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Fast gas chromatography negative chemical ionization tandem mass spectrometry of explosive compounds using dynamic collision-induced dissociation

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ABSTRACT

The analysis of nine explosive compounds by gas chromatography tandem mass spectrometry (GC–MS/MS) using negative chemical ionization (NCI) was performed under two different conditions: first, a conventional GC separation coupled with a standard ion dissociation method in a quadrupole ion trap (QIT) was performed in segmented selected reaction monitoring mode; second, a fast GC separation on a microbore capillary column was combined with a faster method of collisional activation in ion traps wherein fragmentation is deliberately accomplished during the mass acquisition scan. The conventional GC–MS/MS method provided separation times in 10 min with detection limits between 0.8 and 280 pg on column. The fast GC method with dynamic collision-induced dissociation (DCID) offered a confirmatory method for the analysis of high explosives with separation times under 2.5 min and detection limits between 0.5 and 5 pg on column, without any hardware modifications to the instrument. The implementation of DCID in combination with three-times-faster mass scanning allows the acquisition of tandem mass spectra to at least 5 Hz (while averaging three scans per spectrum). Although detection limits for GC-NCI–MS/MS using conventional CID or DCID are not quite on par with LODs achieved by GC-ECD, the combination of NCI with DCID tandem MS leads to detection limits at least comparable, if not superior, to other mass spectrometric methods. Selected reaction monitoring in the negative ionization mode is anticipated to offer the most selective approach to detecting explosives and eliminating potential interferences, which could ultimately lead to the best detection limits for real, contaminated samples.

1. Introduction

The analysis of explosives requires highly selective and sensitive analytical methods that can detect trace amounts of residues in diverse complex matrices. To eliminate or reduce matrix interference, chromatography is often employed to separate the various components; both gas and liquid chromatographic methods have been developed for this purpose. Mass spectrometry (MS) has long been used to study explosives compounds [1–3] and has always been perceived as the ideal confirmatory detection method for explosive compounds because of its selectivity and confirmatory power. However, the limits of detection (LODs) achievable by MS were not always compatible with the trace analysis requirements of a forensic laboratory on a routine basis. For this reason, screening methods relying on detectors with no confirmatory power are often used prior to confirmation with MS, and concentration procedures are applied to the positive samples in order to bring the explosives into a concentration range that can be detected by the mass spectrometer. Screening methods are also important to provide a double check mechanism and insure that samples are not mishandled. Low detection limits for explosive compounds have made electron capture detectors (ECD) [4–8] and chemiluminescence detectors (CL) [9–11], the most common types of detectors for gas chromatography screening methods.

Modern mass spectrometers now offer improved detection limits and have been combined with LC and GC separations for the analysis of explosives at low levels [12,13], reducing the needs for pre-concentration procedures. LC analyses often offer the ability to screen for a larger number of explosives simultaneously because, unlike GC separations, there is no thermal degradation of the explosives in an LC separation. GC analysis of explosives is nonetheless favored in many forensic laboratories because of the lower cost and greater availability of instrumentation. Analysis of explosives by GC–MS has previously been performed using electron ionization (EI) and chemical ionization (CI) in both positive and negative mode

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[14]. EI of explosives tends to provide limited information regarding the nature of the explosive because a number of organic high explosives have analogous structures and fragmentation patterns.

Chemical ionization, being a softer ionization method, can reveal more information regarding the structure of a particular explosive and can also allow an increase in the selectivity of the method when used in the negative mode. Electron-capturing compounds are relatively uncommon in nature, so nitro-containing explosive compounds possess a unique chemical property that favors the elimination of matrix interferences when analysed via negative chemical ionization (NCI) [15,16].

The use of tandem MS for the analysis and identification of explosives has also been reported using positive chemical ionization (PCI) [12,17] and NCI [18]. Tandem MS has the advantage of improving the selectivity of the analysis, while maintaining the identification power inherent to all mass spectrometric techniques. Tandem MS can be performed in conjunction with GC separation, but the needs for reduced turn-around time and increased efficiency in laboratories require faster separation methods, which are now achievable on conventional gas chromatographs. Fast GC methods have been developed for the analysis of explosives [7,8], but the acquisition rates required to obtain sufficient data points per chromatographic peaks are not fully compatible with conventional tandem MS sampling rates [19]. The ability to perform tandem MS in the time frame required by fast GC in a simple manner is a step toward making the technology available to a larger number of laboratories, without requiring expensive equipment. Ion-traps are the least expensive mass spectrometers that permit tandem mass spectrometry. The analyses of explosives and other analytes often involve samples with complex matrices and the selectivity of tandem MS becomes an advantage in these analyses by reducing the effect of interferences.

