X-RAY DIFFRACTION IN FORENSIC SCIENCE

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X-ray powder diffraction (XRD) is used widely in forensic science. Its main strengths are its non-destructive nature, thus preserving evidence, its ability to identify compounds and not just elements, and its ability to analyse many types of different materials—organic, inorganic and metallic. A selection of evidence types and their analysis by XRD is described.

Introduction

The task of identifying an individual suspected of involvement in a crime usually comes down to answering the question “Are the accused person and the person characterized as having committed the crime in fact one and the same person?” The question may be answered in one of two ways: (a) it may be possible to establish a connection between some physical evidence associated with the crime and some personal characteristic of the accused e.g. his DNA profile, his fingerprints, or a video surveillance camera image of him, and (b) it may be possible to show a connection between the scene of the crime and something which is definitely linked with the accused e.g. textile fibres from his clothing, tool marks made by a case opener or screwdriver belonging to him, or his shoeprints.

Of these two ways of answering the original question, the former tends to provide the more compelling evidence. DNA profiling yields near unequivocal identification of an individual, and a clear fingerprint left at a scene is also one of the most reliable forms of evidence. If the perpetrator of the crime is careless or unfortunate enough to leave a body fluid or fingerprints at the scene, there is a good chance of him being apprehended. Alternatively, a high quality video camera image of the individual’s face at the scene may result in his rapid identification, without the need for the expense of DNA profiling or for a fingerprint search.

There will be occasions, however, when there is no photographic, DNA, or fingerprint evidence available, and the task of identifying or exonerating the accused may rely upon analysis of contact trace evidence. The oft-quoted guiding principle in forensic science is that “…every contact leaves a trace…” so if we can identify the trace, we provide evidence of the contact. Simple examples might be the collision of a red car with a blue car, in which blue and red paint will be transferred from one car to the other, and the transfer of clothing fibres from assailant to victim and vice versa during an assault.

X-ray diffraction (XRD) in forensic science [1–4] usually implies the use of powder diffraction as opposed to single crystal diffraction. The latter is rarely used, because full structural analyses are seldom required, and the expense of maintaining or leasing a facility for this purpose could not be justified. Qualitative phase analysis of polycrystalline organic, inorganic and metallic substances is the bread and butter of the forensic diffractionist, who may be dealing with anything from microgram specimens to kilogram seizures of drugs. XRD is concerned largely with the identification of these so-called “contact traces”. As might be expected, there are many types of material (Table 1) which...
occur as contact traces and which can be analysed satisfactorily by XRD. The only prerequisite is that the material should be crystalline or at least partially crystalline.

This is a comprehensive list showing the different types of materials which at one time or another have been analyzed by XRD in various forensic science laboratories. Users of XRD in private industry, or for that matter in academic circles, may concentrate on just one of the types of materials listed here, whereas the forensic analyst may be called upon to analyse any of these materials. A brief discussion follows, in which the examination of a selection of these materials (paints/pigments, plastics/polymer, metals/alloys, drugs, paper, miscellaneous) is described, some illustrated with suitable examples.

The choice has been made to reflect the versatility of XRD, because it can be used to analyse all crystalline material, from organic compounds such as drugs, through minerals, to heavy metals. As a general rule, a diffractionist in a forensic science laboratory will be asked to either (a) identify a single substance e.g. a powder found on someone suspected of carrying restricted substances, or (b) compare two specimens to see whether or not they could have come from the same source e.g. paint flakes from a window sill (control), and paint flakes from the clothing of a person suspected of having gained unlawful entry through that window (suspect).

Most contact trace specimens encountered in forensic science are very small, so the XRD instrumentation must be capable of small specimen analysis. This can mean samples weighing a few microgrammes (μg). Powder photography was always the method of choice for such small samples until latterly, when powder diffractometers truly capable of small specimen analysis (capillary-focused parallel beams and high resolution area detectors) became available. The types of powder cameras deployed are Debye–Scherrer (57.3 and 114.6 mm diameter), Guinier, and Gandolfi. The Gandolfi camera is especially suited to the analysis of materials which for one reason or another cannot, or should not, be ground up—for example, very hard abrasive materials, gemstones, explosives, and materials that convert from one polymorphic form to another on grinding [5–10].

