoms of the tungsten metal target, discussed in §3.2.2.1.

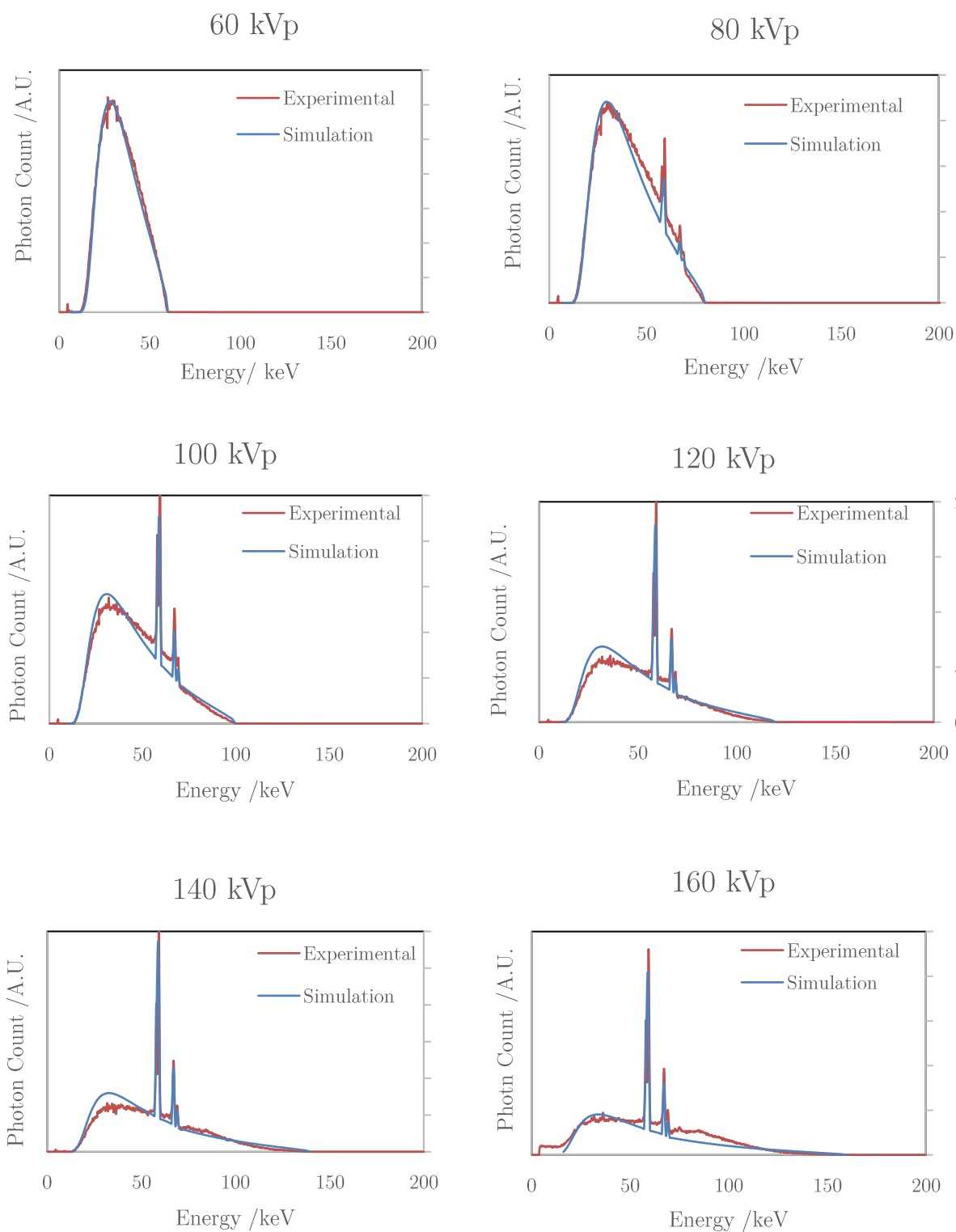


Figure 8.12 Graphs demonstrating the agreement between experimental data and *SpekCalc* simulated spectra at 60 kVp, 80 kVp, 100 kVp, 120 kVp, 140 kVp and 160 kVp.

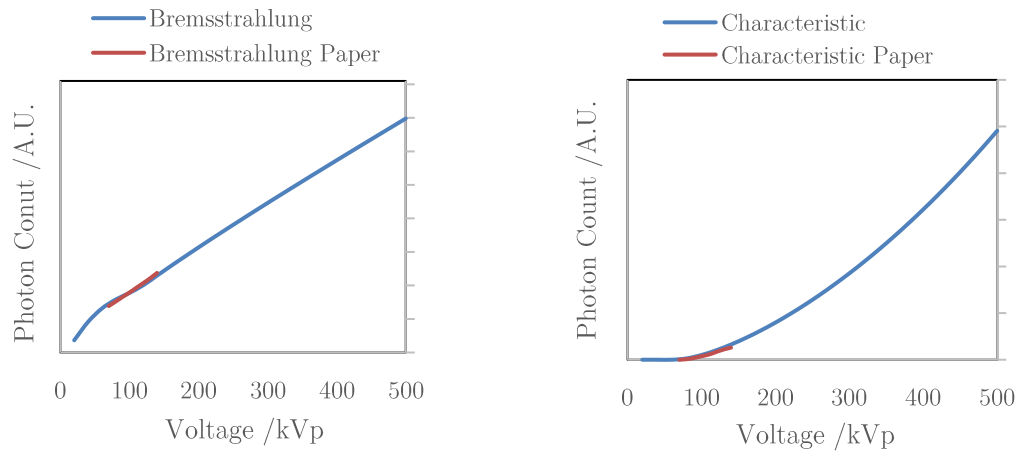


Figure 8.13 Estimated Bremsstrahlung and characteristic contributions from the output tube at various tube potentials overlaid with results from Tucker *et al.* (1991)¹⁵⁸ referred to as ‘Paper’.

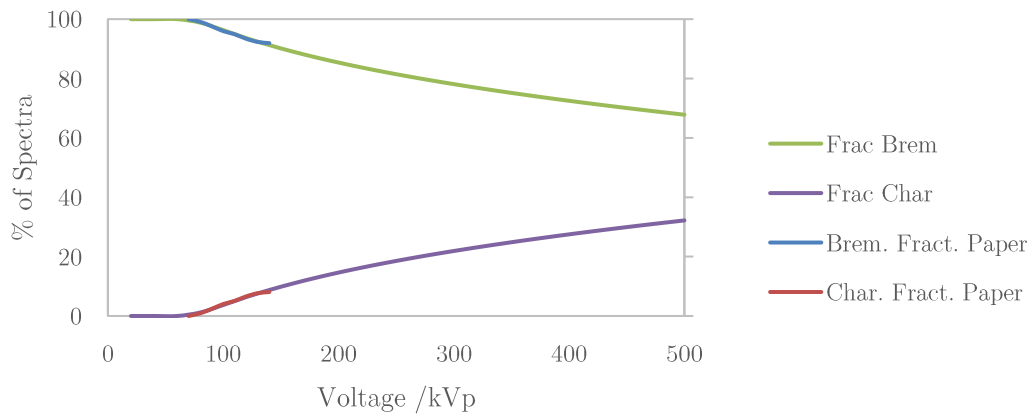


Figure 8.14 Contributions of Bremsstrahlung and characteristic radiation as a proportion of the overall spectra up to 500 kVp overlaid with results from Tucker *et al.* (1991)¹⁵⁸ referred to as ‘Paper’.

As the voltage of the X-ray source is increased, the amount of characteristic radiation increases. Figure 8.14 demonstrates how the contributions of Bremsstrahlung and characteristic radiation change as a proportion of the spectra as the tube potential is increased. Although it is clear from Figure 8.14 that the proportion of Bremsstrahlung radiation decreases as the voltage increases, Figure 8.13, the overall contribution from Bremsstrahlung radiation is still greater than

that of characteristic radiation. Thus, when working at high voltages it is more efficient to employ energy dispersive diffraction.

8.4 ED-FCG

With access to higher energy photons, for increased penetration ability, FCG was combined with energy dispersive methods to create energy dispersive FCG, ED-FCG. The energy dispersive detector was employed and placed along the primary axis, centrally placed in relation to the annular beam, described in §6.4.5.

In contrast to AD-FCG the energy dispersive detector remains stationary but, as with the pencil beam geometry, the use of the polychromatic beam means the diffraction from various d -spacings within the sample are distributed along the z -axis, discussed in further detail in §3.4.2.

To demonstrate the ED-FCG technique, the high energy tungsten source was employed with the energy dispersive X-123CdTe Amptek detector. Initially, a sheet of 1 mm Fe was analysed, $D_S = 150$ mm away from the source with the detector placed $D_{SD} = 475$ mm away from the sample on the opposite side, along the symmetry axis, as shown in **Error! Reference source not found.** The energy spectrum obtained was converted into d -space via Equation (3.6). Figure 8.15 shows the result of this analysis, displaying the high intensity Fe 110 peak.

Petri dishes filled with Al_2O_3 and NaCl, detailed in §6.3.1, were separately analysed and linearly translated along the primary axis, through the annular beam. The measured diffraction profiles obtained when the source-to-sample distance, $D_S = 143$ mm, $D_S = 160.8$ mm, $D_S = 174.5$ mm and $D_S = 194$ mm, are shown in Figure 8.16(a) for Al_2O_3 . NaCl was also translated along the z -axis with diffraction profile obtained at $D_S = 150.0$ mm, $D_S = 167.8$ mm, $D_S = 186.5$ mm and $D_S = 206.0$ mm, shown in Figure 8.17(a).

Analysing Figure 8.16(a) and Figure 8.17(a), the diffraction profiles appear to shift to a lower energy as the source-to-sample distance, D_S , increases. This is due to the geometry of the system, as detailed in §3.4.2. Since the conversion to d -spacing values, using Equation (3.6), is dependent on the sample position, the conversion

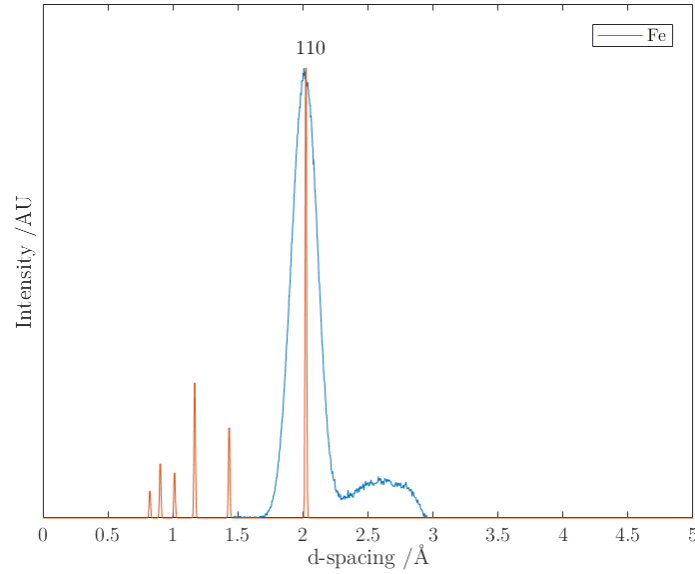


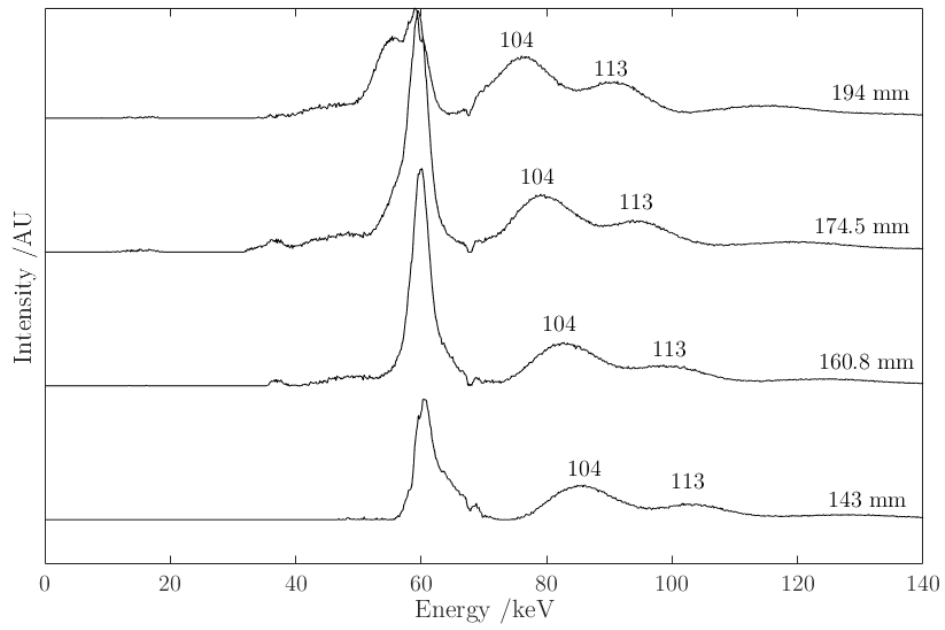
Figure 8.15 Diffraction profile of 1 mm Fe obtained using ED-FCG, 60 s exposure.

shifts all the spectra back to correct d -spacing, seen in Figure 8.16(b) and Figure 8.17(b). This has similarities with the with equivalent energy dispersive pencil beam geometry where the scattering angle is narrowly defined and utilised to determine the d -spacing.

Multiplex sampling was then considered, employing NaCl and a 1mm sheet of Fe, placed together in the incident beam, **Error! Reference source not found..** The thickness of the Fe was systematically increased by adding additional 1 mm sheets of Fe, resulting in the diffraction patterns shown in Figure 8.18. The intense peak at ~ 2 Å is a combination of the 110 Fe (2.028 Å) and 220 NaCl (1.987 Å) which is why, unlike the 200 NaCl peak (2.81 Å), it is prominent throughout each iteration. The NaCl dominant peak 200, is initially prominent when no Fe is included, but significantly reduces in intensity when more than 4 mm of Fe are present.

This indicates the need for a method to enable depth perception within the sample volume. The summation of scattering originating from an inspection volume, which includes a strongly coherent scattering metal such as Fe, would be dominated by the scatter originating from the metal, overshadowing the coherent scatter from the polycrystalline material.

(a)



(b)

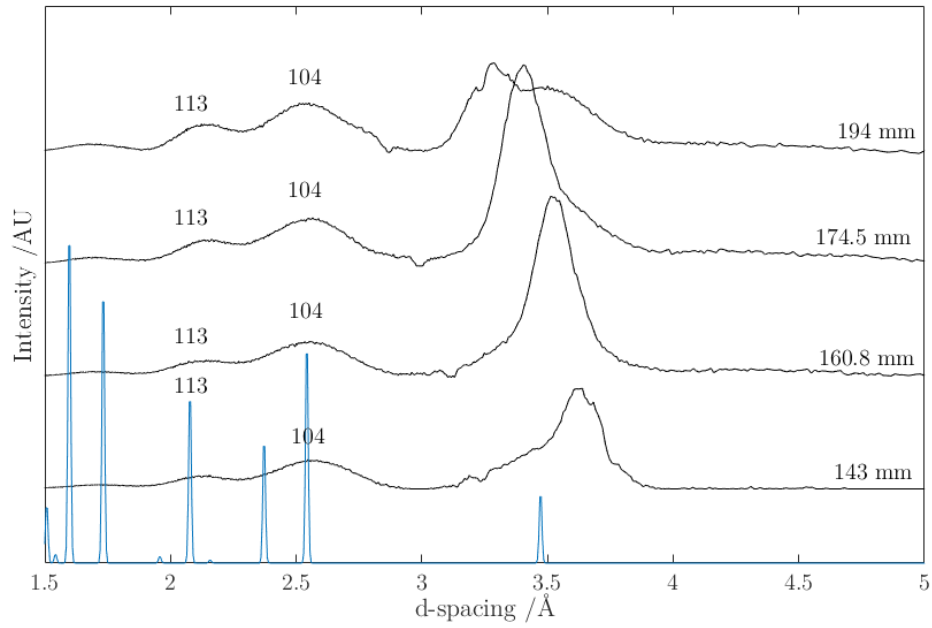
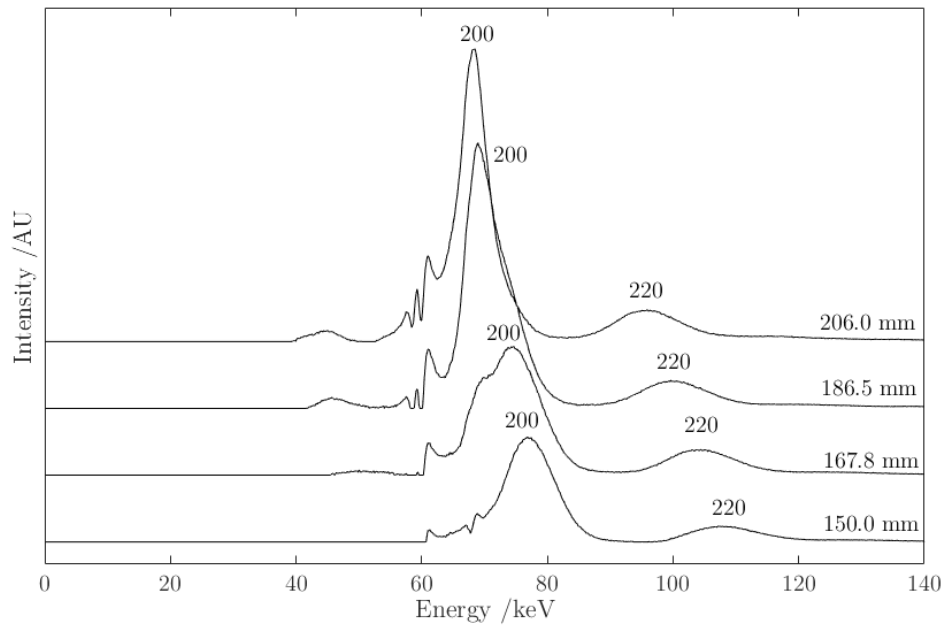


Figure 8.16 (a) Diffraction profile obtained from a sample of Al_2O_3 , translated through the primary axis when $D_G = 143, 160.8, 174.5$ and 194 mm (b) Diffraction profile as a function of d -spacings.

(a)



(b)

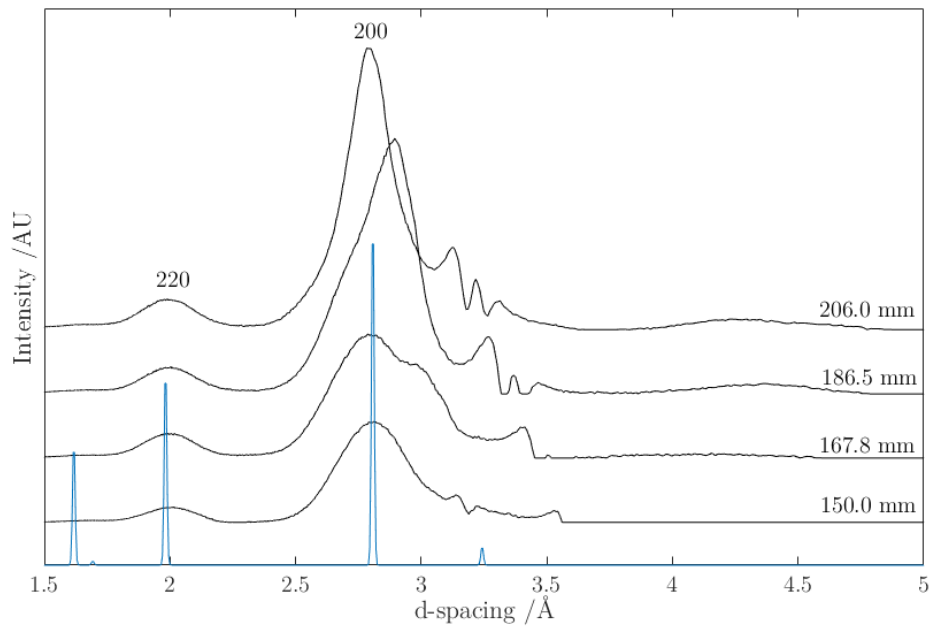


Figure 8.17 (a) Diffraction profile obtained from a sample of NaCl, translated through the primary axis when $D_S = 150.0, 167.8, 186.5$ and 206 mm (b) Diffraction profile as a function of d -spacings.

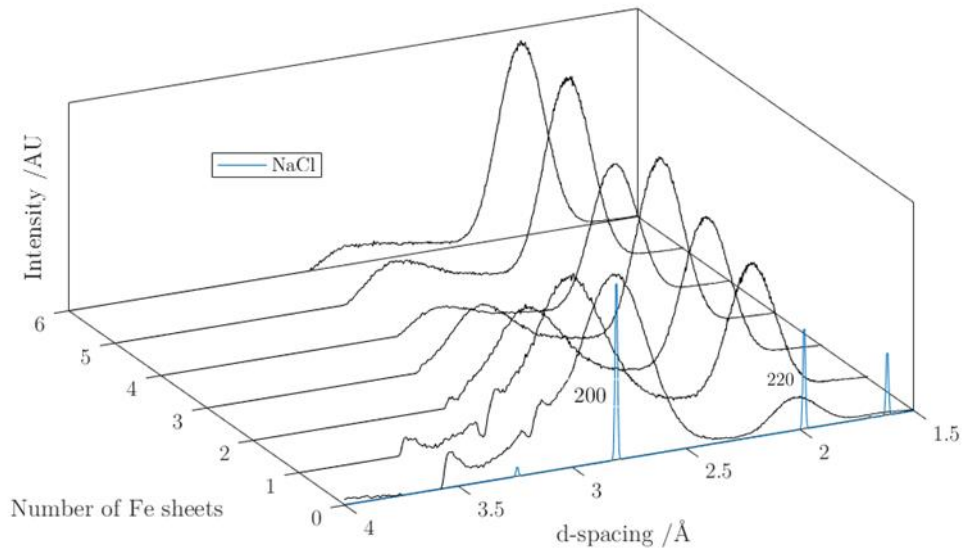


Figure 8.18 Diffraction profiles from combination of 15 mm NaCl and 1 mm Fe sheets, with increasing numbers of Fe sheets.

The NaCl 220 peak appears to shift slightly to higher d -spacings when the additional sheets of iron are employed. This is due to the conversion to d -spacing values depending on the position of the sample. As the additional Fe sheets were added, the NaCl was also moved due to the increasing thickness of Fe. However, the conversion did not account for this, using $D_S = 150$ mm, where the Fe sample was placed, hence why the intense 110 Fe peak, seen in Figure 8.15, at ~ 2 Å is consistent.

8.5 HEXITEC detector

The capabilities of the HEXITEC detector were investigated, initially assessing its AD functionality by using a pencil beam geometry before using AD-FCG. Figure 8.19 demonstrates the use of the HEXTEC detector as an angular dispersive detector using transmission pencil beam geometry with samples (a) 1.30 mm Al and (b) 1.53 mm Al_2O_3 using 0.125 mm radius pin-hole collimator.

As previously seen in Figure 7.9, §7.2.1, the Al_2O_3 sample (Figure 8.19 (b)) exhibits large grain size, identifiable by the speckled appearance of the Debye cones.

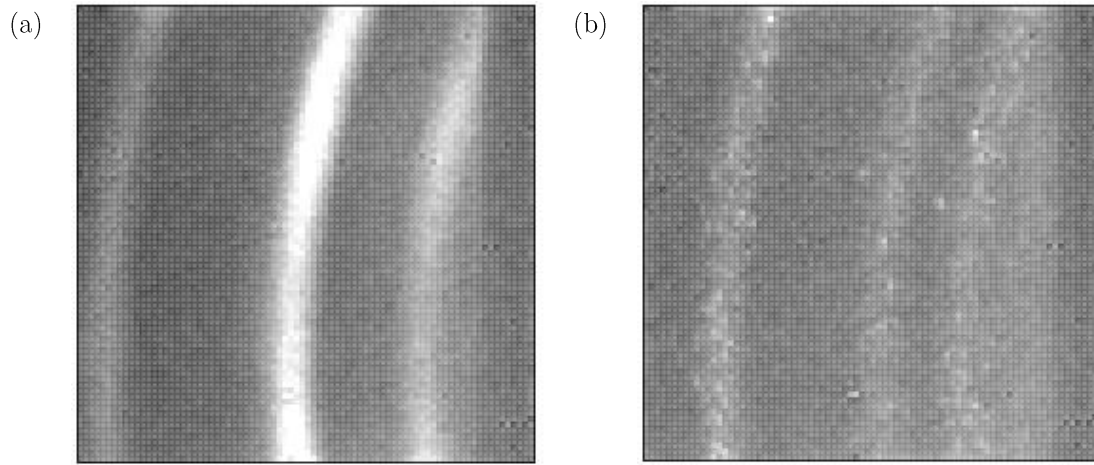


Figure 8.19 Angular dispersive images acquired from the HEXITEC detector using a pencil beam geometry in conjunction with the Mo Source. (a) 1.30 mm Al (b) 1.53 mm Al_2O_3

AD-FCG was investigated at low energy (Mo) employing the $\varphi_m = 5.29^\circ$ annular collimator, to prevent the primary annular beam impinging on the larger area of the HEXITEC detector window. Samples of 1.53 mm Al_2O_3 and 0.10 mm CaCO_3 were placed in the beam at $D_S = 135$ mm. Figure 8.20 and Figure 8.21 present the obtained diffraction patterns from translating the detector along the z -axis in 1 mm increments between $D = 175$ mm and $D = 204$ mm. Measuring the intensity of the central pixels of each image, the diffraction profile of each sample can be determined, Figure 8.22.

Multiplex sampling was then considered, observing the 1.53 mm Al_2O_3 and 0.10 mm CaCO_3 samples simultaneously, placed at $D_S = 135$ mm and $D_S = 155$ mm respectively. The detector was translated in 1 mm increments over $D = 180$ mm and $D = 214$ mm. The resulting images are presented in Figure 8.23. Subsequent analysis, Figure 8.24 indicates the formation of two condensation foci; one from Al_2O_3 and one from CaCO_3 .

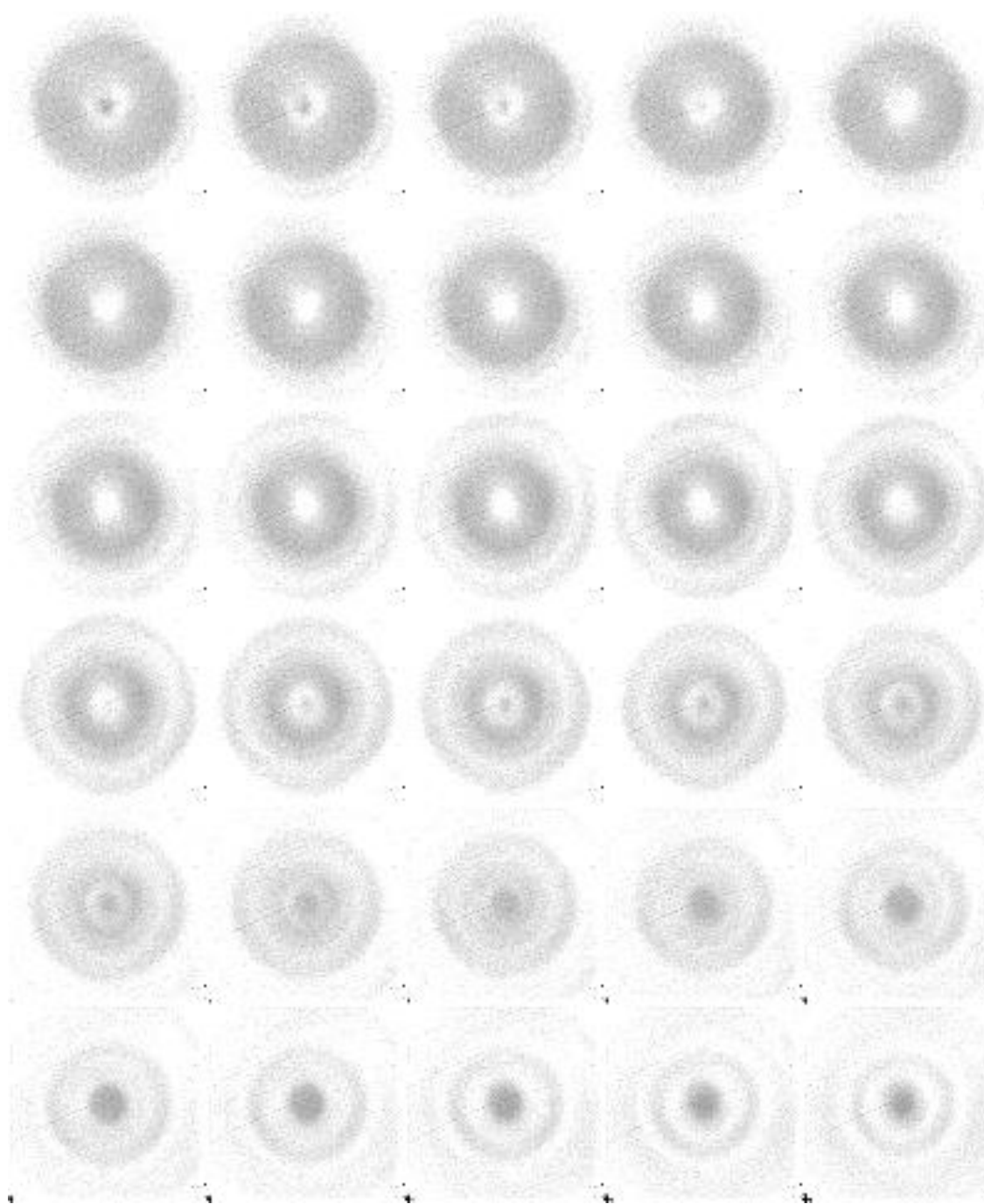


Figure 8.20 Sequence of diffraction patterns obtained from 1.53 mm Al₂O₃ employing Mo source and HEXITEC detector, incrementally translated between $D = 175$ mm to $D = 204$ mm in 1 mm increments.

