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# 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

**ABSTRACT:** A highly sensitive screening method based on high performance liquid chromatography atmospheric pressure ionization mass spectrometry (HPLC-API-MS) has been developed for the analysis of 21 nitroaromatic, nitramine and nitrate ester explosives, which include the explosives most commonly encountered in forensic science. Two atmospheric pressure ionization (API) methods, atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI), and various experimental conditions have been applied to allow for the detection of all 21 explosive compounds. The limit of detection (LOD) in the full-scan mode has been found to be 0.012–1.2 ng on column for the screening of most explosives investigated. For nitrobenzene, an LOD of 10 ng was found with the APCI method in the negative mode. Although the detection of nitrobenzene, 2-, 3-, and 4-nitrotoluene is hindered by the difficult ionization of these compounds, we have found that by forming an adduct with glycine, LOD values in the range of 3–16 ng on column can be achieved. Compared with previous screening methods with thermospray ionization, the API method has distinct advantages, including simplicity and stability of the method applied, an extended screening range and a low detection limit for the explosives studied.

**KEYWORDS:** forensic science, explosives, post-explosion residues, high performance liquid chromatography-atmospheric pressure ionization-mass spectrometry, atmospheric pressure chemical ionization, electrospray ionization, screening method, nitroaromatics, nitramines, nitrate esters

Detection and screening of explosives remains a highly relevant analytical problem and an ever developing field because of the increased demand for security checks in public locations, such as airports and governmental or commercial premises. Also, the analysis of post-explosion debris continues to be a challenge, because of the combination of low levels of explosive material, the complicated and often contaminated matrix, and the poor thermal stability of the compounds to be detected.

Generally, the low vapor pressure of explosive compounds complicates detection and analysis. Therefore, sensitive analytical methods are required. Commonly, detection is based on the strong electronegativity of nitrogen containing compounds (electron-capture detectors) or the chemiluminescence of nitrogen dioxide monitored by a photomultiplier (thermal energy analysers). Mass spectrometry has been used for identification of low levels of explosives for many years and its applications continue to increase with new spectrometer designs and improved interfaces with either gas or liquid chromatography. High performance liquid chromatography (HPLC) coupled with mass spectrometry (MS) remains a useful technique, especially for thermally sensitive explosives. An overview of recent developments in the analysis of explosives was presented by Byall at the 13th INTERPOL Forensic Science Symposium (1).

For the presently investigated method, a combination of HPLC and MS has been applied. This technique is ideally suited for the analysis and identification of a series of organic explosive compounds in post-explosion residues. Different ionization methods that serve as an interface between the HPLC system and the mass spectrometers will be compared. Changing this part of the method will be shown to have a distinct effect on the performance and detection limits.

High performance liquid chromatography, thermospray ionization, mass spectrometry (HPLC-TSP-MS) has long been used for forensic identification of explosives (2). The detection limits of a series of six explosives were found to range from 0.2 ng (on column) for trinitrotoluene (TNT) to 5 ng for ammonium picrate under full scan MS conditions. Comparable ranges of 0.5–5 ng on column (with a signal-to-noise ratio of three) were found for EGDN, HMX, RDX, DEGDN, NG, 2,4-, 2,6-, 3,4-DNT, TNT, and PETN (for abbreviations see Experimental) in our institute (3). With the TSP ionization method, most of these explosives were detected in one run.

In the 1990s, the TSP system was gradually replaced by the atmospheric pressure ionization (API) system because of its user-friendliness, better sensitivity and improved reliability (4). API is a soft ionization technique which causes little fragmentation. Therefore, both the molecular and the adduct ions can be easily detected. API can be operated in two ionization modes, namely, ESI (electrospray ionization) and APCI (atmospheric pressure chemical ionization). The selectivity for a compound changes with the ionization method, because the two techniques are based on different physical

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phenomena. ESI is based on liquid-phase ion-molecule reactions and APCI on gas-phase ion-molecule interactions. Although the conversion from APCI to ESI is quick and easy, necessary changes in the conditions of the HPLC system, such as a different buffer or column can be time consuming and limit the ease of operation in a screening application.

In an attempt to improve the sensitivity and robustness of an analytical technique for forensic research, the mass spectrometer Finnigan MAT TSQ 700 used in our laboratory was recently upgraded from the standard API interface, i.e., API-1, to the API-2 interface. API-2 is a second-generation API interface originally developed for TSQ7000, which allows more ions to be introduced into the MS system and thus provides higher sensitivity. In addition to this improvement in the interface, new conditions such as a three to five times higher full scan sensitivity, a two to four times improved precision, less limitations to the sample quantity that can be introduced (an improvement of a factor five to ten compared to previous conditions), and a longer operation time when using non-volatile buffers and contaminated samples, were demonstrated (5).

In the last decade, reports on the use of the API method for the analysis of explosives have appeared in literature (6–10). However, to our knowledge, a clear and full comparison between the API and TSP method was not published. Schilling suggests better sensitivity of explosives with the APCI and ESI method compared with the TSP technique (6). However, nitrate esters were not included in his study. Snow et al. have evaluated several buffer systems to establish stable and reproducible signals for nine explosive compounds (7). Again, nitrate esters were not included. Engewald et al. tried to establish a spectral library consisting of 48 explosives, which were acquired by flow injection into an eluent consisting of methanol-water and ammonia acetate (8). However, some explosives, that are of major importance in forensic science, were not included and no detailed information such as detection limits was presented. Recently, Yinon has reviewed the forensic analysis of explosives by HPLC-MS (9). He concluded that for TNT, RDX, HMX, tetryl and PETN, HPLC-ESI-MS in the negative mode is the most appropriate method for the analysis and identification of these compounds. Recently, Zhao and Yinon have demonstrated a more reliable identification and an enhanced sensitivity for the analysis of several nitrate ester explosives by using post-column additives (10).

Although the API method has been shown to improve the detection of certain explosive compounds, it has not yet been proven to be a method that is generally applicable for a number of different explosive compound classes. This is a prerequisite for a useful screening method in forensic research. Therefore, we have studied nitroaromatic, nitramine, and nitrate ester explosives in order to develop a workable HPLC-API-MS method to replace the previously used HPLC-TSP-MS method for the screening and identification of explosives. This new method offers higher sensitivity and an extended screening range for explosive components that are of forensic interest.

