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Gas chromatography positive chemical ionization and tandem mass spectrometry for the analysis of organic high explosives

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Abstract

The characteristic ions or the parent ion resulting from ionization can be isolated in an ion trap and subjected to further fragmentation during a gas chromatography–tandem mass spectrometry (GC/MS/MS) experiment. This approach can improve the selectivity and sensitivity of explosive compounds over gas chromatography–mass spectrometry (GC/MS) by improving the differentiation of the target compounds from interfering and co-eluting compounds and reducing the background noise within an explosive debris sample. The optimization of the operating parameters for GC/MS and GC/MS/MS experiments with an ion trap mass spectrometer were conducted using a mixture of explosive compounds and 3,4-dinitrotoluene as an internal standard. The level of detection (LOD) and limit of quantitation (LOQ) for these compounds was determined by GC/MS with electron ionization, GC/MS with positive chemical ionization, and GC/MS/MS with positive chemical ionization. The LOD range was found to be 3.6 pg for 2,4-dinitrotoluene to 2.23 ng for hexahydro-1,3,5-trinitro-s-triazine (RDX) using GC/EI/MS; 0.4 pg for 2,4-dinitroltoluene to 19.0 pg for 1,3,5-trinitrobenzene using GC/PCI/MS; and 0.5 pg for 4-nitrotoluene to 41.4 pg for RDX using GC/PCI/MS/MS. The LOD results for GC/PCI/MS and for GC/PCI/MS/MS are very similar for most of the compounds except the GC/PCI/MS LOD results are lower for RDX and 1,3-dinitrobenzene while the GC/PCI/MS/MS LOD results are lower for 1,3,5-trinitrobenzene. The GC/PCI/MS/MS method offers improved selectivity when analyzing real world samples containing interfering products and matrix noise thereby improving sensitivity for complex samples.

Keywords: Gas chromatography; Tandem mass spectrometry; Organic high explosive

1. Introduction

Post-detonation organic explosive compounds are difficult to analyze and detect because a detonation results in trace amounts of explosives spread over a large debris field. The detonation not only consumes most of the explosive material but also produces interfering compounds and a complex matrix. Clean up and sample concentration procedures, such as solid phase extraction (SPE) [1,2], solid phase microextraction (SPME) [3–6], and single drop microextraction (SDME) [7] are used to improve the isolation of explosive compounds away from the debris matrix. Clean up and sample pre-concentration procedures are time consuming, can cause contamination [8], and may not reduce the background sufficiently or remove interfering products to an acceptable level.

Once the explosive compounds have been isolated, they are separated through chromatography. Typical chromatographic techniques used for the separation of organic explosives include capillary electrophoresis (CE) [9,10], high-performance liquid chromatography (HPLC) [11,12], and gas chromatography (GC) [13]. GC can be interfaced to many different types of detectors and can resolve multiple explosive compounds giving it two distinct advantages over CE and HPLC. However, some organic explosives can be degraded by small increases in energy, such as the heat of the GC injection port or oven.

The GC separation of tetryl produces 2,4,6-trinitro-*N*-methyl-aniline (*N*-methylpicramide) due to a complete hydrolytic decomposition reaction [14]. When 2,4,6-trinitro-*N*-methyl-aniline, molecular mass of 242.15 g, undergoes

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chemical ionization a fragment of *m*/*z* 243 is produced [15–17]. Typically, the acid strength of the reagent gas used in chemical ionization influences the ion intensities of the fragments produced but not the *m*/*z* of the fragments. In the chemical ionization of hexahydro-1,3,5-trinitro-s-triazine (RDX), different fragments are produced depending on the acid strength of the reagent gas [18]. Weak Brønsted acids such as ammonia and isobutene transfer just enough ionization energy to cause rearrangement reactions producing RDX fragments *m*/*z* 84, 131, and 176. Strong Brønsted acids such as hydrogen and methane impart more ionization energy leading to cleavage reactions producing RDX fragments *m*/*z* 75 and 149. Octahydro-1,3,5,7-tetranitro-1,3,4,5-tetrazocine (HMX) is difficult to analyze by GC/MS because the compound is either not detected due to thermal degradation in the GC [19] or produces a MS fragmentation that is not sufficient to positively identify the compound as HMX [20,21].

