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TRACE ANALYSIS OF EXPLOSIVES BY THERMOSPRAY HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY–MASS SPECTROMETRY

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SUMMARY

A series of explosives were analyzed by thermospray high-performance liquid chromatography–mass spectrometry (TSP-HPLC–MS). Both positive and negative ion spectra were acquired in thermospray and chemical ionization (filament-on) modes. The explosives proved most sensitive in the negative ion mode under chemical ionization conditions. The spectra for the explosives analyzed provided molecular weight information with few fragment ions. Detection limits from 200 pg for trinitrotoluene to 5 ng for ammonium picrate were obtained under full scan mass spectrometer conditions. TSP-HPLC–MS proved useful in separating and identifying components in commercial explosive mixtures without interferences from plasticizers as well as in detecting explosives from hand swabs with excellent sensitivity and specificity. The plasticizers primarily were detected in the positive ion mode while the explosives were most sensitive with negative ion detection.

INTRODUCTION

The analysis of explosives has become of increasing importance in both forensic and environmental applications¹. The analysis of post-explosion residues in debris material is important in the criminalistic investigation of a bombing because it can help find the link between the explosive used and the suspect. The resulting analysis of the explosive could later on be used as evidence in judicial proceedings. The identification of the type of explosive is often complicated by the small quantities of material available after separation from the debris on the explosion site.

During the handling of explosives, particles of explosives may adhere to the person's hands. Removal of explosive residues from the hands of suspects and their identification is therefore important. The suspect's hands are swabbed with cotton swabs soaked in a solvent. The extracts are then analyzed for traces of explosives. Only trace amounts of explosives, mixed with a variety of other organic compounds, are expected in such cases².

Environmental contamination by explosives is becoming an important issue in the manufacturing and disposal of explosives. Environmental trace analysis of water and soil contaminated by explosives has become necessary due to the discharge of wastewaters produced in ammunition manufacturing and burial of obsolete ammunition and explosives in the soil.

The requirements of an analytical method for these applications should include good separation, high specificity and sensitive detection. The liquid chromatography-mass spectrometry (LC-MS) system seems to be the method of choice for these applications as it is also suitable for thermally sensitive and involatile compounds.

Several LC-MS systems have been used for the analysis of explosives³⁻⁶. These systems used the split-type direct liquid introduction (DLI) high-performance liquid chromatography (HPLC)-MS interface with either positive or negative chemical ionization or HPLC with off-line chemical ionization MS detection. The sensitivity of the DLI system is limited because only 1-2% of the effluent enters the mass spectrometer. On the other hand, off-line techniques require a much greater effort to collect and concentrate the fractions and can suffer a loss of the HPLC resolution.

In an effort to find a more sensitive LC-MS method for these applications, a thermospray (TSP)-LC-MS system has been used for the separation and identification of a series of standard and technical explosive mixtures, using positive and negative ion detection, with and without filament chemical ionization. The TSP interface appears to offer the greatest capability for analyzing explosives separated by HPLC with high sensitivity. The interface allows high flow-rates (near 2.0 ml/min) of aqueous solvents and volatile buffers into the system and provides the gentle ionization necessary to obtain molecular ion⁷⁻¹⁰.

The pure compounds studied included 2,4,6-trinitrotoluene (TNT), 2,4,6-N-tetranitro-N-methylaniline (tetryl), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX), pentaerythritol tetranitrate (PETN) and ammonium nitrate. Two technical mixtures were examined, one an explosive used in letter bombs containing RDX and PETN and another explosive containing TNT, nitroglycerin (NG), 2,4,6-trinitrophenol (picric acid), ammonium nitrate and 2,4-dinitrotoluene (DNT).

EXPERIMENTAL

Samples

Pure and technical explosives were obtained from the Israeli Police Analytical Laboratory. The standards were dissolved in acetone or acetonitrile (HPLC-grade) to known concentrations. Solvent used in this study were HPLC-grade and were filtered through 0.45- μ m filters before use. Hand swabs on commercial explosive mixtures were performed by holding about 1 g of explosive in one of the author's hands for 1 min followed by wiping the hands with a paper towel. After 2 min a cotton swab soaked in acetone was wiped across the hand. This swab was washed in 4 ml acetone to remove the residual explosives from the cotton and then the acetone was evaporated with nitrogen to about 0.2 ml. About 50% of the extract was injected for HPLC-MS analysis.

HPLC-MS

Many details of the HPLC-MS system and operation have been given earlier¹¹. The HPLC separations were performed on a Zorbax C₈, 25 cm × 4.6 mm I.D. column using a gradient of 25% methanol to 75% methanol in water containing 0.1 M ammonium acetate at 1.4 ml/min in 15 min. The final conditions were held for 10 min before cycling back to the initial conditions for the next analysis.

The Vestec thermospray interface (Vestec, Houston, TX, U.S.A.) was used for the HPLC-MS analysis of explosives. The vaporizer was operated at 170–180°C which resulted in the most intense and stable ion current for TNT. Source block temperatures from 120 to 300°C (by 50°C) were evaluated for both positive and negative ion detection of explosives. Low temperatures were preferred if molecular weight information was to be obtained from these thermally unstable compounds. However, temperature played an important role in negative ion detection. Electron-capture ionization of explosives showed the best sensitivity at the lowest operating temperatures (120°C) while providing abundant molecular weight information. Positive ion detection was less temperature-dependent and the source could be operated at 120–180°C without significant changes in the spectra or sensitivity. When the TSP interface was operated in the chemical ionization mode, a 1000 eV filament was turned on and the emission set to 0.15 mA. The mass spectrometer was operated under full scan acquisition (m/z 150–650) with a 2-s scan. All detection limits were obtained using full scan acquisition.