## Methods

### Materials

The following three groups of explosives were investigated: (1) Nitroaromatic compounds: picric acid (PA), nitrobenzene (NB), 2-nitrotoluene (2NT), 3-nitrotoluene (3NT), 4-nitrotoluene (4NT), 2,4-dinitrotoluene (24DNT), 2,6-dinitrotoluene (26DNT), 3,4-dinitrotoluene (34DNT), 1,3,5-trinitrobenzene (TNB), 1,2-dinitrobenzene (12DNB), 1,4-dinitrobenzene (14DNB),

1,3-dinitrobenzene (13DNB), toluene 2,4,6-trinitrotoluene (TNT), 2,4,6-N-tetranitro-N-methylaniline (tetryl); (2) Nitrate esters: Ethylene glycol dinitrate (dinitro ethylene glycol) (EGDN), Diethylene glycol dinitrate (DEGDN), 1,2,3-propanetriol trinitrate (Nitroglycerin) (NG), pentaerythritol tetranitrate (PETN); (3) Nitramines: hexanitrohexaazaisowurtzitane (HNIW or CL-20), 3,5-trinitro-1,3,5-triazacyclohexane (Cyclotetramethylene tetranitramine) (RDX), 1,3,5,7-Tetranitro-1,3,5,7-tetraazacyclooctane (HMX). CL-20 was obtained from TNO, The Netherlands. PA and 3NT were purchased from Aldrich, Steinheim, Germany, 2NT and 3NT from Merck-Schuchardt, Germany and the other compound from Cerilliant, Austin, USA. Glycine was purchased from Sigma (MO, USA). All the materials used were of purity better than 98 % (w/w). All solvents used were of HPLC or glass distilled grade (Rathburn). Water was purified by a Milli-Q/Organex Q system (Millipore). All other reagents were of analytical grade.

### *Explosive Reference Solutions and Determination of Limit of Detection*

Explosive reference mixtures were prepared from individual standard stock solutions with a concentration of typically 1000 ng/ $\mu$ L in methanol. Mixtures were further diluted to a desired concentration by a series of dilutions with methanol. By working at low concentration near the detection limit for the determination of the limit of detection (LOD) of an explosive compound, a blank is always checked before it. The LOD was measured by the height of a peak in the MS-chromatogram at a signal-to-noise ratio of three.

### *Sample Treatment*

Samples were prepared, as in the same way as described in Ref 3, by extraction of post-blast debris (e.g., small pieces of metal or shrapnel) or small objects. The extraction was performed with several millilitres of methanol by sonification for 10 min. The extracts were reduced to about 100  $\mu$ L by evaporation under nitrogen at room temperature. Alternatively, visible residues present on large objects were scrapped off or removed by swabbing. These samples were extracted in the same way as for debris. Subsequently, the samples were filtered through a membrane filter (Spartan 13/0.45 RC, 0.45  $\mu$ m from Schleicher & Schuell, Dassel, Germany) and injected into the HPLC system.

### *Instrumental*

A HPLC/API/MS System, as shown in Fig. 1, was used throughout this work.

*High Performance Liquid Chromatography (HPLC)*—A Waters 600-MS programmable pump equipped with a Waters 717 plus Autosampler and a Waters 486 UV detector (at 254 nm) was used with a Waters Nova-Pack 4  $\mu$ m C18 3.9  $\times$  150 mm HPLC cartridge column. The eluent in the reservoir was flushed with helium at a speed of 25 mL/min.

*Mass Spectrometry*—A Finnigan MAT TSQ (Triple Stage Quadrupole) 700 mass spectrometer was used as a detector. A Finnigan MAT API ion source was connected to the mass spectrometer.

*Upgrade of the API Ion Source*—The TSQ 700 was originally equipped with an API interface (a set-up called API-1). The system was later upgraded with a new API interface (called API-2). The upgraded system uses the same APCI and ESI probe assemblies as the API-1. However, it uses a new heated capillary, a new skimmer

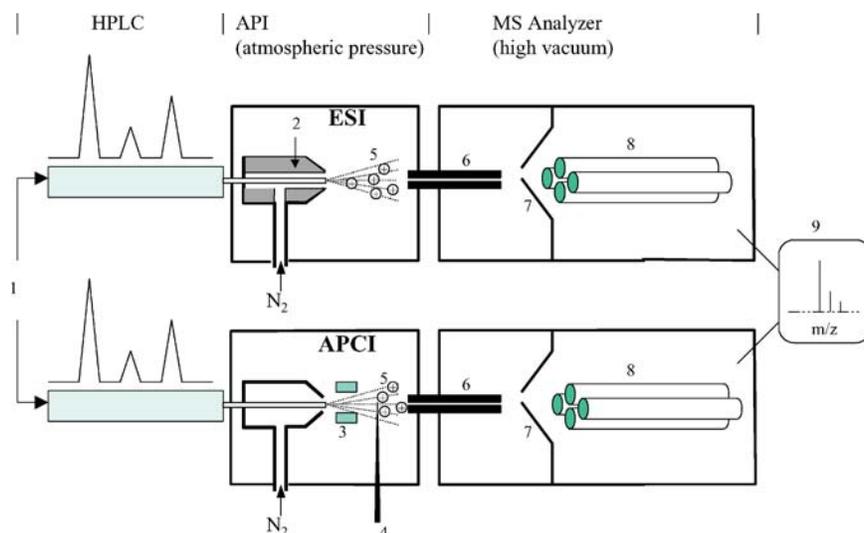


FIG. 1—A general schematic of an API HPLC/MS system composed of HPLC separation, API ionization and MS detection: 1. HPLC column; 2. Electrode (3–8 kV) for electrospray; 3. Heater block (100–500°C); 4. Corona (2–6 kV) for APCI; 5. Ionized analytes by API; 6. Heated capillary; 7. Skimmer; 8. Quadrupole mass (ion) filter; 9. MS detector (ESI stands for electrospray ionization and APCI stands for atmospheric pressure chemical ionization).

TABLE 1—HPLC-API-MS modes and abbreviations.

Abbreviations*	Mobile Phase	Ionization Mode
MeOH/H <sub>2</sub> O-APCI(–)-MS	methanol/water, v/v = 1:1	APCI in the negative mode
MeOH/H <sub>2</sub> O-ESI(–)-MS	methanol/water v/v = 1:1	ESI in the negative mode
MeOH/H <sub>2</sub> O/NH <sub>4</sub> Ac-APCI(–)-MS	methanol/water v/v = 1:1 with 2.5 mM ammonium acetate	APCI in the negative mode
MeOH/H <sub>2</sub> O/NH <sub>4</sub> Ac-ESI(–)-MS	methanol/water v/v = 1:1 with 2.5 mM ammonium acetate	ESI in the negative mode
MeOH/H <sub>2</sub> O/gly-APCI(+)-MS	methanol/water v/v 1:1 with 1.0 mM glycine	APCI in the positive mode

\* Ac stands for acetate.  
\* Gly stands for glycine.

TABLE 2—API-MS conditions.

