CHAPTER 17
DETECTION AND ANALYSIS OF EXPLOSIVES

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17 DETECTION AND ANALYSIS OF EXPLOSIVES

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17.1 AWARENESS SUMMARY

Detection and analysis are important at all stages in the life-cycle of an energetic material, from manufacture through storage to deployment, the actual technique employed for a particular activity being dependent upon the type of information required.

Some common applications are:

a. Detection of hidden explosives as part of security procedures
b. Analysis of explosives as part of quality control procedures during the manufacture and filling of explosive munitions
c. Identification of explosives of unknown composition. This includes examination of post explosion residues, foreign ammunition and recovered terrorist devices
d. Critical examination of materials and stores in support of accident or defect investigations
e. Examination of materials after periods of service or after undergoing trial programmes, for example during trials and in support of in-service surveillance programmes

Information at the simplest level is provided by detection techniques. These are able to establish whether or not a substance is present. Some are also capable of distinguishing between types of compound but, in general, detection techniques provide no detailed chemical information. It should be noted, however, that while the information obtained from detection techniques is simple the technique itself might be extremely complex. Thus detection techniques range from colour, or 'spot', tests to the combined x-ray and neutron activation devices used for explosives detection at airports.

The number of techniques available for the detection and analysis of energetic materials is vast and this chapter does not seek to give a comprehensive description of each of them. What it does attempt to do is provide a broad introduction to the major techniques, their applications and advantages, at a level that does not assume a detailed technical knowledge.

17.1.1 Instrumental Techniques for detection and analysis

Instrumental techniques are normally used for the detection of concealed explosives in, for example, airports and public buildings. The main requirements of an instrumental explosives detector in these circumstances are therefore:

i. Sensitivity
ii. High success rate
iii. Low false alarms
iv. Rapid Response
vi. High reliability
vii. Non-intrusive
viii. Non hazardous
ix. Multiple parameter

v. Simplicity in use

x. Low cost

Instrumented detection techniques can be further subdivided into techniques for vapour detection and bulk detection.

17.1.1.1 Vapour Detection Techniques

Vapour detection techniques, commonly called Explosive Trace Detection (EDS) systems are designed to detect very small quantities of explosives often in the vapour phase or from material (cotton) swabs. The two leading technologies, Ion Mobility Spectroscopy (IMS) and Mass Spectroscopy (MS), both detect explosives in the vapour phase. In the border security applications the samples are either taken directly from the air near to a suspected contaminated area or the explosive is concentrated onto a fabric swab, which is then vaporised into a gas stream for analysis. When in the gas phase both techniques ionise the molecules and then detect the ions generated. IMS determines the time taken for an ionised molecule to reach the detector, enabling detection of the explosive by calibrating the detection (drift) time against known standards. The MS uses a magnetic field to separate the ions into their separate mass to charge ratios, enabling identification by determination of their molecular mass. Whilst MS is the more accurate and elegant analytical tool, IMS is the market leader for Explosive Trace Detection systems because it is easy of miniaturise, simple to use and has low cost.

17.1.1.2 Bulk Detection Techniques

Bulk detection techniques, commonly called Explosive Detection Systems (EDS) are design to detect large quantities of explosives sealed within containers. To obtain information from within the sealed container it is normal to use the short wavelength parts of the electromagnetic spectrum that can penetrate through solid objects, such as X-rays. Conventional transmission X-ray devices have been used for many years to detect for explosives. However, simple X-ray techniques cannot easily distinguish between a block of plastic explosive and a paperback book of similar size. Effective bulk detectors therefore require a more discriminating method for distinguishing explosives.

Dual energy X-ray systems are able to discern between materials based on the atomic numbers of atoms that make up the material (z-numbers) but have great difficulty discerning density. X-ray scattering, either back towards the X-ray source (back scatter) or passed forward through the object (forward scatter) has been proposed as an effect way of luggage inspection. A scattered image will give information about z-numbers and the density of the object, meaning plastic explosives can now be distinguished from common plastics and clothing. A major problem is the position of the object relative to the X-ray source and the detector has a strong influence on the scattered signal and this can cause errors in interpreting the data.

X-ray technology continues to be the preferred method of explosive screening because it is safe to humans and luggage, and is relatively cheap to buy and operate. However it is by no means the best option and suffers from high false

alarm rates. Duel Energy X-ray instruments and X-ray Scattering will significantly reduce the false alarm rates, but at a greatly increased cost and complexity.

17.1.2 Chemical Analysis Techniques

Chemical analysis techniques for energetic materials are capable of providing detailed qualitative and quantitative information. Thus analysis can establish both the identity and the concentration of a component in an energetic material.

While traditional "wet" chemical methods of analysis are still useful for some energetic materials the vast majority of analyses are these days carried out using instrumental techniques. One area where chemical methods remain appropriate is the analysis of simple inorganic materials in, for example, pyrotechnics. However new instrumental techniques such as ion chromatography are now beginning to replace the traditional chemical methods for these determinations.

The two most widely used types of instrumental technique employed in the analysis of energetic materials are spectroscopy and chromatography. They complement one another to a large extent since spectroscopic techniques are most useful for qualitative analysis while chromatography is used mainly for quantitative analysis. The two techniques are often linked to provide a particularly powerful analytical device.

Chromatography encompasses a range of related analytical techniques, each of which involves the separation of a mixture of components by exploiting differences in the equilibrium distribution of the components between a mobile and a stationary phase. As well as separating complex mixtures into components parts to allow for identification by a spectroscopy technique it can be used in its own right to identify materials, based on comparing the equilibrium distribution of the explosive in the mobile and station phase compared to a known standard.

Infrared Spectroscopy (IR) and Mass Spectroscopy (MS) are two key spectroscopic techniques. If the explosive is a pure form IR is an important technique that is very quick, cheap, and easy to perform. It will quickly identify the number and types of chemical bonds within a covalent molecule. However if the explosive is ionic this technique will not be able to identify the explosive. In addition since most energetic materials are mixtures, the IR data will be very difficult to interpret because the data for each component will overlap.

Reference has already been made to the use of detectors based on mass spectrometry (MS). However, MS is also widely used analytical technique and as such can provide one of the most powerful methods for characterizing an unknown material. Mass spectrometric detectors are now used routinely in Gas Chromatography (GC) and Liquid Chromatography (LC) separations as they offer high sensitivity and an ability to provide compound identification.

17.2 DETECTION OF EXPLOSIVES

17.2.1 Explosive Trace Detection (ETD) - Vapour Detection

Vapour detectors rely on the fact that every substance has a characteristic vapour pressure, defined as the pressure exerted by the vapour of the substance when it is in equilibrium with its solid or liquid phase. Many organic compounds have high vapour pressures while inorganic salts such as ammonium nitrate have negligibly low vapour pressures. The vapour pressure of a substance increases with temperature and in general the smaller the molecule the higher the vapour pressure at any given temperature. Liquid explosives will have significant vapour pressures at ambient temperature and solid explosive less so.

