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TECHNICAL NOTE

CRIMINALISTICS

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Rapid Quantitative Analysis of Multiple Explosive Compound Classes on a Single Instrument via Flow-Injection Analysis Tandem Mass Spectrometry†,‡

ABSTRACT: A flow-injection analysis tandem mass spectrometry (FIA MSMS) method was developed for rapid quantitative analysis of 10 different inorganic and organic explosives. Performance is optimized by tailoring the ionization method (APCI/ESI), de-clustering potentials, and collision energies for each specific analyte. In doing so, a single instrument can be used to detect urea nitrate, potassium chlorate, 2,4,6-trinitrotoluene, 2,4,6-trinitrophenylmethylnitramine, triacetone triperoxide, hexamethylene triperoxide diamine, pentaerythritol tetranitrate, 1,3,5-trinitroperhydro-1,3,5-triazine, nitroglycerin, and octohy-dro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine with sensitivities all in the picogram per milliliter range. In conclusion, FIA APCI/ESI MSMS is a fast (<1 min/sample), sensitive (~pg/mL LOQ), and precise (intraday RSD < 10%) method for trace explosive detection that can play an important role in criminal and attributional forensics, counterterrorism, and environmental protection areas, and has the potential to augment or replace several of the existing explosive detection methods.

KEYWORDS: forensic science, FIA APCI/ESI MSMS, RDX, TATP, HMTD, PC tetryl, HMX, TNT

Explosive materials are an important class of chemicals whose breadth of detection methods reported in the literature has been driven by a wide range of applications. Explosive detection methods have been developed for humanitarian demining (1,2), groundwater and soil remediation (3,4), security screening (5–7), tactical forensic and intelligence (8–10), criminal forensic, (11) rapid sample screening, (12–15), and trace-evidence chemical imaging (16–18). Explosive detection method has also provided motivation for the development of several technologies based on an olfaction-like mechanism. (19–22) Although these reports encompass a wide range of applications, this work can largely be divided into two categories, one that prioritizes rapid detection at the expense of quantification (for tactical, field, and evidence screening applications), and the other that prioritizes sensitivity and quantification at the expense of analysis time (for probative criminal forensic). This paper focuses on the latter, where current forensic methods used in criminal prosecution typically require a range of instruments (GC-MS, GC-NCI, GC-ECD, LC-MS, LC-MS/MS, IC, etc.) to cover all the possible explosive compounds, and often have analysis times of at least several minutes per sample, if not longer. Examples of current quantitative methods approved by the Environmental Protection Agency (EPA) for organonitrate explosives detection include Methods 8095 (23) and Method 529 (24) which employ gas chromatography (GC) with electron capture (ECD) and mass spectrometry (MS) detection, respectively, and Method 8330 (25) that employs high-performance liquid chromatography with UV detection (HPLC-UV). The reported limits of quantitation (LOQ) for these methods varied from 0.084 ng/mL for TNT by Method 529 to 13 ng/mL for tetryl by Method 8330, with the analysis times ranging from 1.2 min for detection of NG by GC-ECD to 14 min for TNT detection by HPLC-UV.

The need for multiple analytical instruments is exacerbated further by the variety of common chemicals that can be repurposed for use in homemade explosives and thus also need to be detected, but that are either not considered in many of the previous reports or not detectable using the aforementioned methods. Several such compounds are the alkali salts of nitrates, chlorates, and perchlorates. EPA Method 300.1 (26) describes an IC technique for chlorate detection with a reported LOQ of 1.3 ng/mL and an analysis time of 30 min. Another example of a homemade explosive is urea nitrate (UN), and ion chromatography (IC) has been reported for detection of UN as nitrate ion, but due to the ubiquity of nitrates this analysis is not sensitive for trace detection. de Perre et. al (27) demonstrated detection of UN by liquid chromatography with ultraviolet/fluorescence (LC-

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UV/fluorescence) detection by derivatizing uronium ion with a fluorophore, xanthydrol. The LOQ for this method was determined to be 21 ng/mL with an analysis time of 5 min. There are numerous other examples of methods developed to detect a subset of both conventional explosives, homemade explosives, and their related compounds, and many of these methods require special instrumentation. A complete review is beyond the scope of this paper.

For a laboratory charged with providing rapid, quantitative analysis across this full range of explosive materials, the consolidation and/or simplification of their analysis would be desirable. Therefore, an opportunity exists for an analytical method that (a) can provide data that are both quantitative and have redundant detection channels for reduced error rates necessary for probative use, (b) is more rapid than existing methods to allow for processing large sample sets for applications such as crime scene or soil mapping, and (c) can meet these requirements for many explosives, both conventional and homemade, on a single instrument to minimize capital costs and laboratory space requirements.