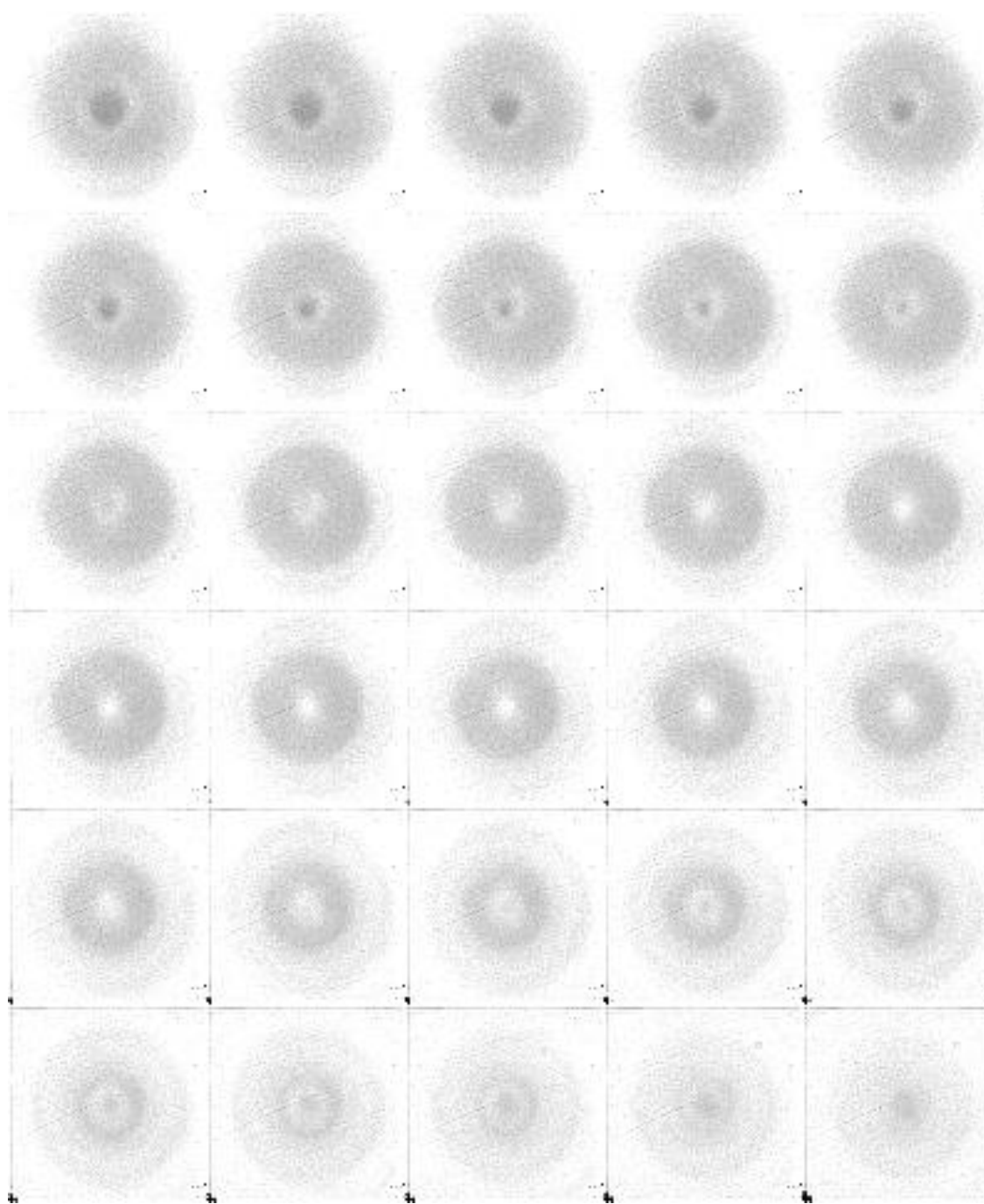


Figure 8.21 Sequence of diffraction patterns obtained from 0.10 mm CaCO_3 employing Mo source and HEXITEC detector, incrementally translated between $D = 175$ mm to $D = 204$ mm in 1 mm increments.

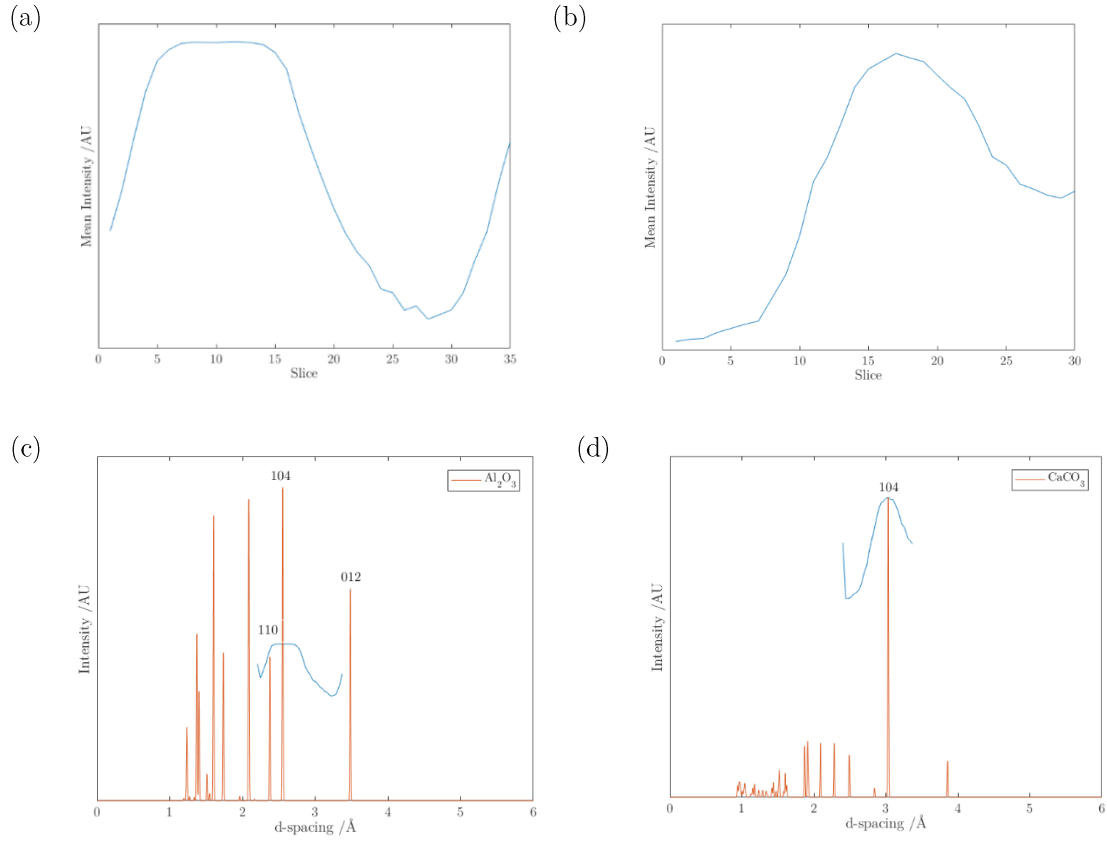


Figure 8.22 Intensity profiles obtained from integration of the centre of each image presented in (a) Al_2O_3 , Figure 8.20 and (b) CaCO_3 Figure 8.21. (c) and (d) show the resultant diffraction patterns.

As previously demonstrated when introducing AD-FCG, §8.2, the observation of small d -spacings is inhibited by the geometry of the system. Additionally, the HEXITEC noticeably does not possess the same angular resolution as the previously employed PIXIS, this is due to the larger detection window but comprising of far fewer pixels. The HEXITEC operates with 80×80 pixels over 25 mm^2 whereas the PIXIS uses 1024×1024 over an active area of 176.89 mm^2 , the difference in pixel size is ~ 24 times.

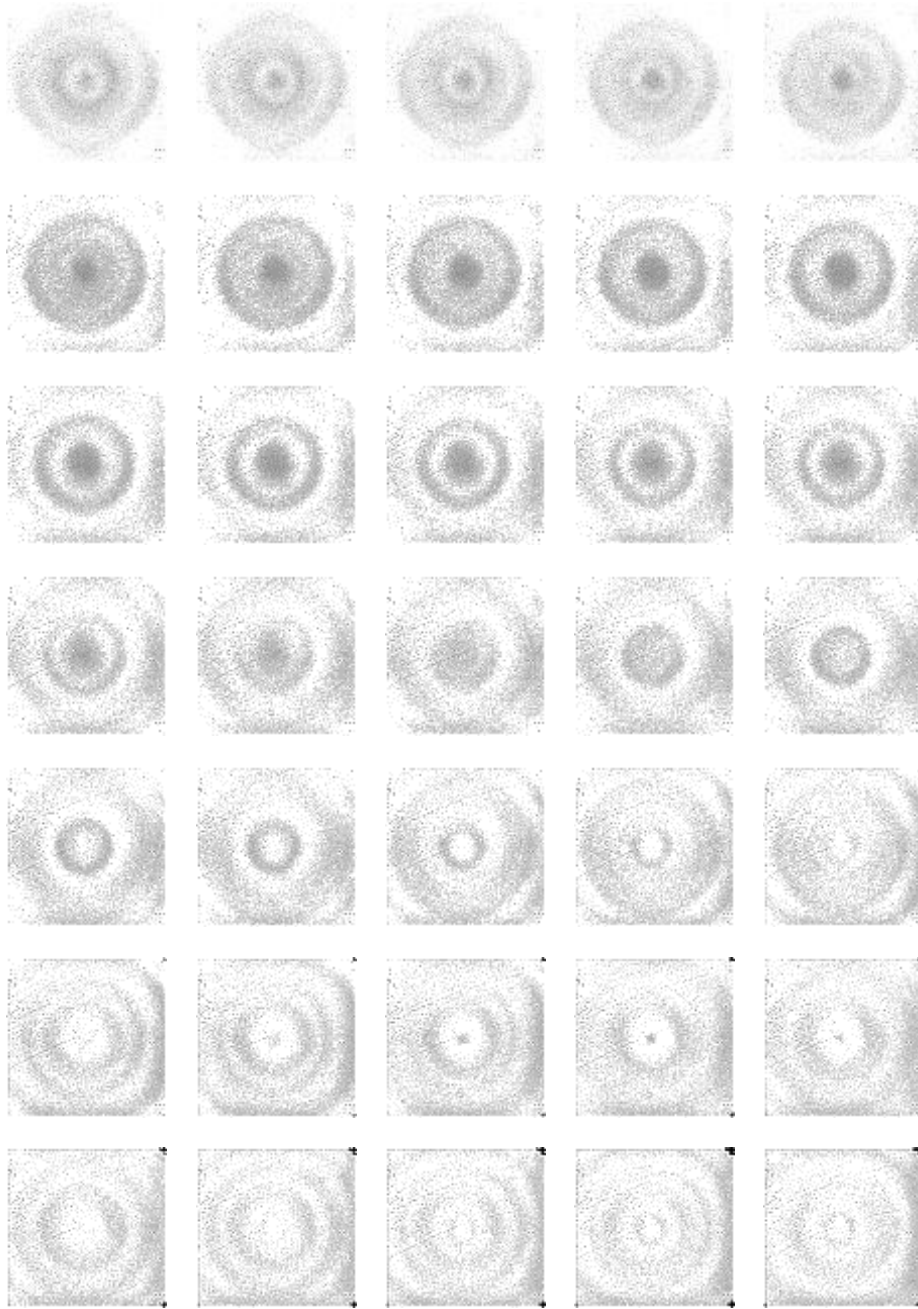


Figure 8.23 AD images obtained from analysing Al_2O_3 and CaCO_3 simultaneously, employing the Mo source and HEXITEC detector translated in 1 mm increments over $D = 180$ mm to $D = 214$ mm.

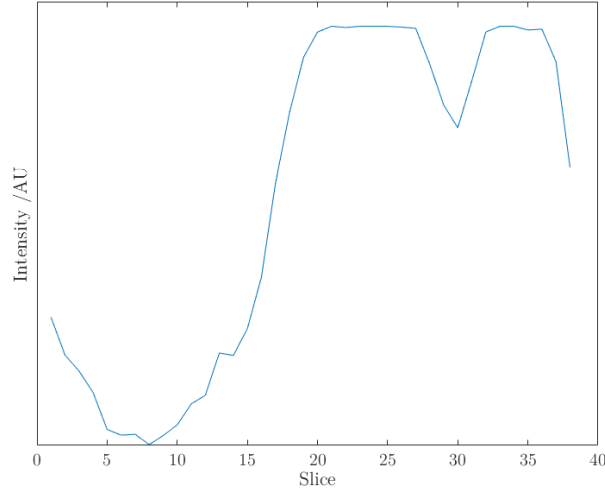


Figure 8.24 Intensity profile plot through the centre of the images presented in Figure 8.23, simultaneously analysing Al_2O_3 and CaCO_3 .

The functionality of the HEXITEC detector was examined by conducting high energy ED-FCG experiments. A 0.5 mm Fe sample placed at $D_S = 138$ mm in an annular beam of $\varphi_m = 2.5^\circ$ was analysed with increasing exposure times. A 120 s exposure was initially obtained, and subsequent exposures were increased by 120 s, until a maximum 600 s exposure was obtained. The resultant diffraction profiles are displayed in Figure 8.25, with corresponding normalised diffraction profiles presented in Figure 8.26, clearly demonstrating the increased SNR associated with longer exposure time, indicated by the smoother diffraction profile.

To gain an understand of how increasing the exposure time affects the level of noise within the diffraction pattern, the noise was measured as described in §6.5.3.

The best fit model was subtracted from the normalised data to obtain the residuals from the best fit. The difference between the minimum and maximum residual for each exposure time was determined, the results of which are seen in Figure 8.27. As expected, Figure 8.27 indicates that there is a decrease in noise as the exposure time is increased, modelled by the exponential function $y = 0.2646e^{-0.01x}$, where

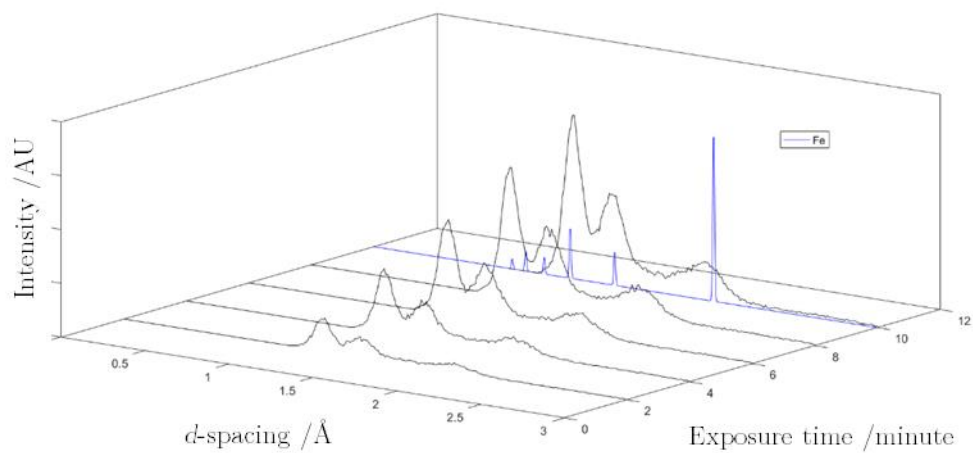


Figure 8.25 Diffraction profiles of 0.5 mm Fe, with increasing exposure time obtained using the HEXITEC detector.

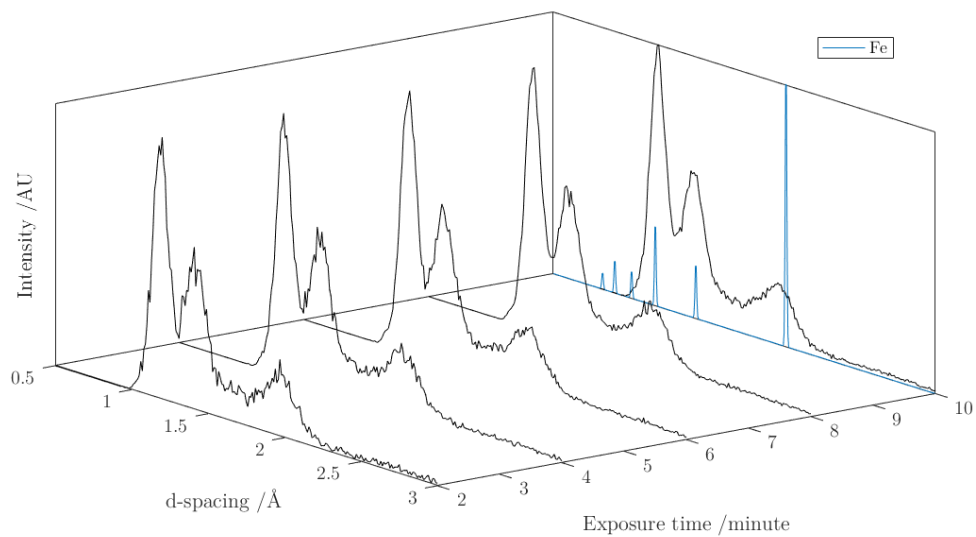


Figure 8.26 Normalised diffraction profiles of 0.5 mm Fe, with increasing exposure time obtained using the HEXITEC detector.

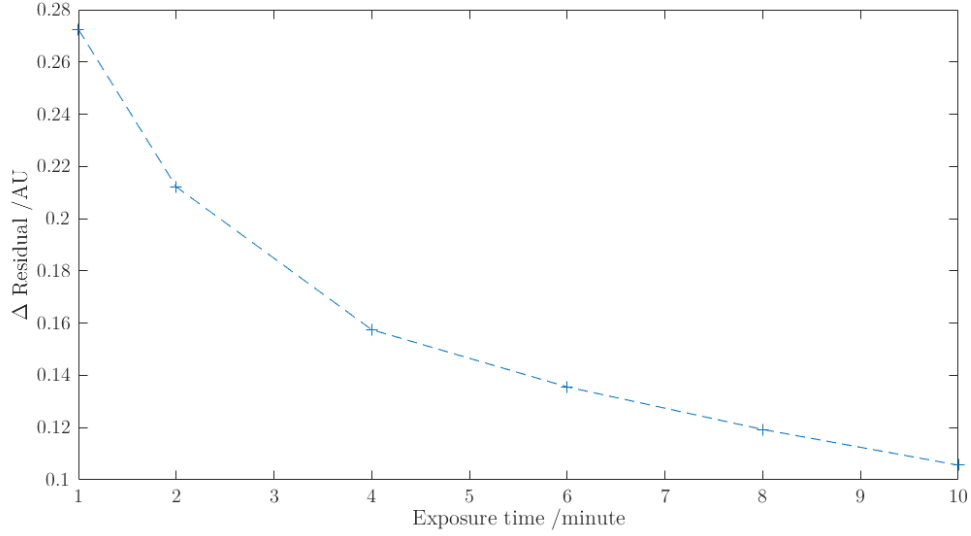


Figure 8.27 Plot demonstrating the difference in residuals from increasing the exposure time, analysing a sample of 0.5 mm sheet of Fe from Figure 8.26.

y is the measured range of the calculated residuals i.e. the measure of noise and x is the exposure time. An exponential model was fitted as the magnitude of noise will never reach zero and can never be negative i.e. $y > 0$.

8.5.1 Depth Awareness

As described in §6.4.6.1, a post-sample pin-hole aperture, detailed in §6.2.1.2, was employed at high energy using the W source in conjunction with the HEXITEC detector, to not only use the material identification capabilities of ED-FCG but to additionally introduce depth awareness utilising the position sensitive capabilities. The depth perception allows the origin of scatter to be determined but also provides a method to isolate the scatter from polycrystalline materials that are otherwise lost in high intensity diffraction from metal objects.

The pin-hole aperture is placed post-sample along the symmetry axis, prior to the detector enabling focusing of the scattered photons through the aperture, onto the detector plane, illustrated in Figure 8.28.

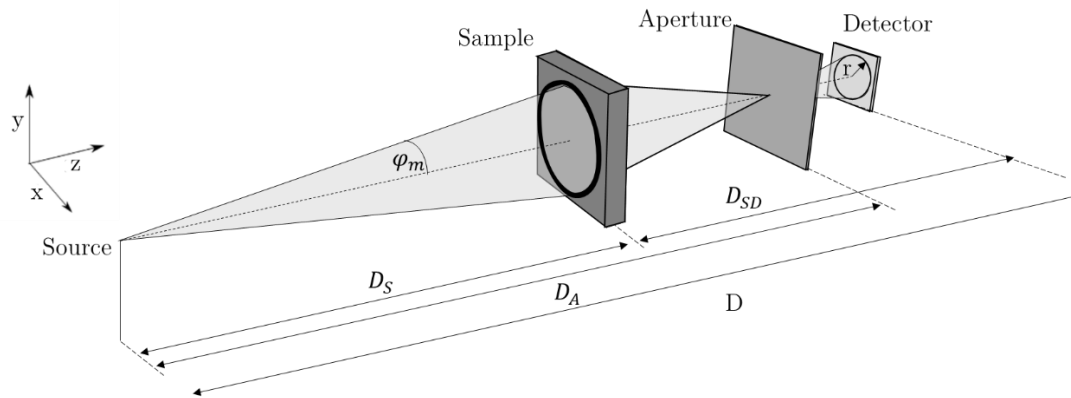


Figure 8.28 Diagram illustrating the geometry of the system, comprising of a conical shaped beam incident on a sample at a distance D_s from the source, proceeded by a pin-hole aperture and a HEXITEC detector at distances D_A and D , respectively, from the source.

Figure 8.29 provides two example images obtained from the HEXITEC detector with the addition of the pin-hole aperture, with the source-to-detector position fixed, D . Due to the focusing of the diffracted photons, a hollow conical beam is generated for each sample, creating a ring footprint within the detector plane. Figure 8.29 (left) displays the result when a 15 mm deep petri dish filled with powdered Al_2O_3 , is placed 149.3 mm away from the source and Figure 8.29 (right) 206.9 mm away from the source, so the sample is simply translated along the primary axis. The inner ring in Figure 8.29 (right) is due to diffraction originating from a metal bar within the system used as a sample shelf so can be disregarded.

The difference in source-to-sample distance, D_s , initially results in a larger footprint impinging on the sample and thus generates a difference in the radius of the resultant focused diffraction beam within the sample plane. However, the radius of the diffracted beam within the detector planes relates to the sample-to-aperture distance.

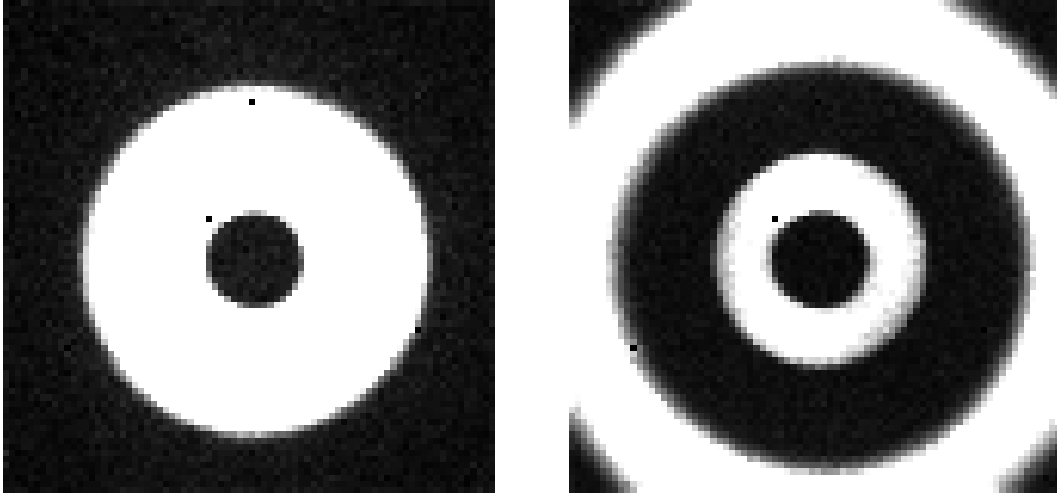


Figure 8.29 Images obtained from the HEXITEC detector for a sample of 15 mm Al_2O_3 when the sample is placed at a) 149.3 mm away from the source and b) 206.9 mm away from the source.

The closer the sample to the pin-hole aperture, the larger the resulting diffraction condensation ring in the detector plane, this is illustrated in Figure 6.17, §6.4.6.1.

Obtained images, like those in Figure 8.29, can be converted into a 2D map evaluating the origin of the scatter within the inspection volume and the d -spacings originating from each voxel, thus is called (d, z) space. This is achieved by using a combination of the position sensitive pixels and ED capabilities allowed by the HEXITEC detector.

Each pixel of the detector is associated with a sample position, indicated by the position of the pin-hole aperture in relation to the detector plane. The smaller the pin-hole aperture-to-detector, D_A , distance the smaller the obtained diffraction condensation ring radii. This can be seen analytically by rearranging Equation (6.15) making the relationship between radius and aperture position is easier to comprehend:

$$r = \frac{D_S \tan \varphi_m}{D_A - D_S} (D - D_A)$$

When the opening angle φ_m , sample position, D_S , and detector position, D , are all fixed, the radius of the resultant diffraction condensation ring depends on the

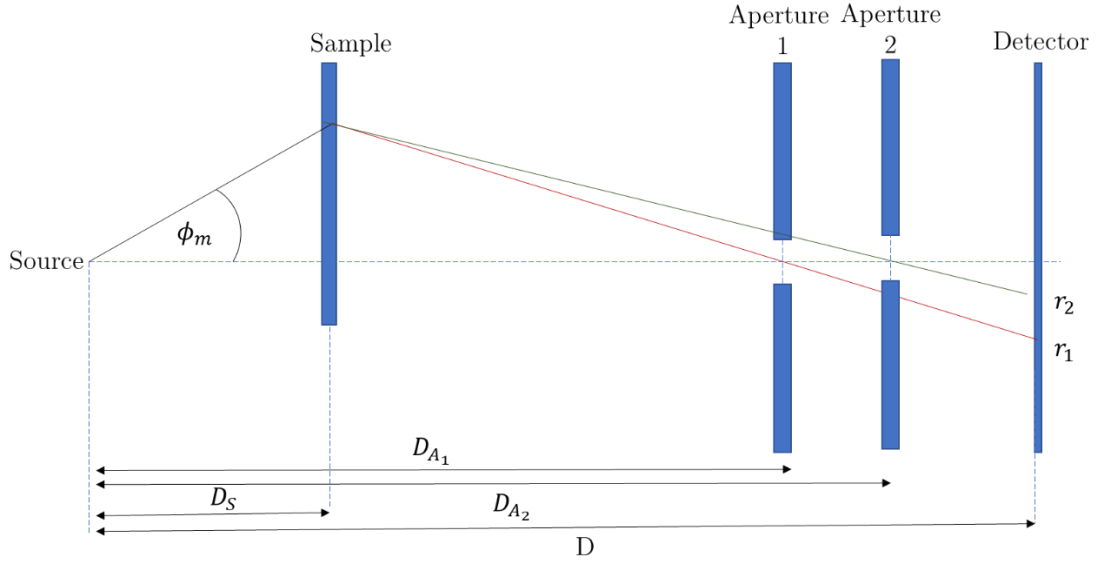


Figure 8.30 Schematic demonstrating how the position of the aperture, D_A , in relation to the sample ($D_A - D_S$) and the detector ($D - D_A$) affects the radius of the diffraction condensation ring within the detector plane.

aperture position, D_A . These are illustrated in Figure 8.30, where two aperture positions, D_{A_1} and D_{A_2} are presented with their corresponding resultant radii r_1 and r_2 . Using this relationship, each pixel can be associated with a sample position when the aperture-to-detector distance, D_A , is known.

The ED-function of the HEXITEC detector allows each one of these pixels, now associated with a voxel within the inspection volume, to provide an energy spectrum corresponding to the material occupying that volume in space.

MATLAB was used to convert the obtained HEXITEC images to (d, z) maps, examples of which are shown in Figure 8.31 (top) where powdered samples of (a) CaCO_3 and (b) Al_2O_3 were placed in petri dishes (shown in §6.3.1) $D_S = 150$ mm away from annular collimated W source with the detector placed at $D = 551.3$ mm and pin-hole aperture at $D_A = 376.66$ mm. Data from each exposure was subject to a background subtraction and Savitzky-Golay filtering using built-in *MATLAB* functions. Each horizontal row of the (d, z) map corresponds to an integrated conic

(a)

(b)

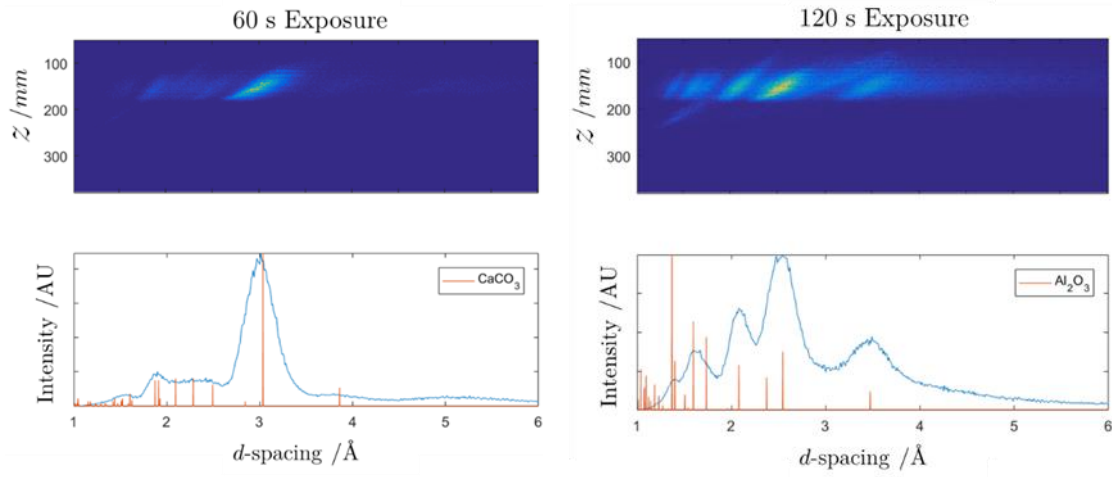


Figure 8.31 2D maps of (d,z) space from (a) calcium carbonate and (b) aluminium oxide collected using a HEXITEC detector in conjunction with an annular collimator and corresponding diffraction profiles.

section through an annular gauge volume of the obtained HEXITEC image. The material phase signature, d -spacings, for each sample are contained within the vertical channels of the (d,z) map.

The material phase signatures, or d -spacing values, can be represented as a conventional diffraction profile, Figure 8.31 (bottom), by using Equation (6.17), §6.4.6.1, where obtained ED-FCG patterns from each pixel are translated into d -spacings. A composite of d -spacing contributions calculated from successive conic sections through an annular gauge volume can be presented as a single diffraction profile as demonstrated with the bottom images within Figure 8.31 (a) CaCO_3 and (b) Al_2O_3 , presented with overlaid reference profiles. No *a priori* sample position information was used in the production of the diffraction patterns which exhibit good correspondence with the standard peak positions.