Figure 1 gives an idea of the actual size of specimens, and the way in which they are mounted for examination in a Debye–Scherrer powder camera. Paint flakes (or any monolithic specimens) are mounted on the end of glass fibres, whilst powders are sealed inside thin-walled glass capillary tubes. Here, the loose paint flakes weigh 150 and 30 μg and the brass specimens 500 and 200 μg respectively.

The analysis of examples of the six types of materials described earlier now follows—paints, polymers, metals, drugs, papers and others.

**Paints and Pigments [11,12]**

When a case is submitted to the laboratory, it is assigned to one scientist who will decide on how best to tackle the case and answer the investigating officer’s questions. If paints are involved, for example in a typical break-in or road traffic accident, the first step is to compare control and suspect specimens visually—by eye and by low power visible light microscopy. If they appear identical in colour, then their chemical composition must be checked, and this is where Fourier Transform Infrared Spectroscopy (FTIR) or XRD may be used.

As a rule, single layer control and suspect paint flakes are sent in for analysis with the request to compare them and to establish whether or not they are similar according to their diffraction patterns. Part of the comparison naturally involves identification of as many of the crystalline components as possible, either by reference to the ICDD Powder Diffraction File [13], or to a local collection of standard reference diffraction patterns.

Figure 2 illustrates the importance of a technique such as XRD, because the two blue paints (ICI Royal Blue and ICI Admiralty Blue) are visually identical, as are the two red paints (ICI Signal Red and ICI Post Office Red)—this is termed a metameric match. ICI Royal Blue contains Prussian Blue as its main pigment, and ICI Admiralty Blue contains β-copper phthalocyanine. The red paints do have some similarities in...
composition—ICI Signal Red contains cadmium sulphide and barium sulphate with an organic pigment Monolite Fast Scarlet (Colour Index (CI) Pigment Red 3). ICI Post Office Red contains cadmium sulphide with either CI Pigment Red 48 or 52.

The XRD results obtained from the control paint samples (i.e. known source) are classified in terms of the categories household, vehicle and other, and these categories are subdivided into eight colours. The analytical results are added to a small database of paint compositions as determined by XRD. The purpose of this database is to provide simple statistics on the frequency of occurrence of a particular combination of pigments or extenders within a given colour category. These statistics form the basis of the so-called evidential value of the analytical results. For example, suppose two paints (control and suspect) match each other in diffraction pattern. What is the significance of this match? If the paints contain only one crystalline component e.g. rutile (titanium dioxide), which is very common in white gloss paints—the significance of the match and its evidential value are low.

If, however, the paints contain maybe four or five crystalline components, some of them unusual, then the significance of the match and its evidential value is high. Reference to a database may reveal that a particular combination of pigments and extenders occurs only once in, say, fifty red paints analyzed during the last seven years. Frequently the resins in the paints are analyzed too, and in this respect the non-destructive nature of XRD is very useful. The paint is first analyzed by XRD and is then examined using Pyrolysis Gas Chromatography (PGC) or by Pyrolysis Mass Spectrometry (PyMS), providing information about both the crystalline and non-crystalline components before the sample is destroyed.

Polymers [11,14]

XRD was used in this laboratory to identify the crystalline pigments and fillers present in electrical wire insulation, without really paying much attention to the broader, more diffuse diffraction maxima from the polymeric material. As there are already a number of well-established techniques for the analysis of polymers, for example PyMS, PGC and FTIR spectroscopy, these methods, in the majority of cases, would be employed before using XRD if a sample were suspected of being polymeric. However, the non-destructive nature of XRD gives it a distinct advantage over these other techniques, and henceforth considerable use was made of XRD for plastics/polymer analysis—mainly as a screening technique.

