Advances in chemistry applied to forensic science

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Acts of terrorism, an increase in the use of firearms, drug abuse, the use of so-called date-rape drugs, and driving whilst under the influence of drugs, are just some of the subjects frequently in the news. In the absence of fingermarks and of material leading to the recovery of DNA, the forensic scientist has to rely upon chemical analysis of trace amounts of materials including explosives, drugs, toxicological specimens, firearms discharge residues, fibres, glass, paint, soil *etc.*, in order to establish or eliminate links between suspect and victim and/or scene. This *tutorial review* describes analytical problems facing the forensic chemist, and the current methods and techniques employed to tackle them.

Introduction

Of late the general public has become more aware of the application of science to crime solving, due mainly to the proliferation of television programmes, both documentary and fictional, and accounts of high-profile court cases in national newspapers, each describing detailed aspects of forensic science. Acts of terrorism, an increase in criminal use of firearms, drug trafficking, the use of so-called date-rape drugs, and driving whilst under the influence of drugs, are just some of the subjects frequently in the news.

Since the discovery of individual-specific "fingerprints" of human DNA and subsequent forensic application of DNA fingerprints[1] in 1985, forensic science laboratories have committed considerable resources to the development of DNA profiling methods. The highly-specific nature of DNA evidence renders it invaluable as a means of identification. Fingermarks at the scene of a crime are also individual-specific, but however careful the criminal may be to avoid leaving his fingerprints, inadvertent contact with other parts of his person may result in his leaving body fluids or tissue at the scene, each of which will yield his DNA. In the absence of fingermarks and of material leading to recovery of DNA, however, the forensic scientist has to rely upon chemical analysis of trace amounts of materials including explosives, drugs, firearms discharge residues, fibres, glass, paint, soil *etc.*, in order to establish or eliminate links between suspect and victim and/or scene. This review will examine the current methods of forensic analytical chemistry for evidence types including those listed above. General textbooks such as those of White[2] and Saferstein[3] provide excellent introductory information.

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Firearms discharge residues

The gases and particulate matter generated when a firearm is used are known as firearms discharge residues (FDR). In order to understand why and how they arise, it is necessary to consider the make up of a typical cartridge. A cartridge case contains three components: primer, propellant and projectile (bullet). The primer is ignited by the percussive effect of the weapon's firing pin striking the primer cap on the end of the cartridge. The primer burns rapidly and ignites the propellant, which in turn burns very quickly, producing a large volume of gases inside the cartridge case which forces the bullet down the barrel. When a weapon is fired, in addition to the forward propulsion of the bullet, residues of primer and propellant chemicals from the cartridge are propelled both forwards toward the target and backwards toward the firer. The disposition and subsequent analysis of these residues can be used to (a) help in identifying the firer, or persons close to the firer, and (b) estimate the distance from which the weapon was fired.

Primers tend to be inorganic, and propellants organic compounds. A typical primer consists of lead styphnate (explosive), antimony sulfide (fuel) and barium nitrate (oxidizer). The propellant is usually a smokeless powder containing nitrocellulose. There are different types of

propellants, those termed ''single base'' which consist only of nitrocellulose, and ''double base'', containing nitrocellulose and nitroglycerine. There are triple base propellants, containing nitrocellulose, nitroglycerine and nitroguanidine, but they are usually restricted to large calibre ammunition. Complete combustion of the propellant is rare, and organic residues consist of unburnt or partially burnt nitrocellulose and nitroglycerine. Inorganic residues are formed from condensation of vapours from the hot primer compounds, and comprise hollow spherical particles, whose elemental composition (Pb, Sb, Ba) is critical to their identification as firearms discharge residues.

Collection of the residues is made in a number of ways, *e.g.* swabbing and vacuuming, and taping. The most convenient method for collecting primer residues is by ''taping'' the hands and forearms of suspects with adhesive tapes. Analysis[4] of the tapes is undertaken in a scanning electron microscope with energy dispersive spectroscopy (SEM-EDS) for the presence of lead, antimony and barium in individual particles. The morphology of the particles as hollow spheres in combination with their elemental composition identifies them uniquely as firearms discharge residue particles. Lead-free ammunition (Sintox) has zinc and titanium as its main elements, and after discharge, the similar morphology of spheroidal particles together with elemental composition Zn and Ti distinguishes them from environmental particles of the same composition. Swabbing and vacuuming is used for recovery of both propellants and primers. Swabs and micro-filters are extracted for propellants and retained for primer analysis. Analytical methods[4] for propellants, with detection limits of 100 pg to 1 ng, include high performance liquid chromatography (HPLC) with amperometric detection, gas chromatography with thermal energy analysis (GC-TEA), and liquid chromatography with mass spectrometry (LC-MS).[5] A recent method[6] for dual analysis (organic and inorganic components) has been suggested using adhesive tape.

Distinguishing between genuine firearms discharge residue particles and those of aggregates of environmental occupational origin is important. The possibility of occurrence of other, non-firearms residue particles with elemental content Pb, Sb and Ba has encouraged research and various surveys. Of particular interest is the elemental composition of automobile brake pads[7], pyrotechnics[7,8] and fireworks. Another aspect of FDR analysis concerns detection and identification at the crime scene. To this end, portable X-ray fluorescence (XRF) equipment[9] for general crime scene work has been developed and successful detection of FDRs and identification of Sb, Pb and Ba has been achieved on a variety of surfaces.