A tandem mass spectrometry (MS/MS) experiment improves the selectivity and sensitivity of the method by selecting only the compounds of interest for detection and ejecting any interfering compounds [22–25]. Extraction and separation of the explosive compounds of interest away from the matrix is typically conducted through solid phase extraction followed by gas or liquid chromatography (LC) [1]. MS/MS experiments eliminate the need for this procedure by relying on the second MS experiment to select the molecular ion of the explosive compound of interest away from the matrix and fragment the selected ion a second time to produce a characteristic mass spectra for identification.

Because a sample does not need to undergo any other extraction technique other than to eliminate compounds that could possibly foul the separation column, the analysis time and the number of sources for potential contamination are reduced. In an ion trap MS/MS experiment, the molecular ion and/or characteristic fragment(s) of choice are stored within the hyperbolic ion trap for further analysis. Collisional induced dissociation (CID) is used to fragment the molecular ion or characteristic fragment stored within the trap at a lower energy than electron ionization. CID results in a different fragmentation pattern from electron ionization and chemical ionization requiring the user to build a library or to analyze a known standard for comparison purposes. The daughter ions created by the CID in the second mass spectral experiment are then selectively ejected and detected.

One of the first reported uses of tandem mass spectrometry for the analysis of explosives was the introduction of sample by direct insertion probe and analysis by a VG gas analysis ZAB mass spectrometer converted for organic compound analysis [26]. The MS/MS spectra were derived from daughter ion scans after electron ionization, isobutane positive chemical ionization, and isobutane negative chemical ionization. In 1990, the sample introduction and mass spectrometer types were varied when an atmospheric sampling glow discharge ionization (ASGDI) source was used in conjunction with a linear quadrupole/time-of-flight mass spectrometer [27]. The first mass spectrometer, the quadrupole, was used to isolate the molecular ion of the explosive sample, while the second mass spectrometer, the time-of-flight, optionally fragmented the ions with air and analyzed the isolated ion. Chromatography before analysis by tandem mass spectrometry occurred in 1993 when LC was used before a Finnigan MAT TSQ 700 tandem quadrupole mass spectrometer [28]. MS/MS experiments were conducted in the daughter ion mode with argon as a collision gas. MS/MS for the analysis of explosives found additional application in 1994 when it was used to study the fragmentation pathways of glycoluril type explosives [29]. Tandem mass spectrometry analysis of explosives increased in sophistication when high-pressure liquid chromatography with electrospray ionization (ESI) was applied as a separation and sample introduction technique [30]. A triple quadrupole instrument was used in 1998 to identify chemical structures of explosives and to differentiate and quantify species at the same *m*/*z* value for the materials through the use of high and low collision energy [31]. LC atmospheric pressure chemical ionization (APCI) with a supplemental feed of dichloromethane used chloride adduct ions for the MS/MS ions of interest increasing response and minimizing decomposition [32]. A fragile ion exhibits a chemical mass shift because it fragments during resonance ejection of mass analysis [33]. The effect of scan speed was used to study fragile ions and their effect on mass resolution and the intensity of the MS/MS isolated explosive ions in 2002 [33]. Also in 2002, MS/MS was used to monitor for degradation products of RDX in ground water expanding the applications for MS/MS of explosives to the environment [34]. More recently, HPLC/APCI/MS/MS has been used for the trace analysis of peroxide explosives [35]. This paper focuses on the development of a GC/MS/MS method for the analysis of explosives using positive chemical ionization.

2. Experimental

A Varian (Walnut Creek, CA) 8200 auto sampler 3400cx gas chromatograph Saturn 2000 ion trap mass spectrometer was used in electron ionization mode (GC/EI/MS), positive chemical ionization mode (GC/PCI/MS), and positive chemical ionization tandem mass spectrometry mode (GC/PCI/MS/MS). 99.999% purity methane reagent gas (Air Products, Allentown, PA) was used in GC/PCI/MS and GC/PCI/MS/MS modes. A 25 m × 0.25 mm × 0.25 μm Equity^{TM}-1 GC column from Supelco (Bellefonte, PA) was used in conjunction with a Siltek^{TM}-deactivated splitless liner from Restek (Bellefonte, PA). The GC temperature program used was 80–115 °C at a rate of 10 °C/min followed by 115–234 °C at 15 °C/min with a hold for 1.34 min. The transfer line and manifold temperatures remained at 280 and 120 °C, respectively for all experiments. A 1 μL amount of sample was injected via auto sampler and an acetonitrile blank (Fisher Chemicals, HPLC grade, Fair Lawn, NJ) was run before each sample injection.