Plastics and polymers, perhaps because of their physical appearance, are sometimes thought of as being non-crystalline, and in some cases this is true. However, the majority of the more common polymers and plastics are at least partially crystalline, and therefore lend...
themselves to analysis by XRD.

The powder patterns shown in Fig. 3 of PTFE, polypropylene, and low- and high-density polyethylene are typical of polymers, with broad, diffuse lines. If pigments were present in any plastic item made of these polymers, their diffraction patterns would consist of much sharper lines than those of the polymers.

Two cases illustrate the use of XRD in polymer analysis:

1. Some pieces of unknown material were submitted for analysis and they yielded diffraction patterns similar to that of polyvinyl chloride (PVC). PyMS then confirmed the presence of a copolymer with a high PVC content.

2. A “crystalline” deposit was found on a chair. The deposit was in fact found to be largely amorphous, but a weak diffraction pattern present matched that of polymethylmethacrylate. The deposit was later identified by PyMS as poly-methylcyanoacrylate.

Metals and alloys

Generally speaking, metals and alloys are identified by elemental analysis, for example using X-ray fluorescence (XRF) or by microprobe analysis in the scanning electron microscope. However, these methods yield no information about the phases present, and this is where XRD is most useful.

One of the most frequently-encountered metals in everyday life is brass [15], perhaps because its composition is so variable which gives rise to variable physical properties to suit different applications.

Figure 4 shows a phase diagram of the copper/zinc system. On the left is the $\alpha$ phase, a solid solution of zinc in copper ranging from 0 to 38% zinc by weight. Next to this is the duplex phase ($\alpha+$),$\beta$), and further to the right is the $\beta$ phase in the region of 50% zinc. Brasses of the type $\alpha$ and $(\alpha+\beta)$ are the most common, whilst...
those with over 50% zinc are rarely used commercially on account of their brittle nature. The two phases, $\alpha$ and $\beta$, have quite different crystal structures. Alpha brass has a face-centred cubic structure with continuously variable occupancy of each site by copper and zinc whilst beta brass has a CsCl cubic structure with zinc at the centre and copper at the corners.

Figure 5 shows powder photographs of a selection of different brass compositions. The powder pattern at the bottom of Fig. 5 stands out because it has two diffraction patterns on it, one from $\alpha$ brass and one from $\beta$ brass. It is of a duplex 60/40 Cu/Zn brass, a common machine brass. The remaining patterns are of pure alpha ($\alpha$) brass with varying Cu/Zn ratios. As more zinc is added, the unit cell expands and the effect on the powder pattern is best seen by looking at the diameter of the 400 reflection in the back reflection region of these powder photographs.

A rough estimate of the percentage of zinc in a single phase $\alpha$ brass may be obtained by straightforward comparison of its powder photograph with these standards. A more accurate estimate (±1%) can be obtained by plotting unit cell dimensions versus %Zn for each of the pure standards.

The variation in composition of a number of common brass objects is quite surprising, and as a result they can be readily distinguished by XRD analysis.

Figure 6 shows a Yale lock, Yale lock retaining ring, Yale lock cylinder, door keys (Chubb and Yale), an electric light fitting, a wood screw, brazing rod, a .303 cartridge case and a cupboard hinge. Although all these items are made of brass, the composition in each is different. In addition to identifying the phases of brass and providing the % zinc in single phase $\alpha$ brasses, an estimate of the ratio of the $\alpha$ to $\beta$ phases within a duplex ($\alpha+\beta$) brass can be made by measuring the relative intensities of the major lines of these phases. The presence of lead (to improve machinability) in some of the alloys is also detectable.
An example of the use of brass analysis in casework was the attempted theft of a ship’s propeller. A worker in a small dockyard repair shop on the River Thames near Woolwich, south London had seen a tugboat propeller (Fig. 7 below shows an example) being brought to a neighbouring shop for repair. He decided to steal the propeller and sell it for scrap. The propeller was four-bladed in cast brass, weighing approximately a ton (950 kg) and measuring 5 ft (1.5 m) from blade tip to blade tip.

