



Application of LC-MSD and GC-ECD Techniques in the Analysis of Post-explosion Residues of Explosives with Content of 1,3,5-Trinitroso-1,3,5-triazinane^{*)}

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Abstract: The paper deals with possible applications of the connection of liquid chromatography with atmospheric pressure chemical ionization (APCI) mass spectrometry (Agilent 1100 series LS-MSD system) and gas chromatography with electron capture detector (GC-ECD) in the analysis of some common available or improvised explosives. The analysis of selected types of individual explosives, 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitroso-1,3,5-triazinane (TMTA) and analysis of their mixtures (TNT/TMTA and RDX/TMTA) in their post-explosion residues on the basis of generated characteristic mass spectra by using LC-MSD system is the aim of this work. Post-explosion analysis of TMTA and its explosive mixtures can be similarly complicated, like that of the well-known plastic explosive on the basis of pentaerythritol tetranitrate, Semtex-1A.

Keywords: explosive, LC-APCI/MS, GC-ECD, 1,3,5-trinitroso-1,3,5-triazinane, TMTA, trace analysis, 2,4,6-trinitrotoluene, TNT

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Introduction

Forensic identification of post-explosion residues in debris material is the major interest of the criminalistic investigation of the bombing because it will help to find the connection between the used explosive and the suspect [1].

Today the mass spectrometry (MS) belongs to significant methods of investigation of explosives. The utilization of new methods of molecular ionization makes possible to measure the mass spectra of substances, which are considerably thermally instable or have very low volatility [2]. The sensitivity and specificity of the mass spectrometer make it a suitable technique for this application [1].

Currently accepted analytical methods for the determination of trace levels of explosive residues rely almost exclusively on liquid or gas chromatography. Generally, gas chromatography with electron capture detector or mass spectrometry is sensitive technique, but reproducibility suffers especially from the thermally labile compounds. The evolution of the LC-MS interface has also allowed development of sensitive and selective methods for a variety of polar and thermally labile compounds including explosives [3]. LC-MS, with atmospheric pressure chemical ionization (APCI), in the negative-ion mode, was found to provide best sensitivity and selectivity for nitroaromatic compounds [4].

Cassada *et al.* described the development of a simple method for the determination of munitions residues and RDX-metabolites in water using atmospheric pressure ionization (API) and electrospray ionization (ESI) techniques [3]. Liquid chromatography-atmospheric pressure chemical ionization mass spectrometry (LC-APCI/MS) has been used for the identification and characterization of by-products of industrial 2,4,6-trinitrotoluene (TNT) in the work of Zhao *et al.* [4]. Several applications of LC-APCI/MS for the analysis of explosives and explosive residues are described by Schreiber *et al.* and Varga *et al.* [5, 6]. A series of explosives were studied by combined high-performance liquid chromatography-mass spectrometry (HPLC-MS) in the paper of Yinon *et al.* [7].

GC detectors suitable for determination of explosives is reviewed by Yinon and Zitrin [8] include the flame-ionization detector (FID), mass spectrometer (MS), nitrogen phosphorous detector (NPD), electron capture detector (ECD), and thermal energy analyzer (TEA). The ECD, widely used for the determination of halogenated compounds, is less selective, but is more sensitive for nitro aromatics than the TEA or NPD. There are described applications of GC-ECD for the identification of traces of nitroaromatic, nitramine, and nitrate ester explosives [9-11].

However, literature does not contain information about detection and post-explosion analysis of 1,3,5-trinitroso-1,3,5-triazinane (TMTA or R-salt). This

substance is easy available high explosive, which can be exploitable as a part of improvised explosive mixtures. From the point of the said fact this paper deals with possibility of applications of the liquid chromatography with atmospheric pressure chemical ionization (APCI), mass spectrometry (Agilent 1100 series LS-MSD system) and the gas chromatography with electron capture detector (GC-ECD).

