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Trace Analysis of Peroxide Explosives by High Performance Liquid Chromatography-Atmospheric Pressure Chemical Ionization-Tandem Mass Spectrometry (HPLC-APCI-MS/MS) for Forensic Applications

ABSTRACT: An HPLC-APCI-MS/MS method for the (trace) analysis of the most commonly encountered peroxide explosives, hexamethylenetriperoxidodiamine (HMTD) and triacetoneperoxide (TATP), has been developed. With this method, HMTD and TATP have been analyzed in the same run. (Pseudo-)molecular ions of these peroxides have been obtained as base peak under the same condition. A series of product ions was produced from these pseudo-molecular ions ($[\text{HMTD} - 1]^+$ and $[\text{TATP} + \text{NH}_4]^+$) in the MS/MS analysis. We also pioneered in showing that a TATP molecular ion $[\text{TATP} + \text{H}]^+$ can be observed with HPLC-MS/MS. The limit of detection for HMTD and TATP was 0.26 and 3.3 ng, respectively, on column by HPLC-MS in the Full Scan mode and 0.08 and 0.8, respectively, by HPLC-APCI-MS/MS in Selected Reaction Monitoring (single mass unit) mode. The method presented has been applied successfully for the identification of peroxides in the bulk solid state (powder sample), as well as in post-blast extracts originating from a forensic case. For the post-blast extracts, the use of tandem MS has been shown clearly to be of crucial importance for the identification and detection of the peroxide explosives.

KEYWORDS: forensic science, peroxide explosives, HMTD, TATP, post-blast, post-explosion residues, high performance liquid chromatography, atmospheric pressure ionization, mass spectrometry, atmospheric pressure chemical ionization, screening method

In recent years, the analysis and detection of one class of explosives, namely peroxide explosives, has become particularly important in forensic investigations because of the emergence of terrorist threats and crimes in which these explosives were applied. A peroxide explosive is an organic compound that contains one or more peroxide functional groups (R-O-O-R) often in a cyclic form. Peroxides can display an explosive power, which can be on the same order of magnitude as high explosives. Peroxide explosives are usually unstable and are highly sensitive to heat, friction, shock, and impact (1), which makes the use of an initiator redundant. TATP itself is a primary explosive.

Several peroxide explosives (see Fig. 1) have been known, such as hexamethylene-triperoxidodiamine (HMTD), triacetoneperoxide (TATP), diacetoneperoxide (DADP) and tetramethylenediperoxididecarbamide (TMDD).

Although TATP and HMTD already were prepared by German chemists in the late nineteenth century, they only occurred in terrorist cases in the 1980s and 1990s (2–4), with the most recent example being the so-called shoe bomber (5).

DADP appears mostly as a by-product of the synthesis of TATP (6,7). The successful synthesis of TMDD, however, is mentioned on the Internet, but as far as we know, it has not been published in an official manner.

Peroxide explosives generally can be made from hydrogen peroxide and a few other well-known chemicals, such as acetone for

TATP and DADP, hexamine (or ammonia and formaldehyde) for HMTD, and formaldehyde and urea for TMDD. A small amount of acid (such as hydrochloric, sulphuric, or citric acid) is added as a catalyst. Most of these ingredients can be obtained easily from local pharmacies. Alarmingly, many procedures for the synthesis of these peroxides can be obtained from the Internet.

Techniques for analyzing and identifying peroxide explosives include mass spectrometry under electron impact (EIMS) and chemical ionization (CIMS) conditions (2,3,8,9), gas chromatography–mass spectrometry (GC-MS) (8), high performance liquid chromatography–mass spectrometry (HPLC-MS) (8), infrared (IR) spectrometry (2–4,8), nuclear magnetic resonance (NMR) (3), thin layer chromatography (TLC) (8) and HPLC-fluorescence (7). Since peroxide explosives lack chromophores and nitro- (NO_2) groups, the common techniques for the detection of trace explosives, such as HPLC-Photo Diode Array Detection (HPLC-PDA) and GC-thermal energy analysis (GC-TEA), are not feasible.

Generally, GC-MS and HPLC-MS are techniques that are particularly suitable for the trace analysis and identification of explosives (10,11), e.g., post-blast samples or hand swabs taken from a person who has handled explosives recently. Lately, researchers from the Forensic Explosives Laboratory (FEL) in the UK have carried out extensive studies on the analysis of TATP, DADP, and HMTD using the abovementioned techniques (6,8,12,13). It was shown that HPLC-MS is a suitable technique for the identification and quantification of HMTD and TATP at trace levels. On the other hand, serious problems with GC-MS, such as GC column activation by organic peroxide explosives and thermally induced decomposition (e.g., HMTD), were encountered. However, detection of DADP was shown to be possible with GC-MS, but not with HPLC-MS.

