

Identification of nitrate ester explosives by liquid chromatography–electrospray ionization and atmospheric pressure chemical ionization mass spectrometry

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Abstract

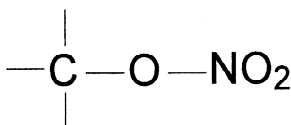
Liquid chromatography–mass spectrometry (LC–MS) with electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI), in the negative-ion mode, was investigated for the analyses of three widely used nitrate ester explosives, pentaerythritol tetranitrate, nitroglycerin and ethylene glycol dinitrate, as well as six additional nitrate esters, using post-column additives. In ESI, ammonium nitrate, sodium nitrite, propionic acid and ammonium chloride promoted formation of characteristic adduct ions of the respective nitrate esters. In APCI, chlorinated agents, dichloromethane, chloroform, carbon tetrachloride and ammonium chloride, were employed, forming chloride attachment adduct ions. Three forensic samples, Booster DYNO, Semtex and Smokeless Powder, were analyzed to demonstrate the validity of the developed LC–MS methods.

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1. Introduction

The major nitrate ester explosives, pentaerythritol tetranitrate (PETN), nitroglycerin (NG) and ethylene glycol dinitrate (EGDN), are characterized by structure **a**.



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PETN is a white, crystalline explosive used as a base charge in blasting caps and detonators, as the core explosive in detonating cord, in booster charges and as a major ingredient in plastic explosives. NG is a colorless, odorless, viscous liquid explosive, used in industrial explosives. It has been the main component in many dynamites and an ingredient in multi-base propellants. EGDN is a transparent, colorless, liquid explosive. It is a good solvent for low-grade nitrocellulose and has been used in mixtures with NG for low-temperature dynamites [1,2].

Due to their widespread use in explosive formulations, the analysis of these nitrate esters is of importance, not only in forensic identification of post-blast debris at bombing scenes, but also in

detection of trace amounts released into the environment. Accordingly, an effective analytical procedure is required for their unambiguous characterization. Although belonging to the same chemical group, these nitrate esters have different vapor pressures, ranging from $1.4 \cdot 10^{-8}$ Torr for PETN, $3.1 \cdot 10^{-4}$ Torr for NG to $7.0 \cdot 10^{-2}$ Torr for EGDN [2], which make their analysis and identification by a single method difficult (1 Torr = 133.322 Pa).

The analysis of nitrate esters with conventional gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS) could be problematic due to their thermal instability and/or sorption in the analytical system [3,4]. Electron ionization mass spectra of these compounds are characterized by a lack of a molecular ion, but by the presence of two fragment ions, m/z 46 (NO_2^+) and m/z 62 (NO_3^+). Some of these difficulties can be overcome to some extent by using temperature-programmed injection [5] or short columns [6].

In an effort to find a suitable analytical method for the identification of the nitrate esters, we have studied the electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) mass spectrometry of PETN, NG and EGDN, as well as six additional nitrate ester compounds (Table 1 and Fig. 1). Previous studies [7,8] show that the negative-ion ESI and APCI of nitrate esters are susceptible to any impurities in the analytical system and promote the formation of a variety of adduct ions instead of molecular-type ions. This sometimes makes the identification of the targeted compound in a complicated sample mixture problematic. Several studies [9–14] pointed to the use of additives in obtaining adduct ion formation in explosives. There-

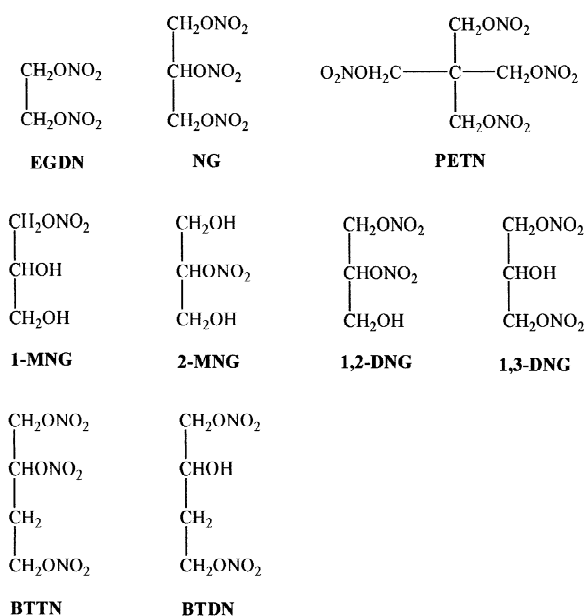


Fig. 1. Chemical structures of investigated nitrate esters.

fore, the potential of several inorganic and organic additives for the formation of characteristic adduct ions was investigated in order to enhance sensitivity and improve unambiguous identification of the explosives. Identification was supported by tandem mass spectrometric determination with collision-induced dissociation (MS–MS–CID) of the adduct ions.