Mode	Vaporizing Temperature (°C)	Vaporizing Spray (kV)	Capillary Temperature (°C)	Sheath Gas (psi)	Auxiliary Gas	Multiplier Voltage (kV)	Scan Range (Mass Unit (mu))
APCI(–)	275	3.5	150	80	off	1.5	40–400
APCI(–)*	140	3.5	120	80	off	1.5	40–400
APCI(+)	150	3.5	150	80	on	1.5	100–400 <sup>†</sup>
ESI(–)	...	...	205	80	off	1.5	100–400
ESI(–)*	...	...	150	80	off	1.5	100–400

\* conditions used for the analysis of EGDN. <sup>†</sup> or 213 in the single mass mode.

and an additional turbo-molecular pump to improve the signal response in HPLC-MS and HPLC-MS/MS analyses. The orifices of the new heated capillary and the new skimmer are almost twice as large as the older one, allowing them to transmit more ion current from the heated capillary. The additional turbo-molecular pump handles the increased gas load from these larger orifices (11). This upgrade will lead to a general increase in sensitivity by a factor of three to five.

**HPLC-MS Interfaces**—The HPLC was coupled to the mass spectrometer through the API ion source (interface) in either an APCI or ESI mode. The eluted components with solvent from the HPLC system were ionised in the API source and introduced into the MS/MS detector, where the intensities of the mass to charge ratio (m/z) of the ionised components and fragments were recorded. This coupling technique is known as (HP)LC-API-MS with two sub-modes: the HPLC-ESI-MS and the HPLC-APCI-MS. The API

can work in either a negative (–) or a positive (+) ion mode, which can be represented as APCI(–), ESI(–), APCI(+) and ESI(+), respectively. Most nitrogen-containing explosives are easily ionised to a negative ion due to the strong electron affinity of the nitro group of these compounds. Therefore, the negative ion mode is commonly applied for these explosive compounds. Five different HPLC-API-MS modifications have been studied in this work. They are listed in Table 1.

For screening and other general applications, sample volumes of 10 µL were injected into the HPLC system. The HPLC mobile phase was pumped through the HPLC column at a flow rate of 0.4 mL/min with the silk function on. When buffers were used as the mobile phase, the column was equilibrated with the mobile phase at a flow rate of 0.05 mL/min for at least 12 h in order to obtain a steady HPLC condition. The optimized MS conditions for both API-1 and API-2 set-ups in the negative ion (–) or positive ion (+) mode are listed in Table 2.

TABLE 3—Screening method for the analysis of 21 explosives based on the combination of three HPLC-API-MS systems.

HPLC-API-MS System	MeOH/H <sub>2</sub> O-APCI(-)-MS Full Scan 40–400 Mass Unit			MeOH/H <sub>2</sub> O/NH <sub>4</sub> Ac-ESI(-)-MS Full Scan 100–500 Mass Unit			MeOH/H <sub>2</sub> O/gly-APCI(+)-MS Single Mass 213 Mass Unit		
	RT (min)	m/z	LOD (ng) API-1/API-2	RT (min)	m/z	LOD (ng) API-1/API-2	RT (min)	m/z	LOD (ng) API-1/API-2
Explosive									
PA	2.38	nd	nd	3.32	228	0.07/0.06	...	...	...
HMX	3.56	nd	nd/5.2	3.66	355	1.5/1.2	...	...	...
RDX	5.28	267/281 <sup>†</sup>	4.0/1.0	5.72	281	0.16/0.12	...	...	...
EGDN*	5.36	94	4.0/0.8	5.54	nd	nd	...	...	...
DEGDN	6.21	62	0.30/0.30	7.10	255	4.0/3.0	...	...	...
TNB	6.88	244	1.7/0.20	7.92	244	1.3/0.28	...	...	...
12DNB	7.27	168	0.15/0.040	8.91	nd	nd	...	...	...
14DNB	7.82	168	0.40/0.06	9.23	nd	nd	...	...	...
CL-20	...	...	...	9.39	497	0.09	...	...	...
13DNB	8.45	168	1.2/0.31	10.15	nd	nd	...	...	...
Tetryl	9.26	241	4.0/0.55	11.45	318	0.50/0.50	...	...	...
NB	9.89	123	20/10	...	nd	nd	...	...	...
NG	10.38	289	21/2.1	11.79	286	2.4/0.15	...	...	...
34DNT	10.89	182	0.060/0.012	...	nd	nd	...	...	...
TNT	11.07	227	0.49/0.16	12.35	226	0.40/0.50	...	...	...
24DNT	13.57	182	0.35/0.063	15.23	nd	nd	...	...	...
26DNT	13.74	182	0.35/0.076	15.23	nd	nd	...	...	...
2NT	17.04	nd	nd	...	nd	nd	17.04	213	50/16
4NT	18.31	nd	nd	...	nd	nd	18.31	213	8.0/3.1
PETN	19.18	315	18/2.2	22.27	375	0.35/0.084	...	...	...
3NT	19.67	nd	nd	...	nd	nd	19.67	213	15/7.4

nd = not detected. \*analysis of EGDN with different measuring conditions as specified in Table 2. <sup>†</sup>found with the API-1 method/ found with the API-2 method. RT = retention time in minute. LOD = limit of detection in ng on column.

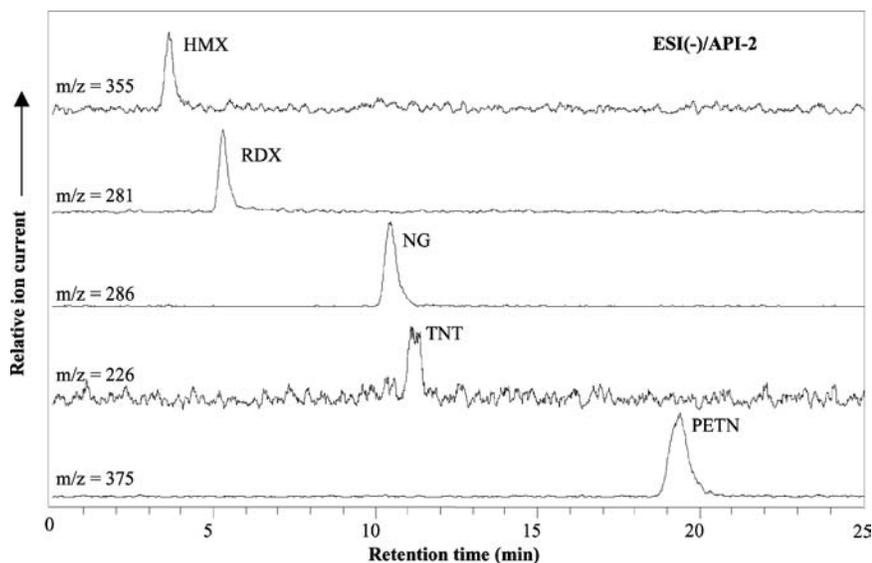


FIG. 2—Typical MS chromatograms of some explosives for m/z-values of 355, 281, 286, 226, and 375 obtained by using the MeOH/H<sub>2</sub>O/NH<sub>4</sub>Ac-ESI(-)-MS method with the API-2 set-up. Sample amount on column: HMX 1.5 ng, RDX 0.5 ng, NG 3 ng, TNT 0.5 ng and PETN 3 ng.

