

## 6

### X-Ray Diffraction and Focal Construct Technology

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This chapter examines the background and practice of X-ray diffraction (XRD) and considers this phenomenon principally in the context of X-ray-based security screening. The focus will be upon the practical aspects of XRD as many texts already provide comprehensive descriptions of the relevant theoretical background and that of the closely associated area of crystallography. X-ray diffraction and its development from simple materials identification to dynamic imaging will be considered, followed by a similar view of aviation screening. Subsequently, a new approach to the harvesting of diffraction signatures (*Focal Construct Technology*) will be introduced and consequent potential applications summarised.

The text provides a starting point for those interested in developments that exploit X-ray diffraction, particularly in the security screening sector.

#### 6.1 X-Ray Diffraction

Following the discovery of X-rays in 1895 by Roentgen [1], their exploitation produced two, almost irreconcilable, distinct disciplines: imaging (radiography) and X-ray diffraction. Von Laue, after demonstrating the wave nature of the rays, showed that the intriguing scatter patterns could be thought of as arising from a three-dimensional diffraction grating. When single crystals were illuminated by a pencil beam of X-rays, they produced discrete spots (intensity maxima) in regular patterns remote from the beam path on a photographic film. Von Laue [2] developed a series of relationships to interpret these patterns and they remain a cornerstone of crystallography

today. Simply, and in one dimension, the condition for constructive interference from a row of coherently scattering centres separated by a vector distance,  $\mathbf{a}$ , is that  $\mathbf{a} \cdot \mathbf{s} = h$ , where  $\mathbf{s}$  is a scattering vector and ' $h$ ' an integer. For three-dimensional regular arrays of atoms, three such equations exist (the 'Laue equations') that fully describe the conditions for diffraction. The spatial distribution of the intensity maxima is related to a crystal's internal structure, i.e. the three-dimensional spatial arrangement of atoms. Structure determination was an early application for X-ray diffraction and remains the dominant activity for diffractionists and crystallographers [3]. A further interpretative breakthrough arose from Laurence Bragg's thesis that X-ray diffraction may be considered as simple specular reflection (at least in terms of direction) from sets of equi-spaced parallel lines intersecting with all the scatter centres as embodied within Bragg's law [4],

$$\lambda = 2d \sin \theta \quad (6.1)$$

which establishes the simple relationship between interplanar spacing (' $d$ ', or ' $d$ -spacing'), X-ray wavelength ( $\lambda$ ), and direction of scatter relative to the incident beam,  $2\theta$ . For most diffractionists, perhaps with the exception of those studying large-scale structures using small angle scattering [5], only the first order of any atomic plane series is considered and therefore any integer order term is redundant. Bragg's law also indicates a key experiment condition that the X-ray wavelength employed for most crystallography is practically optimised when it is approximately that of the interplanar spacing, i.e.  $\sim 10^{-10}$  m. In practice, Bragg's law illustrates elegantly the reciprocal relationship between Euclidian space (the separation of atomic planes) and diffraction space ( $\theta$ ); scattering occurs at relatively low angles for large-scale repeat distances.

Polycrystalline materials may be thought of as orientationally random collections of small (typically  $<100 \mu\text{m}$ ) single crystals. Thus, when interrogated by a narrow pencil beam of X-rays, scatter follows the form of concentric hollow cones (Debye cones) shown in the forward direction in Figure 6.1. At normal incidence, these cones produce rings of relatively high intensity.

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Under ideal conditions, the circumferential intensity is constant around each of the rings. Plotting the intensity against scatter angle produces an identical 1D graph regardless of the azimuth angle chosen. However, in practice, this ideal is met rarely; Figure 6.2 illustrates a conventional pencil beam system configured in transmission mode with a number of non-ideal scattering examples from samples with preferred orientation and large (relative to the interrogating X-ray beam) grain size. This type of data collection and its interpretation is the basis for all powder diffraction applications [6]. Plotting the relative intensity or photon counts over a chosen integration period against  $2\theta$  (i.e. the half-opening angle) of the different Debye cones produces a diffractogram.

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To derive the atomic distributions within a crystal (and thus solve its structure), it is necessary to determine (a) the relationships between directions of scatter and (b) the amplitude of each maximum. Using the Fourier transform relationship, expressed in Eq. (2), the electron density distribution,  $\rho(x, y, z)$ , may be calculated from the scatter amplitudes,  $F_{hkl}$  if the phase,  $\phi_{hkl}$ , of each reflection (intensity maxima) is known [7].

$$\rho(xyz) = \frac{1}{V} \sum_{h=-\infty}^{\infty} \sum_{k=-\infty}^{\infty} \sum_{l=-\infty}^{\infty} |F_{hkl}| e^{i\phi_{hkl}} e^{-2\pi i(hx+ky+lz)} \quad (6.2)$$

where  $h, k, l$  are Miller indices defining a set of planes,  $V$  is the unit cell volume and  $x, y, z$  are unit cell fractional coordinates.