2. Experimental

2.1. Chemicals and reagents

The following nitrate ester standards stored in ampules and dissolved in 1 ml acetonitrile (Cerilliant or Radian International, Austin, TX, USA) were employed: pentaerythritol tetranitrate (1000 $\mu\text{g/ml}$), nitroglycerin (1000 $\mu\text{g/ml}$), ethylene glycol dinitrate (100 $\mu\text{g/ml}$), 1,2,4-butanetriol trinitrate (100 $\mu\text{g/ml}$), 1,2,4-butanetriol 1,4-dinitrate (100 $\mu\text{g/ml}$), 1,2-dinitroglycerin (100 $\mu\text{g/ml}$), 1,3-dinitroglycerin (100 $\mu\text{g/ml}$), 1-mononitroglycerin (100 $\mu\text{g/ml}$), and 2-mononitroglycerin (100 $\mu\text{g/ml}$). Ammonium nitrate (99.999%) and carbon tetrachloride (99.9%) were purchased from Aldrich (Milwaukee, WI,

Table 1
Investigated nitrate esters

Nitrate ester	M_r
Pentaerythritol tetranitrate (PETN)	316
Glycerol trinitrate (Nitroglycerin; NG)	227
Ethylene glycol dinitrate (EGDN)	152
1,2,4-Butanetriol trinitrate (BTTN)	241
1,2,4-Butanetriol 1,4-dinitrate (BTDN)	196
Glycerol-1,2-dinitrate (1,2-dinitroglycerin; 1,2-DNG)	182
Glycerol-1,3-dinitrate (1,3-dinitroglycerin; 1,3-DNG)	182
Glycerol-1-nitrate (1-mononitroglycerin; 1-MNG)	137
Glycerol-2-nitrate (2-mononitroglycerin; 2-MNG)	137

USA); ammonium chloride (99.5%) was obtained from Sigma (St. Louis, MO, USA); sodium nitrite (99%) from Sigma–Aldrich (Seelze, Germany); propionic acid ($\geq 99.5\%$), dichloromethane (99.8%) and chloroform ($\geq 99.8\%$) from Fluka (Buchs, Switzerland). B&J Brand high-purity methanol (Burdick & Jackson, Muskegon, MI, USA) and Milli-Q purified water were used throughout the experimental procedures.

The nitrate ester compounds were diluted with methanol–water (50:50) to the desired concentrations. The forensic samples, Booster DYN0, Semtex and Smokeless Powder, were first dissolved in methanol, filtered through 0.45- μm membrane filters and then diluted to the desired concentrations with methanol–water (50:50).

2.2. LC–MS conditions

LC–MS analyses were conducted on a Thermo-Finnigan LCQ_{DUO} ion trap mass spectrometer (San Jose, CA, USA), using either one of the ESI and APCI interfaces, in the negative-ion mode. A Finnigan-MAT SpectraSystem HPLC system consisting of a SCM 1000 vacuum membrane degasser, a P4000 gradient pump and an AS 3000 autosampler, was coupled to the mass spectrometer. Helium was used as damping and collision gas for the ion trap, while nitrogen served as sheath and auxiliary gas for the ion source.

In LC–ESI-MS, spray voltage was set at -4.2 kV, sheath gas (nitrogen) pressure was 100 ± 20 p.s.i. (690 ± 140 kPa). The temperatures of the heated capillary ranged from 125 to 140 °C, depending on the additives used (Table 2). HPLC separation was achieved with a Restek Allure C₁₈ column (100×2.1 mm, 5 μm particle size) (Bellefonte, PA, USA) using an isocratic mobile phase of methanol–water (70:30) at a flow-rate of 150 $\mu\text{l}/\text{min}$. Sample injection volume was 10 μl . Ammonium nitrate, sodium nitrite, propionic acid and ammonium chloride, dissolved in methanol–water (70:30), were introduced post-column by a syringe pump (flow-rate 5 $\mu\text{l}/\text{min}$) through a T union into the LC flow before entering the mass spectrometer. Their final concentrations were 0.05, 0.1, 0.2 and 0.1 mM, respectively.

In LC–APCI-MS, discharge current was 5.5 μA , sheath and auxiliary gas pressure was 100 ± 20 p.s.i.

Table 2
Temperatures of heated capillary and vaporizer

Temperature of heated capillary (°C)	Temperature of vaporizer (°C)	Additive
ESI-MS		
125		Ammonium nitrate
130		Sodium nitrite
140		Propionic acid
140		Ammonium chloride
150		No
APCI-MS		
125	330	Dichloromethane
125	150	Chloroform
125	150	Carbon tetrachloride
130	150	Ammonium chloride
140	200	No

(690 ± 140 kPa). Vaporizer and heated capillary temperatures were selected according to the additives used (Table 2). A Restek Allure C₁₈ column (150×3.2 mm, 5 μm particle size) was used, with an isocratic mobile phase of methanol–water (70:30) at a flow-rate of 400 $\mu\text{l}/\text{min}$. Sample injection volume was 10 μl . Dichloromethane, chloroform, carbon tetrachloride and ammonium chloride, dissolved in methanol–water (70:30), were introduced post-column by a syringe pump (flow-rate 5 $\mu\text{l}/\text{min}$) through a T union into the LC flow before entering the mass spectrometer. Their final concentrations were 0.2, 0.1, 0.05% (v/v) and 0.3 mM, respectively.

