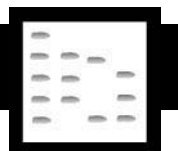# EXPLOSIVES

## Gas Chromatography

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## Introduction

Although some explosives are thermally labile and others are not volatile enough, gas chromatography (GC), with a variety of detectors, has been found to be a good method for separation and analysis of a certain number of organic explosives. This can be achieved when using the GC under controlled experimental conditions, such as the temperature of the column, injector and detector, type and length of the column, special injection techniques and the use of selective detectors.

In this article we will describe some of the GC methods used for the analysis of explosives – the preferred columns, the injection techniques and the preferred detectors. In order to be able to evaluate GC as a method for the analysis of explosives, it is necessary to present a short overview of the main organic explosives (**Figure 1**). These explosives can be divided into the three following groups:

1. Nitroaromatic compounds
2. Nitrate esters
3. Nitramines

The most widely used nitroaromatic explosive is 2,4,6-trinitrotoluene (TNT). Nitrate esters include ethylene glycol dinitrate (EGDN), glycerol trinitrate (nitroglycerin, NG) and pentaerythritol tetranitrate (PETN). Nitramine explosives include 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) and 2,4,6-$N$-tetranitro-$N$-methylaniline (tetryl).

Additional nitroaromatic compounds encountered are 2-, 3- and 4-nitrotoluene, 2,4- and 2,6-dinitrotoluene (DNT) and degradation products of TNT such as 2-amino-4,6-dinitrotoluene and 4-amino-2,6-dinitrotoluene.

## Extraction Procedures

Various extraction procedures can be used. Several of them are described as follows.

### Extraction of Explosives from Water

1. Liquid–liquid extraction is carried out with a separation funnel using 1 L of water (containing TNT and other nitroaromatic compounds) and shaking three times with 30 mL of methylene chloride. The combined organic phases are dried over anhydrous sodium sulfate and reduced in volume to 1 mL in a rotary evaporator at 40°C, after the exchange of the methylene chloride with methanol. Other solvents can be used, such as benzene or toluene for nitroaromatic compounds, or isoamyl acetate for nitramines. Extraction can also be carried out using 100 mL of water. In that case only about 6 mL solvent are required.
2. Solid-phase extraction is carried out using Amberlite XAD-2, XAD-4, XAD-8 resins (1 : 1 : 1), C18 phases, phenyl phases and cyano phases, 2.5 g of XAD resin is placed in a $15 \times 1$ cm i.d. glass column plugged with silanized glass wool and flushed with methanol and water. 1 L of water, containing the explosives, is forced through the column at a flow rate of 30 mL min$^{-1}$, using nitrogen pressure. The column is then dried with a stream of nitrogen and eluted twice with 15 mL of methylene chloride. Drying, concentration and solvent exchange are carried out as in the liquid–liquid extraction method. Recovery for TNT is 95%.

### Extraction of Explosives from Soil

1. 10 g of undried, homogenized soil is extracted with 25 mL acetone in an ultrasonic bath for 30 min. The extract, after passing through filter paper, is ready for analysis. Recovery for RDX is 95%.
2. Supercritical fluid extraction (SFE) can be used for the extraction of explosives from soil. Extraction is made with supercritical $CO_2$ at 5000 psi and 50°C. The dynamic SFE mode is being used, where fresh supercritical fluid is flushed continuously through the sample matrix and then passes through a trap in which the analytes of interest are collected. This mode of operation gives a better recovery than the static mode.