Experimental

Used substances

In this paper the following explosives were tested:

- casting military 2,4,6-trinitrotoluene (TNT),
- casting system of 1,3,5-trinitroso-1,3,5-triazinane (TMTA or R-salt) and additives,
- casting mixture of TNT and TMTA,
- casting matrix of RDX, TMTA and additives.

Compositions of these mixtures are summarized in Table 1.

Table 1. Composition of studied casting explosive mixtures

Explosive	Composition [%]	Density [g cm ⁻³]
TNT	100% TNT	1.56
TMTA cast	92% TMTA, 4% diphenylamine, 4% anthracene	1.47
TNT/TMTA	58% TNT, 42% TMTA	1.64
RDX/TMTA	75% RDX, 23% TMTA, 1% diphenylamine, 1% anthracene	1.37

The used standards for the identification of individual components of explosive mixtures were as follows: 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitroso-1,3,5-triazinane (TMTA or R-salt), 1,3,5-trinitro-1,3,5-triazinane (RDX) and pentaerythrytol tetranitrate (PETN). The molecular structures of these explosives are shown in Figure 1.

TMTA, a trinitroso analogue of RDX, is the only representative of nitrosamines interesting as a military high explosive [12, 13]. The TMTA manufacture was based on nitrosolysis of hexamethylenetetramine (or aqueous mixture of ammonia and formaldehyde) with sodium nitrite and mineral acid (sulphuric, hydrochloric), in cooled diluted water solution. There was no need to use concentrated nitric or sulphuric acids in the manufacture of the explosive; the process seemed to be safe and could be successfully realized also under improvised conditions [14].

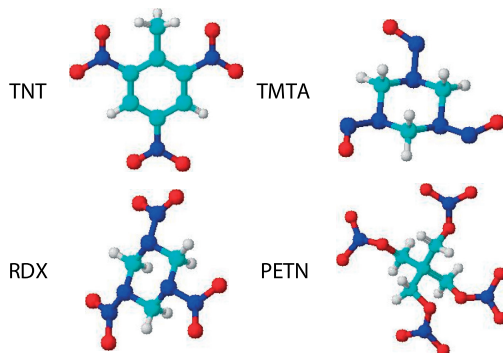


Figure 1. Molecular structures of investigated explosives.

Apparatus for analyses of samples

Liquid chromatography-mass spectrometry (LC-MS) conditions

All analyses were performed by means of Agilent 1100 series LC-MSD system with the atmospheric pressure chemical ionization (APCI) source, in the negative-ion mode. The used chromatographic and mass spectrometric conditions are shown below.

Chromatographic conditions:

Column: Zorbax Eclipse XDB-C8; 4.6 x 150 mm; 5 mm (Agilent Technologies)
 Mobil phase: Methanol/water; 70 : 30, v/v, with addition of ammonium chloride and formic acid
 Flow rate: 1 mL min⁻¹
 Injection vol.: 20 μL

MS conditions:

Source: APCI	Vaporizer temp: 300 °C
Mode: SCAN and SIM	Dry gas flow: 5 L min ⁻¹
Ionization polarity: Negative	Drying gas temp: 330 °C
Capillary voltage: 3000 V	Fragmentor: 30 V
Nebulizer: 60 psi	

Gas chromatograph with electron capture detector (GC-ECD)

The standards of explosives (TNT, TMTA, RDX and PETN) were analyzed on a Hewlett Packard 5890 II chromatograph, using a capillary column HP-5 of 5 m length, 0.53 mm inner diameter, and 0.88 μm film thickness. An electron capture detector (ECD) was used for the detection, and the carrier gas was nitrogen of 20 kPa overpressure. The

Mass spectra of TNT, RDX and PETN are described in detail in the paper [6]. TMTA features mainly adduct and fragment ions in the APCI mass spectrum. TMTA also produces like RDX adduct ions $[M+Cl]^-$ with the isotopes ^{35}Cl and ^{37}Cl at m/z 209 $[M+^{35}Cl]^-$ and m/z 211 $[M+^{37}Cl]^-$. Mass spectrum of TMTA does not contain molecular ion, but its characteristic ions are fragments rising by the loss of 30 mass units $[M-NO]^-$ at m/z 144. Adduct ions at m/z 318, 383 and 385 were $[2M-NO]^-$, $[2M+^{35}Cl]^-$ and $[2M+^{37}Cl]^-$. The determination of the presence of PETN in some organic extracts from the priming charge (booster) was based on the SIM method, which included the ions of PETN at m/z 315, 351 and 378.