Table 17-1 Vapour Pressure of Some Explosives (20 °C)

Compound	Vapour pressure (mm Hg)	Concentration of vapour (g cm^{-3})
NG	5.8×10^{-4}	7.7×10^{-9}
EGDN	4.2×10^{-2}	3.8×10^{-7}
HMX	9.5×10^{-16}	1.7×10^{-20}
RDX	2.1×10^{-7}	2.7×10^{-12}
PETN	1.8×10^{-6}	3.3×10^{-11}
TNT	2.5×10^{-6}	3.4×10^{-11}

A number of common explosives substances have high enough vapour pressures to generate a detectable concentration of vapour in air. Some typical figures are shown in **Table 17-1**. It can be seen that the nitrate esters nitroglycerine (NG) and ethyleneglycol dinitrate (EGDN) are likely to be most readily detected using a vapour detector and explosives containing RDX or PETN, often found in plastic explosives, not susceptible to vapour detection. TNT at first sight would seem to be in the same category as RDX and PETN; however, minor impurities such as dinitrotoluene (DNT) have a much higher vapour pressure than TNT and can be detected by this method. Apart from the vapour pressure of the explosive substance, the performance of the detector is also affected by the background against which the detector has to operate and by the packaging in which the explosive is concealed.

17.2.1.1 Animals

There are two types of olfactory sensors, natural and artificial. Dogs are commonly used to detect explosives, but the time and cost of training animals, the lack of quantitative information and their lack of flexibility means alternatives are being developed. Several different types of electronic noses are currently under development, but there needs to be an improvement in their specificity, reliability and portability before they will be suitable for fieldwork.

Dogs have a highly developed sense of smell and this has been exploited for the detection of explosives since World War II. Today the use of sniffer dogs to detect volatile explosive vapours is still widespread. They are fast, directional and able to be deployed in real time over large areas. Other animals have also been investigated for the detection of explosive vapour.

17.2.1.2 Electronic Noses

Artificial olfactory sensors ‘electronic noses’ usually consist of an array of chemical sensors that interact with an explosive vapour in different ways. Each sensor will give a different response depending upon the nature and concentration of the vapour present and combining this with a pattern recognition system will allow the identification of the explosive vapour. The chemical sensor can be electronic, piezoelectric or optical and could be either organic or inorganic.

17.2.1.3 Chemical

Detection techniques for energetic materials can be subdivided into a number of types. The simple type is that which involves a chemical reaction between the energetic material (or a component of it) and a prepared reagent. This may occur in solution, as in the case of a soluble solid energetic material, or in a detector tube in the case of an explosive vapour. Such detector tubes, which are packed with the prepared reagent, are commercially available.

There is a wide range of chemical reactions that are suitable for energetic materials detection. Most of these yield a coloured product and are known as colour or 'spot' tests when they are applied to small quantities of an energetic material in solution. For example di- and tri-nitroaromatic compounds develop characteristic red colours with 30 % v/v potassium hydroxide solution. This reaction and, numerous variations on it, is widely used for the detection of nitroaromatic high explosives such as TNT.

Nitrate esters and nitramines can also be detected using spot tests. One of the most frequently used employs the Griess reaction in which the nitrate ester or nitramine is first hydrolysed in alkaline solution to the nitrite ion (NO_2^-). This then forms a highly coloured azo compound in the presence of an aromatic amine and a suitable coupling reagent, as shown in Figure 17-1.

Another common spot test for nitrate esters and nitroaromatics uses diphenylamine. In this case, the reagent is a 1 % (v/v) solution of diphenylamine in sulphuric acid that reacts with nitrate esters and nitramines to give a deep blue colour. This reaction is also frequently used to develop component spots in the thin layer chromatography of high explosives.

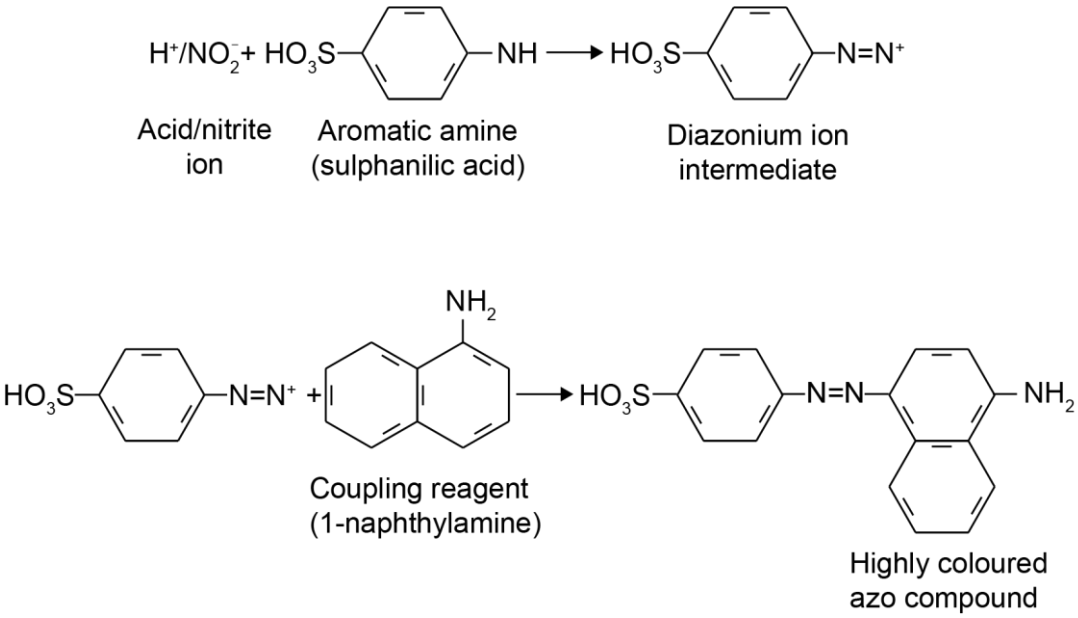

Figure 17-1 Reaction of nitrite ion to produce a highly coloured compound

Spot tests are particularly useful in identifying inorganic ions such as those found in pyrotechnics. For example, spot tests are available (Table 17-2) for most of the common anions such as nitrate (NO_3^-), chlorate (ClO_3^-) and perchlorate (ClO_4^-) and the common metal ions such as potassium (K^+) and sodium (Na^+).

Table 17-2 Selected Spot Tests for Some Ions Found in Energetic Materials

Ion	Reagent/Conditions	Ion indicated by
Na^+	Zinc uranyl acetate in acetic acid solution	Yellow precipitate
K^+	Sodium tetraphenylboron in water (2 %)	White precipitate
NO_3^-	Conc. sulphuric acid droplet on a ferrous sulphate crystal in a pool of test solution	Brown ring around crystal
ClO_3^-	Manganese (II) sulphate in strong phosphoric acid solution, warmed	Violet colouration

Vapour detection is normally carried out using a commercially available detector tube designed for a particular compound or class of compounds. The tube is used with the same manufacturer's sampling pump. A certain amount of air containing the vapour is thereby pulled across the reagent in the tube and a colour change occurs, the extent of which gives an indication of the vapour concentration.

