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Analysis of Explosives by Liquid Chromatography/Thermospray/Mass Spectrometry

ABSTRACT: We have investigated the application of liquid chromatography/thermospray/ mass spectrometry (LC/TSP/MS) to the separation and identification of commercial and military explosives. The LC was performed using a reverse phase column with an isocratic mobile phase and a flow rate of 1.5 mL/min. These conditions resulted in retention times of less than 3 min for common explosives, permitting rapid analysis. The TSP was operated in the filament-on ionization mode which yielded unique spectra for the following explosive compounds: 1,3,5-trinitrotriazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,4,7-tetraazacyclooctane (HMX), trinitrotoluene (TNT), dinitrotoluene (DNT), pentaerythritoltetranitrate (PETN), nitroglycerin (NG), diphenylamine (DPA), and monomethylaminenitrate (MMAN). The majority of explosives yielded only negative ion thermospray mass spectra, which exhibited a strong $[M+CH_3COO]^-$; however, components of double-based smokeless powders also yielded positive ion spectra. An important forensic science application of this work is the identification of commercial and military explosives. Spectra which were obtained from the residues of improvised explosive devices of military C4 and a double-based smokeless powder allowed identification of the pure explosive compounds. LC/TSP(filament-on)/MS provided limits of detection less than 2.5 picograms for PETN.

KEYWORDS: forensic science, explosives, chemical analysis, liquid chromatography, thermospray, mass spectrometry

The analysis of explosives (Table 1) has become increasingly important in several analytical areas. In forensic science, the increase in terrorist activity in recent years has generated the need for improved analytical methods that can accurately identify explosives and explosives residue. The analysis of postblast residues in debris material is an important aid for a bombing investigation because it may provide the link between the explosive used and a suspect. The discovery that some explosives are mutagenic has increased the environmental need to monitor explosives [1]. Environmental analysis of water and soil contaminated by explosives has become necessary because of the waste waters produced in ammunitions manufacturing and to the burial of ammunitions and explosives in the soil. In the medical field, there is an increasing need to monitor vasodilators such as PETN, NG, and their metabolites

TABLE 1—*Pure explosive compounds and molecular information.*

Common Name	Proper Name	Molecular Formula	Nominal Molecular Weight
TNT	2,4,6 trinitrotoluene	$C_7H_5N_3O_6$	227
DPA	diphenylamine	$C_{12}H_{11}N$	169
HMX	1,3,5,7-tetranitro-1,3,4,7-tetraazacyclooctane	$C_4H_8N_8O_8$	296
RDX	1,3,5-trinitrotriazacyclohexane	$C_3H_6N_6O_6$	222
MMAN	monomethylaminenitrate	$CH_4N_2O_3$	92
NG	nitroglycerin	$C_3H_5N_3O_9$	227
Tetryl	2,4,6-N-tetranitro-N-methylaniline	$C_7H_5N_5O_8$	287
PETN	pentaerythritol tetranitrate	$C_5H_8N_4O_{12}$	316
Ethyl centralite	ethyl centralite	$C_{17}H_{20}N_2O$	268

in blood [2]. In addition, many explosives are toxic, and the inhalation of their vapors presents a health hazard. It is necessary, therefore, to analyze blood samples of personnel working in munitions manufacturing plants for traces of explosives and their metabolites. Thus, the need for a method of analysis for explosives is evident.

The thermal instability of most explosives, along with the requirements of high sensitivity of the analysis, limit the number of analytical methods that can be used for explosive analysis. The requirements of an ideal analytical method for these applications should include good separation, high selectivity, and high sensitivity. This method should work equally well on complex samples from the real world and on lab standards made up in pure solvents.

The very nature of explosives precludes the application of certain chromatographic procedures. High-temperature gas chromatography is generally difficult to use since most explosives will not survive the thermal conditions required for their vaporization and separation. Some of these difficulties can be reduced using cold on-column capillary injection techniques. A more suitable separations technique, one that is not based upon the boiling points of the compounds, is desirable.

The majority of recent published reports dealing with the analysis of explosive material has involved high performance liquid chromatography (HPLC) with a variety of detection systems. These detection systems include ultraviolet (UV) absorption, electrochemistry, thermal energy analysis, electron capture, and mass spectrometry. The majority of these publications has cited variable-wavelength UV absorption as the detection method. The lower limit of detection (LOD) for explosives in one study was between 24 and 50 ppb, with 400 µL of sample injected at one time [3]. UV detection does have inherent limitations: it is suitable only for the determination of trace levels of strongly UV absorbing materials, it is relatively nonselective, and confirmation remains an obstacle.

LC with electrochemical detection (LC/EC) is suited to trace analysis of nitramines, nitrated esters, and nitroaromatics [4]. Limits of detection for nitro-aromatics by LC/EC are in the low nanogram or subnanogram range, while selectivity is considered better than in UV detection [5]. LC coupled with thermal energy analysis detection (LC/TEA) has been used in recent years for the trace analysis of nitro-containing compounds [6]. Although TEA detection is sensitive to picogram amounts of material, it is not a completely selective system, since it is known that other types of organic compounds provide significant responses [7]. Another inherent limitation is that water based solvent systems are not fully compatible with the detector, essentially excluding ion-exchange, paired ion, and reversed phase HPLC. LC with electron capture detection (LC/ECD) has a LOD for nitro compounds in the picogram range [8]. However, linearity and sensitivity are significantly dependent upon the electron capturing properties of the solvent and any impurities that may be present [5]. Another disadvan-

tage of this technique is that an increase in the flow rate decreases the signal height. This is due to quenching of the analytical signal by the mobile phase.