RESULTS AND DISCUSSION

The positive ion and mass chromatograms (TSP ionization) of a standard mixture are shown in Fig. 1. Only three components were observed: RDX, HMX and tetryl. The others (PETN, ammonium picrate and TNT) were not amenable to TSP ionization in the positive ion mode. The mass spectrum of RDX contained one major ion at m/z 240 which is due to $[M + NH_4]^+$. These types of ions are typical to TSP-LC-MS where ammonium acetate is used as a buffer^{9,11}. Similarly, the mass spectrum of HMX contained one major ion at m/z 314, again due to $[M + NH_4]^+$.

The mass spectrum of tetryl (Fig. 2) had its base peak at m/z 290 due to $[M + NH_4 - CH_3]^+$, a common ion in TSP-LC-MS. Other major ions were $[M + NH_4]^+$ at m/z 305 and the ion at m/z 242 which is a typical ion in both the electron ionization and chemical ionization mass spectra of tetryl^{12,13}. This ion is due to loss of CH_3NO from the molecular ion.

Switching on the filament in positive ion detection mode did not produce any different mass spectra in this mixture other than some additional low abundance fragment ions.

The negative ion and mass chromatogram (TSP ionization) of the same standard mixture (Fig. 3) detected all six components. The mass spectrum of TNT contained one major ion, $[M - H]^-$, at m/z 226. The mass spectrum of tetryl (Fig. 4) had its base peak at m/z 241 due to the $[M - NO_2]^-$ ion. It contained another major ion at m/z 257, due to $[M - NO]^-$. Other characteristic ions, but of low abundance, were $[M + CH_3O]^-$ at m/z 318 and $[M + H]^-$ at m/z 288.

The mass spectrum of RDX contained mainly one ion, $[M + CH_3COO]^-$, at m/z 281 (typical to TSP-LC-MS) and a low abundance ion (<2%)

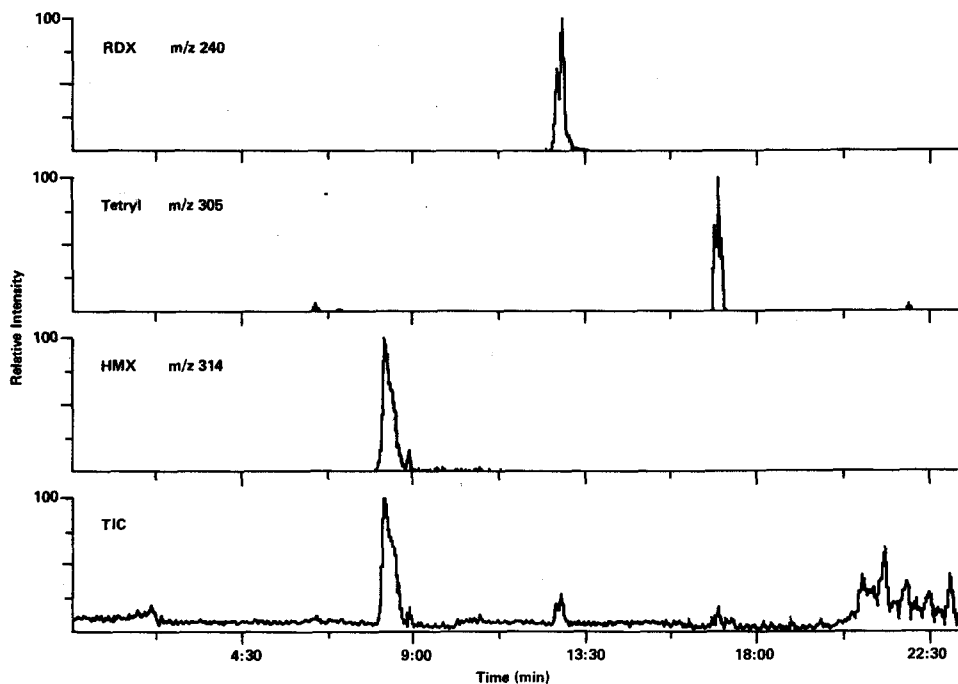


Fig. 1. Ion chromatogram and total ion current (TIC) for positive ion TSP ionization HPLC-MS analysis of the standard explosive mixture ($5 \mu\text{g}$ injected). Note only RDX, HMX and tetryl were detected in the mixture. TNT, ammonium picrate, and PETN were not detected in the positive ion mode.