His plan was to enter the repair shop after dark, cut the blades off the propeller with a gasoline-powered abrasive disc cutter/grinder, and load the severed parts into the back of his truck and make off with them. Unfortunately he forgot to check how much gasoline he had in the tank of the cutter/grinder, and before he had even cut through one blade of the propeller, the cutter ran out of gasoline. The man ran to his truck with the cutter/grinder and made off. The noise of the cutter had attracted attention and he was seen by a witness who reported his vehicle registration number to the police. Within 10 min the police were knocking at the man’s door. They found him inside with his overalls off, standing in jeans and a singlet, and from the neck up he was covered in a layer of fine brass particles—from the action of the cutter/grinder on the propeller blade. The man was arrested and taken away. Samples of the brass particles from his body and clothing, together with a sample of control brass from the ship’s propeller were submitted to the laboratory for examination.

The powder photographs in Fig. 8, which were both of a duplex \((\alpha+\beta)\) brass, seemed quite different at first which was surprising, but reference to the phase diagram provided an explanation. The cutting action of the abrasive disc on the metal would have generated a great deal of heat—probably raising the temperature to 300–400°C, and brass particles at this temperature would have had their \(\alpha/\beta\) phase ratio shifted in favour of the \(\beta\) phase. When both samples were annealed at 500°C, the resulting powder patterns (Fig. 9) agreed very well indeed.

Particles of abrasive material found on the
man’s clothing were compared with control grit from the cutter/grinder, and they were also found to be identical, consisting of silicon carbide (SiC).

**Drugs**

It would be misleading to imply that all drugs seizures are analysed by XRD alone, but a considerable amount of analytical data have been amassed by forensic science laboratories around the world [16–21]. Some of the drugs most frequently encountered are cocaine, heroin, morphine and the amphetamines. These drugs occur as loose powders or tablets in which the drug is mixed or “cut” with some other substance termed a diluent or adulterant (Table 2).

The initial examination is by eye and occasionally by low power visible light microscopy. Simple chemical tests are then used to identify the drugs present, and confirmation is by Gas Chromatography-Mass Spectrometry (GCMS). If the drugs present are to be quantified, this will usually be achieved with Nuclear Magnetic Resonance (NMR), GCMS, or High Performance Liquid Chromatography (HPLC). FTIR is used to distinguish between cocaine base (Crack) and the main salt of cocaine, cocaine hydrochloride.

XRD is usually employed (a) to identify the precise chemical form (salt, base, acid) of the drug, (b) to identify any diluents or adulterants, and (c) in some cases to compare one seizure with another, or with several others. The amount of a seizure can vary enormously, from a few milligrams to kilograms depending upon the source. If XRD analysis is required, a sub-sample of a few milligrams is submitted to the X-ray Section once the initial examination has been completed by the Drugs Section. Powdered specimens are hand-ground using an agate mortar and pestle, and for diffractometry are loaded into flat specimen holders using the side loading technique of McMurdie et al. [22]. If powder photography is to be used, they are loaded into thin-walled glass capillary tubes (0.3 mm diameter). Iron-filtered Cobalt Kα radiation is used in the London Laboratory of the FSS. Its wavelength (1.79026 Å) provides better angular dispersion than Cu radiation, at the expense of intensity and count rates.

Identification of as many of the components as possible in a mixture can provide a wealth of information, for example trends in usage of particular drugs, changes in diluents or adulterants, and changes in the purity of a synthesized product. These aspects may reflect changes in social habits, changes in sources and suppliers, and demand for better, purer products respectively. Identification of the salt, base or acid of drugs such as cocaine (free base (Crack) and hydrochloride), heroin (base and hydrochloride), morphine (base, hydrochloride and sulphate) are a matter of routine. Distinction between the optically active form(s) and the racemic form of drugs such as amphetamine (d- or l-amphetamine sulphate and dl-amphetamine sulphate) is also a relatively simple process by XRD. Powder diffraction will not permit distinction of the d-form of any compound from its l-form, however, and single crystal diffraction experiments would be required for this. In some cases FTIR spectroscopy will distinguish salts from bases in high purity mixtures, but if the drug is mixed with certain diluents, it may be impossible to state with certainty whether the drug is present as a base or salt.