An example of a chemical reaction that is used in vapour detector tubes is the hydrolysis of ethylene glycol dinitrate (EGDN), a common explosive ingredient with the reaction scheme shown in Figure 17-2.

$$(CH_2ONO_2)_2 + H_2SO_4 \rightarrow HNO_3$$

$$HNO_3 + \text{aromatic amine} \rightarrow \text{Yellow/orange reaction product}$$

Figure 17-2 Hydrolysis of EGDN and reaction to give coloured reaction product

The EGDN detector tube containing the aromatic amine can detect 0.25 ppm of the vapour through the observed colour change.

17.2.1.4 Electrochemical

Electrochemical sensors can be categorised into potentiometric (measurement of potential difference/voltage); amperometric (measurement of current) and conductimetric (measurement of conductivity) type devices according to the transduction approach adopted. These types of sensor are fast, inexpensive with high sensitivity and a viable option for miniaturisation. Electrochemical detection techniques can respond to substances that can undergo chemical oxidation or reduction (redox); the electrical output results from a flow in electrons or ions caused by the chemical reaction that takes place at the surface of the electrode. Due to this, the redox properties of nitroaromatic explosive substances ideally lend themselves to electrochemical detection. The detection of peroxide-based explosives by other techniques is more challenging due to the fact they do not fluoresce, have minimal UV absorption and a lack of nitro groups, all necessary parameters upon which traditional detection techniques are based. Electrochemical sensors in this context offer an opportunity to detect peroxide-based explosives that would otherwise prove problematic.

17.2.1.5 Immunochemical

Immunochemical sensors exploit characteristics of the antibody–antigen reaction in such a manner that produces a device that can be highly specific to its target molecule. This feature and the fact that it is possible to produce antibodies for a specific purpose make this an expanding field of research into explosives detection.

17.2.1.6 Luminescence

Luminescence-based sensors for detecting explosive compounds may be described as utilising either direct or indirect detection methods. Direct detection techniques utilises any fluorescence which the sample may emit itself or through inducement with a chemical reaction. Indirect detection involves the evidence of explosives being present through their effect on a fluorescent material such as, for example, via quenching where the fluorescence is reduced by the explosive.

17.2.1.7 Nanotechnology

Nanotechnology has become a rapidly expanding area of research over recent years as techniques and knowledge have developed. Materials often possess unique characteristics when in a nanoscale form as compared to bulk materials

and as such, the incorporation into existing techniques is an active area of research to enhance sensitivity and selectivity. For example, the benefits of using such materials as carbon nanotubes are that they display enhanced detection sensitivity compared to sensors incorporating other carbon platforms (possibly due to increased surface area), they have electrocatalytic effects, are mechanically strong and flexible and have excellent electrical and thermal conductivity. Nanoparticle systems have also been used such as metal nanoparticles, again they can lead to enhanced sensitivities especially in electrochemical systems due to increased surface areas, catalytic effects and improving electrical conductivity. Metal nanoparticles can also have beneficial effects in optical sensors due to increased surface areas and a number of optical effects such as surface enhanced Raman spectroscopy.

17.2.1.8 Molecularly imprinted polymers

Molecularly imprinted polymers (MIPs) are generated through both covalent and non-covalent interactions of functional monomers with the molecule of interest or its analogues, acting as a template. MIPs allow the formation of molecules with recognition sites specific for a target analyte producing a substance specific coating that may then be incorporated onto a sensing platform. MIPs are stable and robust which accounts for the interest in researching possible uses for them as sensing materials.

17.2.1.9 Quartz crystal microbalance

The quartz crystal microbalance utilises the resonance frequency change due to changes in mass upon the crystal surface as a means to detect the presence of a substance of interest. This technique is further enhanced through coating the surface with various compounds that help provide specificity to the system.

17.2.1.10 Electron capture detectors

One of the most widely used instrumental vapour detectors is the electron capture detector. In this device electrons are produced from a radioactive β-emitter (usually nickel-63), which forms the cathode of an ionization chamber. An inert carrier gas (nitrogen or argon) is contained within the chamber and the electrons collide with the carrier gas molecules and thereby lose much of their energy, becoming in the process 'thermal' electrons. These thermal electrons then migrate to the anode under a fixed voltage, thus producing a constant (baseline) current between the electrodes. When an electron-capturing gas or vapour is introduced into the ionisation chamber it causes a decrease in the baseline current due to the interaction of the thermal electrons with the electron-capturing molecules. The extent of the decrease in current is an indication of the concentration of the electron-capturing molecules present.

An electron capture detector is very sensitive towards compounds with a high affinity for electrons. These include compounds containing highly electronegative groups such as -F and $-NO_2$. Although electron capture detectors are, therefore, by no means specific for explosives, they respond well to explosive compounds that contain the nitro group.

Electron capture detectors have a fast response and a limiting sensitivity of about 1 x 10^{-3} g for an electron- capturing compound. Their major drawback as detectors for explosive vapours is their lack of specificity. A number of methods have been used to improve this. The most successful is to install a separating column upstream of the detector so that the components in a mixture of vapours are separated before they reach the detector. The detector then becomes part of an analytical device incorporating gas chromatography and electron capture detection. This technique, which is the basis of a number of commercial devices, is discussed more fully in a later section.

17.2.1.11 Ion mobility spectrometers (IMS)

Another type of instrumental vapour detector for explosives is the ion mobility detector. In this device air is drawn through the detector continuously by means of a small fan. Electrons are produced inside the detector chamber by a high voltage (typically 3 kV) discharge. Some of these electrons are captured by molecules of the explosive forming negative ions which, in turn, pick up water molecules from the air to produce large 'ion clusters'. The ion-laden air is then passed through an ion mobility electrode grid that is optimised to allow only the passage of ions in a certain mass range corresponding to explosive compounds. A further electrode then collects the ions allowed through the grid and the resulting current is processed and fed to a signal device.

17.2.1.12 Mass spectrometry (MS)

Mass spectrometry (MS) has been extensively used as the basis of detectors for explosive vapours. In the majority of such devices the sample molecules are bombarded by electrons that are emitted from a hot rhenium or tungsten filament and accelerated to an energy of 70 eV. The electrons cause fragmentation of the sample molecules and generate positive ions from the fragments. The ion fragments are then filtered according to their mass/charge ratio while being accelerated through a magnetic field. They are detected using an electron multiplier and the fragmentation pattern (mass spectrum) is characteristic of the original sample molecule. Complex mixtures of vapours may not be readily analysed using mass spectrometry because of overlapping spectra, but if separation is carried out beforehand, for example using a gas chromatography (GC) column, then the technique (GC-MS) becomes a useful analytical tool.

17.2.2 Explosive Detection Systems (Bulk Detection)

Vapour detectors have an obvious disadvantage in that they are suitable only for those components in an energetic material, which have an appreciable vapour pressure. Bulk detectors are therefore necessary, particularly in the context of the growing demand for the detection of all types of concealed explosives.

17.2.3 Conventional Transmission X-ray

X-ray devices have been used for the bulk detection of explosives for many years at airport baggage checks. Conventional X-ray screen systems measure the attenuated X-ray energy after it has passed through a scanned object. A standard airport hand-baggage scanner has a fan shaped or scanning X-ray beam whose absorption is measured by a line of detectors, and a high quality image is derived from the degree of absorption is produced. Simple X-ray techniques, however, cannot easily distinguish between a block of plastic explosive and, for example, a paperback book of similar size. Effective bulk detectors therefore require a more discriminating method for distinguishing explosives.