## Capillary Columns

Low polarity columns are used, because the polar interaction of the nitro groups can produce irreversible adsorption on the stationary phase or decomposition of the explosives at higher temperatures.
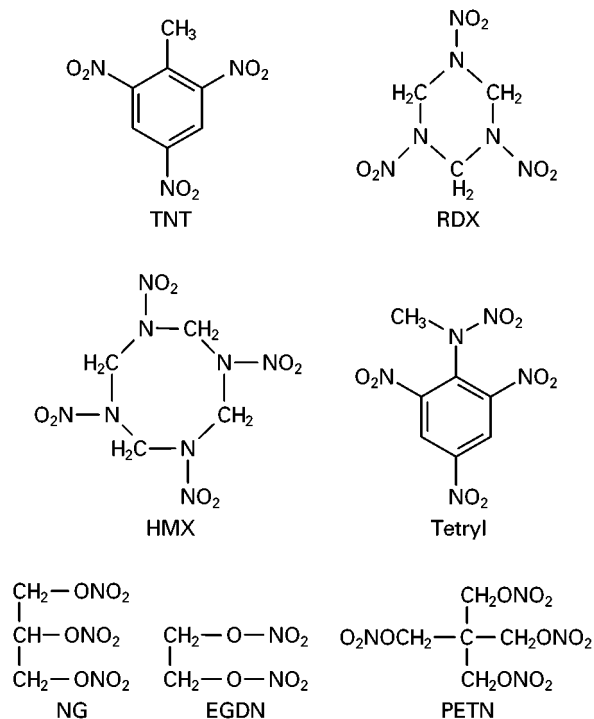
**Figure 1** Structure of commonly used explosives (see text for abbreviations used).

Columns commonly used for the separation and analysis of explosives include DB-1 (BP-1 or CP-Sil 5CB) (100% dimethylpolysiloxane) and DB-5 (5% phenylmethylpolysiloxane). Other columns, such as DB-17 (50% phenylmethylpolysiloxane) and OV-225 (50% cyanopropylphenylmethylpolysiloxane) have also been used, but only for separation of nitroaromatic compounds.

Another important factor is the column length. Compounds which evaporate at higher temperatures, such as RDX and PETN, should be eluted from the column as fast as possible in order to minimize their decomposition. This can be done by either increasing the flow rate of the carrier gas or decreasing the length of the column. Columns as short as 1.5 m have been used although short columns will, of course, have a poorer separation capability.

**Table 1** shows a summary of GC columns and conditions which have been used for the separation of a variety of explosives.

## Injectors

Injectors used include split–splitless injectors at temperatures ranging from 170°C to 250°C, a flash vaporizing injector at 270°C and a temperature-programmable injector (cooled with liquid $CO_2$),

programmed from $-5°C$ to 250°C at a rate of 200°C min$^{-1}$. A temperature-programmed injector is much better suited for GC analysis of thermally labile compounds, as it will minimize decomposition in the injector.

## Detectors

### Electron-Capture Detector (ECD)

An electron-capture detector is an ionization chamber in which electrons are produced from a radioactive source (usually tritium or nickel-63). These electrons are injected into a stream of inert carrier gas (helium or nitrogen), where they reach thermal energy equilibrium through collisions with the carrier gas. The thermal electrons are collected at an anode, thus producing a standing current. When an electron-capturing compound (the sample), such as a halogen- or a nitro-containing compound, is introduced into the carrier gas, the standing current is reduced. The reduction in current is proportional to the concentration of the sample. Electron-capture detectors have a fast response and are highly sensitive for most electron-capturing compounds. However, their specificity for explosives is low. Detection limits are in the 5–50 pg range for the various explosives.

An example is presented in **Figure 2**, which shows the GC-ECD chromatogram of a soil sample taken from a former explosives storage bunker. The column used was a 30 m, DB-5 capillary column, held at 180°C isothermal. The dinitrotoluenes were by-products of TNT, while the aminodinitrotoluenes were microbial degradation products of TNT.

### Thermal Energy Analyser (TEA) Detector

The TEA detector, also known as a chemiluminescence detector, is a nitrogen-specific detector. In the TEA detector, nitro compounds are pyrolysed to form $NO^·$ radicals, which pass into a reaction chamber where they are oxidized by ozone to form electronically excited nitrogen dioxide ($NO_2^*$). The excited nitrogen dioxide decays back to its ground state with emission of chemiluminescent light in the near-infrared region ($\lambda \cong 0.6–2.8\ \mu m$). The intensity of the emitted light is proportional to the NO concentration and hence to the nitro compound concentration. The TEA detector, although more specific for explosives than the ECD, is less sensitive by one to two orders of magnitude. An example is presented in **Figure 3**, which shows the GC-TEA chromatograms of pure PETN and of a sample taken from the debris of a bombing, containing traces of PETN.

