Handheld Portable DAPCI Ion Source for *in-situ* Analysis of Nitroaromatic Explosives

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Keywords: in-situ mass spectrometry; field analysis; portable instrument; ambient ionization; explosives analysis; real time analysis; desorption atmospheric pressure chemical ionization

Abstract

A novel, lightweight (0.6 kg), solvent and gas-cylinder free, handheld ion source based on desorption atmospheric pressure chemical ionization (DAPCI) has been developed and deployed for the analysis of nitroaromatic explosives on surfaces in open air, offering portability for in-field analysis. A small, inexpensive, rechargeable lithium polymer battery was used to power the custom-designed circuitry within the device, which generates up to ±5 kV dc voltage to ignite a corona discharge plasma in air for up to 12 hours of continuous operation, and allowing positive and negative ion MS. The generated plasma is pneumatically transported to the surface to be interrogated by ambient air at a rate of 1 - 3.5 L/min, compressed using a small on-board diaphragm pump. The plasma source allows liquid or solid samples to be examined almost instantaneously without any sample preparation in the open environment. Advantages of low carrier gas and low power consumption (< 6 W), as well as zero solvent usage have aided in developing the field-ready, handheld device for trigger-based, "near real-time" sampling/ionization. Individual nitroaromatic explosives (such as 2, 4, 6-trinitrotoluene (TNT)) can easily be detected in amounts as low as 5.8 pg with a linear dynamic range of at least 10 (10 to 100 pg), a relative standard deviation (RSD) of ca. 7% and an R^2 value of 0.9986. Direct detection of several nitroaromatic compounds in a complex mixture without prior sample preparation is demonstrated and their identities were confirmed by tandem mass spectrometry fragmentation patterns.

Introduction

Increases in terrorism and security threats around the world necessitate the development of highly sensitive and chemically specific analytical techniques capable of detecting extremely low vapor pressure explosives *in situ* at the source. These analytical tools should be capable of high throughput analysis in "near real time"; however, such methods are not currently available. Any method which can operate *in situ* providing near instantaneous analysis would have significant implications for homeland security, border control, transportation security, national defence, and forensic investigations[1]. Condensed phase explosives are difficult to ionize due to their wide range of volatilities while their presence on surfaces makes it difficult for direct analysis and detection. *In-situ* analysis of condensed phase explosives and their residues with low vapor pressure with little or no sample preparation is therefore highly desirable .[2,3]

Currently the most widely adopted technology for the trace analysis and detection of explosives at border and transport checkpoints is wipe sampling coupled with ion mobility spectrometry (IMS).[4-7] Ionization can be achieved using a number of atmospheric pressure ionization techniques such as corona discharge[8] and electrospray ionization (ESI)[9,10], which are well used by IMS. Although very high sensitivity, portability, instant detection and low detection limits can be achieved, poor peak capacity of IMS makes it prone to poor selectivity, nonlinear response and difficulties associated with identification and confirmation of analyte(s) in complex mixtures.[11-13]

Solid phase extraction (SPE)[2,14] followed by gas chromatography (GC) or liquid chromatography (LC) mass spectrometry (MS)[15,16] is the most widely adopted method for both qualitative and quantitative analysis of explosives. High sensitivity and specificity can be achieved using SPE-GC/LC-MS for explosives analysis.[17-20] With the aid of tandem mass spectrometry (MS/MS), higher selectivity and specificity of trace amounts of explosives in complex mixtures can be achieved.[21-23] Despite all these advantages a significant amount of time is required for sample pre-concentration and pre-treatment. Moreover, the sample must also be transported to the laboratory for analysis.

Recently, ambient ionization methodology [24,25] in conjunction with mass spectrometry has beed deployed for the trace analysis and detection of a wide range of explosives measured *in situ* at the site of interest.[26,27] Ambient ionization (AI) is a relatively new paradigm that facilitates both sampling and ionization of analyte(s) in their native environment in one step outside the mass spectrometer with little or no sample preparation.[28] AI-MS analysis can be performed directly on unmodified samples in air outside the vacuum system and is capable of providing nearly instantaneous data while minimizing sample preparation.[29-33]

AI-MS methods have shown extraordinary performance due to their simplified analysis procedures.[24,34-36] For instance, in the past 10 years desorption electrospray ionization (DESI),[37,38] direct analysis in real time (DART),[39-41] plasma-assisted desorption/ionization (PADI),[42] low temperature plasma (LTP),[43-45] desorption electro-flow focusing ionization (DEFFI)[27] and desorption atmospheric pressure chemical ionization (DAPCI)[41,46-48] have been exploited in the trace detection and analysis of a wide range of explosives. However, these AI sources are usually limited to the laboratory settings due to the bulky gas cylinders, high electrical power, and high gases/solvent flow rates required for operation. These requirements make size reduction difficult and often lead to an increase in setup time. For example, the DESI ion source requires a syringe pump to provide ~3 μL/min solvent feed and high pressure gas flows.[31,34] Desorption ionization sources based on photo ionization, such as desorption atmospheric pressure photoionization (DAPPI)[49] and Laser-based standoff systems[50,51], have the ability to perform rapid analysis of a wide range of analyte(s) including explosives from surfaces,[52] however, they are not amenable for in-field analysis due to lack of portability. Optical spectroscopy methods also exists for the detection of explosives but they often require concentrate samples, intense lasers, or enhancing functional surfaces[53,54]. As such there exists a need for small, handheld, portable ambient ionization sources that can be integrated with small footprint, portable mass spectrometers[55-57] for in field applications to interrogate different surfaces for the presence of explosives.