17.2.4 Dual-energy X-ray

At higher energy levels (over 100 kV) the energy absorbed by an object depends primarily on the density of the material. The higher the density, the more energy is absorbed by the object and the darker the image. Metals would appear very dark in the transmission image, however an explosive behind a denser material remains difficult to detect. At lower energies (approximately 80 kV) the absorption depends mainly on the effective atomic number as well as the thickness of the material.

A system that uses two X-ray energy levels is called a dual energy system. Heavy metals will appear dark in both views, but areas of light elements are darker in the lower energy view. Comparing both views means light elements such as carbon, nitrogen and oxygen can be detected. Using a dual energy method can give density and thickness information about the sample; the challenge is that the actual density of objects is poorly known for real luggage items and theory only generates an estimate of atomic number.

Dual energy X-ray systems are now widely used in airports and organic materials (low z) can theoretically be distinguished from inorganic materials and metals (high z), where z denotes the atomic number of an atom. However, X-ray intensities are not only related to its material composition but also its position, orientation and thickness. So unless they are combined with volume imaging (e.g. CT or stereoscopic imaging), they only provided an indication of the atomic number of the object. Even when used with volume imaging, the sensitivity and specificity are low and only allows materials to be characterized broadly as inorganic or organic.

17.2.5 Scatter Imaging

Image data from an object that is collected from scattered X-ray energy back towards the X-ray source (back scatter) or passed forward through the object (forward scatter) has been proposed as an effect way of luggage inspection. Dual energy X-ray systems are able to discern between materials based on the atomic numbers of atoms that make up the material (z-numbers) but have difficulty discerning density. A scattered image will give information about the z-

numbers and the density of the object, meaning plastic explosives can now be distinguished from common plastics and clothing.

The backscatter signal depends on the competition between photoelectric absorption and Compton scattering. The photoelectric cross-section increases with the atomic number of the object, while the Compton cross-section is relatively independent of the atomic number. So the backscattering signal favours low atomic elements of high density, such as plastic explosives and provides a direct measurement of the density of elements with low atomic number.

Image scatter can be characterised as coherent (elastic) or incoherent (inelastic or Compton) scattering. Forward scatter in the region of 3-10° contains predominately coherently scattered photons and at large angles the scattered beam is dominated by incoherent scattered photons. Measurement of both of these is useful. Coherent scatter leads to diffraction effects whose intensity gives information on atomic number and physical density. Incoherent scatter intensity is dependent on density and hence both of these can be combined to isolate atomic number information.

This technology has been used successfully on cars and trucks (cargo) where explosives can be present in large quantities, but airport luggage has presented a more difficult problem due to the smaller quantities involved. A major problem is the position of the object relative to the X-ray source and the detector has a strong influence on the scattered signal and this can cause errors in interpreting the data.

X-ray technology continues to be the preferred method of explosive screening because it is safe to humans and luggage, cheap to buy and operate, and is well understood. However it is by no means the best option and suffers from relatively high false alarm rates.

17.2.6 Terahertz

Terahertz radiation also known as submillimeter radiation and T-waves lies in the far infrared region from 0.1 to 10 THz. In this range waves can penetrate through many non-polar dielectric materials, such as wood or leather, and the low photon energies are at a level one million times less than that of X-ray photons. Most explosives and explosive related compounds have spectral fingerprints within this range and, as many apparatus operate within the range 0.1–2.0 THz, this highlights THz radiation as a prospective sensor and imaging agent for the detection of concealed explosive substances.

Terahertz radiation can penetrate fabrics and plastics, so it can be used in surveillance, such as security screening, to uncover concealed weapons on a person, remotely. This is of particular interest because many materials of interest have unique spectral "fingerprints" in the terahertz range. This offers the possibility to combine spectral identification with imaging.

17.3 CHEMICAL ANALYSIS

The chemical analysis of energetic materials seeks to provide more information than simple detection and, unlike detection, generally requires some sample preparation. The principal aims of analysis are to identify the components of an energetic material (qualitative analysis) and to establish how much of each is present (quantitative analysis).

While traditional "wet" chemical methods of analysis are still useful for some energetic materials the vast majority of analyses are these days carried out using instrumental techniques. One area where chemical methods remain appropriate is the analysis of simple inorganic materials in, for example, pyrotechnics. However new instrumental techniques such as ion chromatography are now beginning to replace the traditional chemical methods for these determinations.

The two most widely used types of instrumental technique employed in the analysis of energetic materials are spectroscopy and chromatography. They complement one another to a large extent since spectroscopic techniques are most useful for qualitative analysis while chromatography is used mainly for quantitative analysis. The two techniques are often linked to provide a particularly powerful analytical device.

17.3.1 Spectroscopy

Spectroscopic techniques of analysis depend upon the absorption of electromagnetic radiation by matter leading to excitation of energy levels (nuclear, electronic, vibrational, etc.) within atoms and molecules. A technique is characterised by the region of the electromagnetic spectrum used in its application since this determines the nature of the excitation.

In a typical investigation the prepared sample is irradiated by scanning through consecutive wavelengths over the chosen region of the electromagnetic spectrum. Energy is absorbed at certain wavelengths and this gives rise to a characteristic absorption spectrum. The spectrum may help to identify an unknown compound or, less frequently, it may be used, by calibration of a suitable absorption band, for quantitative analysis.

17.3.1.1 Infrared (IR) and RAMAN spectroscopy

Infrared spectroscopy is one of the most widely used spectroscopic techniques in energetic materials analysis. When a molecule absorbs energy in the infrared region of the electromagnetic spectrum excitation of its vibrational energy levels occurs. Particular groups of atoms can therefore be identified from their characteristic absorption frequencies. For example the infrared spectrum of TNT contains various absorption bands at wavelengths (or frequencies) characteristic of the nitro ($-NO_2$) group. Similar bands are found in the infrared spectra of all molecules containing this group but the precise position depends upon the molecular environment of the NO_2 group. The overall infrared spectrum of a molecule provides a "fingerprint" of that molecule.

Infrared spectroscopy is particularly useful for the identification of inorganic oxidisers in pyrotechnics. These are relatively simple molecules (e.g. KNO_3, $NaClO_3$) and have uncomplicated and characteristic infrared spectra.

Infrared spectrometers are relatively inexpensive items of equipment, the basic components being an infrared source, a sample compartment and a detector for sensing the infrared radiation not absorbed by the sample. Spectra are easy to obtain and the technique is widely applicable across the range of energetic materials. Fourier transform infrared (FTIR) spectrometers, in which the whole of the infrared spectrum impinges on the sample at the same time rather than wavelength-by-wavelength, are able to generate spectra in fractions of a second.

Modern IR spectrometers are the standard way of obtaining the reflected spectra of energetic materials (or separated components thereof). Either discrete spectra of specific sample sites or mapping to provide multiple spectra from an even larger area, offering data about the spatial location of the components in a multicomponent sample as well as the component spectra.

Mapping data obtained from attenuated total reflectance (ATR) objectives also can provide similar data as acquired using transmission or reflection methods, but without the sample preparation required for transmission or reflection experiments, eliminating the requirement to grind the sample to a fine powder and press in a KBr disc or mix with a mulling agent (usually Nujol, a viscous hydrocarbon mixture).