This report presents the results obtained for the analysis of explosive compounds using NCI and tandem MS in a quadrupole ion-trap (QIT). Results obtained using conventional gas chromatographic conditions are compared to fast GC data. To be able to achieve the duty cycle required by the fast GC separation, these experiments were conducted using fast mass scan rates and dynamic collision-induced dissociation (DCID). The principles behind DCID are described in detail in previous reports [20–22]. DCID is a modified collision-induced dissociation (CID) method, which activates ions for dissociation during the mass scan, without requiring a separate ion activation period.

2. Experimental

2.1. Operating conditions

A PolarisQ ion trap mass spectrometer (Thermo Scientific, Austin, TX) in combination with a Trace GC Ultra (Thermo Scientific, Austin, TX) were used throughout this study. Both were used without hardware modifications; the scan functions of the mass spectrometer were modified to accommodate the requirement of the fast separation and non-conventional ion excitation technique. These software modifications were made possible by accessing the source code furnished by Thermo Scientific through the Xcalibur Development Kit (XDK) using Visual Basic 6.0 (Microsoft Corp., Redmond, WA). In brief, the software was modified to eliminate down time in-between scans. The scan function was also modified to eliminate the conventional CID excitation step in tandem MS mode and to add the DCID excitation waveform to the existing waveform during the mass scanning period. Conventional CID was used with the conventional GC separation while DCID was used for the fast separation. To perform conventional CID, no modifications were made to the software and the CID excitation amplitude was set at 1 V_{pp} at a q_z = 0.45 for 15 ms. For DCID experiments, excitation was performed at a frequency of 171 kHz ($q_z \sim 0.45$) with an amplitude of 3 V_{pp}.

For conventional GC, a 30 m × 0.25 mm i.d. × 0.25 μm RTX-5MS (5% diphenyl/95% dimethyl polysiloxane) column was used with a 30 °C/min ramp between 70 and 220 °C with a 1.5 min hold at the beginning and a 4 min hold at the end. Ultra high purity (UHP) helium (Airgas, Parkersburg, WV) was further purified using a helium gas purifier (model HP2, VICI, Houston, TX) at a flow rate of 2 mL/min. 1 μL injections were split 10:1 prior to separation. Other parameters are the same as described below for the fast GC. For fast GC, the chromatographic settings of a previously published method [7] were adapted to this system. The column was a DB-5 (Agilent J&W Scientific, Santa Clara, CA) with the following dimensions: 5 m × 0.1 mm i.d. × 0.2 μm stationary phase thickness. UHP helium was used as the carrier gas at a flow rate of 1.5 mL/min. The injector was kept at 180 °C with a 10:1 split. The oven temperature program was a linear ramp from 70 to 220 °C at 70 °C/min with a 0.2 min hold at the beginning and 1.5 min at the end. The transfer line was kept at 220 °C and the ion source at 150 °C. In the mass spectrometer, negative chemical ionization was performed via electron capture using methane (99.995%, Airgas, Parkersburg, WV) as a moderating gas at 1.2 mL/min. An autosampler (AS3000, Thermo Scientific, Waltham, MA), was used to perform 1 μL injections. For the results shown in Section 3, a minimum of five injections were performed.

2.2. Chemicals

A working standard of a mixture of nine explosives compounds at 1 μg/mL in HPLC grade acetone (Fisher Scientific, Fair Lawn, NJ) was prepared from individual standards. The following standards were all purchased from Cerilliant Corporation (Round Rock, TX): ethylene glycol dinitrate (EGDN), 4-nitrotoluene (4-NT), nitroglycerine (NG), 2,6-dinitrotoluene (2,6-DNT), 2,4-dinitrotoluene (2,4-DNT), 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), cyclotrimethylenetrinitramine (RDX), and 2,4,6-trinitrophenylmethylnitramine (Tetryl) at a concentration of 1 mg/mL in acetonitrile except for EGDN, which was at 100 μg/mL. The working standard was used to produce a series of standard solutions with concentrations varying between 1 and 500 ng/mL by performing serial dilution in acetone.