3. Reagents

EPA Mix A and EPA Mix B were obtained from Supelco (Bellefonte, PA). EPA Mix A contained the following compounds in concentrations of 100 ppm: nitrobenzene (NB), 1,3-dinitrobenzene (1,3-DNB), 2,4-dinitrotoluene (2,4-DNT), 1,3,5-trinitrobenzene (1,3,5-TNB), 2,4,6-trinitrotoluene (2,4,6-TNT), hexahydro-1,3,5-trinitro-s-triazine (RDX), 2-amino-4,6-dinitrotoluene (2-A-4,6-DNT), and octahydro-1,3,5,7-tetranitro-1,3,4,5-tetrazocine (HMX). EPA Mix B contained the following compounds in concentrations of 100 ppm: 2-nitrotoluene (2-NT), 3-nitrotoluene (3-NT), 4-nitrotoluene (4-NT), 2,6-dinitrotoluene (2,6-DNT), 4-amino-2,6-dinitrotoluene (4-A-2,6-DNT), and *N*-methyl-*N*-2,4,6-tetranitroaniline (tetryl). An internal standard, 1000 ppm 3,4-dinitrotoluene (3,4-DNT), was purchased from Protocol Analytical (Middlesex, NJ). HPLC grade acetonitrile obtained from Fisher Chemicals (Fair Lawn, NJ) was used in the dilution of the stock solutions for method limit of detection samples. Stock solutions were stored in the freezer at 0 °C and were used to prepare the method limit of detection samples just before analysis.

4. GC/PCI/MS/MS method development

Creation of an MS/MS method requires optimization regarding: non-resonant waveform ejection versus resonant waveform ejection, collision induced dissociation excitation storage level (*m*/*z*), excitation amplitude (V), and selection of an ion that increases selectivity for that compound. A GC/PCI/MS/MS method using non-resonant waveform ejection was created using the automated method developer (AMD) in Varian's Saturn GC/MS workstation Version 5.52. In non-resonant CID, a dipole wave form is applied exciting all ions in the trap simultaneously. In resonant CID, a single frequency corresponding to the selected ion is applied to excite the ions in the trap. Method creation using non-resonant waveform ejections is simplified and produces consistent spectra over time when compared to resonant waveform ejections [36].

Storage radio frequency (rf) values are typically reported in terms of the Mathieu "*q*" parameter. The Mathieu "*q*" parameter mathematically describes the stability of the ion trajectory with values ranging from 0 to 0.908 [37]. A value of 0.4 has been determined to produce the optimum yield of most product ions and their daughter ions by the Varian instrument manufacture because it is in the middle of the two extreme "*q*" values. The CID rf storage value (*m*/*z*) depends on the *m*/*z* of the ion and is determined using the "*q*" calculator provided in the workstation Version 5.52 software: CID rf storage value (*m*/*z*) = 0.4233 × (*m*/*z* of selected ion) − 0.3944. This equation was used to determine the storage radio frequency used in trapping the MS/MS ion of interest.

The excitation amplitude (V) was experimentally determined. The excitation amplitude is the amplitude of the ejection waveform used during the coarse isolation step. The excitation amplitude was optimized to produce the best signal and the most structural information through fragmentation. The isolation window used was 3.0 *m*/*z*. The isolation window is the total *m*/*z* range to be isolated with the selected *m*/*z* at the center. The scan time was 0.7 (s/scan) for the GC/EI/MS and GC/PCI/MS methods while the scan time for the GC/PCI/MS/MS method was 0.51 (s/scan). The low *m*/*z* to the high *m*/*z* scanned for the GC/EI/MS and GC/PCI/MS methods were 40–450 *m*/*z* while the low *m*/*z* to the high *m*/*z* scanned for the GC/PCI/MS/MS method was 40–250 *m*/*z*. The emission current for all methods was 10 μA. The final GC/PCI/MS/MS conditions are listed in Table 1.