As discussed in §6.4.6.1, measuring the radius, r , on the detector, and knowing the geometry of the system (D, D_A, φ_m) , illustrated in Figure 8.28, the source-to-sample mid plane, D_S , can be determined by using Equation (6.15). The movement within the (d,z) map was demonstrated by traversing a 15 mm sample of Al_2O_3 along the z -axis, in 9.6 mm increments, resultant (d,z) maps, with corresponding diffraction profiles are shown in Figure 8.32.

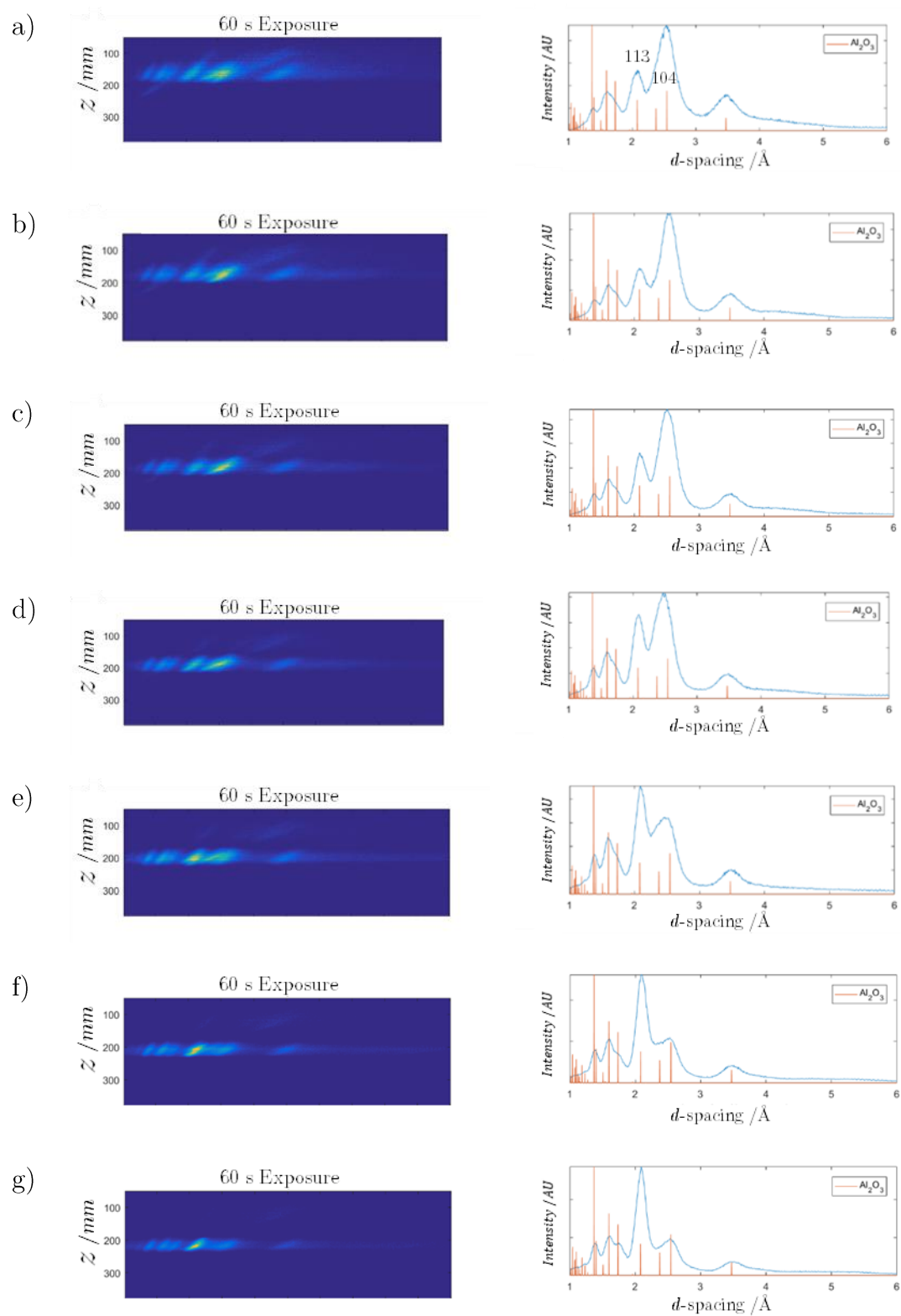


Figure 8.32 Resultant (d, z) maps (left) from traversing a 15 mm sample of Al_2O_3 along the z -axis, varying D_S in increments of 9.6 mm and the corresponding diffraction profiles.

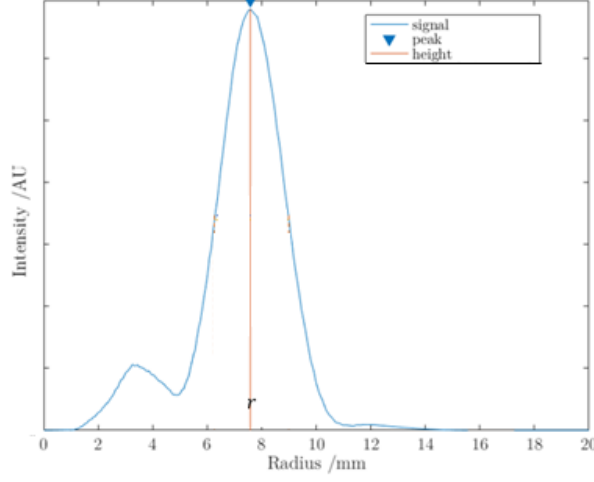


Figure 8.33 Radial intensity plot of resultant scatter from Al_2O_3 , where $D_S = 185.25$ mm with annotations of measurements obtained to analyse sample position.

Analysing the (d, z) , maps in Figure 8.32 the origin of scatter can be seen to change in each of the images, with the bright spots, representing the d -spacings of the material under inspection shifting downward within the map indicating a larger D_S i.e. the sample moved further away from the source.

The relative intensities of the peaks within the diffraction profile can be seen to vary depending on the samples position within the system, for example peaks 104 and 113, labelled on the diffraction pattern in Figure 8.32 (a). This variation is due to the change in the angle at which the diffracted beams from the sample form with the aperture pin-hole at the varying sample positions. At smaller sample-to-aperture distances ($D_A - D_S$ is smaller) the diffraction angle, 2θ , fixed in ED-FCG, is larger. At larger 2θ 's, diffracted beams have a longer wavelength, following Braggs Law, Equation (3.2), therefore the obtained diffraction is dependent on the position of the sample in relation to the pin-hole aperture.

Table 8.2 Calculated D_S values from measurement of radii within detector plane.

Source-to-sample mid-plane distance /mm (D_S)	Recovered source-to-sample mid-plane distance /mm		Source-to-sample mid-plane distance /mm (D_S)	Recovered source-to-sample mid-plane distance /mm Fe
	CaCO ₃	Al ₂ O ₃		
157.25	161.00 ± 3.9	165.00 ± 3.7	149.50	151.00 ± 4.2
164.25	165.00 ± 3.7	167.00 ± 3.6	156.50	158.08 ± 4.0
171.25	173.00 ± 3.4	173.00 ± 3.4	163.50	165.00 ± 3.7
178.25	179.00 ± 3.2	178.00 ± 3.2	170.50	171.00 ± 3.5
185.25	185.00 ± 3.0	184.00 ± 3.0	177.50	181.00 ± 3.1
192.25	192.00 ± 2.8	192.00 ± 2.8	184.50	188.00 ± 2.9

To evaluate the precision of calculating the sample position from this technique three samples, CaCO₃, Al₂O₃ (both 15 mm filled petri dishes) and Fe (1 mm sheet), were employed. Each sample was individually centrally positioned within the incident beam and translated along the z -axis in increments of 7 mm. Obtained images, like those displayed in Figure 8.29, were azimuthally integrated to produce radial intensity plots, an example is shown in Figure 8.33. The maximum peak value, indicated by the blue arrow, is the radius value of the resultant scatter distribution within the detector plane.

The measured radii were then converted into D_S using Equation (6.15), where $\varphi_m = 2.5^\circ$, $D_A = 376.66$ mm and $D = 551.25$ mm. The measured radii are shown in Table 8.2. Error propagation, as conducted with spiral and linear encoder in §7.2.2, was used to calculate the uncertainty in measurement of D_S , using Equation (8.1).

$$\sigma D_S = \left[\left(\frac{\partial D_S}{\partial r} \sigma r \right)^2 + \left(\frac{\partial D_S}{\partial D} \sigma D \right)^2 + \left(\frac{\partial D_S}{\partial D_A} \sigma D_A \right)^2 + \left(\frac{\partial D_S}{\partial \varphi_m} \sigma \varphi_m \right)^2 \right]^{1/2} \quad (8.1)$$

where,

$$\frac{\partial D_S}{\partial r} = \frac{D_A}{D - D_A \tan \varphi_m} \frac{D - D_A \tan \varphi_m}{(D - D_A \tan \varphi_m + r)^2}$$

$$\frac{\partial D_S}{\partial D_A} = \frac{r}{D - D_A \tan \varphi_m} \frac{D \tan \varphi_m + r}{(D - D_A \tan \varphi_m + r)^2}$$

$$\frac{\partial D_S}{\partial D} = - \frac{D_A r \tan \varphi_m}{(D - D_A \tan \varphi_m + r)^2}$$

$$\frac{\partial D_S}{\partial \varphi} = \frac{D_A r}{D - D_A \tan \varphi_m} \frac{D - D_A \sec^2 \varphi_m}{(D - D_A \tan \varphi_m + r)^2}$$

The results in Table 8.2 are presented in Figure 8.34 (CaCO_3), Figure 8.35 (Fe) and Figure 8.36 (Al_2O_3). $y = x$ is included to clearly illustrate where the sample location should ideally equal the recovered position. Table 8.2 and Figure 8.33, Figure 8.34 and Figure 8.35 illustrate the respective graphs, as the source-to-sample distance, D_S , increases, the precision of measurement increases, indicated by the decrease in the magnitude of error observed.

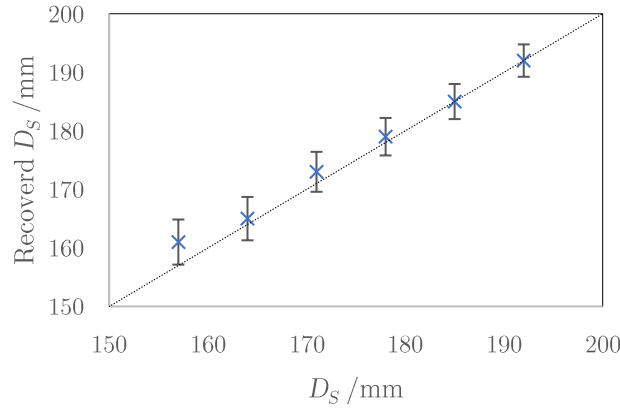


Figure 8.34 Calculated D_S values for 15 mm sample of CaCO_3 translated along the primary axis in increments of 7 mm.

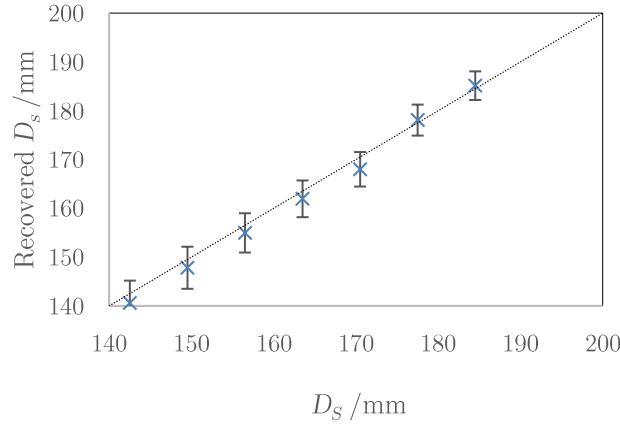


Figure 8.35 Calculated D_S values for 1 mm sample of Fe translated along the primary axis in increments of 7 mm.

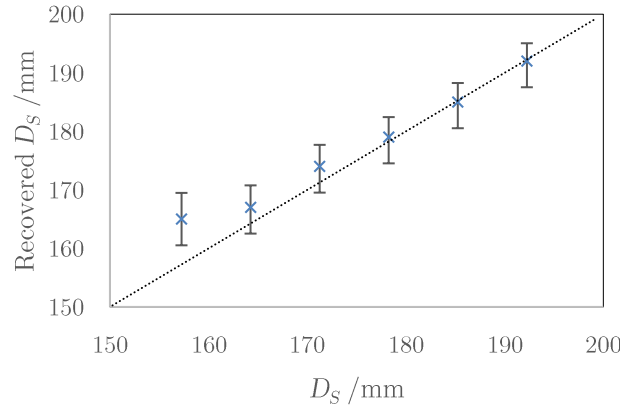


Figure 8.36 Calculated D_S values for 15 mm sample of Al_2O_3 translated along the primary axis in increments of 7 mm.

The determined recovered sample position, D_S , shows good correspondence with known sample location at all sample positions. The recovered position is most precise, and closest to the actual value, when the sample-to-detector distance ($D - D_S$) is minimum i.e. D_S is large.

Multiplex sampling was investigated, involving multiple samples simultaneously in the primary beam at spatially separated positions along the z -axis. Initially a single CaCO_3 filled petri dish with a 1 mm sheet of Al was placed in the beam CaCO_3 at

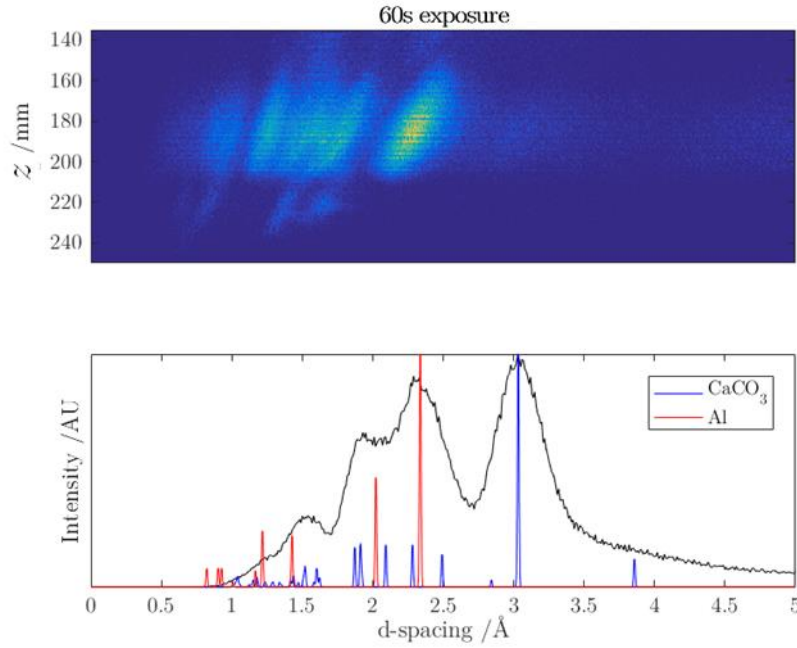


Figure 8.37 (d,z) map from spatially separated 15 mm samples of CaCO_3 and 1 mm Al placed at $D_S = 180$ mm and $D_S = 220$ mm, respectively, with the respective diffraction profile.

$D_S = 180$ mm and Al at $D_S = 220$ mm. The recovered (d,z) map is presented in Figure 8.37 with the resulting diffraction pattern from summation of the d -space values though all of the observable z -space.

Figure 8.37 is composed of a combination of scatter originating from both CaCO_3 and Al, integrating select conic sections through an annular gauge volume, i.e. summing a select number of rows within the (d,z) map can produce individual diffraction patterns of the different materials within the inspection volume, presented in Figure 8.38.

Observing 10 mm sections throughout the inspection volume can see the CaCO_3 profile at $D_S = 180$ mm morph into the Al profile, presented in Figure 8.39, with the diffraction profiles for the intermediate D_S values. Analysing Figure 8.39 the change in intensity over the various sections can also be seen, with a decrease in intensity as the scattering from the CaCO_3 is excluded the further away the samples' central plane from the integrated section.

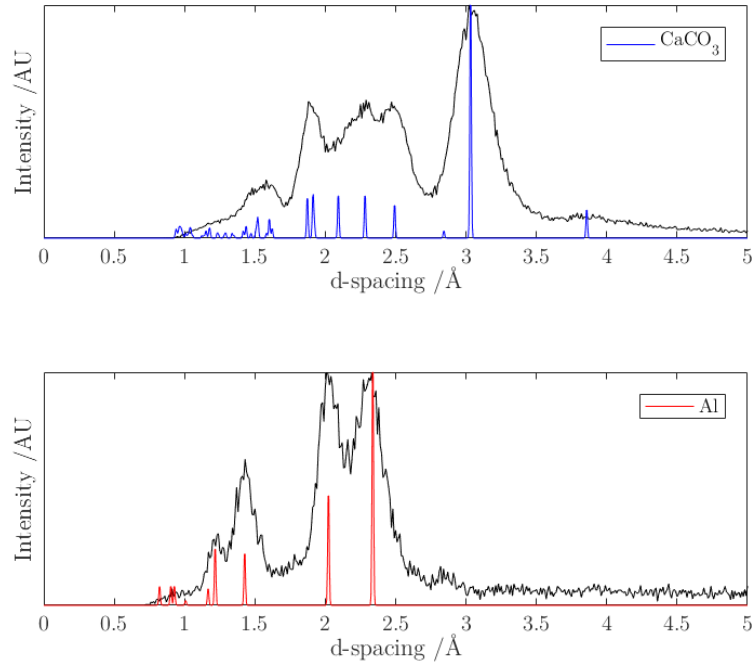


Figure 8.38 Diffraction profiles obtained from summation of 10 mm of z -space from the (d, z) map in Figure 8.37 centred around $D_S = 180$ mm for CaCO_3 and $D_S = 220$ mm for Al.

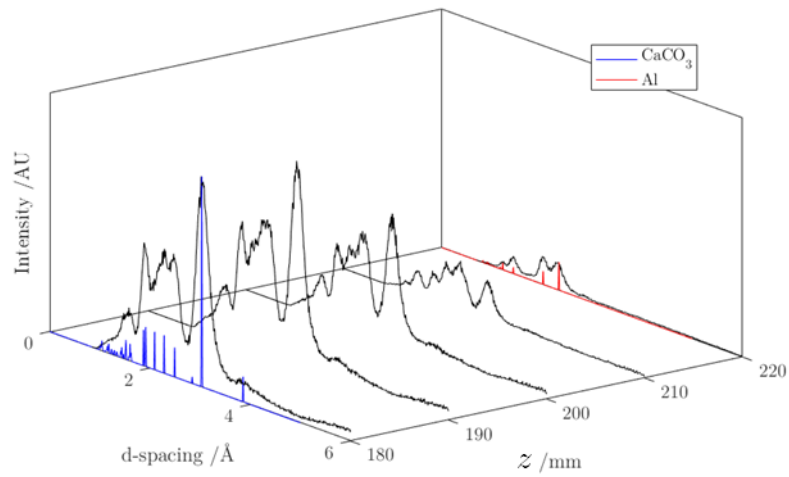


Figure 8.39 3D plot of integrated 10 mm sections from interrogation volume containing 15 mm CaCO_3 sample at $D_S = 180$ mm and Al at $D_S = 220$ mm.

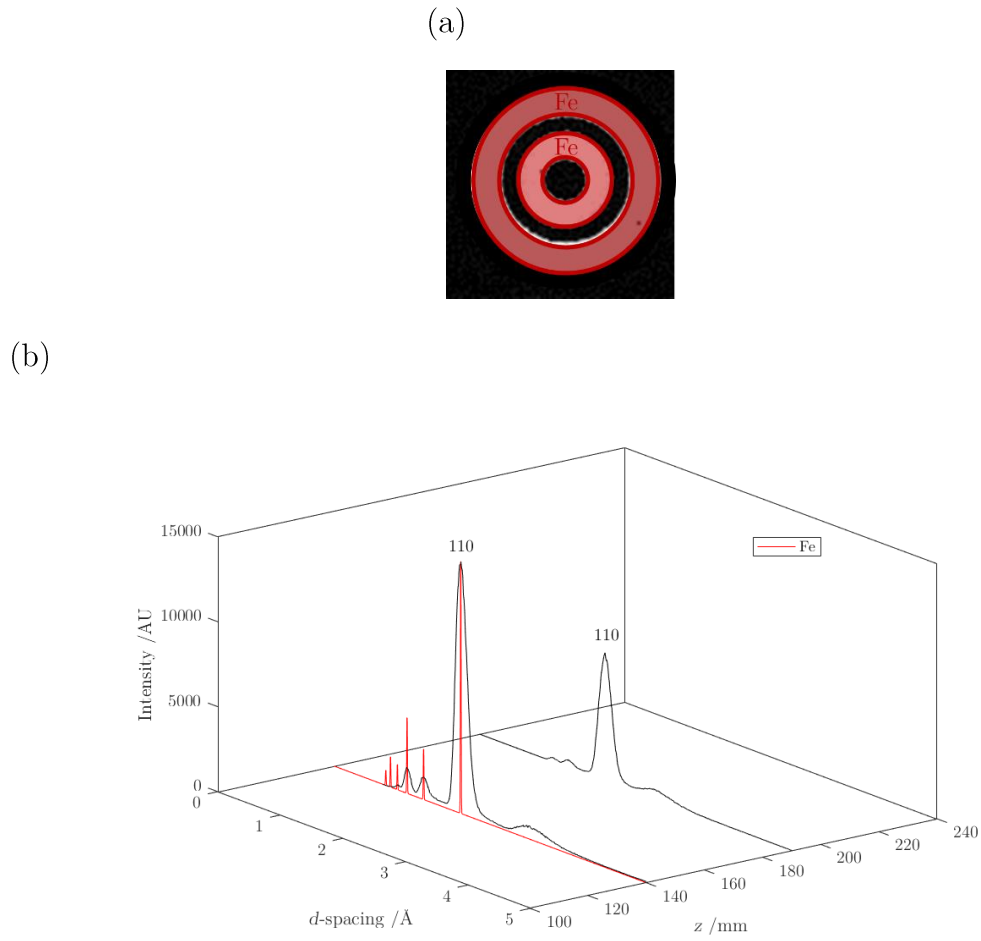


Figure 8.40 (a) HEXITEC image, presenting two conic gauge volumes from the two samples of Fe, placed in the annular beam path. Torus shaped colours overlays indicate the resultant scatter from each of the samples. (b) 3D plot of the resultant diffraction profiles from integration of each of the conic sections identified in (a).

An empty box was simulated with two sheets 2 mm sheets of Fe, separated by 50 mm. The obtained HEXITEC image is shown in Figure 8.40, with the corresponding diffraction profiles from integration of the conic sections associated with each of the Fe samples.

The difference in intensity between the two plates could be due to the change in angle at which the diffracted beams from the sample form with the aperture pin hole at the varying sample positions, as with the variation in relative peak intensity shown in Figure 8.32.

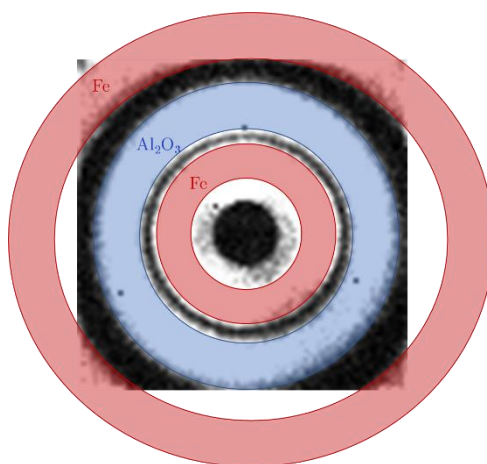


Figure 8.41 Obtained HEXITEC image, presenting the conic gauge volumes from the three samples - Fe, Al_2O_3 and Fe - placed in the annular beam path. Torus shaped coloured overlays identify which conic section originates from which sample and corresponds to reference profile colours used in Figure 8.43.

The number of samples was increased to model walls of a metal container, containing an explosive simulant, Al_2O_3 . Two samples of 1 mm Fe were placed either side of a petri dish filled with Al_2O_3 , spatially separated by 50 mm (between the mid-plane of each sample). The resultant HEXITEC image from a 60 second exposure is presented in Figure 8.41.

The HEXITEC image was integrated to form the (d,z) map, as previously discussed, presented in Figure 8.42 (top), as clearly shown the resultant scatter from three spatially separated samples, separated across several z rows. The summation of all the obtained scatter from the sample volume was converted into the resultant diffraction profile seen in Figure 8.42 (bottom). As with the two sample example above, the conic section can be individually integrated to form individual diffraction profiles from each sample, these are shown in the 3D plot of diffraction profiles in Figure 8.43 created selecting 10 mm sections from the (d,z) map.

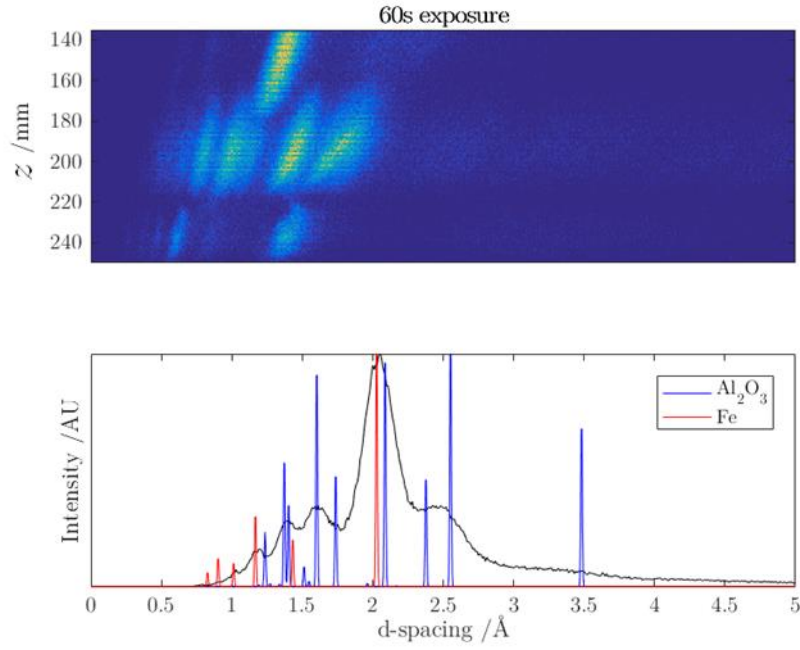


Figure 8.42 (d,z) map from spatially separated samples from the three samples - Fe, Al_2O_3 and Fe - placed in the annular beam path placed at $D_S = 140$ mm, $D_S = 190$ mm and $D_S = 240$ mm respectively, with the respective diffraction profile integrating the full observable interrogation volume.

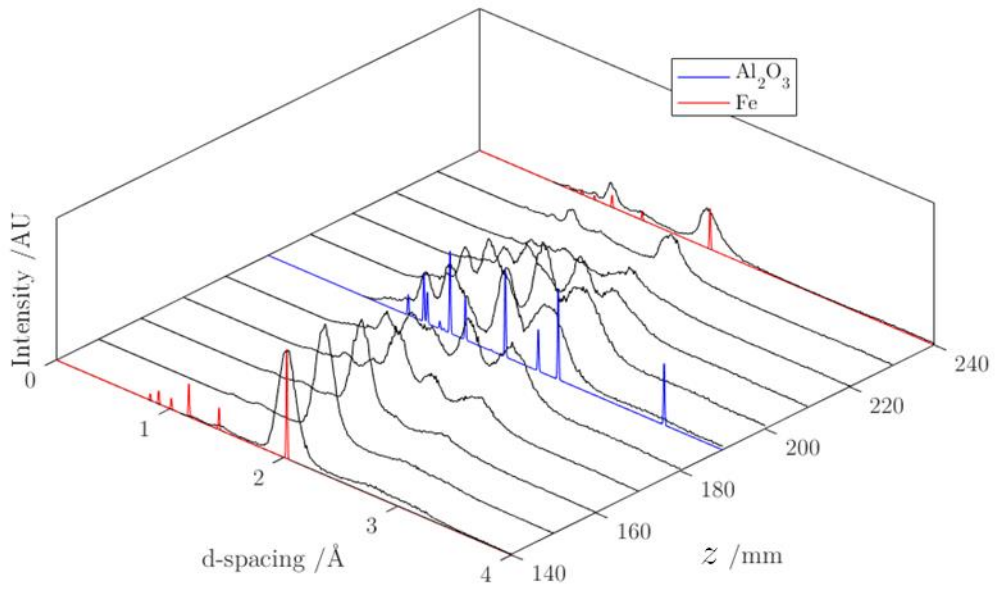


Figure 8.43 3D plot of integrated 10 mm sections from spatially separated samples from the three samples - Fe, Al_2O_3 and Fe - placed in the annular beam path placed at $D_S = 140$ mm, $D_S = 190$ mm and $D_S = 240$ mm respectively, with the respective diffraction profile integrating the full observable interrogation volume.

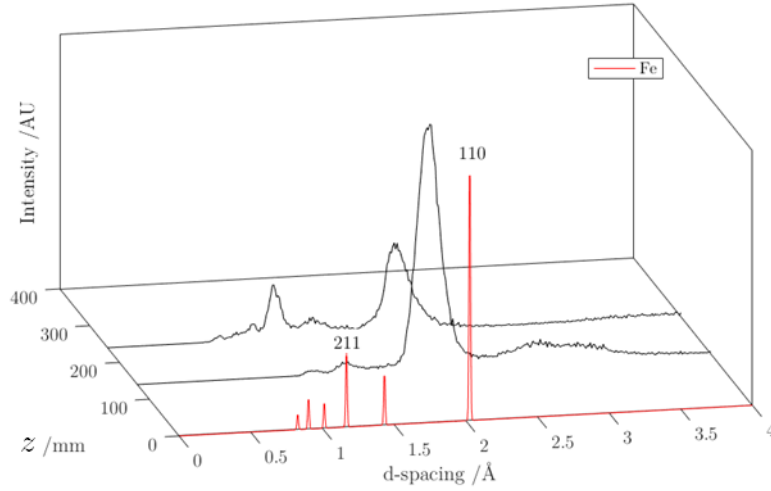


Figure 8.44 Comparison of the two diffraction profiles produced from spatially separated samples of 1 mm Fe at $D_S = 140$ mm and $D_S = 240$ mm.