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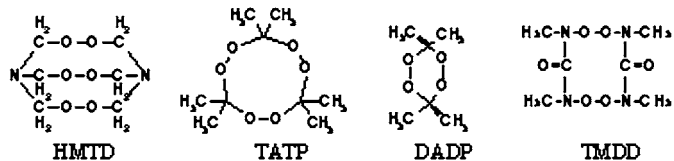


FIG. 1—Peroxide explosives: hexamethylenetriperoxidetriamine (HMTD), triacetoneperoxide (TATP), diacetonediperoxide (DADP), and tetramethylenediperoxidecarbamide (TMDD).

Recently, we have developed a screening method for the detection of twenty-one explosives in different classes by HPLC-MS (14,15). In this paper, we expand this screening method with organic peroxide explosives. This is also the first method in which HMTD and TATP can be screened in the same HPLC-APCI-MS(/MS) run. Furthermore, we have shown that the MS/MS mode largely increases reliability and that this mode is essential to the trace analysis and identification of HMTD and TATP in post-blast samples. In addition, ideas for further development of the analysis of other peroxides, such as DADP, are discussed.

Methods

Materials

Explosive standards (reference materials) of hexamethylenetriperoxidetriamine (HMTD) and triacetoneperoxide (TATP) were obtained from AccuStandard Inc., New Haven, CT (www.accustandard.com). Both materials were supplied as 0.1 mg/ml solutions in acetonitrile (catalogue numbers M-8330-ADD-24 and M-8330-ADD-25). The identification of the seized (powder) material was confirmed with Fourier transform-infrared spectrometry (FT-IR) (reference spectra from (3)). All other materials used were of purity better than 98% (w/w). All solvents used were of HPLC or glass distilled grade (Rathburn). Water was purified with a Milli-Q/Organex Q system (Millipore). All other reagents were of analytical grade.

Preparation of Samples

White powder material seized from a crime scene and presumably containing peroxide explosive was dissolved and diluted with acetone. In case of post-blast analysis, the explosive residues were extracted from debris, e.g., shrapnel of a (letter) bomb obtained from a crime scene or residues from a controlled explosion of an improvised explosive device (CE-IED), with several milliliters of acetone or methanol by sonification for 10 min. The collected extract was about 1 ml. If necessary, the extract was reduced further to a smaller volume by evaporation at room temperature. Subsequently, the samples were filtered through a membrane filter (Spartan 13/0.45 RC, 0.45 μm from Schleicher & Schuell, Dassel, Germany) and injected into the HPLC system.

Instrumental

All analyses were performed using high performance liquid chromatography separation and single or tandem mass spectrometry

detection with atmospheric pressure chemical ionization (HPLC-APCI-MS(/MS)). The HPLC system consisted of a Waters 600-MS programmable pump equipped with a Waters 717 plus Autosampler and a Waters 486 UV detector (at 220 nm). The mass spectrometer was a model Finnigan MAT TSQ (Triple Stage Quadrupole) 700. The HPLC was connected to the mass spectrometer by the upgraded Finnigan MAT API interface, which is equivalent to API-2 for Finnigan TSQ 7000. This upgrade has led to a general increase in sensitivity of a factor three to five compared to the standard one (14).

Procedures of HPLC-APCI-MS(/MS) Analysis

A sample volume of 10 μL acetone or methanol solution was injected into the HPLC system. Chromatographic separation was achieved with a Waters Nova-Pack 4 μm C18 3.9×150 mm HPLC cartridge column using an isocratic mobile phase of a methanol-water mixture (75:25) with 2.5 mM ammonium acetate at a flow-rate of 0.4 mL/min. The API was operated in the atmospheric pressure chemical ionization positive ion mode (APCI+) with the vaporizing temperature being 360°C, heated capillary 150°C, vaporizing spray voltage 3.5 kV, and sheath gas 80 psi. The positive ions generated by the APCI ion source were detected by the MS or MS/MS system, where the current intensities of the mass to charge ratio (m/z) of the ionized components and fragments (ions) were recorded.

When analyzing by single MS detection, MS spectra were recorded in the Full Scan (FS) or in the Single or Selected Ion Monitoring (SIM) mode. In the SIM mode, only a few target ions are monitored. This results in lower detection limits, because more time is spent with monitoring significant ions that are known to occur in the mass spectrum of the target analysis.

Only the Product Ion mode was used for experiments with the MS/MS detection. In this mode a precursor ion selected by the first MS analyzer is fragmented in the collision cell with argon as collision gas to produce product ions, which are then mass-analyzed by the second MS analyzer in Full Scan (FS) or Selected Reaction Monitoring (SRM) mode. In the FS mode, the second MS analyzer scans a mass range to obtain a mass spectrum of the selected precursor ion. In the SRM mode, a limited number of precursor-ion/product-ion pairs is monitored. Because of the same reasons as with the SIM mode in the single MS case, lower detection limits can be obtained in the SRM mode than in the FS mode.