The molecular ion represents a particular compound better than any characteristic fragment and should be used if at all possible. The selected ions for the MS/MS experiment were the same as the protonated molecular ion for all of the explosive compounds except for tetryl and RDX. A characteristic ion from both of these compounds was used instead. Tetryl decomposes from the heat in the GC to form 2,4,6-trinitro-

Table 1
GC/PCI/MS/MS conditions

Explosive compounds	Molecular weight (g/mol)	MS/MS ion	Excitation storage level (*m*/*z*)	Ejection amplitude (V)
Nitrobenzene	123.11	124	54.5	41.41
2-Nitrotoluene	137.14	138	60.6	35.13
3-Nitroltoluene	137.14	138	60.6	40.07
4-Nitrotoluene	137.14	138	60.6	42.30
1,3-Dinitrobenzene	168.11	169	74.4	63.66
2,6-Dinitrotoluene	182.13	183	80.5	49.90
2,4-Dinitrotoluene	182.13	183	80.5	56.56
3,4-Dinitroltoluene	182.13	183	80.5	62.09
1,3,5-Trinitrobenzene	213.10	214	94.3	71.16
2,4,6-Trinitrotoluene	227.13	228	100.5	66.86
RDX	222.12	75	35.0	26.40
4-Amino-2,6-dinitrotoluene	197.15	198	87.2	45.95
2-Amino-4,6-dinitrotoluene	197.15	198	87.2	58.16
Tetryl	287.15	243	107.0	71.50
HMX	296.16	ND	NA	NA

ND, not detected; NA, not applicable.

Table 2
GC/EI/MS results

Explosive compounds	R.S.D.	Slope	R^2	LOD (ng)	LOQ (ng)
Nitrobenzene	26.3	11601	0.862	0.0254	0.0850
2-Nitrotoluene	17.9	18310	0.973	0.0292	0.0970
3-Nitroltoluene	17.8	20058	0.978	0.0089	0.0300
4-Nitrotoluene	16.3	18752	0.956	0.0118	0.0390
1,3-Dinitrobenzene	4.2	11549	0.986	0.0059	0.0200
2,6-Dinitrotoluene	7.5	21094	0.960	0.0054	0.0180
2,4-Dinitrotoluene	4.7	18869	0.942	0.0036	0.0120
1,3,5-Trinitrobenzene	5.3	3868	0.953	0.0135	0.0450
2,4,6-Trinitrotoluene	5.7	10070	0.953	0.0073	0.0240
RDX	24.2	32	0.777	2.2322	7.4410
4-Amino-2,6-dinitrotoluene	12.6	3201	0.966	0.0043	0.0140
2-Amino-4,6-dinitrotoluene	9.3	2117	0.979	0.1002	0.3340
Tetryl	27.4	350	0.981	0.2803	0.9340
HMX	ND	ND	ND	ND	ND

N-methyl-aniline [14] that creates *m*/*z* 243 when ionized by chemical ionization [15–17]. The most characteristic ion and the MS/MS selected ion of choice for tetryl is *m*/*z* 243. Chemical ionization of RDX with methane leads to cleavage reactions producing RDX fragments of *m*/*z* 75 and 149 [18]. The most abundant ion, *m*/*z* of 75, was selected for the MS/MS experiment. The *m*/*z* 75 ion is created from the protonation of the $[CH_2NNO_2]$ fragment. HMX was not detected using any of the different methods discussed in this paper because it tends to decompose at elevated temperatures [38].

5. Results and discussion

Optimization experiments were conducted for injector and trap temperature, flow rate, and injector mode. The optimal injector temperature conditions were selected based upon signal and relative standard deviation (R.S.D.). The optimal injector port temperature was found to be 175 °C. Results obtained for the ramped temperature program injector condition (4–220 °C at 200 °C/min) improved the signal for certain compounds but the reproducibility was poor. Injector port temperature had no effect on the mass spectra produced. The optimal trap temperature conditions were selected based on the amount of molecular ion obtained and chromatographic quality. The optimal trap temperature was found to be 180 °C. Lower trap temperatures produced more molecular ion while higher trap temperatures improved chromatography. The optimal flow rate was found to be 1.3 mL/min while the optimal injector mode was found to be splitless for 2 min for the EI/MS and PCI/MS modes and split (12.5:1) for the PCI/MS/MS mode.

The precision was determined for the liquid injections of each method by calculating the relative standard deviation of each explosive using 3,4-dinitrotoluene as an internal standard. The concentration of 3,4-dinitrotoluene in each sample was 25 μg/mL. The R.S.D. is calculated by dividing the standard deviation by the mean and multiplying by 100. The average R.S.D. of each explosive, except for the internal standard, is reported in Tables 2–4. The linearity of the liquid injection for each of the mass spectral methods was determined by plotting the response of each of the explosive analytes in Microsoft Excel and using equations within Excel to determine the calibration slope and the calibration linearity (R^2). The calibration slope (*m*) and the calibration linearity (R^2) are also reported in Tables 2–4.

