

Chapter 1

The Chemistry of Forensic Evidence

Learning Objectives

- To gain knowledge of the different classes of materials examined as forensic evidence, including fibres, paint, polymers, documents, glass, soil, explosives, firearms, arson residues, body fluids, drugs, toxicological specimens and fingerprints.
- To understand the chemistry of common types of forensic evidence.
- To gain an understanding of the analytical tools used to interpret forensic data.

1.1 Introduction

Forensic science pertains to science applied to the law, including criminal investigation, with results being presented as evidence in the law courts. Within this discipline is *forensic chemistry*, which is regarded as the application of analytical chemistry – the analysis of compounds and elements – to legal matters. Forensic chemists are asked to analyse samples to be used as evidence and draw appropriate and accurate conclusions about such evidence.

A major aspect of forensic chemistry is the analysis of physical evidence to connect a criminal to a crime. A fundamental idea in forensic science is the Locard principle, which states that every contact leaves a trace. The evidence collected from a crime scene or a victim may be matched with the evidence found on or in the possession of an individual accused of a crime.

Important questions that can be asked about evidence are: what is the evidential material, and can it be linked to a crime? It is the role of a forensic chemist to identify and characterize the nature of the evidence and whether it is possible to predict the source of the material based on its chemistry. An array of laboratory techniques is used to solve these problems.

There are important considerations to be made when analysing forensic evidence as it frequently consists of very small samples and sensitive analytical techniques are required for an accurate analysis. Another challenge for forensic chemists is that specimens submitted as evidence are usually not pure substances, but are mixtures or may contain contaminants. However, the identification of a unique mixture of chemical compounds can be a positive advantage for connecting evidence to a crime scene.

1.2 Evidence Types

The type of evidence collected from a crime scene depends on the nature of a crime. *Evidence* can be categorized based on its origins and/or composition. An overview of the chemistry of commonly encountered types of evidence is provided here.

1.2.1 Polymers

Polymers are molecules consisting of a large number of repeated chemical structural units [1]. Polymers are constituents of fibre, paint and document evidence (to be described in other sections of this chapter), so they play an important role in forensic evidence. Polymers are also found in other types of evidence including packaging, adhesive tapes and vehicles. Many commercial polymers are produced, and the polymer type will depend very much on the product type and application. The majority of commercial polymers are carbon based, but some are based on inorganic structures such as silicon. Figure 1.1 illustrates the structures of regularly encountered polymers.

Although polymers are commonly referred to as plastics, this term refers to one class of polymers more correctly known as *thermoplastics*. Thermoplastics melt when heated and re-solidify when cooled. Two other classes of polymer are *thermosets*, which have cross-linked structures and decompose when heated, and *elastomers*, which are also cross-linked but with rubber-like characteristics. Some polymer materials may also be *copolymers*, where the polymer molecules consist of two or more different monomer structures. There are also polymer *blends* that are mixtures of at least two different polymers or copolymers, and composites, which are a mixture of two or more materials with a polymer being a fibre or matrix component. Additives are very often present in commercial polymers, and these can include fillers (e.g. calcium carbonate; used to improve the mechanical properties), plasticizers (e.g. esters; used to modify flexibility),

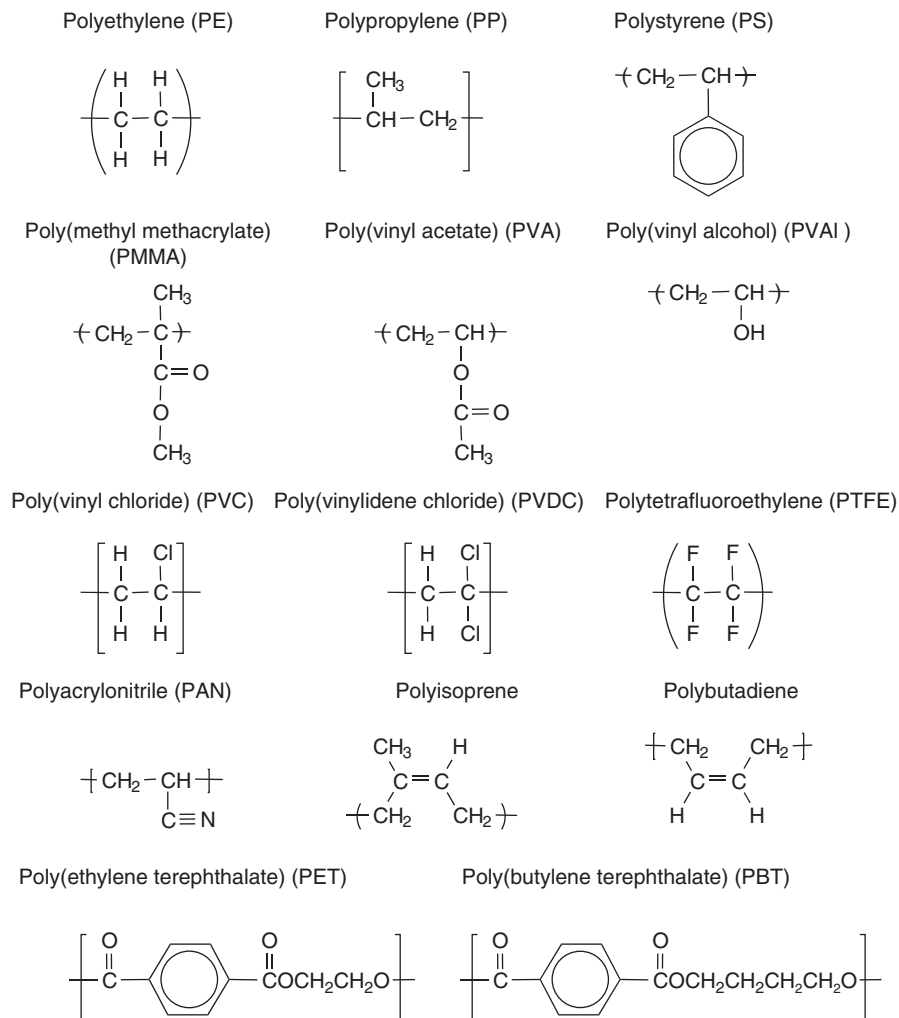


Figure 1.1 Chemical structures of common polymers.

stabilizers (e.g. carbon black; used to counteract degradation) and dyes or pigments (to impart colour).

