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Analysis of nitrogen-based explosives with desorption atmospheric pressure photoionization-mass spectrometry

Short title: Analysis of explosives by DAPPI-MS

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Abstract

RATIONALE

Fast methods that allow the *in situ* analysis of explosives from a variety of surfaces are needed in crime scene investigation and home-land security. Here, the feasibility of ambient mass spectrometry technique desorption atmospheric pressure photoionization (DAPPI) in the analysis of the most common nitrogen-based explosives is studied.

METHODS

DAPPI and desorption electrospray ionization (DESI) were compared in the direct analysis of trinitrotoluene (TNT), trinitrophenol (picric acid), octogen (HMX), cyclonite (RDX), pentaerythritol tetranitrate (PETN), and nitroglycerin (NG). Effect of different additives in the DAPPI dopant and in DESI spray solvent on the ionization efficiency was tested, as well as the suitability of DAPPI to detect explosives from a variety of surfaces.

RESULTS

The analytes showed ions only in negative ion mode. With negative DAPPI, TNT and picric acid formed deprotonated molecules with all dopant systems, while RDX, HMX, PETN and NG were ionized by adduct formation. The formation of adducts was enhanced by addition of chloroform, formic acid, acetic acid or nitric acid to the DAPPI dopant. DAPPI was more sensitive than DESI for TNT, while DESI was more sensitive for HMX and picric acid.

CONCLUSIONS

DAPPI could become an important method for the direct analysis of nitroaromatics from a variety of surfaces. For compounds that are thermally labile, or that have very low vapor pressure, however, DESI is better suited.

Introduction

Efficient analytical methods for detection of explosives are increasingly needed in crime scene investigations, homeland security and environmental analysis.[1,2] Due to the obvious threat that explosives pose to people, speed, sensitivity and reliability are often of the essence when developing the methods of analysis. Mass spectrometry (MS) has the advantage of being able to give specific information about the identity of the analytes. Traditionally, MS analysis of explosives is performed by GC- or LC-MS.[1] GC-MS is amenable only to explosives that are thermostable, whereas LC-MS can be used also for compounds that have low vapor pressures or are thermally labile. However, both GC- and LC-MS require the explosive traces to be manually sampled from the contaminated surface by wiping or extraction, which slows down the analysis process, and increases the possibility of error or contamination of the samples.

Recently, new mass spectrometric (MS) technology that is especially suitable for forensic surface analysis has emerged, namely ambient MS techniques.[3–5] The first two techniques to emerge were desorption electrospray ionization (DESI),[6] and direct analysis in real time (DART),[7] in 2004 and 2005, respectively. In ambient ionization techniques the sampling and ionization take place outside the mass spectrometer, directly from the sample surface. This means that also samples of unconventional size and form can be analyzed without time-consuming sample preparation steps. Ambient MS techniques are especially useful in high-throughput qualitative analyses due to their high speed and high tolerance of impurities. Even in the case of complex samples the analyses are usually performed practically without any sample preparation, which shortens the analysis time further. In the analysis of explosives, ambient MS techniques have a significant advantage, since they can be used for the *in situ* analysis of explosives directly from the contaminated surface, without the need to extract and enrich the analytes from the surface. Ambient MS techniques can also be used with portable MS instruments, as has been done with DESI,[8] which allows the analysis of explosives at e.g. airports or environmental sites, where levels of explosives have to be monitored from soil. A number of reports exist on the application of DESI, DART and other ambient MS techniques, such as dielectric barrier discharge and low temperature plasma (LTP), to the analysis of explosives.[7–17] DESI is thus far the most extensively studied technique, and it has been applied to the analysis of nitroaromatic and nitroamine explosives from a number of surfaces, such as paper, plastic, metal, skin, glass, and clothing.[8–11,13,18,19]

DAPPI is an ambient ionization technique, which has been shown to detect efficiently both polar and non-polar compounds, and therefore it broadens the group of compounds that can be analyzed by direct ionization techniques towards compounds of lower polarity.[20] In DAPPI, the sample is thermally desorbed from the sample surface using hot solvent vapor, after which the analytes are ionized in the gas-phase by photon-initiated gas-phase reactions, similar to those in APPI.[21,22] In comparison with DESI, the sensitivity of DAPPI has been (at least) on the same level when analyzing polar analytes, and better when analyzing neutral or non-polar analytes.[20,23,24] DAPPI is also less susceptible to biological matrices than DESI.[25] In comparison with DART, DAPPI was more sensitive and showed lower background.[26] Thus far, DAPPI has been shown to be suitable for the analysis of illicit drugs from tablet, plant, resin, powder and paper,[27–30] pharmaceuticals from tablets and urine,[20,25,26] polyaromatic hydrocarbons and pesticides from environmental and food matrices,[24,31,32] vitamins, steroids and other lipids [23,26,32,33], atmospheric aerosols from filter [34] and insect defense chemicals.[35] Despite the wide range of applications with DAPPI and the obvious interest in fast, direct methods for the analysis of explosives, this area has not been explored. The aim of this study was to test the feasibility of DAPPI in the analysis of the most common nitroaromatic, nitroamine and nitroester explosives from various surfaces, and to compare DAPPI to DESI, which is the most popular ambient MS technique in the direct analysis of explosives.