Comparing the relative peak intensity difference between the first Fe diffraction profile, $D_S = 140$ mm with the second diffraction profile $D_S = 240$ mm, there is a decrease in intensity when observing the 110 peak. In part this could be due to the scatter overlapping with the edges of the detector, but is also a demonstration of the effect shown in Figure 8.40. Inspection of the 211 peak, reveals there is an increase in the peak intensity, indicating the effect demonstrated in Figure 8.32 is again present here, so relative peak intensity cannot be used to aid the identification of the samples present.

The effect of increasing the thickness of the container wall was investigated by increasing the number of Fe sheets surrounding the sample of Al_2O_3 . Fe sheets were centrally placed at $D_S = 150$ mm and $D_S = 230$ mm, with the Al_2O_3 sample consistently placed at $D_S = 190$ mm. Figure 8.45 presents the HEXITEC images from each of the 60 second exposures when increasing the thickness of the Fe sheets. The top left image within Figure 8.45, presents the image from when the sample geometry consisted of single sheets of 0.5 mm Fe surrounding the 15 mm Al_2O_3 sample. Subsequent images incrementally increase the thickness of Fe by 0.5 mm

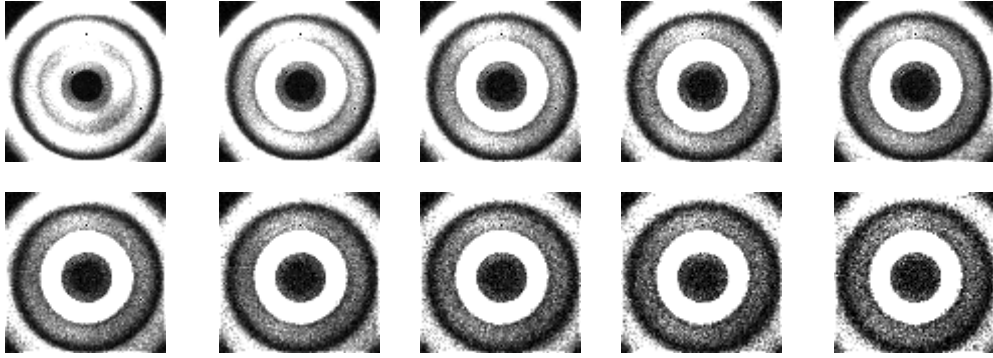


Figure 8.45 Images obtained from the HEXITEC detector when a model containing Al_2O_3 ($D_S = 190$ mm) between two sheets of Fe ($D_S = 150$ mm and $D_S = 230$ mm), the two bright ring of the Fe sheets and a darker ring of the Al_2O_3 in between. The top left is when 0.5 mm of Fe was used on either side, increasing the thickness in increments of 0.5 mm until the bottom right image where 5 mm of Fe was used on either side.

on each side of the Al_2O_3 . Referring back to the previous HEXITEC image containing the same three spatially separated samples, Figure 8.41, the same three conic sections - one for each sample - are clear in each image within Figure 8.45.

The middle conic section within each image of Figure 8.45, corresponding to Al_2O_3 , shown in blue in Figure 8.41, appears to decrease in intensity with each additional sheet of Fe. Isolating 10 mm of z space centrally positioned around 190 mm and converting to produce diffraction profiles of each iteration, results in the diffraction profiles presented in Figure 8.46, where the decrease in intensity can clearly be seen. The maximum intensity of each interaction was determined and compared in Figure 8.47, where a trendline has been fitted to the data modelled by $y = 1170.6e^{-0.502x}$, where y is the maximum intensity of the Al_2O_3 sample and x is the thickness of the Fe container wall.

Using the same data, the effect of the thickness of the container wall on the noise associated with the obtained diffraction pattern of the concealed sample was evaluated. The process of measuring the noise detailed in §6.5.3 and employed previously in §8.5, to investigate the effects of exposure time when observing a single sample with the HEXITEC detector, was used again here to investigate the

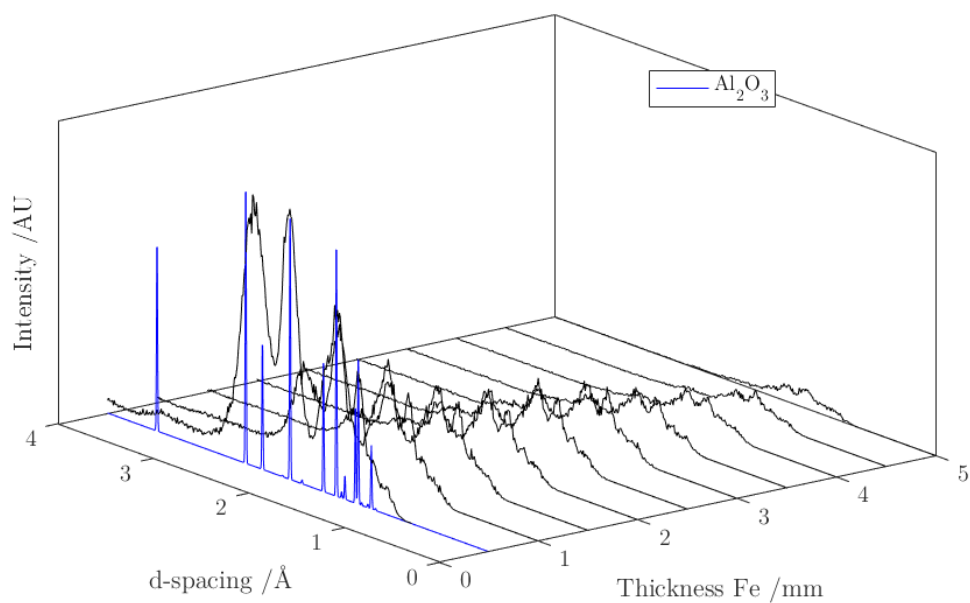


Figure 8.46 3D plot of diffraction profiles obtained from central 10 mm around 190 mm within z space from each image obtained when modelling an increasing thickness Fe container containing centrally positioned Al₂O₃.

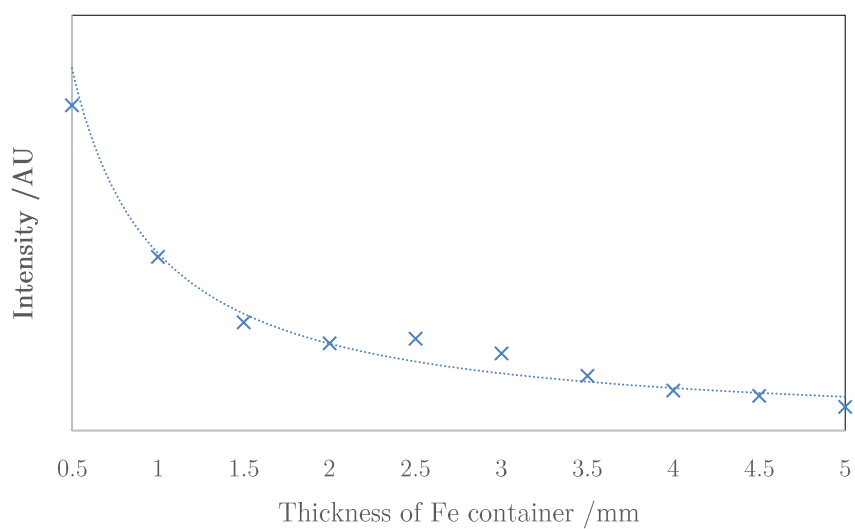


Figure 8.47 Comparison between thickness of the Fe container wall and measured maximum intensity of concealed Al₂O₃ sample.

effect of increasing the thickness of a container wall of the noise of the acquired diffraction pattern from the concealed sample.

As detailed in 6.5.3, the best fit model employed a Gaussian with 5 terms. The resulting residual plot is presented in Figure 8.48, where a logarithmic trendline has been used to model the trend, corresponding to $y = 0.5736 \ln x + 0.7084$, where y is the measure of noise and x is the thickness of the container wall. This trend was anticipated as it will reach a point where the difference between the residuals (Δ residuals) is at a maximum between the normalised profiles.

When a 5 mm thick container was modelled i.e. 10 mm of Fe in total. The two 5 mm Fe samples were placed at $D_S = 150$ mm and $D_S = 230$ mm, with the Al_2O_3 sample placed in the middle at $D_S = 190$ mm and the image was obtained with an exposure of 300 seconds.

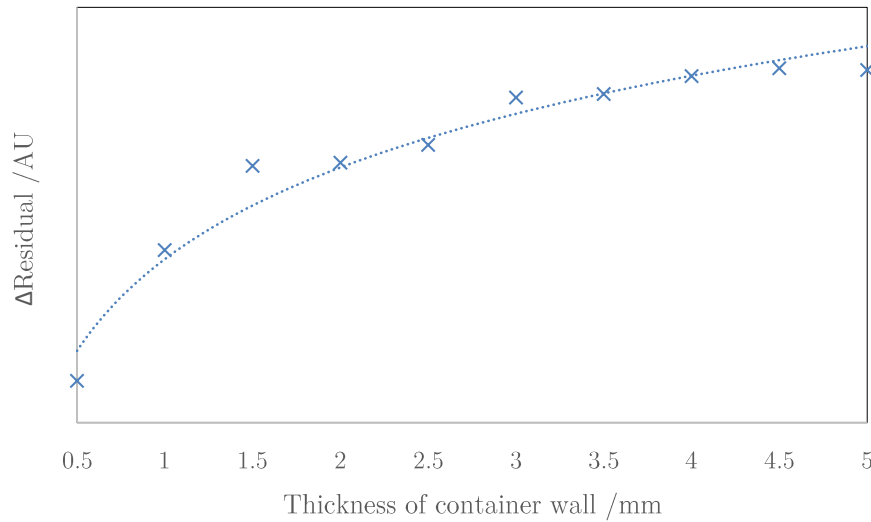


Figure 8.48 Graph produced measuring the difference in residuals from analysing a concealed sample of Al_2O_3 when increasing the thickness of the walls of an Fe container in increments of 0.5 mm.

The corresponding (d,z) map is presented with the corresponding diffraction profile, integrating through the whole gauge volume in Figure 8.49. From the diffraction profile within Figure 8.49, it is clear the diffraction from Al_2O_3 is completely overshadowed from predominant diffraction from the Fe container walls.

A 3D plot was created isolating 10 mm in increments of 10 mm sections through z space, Figure 8.50. Here, the diffraction originating from the Al_2O_3 sample can be seen at $z = 190$ mm, where the scatter originates from. The reduced intensity of the final diffraction profile within Figure 8.50, illustrates that the resultant diffraction overlapping with the edge of the detector window.

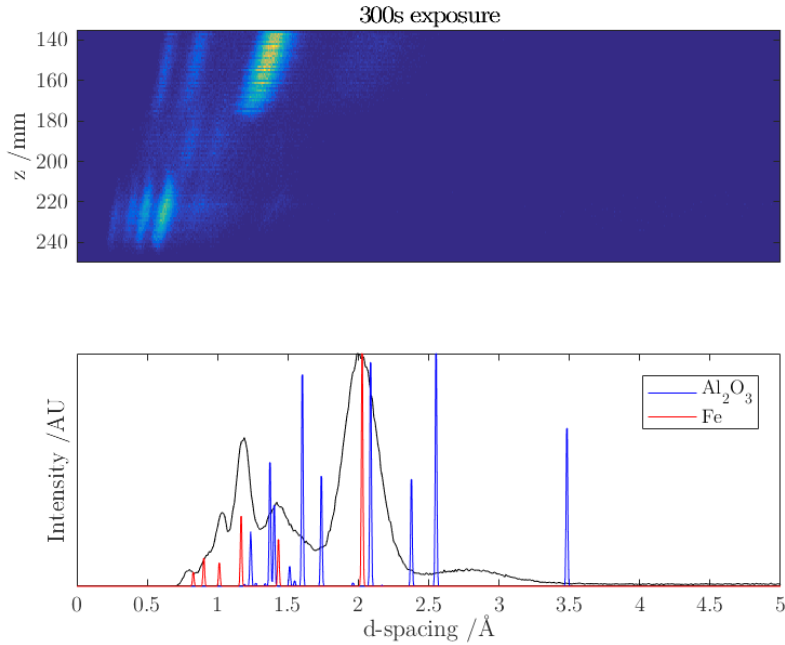


Figure 8.49 (d,z) map and corresponding diffraction profile from gauge volume with Al_2O_3 at $D_S = 190$ mm with two 5 mm Fe samples, modelling container walls placed at $D_S = 150$ mm. and $D_S = 230$ mm with overlaid reference profiles of Al_2O_3 and Fe.

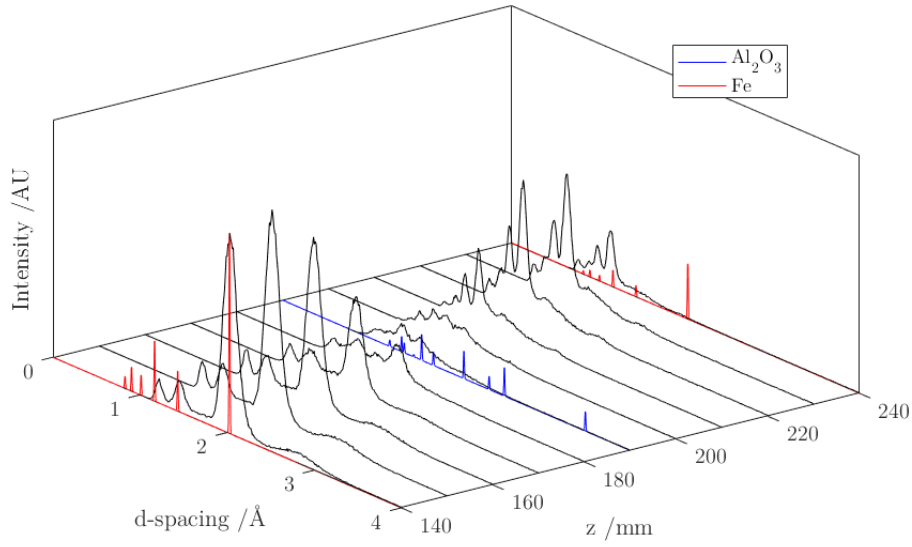


Figure 8.50 3D plot of diffraction profiles analysing 10 mm sections from the gauge volume containing 15 mm Al_2O_3 sample at $D_S = 190$ mm and 5 mm Fe, either side at $D_S = 150$ mm and $D_S = 230$ mm.

The same sample geometry was observed at different exposure times to evaluate the effect of exposure time on the magnitude of noise within the obtained diffraction patterns from the Al_2O_3 sample. The extracted diffraction patterns from integrating the 10 mm volume around the Al_2O_3 samples for each of the exposure times obtained - 60 s, 120 s, 180 s, 240 s and 300 s - are presented Figure 8.51 (top) along with the normalised diffraction profiles Figure 8.51 (bottom).

The noise was measured, as described in §6.5.3, and the results shown in Figure 8.52. The trendline shown is modelled by the exponential equation $y = 0.4073e^{-0.002x}$ where y is equal to the measure of noise and x is the exposure time.

Both functions presented model the magnitude of noise when evaluating the effect of exposure time, the first in §6.4.6 analysing a single sample and the second here analysing exposure time on a concealed sample, follow an exponential decay which is expected; when the exposure time is increased the noise contained within the diffraction profile decreases.

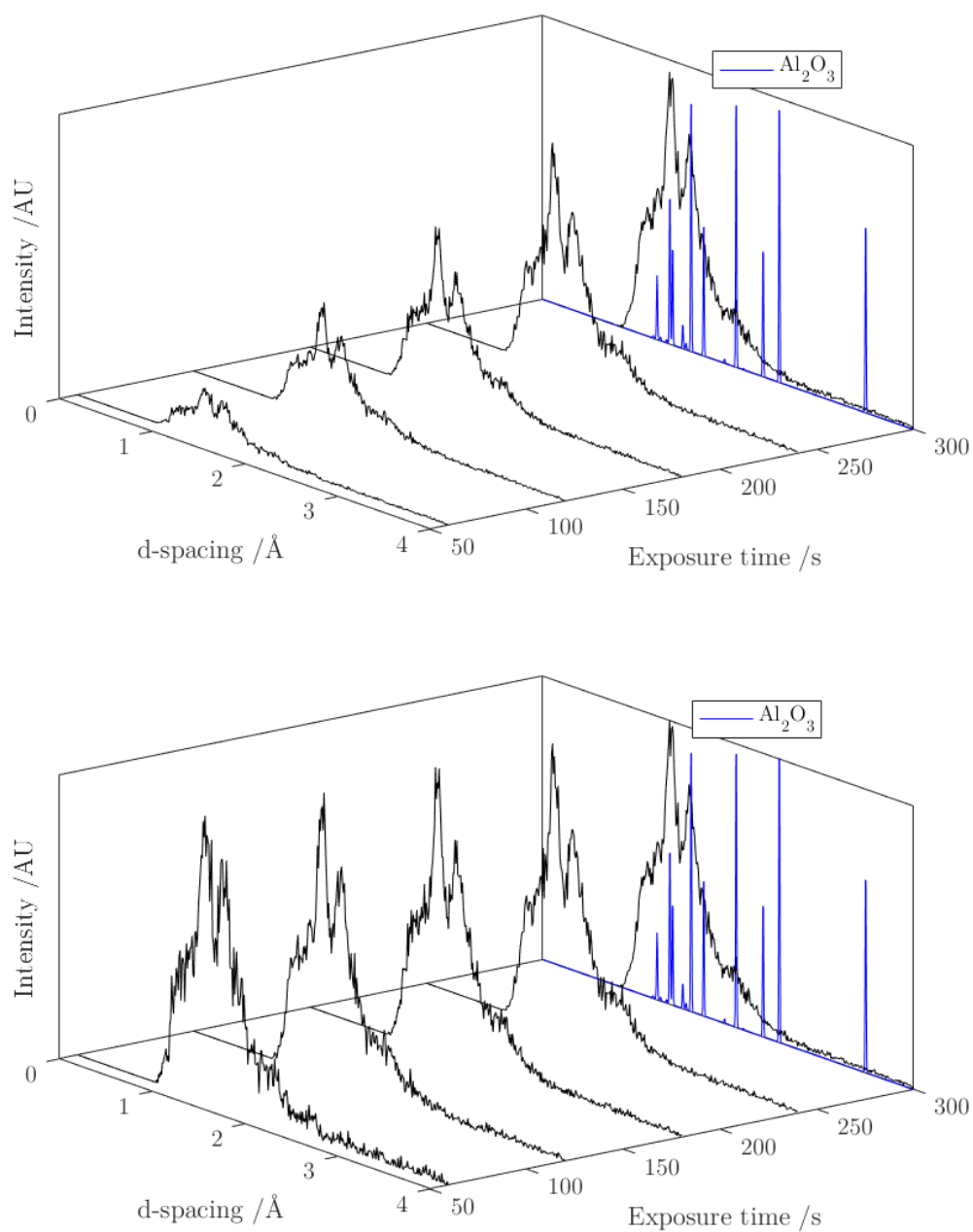


Figure 8.51 Obtained diffraction profile from 10 mm volume around Al_2O_3 sample with increasing exposure times (top) normalised diffraction profiles (bottom).

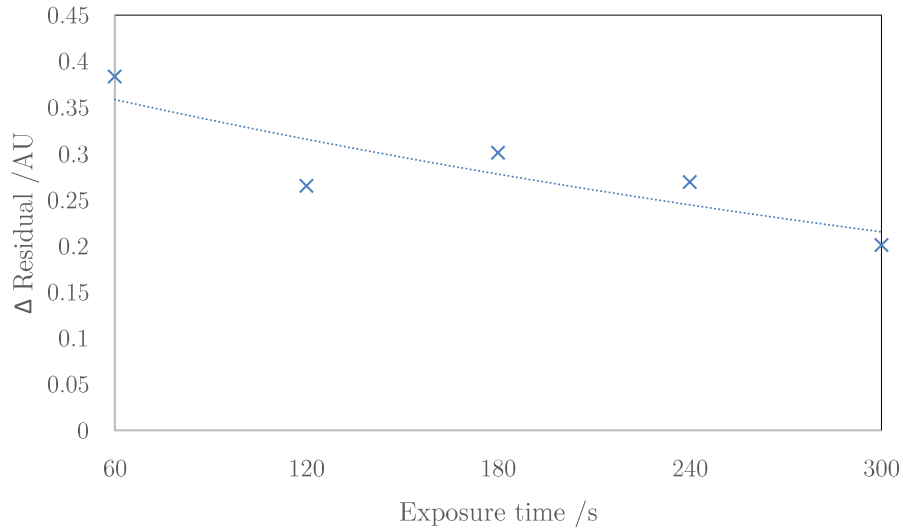


Figure 8.52 Plot illustrating the difference in residuals as a measure of noise from increasing the exposure time, of a concealed 15 mm sample of Al_2O_3 between spatially separated 5 mm Fe samples.

Analysing the two functions, the first presented for one sample, has a higher decay factor (or negative growth factor) than the second, indicating a shorter exposure time is required to achieve a diffraction pattern where the noise is negligible. The functions also demonstrate that the noise for multiple samples will always be higher than when there is a single sample. However, the noise within the diffraction pattern depends on many factors including the material, the sample position, the source, the geometry of the system, the thickness of the container wall, the proximity to other samples as well as the exposure time.

It is apparent from analysing 3D plots, such as those presented in Figure 8.43 and Figure 8.50 that within (d,z) space samples appear thicker than their physical dimensions. This may have impact on the performance of the technique, restricting the use when samples are in close proximity with intensely scattering objects overshadowing weakly scattering samples.

8.5.1.1 Depth Resolution

An experiment was conducted to observe how the placement of two samples, at a fixed distance apart, appeared in the recovered (d,z) map when translated along

the z -axis, employing the W source. Two filled petri dishes of Al_2O_3 were analysed at a fixed distance apart of 36 mm and translated along the z -axis in 12 mm increments, initially at $D_S = 138$ mm from the source. The acquired HEXITEC images, with the corresponding calculated (d, z) , are presented in Figure 8.53.

Analysing the HEXITEC images, it is apparent that the two samples appear further apart when they are placed closer to the detector, even though they are the same 36 mm apart as in Figure 8.53(a).

Summing each z (row) of the (d, z) map to produce the plots presented in Figure 8.54, demonstrated how the two samples appear as a single sample at the detector plane i.e. when the sample-to-detector distance, D_{SD} , is large. The single peak separates to form two peaks, the closer the sample is to the detector indicating an enhanced depth resolution when sample-to-detector distance, D_{SD} , is small.

To understand why two samples of Al_2O_3 appear as one sample when placed close to the X-ray source i.e. when D_S is a minimum, a study was undertaken to determine the apparent sample thickness, Δz , and compare analytical calculation to experimental results. Equation (6.15) has been successfully employed to identify the mid-plane position of the sample, D_S , when the location and dimensions of the sample are unknown.

For the purpose of analysing acquired scatter broadening within the detector plane, an equation was sought which included all possible physical parameters that could be contributable to the broadening: sample thickness, position of the sample (i) and radius, depth and location of the aperture, (a , b and j respectively) and the position of the detector, D . Figure 8.55 and Figure 8.56 illustrate the geometry of the system and identify the additional variables used in this analysis.

The first equation to be constructed examined the source-to-sample distance, D_S , using the newly devised parameters. Using the central path of the source, φ_m , and modelling the diffraction emanating from the mid-sample plane, the radius of the resulting diffraction maxima, which appears at the detection plane, can be calculated using geometry. Initially calculating the radius of incident beam within the mid-sample plane, by trigonometry it can be understood that:

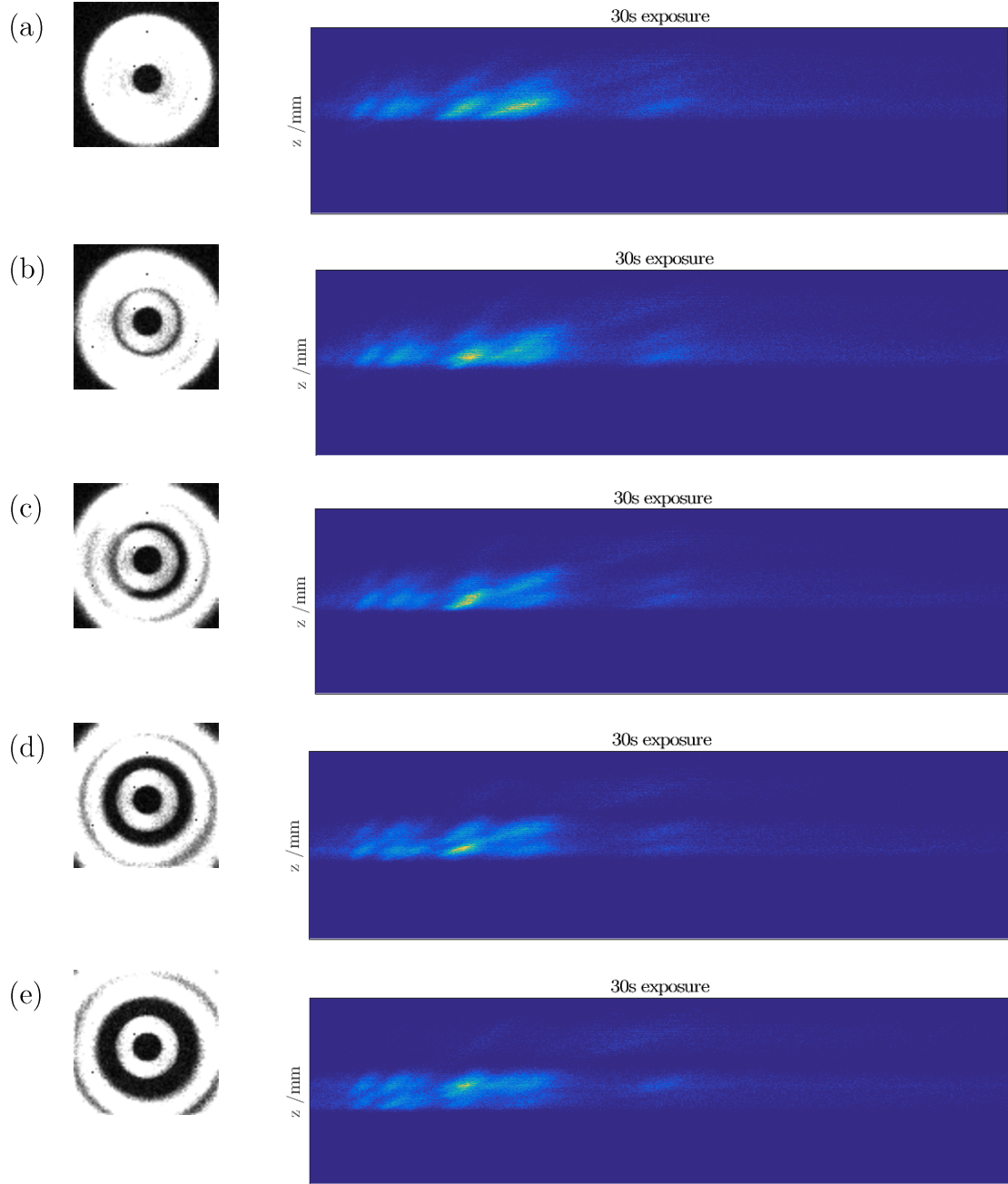


Figure 8.53 Resultant (d, z) maps for two samples of Al_2O_3 separated by a fixed distance 36 mm, translated via increments of 12 mm, along the primary axis, z , from $D_S = 138$ mm to $D_S = 198$ mm.

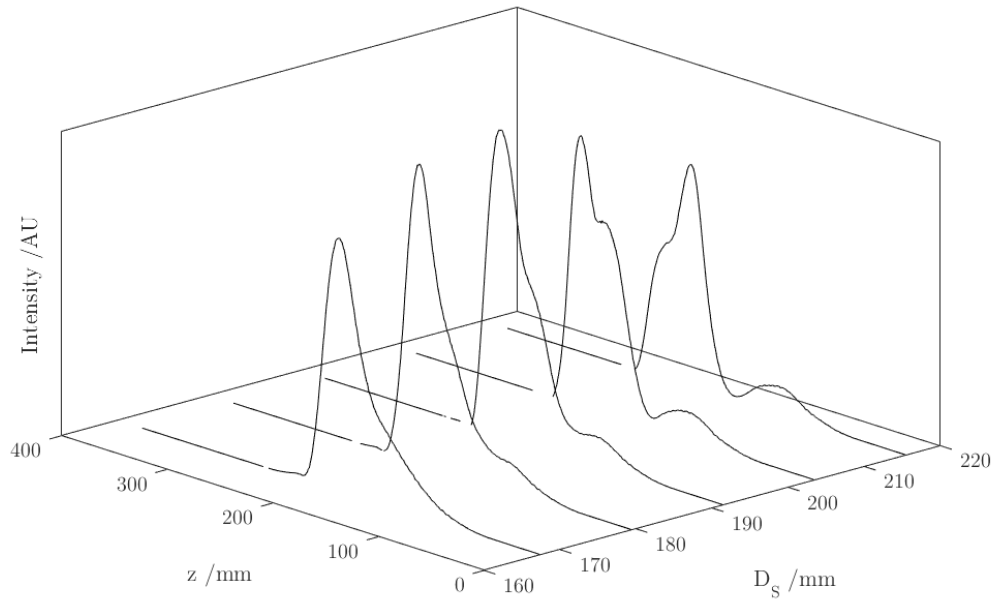


Figure 8.54 Intensity of scatter summed along each z of the (d,z) map from two samples of Al_2O_3 at a fixed distance of 36 mm apart placed centrally placed at D_s , translated along the primary axis, z , employing the W source.