Toxicology

The forensic toxicologist's role[2,3] is to detect and identify the presence of drugs and poisons in body fluids, tissues and organs. As in the detection and analysis of firearms discharge residues, the amount of material the toxicologist is expected to work with is low, being of the order of nanograms or at best micrograms. Widespread use and abuse of drugs means that the majority of toxic materials are drugs, so the analyst has to devise a means of extracting the drugs and their metabolites, identifying them, and if necessary quantifying them. Occasionally, the forensic toxicologist has to deal with cases of heavy metal poisoning. The metals may have to be extracted from body fluids or from contaminated foodstuffs, and identified by techniques such as X-ray fluorescence.[10]

When the type and/or number of drugs in the toxicological sample is unknown, a screening procedure, for example enzyme immunoassay (EIA), is initially employed. Screens for opiates, cannabis, amphetamines, cocaine, methadone and benzodiazepines are usually run as a matter of routine, together with any others if prior knowledge indicates specific drug usage. Positive screening results provide the analyst with a list of drugs to be extracted, confirmed and quantified. A fresh sample is taken and the drugs of interest are then extracted.

Drugs are classified broadly as acidic (*e.g.* barbiturates), basic (*e.g.* the amphetamines, cocaine and methadone), and neutral or amphoteric (*e.g.* morphine and the opiates). They, and their main metabolites, are extracted from body fluids by controlling the pH of the aqueous solution in which they are dissolved. Solid phase extraction (SPE) is widely used now in preference to liquid/liquid extraction, mainly because it is amenable to automation, and SPE equipment manufacturers will often provide method sheets for users. SPE cartridges may be used for small scale bench-top work, or for larger scale automated process operation. After extraction and clean-up, the presence of the drug(s) is confirmed by a spectroscopic method, either Gas Chromatography-Mass Spectrometry (GC-MS) or LC-MS. Confirmation by either of these methods[11] is essential, because the screening technique may not be specific enough. These hyphenated techniques are highly specific and they enable quantification to the required levels of sensitivity. GC-MS methods generally require derivatisation of the extracts in order to render them volatile, whilst LC-MS methods do not. LC-MS is particularly useful when the compounds in question are thermally labile.

Driving whilst under the influence of drugs is a problem, the seriousness of which has only relatively recently been recognized. In the UK between 1985 and 2000, the proportion of road traffic fatalities with illicit drugs in their bodies[12] increased from 3% to 18%. This research evidence supported a growing public perception that ''drug driving'' was contributing to death and injury on the road. The Police Service has adapted standardized field sobriety tests (SFST) and drug recognition examinations (DRE)[3] for use in the UK, and Field Impairment Testing (FIT) was introduced in 2000. In 2001 the UK Forensic Science Service (FSS) introduced a streamlined analytical procedure[13] which enabled it to process a large number of motorists' samples following positive FIT. This is based upon the procedures described above: screening, extraction and confirmation. The use of oral fluid, as opposed to blood or urine, for the detection of drugs of abuse has increased. The collection of oral fluid is non-invasive and the testing detects primarily the parent drug and lipophilic metabolites. It has the potential to provide a convenient, rapid, roadside detection system[14] similar to that used to detect alcohol. A minimum of 1 ml oral fluid enables roadside

immunoassay screening with sufficient fluid left for laboratory GC-MS, LC-MS, or LC-MS/MS confirmation.

Drug-facilitated sexual assault, or the use of so-called ''date rape'' drugs, is a crime in which the perpetrator surreptitiously administers drugs (usually through alcoholic drinks) to the victim prior to a sexual assault. The drugs work in a way that renders the victim physically helpless and unable to remember what has happened. There are three well-known date rape drugs: GHB (gamma hydroxybutyrate), Rohypnol (flunitrazepam) and Ketamine (ketamine hydrochloride). Rohypnol is legal in Europe and is prescribed for sleep problems and as an anaesthetic, but it is illegal in the United States of America. Ketamine is an anaesthetic for humans and for animals, and GHB is also used to treat sleep problems. Other hypnotic drugs such as Zolpidem[15] and Zopiclone[16] have also been reported in cases of date rape. The low levels of these substances have been detected and measured using LC-MS/MS. Despite all the publicity given to date rape drugs, in a substantial proportion[17] of alleged date rape cases it was found that the only drug involved was alcohol.

Drug analysis

The main types of drugs of abuse[2,18] likely to be encountered by a forensic drugs analyst are: cannabis, amphetamines, benzodiazepines, heroin, and cocaine. They appear in sub-gram quantities as so-called ''street seizures'' in the possession of individual users, in larger amounts in the hands of local drug dealers, and in kilogram quantities as imported drugs (mainly cannabis, heroin and cocaine). With regard to their analysis, the forensic scientist's main tasks are to (a) determine whether or not a controlled substance is present, (b) determine how much of the substance is present, and (c) determine, on occasion, the relationship of drug samples to each other[19] through comparison or ''profiling''.

Cannabis samples submitted to the laboratory can be in one of three forms: herbal material, resin and oil. The main physiologically active ingredient of cannabis is Δ^9-tetrahydrocannabinol (Δ^9-THC). Identification of herbal cannabis is achieved by visual inspection under low power magnification. Ethanol extracts of the herbal material, resin and oil are subjected to thin layer chromatography (TLC) for rapid screening and simple comparison purposes. For identification and confirmation, trimethylsilyl derivatives of the main components Δ^9-THC, cannabidiol, cannabinol and the lesser components Δ^8-THC and Δ^9-tetrahydrocannabinolic acid are analysed by GC-MS. The technique will identify, unequivocally, the derivatised compounds. HPLC or GC-MS can be used for profiling purposes. The preliminary screen by TLC will provide a good indication as to whether or not the blocks of resin are from the same batch, and reversed-phase HPLC will confirm this. HPLC is particularly useful because unlike GC-MS, it does not require the samples to be derivatised. Tetrahydrocannabinolic acids are thermally labile and would decompose under GC-MS conditions. The chromatogram serves as the profile of the drug.

