

# Gas chromatography, liquid chromatography and ion chromatography adapted to the trace analysis of explosives

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## Abstract

The potential of gas chromatography, high-performance liquid chromatography and ion chromatography for application to the determination of traces of explosives was investigated. The most important aspect is the combination of the chromatographic technique with selective detection methods. In gas chromatography a chemiluminescence detector is preferred and for high-performance liquid chromatography the advantages of postcolumn derivatization are described. Problems and possible solutions in the trace analysis of explosives which depend on matrix effects and chemical properties are discussed.

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## 1. Introduction

Chromatographic methods are important in the trace analysis of explosives. The utility of chromatography is based on the selective separation of sought compounds from unwanted accompanying substances. Traces of explosives have usually to be determined in very complex matrices, such as debris from a bomb scene or environmental dirt from cars or houses. The chromatographic method can be selected to match the characteristics of the explosives and eliminate interfering substances from the matrix. Also, chromatographic methods can be combined with special detectors for sensitive and specific detection of the explosive constituents. An extensive review on the detection and identification of explosive residues has been written by Beveridge [1]. There is also an excellent book on modern methods and their applications in the analysis of explosives [2].

Gas chromatography (GC), liquid chromatography (LC) and ion chromatography (IC) can be

applied to the analysis of explosives depending on the characteristics of each constituent. The application of supercritical fluid chromatography (SFC) has also been reported [3], but this is not discussed in this paper. Gas chromatography is preferred for the organic compounds, which can be vaporized without decomposition. To this group belong the explosive oils, *e.g.* ethylene glycol dinitrate (EGDN), diethylene glycol dinitrate (DEGN) and nitroglycerine (NG), also nitroaromatics such as dinitrotoluene (DNT), trinitrotoluene (TNT) and tetryl (CE), and even high explosives such as pentaerythritol tetranitrate (PETN) and hexogen (RDX).

Gas chromatography has the advantage of a high resolving power. Several isomers of nitroaromatics can be separated with narrow peaks in one run together with explosive oils and high explosives in a reasonable time. The importance of gas chromatography is based on its compatibility with mass spectrometric [4] and chemoluminescence (TEA) [5] detectors. These detectors make the identification of small

amounts possible by selective detection at reproducible retention times.

Liquid chromatography has a wide range of applications. The trace analysis of explosives is preferably done by high-performance liquid chromatography (HPLC), because it can be coupled to sensitive detectors. Even coupling to a chemiluminescence detector (TEA) is possible [5]. HPLC is important for the determination of thermolabile compounds or explosive constituents that cannot be vaporized. The separation mechanism in LC is totally different from that in GC, and the methods can be used alternatively to confirm the results. Usually HPLC is less sensitive than GC because of the broad peak shape and lower peak heights. Also, the resolution between substances of similar polarity such as isomers is lower than in GC.

Thin-layer chromatography (TLC) can be used for the trace analysis of explosives with the disadvantage of about a 100 times lower sensitivity than GC. However, TLC is an inexpensive technique that can often be applied successfully if the amount of explosive is large enough and the detection is made fairly selective with spray reagents.

Ion chromatography is the method of choice for the ionic constituents of explosives. Preferably IC is used for inorganic anions such as nitrite, nitrate and chlorate [6]. Inorganic cations with the exception of ammonium are not typical components of explosives and cation chromatography is not often applied. Recently capillary electrophoresis has been introduced for the determination of inorganic anions and it seems to be superior to IC because of its higher efficiency and shorter analysis times [7].

The trace analysis of explosives has to be applied to samples from bomb scenes (post-blast analysis), to samples from cars of premises and to samples from suspects. Each sample source has its own characteristics, but accompanying substances having a higher concentration than the explosive itself are the greatest problem for the analysis. Therefore, the adaptation of the chromatographic techniques to the trace analysis of explosives must be focused, in addition to optimization of the chromatographic conditions, on a selective detection method. The detector

should only respond to explosives and should give no signal for all substances that are not related to explosives. This requirement cannot be met ideally, because the structural properties of the different explosives are not so unique that other substances cannot interfere. Only the nitroaromatics can be easily identified by mass spectrometry. The structural property that contrasts with most of the compounds in the matrix is the high content of nitro groups in organic explosives. In addition to spectrometric methods, selective detection can also be based on the recognition of nitro groups in the eluate.