One technique that has drawn considerable attention for both rapid analysis of explosive traces (28) and, more broadly, for forensic applications in general (29) is ambient ionization mass spectrometry (AI-MS). These reports have demonstrated that AI-MS is capable of rapid, direct analysis of surface residues without sample preparation. However, these reports also indicate that method sensitivity is affected by the substrate composition and that the inter-day residual standard deviation is "less than 30%" (28), which is higher than values for the existing validated methods. These factors, along with other non-technical reasons, have resulted in the acknowledgment that AI-MS may, at least initially, be better suited for "evidence preselection" than for quantitative work appropriate for adjudication in a court of law. (29) One of the challenges noted in Ref. (29) is that probative analytical methods must pass the Daubert criteria, (30) the most applicable to AI-MS being that the error rate must be quantifiable and acceptably low, and the error origins understood and controllable (31).

As an alternative to AI-MS, for applications where probative-quality quantitative data are more important than direct surface analysis and where sample extraction is permissible, flow-injection analysis tandem mass spectrometry (FIA-MS/MS) offers high throughput (<1 min/sample), is well recognized in speed and performance as intermediate between AI-MS and conventional quantitative LC-MS/MS, and has recently been extensively reviewed. (32) In this review (32), it was also noted that the newer generation of mass spectrometers is continuously making FIA-MS/MS methods ever more capable. To date, FIA-MS/MS has been used for rapid quantitative analysis of pharmaceuticals (33), pesticides (34), environmental contaminants (35), medical tests (36), drugs of abuse (from both urine and serum) (37), and, since the 1990s, diagnosis and screening of metabolic diseases. (38) Surprisingly, we found no reports of FIA-MS/MS use for explosives detection. In contrast, there are still reports of using conventional LC-MS/MS with an 8-min analysis times for explosives detection. (39) This is surprising, as a recent review of the use of forensic mass spectrometry (40) concluded:

> Critical to reducing the backlog problems at crime laboratories across the United States will be the implementation of higher-throughput techniques such as fast GC, UPLC, or ambient ionization methods.

In this paper, we apply FIA-MS/MS methods to 10 explosives across multiple explosive classes (organonitrates, organic peroxides, and oxidizer salts) and report sensitivity to pg/mL levels with 20-sec analysis times. We report primary and backup MS-MS transitions and also characterize and report the inter-day and intra-day relative standard deviations of these methods so they can be compared with currently acceptable LC- and GC-based explosive detection methods. We feel that by laying the groundwork for FIA-MS/MS of explosives, we might inspire the forensic community to consider this powerful method for the collection and admission of probative evidence when prosecuting crimes involving illicit use of energetic materials. We also feel that this method's versatility would easily allow addition of new compounds for analysis, and thus be adaptable to continuously evolving security challenges.

Experimental

Chemicals

Two concentrations (1 mg/mL and 0.1 ng/mL) of standard solutions of RDX, PETN, TNT, HMX, tetryl, HMTD, TATP, and erythritol tetranitrate (ETN) in acetonitrile and methanol were obtained from AccuStandard Inc. (New Haven, CT). Solid urea nitrate was purchased from TCI America (Portland, OR). Solid isotopically labeled Urea ^{13}C, 1 mg/mL solution of perchloric acid sodium salt ($NaCl^{18}O_4$) in water, and 1 mg/ml solution in 50%/50% acetonitrile/methanol of isotopically labeled TNT ($^{13}C_7{}^{15}N_3$) were obtained from Cambridge Isotope Laboratories (Tewksury, MA). Solid potassium chlorate and 18-Crown-6 ether were purchased from Sigma-Aldrich Co. (St. Louis, MO). LCMS grade methanol, acetonitrile, water, and dichloromethane (>99.8%) were obtained from VWR (Radnor, PA). Isotopically labeled TATP ($C_9D_{18}O_6$) and isotopically labeled HMTD ($^{13}C_6H_{12}{}^{15}N_2O_6$) were synthesized by MIT Lincoln Laboratory (Lexington, MA).

