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Identification of simulants for explosives using pixellated X-ray diffraction

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Abstract

A new method of material identification has been developed utilising pixellated X-ray diffraction (PixD) to probe the molecular structure of hidden items. Since each material has a unique structure, this technique can be used to “fingerprint” items and has significant potential for use in security applications such as airport baggage scanning. The pixellated diffraction technique allows two distinct forms of diffraction, angular-dispersive and energy-dispersive X-ray diffraction, to be combined, exploiting the benefits of both. Thus, fast acquisition times are possible with a small system which contains no moving parts and can be easily implemented. In this work, the capability of the system to identify specific materials within a sample is highlighted. Such an approach would be highly beneficial for detecting explosive materials which are concealed amongst or inside other masking items. The technology could easily be added to existing baggage scanning equipment and would mean that if a suspicious item is seen in a regular X-ray image, the operator of the equipment could analyse the object in detail without opening the bag. The net result would be more accurate analysis of baggage content and faster throughput, as manual searching of suspicious objects would not be required.

Background

Current X-ray based baggage scanning techniques are based on the measuring the amount of X-ray absorption due to different hidden materials. The absorption is due to the atomic number, Z , and the density of the materials, and as such it is easy with such techniques to distinguish metal items from clothes, shoes, etc. However, plastic explosives are composed of low Z materials, and as such can be difficult to identify when hidden inside packages or baggage. A new method is therefore needed which is sensitive to materials based on some different intrinsic property. X-ray diffraction (XRD) is a technique which can be used to probe the atomic and molecular structure of materials. (Cook et al. 2007, 2009; Farquharson et al. 1997; Kämpfe et al. 2005; Luggar et al. 1998; Malden and Speller 2000; Phadnis et al. 1997). Since every material has a different structure, XRD can be used to “fingerprint” samples and to resolve materials which may look similar using, for example, X-ray absorption or millimetre-wave imaging.

Diffraction occurs when X-rays are scattered from different atomic planes within a material before constructively interfering, and is described by Bragg's law:

$$n\lambda = 2d \sin\left(\frac{\theta}{2}\right) \quad (1)$$

where λ is the X-ray wavelength, d is the inter-atomic distance in the material and θ is the angle through which the incident X-rays are scattered. There are two different methods which can be implemented in order to measure XRD. In angular-dispersive XRD (ADXRD), the X-ray source and detector are rotated with respect to the sample surface, and a narrow window of incident X-ray energies is selected (λ is approximately constant). The different d values present within the material produce high intensity diffraction peaks at the incident X-ray angles which satisfy Bragg's law for the selected value of λ . ADXRD can also be performed with a pixellated detector array, such that monoenergetic photons are collected over a range of angles simultaneously. An alternative method is to keep the scattering angle fixed, and use a polychromatic X-ray beam (a wide range of λ) - this approach is called energy-dispersive XRD (EDXRD). ADXRD can give a very high angular resolution, but the standard approach of rotating

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the X-ray source and detector about the sample is impractical for most security-based scenarios. EDXRD uses a fixed experimental setup, but requires a strict collimation of the incident and scattered X-ray beams in order to have a well defined θ . This collimation leads to a large drop in the detected X-ray flux, and thus long counting times are required.

A novel technique has been developed in which features of both ADXRD and EDXRD are simultaneously combined (Christodoulou et al. 2011; O'Flynn et al. 2012; O'Flynn et al. 2013). This is achieved by using a pixellated detector which is bonded to a CdTe crystal. The active detector area is 20×20 mm, and is composed of 80×80, 250 μm pitch pixels. The CdTe enables the energy of incident X-ray photons to be observed, such that each pixel generates an individual energy spectrum for an acquisition (Jones et al. 2009; Seller 2011). The pixel array gives spatial resolution to the system, and is utilised for measuring angular-dispersive diffraction.

In this work, we present pixellated XRD (PixD) data from simulants for explosives provided by the Home Office Centre for Applied Science and Technology (CAST), UK. The simulants were designed to look similar to a particular plastic explosive when examined using passive millimeter-wave imaging. The results presented demonstrate the ability of pixellated XRD to identify a sample based on the molecular structure of its constituent materials, and therefore the potential to search for specific compounds/substances amongst other masking materials.