Polymers are used as drug *packaging* or for the disposal of remains, so linking bags to a source can provide valuable information. The most commonly used polymers in packaging are polyethylene (PE) (e.g. bags and bottles), polypropylene (PP) (e.g. bottles and containers), polystyrene (PS) (e.g. containers and foam insulation) and poly(ethylene terephthalate) (PET) (e.g. food containers and bottles). Other types of bulk polymers that might be collected as evidence

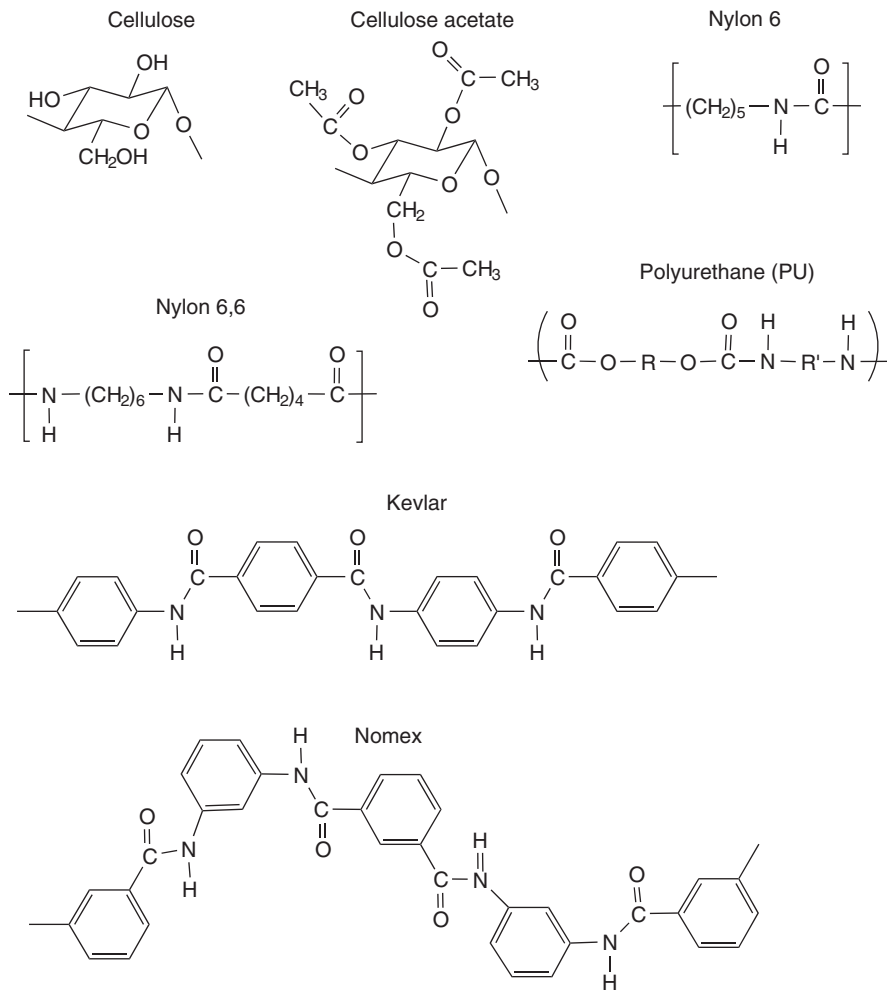


Figure 1.1 (continued)

include poly(vinyl chloride) (PVC), which is used to produce pipes and electrical insulation.

Adhesive tapes are also polymer based and are used in drug packaging as well as in robberies or explosive devices. Both the adhesive and tape components are manufactured using polymers. A range of tapes are commercially produced including cellotape (regenerated cellulose), packaging tape (e.g. PP) and electrical tape (e.g. PVC). The adhesives generally fall into several

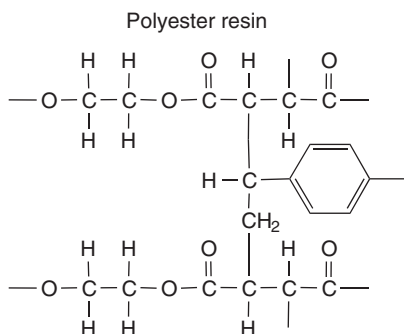
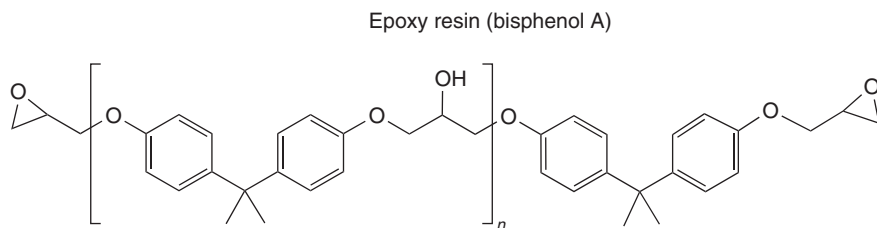


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main categories: acrylic (polymers derived from acrylate and methacrylate monomers), elastomer based (e.g. butadiene and isoprene) and copolymers of styrene with butadiene and isoprene.

Polymers are increasingly used in *automobile* design and can be used as evidence in accident investigation. Copolymers such as styrene–acrylonitrile (SAN) and styrene–butadiene rubber (SBR) are used in tyre manufacture and in bumper bars. Car light enclosures are produced using poly(methyl methacrylate) (PMMA).

SAQ 1.1

Suggest possible polymer types that may be identified in each of the following evidence types:

- (a) plastic shopping bags
- (b) adhesive tape
- (c) car tyres.

1.2.2 Fibres

Fibres are a common form of physical evidence and their value comes from the fact that they are readily transferred between surfaces, thus providing the ability to link a suspect to a crime scene [2–6]. Fibre examination involves identifying comparing specimens. Fibres may be collected from materials such as clothing, carpets and car interiors and are directly retrieved by the use of adhesive tape pressed onto the surface of interest.

An extensive range of fibres are classified into two groups: natural and man-made. Natural fibres can derive from animal sources (e.g. hair, wool or silk), plant sources (e.g. cotton, linen, hemp, jute or ramie) or mineral sources (e.g. asbestos). Man-made fibres are subdivided into synthetic fibres (made by synthetic polymers) and regenerated fibres (made from chemically modified naturally occurring polymers). Other fibres including glass, metal or carbon fibres may also be encountered. Table 1.1 lists the common types of man-made fibres and their compositions.