A detection system that can overcome the disadvantages of EC, TEA, and ECD is mass spectrometry. The combination of LC, which is a widely used separation technique for explosive mixtures, and mass spectrometry, which is a sensitive and selective detection method, in theory, should be ideal for the separation and identification of explosives. In addition, LC/MS provides two points of comparison with standard explosives for identification, one based upon the LC retention times and the other based upon the specific mass spectra obtained. Several LC/MS systems have been used for analysis of explosives. These systems are the LC/direct liquid introduction/MS (DLI), with either positive or negative chemical ionization (CI), and LC with off-line CI/MS detection. Sensitivity of the DLI system is limited because only 1 to 2% of the effluent enters the mass spectrometer. The off-line technique suffers from the inconvenience of sample collection and ineffective time utilization. LODs are in the nanogram to subnanogram range for CI/MS [9,10].

Recently, a thermospray (TSP) LC/MS interface has been introduced which significantly improves the sensitivity, reliability, and applicability of LC/MS [11]. The principles and applications of TSP have been reviewed by Vestal and coworkers [11-14]. The complete or partial vaporization of a liquid as it flows throuugh a heated capillary has been defined as thermospray. TSP provides stable vaporization of a wide variety of solvent systems including volatile aqueous buffers with flow rates up to 2.0 mL/min. The TSP is capable of producing intact molecular ions for many molecules which can be ionized in solution. Intact molecular ions up to 1758 daltons have been generated using TSP [15]. One of the most significant aspects of LC/TSP/MS is the ability to detect nonvolatile and thermally labile compounds such as drugs and their metabolites [15], glucuronides [16], nucleosides and nucleotides [17], peptides [18], pesticides [19], dyes [20], and antibiotics [13].

Recently, Voyksner and Yinon demonstrated that thermospray is applicable to the trace analysis of explosive compounds, technical explosives mixtures, and hand swabs [21]. They also observed that the gentle ionization provided by TSP allows for the production of molecular or pseudo-molecular ions for explosives compounds as opposed to the highly fragmented spectra observed for explosives under electron impact or chemical ionization conditions.

In this paper we confirm and expand upon the original work performed by Voyksner and Yinon [21]. In addition to the use of LC/TSP/MS for separation and identification of standard explosive mixtures, we have extended the range of applications to include a number of commercial and military explosives, stabilizers in double-based smokeless powders as well as explosives residue. In addition, we have attempted to better understand the differences observed in the spectra generated by the various ionization modes available in thermospray. The isocratic chromatographic conditions used in this paper also provided for a rapid separation of explosive mixtures.

Materials and Methods

All experiments were performed using a Vestec thermospray (TSP) (Fig. 1) (Vestec, Houston, TX) interfaced to a Finnigan-MAT triple-stage quadrupole mass spectrometer (TSQ45) (Finnigan-MAT, San Jose, CA) [12]. The vaporizer of the thermospray probe (Fig. 1) consists of 0.15 mm inside diameter by 1.5 mm outside diameter stainless steel tubing which is resistively heated. The probe has two thermocouples which are used to regulate and monitor the temperature of the probe. The thermocouple located near the probe handle measures the control temperature (T1); the other thermocouple, located near the exit aperture of the probe, measures the tip temperature (T2). T2 is located in a feedback loop which is used to control the temperature at T1. The temperature of the source block is measured by a thermocouple embedded into the block. The vaporization produces a supersonic jet of vapor that
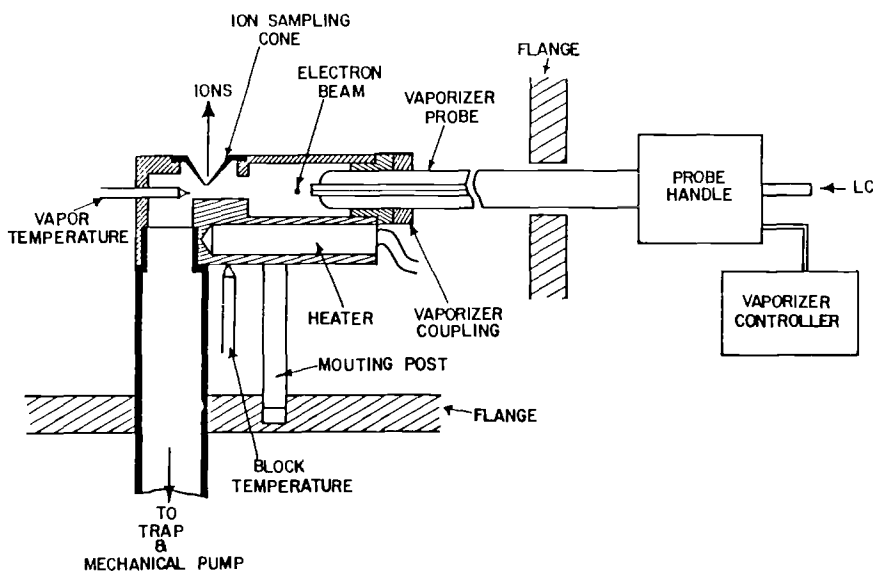
FIG. 1—*Schematic diagram of thermospray apparatus using a resistively heated vaporizer. Reprinted by permission of M. Vestal (Vestec Corp., Houston, TX).*

traverses the ion source into a pumping line of an external mechanical pump. The ions are sampled into the mass spectrometer through the conical exit port.