## Results and Discussion

An operational method based on HPLC-API-MS was established for the screening of the 21 selected explosives as shown in Table 3. A combination of three HPLC-API-MS systems was used to obtain a satisfactory detection of all 21 explosives. The analysis of some explosives by one of the systems is shown in Fig. 2.

The limit of detection (LOD) in the full-scan mode and at a signal-to-noise ratio of three was found to be 0.060–4 ng on column with the API-1 method and 0.012–1.2 ng on column with the upgraded API-2 method for most of the explosives, excluding NB, 2NT, 3NT, 4NT, and EGDN. EGDN was only successfully detected at a lower

vaporising temperature of 140°C. The detection of nitrotoluenes was performed by forming an adduct ion with glycine, resulting in an LOD in the range of 8–50 ng by API-1 and 3–16 ng by API-2 in the single mass mode.

### Comparison of Screening with the Different HPLC-API-1-MS Systems

In a preliminary stage of the present research project, it was found that nitroaromatic explosives with one or two nitro groups attached to the aromatic ring often have a poor sensitivity when

TABLE 4—Comparison of limits of detection (LODs) obtained by different HPLC-API-1-MS conditions for 21 explosive compounds.

Ionization Mode HPLC Mobile Phase Scan Range*	LODs (ng on Column)					
	ESI(-)		APCI(-)		APCI(+)	
	MeOH/H <sub>2</sub> O 100–400	MeOH/H <sub>2</sub> O/NH <sub>4</sub> Ac 100–400	MeOH/H <sub>2</sub> O 40–400	MeOH/H <sub>2</sub> O/NH <sub>4</sub> Ac 40–400	MeOH/H <sub>2</sub> O/gly 40–400	MeOH/H <sub>2</sub> O/gly 213
Explosive						
PA	0.02	0.07	nd	nd	...	...
HMX	4	1.5	nd	10	...	...
RDX	0.2	0.16	4	0.2	...	...
EGDN <sup>†</sup>	...	...	4	...	...	...
DEGDN	nd	4	0.3	nd	...	...
TNB	nd	1.3	1.7	nd	...	...
12DNB	nd	nd	0.15	nd	...	...
14DNB	nd	nd	0.4	nd	...	...
CL20	...	0.09	...	...	...	...
13DNB	nd	nd	1.2	nd	...	...
Tetryl	0.9	0.5	4	...	...	...
NB	nd	nd	20	...	...	...
NG	2.3	2.4	21	60	...	...
34DNT	nd	nd	0.06	5	...	...
TNT	0.65	0.4	0.49	0.25	...	...
24DNT	nd	nd	0.35	nd	...	...
26DNT	nd	nd	0.35	nd	...	...
2NT	nd	nd	nd	nd	250	50
4NT	nd	nd	nd	nd	40	8
PETN	1.2	0.35	18	18	nd	...
3NT	nd	nd	nd	nd	75	15

nd = not detected. \* full scan mode in the range indicated or single mass mode of 213 indicated in mass units. <sup>†</sup>analysis of EGDN with different measuring conditions as specified in Table 2.

using the HPLC-API-MS systems described in the literature (6–10). The sensitivity is mainly determined by the ionization efficiency of the analytes in the ion source, which depends on the ionization environment in the source created by the solvent and buffer components or additives of the HPLC mobile phase or buffer. In our search for a general screening method, we first attempted to find a buffer that was suitable for both nitroaromatic and other explosive compounds. Unfortunately, we were not able to create an appropriate ionization environment for the formation of an adduct ion that was easily detected, particularly for nitroaromatics. The different HPLC-API-1-MS conditions investigated include mobile phases consisting of methanol-, propanol- and acetonitrile-water mixtures with or without a buffer component or additive, such as nitrate, acetate, formate, chloride, hydrogencarbonate, trichloroacetate, and trifluoroacetate. All possibilities were tested with the two ionization modes, APCI, and ESI. Nitroaromatics were found to be detected in the easiest manner when a pure solvent as the mobile phase was used. Any buffer component or salt present in the mobile phase was found to dramatically suppress the signal of the one and two nitro-containing aromatic compounds.

Although certain HPLC-API-1-MS conditions seemed ideally suited for a particular explosive, the need for a generally applicable screening method did not justify the use of this set-up in the general screening method. In Table 4, an overview is given of those conditions that were the most appropriate for general screening purposes. As can be concluded from the table, the MeOH/H<sub>2</sub>O/NH<sub>4</sub>Ac-APCI(-)-MS condition is not broadly applicable. We included this method for comparison.

As can be seen from Table 4, the MeOH/H<sub>2</sub>O-APCI(-)-MS set-up is the most appropriate system for the detection of nitroaromatics. However, for most of the other explosives, the MeOH/H<sub>2</sub>O/NH<sub>4</sub>Ac-ESI(-)-MS set-up is the most suitable one. Interestingly, the explosives 2-, 3-, and 4-NT could only be detected

with the newly developed method MeOH/H<sub>2</sub>O/gly-APCI(+)-MS based on the formation of glycine adduct ions. In the single mass mode, instead of the full-scan, the LOD of NTs decreased approximately five times.

#### Advantages of Upgrading the API-1 System to the API-2 System

The limits of detection of the explosives studied were measured on the API-2 system under the same conditions as the API-1 set-up. It can be seen from Table 5 that the sensitivity with the API-2 set-up has considerably increased. For most explosives, an increase in sensitivity by a factor three to eight compared to the API-1 system has been found. This enhancement can be attributed to the larger orifice of the heated capillary and skimmer (see Fig. 1), which allow a higher ion current to enter the MS system. On using the MeOH/H<sub>2</sub>O-ESI(-)-MS system with the API-2 set-up for the analysis of HMX, NG, and PETN, a considerably higher sensitivity has been found. This may result from different ionisation mechanisms in case of API-1 and API-2. The ionisation environment in API-1 is thought to be more favourable for the formation of (M + ONO<sub>2</sub>)<sup>-</sup> base ions, while in API-2 the (M + NO<sub>2</sub>)<sup>-</sup> ion is more easily generated. When using the MeOH/H<sub>2</sub>O/NH<sub>4</sub>Ac-/ESI(-) system a significant increase in sensitivity for TNB, NG and PETN was obtained.