The title ''amphetamines'' includes amphetamine itself, methylamphetamine, 3,4-methylenedioxyamphetamine (MDA), 3,4-methylenedioxymethylamphetamine (MDMA, Ecstasy) and 3,4-methylenedioxyethylamphetamine (MDEA). These drugs are usually synthesized, and when sold as powders are adulterated or diluted with a variety of compounds including glucose monohydrate, mannitol, Epsom Salts ($MgSO_4 \cdot 7H_2O$), caffeine and starch. The drugs are usually taken orally, in either powder or tablet form. The Marquis test[19] is a useful presumptive test for amphetamines and other drugs, relying on a colour reaction. In the presence of amphetamine and methylamphetamine, a yellow-orange coloration results. With ring-substituted amphetamines, a blue-purple coloration is obtained. TLC is then used to determine the amphetamine present.

Confirmation of the drugs is by GC-MS, with suitable derivatisation. Nuclear magnetic resonance (NMR)[20] or HPLC is used to quantify the drugs, but comparison of samples requires GC-MS. The methods of synthesis of the drugs are well known, and levels of impurities expected for each route are known. These impurities which constitute the ''fingerprint'' or profile are numerous and not all have been identified, but the resulting chromatograms from samples are easily compared visually, and the components identified by the mass detector. Isotopic characterization of MDMA using the δ^{15}N ratio successfully discriminated between batches of the illicit material. Raman spectroscopy[21] has also been used for composition profiling of Ecstasy tablets. Far-red excitation (785 nm) has been investigated as a simple and rapid technique for MDMA tablet profiling. The spectra obtained are rich in vibrational bands and permit identification of the active drug and excipients used to bulk the tablets. Relative band heights can be used to determine drug/excipients ratios and the degree of hydration of the drug. Some 50 tablets per hour were analysed, demonstrating the high throughput nature of the technique. In one case, a sample of 400 tablets from a seizure of $>$50,000 could be classified on the basis of excipients used. Some were diluted with sorbitol, some with cellulose and the remainder with glucose. Further, more detailed analysis revealed differing drug/excipient ratios within a particular drug/excipient combination, and also a difference in the degree of hydration in the MDMA feedstocks used to manufacture the cellulose-, glucose-, and sorbitol-based tablets.

Benzodiazepines, unlike heroin, cocaine, cannabis and amphetamines, are controlled pharmaceutical drugs. They are usually encountered as tablets or capsules containing controlled amounts of drug. A seizure may consist of a few, or hundreds or thousands of capsules, and a representative number[19] will be selected for analysis. A detailed description of the capsules or tablets is made first, and compared with manufacturers' information, and then analysis is undertaken. Presumptive tests, if positive for benzodiazepines, are followed by thin layer chromatographic analysis.

Benzodiazepines do not require derivatisation and are straightforward to analyse by GC-MS. If chromatographic retention times and spectral information match, then the identification is confirmed. Quantification is conveniently obtained through HPLC with UV detection. Profiling of such compounds is not appropriate because the drugs are manufactured under strict quality control conditions, and will be of high purity.

Heroin, or diamorphine (diacetylmorphine), is produced by acetylating morphine which is isolated from the opium poppy. The occasional ''vinegary'' smell of a powder containing heroin is due to hydrolysis and the subsequent formation of monoacetylmorphine, morphine and acetic acid. The purity of street level drugs varies considerably, but the average street seizure contains 35 wt% diamorphine. The most common forms of heroin are the salt (the hydrochloride hydrate), which is water soluble, and the base which is insoluble in water. The salt is therefore the form of choice for injection, whilst the base is usually snorted or smoked. A decade's worth (1980–89) of heroin analysis[22] by X-ray powder diffraction (XRD) revealed an interesting trend, in that street seizures containing the hydrochloride were prevalent at the beginning of the decade, but its use was supplanted by that of the base by the end of the period. The decade concerned also happened to be that in which awareness of the disease AIDS was raised, so one may speculate that the move by addicts from injection to smoking the drug was motivated in part by a desire to avoid contracting the disease through use of shared hypodermic needles.

Street seizures comprise the drug, as salt or base, mixed or ''cut'' with various materials such as phenobarbitone, paracetamol, caffeine, procaine, lignocaine, codeine, phenolphthalein, calcite and lactose monohydrate. Heroin itself usually consists of diamorphine, 6-*o*-monoacetylmorphine, morphine and codeine, so most ''heroin'' samples are quite complex if adulterated with some of the aforementioned compounds. The usual presumptive test for heroin is Marquis Reagent, with which opiates react[19] to give a blue-violet colour. Thin layer chromatography with a suitable elution solvent reveals most of the components of the mixture, whilst GC-MS is the method of choice again for heroin confirmation/identification.

Quantification of heroin samples may be achieved by either GC or HPLC. GC of course will require derivatisation of samples, but HPLC requires only the dissolved samples. Either method proceeds with the simultaneous analysis of sample complete with internal standard, and then analysis of a set of calibration standards whose concentration range encompasses the range of heroin concentrations anticipated. If comparison of heroin seizures is required, the comparison has to be both qualitative and quantitative, and GC-MS is the method used. TLC will suffice as a simple means of comparison, and it is most effective for a large number of samples in that it will quickly identify samples that are *not* similar, but it is not quantitative. HPLC is quantitative but does not provide the analyst with a definitive identification of each chromatographic peak. Comparison of samples demands exactly the same treatment of each sample, and if, as a result, the chromatograms and mass spectral data are indistinguishable, the samples are deemed to have come from the same source.

Cocaine is listed as a Class A drug in schedule 2 of the Misuse of Drugs Act 1971.[18] It occurs naturally in plant material and is extracted from coca leaves. One form of cocaine that has gained widespread popularity is known as *crack*. It is the free base form of cocaine and is prepared from cocaine hydrochloride by mixing the salt with sodium bicarbonate and water, and heating it. Crack is smoked or snorted. The salt, cocaine hydrochloride is a white powder known as *snow*. Both the hydrochloride and the base are sold on the street as powders cut with various adulterants such as mannitol, glucose monohydrate, and local anaesthetics lignocaine and procaine base and hydrochloride. Presumptive tests[19] for cocaine include the cobalt isothiocyanate test, which is not completely cocaine specific. This test, and a modified version, called the Scott test, which is more specific, are both based on reactions which produce colour changes. TLC is performed on methanol solutions of the street seizures, and will identify cocaine, its related compounds and lignocaine and procaine. GC-MS is used to confirm the presence of cocaine and also to quantify it.