Fibres are principally coloured by dyes. Dyes are colouring agents that are soluble in the solvent employed in an application. There is an extensive range of commercial synthetic dyes, and these are standardized by a Colour Index (CI) number that is referenced by professional colourists' associations [7]. Dyes can be classified by their structure type or the method of application. Some common structural types used as dyes include azos (containing an —N=N— structure),

Table 1.1 Common man-made fibres

Fibre type	Composition
<i>Regenerated</i>	
acetate	cellulose acetate
triacetate	cellulose triacetate
viscose rayon	regenerated cellulose (precipitated from acidic solution)
lyocell	regenerated cellulose (precipitated from organic solution)
azlon	regenerated protein
<i>Synthetic</i>	
acrylic	> 85 % acrylonitrile
modacrylic	35–85% acrylonitrile
polyester	PET, PBT
nylon	nylon 6, nylon 6,6, nylon 11
aramid	Kevlar, Nomex
urethane	polyurethane (e.g. Spandex and Lycra)
olefin	PE, PP
chlorofibre	PVC, PVDC
vinyon	PVC
fluorofibre	PTFE
vinal	PVAI

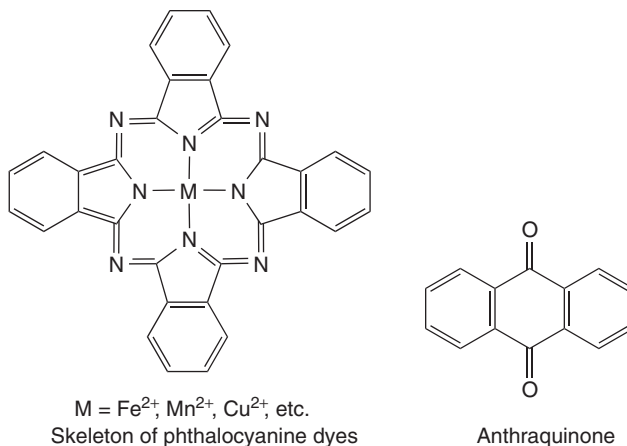


Figure 1.2 Base structures of phthalocyanines and anthraquinones.

phthalocyanines (Figure 1.2), anthraquinones (Figure 1.2), carbonyls and polymethines. Dye groups are also classed by the method of application, and Table 1.2 summarizes the properties of the main dye classes.

SAQ 1.2

A blue polyester fibre is collected as evidence. What is the likely class of dye used to colour this fibre? What is the possible nature of the bonding between the dye and the fibre in this case?

1.2.3 Paint

Paint is used to cover a range of surfaces, but the types that are of most interest in forensic science are automotive and architectural paints [8–11]. Automotive paint is often collected as evidence for car accidents or incidents. Architectural paints can be transferred during robberies, for instance. Due to the enormous range of commercial paints available with different compositions, paint is a valuable form of evidence. Additionally, because paint specimens are commonly multi-layered, more discriminating information can be provided.

Paints are composed of pigments, binders, solvents and additives. *Pigments* are colouring agents that are suspended particles in a solvent. There is an array of commercial pigments available used to impart colour, and some common paint pigments are listed in Table 1.3. Metals can also be added to certain paint types, such as metallic automobile paints. Pigments may be inorganic or organic compounds and synthetic or naturally occurring in origin. The *binder* provides the supporting medium for the pigment and additives, and enables a film to be formed

Table 1.2 Dye classes used for fibres

Dye class	Properties	Common fibre substrates
<i>Acid</i>	anionic dye; ionically bonds with cationic fibre groups; water soluble	nylons, PP, wool, silk
<i>Basic</i>	cationic dye; ionically bonds with anionic fibre groups; water soluble	acrylic, PAN
<i>Direct</i>	cationic dye in electrolytic solution; attracted to anionic fibre; water soluble	acetate, rayon, cotton
<i>Disperse</i>	van der Waals forces and hydrogen bonding between dye and fibre; water insoluble	polyester, acetate
<i>Reactive</i>	covalent bonding between dye and fibre; water soluble	cotton, wool, cellulose-based
<i>Vat</i>	reductant used to solubilize dye; oxidized in fibre; water insoluble	cellulose-based
<i>Sulfur</i>	reductant used to solubilize sulfur-based dye; oxidized in fibre; water insoluble	cellulose-based

Table 1.3 Common paint pigments and extenders

Compound	Properties
aluminium silicates (clays)	extenders
anatase (TiO ₂)	white pigment
barium chromate (BaCrO ₄)	yellow pigment
barium sulfate (BaSO ₄)	white pigment
cadmium sulfides (CdS)	yellow, red and orange pigments
calcium sulfates (CaSO ₄ ·xH ₂ O)	extenders
calcium carbonates (CaCO ₃)	extenders
cerulean blue (CoO, SnO ₂)	blue pigment
chrome reds (PbCrO ₄ , Pb(OH) ₂)	red pigments
chrome yellows (PbCrO ₄ , PbSO ₄)	yellow pigments
chromium oxide (Cr ₂ O ₃)	green pigment
cobalt blue (CoO, Al ₂ O ₃)	blue pigment
magnesium carbonate (MgCO ₃)	extender
magnesium silicate (Mg ₃ Si ₄ O ₁₀ (OH) ₂)	extender
ochres (Fe ₂ O ₃)	yellow, red and brown pigments
Prussian blue (Fe ₄ (Fe(CN) ₆) ₃)	blue pigment
red lead (Pb ₃ O ₄)	red pigment
rutile (TiO ₂)	white pigment
viridian (Cr ₂ O ₃ ·2H ₂ O)	blue-green pigment

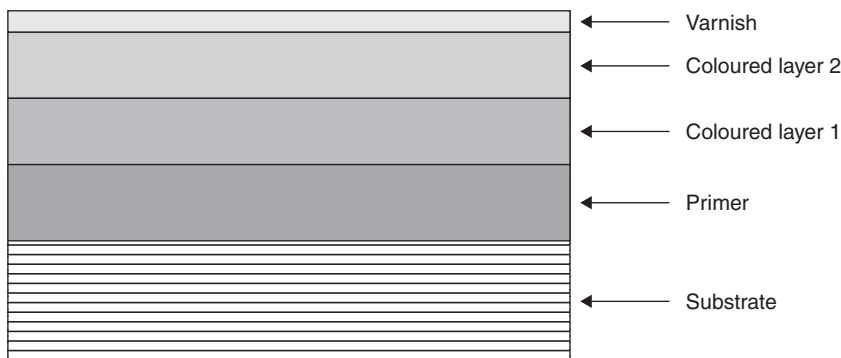


Figure 1.3 Paint layer structure.

when the paint dries. Alkyds and acrylic resins are common binders. Alkyd resins are cross-linked or linear polymers produced from alcohols and acids, and are usually modified with oil. There is a broad range of organic *solvents* used in paint, and the use of a solvent assists in the formation of a uniform film. The drying process is usually a combination of solvent evaporation and a polymerization process. Drying oils, such as linseed oil, are sometimes present to produce films resulting from the oxidation of the oil. Common additives that can be present in paint include extenders and plasticizers. *Extenders* are often low-cost pigments used to reduce the cost of the paint. *Plasticizers* are compounds, such as phthalate esters, that are used to increase flexibility.