For full scan MS–MS–CID analyses, the collision energy was set to 10–30% of 5.0 V.

3. Results and discussion

Nitrate esters have a strong electron affinity [3], which makes them excellent candidates for analysis in the negative-ion mode. However, in the absence of any additives, the mass spectra are usually characterized by various adduct ions formed from the decomposition fragments of the nitrate esters themselves or the impurities present in the analytical system. The lack of specificity in the mass spectra sometimes makes the unambiguous identification of these nitrate esters difficult. Especially in the case of EGDN, no characteristic ions can be detected either in the ESI or APCI mass spectra. In order to solve

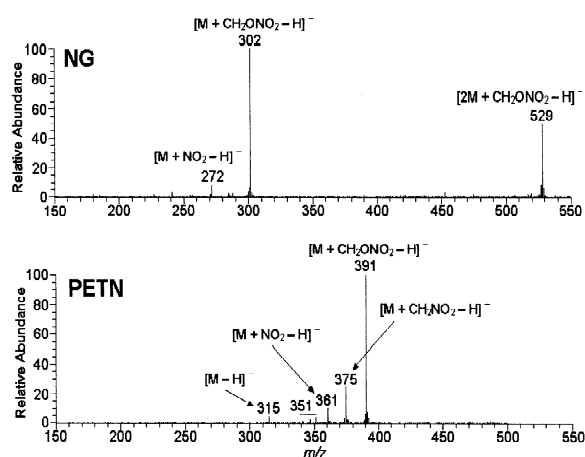


Fig. 2. Negative-ion ESI mass spectra of NG and PETN without additive.

this problem, we investigated different kinds of additives and their effectiveness in promoting the formation of characteristic adduct ions for the identification of the analyzed nitrate esters.

3.1. Electrospray ionization mass spectrometry of nitrate esters

Typical examples of ESI mass spectra without additives are the mass spectra of NG and PETN, shown in Fig. 2. Mass spectra contain adduct ions formed by addition reactions between the nitrate ester and its decomposition fragments.

In order to investigate adduct ion formation in nitrate esters, ammonium nitrate, sodium nitrite,

propionic acid and ammonium chloride were chosen as additives. Optimal concentrations of the additives for LC–ESI–MS analyses, at the flow-rate 150 $\mu\text{l}/\text{min}$, were 0.05 mM NH_4NO_3 , 0.1 mM NaNO_2 , 0.2 mM propionic acid, and 0.1 mM NH_4Cl . Another experimental parameter crucial for the efficient detection of the adduct ions was the temperature of the heated capillary. The higher the vapor pressure of the nitrate ester, the lower the required temperature of the heated capillary for the adduct ion to be detected. This was especially critical for EGDN, which was preferentially detected at a heated capillary temperature below 140 $^\circ\text{C}$, while a slightly wider temperature range was acceptable for the other nitrate ester compounds. However, for cases where the analyte includes all three explosives, a specific temperature of the heated capillary temperature was set, according to the additive used, as described in the Experimental section.

Table 3 lists the m/z of the detected adduct ions formed for all the investigated nitrate esters with different additives and the corresponding limits of detection. No adduct ions were formed in EGDN when using propionic acid as additive. With sodium nitrite, adduct ion formation in EGDN was not effective. Propionic acid and sodium nitrite proved to be effective additives for some of the other nitrate esters. When analyzing 1,2- and 1,3-dinitroglycerin with ammonium nitrate as additive, one has to be careful not to confuse the adduct ion at m/z 244 ($[\text{M} + \text{NO}_3]^-$) with a cluster ion at the same m/z , resulting from ammonium nitrate itself, as previously reported [15]. Unambiguous identification of these

Table 3
Mass spectral ions and limits of detection of nitrate esters in LC–ESI–MS