Methods

The experimental setup used for pixellated diffraction was the same as that described in a previous paper (O'Flynn 2013). The incident X-ray beam was shaped by two primary pinhole collimators measuring 0.5×0.5 mm, and upon reaching the sample the cross-sectional area of the X-ray beam was approximately 1 mm². As shown in Figure 1, the detector was positioned such that the primary X-ray beam did not hit it, and so only scattered X-rays were observed. With a well-defined scattering geometry, a specific scattering angle could be assigned to each pixel. Knowledge of both the scattering angle and energy of X-ray events allows momentum transfer values, x , for interactions to be determined by using the following equation:

$$x = \frac{E}{hc} \sin\left(\frac{\theta}{2}\right) \quad (2)$$

where E is the incident X-ray energy (elastic scattering is assumed). The momentum transfer values at which diffraction peaks are measured give us information on the atomic structure of the material under observation. Since values of x for a material are absolute, i.e. they are position and energy invariant, it is possible to sum the

momentum transfer plots from all pixels to give an overall spectrum for an acquisition without a loss of information. The resolution of this spectrum is determined by the 250 μm pixel size, and its counting statistics are governed by the overall detector size. This data processing method therefore enables greater detection efficiency whilst maintaining resolution, and vastly reduces the amount of data to be examined.

Three simulants were studied, which each consisted of polycrystalline hexamine and pentaerythritol embedded in a plastic binding material. Although the ratios of the two powders were the same for each simulant, there were slight variations in the polymer coating and crystalline grain sizes. The simulants were approximately 24 mm thick. Due to this thickness, peak broadening was expected due to an underestimation of the scattering angle for photons which were scattered from deeper within the sample. The scattering angles assumed for each pixel are dependent on the sample-detector distance, therefore scattering from closer to the detector will be detected at pixels representing lower scattering angles than scattering from the front of the sample (see Figure 2). For this initial study, measurements of the simulants were taken with 10 minute acquisition times. The diffraction data were corrected by performing a subtraction of the background signal (measured with no sample in place).

Results and discussion

Pixellated X-ray diffraction intensity maps for an example simulant sample are shown in Figure 3(a)-(c). It can be seen that as higher energy windows are observed, the areas of high intensity move towards a lower scattering angle (with the incident beam position a small distance outside the top right hand corner of the detector). This diffraction behaviour is as expected according to Bragg's law. There are small regions of high intensity which can be seen within the broad ring of lower intensity diffraction. These regions are thought to be due to relatively large crystalline regions within the simulants which effectively act as single crystals rather than powders due to their comparable size with the incident X-ray beam (of the order of 1×1 mm²). The positions of these regions as a function of energy behave in a similar manner to a diffraction ring, and thus can still be used to give information on the momentum transfer values for the diffraction.

Figure 3(d)-(f) show the diffraction intensity as a function of the scattering angle. By applying the method described in the previous section, the data were converted into momentum transfer space, giving one plot which describes the diffraction recorded across all pixels (Figure 4). The constituent materials of simulants - and plastic explosives - tend to be distributed in a non-uniform manner. This is reflected in the XRD measurements

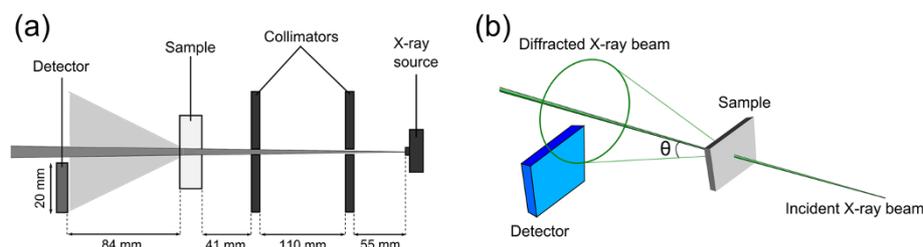


Figure 1 Experimental setup. (a) Schematic diagram of the pixellated diffraction setup (plan view). (b) The detector measures diffraction from a powder sample in the form of a portion of the diffraction ring. The angle of scatter is dependent on the sample's molecular structure and the X-ray energy, as given by Equation 2.