However, as the phase cannot be determined directly from measurements of intensity, a direct calculation of electron density distribution is not possible from experiment. Many methods have been developed to solve this ‘phase problem’ and the reader is referred to excellent texts for further discussion [8]. It becomes apparent when studying the distribution of intensity maxima that atomic planes may appear to possess scattering amplitudes equal to zero; they are absent from the diffractogram. This result arises due to the specific inherent symmetry of regular atomic arrangements; determination of the symmetry components is a critical step in determining structures. The structure determination process is the dominant activity for diffractionists and crystallographers and has led to several celebrated discoveries including the elucidation of the DNA structure [9] and that of haemoglobin [10] where structure–function relationships have

been shown to be critical to our understanding of biochemistry. Structure solution of proteins is now almost routine with perhaps the most challenging component being the crystallisation stage. Phase retrieval methods can be applied to data from single crystals and also polycrystals although powder diffraction is described by a one-dimensional diffraction space (i.e. planes of the same family with identical  $d$ -spacings are generally indistinguishable from one another) and thus single crystal diffraction is the preferred choice especially for large molecular structure elucidation. The historical limitation that many materials do not easily form large single crystals is rapidly being superseded with the combination of bright X-ray sources (especially synchrotrons) and environmental control enabling structure solution from single, micron-sized crystals [11].

In contrast to structure determination, materials identification from diffraction signatures is most often undertaken using polycrystalline materials with reference to a database of ‘known’ (empirical or calculated) diffraction patterns [12]. The term ‘phase’ is used in this context to describe the unique structures of a material species. For example, calcium carbonate may form as calcite or aragonite structural phases. Interestingly, a significant biological mystery is how cells engineer the formation of one phase rather than the other [13]. Although the stoichiometry of  $\text{CaCO}_3$  is identical for calcite and aragonite, their atomic arrangements are quite different and thus they possess very distinct diffraction patterns as illustrated in Figure 6.3. Thus, one of the strengths of diffraction for materials discrimination is its ability to discriminate between such ‘polymorphs’.

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In principle, the process of materials identification involves recording the directions of scatter and relative intensities for each Bragg maxima and then comparing them with those of previously collected data. This is a ‘fingerprint’ approach to identification that originated

through systematic procedures developed, for example, by Hanawalt [14]. The first database, or 'powder diffraction file' (PDF), was produced in 1941, and this has developed into a significant (>384,000 entries) commercial database, 'PDF4+', available from the International Centre for Diffraction Data (ICDD) [15].

For several years, powder diffraction languished as a technique in the shadow of single crystal methods principally due to the problems of extracting accurate integrated intensities from overlapping sets of intensity maxima. However, something of a revolution occurred when Hugo Rietveld showed how each individual intensity point within a dataset could be exploited [16].

His method involves a non-linear least squares fit of the experimental data points to those calculated from an initial or prototype crystallographic structure. The 'Rietveld refinement method' [17] has now become a ubiquitous tool and, despite producing parameter standard deviations that possibly underestimate probable errors, it continues to be a very successful approach to structural refinement.

Contemporary analysis methods applied to data from powder diffraction experiments enable derivation of features well beyond simply material phase. For example, it is possible to extract microstructural, quantitative information such as micro-strain, macro-strain, coherent domain size (crystallite size), and preferred orientation [6]. Indeed, any physical characteristic that can be mathematically modelled can be included within a Rietveld refinement and quantified. This has led, for example, to standardless quantification of phases within a mixture, i.e. without reference to external calibration curves [18]. Consequently, powder X-ray diffraction has become a powerful tool in the materials analysis armoury.

In contrast to crystalline materials, amorphous materials (including liquids) do not possess long-range structural order and therefore do not produce scattering distributions with well-defined

(sharp) diffraction maxima. However, a degree of short range, local order does persist (e.g. from inter-atomic and intra-molecular bonds) and thus corresponding scattering distributions are characterised by broad, diffuse halos [19]. Analytically, these are considered through radial or pair distribution functions that describe the average atomic or electron density as a function of the radial distance from any reference atom; interatomic vector directions are meaningless within a structurally disordered system, only their magnitudes have relevance. Thus, the scattering intensity distribution  $I(q)$  from a non-crystalline array of atoms may be described by:

$$I(q) = \sum_m \sum_n f_m * f_n \sin qr_{nm} / qr_{nm} \quad (6.3)$$

where  $q = 4\pi \sin \theta / \lambda$ ,  $r_{nm}$  is the magnitude of the vector separating atoms  $m$  &  $n$ , and  $f_m$  &  $f_n$  are the respective atomic scattering factors for each atom.

For example, water produces a dominant broad peak with a maximum at  $\sim 0.324$  nm [20] that arises from the intermolecular interference of the nearest neighbour oxygen–oxygen (O–O) atoms. Examples of X-ray scattering from liquids is provided in Figure 6.4.