Plasma based AI sources are good candidates for portability due to their inherent lack of solvent and generated waste as well as the ability to change the discharge gas composition for improved desorption and ionization capability.[58] For example, low temperature plasma (LTP), a plasma AI source based on dielectric barrier glow discharge, has been successfully miniaturized and its performance demonstrated on both a commercial bench-top and on a miniature mass spectrometer.[59] Desorption atmospheric pressure chemical ionization (DAPCI) is another plasma-based AI source that is relatively underutilized. DAPCI is based on atmospheric pressure chemical ionization (APCI).[60] DAPCI has been successfully utilized in the analysis of complex molecules including melamine in powdered milk,[61] for the differentiation of variants of Chinese tea,[62] analysis of fuels and petroleum oil mixtures,[63] and analysis of alkylated benzenes and polycyclic aromatic hydrocarbons.[64] In a typical DAPCI experiment, a corona discharge is generated by applying a high DC voltage to a sharp needle and the gas-phase reagent ions produced are directed pneumatically towards a surface using a carrier gas (e.g. nitrogen, helium, argon). The analyte(s) is desorbed and ionized directly from the surface, presumably by a two-step mechanism involving thermal desorption followed by gas-phase ionization, through proton or electron transfer, electron capture or other ion molecule reactions under ambient conditions in open air.[38]

Herein, we describe the development of the first handheld DAPCI ion source and its application to the direct analysis of nitroaromatic explosives from surfaces in the open environment. The complete handheld DAPCI ion source, including the air pump, battery and electronic circuitry is enclosed in a 3D printed plastic enclosure. The handheld DAPCI is applied for “near real time” *in situ* detection and analysis of nitrobenzene explosives under ambient conditions without sample treatment and their chemical identity is confirmed using tandem mass spectrometry (MS/MS).[22,65] Results obtained from the handheld DAPCI experiments using a bench-top mass spectrometer show that the handheld DAPCI ion source can be used to detect model nitroaromatic explosive compounds (in the low pg range for TNT) from a paper surface (surface area <~1 cm^2). The sample preparation is limited to the dilution of the explosive standards in methanol/acetonitrile solvent (v/v, 1:1) to simulate different levels encountered in real scenarios.

Experimental Section

Chemicals and Reagents All analytical explosive standards of 2, 4, 6-trinitrotoluene (TNT), 1, 3, 5-trinitrobenzene, 2, 4-dinitrotoluene, 1, 3-dinitrobenzene, 2-amino-4, 6-dinitrotoluene and 2, 4, 6-trinitrophenylmethylnitramine (Tetryl) were purchased as 1 μg/mL solutions in methanol/acetonitrile (1:1) from AccuStandards Inc. (New Haven, CT). Explosive stock solution multicomponent mixture of 2, 4, 6-trinitrotoluene (TNT), 1, 3, 5-trinitrobenzene, 2, 4-dinitrotoluene, 1, 3-dinitrobenzene, 2-amino-4, 6-dinitrotoluene, 2, 4, 6-trinitrophenylmethylnitramine (Tetryl) (100 μg/mL each component) in methanol/acetonitrile (1:1) solution was also purchased from the same supplier. HPLC grade solvent (methanol and acetonitrile) was purchased from Mallinckrodt Baker Inc. (Phillipsburg, NJ). Working solutions of the samples (10-100 pg/μL) were made up in methanol and acetonitrile (1:1) to the target concentration using stepwise dilution.

Sample Preparation In all experiments the sample preparation step was limited to dilution of explosive stock solutions in methanol/acetonitrile (1:1) to the desired concentration. From each solution 1 μL was applied onto a cellulose filter paper (Whatman, Maidstone, UK Grade 1) (1 cm^2 total surface area) using a pipettor (Brand Gmbh, Germany). All samples were analyzed immediately in open air using the newly developed handheld, portable DAPCI device coupled to a commercial mass spectrometer.