from different regions of the same simulant sample (moving the sample perpendicular to the X-ray beam), which show similar diffraction patterns, but with some slight differences in the peak intensities and positions. The differences in peak intensity are thought to be due to either the amount of crystalline material in the scattering volume, or the size of the crystalline grains. The peak position is dependent on the sample-detector distance - e.g. if more crystalline regions are present towards the rear of the sample (closer to the detector), the diffraction will be measured at a lower momentum transfer value. Figure 4 also shows that similar XRD data were measured for each of the three simulants; this was expected since each simulant was composed of the same base materials in the same ratios.

The nature of the peaks present in the simulant XRD pattern can be explained by relating it to the constituent materials present - hexamine and pentaerythritol. Using the same experimental setup, diffraction data was also taken for base hexamine and pentaerythritol powders. As shown in Figure 5, it can be seen that peaks occur for the two constituents in the same regions of momentum transfer space as those features seen for the simulant samples. The peaks are sharper for the base samples,

since they were 3 mm thick, rather than the 24 mm thick simulants. Broader peaks are observed with the simulants due to scattering from deeper within the sample, as discussed in the previous section. The multiple diffraction peaks from the pentaerythritol present in the simulant are thought to become merged into one broad peak covering a similar momentum transfer range ($1.3\text{-}2.2\text{ nm}^{-1}$) due to this individual peak broadening. In addition, there appears to be a further broad, low intensity feature in the simulant diffraction patterns which spans the momentum transfer range of interest. The data are corrected for background contributions, and this feature does not appear in the data for the base samples, so it is assumed that this feature is due to scattering from the amorphous binding material present in the simulants. The overall higher intensity for the simulant sample compared to the base materials is explained due to the thicker simulant giving a larger scattering volume, which outweighs the additional X-ray attenuation. Using the information from the hexamine and pentaerythritol samples, it appears that the differences in the intensity of the diffraction peak at $\sim 1\text{ nm}^{-1}$ (for example, between the measurements at positions 1 and 2 for simulant

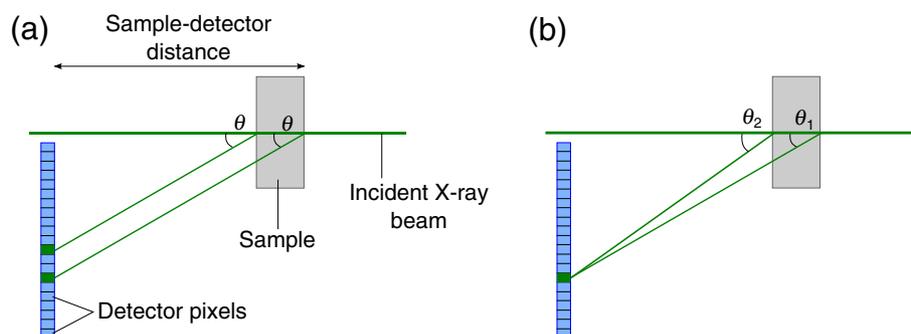
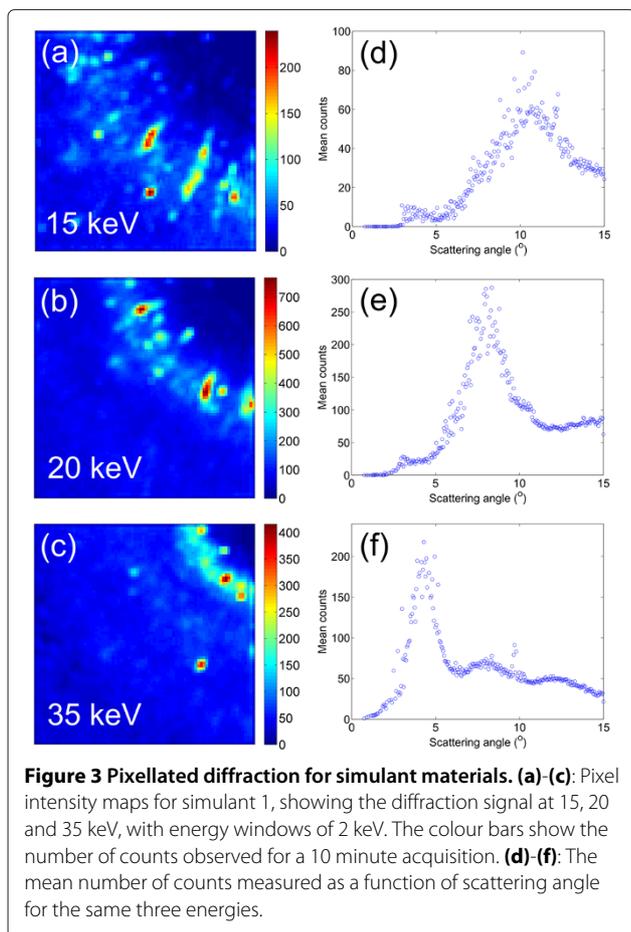