3. Results and discussion

In fast GC, chromatographic peaks typically exist for approximately one second or less in the detector, so the detector must have a sufficiently fast acquisition rate in order to appropriately sample the analyte multiple times during the eluting peaks. To achieve a minimum of five data points with an ion trap combined with fast-GC, the ion trap duty cycle must be improved to at least 5 Hz. Conventional full-mass-scanning scan rates in QITs are not fast enough and conventional tandem MS scans are typically much slower than this minimum requirement. Typically, in ion traps, mass scans are averaged to improve the signal-to-noise ratio of ions of interest. This averaging is partially responsible for the slow data acquisition rate inherent with ion traps. Fig. 1 shows the improvements in scan times achieved by changing the mass scan rate from 0.18 to 0.06 ms/u and by reducing the down-time between scans. Fig. 1a and b shows that up to twice as many data points (average of 3 microscans) can be obtained using the modified scanning program when compared to the standard scan rate. The increase in mass scan rate results in a loss in mass resolution, discussed in more detail later in this section, which may or may not be an acceptable

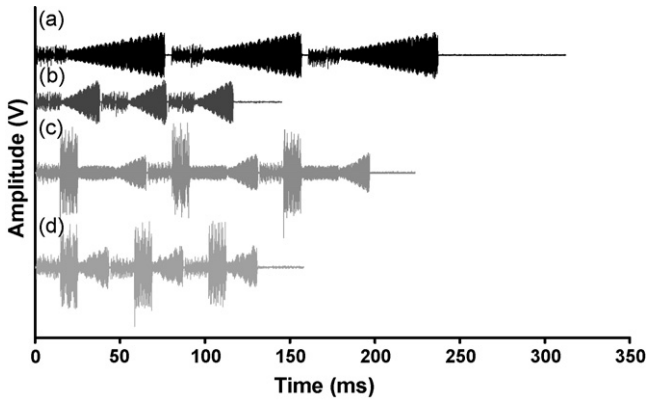

Fig. 1. Scan function on end-cap of PolarisQ ion-trap. Pre-ion and injection times of 5 ms each for all the scans between *m/z* 50 and 300 (3 microscans). Full scan MS acquisition at (a) normal 0.18 ms/amu scan rate parameter and (b) 0.06 ms/amu scan rate parameter; tandem MS acquisition at a fast scan rate parameter of 0.06 ms/amu with (c) conventional CID (10 ms isolation and 20 ms excitation) and (d) DCID (10 ms isolation).

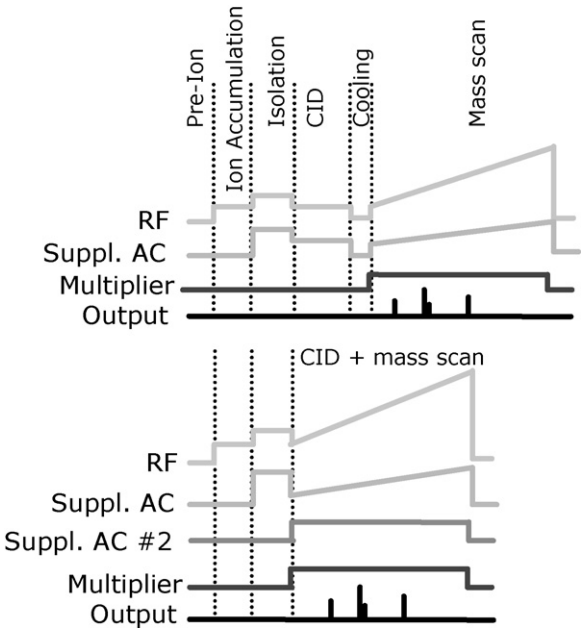

Fig. 2. Ion trap scan functions for operation in (a) conventional CID mode and (b) in DCID mode. RF represents the amplitude applied to the ring electrode. Supplementary AC is applied to the end-caps for isolation, CID and resonance ejection purposes. Supplementary AC #2 represents the excitation waveform applied to the end-caps to perform DCID.

effect of fast scanning, depending on the application. Because tandem MS is performed in conjunction with a separation step, and because the ion isolation stage, which is the crucial step in determining which precursor ion is being fragmented, is not affected by the modifications to the scan function, the slight loss in mass resolution in the mass acquisition step of the analysis is unlikely to significantly decrease the selectivity of the method. In theory, then, the selectivity lost through rapid mass scanning can be regained through the use of selected reaction monitoring.