Paint can be applied to nonporous surfaces, such as metals, or to porous surfaces, such as wood. A layered system is usually found, with primer, coloured and varnish (or clearcoat) layers regularly used. The primer is used to prepare the substrate for the application of paint; the varnish protects the paint layer and also provides gloss and/or colour improvement. The number and nature of layers will vary between applications. Figure 1.3 illustrates a typical paint layer structure.

Automotive paint is a common type of paint evidence and can have a complex layering system that usually consists of at least four coatings. The first layer is an electrocoat polymer consisting of epoxy resin that is electroplated onto steel to provide corrosion resistance. The second layer is usually a primer surface composed of epoxy–polyester resin or urethane and pigments to provide an even surface. The next layer is the basecoat (or colourcoat), which determines the paint colour and often has an acrylic-based binder. The final clearcoat is often acrylic based or urethane based.

1.2.4 Documents

Questioned documents are a well-known form of evidence. Analysis of the chemical composition of documents provides information about the origins and whether

or not modifications have been made [12–14]. The document materials that provide valuable information are paper, ink and toner.

Paper is produced from fibre pulp, with wood being a major source of fibre. During paper manufacture, sizing agents are usually added to make the cellulose component more hydrophobic to prevent ink from running. An array of minerals, resin and colourants can be present in paper and as the composition varies between manufacturers, paper chemistry can be used to connect a paper specimen to a source.

Analysis of *inks* used in questioned documents can provide various types of useful information for document examiners. The analyses can determine if two inks are of the same origin, if they were made by the same manufacturer or when the ink was manufactured. Ink is a complex medium for imparting colour and can include dyes, pigments, solvents, resins and lubricants. Modern writing instruments fall into two main categories: ballpoint pens and non-ballpoint pens. Ballpoint pens contain oil-based inks and use dyes as colourants. Non-ballpoint pens contain water-based inks and include fountain, rollerball and gel pens.

Toner is in widespread use in printed documents, and the variation in ingredients means that analyses can be used to determine if documents are printed or copied with the same toner, the source of a printed or copied document or if alterations have been made to a document. Dry toners can consist of pigments (e.g. carbon black), polymer binders (e.g. styrene–acrylate copolymer, styrene–butadiene copolymer, polyester resin and epoxy resin) and additives (e.g. ferrite and magnetite).

1.2.5 Glass

Glass is a hard, brittle material that can be broken into small fragments and is a common form of evidence [15, 16]. Glass may be recovered from the clothing of a suspect, for instance, or be found at the scene of car accidents. Glass is produced when silica (SiO_2) (most commonly) and other metal oxides are melted at a high temperature and then quickly cooled to produce an amorphous structure. Fluxes, such as Na_2O or K_2O , are added to lower the melting temperature of the mixture, and work by disrupting the Si—O network produced by silica. The oxygen atoms become negatively charged and loosely hold the monovalent cations within the network (Figure 1.4). As the bonding is weak, cations can migrate out of the network in water, so a stabilizer such as lime (CaO) or magnesia (MgO) is added to make the glass water resistant. Stabilizers are divalent and so are held more tightly in the glass structure. A number of trace elements are also present in glass, and these can be natural impurities or deliberately added to produce colour.

There is a vast number of glass formulations, but glass can be classified by several main compositional classes. *Soda–lime glass*, also known as soda–lime–silicate glass, is the most common class encountered in forensic evidence. Soda–lime glass is formed from SiO_2 with Na_2O and K_2O added as fluxes and CaO , Al_2O_3 and MgO added as stabilizers. This is the most common

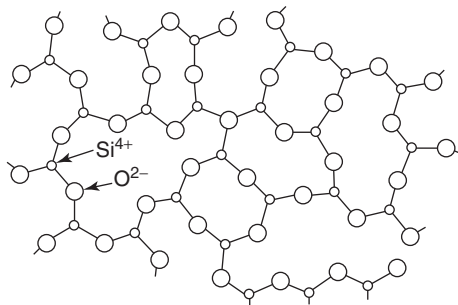


Figure 1.4 Silica glass structure.

composition of glass used for flat glass, bottles or containers. Borosilicate glass is a soda–lime glass containing more than 5% boric acid (B_2O_3) and is used in automobile headlights and heat-resistant glass such as Pyrex.

Different manufacturing processes are used to produce glass for its various applications. Float glass is produced by layering molten glass on a bath of molten tin in an inert atmosphere to produce a flat surface, and this type of glass is widely used in buildings and vehicles. Toughened or tempered glass is stronger than regular glass due to the rapid heating and cooling process during manufacturing to introduce stress. Toughened glass is used for safety glass and in vehicles. Glass can also be laminated when multiple layers of glass are bonded with a plastic film, and this form is used for windscreens and security glass. Glass for containers is produced using a blow-moulding process.

SAQ 1.3

What manufacturing process is used to produce the following glass types?

- (a) car windscreen.
- (b) wine bottle.

1.2.6 Soil

Soil is used as evidence as it may be found adhering to shoes, clothing or vehicles and can link a suspect to a crime scene [17–19]. The most common forensic soil examination involves a comparison of soil samples from known locations with soil collected as evidence. Soil is a complex mixture of minerals and organic matter, as well as man-made materials such as glass. Minerals form the inorganic component of soil, which is the major constituent. The inorganic component of soils results from the weathering of rocks and consists of minerals of various sizes

Table 1.4 Common soil minerals

Mineral class	Mineral names
feldspars	albite, oligoclase, anorthite, orthoclase, microcline
oxides	goethite, haematite, magnetite, quartz, anatase, gibbsite
micas	muscovite, biotite
carbonates	calcite, dolomite, siderite
clay minerals	illite, montmorillonite, kaolinite, halloysite, smectites
sulfates	gypsum, jarosite

and compositions. The inorganic component can be categorized by size: sand (2–0.02 mm), silt (0.02–0.002 mm) and clay (< 0.002 mm). Certain minerals are more commonly found in soil (these are shown in Table 1.4), but the exact composition will vary between locations. Organic matter is a minor component of most soils (< 5 %) and can derive from seeds, pollen and decomposing plants and animals. Due to the variation of soil composition over relatively small distances, it is important to check for variability of composition in the vicinity of the source.