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In parallel to analytical innovations, developments in hardware have enabled elucidation of increasingly complex molecular structures and have reduced data collection times. For example, digital area detectors, including those with pixelated energy-resolving capability [21], have replaced photographic film, and synchrotrons have become the X-ray source of choice for many experimentalists especially those wishing to achieve high-spatial resolutions or observe stimulated structural changes dynamically [22]. Further the use of engineered optical elements (e.g. graded layers, polycapillaries, etc.) has also enhanced the diffraction experiment [23]. For routine, laboratory-based powder diffraction in reflection mode, the sample is illuminated with a collimated, monochromatised X-ray beam, and a moving detector rotates as illustrated in Figure 6.5. As dispersion occurs spatially, this is known as angular dispersive X-ray diffraction (ADXRD). Conventionally, the Bragg–Brentano parafocusing geometry is employed and the sample is rotated around an axis parallel to the detector rotation axis to maintain a fixed  $\theta/2\theta$

relationship [6]. This reflection geometry results in only those planes parallel to the sample surface being measured. The sample may also be rotated around an axis normal to sample plane to improve counting statistics.

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The choice of interrogating wavelength is an important feature of any diffraction experiment.

Typically for thermionic X-ray sources, a compromise is found between the anode melting points (high-power density & inefficient energy conversion), cost, and emission line energy. The CuK $\alpha$  line (0.154 nm) is the most frequently used and produced by the monochromatisation of radiation from a Cu anode. However, the energy of this radiation results in very little penetration into materials. For example, 99% of the X-ray photons contributing to the diffraction pattern of rhombohedral Al<sub>2</sub>O<sub>3</sub> arise within the uppermost ~52  $\mu$ m of the sample surface. This lack of penetration limits the use of diffraction for applications involving extended absorption paths encountered within practical objects, in particular, aviation security (see later).

An alternative, analogous method of data collection is to employ energy dispersive diffraction (EDXRD) where the sample is illuminated with a polychromatic beam and an energy-resolving detector placed to receive diffracted radiation at a fixed position,  $\theta$  [24]. Considering Bragg's law, the interplanar spacing can then be calculated from the wavelength of the intensity maxima. In contrast to ADXRD where data is most frequently presented in terms of  $2\theta$ , EDXRD employs 'momentum transfer', i.e.  $E \sin \theta/hc$ . In practice, data can be measured at significantly greater speeds using EDXRD. However, it is not often the method of choice as the d-spacing discrimination is compromised by the energy resolution and finite acceptance angle of the detector. Thus, when applied within a typical materials identification protocol, the EDXRD approach produces significantly less confidence than that of the corresponding ADXRD data.

This limitation impacts detrimentally upon the discrimination power of such systems particularly for materials with larger unit cells.

As a testament to the success of X-ray diffraction, the technique has remained (albeit with some refinement) essentially unmodified for over 100 years. The relatively high resolution (in the sense of *d*-spacing discrimination) and other advances now enable structure determinations from polycrystalline samples [25]—an achievement previously confined to the domain of single crystal crystallography. Furthermore, the growth in X-ray powder diffraction can be evidenced by diffractometer and database sales that have been annually double digit for the past decade. In summary, X-ray diffraction is a powerful probe enabling unprecedented materials discrimination, identification, and characterisation. However, for potential applications that require high-speed data acquisition and perhaps the interrogation of materials requiring substantive X-ray penetration (most ADXRD experiments are performed in reflection mode), XRD in its current form is limited. High-speed/large area detectors and high-power sources may be prohibitively high cost for some industrial applications [26]. By employing a source of parallel X-rays, the illuminated footprint on the sample can be extended from a small area to a larger rectangular area to improve the signal-to-noise ratio, speed, and particle statistics. The usefulness of this approach is limited since the detector active area must be expanded with the X-ray footprint, resulting in a concomitant increase in the measured incoherent scatter. Furthermore, this approach causes peak asymmetry, particularly at low-scattering angles.

## **6.2 Aviation Screening**

Over the last four decades, there has been a growing worldwide interest in aviation security technologies. This interest has been driven and directed by politics, technology developments, and terrorist threats. Many innovations arise and are implemented as a direct reaction to specific



events, several of which are illustrated in Table 6.1. Between 1985 and 1997, around 1,100 people lost their lives due to aviation terrorist bombings. The tragic events of 9/11, when almost 3,500 died, further increased global awareness and the demand for development of improved screening techniques.