#### Selection of the Different HPLC-API-MS Systems

As can be seen in Table 4, no single HPLC-API-MS set-up can cover the detection of all twenty-one explosives. A combination of different set-ups is necessary for a complete screening of the explosives studied in this paper. The conversion of interface from APCI to ESI is not time consuming and takes

TABLE 5—Increase in sensitivity on upgrading HPLC-API-1-MS to HPLC-API-2-MS.

HPLC-API-MS System Scan Range*	Ratio of LOD (API-1)/(API-2)			
	MeOH/H <sub>2</sub> O- ESI(-)-MS 100–400	MeOH/H <sub>2</sub> O/NH <sub>4</sub> Ac- ESI(-)-MS 100–400	MeOH/H <sub>2</sub> O- APCI(-)-MS 40–400	MeOH/H <sub>2</sub> O/gly- APCI(+)-MS 213
Explosive				
PA	1.3	1.2	nd	...
HMX	13	1.3	‡	...
RDX	4.3	1.3	4	...
EGDN <sup>†</sup>	nd	nd	5	...
DEGDN	nd	1.3	1	...
TNB	nd	4.8	8.5	...
12DNT	nd	nd	3.8	...
14DNT	nd	nd	6.7	...
13DNT	nd	nd	3.9	...
Tetryl	2.3	1	7.3	...
NB	nd	nd	1.9	...
NG	21	16	10	...
34DNT	nd	nd	5	...
TNT	2.1	0.8	3.1	...
24DNT	nd	nd	5.6	...
26DNT	nd	nd	4.6	...
2NT	nd	nd	nd	3.2
4NT	nd	nd	nd	2.6
PETN	22	4.2	8.2	...
3NT	nd	nd	nd	2

nd = not detected. \* full scan mode in the range indicated in mass units or single mass mode at 213 mass units. <sup>†</sup> analysis of EGDN with different measuring conditions as specified in Table 2. <sup>‡</sup> not detected with the API-1 set-up.

less than 3 min. Therefore, we have decided to combine the MeOH/H<sub>2</sub>O-APCI(-)-MS, the MeOH/H<sub>2</sub>O/NH<sub>4</sub>Ac-ESI(-)-MS and the MeOH/H<sub>2</sub>O/gly-APCI(+)-MS methods to establish a general screening test for explosives.

The MeOH/H<sub>2</sub>O-APCI(-)-MS method is the most suitable option for the analysis of the nitroaromatics. Because the nitrotoluenes show a poor to no sensitivity in the other systems, the MeOH/H<sub>2</sub>O/gly-APCI(+)-MS is the method of choice for analysis of these compounds. The MeOH/H<sub>2</sub>O/gly-APCI(+)-MS method is only required when a suspect peak has been found by UV detection, because UV detection is more sensitive than MS detection in this case.

Although the MeOH/H<sub>2</sub>O-ESI(-)-MS method provides the highest sensitivity for compounds such as PA, HMX, RDX, tetryl, PETN, and NG, it can not be implemented in the general screening method because of its lack of reproducibility and stability. In summary, we decided that for the general screening method, a combination of the MeOH/H<sub>2</sub>O-APCI(-)-MS, the MeOH/H<sub>2</sub>O/NH<sub>4</sub>Ac-ESI(-)-MS and the MeOH/H<sub>2</sub>O/gly-APCI(+)-MS set-ups is the most practical choice.

#### Mass Spectroscopic Data Observed with the Different HPLC-API-MS Systems

Because API is a soft ionization method, most explosives react to form molecule-related ions, i.e., (M)<sup>-</sup>, (M + H)<sup>+</sup>, (M - H)<sup>-</sup> and/or an adduct ion form, such as (M + X)<sup>+</sup> and (M + X)<sup>-</sup>. A base ion (which is the ion with the highest abundance) of an explosive compound is usually one of those and thus related to the mass of the molecule. However, EGDN and DEGDN have been found to be rather fragile and thermally labile compounds. Therefore, these molecules are readily fragmented during ionization. The most abundant ions detected (base ions) of these two compounds are frag-

ments. Therefore, detection of these compounds is more indirect. In Tables 6a–d both the molecule-related and fragment ions that have been detected for the explosive compounds investigated are given.

In most cases, besides molecule-related ions, several ionic fragments are generated by the API. By studying these ions, we can not only increase our knowledge of the ionization process, but also confirm the identification by checking all the ions formed. The ions generated (molecule, adduct or fragment) can be regarded as a kind of fingerprint of the explosive. The importance of these fragments and adduct ions is also emphasised by Yinon (9). The results obtained with the API HPLC/MS methods are listed in Tables 6a–d, respectively. As can be seen from these tables, the ions formed by making use of the upgraded API-2 set-up differ in many cases from those obtained with the former API-1 set-up. This implies that not only the physical dimension of the API has changed but also the ionization conditions have changed. This may also be a reasonable explanation for the differences in sensitivity increase for the various explosive compounds.

#### Optimization of HPLC and MS Conditions

The HPLC conditions for the MeOH/H<sub>2</sub>O/NH<sub>4</sub>Ac conditions were optimized previously (3). It is generally satisfactory to use an isocratic flow for the separation of the explosives studied here. An insufficient separation of the explosive components can normally be compensated for by the highly selective MS detector. The only exception is the 24DNT/26DNT pair that can neither be separated by HPLC, nor distinguished by MS.

The API-MS conditions used for the screening method coincide for almost all explosives with the conditions found when optimizing the explosives separately. EGDN is the only exception. For this compound a lower vaporization temperature is necessary, see Table 3 and Ref 9.

TABLE 6a—Mass spectroscopic data of the explosives analyzed by the MeOH/H<sub>2</sub>O-APCI(–)-MS system.