Experimental

Chemicals and samples

2,4,6-Trinitrophenol (picric acid) and acetone were purchased from Merck KGaA (Darmstadt, Germany), toluene, chloroform (VWR International S.A.S., Fountenay sous Bois, France) and formic acid were from Sigma-Aldrich (Steinheim, Germany), and methanol, acetic acid and nitric acid were from J.T.Baker (Deventer, the Netherlands). 2-Methyl-1,3,5-trinitrobenzene (trinitrotoluene, TNT), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (octogen, HMX), 1,3,5-trinitroperhydro-1,3,5-triazine (cyclonite, RDX), pentaerythritol tetranitrate (PETN) and 1,2,3-trinitroxypropane (nitroglycerin, NG) were obtained from the Finnish Defense Forces Technical Research Centre. All the explosives were weapons grade. Water was purified with a Millipore purification system (Millipore, Molsheim, France).

The standard samples were diluted to water/methanol (50/50 %) to final concentrations of 10-100 µM. For analysis with DAPPI 1-µL droplets were applied on polymethylmethacrylate

(PMMA, Vink Finland, Kerava, Finland) surface and the dried spots were analyzed as described previously.[20,31] For glass, metal, wood, bills, oil cloth and Mesoft wiping cloth (Mölnlycke Health Care AB, Göteborg, Sweden) the sample volume was 1-10 µL.

Mass Spectrometry

The explosives were analyzed using an Agilent 6300 Series ion trap mass spectrometer (Agilent, Santa Clara, CA, USA) in negative ion mode. For microchip-APPI (µAPPI), DAPPI and DESI experiments the spray shield of the MS was replaced by a capillary extension part (Agilent Technologies, Santa Clara, CA).

Heated nebulizer microchip

The fabrication process of the heated nebulizer microchip used to heat and deliver the DAPPI spray solvent and gas flow has been described thoroughly in previous papers and is therefore not discussed here.[36] This study used the multifunctional clamp described by Luosujärvi et al.[31] made of amorphous polyimide (TECASINT 2011, Ensinger GmbH, Nufringen, Germany) to connect the microchip to the gas line and the heater wires.

DAPPI setup and experimental parameters

A DAPPI housing, designed and built by Protoshop (Espoo, Finland) was attached to a Nanospray stand (Proxeon Biosystems A/S). The stage contained holders for mounting a lamp and the microchip, and 2 xyz-stages (Proxeon Biosystems A/S, Odense, Denmark) for moving the sample stage and the microchip. A krypton discharge vacuum ultraviolet (VUV) lamp (Heraeus Noblelight, Cambridge, UK) emitting 10.0 and 10.6 eV photons was used to initiate the ionizing reactions. The microchip was aligned parallel to the MS inlet, and the microchip nozzle was set at approx. 3 mm above the capillary extension. The spray angle was approx. 45°. The plume was aimed at the sample at approx. 2.5 mm distance from the tip of the capillary extension. The nebulizer gas (nitrogen) flow rate was adjusted to 220 mL/min using an Aalborg model GCF17 mass flow controller (Orangeburg, NY). The microchip heating power was set to 5 W using an adjustable DC power supply (Thurlby-Thandar Instruments Ltd, Huntingdon, UK) or an IPS-603 Iso-Tech programmable power supply (Northants, UK). Vaporized dopant was delivered through the heated nebulizer microchip at 10 µL/min flow rate using a syringe pump (KD Scientific, Holliston, MA or Cole Palmer, Vernon Hills, IL). The capillary voltage was set to +2000 V (TNT +1500), the skimmer plate to -20 V and the capillary exit to -80 V (NG -70 V). Nitrogen drying gas flow rate was 4 L/min and it was heated to 120 °C (PETN

and NG) or 140 °C (the rest of the compounds). A schematic of the DAPPI setup is provided in Figure S1 (Supporting material).

µAPPI experimental parameters

For optimization of the ion trap parameters 10-100 µM solutions of the analytes were delivered continuously at 10 µL/min flow rate using a syringe pump and ionized with µAPPI (see schematic in Figure S1, Supporting material). The same heated nebulizer microchip, VUV lamp and Aalborg mass flow controller were used as in the DAPPI experiments (see above). Nitrogen nebulizer gas was delivered through the gas line at 70 mL/min. A 2 W power was set to the nebulizer microchip by the IPS-603 Iso-Tech programmable power supply.

The DESI setup and experimental parameters

The DESI ion source consisted of a grounded solvent delivery line connected to a syringe pump and a coaxial line for delivering the nebulizer gas (nitrogen at 10 bar). The spray was directed at the sample spot using an impact angle of 45°. The collection angle was <10°. The distance between the sprayer tip and the surface was 1-2 mm and the distance between the sample spot and the MS inlet was 1-2 mm. The spray solvent was infused with a flow rate of 3 µL/min. The ion trap voltages used in DESI were optimized for the studied compounds using a commercial ESI (Agilent Technologies) source in continuous flow mode at 10 µL/min. The optimized parameters are shown in Table S1 in Supporting material.