1.2.7 Explosives

An explosion is the result of a chemical or mechanical process that results in the rapid expansion of gases. The chemical identification of explosives is used to link a suspect to an explosion or an attempted explosive incident [20–22]. Explosive evidence may be collected pre-blast, for instance from a disarmed device, or post-blast from debris collected from the scene of an explosion. Explosives are classified as low or high based on the speed of decomposition. Low explosives are ignited by a spark or a flame in a confined environment, and propagation occurs from particle to particle. High explosives generally require an initiator for detonation to occur and produce high-pressure shock waves. High explosives are generally more powerful than low explosives.

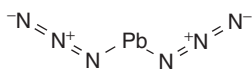
Explosives can be distinguished by their chemical structure. Figure 1.5 illustrates the structures of common explosives. Nitro compounds containing three or more nitro groups on one benzene ring and some compounds with two nitro groups are used as explosives. Nitric esters which contain a nitroxy group ($-C-O-NO_2$) and nitramines ($-C-N-NO_2$) are also compound classes used for the production of explosives. The salts of nitric, chloric or perchloric acids are also used as explosives or in explosive mixtures. Azides are another class of compounds used.

SAQ 1.4

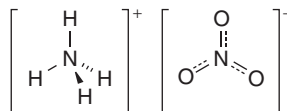
Which of the explosives shown in Figure 1.5 are nitramines?

Low explosives

Lead azide

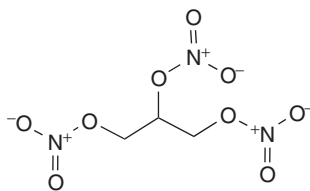


Ammonium nitrate

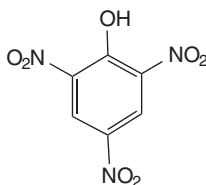


High explosives

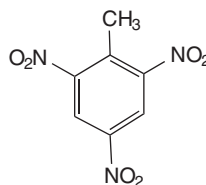
Nitroglycerine (NG)



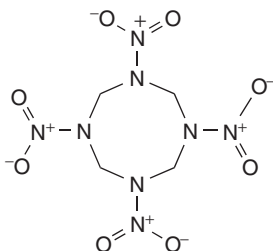
Picric acid



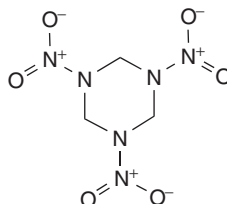
2,4,6-trinitrotoluene (TNT)



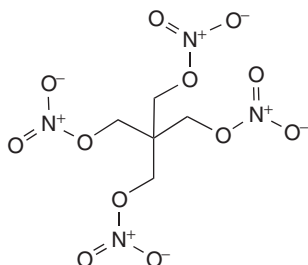
1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX)



1,3,5-trinitro-1,3,5-triazacyclohexane (cyclotrimethylenetrinitramine) (RDX)



Pentaerythritol tetranitrate (PETN)



2,4,6-trinitrophenylmethylnitramine (tetryl)

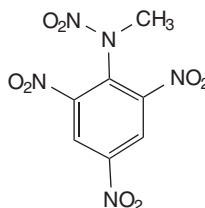


Figure 1.5 Common explosive structures.

1.2.8 Firearms

In the field of firearm examination, information about a crime can be obtained from the fired projectiles, the fired weapon itself and the residues that result from the firing of a weapon [23, 24]. The general components of a firearm cartridge are a primer, a propellant and a projectile. The primer is a chemical designed to be sensitive to shock, and when the trigger of the weapon is applied an explosion of the primer is initiated. The explosive primer causes the propellant to combust, and high temperature and pressure gases are produced. The increased gas pressure allows the projectile to travel at high speed down the barrel. For shot cartridges, there is an additional layer of material (a wad) to separate the shot from the shot pellets.

Table 1.5 lists the structures of the common materials found in primers, propellants, bullets, shot and casings. The main components of primers are initiators, fuel and oxidizing agents. Propellants are often based on nitrate esters such as nitrocellulose and nitroglycerine. Additives such as plasticizers or stabilizers are also present in propellants.

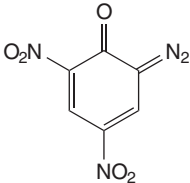
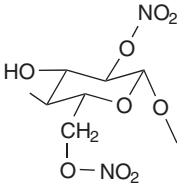
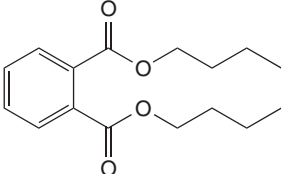

Forensic chemistry comes into play for the identification of gunshot residue (GSR). GSR results from the cooling and condensation processes of the gases of the combustion reactions that occur within a firearm. The particles produced can be expelled through various openings in a weapon and deposited on all sorts of surfaces. GSR may be produced by the propellant, primer, bullet or cartridge casing, lubricant or firearm barrel. The most common method for the collection of GSR is to swab the residue with a moistened fabric swab. GSR may also be collected using tape lifting, where residues are simply collected using adhesive tape. Alternatively, vacuum lifting, involving vacuuming via a series of filters, may be utilized. The identification of GSR can be used to connect a suspect to a recently fired weapon and can be used to identify bullet holes and aid in the determination of firing distance.

1.2.9 Arson

Arson is the deliberate burning of property and provides a challenge from the point of view of evidence as this can be largely destroyed at the crime scene [21, 25]. The challenge from a chemistry perspective is to obtain sufficient evidence from the scene to determine the cause of the arson. The agent used to initiate a fire or to increase the rate of growth of fire is known as accelerant. The identification of an accelerant at the scene of a fire demonstrates that arson has been committed. After the fire is extinguished, the residues of an accelerant remain from hours to days after the incident, so an expedient collection of evidence is required. Porous materials, such as carpets and soft furnishings, that can potentially contain flammable residues can be collected at the scene and stored in airtight containers.