Handheld DAPCI Ion Source A custom-designed handheld, DAPCI ion source was developed; it differs from the DAPCI ion source reported previously[60,63] in that it is battery powered, gas cylinder free and weighs less than 1 kg. It consists of a tapered tip stainless steel needle (80 mm long and 3.2 mm diameter tapered to a fine point) inserted coaxially into a Swagelok 1/8” Teflon tee piece with a custom designed ceramic exit nozzle attached to a grounded electrode. The stainless steel needle was connected via a barrel connector to the high voltage output module. A small diaphragm pump (Schwarzer Precision, 12FC35A) with a maximum flow rate of 6 L/min was used to generate and compress an air flux inside the handheld DAPCI device (see Figure 1 b for more details). The generated air is ionized by the corona discharge and pneumatically transported to the surface to desorb and ionize analyte(s) that may be present. The corona discharge is formed by applying a high voltage, typically ± 2.5 – 3kV, generated using a high voltage DC to DC converter (EMCO High Voltage, c50/c50N) to a tapered tip stainless steel needle powered using a lithium polymer battery (Tracer Power, 12 V, 4 Ah).

Figure 1 a shows the custom-designed high voltage control circuit used to generate the high voltage in the range of ±1 - 5 kV. The circuitry of the handheld DAPCI is powered from a 12 V, 4 Ah lithium Polymer battery with a built-in charging circuit and a power level indicator that displays when re-charging is necessary. From a fully charged state the battery can power the device for up to 12 hours of continuous use and for as much as 3-4 days when used intermittently. It should be noted that the total operation time of the handheld DAPCI ion source in the field is much longer, since the power supply is only triggered as needed and that the diaphragm pump may also be turned off while not in use. The high voltage regulated DC-to-DC converter module (EMCO HIGH VOLTAGE, c50/c50N, UK) and the diaphragm pump require a minimum 12V supply to operate correctly. Due to the battery discharge rate, it was necessary to include a buck-boost DC-to-DC converter to ensure precise voltage regulation. An ARM based microcontroller board (Teensy 3.1, PJRC, USA) handles all internal command communication and receives user inputs via a 2.4” touch screen interface (4D-Systems, 24PT-uLCD, UK). This enables the user to switch between ion polarities (positive or negative) and to regulate voltage in either positive or negative mode. The exact voltage applied to the needle and the flow rate of the compressed air exiting the diaphragm pump can also be regulated via the touch screen. The pump speed is controlled by digitally altering the duty cycle of the Pulse Width Modulated (PWM) signal that turns on the MOSFET driver for the diaphragm pump. A summary of the handheld DAPCI specification is given in Table S 1 (supporting information).