Apparatus

All measurements were performed on an AB SCIEX 4000 QTrap hybrid triple-quadrupole linear ion-trap mass spectrometer (Applied Biosystems, Framingham, MA) in combination with an ABSCIEX TurboV™ ion source equipped with both APCI and ESI probes. All data were acquired in multiple reaction monitoring (MRM) mode, in positive and negative polarity, with a dwell time of 100 msec per transition. The curtain gas pressure setting was 10 psi, the source gas pressure setting was 40 psi, and the collision gas flow was set to "high." The source temperature was optimized for each explosive compound and is specified in Table 1. The APCI corona voltage was set at ±5 KV, whereas the ESI nebulizer current was set at 5500 V in positive polarity and 4500 V in negative polarity. The entrance potential was ±10 V and the collision cell exit potential was set at ±15 V. The precursor ion *m/z* (Q1 mass) and product ion *m/z* (Q3 mass) were identified by performing a product-ion MSMS scan. The de-clustering potential (DP) and collision voltage (CE) were optimized for the best instrument response for each analyte by infusing 100 ng/mL of the compounds into the V-Source via a syringe pump at 10 µL/min. The Q1 and Q3 mass-to-charge ratios and, DP, and CE voltages for both explosives and internal standards (IS) are listed in Table 1. The software to control the instrument was Analyst Version 1.5.1.

TABLE 1—*FIA APCI/ESI MSMS explosives detection. MRM transitions and optimized MS parameters.*

Compound	Ionization	Polarity	Source T(°C)	DP (V)	CE (V)	Q1 (amu)	Q3 (amu)	Q1 ion	Q3 ion	Chemical Ionization Reagent
UN	ESI	POS	150	70	12	325	265	$C_{13}H_{29}N_2O_7^+$	$C_{12}H_{25}O_6^+$	18-Crown-6
UN IS[a]				70	12	326	265	$C_{12}{}^{13}CH_{29}N_2O_7^+$	$C_{12}H_{25}O_6^+$	
PC	ESI	NEG	300	−50	−30	83	67	ClO_3^-	ClO_2^-	None
PC IS[b]				−50	−38	107	89	$Cl^{18}O_4^-$	$Cl^{18}O_3^-$	
TNT	APCI	NEG	250	−35	−40	227	46	$C_7H_5N_3O_6^-$*	NO_2^-	
TNT IS[c]				−35	−40	237	47	$^{13}C_7H_5{}^{15}N_3O_6^-$*	$^{15}NO_2^-$	
TATP	APCI	POS	300	60	15	91	74	$C_3H_7O_3^+$	$C_3H_6O_2^+$	
TATP IS[d]				60	15	97	80	$C_3HD_6O_3^+$	$C_3D_6O_2^+$	
HMTD	APCI	POS	200	35	15	209	88	$C_6H_{13}N_2O_6^+$	$C_3H_6NO_2^+$	
HMTD IS[e]				35	15	217	92	$^{13}C_6H_{13}{}^{15}N_2O_6^+$	$^{13}C_3H_6{}^{15}NO_2^+$	
RDX	APCI	NEG	200	−38	−33	257	46	$C_3H_6N_6O_6Cl^-$	NO_2^-	DCM
PETN	APCI	NEG	200	−38	−20	351	62	$C_5H_8N_4O_{12}Cl^-$	NO_3^-	
NG	APCI	NEG	200	−30	−15	262	62	$C_3H_5N_3O_9Cl^-$	NO_3^-	
Tetryl	APCI	NEG	150	−30	−30	322	46	$C_7H_5N_5O_8Cl^-$	NO_3^-	
HMX	APCI	NEG	250	−40	−25	331	109	$C_4H_8N_8O_8Cl^-$	$C_4H_5N_4^-$	
ETN IS[f]	APCI	NEG	*	−30	−23	337	62	$C_4H_6N_4O_{12}Cl^-$	NO_3^-	

a,b,c,d,e,f – denotes transitions used for internal standards (IS): 13C urea(a) used as IS for UN, ^{18}O sodium perchlorate (b) used as IS for PC, $^{13}C_7{}^{13}N_3$ TNT (c) used as IS for TNT, D_{18} TATP (d) used as IS for TATP, $^{13}C_6{}^{15}N_2$ HMTD (e) used as IS for HMTD, ETN (f) used as IS for RDX, PETN, Tetryl, NG, and HMX. DCM, Dichloromethane.

*ETN IS detection temperature was the same as analyte.