Results and discussion

Six nitrogen-based explosives: [2-methyl-1,3,5-trinitrobenzene (trinitrotoluene, TNT), 2,4,6-trinitrophenol (picric acid), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (octogen, HMX), 1,3,5-trinitroperhydro-1,3,5-triazine (cyclonite, RDX), pentaerythritol tetranitrate (PETN) and 1,2,3-trinitroxypropane (nitroglycerin, NG) were chosen for the study (Figure 1). µAPPI and ESI were used to optimize the ion trap voltages for each compound, while typical DAPPI and DESI parameters were adopted from previous studies,[20,31] and their suitabilities for the compounds under study were briefly tested. For DAPPI and DESI analyses, 10-100 µM samples of the explosives in water/methanol (50/50%) were applied on PMMA surfaces, from which they were analyzed directly as described before.[6,20]

Ionization of the explosives in DAPPI

The studied analytes showed no signals in positive ion mode, and therefore all the experiments were performed in negative ion mode. First, commonly used DAPPI spray solvents toluene and acetone were tested as spray solvents. Only TNT showed intense negative ions with pure toluene and acetone, whereas for the rest of the compounds the ionization with pure dopants was poor. Since previous studies with ESI, APCI, APPI, DESI and DART have reported that ionization of nitroesters and nitroamines can be improved by formation of anionic adducts,[7–11,37–45] the addition of low concentrations of different additives to the dopant was tested. The studied additives were chloroform (0.5-5%), formic acid and acetic acid (0.005-0.05%), and nitric acid (50-200 µM) (Table S2 in Supporting material). Addition of ammonium acetate and ammonium chloride salts to the dopant was also experimented, but not explored further due to clogging of the nebulizer microchip. Acetone with additives gave higher signals than toluene and was therefore chosen for the rest of the study. Since the adducts are thermally unstable, the drying gas temperature was set to 120-140 °C, which is lower than conventionally used. Sufficient heat was, however, needed for the desorption of the analytes, and the heating power of the heated nebulizer microchip was set to 5 W, similarly to most previous studies.

TNT formed in all cases a deprotonated molecule ($[M-H]^-$) as has been reported before with ESI and APPI.[37,38,43,44] In addition, a fragment corresponding to $[M-NO]^-$ was observed at *m/z* 197. The ionization efficiency for TNT was high with all dopant systems, but the highest signal was achieved with acetone containing 5% $CHCl_3$ (Figure 2). Picric acid showed a deprotonated molecule ($[M-H]^-$) and a $[M-NO]^-$ fragment at *m/z* 199 with all solvents. The highest signal was achieved with acetone containing 100 µM HNO_3. Despite the high gas-phase acidity of picric acid (1267 kJ/mol)[46], the ionization efficiency for picric acid was an order of magnitude lower than e.g. for TNT.

RDX, HMX, PETN and NG formed ions mainly through adduct formation, even without additives in the dopant. Intense adducts that could be assigned with high probability included $[M+59]^-$, $[M+45]^-$, $[M+46]^-$, $[M+62]^-$, $[M+61]^-$, $[M+89]^-$ and $[M+32]^-$ corresponding to $[M+CH_3COO]^-$, $[M+CHOO]^-$, $[M+NO_2]^-$, $[M+NO_3]^-$, $[M+NO_3\text{-}H]^-$, $[M+CH_3COO+H_2CO]^-$ and $[M+O_2]^-$, respectively.[37] In addition, a number of unrecognized adducts, such as $[M+60]^-$, $[M+1]^-$, and $[M+77]^-$ were observed in a number of cases. Besides the adducts, minor ions corresponding to $[M-H]^-$ (PETN and RDX) or $M^{-\cdot}$ (NG) were shown. It has been reported that

trace amounts of anions, such as acetate, formate and chloride are present in solvents and glassware as impurities, and can contribute to the analyte signals.[37,41] NO_2^- and NO_3^- ions could also have been formed by decomposition of the analytes, as has been reported before for RDX, HMX, PETN and NG (ions of type $[M+NO_3]$- and $[M+NO_2]$-) in APCI.[41,47] However, deliberately added volatile additives in the acetone dopant directed the route of ionization towards one route only: the formation of adduct ions with the additive, which resulted in cleaner spectra and significantly improved sensitivity (Figures 2 and 3). An especially good additive was nitric acid (100 µM), which gave the best ionization efficiency for RDX, HMX and PETN. Since nitric acid gave high signals also for TNP and NG, it would be a good candidate for field screening applications, where broad coverage of explosives is required. The main ions observed in DAPPI with the optimum solvent systems are listed in Table 1.