This paper describes optimized combinations of chromatographic methods with selective detection techniques for the trace analysis of explosives.

## 2. Experimental

### 2.1. Gas chromatography

The gas chromatograph was a Varian 3400 coupled to a TEA detector from Thermedics, as described by Kolla [8]. Injection was performed with a split-splitless injector operated at 170°C. The column was a 10 m DB-5 capillary column. The column temperature was initially 50°C and was increased at 10°C/min to 250°C.

### 2.2. Liquid chromatography

Liquid chromatography was carried out with modular equipment. An LDC Analytical 3200 pump was used. The column was Lichrospher RP-8 and the eluent was water-methanol (1:1). Postcolumn derivatization was performed as described by Engelhardt *et al.* [9] with a low-pressure mercury lamp behind the column and mixing sulphanilamide and naphthylethylenediammonium chloride sequentially with the eluent. The detector was a Shimadzu UV-Vis detector operated at 540 nm.

### 2.3. Ion chromatography

Ion chromatography was performed with a Metrohm IC 690 instrument, which operates on

the single-column principle without chemical suppression. The anion-exchange column was a Hamilton PRP-X100 and the eluent was 4 mM potassium hydrogenphthalate (pH 4.5).

### 3. Results and discussion

#### 3.1. Gas chromatography

In general analytical operations, GC is the method of choice because it is easy to handle, the conditions are stable and reproducible, the analysis is fast and many different detectors can be coupled to the system. Therefore, GC is also well suited to the analysis of organic explosives. However, the usual GC systems cannot be applied to explosives without slight modifications, because not every explosive is stable at higher temperatures. In Table 1 the deflagration temperatures of explosives and their vapour pressures at GC temperatures are given. At the deflagration temperature sudden decomposition of the explosive takes place, but partial decomposition starts at much lower temperatures with the lowest stability for nitrate esters. Nitroglycerine shows significant decomposition at 135°C, turning red because of the formation of nitrosic gases. There is a dilemma especially for explosives with very low vapour pressures such as PETN and RDX, which decompose at elevated temperatures. No problems arise for the more stable nitroaromatics (the C–NO<sub>2</sub> bond is more stable than the O–NO<sub>2</sub> or the N–NO<sub>2</sub> bond), which have fairly high vapour pressures.

Table 1  
Deflagration temperatures and vapour pressures of explosives

Explosive	Deflagration temperature (°C)	Vapour pressure at 100°C (Torr) <sup>a</sup>	Vapour pressure at 200°C (Torr) <sup>a</sup>
EGDN	200	22.2	2582
NG	200	0.39	78.6
TNT	333	0.069	360
PETN	209	0.0008	26.9
RDX	229	0.00016	0.31

<sup>a</sup> Vapour pressures from ref. 10 were recalculated. 1 Torr = 133.322 Pa.

Also, the explosive oils NG and EGDN with their high vapour pressures can be determined by GC despite their thermal instability. In order to be able to analyse all explosives, the explosive oils and the nitroaromatics together with PETN and RDX, a compromise has to be found for the GC conditions.

#### 3.2. Injection port

The large amounts of compounds of higher molecular mass and salts in the matrices, which cannot be vaporized, prevent the use of on-column injection, otherwise serious contamination of the column would occur. An injection port with an insert that traps the non-vaporizable substances should be used. The easiest system for this purpose is a split-splitless injector with a fritted glass insert. Its inner surface is small and inactive, so that possible decomposition is prevented and it is not adsorptive for explosives. It can be replaced very quickly if it is dirty and the analysis deteriorates. The effect of a dirty insert can be seen when determining PETN and RDX, which evaporate only at higher temperatures and are simultaneously unstable if polar substances are present [8] in the injector (Fig. 1). The PETN peak decreases and the RDX peak tails badly. Often the beginning of the column (about 20 cm) has to be cutoff to restore the original sensitivity. The quality of the separation should be checked periodically with a standard mixture.