**Table 1** GC columns used for separation of explosives

| Column type | Column dimensions | Temperature programme | Carrier gas | Detector/s used | Explosives analysed |
|---|---|---|---|---|---|
| DB-1 | 30 m × 0.32 mm i.d. 0.25 μm film | 70–250°C at 3°C min$^{-1}$ | He | MS | DNT, TNT |
| DB-1 | 5 m × 0.20 mm i.d. 0.33 μm film | 75–225°C at 20°C min$^{-1}$ | He | ECD, MS | Semtex[a], PETN, RDX |
| DB-1 | 15 × 0.25 mm i.d. 0.25 μm film | 80–250°C at 25°C min$^{-1}$ | He | MS | TNT. Tetryl, RDX, HMX, PETN |
| BP-1 | 12.5 m × 0.22 mm i.d. 0.25 μm film | 60–240°C at 40°C min$^{-1}$ | He | TEA | NG, TNT, RDX |
| BP-1 | 12 m × 0.25 mm i.d. 0.25 μm film | 60–250°C at 40°C min$^{-1}$ | He | ECD | EGDN, NG, PETN, DNT, TNT, RDX |
| DB-5 | 10 m × 0.32 mm i.d. 0.25 μm film | 50–250°C at 10°C min$^{-1}$ | He | TEA | EGDN, NG, PETN, DNT, TNT |
| DB-5 | 15 m × 0.25 mm i.d. 0.25 μm film | 50–260°C at 25°C min$^{-1}$ | He | MS | DNT isomers |
| DB-5 | 1.5 m × 0.25 mm i.d. 0.25 μm film | 60–220°C at 20°C min$^{-1}$ | He | MS | NG, PETN |
| CP-Sil 5CB | 20 m × 0.25 mm i.d. 0.25 μm film | 50–90°C at 5°C min$^{-1}$ 90–250°C at 3.5°C min$^{-1}$ | H$_2$ | ECD | DNT, TNT |
| DB-17 | 30 m × 0.32 mm i.d. 0.25 μm film | 70–250°C at 3°C min$^{-1}$ | He | ECD, TEA | DNT, TNT |
| OV-225 | 30 m × 0.32 mm i.d. 0.25 μm film | 70–250°C at 3°C min$^{-1}$ | He | ECD, TEA | DNT, TNT |
| OV-101 | 25 m × 0.25 mm i.d. 0.1 μm film | 50–240°C at 40°C min$^{-1}$ | He | ECD | EGDN, NG, PETN, DNT, TNT, RDX, HMX, Tetryl |
| DB-1301 | 4.5 m wide bore 1.0 μm film | 128–225°C at 30°C min$^{-1}$ | He or H$_2$ | ECD | DNT, TNT, RDX, HMX |

[a] Semtex is a plastic explosive containing RDX and PETN.

The chromatograms were recorded at two different injection temperatures: 170°C and 250°C. At 250°C PETN decomposes, therefore a decomposition peak appears in the chromatogram. The column used was a 10 m, DB-5 capillary. Injections at 170°C and 250°C were done with a split–splitless injector, in the splitless mode.

## Gas Chromatography–Mass Spectrometry (GC-MS)

The good separation capability of capillary column GC, together with the high sensitivity and identification capability of the mass spectrometer, have made GC-MS a powerful method in analytical chemistry. The use of GC-MS for the analysis of explosives is limited by the thermal decomposition characteristics of some of the explosives. Precautions to be taken when analysing explosives by GC-MS are similar to those taken when using GC with any other detector.