Product ion spectra of the most intense ions in the optimized dopant systems were collected in MS/MS mode (Table 1). For TNT and picric acid the main product ions were formed due to loss of NO (*m/z* 196 and 198, respectively), in addition TNT showed intense ions at *m/z* 210 (loss of O) and *m/z* 183, and picric acid an intense ion at *m/z* 182 (loss of NO_2). Previous reports of TNT MS^2 products in APCI and LTP report major product ions at *m/z* 210, 197 (loss of NO from $M^{-\cdot}$), and in DESI also at *m/z* 183.[10,16,39] The major product ion in the MS^2 spectra of RDX, PETN and NG was the NO_3^- ion at *m/z* 62; for PETN and NG it was also the only product ion. For HMX, also product ions at *m/z* 147 and 221 were observed, and for RDX an ion at *m/z* 283 (loss of H). The NO_3^- ion has also been reported as a product ion in APCI-MS/MS spectra of PETN and NG.[39] In ESI, the ion at *m/z* 62 was observed in the MS spectra of nitroesters, but not in the MS^2 spectra,[42], and this was explained to be due to the low-mass cut-off of the instrument. Here, the fragmentation cut-off of the ion trap was manually set to *m/z* 50, to allow monitoring of low mass ions in case of RDX, HMX, PETN and NG. The ion at *m/z* 62 was formed with high efficiency, and would thus be a good product ion candidate for MRM transitions.

Ionization of the explosives in DESI

Similarly to DAPPI, all the analytes were successfully ionized in negative ion DESI. Spray solvents with additives that previously have been reported to function well in the analysis of explosives in DESI[9–11] were experimented: 1) water/MeOH (50/50%) without additives, and with 2) 1 or 3) 10 mM NaCl, 4) 0.05% HCl, and 5) 0.05% trifluoroacetic acid (TFA). Somewhat similar signal intensities for all the ions were achieved with pure water/methanol (50/50%) and

with HCl and NaCl additives (results not shown). TNT and picric acid gave $[M-H]^-$ ions similarly to DAPPI, while RDX, HMX, PETN and NG showed adduct ions (mainly $[M+Cl]^-$ and $[M+NO_3]^-$). Representative DESI spectra of the explosives are shown in Figure S2 of Supporting Material. The presence of TFA (0.05%) completely suppressed the ionization of the analytes, and only TFA-derived ions (*m/z* 113 and 227) were observed, unlike in previous DESI reports,[9,11] where dilute concentration of TFA (0.05%) in the spray solvent has been reported to lead to formation of intense TFA adduct ions.

Comparison of DAPPI and DESI

To roughly compare the sensitivities of DESI and DAPPI towards the explosives, the LODs for the studied compounds were estimated. This was done by extrapolating the instrument-derived signal-to-noise (S/N) ratios obtained for the 10-100 pmol samples to concentration values corresponding to S/N=3. For both techniques, the extrapolated LODs were approx. in the range of 10-300 pg (approx. 40-1400 fmol; Table 2). DAPPI was more sensitive towards TNT, while DESI was more sensitive towards picric acid and HMX. For the rest of the compounds the LODs with DAPPI and DESI were in the same order of magnitude. The low sensitivity of DAPPI towards HMX could be due to the very low vapor pressure of HMX (3.01×10^{-15}, Table 2). In DAPPI, thermal desorption is used to desorb the analytes from the surface, and compounds with low vapor pressure are not efficiently desorbed by the heat. DESI, on the other hand, can desorb the compounds by droplet-mediated processes.[48] Figure S3 (Supporting material) shows the extracted ion chromatograms (XIC) for measurements of HMX and RDX in DAPPI, and HMX in DESI. For RDX in DAPPI and HMX in DESI, four sample spots were analyzed, and their analyses result in formation of clear ion peaks, indicating efficient desorption from the surface. For HMX in DAPPI, three sample spots were analyzed, and a steady, long-lasting signal of the ion was formed, resulting from the inefficient thermal desorption of HMX. HMX has also been reported to be thermally unstable,[49] and therefore its low signal in DAPPI may also partly be explained by the high temperature used for the desorption. A similar long-lasting signal was also observed for picric acid (results not shown), indicating that also picric acid is poorly desorbed from the surface in DAPPI. The vapor pressure of picric acid has been reported to be considerably higher (7.48×10^{-7}) than for HMX, and therefore it does not explain the phenomenon. In GC, picric acid has been reported to adsorb strongly on polar surfaces (e.g. the GC column), which causes serious peak tailing and prevents its analysis by GC.[50] Therefore, we suggest that also here picric acid is strongly

adsorbed on the sampling surface and/or surfaces of the MS inlet, which leads to poor desorption efficiency. In DESI, picric acid is efficiently desorbed from the surface by the droplet-mediated process, after which picric acid is efficiently ionized due to its high acidity. For TNT, however, DAPPI was found more sensitive than DESI, due to efficient desorption and ionization processes in DAPPI. Also previous reports using APPI have shown high sensitivity towards TNT.[43,44]