The liquid chromatographic separation was performed using dual Gilson Model 302 pumps and a C-18 column (Supelco 5 mm by 15 cm, 5-μm packing). The column was operated using a premixed isocratic mobile phase consisting of 60/40 methanol (Burdick and Jackson)/0.10M ammonium acetate (Aldrich) aqueous buffer.

All explosives were obtained from a Federal Bureau of Investigation (FBI) standards collection and are listed in Table 1. The standards were prepared in LC grade acetone or methanol. All solvents and samples were filtered using a 0.45-μm filter before use.

The various operating conditions of the LC/TSP/MS were optimized to yield the maximum sensitivity for the ions produced by LC/TSP(filament-on)/MS of TNT and PETN (Table 2). The parameters which were optimized included the following: LC flow rate; T1;

TABLE 2—*Optimum operating conditions for LC/TSP/MS of explosive compounds.*

Parameter/Condition	Optimum Value/Condition
T1[a]	110°C
T2[b]	~172°C
Block temperature	225°C
Flow rate	1.5 mL/min
Mobile phase	60/40 MeOH/0.10M ammonium acetate buffer
Ionization mode	filament on
+/− Ions detected	− ions

[a]T1 is the control temperature on the thermospray probe, measured at the base of the probe.

[b]T2 is the tip temperature on the thermospray probe, measured at the tip of the probe, which is inserted into the mass spectrometer.

T2; block temperature; ionization mode; and polarity of the ions detected (Table 2). Since the optimum operating conditions for the two explosives were found to be nearly identical, all subsequent specimens were analyzed at these conditions.

Results and Discussion

The results and discussion portion of this paper will include two major topics: (1) operation modes (mass spectrometry and thermospray) and (2) discussion of spectra obtained using LS/TSP(filament-on)/MS (pure explosives, mixture analysis, military and commercial products, and residue analysis).

Mass Spectrometer Modes of Operation

In this research, the TSQ45 was operated in the quadrupole 3 normal MS mode. In this mode, all ions pass through the first two quadrupoles and are mass analyzed by scanning the third quadrupole over a selected mass region. Two different scan modes were utilized: full scan (normal MS) and selected ion monitoring (SIM). The lower mass limit for the full scan MS was m/z 150 and the upper mass limit was m/z 400. The lower mass limit was selected above the unwanted interference ions from the mobile phase reagent ions. In SIM, the third quadrupole was set to pass ions of a particular m/z ratio.

Thermospray Modes of Ionization

Currently there are three modes of ionization available for use with the TSP interface: thermospray (filament-off), filament-on, and discharge ionization. With TNT as the reference compound, a sensitivity ratio of 1:3:1.4, with respect to base peak intensity, was observed for these ionization modes, respectively. The greatest sensitivity for explosive compounds was obtained in the negative ion mode with filament-on ionization. This agrees with the findings of Voyksner and Yinon [21]. The positive ion mode of ionization yielded virtually no signal for the majority of explosive compounds. The effect of the various ionization modes on the resulting negative ion mass spectrum of TNT are shown in Fig. 2. The greater sensitivity in the negative ion mode may be attributed to the presence of the nitro groups in the explosive compounds. The nitro groups are strongly electrophilic and therefore should produce intense negative ion signals.

The ability of explosive compounds to capture electrons has been documented [8]. One of the major distinctions between the three ionization modes for TSP is that with filament-off ionization there is no external source for the production of electrons. Filament-on and discharge ionization have an external source of electrons which can produce thermal electrons. The presence of thermal electrons with filament-on ionization has been reported by Gartiez and Vestal [14]. Therefore, the relative lack of sensitivity in the TSP(filament-off) mode may be attributed to the absence of thermal electrons which contribute to filament-on and discharge ionization modes. The lack of thermal electrons in the TSP mode also accounts for different ions being observed in the various mass spectra of TNT. With TSP ionization, the most abundant ion for the TNT spectra is m/z 226 $[M-H]^-$, while in the other ionization modes the most abundant ion is m/z 227 $[M]^-$ due to electron capture by the highly electronegative nitro groups.