Cocaine, like heroin, is produced in batches whose impurities, and level of impurities, will differ. As a result, seizures from different batches are unlikely to have the same overall composition at trace level, and the makeup of a sample can act as a ''signature'' for its batch, and in some cases, indicate its geographical source. Cocaine profiling, like heroin profiling, can result in the linking of seizures and identification of probable source. The cocaine ''profile'' includes cocaine, ecgonine, benzoylecgonine, nor-cocaine, the truxillines and cinnamoyl cocaines. An account of the recent advances in cocaine profiling methodology[23] provides an interesting insight to the subject.

Stable isotope ratio mass spectrometry (SIRMS) is an analytical technique which has found wide application[11,24] in forensic science. It is appropriate to mention it in some detail here, because its use in drug analysis is of considerable importance. The sample to be analysed has first to be converted into simple gases *e.g.* CO_2, N_2, CO, H_2 and SO_2, and these gases are led to a dual input mass spectrometer together with gas produced from a reference material. Gas isotope ratio mass spectrometers are single focusing magnetic sector instruments in which the isotopes are detected continuously and simultaneously by a multi-collector array. Stable isotope measurements are expressed in delta (δ) values according to the formula:

$$\delta^{13}C(‰) = ((R^{13}_{sample} - R^{13}_{standard}) \times 10^3)/R^{13}_{standard}$$

where $R^{13} = {}^{13}C/{}^{12}C$.

The abundance of the largest trace isotope of carbon (^{13}C) is 11,000 ppm (0.011) relative to the major isotope (^{12}C). Other abundances are: $^{2}H/^{1}H$ = 158 ppm, $^{15}N/^{14}N$ = 3,700 ppm, $^{18}O/^{16}O$ = 2,000 ppm and $^{34}S/^{32}S$ = 42,000 ppm. Positive delta values indicate that there is a greater percentage of the heavier isotope present relative to the standard. Cocaine originating from different geographic regions in South America[25] can be identified by its isotope ratio signature. By combining the carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$) isotope ratios with detectable differences in the patterns of trace alkaloids, the source of cocaine samples can be correctly identified. A similar approach has been adopted for sourcing heroin.

Explosives

The majority of chemical explosives (energetic materials)[26,27] contain oxygen, nitrogen and oxidizable elements (fuels) such as carbon, hydrogen, and sulfur. Explosives may be classified in terms of their chemical composition (those containing molecular groups such as peroxides, ozonides, nitrates, nitrites,

chlorates, perchlorates, azides, fulminates and acetylides), but a more useful classification is by their performance and uses. Three convenient classes are: primary explosives, secondary explosives and propellants.

Primary explosives differ from secondary explosives in that they undergo a very rapid transition from burning to detonation, and they have the ability to transmit the detonation to less sensitive explosives. On detonation, the primary explosives produce a great deal of heat and shock, which can be used to initiate a secondary, more stable explosive. For this reason, the primary explosives are used as initiators, or detonators. Primary explosives are sensitive to detonation through shock, friction, electric spark or high temperatures and will explode whether they are confined or unconfined. Examples of primary explosives are: lead styphnate (lead trinitroresorcinate), lead azide, tetrazene, and mercury fulminate.

Secondary explosives (high explosives) are less sensitive than primary explosives and are only detonated by the shock produced by the explosion of a primary explosive. A secondary explosive, on detonation, decomposes instantaneously into other more stable compounds (usually gases). RDX decomposes into carbon monoxide, steam and nitrogen. Examples of secondary explosives are: nitrocellulose, TNT (trinitrotoluene), nitroguanidine, picric acid, tetryl (trinitrophenylmethylnitramine), RDX (cyclotrimethylenetrinitramine), PETN (pentaerythritol tetranitrate), HMX (cyclotetramethylenetetranitramine), and TATB (triamino-2,4,6-trinitrobenzene). Propellants are combustible materials containing within themselves all the oxygen needed for their combustion. They can be initiated by a flame or a spark, and change from a solid to a gaseous state relatively slowly, *i.e.* in milliseconds. Black powder (potassium nitrate, charcoal and sulfur) and smokeless powder (nitrocellulose) are examples of propellants.

A forensic chemist can be faced with a number of requests[2,28] with regard to explosives. He/she may be asked to identify (a) bulk material, as in the case of seizure of an unexploded device, or (b) traces of explosives in order to establish links between suspect(s) and the crime scene. Such traces can occur in almost any setting—open spaces, commercial buildings and private dwelling places, in and on motor vehicles, on public transport systems, on individuals, their clothing, and their private property. Analysis of post-blast residues is also important, enabling the scientist to identify the explosives that caused the blast, together with their likely origin. Systematic procedures[3] are followed in order to recover whatever evidence may be present, both in linking suspect and scene, and following an explosion.

Recovery of traces of explosives, or explosives residues, is achieved by swabbing (dry or with a solvent), solvent washing of items, vacuum sampling, or by adhesive tape. A rapid and convenient screening method at the crime scene or in the laboratory is ion mobility spectrometry[29] (IMS). A portable IMS instrument uses a vacuum to collect explosive residues from suspect surfaces. Alternatively, the surface suspected of containing explosive residues is wiped down with a cellulose or Teflon filter disc, and the collected residues are then sucked into the spectrometer. The residues are vaporized by the application of heat, and converted into electrically charged molecules or ions by means of metal foil containing ^{63}Ni, whose β-particles initiate ionization of the air. The ions then pass along a cylindrical drift tube under the influence of an electric field of $\sim$200 V cm^{-1}. The ions traverse the drift region in a few milliseconds, and the detector signal from the different ions with characteristic drift times constitutes the mobility spectrum.