Feasibility of DAPPI in the analysis of explosives from a variety of surfaces

In real life, it may be necessary to detect explosives from a wide variety of surfaces, and therefore the feasibility of DAPPI to detect explosives from different types of surfaces besides PMMA was tested. Compounds of the study were applied on typical materials that could be found on crime scenes or explosion sites (glass, metal, wood, bills), or could be used by criminal investigators to collect traces of explosives from the same sites (oil cloth and Mesoft wiping cloth). The spiked materials were then analyzed by DAPPI similarly as above. The sensitivity of analysis was shown to depend on the nature of the material: smaller amounts of sample could be detected from a smooth, even surface, such as glass, while more porous surfaces, such as metal and especially wood required larger amounts of material for detection (Figure 4 and Figure S4). Intense signals were also obtained from the Mesoft wiping cloth (Figure S4 in Supporting material), which therefore could be feasible for collecting samples from the surfaces of a crime scene, or even the skin of a suspect, after which the cloth could be brought to the forensic laboratory for analysis by DAPPI

Conclusions

DAPPI was shown to ionize most of the nitroaromatic, nitroamine and nitroester explosives with high efficiency. The ionization of nitroamines and nitroesters took place by adduct formation and was significantly improved by addition of dilute salts to the dopant. The poor signal for HMX is suggested to be due to its low vapor pressure, which prevents its thermal desorption in the DAPPI process. Picric acid, on the other hand, was suspected to adsorb too strongly on the sampling surface. For HMX and picric acid DESI was therefore found to be a better suited technique, although the sensitivity of DESI and DAPPI for the rest of the compounds was at the same level. Analyses of explosives from a variety of surfaces show that DAPPI is a promising technique for the *in situ* analysis of explosives, especially for neutral nitroaromatics. Connection of DAPPI to rugged portable mass spectrometers[51,52] as has

already been done with DESI and some other ambient MS methods, may allow the direct analysis of explosives on crime scenes or in homeland security applications.

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Figure captions

Figure 1. Structures of the studied analytes.

Figure 2. Signal-to-noise ratios (average of 4 measurements) of the main ions of the studied explosives with acetone dopant and different additives. For TNT and picric acid the main ion in all cases was $[M-H]^-$.

Figure 3. DAPPI spectra of the studied explosives using the optimum dopants. The dopant was acetone + $CHCl_3$ (5%) for TNT and NG, and acetone + HNO_3 (100 µM) for the rest of the compounds. The amount analyzed per compound was 100 pmol.

Figure 4. DAPPI analysis of 100 pmol and 1 nmol of PETN from glass and wood surfaces, respectively. The dopant was acetone + HNO_3 (100 µM) at 10 µl/min.

Tables

Table 1. The main analyte ions observed in full scan and MS/MS modes in DAPPI using 100 µM concentrations and the optimum solvents.

Compound	**Optimum solvent**	**Main ion (*m/z*)**	**Identity**	**MS^2 products**	**MS^2 amplitude (V)**
TNT	acetone + $CHCl_3$ (5%)	226	$[M-H]^-$	196, 210, 183	0.85
TNP	acetone + HNO_3 (100 µM)	228	$[M-H]^-$	198, 210, 182, 183	1.10
RDX	acetone + HNO_3 (100 µM)	284	$[M+NO_3]^-$	62, 283	0.95
HMX	acetone + HNO_3 (100 µM)	358	$[M+NO_3]^-$	147, 62, 220	1.05
PETN	acetone + HNO_3 (100 µM)	378	$[M+NO_3]^-$	62	1.00
NG	acetone + HNO_3 (100 µM)	289	$[M+NO_3]^-$	62	0.85

Table 2. Vapor pressures and extrapolated LODs for the studied explosives in DAPPI and DESI.

Compound	Vapor pressure (at 25 °C/Torr)[a]	DAPPI		DESI	
		Ion	LOD[b] (pg)	Ion	LOD[b] (pg)
TNT	$5.50 \rangle 10^{-6}$	$[M-H]^-$	43	$[M-H]^-$	310
picric acid	$7.48 \rangle 10^{-7}$	$[M-H]^-$	160	$[M-H]^-$	9.3
RDX	$3.30 \rangle 10^{-9}$	$[M+NO_3]^-$	17	$[M+Cl]^-$	38
HMX	$3.01 \rangle 10^{-15}$	$[M+NO_3]^-$	280	$[M+Cl]^-$	37
PETN	$1.16 \rangle 10^{-8}$	$[M+NO_3]^-$	37	$[M+Cl]^-$	71
NG	$4.81 \rangle 10^{-4}$	$[M+Cl]^-$	180	$[M+NO_3]^-$	160

[a] according to [53]

[b] extrapolated to S/N = 3 from the S/N for 10-100 µM sample concentrations.