The injection temperature is chosen in the range between optimum evaporation and the beginning of decomposition for the most difficult explosives (PETN and RDX). In Fig. 2, peak area *versus* injection temperature plots for some important explosives are shown. To determine the optimum injection temperature, the area of the peaks was calculated. The optimum temperature occurs near 170°C, where the peaks for the explosive oils have already decreased. The injection temperature can even be used for confirmation, *e.g.*, PETN decomposes at a temperature higher than 200°C and a new peak appears at a low retention time. To confirm PETN, the peak at 170°C must decrease with increasing injector temperature and a new peak must be observable (Fig. 3). The injector is operated in

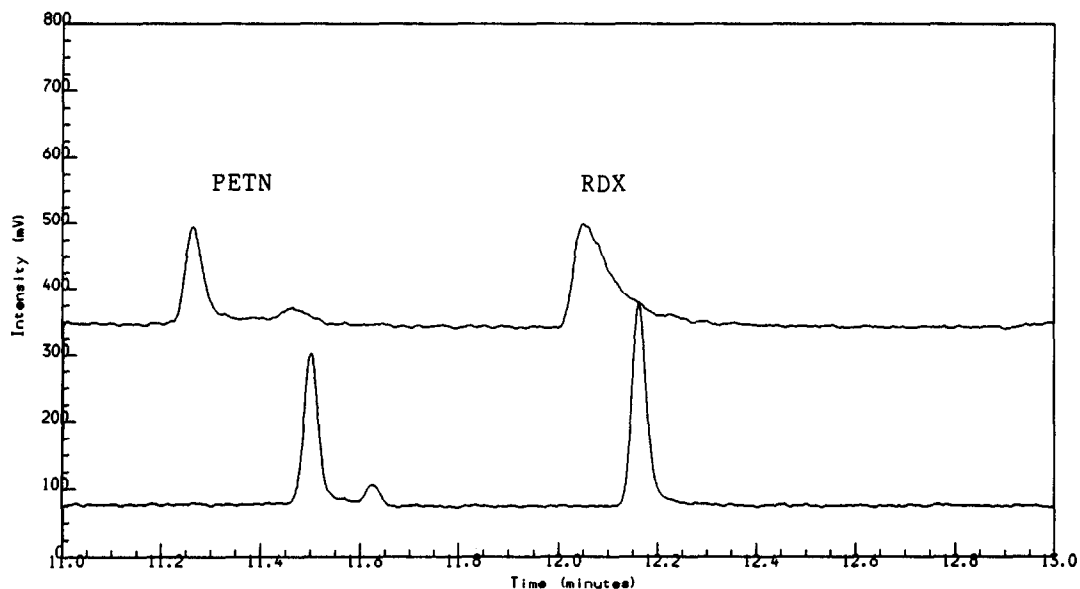


Fig. 1. Worsening of the peak shape of PETN and RDX because of contamination of the injector with polar substances.

the splitless mode in order to avoid any losses of explosives in the sample.

### 3.3. Capillary column

The column should have only a low polarity because the polar interaction of the nitro group, especially with PETN and RDX, can lead to irreversible adsorption on the stationary phase or decomposition of the explosives if the temperature is increased. However, it is necessary to have some functional groups in the stationary phase for selective interaction. This is because

with a pure polymethylsiloxane (OV-1) the separation of PETN and RDX is not possible. A small amount of phenyl groups in the stationary phase such as that found in a polymethylphenyl(5%)siloxane (DB-5) enhances the selectivity of the column for the nitro compounds and good separations are obtained. Another problem is the column length. At the temperature at which PETN and RDX evaporate, the decomposition of these two compounds begins to take place. The decomposition is fairly slow, but these compounds should be eluted from the column as fast as possible if the temperature programme reaches this limit. There are two methods to achieve fast elution: the gas velocity can be increased or the column length can be shortened. Both are applied in the GC of explosives. The inlet pressure in the injector is increased to the point where injection by the usual type of syringe is just possible and the capillary column is not made longer than 10 m for DB-5. Columns of higher polarity should be shorter. In order to have a sufficient number of theoretical plates, *i.e.*, narrow peak shapes, the inner diameter of the columns should be only 250  $\mu\text{m}$ . The film thickness should be small to prevent peak broadening because of low diffusion velocities.