Instrumental conditions of the TSQ for the MS and MS/MS analysis have been listed in Tables 1 and 2, respectively.

Results and Discussion

The results of the HPLC-APCI-MS(/MS) analysis of HMTD and TATP are given in Table 3.

HPLC-MS Analysis for Screening

In the single MS analysis, HMTD and TATP were detected as $[\text{HMTD} - 1]^+$ and $[\text{TATP} + \text{NH}_4]^+$, respectively. As shown in

TABLE 1—Data acquisition for the single MS analysis of HMTD and TATP.

Scan Modes	Ionization	Vaporizing Temperature (°C)	Vaporizing Spray (kV)	Capillary Temperature (°C)	Sheath Gas (psi)	Multiplier Voltage (kV)	Monitored Mass-Charge Ratio (m/z)
Full scan (FS)	APCI (+)	360	3.5	150	80	1.0	80–255

TABLE 2—Data acquisition for the MS/MS analysis of HMTD and TATP.

Scan Modes	Multiplier Voltage (kV)	Monitored Mass-Charge Ratio (m/z) Precursor Ion → Product Ions (Scan Rate 1 s)
Product Ion mode in Full Scan (FS)	1.0	207[HMTD-1] ⁺ → 40–210 240[TATP + NH ₄] ⁺ → 70–245
Product Ion mode in Selected	1.8	207[HMTD-1] ⁺ → 118 (and/or 88,58)
Reaction Monitoring (SRM)		240[TATP + NH ₄] ⁺ → 74 (and/or 223,240)

Collision-induced dissociation (CID) or fragmentation takes place in the collision cell with the collision-offset voltage of -12V and collision gas argon (99.999%) pressure of 1.8 milli Torr. Other conditions as in Table 1.

TABLE 3—Results of the HPLC-APCI-MS(/MS) analysis of standard HMTD and TATP.

HPLC Retention Time (min)	Limit of Detection (S/N ^a = 3), ng on Column in Different MS(/MS) Data Acquisition (Scan) Modes ^b		
	MS in FS	MS/MS in FS	MS/MS in SRM ^c
Solvent	2.50–2.80
HMTD	3.00	0.26	0.08
TATP	7.60	3.3	0.8

^a S/N = signal-to-noise ratio.

^b Abbreviations for scan modes: FS = full scan mode, SRM = selected reaction monitoring mode.

^c The LOD can be further improved by a factor of three when the first MS Q1 is set to a lower resolution.

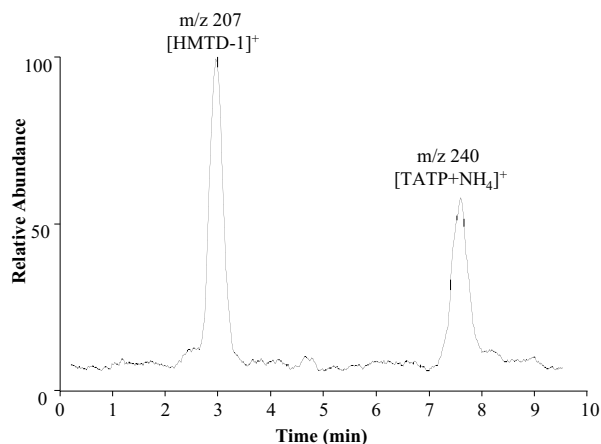


FIG. 2—HPLC-MS chromatograms of HMTD and TATP with m/z of 207 and 240. Signals at m/z 207 and 240 were extracted from the Full Scan mass spectrum in the scan range of m/z 80–255 and plotted in the base peak plot mode (plot only the highest signal of those at the two m/z-values at any moment). Injection: 10 μ L of 4 ng/ μ L TATP and 0.5 ng/ μ L HMTD. The ions found in the mass spectrum of the HMTD peak were [HMTD-1]⁺ with m/z 207 (100%) and [HMTD-O-O]⁺ with m/z 176 (9%), and in the TATP peak were [TATP + NH₄]⁺ with m/z 240 (100%) and m/z 89 (7%).

Fig. 2, the HPLC separation was completed within 10 min with the HMTD peak appearing at 3.0 mins and TATP at 7.6 min. The full scan spectrum of the HMTD showed a base peak of a molecular-weight related ion or pseudo-molecular ion [HMTD-1]⁺ with m/z 207 and a peak of a fragment ion [HMTD-O₂]⁺ (9) with m/z

176 with abundance 9%.² The TATP showed a base peak of a pseudo-molecular ion [TATP + NH₄]⁺ with m/z 240 and a peak of fragment ion [TATP-133]⁺ with m/z 89 with an abundance of 7%. The molecular structure belonging to this mass-charge ratio of 89 is unknown to date (13).