Results and Discussion

Results of LC-APCI/MS and GC-ECD analyses of post-explosion extracts

All organic extracts of post-explosion debris of TNT, TMTA and explosive mixtures of TNT/TMTA and RDX/TMTA by means of LC-APCI/MS in SIM mode and GC-ECD techniques were measured. In the case of liquid chromatography the used mobile phase, methanol-water, allowed the identification of components in organic and water extracts, too. Results of LC-APCI/MS measuring of investigated explosives are summarized in Table 2.

Table 2. Results of LC-APCI/MS analyses of post-explosion products of tested explosives

Explosive	Major ions of original explosive	LC-APCI/MS analyses of post-explosion samples			
		Methanol extract (M)		Water extract (W)	
		M ₁	M ₂	W ₁	W ₂
TNT	$[M]^-$, $[M-H]^-$, $[M-NO]^-$	$[M]^-$, $[M-H]^-$, $[M-NO]^-$			$[M-H]^-$
TMTA	$[M+^{35}Cl]^-$, $[M+^{37}Cl]^-$, $[M-NO]^-$	-	$[M+^{35}Cl]^-$, $[M+^{37}Cl]^-$, $[M-NO]^-$	$[M+^{35}Cl]^-$, $[M+^{37}Cl]^-$	-
TNT/TMTA	$[M]^-$, $[M-H]^-$, $[M-NO]^-$ (TNT), $[M+^{35}Cl]^-$, $[M+^{37}Cl]^-$, $[M-NO]^-$	$[M]^-$, $[M-H]^-$	$[M-H]^-$	-	-
RDX/TMTA	$[M+^{35}Cl]^-$, $[M+^{37}Cl]^-$ (RDX), $[M+^{35}Cl]^-$, $[M+^{37}Cl]^-$, $[M-NO]^-$	-	$[M+^{35}Cl]^-$, $[M+^{37}Cl]^-$ (RDX)	-	-

LC-APCI/MS analysis showed that the concentration of TNT in post-explosion residues reliably exceeds its limit of detection at the usage of the solvent of organic as well as water origin. The corresponding LC-APCI/MS

chromatograms are shown in Figures 3A and 3B. The traces of TNT in the post-explosion residues were confirmed by GC-ECD technique, too. The results of GC-ECD measurements are summarized in Table 3.

Figure 5A shows the chromatogram obtained by the GC-ECD technique for post-explosion residues of TNT and identified component of PETN from the priming charge of Semtex-1A.

Table 3. Results of GC-ECD analyses of methanol post-explosion extracts of investigated explosives

Post-explosion samples of explosives	Identification of original components		Identification of priming charge (Semtex-1A)
	Samples 1	Samples 2	
TNT	TNT	TNT	PETN
TMTA	TMTA	TMTA	PETN
TNT/TMTA	TNT	TNT	PETN
RDX/TMTA	RDX	RDX	PETN

LC-APCI/MS post-explosion analysis of TMTA already was not as successful as LC/MS identification of TNT. From the two analyzed organic extracts only one sample contained all ions of TMTA. In the case of water samples of TMTA the situation was similar as in the case of organic extracts. The positive LC-APCI/MS chromatograms of methanol and water post-explosion extracts of TMTA are shown in Figures 3C and 3D. At the samples of post-explosion residues of TMTA by using of GC-ECD technique better results were obtained (Figure 5B) than by using LC/MS technique. It is caused by higher sensitivity of electron capture detector to the TMTA.