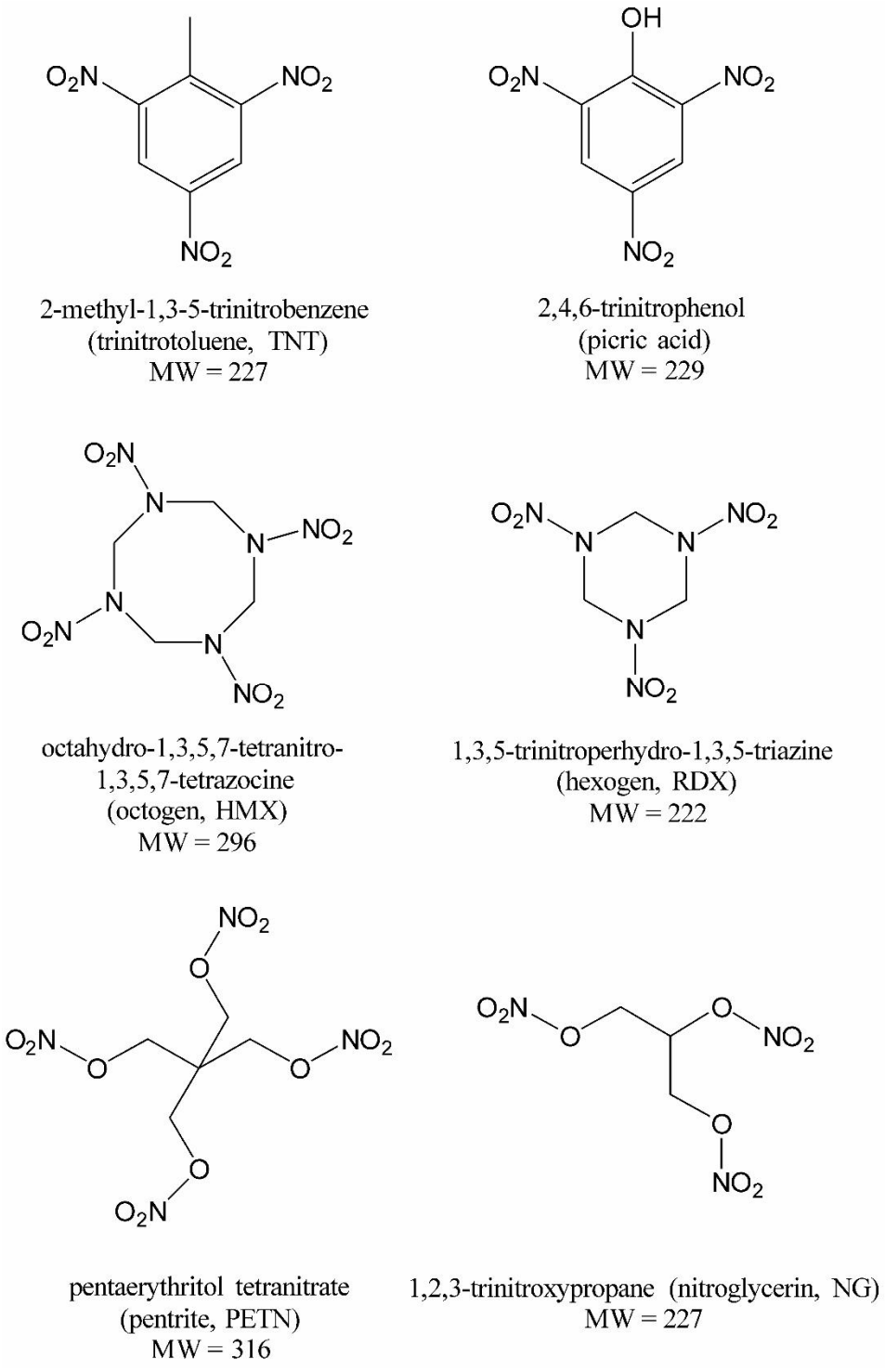
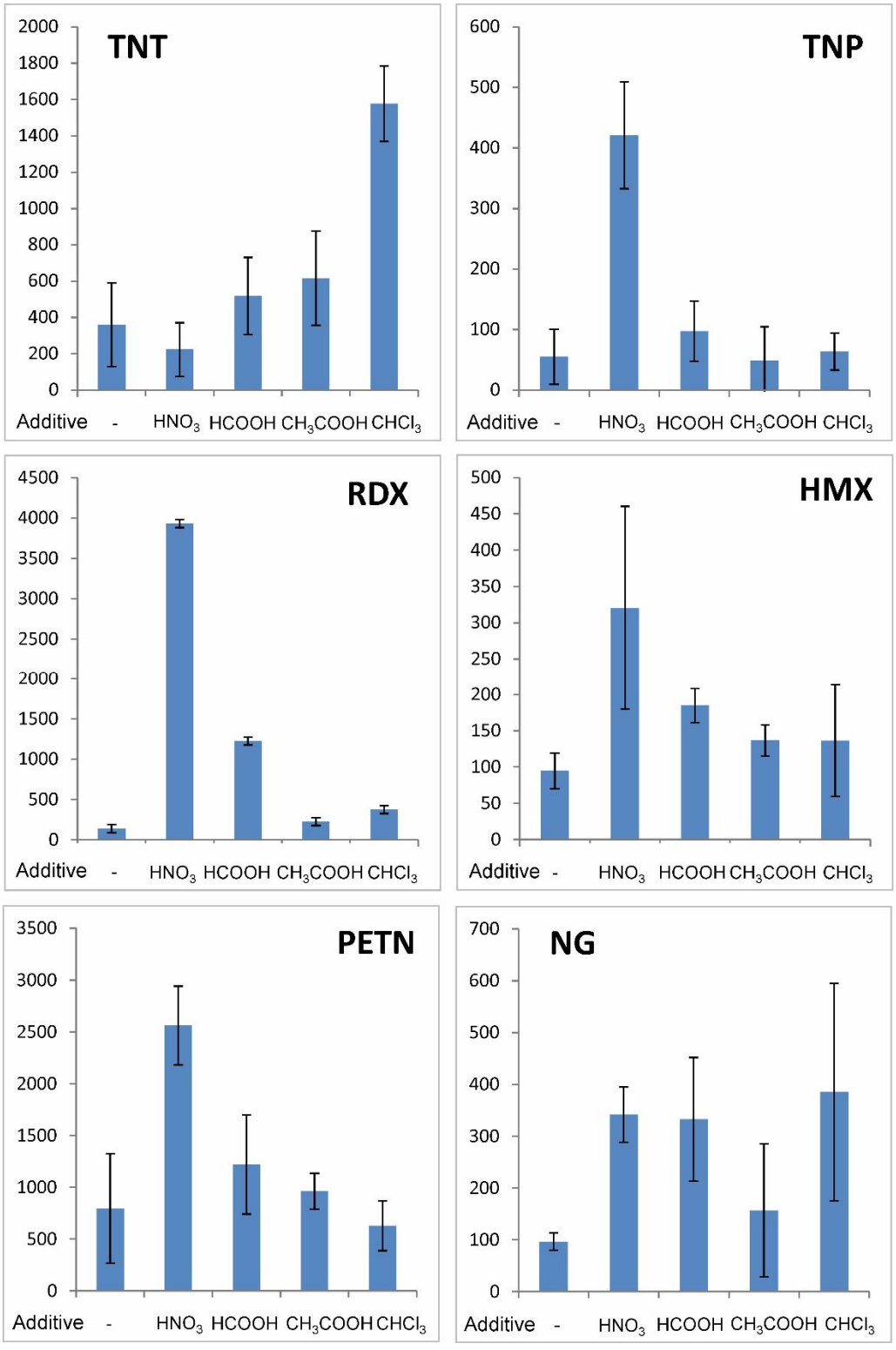