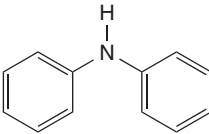
The most common means of arson is the use of an ignitable liquid with ignition via a flame. The majority of arson cases are started with petroleum-based

Table 1.5 Chemical composition of common firearm projectiles

Component type	Substance	Structure
primer initiator	lead styphanate	$\text{Pb}^{2+} \left[\begin{array}{c} \text{O}^- \\ \\ \text{O}_2\text{N}-\text{C}_6\text{H}_2-\text{NO}_2 \\ \\ \text{NO}_2 \\ \\ \text{O}^- \end{array} \right]^{2-}$
	diazodinitrophenol (dinol)	
primer fuel	antimony sulfide	SbS
primer oxidant	barium nitrate	Ba(NO ₃) ₂
primer cap	brass	Cu—Zn
	copper	Cu
propellant	nitrocellulose	
		nitroglycerine
propellant plasticizer	dibutylphthalate	
	camphor	

(continued overleaf)

Table 1.5 (continued)

Component type	Substance	Structure
propellant stabilizer	diphenylamine	
bullets or shot	lead	Pb
	lead-antimony	Pb—Sb
bullet jacket	copper	Cu
	copper-zinc	Cu—Zn
	copper-tin	Cu—Sn
shot cartridge	polyethylene	—(CH ₂ -CH ₂) _n —

accelerants, such as petrol (gasoline) or kerosene. Accelerants can be broadly grouped according to their physical state: gases (e.g. propane, butane and natural gas), liquids (gasoline and kerosene) and solids (flash powder and gunpowder). Although an ignitable liquid is consumed in the fire, ignitable liquid residues (ILRs) can be detected in fire debris.

1.2.10 Body Fluids

Body fluids, including blood, semen and saliva, can provide valuable physical evidence. The presence and distribution of the dried stains of body fluids can substantiate a crime [26, 27]. *Blood* is a biological fluid comprising plasma (containing proteins, lipids and electrolytes), erythrocytes (red blood cells), leukocytes (white blood cells) and thrombocytes (platelets). *Semen* is a suspension of spermatozoa cells in seminal fluid excreted by exocrine glands. The fluid can contain sugar, citric acid, calcium and proteins. *Saliva* is the secretion produced by the salivary glands and contains enzymes including amylase.

1.2.11 Drugs and Toxicology

Drug abuse has an enormous social cost, and drugs are a major source of forensic evidence [28–30]. There are many drugs of interest, each with different chemical properties to address. Forensic drug analysis can involve the examination of bulk or trace amounts of illicit or controlled substances. *Forensic toxicology* also involves the analysis of drugs and poisons in the body [31, 32]. Toxicological samples may be collected ante-mortem or post-mortem. Various body fluids including blood, urine, saliva and sweat and tissues, organs and hair can be used for drug analysis.

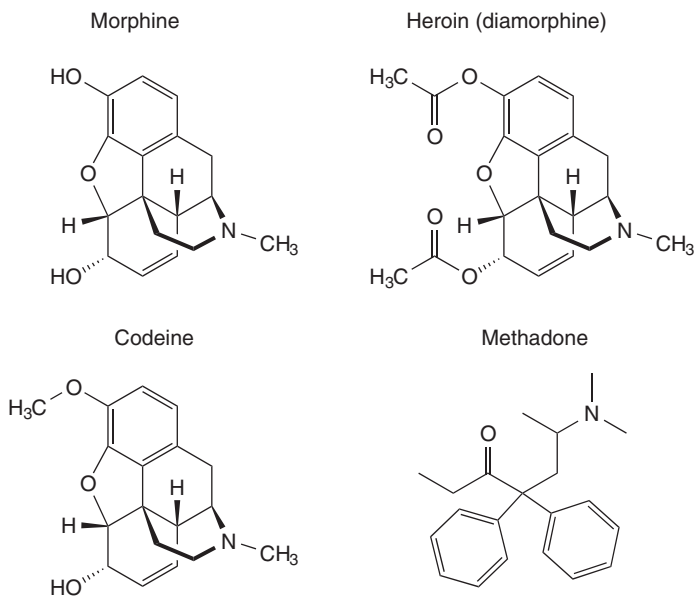


Figure 1.6 Chemical structures of main opioids.

Opiates, naturally occurring alkaloid analgesics, are obtained from the opium poppy (*Papaver somniferum*) and have been in use for thousands of years [28, 29, 33–34]. Opioid is the term used to describe the natural and semi-synthetic alkaloids prepared from opium. The structures of the main opioids are shown in Figure 1.6. Morphine is the principal opium alkaloid. There are several purification methods for morphine including the addition of calcium hydroxide or a pH adjustment approach. Codeine is also present in opium. Heroin is a semi-synthetic derivative of morphine that was first synthesized in the 19th century. To produce heroin, morphine is acetylated to produce diamorphine. Opiates are commonly found in a hydrochloride salt form. Given that raw opium contains a mixture of compounds, the final product will contain a variety of products. Heroin is also diluted with sugars, caffeine or barbiturates. Fully synthetic opioids without morphine structures have also been developed, including methadone.

SAQ 1.5

Heroin (diamorphine) can be produced by refluxing morphine in acetic anhydride. Given that codeine is also present in the opium poppy, what will be the by-product formed as a result of the reaction with acetic anhydride?

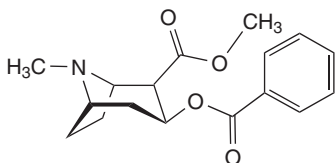


Figure 1.7 Chemical structure of cocaine.

Cocaine is an alkaloid from the *Erythroxylon coca* plants and has been recognized as a drug for thousands of years [28, 29, 33]. The cocaine structure is shown in Figure 1.7. Alkaloids are extracted from the leaves by solvent extraction and precipitation. Hydrolysis is used to convert alkaloids to ecgonine, which is treated to produce ecgonine methyl ester, to which a base is added to produce cocaine. Cocaine can form salts, such as the hydrochloride. The hydrochloride form of cocaine is the most common form, and a version of the free base form is known as crack cocaine.

Amphetamines form a group of synthetic drugs that act as stimulants for the central nervous system (CNS) [28, 30, 33, 35]. Amphetamine was first synthesized in 1887, and a number of derivatives have been subsequently produced. Amphetamines can be found in powder, liquid, crystal, tablet or capsule form. The commonly encountered derivatives include methamphetamine, 3,4-methylenedioxyamphetamine (MDA), methylenedioxymethylamphetamine (MDMA, also called Ecstasy) and 3,4-methylenedioxyethylamphetamine (MDEA). The structures of amphetamine and common derivatives are shown in Figure 1.8. Sulfate salts are commonly found forms of amphetamines. There are many synthetic routes used in clandestine laboratories to produce amphetamines. For instance, common synthetic methods for methamphetamine involve reduction reactions that add an amine group to a phenethylamine structure (known as reductive amination). Ephedrine and pseudoephedrine (Figure 1.8) have been common precursors in the reactions, and the Leuckart reaction and the Birch method are well-known synthetic routes.