LC-APCI/MS and GC-ECD chromatograms of explosive mixtures of TNT/TMTA and RDX/TMTA (Figures 4A, 4C and Figures 5C, 5D) showed that amounts of non-reacted particles of TMTA in the post-explosion debris are below the sensitivity of both instruments.

High detonation velocities of the mixtures TNT/TMTA and RDX/TMTA (6.95 km s^{-1} for TNT/TMTA and 8.00 km s^{-1} for RDX/TMTA, that are the experimentally determined values) are probably the reasons of absence of TMTA in post-explosion residues of these mixtures. It means that in comparison with TNT (6.47 km s^{-1}) the detonation is forwarded to more ideal conditions with the results of smaller part of TMTA after the detonation. The trace amount of TMTA in post-explosion residues is considerably influenced by the substitution of this component in the explosive mixtures.

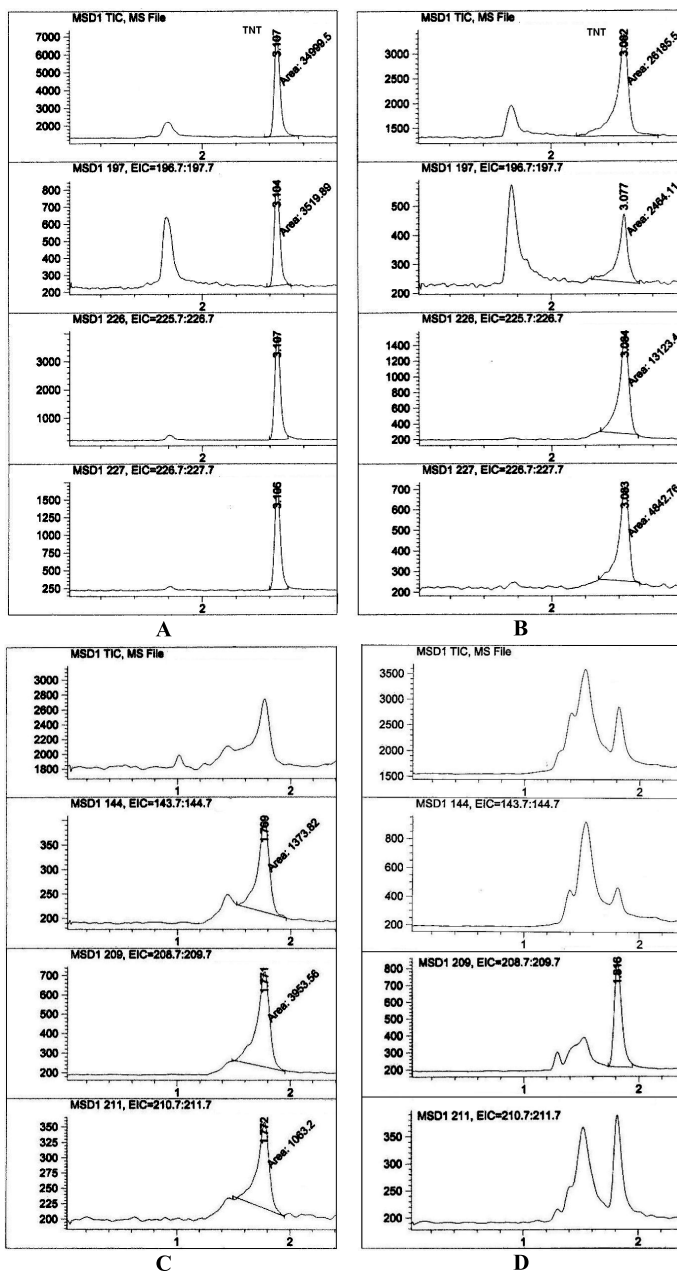


Figure 3. Comparison of LC-APCI/MS chromatograms of post-explosion residues of TNT and TMTA in water (A and D) and in methanol (B and C).