$[2M + \text{CH}_3\text{COO}]^-$ at m/z 503. The mass spectrum of HMX contained one major ion, $[M + \text{CH}_3\text{COO}]^-$, at m/z 355. Also, an ion at m/z 651, due to $[2M + \text{CH}_3\text{COO}]^-$, having an abundance of about 1% was observed. The mass spectrum of PETN (Fig. 5A) had a base peak at m/z 375, due to $[M + \text{CH}_3\text{COO}]^-$ and major ions at m/z 378, due to $[M + \text{ONO}_2]^-$, and at m/z 315, due to $[M - \text{H}]^-$ (ref. 14). An additional series of ions were observed at m/z 330, 285, 240 and 195. These ions were formed by

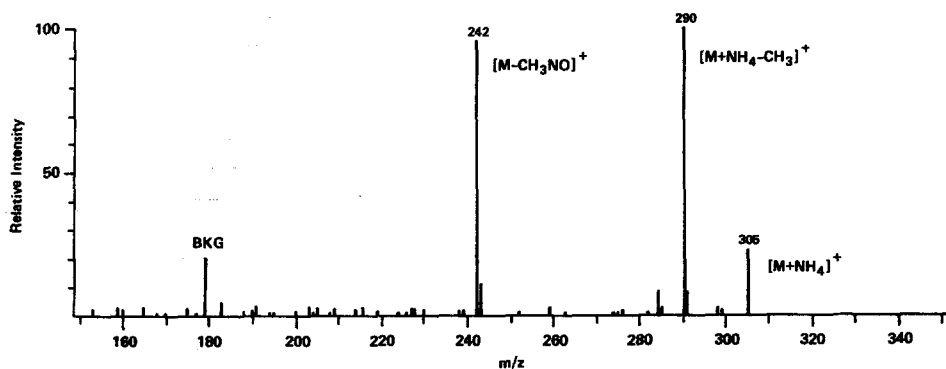


Fig. 2. TSP ionization positive ion spectrum of tetryl.

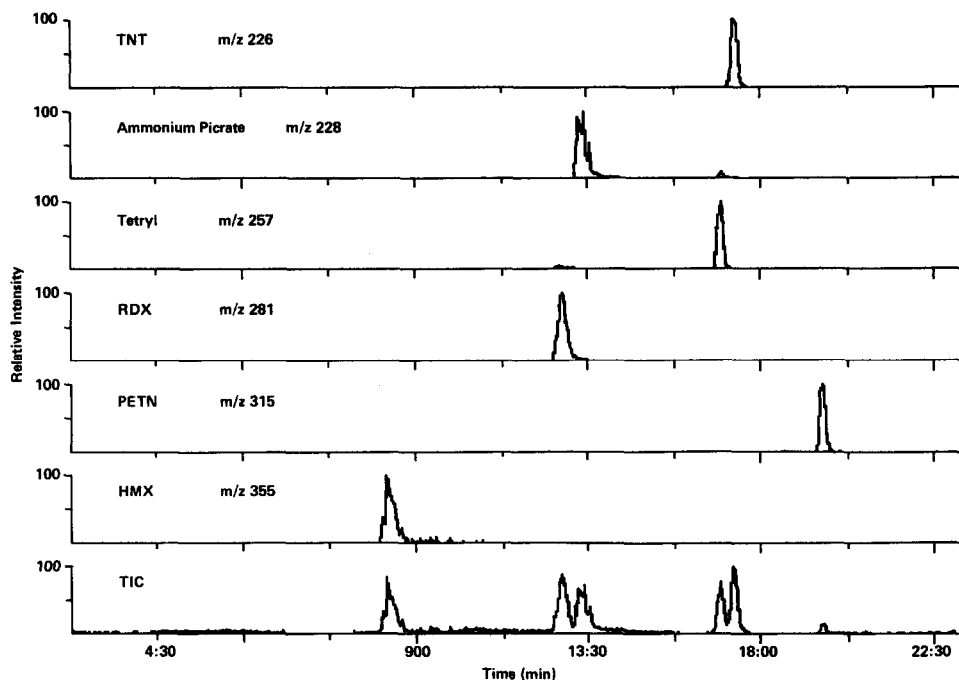


Fig. 3. Ion chromatograms and TIC chromatogram for negative ion TSP ionization of standard explosive mixture (5 μg injected).

consecutive losses of 45 mass units from the $[\text{M} + \text{CH}_3\text{COO}]^-$ ion at m/z 375. In order to explain the mechanistic formation of these ions we looked at the negative ion mass chromatogram of pure PETN (Fig. 5B). The chromatographic mass peak due to $[\text{M} + \text{CH}_3\text{COO}]^-$ was broader than the $[\text{M} - \text{H}]^-$ peak. Each consecutive loss of 45 mass units produced an even broader peak: the peak at m/z 330 was broader than the one at m/z 375, and the peak at m/z 285 was broader than the one at m/z 330. This consecutive loss of 45 mass units could be due to losses of COOH from

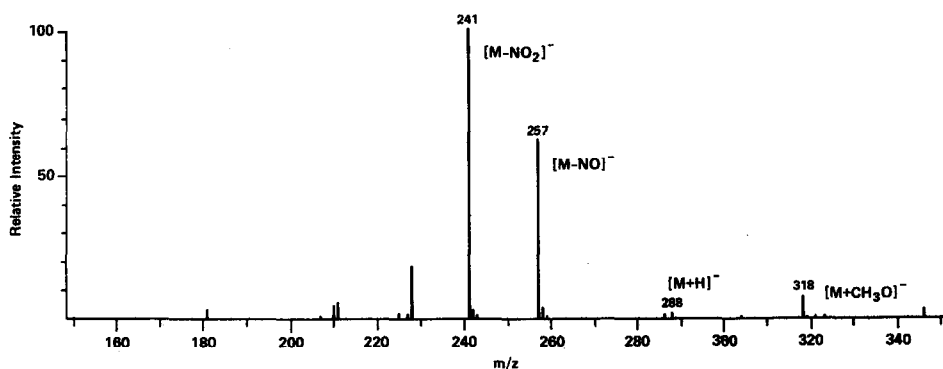


Fig. 4. TSP ionization negative ion spectrum of tetryl.