All analytical samples were delivered directly into the ESI or APCI probe by LC injection. The LC system consisted of 1260 Infinity capillary pump with degasser G1382A, high-performance micro autosampler G1377A, and autosampler thermostat G1330B (Agilent technologies, Santa Clara, CA). The autosampler temperature was held at 10°C for all samples. The typical flow rate used for the flow-injection analysis was set at 350 μL/min; the injection size was 40 μL for all analytes except HMTD, where 20 μL was used to avoid carryover. An 80%/20% acetonitrile/water mixture was used as a flow solvent for UN and PC analysis, 100% acetonitrile for the detection of TNT and HMTD, 100% methanol was used for TATP, and 95%/5% acetonitrile/water was used as a flow solvent for the RDX, PETN, tetryl, NG, and HMX analysis. The flow solvents varied to achieve the best sensitivity of detection; however, a single solvent -100% acetonitrile can be used for all explosives for chemical identification of explosive in the mixture. Figure S1 in the supporting information shows the spectrum of 0.4 ng explosives mix containing 10 components, such as 2-amino 4, 6-dinitrotoluene, 4-amino 2, 6-dinitrotoluene, 1,3-dinitrobenzene, 2,6-dinitrotoluene, 2,4-dinitrotoluene, 1,3,5-trinitrobenzene, TNT, RDX, Tetryl, and HMX.

Results and Discussion

MSMS Analysis

MSMS MRM transitions for each analyte were identified by infusing 100 ng/mL individual solutions of analytes via syringe pump at a rate of 10 μL/min in full-scan Q1-MS mode, and then performing an MSMS product-ion scan on the peaks different from the background to identify the most sensitive MRM transitions. Table 1 lists the ions used for explosives detection.

Chemical ionization reagents such as 18-crown-6 ether (18C6) and dichloromethane (DCM) were used to improve detection for some analytes. For example, for the detection of urea nitrate, we used 2 mM solution of 18C6 in acetonitrile to complex with uronium ion as described in Ref. (41). The MSMS product-ion scan acquired in positive polarity ESI ionization mode in Fig. 1 shows [18C6+uronium] $^+$ ion at *m/z* 325 as a precursor ion with $[18C6+H]^+$ at *m/z* 265 product ion with greatest intensity.

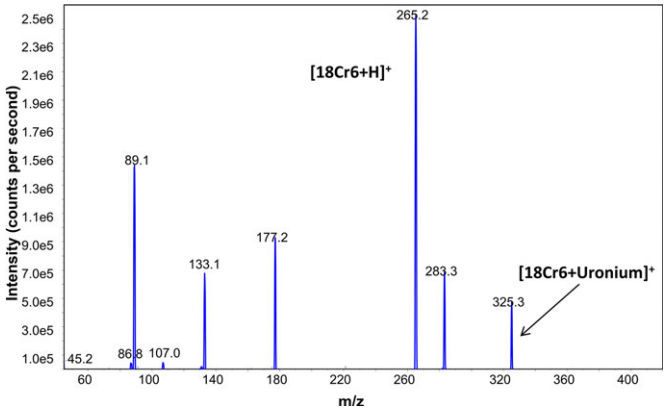

FIG. 1—*ESI spectrum of the product-ion scan of UN in the presence of 18C6 shows the primary ions used for UN detection: [18C6-uronium]$^+$ and [18C6+H]$^+$.*

Detection of PETN, NG, HMX, tetryl, and RDX as chlorinated adducts of the molecular ion in the presence of DCM (42) provided the best limit of quantitation (LOQ). Figure 2 shows an APCI product-ion scan of 100 ng/mL of HMX in the presence of 10% DCM in acetonitrile. The spectrum was acquired in negative polarity APCI mode by syringe infusion of HMX with DCM solution at a rate of 10 μL/min. The molecular ion at *m/z* 331 was assigned as HMX chlorinated adduct ($C_4H_8N_8O_8Cl^-$). The MSMS product-ion scan identified the main fragment ion for HMX detection at *m/z* 109 as a loss of chloride, four nitrite groups, and four hydrogens ($C_4H_5N_4^-$).

No chemical ionization reagents were used for the detection of PC, TNT, HMTD, and TATP. PC was detected in ESI negative polarity as chlorate (ClO_3^-) at *m/z* 83 fragmented to chlorite (ClO_2^-) at *m/z* 69 via collision-induced dissociation (CID). TNT was detected in APCI negative mode as TNT M*, the same transition as reported by Xu et.al (43). The most sensitive transition for HMTD detection was determined in APCI positive polarity as an HMTD molecular ion's protonated adduct $[HMTD+H]^+$ at *m/z* 209 to an HMTD fragment ion at *m/z* 88 assigned as