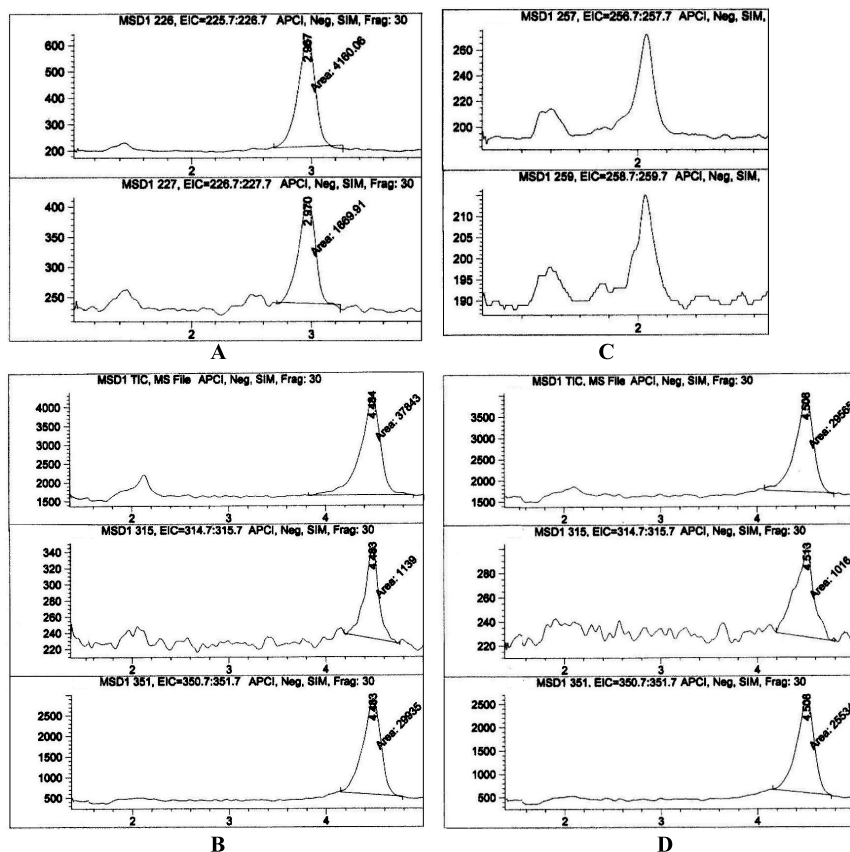


Figure 4. The positive results of LC-APCI/MS analyses of post-explosion residues of mixtures of TNT/TMTA (**A** - TNT), (**B** - PETN) and RDX/TMTA (**C** -RDX), (**D** - PETN) in methanol extracts.

High detonation velocity of these mixtures causes increasing, in ideal conditions of detonation, at the expense of amount of post-explosion residues. Reduced amount of components can also complicate the analysis of TNT and RDX in these explosive mixtures (lower response of the detector for these components after detonation of explosive mixtures).

In all samples of organic extracts of TNT/TMTA and RDX/TMTA the presence of PETN comes from the priming charges of Semtex-1A by means of GC-ECD and LC-APCI/MS (Figures 4B a 4D) was confirmed.