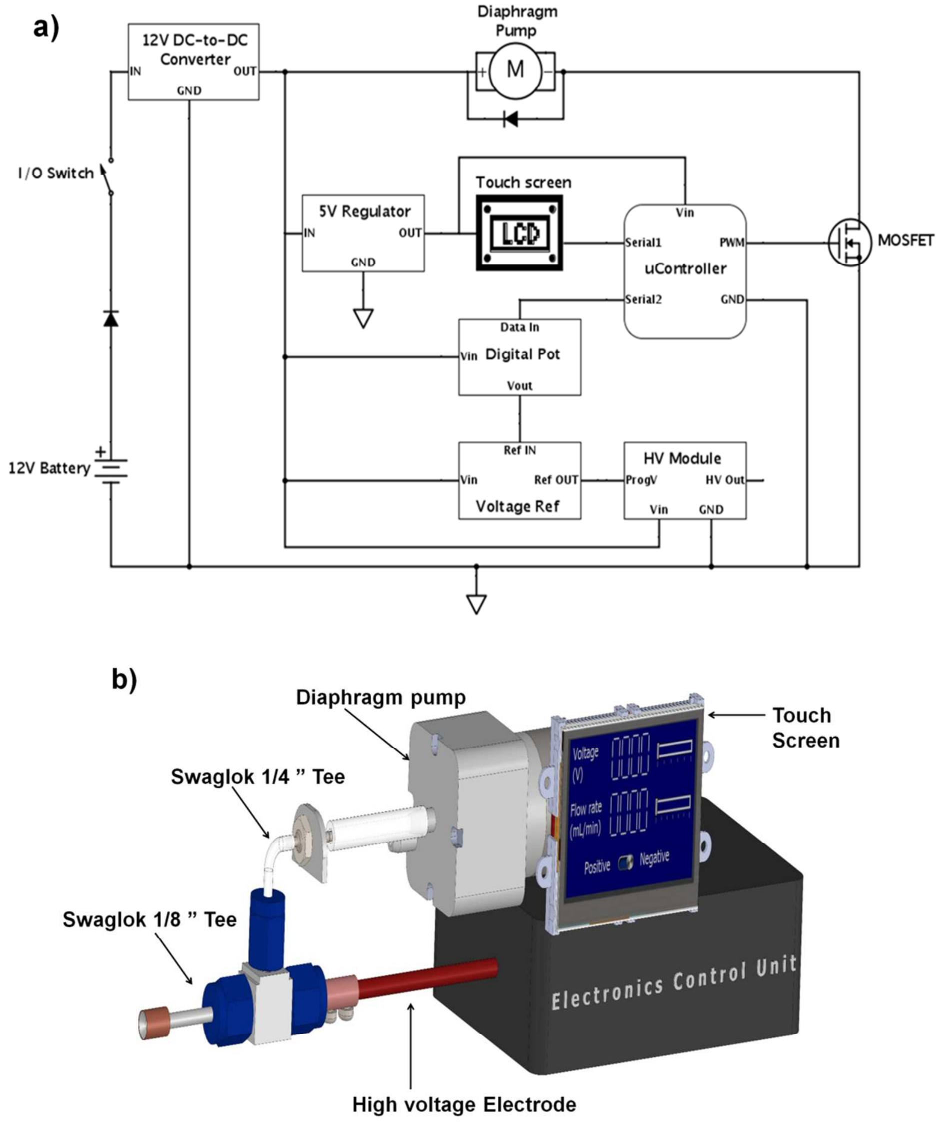

Figure 1. Handheld, desorption atmospheric pressure chemical ionization (DAPCI) source for direct analysis of explosives: a) circuit block diagram, b) CAD model of internal DAPCI components.

Handheld DAPCI Coupled to a Mass Spectrometer In a typical DAPCI MS experiment, a corona discharge is generated by applying a high DC voltage to a sharp needle and the reagent ions produced are directed pneumatically towards a surface using a carrier gas (e.g. air, nitrogen, helium).[38,63] The carrier gas is directed towards a substrate/surface at a rate of ~3 L/min to desorb and ionize analytes which may be present. The voltage applied to the electrode was typically ±~2.5 - 3 kV so as to produce a corona discharge in close proximity at the tip of the electrode. The handheld ion source is optimally coupled to the atmospheric pressure inlet of a commercial benchtop mass spectrometer placed at a distance of ~2.5 mm (Figure 2). The analyte(s) ions formed are transported to the mass spectrometer through the atmospheric pressure interface. The transport mechanisms for this action includes static charge accumulation on the insulating surface, momentum transfer from gaseous ion impact on the molecular species on the surface, and the suction of the vacuum at the inlet of the transfer capillary.

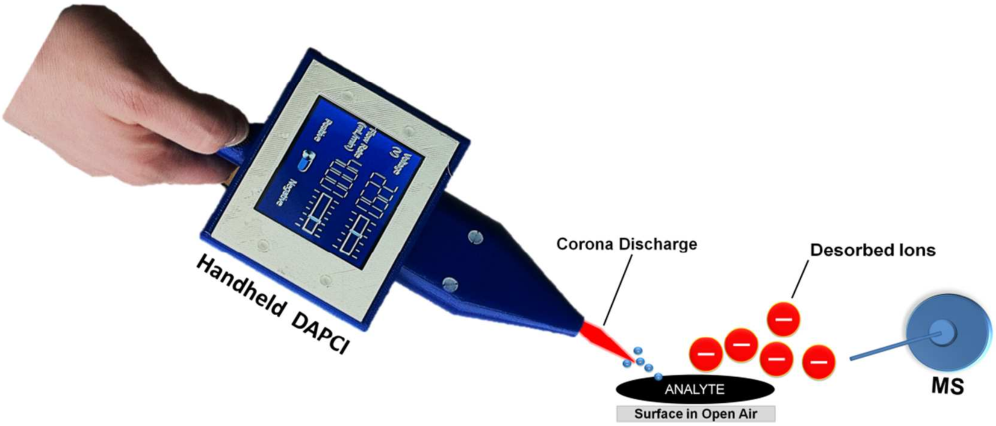

Figure 2. Schematic of the handheld DAPCI experimental setup used in the analysis of nitroaromatic explosives.

Experiments were conducted using a commercial linear ion trap (Thermo LTQ, San Jose, CA USA) mass spectrometer with an atmospheric pressure interface, tuned for optimum detection of the precursor ion of interest. Data processing was carried out using the commercial instrument software interface (Xcalibur, version 4.1). The experimental conditions for operation of the handheld DAPCI-MS for nitroaromatic explosives (2, 4, 6-trinitrotoluene (TNT), 1, 3, 5-trinitrobenzene, 2, 4-dinitrotoluene, 1, 3-dinitrobenzene,2-amino-4, 6-dinitrotoluene, 2, 4, 6-trinitrophenylmethylnitramine (Tetryl)) and the multi-component explosive mixture for analysis in the positive mode were as follows: ion source voltage applied to the tapered tip stainless steel needle of +3 kV; tube lens voltage, 200 V; heated capillary voltage, 25 V; capillary temperature, 200 ^{o}c; multipole rf amplitude ($V_{p\text{-}p}$), 400 V; multiplier voltages 1 and 2, -800 V; ion injection time, 100 ms and 3 microscans. For the analysis of the same standard model compounds and the multi-component explosive mixture in negative mode the conditions were as follows: handheld DAPCI ion source voltage applied to the tapered tip stainless steel needle of -2.5kV; tube lens voltage, -102 V; heated capillary voltage, -20 V; capillary temperature, 200 ^{o}c; multipole rf amplitude (V_{p-p}), 400 V; multiplier voltages 1 and 2, -800 V; ion injection time, 100 ms and 5 microscans. For all experiments in both positive and negative ion modes the instrument was set to record mass spectra in the automatic gain control mode for a maximum ion trap injection time of 100 ms. All mass spectra were recorded as peak profiles in an averaging time of 1 min and are presented with the background subtracted unless otherwise stated. For structural confirmation MS/MS was performed on the isolated molecular ion signals of interest using collision-induced dissociation (CID) to confirm the presence and identity of the analyte(s)[16]. These experiments were performed using an isolation window of 1.5 Thomson (Th. mass/charge units) and using normalized collision energy of 25-40% (manufacturer's unit). Mass and collisional energy calibration were carried out following the manufacturer's instructions.