The limits of detection (LOD) for the analysis of the peroxides were determined at a signal-to-noise ratio (S/N) of three and are listed in Table 3. Compared to the literature (12), the LOD of HMTD in the SIM mode (result not shown) has improved with a factor of five. However, the LOD of TATP in the FS mode is about three times worse than the value in a previously published paper (13). In that paper, a splitting of the flow rate 3:1 (0.05 mL/min) of the HPLC was carried out to achieve better peak shape and response. Since we were using very similar conditions as those in the literature for the detection of the TATP, but without splitting the flow rate, the worse LOD value may be attributed to the instrumental differences. The LOD values obtained with the SIM mode are approximately 25 times lower than those obtained with the Full Scan (FS) mode, due to the reason described earlier.

For the screening and identification, full mass scans always should be performed if detection limits permit, in order to gain maximum specificity, while the MS in SIM mode has little practical meaning except for an indicative screening. This will be discussed further in HPLC-MS/MS Analysis.

HPLC Optimization

In the screening method used for the peroxide explosives, the same HPLC column and mobile phase are applied as used for the screening of 21 other nitro-explosives (14). The composition of the mobile phase was chosen and optimized in order to (simultaneously) obtain a base peak of a pseudo-molecular ion both for HMTD and TATP by the MS detection and to achieve the best sensitivity.

The ratio of methanol-water of the HPLC mobile phase was 75:25. At isocratic elution, HMTD was only just separated from the solvent peak. Increasing the water content in the mixture will separate it more from the solvent peak, but with the cost of having a longer or even unreasonably long retention time for TATP. We also have tried gradient elution for the separation of the two peroxides. Unstable base lines under these conditions render this modification unattractive. The ammonia concentration in the mobile phase was 2.5 mM and was the same as the one for the screening of the other nitro-explosives. This facilitates quick equilibration of the HPLC column after switching between the two screening methods.

MS Optimization

It was reported (12,13) that HMTD and TATP have a good MS response when using a methanol-water mixture (without addition of buffer) as the mobile phase. Therefore, it should be possible in principle to detect both peroxides in the same HPLC-MS run. However, since TATP is a very fragile compound, only the fragment ions, e.g., m/z 89, could be obtained under these conditions. Fortunately, TATP was shown to be detected as a molecular adduct ion, such as [M + NH₄]⁺ (13), [M + K]⁺, or [M + Na]⁺ (noticed in a personal communication, see Acknowledgments) in the presence of these ions in the mobile phase. Having compared these adduct ions, we found that the ammonia adduct was the most promising option with respect to sensitivity. Moreover, under the same conditions

² A “base peak” denotes an ion of 100% relative abundance in the MS spectrum.

HMTD also could be detected with a good sensitivity in the form of $[M - 1]^+$. However, the usually encountered ions $[M + \text{NH}_4]^+$, M^+ , or $[M + \text{H}]^+$ could not be found. The ion $[M - 1]^+$ with m/z 207 was reported to be found under HPLC-MS conditions (8,12), although the precise molecular structure is still not revealed. The concentration of ammonia in the solvent has no significant influence on the sensitivity and separation when it varies from 1–10 mM.

The conditions of the APCI interface, such as the vaporizing temperature, heated capillary temperature, vaporizing spray voltage, and sheath gas pressure, were optimized for the base peak of the pseudo-molecular ion of HMTD and TATP, respectively. Surprisingly, the detection behaviors of the both base peaks of the pseudo-molecular ion have almost the same trends with the variation of the APCI parameters. In addition, the values of the optimized key parameters are rather constant over a wide range with regard to the vaporizing temperature, which varied from 330–420°C and with regard to the heat capillary temperature, which varied from 120–180°C.

The APCI variation in the negative ion mode and the ESI (electrospray ionization) variation in both the positive and negative modes, in combination with the buffers mentioned above, also were tested. Under none of these conditions could both peroxides be detected with reasonably high responses.

HPLC-MS/MS Analysis

As shown in the single MS analysis, there are no peaks in the mass spectrum with relative abundances above 20% of the base peak for HMTD and TATP. This poses a problem when trying to select three (meaningful) ions for selected ion monitoring as specified by the Food and Drug Administration (FDA) mass spectra acceptance criteria (16). Thus, MS in SIM mode is not regarded as sufficiently specific for identification in this case. However, the acquired molecular-weight related ions of the peroxides provide the possibility to obtain a full range mass spectrum by the fragmentation of the molecular ion in the MS/MS analysis. The MS/MS analysis was operated in the Product Ion mode in which the precursor ions $[\text{HMTD} - 1]^+$ (m/z 207) and $[\text{TATP} + \text{NH}_4]^+$ (m/z 240) were selected for the fragmentation with argon as collision gas to produce the product ions.