Hallucinogens form a group of drugs that alter the perception of reality [28, 29, 33]. Figure 1.9 shows the structures of commonly encountered hallucinogenic drugs. Cannabis (also referred to as marijuana or hashish) is a widely used drug and is obtained from the *Cannabis sativa* plant. Cannabis is usually in the form of plant materials or resin, and the active ingredient is Δ^9 -tetrahydrocannabinol (THC). Lysergic acid diethylamide (LSD) is a potent hallucinogen that has been known since the 1930s. LSD is a semi-synthetic drug, with lysergic acid being a naturally occurring ergot alkaloid. LSD is a colourless liquid and is usually found impregnated in a substance such as paper. Psilocybin and psilocin are found in a number of species of mushrooms (i.e. 'magic mushrooms'). Mescaline (3,4,5-trimethoxyphenethylamine) is also a potent hallucinogen obtained from a natural

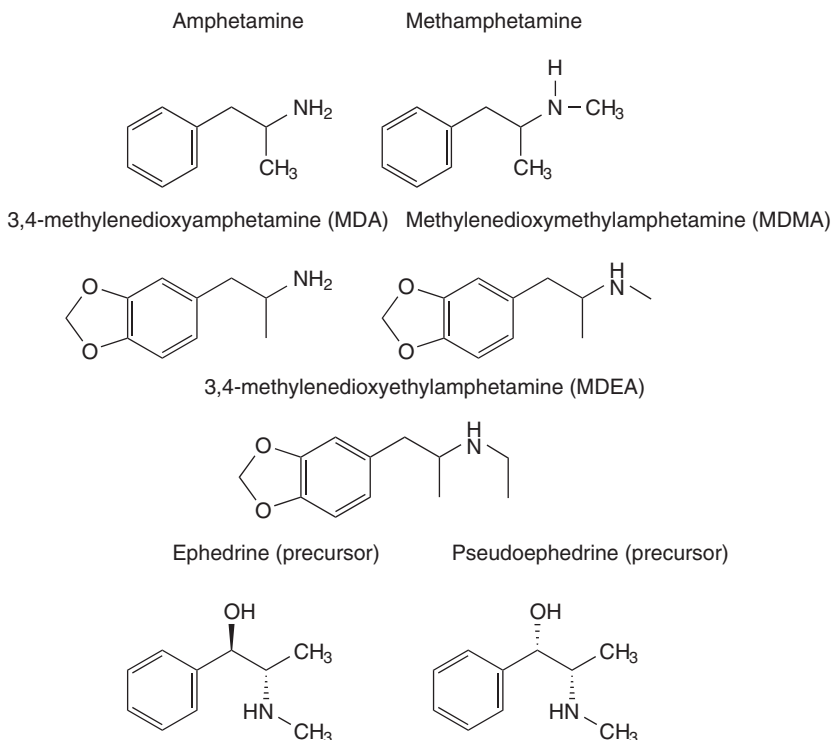
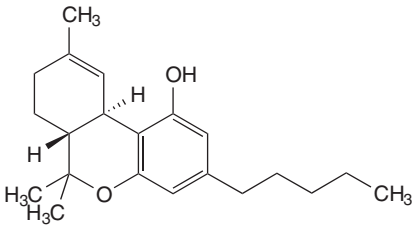


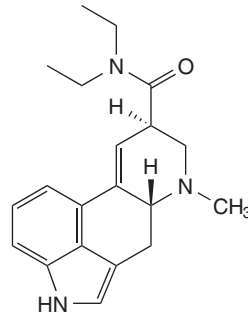
Figure 1.8 Chemical structures of amphetamines.

source, an American cactus species (commonly known as peyote). Phencyclidine (PCP) (1-(1-phenylcyclohexyl)piperidine) was first synthesized as an anaesthetic in the 1950s, but was adopted as a recreational drug in the 1960s for its hallucinogenic properties. A structurally related anaesthetic, ketamine, has also been more recently adopted for its hallucinogenic properties.

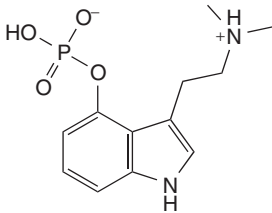
Alcohol commonly refers to ethanol, which is found in alcoholic drinks, and is the most common toxic substance encountered in forensic toxicology [28, 36–38]. Alcohol acts as a depressant. Excessive consumption of alcohol is associated with many accidents, so the ability to measure the concentration of alcohol in body fluids is of major forensic importance. For ante-mortem specimens, alcohol levels in breath, blood and urine are used. Various body fluids, such as bile, are collected post-mortem in addition to blood and urine for alcohol analysis. Alcohol is initially absorbed via the stomach and into the bloodstream. Elimination of alcohol is accomplished via oxidation and excretion. Oxidation occurs in the liver, where the enzyme alcohol dehydrogenase converts the alcohol into acetaldehyde and then acetic acid, which is oxidized to carbon dioxide (CO₂)

Δ^9 -tetrahydrocannabinol (THC)

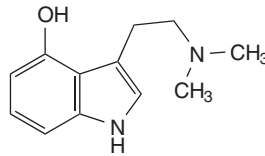
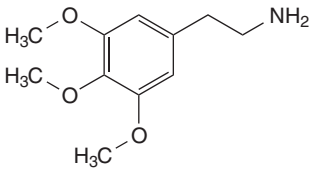
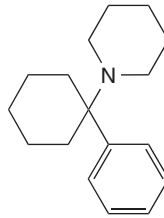
Lysergic acid diethylamide (LSD)



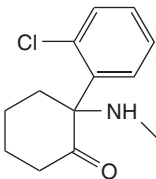
Psilocybin



Psilocin

Mescaline
(3,4,5-trimethoxyphenethylamine)Phencyclidine
(1-(1-phenylcyclohexyl)piperidine) (PCP)

Ketamine

**Figure 1.9** Chemical structures of hallucinogens.

and water. The remainder of the alcohol is excreted in breath, urine and sweat. The amount of alcohol in breath is directly proportional to the blood alcohol concentration (BAC).

Inhalants are volatile chemicals that are inhaled to produce the desired effect [28, 39]. Examples of substances used as inhalants include paint thinners and petrol. Inhalants produce effects similar to those of alcohol. Some common substances found in inhalants are toluene, butane and halogenated hydrocarbons.

A number of synthetic *CNS depressants* are encountered in forensic samples and may be diverted from legitimate sources [28–30, 33]. Barbiturates have been in use for an extended period and are prescribed for a variety of purposes including as tranquilizers, muscle relaxants or hypnotics. They may be in the form of powders, tablets, capsules or solutions. The widely prescribed benzodiazepines were introduced to replace barbiturates and are commonly found in tablet or capsule form. Gamma-hydroxybutyric acid (GHB) is a hydroxylated short-chain fatty acid and can act as a CNS depressant [28, 33]. The salt can be in the form of powders, tablets or solution. Figure 1.10 shows the structures of some common CNS-depressant drugs.