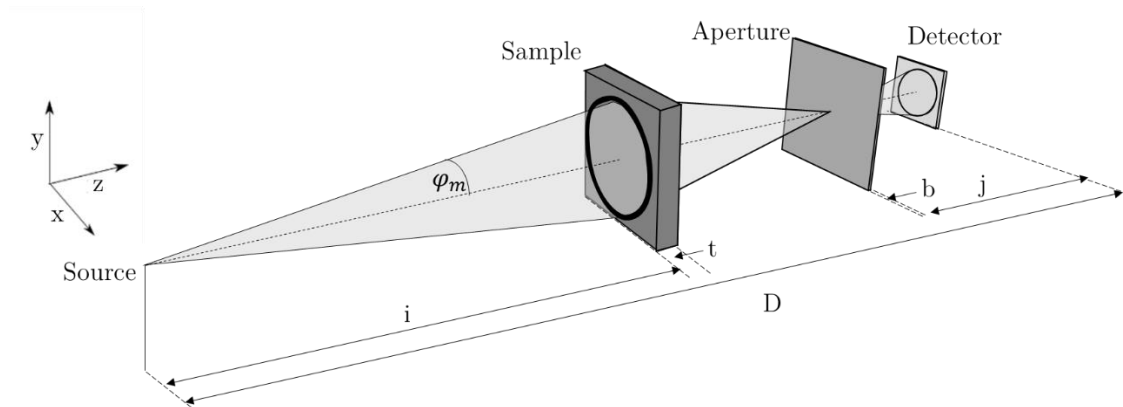


Figure 8.55 Geometry of the system including additional geometric components.

$$r_s = D_S \tan \varphi_m$$

Where $D_S = i + t/2$. By using similar triangles, it can be shown that around the central point of the pin-hole aperture, circled in Figure 8.56, on the z -axis:

$$\frac{r_s}{D - b/2 - j - D_S} = \frac{r}{j + b/2}$$

Rearranging, an equation for the radius of the diffraction within the detector plane can be found:

$$r = \frac{r_s [j + b/2]}{D - b/2 - j - D_S} = \frac{[j + b/2] D_S \tan \varphi_m}{D - b/2 - j - D_S}$$

This equation is a good indication of the average path of the rays, however, the radius of the aperture, a , is not included and b would cancel out due to symmetry.

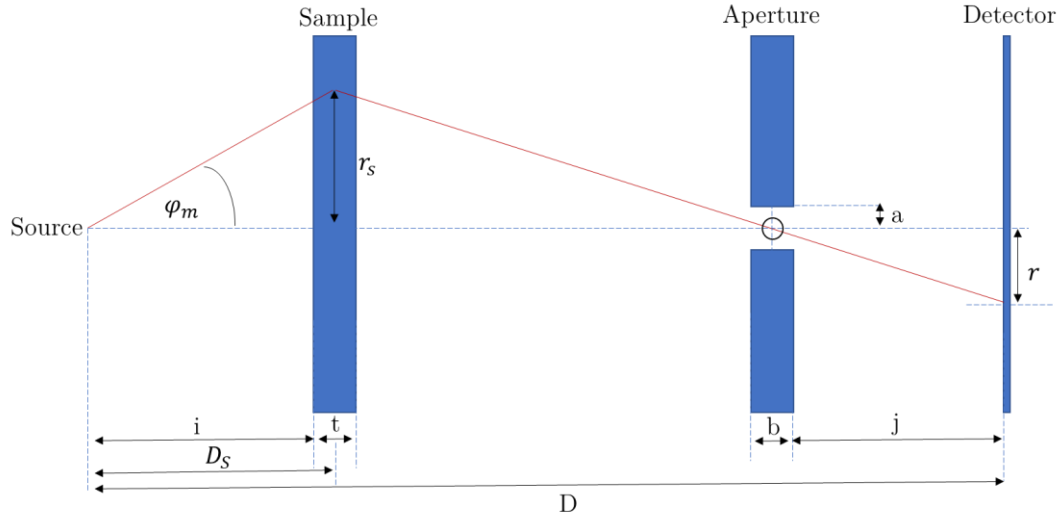


Figure 8.56 Central beam path of a single incident beam from the hollow conical beam and resultant diffraction.

To include the radius of the aperture, a , in the final equation points 1 and 2, labelled on Figure 8.57 were identified to find the minimum and maximum possible position of the rays traversing through the aperture with incident angle, φ_m . Using these points and similar triangles it can be deduced that at:

1. $\frac{r_s - a}{D - b - j - D_s} = \frac{r_{min} + a}{j + b}$
2. $\frac{r_s + a}{D - j - D_s} = \frac{r_{max} - a}{j}$

To find the average radius, r_{av} , the mean of r_{min} and r_{max} can be calculated, either using D_s as the sample mid-plane position, Equation (8.2), or including the thickness of the sample, Equation (8.3).

$$r_{av} = \frac{[D_s \tan \varphi_m - a] j + b}{2[D - D_s - b - j]} + \frac{j[D_s \tan \varphi_m + a]}{2[D - D_s - j]} \quad (8.2)$$

$$= \frac{[(i + t/2) \tan \varphi_m - a] j + b}{2[D - (i + t/2) - b - j]} + \frac{j[(i + t/2) \tan \varphi_m + a]}{2[D - (i + t/2) - j]} \quad (8.3)$$

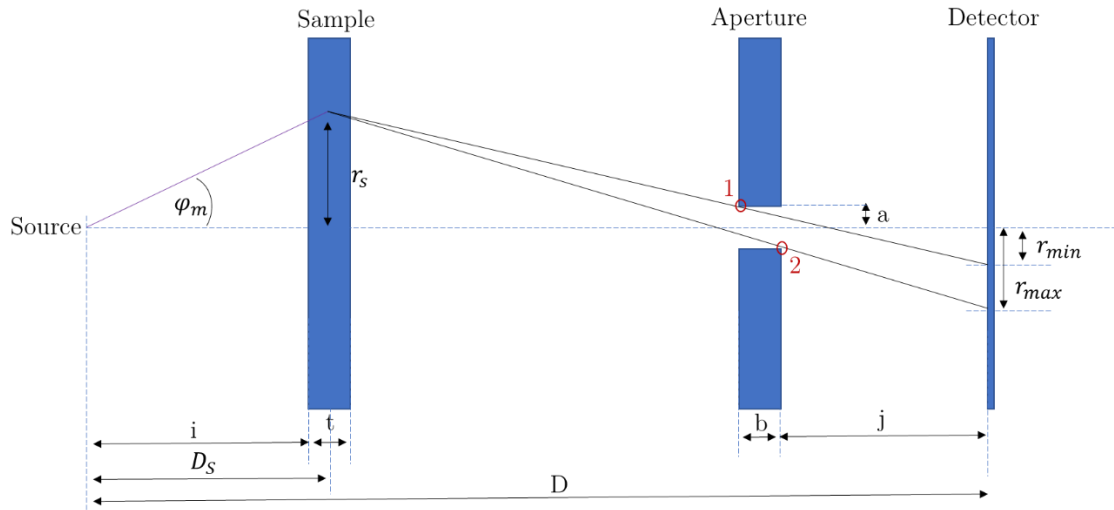


Figure 8.57 Beam paths of an incident hollow conical beam with incident angle φ_m and resultant diffraction passing through the pin-hole aperture.

Equation (8.3) was used to predict the radius of the resulting scatters' conic section at the detector plane when a 1 mm sample of Fe was traversed along the z -axis. The associated errors, calculated by error propagation, for each variable when measuring the average radius in the detector plane, r_{av} , can be calculated via Equation (8.4) using the standard deviations $\sigma\varphi_m = 0.1^\circ$, $\sigma a = 0.05$ mm, $\sigma j = 0.00005$ mm, $\sigma b = 0.1$ mm, $\sigma D = 0.00005$ mm, $\sigma i = 0.0005$ mm and $\sigma t = 0.1$ mm.

$$\sigma r_{av} = \left[\left(\frac{\partial r_{av}}{\partial i} \sigma i \right)^2 + \left(\frac{\partial r_{av}}{\partial t} \sigma t \right)^2 + \left(\frac{\partial r_{av}}{\partial \varphi_m} \sigma \varphi_m \right)^2 + \left(\frac{\partial r_{av}}{\partial a} \sigma a \right)^2 + \left(\frac{\partial r_{av}}{\partial j} \sigma j \right)^2 + \left(\frac{\partial r_{av}}{\partial b} \sigma b \right)^2 + \left(\frac{\partial r_{av}}{\partial D} \sigma D \right)^2 \right]^{1/2} \quad (8.4)$$

where,

$$\begin{aligned} \frac{\partial r_{av}}{\partial i} &= \frac{[(i + t/2) \tan \varphi_m - a] j + b}{2(D - b - i - j - t/2)^2} + \frac{j[(i + t/2) \tan \varphi_m + a]}{2(D - i - j - t/2)^2} + \frac{b + j \tan \varphi_m}{2(D - b - i - j - t/2)} \\ &\quad + \frac{j \tan \varphi_m}{2(D - i - j - t/2)} \\ \frac{\partial r_{av}}{\partial t} &= \frac{[(i + t/2) \tan \varphi_m - a] j + b}{4(D - b - i - j - t/2)^2} + \frac{j[(i + t/2) \tan \varphi_m + a]}{4(D - i - j - t/2)^2} + \frac{b + j \tan \varphi_m}{4(D - b - i - j - t/2)} \\ &\quad + \frac{j \tan \varphi_m}{4(D - i - j - t/2)} \\ \frac{\partial r_{av}}{\partial \varphi_m} &= \frac{(i + t/2) b + j \sec^2 \varphi_m}{2(D - b - i - j - t/2)} + \frac{j(i + t/2) \sec^2 \varphi_m}{2(D - i - j - t/2)} \\ \frac{\partial r_{av}}{\partial a} &= \frac{b - 2D + t + 2i}{-2D + 2j + t + 2i} \frac{b - 2D + 2j + t + 2i}{2b - 2D + 2j + t + 2i} \\ \frac{\partial r_{av}}{\partial j} &= \frac{[(i + t/2) \tan \varphi_m - a] j + b}{2(D - b - i - j - t/2)^2} + \frac{j[(i + t/2) \tan \varphi_m + a]}{2(D - i - j - t/2)^2} + \frac{(i + t/2) \tan \varphi_m - a}{2(D - b - i - j - t/2)} \\ &\quad + \frac{(i + t/2) \tan \varphi_m + a}{2(D - i - j - t/2)} \\ \frac{\partial r_{av}}{\partial b} &= \frac{[(i + t/2) \tan \varphi_m - a] j + b}{2(D - b - i - j - t/2)^2} + \frac{(i + t/2) \tan \varphi_m - a}{2(D - b - i - j - t/2)} \\ \frac{\partial r_{av}}{\partial D} &= -\frac{[(i + t/2) \tan \varphi_m - a] j + b}{2(D - b - i - j - t/2)^2} - \frac{j[(i + t/2) \tan \varphi_m + a]}{2(D - i - j - t/2)^2} \end{aligned}$$

Table 8.3 Measured and calculated conic section radii values within the detector plane from traversing a 1 mm sample of Fe along the z -axis.

i /mm	Measured r_{av} /mm	Predicted r_{av} /mm
142.00	4.79 ± 0.06	4.80
149.00	5.20 ± 0.06	5.21
156.00	5.63 ± 0.06	5.64
163.00	6.08 ± 0.07	6.10
170.00	6.50 ± 0.08	6.59
177.00	7.26 ± 0.08	7.13
184.00	7.84 ± 0.09	7.70

The analytical radial average, r_{av} , corresponds to the measured radius of the conic section within the detector plane. This is determined by measuring the peak intensity of the radial plot calculated from azimuthally integrating the HEXITEC image, radial plot shown in Figure 8.58. Translating a 1 mm sample of Fe along the z -axis, HEXITEC images were obtained with 30 s exposure and azimuthally integrated to determine the peak intensity corresponding to the radial values, presented in Table 8.3.

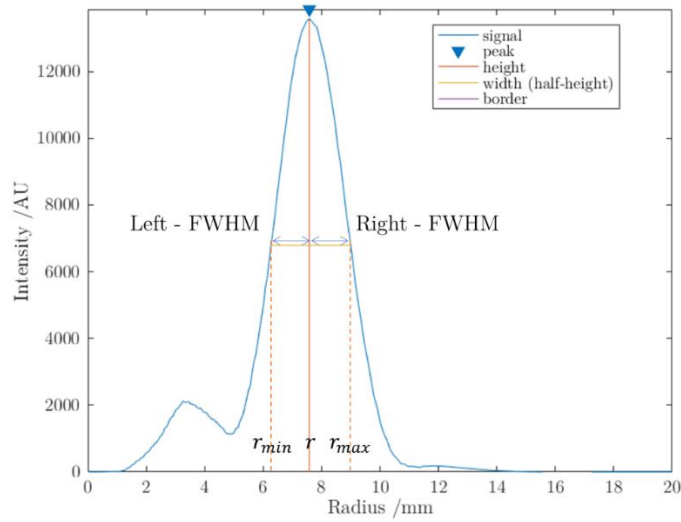


Figure 8.58 Radial plot from azimuthally integrating scatter from HEXITEC image from Al_2O_3 , where $D_S = 185.25$ mm with annotations of measurements obtained to analyse peak broadness.

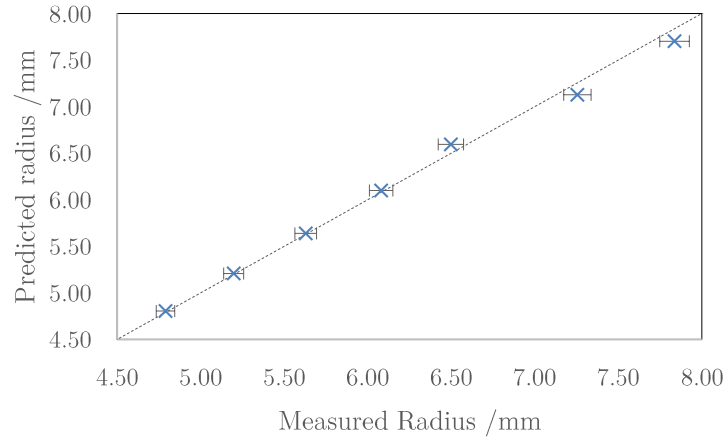


Figure 8.59 Measured radii values compared to predicted radii values from using 1 mm thick Fe samples translated along the z -axis with $y = x$ included for reference.

The measured values were compared to predicted radii values, calculated at each placement along the z -axis for the 1 mm Fe sample employing Equation (8.3). The measured and predicted values are displayed in Figure 8.59. The predicted radii values, at each i , correspond well to the measured values. The larger radii, corresponding to the larger i values differ from the corresponding predicted values. This could be due to the resulting conic section overlapping the detector window.

Employing a similar methodology, the recovered sample thickness was evaluated when individual samples were translated along the primary z -axis. Using obtained HEXITEC images from sampled of Fe, CaCO_3 and Al_2O_3 , and azimuthally integrating them to produce the radial plots - as previously produced to find the average radii resultant scatter - the recovered thickness can be measured by determining the left-full width at half maximum (FWHM) and right-FWHM of the intensity peak, as previously shown in Figure 8.58. Examples of the determined radial plots from a 15 mm CaCO_3 sample translated along the z -axis in increments of 14 mm are presented in Figure 8.60, with their corresponding (d, z) maps. Once the left-FWHM and right-FWHM were converted into z -space values, z_{min} and z_{max} respectively, using Equation (8.5), a variation of Equation (6.15), employing all the

variables introduced in Figure 8.61, the apparent thickness $\Delta z = z_{max} - z_{min}$, can be calculated.

$$z = \frac{(D - j - \frac{b}{2})r}{r + (j + \frac{b}{2}) \tan \varphi_m} \quad (8.5)$$

To analytically predict the thickness of the sample the extreme beam paths were determined, a schematic diagram of which is presented in Figure 8.61. To determine the radii limits of the conic section that would be produced within the detector plane, the opening of the annular collimator was considered. Due to the finite aperture of the annular collimator the opening angle possesses uncertainty. At the high energy, W, experiments conducting this equates to $\varphi_m = 2.5^\circ \pm 0.1^\circ$, i.e. $\varphi_{min} = 2.4^\circ$ and $\varphi_{max} = 2.6^\circ$.

The radii of the conic section within the detector plane depends on the opening angle, φ_m , the placement of the sample, i , the thickness of the sample, t , and shape and location of the pin-hole aperture (radius, $r = 0.75$ mm and depth, $b = 4$ mm), $j = 167.4011$ mm from the detector, which have all been incorporated into Equations (8.6) and (8.7), to determine r_{min} and r_{max} respectively, derived using the geometry in Figure 8.61.

$$r_{min} = \frac{b + j \tan \varphi_{min} - a}{D - j - b - i - t} - a \quad (8.6)$$

$$r_{max} = \frac{j \tan \varphi_{max} + a}{D - j - i - t} + a \quad (8.7)$$

Using Equation (8.5), r_{min} and r_{max} can be converted into z_{min} and z_{max} resulting in Equations (8.8) and (8.9), respectively. These were employed to analytically predict the apparent thickness of the sample in z -space i.e. the thickness a sample appears to be within the determined (d, z) map.

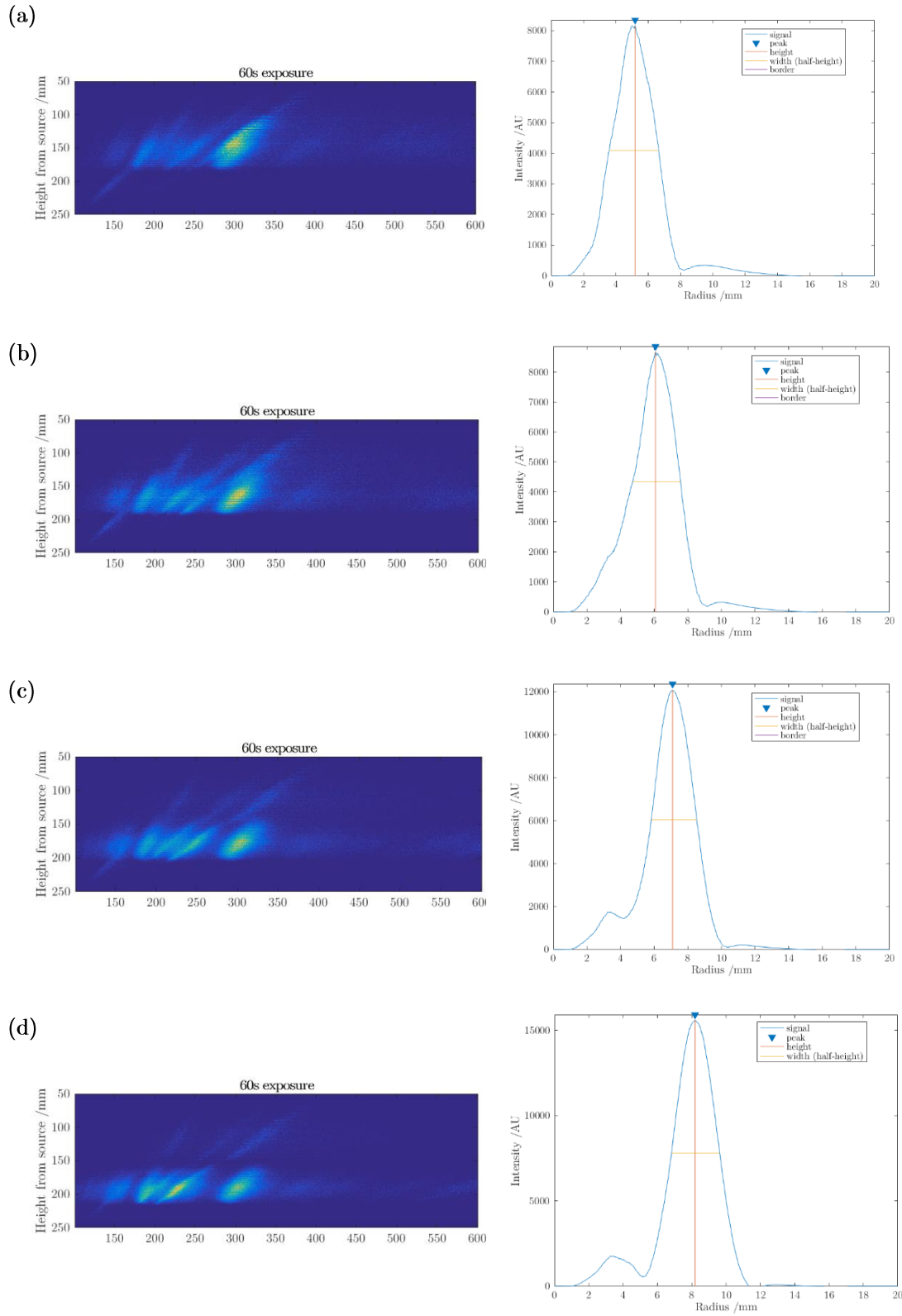


Figure 8.60 (d,z) maps and corresponding radial plots for a 15 mm sample of CaCO_3 translated along the z -axis by 14 mm increments.

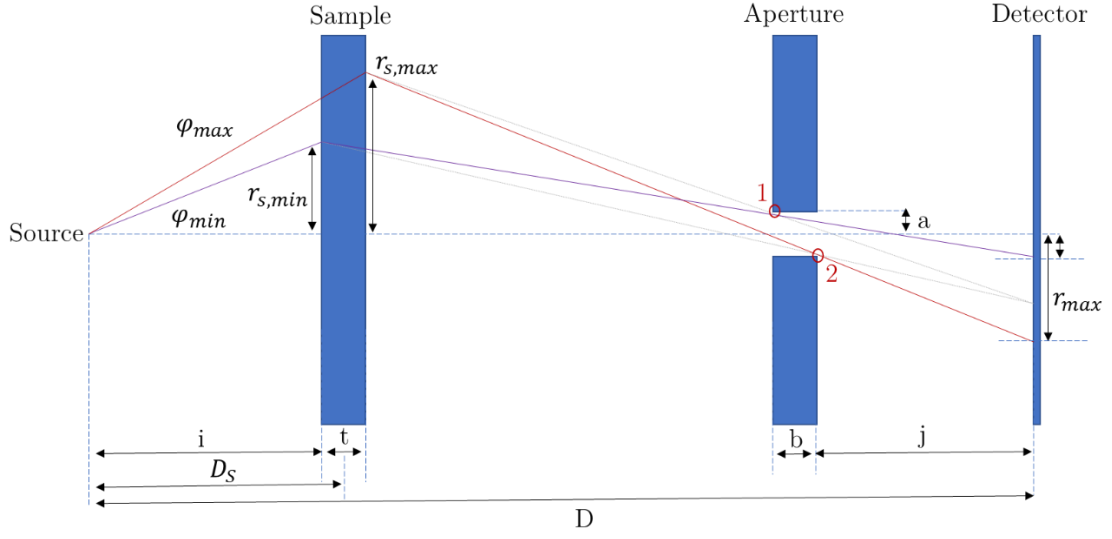


Figure 8.61 Extreme beam paths of an incident hollow conical beam considering the diffraction scatter produced from the limits of the opening angle, φ_{min} and φ_{max} and resultant diffraction passing through the pin-hole aperture.

$$z_{min} = \frac{(D - j - \frac{b}{2})r_{min}}{r_{min} + (j + \frac{b}{2})\tan\varphi_{min}} \quad (8.8)$$

$$= \frac{(D - j - \frac{b}{2}) \left[\frac{b + j}{D - j - b - i - t} \frac{i \tan\varphi_{min} - a}{-a} - a \right]}{\left[\frac{b + j}{D - j - b - i - t} \frac{i \tan\varphi_{min} - a}{-a} - a \right] + (j + \frac{b}{2})\tan\varphi_{min}}$$

$$z_{max} = \frac{(D - j - \frac{b}{2})r_{max}}{r_{max} + (j + \frac{b}{2})\tan\varphi_{max}} \quad (8.9)$$

$$= \frac{(D - j - \frac{b}{2}) \left[\frac{j((i + t)\tan\varphi_{max} + a)}{D - j - i - t} + a \right]}{\left[\frac{j((i + t)\tan\varphi_{max} + a)}{D - j - i - t} + a \right] + (j + \frac{b}{2})\tan\varphi_{max}}$$

Values corresponding to the placement of samples, Fe (1 mm), CaCO_3 and Al_2O_3 (15 mm), are presented with the measured and calculated recovered thickness $\Delta z = z_{max} - z_{min}$ as the sample is incrementally translated through the z -axis, in Table

8.4, Table 8.5 and Table 8.6, respectively together with the errors. Errors are calculated by error propagation, shown below for calculating Δz via Equation (8.10), formed from combining Equations (8.8) and (8.9), using the standard deviations $\sigma D = 0.0005$ mm, $\sigma \varphi_{min} = 0.1^\circ$, $\sigma \varphi_{max} = 0.1^\circ$, $\sigma j = 0.0005$ mm, $\sigma b = 0.1$ mm, $\sigma r_{max} = 0.5$ mm and $\sigma r_{min} = 0.5$ mm.

$$\Delta z = \frac{(D - j - \frac{b}{2})r_{min}}{r_{min} + (j + \frac{b}{2})\tan \varphi_{min}} - \frac{(D - j - \frac{b}{2})r_{max}}{r_{max} + (j + \frac{b}{2})\tan \varphi_{max}} \quad (8.10)$$

$$\sigma \Delta z^2 = \left[\left(\frac{\partial \Delta z}{\partial D} \sigma D \right)^2 + \left(\frac{\partial \Delta z}{\partial j} \sigma j \right)^2 + \left(\frac{\partial \Delta z}{\partial b} \sigma b \right)^2 + \left(\frac{\partial \Delta z}{\partial r_{min}} \sigma r_{min} \right)^2 + \left(\frac{\partial \Delta z}{\partial \varphi_{min}} \sigma \varphi_{min} \right)^2 + \left(\frac{\partial \Delta z}{\partial r_{max}} \sigma r_{max} \right)^2 + \left(\frac{\partial \Delta z}{\partial \varphi_{max}} \sigma \varphi_{max} \right)^2 \right]^{1/2}$$

$$\begin{aligned} \frac{\partial \Delta z}{\partial D} &= \frac{r_{min}}{(b/2 + j)\tan \varphi_{min} + r_{min}} - \frac{r_{max}}{(b/2 + j)\tan \varphi_{max} + r_{max}} \\ \frac{\partial \Delta z}{\partial j} &= \frac{r_{max}\tan \varphi_{max}(D - b/2 - j)}{\left((b/2 + j)\tan \varphi_{max} + r_{max}\right)^2} - \frac{r_{min}\tan \varphi_{min}(D - b/2 - j)}{\left((b/2 + j)\tan \varphi_{min} + r_{min}\right)^2} \\ &\quad + \frac{r_{max}}{(b/2 + j)\tan \varphi_{max} + r_{max}} - \frac{r_{min}}{(b/2 + j)\tan \varphi_{min} + r_{min}} \\ \frac{\partial \Delta z}{\partial b} &= \frac{r_{max}\tan \varphi_{max}(D - b/2 - j)}{2\left((b/2 + j)\tan \varphi_{max} + r_{max}\right)^2} - \frac{r_{min}\tan \varphi_{min}(D - b/2 - j)}{2\left((b/2 + j)\tan \varphi_{min} + r_{min}\right)^2} \\ &\quad + \frac{r_{max}}{2\left((b/2 + j)\tan \varphi_{max} + r_{max}\right)} - \frac{r_{min}}{2\left((b/2 + j)\tan \varphi_{min} + r_{min}\right)} \\ \frac{\partial \Delta z}{\partial r_{min}} &= \frac{b + 2j \tan \varphi_{min}}{(b + 2j \tan \varphi_{min} + 2r_{min})^2} \\ \frac{\partial \Delta z}{\partial \varphi_{min}} &= \frac{r_{min} \sec^2 \varphi_{min}}{(b + 2j \tan \varphi_{min} + 2r_{min})^2} \\ \frac{\partial \Delta z}{\partial r_{max}} &= \frac{b + 2j \tan \varphi_{max}}{(b + 2j \tan \varphi_{max} + 2r_{max})^2} \\ \frac{\partial \Delta z}{\partial \varphi_{max}} &= \frac{r_{max} \sec^2 \varphi_{max}}{(b + 2j \tan \varphi_{max} + 2r_{max})^2} \end{aligned}$$

Table 8.4 Measured and predicted recovered thicknesses, Δz , when a 1 mm sample of Fe is translated though the z -axis.

D_S /mm	z_{min} from measured l- FWHM /mm	z_{max} from measured r- FWHM /mm	Δz from obtained data/mm	Predicted Δz /mm
142.5	120.8 ± 5.6	162.9 ± 3.6	42.1 ± 9.3	45.7
149.5	128.7 ± 5.3	168.1 ± 3.4	39.4 ± 8.7	43.1
156.5	136.1 ± 4.9	173.4 ± 3.2	37.3 ± 8.2	40.6
163.5	146.7 ± 4.5	179.0 ± 3.1	32.3 ± 7.5	38.2
170.5	154.0 ± 4.2	184.9 ± 2.9	30.9 ± 7.0	35.8
177.5	161.9 ± 3.9	192.2 ± 2.6	30.3 ± 6.5	33.5
184.5	171.0 ± 3.5	195.9 ± 2.5	24.9 ± 6.0	31.2

Table 8.5 Measured and predicted recovered thicknesses, Δz , when a 15 mm sample of CaCO_3 is translated though the z -axis.

D_S /mm	z_{min} from measured l-FWHM /mm	z_{max} from measured r-FWHM /mm	Δz from obtained data/mm	Predicted Δz /mm
149.5	119.9 ± 5.7	173.2 ± 3.4	53.3 ± 9.2	50.9
157.5	130.0 ± 5.3	180.9 ± 3.2	50.9 ± 8.5	47.6
164.5	142.6 ± 4.7	185.0 ± 3.0	42.4 ± 7.7	44.8
171.5	154.1 ± 4.2	190.0 ± 2.9	35.9 ± 7.1	42.1
178.5	161.2 ± 3.9	196.0 ± 2.7	34.8 ± 6.6	39.5
185.5	168.5 ± 3.6	201.5 ± 2.5	33.0 ± 6.2	37.0
192.5	175.4 ± 3.4	206.6 ± 2.4	31.2 ± 5.7	34.5

Table 8.6 Measured and predicted recovered thicknesses, Δz , when a 15 mm sample of Al_2O_3 is translated though the z -axis.