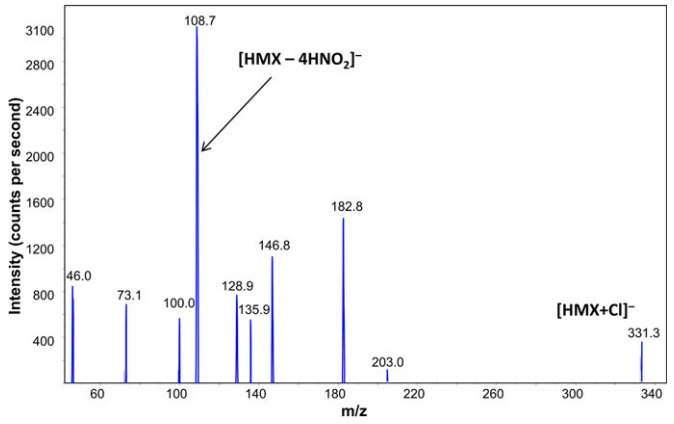

FIG. 2—*APCI spectrum of the product-ion scan of HMX in the presence of DCM shows the primary ions used for HMX detection: [HMX+Cl]⁻ and [HMX-4HNO₂]⁻.*

$C_3H_6NO_2^+$. (44) For TATP detection, we used the TATP fragment ion at *m/z* 91 ($C_3H_7O_3^+$) first reported by L. Widmer et. al. (45) which in turn produced a fragment by CID at *m/z* of 74 assigned as $C_3H_6O_2^{+*}$ radical. Figure 3*a* shows the APCI positive-polarity MSMS product-ion scan of 100 ng/mL of TATP, yielding a TATP ion at *m/z* 91 and its fragment at *m/z* 74. Because both precursor and product ions are TATP fragments, we confirmed identification using isotopically labeled TATP. A product-ion scan of isotopically labeled D_{18}-TATP ($C_9D_{18}O_6$) shown in Fig. 3*b* confirms the TATP ion assignments.

Matrix Interferences

Matrix effects can influence the quantitative analysis by suppressing or increasing the signal due to the presence of interfering compounds (46). Suppression is an important factor to consider for FIA because there is no chromatographic separation prior to ionization. Signal suppression matrix effects were observed for HMTD in the presence of water. Solubility of HMTD in water is very limited and according to Gosetti et al. (46) "*suppression in APCI is due to formation of solid matter: a precipitate could form as the concentrations of both analyte and nonvolatile components increase with solvent evaporation*." Figure 4 shows 0.1 ng/mL of HMTD in 100% acetonitrile (blue trace) and 30% water/70% acetonitrile (red trace). The presence of water decreased HMTD signal intensity by 70%.

Signal enhancement due to a matrix interferent was observed for detection of RDX and PETN in APCI MSMS negative polarity mode. Given the unit mass resolution of the triple-quadrupole mass spectrometer, it may present an erroneous assignment of the interfering peaks as a compound of interest. For example, Fig. 5 shows the precursor ion scan of *m/z* 62 of the Acrodisc™ filter extract with a small peak at 350.2 interfering with the transitions used for PETN detection. In these circumstances, the use of the backup MSMS transitions (Table S1, Supporting Information) can be helpful to reduce the uncertainties in assignments causes by such interferences.

In addition, as recently reported by J. Oxley (47), an acetonitrile may suppress ionization in positive ionization mode by suppressing formation of the protonated ions. Methanol was used for TATP analysis. In case of HMTD and urea nitrate detected as an adduct to 18Crown6 ether, acetonitrile was used as a flow solvent, since these compounds have a limited solubility in