GC-MS for the analysis of explosives has been used in three different ionization modes: electron ionization (EI), chemical ionization (CI) and negative-ion chemical ionization (NCI). The produced ions are mass separated by a mass analyser (magnetic sector, quadrupole or ion trap), detected by an electron multiplier, recorded by a data system and stored in the computer as a mass spectrum. There are different ways to display the results: (i) as a total ion
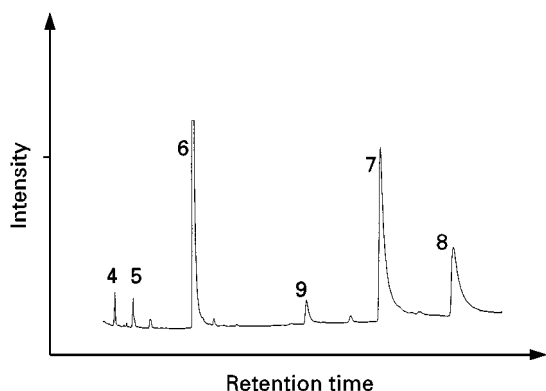


**Figure 2** GC-ECD chromatogram of a sample taken from a former explosives storage bunker. Peak identity: 4: 2,6-dinitrotoluene; 5: 2,4-dinitrotoluene; 6: TNT; 7: 4-amino-2,6-dinitrotoluene; 8: 2-amino-4,6-dinitrotoluene; 9: RDX. (Reproduced from Haas R *et al.* (1990) *Fresenius Journal of Analytical Chemistry* 338: 41–45, by permission of Springer-Verlag.)
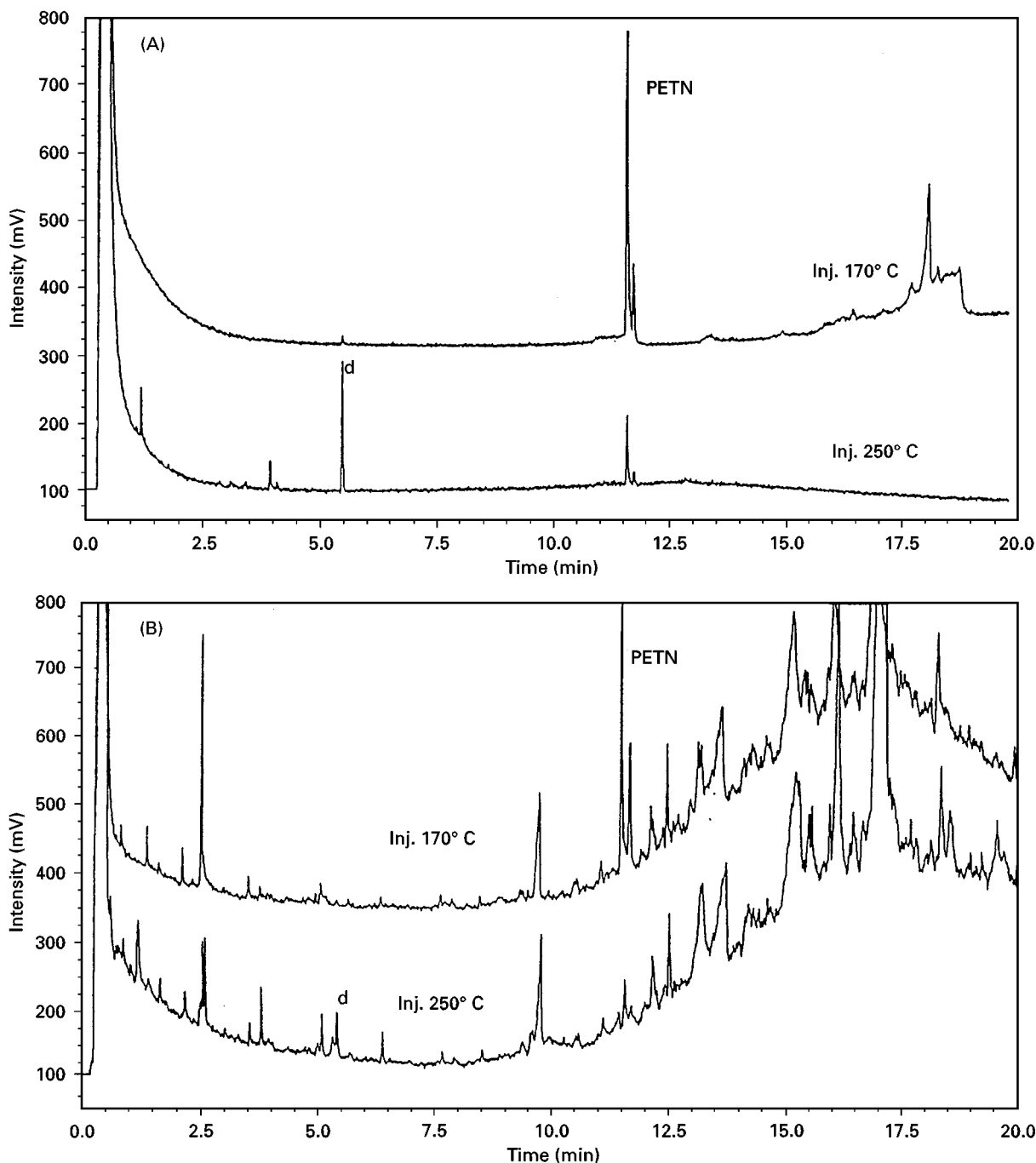
**Figure 3** GC-TEA chromatograms. (A) Pure PETN. (B) A sample from a bombing scene, containing PETN. Chromatograms were run at injection temperatures of 170°C and 250°C. Peak d is a decomposition product of PETN. (Reproduced from Kolla P (1994) *Journal of Chromatography A* 674: 309–318, by permission of Elsevier Science Publishers.)