LC/TSP/MS Spectra

The negative ion LC/TSP(filament-on)/MS mass spectra for RDX, HMX, PETN, and tetryl are displayed in Fig. 3 and Table 3. These spectra all exhibit abundant molecular or pseudo-molecular ions and little fragmentation allowing for easy identification. The mass
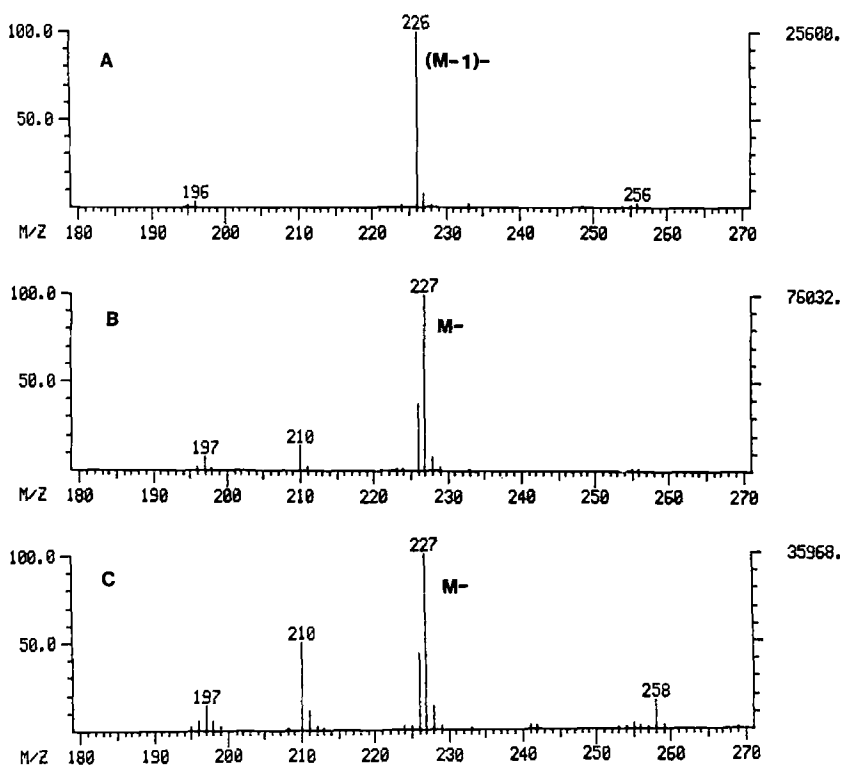
FIG. 2—*Negative ion LC/TSP/MS spectra of TNT with different ionization modes:* (A) *TSP fila-ment-off.* (B) *TSP filament-on.* (C) *discharge.*

spectrum of RDX contained one major ion, $[M+CH_3COO]^-$, at m/z 281. The mass spectrum of tetryl had its most abundant ion at m/z 257, as a result of $[M-NO]^-$, and an ion at m/z 318, corresponding to $[M+H+NO]^-$. The mass spectrum of HMX contained one major ion, $[M+CH_3COO]^-$, at m/z 355. The mass spectrum of PETN had its most abundant ion at m/z 375, as a result of $[M+CH_3COO]^-$. The mass spectrum of PETN contained two other major ions, $[M+CH_3COO-COOH]^-$ at m/z 330, and $[M-H]^-$ at m/z 315. The negative ion LC/TSP(filament-on)/MS mass spectrum for NG is summarized in Table 3. The mass spectrum for NG had its most abundant ion at m/z 289 as a result of $[M+NO_3]^-$, and an ion at m/z 241, corresponding to $[M+14]^-$. In addition to the spectra of pure explosive compounds, mixtures of explosives and additives can also be determined via the same analytical technique.

A number of compounds play a significant role in the manufacturing of smokeless and double-based smokeless powders. In contrast to the nitro containing high explosives, this particular group of compounds produced intense positive ion spectra. The positive ion LC/TSP(filament-on)/MS mass spectra of diphenylamine (DPA) and ethyl centralite were characterized by $[M+H]^-$ ions of m/z 170 and 269, respectively (Table 3). The positive ion LC/TSP(filament-on)/MS spectrum of MMAN had its most abundant ion at m/z 108 as a result of $[M+16]^+$ and an ion at m/z 92, corresponding to $[M]^+$ (Table 3). A summary of the major ions for the LC/TSP(filament-on)/MS mass spectra of explosives and additives are presented in Table 3.

The LC/TSP(filament-off)/MS spectra for RDX, HMX, Tetryl, and PETN have recently been published. The spectra of RDX and HMX presented in this paper correspond very
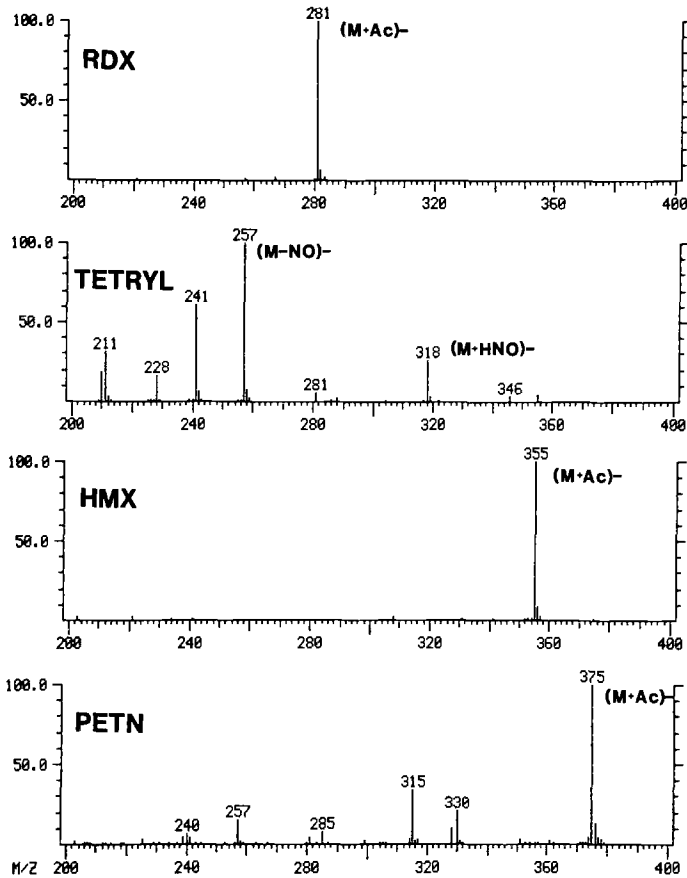
FIG. 3—*Negative ion LC/TSP(filament-on)/MS mass spectra of RDX, Tetryl, HMX, and PETN.*

closely to the spectra published by Voyksner and Yinon [21]. The reproducibility of spectra for explosive compounds from laboratory to laboratory is a significant improvement over the analysis of explosives using mass spectrometry via electron impact ionization, which produces highly fragmented spectra and chemical ionization, which is often difficult to reproduce [10,11,22].