IMS permits fast, highly sensitive and specific detection, but relies upon the measurement of mobility as the sole characteristic for identification, so the results of an IMS screening test need to be confirmed. Residues submitted to the laboratory are first examined microscopically and then dissolved in a solvent such as ethanol or acetone prior to colour spot tests and chromatographic analysis. The combination of the separation power of HPLC with the identification capability of mass spectrometry (MS) is the most widely used[11] analytical system. The high explosives TNT, NG, PETN and RDX are efficiently ionized under negative ion atmospheric pressure chemical ionisation (APCI) conditions.[30] The limit of detection is improved, in some cases by several orders of magnitude, by complexation with chlorine, demonstrating this to be a highly suitable method for enhancing the detection capabilities for explosives.

Any detection of explosives or explosive residues must take into account the background level at a specific site. A recent survey[31] of background levels of explosives in public places was undertaken in four major UK cities: Birmingham, Cardiff, Glasgow and Manchester. The survey concentrated mainly on public means of transport (taxis, buses and trains), but also included samples collected from airports, hotel rooms, private houses, private vehicles, and clothing purchased from charity shops. Samples were collected by wiping non-porous surfaces with swabs impregnated with 1 : 1 ethanol : water, and by vacuuming porous surfaces. GC-TEA and GC-MS were used to detect, identify and confirm the presence of traces of NG, TNT, PETN and RDX. LC-MS was used to analyse samples for the presence of cyclotetramethylene tetranitramine (HMX). Only one low-level trace (7.5 ng) of RDX was detected on a collective swab of nine train seats. Nitroglycerine (3.6 ng), possibly associated with the use of firearms, was found on the floor of a taxi, and 2,4-dinitrotoluene (15.2 ng) was detected on the back of an X-ray machine at Glasgow airport. The overall conclusion was that it is unlikely that persons visiting public areas could become significantly contaminated with explosives.

Classical trace evidence

This refers to evidence[2,3] such as textile fibres, paint, glass and soil. Prior to the advent of DNA profiling, these materials constituted the main types of so-called trace evidence. The search for evidence at a crime scene, or on a victim's or suspect's clothing for textile fibres, paint flakes, and glass fragments is highly labour-intensive, and some might say not cost-effective. In the absence of DNA evidence and finger marks, however, trace evidence of this nature may be the only means of solving of a crime.

Textile fibres. Textile fibres may be classified in broad terms as either natural or man-made. Further subdivision of natural fibres leads to animal, vegetable and mineral fibres.

Sub-classification of man-made fibres leads to: *synthetic polymer* (polyester, polyamide, polyurethane, polyolefin, polyvinyl), and *natural polymer* (rubber, cellulose ester, regenerated cellulose, regenerated protein). Textiles are ubiquitous and they can be involved in crimes[32] in many ways, and can occur as evidence also in a variety of ways.

Forensic examination of any trace evidence, including textile fibres, is based upon Locard's Exchange Principle. This states that "every contact leaves a trace". In practice, even though a transfer of material has taken place (in one or both directions), it may be impossible to detect, because the amount transferred may be so minute. Also, some surfaces, because of their disposition and texture, may shed transferred material easily and quickly. As a consequence it is important to collect clothing from suspects and victims as soon as possible after an alleged offence, because evidence of contact (and hence association) found through comparison of fibres, will generally involve recent transfers.

Recovery or retrieval of fibres from a crime scene is achieved through the use of forceps when they are easily visible, through adhesive tape lifts, or vacuuming. The procedure for examination and analysis of fibres consists of microscopic comparison, fibre identification and colour analysis. Known, or control fibres are subjected to UV/visible comparison microscopy with those extraneous (suspect) fibres recovered loose or from tape lifts. The fibre type (man-made or natural) can be determined, with morphological detail from optical microscopy usually sufficient for identification of natural fibres, and Pyrolysis Gas Chromatography (PGC) and Pyrolysis Mass Spectrometry (PyMS) for identification of man-made fibres. If, after comparison microscopy there are similarities, known and suspect fibres are examined by visible light microspectrophotometry. If the resulting spectra are similar, FTIR examination follows, which yields unequivocal fibre polymer identification and some information concerning the dyes.

Dye extraction is the next stage, and the methods used will depend upon the type of fibre and dye used. Solvent extraction, enzymatic hydrolysis, and alkaline hydrolysis are techniques used for the release of dyes from the various types of fibre. Visually similar colours may consist of different component dyes (a so-called "metameric match") which can be readily distinguished by TLC. Thin layer chromatography does have its limitations, particularly with pale yellow dyes and with low concentrations of dye, and HPLC[32] and Surface Enhanced Resonance Raman Scattering Spectroscopy (SERRS)[32,33] have been used to good effect. SERRS[33] is a combination of Resonance Raman Spectroscopy (RR) and Surface Enhanced Raman Scattering (SERS), and is a very sensitive technique, possibly up to ten orders of magnitude more sensitive than traditional Raman spectroscopy. Silver colloids are used to obtain the surface enhanced effect. Aggregation of these colloid particles and ensuring that the analyte molecules are in close proximity to the colloid surface are essential for achieving high sensitivity and reproducible SERRS spectra.. An organic compound such as poly(L-lysine) has proved to be an excellent aggregating agent. For fibre dye analysis, a single strand of fibre is pre-soaked in sodium hydroxide, rinsed and then soaked in an aqueous solution of poly(L-lysine), rinsed again, and then treated with the concentrated silver colloid. The fibre is placed on a microscope slide and the SERRS spectrum of the colorant is recorded. This *in situ* analysis of the dye is worthy of note because the fibre remains intact (the method can be considered to be non-destructive) and can be retained for further complementary methods of examination. LC-MS has more recently been used to identify dyes extracted from textile fibres.[34]