D_S /mm	z_{min} from measured l-FWHM /mm	z_{max} from measured r-FWHM /mm	Δz from obtained data/mm	Predicted Δz /mm
149.5	112 ± 6.2	171.5 ± 3.5	59.5 ± 9.7	50.9
157.5	133.7 ± 5.1	181.4 ± 3.2	47.7 ± 8.3	47.6
164.5	147.5 ± 4.5	185.9 ± 3.0	38.4 ± 7.5	44.8
171.5	156.0 ± 4.1	190.3 ± 2.9	34.3 ± 7.0	42.1
178.5	161.4 ± 3.9	195.4 ± 2.7	34.0 ± 6.6	39.5
185.5	167.8 ± 3.7	200.5 ± 2.5	32.7 ± 6.2	37.0
192.5	174.5 ± 3.4	206.9 ± 2.4	32.4 ± 5.8	34.5

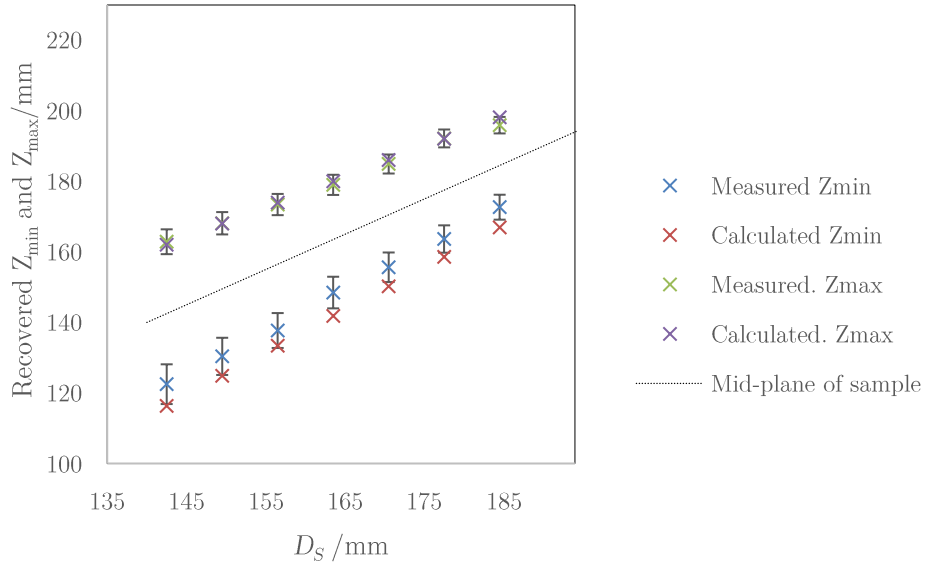


Figure 8.62 Plot illustrating the experimental and calculated z_{max} and z_{min} for 1 mm thick Fe translated along the primary axis.

The obtained z_{min} and z_{max} values for each of the samples Fe, CaCO_3 and Al_2O_3 along with the predicted corresponding values are represented in graphical form in Figure 8.62, Figure 8.63 and Figure 8.64, respectively, with the mid-plane of the sample included for reference.

For each sample, the recovered thickness of each was analytically predicted and compared to the determined Δz from the measured data and displayed in Figure 8.65. The graphs within Figure 8.65 show good correlation between the analytical results and the measured data, verifying the model. The displayed results additionally demonstrate that as D_S is increased, Δz decreases in all samples analysed.

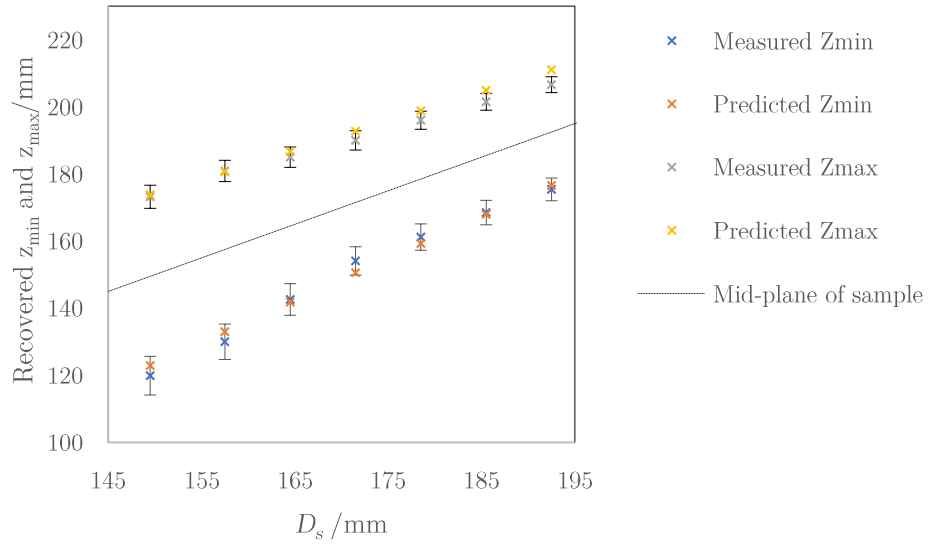


Figure 8.63 Plot illustrating the experimental and calculated z_{max} and z_{min} for 15 mm thick CaCO_3 translated along the primary axis.

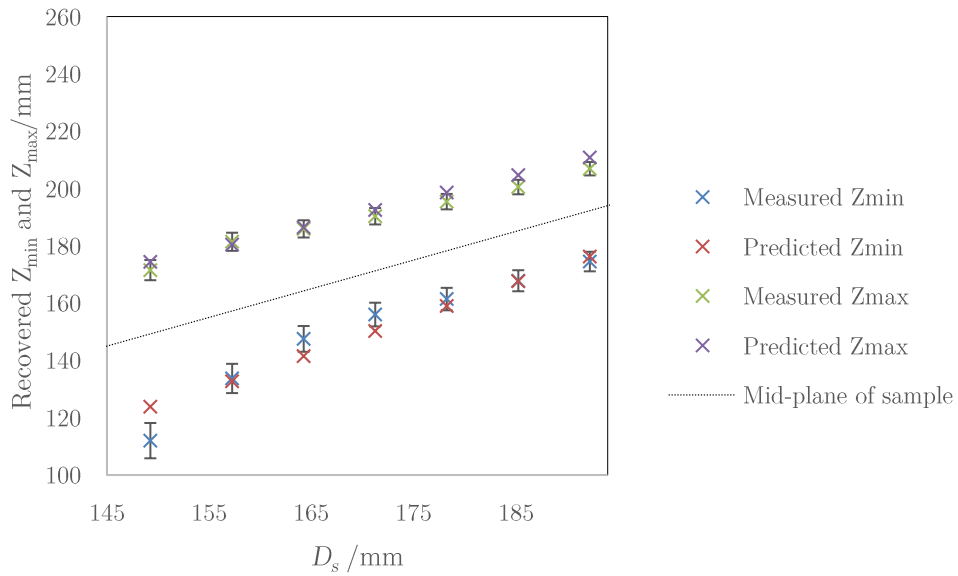


Figure 8.64 Plot illustrating the experimental and calculated z_{max} and z_{min} for 15 mm thick Al_2O_3 translated along the primary axis.

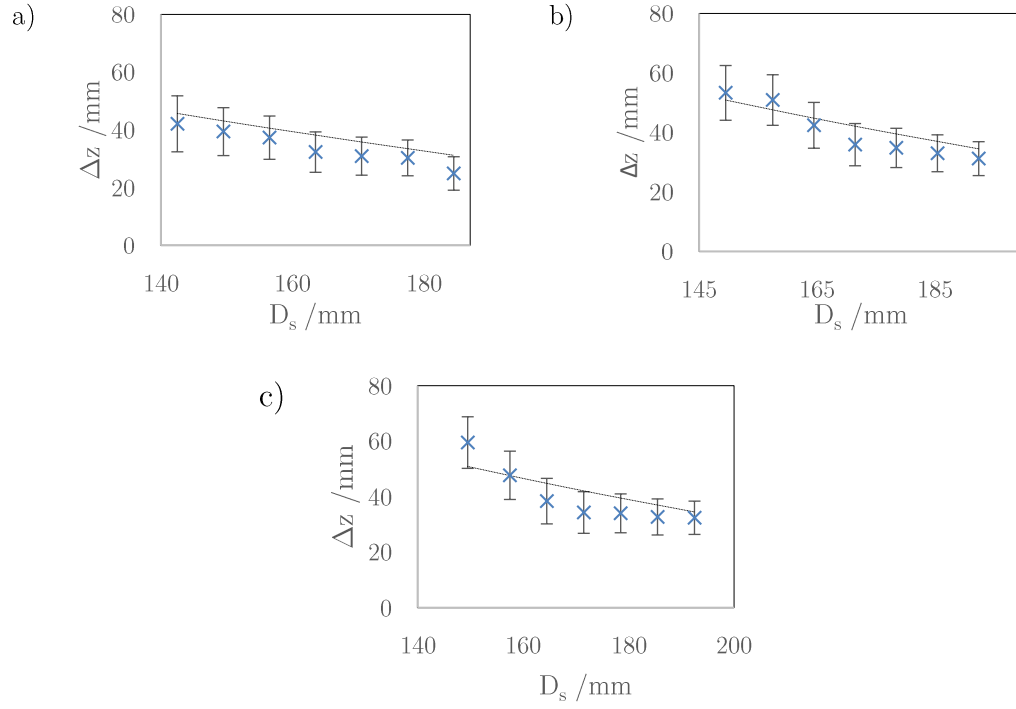


Figure 8.65 The recovered thicknesses, Δz , of a) Fe (1 mm) b) CaCO₃ (15 mm) c) Al₂O₃ (15 mm) translated along the z-axis at source-to-sample distances, D_s , with the corresponding predicted thickness, shown in dashed black.

Considering an infinitely thin sample ($t = 0$ mm) traversing through the sample space from $D_s = 140$ mm to $D_s = 250$ mm, in increments of 5 mm, the samples apparent thickness, Δz , was calculated i.e. the calculated thickness from using the minimum and maximum radius (r_{min} and r_{max} respectively) that would be produced from a $\varphi_m = 2.5^\circ \pm 0.1^\circ$ beam, as used in acquiring the preceding data, Figure 8.66.

This indicates that an infinitely thin sample ($t = 0$ mm), placed at $D_s = 140$ mm, at the base of the system will be observed as being ~ 48 mm thick in the recovered sample thickness from analysing the obtained radii of the resultant HEXITEC image. This decreases to 0 mm as the sample is translated along the z-axis, towards the detector, reaching 0 mm when placed directly preceding the pin-hole aperture at $D_s = D - j = 363.3408$ mm. This poor depth resolution demonstrates why the Al₂O₃ samples analysed in Figure 8.54 appear more distinct when placed closer to the detector.

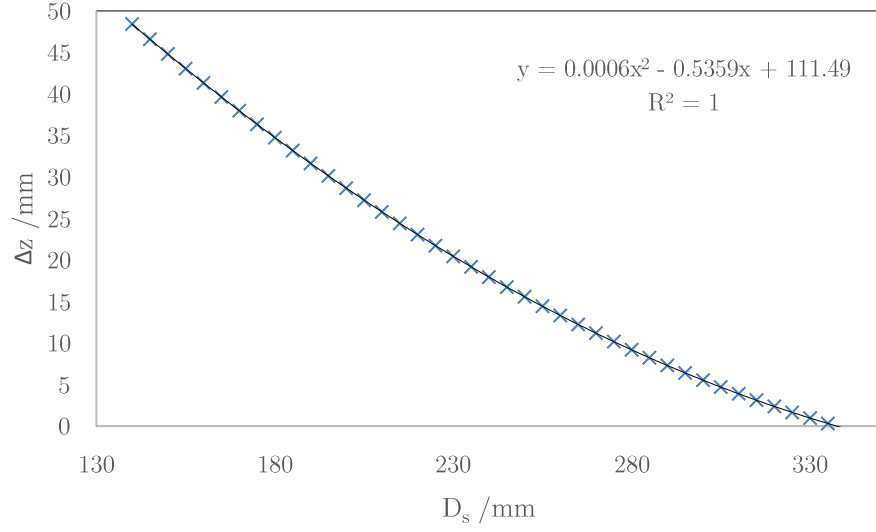


Figure 8.66 Graph indicating the recovered thickness, Δz , of an infinitely thin sample, ($t = 0$). Incrementally translated through the samples space at D_s along the z-axis. A trendline is included with the equation displayed.

Multivariate analysis was performed to consider not only the significance of each parameter but to evaluate the most dominant variables in the system. *MiniTab*© was used to assess the coefficients in the model. P-values for all parameters were determined to be significant so all parameters were used in the regression equation.

$$\Delta z = 26.385 - 0.24052 i + 0.154416 D + 0.3586 t - 1.0720 b - 0.19062 j + 34.257 a - 2360.76 \varphi_{min} + 1596.00 \varphi_{max}$$

The most dominant parameters were determined to be the related to the opening angle of the annular beam, φ_{min} , followed by φ_{max} . When considering just the geometry of the encoder (a , b and j) the most influential variable was the radius of the pin-hole, a .

8.5.2 Extending to Higher Energy

For this technique to be applied to real world situations, it would be required to work at higher energies to penetrate thick metal containers. A series of simple

simulations were conducted at higher energies to provide an indication of the performance at higher energy and indicate any limitation that might affect the use of the system.

As mentioned in §3.2.2.1, X-ray tubes are limited to producing X-rays up to 450 kVp so simulations were conducted up to 500 kVp. The high energy input spectrum was created using *SpekCalc* using the same parameters as was previously used in §8.3, presented in Figure 8.67. The energy range was chosen due to the capabilities of portable X-ray sources.

A simple model was used comprising of 1 mm Fe either side of 15 mm Al_2O_3 , simulating the petri dish, as used in §8.5.1, where the samples were placed at $D_S = 150$ mm (Fe), $D_S = 190$ mm (Al_2O_3) and $D_S = 230$ mm (Fe) from the source.

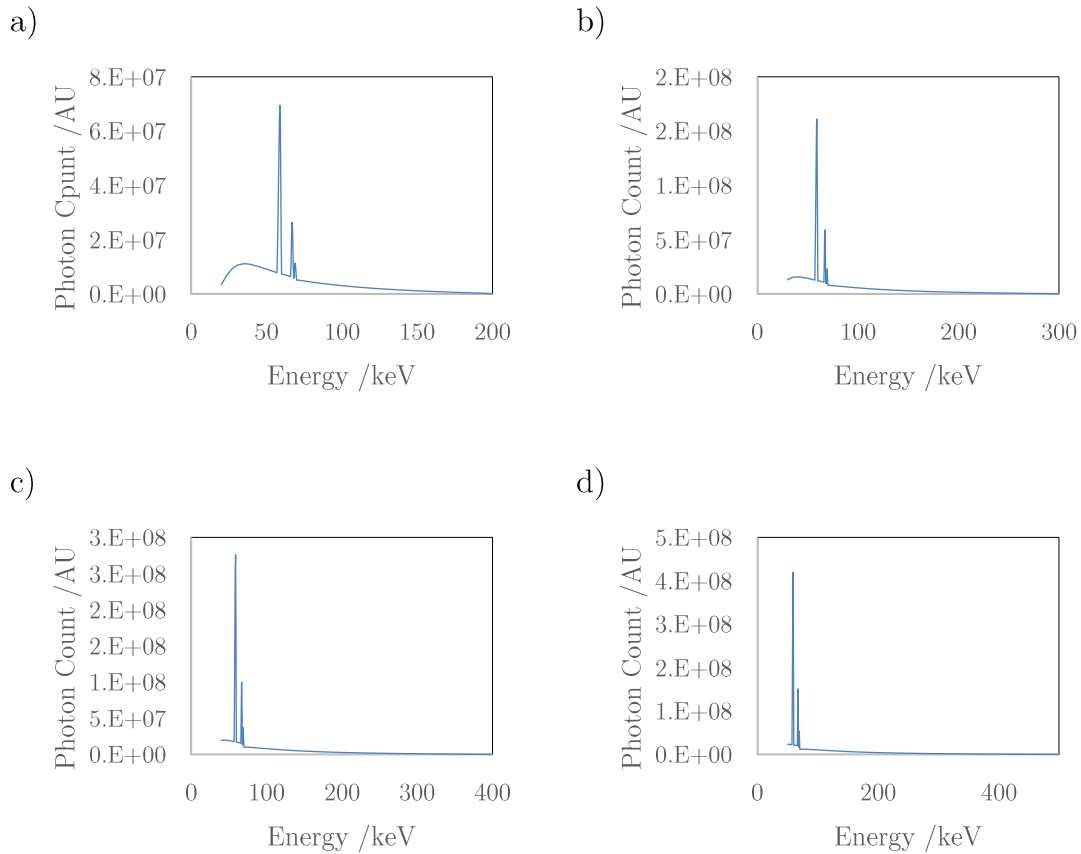


Figure 8.67 Simulated energy profiles computed by *SpekCalc* a) 200 kVp, b) 300 kVp, c) 400 kVp, d) 500 kVp.

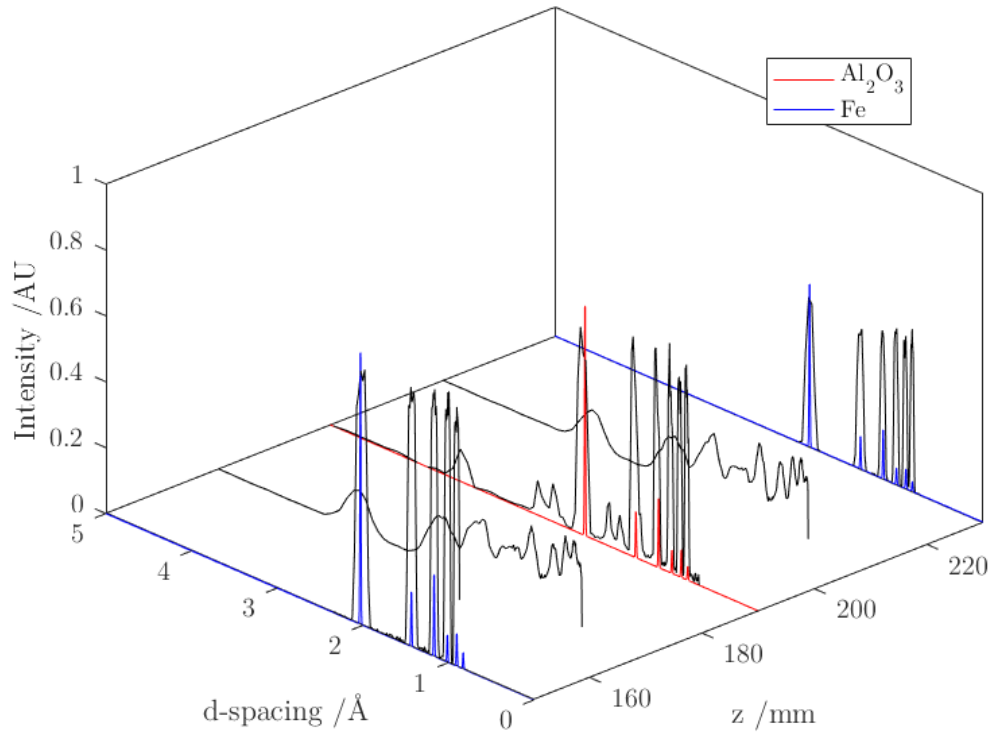


Figure 8.68 3D plot of diffraction patterns generated from simulation of two 1 mm samples of Fe placed at $D_S = 150$ mm and $D_S = 230$ mm, with a 15 mm sample of Al_2O_3 at $D_S = 200$ keV.

Five spectra were extracted from the simulation, equating to $z = 150$ mm, $z = 170$ mm, $z = 190$ mm, $z = 210$ mm and $z = 230$ mm, displayed in Figure 8.68 where the individual samples can be identified with a mixture of both spectra present in the two middle spectra, $z = 170$ mm and $z = 210$ mm.

As with the experimental observations, the spectra obtained from the sample closest to the detector $D_s = 230$ mm is less intense than the one placed at $D_s = 150$ mm.

The simulation was repeated with a larger area detector, so all the scatter originating from the samples is captured by the detector i.e. not overlapping with the edges within the detector plane, Figure 8.69. From this, the same intensity

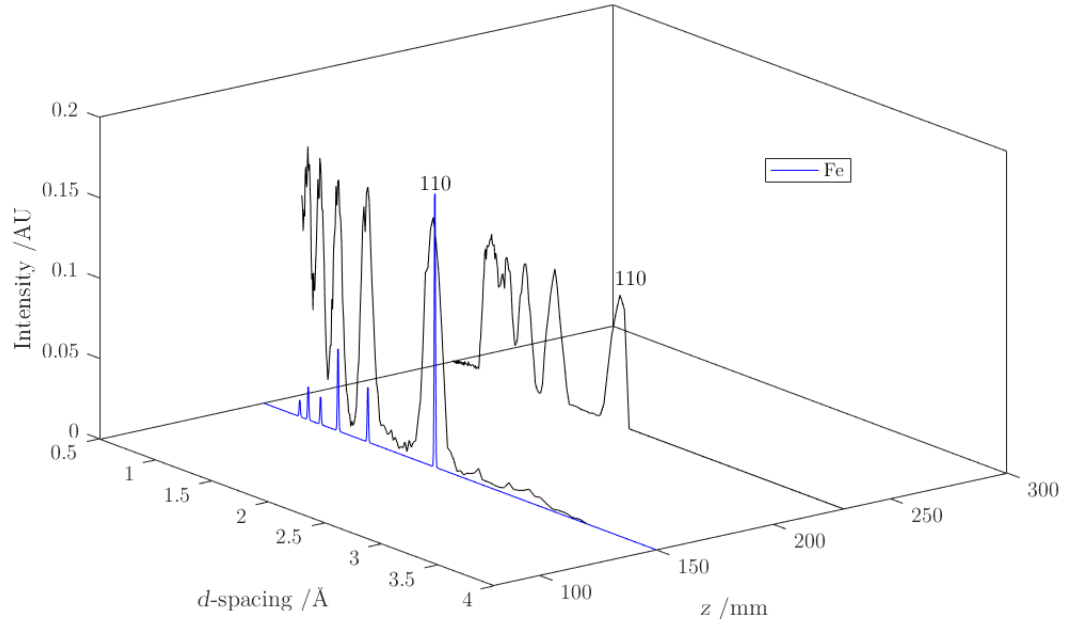


Figure 8.69 3D plot of diffraction patterns generated from simulation of two 1 mm samples of Fe placed at $D_S = 150$ mm and $D_S = 230$ mm.

difference between the front and back Fe sheets can be seen as with the experimental model when analysing an empty box, Figure 8.40. As discussed in §8.5.1, when analysing the relative peak intensity of a sample of Al_2O_3 traversing through the annular beam, the variation of relative peak intensities is due to the change in the angle at which the diffracted beams from the sample form with the aperture pin-hole at the varying sample positions, but further work is needed to know if this is the only cause of the intensity loss.

The geometry was simulated at the four different energy levels up to a source with 500 kVp. The middle spectra, when $r = 8$ mm i.e. $z = 190$ mm, were extracted from each simulation and compared within Figure 8.70. The intensity of the spectra, from the Al_2O_3 sample, can be seen to decrease as the energy of the source increases. This is thought to be due to the number of photons at the low energy level decreasing in the simulated energy profiles.

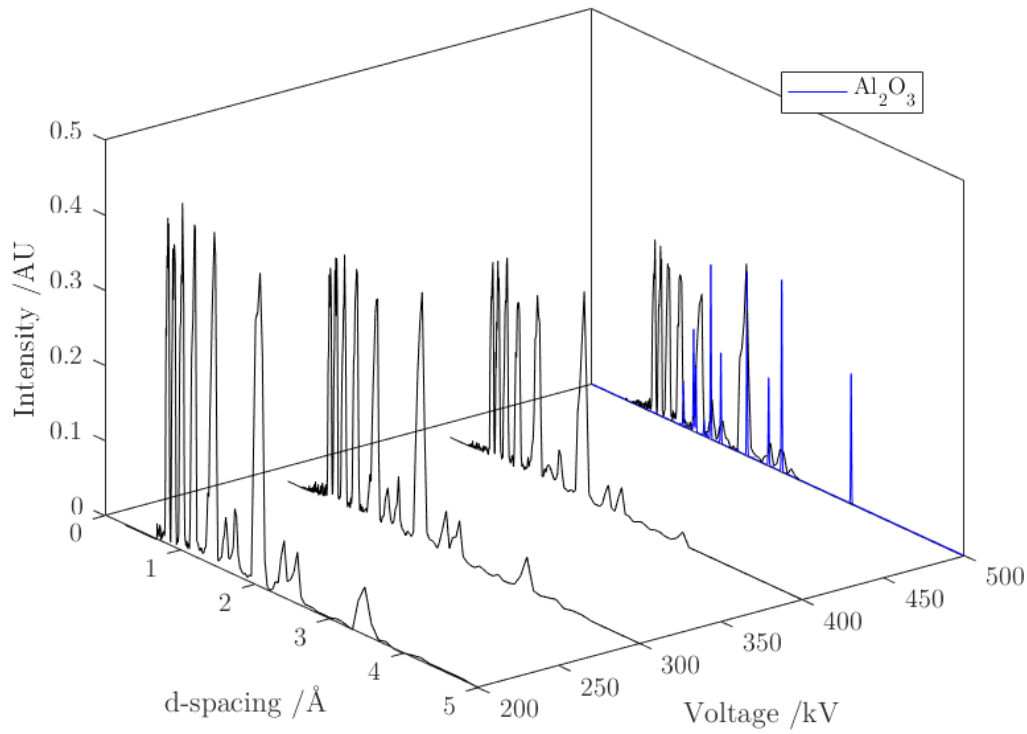


Figure 8.70 3D plot of the acquired energy spectra obtained from simulated FCG -pin hole technique measured at $r = 8$ mm, equating to $z = 190$ mm.

8.6 Concluding Remarks

This chapter presents the results from adopting Focal Construct Geometry (FCG) as a method to increase the intensity of the resultant diffraction maxima from the weakly scattering material. This was initially demonstrated analytically by comparison of pencil beam geometry and FCG, to demonstrate the increase in flux incident on the sample, thus increase in the interaction cross section area, resulting in diffraction maxima of enhanced intensity. This was calculated to be 408 times that of the pencil beams intensity.

The increased intensity of the diffraction maxima obtained employing FCG was further investigated using angular dispersive diffraction employing the Mo source, comparing the intensity of the resultant maxima from a sample of Al_2O_3 . In the pencil beam geometry, the diffraction profile was obtained via a stationary 2D detector array, whereas in FCG the detector was translated along the primary axis

in order to capture each on the condensation foci, which directly relates to each maxima in the pencil beams profile. This validates the analytical calculation by demonstrating the increase of intensity for each reflection for the annular beam geometry.

An additional benefit of using FCG, demonstrated with a sheet of Al, is the mitigation of effects caused by preferred orientation and large grain size, characteristic of some explosive powders.⁹⁰ When using pencil beam geometry, it is well known that the effects of preferred orientation and large grain size distort the resultant diffraction profile, often missing certain reflections and the relative peak intensity varying. With FCG it was demonstrated that although the sample contained preferred orientation, shown by the broken condensation rings, they still can be seen to converge, mitigating the effects of preferred orientation as the maxima can still be observed in the resultant profile.

Angular dispersive FCG was modelled with *McXtrace* and validated with a sample Al. Although *McXtrace* does not account for preferred orientation of the sample, the simulation showed good agreement to experimental results.

The use of ED techniques to gain access to higher energy photons was evaluated in terms of efficiency of the technique. High energy X-ray source spectra were simulated with the proportion of photons contributing to characteristic (AD) and Bremsstrahlung (ED) radiation assessed. It was shown that using higher voltage X-ray sources, up to 500 kVp, provides a greater proportion of photons contributing to the Bremsstrahlung radiation, indicating ED techniques are more efficient. ED-FCG is demonstrated, employing the high energy W source, realising the need for a method to enable depth perception due to highly coherent scattering metal samples overshadowing the weaker scattering polycrystalline explosive simulant.

ED-FCG was then demonstrated with both samples of NaCl and Al₂O₃ with the high energy W source. The samples were each individually translated along the primary axis to show the shift in energy of the peaks as the sample is translated. When the energy was converted into *d*-spacing the peaks align, due to the conversion relying on knowledge of the sample's location.

Multiplex samples were observed, namely sheets of Fe and NaCl, to demonstrate the reduction of the weakly scattering NaCl profile when individual sheets of Fe are incrementally added. In the experiment shown, the NaCl scatter was indistinguishable from the Fe scatter when there was 3 mm of Fe present.

In order to explore the possible separation of the individual materials scatter, a combination of AD and ED was investigated, by employing the HEXITEC detector as previous research, detailed in §4.1.2, suggested this as a potential method. The AD and ED functionalities of the HEXITEC detector were analysed before employing it in conjunction with a post-sample pin-hole aperture to enable depth perception.

This technique, employing both the post-sample pin-hole aperture and the HEXITEC detector was demonstrated employing multiplex sampling. The different samples, each with a different source-to sample distance, generate diffraction condensation rings with varying radii within the detector plane. This AD functionality of the HEXITEC detector allows each of the radii, within the detector plane to be associated with a voxel within the inspection volume. The ED functionality of the HEXITEC detector provides an energy spectrum corresponding to the material occupying that volume in space. *MATLAB* was utilised to convert the HEXITEC images to (d,z) maps, where the material phase signatures, or d -spacing values, can be represented as conventional diffraction profiles. This is demonstrated with individual samples of Al_2O_3 and NaCl, before demonstrating the recovery of the samples position by traversing a sample of Al_2O_3 along the primary axis. The variation of relative peak intensities is due to the change in the angle at which the diffracted beams from the sample form with the aperture pin-hole at the varying sample positions. At smaller sample-to-aperture distances ($D_A - D_S$ is smaller) the diffraction angle, 2θ , fixed in ED-FCG, is larger. At larger 2θ 's, diffracted beams have a longer wavelength, following Braggs Law, Equation (3.2), therefore the obtained diffraction is dependent on the position of the sample in relation to the pin-hole aperture.

Multiplex sampling was analysed, first by modelling an empty box, with two sheets of Fe, before modelling a metal container with a polycrystalline sample - explosive simulant - inside. Additional Fe sheets were added, as with the ADFCG method in §8.4, to evaluate the effect of increase thickness of a container on the obtainable scatter from the weakly scattering concealed material. In the images captured from the HEXITEC, the scatter from the polycrystalline material inside the simulated metal box, appeared to decrease in intensity as the thickness increases. This is the first time this technique has been implemented as a separation technique, i.e. used to remove the strong scatter originating from the metal container as opposed to location of the sample.

The effect of exposure time was evaluated, concluding that longer exposure times can achieve a diffraction pattern where the noise is negligible however the noise within the pattern is dependent on many factors within the system including the material, the source, the sample position, the geometry of the system, the thickness of the container wall and the proximity of the samples as well as exposure time.

The depth resolution of the high energy FCG, pin-hole system is evaluated analytically and compared to experimental data from samples of Fe, CaCO_3 and Al_2O_3 . Both analytically and experimentally, it was shown that the recovered sample appears significantly thicker than the actual sample and in the current geometry the samples need to be placed 30 mm apart to be recovered separately.