Table 3
GC/PCI/MS results

Explosive compounds	R.S.D.	Slope	R^2	LOD (ng)	LOQ (ng)
Nitrobenzene	11.4	7088	0.893	0.0008	0.0030
2-Nitrotoluene	5.6	4480	0.916	0.0008	0.0030
3-Nitroltoluene	5.2	5020	0.969	0.0014	0.0050
4-Nitrotoluene	3.4	4647	0.881	0.0015	0.0050
1,3-Dinitrobenzene	3.1	2740	0.989	0.0008	0.0030
2,6-Dinitrotoluene	4.3	3819	0.968	0.0005	0.0020
2,4-Dinitrotoluene	3.1	3824	0.966	0.0004	0.0010
1,3,5-Trinitrobenzene	2.8	1369	0.989	0.0190	0.0630
2,4,6-Trinitrotoluene	3.5	2550	0.991	0.0024	0.0080
RDX	9.4	261	0.886	0.0133	0.0440
4-Amino-2,6-dinitrotoluene	4.8	2272	0.998	0.0015	0.0050
2-Amino-4,6-dinitrotoluene	8.3	2834	0.986	0.0027	0.0090
Tetryl	18.2	1130	0.941	0.0031	0.0100
HMX	ND	ND	ND	ND	ND

Table 4
GC/PCI/MS/MS results

Explosive compounds	R.S.D.	Slope	R^2	LOD (ng)	LOQ (ng)
Nitrobenzene	5.7	4517	0.940	0.0007	0.0020
2-Nitrotoluene	6.8	2945	0.982	0.0010	0.0030
3-Nitroltoluene	5.9	5041	0.945	0.0006	0.0020
4-Nitrotoluene	3.7	5631	0.950	0.0005	0.0020
1,3-Dinitrobenzene	12.7	226	0.982	0.0133	0.0440
2,6-Dinitrotoluene	4.0	2216	0.953	0.0014	0.0050
2,4-Dinitrotoluene	3.9	3111	0.917	0.0010	0.0030
1,3,5-Trinitrobenzene	4.6	3341	0.966	0.0009	0.0030
2,4,6-Trinitrotoluene	11.1	2188	0.963	0.0014	0.0050
RDX	8.5	72	0.890	0.0414	0.1380
4-Amino-2,6-dinitrotoluene	6.7	2330	0.999	0.0013	0.0040
2-Amino-4,6-dinitrotoluene	5.6	5403	0.997	0.0006	0.0020
Tetryl	13.1	651	0.942	0.0046	0.0150
HMX	ND	ND	ND	ND	ND

The method limit of detection (LOD) is the smallest quantity of analyte that can be detected [39]. The method limit of quantitation (LOQ) is the smallest quantity of analyte that can be quantified [39]. The level of detection was calculated as $3\times(\text{S.D.}/S)$ where S.D. is the standard deviation of the response acquired for the 15 μg/mL triplicate samples and S is the slope of the calibration curve not set with an intercept of 0. The method limit of quantitation was calculated as $10\times(\text{S.D.}/S)$. The LOD and the LOQ for each explosive compound are listed in Tables 2–4 for GC/EI/MS, GC/PCI/MS, and GC/PCI/MS/MS, respectively. The LOD for the explosive compounds are visually compared for the three different mass spectral methods in Fig. 1. The LOD for EI and PCI were also compared to limits of detection previously reported in the literature obtained with a quadrupole [40]. When the GC/EI/MS, GC/PCI/MS, and GC/PCI/MS/MS results obtained from this work are compared to the GC/EI/MS, GC/PCI/MS, and GC/NCI/MS results obtained with the Hewlett-Packard 5989 gas chromatograph quadrupole mass spectrometer from the previous reference respectively, the LOD results show that greater sensitivity is obtained by the ion trap mass spectrometer. The mass spectra obtained