Nitrate ester	NH_4NO_3		NaNO_2		Propionic acid		NH_4Cl	
	m/z of $[\text{M} + \text{NO}_3]^-$	LOD (pg/ μl)	m/z of $[\text{M} + \text{NO}_2]^-$	LOD (pg/ μl)	m/z of $[\text{M} + \text{CH}_3\text{CH}_2\text{CO}_2]^-$	LOD (pg/ μl)	m/z of $[\text{M} + \text{Cl}]^-$	LOD (pg/ μl)
PETN	378	5	362	10	389	10	351, 353	10
NG	289	5	273	20	300	25	262, 264	10
EGDN	214	2000	198	10 000	n.d.	–	187, 189	2500
BTTN	303	10	287	10	314	5	276, 278	10
BTDN	258	10	242	10	269	5	231, 233	10
1,2-DNG	244	75	228	10	255	5	217, 219	10
1,3-DNG	244	75	228	10	255	5	217, 219	20
1-MNG	199	50	183	30	210	25	172, 174	75
2-MNG	199	75	183	25	210	25	172, 174	100

two nitrate esters can be done by using other additives. The adduct ions resulting from ammonium chloride as additive were characterized by two ions with a difference of 2 mass units and an abundance ratio of 3:1 due to the naturally occurring isotopes of ^{35}Cl and ^{37}Cl . Based on the results obtained, ammonium nitrate and ammonium chloride proved to be the most effective additives for LC–ESI–MS of the three nitrate esters explosives PETN, NG and EGDN. The mass chromatograms of a mixture of these three compounds with ammonium nitrate as additive are shown in Fig. 3.

The identity of the observed adduct ions was further supported by the MS–MS–CID results of some adduct ions, which are listed in Tables 4 and 5. The fragment ion at m/z 62 ($[\text{NO}_3]^-$) was always observed in the mass spectra of the nitrate esters with lower parent adduct ion mass, such as in the case of EGDN, 1- and 2-mononitroglycerin. The reason for the absence of $[\text{NO}_3]^-$ in the CID mass spectra of other nitrate esters was the cut-off at one-third of the m/z of the parent ion, below which no daughter ions can be observed. This phenomenon is inherent to the Thermo-Finnigan LCQ_{DUO} ion trap mass spectrometer. In the MS–MS–CID analysis of PETN with various additives, all adduct ions produced the most intense daughter ion at m/z 315, corresponding to $[\text{M}-\text{H}]^-$. The MS–MS–CID spectra of NG adduct ions were characterized by several daughter ions in

the lower mass range. The ion at m/z 226, $[\text{M}-\text{H}]^-$, was either at a very low intensity or not observed at all. No daughter ions were observed in the MS–MS–CID of the adduct ion formed in NG with propionic acid. The MS–MS–CID mass spectra of the EGDN adduct ions only produced an ion at m/z 62 ($[\text{NO}_3]^-$). For the other nitrate esters investigated, their MS–MS–CID exhibited similar fragmentation processes as PETN, NG and EGDN. No daughter ions were observed in the MS–MS–CID mass spectra of $[\text{M}+\text{NO}_3]^-$ of BTTN and BTDN as well as $[\text{M}+\text{Cl}]^-$ of BTDN. Probably the daughter ions are in the low mass range, below the cut-off of the ion trap. It is noteworthy to point out that $[\text{M}+\text{CH}_3\text{CH}_2\text{CO}_2]^-$ of both 1- and 2-mononitroglycerin fragmented into three high abundant characteristic daughter ions at m/z 136, 73 and 62, corresponding to $[\text{M}-\text{H}]^-$, $[\text{CH}_3\text{CH}_2\text{CO}_2]^-$, $[\text{NO}_3]^-$, respectively, which supports the involvement of both the additive and the nitrate ester molecule in the adduct ion formation.

3.2. Atmospheric pressure chemical ionization of nitrate esters

When using dichloromethane, the detection of EGDN vapors by ion mobility spectrometry was facilitated through the specific formation of $[\text{EGDN}+\text{Cl}]^-$ [16]. Recently, Reich and Yost [17] reported the application of dichloromethane, chloroform and carbon tetrachloride additives, introduced as a solution in LC–APCI–MS analysis of several explosives (e.g., HMX, RDX, PETN, TNT). Except for TNT, with $[\text{M}-\text{H}]^-$ as the dominant ion, $[\text{M}+\text{Cl}]^-$ was the preferentially formed adduct ion for all the other explosives. Based on these previous studies, an attempt was made to investigate the adduct ion formation in the nitrate esters, using LC–APCI–MS in the negative-ion mode with dichloromethane, chloroform, carbon tetrachloride and ammonium chloride. Like in LC–ESI–MS, an important parameter was the concentration of each one of the post-column introduced additives. The optimal final concentrations were found to be 0.2% for dichloromethane, 0.1% for chloroform, 0.05% for carbon tetrachloride and 0.3 mM for ammonium chloride. In APCI, both vaporizer and heated capillary temperatures have great impact on the adduct