Figure 1. Structures of the studied analytes.



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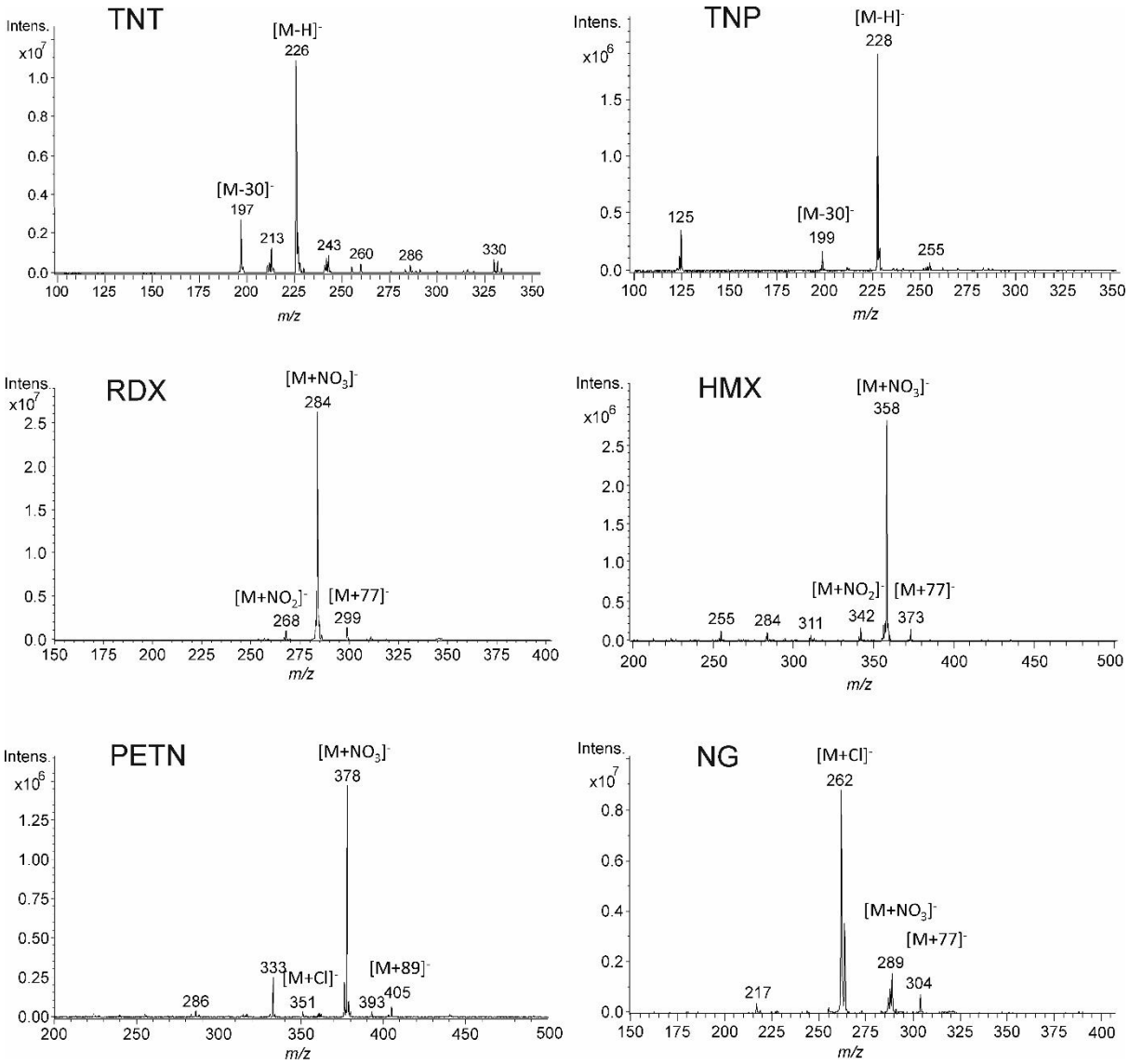