An infinitely thin sample was considered to indicate the depth resolution of the system, with multivariate analysis conducted to determine the most influential parameter for systematic broadening along the z -axis, revealed to be the radius of the pin-hole. Simulations were conducted to extend the system to higher energy, beyond the capabilities of the laboratory, to observe the affects and evaluate the potential restrictions. The intensity of the spectra can be seen to decrease as the voltage of the source increases, thought to be due to the number of photons at low energy levels decreasing in the simulated energy spectra.”

Chapter 9

Discussion

This chapter presents a critical analysis of the research undertaken throughout this study. It encompasses the initial validation experiments before moving on to the interpretation of scatter when no *a priori* information is known about the sample or its position, and evaluation of FCG at high energy.

XRD was identified as a potential technology to identify an explosive component within a highly absorbing metal container without disclosing sensitive information, and so was investigated for use as a tool within a weapons verification dismantlement regime. XRD offers superior specificity and safety advantages over the discussed Gamma and neutron techniques, detailed in Chapter 2.

Low energy conventional pencil beam ADXRD was employed to validate the use of the simulation software *McXtrace*. The capability of ADXRD to interpret coherent scatter originating from an unknown material at an unknown location was assessed. Three methods were introduced to locate the origin of scatter to aid the retrieval of material phase for material identification. All presented techniques - analytical, encoders and algorithmic - were successfully demonstrated and compared in terms of accuracy and reliability.

Focal construct geometry was considered, as a previously reported technique, to enhance diffraction flux and mitigate the effects of preferred orientation and large

grain size, characteristic of explosive compounds. AD-FCG was implemented at low energy and the resultant intensity compared to pencil beam ADXRD, both analytically and through experimental investigation, to demonstrate the increased scattering flux capabilities. A sample exhibiting preferred orientation was analysed demonstrating FCGs capability to mitigate its disruptive effects in conventional pencil beam ADXRD.

ED techniques were considered due to availability of high energy photons within the Bremsstrahlung portion of the X-ray source spectrum, increasing the penetration capabilities. Furthermore, ED techniques were revealed to be more efficient than AD techniques, when analysis was conducted measuring the proportions of the X-ray source spectra contributing to the characteristic lines (AD) and Bremsstrahlung (ED) radiation.

ED-FCG was implemented at high energy with a W X-ray source, demonstrating the capability to penetrate thick metal sheets (> 10 mm at 60 s exposure). Analysis of multiple samples demonstrated the diminished ability of the technique to identify weakly coherent scattering polycrystalline materials when a highly coherent scattering material was present.

The use of an energy sensitive pixelated detector, to combine spatial capabilities of ADXRD with the penetration abilities of EDXRD, was evaluated due to successful implementation reported in previous research, discussed in §4.1.3.

To enable depth perception, i.e. the ability to separate scatter originating from different positions along the z -axis, a post-sample pin-hole aperture was employed in conjunction with the HEXITEC detector. This technique was implemented using a high energy W source and demonstrated with multiple different sample geometries. The accuracy and precision of the technique were evaluated by translating samples along the z -axis and conducting an error study by error propagation.

The ability to isolate select conic sections of the AD-FCG images was demonstrated utilising a model mirroring a concealed explosive in a container, comprised of an explosive simulant between two metal sheets, representing the container walls.

The depth resolution of the system was evaluated analytically before being compared to obtained experimental data. The analytical model was then used to assess the thickness of an infinitely thin sample, indicating the depth resolution of the system is ~ 30 nm. Multivariate analysis was conducted to determine the significance of each variable within the analytical model. When only geometric parameters are considered, the radius of the pin-hole was established to be the most influential variable. Improving the depth resolution of the technique would enable objects of close proximity, to be distinguished and hence enhance the detection capability.

Finally, the technique was simulated at high energy, demonstrating its potential for use at higher energies, required for the potential use in real world applications.

9.1 Viability of *McXtrace*

McXtrace, the main simulation software employed for this study, was initially compared to pencil beam ADXRD experimental data obtained from low energy Cu experiments with the Bruker D8-GADDS diffractometer. The simple tests were designed to assess the basic functionalities of the software to confirm it was fit for purpose. The software was deemed capable of modelling the geometries needed for this research.

9.2 Interpretation of scatter

ADXRD methods were initially considered due to its superior material specificity and spatial awareness capability compared to EDXRD, the primary advantage of which is its speed, considered to be of less importance.

In XRD, knowledge of the origin of scatter (i.e. the position of the detector) in relation to the detector plane is crucial for determining the diffraction angle and thus identify unknown substances. The first half of this project, Chapter 7, focused on utilising pencil beam ADXRD to interpret the scatter from an unknown scattering source when no *a priori* information is known about the sample or its location.

Three techniques were introduced - analytical, encoders and algorithmic - which enabled the scattering origin to be determined aiding interpretation of the coherent scatter to recover material phase, to in turn identify the sample. Firstly, the analytical method alters the position of the detector along the primary axis by a known amount, obtaining a minimum of two diffraction patterns at difference locations. By measuring the change in the Debye cone radius, the distance between the sample and the detector can be calculated through the use of geometry and simultaneous equations, as described in §6.4.2.1.

The technique was demonstrated experimentally with a sample of Al_2O_3 placed an unknown distance from the detector. Both the samples location and the identity of the material were recovered independently. The same experiment was modelled via simulation and showed good agreement with the experimental result. Spatial differential is achieved without the use of post sample collimation which can result in a loss of up to 99% of the scattered beam flux.⁹⁸

Although this technique performed well when only two samples were included within the sample volume, ADXRD patterns become difficult to interpret due to the overlapping diffraction maxima meaning peak amplitude is an unreliable characteristic, thus no reliable coincidence information can be used to measure common maxima between each pattern. Furthermore, this technique relies on all peaks being measured in both diffraction patterns obtained at the two different positions. Here, visual inspection was used to find common maxima however if this was to be used in the future a computation method could be developed to detect and interpret the peaks within the different images collected.

Additional problems within this technique include the need to rely on moving parts, obtaining two images with one detector from different positions along the z -axis. To overcome this, more detectors could be used to each obtain part of the diffraction pattern. Dicken *et al.* developed a method using four detector positions to increase reliability, but this reduces the possibility for detecting compounds with preferred orientation or large grain size which was the main difference discovered when comparing the simulated results conducted with ideal samples than with the experimental results which exhibited large grain size, Figure 7.9.¹¹⁵

Like the analytical method, the encoder technique is a similar geometry dependent method. It introduces a post-sample reference structure to ‘encode’ the scatter originating from the sample. The encoder absorbs a proportion of the diffraction scatter, leaving a “shadow” in the transmitted diffraction pattern. Since the position of the coded aperture mask is known in relation to the detector, it acts as a reference structure, unambiguously modulating the diffraction.⁶⁰ The encoders employed here function the same way the comb-like structures work, developed by MacCabe *et al.* (2012⁶⁰, 2013¹¹⁷). As with the comb-like structures, encoders are utilised to determine the position of the sample along the primary axis. The primary advantage gained over using the encoders is the intensity of the resultant scatter within the detector plane is increased due to the open fraction of the encoders as the comb-like structures would absorb ~50% of the scattered photons before reaching the detector plane.

The encoders were successfully employed for recovery of sample position to aid material phase recovery without the need for moving components. A linear wire was used as a post-sample encoder, the distinctive feature of which is its off-centre location, giving rise to unique polar angles with respect to the radius of the Debye cone. It was demonstrated through both simulation and experimental tests that determination of the sample’s location can be achieved when no *a priori* knowledge of the sample’s position relative to the detector.

As the dimensions of the linear encoder appear greater within the detector plane when the sample is close to the encoder, greater human and experimental errors arise leading to lower system specificity. The uncertainties associated with the position of each of the components were calculated using error propagation to determine the optimal geometry to gain the most accurate values for both D_{SD} and 2θ . The associated errors when calculating the sample position and diffraction angle are minimised when the offset distance, α_{LE} , and encoder-to-detector distance, $D_{LE:D}$, are maximised. This means that when α_{LE} is increased, the sensitivity of the encoder for spatial resolution is increased due to the measurement of the encoding angle being more distinguishable. The α_{LE} is limited by the low angle scattering photons, 2θ , which need to intersect the encoder in order to ‘encode’ the

Debye cones. Thus, a compromise between sensitivity and specificity has to be made with this system.

The Archimedean spiral encoder, the geometry of which is described in §6.4.2.2, was introduced as a way of overcoming this limitation of the linear encoder. The same analysis as for the linear encoder was conducted and it was determined that the optimum position of the spiral encoder (error is minimised) is when the Archimedean spiral encoder is close to the sample, i.e. the spiral encoder is more sensitive when the sample is placed closer to the encoder. When calculating the sample-to-detector distance, D_{SD} , the most significant error arose from measuring the spiral-to-detector distance, $D_{AS:D}$. Considering the diffraction angle calculation, the most dominant errors were seen in the measurement of the radius in the detector plane, r . This can be decreased employing a higher resolution energy detector.

Linear and spiral post-sample encoders were shown to be effective at providing geometric and structural information and experimental results showed good agreement with analytically calculated results. Both linear and spiral encoders were shown to provide single axis positions with $\sim 1\%$ precision.

The final method introduced, the algorithmic method presents an algorithm by which the diffraction data is compared to a set database of materials to produce a likelihood of materials at specific locations. As with the two previous techniques, the sample to detector distance, D_{SD} , was calculated. This was compared to the actual sample-to-detector distance and the absolute precision error calculated for each sample at every position. The absolute precision errors for two samples placed within a sample volume were determined by simulating the samples throughout the volume. The radii at two different detector positions were measured, and the algorithm used to retrieve the positions of the samples. The errors were seen to be greatly reduced when the detector was placed furthest away from the sample. This was expected as the Debye cones for each pattern will be further apart making them more perceptible. The specificity of the technique can be tailored by altering the minimum threshold distance between peaks before they are considered a match. No post-sample collimation is used to ensure that the scattered X-rays contribute

to the resulting diffraction pattern. This increase in intensity decreases the effects of preferred orientation.

Comparing all three techniques, the analytical method produces the greatest average variation from the true sample location and is also the least reliable, incorrectly determining the location 13.3 % of the time. The encoders both have less variation between the calculated and true value of the sample location and are also more reliable than the analytical technique. The spiral encoder is seen to be more reliable than the linear encoder, this was primarily due to the inability to determine the location in some linear encoder geometries due to the Debye cone bypassing the encoder. The algorithmic technique located the sample 100% of the time and produced the least variation, indicating the highest accuracy amongst the techniques presented.

All these techniques are limited by elongated (thick) samples, extending along the primary axis as this would result in the broadening of the peaks within the diffraction plane impeding the performance of all the techniques due to overlapping peaks in the resulting diffraction profiles. These methods are used assuming that:

- i) angular dispersive diffraction is used
- ii) three diffraction peak positions are required for 1D materials
- iii) three Debye rings are always measurable on the detector and
- iv) intensities are irrelevant.

9.3 FCG

Focal construct geometry, FCG, detailed in §3.4.2, is adopted as a method of increasing the diffraction flux and mitigating the effects of preferred orientation and large grain size, characteristic of explosive compounds.⁶⁸

9.3.1 Pencil beam vs. FCG

FCG involves the use of a pre-sample collimator, in place of a pencil beam optic, to modify the morphology of the incident beam.

The geometries were analytically compared by calculating the relative open fraction area allowing the incident X-ray to reach the sample plane. The FCG:PB ratio was

calculated, using the parameters employed in the equivalent experimental comparison, detailed in §6.4.3.1. Analytically, the increased interaction cross section area results in the FCG geometry having an enhanced diffraction flux of 408 times.

Data for the experimental comparison was attained using the low energy Mo source (25 kV and 20 mA) in conjunction with the PIXIS detector, analysing a 1.53 mm Al_2O_3 sample. The measured FCG:PB ratio ranged from 382-1062, depending on the reflection used, encompassing the calculated analytical value. Rogers *et al.*(2010)¹⁰⁶ noted on the differences between the intensities arising from the annular beam geometry and the pencil beam arrangement concluding that the differences are primarily due to the Lorentz factor which varies with beam geometries. This could explain the inconsistencies in the FCG:PB ratio determined from experimental data.

Analysing the two different geometries it is worth noting that if a sample is smaller than the diameter than the annular beam, i.e. only a small part of the annulus interacts with the sample with most of the photons missing the sample, no significant increase in intensity would be observed when compared to a pencil beam of the same diameter as the annular wall thickness. Therefore, if a pencil beam of a cross-sectional area equating to the cross-sectional area of an annular beam within the detector plane, there would be no significant difference in intensity. However, a pencil beam with a large beam divergence would generate significantly broader diffraction peaks. FCG brings together the high intensity achieved from increasing the incident beam cross-sectional area with its capability of converging the scattered photons, focussing the scattering maxima.

9.3.2 AD-FCG

Simulations of AD-FCG were conducted in *McXtrace*, modelling the Mo source and PIXIS detector, to demonstrate the capability of the simulation software. Condensation rings emitted from the Al_2O_3 sample can be seen converging towards the centre of the image as they approach their condensation focus and then diverging away from the centre, Figure 8.6. Once the intensity of the centre pixel of each image was summed to generate a z -axis profile a good correlation was seen to the reference profile for Al_2O_3 .

To demonstrate the capability of FCG to mitigate the effects of preferred orientation, which impedes the use of conventional pencil beam ADXRD, due to the omission of d -spacings in the resulting pattern, a sample of 1.3 mm Al exhibiting preferred orientation was investigated. Due to the preferred orientation the Al diffraction images exhibit broken condensation rings. The broken condensation rings can still be seen converging as they approach their condensation focus and then diverging in opposite directions, Figure 8.8.

Conducting the low energy experiments revealed difficulty in acquiring small d -spacings, due to their associated large scattering angles. The ability to detect small d -spacings is reliant of several factors of the setup. Condensation foci from small d -spacings form close to the sample plane. Decreasing the sample-to-detector distance, theoretically allows the observation of the condensation foci at this close proximity. Practically this results in the primary annular beam impinging on the detector window, flooding the detector.

Without decreasing the size of the detector window, several geometric alterations can be considered. The radii of annular collimator can be increased by increasing the radius of the annular collimator creating a larger opening angle, φ_m , this can also be achieved by moving the annular collimator closer to the source. Increasing the opening angle incidentally increases the dimensions of the whole system, extending along the z -axis. However, in extreme situations, this can cause the diffracted Debye cones to diverge, rather than converge, meaning a condensation focus cannot form, illustrated in Figure 9.1. *McXtrace* was used to simulate Al with the primary annular beam removed from the simulation after diffraction, allowing acquisition of the lower d -spacings.

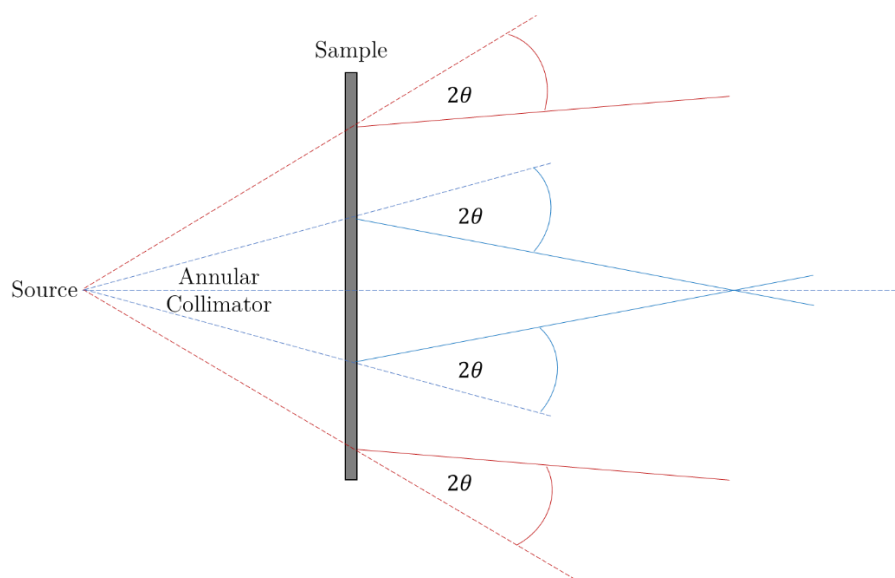


Figure 9.1 Schematic demonstrating the extreme geometry when the radius of the annular collimator is increased to a point where the diffracted beams, shown in solid red, will never converge. The blue trace demonstrates the formation of a condensation focus when the radius of the annular collimator is small.

9.4 High energy: AD vs. ED

Although useful in applications where high resolution is required such as pharmaceuticals and forensics, AD techniques are limited by the energy of the characteristic peak, meaning their penetration ability is limited. As discussed in §3.3, energy dispersive methods employ the polychromatic Bremsstrahlung portion of the spectrum and thus is only limited by the maximum voltage applied across the X-ray tube, §3.2.2.1. Producing X-rays via an X-ray tube the maximum voltage is limited to 450 kVp, to gain higher energies an accelerator is used.^{33,93} Tungsten sources were analysed due to being the highest energy portable sources commercially available.^{93,140}

ED techniques were considered due to the increased penetration capability offered, due to the higher energy photons obtainable by using the Bremsstrahlung portion of the X-ray spectrum. The efficiency of the two techniques was compared by analysing the proportions of each radiation in the X-ray source spectra generated by increasing the source voltage.

Experimental source spectra, obtained from the high energy VJ Technology W source, were compared to data from *SpekCalc* at various peak voltages which clearly illustrates a strong agreement to the simulated spectra, Figure 8.12. *SpekCalc* was employed to extend the voltage of the source beyond the capability of the lab to 500 kVp and the spectra evaluated. The higher the proportion of contributed photons, the higher the incident flux thus greater efficiency.

Analysing Figure 8.13, the proportion of Bremsstrahlung radiation decreases as the voltage increases, however the overall contribution from Bremsstrahlung is still greater than that of characteristic at 500 kVp. Thus, when working at high voltages, considered here, it is more efficient to utilise energy dispersive diffraction than angular dispersive diffraction.

In §7.1.4 it was shown that employing conventional pencil beam geometry at high energy results in the Debye cones generated having a smaller diffraction angle, 2θ . This either results in patterns with poor resolution or extended geometry set-up with the detector being placed far away from the scattering source.

Employing AD-FCG has a similar restriction; as the diffraction angle decreases the condensation foci translate further along the primary axis, extending the geometry of the system. To demonstrate this effect, simulations of a 15 mm Al_2O_3 sample placed at $D_S = 135$ mm, $\varphi_m = 2.5^\circ$ and the detector fixed in place at $D = 210$ mm, were conducted. The results of increasing the energy source can be seen in Figure 9.2, where the condensation rings increase in diameter in the detector plane indicating the foci are forming further along the primary z axis.

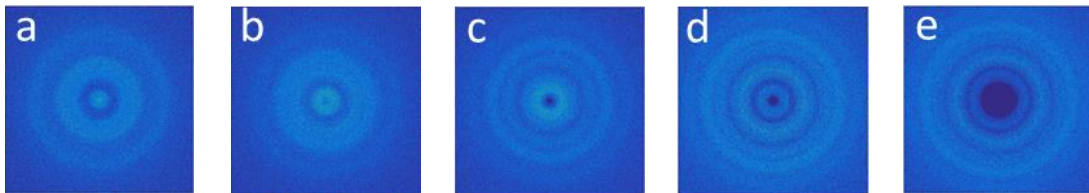


Figure 9.2 Simulated AD-FCG images with increasing energies a) 50 keV b) 60 keV c) 70 keV d) 80 keV e) 90 keV.

In extreme cases the Debye cones will not converge. This effect can be counteracted by decreasing the opening angle of the angular beam, φ_m , producing a narrower hollow conical incident beam.

It is worthwhile analysing Braggs' Law to evaluate the limitations, if any, that would be imposed by increasing the energy. For a diffracted beam, θ is limited between 0° and 90° . Evaluating the consequence of this within Braggs' law results in:

$$\lim_{\theta \rightarrow 0} \sin \theta = 0$$

$$\lim_{\theta \rightarrow 90} \sin \theta = 1$$

When $\sin \theta = 0$ the corresponding d -spacing is infinite, meaning practically there is no distance between planes that gives a phase change resulting in no diffraction and therefore no spatial information. At $\sin \theta = 1$, $d = \lambda/2$, meaning information can be obtained about d -spacings equal to half the wavelength of the incident beam or greater. Since the wavelength-energy relationship shows that an increase in energy results in a shortening of the wavelength incident on the sample, it can be used along with the previous deduction to demonstrate that as the energy is increased, the resolution of the data also increases.

9.5 Energy Dispersive-FCG

With access to higher energy photons for increased penetration ability, FCG was combined with energy dispersive methods to create energy dispersive FCG, ED-FCG. To demonstrate the ED-FCG technique a high energy system was built employing a W source in conjunction with an energy dispersive X-123CdTe Amptek detector. The energy dispersive detector was centrally placed along the primary axis. Unlike the ADFCG technique, the detector remains stationary as there is no requirement to take multiple measurements long the principle axis of the annular beam to obtain structural information, much like the pencil beam system.

No scattering collimators are employed for this technique, meaning knowledge of the sample position, along the primary axis is crucial to retrieving material phase; a parallel that exists with pencil beam EDXRD where the scattering angle is

narrowly defined to determine the d -spacing. Studies by Dicken *et al.* have shown ED-FCG technique is limited by the geometric blurring evidenced via peak broadening.

The technique was initially demonstrated with a single 1 mm sample of Fe before investigating the placement of the sample on the resulting diffraction profile by translating 15 mm NaCl and Al₂O₃ samples through the annular beam along the z -axis. This demonstrated the ability to retrieve material phase with *a priori* knowledge of the sample position. The diffraction profiles appear to shift to a lower energy as the source-to-sample distance, D_S , increases. This is due to the geometry of the system, as detailed in §3.4.2. Since the conversion to d -spacing values is dependent on knowledge of the sample position, the conversion shifts the profiles to correct d -spacings, observed in Figure 8.16(b) and Figure 8.17(b), which show good agreement with the respective reference profile.

To observe the effect of an increased presence of a highly scattering metal within the sample volume, a 15 mm sample of NaCl was placed in the annular beam, with a diffraction profile obtained after each subsequent addition of 0.5 mm Fe samples. The resulting diffraction profiles, Figure 8.18, show the reduced intensity of the NaCl profile with each addition of Fe. The diminished ability of the technique to identify weakly coherent scattering polycrystalline materials when a highly coherent scattering material was present indicates the need for depth awareness, enabling the isolation of scatter from weakly scattering polycrystalline materials.

9.6 HEXITEC detector

A combination of both AD and ED techniques was sought, as previous research, Greenberg *et al.* (2013)^{37,104} detailed in §4.1.3, suggested this as a possible method to enable depth awareness.

The HEXITEC detector was introduced, offering simultaneous acquisition of AD and ED data through an array of 80×80 pixels, each capable of measuring a diffraction pattern. Previously used by Christodoulou *et al.* (2011)⁹⁹ and O’Flynn *et al.* (2017)⁸⁹, the HEXITEC has a large angular window, offering the simultaneous acquisition of spatially and energy resolved data, contrasting standard EDXRD

systems where the scatter beam is usually highly collimated to obtain scatter from specific voxels.

The HEXITEC detector is initially demonstrated with a pencil beam ADXRD geometry, observing a sample of Al and a sample of Al_2O_3 , exhibiting large grain size. AD-FCG was implemented with individual CaCO_3 and Al_2O_3 samples before investigating multiplex sampling where the CaCO_3 samples were spatially separated along the z -axis. The HEXITEC detector has noticeably lower angular resolution than the previously employed PIXIS, due to the larger pixel size.

The functionality of the HEXITEC detector to conducted high energy ED-FCG was investigated employing the high energy VJ Technology IXS1680 (W source). Diffraction profiles were obtained increasing the exposure time of each one by 120 s, up to a maximum of 600s. As expected, the diffraction profile acquired over a longer exposure time contained less noise, due to the increase in diffraction flux enhancing the SNR ratio.

The HEXITEC detector enables the detection of both AD and ED scattered photons simultaneously, but the sole use of the detector doesn't enable the depth awareness required. Previous work using energy sensitive pixelated detection to identify spatial information from voxels in the extended sample have required pre- and post-sample collimation to precisely define the point of intersection.^{57,112,159}

9.6.1 Depth Awareness

The HEXITEC detector was introduced as a method to simultaneous measure both AD and ED scattered photons. When used in conjunction with a post-sample pin-hole encoder, the material identification capabilities of EDXRD and the spatial awareness capabilities of ADXRD, enable depth perception along the z -axis.

The pin-hole aperture is placed between the sample and the detector to modify the resultant scattering diffraction. The technique not only enables depth perception but additionally offers a method to isolate scatter originating from specific sample-to-detector distances. This provides the method needed to isolate scatter originating from weakly coherent scattering polycrystalline materials from highly coherent scattering materials, that would otherwise dominate the diffraction pattern.

Contrasting previous FCG single snapshot techniques - AD-FCG and ED-FCG - no previous knowledge of the sample location is required to determine the phase of each sample.

To demonstrate the capability of the technique to recover the sample position a 15 mm Al_2O_3 sample was incrementally translated through the annular beam with a 60 s exposure obtained at each position. Analysing the resulting diffraction patterns from each position, the relative peaks widths can be seen to vary depending on the samples position within the system. Narrower diffraction peaks are seen when the sample is closer to the detector. This variation is due to the change in the angle at which the diffracted beams from the sample form with the pin-hole aperture at the varying sample positions. At smaller sample-to-aperture distances ($D_A - D_S$ is smaller) the diffraction angle, 2θ , fixed in ED-FCG, is larger. At larger 2θ s, diffracted beams have a longer wavelength, following Braggs Law, Equation (3.2), therefore the obtained diffraction is dependent on the position of the sample in relation to the pin-hole aperture.

The accuracy of technique to recover the samples position was evaluated, employing the 15 mm Al_2O_3 and CaCO_3 samples and additionally a sample of 1 mm Fe. The samples were individually translated along the z -axis with exposures obtained at each increment. The obtained AD images were azimuthally integrated to produce radial plots. The measured radius, associated with the sample position, was taken to be at the maximum intensity, Figure 8.33. The radial values were converted into source-to-sample distance, D_S . The recovered sample position, D_S , shows good correspondence with known sample locations particularly when the sample is placed close to the detector, i.e. D_S is large.

Error propagation was used to calculate the uncertainty in measurement of D_S , indicating the precision of the technique. As the source-to-sample distance, D_S , increases, the precision of the measurement increases, indicated by the decreasing magnitude of the error, seen in Figure 8.34, Figure 8.35 and Figure 8.36. The

recovered position is most precise, and closest to the actual value, when the sample-to-detector distance, D_{SD} , is minimum i.e. D_S is large.

Multiplex sampling was investigated, observing multiple samples simultaneously in the primary beam at spatially separated positions along the z -axis. Individual samples were shown to produce polychromatic, range dependent rings in the detector plane. This was demonstrated using spatially separated samples of 1 mm Al and 15 mm CaCO_3 . Integrating select conic sections through an annular gauge volume, i.e. summing a select number of rows within the (d,z) map enables individual diffraction patterns of the different materials spatially separated within the inspection volume to be obtained.

A container was modelled with sheets of Fe either side of an explosive simulant, Al_2O_3 , to show that by isolating individual conic sections, the individual pattern of the concealed material can be distinguished. This is presented in a 3D plot Figure 8.43, where 10 mm conic section were selected throughout the gauge volume. The obtained diffraction pattern can be seen to initially represent the Fe sample before merging into Al_2O_3 , placed at the centre, before displaying Fe again.

An investigation was conducted evaluating the thickness of the metal container. This was modelled by increasing the number of Fe samples, either side of the explosive simulant. As the number of Fe sheets increased, modelling a thicker container, observation of the AD images shows the middle conic section corresponding to Al_2O_3 decreasing in intensity with each additional sheet of Fe, Figure 8.45. Integrating the conic section surrounding the Al_2O_3 sample and measuring the maximum intensity of each, confirmed the decrease in intensity of Al_2O_3 when each additional Fe sheet was added, Figure 8.46.

A study was conducted evaluating the effect of the thickness of the container wall on the noise associated with the obtained diffraction pattern of the concealed sample, Al_2O_3 . The process of measuring the noise detailed in §6.5.3 and previously employed in §8.5. As the thickness of the container increases, the noise measured from each of the Al_2O_3 conic section increases. A logarithmic correlation was used to model the trend. This trend was expected as it will reach a point where the difference between the residuals (Δ residuals) is at a maximum between the

normalised profiles indicating a very poor SNR, where the diffraction pattern can not be distinguished from the noise.

Results are presented when a 5 mm thick container was modelled, and the image obtained with an exposure of 300 s. The corresponding (d,z) map is presented with the corresponding diffraction profile, integrating through the whole gauge volume. Analysing the diffraction profile within Figure 8.49, it is clear the diffraction from Al_2O_3 is completely overshadowed from predominant diffraction from the Fe. A 3D plot was created isolating 10 mm sections through z space, Figure 8.50, where the diffraction originating from the Al_2O_3 sample can be seen.

The same 5 mm thick container geometry was observed at different exposure times to evaluate the effect of exposure time on the magnitude of noise within the obtained diffraction patterns from the Al_2O_3 sample. The extracted diffraction patterns from integrated 10 mm volumes around the Al_2O_3 sample for each exposure time is presented with the normalised diffraction profiles. The noise was measured, as described in §6.5.3, trendline shown is modelled by an exponential decay which is expected; when the exposure time is increased the noise contained within the diffraction profile decreases. The noise within the diffraction pattern depends on many factors including the material, the samples position, the source, the geometry of the system, the thickness of the container wall, the proximity to other samples as well as the exposure time.

The novel FCG technique presented here, minimises the need for mechanical movement as one snapshot image contains energy dispersive data for compounds throughout the entire volume, through the path traversed by the incident annular beam.

As is apparent from the 3D plots, such as those presented in Figure 8.43 and Figure 8.50, within (d,z) space samples appear thicker than their physical dimensions. The peaks in the determined diffraction profiles exhibit systematic broadening due to associated effects of the physical parameters, which describe the primary/diffracted beam collimation and energy/spatial resolution. This may have impact on the performance of the technique, restricting the use when samples are in close

proximity with intensely scattering objects overshadowing weakly scattering samples i.e. a sample is close to its container wall.