Explosive	Molecular Weight (g/mol)	m/z (Ion Abundance) [Suggested Ion]*	
		APCI-1 Set-up	API-2 Set-up
RDX	222.1	267 (100%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 254 (76%) [M + CH <sub>3</sub> OH] <sup>-</sup> , 221 (68%) [M - H] <sup>-</sup> , 283 (31%) [M + ONO <sub>2</sub> -H] <sup>-</sup> , 297 (29%) [M + CH <sub>2</sub> ONO <sub>2</sub> -H] <sup>-</sup>	281 (100%) [M + CHNO <sub>2</sub> ] <sup>-</sup> , 221 (78%) [M - H] <sup>-</sup> , 267 (50%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 297 (37%) [M + CH <sub>2</sub> ONO <sub>2</sub> -H] <sup>-</sup> , 268 (33%) [M + NO <sub>2</sub> ] <sup>-</sup>
EGDN <sup>†</sup>	152.1	94 (100%) [CH <sub>3</sub> OH + NO <sub>3</sub> ] <sup>-</sup> , 62 (60%) [NO <sub>3</sub> ] <sup>-</sup>	94 (100%) [CH <sub>3</sub> OH + NO <sub>3</sub> ] <sup>-</sup> , 64 (30%) [M-2CHNO <sub>2</sub> ] <sup>-</sup> , 62 (10%) [NO <sub>3</sub> ] <sup>-</sup>
DEGDN	196.1	78 (100%) [M-2CHNO <sub>2</sub> ] <sup>-</sup> , 62 (96%) NO <sub>3</sub> <sup>-</sup> , 46 (88%) NO <sub>2</sub> <sup>-</sup> , 64 (86%) [M-CHNO <sub>2</sub> -CH <sub>2</sub> CHNO <sub>2</sub> ] <sup>-</sup> , 94 (36%) [CH <sub>3</sub> OH + NO <sub>3</sub> ] <sup>-</sup> , 242 (20%) [M + NO <sub>2</sub> ] <sup>-</sup> , 258 (10%) [M + NO <sub>3</sub> ] <sup>-</sup>	62 (100%) [NO <sub>3</sub> ] <sup>-</sup> , 46 (50%) [NO <sub>2</sub> ] <sup>-</sup> , 94 (38%) [CH <sub>3</sub> OH + NO <sub>3</sub> ] <sup>-</sup> , 78 (33%) [M-2CHNO <sub>2</sub> ] <sup>-</sup> , 242 (28%) [M + NO <sub>2</sub> ] <sup>-</sup> , 64 (26%) [M-CHNO <sub>2</sub> -CH <sub>2</sub> CHNO <sub>2</sub> ] <sup>-</sup> , 258 (13%) [M + NO <sub>3</sub> ] <sup>-</sup>
TNB	213.1	244 (100%) [M + CH <sub>3</sub> O] <sup>-</sup> , 213 (85%) [M] <sup>-</sup> , 182 (40%) [M-NO-H] <sup>-</sup>	244 (100%) [M + CH <sub>3</sub> O] <sup>-</sup> , 213 (90%) [M] <sup>-</sup> , 183 (14%) [M-NO] <sup>-</sup> , 182 (14%) [M-NO-H] <sup>-</sup>
12DNB	168.1	168 (100%) [M] <sup>-</sup> , 138 (5%) [M-NO] <sup>-</sup>	168 (100%) [M] <sup>-</sup>
14DNB	168.1	168 (100%) [M] <sup>-</sup> , 138 (9%) [M-NO] <sup>-</sup>	168 (100%) [M] <sup>-</sup>
13DNB	168.1	168 (100%) [M] <sup>-</sup> , 200 (31%) [M + CH <sub>3</sub> OH] <sup>-</sup> , 138 (7%) [M-NO] <sup>-</sup>	168 (100%) [M] <sup>-</sup>
Tetryl	287.2	241 (100%) [M-NO <sub>2</sub> ] <sup>-</sup>	241 (100%) [M-NO <sub>2</sub> ] <sup>-</sup>
NB	123.0	123 (100) [M] <sup>-</sup>	123 (100) [M] <sup>-</sup>
NG	227.1	[288 (100%) [M + ONO <sub>2</sub> -H] <sup>-</sup> , 289 (98%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 302 (89%) [M + CH <sub>2</sub> ONO <sub>2</sub> -H] <sup>-</sup> , 273 (74%) [M + NO <sub>2</sub> ] <sup>-</sup> , 227 (30%) [M] <sup>-</sup>	289 (100%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 62 (90%), [NO <sub>3</sub> ] <sup>-</sup> , 227 (30%) [M] <sup>-</sup> , 288 (13%) [M + ONO <sub>2</sub> -H] <sup>-</sup> , 302 (13%) [M + CH <sub>2</sub> ONO <sub>2</sub> -H] <sup>-</sup> , 273 (8%) [M + NO <sub>2</sub> ] <sup>-</sup>
34DNT	182.1	182 (100%) [M] <sup>-</sup> , 181 (40%) [M - H] <sup>-</sup>	182 (100%) [M] <sup>-</sup> , 181 (40%) [M - H] <sup>-</sup>
TNT	227.1	227 (100%) [M] <sup>-</sup> , 226 (28%) [M - H] <sup>-</sup>	227 (100%) [M] <sup>-</sup> , 258 (15%) [M + CH <sub>3</sub> O] <sup>-</sup> , 226 (13%) [M - H] <sup>-</sup> , 197 (6%) [M-NO] <sup>-</sup>
24DNT	182.1	182 (100%) [M] <sup>-</sup> , 181 (40%) [M - H] <sup>-</sup>	182 (100%) [M] <sup>-</sup> , 181 (48%) [M - H] <sup>-</sup>
26DNT	182.1	182 (100%) [M] <sup>-</sup> , 181 (47%) [M - H] <sup>-</sup>	182 (100%) [M] <sup>-</sup> , 181 (81%) [M - H] <sup>-</sup>
PETN <sup>‡</sup>	316.1	315 (100%) [M - H] <sup>-</sup> , 361 (60%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 378 (30%) [M + ONO <sub>2</sub> ] <sup>-</sup>	315 (100%) [M - H] <sup>-</sup> , 378 (100%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 62 (20%) [NO <sub>3</sub> ] <sup>-</sup>

\* An explosive compound may be ionized into molecule-related ions (such as [M]<sup>-</sup>, [M + H]<sup>+</sup>, [M - H]<sup>-</sup>, [M + X]<sup>+</sup> and/or [M + X]<sup>-</sup> where M denotes the molecule, H the proton and X the adduct ion) and fragment ions (such as [M-fragment]<sup>-</sup> and/or [M-fragment]<sup>+</sup>). They appear in the mass spectrum at different mass-to-charge values (m/z) in different abundances (represented in percentage).

<sup>†</sup> see Table 2 for the different experimental conditions used to analyse EGDN.

<sup>‡</sup> Due to the possible presence of acetic acid as an impurity in the eluent the m/z signal of the adduct ion of [M + Ac]<sup>-</sup> can be a factor of 40 higher than that of [M - H]<sup>-</sup>.

TABLE 6b—Mass spectroscopic data of the explosives analyzed by the MeOH/H<sub>2</sub>O-ESI(–)-MS system.