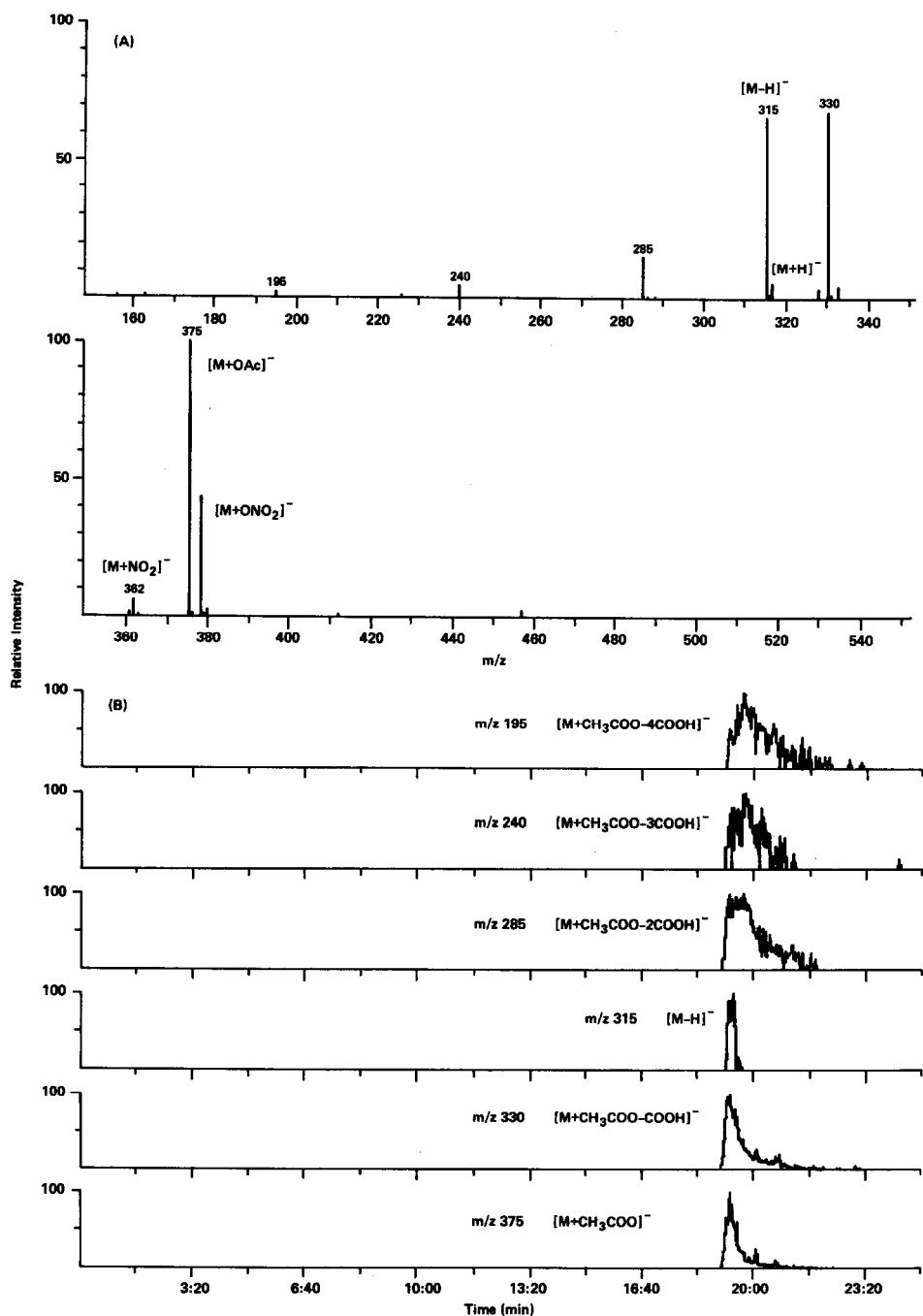


Fig. 5. (A) TSP ionization negative ion spectrum of PETN. (B) Ion chromatograms for PETN showing $[M+CH_3COO]^-$ anion with consecutive losses of 45 mass units (m/z 330, 285, 240, 195). These decomposition ions exhibit an increasing peak width with decreasing mass compared to the $[M-H]^-$ ion at m/z 315.