Raman spectroscopy, which like IR spectroscopy depends upon the excitation of vibrational modes in a molecule, is of growing importance in explosives analysis. The technique is useful because it is non-destructive, potentially very sensitive and can identify molecules *in situ*, without any sample preparation or pre-treatment.

Raman spectroscopy involves the scattering of light by molecules. Most light that hits a sample is transmitted or reflected but some is scattered elastically (Rayleigh scattering, where no net energy is absorbed or emitted), and an even smaller amount is absorbed and then scattered inelastically (with energy being absorbed or emitted). This inelastic scattering is Raman scattering. Only about 1 photon in 10^9 is Raman scattered and so an intense light source (e.g. a laser) and complicated optics are required to study the effect.

Although they both relate to changes within vibrational energy levels, IR and Raman methods do not produce identical vibrational spectra. The selection rule for Raman activity is that the polarizability of the molecule must change (compare IR which requires a change in dipole moment). This means that IR produces stronger bands from vibrations of polar bonds while for Raman the stronger bands arise from non-polar bonds. Raman spectroscopy has the advantage over IR in that specialized sample preparation is not required. It can be used to investigate samples in situ (e.g. drugs still in a plastic bag) and for process monitoring by the use of optical fibres.

17.3.1.2 Ultraviolet-Visible (UV-Vis) spectroscopy

Excitation of electrons within molecules is caused by the absorption of ultraviolet or visible radiation by matter. The absorption bands in the spectrum of a compound are, as in infrared spectroscopy, characteristic of particular groups of atoms. However the technique of UV-Vis. spectroscopy does not distinguish clearly between molecules and groups of atoms and it is generally not as useful as infrared spectroscopy for the qualitative analysis of energetic materials.

UV-Vis absorption bands are very intense and therefore the technique is useful for quantitative work and for the trace analysis of pure compounds or the separated components of a mixture. Spectra are normally recorded in solution in a non-absorbing solvent. UV-Vis. spectrometers are commonly used as detection devices for high performance liquid chromatography (HPLC).

17.3.1.3 Nuclear Magnetic Resonance (NMR) spectroscopy

In the technique of NMR spectroscopy the sample is dissolved in a suitable solvent and held in a glass tube between the poles of a powerful magnet. It is then irradiated with energy in the radio frequency region of the electromagnetic spectrum. Depending upon the energy (or frequency) of the impinging radiation, transitions occur between spin states of certain nuclei in the sample (those of the element to which the spectrometer has been "tuned") at frequencies that are characteristic of the chemical environment of the nuclei.

Thus if a particular nucleus, say C-13, is present in a compound in six different environments then, in general, the C-13 NMR spectrum of that compound will contain six absorption peaks. In practice the spectrum may be more complex than this as a result of nuclear - nuclear interactions.

Nuclei that are amenable to study by NMR spectroscopy include H-1, C-13, F-19 and P-31. However it is a technique that requires expensive instrumentation and a skilled and knowledgeable operator. It is used mainly for determining the molecular structure of new compounds but it is also useful for the identification of unknown organic components in, for example, an energetic material. Because of its great expense NMR is not normally used for the routine analysis of explosives.

17.3.1.4 Laser induced breakdown spectroscopy (LIBS)

Laser-induced breakdown spectroscopy (LIBS) uses a high intensity laser to vaporise a sample creating a plasma plume. The subsequently emitted light from this plasma enables the characterisation of the sample. LIBS, as a detection technique, holds many advantages, especially in the field of explosives detection, such as: no need for sample preparation, the ability for real time results, apparatus that may be ruggedised and miniaturised for field work, a sensitive technique requiring only a small sample and the capacity for stand-off detection approach.

17.3.1.5 X-ray fluorescence (XRF) spectroscopy

X-ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X-rays from a material that has been excited by bombarding with high-energy X-rays or gamma rays. The phenomenon is widely used for elemental analysis and chemical analysis. In principle, the lightest element that can be analysed is beryllium (Z = 4), but due to instrumental limitations and low X-ray yields for the light elements, it is often difficult to quantify elements lighter than sodium (Z = 11), unless background corrections and very comprehensive inter-element corrections are made. The technique is usually combined with optical microscopy enabling the mapping of elements on or just below the surface of the sample.

17.3.1.6 Mass spectrometry

Reference has already been made to the use of detectors based on mass spectrometry (MS). However, MS is also widely used analytical technique and as such can provide one of the most powerful methods for characterizing an unknown material. Mass spectrometric detectors are now used routinely in GC and HPLC separations as they offer high sensitivity and an ability to provide compound identification.

In a mass spectrometer the molecules of the sample, which may be a directly-injected pure compound or a separated component from a GC or HPLC column, are firstly ionized, usually by a source of energetic particles. This normally leads to the formation of a ‘molecular ion’ from which the molar mass of the compound (M) may be determined as shown in Equation (17-1).

$$M + \text{energy} \rightarrow M^{+\cdot} + e^{-} \qquad \textbf{(17-1)}$$

In some modes of MS the high energies used also cause bond cleavage and hence fragmentation of the molecular ion ($M^{+\cdot}$). These fragment ions, together with the molecular ion, are then separated in a magnetic field by virtue of their different mass/charge ratio with most ions being singly charged. It is this pattern of separated ions, which constitutes the mass spectrum and which, through a library search or by interpretation, can help to identify an unknown compound.

High-energy electrons are a common means of bringing about sample ionization in mass spectrometers. This technique is known as electron (impact) ionisation (EI) mass spectrometry. At the energies normally employed it leads to considerable fragmentation and hence much structural information but does not always yield a molecular ion. This is particularly the case with compounds of low thermal stability such as explosives. Chemical ionisation (CI) provides an alternative means of generating ions from gas phase species. In this case ionized molecules of a simple gas e.g. methane, ammonia are made to react with the sample to cause ionization by proton transfer. CI is a ‘soft’ ionization method and gives a clearly defined molecular ion or pseudo-molecular ion such as MH^{+} but provides less structural information than EI.

Ions can also be generated from species in solution. These might be compounds dissolved in the mobile phase of an HPLC system. In Electrospray Ionisation (ESI) the solvent is evaporated from charged droplets to produce molecular ions that are then passed into the mass analyser. ESI is a ‘soft’ ionisation technique and produces mainly molecular ions.

In recent years there have been major developments in desorption ionisation (DI) methods, where ions are formed at surfaces. Two important sampling and ionisation methods have emerged, Desorption Electrospray Ionisation (DESI) and Direct Analysis in Real Time (DART). In DESI the ions are formed by directing a solvent spray at trace species on a surface while in DART a jet of ionised gas is used. Both techniques are ‘soft ‘ionisation methods.

17.3.2 Chromatography

Chromatography encompasses a range of related analytical techniques, each of which involves the separation of a mixture of components by exploiting differences in the equilibrium distribution of the components between a mobile and a stationary phase. The International Union of Pure and Applied Chemistry (IUPAC) have defined chromatography as: “A physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary (the stationary phase) while the other (the mobile phase) moves in a definite direction. The stationary phase may be a solid, or a liquid supported on a solid, or a gel. The stationary phase may be packed in a column, spread as a layer, or distributed as a film, etc.; in these definitions ‘chromatographic bed’ is used as a general term to denote any of the different forms in which the stationary phase may be used. The mobile phase may be gaseous or liquid”.