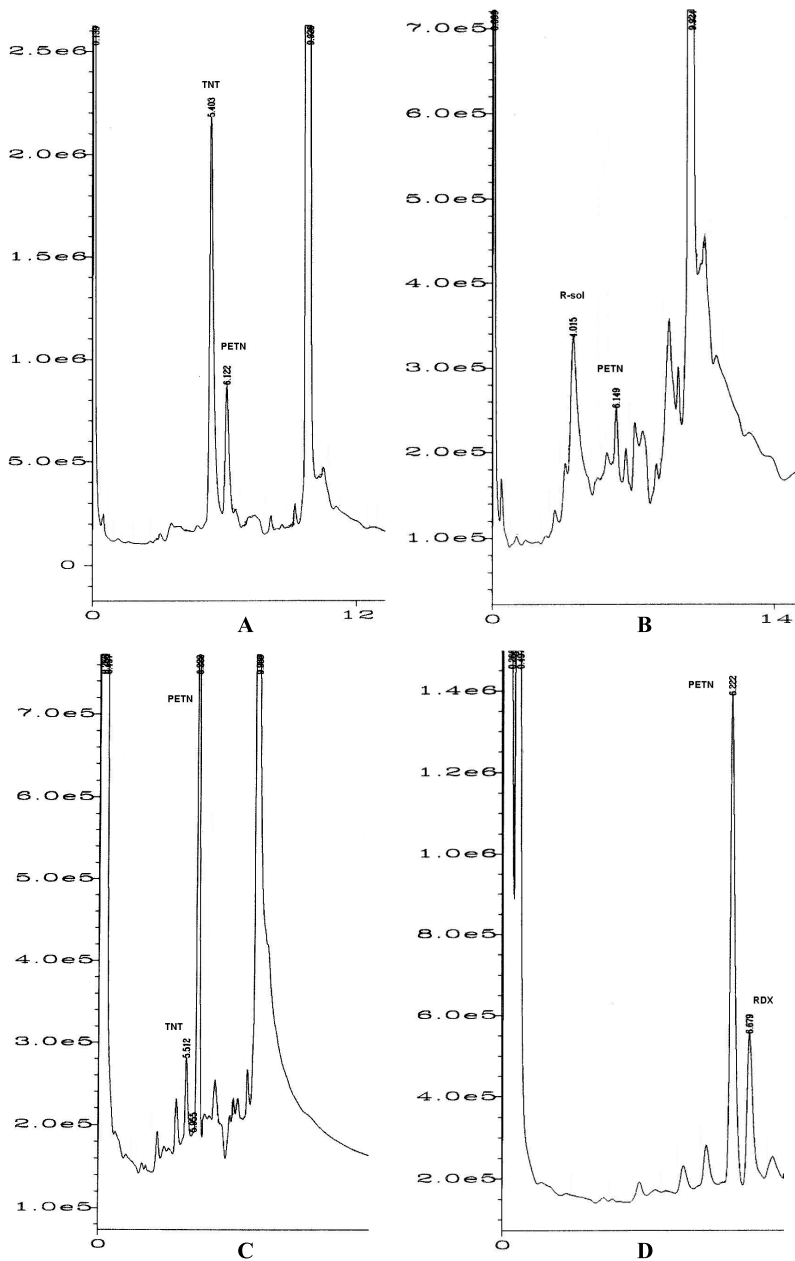


Figure 5. GC-ECD chromatograms of post-explosion residues of TNT (A), TMTA (B), mixtures of TNT/TMTA (C) and RDX/TMTA (D).

Conclusions

On the bases of LC-APCI/MS and GC-ECD analyses of post-explosion residues of 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitroso-1,3,5-triazinane (TMTA) and two explosive mixtures TNT/TMTA and RDX/TMTA we found the following results:

- 1) Analysis of TNT after detonation compared with TMTA, but mainly mixtures of TNT/TMTA and RDX/TMTA, is relatively simple. TNT is the common well-known detectable explosive. Both tested solvents (methanol and water) were suitable for its post-explosion analysis.
- 2) Analysis of TMTA is becoming complicated, because compared to TNT, it detonates with higher detonation velocity and that is why after its detonation stays lower amount of post-explosion products (superior process of detonation). Volatility of TMTA is relatively high which can also complicate its detection after explosion.
- 3) TMTA in post-explosion products of explosive mixtures of TNT/TMTA and RDX/TMTA was not detected. However, these samples were positive for TNT and RDX. The results of this experiment showed that very strong explosives, which post-explosion analyses can be complicated for the absence of TMTA, is possible to obtain by using the casting technology from TMTA with TNT or RDX. In the analysis of investigated explosives higher sensitivity of GC-ECD technique was confirmed, but their LC/MS analysis was simpler on the basis of known APCI mass spectrum of individual explosives.
- 4) Collection of samples of post-explosion residues of the tested explosives was carried out under idealized conditions (sampling done immediately from the metal plate of the construction). In reality the time between the detonation and sampling and weather conditions can also influence the success of analyses of these explosives.

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