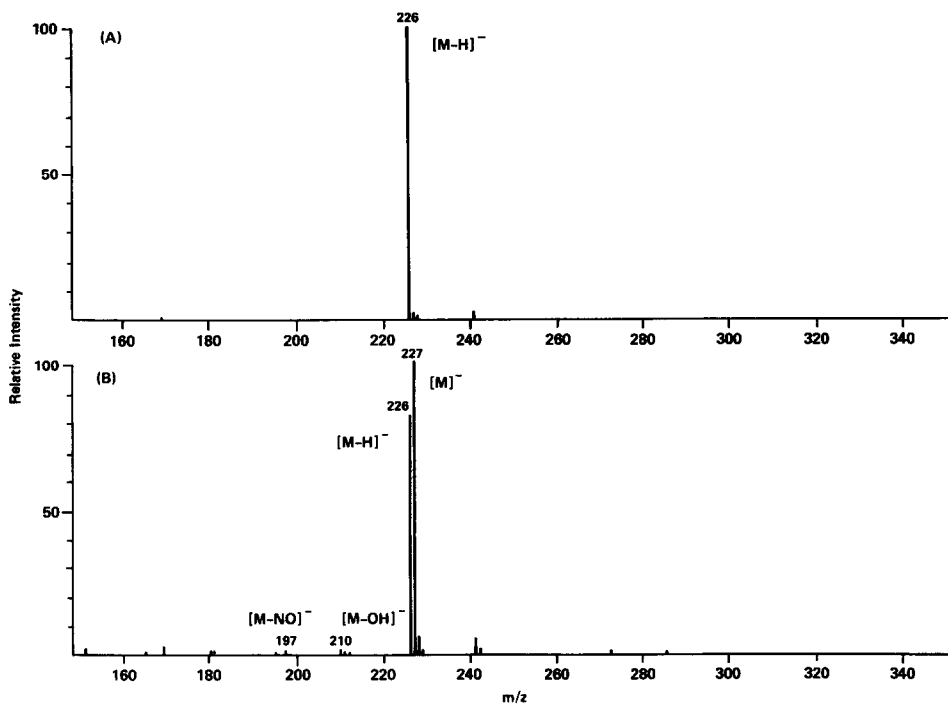


Fig. 6. HPLC-MS spectra of TNT. (A) Negative ion detection TSP ionization. (B) Negative ion detection filament ion chemical ionization.

$[\text{C}(\text{CH}_2\text{ONO}_2)_4 + \text{CH}_3\text{COO}]^-$ ion followed by rearrangements. Also, this could have occurred through thermal decomposition of $[\text{PETN} + \text{CH}_3\text{COO}]^-$ on the hot source block surface. The peak broadening and tailing behavior is probably explained by the condensation of PETN aerosol on the source block wall with subsequent thermal decomposition and possible reaction with the solvent system¹⁵. More experiments with isotopically-labelled PETN need to be performed to verify these assumptions.

The mass spectrum of ammonium picrate had one major ion, $[\text{M} - \text{NH}_4]^-$, at m/z 228. The loss of NH_4 from ammonium picrate had been observed in its positive ion mass spectra in both electron ionization¹² and chemical ionization¹⁶.

When switching on the filament, the only difference was in the mass spectrum of TNT. Fig. 6A and B shows the mass spectra of TNT without and with filament-generated reagent ions respectively. In addition to the $[\text{M} - \text{H}]^-$ ion, an $[\text{M}]^-$ ion at m/z 227 was produced, forming the base peak. Low abundance ions^{17,18} were observed at m/z 210, $[\text{M} - \text{OH}]^-$, and at m/z 197, $[\text{M} - \text{NO}]^-$.

Sensitivity

Better sensitivity was obtained in both positive and negative ion mode with filament-on. In the positive ion mode, when a sample of the standard mixture was injected, only RDX, HMX and tetryl were observed, as stated earlier. Less than 5 ng of RDX and HMX could be detected. However, the minimal amount of tetryl which

could be detected was more than 50 ng. In the negative ion mode, 200 pg of TNT, 1 ng of RDX, HMX, and PETN (Fig. 7) could be detected. The detection limits for tetryl were determined to be 5 ng and ammonium picrate to be 50 ng.

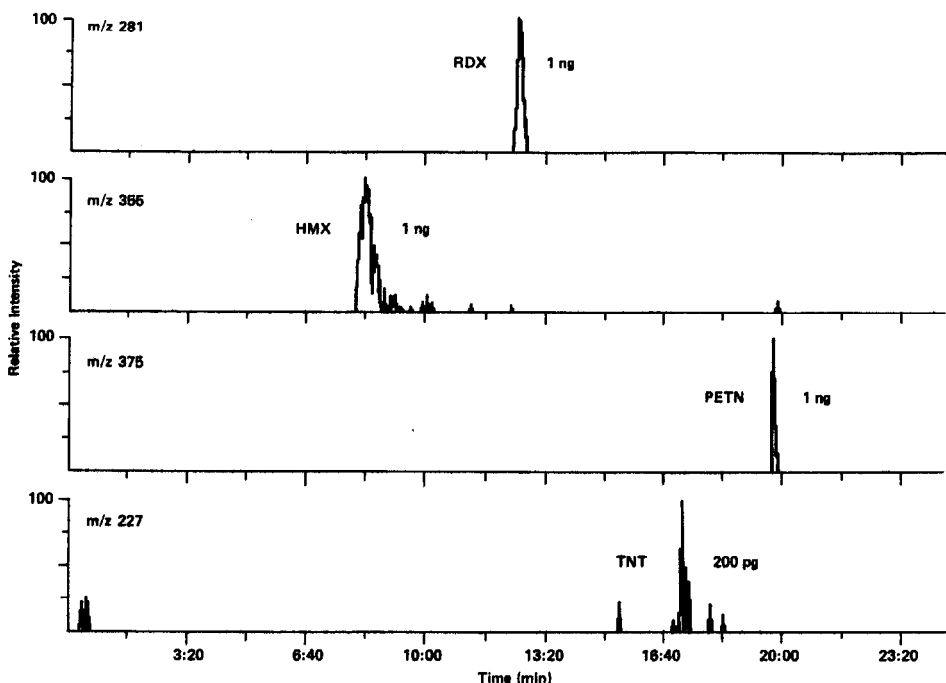


Fig. 7. HPLC-MS ion chromatograms for 200 pg of TNT and 1 ng of each of RDX, HMX and PETN using negative ion detection with filament chemical ionization.