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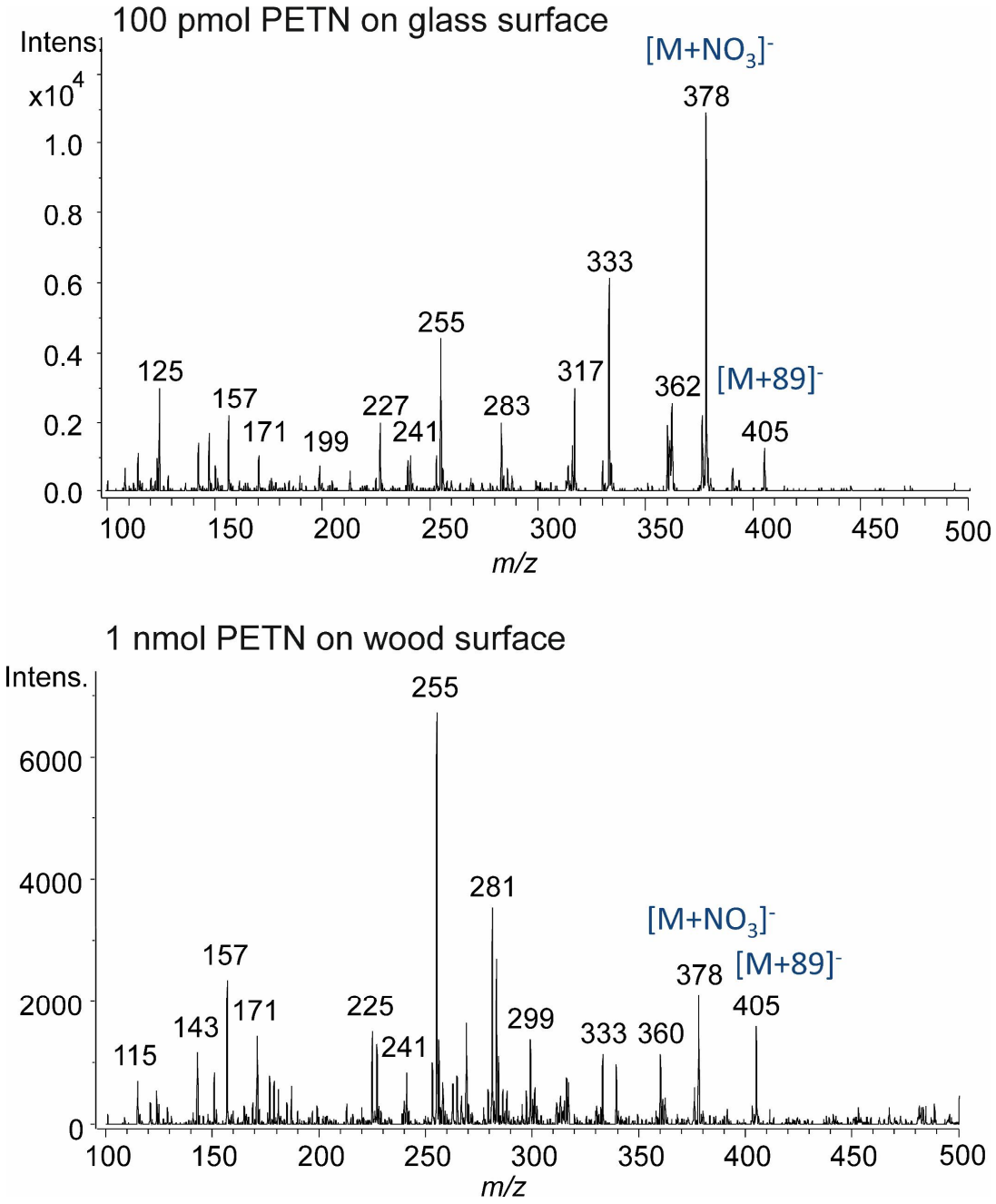

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