Adding conventional tandem mass spectrometry to the fast scanning method would negate any improvements in data acquisition rate, because the collisional activation time would add significant time to each scan. Therefore, dynamic collision-induced dissociation (DCID) was implemented as a more appropriate technique that would only add a minimum amount of time to the scan function, while still allowing the acquisition of tandem mass spectra. DCID is a fragmentation method that was developed by Jackson and co-workers [20–23]; and has been described thoroughly in these publications. In brief, DCID is a form of collisional activation in which an ac-waveform is applied to the end-cap electrodes to excite the isolated ions of interest at their secular frequency and force collisions with the helium bath gas. However, instead of executing fragmentation in a separate excitation period, as is done in conventional CID, the excitation occurs during the mass analysis scan. The result is that only a short isolation period must be added to the scan function prior to mass analysis, resulting in a time saving of approximately 15–30 ms per microscan, which is equivalent to the typical duration of the excitation step and cooling period in conventional CID. Schematics of the scan functions required to operate the ion trap in both fragmentation modes are presented in Fig. 2 and the actual waveforms are presented in Fig. 1c and d. When using a faster mass acquisition scan ramp of 0.06 ms/u, DCID offers time-savings of 65 ms per 3 microscans cycle compared to standard CID, which represents a 30% time saving or more than one microscan every cycle.

One benefit of increasing the scan rate in QITs is that the scan rate increase positively influences the absolute intensities of the observed peaks. This enhancement is observed because the same number of ions (potential signal) are integrated over a shorter period of time, which therefore makes it easier to distinguish real signals from background noise. In some cases, especially for very narrow peaks, the faster integration leads to an improved signal-to-noise ratio [24], and therefore to lower detection limits. This was especially observed in the case of PETN. PETN could not be observed under the conventional chromatographic conditions used, but could easily be detected in the chromatogram when using fast-scanning DCID. The scan rate definitely had an influence, but the difference in observation of PETN could also be related to the difference in chromatographic separation, because PETN is prone to on-column degradation.

Fast mass scanning also results in a loss of mass resolution. This loss in mass resolution is caused by to the fact that fewer mass data points can be acquired at the faster scan rates. At the typical scan rate of 0.18 ms/amu, 15 samples/amu are typically acquired (software default), but at a scan rate of 0.06 ms/amu a maximum of 10 samples/amu can be acquired. At the standard scan rate (0.18 ms/amu) the average mass peak full width at half height (FWHM) is 0.37 amu, while at 0.06 ms/amu it is around 0.67 amu. These values are averaged peak widths for the molecular peaks of TNT, 2,6-DNT and 2,4-DNT. In this specific case, increasing the scan rate by a factor of three results in approximately a twofold loss in mass resolution. This reduction in mass resolution agrees with Yang and Bier [24], who have previously reported a six times reduction in mass resolution for a 12-fold increase in scan rate: a comparable ratio. Goeringer et al. [25] published a theoretical relation between scan rate and mass resolution, but it does not take into account instrumental acquisition parameters such as losses caused by analog-to-digital conversion limitations.

Fig. 3 shows typical total ion chromatograms obtained using (a) the conventional chromatographic separation with conventional tandem MS and (b) fast GC with DCID of the standard mixture of nine explosives. These chromatograms were reconstructed from the segmented selected reaction-monitoring scans, preprogrammed based on the known retention times of each analyte on these columns, as would be employed in a screening method. Due to the segmented nature of the reconstructed plot, the noise level in this total ion chromatogram (TIC) appears to display instantaneous increases and decreases mid-way between chromatographic peaks. The variation in noise level is caused by the program switching