Figure 2 Thickness effect. The effect of sample thickness on the observed diffraction pattern. (a) Photons scattered from the rear of the sample will arrive at a different pixel to those scattered through the same angle from the front of the sample. (b) Alternatively, this effect can be thought of as different scattering angles being measured at the same pixel. The scattering angle assigned to each pixel is based on the sample-detector distance as shown.

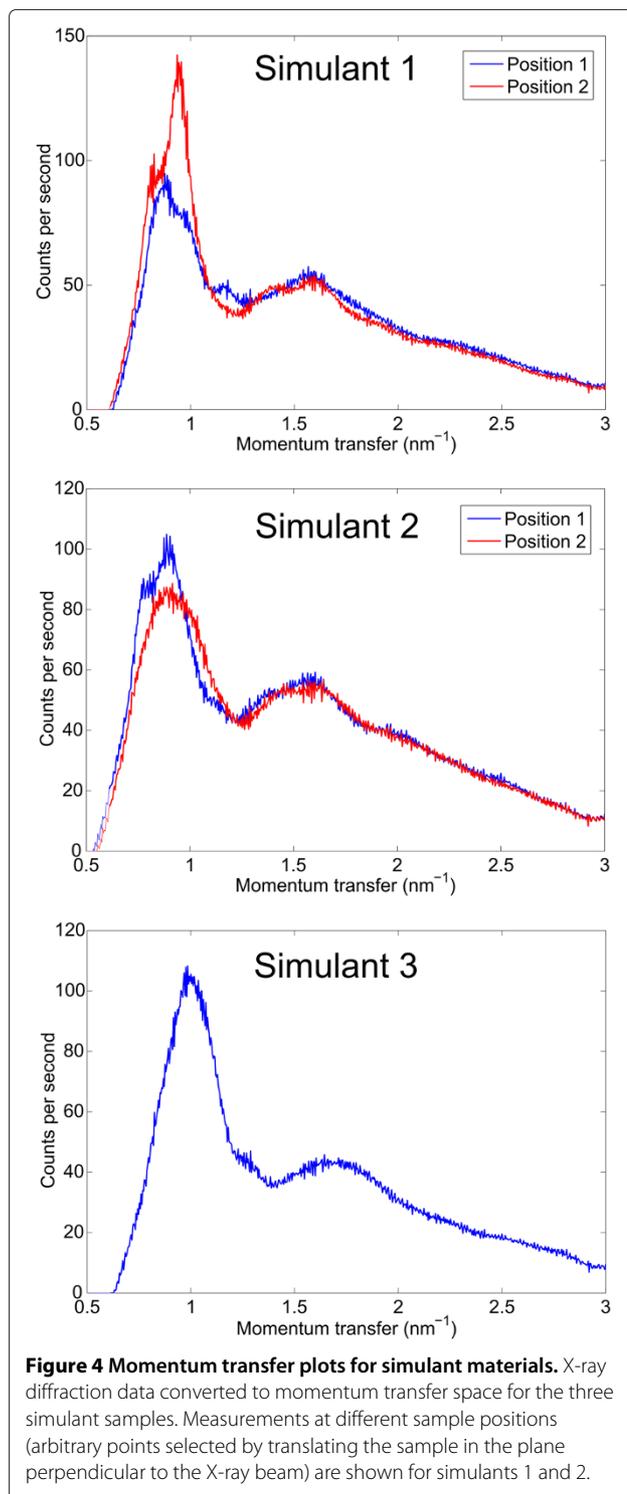


1) is due to the amount of hexamine present in the scattering volume.