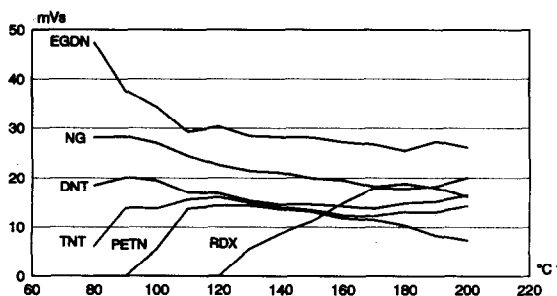


Fig. 2. Peak areas of explosives vs. injection temperature.

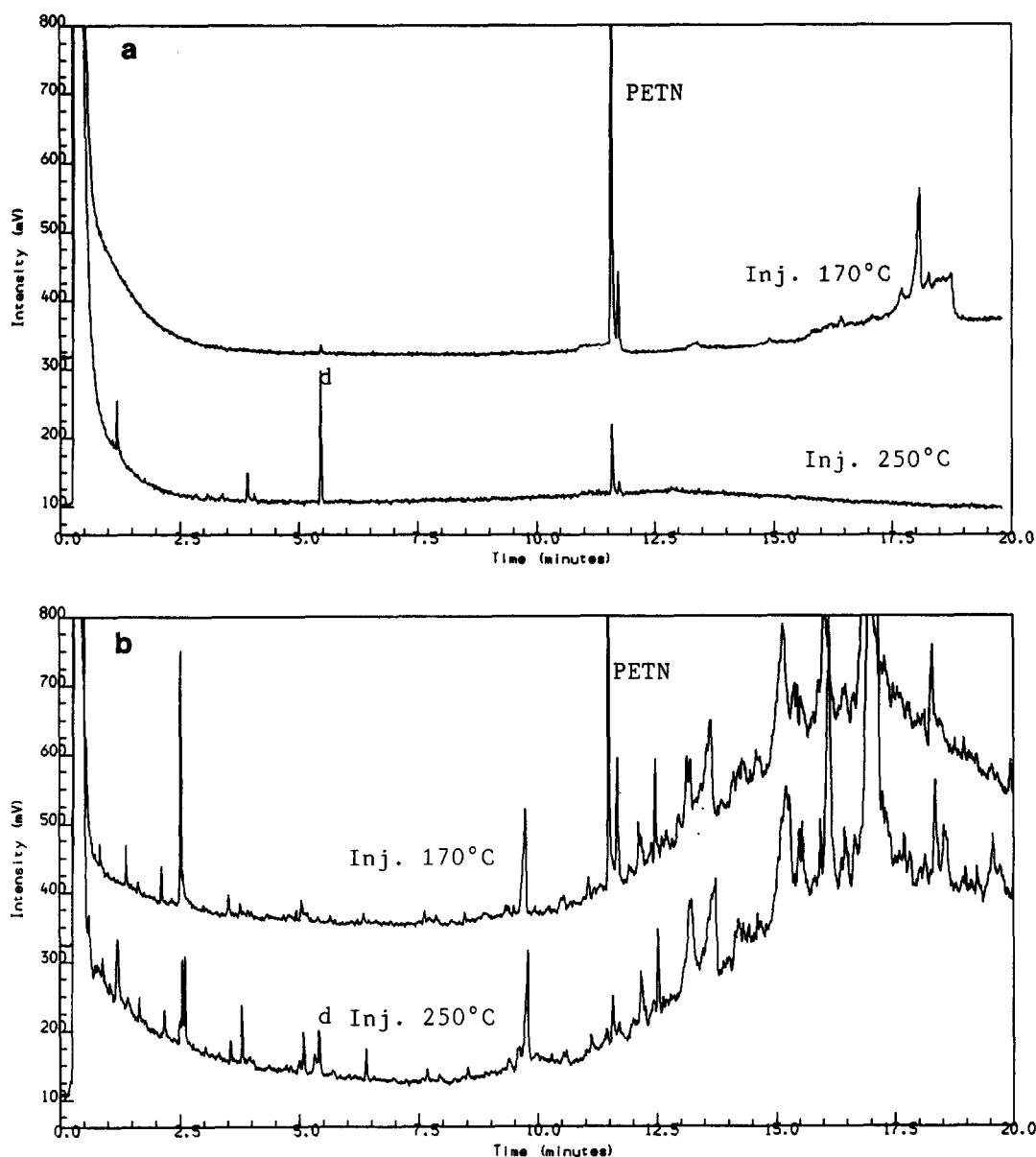


Fig. 3. (a) GC-TEA of pure PETN at injection temperatures of 170 and 250°C. d = Decomposition product of PETN. (b) GC-TEA of a real sample containing PETN traces at injection temperatures of 170 and 250°C.

### 3.4. GC detector

As described above, the detector has to be selective for explosives because of possible interferences from accompanying substances in the matrix. The mass spectrometer is well suited for

the determination of nitroaromatics, especially with negative chemical ionization (NCI) [11]. Problems with MS may arise in the identification of nitrate esters or RDX in complex matrices because the spectra are often not unequivocal if there is co-elution with other substances. In

addition, GC–MS is usually used for many other analytical problems in a laboratory and the system cannot be modified each time for the trace analysis of explosives. As an alternative the TEA, a chemiluminescence detector, has been introduced. This detector responds specifically to nitro and nitroso compounds. The eluting substances are pyrolysed at high temperature and nitrogen monoxide is formed. The reaction of nitrogen monoxide with ozone is followed by the emission of light, which can be measured by a photomultiplier. This operating principle produces only peaks for substances containing nitro or nitroso groups. A commercially available TEA was modified [8,12] to make the TEA compatible with capillary columns with small inner diameters and to enhance significantly both the sensitivity and the resolving power.

Despite the specificity for nitro and nitroso compounds, in some samples, in addition to the explosive constituents, many unidentified peaks appear in the chromatogram (Fig. 4). Therefore, confirmation with at least one different method is necessary. To confirm explosive traces, the alternative analysis must have a similar sensitivity and should have also a selective detector. A simple column change to a stationary phase of

different polarity in the GC–TEA system is one way of confirmation. If the identified peak has the same retention time on the new column as the standard, the probability is very high that the peak comes from the same substance. This polarity change of the column can be achieved with a stationary phase of higher phenyl content or with an additional content of cyanopropyl groups in polymethylsiloxane. In the latter column the interaction of the nitro compounds is stronger and retention changes will be observed depending on the chemical structure. The TEA detector can also be coupled to HPLC, which is based on a totally different separation mechanism. The greatest disadvantage of this approach is the lower sensitivity, which results from broad peak shapes and poor resolution.

Confirmation is also possible by GC–MS as already mentioned. Other GC detectors with lower selectivity such as the electron-capture detector or a nitrogen-specific detector can only be used if the matrix is relatively clean. When combined with high concentrations of chloro compounds or nitrogen-containing compounds the explosives peaks are often overlapped by these contaminants and identification of the explosive is impossible. For compounds such as