The LC/TSP(filament-on)/MS spectra for PETN and Tetryl presented in this paper, however, differ slightly from the LC/TSP(filament-off)/MS spectra previously reported [21]. Voyksner and Yinon reported the most abundant ion for PETN at m/z 375 with other major ions at m/z 378, 330, and 315. The most abundant ion in our study varied between m/z 378, as a result of $[M+NO_3]^-$, and m/z 375, as a result of $[M+CH_3COO]^-$. The different modes of ionization (filament-off versus filament-on) may account for the slight difference in the spectra.

Chromatographic Separation

The use of a 15-cm C-18 column and a premixed isocratic mobile phase at a flow of 1.5 mL/min resulted in adequate separation of the explosives studied in just over 2 min. This is approximately 10 times faster than the separation reported using a 25-cm column with sol-

TABLE 3—*Major ions in LC/TSP(filament-on)/MS mass spectra.*

Compound Injected	Peak		Identity
	Mass	% Relative Abundance	
TNT	227	100	$[M]^-$
	226	42	$[M-H]^-$
	210	51	$[M-OH]^-$
	197	15	$[M-NO]^-$
RDX	281	100	$[M+CH_3COO]^-$
HMX	355	100	$[M+CH_3COO]^-$
PETN	378[a]	100	$[M+NO_3]^-$
	375[a]	100	$[M+CH_3COO]^-$
	330	22	$[M+CH_3COO-COOH]^-$
	315	36	$[M-H]^-$
Tetryl	346	5	$[M+CH_3COO]^-$
	318	29	$[M+H+NO]^-$
	257	100	$[M-NO]^-$
	241	62	$[M-NO_2]^-$
NG	289	100	$[M+NO_3]^-$
	241	21	$[M+14]^-$
MMAN	108	100	$[M+16]^+$
	92	10	$[M]^+$
DPA	170	100	$[M+H]^+$
Ethyl centralite	269	100	$[M+H]^+$

[a]See text for discussion.

vent programming [21]. A typical separation is shown by the reconstructed ion chromatogram (RIC) and ion chromatograms in Fig. 4. The sample injected contained approximately 200 ng each of RDX, HMX, TNT, PETN, and Tetryl. The ions at m/z 226 and 241 correspond to TNT $[M-H]^-$ and Tetryl $[M-NO_2]^-$, respectively. The ions at m/z 281, 355, and 375 correspond to the acetate adduct $[M+CH_3COO]^-$ of RDX, HMX, and PETN, respectively.

It is also possible to make direct injections without the use of a column, to reduce further the time of analysis. The nature of the LC/TSP/MS spectra of explosives, exhibiting only a few major ions, lends itself to selected ion monitoring (SIM) which offers increased sensitivity without a significant loss in selectivity. Triplicate (direct) injections of 2.5 pg of PETN with selected ion monitoring of m/z 375 and 315 yielded a signal-to-noise ratio of 50:1 based upon peak areas. This provides a limit of detection ($S/N = 3$) of less than 2.5 pg under SIM conditions while maintaining a high degree of selectivity. As expected, this is an improvement over the full scan limit of detection of 1 ng previously reported [21]. Figure 4 clearly shows that PETN has the lowest response factor for the explosives analyzed. Hence, the detection limit for the other explosives should be even lower than 2.5 pg.

Analysis of Military and Commercial Products

Although the analysis of pure explosive compounds is of significance to the scientific community, of equal importance is the ability to characterize commercial or military explosives. A number of high explosives were analyzed including military C4 and PE2. Tovex 300 (Dupont), a commercial blasting agent sensitized with monomethylaminenitrate (MMAN), and NONEL (Ensign Bickford), a water-resistant primer/detonating lead containing HMX and aluminum dust, were also examined. The RICs for C4 shown in Fig. 5 indicate the presence of HMX in the RDX based explosive. Figure 6 shows the sequential analysis of a
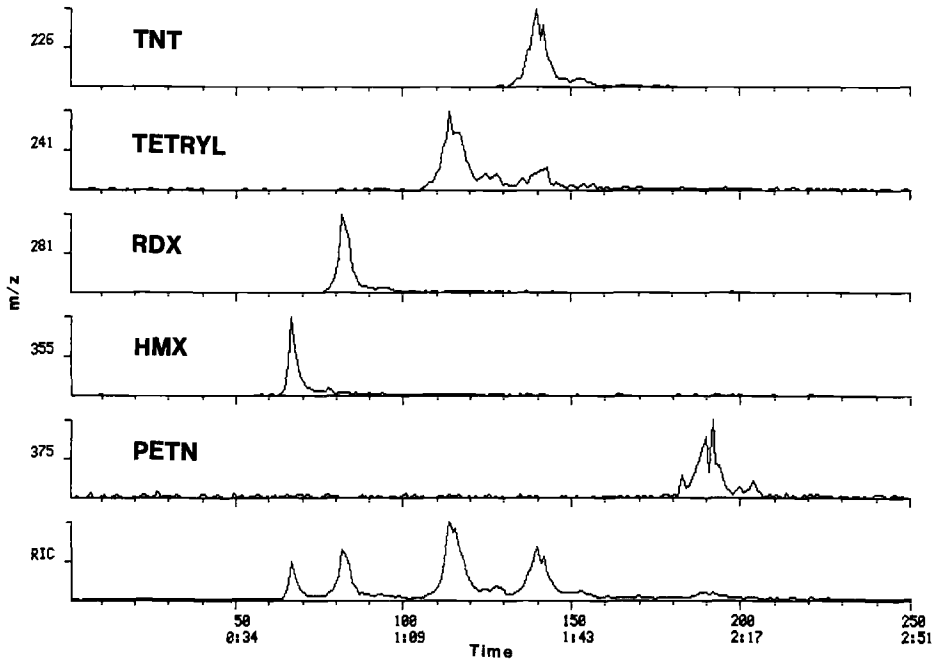
FIG. 4—*Ion chromatograms and reconstructed ion current (RIC) for negative ion LC/TSP(filament-on)/MS analysis of a standard explosive mixture.*