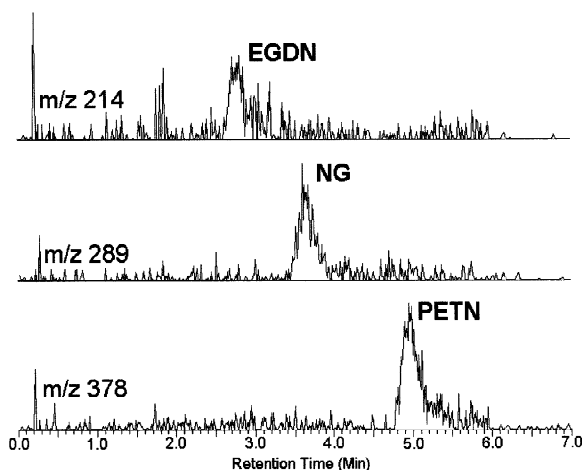


Fig. 3. Mass chromatograms of a mixture of 2 ng/ μl EGDN, 10 pg/ μl NG and 10 pg/ μl PETN with post column introduction of ammonium nitrate in LC–ESI–MS.

Table 4
MS–MS–CID ions of PETN, NG and EGDN

Parent ion (P)		CID energy (%)	Daughter ions		Suggested composition
<i>m/z</i>	Ion		<i>m/z</i>	%	
PETN					
378	[M+NO ₃] [−]	23.00	315	100	[P–NO ₃ –H] [−]
			192	22	[P–NO ₃ –2ONO ₂] [−]
362	[M+NO ₂] [−]	25.00	315	100	[P–NO ₂ –H] [−]
			192	10	[P–NO ₂ –2ONO ₂] [−]
			109	30	[ONO ₂ +NO ₂ +H] [−]
389	[M+CH ₃ CH ₂ CO ₂] [−]	20.00	315	100	[P–CH ₃ CH ₂ CO ₂ –H] [−]
			293	15	[2CH ₃ ONO ₂ +2ONO ₂ +OH] [−]
			192	6	[P–CH ₃ CH ₂ CO ₂ –2ONO ₂] [−]
351	[M+ ³⁵ Cl] [−]	15.00	315	100	[P– ³⁵ Cl–H] [−]
			193	12	[P– ³⁵ Cl–2ONO ₂ +H] [−]
			109	7	[ONO ₂ +NO ₂ +H] [−]
NG					
289	[M+NO ₃] [−]	17.00	125	15	[2ONO ₂ +H] [−]
			109	28	[ONO ₂ +NO ₂ +H] [−]
			93	7	[2NO ₂ +H] [−]
			86	100	[2CHNO] [−]
273	[M+NO ₂] [−]	11.00	226	3	[P–NO ₂ –H] [−]
			180	40	[P–2NO ₂ –H] [−]
			109	100	[ONO ₂ +NO ₂ +H] [−]
			93	12	[2NO ₂ +H] [−]
			86	28	[2CHNO] [−]
262	[M+ ³⁵ Cl] [−]	19.00	226	3	[P– ³⁵ Cl–H] [−]
			109	30	[ONO ₂ +NO ₂ +H] [−]
			93	20	[2NO ₂ +H] [−]
			86	100	[2CHNO] [−]
EGDN					
214	[M+NO ₃] [−]	10.00	62	100	[ONO ₂] [−]
198	[M+NO ₂] [−]	23.00	62	100	[ONO ₂] [−]
187	[M+ ³⁵ Cl] [−]	12.00	62	100	[ONO ₂] [−]

ion formation. It was noted that except for dichloromethane which required a higher vaporizer temperature (330 °C), the other additives produced intense [M+Cl][−] ions at lower vaporizer temperature (150 °C). Moreover, lower temperatures of the heated capillary (125 or 130 °C) were favorable to the adduct ion formation.

Chloroform and ammonium chloride produced the best sensitivity of adduct ion formation. Lowest detection limits for PETN, NG and EGDN were 10, 20 pg/μl and 2.5 ng/μl, respectively. Although carbon tetrachloride was acceptable for most nitrate esters, it produced low intensity adduct ions of EGDN. Dichloromethane was not efficient in the formation of the adduct ions. Fig. 4 shows the APCI

mass spectrum of NG with additive carbon tetrachloride. [M+Cl][−] has been observed in all APCI mass spectra of nitrate esters, when using chlorinated additives. Experiments were also conducted on EGDN, NG and PETN without any additive. Mass spectra of NG and PETN are shown in Fig. 5. No ions were observed in the mass spectrum of EGDN. In addition, the lowest limits of detection were much higher than those with the chlorinated additives. The mass chromatograms of a mixture of PETN, NG and EGDN with post-column introduction of chloroform are shown in Fig. 6. As in ESI, MS–MS–CID mass spectra of adduct ions produced a major daughter ion at *m/z* 315, [M–H][−], in PETN, low mass daughter ions in NG and an ion at *m/z* 62, [NO₃][−], in EGDN.