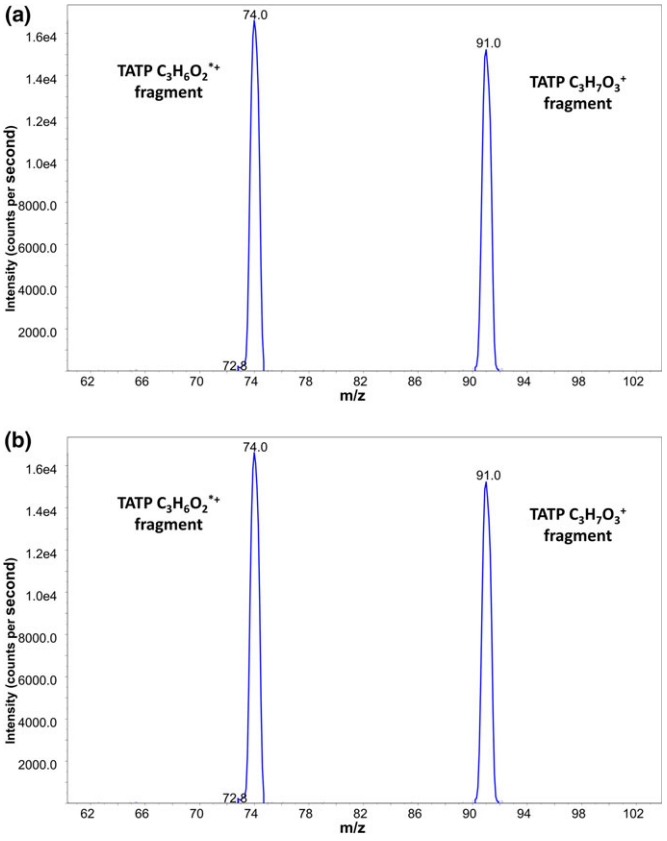

FIG. 3—*(a) APCI spectrum of the product-ion scan of the TATP fragment ion* $C_3H_7O_3^+$ *shows the primary ions used for TATP detection:* $C_3H_7O_3^+$ *and* $C_3H_6O_2^{+*}$. *(b) APCI spectrum of the product-ion scan of the* d_{18}*-TATP fragment ion* $C_3HD_6O_3^+$ *confirms the main ions used for TATP detection:* $C_3HD_6O_3^+$ *and* $C_3D_6O_2^{+*}$.

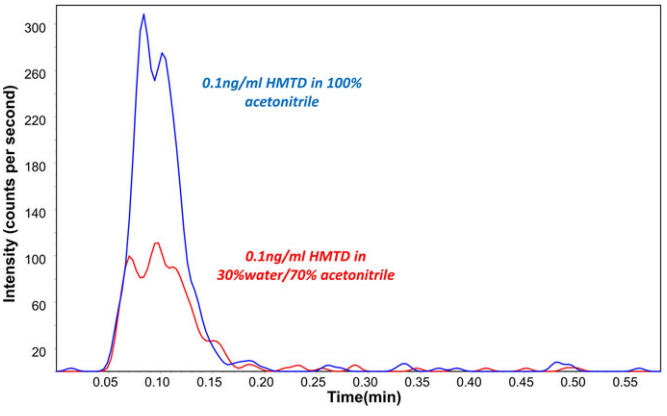

FIG. 4—*0.1 ng/mL HMTD in acetonitrile (blue trace) and 30%water/70% acetonitrile (red trace) showing signal suppression in the presence of water.*

methanol. Solvents alternative to ACN may be investigated to improve LOD further.

Internal Standard

To account for matrix interferences and improve the accuracy, we introduced internal standards that are chemically similar to the compounds of interest, such as isotopically labeled HMTD,

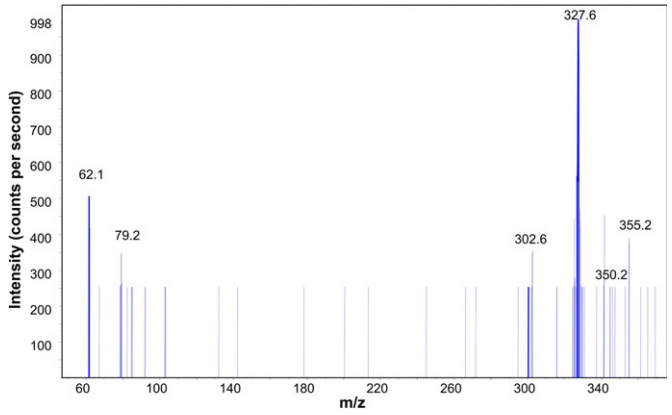

FIG. 5—*APCI MSMS precursor ion scan of m/z 62 of the Acrodisc™ filter extract in acetonitrile.*

TABLE 3—*Methods sensitivity, FIA APCI/ESI MSMS compared with other methods.*

	LOQ (ng/mL)/[retention time (min)]		
Analyte	FIA APCI/ESI MSMS	EPA Methods	Published Methods
UN	0.84/[0.3]		21/[5][27]
PC	0.08/[0.3]	1.31/[30][26]	
TATP	0.43/[0.3]		100/[11][45]
HMTD	0.04/[0.3]		20/[15][44]
TNT	0.10/[0.3]	0.11/[14][25], 2/[7][50], 0.08/[10][24]	0.25/[20][43]
RDX	0.10/[0.3]	0.84/[4][25], 0.2/[8.7][50], 0.08/[22][24]	0.2/[5.3][43]
PETN	0.03/[0.3]		0.35/[19.8][43]
NG	0.12/[0.3]	1/[1.2][23]	2/[4][51]
HMX	0.08/[0.3]	0.2/[11][23]	1.5/[3.6][43]
Tetryl	0.20/[0.3]	4/[7][25], 2/[8][23], 0.18/[25][24]	0.5/[9.3][43]

The numbers in superscripts denote the literature reference listed in the reference section of this paper.