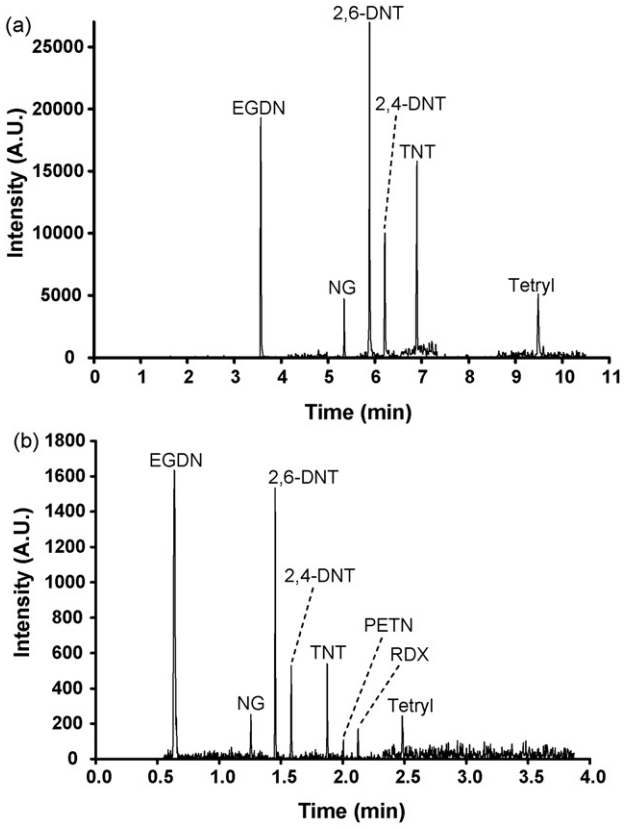

Fig. 3. Total ion chromatograms (TIC) of a mixture of nine explosive compounds using (a) conventional GC–MS/MS with CID (100 ng/mL, $q_z = 0.45$) and (b) fast GC–MS/MS with DCID (75 ng/mL, $q_z = 0.45$, 171 kHz). No fragmentation of EGDN, 4-NT, NG and PETN.

between the isolation of different precursor ions at the mid-point between the analyte retention times. The chromatogram over the entire duration may not be fully representative of the noise level, but the individual segments are representative for the analysis of each individual target compound. Within each segment it is possible to perform selected reaction monitoring (SRM) and extract a chromatogram representing the expected product ion(s) for any given target compound. Examples of SRM acquired using Fast GC and DCID are compared with the total ion chromatogram (TIC) for the same segment in Fig. 4. The visual representation for the different scans is based on a system proposed by Schwartz et al. in 1990 [26], which is gaining in popularity and allows for uniformity in the description of different scanning modes. Filled circles represent selected ions, while open circles indicate an analysis scan over a described mass-to-charge range.

The major ion observed for all the nitrate esters (EGDN, NG, PETN) is m/z 62, which corresponds to NO_3^-, the main product of the dissociative electron capture. Chemical ionization with methane as a moderating gas is not sufficiently soft to obtain molecular ions for these compounds under our operating conditions, although an adduct of the form $[M+NO_3]^-$ is occasionally observed as a very weak peak. Fragmenting the NO_3^- ion would not give any more information on the identity of the precursor. In this case, the retention time combined with a mass spectrum showing a peak at m/z 62 is used to tentatively identify the presence of individual nitrate esters. Moreover, using a scan window of m/z 50–300 while performing DCID at a frequency of 171 kHz means that m/z 62 starts at a secular frequency that is already beyond that of the excitation frequency and could not be excited under these specific conditions.

Table 1
Precursors and related product ions for analysis of explosives by negative chemical ionization with tandem MS.

Compounds	Precursor m/z	Product(s) m/z
EGDN	62	–
4-NT	137	–
NG	62	–
2,6-DNT	182	152
2,4-DNT	182	165, 152
TNT	227	210, 197
PETN	62	–
RDX	129	85
Tetryl	242	212, 225

Table 1 lists the precursor and product ions observed for each of the explosives studied. The nitroaromatics form mostly $M^{\bullet-}$ radical ions, while the nitrate esters as mentioned above rapidly degrade to form NO_3^- as their major peak. RDX is not known to form a molecular peak under negative chemical ionization but usually an adduct, $[RDX + NO_2]^-$, and fragments [27]. The adduct formation was not observed under our operating conditions. The main fragment, the one used in this study as a precursor ion, was the $[RDX–NO_2–HNO_2]^-$ (m/z 129); another major ionization product was $[C_2H_4N_2O_2]^-$ at m/z 102. In a similar manner, Tetryl is known to undergo hydrolysis during chromatography to form *N*-methylpicramide [28], which produces a molecular ion at m/z 242 as the base peak in the mass spectrum.