specimen of PE2 (RDX) and Nonel (HMX). The positive ion RIC for a Tovex (MMAN) specimen is shown in Fig. 7. All the specimens studied yielded mass spectra which were predictable based upon their composition and comparison to pure standards.

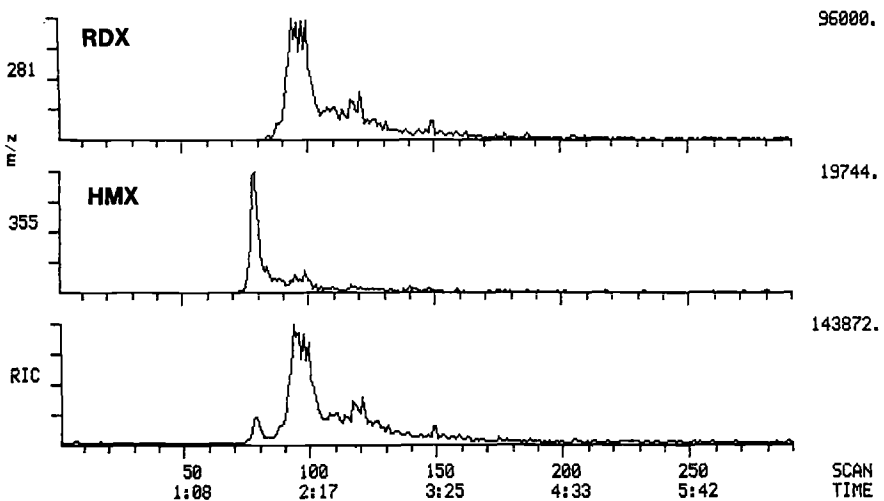Figure 8 demonstrates the advantages offered by simultaneous positive and negative ion

FIG. 5—*Ion chromatograms and reconstructed ion chromatogram for negative ion LC/TSP(fila-ment-on)/MS analysis of C4. LC peak in the m/z 355 ion chromatogram indicates presence of HMX in RDX-based explosive.*
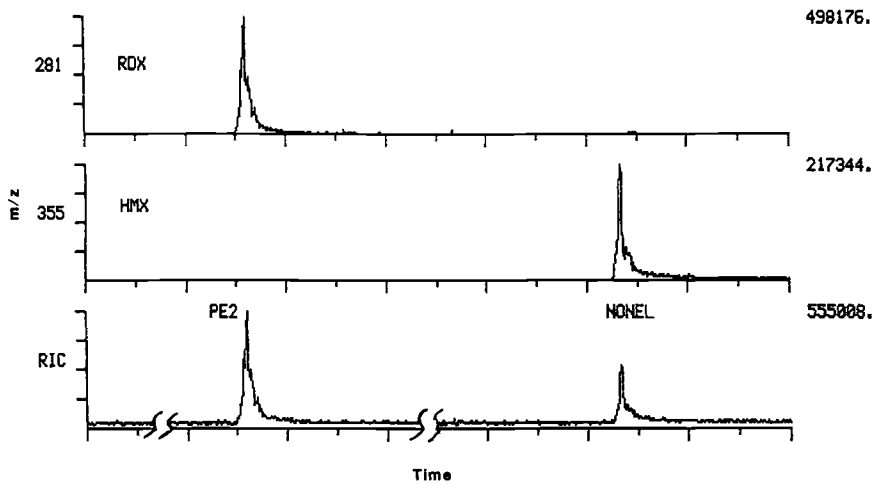
FIG. 6—*LC/TSP(filament-on)/MS negative ion chromatograms and reconstructed ion chromatogram for sequential analysis of samples of PE2 (RDX) and Nonel (HMX).*

detection capabilities in which a sample of Hercules Red Dot, a double-based smokeless powder, is characterized. The negative ion trace indicates the presence of NG, while the diphenylamine and ethyl centralite are observed only in the positive ion mode.