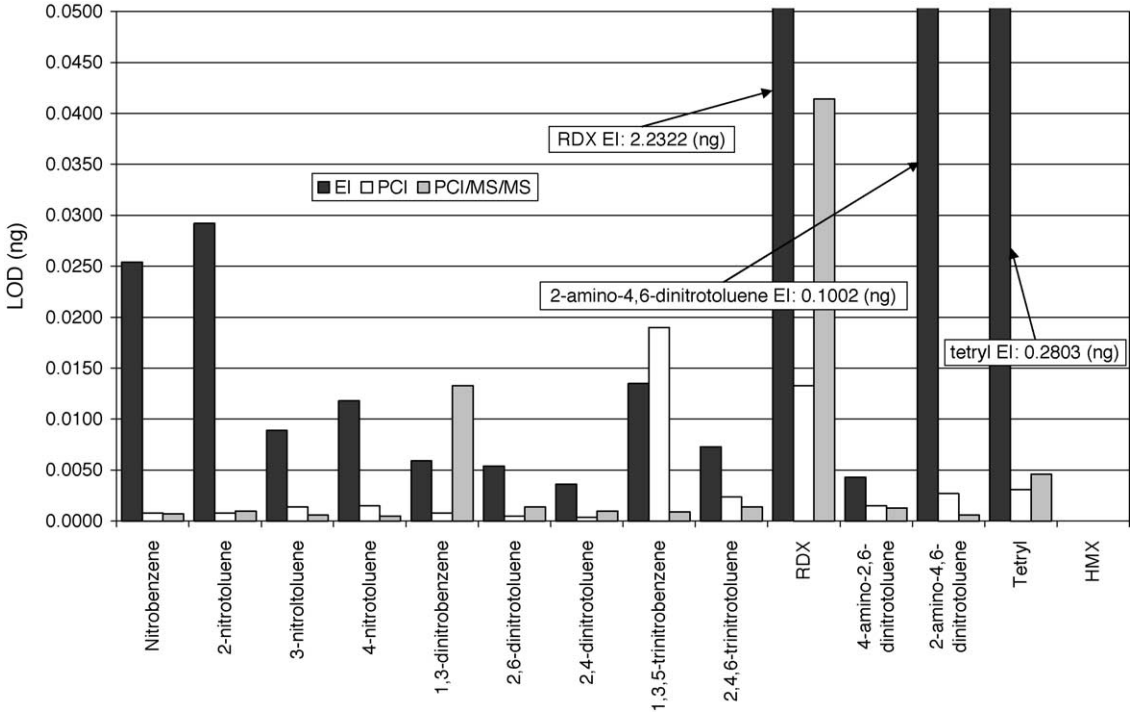

Fig. 1. Visual comparison of LOD for different mass spectral methods.

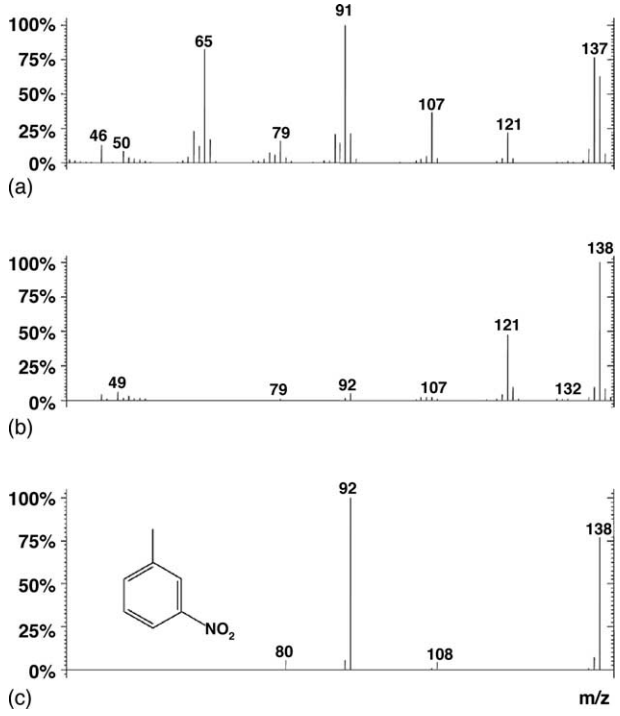

Fig. 2. Mass spectra obtained for 3-nitrotoluene in (a) GC/EI/MS (b) GC/PCI/MS and (c) GC/PCI/MS/MS.