chromatogram (TIC) or reconstructed ion chromatogram (RIC), which is equivalent to a GC chromatogram – a mass spectrum of each one of the GC peaks can be displayed; (ii) as mass chromatograms, which are GC chromatograms including only preselected masses. Each one of the GC separated compounds can be represented by one or several masses which are characteristic of the full mass spectrum.

**Electron Ionization (EI)**

The basic form of ionization in mass spectrometry is electron ionization (EI), where an electron beam, usually at an energy of 70 eV, collides with the molecules of the sample to transform them into positively charged ions. In addition, extensive fragmentation of the ions occurs, resulting in a mass spectrum which
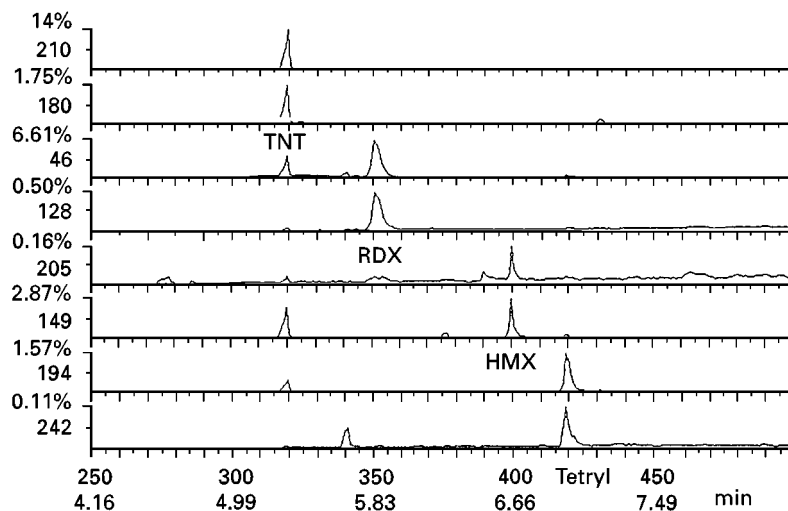
**Figure 4**  GC-MS EI mass chromatograms of a mixture of explosives (10 ppb each), extracted from water by liquid–liquid extraction. (Reproduced from Yinon J (1996) *Journal of Chromatography A* 742: 205–209, by permission of Elsevier Science Publishers.)

does not always contain a molecular ion. The fragmentation patterns thus obtained can be correlated with specific functional groups, enabling recognition of many structural features in the analysed molecule. An EI mass spectrum of a molecule can, therefore, be considered a 'fingerprint' of that molecule and can be used as an identification tool.