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Prior to the Lockerbie event in 1988, airport security concentrated on the detection of high atomic number objects such as weapons including guns and ammunition through the employment of metal detectors and single view X-ray screening. Subsequently, events involving passengers carrying explosive materials directed technology development towards detection of lower atomic number substances in highly shape variant formats. A significant issue has been identifying and adapting detection systems to deliver the necessary performance fidelity within the operational constraints demanded by the industry. A viable technology has to offer a cost-effective and preferably small footprint design, which is capable of being integrated into a high passenger throughput environment. Furthermore, the London transatlantic bomb plot of 2006 and the 'printer cartridge bomb plot' of 2010 are evidence for the requirement of systems to be capable of identifying liquids, aerosols, and gel explosives (LAGs), concealed home-made explosives (HMEs), respectively. In particular, the sophistication and inherent variability within the makeup of HMEs and their concealment is also increasing. The growing uncertainty associated with this threat vector is driving the demand for technologies with high throughput, sensitivity, and specificity to meet the required low false negatives and false alarm rates. Both bulk and trace methods of explosives detection are components of aviation security screening systems. Explosive trace detection (ETD) techniques include mass spectrometry [27], chemiluminescence [28], ion mobility spectrometry [29], immunoassay [30], and bio-sensor technologies [31]. In general, these detect minute concentrations of an illicit substance (<1 mg) present on the exterior surface of luggage or vapours emitting from the substance. The primary

detection ETD methods are inherently slow processes and produce an unacceptably low throughput for busy airports. In contrast, bulk detection systems, usually referred to as explosive detection systems (EDS), identify weapons and/or volumes of illicit substances, such as explosives and drugs, whilst screening 100% of checked baggage. These methods are frequently X-ray based and capture images of the inside of luggage. Other non-X-ray-based screening systems include neutron techniques [32], nuclear quadrupole resonance [33], and terahertz time domain spectroscopy [34].

X-radiographic transmission screening is ubiquitous throughout the aviation security sector. The simple, single view systems have been enhanced by the addition of multiple views (providing some depth decoupling) and dual energy X-ray detectors enabling some material discrimination. However, there remain challenges for these technologies. For example, materials in sheet form are difficult to detect and the discrimination of materials based upon density/absorption characteristics is too inaccurate to prevent high levels of false positives.

The detection of sheet materials can be achieved through computer tomography (CT) where volumetric representations of objects are mathematically reconstructed from multiple views. Translation of this technology from the medical arena to the aviation security sector has been possible due to improvements in processor and data acquisition speeds. CT systems are commonly employed as a level-2 intervention, i.e. post-conventional X-ray scanning or in cargo screening. CT may also be coupled with dual energy detectors to produce greater, material discrimination, and thus reduced false alarm rates [35]. The cutting-edge RTT™ systems of Rapiscan are fast (scan speed of  $0.5 \text{ ms}^{-1}$ ) and feature a novel stationary gantry. However, disadvantages of CT systems include their relatively high cost (capital and maintenance) and large footprint. Furthermore, regardless of superior imaging performance, sufficient material discrimination fidelity remains a significant hurdle to achieving low false alarm rates.

X-ray diffraction may be considered as providing orthogonal material information to that of absorption-based processes. As discussed previously, diffraction signatures are unique within materials space and could in principle be used for high-specificity detection and identification. This feature has promoted several attempts to exploit diffraction in security screening although

there is only one notable commercial system incorporating a diffraction probe currently available. The ‘XRD 3500™’, commercialised by Morpho (Safran) is employed in a ‘system of systems’ approach as a secondary screening technique, upon identification of suspicious materials within an inspection volume by CT. It is a relatively high cost system (GPB ~ 0.5 M) requiring substantive maintenance. It employs high-power X-ray sources to increase the amount of diffracted flux available for analysis. Any discussion of XRD applied within aviation screening would not be complete without consideration of the work of Geoffrey Harding who has consistently promoted diffraction-based imaging systems through numerous elegant patents and publications. For example, the multi-generational X-ray diffraction imaging (XDI) technique was introduced in 2005 [36] as a concept system for security screening, combining the ability of X-rays to form an image and to analyse the material under inspection. This was superseded by the ‘multiple inverse fan beam’ (MIFB) topology [37].

Despite these innovations, practical solutions that enable the deployment of XRD within mass transit screening systems have remained elusive. The principal barrier has been the relatively small amount of diffracted flux collected during operationally relevant exposure times leading to low signal-to-noise ratio. The relatively small amount of signal collected is usually due to the compound effect of high aspect ratio collimation (photons collected over a small solid angle) and the low exposure times required for operationally relevant speeds. Consequently, many approaches require higher powered X-ray sources to increase the probability of collecting diffracted photons in order to make a material call.

### **6.3 Focal Construct Technology (FCT): Background**

Traditional diffractometer methods measure the intensity and angular distribution of Debye cones from a sample using a point detector that cuts through each cone footprint or ring. In practice, point detectors have a finite detection area, and the intensity over a small, approximately annular sector of each ring is measured. The remaining fractions of the rings are usually not examined even though important data can be collected by measuring a whole ring. To

measure complete Debye rings requires a spatially resolving area detector, which can be bulky and prohibitively high in cost. Furthermore, there is a trade-off between  $d$ -spacing resolution and sample to detector separation. For example, to capture rings over a wide range of Bragg angles requires either a very large area detector or a smaller detector positioned closer to the sample, i.e. to conserve the solid angle under consideration. In such a scenario, with fixed detector parameters, the larger detector will provide improved angular resolution and better estimation of  $d$ -spacing values. In conclusion, the layout and relatively large physical size of standard instruments such as powder diffractometers are dictated by the divergence of the diffracted flux from the samples necessitating off axis measurement.