The word chromatography (‘colour writing’) was coined by the Russian scientist Mikhail Tsvet (1906) and arises from the original use of the technique to separate coloured pigments (Greek chroma = colour). From these beginnings it developed slowly until the work of Synge and Martin (1941) laid the foundations of modern gas chromatography. Modern (high pressure) liquid chromatography was a later development and is generally reckoned to start with the publication of work by Huber and Hulsman (1967). Today chromatographic techniques play a major part in the chemical analysis of a wide range of materials, including pharmaceuticals, biochemicals, foods, petroleum products, dye-stuffs, environmental pollutants, pesticides, fertilizers, explosives and various other materials of forensic interest.

The essence of modern chromatography is very simple. A sample of the mixture to be analysed is introduced into a stream of mobile phase (a gas or a liquid) that flows over a stationary phase (a solid or a liquid coated on to a solid, usually contained within a tube or “column”). The sample molecules are distributed between the phases so that they each spend some time in the mobile phase and some time in the stationary phase. This is illustrated in Figure 17-3. All molecules are in dynamic equilibrium between the two phases. Certain molecules (those chemically dissimilar to the stationary phase molecules)

spend relatively less time in the stationary phase and are therefore swept forward rapidly by the mobile phase. Others (those more chemically similar to the stationary phase molecules) spend relatively more time in the stationary phase and move forward more slowly.

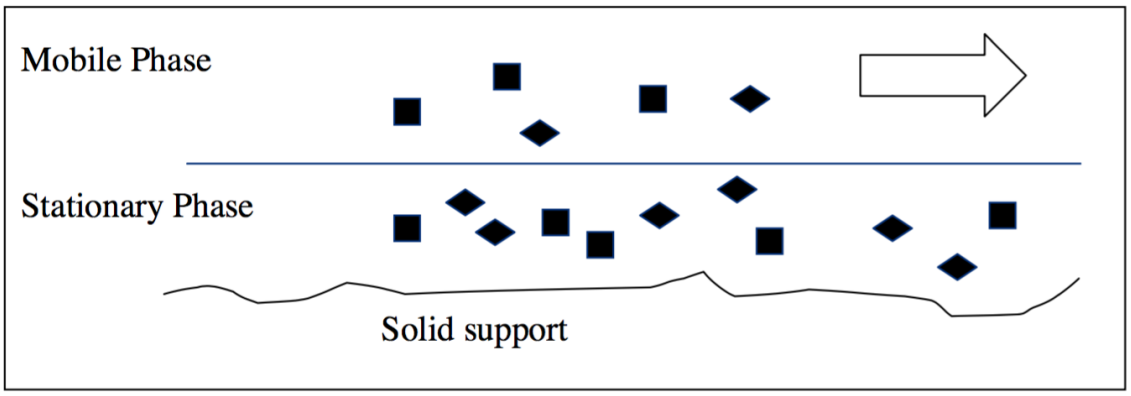

Figure 17-3. Distribution of different molecules between phases in chromatography

After the successful separation of the various components of a mixture into bands on the chromatographic column each band, as it emerges, is detected by a suitable device that responds to some property of the molecules present (e.g. ultraviolet absorption, thermal conductivity, refractive index, ion current following ionization etc.). The responses are then fed into a recorder to produce a series of peaks called a chromatogram (Figure 17-4).

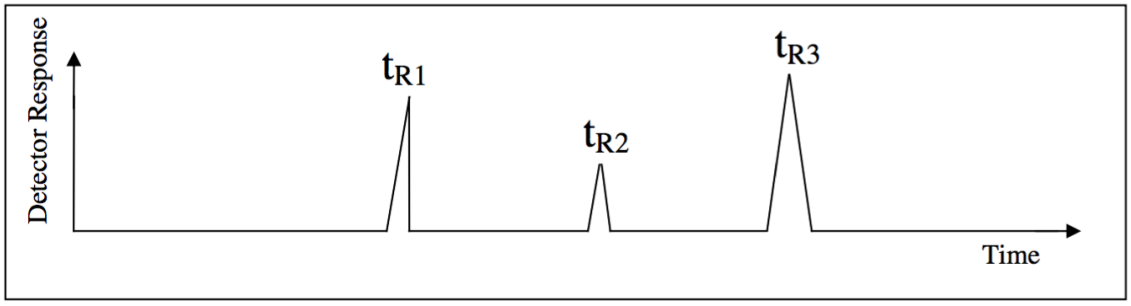

Figure 17-4. A simple chromatogram

Different kinds of molecule present in the mixture are therefore separated into bands as a result of differences in their distribution between the two phases. The time taken for a particular band to progress through the column (from injection to detection) is called the retention time, t_R. It is dependent on a large number of factors such as column temperature, mobile phase flow-rate, stationary phase composition and column length. Retention time is not in itself a reliable means of identifying separated components although a number of indices have been devised for use with some types of compound.

The basic components of a modern column chromatograph are a source of mobile phase (liquid or gas), a sample injection device, the column (usually contained within a temperature controlled oven), a detector and a recorder plus data handling facilities within a PC (or data station). An HPLC also incorporates

a pump between the mobile phase reservoir and the injector to pump the mobile phase through the system.

The most general classification of chromatographic techniques is in terms of the mobile phase so the two major divisions are gas chromatography and liquid chromatography. For most separations gas chromatography is used with helium or nitrogen as the mobile phase (carrier) gas in conjunction with a liquid stationary phase coated (or chemically bonded) on to a suitable solid support. This particular subdivision of gas chromatography depends upon partition as the distribution mechanism and is sometimes called gas-liquid chromatography.

Other distribution mechanisms used in gas and liquid chromatography are illustrated in Figure 17-5. Adsorption is used in gas chromatography for the separation of permanent gases.