Results and Discussion

Handheld DAPCI-MS Characterization The handheld DAPCI ion source was first characterized by recording the background mass spectrum of the corona discharge using air as the discharge gas generated using a small diaphragm pump in the open laboratory environment in both positive and negative ion modes (for more details see supporting information Figure S 1). The primary reagent ions from the handheld DAPCI source are protonated water clusters $[(H_2O)_nH]^+$, and anions (O_2^-, OH^-, NO_2^-). These ions facilitate analyte(s) ionization via proton transfer and electron capture reactions in positive and negative ion modes respectively.[66] The anions NO_2^-, O_2^-, CO_3^- are highly reactive species and can undergo a variety of ion molecule reactions including nucleophilic addition, proton abstraction, charge exchange, and oxidation. The dominant water cluster protonated ions are known as the "first hydrated shell" and are formed by the core ions H_3O^+ and OH^- becoming hydrated with water vapor in ambient air.

Analysis of Nitrobenzene Explosives in Air using the Handheld DAPCI in Negative Ion Mode When air is used as the handheld DAPCI carrier gas under the conditions in Figure S 1 b (supporting information); the ionization of oxygen gas in the presence of water clusters generates reactant anions as observed in Figure S 1 b at *m/z* 46, 32, and 60 (NO_2^-, O_2^-, CO_3^-) which readily react with the vapors of nitroaromatic explosives.[66,67] Such reactions are likely due to their high electron affinities (EA), a well-known feature of the nitro or nitrate functional groups present in most common explosive formulations.[68,69] This means that these analytes can readily form negative ions by electron capture.[70,71] This attribute of explosives has been previously exploited by other ambient ionization methods such as DESI,[27,72,73] LTP,[43,74] and DART.[75] Just as DESI, DART and LTP have been used in the negative ion mode to detect TNT at trace levels, so also the handheld DAPCI ion source was used in the negative ion mode to detect and record a mass spectrum of TNT in full MS mode, when 10 pg (absolute concentration) of TNT in methanol/acetonitrile was deposited onto a filter paper surface are of approximately 1 cm^2 (Figure 3).

The mass spectra recorded in the negative ion mode for both TNT (Mw 227) and 1,3,5-trinitrobenzene (TNB) (Mw 213) included both molecular radical cations and deprotonated by molecular anions, viz. $M^{-\cdot}$ and $[M-H]^-$ at *m/z* 227 and 213 for the former and *m/z* 226 and 212 for the latter, as displayed in Figure 3. The TNT molecular radical cation fragments with neutral loss of NO to give *m/z* 197 ($[TNT-NO]^-$) or OH to give *m/z* 210 ($[TNT-OH]^-$). These dissociations are confirmed by tandem mass spectrometry (insert (i) Figure 3). Note too that fragmentation is accompanied by evidence of ion-molecule reactions, e.g. oxidation of TNT to give $[M + O]^-$. It is important to note that the mass spectrum of TNT was similar to that previously observed in the negative ion mode using DESI[74] and LTP[43] but with increased fragmentation. Similarly, for TNB which gives in addition to the low intensity molecular anion at *m/z* 213 an intense deprotonated ion $[M-H]^-$ at *m/z* 212. The molecular radical cation fragments by loss of OH at *m/z* 196 $[TNB\text{-}OH]^-$ and NO at *m/z* 183 $[TNB\text{-}NO]^-$ is confirmed by CID MS/MS data (Insert (ii) Figure 3 b).