Figure 10 shows three forms of amphetamine salts which are easily distinguishable by XRD. The same applies to different forms of the other common drugs of abuse. Other salts exist, e.g. phosphates, tartrates, and citrates but they are not seen as frequently as sulphates, hydrochlorides and the base forms of heroin, morphine and cocaine. XRD is an excellent way of identifying these and other forms of drugs, through reference to the ICDD Powder Diffraction File (PDF) [13] or to a local database of patterns.

In general, sugars are the favoured adulterants, with Epsom Salts (MgSO₄·7H₂O) being the most common inorganic substance (see Fig. 16). Useful information concerning synthetic routes of drug manufacture may sometimes be obtained from XRD analyses. For example, Crack cocaine (cocaine base) may be prepared from its hydrochloride by heating with sodium bicarbonate. The sole end products should be cocaine base and sodium chloride, so the presence of all four compounds in a seizure points to a rather amateurish, incomplete attempt at synthesis from cocaine hydrochloride and sodium bicarbonate.

If a record is maintained of the diluents or

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<th>Table 2. List of common diluents/adulterants.</th>
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<tr>
<td>Mannitol (β, and occasionally α and δ)</td>
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<tr>
<td>a-Lactose monohydrate</td>
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<tr>
<td>Glucose monohydrate</td>
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<td>Sucrose</td>
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<td>Fructose</td>
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<td>Boric acid</td>
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<td>Citric acid</td>
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<td>Magnesium sulphate</td>
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<td>Sodium chloride</td>
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<td>Flour, talc</td>
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adulterants identified over a period of time, trends appear, and it is apparent that certain diluents are preferred for particular drugs. For example, the favoured carbohydrate for amphetamine sulphate appears to be glucose monohydrate, whilst that for cocaine is β-d-mannitol.

In a particular case study, an off-white powder was submitted for analysis. The Drug Section's preliminary analysis revealed heroin, glucose, and sodium chloride. A sub-sample was submitted to the X-ray Section with the request to confirm this analytical result, and to identify the chemical form of heroin, i.e. base or hydrochloride.

The XRD result confirmed the presence of heroin (as the hydrochloride hydrate), and also sodium chloride, but no glucose. Instead, a strong powder pattern was present which could not be identified, either by reference to our local database or to the PDF. A record of the d-spacings and relative intensities was kept for future reference. Within a few months the same unknown pattern had appeared in four unrelated street seizures. In one seizure, this pattern occurred together with that of glucose monohydrate, and this led us to consider that glucose might be forming a complex with sodium chloride. A literature survey revealed a paper published in 1947, in which the crystal and molecular structures of complexes between sucrose and sodium chloride and sucrose and sodium bromide were reported [23].

We attempted a synthesis of such a complex between glucose and sodium chloride by mixing weighed amounts of glucose monohydrate and sodium chloride in molecular weight ratios such as 1:1, 1:2, and 2:1. The powders were mixed dry and left to stand in glass tubes. Within two hours each mixture had “caked” into a solid lump. The lumps were analysed by XRD revealing the pattern of the hitherto unidentifiable material together with those of either excess glucose monohydrate or excess sodium chloride (Fig. 11).

The final stage of analysis was completed with the determination of the crystal and molecular structure [24]. Crystals belonged to the trigonal space group P3, and the empirical formula proved to be C₆H₁₂O₆·1/2NaCl·1/2H₂O (the coordination sphere of the sodium ion in the crystal structure is shown below in Fig. 12).