Just as with explosives, there is a need to take into account the level of background fibre "contamination". The common occurrence of textiles in daily life constitutes a major source of background fibres. Knowledge of the frequency of occurrence of fibre types in a given population is required in order to assess the evidential value of finding fibres that could not be differentiated from a suspect source. For example, studies of the population of coloured fibres in human head hair,[35] revealed that natural fibres (mainly cotton) at 72% were the most prevalent with the balance of man-made fibres. Black/grey cotton (48%), blue cotton (29%) and red cotton ($\sim$13%) were the most common colours. A similar survey, but in a different country, looking at the population of coloured textile fibres in domestic washing machines[36] revealed strikingly similar results in that cotton fibres ($\sim$70%) were the most prevalent followed by man-made fibres ($\sim$24%). Black/grey cotton (27%), blue cotton (20%) and red cotton ($\sim$16%) were the most common colours.

In general, the more common the fibres, the lesser the value of the evidence. Conversely, fibres which are rare by virtue of an unusual morphological characteristic, specific usage, limited production or obsolescence will have strong evidential value, even when they are present in low numbers.

Paint. Paint[37] has a dual role, and that is to decorate and to protect. The protective role is to shield the surface from its environment. Decorative household paints must have properties that protect against the sun (ultraviolet radiation), rain (moisture) and the atmosphere (oxygen), whilst vehicle paints, as well as being required to resist the elements, must resist chemical attack from salt, fuel and lubricants. It is clear that these two types of paints, together with tool paints and specialist paints such as security and anti-climb paints, will therefore have differing compositions. Irrespective of minor differences, however, all paints are composed of pigments, extenders and binders as well as other additives, dissolved or dispersed in a solvent. After the paint has been applied to a surface, the solvent evaporates, leaving behind a hard polymeric binder and any pigments that were suspended in it.

Paint occurs as trace evidence[38] in a number of circumstances. It may occur as small flakes on the outer garments of a person who has broken into property and damaged paintwork, or as smears of vehicle paint transferred from one vehicle to another in a traffic accident, or from a vehicle to a victim in a hit-and-run accident. If a tool such as a jemmy has been used in a break-in, it may well have smears of paint on its tip. In some cases, usually hit-and-run cases, enough information may be obtained from a paint flake left on the victim, to enable identification of the colour, make, and model of the vehicle involved. This does require cooperation from the vehicle manufacturer, who will have records of paint batch compositions and layer sequences.

The analytical approach to such evidence begins with microscopic examination of control paint, for example from the point of entry in the case of a break-in, and suspect samples (found on the garments of the suspect). Polarized light microscopy and fluorescence microscopy are used as well as visible light microscopy because much information can be obtained concerning the overall appearance of the samples—the presence of a layer structure, the colour and texture of the layers, particle size information, and the presence of contamination. Most forensic paint specimens encountered are single layer, so after colour comparison, the chemical composition of the pigments, extenders and binders must be determined.

Colour comparison is usually undertaken by microspectrophotometry. It is important that the control paint specimen be taken from as close as possible to the suspect sample, to eliminate differences in top-surface measurements caused by light, weathering and ageing. Pigments can be organic or inorganic, but only inorganic pigments are used for black or white paints. Extenders, like pigments are particulate in nature, and are usually cheap, synthetic inorganic materials or minerals, and they are present to add bulk to the paint.

Analysis of paint pigments and extenders is undertaken by Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), X-ray fluorescence (XRF) and Scanning electron microscopy/energy dispersive spectrometry (SEM/EDS). Scanning electron microscopy is particularly useful because it provides a magnified image of the paint flake specimen, together with the capability of elemental analysis. The electron beam can be focused directly on individual paint layers and on individual particles, and an elemental analysis obtained. Inferences can be drawn as to which extenders or pigments are present in the specimen, but SEM/EDS alone will not provide definitive pigment identification. XRD is a useful non-destructive method[22] for paint analysis in that it does provide definitive identification of the pigments (organic or inorganic) and extenders, although multilayer paints require separation of the layers prior to analysis. Its chief drawback by comparison to the other techniques is its relative insensitivity. Laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) has also been used[39] for elemental analysis. The laser ablation method is capable of simultaneously sampling several layers directly before analysis by ICP-MS for the identification and quantification of trace elements present in different layers of the sample. Trace element analysis adds a further means of discrimination. Analysis of the binders in a paint specimen is undertaken by pyrolysis methods[38] such as Pyrolysis Gas Chromatography (PGC) and Pyrolysis Mass Spectrometry (PyMS), and FTIR.

Glass. Glass that is broken during the commission of a crime[38] can be a useful source of trace evidence, linking a suspect with the crime scene. Splinters or fragments of glass may be found in a suspect's hair, on his outer garments, or embedded in his shoes as a result of breaking and entering. In a hit-and-run accident, fragments of glass from a broken headlamp, like paint fragments, found on the victim, may help to identify the vehicle involved.

Glass is an amorphous material, consisting of silicon oxides mixed with metal oxides such as sodium, calcium, magnesium and aluminium. The combination of these oxides is used in the manufacture of the most common types of glass—window and bottle glass. The forensic scientist will generally classify glasses as sheet (window or "float"), container (bottle, jar), tableware (including lead glass), vehicle window, and vehicle headlamp (borosilicate glass).

The majority of glass evidence usually consists of small fragments recovered from clothing, and the task of comparing them with a control sample from a window or bottle, for example, comes down to physical and chemical analysis. The physical properties of density and refractive index (RI) have been used for characterizing glass fragments for many years, whilst SEM-EDS, XRF and inductively coupled plasma atomic emission spectroscopy (ICP-AES) and LA-ICP-MS are used for elemental analysis. Refractive index is measured by an automated system[3,38] called GRIM (glass refractive index measurement).