Table 5
MS–MS–CID ions of nitrate esters

Parent ion (P)		CID energy (%)	Daughter ions		Suggested composition
<i>m/z</i>	Ion		<i>m/z</i>	%	
BTTN					
287	[M+NO ₂] ⁻	13.30	240	2	[P–NO ₂ –H] ⁻
			194	40	[P–2NO ₂ –H] ⁻
			125	60	[2ONO ₂ +H] ⁻
			109	100	[ONO ₂ +NO ₂ +H] ⁻
			93	27	[2NO ₂ +H] ⁻
314	[M+CH ₃ CH ₂ CO ₂] ⁻	12.70	240	43	[P–CH ₃ CH ₂ CO ₂ –H] ⁻
			194	42	[P–CH ₃ CH ₂ CO ₂ –NO ₂ –H] ⁻
			136	10	[P–CH ₃ CH ₂ CO ₂ –ONO ₂ –CHNO] ⁻
			125	32	[2ONO ₂ +H] ⁻
			109	100	[ONO ₂ +NO ₂ +H] ⁻
			93	8	[2NO ₂ +H] ⁻
276	[M+ ³⁵ Cl] ⁻	19.00	240	5	[P– ³⁵ Cl–H] ⁻
			109	100	[ONO ₂ +NO ₂ +H] ⁻
			93	10	[2NO ₂ +H] ⁻
BTDN					
242	[M+NO ₂] ⁻	15.00	195	2	[P–NO ₂ –H] ⁻
			109	100	[ONO ₂ +NO ₂ +H] ⁻
269	[M+CH ₃ CH ₂ CO ₂] ⁻	18.00	195	6	[P–CH ₃ CH ₂ CO ₂ –H] ⁻
			136	100	[P–CH ₃ CH ₂ CO ₂ –CH ₂ NO ₂] ⁻
1,2-DNG					
228	[M+NO ₂] ⁻	18.00	181	1	[P–NO ₂ –H] ⁻
			135	65	[P–2NO ₂ –H] ⁻
			125	10	[2ONO ₂ +H] ⁻
			109	57	[ONO ₂ +NO ₂ +H] ⁻
			93	2	[2NO ₂ +H] ⁻
			87	100	[CH ₂ NO+CHNO] ⁻
255	[M+CH ₃ CH ₂ CO ₂] ⁻	18.00	181	3	[P–CH ₃ CH ₂ CO ₂ –H] ⁻
			136	20	[P–CH ₃ CH ₂ CO ₂ –NO ₂] ⁻
			135	60	[P–CH ₃ CH ₂ CO ₂ –NO ₂ –H] ⁻
			118	12	[P–CH ₃ CH ₂ CO ₂ –NO ₂ –H ₂ O] ⁻
			87	100	[CH ₂ NO+CHNO] ⁻
			73	6	[CH ₃ CH ₂ COO] ⁻
217	[M+ ³⁵ Cl] ⁻	17.00	62	100	[ONO ₂] ⁻
1,3-DNG					
228	[M+NO ₂] ⁻	20.00	181	7	[P–NO ₂ –H] ⁻
			109	100	[ONO ₂ +NO ₂ +H] ⁻
255	[M+CH ₃ CH ₂ CO ₂] ⁻	21.00	181	12	[P–CH ₃ CH ₂ CO ₂ –H] ⁻
			136	100	[P–CH ₃ CH ₂ CO ₂ –NO ₂] ⁻
217	[M+ ³⁵ Cl] ⁻	16.00	62	100	[ONO ₂] ⁻
1-MNG					
199	[M+NO ₃] ⁻	16.00	62	100	[ONO ₂] ⁻
183	[M+NO ₂] ⁻	19.00	136	2	[P–NO ₂ –H] ⁻
			109	7	[ONO ₂ +NO ₂ +H] ⁻
			108	75	[ONO ₂ +NO ₂] ⁻
			62	100	[ONO ₂] ⁻

Table 5. Continued

Parent ion (P)		CID energy (%)	Daughter ions		Suggested composition
<i>m/z</i>	Ion		<i>m/z</i>	%	
210	$[M + \text{CH}_3\text{CH}_2\text{CO}_2]^-$	19.00	136	60	$[\text{P} - \text{CH}_3\text{CH}_2\text{CO}_2 - \text{H}]^-$
			73	78	$[\text{CH}_3\text{CH}_2\text{COO}]^-$
			62	100	$[\text{ONO}_2]^-$
172	$[M + ^{35}\text{Cl}]^-$	17.00	62	100	$[\text{ONO}_2]^-$
2-MNG					
199	$[M + \text{NO}_3]^-$	15.00	62	100	$[\text{ONO}_2]^-$
183	$[M + \text{NO}_2]^-$	24.00	136	1	$[\text{P} - \text{NO}_2 - \text{H}]^-$
			109	23	$[\text{ONO}_2 + \text{NO}_2 + \text{H}]^-$
			62	100	$[\text{ONO}_2]^-$
210	$[M + \text{CH}_3\text{CH}_2\text{CO}_2]^-$	21.00	136	42	$[\text{P} - \text{CH}_3\text{CH}_2\text{CO}_2 - \text{H}]^-$
			73	88	$[\text{CH}_3\text{CH}_2\text{COO}]^-$
			62	100	$[\text{ONO}_2]^-$
172	$[M + ^{35}\text{Cl}]^-$	19.00	62	100	$[\text{ONO}_2]^-$

Fig. 7 shows the APCI-MS-MS-CID mass spectrum of the $[M + ^{35}\text{Cl}]^-$ ion of PETN.