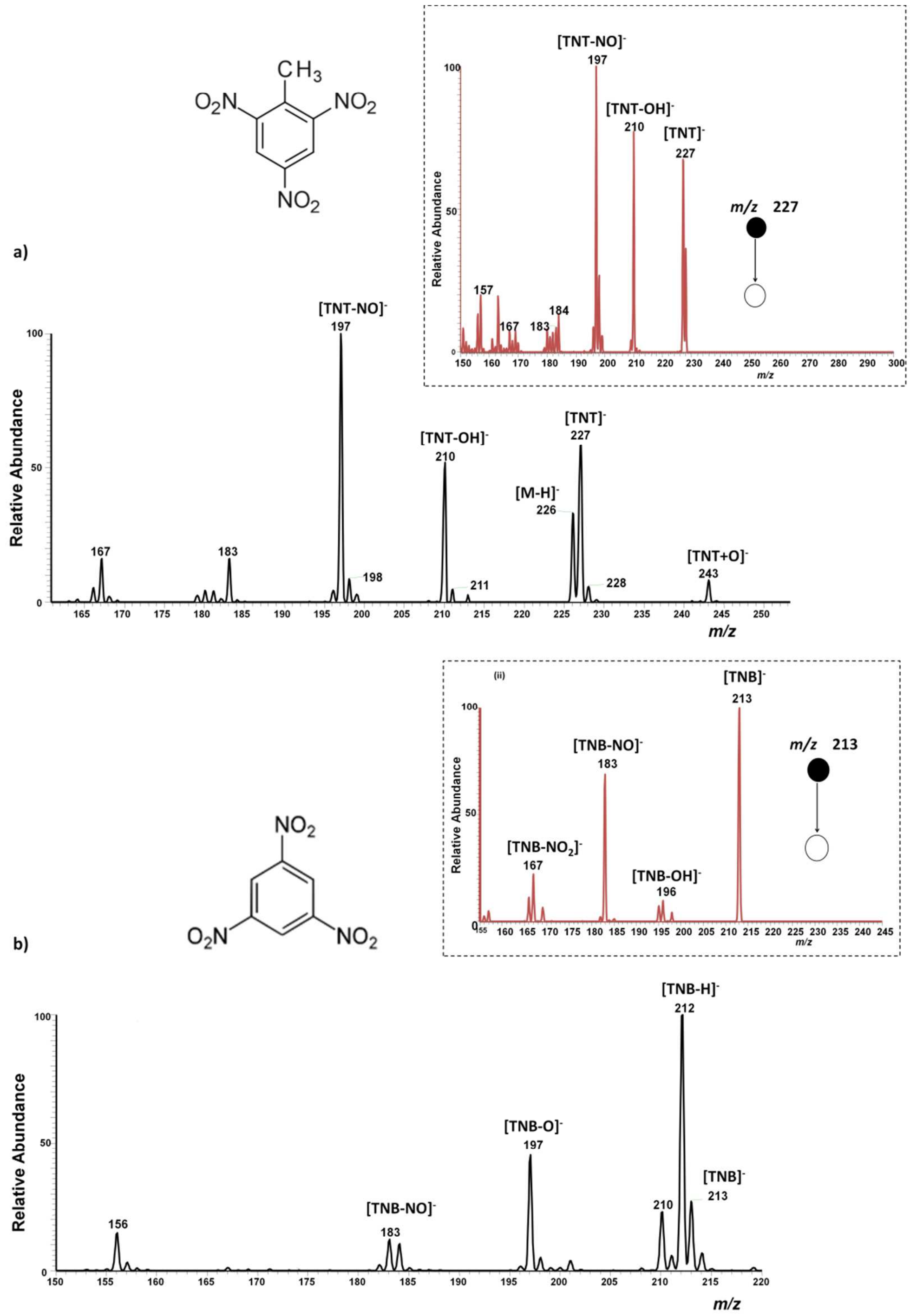

Figure 3. Typical handheld DAPCI ion source negative mass spectra obtained using a bench-top ion trap mass spectrometer instrument. 10 pg of TNT (Mw 227) and TNB (Mw 213) model explosive compounds in methanol

solution were spotted onto paper (~ 1 cm^2 surface area) surface and ionized in the open environment; a) 2, 4, 6-trinitrotoluene (TNT) molecular anion $[M]^-$ (*m/z* 227) and deprotonated ion at *m/z* 226 b) TNB $[M]^-$ (*m/z* 213) and deprotonated ion $[M-H]^-$ at *m/z* 212.. Inserts (i) and (ii) shows the CID MS/MS mass spectra of TNT (Mw 227) and TNB (Mw 213) radical anion $[M]^-$ at *m/z* 227 and 213 respectively.

As can be observed from Figure 3 above, the handheld DAPCI ion source gave a stable signal in the negative mode, with a high signal-to-noise (S/N) ratio even for small amounts of the explosive analyte(s) deposited on the paper surface at room temperature. In subsequent experiments other explosive nitrobenzene compounds such as 2, 4-dinitrotoluene (Mw 182), 1, 3-dinitrobenzene (Mw 168), 2-amino-4, 6-dinitrotoluene (Mw 197) , 2, 4, 6-trinitrophenylmethylnitramine (Tetryl) (Mw 287) were analyzed, in the negative mode, under conditions that favored electron capture and proton abstraction as the ionization mechanisms as shown in Figure S 2 (supporting information).