Elemental analysis[38] is the final stage in glass comparison and this will enable discrimination of glasses similar in density and refractive index. Glass fragments are mounted in resin blocks, polished, and examined in the SEM where energy dispersive spectrometry yields elemental concentrations. XRF, and in particular micro-XRF which employs capillary optics to produce an intense, focused beam of X-rays, is used on small irregularly-shaped fragments of glass. This experimental configuration enables quantitative elemental analysis normally associated only with flat polished surfaces of the fragments in the SEM. Total reflection X-ray fluorescence (TXRF) is another variant of conventional XRF, which uses grazing incidence (instead of the usual 45°) for the incoming X-ray beam. The signal to noise ratio is improved and dissolved glass samples yield quantitative results as good as any other technique.

Of the two inductively coupled plasma techniques, ICP-MS is more sensitive than ICP-AES, and when combined with laser ablation (LA-ICP-MS), is non-destructive. Samples for ICP-AES have to be dissolved prior to analysis. Typical analyses of float glasses and container glasses reveal similar amounts of Si ($\sim$34%) and Na ($\sim$10%), but quite different levels of Mg ($\sim$2.5% & 0.5% respectively) and Al ($\sim$0.4% & $\sim$1% respectively). The detection limit of ICP-MS (0.01 μg l^{-1}) is an order of magnitude lower than that of ICP-AES.

Soil. Soil[2,3] has long been regarded as potentially one of the most useful evidence types, but also as one whose significance has been one of the most difficult to interpret. Soil or mud sticking to a suspect's shoes and clothes, and soil on a vehicle's tyres may be used to link a person or vehicle to a crime scene. Forensic soil analysis, just as paint and glass analysis, is comparative, with soil found on a suspect being compared with that from a crime scene. Soil found on a suspect may suggest a particular locality, because of its unique or unusual chemical composition. This is specialist work and would normally be undertaken by a geologist.

Procedures for soil examination will depend upon just how much sample is available. Side-by-side comparison of control and suspect samples (if they are bulk samples) will quickly establish similarity or dissimilarity. Before colour comparison

can be made, however, both samples must be dried thoroughly because wet soils appear darker than dry soils. Low power microscopic examination will reveal vegetation content, animal remains and man-made debris. Greater magnification reveals the mineral content of the soil. If only smears of soil make up the suspect sample, then high magnification microscopy will probably be the main means of comparison.

The real difficulty with soil as evidence is its compositional variability. If the soil composition does not vary significantly for a considerable area around the crime scene, then its evidential value in linking soil on a suspect to soil at the scene is very low. Even when variations in composition do occur within metres of the scene, the significance of a match between suspect soil and crime scene soil must be viewed with caution. This is where detailed mineralogical analysis and trace element analysis becomes important.[40] Combining ICP-AES and ICP-MS allows the abundance of up to 50 elements to be determined in small samples. For most elements, ICP measurement precision is good, but a degree of variation can arise as a result of sub-sampling procedures, and selective transfer mechanisms relating to forensic samples as well as the degree of spatial variation existing in nature. If the sample size is sufficiently large, the analysis of several different size fractions can be attempted, but usually analysis of a standardized <150 μm fraction separated from a bulk sample provides sufficient discrimination between samples, and is the most practical means for the mass screening of samples. Stable isotope ratio variation in soils has been examined in order to determine its usefulness in forensic soil investigations. Carbon and nitrogen abundance and ^{13}C and ^{15}N isotopic values were determined from six different locations using continuous flow isotopic ratio mass spectrometry.

Other trace materials. In cases of assault, trace evidence such as smears of cosmetics (face powder, lipstick, mascara, eye liner *etc.*) and smears of shoe polish are occasionally encountered. These materials usually contain wax-like substances together with pigments or dyes. The composition of these materials can be obtained by methods including XRD, XRF, SEM/EDS and SERRS. The *in situ* capability of SERRS[33] permits analysis of, for example, lipstick and shoe polish smears without removing them from a substrate. An aqueous solution of poly(L-lysine) is applied to the smear followed by concentrated silver colloid solution which is allowed to dry naturally. The SERRS spectrum is obtained by excitation of the sample at 514.5 nm.

Arson

Fire investigation consists of establishing how, where, and when a fire started. In reality arson is one of the most difficult crimes to investigate.[2,3] There is always the chance that the fire could have been started accidentally, by a discarded cigarette butt, or by a faulty electrical appliance, but the physical evidence of this may well have been destroyed in the fire. Even if it had been started deliberately, the link between a suspect and the crime scene may be difficult to prove, and often the consequences of extinguishing the fire may hamper the forensic scientist's investigation.

If the cause of the fire is thought to have been accelerants (ignitable liquids), detection and identification of these substances, or their residues, is one of the scientist's first tasks. Most arson attacks are started with accelerants such as petrol (gasoline) or paraffin (kerosene), with occasional use of paint thinners, and if any residues of these substances are left after the fire has been extinguished, they may evaporate quickly. It is important that the scientific investigation begins as soon as possible. Since ignitable liquids always flow to the lowest point, the most severe burning would be expected on the floor rather than on the ceiling. The suspect may have spread a trail of petrol or paraffin from a pile of debris to a point of relative safety for himself, such that once the trail was ignited, he could make good his escape without fear of injury.