Explosive Residue

Developing a method of analysis for identifying postblast residues is of equal utility as the characterization of unexploded materials. For us to evaluate the effectiveness of LC/TSP/ MS for residue analysis, a number of improvised explosive devices were constructed and detonated under controlled conditions. Figure 9 shows a photograph of a propane tank re-
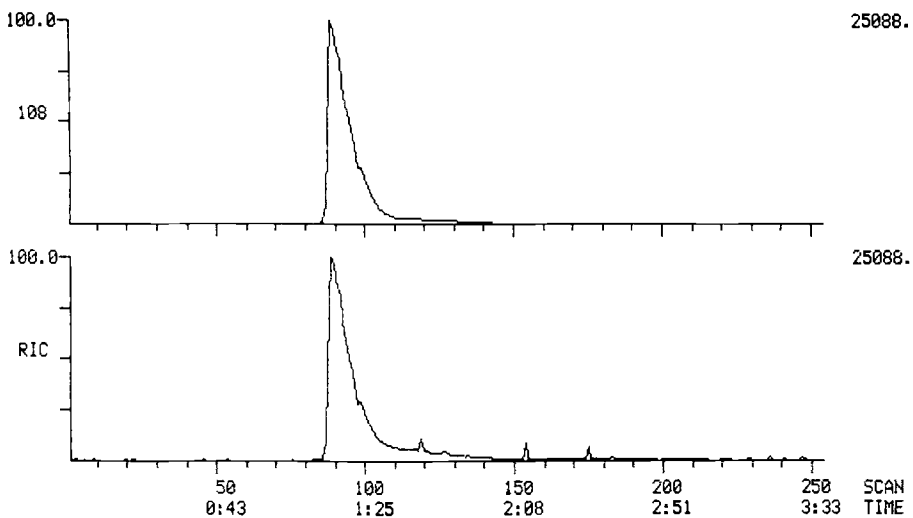

FIG. 7—*LC/TSP(filament-on)/MS positive ion chromatogram and reconstructed ion chromatogram for a sample of Tovex.*
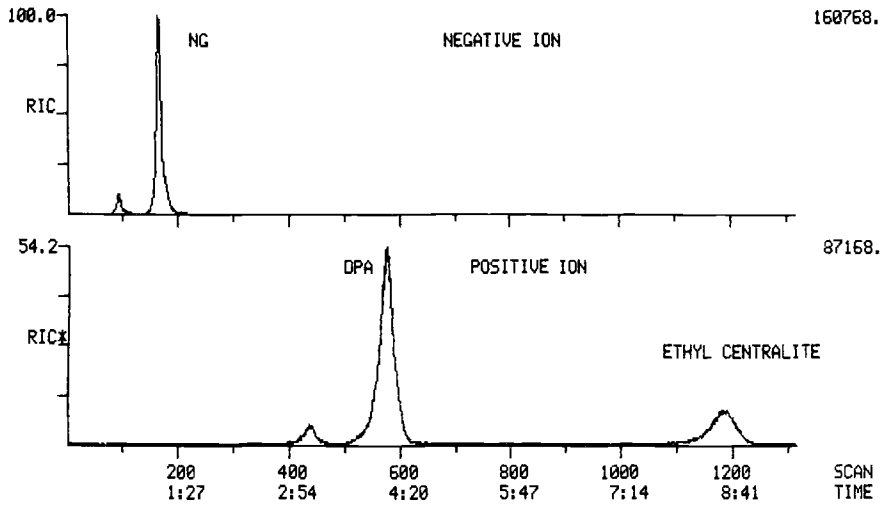
FIG. 8—*Reconstructed positive and negative ion chromatograms for a sample of smokeless powder. Retention times shown are half of the actual times due to dual positive and negative acquisition.*

covered from near the seat of a C4 explosion. The areas labeled 1 to 3 were swabbed with acetone. Extracts of the cotton swabs were examined for the presence of RDX and HMX residue with selected ion monitoring. The chromatogram in Fig. 10 indicates the presence of RDX and HMX. This profile can be compared with the standard C4 sample as shown in Fig. 5.

FIG. 9—*Photograph of propane tank recovered from near seat of a C4 explosive. Areas labeled 1 to 3 are regions which were examined for presence of RDX and HMX residue with selected ion monitoring.*
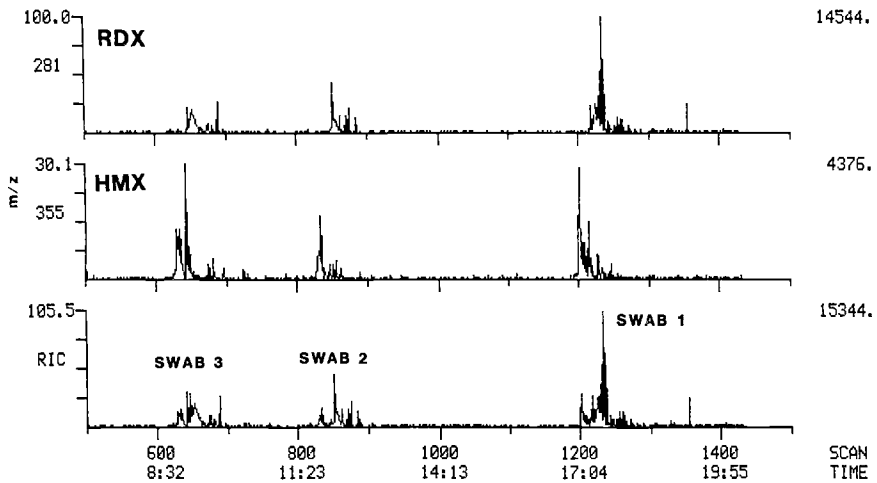
FIG. 10—*LC/TSP(filament-on)/MS negative ion chromatogram for selected ion monitoring of* m/z *281 (RDX) and 355 (HMX) from residue (Regions 1 to 3) of propane tank in Figure 9.*