The abundance of the TNT molecular radical cation $[TNT]^-$ at *m/z* 227 was used to prepare a five point calibration curve covering the range from 10 pg to 100 pg. A limit of detection (LOD) of 5.8 pg (absolute) was obtained under ambient conditions in the open environment (Figure S 3, Supporting Information). The analytical performance of the handheld DAPCI ion source for the analysis of nitroaromatic explosives was evaluated using full scan mass spectra of TNT in the negative mode over a range of absolute amounts from 10 to 100 pg and triplicate measurements showed good reproducibility with an RSD of 7% for a 10 pg/µL sample deposited on the paper surface (for more information see Figure S 3). The handheld DAPCI ion source response was linear over the range 10 to 100 pg ($y = 2.786x+0.0$ with an R^2 value of 0.999). Using the handheld DAPCI ion source the LOD for the model nitroaromatic explosive compounds studied was similar to that obtained using a handheld LTP ion source[59], as summarized in Table 1. Note that quantitation based on MS/MS data is also possible but was not utilized.

Table 1. LOD of analyzed nitroaromatic explosive model compounds in pg (absolute). Comparison between handheld DAPCI using air and handheld LTP using helium.[59]

Compound	***LOD using a handheld ambient ion source (pg)**	
	DAPCI Using Air	**LTP Using Helium**
2,4,6-trinitrotoluene (TNT)	5.8	20
2,4-dinitrotoluene	6.5	n.d
Tetryl	1500	2000

***LOD** was calculated as, $LOD = 3.3\frac{standard\ error}{slope}$ taken from a calibration curve of 5 points with three repetitions for each point.
n.d = not detected

Identification of each individual intact radical anion and deprotonated molecule was again achieved using MS/MS through CID experiments. For example the dissociation of 1,3-dinitrotoluene (Mw 168) radical anion at *m/z* 168 provided an abundant fragment ion at *m/z* 138 via a neutral loss of NO as shown in insert (ii) (Figure S 2 b). Table S 2 (supporting information) provides a summary of data for all the explosive compounds detected using the handheld DAPCI including their structures, vapor pressure and CID fragmentation patterns sampled at ambient conditions in the open environment using a cylinder and solvent-free handheld DAPCI ion source. When air is used as the handheld DAPCI ion source carrier gas to generate a corona discharge; ionic species corresponding to OH and O adducts were observed together with their characteristic fragmentations by OH and NO losses (for more detail see Figure S 2 d). The increased fragmentation observed from the handheld DAPCI, with the model explosive compounds studied, is possibly a consequence of increased internal energy afforded to the primary ionizing species as a result of using atmospheric air as the carrier gas. Formation of these complexes/adducts and their characteristic fragmentation patterns provides reliable and complementary chemical information which facilitates nitrobenzene explosives identification in complex mixtures with enhanced sensitivity.

Analysis of Nitro Explosive Mixture using Handheld Portable DAPCI Ion Source

In this experiment a multicomponent stock solution of the explosive mixture consisting of ~10 pg/μL of each component; TNT (Mw 227), TNB (Mw 213), 2, 4-dinitrotoluene (2,4-DNT) (Mw 182), 1, 3-dinitrobenzene (1,3-DNB) (Mw 168), 2-amino-4,6-dinitrotoluene (Mw 197), 2, 4, 6-trinitrophenylmethylnitramine (Tetryl) (Mw 287) in methanol/acetonitrile solution (v/v, 1:1) was utilized. The mixture was then analyzed using the handheld DAPCI ion source operated in negative ion mode. Approximately 1 μL of the matrix solution was spotted onto the paper substrate and analyzed using the commercial ion trap bench-top mass spectrometer. Figure 4 shows the mass spectra obtained from the analysis of the nitrobenzene explosive mixture using the handheld DAPCI ion source. Again, as observed for the standard individual nitrobenzene explosive analyte(s), intact radical anions $[M]^-$ and deprotonated molecular $[M-H]^-$ species were observed and each ion was characterized using MS/MS CID to identify each component in the mixture. Insert (i) Figure 4 displays the MS/MS CID mass spectrum for the tetryl (Mw 287) molecular anion $[M]^-$ at *m/z* 287, which experiences a neutral loss of OH upon CID activation to yields the intense peak at *m/z* 270 and that of deprotonated TNT at *m/z* 226. In the case of TNT, the molecular anion $[M]^-$ at *m/z* 227 together with its fragment $[TNT-OH]^-$ at *m/z* 210 and ion-molecule reaction product $[TNT+O]^-$ at *m/z* 243 were observed, in unexpectedly high intensity.