Tandem mass spectra obtained using DCID qualitatively match spectra obtained via conventional tandem MS and those found in the literature for all compounds studied [18,29]. For the nitroaromatics, the major dissociation products correspond to the losses of m/z 17 ($[M–OH]^-$) and losses of m/z 30 ($[M–NO]^-$), the loss of OH from 2,6-DNT does not occur in a significant amount. For RDX, the $[C_3H_5N_4O_2]^-$ (m/z 129) formed a product at m/z 85, which was previously observed by McLuckey et al. [18] for the CID of the same ion in ion traps and is attributed to the loss of N_2O. This fragmentation pathway, although different from the one observed in higher energy CID experiments in sector instruments, where $[C_2H_4N_3O]^-$ (m/z 86) and $[C_2H_2N_3O]^-$ (m/z 84) are the main dissociation products [17,30], is an acceptable product for the detection and identification of RDX in ion traps. The difference in activation energy most probably leads to the difference in product ions.

Examples of tandem mass spectra using DCID are shown in Fig. 5. As previously demonstrated for other types of samples, fragmentation efficiencies are not optimal using DCID because of the very short amount of time that is available to perform fragmentation [20,31], but the fragmentation patterns are similar to those acquired with conventional CID. The relative intensities of certain peaks may vary depending on the excitation method, but the same major products are usually formed. In DCID, the precursor ion is usually still visible in the product spectrum, since only a fraction is dissociated; the presence of the precursor ion can be helpful for identification purposes, although not necessary.

The detection limits achieved using conventional GC with conventional MS/MS and fast GC with DCID MS/MS with NCI are shown in Table 2 along with results from previously published studies [12,14]. The values obtained using conventional GC–MS/MS were on average an order of magnitude higher (i.e., worse) than the values achieved using fast GC with DCID. The large difference is most probably related to the increased thermal degradation on the long column and to the slower data acquisition rates leading to fewer data points per peak. Perr et al. [12] report quantitative values for the analysis of explosives by GC followed by EI-MS, PCI-MS and PCI-MS/MS, all performed on a ion trap instrument. It is assumed