Using the Full Scan data acquisition, as shown in Fig. 3a, six product ions with m/z 191, 147, 118, 88, 72, and 58 in the full scan mass spectrum were obtained from the precursor ion $[\text{HMTD} - 1]^+$, where 191, 118, and 88 might be assigned to $[\text{HMTD} - 1\text{-O}]^+$, $[\text{O}_3(\text{CH}_2)_4\text{N}]^+$, and $[\text{O}_2(\text{CH}_2)_3\text{N}]^+$, respectively. Similarly, as shown in Fig. 3b, four product ions with m/z 223, 132, 91, and 74 were obtained from the precursor ion $[\text{TATP} + \text{NH}_4]^+$, where m/z 223 and 74 were assigned to $[\text{TATP} + \text{H}]^+$ and $[\text{TATP}/3]^+$ (mono-acetone mono-peroxide), respectively. To our knowledge, it is the first time that a TATP molecular ion has been observed under HPLC-MS and/or MS/MS circumstances.

Using Selected Reaction Monitoring (SRM) data acquisition, a number of precursor-ion/product-ion pairs can be monitored simultaneously. For instance, m/z 207/118 and 240/74 can be monitored for the analysis of HMTD and TATP in the same analysis run, or m/z 240, 240/223, and 240/74 can be monitored for double identification of TATP in one run. Similarly to the SIM mode, an improved detection limit can be obtained in the SRM mode compared to the FS mode.

In Table 3, the limits of detection (LODs) of the MS/MS analysis in the Product Ion mode have been given. Obviously, the LODs in the Full Scan (FS) acquisition mode are rather poor due to the

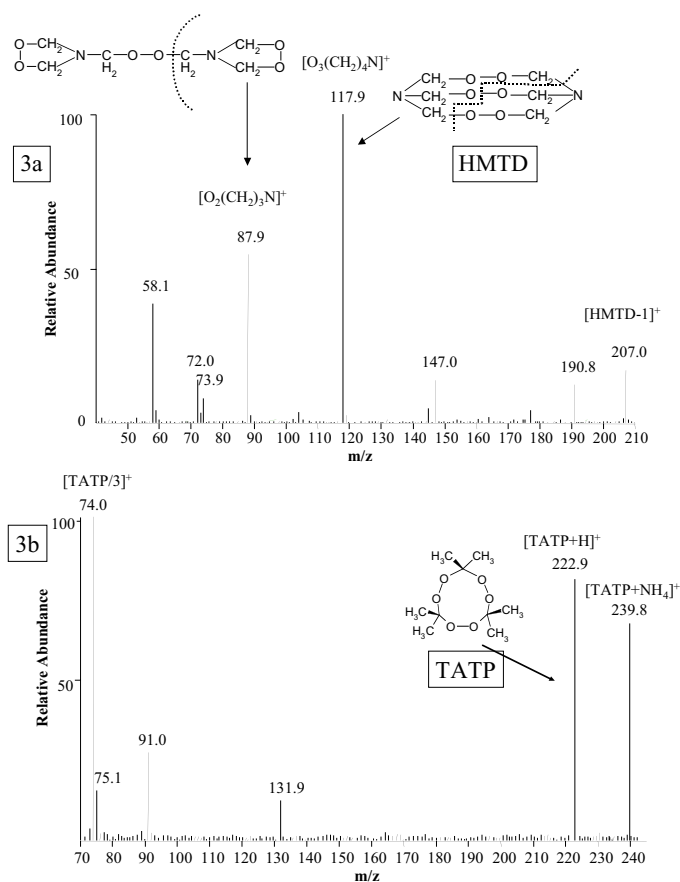


FIG. 3—HPLC-MS/MS spectra of the reference peroxide HMTD (a) and TATP (b) obtained in the Full Scan mode. The precursor ions selected were for HMTD m/z 207 and for TATP m/z 240.

low fragmentation efficiency of the precursor ion. Thus, this data acquisition mode is not so useful for trace analysis, but it may be useful for bulk peroxide samples. Much improved detection limits were obtained with the Selected Reaction Monitoring (SRM) data acquisition mode.

MS/MS Optimization

The parameters of the collision-induced dissociation (CID) for the MS/MS detection, such as collision gas (argon) pressure and collision offset voltage, were optimized in the case of selective monitoring of the mass-charge ratio of 118 for HMTD and 74 for TATP. It was noticed that under optimized conditions (as given in Table 2), besides the fragment ions with m/z 74 and 223, still many precursor ions $[\text{TATP} + \text{NH}_4]^+$ were observed in the full scan mass spectrum, as seen in Fig. 3b. Further increasing the collision gas pressure and/or collision offset voltage was found to decrease the abundance of the $[\text{TATP} + \text{NH}_4]^+$ ions but not to increase the intensity of the fragments with m/z 74. This may be due to the further fragmentation of the ion under these conditions.