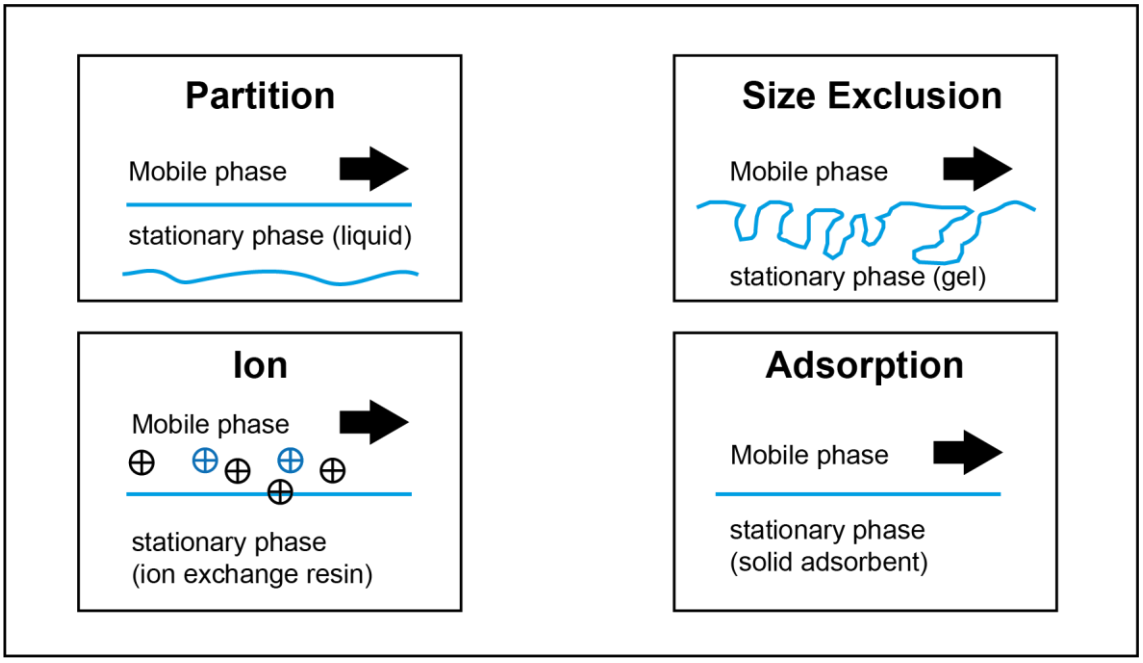

Figure 17-5. Chromatography distribution mechanisms

Liquid chromatography can be operated in a number of formats. These include thin layer chromatography (TLC) in which the stationary phase is alumina or silica coated onto a glass plate, conventional (gravity flow) column chromatography in which the liquid mobile phase passes down a vertical glass column packed with silica or alumina and high performance liquid chromatography (HPLC) in which the mobile phase is pumped under high pressure through a stainless steel column packed with stationary phase. HPLC is the most widely used of the liquid chromatography formats but TLC is often employed for the preliminary qualitative analysis of simple mixtures. TLC and conventional column chromatography both rely on adsorption as the distribution mechanism but in the case of HPLC partition is more important. For the separation of typical organic mixtures two extreme modes are possible. When the stationary phase coating is polar (e.g. an alcohol) and the mobile phase is a non-polar liquid (e.g. hexane) it is called normal phase HPLC. The reverse

situation, when the stationary phase coating is non-polar (e.g. a hydrocarbon) and the mobile phase is polar (e.g. methanol and water), is called reverse phase HPLC. The latter mode is much more widely used. Two important specialist HPLC techniques are Ion Chromatography (IC) in which ion-exchange resins are used for the separation of mixtures of cations or anions and Size Exclusion Chromatography (SEC) that uses the pores in a gel to separate polymer molecules according to their size.

Chromatography is particularly useful for the quantitative analysis of organic components in an energetic material of known composition. Such analyses may be carried out by an external or internal standard method. In the latter case the chromatography detector response of the component of interest is calibrated against that of an internal standard, which is then added to the energetic material sample solution at a known concentration. A plot of simple detector response against time is called a chromatogram.

It is not possible to use chromatography to carry out qualitative analysis on an unknown compound using the simple response detectors normally employed. However using a device such as a mass spectrometer or a Fourier Transform Infrared (FTIR) spectrometer as a detector for GC turns the technique into a very powerful analytical tool, which can be used for both qualitative and quantitative work.

17.3.2.1 Thin layer chromatography

Thin layer chromatography (TLC) is a simple form of liquid chromatography in which the stationary phase is coated on to a glass plate, which is then held vertically in a beaker containing a small amount of mobile phase, enough to cover the bottom few inches of the plate. A spot of the sample solution is then placed on the plate just above the liquid level. As the liquid moves up the stationary phase on the plate the components in the sample become separated. The separated spots are "developed" using a chemical spray that produces a colour by reacting with each component or by irradiating with UV light.

TLC is simple to carry out and requires no complex instrumentation. It is particularly suitable for the preliminary qualitative analysis of explosive mixtures (e.g. RDX/TNT) and for distinguishing between single-base and double-base propellants (link to 12.2.2).

17.3.2.2 Gas chromatography (GC)

GC is the chromatographic method used for the analysis of gases and volatile compounds. The hardware is simpler than for HPLC and it is generally easier to operate successfully. However, since it is often necessary to use GC column temperatures in excess of 250 °C in order to get the analytes (the compounds that are being analysed) into the vapour phase and achieve effective separation, its drawbacks are obvious. In general GC is suitable only for samples that are volatile below about 350 °C and are not thermally degraded.

Following the separation of a mixture of organic compounds by GC the compounds, when they emerge from the column, are detected either by a simple ‘response’ detector, which responds to some property of the compound but is unable to identify it or by a ‘smart’ detector, which is usually able to identify the compound. The most widely used response detector is the flame ionisation detector (FID), which responds to all molecules containing C-H bonds and is fairly sensitive. The response arises from the generation of an ion current when molecules from the compound being detected are passed into a hydrogen/air flame and break down to give ions such as CHO^+. A modified form of the FID called the alkali flame ionisation detector (AFID) is particularly sensitive to nitrogen or phosphorus compounds. It can be “tuned” to either type and can detect them in the presence of non-N or non-P containing compounds. The AFID is often called a Nitrogen Phosphorous detector (NPD).

Another specific GC detector is the Thermal Energy Analyser (TEA). This responds to compounds, which on pyrolysis, release nitric oxide (NO) or a closely related species such as NO_2, which can be readily converted into NO. Detection is by means of the chemiluminescence produced by the reaction of NO with ozone (O_3). Since NO or NO_2 are products of the pyrolysis of many energetic materials the potential usefulness of the TEA can be appreciated. It offers sensitivity similar to that of an ECD but has much greater selectivity for particular types of compound. TEAs are considerably more expensive than other detectors and are not at present (2017) widely used.

Other response detectors used in GC include the thermal conductivity detector (TCD) which is used mainly for permanent gases and is considerably less sensitive than an FID, and the electron capture detector (ECD) which is very sensitive but responds only to molecules containing the most electronegative groups (e.g. –F, $-NO_2$). However, it is becoming easier and more common to interface spectrometers to gas chromatographs as ‘smart’ detectors, leading to techniques such as GC-MS and GC-FTIR. The advantage of these is that the separated components can then be positively identified in most cases rather than simply detected. Response detectors such as the FID, TCD and ECD are therefore becoming less widely used since a mass spectrometer can do everything and more that a response detector can do. Although a mass spectrometer detector is more expensive than a simple response detector the greater power of the MS generally outweighs the extra expense.

In recent times the separation of organic vapours is carried out using mainly wall coated open tubular (WCOT) or ‘capillary’ columns. These are very narrow bore columns made of fused silica in which the stationary phase is chemically bonded onto the inside wall of the column. Porous layer open tubular (PLOT) columns contain adsorbent particles on the column wall and are suitable for the separation of permanent gases. Injection on to such columns, with their very low capacities, is normally carried out via a so called ‘split-splitless’ injector where much of the injected liquid is diverted to waste and only a small proportion enters the column.