Explosive	Molecular Weight (g/mol)	m/z (Ion Abundance) Suggested Ion	
		API-1	API-2
PA	229.1	228 (100%) [M - H] <sup>-</sup> , 229 (23%) [M] <sup>-</sup>	228 (100%) [M - H] <sup>-</sup> , 229 (23%) [M] <sup>-</sup>
HMX	296.1	358 (100%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 331 (85%) [M + 35] <sup>-</sup> , 341 (58%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 385 (20%) [M + 89] <sup>-</sup> , 295 (20%) [M - H] <sup>-</sup>	341 (100%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 355 (69%) [M + NNO <sub>2</sub> ] <sup>-</sup> , 358 (35%) [M + ONO <sub>2</sub> ] <sup>-</sup>
RDX	222.1	284 (100%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 267 (68%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 257 (50%) [M + 35] <sup>-</sup> , 297 (25%) [M + CH <sub>2</sub> ONO <sub>2</sub> -H] <sup>-</sup> , 311 (8%) [M + 89] <sup>-</sup>	267 (100%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 281 (90%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 257 (30%) [M + 35] <sup>-</sup> , 284 (25%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 311 (17%) [M + 89] <sup>-</sup> , 297 (<5%) [M + CH <sub>2</sub> ONO <sub>2</sub> -H] <sup>-</sup>
Tetryl	287.2	318 (100%) [M + CH <sub>3</sub> O] <sup>-</sup> , 322 (22%) [M + 35] <sup>-</sup> , 349 (22%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 376 (8%) [M + 89] <sup>-</sup>	318 (100%) [M + CH <sub>3</sub> O] <sup>-</sup> , 332 (44%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 349 (20%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 322 (20%) [M + 35] <sup>-</sup> , 376 (8%) [M + 89] <sup>-</sup>
NG	227.1	289 (100%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 262 (70%) [M + 35] <sup>-</sup> , 302 (33%) [M + CH <sub>2</sub> ONO <sub>2</sub> -H] <sup>-</sup> , 316 (10%) [M + 89] <sup>-</sup>	272 (100%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 286 (91%) [M + NNO <sub>2</sub> -H] <sup>-</sup> , 289 (32%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 316 (21%) [M + 89] <sup>-</sup> , 262 (20%) [M + 35] <sup>-</sup>
TNT	227.1	226 (100%) [M - H] <sup>-</sup>	226 (100%) [M - H] <sup>-</sup>
PETN	316.1	378 (100%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 315 (74%) [M - H] <sup>-</sup> , 361 (57%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 351 (49%) [M + 35] <sup>-</sup>	361 (100%) [M + NO <sub>2</sub> -H] <sup>-</sup> , 378 (25%) [M + ONO <sub>2</sub> ] <sup>-</sup> , 351 (23%) [M + 35] <sup>-</sup> , 315 (<5%) [M - H] <sup>-</sup>

TABLE 6c—Mass spectroscopic data for the explosives analyzed by the MeOH/H<sub>2</sub>O/NH<sub>4</sub>Ac-ESI(–)-MS system.

Explosive	Molecular Weight (g/mol)	m/z (Ion Abundance) Suggested Ion*	
		API-1	API-2
PA	229.1	228 (100%) [M – H] <sup>–</sup>	228 (100%) [M – H] <sup>–</sup>
HMX	296.1	355 (100%) [M + Ac] <sup>–</sup> , 331 (28%) [M + 35] <sup>–</sup> , 358 (17%) [M + ONO <sub>2</sub> ] <sup>–</sup>	355 (100%) [M + Ac] <sup>–</sup> , 358 (17%) [M + ONO <sub>2</sub> ] <sup>–</sup>
RDX	222.1	281 (100%) [M + Ac] <sup>–</sup>	281 (100%) [M + Ac] <sup>–</sup>
DEGDN	196.1	255 (100%) [M + Ac] <sup>–</sup>	255 (100%) [M + Ac] <sup>–</sup>
TNB	213.1	244 (100%) [M + CH <sub>3</sub> O-H] <sup>–</sup>	244 (100%) [M + CH <sub>3</sub> O-H] <sup>–</sup> , 272 (35%) [M + Ac] <sup>–</sup>
CL-20	438.2	...	497 (100%) [M + Ac] <sup>–</sup> , 483 (21%), 450 (16%), 437 (11%) [M – H] <sup>–</sup> , 390 (10%)
Tetryl	287.2	318 (100%) [M + CH <sub>3</sub> O-H] <sup>–</sup> , 241(57%) [M-NO <sub>2</sub> ] <sup>–</sup>	318 (100%) [M + CH <sub>3</sub> O-H] <sup>–</sup> , 346(50%) [M + Ac] <sup>–</sup>
NG	227.1	286 (100%) [M + Ac] <sup>–</sup> , 241(10%) [M + CH <sub>2</sub> ] <sup>–</sup>	286 (100%) [M + Ac] <sup>–</sup>
TNT	227.1	226 (100%) [M – H] <sup>–</sup>	226 (100%) [M – H] <sup>–</sup>
PETN	316.1	375 (100%) [M + Ac] <sup>–</sup> , 315 (58%) [M – H] <sup>–</sup> , 330 (6%) [M + CH <sub>2</sub> ] <sup>–</sup>	375 (100%) [M + Ac] <sup>–</sup>

\*Ac stands for acetate.

TABLE 6d—Mass spectroscopic data for the explosives analyzed by the MeOH/H<sub>2</sub>O/gly-APCI(+)-MS system.

Explosive	Molecular Weight (g/mol)	m/z (Ion abundance) Suggested Ion by Both API-1 and API-2
2NT	137.1	213 (100%) [M + glycine] <sup>+</sup>
3NT	137.1	213 (100%) [M + glycine] <sup>+</sup>
4NT	137.1	213 (100%) [M + glycine] <sup>+</sup>

### Reproducibility

When using the same HPLC buffer for one column under the same chromatographic conditions, the separation properties of the system with respect to retention time have been demonstrated to be very stable (3). The standard deviations of the retention time were less than 0.02 min. Negligible changes in these retention times have been observed after a period of six months. For the screening method developed in this paper, three buffers are being used. This is a serious drawback of the method, because it is time consuming to equilibrate a column after a buffer change. In our laboratory, we have circumvented this complication by using two columns, one for the mobile phase based on the water-methanol mixture, and one for the water-methanol mixture with ammonium acetate. The use of the water-methanol mobile phase with glycine is only required in cases where the analysis and detection of nitrotoluenes is under investigation.