Forensic Application to a Letter Bomb Case

The developed HPLC-MS(/MS) method was applied to a forensic case. In this case, a letter bomb had exploded. Subsequently, a white powder material and improvised explosive devices (IEDs) were seized from the suspect's house. The IEDs were destroyed by controlled explosion of the IED (CE-IED). The post-blast debris

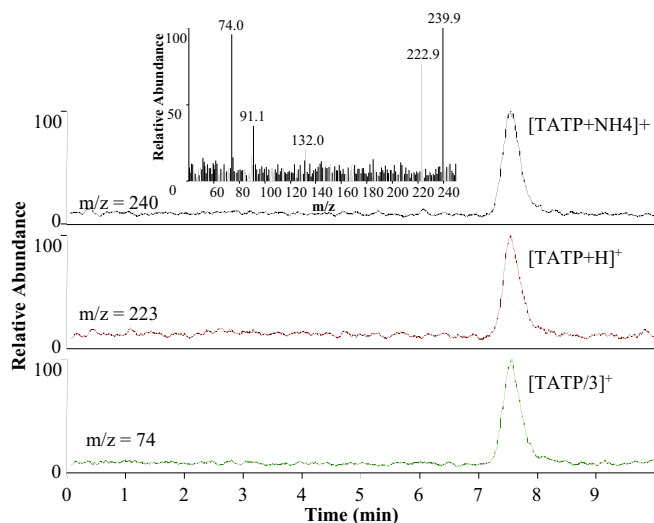


FIG. 4—HPLC-MS/MS chromatograms of the product ions with m/z 240, 223, and 74 obtained in the Full Scan mode for the white powder material seized from a suspect's house (precursor ion m/z 240). The insert of the mass spectrum refers to the peak at 7.6 min, which was identified as TATP by comparing it to Fig. 3b.

from the CE-IEDs and the exploded letter bomb were analyzed in addition to the white powder material.

White Powder Analysis

The white powder was identified as TATP by FT-IR analysis. Further analysis by screening for HMTD and TATP with HPLC-MS showed a small peak at the position of HMTD (m/z 207) and a peak

at the position of TATP (m/z 240). However, the presence of TATP was only confirmed by the HPLC-MS/MS analysis, as shown in Fig. 4. Compared to Fig. 3b, the mass spectrum of the peak in Fig. 4 matches closely with the TATP reference.

Trace (Post-blast) Analysis

The sensitivity for the peroxide explosive TATP with HPLC-MS/MS in the Full Scan mode (see Table 3) is low and usually is not sufficient for trace analysis. Therefore, the post-blast extracts from the CE-IED and the exploded letter bomb have been analyzed by HPLC-MS/MS in the Selected Reaction Monitoring (SRM) mode. In this mode the un-decomposed precursor ion with m/z 240 and the precursor/product-ion pairs with m/z 240/223 and 240/74 were measured simultaneously, as shown in Figs. 5 and 6. The precursor ion with m/z 240 was assigned to $[TATP + NH_4]^+$, and the product ions with m/z 223 and 74 were assigned to $[TATP + H]^+$ and $[TATP/3]^+$, respectively. It was seen that many disturbing peaks occurred in the chromatograms of the ions with m/z 240 and 223. Apparently, identification of TATP by just these two types of measurements is insufficient, since any peak appearing at the position of TATP in the chromatogram has a reasonable chance to originate from an impurity or another disturbing component. Nevertheless, the baseline in case of the ion pair with m/z 240/74 is reasonably clean both for the blanks and for the extracts. The identification of traces of TATP is facilitated by including this ion pair. Combining these three significant ion pairs, TATP was identified exclusively in the post-blast debris of the CE-IED and the letter bomb. Based on the ion pair 240/74, the concentration TATP in the acetone extracts of the copper debris of the CE-IED (Fig. 5) and the letter bomb (Fig. 6) was measured at least as 0.5 and 0.2 $ng/\mu L$, respectively. In addition, methanol extracts of plastic debris of another four