Focal construct geometries employ a novel tubular interrogating or primary X-ray beam to affect a convergent and therefore inherently compact, diffracted ray geometry [38]. Whilst increasing the interrogated or gauge volume in comparison with a pencil beam, this technique produces diffracted rays that converge to a single series of collinear points [39], i.e. on axis measurement.

To illustrate the basic focal construct concept in angular dispersive mode, consider a simple diffraction experiment where a pencil X-ray beam (diameter,  $W_T$ ) strikes an ideal powder sample and produces (for simplicity in transmission) a 'single' Debye cone. If multiple incident beams are incident normally upon the sample such that the loci of their intersections with the sample lie equidistantly on a circle (radius,  $R_s$ ) and the sample to detector distance,  $D_z = R_s \cot 2\theta$ , then the resultant Debye cones will possess a single convergence point along the principal axis of the interrogating tubular beam. This concept is illustrated in Figure 6.6 where only two incident beams and two corresponding Debye cones are shown for clarity. Two spatially separated 'focus points' are formed along the principal axis,  $z$ . Similar focus points are also recorded for a conical shell incident beam (although the equation above becomes modified). Thus, forming a continuous, annular interrogating X-ray footprint on the sample results in a high-intensity point along the principal axis (for each scattering plane) and an increased intensity circle or caustic at

the outer Debye ring terminus with a radius,  $\sim 2R_s$ . Such loci occur due to the superposition of scattering from a continuum of points from a single family (constant two thetas) of Debye cones.

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Systematically translating an area detector along the principal axis records a scattering distribution as illustrated in Figure 6.7. Interestingly, as the detector approaches a ‘focal’ position, it is clear that the extraneous scatter is significantly reduced. Summing the detector pixel intensity in the central region as a function of detector position results in a 1D diffractogram with familiar high-intensity peaks [38]. However, the circular caustics may be equivalently formed from converging or diverging Debye ring rays and thus the abscissa cannot be straightforwardly transformed into scatter angle or  $d$ -spacing.

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There are several advantages of this technique when compared to the traditional pencil beam experiments. The summation of intensity from any Debye family at the detector will provide order(s) of magnitude increase in intensity dependent upon design specification, i.e. intensity will be greater by a factor of  $\sim 8R_s/W_T$  in comparison to an equivalent pencil beam measurement with a diameter,  $W_T$ . Furthermore, the detrimental effects of preferred orientation (e.g. wire texture) and large grain size on the diffraction data may be reduced significantly without the need for any sample preparation [40]. FCT patterns corresponding to materials with preferred orientation and large grain size are illustrated in Figure 6.8 for detector positions at a focal point and also on either side of this maxima position. There are several modes of operation including the linear measurement of intensity along the principal axis and static energy dispersive detectors and, in principle, system elements may be engineered using standard, low-cost techniques. Typical  $d$ -spacing ranges can be measured within a short distance but with resolution comparable to that of conventional angular dispersive systems, i.e. there is a potential for smaller/portable implementation. In contrast to conventional approaches, here the greatest discriminating power occurs for high  $d$ -spacings. Any background signal (e.g. fluorescence) relative to the diffraction signal will be significantly less than that of a conventional system (possessing an equivalent illuminated area) simply due to the smaller detector area required to capture the coherent scatter.

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There are a number of approaches to formalise the scattering process from this geometry. The scattering distribution at the detector may be considered as a convolution of the Debye cones and the annular incident beam. Adopting Gaussian profiles for the Debye cone,  $g(r)$ , and incident beam,  $f(r)$ , cross sections (and assuming no beam divergence and an infinitely thin sample), then, for a single Debye cone the scattering distribution normal to the primary axis is represented by [40],

$$f(r) * g(r) = \frac{1}{\sqrt{2\pi(\sigma_f^2 + \sigma_g^2)}} e^{-\frac{(r - (R - D \tan 2\theta))^2}{2(\sigma_f^2 + \sigma_g^2)}} \quad (6.4)$$

where  $\sigma_f$  &  $\sigma_g$  are the Gaussian width parameters for the incident beam and Debye cone, respectively,  $D$  is the perpendicular sample to detector distance, and  $R$  is the radius of the incident beam at the sample.

This is a continuous function of both  $r$  and  $D$ , and by plotting  $f * g$  against  $D$  at  $r = 0$ , the intensity profile along the principal axis can be calculated. By differentiating this with respect to 'D', the focal point positions along the principal axis can be derived and shown to be entirely coincident with the geometric derivation of focal points provided previously. This approach can also be applied to predict the scattering distributions from non-ideal samples such as those possessing preferred orientation.

Fortuitously, this equation has a form similar to that of a desirable autocorrelation function as provided by coded apertures such as MURA's [41]. In this respect, the beam topological modulation produced by the primary optic may be regarded as a coded aperture. This then has the advantage that the typical FCT ring caustics formed from both diverging and converging scatter cones (making them difficult to interpret as a diffractogram) may be accurately recovered through convolution.