An example is presented in **Figure 4** which shows the GC-MS EI mass chromatograms of a mixture of explosives (10 ppb each), extracted from water by liquid–liquid extraction with methylene chloride. Each of the explosives could be identified by at least one characteristic ion (in most compounds a fragment ion). The column used was a 15 m × 0.255 mm i.d. DB-1 capillary column. Column temperature programme was 80°C to 250°C at 25°C min$^{-1}$. Injector temperature was programmed from − 5°C to 250°C at 200°C min$^{-1}$. The mass spectrometer was an ion trap operated in the EI mode.

### Chemical Ionization (CI)

In chemical ionization (CI) ions are formed by reaction of the sample molecules with a known preselected set of reagent ions. These reagent ions are produced by ion–molecule reactions in a reagent gas introduced in the ion source of the mass spectrometer at a pressure of 0.1 to 1.0 Torr. Common reagent gases are methane and isobutane.

CI mass spectra contain usually an MH$^+$ ion and little fragment ions. It is, therefore, suitable for molecular weight identification. In many cases, in the CI mass spectrum of an explosive an MH$^+$ ion might be observed, while in the EI mass spectrum of the same compound there is no molecular ion. For example, the EI mass spectra of NG and PETN are similar,

containing abundant ions at $m/z$ 30 (NO$^+$), $m/z$ 46 (NO$_2^+$) and $m/z$ 76 (CH$_2$ONO$_2^+$). However, they have different GC retention times, but this means that their identification is based on chromatographic properties. In the CI mass spectra of NG and PETN, MH$^+$ ions are observed, at $m/z$ 228 and $m/z$ 317, respectively.

### Negative-ion Chemical Ionization (NCI)

In negative-ion chemical ionization (NCI) a reagent gas at 0.1 to 1.0 Torr is introduced in the ion source of the mass spectrometer. This reagent gas acts primarily as a moderator in producing high concentrations of low energy electrons. Negative ions are formed in the analysed sample by electron capture. These ions are either molecular ions or (M–H)$^-$ ions. Fragment ions are also formed by dissociation of part of the molecular ions. Special reagents can be introduced into the ion source causing ion–molecule reactions, thus forming characteristic adduct ions. For example, the NCI mass spectrum of TNT will contain abundant anions at $m/z$ 227, M$^-$, $m/z$ 210, (M–OH)$^-$, $m/z$ 197, (M–NO)$^-$ and $m/z$ 181, (M–NO$_2$)$^-$. The detection limit of explosives in the NCI mode is, in general, lower by one order of magnitude then in the positive CI mode.

## Conclusions

While GC is a chromatographic method and needs comparison of retention times with standards, mass spectrometry is an identification method and provides a 'fingerprint' of the investigated compound. The combination of GC with MS incorporates both

separation and identification capabilities, and is therefore superior to GC alone.

Both GC and GC-MS, although being suitable techniques for the separation and analysis of explosives, have a limitation in that the injector and column have to be heated. This fact necessitates taking special precautions when dealing with the more thermally labile compounds. Liquid chromatography–mass spectrometry (LC-MS), where the injector and column are at room temperature, does not have these limitations, and is therefore a better choice when analysing the more thermally labile explosives. However, GC-MS is readily available in most analytical laboratories, while LC-MS is not. This situation is expected to change in the next 5 to 10 years, which will place LC-MS as the method of choice for the separation and analysis of explosives.

In both GC-MS and LC-MS, the addition of tandem mass spectrometry (MS-MS) provides an extra dimension for improved selectivity and therefore improved identification.

**See Colour Plate 83.**

*See also:* **II/Chromatography: Gas:** Detectors: Mass Spectrometry; Detectors: Selective. **Extraction:** Analytical Extractions; Solid-Phase Extraction; Solid-Phase Microextraction. **Explosives:** Liquid Chromatography; Thin-Layer (Planar) Chromatography.

## Further Reading

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# Liquid Chromatography

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## Introduction

Explosive analysis is important in different areas: explosive manufacture (quality and wastewater control), forensic science and toxicology (investigation of explosions or of criminal actions) and environmental monitoring (water and soil analysis at sites intensively used for military purposes). **Figure 1** shows some of the more common explosives.

In the literature various methods and procedures have been described for analysing these compounds. In the last few years, the investigation of explosives in the water and soil around former ammunition plants,