TATP, sodium perchlorate, and urea. The internal standard ETN was used for RDX, PETN, NG, HMX, and tetryl because in the presence of DCM in APCI source they similarly form ion-chlorinated adducts. Internal standards were used to increase precision and robustness of the methods and to suppress matrix effects. The list of internal standards and ions used for their detection, as well as mass spectrometer settings, are shown in Table 1.

Quantitation

Quantitation was accomplished via calibration with external standards, where the instrument response for a given concentration of a particular analyte was determined to be a function of the ratio of the peak areas of the analyte and internal standard. The ratio of the peak area for the analyte to that of the internal standard for each compound was plotted against the concentration of the standards. A seven-point linear regression fit, with an equal weighting for each concentration, was used to determine the slope and intercept of the calibration curve (See Supplemental Information). This was automated using the Analyst 1.5.1 software. A summary of the slopes, intercepts, and coefficient of determination for calibration curve R^2, linear calibration ranges, precision and percent accuracy for each analyte is presented in Table 2. As shown, the linear regression coefficient is above $R^2 > 0.99$ for all analytes, demonstrating excellent correlation between analyte's concentration and instrument response. The linear ranges vary between 0.5 ng/mL and 200 ng/mL for UN to 0.005 ng/mL to 10 ng/mL for PETN and RDX. Percent accuracy was determined by analyzing control samples with a known gravimetric concentration. In most cases,

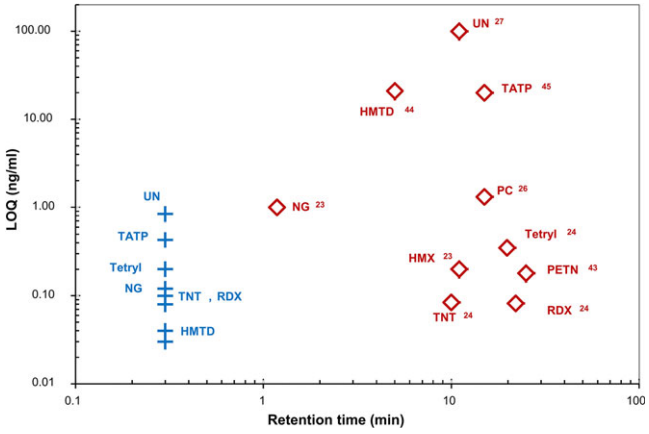

FIG. 6—*LOQ and analysis times of the FIA SPCI/ESI MSMS methods (blue) for explosives detection compared with the EPA and published methods (red). The numbers in superscripts denote the literature reference listed in the reference section of this paper.*

the methods demonstrated a good percent accuracy between 96 and 105% except UN with 117%. We attributed that to a different stock solutions of UN used for standards and control samples preparation; therefore, a minor gravimetric error may have caused that discrepancy. Inter-day %CV was calculated as a relative standard deviation between six replicate measurements of the control samples. Intra-day % CV is a relative standard deviation between

TABLE 2—*Calibration curve summary for the 10 explosives reported.*

Analyte	Linear Range (ng/mL)	Slope	Intercept	R^2	% Accuracy	Inter-day %CV $n = 6$	Intra-day %CV $n = x$	Number of Experiments (x)
UN	0.5–195	0.0196	0.0546	0.9939	117.50	2.03	3.61	7
PC	0.02–20	0.1909	0.0762	0.9950	98.62	6.03	21.66	10
TATP	0.1–200	0.0036	0.0137	0.9994	105.09	0.92	11.72	6
HMTD	0.02–100	0.7341	0.0557	0.9971	102.32	3.82	4.90	14
TNT	0.05–100	0.3135	0.0077	0.9985	96.45	3.38	7.12	11
RDX	0.001–10	0.7571	0.0028	0.9904	101.28	1.74	8.53	17
PETN	0.001–10	2.9500	0.0020	0.9956	95.68	2.09	7.14	19
NG	0.02–100	0.7285	0.0107	0.9968	105.25	1.94	3.95	6
HMX	0.1–100	0.9632	0.0643	0.9967	96.26	2.89	8.33	9
Tetryl	0.1–100	0.2366	0.0274	0.9963	104.11	4.29	9.69	8

the concentrations measurements performed on different days. The FIA APCI/ESI MSMS analysis showed excellent precision with a highest inter-day at 6% and intra-day precision at 22% for PC.