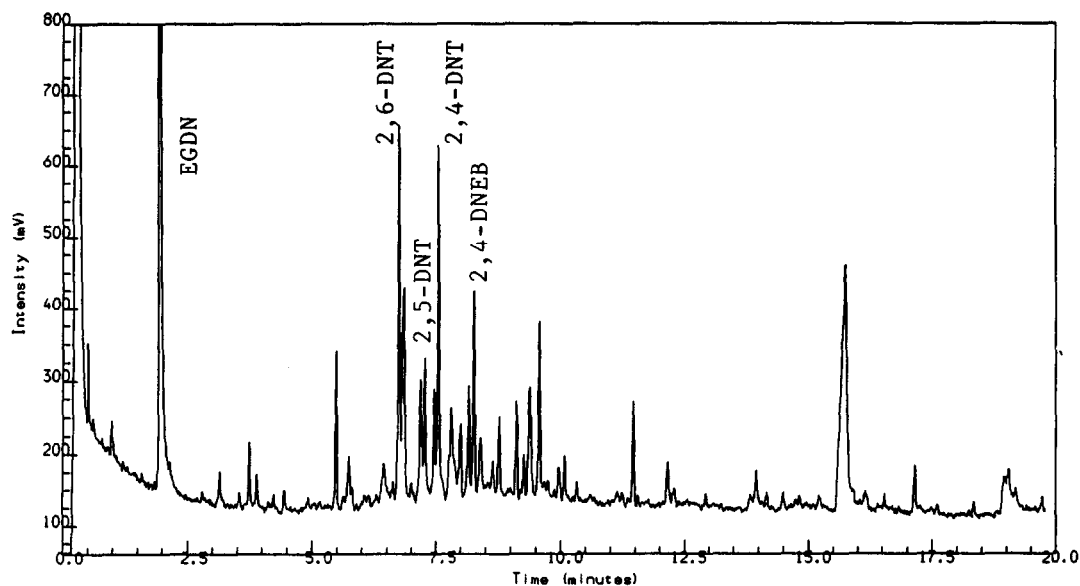


Fig. 4. GC–TEA of a real sample from a scene showing many unknown peaks.

nitrate esters and nitramines an alternative can be found with LC systems as described in the next section.

### 3.5. Liquid chromatography

The term liquid chromatography generally applies to all chromatographic methods with liquid mobile phases. The evolution of techniques in the last few years has concentrated on HPLC, mainly because of the direct coupling to sensitive detectors. For the trace analysis of explosives, detectors with selective responses are necessary. The mostly commonly used UV detector is non-specific for explosives because nitrate esters have very low chromophoric properties and are only detectable at wavelengths below 230 nm. At these wavelengths most organic substances have fairly high molar absorptivities and interfere with trace explosives. Just as in GC, selective detection must be based on reaction or interaction of the nitro group of the organic explosives. The TEA (chemiluminescence) detector can be applied in HPLC also, but it is more suitable for GC. Other selective HPLC detectors are the hanging mercury drop electrode (HMDE) [13] or UV photolysis followed by electrochemical detection [14]. Neither method has the same selectivity as the TEA and there are many substances that may interfere with the constituents of explosives.

Very specific detection can be achieved with a special postcolumn derivatization (PCD) [9]. The eluate from the HPLC column is subjected to UV irradiation and the nitro compounds split off nitrite ions. The nitrite ions are reacted with sulphanilamide and naphthylethyldiamine in a modified Griess reaction. The dye produced is detected in the visible range at 540 nm. This detection procedure is very specific, because only substances that produce nitrite ions by photolysis give peaks. Other dyes with absorption characteristics at 540 nm usually have a totally different HPLC behaviour from that of explosives. In Fig. 5 a chromatogram of a real sample analysed by HPLC–PCD is shown. Additional confirmation can be easily achieved by turning the UV irradiation

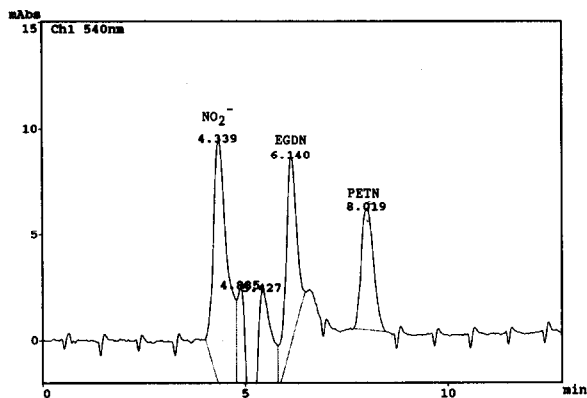


Fig. 5. HPLC–PCD of a sample after the explosion of a car bomb.

off. If the peak of the explosive then vanishes, it must be a nitro compound. The PCD detection shows very good sensitivities for nitrate esters (25–50 ppb) and nitramines (30–100 ppb). The sensitivity for nitroaromatics is ten times lower, because the C–NO<sub>2</sub> bond is fairly stable towards UV irradiation. The O–NO<sub>2</sub> and N–NO<sub>2</sub> bonds are so unstable that the NO<sub>2</sub> is separated very early in the light path and the further conversion of nitrite into nitrate must be suppressed by addition of sodium hydroxide to the eluent in order to have high sensitivity.