Analysis of commercial explosive mixtures

The analysis of a letter bomb explosive using both positive and negative filament chemical ionization is shown in Fig. 8. It is interesting to note that positive ion detection was specific for the plasticizers (early eluting peaks in the total ion current) while negative ion detection was specific for the explosives. The letter bomb explosive was made from a mixture of RDX and PETN (RDX is also detectable in positive ion detection, but with less sensitivity).

Another explosive mixture examined by TSP-HPLC-MS is shown in Fig. 9. This technical explosive mixture contained DNT, TNT, NG, picric acid and ammonium nitrate along with various isomers of the above ingredients. At least three isomers of TNT were observed at m/z 227. The isomer having the highest concentration was the 2,4,6-isomer. This was proven by comparing the retention time of this isomer with the retention time of a standard of 2,4,6-TNT. Similarly, the three isomers of DNT, observed at m/z 182, contain the 2,4-DNT at highest concentration. The mass spectrum of picric acid contained one major ion, $[M]^-$ at m/z 229. The

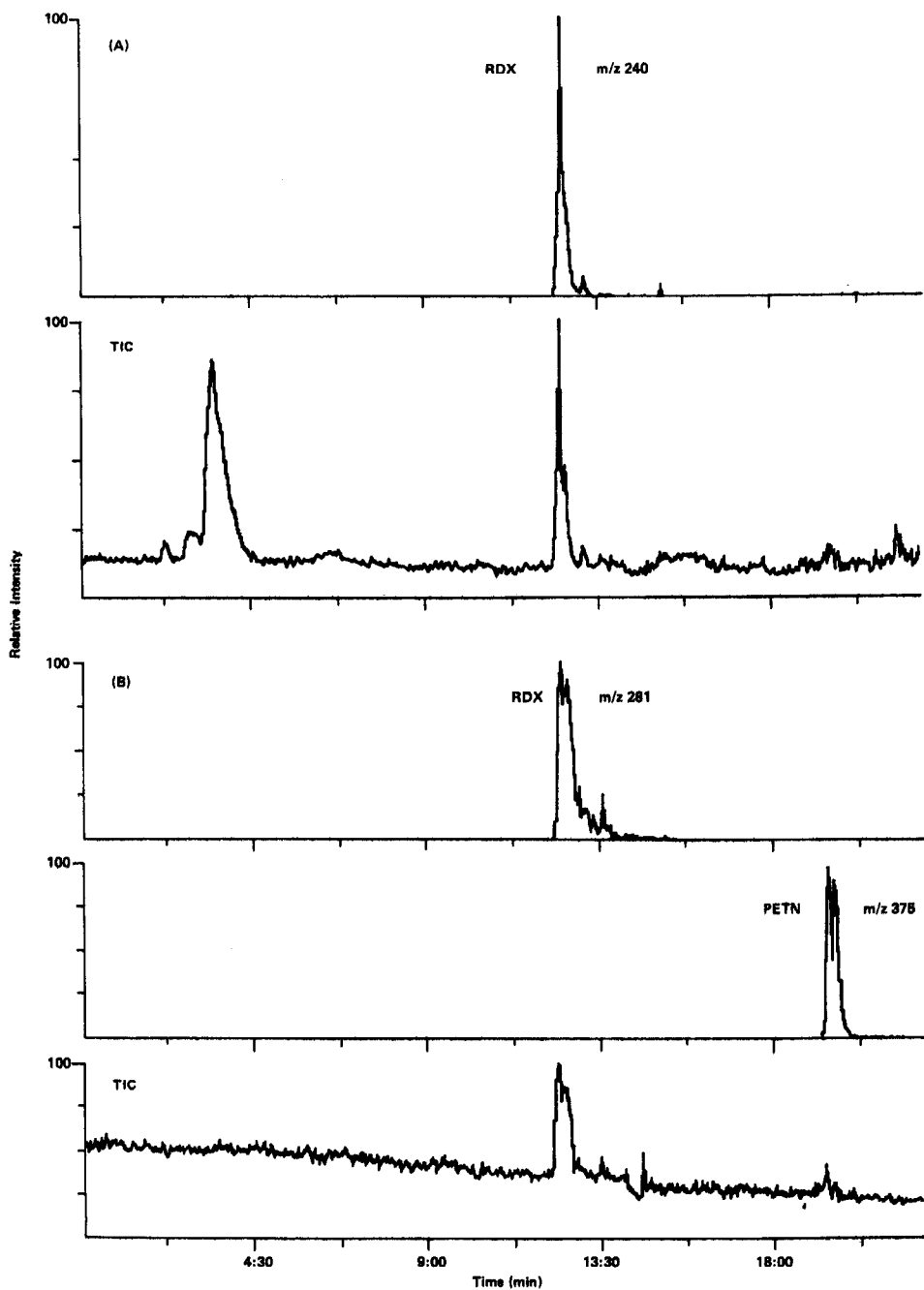


Fig. 8. HPLC-MS ion and TIC chromatograms for the analysis of a commercial letter bomb explosive using filament chemical ionization. (A) Positive ion detection. (B) Negative ion detection.