Once the origin (seat) of the fire has been located, the scientist may use a "sniffer" or portable vapour detector. Accelerants are never totally consumed in the fire, because they may be absorbed in flooring, carpets, plasterboard and upholstery. The sniffer, whilst not specific in its identification, detects combustible vapours, confirming the investigator's suspicions. Gas chromatography (GC) is the technique most widely used to analyse traces of accelerants recovered from fire scenes. The analysis starts with headspace sampling of the bags or jars that contain the debris and clothing. The container is heated, driving any volatile residue into its airspace. A syringe containing an absorbent material, such as the resin Tenax, is pushed through the container into the headspace air and it is used to draw the air containing volatile compounds through the resin. The absorbed volatiles are then thermally desorbed from the Tenax when the sample tube is inserted in the GC. The resulting chromatogram will comprise a mixture of peaks from the accelerants and any pyrolysis products from the thermal breakdown of plastics and natural materials due to the heating effect of the fire. The more volatile components of petrol will not be present in the residues recovered from a fire scene, and at first this may hinder identification, but comparison with chromatograms of standard petrol, paraffin, diesel and white spirit will generally identify the accelerants.

If identification by GC alone proves difficult, GC-MS is used in selective ion mode to identify the components of a particular accelerant. Tandem mass spectrometry[11] has also been used for low levels of accelerants in the presence of a large amount of background material. Gas chromatography/isotope ratio mass spectrometry (GC-IRMS) technology[41] has also been used in an attempt to link the accelerant from fire debris to accelerant identified in samples of the suspect's clothing or containers.

Inks

Forensic document examiners are mainly interested in the identification of signatures and handwriting, but they are also interested in writing materials and printing equipment. The composition of inks, papers and the materials from which documents are produced can be of great significance in a case.

With respect to the identification and interpretation of alterations, deletions and additions to documents, a study of the chemical composition of the ink[2,3] used on documents may confirm whether or not two documents were written using the

same pen. One way of comparing inks is by visible light microspectrophotometry, and viewing the writing under different conditions of illumination (infrared and ultraviolet light) can also reveal differences in the inks. Thin layer chromatography (TLC) is a simple and convenient way of showing the multiple dye components normally present in commercial ballpoint pen inks. As commercial ink formulations tend to change over the years, it is possible to state with some degree of confidence that certain documents are not as old as they are claimed to be, if their inks are shown to contain relatively modern chemical components.

Raman spectroscopy is used when inks cannot be distinguished using more traditional infrared and fluorescence techniques. Surface Enhanced Resonance Raman Scattering (SERRS)[33,42] is used to obtain detailed spectra from ink samples that are either weak Raman scatterers or show dominant fluorescence when analysed by conventional Raman spectroscopy. The *in situ* analytical capability is again important here, as in textile fibre dye analysis, because the technique is virtually non-destructive, but micro-application of the colloid solution to the pen stroke under analysis is essential.

Determination of the relative age of ballpoint pen inks, written on the same paper with the same ink formulation, has been and still is a controversial subject. Ink was extracted from written paper samples taken from 1990 and 2000, made with BIC blue and black pens, and the extracts were analysed by LC-MS and LC-MS-MS methods[5] in an attempt to characterize the ageing of inks on paper. It has long been known that 2-phenoxyethanol (PE), a volatile organic compound found in ballpoint pen inks, evaporates as the inks age. In a study of 633 ballpoint pen inks, GC-MS was used[43] to establish that PE occurs in 237 out of 279 (85%) black inks, and in 293 out of 354 (83%) blue inks. In another study[44] the disappearance of PE was measured (with GC-MS) as a function of time, and curves showing an exponential reduction in PE were obtained for two ballpoint pens each with different inks. Ink solvents were shown to evaporate rapidly, and behave differently depending upon the type of paper used; consequently the method was considered unsuitable for the dating of ballpoint pen inks in forensic document examination.

Summary & future prospects

Forensic analytical chemistry has two main purposes, namely identification and comparison. By-products of the identification process are databases comprising analytical results, qualitative and, where possible, quantitative. The importance of analytical databases in forensic science cannot be emphasized enough, because they will influence the significance placed upon a match between control and suspect samples. In a world where mass production has largely taken over from small, independent manufacturers of, for example, materials such as paint and glass, stringent quality control means little variation in chemical composition from batch to batch. As a consequence, the search for, and identification of, new, more sensitive chemical discriminators, has become important. Any new analytical method offering greater sensitivity, however, brings with it a concomitant increase in the dangers posed by contamination, and method validation must take this into account. Background information on the random occurrence of textile fibres, glass, explosives and drugs in certain environments forms another database that allows a level of significance to be placed upon a particular analytical result. Collection of this information can be tedious and time-consuming, but it is important because it enables the forensic scientist to have confidence in his/her assertion that the presence of trace evidence, however small, is indeed real and significant.

The future of any science is hard to predict, but there are a number of areas in which forensic science will probably advance, including miniaturisation,[5] analysis at the crime scene, and automation of laboratory analytical processes to enable higher throughput of samples. Analysis at the crime scene is currently undergoing trials[45] in the UK with a mobile laboratory for DNA analysis, footwear and fingerprint information, and mobile phone data. Teleforensics, a terrestrial version of the technology used by NASA for non-destructive remote space (planetary) exploration capabilities, has been applied in the United States to crime scene elemental analysis[9] for traces of firearms discharge residues, blood and semen, using portable XRF equipment.

It has been said, not unkindly, that forensic science is not ''rocket science'', but the science *behind* forensic science most certainly is, with the science behind DNA profiling and stable isotope ratio mass spectrometry (SIRMS) as two shining examples. Both techniques have their roots in fundamental science, and their applications in forensic science lead, in their own way, to specific identifications. Surface Enhanced Resonance Raman Scattering Spectroscopy (SERRS), too, shows considerable potential as a virtually non-destructive method of *in situ* trace analysis. Just as the technique of DNA profiling will surely develop further, SIRMS and SERRS undoubtedly will, establishing themselves as key analytical methods for determining, respectively, the source and composition of materials such as explosives, drugs, soils, glass, pigments, dyes, inks, fuels, counterfeit money and many others.

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