HPLC has special advantages in the analysis of very dirty samples because the columns and the eluents are more stable to contamination from accompanying substances in extracts of debris or dust. It is also possible to analyse explosives that cannot be evaporated without decomposition such as octogen (HMX), but the latter seldom appear in real cases. The essential disadvantage of HPLC is the low resolving power and the broad peak shapes. In reversed-phase HPLC, which is the most commonly used phase system, the several isomers of nitroaromatics cannot be completely separated as necessary to allow the calculation of the isomer distribution [15]. This problem can only be solved by using normal-phase HPLC, but with normal-phase systems most of the selective detection methods cannot be used and the column and eluent behaviour is often unstable.

Overall, HPLC is well suited for the trace analysis of explosives, but if GC-TEA is available then HPLC should be used as the second analytical step.

### 3.6. Ion chromatography

In the trace analysis of explosives, IC is applied to the inorganic part. The determination of inorganic ions is primarily concerned with anions. Anion determination is important if the organic tests reveal that no military high explosive or plastic explosive was involved, or that a dynamite is assumed. With a dynamite, nitrate should be found in the anion chromatographic analysis. If no organic traces are found, a purely salt-based explosive can be presumed and anion determination must be performed with respect to chlorate, nitrate, perchlorate or sulphate.

Cation chromatography is also applicable to the trace analysis of explosives, but usually only ammonium is significant. Instead of modifying the ion chromatograph, ammonium can be specifically detected in small amounts using Nessler's reagent.

The presence of nitrate in the water extract from debris or dust is not specific for explosives.

The interpretation of the nitrate content is always very difficult, because there are other sources from which nitrate may have originated, *e.g.*, fertilizers. Nitrate from commercial explosives, especially in post-blast analysis, is at a very low concentration and often in the range of the environmental level, except for low explosives such as flash powder or black powder. Sometimes the ratio to the ubiquitous chloride helps to establish the significance of the nitrate level [16], but in post-blast analysis such determinations are possible only with samples taken at very short distances from the centre of the explosion (Fig. 6). The presence of nitrate can only be related to explosives if there is a fairly large amount and if other analytical results support a nitrate-containing explosive. Other analytical results may be the finding of ammonium; traces of explosive oils and/or nitroaromatics (dynamites/European dynamites); significant amounts of oils and/or waxes (emulsion explosives) [17]; microscopic identification of microballons (emulsion explosives) [18]; unreacted particles of gelatinous nitrocellulose (dynamites) [15]; fragments of explosive wreckage paper (commercial explosives).