3.3. Samples

Based on the analytical procedures developed for the nitrate esters, several explosives of forensic interest were analyzed either by LC-ESI-MS or LC-APCI-MS, using post-column additives.

Fig. 8 shows the mass chromatograms of a Booster DYNO sample at a concentration of 50 $\mu\text{g}/\mu\text{l}$ in

LC-APCI-MS with post-column introduction of chloroform. TNT and PETN were found to be the main explosive ingredients in this formulation. PETN produced $[M + \text{Cl}]^-$ adduct ions, while TNT produced $[M]^-$ and $[M - \text{H}]^-$ ions. A 25 $\mu\text{g}/\mu\text{l}$ Semtex sample analyzed by LC-ESI-MS with post-column introduction of ammonium nitrate, produced RDX and PETN adduct ions, as expected (Fig. 9). A Smokeless Powder sample, at a concentration of 10 $\mu\text{g}/\mu\text{l}$, showed the presence of NG in LC-ESI-MS with post-column sodium nitrite additive (Fig. 10).

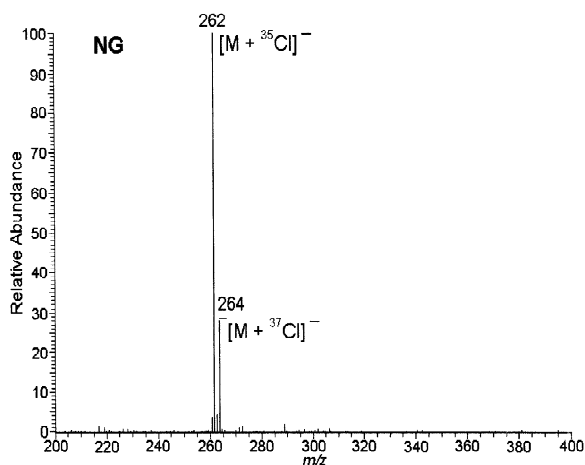


Fig. 4. Negative-ion APCI mass spectrum of NG with carbon tetrachloride additive.

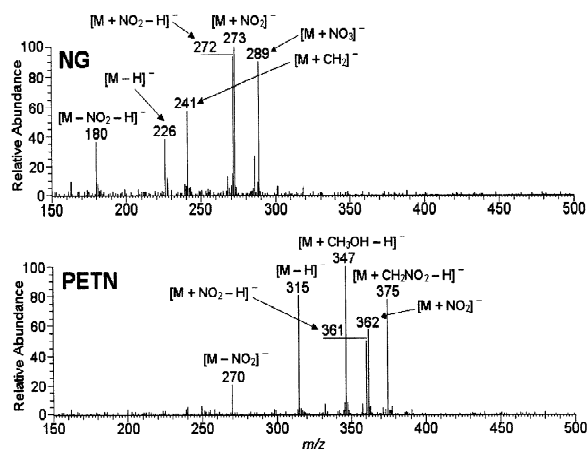


Fig. 5. Negative-ion APCI mass spectra of NG and PETN without additive.

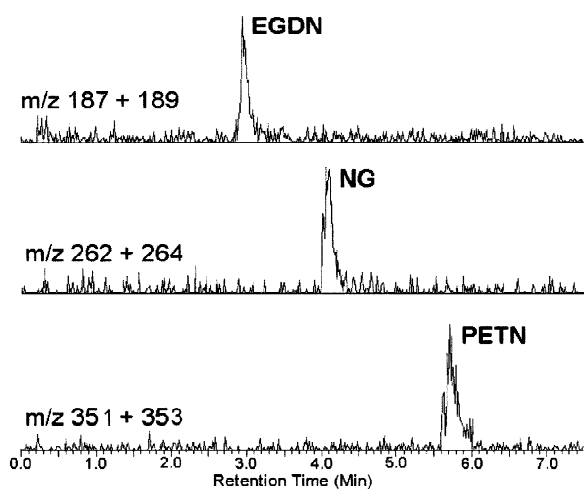


Fig. 6. Mass chromatograms of a mixture of 2.5 ng/μl EGDN, 20 pg/μl NG and 10 pg/μl PETN with post column introduction of chloroform in LC–APCI–MS.