Diffraction data from the explosive material which was the basis for the simulants is shown in Figure 6. It is important to note that the explosive sample was 3 mm thick, so the data cannot be directly compared with those of the simulants. As is the case with the simulants, features are identifiable in the explosive data which correspond to the different energetic materials which are present (O'Flynn 2013).

Conclusion

The X-ray diffraction data presented for the three simulant samples demonstrate the ability of XRD to identify the different materials present in a sample based on their individual molecular structures, and therefore the possibility of implementation in a system which can search for specific materials hidden inside packages or baggage. Examples of such materials are the high energy compounds RDX and PETN which are found in many plastic explosives; if the diffraction patterns for these substances are known, they can be compared with the data obtained from unknown items to provide a "red light/green light"



system. This approach also applies to any potentially dangerous substances, such as ammonium nitrate. Principal component analysis (PCA) is a data processing technique which groups similar datasets together, and has been previously used to accomplish an explosives identification

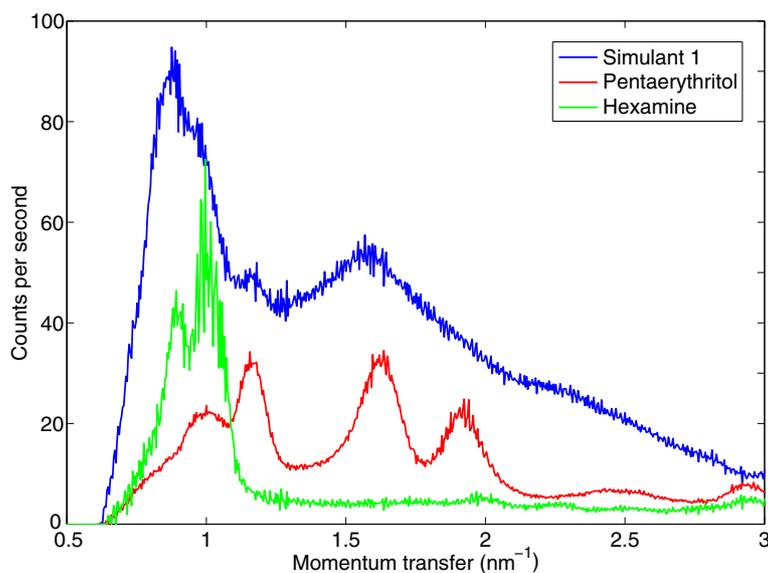


Figure 5 Comparison of XRD for a simulant and its individual powder constituents. X-ray diffraction data in momentum transfer space for a simulant, hexamine and pentaerythritol, with 10 minute acquisition times. It can be seen that the peaks observed for the two base materials are also present in the simulant, albeit with peak broadening in the latter sample due to a larger sample thickness.

system for PixD. Although diffraction data are noisier with short acquisition times (due to less X-rays being measured by the detector), PCA has demonstrated accurate material identification for measurements acquired in one second (O'Flynn 2013). With a large library of XRD datasets from explosive and inert materials, PCA enables diffraction

patterns of unknown samples to be classified based on their similarity to previously measured data.