Sensitivity

According to Mol et al., (48) the sensitivity of the FIA method is strongly dependent on the analyte's peak shape, which in turn depends on the capillary internal diameter, length, and the flow rate of the solvent. In this work, the highest sensitivity was achieved with the 0.13 mm internal diameter capillary of ~1 m length between the autosampler and the ionization source of the mass spectrometer, flow solvent delivery rate was set at 350 μL/min. The sensitivity of the FIA APCI/ESI methods was evaluated as limits of quantitation (LOQ). Nominal LOQs were defined as 10 times the standard deviation at the minimum detectable concentration level (49). Table 3 presents an LOQ of the FIA APCI/ESI MSMS methods compared to the EPA and other published methods. The retention time shown for each LOQ determination does not include the time for injection and needle wash. The total analysis time for FIA APCI/ESI MSMS was under 2 min. The numbers in superscripts denotes the literature reference listed in the reference section of this paper.

As shown in Table 3 and Fig. 6, FIA ESI/APCI MSMS provides quick and sensitive detection for most analytes compared to the EPA (used for environmental monitoring) or other methods published in the literature. For example, detection of UN as an uronium ion adduct to 18C6 ether by FIA ESI MSMS is 25 times more sensitive than the HPLC-UV-Fluorescence detection (27) and 17 times faster. FIA ESI MSMS method for the detection of potassium chlorate is 16 times more sensitive than EPA IC method and 1000 times faster. Detection of TATP as a fragment ion $C_3H_7O_3^+$ is 200 times more sensitive than APCI MS detection of TATP-Ammonium adduct (51) and since no separation required the proposed method is 36 times faster. Compared to the lowest LOQ reported, the FIA APCI MSMS methods are 13 times more sensitive for PETN, 8 times more sensitive for NG detection, and 2.5 times more sensitive for HMX detection. The GCMS technique used in EPA Method 529 is 20% more sensitive for TNT, RDX, and tetryl detection; however, the retention time for the analytes is 30–80 times longer than the FIA ESI/APCI MSMS methods.

Conclusion

FIA APCI/ESI MSMS methods for explosives detection are fast, sensitive, and selective. In terms of sensitivity, it is on par or better than EPA or other published methods. Figure 6 represents a comparison between the most sensitive explosives detections reported by EPA and other published methods and the results of the FIA APCI/ESI MSMS, where *y*-axes are LOQ of the methods and *x*-axes are retention times of the analytes.

Detection by a triple quad provides two-dimensional separations, thus shortening analysis time to under a minute without the need for the column separation of the analytes. With internal standard and external standards calibration curves, FIA APCI/ESI MSMS provides quantitation, which in turn with proper validation produces reliable measurement to be presented in the court of law. FIA MSMS analysis will provide data that are both quantitative and qualitative for reliable identification of explosive compounds, more rapid than existing methods to allow for processing large sample sets for applications such as crime scene or soil mapping, and is suitable for the detection of many explosives, both conventional and homemade, on a single instrument to minimize capital costs and laboratory space requirements.

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Supporting Information

Additional supporting information may be found online in the Supporting Information section at the end of the article:

Table S1. FIA APCI/ESI MSMS explosives detection. MRM transitions and optimized MS parameters for secondary MRM transition used to reduce false positive detection.

Figure S1. APCI MSMS spectrum of the 0.4 ng of explosives mix showing 2,6-dinitrotoluene and 4,6- dinitrotoluene at *m/z* of 182, 2-amino-4, 6-dinitrotoluene and 4-amino-2, 6-dinitrotoluene at *m/z* 197, 1,3, 5-trinitrobenzene at *m/z* 213, TNT at *m/z* 227, Tetryl at *m/z* 242, RDX at *m/z* 268, PETN at *m/z* 315, HMX at *m/z* 342.

Figure S2. urea nitrate calibration curve. Error bars represent 1 standard deviation between 42 measurements at each concentration level.

Figure S3. potassium chlorate calibration curve. Error bars represent 1 standard deviation between 60 measurements at each concentration level.

Figure S4. TATP calibration curve. Error bars represent 1 standard deviation between 36 measurements at each concentration level.

Figure S5. HMTD calibration curve. Error bars represent 1 standard deviation between 84 measurements at each concentration level.

Figure S6. TNT calibration curve. Error bars represent 1 standard deviation between 66 measurements at each concentration level.

Figure S7. RDX calibration curve. Error bars represent 1 standard deviation between 102 measurements at each concentration level.

Figure S8. PETN calibration curve. Error bars represent 1 standard deviation between 114 measurements at each concentration level.

Figure S9. NG calibration curve. Error bars represent 1 standard deviation between 36 measurements at each concentration level.

Figure S10. HMX calibration curve. Error bars represent 1 standard deviation between 54 measurements at each concentration level.

Figure S11. Tetryl calibration curve. Error bars represent 1 standard deviation between 48 measurements at each concentration level.