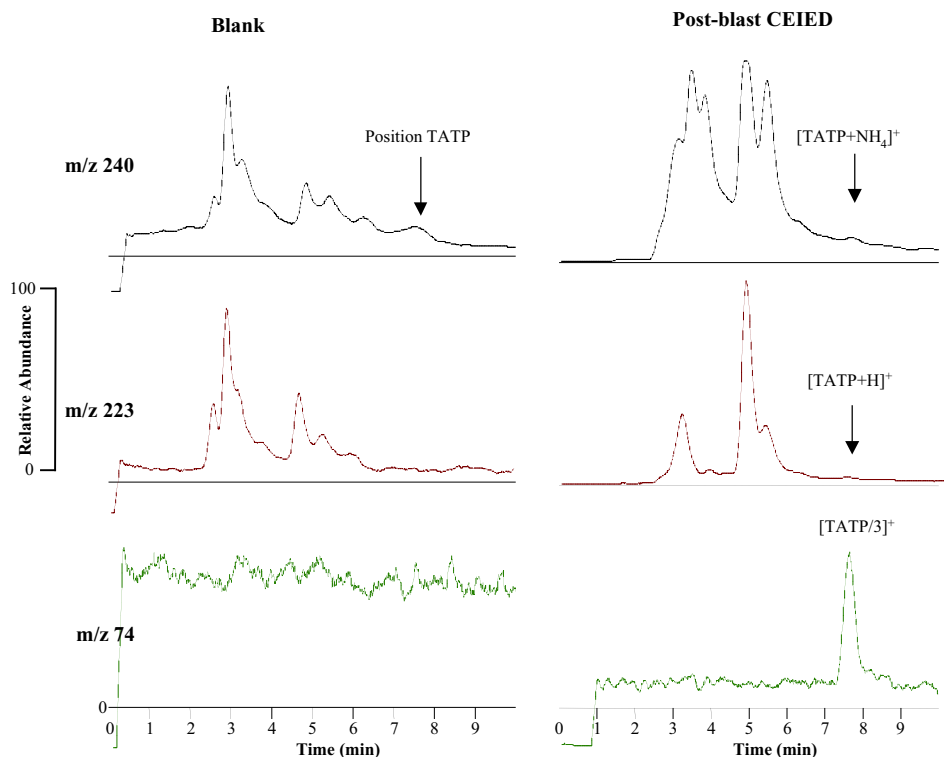


FIG. 5—HPLC-MS/MS chromatograms of the product ions with m/z 240, 223, and 74 obtained in the SRM mode for the analysis of post-blast debris from the controlled explosion of an improvised explosive device (CE-IED)(precursor ion m/z 240). The amount of TATP detected was estimated to be less than approximately 5 ng on column.

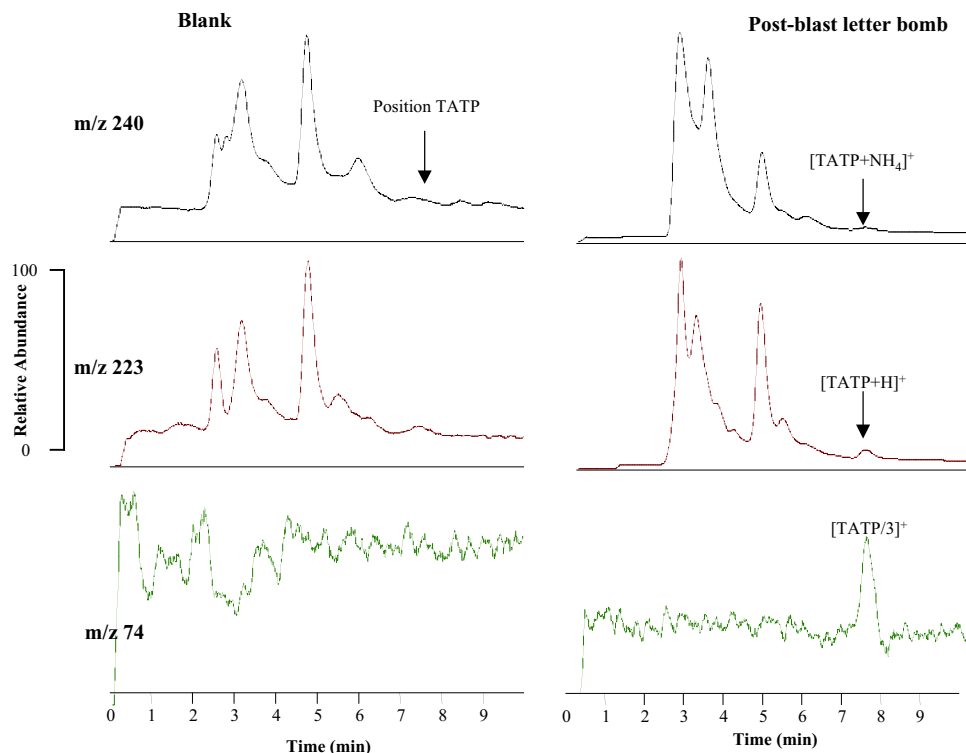


FIG. 6—HPLC-MS/MS chromatograms of the product ions with m/z 240, 223, and 74 obtained in the SRM mode for the analysis of the post-blast debris from the letter bomb (precursor ion: m/z 240). The amount of TATP detected was estimated to be less than approximately 2 ng on column.