The principal disadvantage of GC in relation to energetic materials analysis is the fact that, in order to shorten separation times, it is necessary to heat the column at a constant temperature ("isothermal") or at a steadily increasing temperature ("temperature programming"). This clearly presents problems for the separation of thermally labile compounds such as molecular explosives, which decompose below 250 °C, a typical maximum column temperature. Most GC injector systems also involve raising the temperature of the injected sample to about 250 °C and this further limits the usefulness of GC for explosives analysis. However such materials can often be successfully analysed by GC using short open-tubular columns and cold on-column injection devices. It is nevertheless more common to use HPLC for separations of explosive mixtures.

GC, which is generally more reliable and easier to operate than HPLC is particularly useful for the quantitative analysis of the volatile organic components in a nitrocellulose (NC) based propellant, such as the stabiliser, where an FID and a flash vaporising injector are perfectly adequate.

17.3.2.3 High performance liquid chromatography

The most widely used form of HPLC for the separation of organic materials is reverse-phase HPLC. In this mode the liquid stationary phase is a non-polar material (commonly octadecyl silane, containing $–C_{18}H_{37}$ groups) and is chemically bonded onto tiny particles (3-10 µm diameter) of a silica support, which are then packed into a stainless steel column. The mobile phase used with a typical reverse-phase column is a polar solvent mixture such as water/methanol or water/acetonitrile flowing at about 1-2 cm^3 min^{-1}. In order to speed up separations the mobile phase composition can be changed during a run. This is termed gradient elution and may be seen as analogous to temperature programming in GC. In isocratic elution the composition of the mobile phase remains fixed throughout the run. Since reverse-phase HPLC is carried out at, or just above, ambient temperatures in order to improve temperature control of the column it is suitable for the separation of thermally sensitive and non-volatile compounds that cannot be analysed by GC. Injection in HPLC is carried out using a loop injector, the sample initially being held in the loop (10 – 100 µl) and then flushed on to the column by diverting the mobile phase through the loop.

The most common response detectors used in reverse phase HPLC systems are UV detectors, which depend upon the ability of the detected molecules to absorb ultraviolet radiation, often at a fixed wavelength of 254 nm. Other detectors have been used, but the presence of the liquid mobile phase always create problems and there is no sensitive HPLC response detector as effective as the FID in GC. Variable wavelength UV detectors are capable of being operated at wavelengths as low as 190 nm where weakly absorbing molecules are more likely to be detected, but they are then particularly susceptible to interference from strongly absorbing impurities in the mobile phase solvents. As in GC there is an increase in the use of MS detectors. These are much more effective than UV detectors in providing a positive identification for a compound as UV spectra are considerably less characteristic than mass spectra. It is less

straightforward to interface an MS to an HPLC than to a GC but the efficiency of interfaces such as electrospray ionization is increasing and LC-MS is now a routine technique.

17.3.2.4 Size exclusion chromatography (SEC)

Size exclusion chromatography (SEC) is a type of HPLC used for the separation of polymers. Here the stationary phase is a gel that contains pores of various sizes through which the polymer molecules permeate as they are carried by the mobile phase, hence the former name of gel permeation chromatography. The different sized molecules are retained to different extents and become separated. SEC is used in energetic materials research principally for separating nitrocellulose (NC) molecules covering a range of molecular weights. A molecular weight distribution can then be obtained for an NC sample. A UV detector is not suitable for SEC and instead a refractive index detector is used which responds to differences in refractive index between pure mobile phase and the mobile phase containing a sample.

17.3.2.5 Ion chromatography (IC)

Another type of HPLC used in the energetic materials field is ion chromatography (IC). In this technique the stationary phase within the chromatography separating column is an ion-exchange resin that has a different affinity for each anion, or cation, in the sample. In the case of anion separations the mobile phase is an aqueous alkali, most commonly a mixture of carbonate and bicarbonate, while for cation separations dilute mineral acids can be used.

IC normally makes use of conductometric detection techniques but in order to detect the separated ions in a sample it is necessary to ensure that the background conductivity of the mobile phase as it passes through the detector is low, otherwise that of the sample will be swamped. In most IC separations this is achieved by fitting a so-called "suppressor column" between the separating column and the detector. This contains an ion-exchange resin, which interacts with the ions in the mobile phase. For anion separations the reaction is typically that shown in Equation (17-2).

$$\text{Resin-H}^+ + M^+ + HCO_3^- \rightarrow \text{Resin-M}^+ + H_2CO_3 \qquad \textbf{(17-2)}$$

The background conductivity due to the bicarbonate (M^+ is a metal counter-ion) is thereby reduced to a level at which the sample ions may be detected.

Ion Chromatography is particularly useful for the determination of inorganic ions in pyrotechnics and home-made explosives containing metal nitrates, chlorates or other metal/oxidiser salts and has replaced many of the "wet" chemical methods that have traditionally been used for the analysis of these materials. IC offers greater sensitivity and faster sample throughput.

17.3.3 Thermal Methods

When an energetic material is heated slowly at a constant rate of temperature increase it invariably undergoes a number of detectable changes before it decomposes or ignites. The study of these changes is the basis of a range of analysis techniques known as thermal methods, which can help to identify and characterise energetic materials.

Changes in weight, which occur when a material is heated, are studied by thermogravimetric analysis (TGA). The weight changes are measured on a few milligrams of material and are compared to an inert reference, usually alumina, which is heated at exactly the same rate. The weight changes may be due, for example, to a loss of water of crystallisation or to the breakdown and gasification of a ligand attached to a metal ion.

Changes that result in the release (exotherm) or absorption (endotherm) of heat at a particular temperature, e.g. melting, phase change, decomposition, etc., are recorded in differential thermal analysis (DTA) as shown in Figure 17-6. The melting point of TNT can be seen at 81 °C, that RDX has an endotherm on melting at 204 °C immediately before decomposing exothermically. HMX has a phase change endotherm around 200 °C and melts at 276 °C immediately before decomposing exothermically. As in TGA, the sample is compared to an inert reference. The technique is particularly useful for the study of pyrotechnic compositions since the melting points and crystalline phase changes for many of the ionic oxidisers are very characteristic.

In differential scanning calorimetry (DSC) the sample and reference are maintained at the same temperature as the two are separately heated. The difference in required power between the two heaters is recorded as a function of temperature and this gives a quantitative measure of changes occurring in the sample.

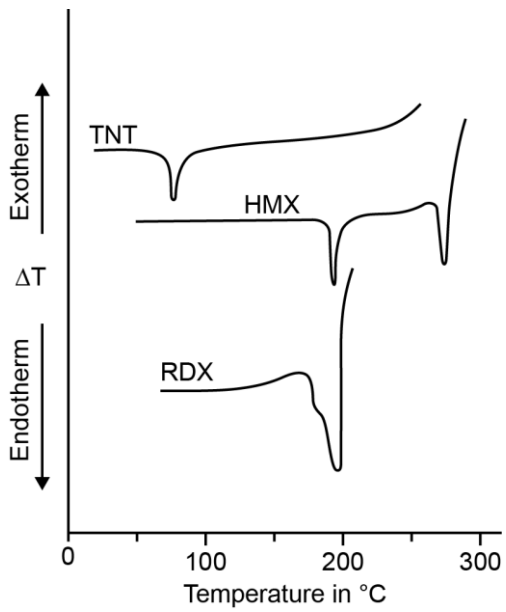

Figure 17-6 Differential thermal analysis of HMX, RDX and TNT

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