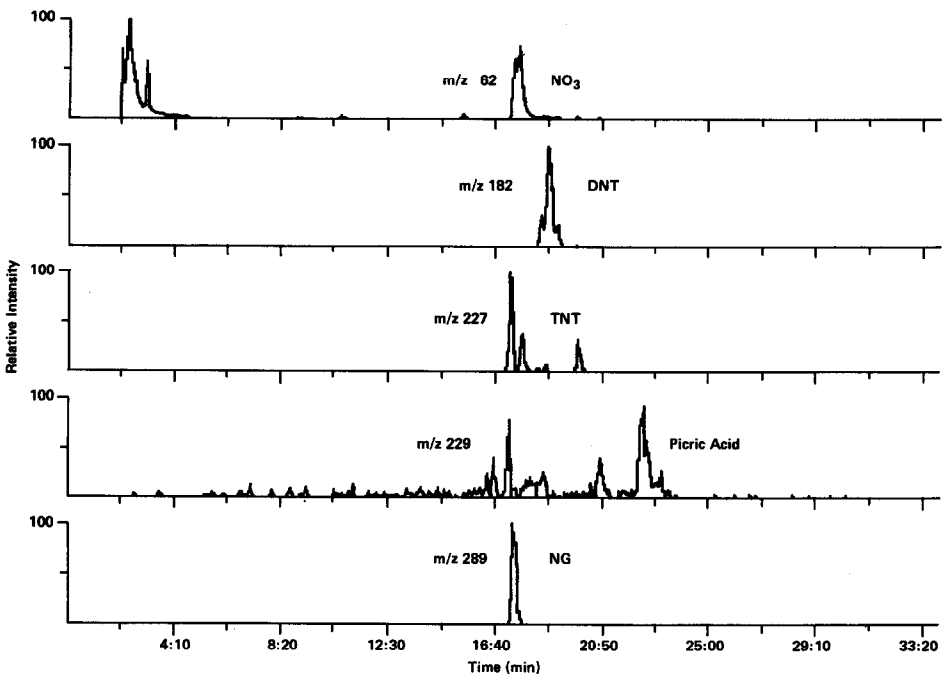


Fig. 9. HPLC-MS ion chromatograms for ammonium nitrate, DNT, TNT, picric acid and NG found in a technical explosive using filament negative ion chemical ionization.

other peaks in the ion chromatogram were due to isotope ions from TNT and isomers of picric acid. Ammonium nitrate produced one major ion, $[\text{NO}_3]^-$, at m/z 62. The mass spectrum of the last component, NG, (Fig. 10) had a base peak at m/z 289, formed by $[\text{M} + \text{ONO}_2]^-$ (ref. 14). Additional major ions in the spectrum were $[\text{M} + \text{CH}_3\text{COO}]^-$ at m/z 286, $[\text{M}]^-$ at m/z 227, and $[\text{M} - \text{H}]^-$ at 226. As in PETN, two ions were also formed by consecutive losses of COOH from the $[\text{M} + \text{CH}_3\text{COO}]^-$

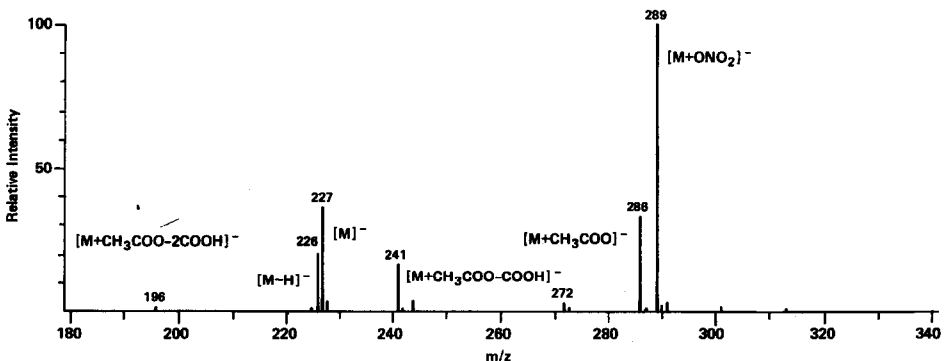


Fig. 10. Negative ion HPLC-MS spectrum of NG from a technical explosive mixture (filament chemical ionization).