4. Conclusions

With post-column introduction of various additives, both LC–ESI–MS and LC–APCI–MS demonstrated high specificity and sensitivity in the identification of PETN, NG and EGDN and additional nitrate esters, through adduct ion formation. Identification of EGDN in LC–MS was not possible without an additive. ESI was found to be more sensitive than APCI for the investigated nitrate esters. Lowest

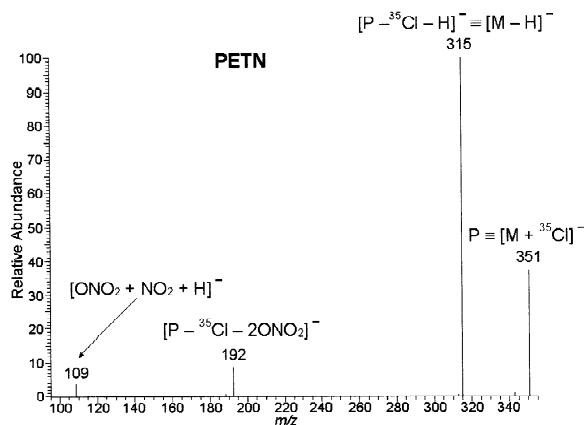


Fig. 7. APCI–MS–MS–CID mass spectrum of the $[M + ^{35}\text{Cl}]^-$ ion of PETN.

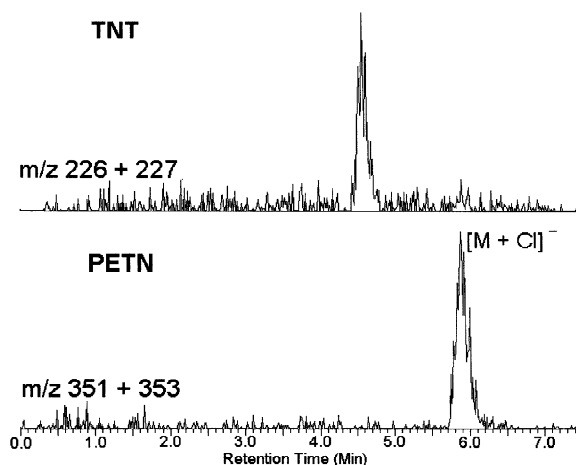


Fig. 8. LC–APCI–MS mass chromatograms of 50 pg/μl Booster DYN0 sample with post column introduction of chloroform.

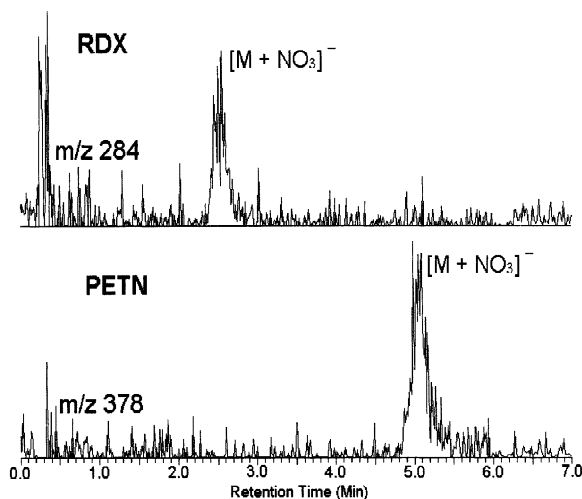


Fig. 9. LC–ESI–MS mass chromatograms of 25 pg/μl Semtex sample with post column introduction of ammonium nitrate.

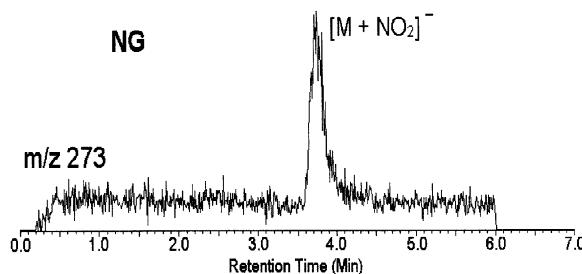


Fig. 10. LC–ESI–MS mass chromatogram of 10 pg/μl Smokeless Powder sample with post column introduction of sodium nitrite.

detection limits in ESI with ammonium nitrate additive for PETN, NG and EGDN were 5, 5 pg/ μ l and 2 ng/ μ l, respectively. The detection limits of EGDN are higher than those of NG and PETN because of the high vapor pressure of EGDN, which makes it more difficult to analyze by LC–MS methods. In LC–ESI–MS, ammonium nitrate provided best sensitivity for the analysis of nitrate esters, while in LC–APCI–MS, chloroform and ammonium chloride provide the highest sensitivity. MS–MS–CID results further confirm the identity of the formed adduct ions. The analysis of three explosive samples of forensic interest demonstrated the effectiveness of using post-column additives in the detection of nitrate ester explosives.

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