Although angular dispersive FCT enables a study of 3D scattering distributions, the corresponding energy-dispersive approach has shown great promise in providing data acquisition

at relatively high speeds [42]. The method exploits an incident conical shell of polychromatic X-rays and a single point or pixelated energy-resolving detector. It has also been shown capable of providing ‘single shot’ diffraction tomography (transmission) for materials identification through barriers (see later).

To date there has been little exploration of FCT when applied in reflection mode analogous to that of conventional X-ray diffraction experiments. However, the ‘focusing’ advantage of the annular beam geometry can also be realised if the incident beam topology is such that it produces a specific footprint shape formed upon an inclined sample surface. In energy-dispersive mode, such a topology can produce a ‘focal’ point on the same side of the sample as the X-ray source and with all diffracted ray paths possessing the same scatter angle. This may be thought of as a 2D Bragg–Brentano geometry. To achieve such a focus, the X-ray source and detector are placed at the same height,  $h$ , from a planar sample, and separated by a distance  $D$ , and the beam topology would be such that an ellipsoidal footprint is illuminated on the sample surface. A powerful feature of this approach, unlike the conventional Bragg–Brentano method, is that that extended planar samples do not degrade the focal spot and there is no requirement for a curved sample.

All the FCT modes above require the formation of a hollow cone of X-rays and several practical options are available for this from a simple annular collimator (low-cost, easy construction but potentially poor uniformity and low intensity), to multilayer diffraction optic elements producing converging X-ray annuli [43]. The potential advantage of this particular approach is that it forms simultaneously converging and diverging X-ray beams.

In summary, FCT is a unique approach to the acquisition of X-ray diffraction data from polycrystalline materials and has inherent speed advantages that are particularly attractive for a number of industrial applications.

## **6.4 Focal Construct Technology: Applications**

In principle, FCT could impact a wide range of sectors that currently exploit X-ray diffraction. However, we shall confine the discussion below to those areas where conventional powder diffraction methods are not ideal and where some progress using FCT has already been made. Currently, there are no commercial systems exploiting FCT, thus we shall consider mostly research data that will form the foundation of future developments.

#### **6.4.1 Security: Aviation Screening**

The principal advantage of FCT applied to aviation security concerns the increased relative intensity (compared to a pencil beam), which translates into a signal acquisition speed that meets the demands of current airport screening. In a high-energy (~150 kV) dispersive mode, FCT also satisfies the requirements for penetration through at least carry-on luggage. A further advantage of FCT is that both the absorption and diffraction caustics may be used in a tomosynthesis approach to direct image objects [44,45]. This is analogous to conventional CT scanning where the object appears to have been rotated about an axis normal to the detection surface in an oblique beam formed from a composite of annular projections. This is an interesting and counter-intuitive result as the conical shell incident beam is produced using a point source, and only linear motion is employed in the image collection process.

The initial application of FCT within a screening environment couples a pre-screening element with a ‘point-and-shoot’ FCT probe. This allows operators to resolve potential material ambiguities that would otherwise be considered threats. In particular, the diffraction probe is able to identify HME materials with a high degree of accuracy. Figure 6.9 schematically illustrates some initial results from this probe. A relatively small mass of ‘target’ material was placed randomly in a suitcase within a cluttered environment and examined with the FCT system. Diffraction signatures from three crystallographically different materials produced using a 10 mAs exposure are also illustrated in Figure 6.9. These materials were easily and uniquely identified from the  $d$ -spacings (energy) of the Bragg maxima to demonstrate the high accuracy materials discrimination.



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### **6.4.2 Security: Envelopes and Packages**

Conventional mailroom X-ray inspection equipment may assist in the detection of suspicious items from their shape using the differential absorption processes of radiography. This inspection task can be slow and cumbersome and requires training to interpret correctly ‘threat’ shapes. Of course, this approach is not appropriate for threats such as explosives and narcotics where shape is irrelevant and X-ray absorption features are poorly discriminating [46]. Government agencies, including the US Postal Inspection Services and the UK Home Office, are acutely aware of this problem but are forced to rely on unsophisticated ‘shape-based’ technologies. Perhaps the three principal advantages of FCT is its interrogating speed, its discriminating ability, and also its potential for automation. Furthermore, as discussed above, FCT lends itself to compact, reduced cost, and high-speed X-ray diffraction instrumentation. Although FCT-based commercial systems are not currently available, initial indications of the materials identification capability of FCT for illicit materials within envelopes are positive.