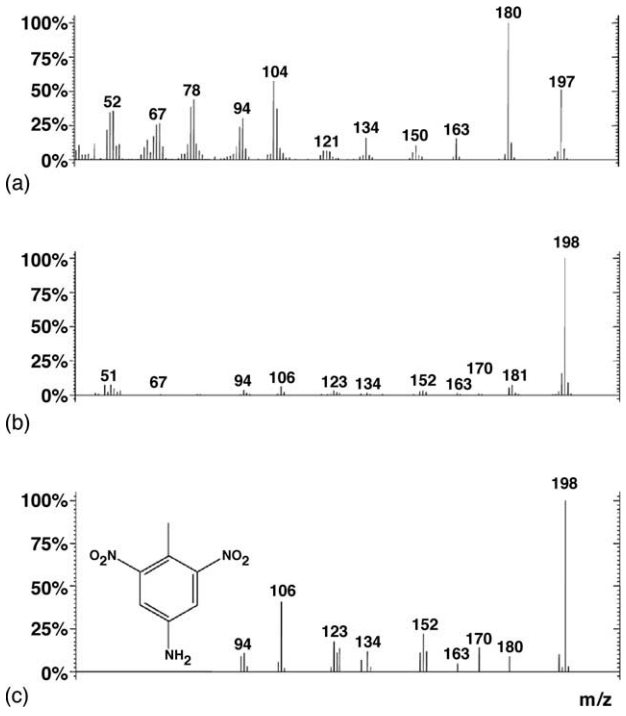

Fig. 4. Mass spectra obtained for 4-amino-2,6-dinitrotoluene in (a) GC/EI/MS (b) GC/PCI/MS and (c) GC/PCI/MS/MS.

for 2-nitrotoluene, 1,3,5-trinitrobenzene, and 4-amino-2,6-dinitrotoluene collected under the different experimental conditions (EI, PCI, and PCI/MS/MS) are presented in Figs. 2–4, respectively. The characteristic *m*/*z* values in the GC/EI/MS and GC/PCI/MS spectra are preserved in the GC/PCI/MS/MS spectra and can be used with standard protocols to identify the compound.

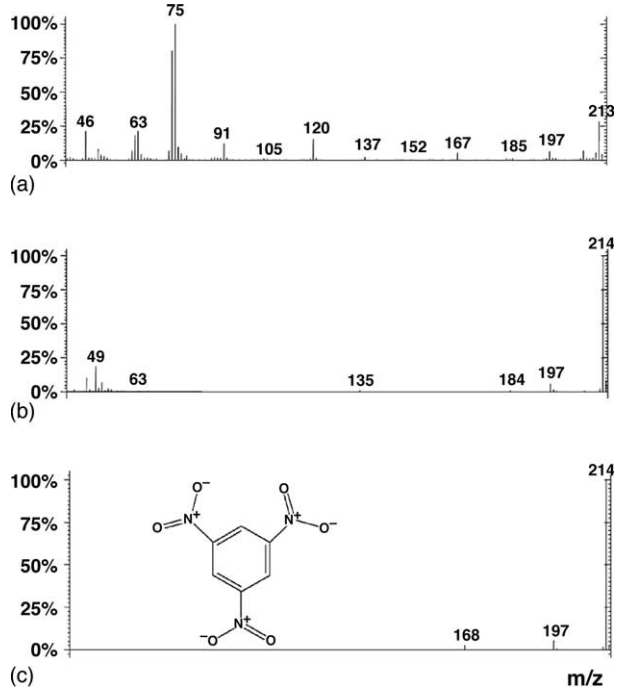

Fig. 3. Mass spectra obtained for 1,3,5-trinitrobenzene in (a) GC/EI/MS (b) GC/PCI/MS and (c) GC/PCI/MS/MS.

6. Conclusion

The GC/EI/MS method produced the highest LOD data. The results obtained between GC/PCI/MS and GC/PCI/MS/MS are similar for all of the compounds except for RDX and 1,3-dinitrobenzene, which are lower by GC/PCI/MS, and 1,3,5-trinitrobenzene, which is lower by GC/PCI/MS/MS. The GC/PCI/MS/MS method however will offer improved selectivity when analyzing real world samples containing interfering products and matrix noise thereby improving sensitivity. Improvements in detection obtained for explosive samples in low concentrations within a complex matrix are the most important aspect of the GC/PCI/MS/MS method. Post-blast debris samples can be analyzed without the need for sample pre-concentration and clean-up thereby reducing the need for sample preparation and the analyte dilution that may result from some sample preparation steps. Reduced sample preparation can also reduce the potential for sample loss or sample contamination. The tandem mass spectrometry experiment presented is shown to be sensitive and selective for the detection of trace level amounts of explosives in complex matrices while easy to use with commercially available instrumentation. The MS/MS spectra fragments can be used in conjunction with retention time to identify the explosive compound.

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