Carbon monoxide (CO) is an odourless, colourless and tasteless gas produced from the partial combustion of organic compounds and can be produced by, for example, fires and the exhaust from petrol engines [28, 40]. The gas can be inhaled in the lungs and absorbed into the blood. The toxicity of CO results from its combination with haemoglobin (Hb) in red blood cells, coordinating with the iron atoms of Hb to produce carboxyhaemoglobin (COHb). Cyanide is also a toxic material that can be produced in fires [28, 40]. Hydrogen cyanide (HCN) can result from the hydrolysis of nitrogen-containing materials such as polyurethanes and polyacrylonitrile. Cyanide is inhaled and transported to blood. The toxicity of cyanide is a result of its ability to affect the cellular processes of cytochrome.

Poisoning due to particular metals can occur via environmental exposure or ingestion [28]. A number of metals can produce detrimental effects when they reach a high enough concentration in the human body. The determination of metal concentrations in biological samples can provide information about a source of poisoning. Metals that are considered in forensic toxicology include aluminium, arsenic, cadmium, iron, mercury, lithium, lead and thallium. The analysis of hair for heavy metals, such as lead, arsenic and mercury, is well established.

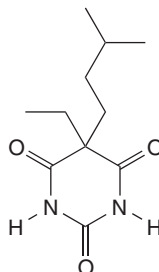
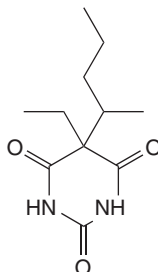
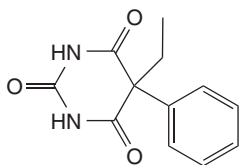
1.2.12 Fingerprints

The detection of fingerprints, or fingermarks, on an object can provide evidence that the object was touched by an individual [41, 42]. Fingermarks are composed of natural secretions and contaminants from the environment. Such impressions are generally invisible, are described as latent and require some form of treatment to make them visible. Hands contain eccrine glands and a deposit produced

Barbiturates

Phenobarbital (5-ethyl-5-phenylbarbiturate)

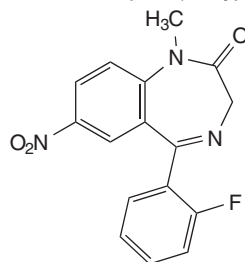
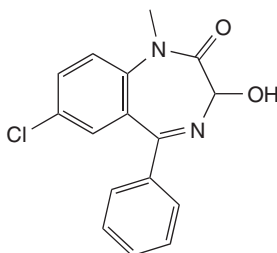
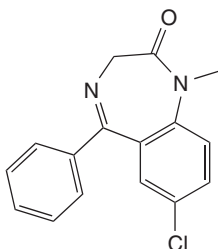
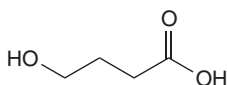
Pentobarbital

Amobarbital
(5-ethyl-5-iso-pentylbarbiturate)*Benzodiazepines*

Diazepam (Valium)

Temazepam

Flunitrazepam (Rohypnol)

*Gamma-hydroxybutyric acid (GHB)***Figure 1.10** Chemical structures of CNS depressants.

by these glands is amino acids. Sebaceous glands (located e.g. on the forehead) also contribute lipid materials, such as fatty acids, due to the contamination of fingers by the touching of the face. Fingermarks can be detected on different surface types. Porous surfaces, such as paper, enable latent fingermarks to be rapidly absorbed onto the substrate. Latent fingermarks are not absorbed into non-porous substrates, such as glass or plastic. Such marks are more easily destroyed. Semi-porous surfaces, such as latex gloves and plastic banknotes, have intermediate properties. Once a fingerprint has been suitably enhanced (as described in Chapter 2), it may be classified based on pattern similarities. Automated fingerprint identification can be carried out to match fingerprints.

1.3 Introduction to Data Analysis

A broad range of experimental techniques are used to collect qualitative and quantitative information about the variety of forensic samples, and the subsequent chapters of this book will detail the methods commonly used. Once data are generated, there is often a need to apply a statistical approach to the data produced. There are two roles for statistics in forensic science. Forensic scientists require statistics to interpret the data obtained from experiments, and this data analysis is the focus in this book. Statistics is also required for the next stage, evidence evaluation – that is, the interpretation of observations from casework. For instance, likelihood ratios can be determined to predict a link between a piece of evidence and a crime scene.

A number of statistical approaches are used in the analysis of the forensic data generated by the techniques discussed in this book. A detailed examination of the origins of these statistical methods is beyond the scope of this book, but a number of useful texts are available and several focus on the application of such methods to forensic problems [43–45]. A starting point is the normal distribution of data, with a mean and standard deviation being used to predict the probabilities of particular measurements. Where the normal distribution is not applicable, a *t*-test can be utilized for the statistical comparison of data.

Linear regression, which involves finding a relationship between two parameters, is also a valuable tool for the quantitative analysis of a variety of forensic data where there is a single dependent variable. Regression lines can be used for calibration purposes and can be produced using an independent variable, *x*, and a dependent variable, *y*. The equation used is:

$$y = mx + b \quad (1.1)$$

where *m* is the slope and *b* is the *y*-intercept. Least squares minimization involves fitting data to a line so that there is a minimum deviation from all data points. The quality of the fit of the line is measured by the squared correlation coefficient, R^2 .

Classification techniques are also very useful for deciphering complex forensic data. Several *multivariate statistical methods* are available that may be used to quantify or classify data, and these are commonly known as chemometric techniques. A widely used method is principal component analysis (PCA), which is an unsupervised method, meaning that no assumptions are made about the data in advance and individual samples are grouped based on the similarity amongst the data. Hierarchical clustering analysis (HCA) is also an unsupervised technique and clusters data in the form of a dendrogram (a tree-like structure) revealing the similarity or dissimilarity of data. There are also supervised methods that utilize prior assumptions about the existence of groups of data and enable a large number of variables to be compared within a data set. Linear discriminant analysis (LDA) and artificial neural networks (ANNs) are examples of supervised methods.

1.4 Summary

An array of material types are encountered as forensic evidence. Such evidence is used to provide a link to a crime scene or to determine how a crime was committed. An understanding of the chemistry of evidence is fundamental to solving such problems – analysis of evidence requires knowledge of the underlying chemical properties. The following chapters deal with the tools used to analyse the chemical properties of forensic evidence.

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