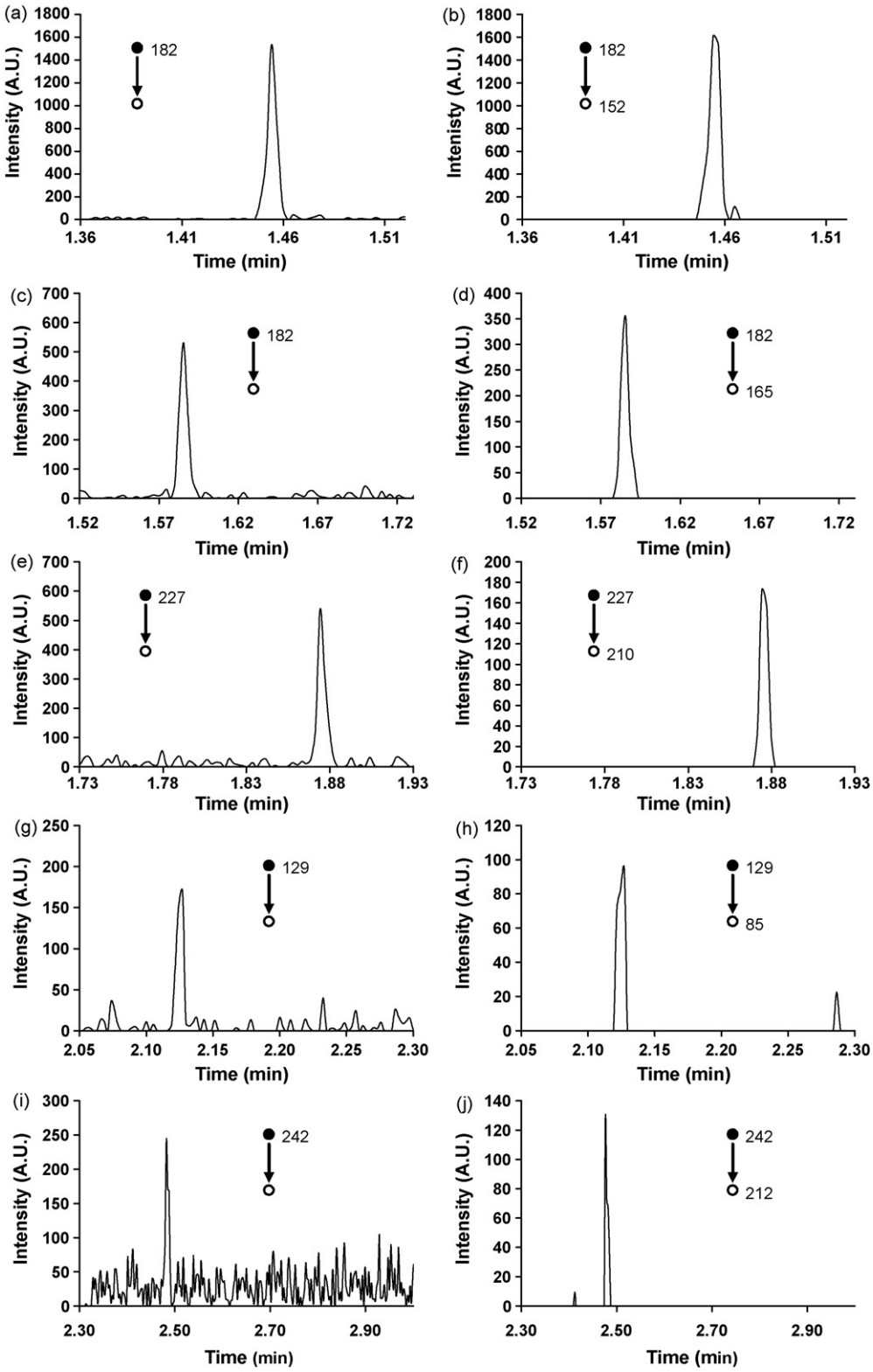

Fig. 4. TIC and SRM of explosives at a concentration of 75 ppb using DCID. 2,6-DNT (a and b); 2,4-DNT (c and d); TNT (e and f); RDX (g and h); and Tetryl (i and j) (q_z = 0.45, 171 kHz).

that their values were obtained from total ion chromatograms since no mention of selected ion monitoring or selected reaction monitoring are made in their paper. Sigman and Ma [14], have also published a report on the analysis of explosives by GC–MS on a single quadrupole instrument in full scan mode and the analyses were performed in EI, PCI, and NCI modes. Their NCI LODs were the lowest of the three modes, but still much higher than the values acquired using ion traps in this study or by Perr et al. The values reported by Perr et al. agree relatively well with the values obtained in the present work using fast GC with DCID, and it is believed