Paper
Forensic paper examination and analysis is usually associated with ransom notes, threatening letters, anonymous hate mail, and wrappings from drug seizures. The examination will more than likely be a comparison of paper from, for example, the ransom note with that found in a suspect’s dwelling. XRD or elemental analysis may be called for, but only after an ini-
tial examination by botanical or fibres experts. XRD is used to identify the fillers present in the paper and it can also yield useful information about the percentage crystallinity of the cellulose [25]. A paper’s mineral content depends upon its use and appearance. A cheap copying paper usually has either no filler (cellulose only) or a clay mineral such as kaolinite, whereas other more expensive papers have rutile or anatase as fillers.

Miscellaneous
A small company specialized in the production of light alloy castings. A supply of the alloy was kept in the factory under lock and key. One night the factory was burgled, and the entire stock of alloy stolen—worth a large sum of money. However, the factory had not been broken into; entry had been effected by someone bearing a key. The only key holders in the company were the three directors. The police interviewed all the factory employees, and the three directors were asked to present their keys for examination. Information on one of the directors was supplied by the other two, both of whom had their reasons for suspecting their colleague of complicity in the burglary. Forensic examination of each of the keys revealed minute traces of a white substance on the key belonging to the director who was under suspicion. The substance was analyzed by XRD (Fig. 15) and found to be aragonite (a polymorph of calcium carbonate).

The director who was under suspicion was then questioned closely by the police and his home searched. Hidden in his garage was part of a cuttlefish bone which he claimed was an aid for sharpening his budgerigar’s beak. This was actually true, because cuttlefish bone (Fig. 13) is sold in pet shops precisely for that purpose, but the man had also used the bone to make an impression of his key for an accomplice to cut a duplicate. The texture of aragonite in cuttlefish bone is excellent for making finely detailed impressions of irregularly shaped objects such as keys (Fig. 14). It emerged that the man had personal financial problems, and in

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**Fig. 11.** Powder photographs of NaCl, heroin hydrochloride hydrate with unknown and NaCl, unknown with glucose monohydrate, and glucose monohydrate.

**Fig. 12.** Molecular structure of the glucose/sodium chloride complex.
order to raise some money quickly, he had enlisted the help of a third party to carry out the burglary and steal and sell the alloy stock.

Powder diffraction’s versatility is one of its greatest attributes. Its ability to analyze mixtures of inorganic, organic and metallic substances is very useful indeed. A smouldering object was pushed through the letterbox of an elderly man’s house. It began to cause the carpet to smoulder but the man stamped on it, managed to extinguish it, and then called the police. Some children found in the vicinity had in their possession a packet of theatrical smoke pellets. XRD analysis of the partially burnt material from the man’s house and an unburnt pellet revealed that they were of similar composition, containing potassium chlorate, ammonium chloride, alpha-lactose monohydrate, and traces of sodium chloride (Fig. 16). The children, in the presence of their parents, were questioned by the police and it transpired that they had been given the smoke pellets by an older boy. This boy had encouraged them to light the pellet and push it through the man’s letterbox. The children were dismissed with a caution but warned that further escapades of this sort would result in them appearing in a Juvenile Court.

Summary

X-ray powder diffraction is a useful and versatile analytical tool in any laboratory, let alone a forensic science laboratory. The purpose of this paper is to raise awareness of its usefulness, in a forensic context, when the sequence...
of analysis can, on occasion, be almost as important as the analysis itself. The preservation of evidence, contact trace evidence, may be vital, so a non-destructive method of analysis is essential.

Specimens from a scene of crime, or from a suspect, are rarely nice, clean, single phase materials—they are mainly multiphase specimens, and often contaminated. This contamination may be regarded by the analyst as a nuisance, but it is nonetheless part of the specimen and may have considerable significance with regard to the specimen’s location at the scene. If it comprises a mixture of organic and inorganic materials, XRD will provide simultaneous analysis regardless.

Powder diffraction is a powerful technique, but it is not the answer to every analytical problem. Its restriction to solid substances and the fact that it is not really a method for trace analysis are its main drawbacks. Analysis of forensic casework specimens requires a careful, well thought out approach to the analytical sequence in order to maximize the information obtainable, before a sample is destroyed in analysis. For this reason alone, XRD is one of the techniques that should be considered more as a first line of attack rather than as a last resort.

References