A common type of improvised explosive device frequently encountered is the pipebomb. Figure 11 shows the debris recovered from an improvised explosive device (pipebomb) which was packed with a double-based smokeless powder and initiated with a squibb or electric match. The chromatogram in Fig. 12 was obtained from an acetone wash of the end cap from the pipe. The presence of DPA shown in the positive ion mode and the presence of NG in the negative ion traces are indicative of the use of a double-based smokeless powder.
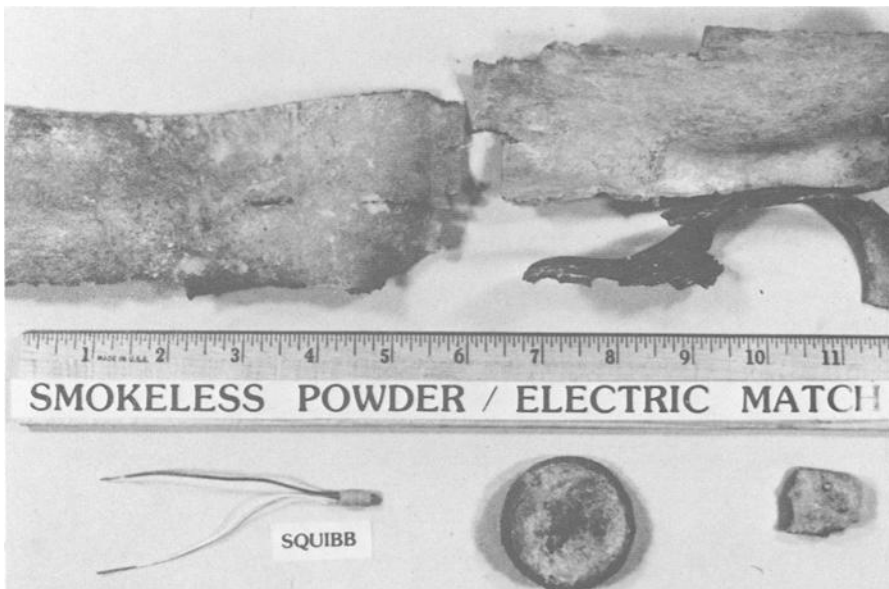

FIG. 11—*Photograph of debris recovered from a pipebomb which was packed with a double-based smokeless powder initiated with a squibb or electric match.*
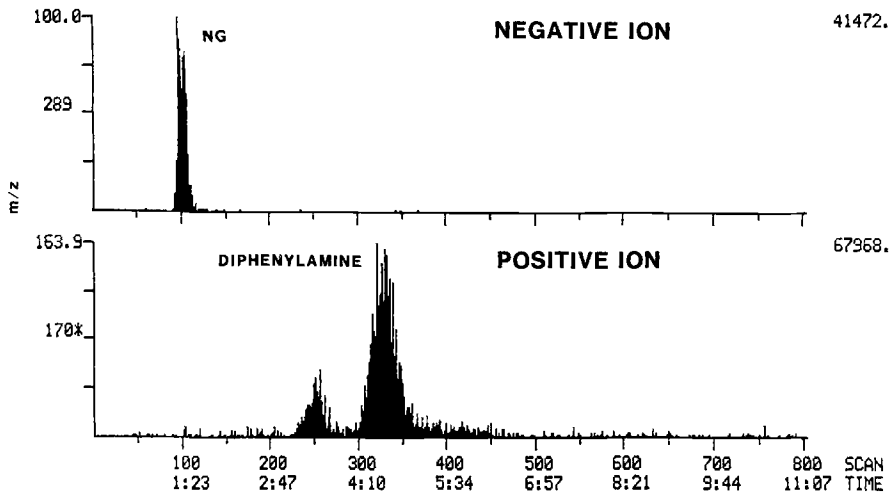
FIG. 12—*Ion chromatograms and reconstructed ion chromatogram from LC/TSP(filament-on)/MS of residue from pipebomb (Fig. 11). Positive ion chromatograms indicate presence of DPA (m/z 170). Negative ion chromatogram indicates presense of NG (m/z 289).*

Conclusions

The data presented here further demonstrate the applicability of LC/TSP/MS for the analysis and characterization of explosives and explosive residues. The spectra observed correspond very closely to those observed by Voyksner and Yinon [21]. The reproducibility of thermospray spectra is significant for the development of standard methods of analysis. In addition, the ability of LC/TSP/MS to produce molecular ions and pseudo molecular ions from explosives allows for easy identification of explosive compounds. Negative ion LC/TSP/MS proved to be very sensitive for a large number of explosive compounds, while providing the high selectivity required to discriminate against interferents which may be present in unknown samples. Positive ion LC/TSP/MS, although not sensitive for explosive compounds, proved to be sensitive for common additives in double-based, smokeless powders.

In addition to confirming the original work of Voyksner and Yinon [21], we have further demonstrated the applicability of LC/TSP/MS by extending the range of applications to include commercial blasting agents, military explosives, double-based smokeless powders, and explosive residue. Separation times of just over 2 min will allow large numbers of samples to be rapidly screened. The limit of detection for PETN in the SIM mode was in the low picogram range. The majority of the other explosive compounds studied exhibited a greater response than PETN; therefore, improved limits of detection are predicted for these compounds.

Acknowledgment

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