One problem with IC is the relatively low

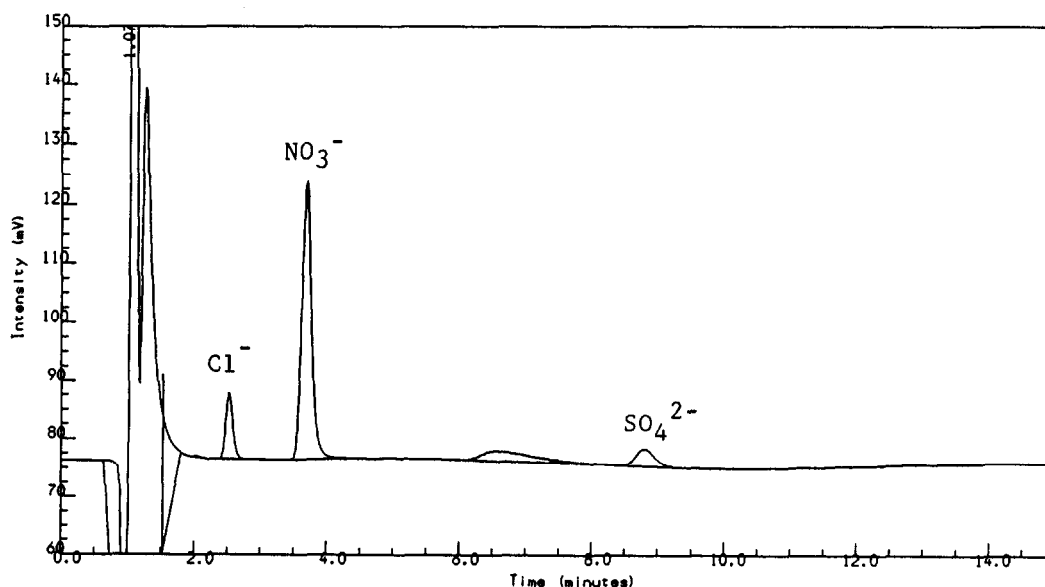


Fig. 6. IC of a swab taken at a 1-m distance after the explosion of 500 g of a dynamite.



sensitivity if it is used as an additional method for the trace analysis of inorganic salts after positive results for explosive oils or nitroaromatics in organic trace analysis. This appearance is typical with European dynamites, which contain several organic nitro compounds in addition to the nitrate salt. The sensitivity of IC with direct conductivity detection is about 1 ppm for nitrate. The injection of 100  $\mu\text{l}$  of the water extract corresponds to 100 ng. Presuming a total amount of 1 ml of concentrated water extract, the limit for a positive result is 1  $\mu\text{g}$  of nitrate in the original sample (assuming 100% recovery). A European dynamite usually contains 5–40% of explosive oils and 2–10% of nitroaromatics. The sensitivity with GC–TEA detection is about 100 pg for an explosive oil. The injection of 1  $\mu\text{l}$  from an extract concentrated to 100  $\mu\text{l}$  corresponds to 10 ng in the original sample (assuming 100% recovery). If there was a very low content of 5% of explosive oil in the dynamite, the nitrate content was 0.2  $\mu\text{g}$  at the most, which is below the limit of detection in IC. The real relationships are often worse for IC.

Inorganic analysis is never successful when explosive traces were found in the organic analysis. The major importance of IC is in the field of home-made mixtures of chlorates, the analysis of residues of black powder or if pyrotechnic mixtures have been used. Mixtures of chlorates with different types of fuels in gas bottles or steel pipes have frequently been used in Europe. In post-blast analysis large amounts of chloride dominate the ion chromatogram. An enrichment of chlorate traces can be achieved by extracting the dried water extract with acetone, and after evaporation of the acetone, making a new water extract [16]. Chlorate salts are more soluble in acetone than chloride salts.

Residues of black powder can be recognized from the unburnt nitrate and the large amount of sulphate [18]. Typical residue components such as thiocyanate are difficult to determine in the residue by simple IC with direct conductivity detection. Pyrotechnic mixtures with fast burning rates usually contain perchlorates and aluminium or magnesium powder. The determination of perchlorate can be performed by IC, but often

the eluent has to be changed to a higher ionic strength and perchlorate tends to have a bad peak shape.

Some of the difficulties with IC can be avoided if the ions are determined by capillary electrophoresis (CE). This method permits a very fast, highly efficient and sensitive determination of ions and will certainly be surely helpful in the analysis of explosives residues [7].

#### 4. Conclusions

The trace analysis of explosives places its own demands on the chromatographic methods applied. The complex matrix of the sample that has to be analysed for explosives traces makes a selective analysis inevitable. The chromatographic separation has to be highly efficient and the detection selective for explosives. GC is the method of choice for the determination of the organic constituents of explosives. GC is easy to combine with MS or nitro/nitroso-specific TEA detection. The highly efficient separation with the capillary column permits the analysis of explosive oils, isomers of nitroaromatics and the high explosive PETN and RDX in one run. HPLC in combination with selective detection can be used as alternative method to GC for confirming explosives traces. HPLC and TLC are very helpful in the trace analysis of explosives with the disadvantage of lower resolving power and lower sensitivity than GC. IC is used for the determination of the inorganic constituents of explosives. In particular, anion chromatography can be applied to determine characteristic salts used as oxidizers in many commercial and home-made explosives.

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