CE-IEDs also were analyzed, with the concentration of TATP found varying from ca. 0.16–1.1 ng/ μ L.

Future Work

Methods for the analysis of other peroxides such as DADP and TMDD by HPLC-MS are still not available. We regard the development of a method to detect DADP as more urgent than a method to detect TMDD, since DADP is expected to be present in TATP case samples and possibly even in TATP reference material. Furthermore, the analysis and detection of DADP may be useful for tracing a source of TATP explosive.

Conclusion

The screening for and identification of both HMTD and TATP in one run by HPLC-MS(/MS) has been made possible for the first time. The base peaks of HMTD and TATP obtained in the single MS detection are of pseudo-molecular ions, i.e., $[\text{HMTD} - 1]^+$ and $[\text{TATP} + \text{NH}_4]^+$. A series of product ions was produced from these pseudo-molecular ions in the HPLC-APCI-MS/MS analysis. It is also the first time that a TATP molecular ion $[\text{TATP} + \text{H}]^+$ has ever been observed in an HPLC-MS/MS analysis. The limit of detection for HMTD and TATP was 0.26 and 3.3 ng on column by HPLC-APCI-MS in full scan mode, respectively, and 0.08 and 0.8 by HPLC-APCI-MS/MS in the Selected Reaction Monitoring (single mass unit) mode. We have shown that the MS/MS mode is essential for the positive identification of TATP. The analysis of TATP was applied successfully to a forensic case, and the method presented was even shown to allow for positive identification of TATP in post-blast debris.

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References

- Fedoroff BT, Sheffield OE. Encyclopedia of explosives and related items. Dover, NJ: Picatinny Arsenal 1975;7:H83.
- Beveridge A. Forensic investigation of explosives, analysis of explosives by IS and MS. London: Taylor & Francis Ltd 1998;257–77, 296.
- Zitrin S, Kraus S, Glattstein B. Identification of two explosives. Proceedings of 1st International Symposium on the Analysis and Detection of Explosives; FBI Academy, Quantico, VA, March 29–31, 1983;137–41.
- Reutter DJ, Bender EC, Rudolph TL. Analysis of an unusual explosive: Methods used and conclusions drawn from two cases. Proceedings of the 1st International Symposium on the Analysis and Detection of Explosives; FBI Academy, Quantico, VA, March 29–31, 1983;149–58.
- Candiotti S. Sources: 'Shoe bomb' suspect claims he used Internet recipe. CNN news. January 8, 2002. Posted at <http://edition.cnn.com/2002/US/01/07/inv.shoe.bomb.probe/>.
- Synthesis, properties and forensic identification of TATP, DADP and HMTD. Forensic Explosives Laboratory: Dstl Fort Halstead, DERA/CES/FEL/CR9704; Internal report, 1997.
- Schulte-Ladbeck R, Kolla P, Karst U. Trace analysis of peroxide-based explosives. Anal Chem 2003;75:731–5. [PubMed]
- McKay GJ. Forensic characteristics of organic peroxide explosive (TATP, DADP and HMTD). Kayaku Gakkaishi 2002;63(6):323–9.
- Oxley J, Zhang J, Smith J. Mass spectra of unlabeled and isotopically labeled hexamethylene triperoxide diamine (HMTD). Propellants, Explos, Pyrotech 2000;25:284–7.

10. Yinon J, Zitrin S. Modern methods and applications in analysis of explosives. 1st ed. New York: Chichester, John Wiley and Sons, 1986.
11. Verweij AMA, de Bruyn PCAM, Choufoer C, Lipman PJJ. [Liquid chromatography, thermospray/negative ion, tandem mass spectrometric \(LC/TSP/MS/MS\) analysis of some explosives](#). Forensic Sci Int 1993;60:7–13.
12. Crowson A, Beardah MS. [Development of an LC/MS method for the trace analysis of hexamethylenetriperoxidediamine \(HMTD\)](#). Analyst 2001;126:1689–93.
13. Widmer L, Watson S, Schlatter K, Crowson A. [Development of an LC/MS method for the trace analysis of triacetone triperoxide\(TATP\)](#). Analyst 2002;127:1627–32.
14. Xu X, van de Craats AM, de Bruyn PCAM. Highly sensitive screening method for nitroaromatic, nitramine and nitrate ester explosives by high performance liquid chromatography-atmospheric pressure ionization-mass spectrometry (HPLC-API-MS) in forensic applications. J Forensic Sci In press.
15. Xu X, van de Craats AM, Kok EM, de Bruyn PCAM. Highly sensitive screening method for high explosives. Poster MeC-178 at 16th IMSC2003, Edinburg, 2003; 31 August–5 September.
16. James SA, Off JA. Use of Mass Spectrometry for Confirmation of Animal Drug Residues. Anal Chem 1978;61:1247–52.

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