A challenge for the pixellated diffraction system is to be able to identify materials in thick samples, as described in the 'Methods' section and demonstrated in 'Results and discussion' section. This issue could be overcome

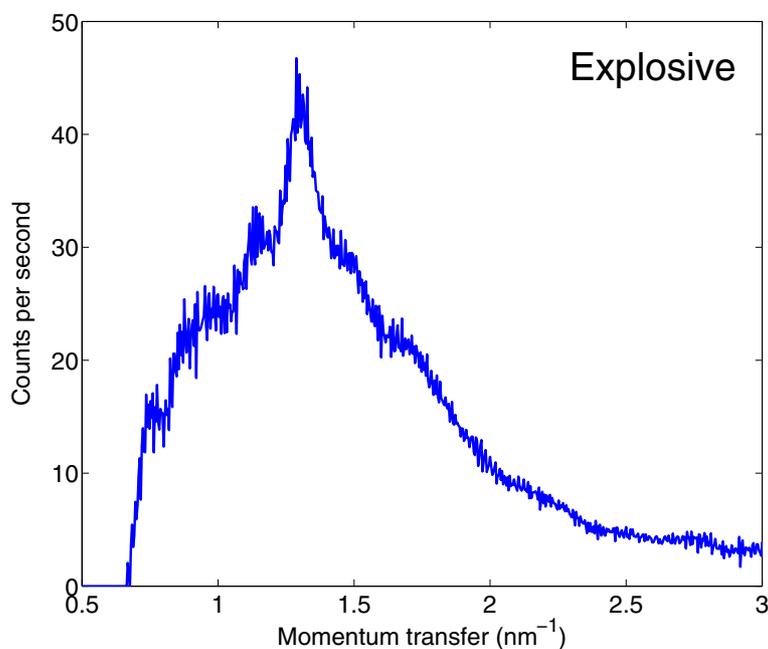


Figure 6 X-ray diffraction pattern for an explosive substance. X-ray diffraction data for the explosive material which the simulants were based upon. The sample was 3 mm thick, and the acquisition time was 10 minutes.

with the use of secondary collimators (positioned between the sample and detector) to more accurately select the scattering angles of photons which reach the detector. One drawback of this approach is the potentially large reduction of photon flux due to the extra collimation, which would lead to longer counting times. Another possible solution is to produce a simulated spectrum for each suspicious material based on the sample thickness, such that more direct comparisons with data from an unknown item can be made. This method would require the thickness of the object under observation to be defined. Attenuation of the incident and scattered X-ray beams due to other materials in front of/behind the object under study would also be a factor to consider in the production of a diffraction based scanning system. Increasing the incident beam peak energy would give greater penetration through the sample, but would have knock-on effects on the resultant diffraction pattern. Further research is required in order to optimise a system for specific material identification in more realistic baggage scenarios.

In conclusion, the pixellated X-ray diffraction technique enables simultaneous measurement of angular and energy dispersive XRD, and utilises the benefits of both methods. The experimental setup is useful for practical situations, since it is compact and contains no moving parts. The pixellated detector enables the counting statistics of a $20 \times 20 \text{ mm}^2$ detector with the angular resolution afforded by the $250 \mu\text{m}$ pixel pitch. It is envisaged that pixellated diffraction would be used alongside conventional baggage imaging methods; due to the small beam size used for diffraction, it would be more efficient to scan suspicious regions within a bag which were initially identified with an image. Radiation protection required for the diffraction setup would be similar to that used for present airport-based scanners.

Competing interests

The authors declare that they have no competing interests.

Authors' contributions

DO set up the pixellated X-ray diffraction (PixD) system, made the measurements, analysed the data and drafted the manuscript. HD synthesised the simulant samples and provided project guidance. CR and CC set up the PixD system and optimised the pixellated detector. MW, MV and PS developed the pixellated detector and provided technical assistance. DH and BW are technical leads for the research project. RS is the principal investigator for the project. All authors read and approved the final manuscript.

Acknowledgements

This project was funded under the Innovative Research Call in Explosives and Weapons Detection (2010) initiative, a cross-government programme sponsored by a number of departments and agencies under the U.K. Government's CONTEST strategy, in partnership with US Department of Homeland Security.

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Received: 11 February 2013 Accepted: 30 June 2013

Published: 6 July 2013

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doi:10.1186/2193-7680-2-4

Cite this article as: O'Flynn et al.: Identification of simulants for explosives using pixellated X-ray diffraction. *Crime Science* 2013 **2**:4.