### Application in Case Investigations

This screening method has been applied to many case investigations mainly for the analysis of post-explosion debris, showing better identification, and sensitivity than the previous HPLC-TSP-MS method. Generally, the magnitude of the explosive compounds in a post-blast extract varies a lot and often is extremely low. However, in most cases, we have been able to detect explosives in the post-blast extracts. In one case a pre- and post-blast sample was analyzed. The pre-blast sample was a methanol solution of a brownish material seized from the suspect. The post-blast samples were extracts of debris. As shown in Fig. 3, due to the complicated composition of the samples, all the three screening systems listed in Table 3 were applied for the analysis. Totally ten to eleven

TABLE 7—Explosive composition of the pre- and post-blast samples in a case as shown in Fig. 3.

Explosives	Found in the Samples (Semi Quantitation, ng/μL)*	
	Pre-blast Sample	Post-blast Sample
HMX	0.37	Near LOD
RDX	5.6	0.68
Tetryl	15	0.76
NG	0.42	0.04
34DNT	0.12	0.009
TNT	7.0	0.95
As 24DNT <sup>†</sup>	4.2	0.34
As 26DNT <sup>†</sup>	2.5	0.2
4NT <sup>‡</sup>	10	1.0
PETN	16.3	1.7
3NT <sup>‡</sup>	30	2.7

\* The quantitation was based on the measurement of the peak height. Because some of the large peaks were out of the linear range the calculated concentration was only semi-quantitative.

<sup>†</sup> 2,4-DNT en 2,6-DNT can neither be discriminated by HPLC or by MS.

<sup>‡</sup> 3-NT and 4-NT were not well separated due to the high concentration in the pre-blast sample. Therefore, the concentration listed here is only indicative.

explosive compounds were found in these samples, where four of them (RDX, Tetryl, TNT, and PETN) were detected in more than one screening system. In a semi-quantitative analysis of the composition (concentration ratios of the compounds in one sample), no significant difference has been found between the pre- and post-blast samples (a proximate ten fold difference in concentration in this case for pre- and post-blast samples in Fig. 3), as shown in Table 7.

### Conclusion

A sensitive screening method has been developed for the analysis of 21 nitroaromatic, nitramine, and nitrate ester explosives, which includes almost all explosives frequently encountered in forensic cases. This method combines three HPLC-API-MS systems to perform the screening, i.e., MeOH/H<sub>2</sub>O-APCI(–)-MS for the detection of the nitroaromatic explosives, MeOH/H<sub>2</sub>O/NH<sub>4</sub>Ac-ESI(–) for the other explosives with the exception of the nitrotoluenes and MeOH/H<sub>2</sub>O/gly-APCI(+)-MS for nitrotoluenes. The limit of

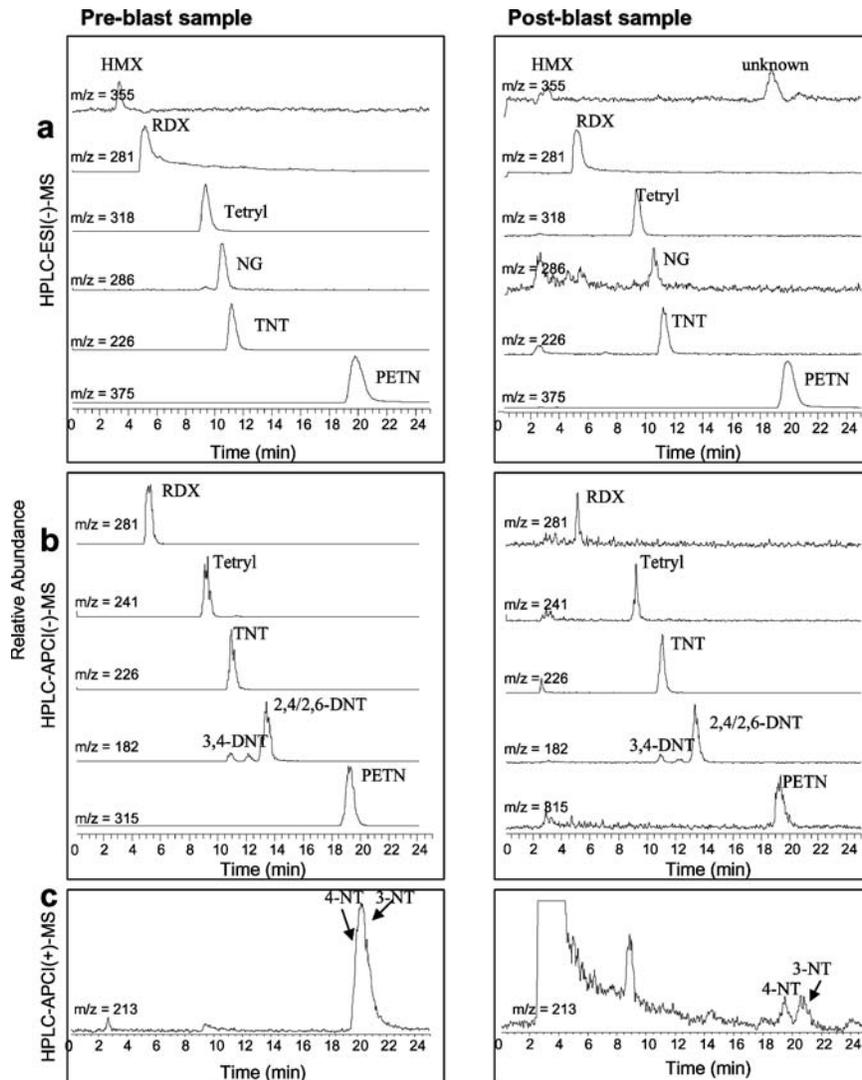


FIG. 3—MS chromatogram of pre- (left) and post- (right) blast explosives in a real case investigation with the three screening HPLC-API(2)-MS systems (a, b, and c) as listed in Table 3. The ratio of the explosive compounds in the pre- and post-blast sample does not significantly change (details see Table 7 and text).

detection (LOD) in the full-scan mode at a signal-to-noise ratio of three has been found to be 0.012–1.2 ng on column (with the exception of nitrobenzene and the nitrotoluenes) for the screening based on the upgraded API ion source of the Finnigan TSQ 700 Mass Spectrometer. For nitrobenzene an LOD of 10 ng was found with the APCI method in the negative mode.

The detection of 2-, 3-, and 4-nitrotoluene is hindered by the difficult ionization of these compounds. However, we have found that the detection limit of these materials can be improved by forming an adduct with glycine, resulting in an LOD in the range of 3–16 ng on column in the single mass mode.

Compared with the screening method based on HPLC-TSP-MS previously developed in our institute, the new method possesses many advantages. For example, the screening range of the new method is doubled. The sensitivity is significantly increased by approximately a factor of ten using the upgraded API-2 system. The API setup is much simpler and thus easier to operate. The method presented is highly sensitive, specific, stable and reproducible and expected to be used as the main analysis method for the identification of forensic explosives in post-explosion debris.

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