### **6.4.3 Medical Diagnostics**

The human body is a highly complex and dynamic assembly of biological, chemical, and ‘engineering’ components. Medical diagnostics attempt to identify, at the earliest stages, when any or all of these components demonstrate atypical behaviour. Unfortunately, due to intrinsic biological variability, such behavioural deviations are often difficult to identify and this often results in diagnoses at late stages of disease progression. Furthermore, diagnostics are often based upon observation of a symptom rather than an original cause. Although the advent of gene

mapping has produced a revolution in medical diagnostics [47], it is often unable to make highly accurate predictions and, naturally, is almost redundant for diseases with environmental causes. X-ray diffraction is not often associated with medical diagnostics. However, its ability to probe structural scales from hundreds of nanometres to Angstroms means that it can characterise both large molecular tertiary structures (such as those formed from fibrous proteins e.g. collagen) and the atomic arrangements in inorganic components, such as apatites in bone. Using ionising radiations is an acceptable practice in medicine when the diagnostic benefits outweigh the exposure risks. FCTs inherent ability to accelerate the data acquisition process has the potential to maintain a low patient radiation dose and further, its innate averaging of interrogation volumes militates against local, sampling inhomogeneity. The subsequent discussion concerns two areas where research is currently being undertaken.

Breast cancer is the most common cancer in women worldwide, and in 2012, almost 1.7 million new cases were diagnosed [48]. The ability of X-ray diffraction to probe wide architectural scales has been shown to enable the early-stage diagnosis of breast cancer [49]. This arises from the discovery that type I/III collagen suprastructure associated with breast tissues becomes significantly compromised as cancer invades surrounding tissues. Of particular interest is that this effect can be observed some distance from the tumour site thus suggesting the possibility of defining tumour margins using this structural characteristic. More recently, X-ray diffraction has also been shown to have diagnostic abilities capable of distinguishing benign and invasive breast cancers [50]. Although patient numbers at this time are relatively small, researchers identified systematic differences in the phase compositions and precise chemistry of breast calcifications (perhaps the most radiologically important early diagnostic markers of breast cancer) by XRD and optical spectroscopies [51]. Thus, characteristics of both soft tissue and calcification

revealed through diffraction signatures may be thought of as constituting a new type of biomarker for breast cancer. Access to such biomarkers in vivo is a significant challenge but given the characteristics of FCT this technology has the potential to play a significant role within this field.

Osteoporosis affects 200 million women worldwide – approximately 75 million people in Europe, USA, and Japan [52]. It is estimated that an osteoporotic fracture occurs every 3 second. This is a condition that produces a major health burden and a mortality risk of between two and ten in the 12 months following a hip fracture. These issues are compounded by the asymptomatic nature of osteoporosis, which often remains undiagnosed until after a fracture occurs. As an engineering problem, one might compare bone mechanical functionality to that of an engineering structure such as a bridge. There are then three principal factors influencing mechanical performance: the architecture, the mass of construction material, and the composition ('quality') of the construction material. The first two of these are accessible through conventional imaging and bone mineral density (BMD) assessments determined by dual energy X-ray absorptiometry (DEXA) [53]. However, it has been consistently demonstrated that BMD alone is a poor predictor of fracture. Data from the Study of Osteoporotic Fractures (NIH: results on-line) showed that 54% of new hip fractures occurred in women who did not have osteoporosis as determined by their BMD, and data from the National Osteoporosis Risk Assessment showed that 82% of post-menopausal women with fractures had bone of 'normal' BMD.

The physicochemical characteristics of bone mineral (similar to calcium hydroxyapatite) are regularly examined by X-ray diffraction [54]. Bone is a composite material wherein the mineral component contributes to bone stiffness and strength, whereas collagen affects toughness. Features such as the degree (and to some extent the type) of lattice substitution, the coherent

domain size, microstrain, and crystallite dimensions can be determined from diffractograms of native bone [55]. These are critical characteristics that contribute to the bone ‘quality’ and therefore impact on its mechanical performance. For example, mineral crystals possessing high levels of carbonate (exchanged for phosphate) are known to be preferentially resorbed under physiological conditions, and therefore if crystallites are precipitated with relatively high amounts of lattice-bound  $\text{CO}_3^{2-}$ , then bone mass is likely reduced [56]. A similar argument can be proposed for crystallites formed with a smaller domain size. Recently, studies have indicated that there are indeed significant differences in several physiochemical features of bone from patients with and without fragility hip fractures [57]. X-ray diffractograms were processed through parameterisation and also data mining methods (e.g. principal component analysis). The data mining approach indicated high accuracy of the data to predict patients within the fracture group [58]. Thus, bone diffraction signatures show great promise as biomarkers for osteoporosis. As with breast cancer, the exploitation of these findings within a practical in vivo test is several years away. However, FCT again offers advantages over conventional X-ray diffraction modes of measurement. Initial results where FCT has been applied to bone phantoms have clearly demonstrated that, at least in transmission, the emerging diffraction signatures are of sufficient quality to enable application of the fracture predictive algorithms, i.e. the magnitude of derived parameter errors are such that fracture and non-fracture groups can be discriminated [59]. Successful commercialisation of this approach holds the promise of portable devices for point-of-patient care thus impacting significantly on the health burden of this condition within an increasingly aging population.