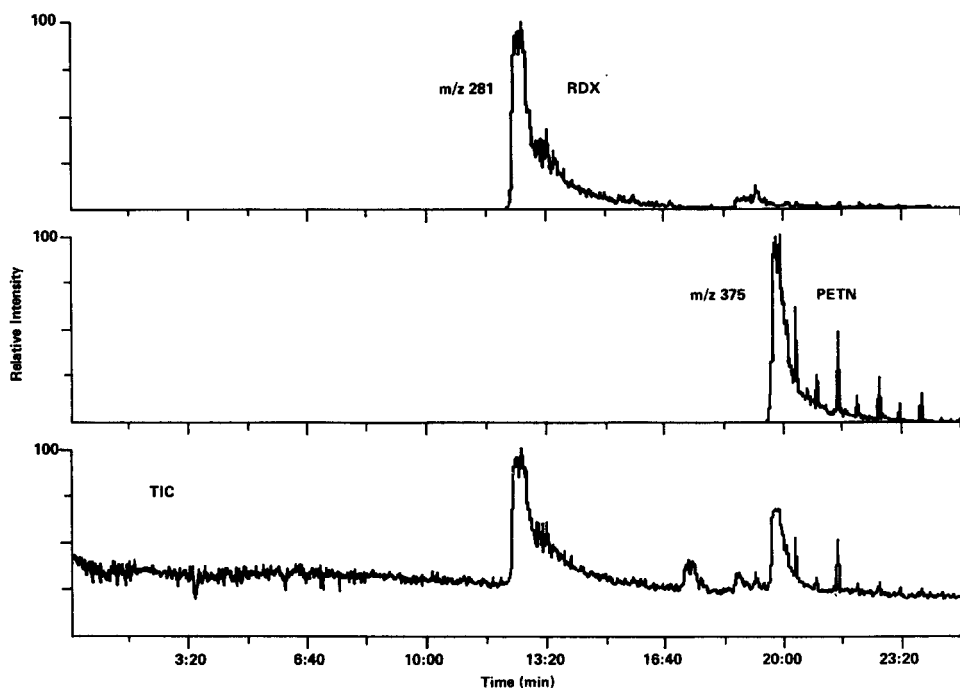


Fig. 11. Hand swab analysis of a letter bomb explosive in negative filament chemical ionization mode. The HPLC-MS ion chromatograms show the presence of RDX and PETN with few interferences.

ion: at m/z 241 and m/z 196. Also, NG exhibited an ion at m/z 62 $[\text{NO}_3]^-$ as seen in Fig. 9.

The positive ion chromatogram (filament chemical ionization) of this mixture does not show any of the explosive components but reveals three peaks which represent the additives (including the plasticizer) of this explosive mixture. The retention times of these three peaks were similar to the retention times of the additive peaks in the ion chromatogram of the letter bomb mixture (Fig. 8A). In order to demonstrate the sensitivity of the system for the detection and identification of traces of explosives, each one of the explosive mixtures was held (in two separate experiments) by one of the authors. The acetone extracts produced the mass chromatogram presented in Fig. 11 (letter bomb explosive) and Fig. 12 (technical explosive). The main explosive ingredients in both experiments can be clearly characterized and match the previous recorded spectra. The high ion count recorded points out that, even in cases where the time of contact with the explosive was shorter, or a longer time has passed between the handling of the explosive and the hand swab, it would be possible to detect the explosives in the extracts. However, this should be the subject of a separate study.

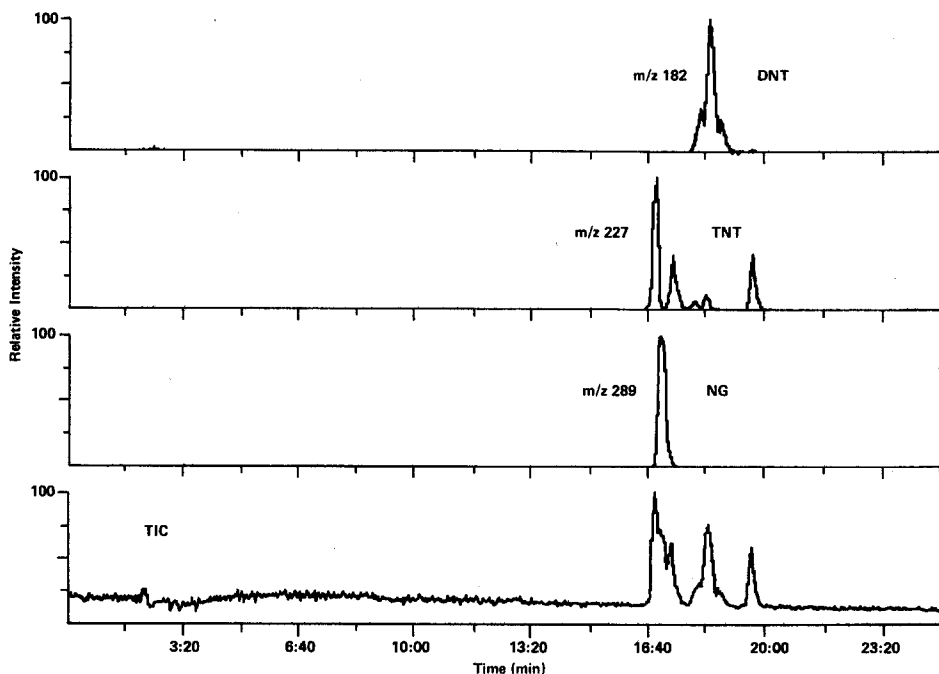


Fig. 12. Hand swab analysis of a technical explosive in negative filament chemical ionization mode. The HPLC-MS ion chromatograms clearly show the presence of DNT, TNT and NG with no interferences.

CONCLUSIONS

TSP-HPLC-MS proved very sensitive and specific for analysis of explosives. Sensitivities of a number of explosives are comparable to other analytical techniques for detection of explosive residues². The real advantage of TSP-HPLC-MS is in the area of specificity. No interference with the target explosive was detected in the commercial mixture or hand swab extracts. Even when components do co-elute or elute very closely (such as in the case of the technical explosive containing DNT, TNT and NG which have very close retention times) the individual components can be resolved by mass.

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