9.6.2 Depth Resolution

FCG XRD was coupled with a post-sample pin-hole aperture to enable depth perception. The geometric limitations of the technique were explored examining the depth resolution along the z -axis. The varying depth resolution within the system was demonstrated by translating two 15 mm Al_2O_3 samples at a fixed 36 mm apart along the z -axis in increments of 12 mm. It is apparent, producing radial plot of the AD images - Figure 8.54, that the two samples appear further apart when they are placed closer to the detector. To understand why the two samples appear as one sample when placed close to the X-ray source, a study was undertaken to determine the apparent sample thickness, Δz , and compare analytical calculation to experimental results.

An equation for the radial average, r_{av} , was constructed which included all possible contributory physical parameters that could be attributable to the broadening. This analytical radial average, r_{av} , corresponds to the measured radius of the conic section within the detector plane. This is determined by measuring the peak intensity of the radial plot calculated from azimuthally integrating the HEXITEC image. The equation was used to predict the radius of the resulting scatters' conic section at the detector plane when a 1 mm sample of Fe was traversed along the z -axis. HEXITEC images were obtained and azimuthally integrated to determine the peak intensity corresponding to the radial value, which showed good agreement with the predicted values.

Employing a similar methodology, the recovered sample thickness was evaluated when individual samples were translated along the primary z -axis. Using obtained HEXITEC images and azimuthally integrating them to produce the radial plots - as previously produced to find the average radii resultant scatter - the recovered thickness can be measured by determining the left-full width at half maximum (FWHM) and right-FWHM of the intensity peak. The calculated depth resolution was shown to have good agreement with the obtained FWHM measured. The depth resolution of the system, whilst also improving in precision, improved with

increasing distance from the source, D_S , demonstrated by the decreasing recovered thickness of the sample.

An infinitely thin sample was considered and analytically translated through the sample space. The sample apparent thickness, Δz , was calculated and indicated that a sample placed at the base of the system will be observed as being ~ 48 mm thick in the recovered sample thickness. This decreased to 0 mm thick as the sample was translated along the z -axis towards the detector, achieving 0 mm when placed directly up against the pin-hole aperture.

Multivariate analysis was performed to consider not only the significance of each parameter but to evaluate the most dominant variables in the system. The most dominant parameters were determined to be the related to the opening angle of the annular beam, φ_{min} , followed by φ_{max} . When considering just the geometry of the encoder the most influential variable was the radius of the pin-hole, a . This indicates that to decrease recovered thickness, the diameter of the pinhole could be reduced. However, this would reduce the flux incident on the detector, increasing the noise, which could in turn be counteracted with longer exposure times.

To obtain the best resolution from the system, the sample needs to be placed far away from the source of the X-rays so multiple samples may be distinguished from one another. Whilst the resolution is still poor, the greatest uncertainty arose from the measurement of r . This could be enhanced with increased detector resolution, improving the resolution and precision of the whole system. The precision of this technique is constrained by the engineering and mechanical tolerances of the collimators and need for translation of the sample through the intersection voxel.

9.7 High Energy

For this FCG pin-hole technique to be applied to real world situations, it would be required to work at higher energies to penetrate thick metal containers. Employing conventional pencil beam geometry at high energy results in the Debye cones generated having a smaller diffraction angle, 2θ . This either results in patterns with poor resolution or extended geometry set-up with the detector being placed far away from the scattering source.

Simulations conducted at higher energies ($< 500\text{kVp}$) provided an indication of limitations that might affect the use of the system. The middle diffraction pattern was extracted from each simulation and compared. The intensity of the diffraction patterns decreased as the voltage of the source increased. The decrease in intensity can be associated with the reduction of Bremsstrahlung radiation in the X-ray spectra as investigated in §8.3. This effect can be overcome by increasing the exposure time when using higher voltage X-ray sources.

In pencil beam XRD higher energy provides a decrease in angular resolution as 2θ diffraction angles decrease with increasing X-ray beam energy. However, by moving the detector further from the diffracting material acts as a positive optical lever, mitigating the loss of angular resolution, though this is at the expense of the system sensitivity given the inverse squared law and additional absorption. However, FCG copes favourably with the angular measurement of relatively long throw focal spots because $\delta\theta/\delta Z$ reduces with increasing sample to detector distance i.e. decreasing values of D_{SD} from simple optical lever considerations.

It is important to note that increasing the energy excessively will result in the scattering angles decreasing to a point where the diffraction condensation rings will diverge and not converge, as illustrated by Figure 9.1, depicting the extreme geometry when the radius of the annular collimator is increased.

Chapter 10

Conclusions and Future Work

The primary conclusions from this research are presented with recommendations for future work. Key contributions of this research to the field are outlined, focussing on the development of weapons dismantlement.

10.1 Research Conclusions

The primary challenge when verifying nuclear disarmament is that there are no established methods to verify that a nuclear weapon (NW) has been dismantled according to international law without revealing sensitive information about the weapon design. The aim of this research was to interrogate a potentially viable technology to aid the identification of the high explosive component within a nuclear warhead container and evaluate its potential utility.

This project has been split into two distinct parts; the first involves the use of pencil beam ADXRD to locate and identify the material inside a given volume, the second looks at improving the intensity of the signal by using focal construct geometry (FCG), before analysing the limitations of the technique by evaluating the constraints, such as the resolution of the system, that could restrict the use of the technique.

Due to its high specificity and advantages over the nuclear techniques, XRD was chosen to investigate the possibility of identifying explosives concealed a highly absorbing metal container without revealing sensitive information and investigate its utility, weapons dismantlement verification.

Pencil beam ADXRD was initially considered due to its higher spatial resolution over EDXRD. Several methods of data interpretation are investigated to recover spatial information of unknown samples along the primary axis.

An analytical method was tested experimentally and compared to simulations to determine the source of the radiation before introducing post sample linear and Archimedean spiral encoders designed to act as a reference structures to determine the origin of scatter. The final method of interpretation, algorithmic, utilised a novel algorithm to determine the presence, or absence, of specific materials held in a database. All three method demonstrated the ability to ascertain the location of the sample to aid the identification of the sample.

An annular beam was employed for FCG experiments, initially being compared to pencil beam ADXRD, demonstrating the increase of flux incident on the sample, increasing the intensity of the resulting diffraction maxima. EDXRD was used to gain access to higher energy photons enabling the penetration of highly absorbing, thick materials. A method was successfully introduced enabling depth awareness along the primary axis employing a post-sample pin-hole aperture in conjunction a HEXITEC detector. Simulations of this geometry were conducted, extending to higher energy to provide an indication of the performance at higher energy and indicate any limitation that might affect the use of the system.

This project is the first research evaluating the use of XRD for the detection of explosives inside nuclear weapons and has outlined the fundamental ability of XRD within the field of weapons dismantlement. Overall the work has demonstrated that XRD is a potential technique to aid weapons dismantlement verification as one component of a toolkit available to the inspectors to verify the dismantlement.

10.2 Recommendations for future work

Whilst this work has demonstrated the feasibility of this technique on a small-scale, real-world application would require a higher energy source to penetrate the larger containers that would need to be evaluated. One of the primary future considerations would be to scale up the experiment, introducing a higher energy source, for greater penetration depth and consideration of a greater variety of metals and materials applicable to weapons dismantlement scenarios.

The system could further be optimised to improve its depth resolution, enabling samples in closer proximity to be individually identified, by altering the dimensions of the pin-hole aperture, optimising the geometric components. In addition, work by Wilson et al. (2015)¹⁴¹ to increase the dimensions of the energy sensitive pixelated detector could vastly improve the magnitude of the inspection volume capable of being imaged.

The use of real explosives in experiments is a subsequent step to bring the technique closer to the real-world application. Although explosives are crystalline materials, the materials chosen for this study are known to be highly scattering materials, explosives will perform differently due to their varied composition. Explosive compounds are frequently combined with other explosives, stabilizers, tagging agents, plasticizers, and other modifiers to increase the stability and efficiency to make it suitable for the required application, this would alter the resulting diffraction pattern.

Commercial explosives such as dynamites, water gels and slurries (e.g. ANFO - a mixture of ammonium nitrate and fuel oil) are used in mining and demolition. Military explosives, for example TNT, RDX and PETN are generally more stable than their commercial counterparts due to less extreme conditions when handling. Military explosives - or combinations of them and their products - are used in warheads or plasticized to form Semtex or C-4. To minimise the volume of explosive necessary to conduct future experiments, a custom-built 3D printed torus shaped container (Figure 10.1) has been designed. The torus shape results in the maximum volume of explosive interacting with the conical shaped beam when utilised in conjunction with the pre-existing system.

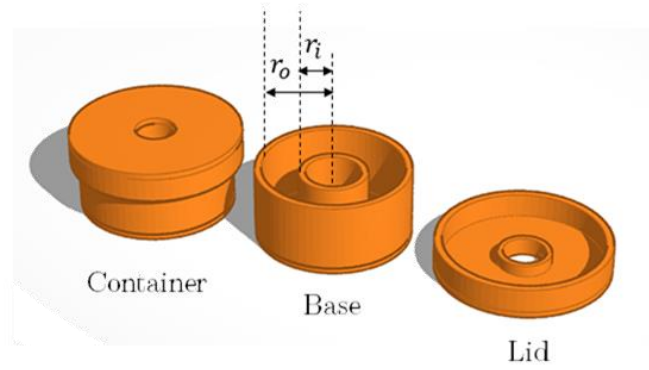


Figure 10.1 Illustration showing the design of the torus shaped container for the testing of explosives. The dimensions shown are the inner, $r_i = 5.5 \text{ mm}$ and outer $r_o = 11.5 \text{ mm}$ radius of the internal volume, to encompass the conical incident beam. The wall thickness was 1mm and internal height is 11 mm.

This work could furthermore be used to design the storage container that the explosive component would be stored in. If a standardised container existed, the confidence of the inspectors verifying the dismantlement could be enhanced to confirm the absence of undeclared design/components within the weapon and the verification of dismantlement.

Furthermore, the novel algorithm used in the algorithmic approach, could be developed to include a larger database of materials to potentially introduce a system of confirming the presence or absence of the explosive component without revealing the specific content. To later use this technique within the field, some form of Information Barrier will be required to hide the exact explosive used within the weapon. A system could be devised where the list of possible explosives is used as a comparison, in the same way the algorithmic method functions, with a simple output stating whether the data obtained matches one or more of the explosives and conforming to the relevant treaty, without revealing the specific material.

10.3 Contributions to knowledge

This research has identified X-ray diffraction as a promising technique which has the potential to identify the explosive component within a nuclear warhead. The techniques demonstrated here have many potential applications, not just in nuclear weapon dismantlement, but also in security environments such as aviation and imported goods, not just limited to explosives but also to other illicit materials.

X-ray diffraction has been evaluated, initially using the conventional pencil beam geometry to solve the long-standing limitation of this technique, the need to know the location of the sample prior to the experiment, to interpret the data. This was performed using a variety of methods which have all been evaluated and compared on the basis of accurately determining the source of the radiation. The effective use of two novel encoders, linear and Archimedean spiral, were demonstrated via simulation, and compared to experimental data. This established the effective recovery of either a single sample or multiple samples position along the primary axis. In turn, this enabled the determination of the samples diffraction angles to identify the concealed materials. Similar encoders proposed by previous studies^{60,160} have the main disadvantage of a ~50% loss of scattered rays due to their ~50% open fraction structure.

A novel algorithm was developed and utilised to search through the diffraction profile of a concealed sample - when no prior knowledge of the location was known - to determine the presence or absence of specific illicit materials held within a database. The accuracy of this technique to determine the scattering source was evaluated and compared to the other techniques used.

By adopting a novel X-ray diffraction technique of focal construct geometry (FCG) utilising an annular beam, the intensity of the resulting diffraction pattern was increased, providing an improved signal-to-noise ratio compared to pencil beam.

Angular and energy dispersive diffraction were compared to analyse the efficiency of using the two techniques at various energy levels. EDXRD was seen to be the highest contributor at higher energy level so further work conducted, focused on utilised EDXRD.

This technique paired with a pin hole aperture and a HEXITEC detector, combining angular and energy dispersive detection, allowed for depth perception along the primary axis. In turn, this meant that the strong signal produced by the highly absorbing metal, could be separated from the weaker scattering signature produced by the explosive material. This research presents the first of its kind to present this technology being implemented as an isolation technique, isolating weakly scattering objects from highly scattering metal structures, as opposed to sample locating technique.

The resolution of this technique was evaluated for the purpose of greater understanding of the system to aid its development. This analysis indicated, that in the current geometry, the concealed explosive would need to be placed ~30 mm away from a highly scattering container wall in order to be clearly identified.

Simulations were used as a comparison to experimental data and then employed to increase the energy of the source, enabling greater depth penetration, giving a proof-of-principle that this technique can be used at higher energies in real-world applications.

Overall, this research is the first of its kind to identify and demonstrate FCG X-ray diffraction as a potential technology with the capability to identify and locate concealed explosives within high absorbing metal containers furthering the possibility to aid the verification of nuclear warhead dismantlement.

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Appendices

Appendix A Peak data

Aluminium oxide, Al₂O₃ (PDF Card number 75-1862)

h	k	l	d-spacing /Å	2θ /°			Intensity /AU
				λ=1.54056 Å	λ=0.7093 Å	λ=0.20899 Å	
0	1	2	3.484	25.54621	11.68496	3.43744	677
1	0	4	2.5541	35.10574	15.96321	4.689553	999
1	1	0	2.382	37.73435	17.12492	5.028585	458
0	0	6	2.1682	41.61906	18.82821	5.524806	5
1	1	3	2.0878	43.30094	19.56027	5.737738	960
2	0	2	1.9663	46.12573	20.78194	6.092605	14
0	2	4	1.742	52.48629	23.49369	6.877978	472
1	1	6	1.6034	57.4236	25.55743	7.47333	908
2	1	1	1.5483	59.66954	26.4832	7.739685	23
1	2	2	1.5164	61.05691	27.05079	7.902758	34
0	1	8	1.5129	61.21331	27.11456	7.92107	85
2	1	4	1.4061	66.43422	29.21813	8.523785	348
3	0	0	1.3752	68.12849	29.88977	8.715676	531
1	2	5	1.3376	70.32077	30.75043	8.961168	11
2	0	8	1.2771	74.19135	32.2459	9.386615	13
1	0	10	1.2407	76.75545	33.21893	9.662648	149
1	1	9	1.2357	77.12313	33.35727	9.701839	86
2	1	7	1.1946	80.3016	34.54032	10.03647	8

Aluminium, Al (PDF Card number 4-787)

h	k	l	d-spacing /Å	2θ /°			Intensity /AU
				λ=1.54056 Å	λ=0.7093 Å	λ=0.20899 Å	
1	1	1	2.338	38.47214	17.44969	5.123283	100
2	0	0	2.024	44.73838	20.18319	5.91876	47
2	2	0	1.431	65.13338	28.69872	8.375201	22
3	1	1	1.221	78.22719	33.77083	9.818927	24

2	2	2	1.169	82.43544	35.32133	10.25684	7
4	0	0	1.0124	99.07759	41.01209	11.84868	2
3	3	1	0.9289	112.0413	44.88991	12.91812	8
4	2	0	0.9055	116.5688	46.11592	13.25343	8
4	2	2	0.8266	137.455	50.81415	14.52501	8

Calcium carbonate, CaCO₃ (PDF Card number 5-586)

h	k	l	d-spacing /Å	2θ /°			Intensity /AU
				λ=1.54056 Å	λ=0.7093 Å	λ=0.20899 Å	
0	1	2	3.86	23.02181	10.54334	3.102515	12
1	0	4	3.035	29.40487	13.42107	3.946165	100
0	0	6	2.845	31.41765	14.32193	4.20982	3
1	1	0	2.495	35.96536	16.34389	4.800701	14
1	1	3	2.285	39.40092	17.85771	5.242198	18
2	0	2	2.095	43.14465	19.49238	5.718003	18
0	2	4	1.927	47.12262	21.21063	6.21698	5
0	1	8	1.913	47.48859	21.36768	6.262524	17
1	1	6	1.875	48.51221	21.80598	6.389574	17
2	1	1	1.626	56.55299	25.19632	7.369313	4
1	2	2	1.604	57.40012	25.54771	7.470531	8
1	0	10	1.587	58.07325	25.82608	7.550671	2
2	1	4	1.525	60.6762	26.89536	7.858121	5
2	0	8	1.518	60.9857	27.02173	7.894415	4
1	1	9	1.51	61.34354	27.16763	7.936307	3
1	2	5	1.473	63.05837	27.86364	8.135989	2
3	0	0	1.44	64.67652	28.51554	8.322763	5
0	0	12	1.422	65.59721	28.88429	8.428304	3
2	1	7	1.356	69.22915	30.32307	8.839328	1
0	2	10	1.339	70.2364	30.71749	8.951779	2
1	2	8	1.297	72.8676	31.73799	9.24228	2
3	0	6	1.284	73.72641	32.06793	9.336061	1
2	2	0	1.247	76.29769	33.04628	9.613715	1
1	1	12	1.235	77.17492	33.37673	9.707351	2

3	1	2	1.1869	80.9302	34.77152	10.10175	1
2	1	10	1.1795	81.54488	34.99669	10.16529	3
0	1	14	1.1728	82.1106	35.20314	10.22352	1
1	3	4	1.1538	83.76462	35.80229	10.39233	3
2	2	6	1.1425	84.785	36.16858	10.49541	1
1	2	11	1.1244	86.48045	36.77146	10.66484	1
2	0	14	1.0613	93.06907	39.04362	11.30093	1
4	0	4	1.0473	94.69749	39.58718	11.4525	3
3	1	8	1.0447	95.00753	39.68984	11.4811	4
1	0	16	1.0352	96.16167	40.0696	11.58682	2
2	1	13	1.0234	97.64397	40.55178	11.72088	1
3	0	12	1.0118	99.15729	41.03751	11.85574	2

Iron, Fe (PDF Card number 6-696)

h	k	l	d-spacing /Å	2θ /°			Intensity /AU
				λ=1.54056 Å	λ=0.7093 Å	λ=0.20899 Å	
1	1	0	2.028	44.64537	20.14297	5.907076	100
2	0	0	1.43401	64.97982	28.63719	8.35759	20
2	1	1	1.17086	82.27608	35.26338	10.24051	30
2	2	0	1.014	98.86582	40.94447	11.82992	10
3	1	0	0.906947	116.2736	46.0381	13.23219	12
2	2	2	0.827926	136.9861	50.72699	14.50162	6

Sodium chloride, NaCl (PDF Card number 5-628)

h	k	l	d-spacing /Å	2θ /°			Intensity /AU
				λ=1.54056 Å	λ=0.7093 Å	λ=0.20899 Å	
1	1	1	3.24471	27.4658	12.55004	3.691028	314.855
2	0	0	2.81	31.8193	14.50127	4.26228	5981.21
2	2	0	1.98697	45.6187	20.56339	6.029166	3387.88
3	1	1	1.69449	54.0756	24.1622	7.071064	69.2725
2	2	2	1.62235	56.6916	25.25395	7.385915	2100.57
4	0	0	1.405	66.493	29.24151	8.530471	1370.9

3	3	1	1.28932	73.3725	31.93207	9.297454	42.1176
4	2	0	1.25667	75.6067	32.78479	9.539566	924.498
4	2	2	1.14718	84.3592	36.01595	10.45247	637.274

Appendix B Attenuation

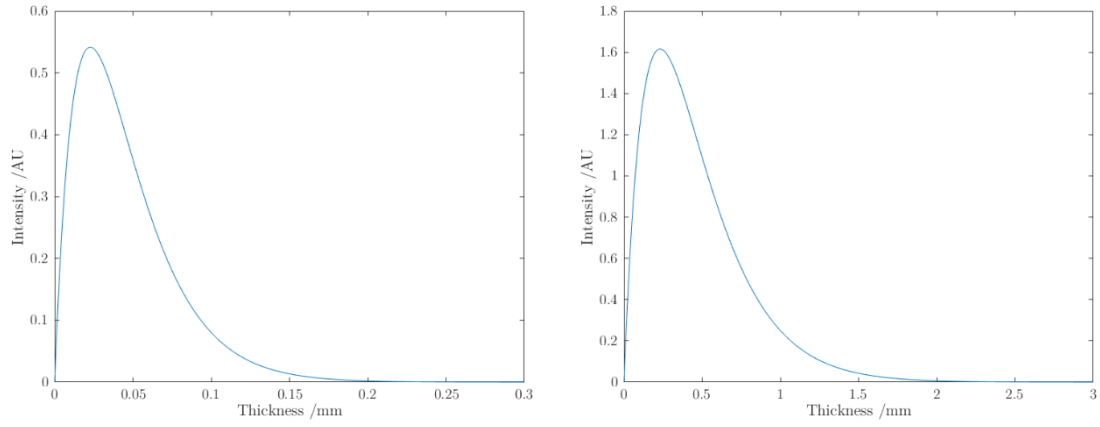


Figure B.1 Attenuation of X-rays of energy 17.5 keV(left) and 40 keV (right) in brass of increasing thickness.

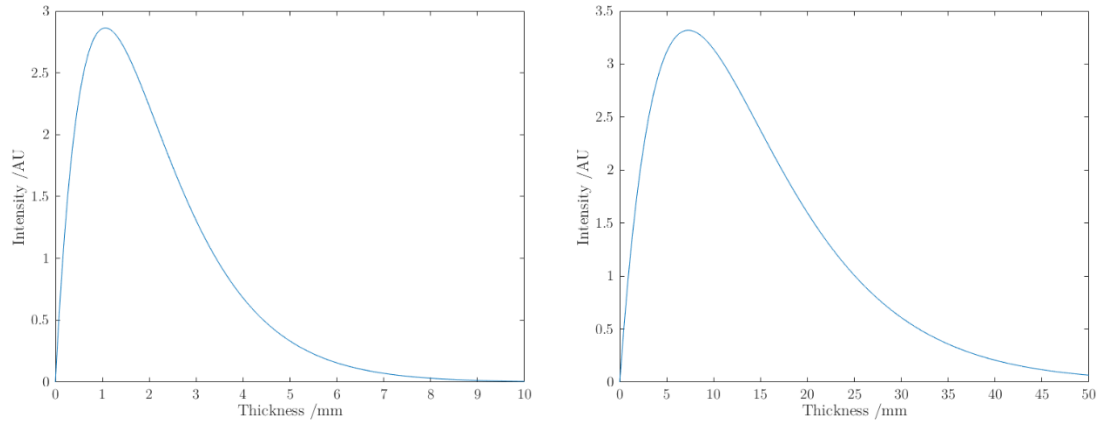


Figure B.2 Attenuation of X-rays of energy 59.3 keV(left) and 160 keV (right) in Fe of increasing thickness.

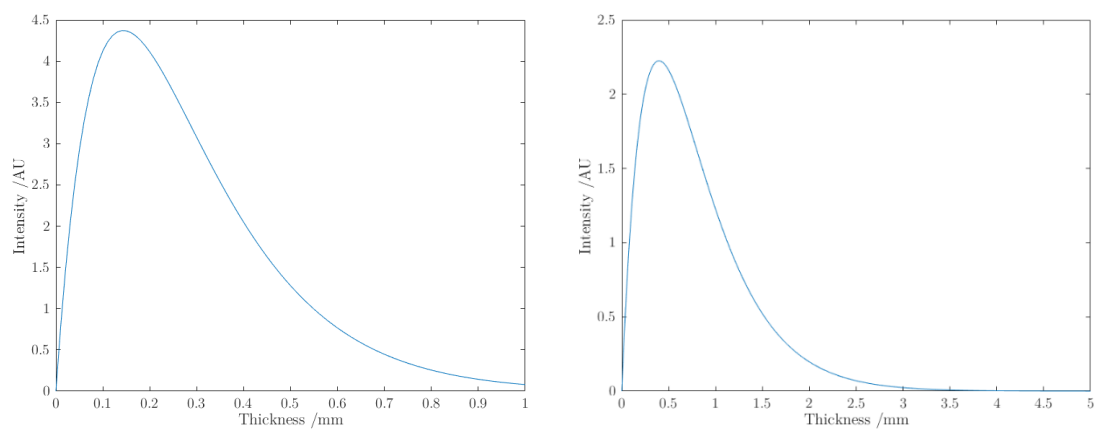


Figure B.3 Attenuation of X-rays of energy 59.3 keV(left) and 160 keV (right) in W of increasing thickness.

Appendix C Calibration

The radii of the Debye cones within the spiral plane (r_{AS}) was calculated based on the known 2θ angle of CaCO_3 (29.4°) - the strongest peak, 104 - in order to determine the relationship between r and the intersection angles, ψ , §6.4.2.2. The sample of CaCO_3 was translated in 1 mm increments from $D_{S:D} = 61$ mm to $D_{S:D} = 83$ mm. Measurements were taken of the radius at the detector, R_D , and the intersection angle, ψ , shown in Table C.1.

Table C.1 Calibration data the spiral encoder, r_{AS} calculated from knowing the sample position.

$D_{S:D}$ /mm	$D_{S:AS}$ /mm	Measured R_D /mm	Measured ψ / $^\circ$	Calculated r_{AS} /mm
61	7	35	117	4
62	8	35	119	5
63	9	36	133	5
64	10	36	142	6
65	11	37	156	6
66	12	37	166	7
67	13	37	176	7
68	14	38	184	8
69	15	39	204	8
70	16	39	214	9
71	17	40	223	10
72	18	41	233	10
73	19	41	243	11
74	20	42	251	11
75	21	42	262	12
76	22	43	265	12
77	23	43	273	13
78	24	44	287	14
79	25	44	295	14
80	26	45	304	15
81	27	45	309	15
82	28	46	314	16
83	29	46	321	16

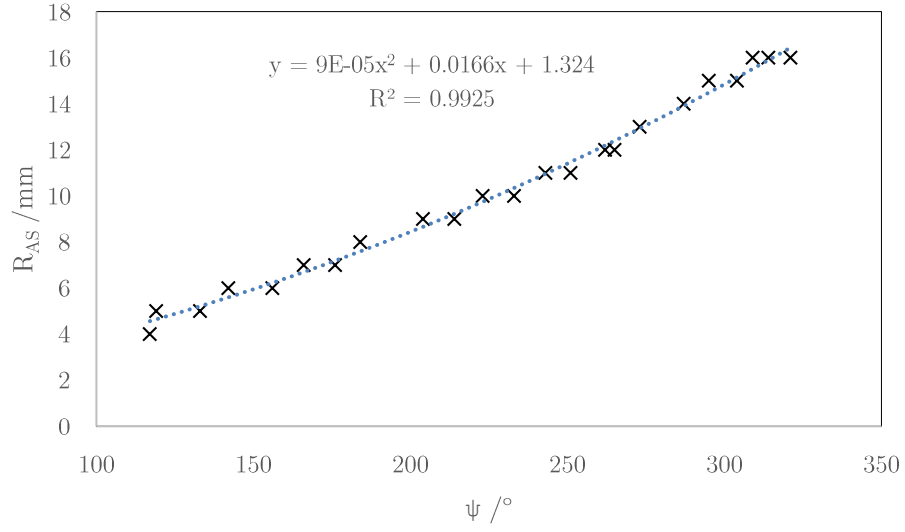


Figure C.1 Graph demonstrating the relationship between measured intersection angles, ψ , and calculated r_{AS} , determined from the known sample position.

The relationship between r_{AS} and ψ was determined by plotting them, Figure C.1. The relationship is represented by a polynomial trend, indicating a non-uniform distortion as it doesn't adhere to the linear relationship of the Archimedean spiral. Calibrated $D_{S:D}$ and scattering angles were calculated and presented in Table C.2. Correlation between the known, Table C.1 and the calculated Table C.2 values of the sample position $D_{S:D}$ and the correct recovery of the sample angle demonstrate successful calibration of the Archimedean spiral.

The calibration was further confirmed by translating a 0.17 mm thick plate of Al_2O_3 and analysing the 012 reflection with scattering angle 25.55° , the data for which is shown in Table C.3, and demonstrates good correlation to measured $D_{S:D}$ and the scattering angle, 2θ .

Table C.2 Calibration data the spiral encoder calculated by $r_{AS} = 0.00009\psi^2 + 0.0166\psi + 1.324$, from the 104 reflection from CaCO_3 .

Measured R_D /mm	Measured ψ /°	Calibrated r_{AS} /mm	Calibrated $D_{S,D}$ /mm	Calibrated 2θ /°
35	117	4	62	29
35	119	5	62	29
36	133	5	63	30
36	142	5	64	29
37	156	6	65	30
37	166	7	66	29
37	176	7	67	29
38	184	7	67	30
39	204	8	69	29
39	214	9	70	29
40	223	10	71	29
41	233	10	72	30
41	243	11	73	29
42	251	11	74	30
42	262	12	75	29
43	265	12	75	30
43	273	13	76	29
44	287	14	78	29
44	295	14	79	29
45	304	15	80	29
45	309	15	81	29
46	314	15	81	30
46	321	16	83	29
Mean				29
Standard deviation				0.3

Table C.3 Calibration data the spiral encoder calculated by $r_{AS} = 0.00009\psi^2 + 0.0166\psi + 1.324$, from the 012 reflection from Al_2O_3

Measured $D_{S:D}$ /mm	Measured R_D /mm	Measured ψ /°	Calibrated r_{AS} /mm	Calibrated $D_{S:D}$ /mm	Calibrated 2θ /°
62	30	99	4	62	26
63	30	110	4	62	26
64	31	125	5	64	26
65	31	136	5	64	26
66	32	146	6	66	26
67	32	157	6	66	26
68	33	165	7	69	26
69	33	174	7	69	26
70	34	184	7	71	26
71	34	195	8	71	26
72	35	205	9	73	26
73	35	217	9	73	26
74	35	225	10	76	25
75	36	233	10	75	26
76	37	241	11	77	26
77	37	246	11	77	26
78	37	254	11	80	25
79	38	260	12	79	26
80	38	266	12	79	26
81	39	276	13	81	26
82	39	286	13	84	25
83	40	295	14	83	26
84	40	301	14	86	25
Mean					26
Standard Deviation					0.3

Appendix D Publications

Prokopiou, D., Smith, K., Rogers, K., Paula, P., Evans, O., Dicken, A., and Godber S. Simulations and experimental demonstrations of encoding for X-ray Coherent Scattering. *Journal of Applied Crystallography*. 50(2). (2017).

Smith, K., Davis, G. and Rogers, K. Material Identification of Objects in *Absconditus* using Interpretation of X-ray Diffraction Profiles. *In preparation*.

Smith, K., Dicken, A. J., Prokopiou, D., Evans, P., and Rogers, K. Spatial resolution of depth resolved snapshot energy-dispersive X-ray diffraction using a conical shaped beam. *In preparation*.