#### **6.4.4 Process Control**

The industrial uses of powder diffraction are extensive and include electronics, optics, aerospace, petroleum, mining, cement, paints, pharmaceuticals, forensic, and medicine. The technique is especially useful in the manufacturing industries that require some measures of quality control. For example, the cement industry employs off-line powder diffraction at several points within the manufacturing process to ensure that the various types of cement are being formed with the appropriate chemistry. The pharmaceutical industry uses diffraction extensively for drug discovery and the fabrication of endoprosthetic implant coatings. The semiconductor sector exercises diffraction techniques to ensure the quality of substrates and active thin films, and the aerospace manufacturing exploits diffraction to ensure the attributes of components such as turbine blades. A comprehensive survey of the industrial use of diffraction can be found elsewhere [26].

In general, industries adopt X-ray diffraction due to its unique ability to provide information such as material phase/composition and preferred orientation. A key feature of any analytical method applied within an industrial process is speed of diagnosis and decreases in analysis turnaround time are continuously sought. This is especially the case for high-energy usage industrial processes. For example, it is common practice in the cement industry to sample typically every 2 hours thus, given the rate of production, any unwanted deviation from an ideal composition can result in significant wastage. This situation is compounded by the concomitant energy, fuel, and CO<sub>2</sub> emission waste. Consequently, this change to an in-line, 'real time' approach would be an attractive option but is currently unavailable due to the inherent data collection speeds of X-ray diffraction.

**Figure 6.1** Idealized distribution of coherent X-ray scatter from a polycrystalline sample illuminated with monochromatic X-ray. Only three Debye cones are illustrated for clarity.

**Figure 6.2** Upper diagram illustrates a typical transmission diffraction experiment where a monochromatic primary beam illuminates a polycrystalline sample, and a section of the coherent scatter is captured upon a planar area detector. In this case, the pattern recorded illustrates that from an 'ideal' sample. The lower diagrams illustrate corresponding scattering from materials

with significantly greater lattice parameters (left), pronounced preferred orientation (middle), and relatively large grain size (right).

**Figure 6.3** Two polymorphs of calcium carbonate illustrating how identical chemical stoichiometry can result in significantly different diffractograms.

**Figure 6.4** X-ray coherent scatter distributions (monochromatic) from a range of materials in liquid form.

**Figure 6.5** A conventional, reflection mode, powder diffraction experimental arrangement. A line source is collimated to direct a ‘ribbon’ of X-rays onto a flat plate sample, and a detector rotates around the sample to receive the scattered photons. Monochromatisation occurs using a filter or highly reflecting crystal placed within the incident or diffracted radiation (not illustrated).

**Figure 6.6** The principle of focal construct technology illustrated for just two points on the continuum of the annular incident beam (at the sample) and two resultant Debye cones. The ‘focus points’ occur along the primary axis.

**Figure 6.7** A sequence of X-ray scatter collected as a planer detector is systematically translated along the primary axis. The focal points are apparent from a central bright intensity point corresponding to scattering from particular sets of crystallographic planes. These Bragg maxima occur when the detector-sample distance is equal to  $R \tan 2\theta$  (assuming parallel incident radiation).

**Figure 6.8** Focal construct coherent scatter distributions for materials measured with the sample-detector distance set to satisfy a focus condition (central column) and a distances slightly less (left column) and more than (right column) the focus condition. The upper row illustrates scattering from an ‘ideal’ polycrystalline sample ( $\text{Al}_2\text{O}_3$ ), the middle row illustrates scattering from a sample with significant preferred orientation (Al) and the lower row illustrates scattering from a sample with large grain size ( $\text{KClO}_3$ ). The focal condition is apparent in all three rows.

**Figure 6.9** A schematic illustrating early results from FCT applied to identify material samples placed within the cluttered environment of a suitcase. Confounding scatter from the suitcase,

benign contents, and other crystalline components were accommodated within the methodology and each material identified with a high degree of specificity from its diffraction pattern.

<b>Table 6.1</b>		
Aviation Terrorist Events		
Year	Event	Reaction
1930	PanAm hijack	
1955	UA terrorist explosion	
1960	NA terrorist explosion	
1961	NA hijack	Armed guards on commercial flights
1969	TWA hijack	FAA metal detectors
1970	PanAm & TWA terrorist explosion	Sky marshals
1971	Northwest Orient hijack	Passenger screening
1972	TWA bomb threat	Explosives Detection Canine Team Program
1973	PanAm & Lufthansa hijack	
1974	Explosion at LAX	Adoption of metal-detectors and X-ray screening for passengers and carry-on bags
1985	TWA hijack	Federal air marshals
1988	PanAm terrorist explosion	Matched search to passengers
1997		Sig uplift in security funding
1998		Pre-screening systems employed
2001	AA & UA terrorist atrocity	TSA formed
2001	Shoe bomber	Shoe inspections, items banned
2002	Gunman at LAX	TSA screens all checked bags
2004		TSA Registered Traveller program
2006	Plot involving liquid explosives	All liquids divested from bags

2009	Northwestern passenger with explosive in underwear	Full-body scanners
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