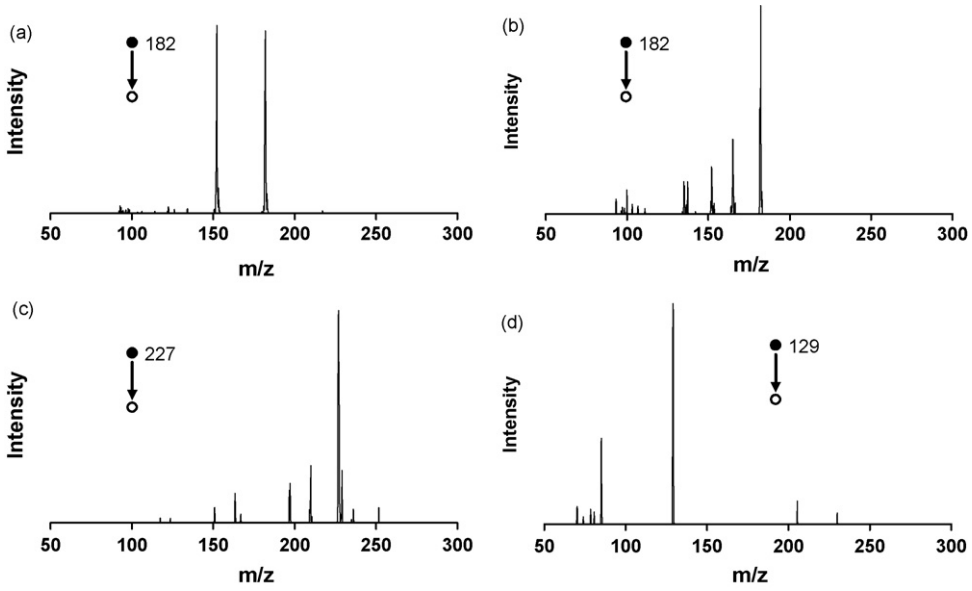

Fig. 5. Mass spectra of (a) 2,6-DNT; (b) 2,4-DNT; (c) TNT; and (d) RDX acquired using DCID tandem MS at a concentration of 75 ng/mL.

Table 2
Reported detection limits for explosives using different tandem mass spectrometric methods.

Compounds	NCI[a] fast GC–MS/MS (DCID, this work) pg	NCI[a] GC–MS/MS (CID, this work) pg	PCI[b] GC–MS/MS [12] pg	NCI[c] GC–MS [14] pg
EGDN	0.5[d]	0.8[d]		750
NG	1.0[d]	13[d]		
PETN	2.0[d]	ND		780
4-NT	ND	150[d]	0.5	
2,6-DNT	0.5	10	1.4	210
2,4-DNT	1.5	10	1.0	180
TNT	2.0	43	1.4	190
Tetryl	2.5	29	4.6	
RDX	5.0	280	41.4	1110

ND = not detected.
[a] Selected reaction monitoring (SRM) values unless otherwise stated.
[b] Data obtained on a Varian Saturn 2000 ion trap (full scan).
[c] Data acquired on a HP 5989 GC–MS (single quadrupole, full scan).
[d] Selected ion monitoring (SIM) values.

that NCI will offer the advantage of increased selectivity over PCI in real samples since fewer compounds in nature have the ability to form negative ions. A report was also published as an application note by Thermo Electron Corp. [32] in which a single quadrupole instrument with NCI was used in conjunction with selected ion monitoring. It states limits of detection varying between 1 and 5 pg for each of the compounds included in this study with the exception of tetryl, which was detected at a 50 pg level. The detection limits determined here are also comparable with published values using electrospray ionization in the negative mode [29].

The limits of detection reported for this work were obtained through SRM, which further increases the selectivity of the method and insures that the peak intensity used to calculate the concentration comes exclusively from the analyte. LODs in the fast GC part of this study are negatively affected by the low fragmentation efficiencies achieved by DCID. In this case the intensity of the signal for the products could be increased by improving the fragmentation efficiency of DCID, which would ultimately lower the detection limits. Currently the fragmentation efficiencies vary between 20% and 25% for the compounds included in this study. The ability to improve the fragmentation efficiency could significantly improve the detection limits and improve the potential of this technique.

4. Conclusion

The analysis of explosives by GC–MS/MS using negative chemical ionization was performed under two different conditions. A more conventional chromatographic and ion dissociation method was contrasted with a fast separation combined with DCID. The conventional method led to longer analysis times with higher detection limits. The fast GC method offered a confirmatory method for the analysis of high explosives with an analysis time under 2.5 min, without any hardware modifications to the commercially available instrument. The implementation of DCID in combination with fast mass scanning allows the acquisition of tandem mass spectrometry data in the time frame of fast gas chromatography. This sampling frequency would not have been possible using conventional CID. Although detection limits are not quite on par with LODs achieved by ECD [7], the combination of NCI with DCID tandem MS leads to detection limits at least comparable, if not superior, to other mass spectrometric methods. Selected reaction monitoring in the negative ionization mode is believed to offer the most selective approach to detecting explosives and eliminating potential interferences, which could ultimately lead to the best detection limits for real, contaminated samples. The poor fragmentation efficiencies achieved by DCID currently act as a limiting factor for the

LODs, but it is likely that the efficiency can be improved by developing a more complex excitation waveforms that would transfer energy over a slightly longer period of time. DCID represents a real option for the implementation of tandem mass spectrometry to fast separation methods and the advantages in speed of analysis and compatibility with existing instrument make it an attractive method for further developments. It is believed that this method could be a valuable asset for performing routine screening analysis looking for known target compounds, such as applications in forensic or environmental laboratories.

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