Insert (ii) displays the CID product ion mass spectrum of $[TNT + O]^-$ which mainly produces m/z 213 by NO loss upon collisional activation together with a hydroxide elimination pathway producing $[TNT-H]^-$ at *m/z* 226. And insert (iii), Figure 4 shows the MS/MS product ion scan spectrum of 4-amino-2,6-dinitrotoluene (Mw 197) which yields an intense fragment ion at *m/z* 167 due to the loss of NO from the molecular anion $[M]^-$ and a less intense peak at *m/z* 180 due to the loss of OH. Again electron capture dominates in ionization of TNT from the complex mixture forming *m/z* 227 molecular anion which upon CID activation forms an intense peak at *m/z* 210 due to the loss of OH, and the loss of NO from the molecular anion forms a peak at *m/z* 197 (Figure S 4), just as seen in the pure compound figure 2 a (insert). The ability to form radical $[M]^-$ and deprotonated $[M-H]^-$ anions in the negative mode simplifies the resulting mass spectra in the case of mixture analysis performed without prior separation.

Selective *in situ* detection of nitrobenzene explosives formulations using a custom-built handheld DAPCI ion source has been demonstrated. Although the actual mechanism leading to the formation of the oxygen associated adducts is not known at present, the results demonstrate the feasibility of employing ambient air as the DAPCI reagent for selective detection of nitroaromatic explosive formulations without the use of any solvents or sample workup. The nitrobenzene model compounds are ionized by the reactant ions formed in the corona discharge; possibly by electron capture in a thermo-chemically controlled chemical sputtering as reported previously[20]. The results presented herein demonstrate that the handheld DAPCI ion source allows *in situ* detection of nitroaromatic explosives from surfaces similar to other ambient ionization methods, such as DESI[20] and LTP.[77] The ability to form radical $[M]^-$ and deprotonated $[M-H]^-$ anions in the negative mode by electron capture processes simplifies resulting mass spectra in the case of mixture analysis without prior separation. This approach is particularly valuable for field applications coupled with miniaturized mass spectrometers.[56]

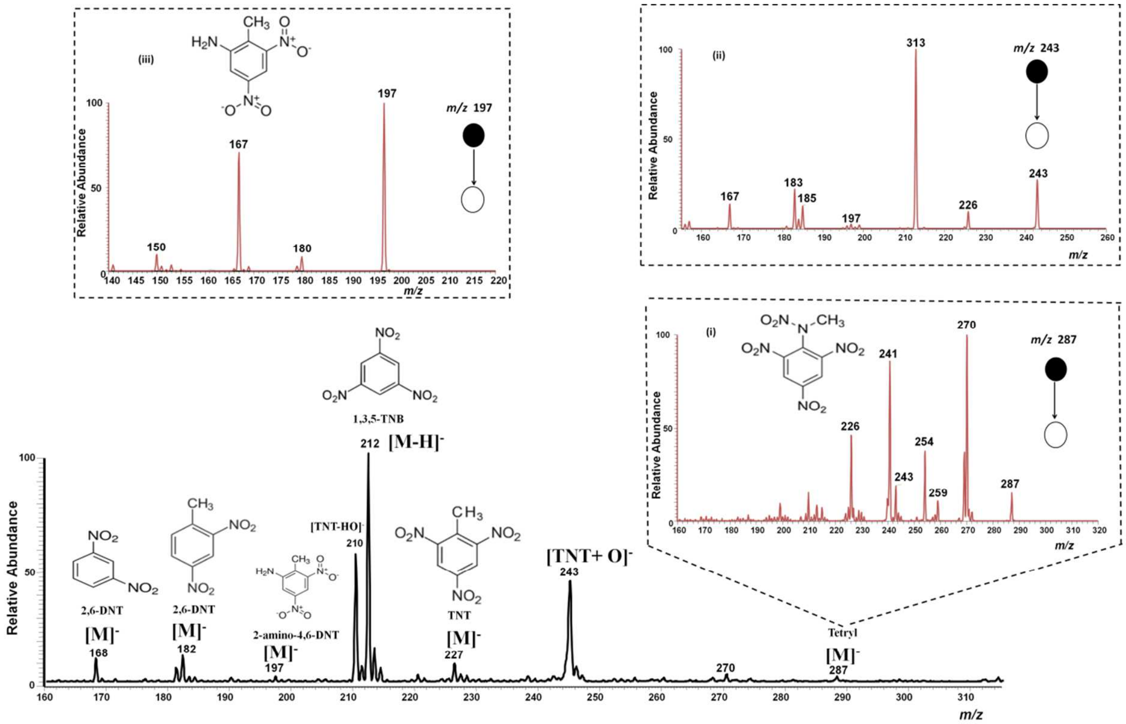

Figure 4. Negative handheld DAPCI ion mode mass spectrum for a mixture of several explosive model compounds analyzed using a bench-top instrument. 10 pg absolute amounts of analytes were contained in the mixture which was deposited onto the surface and ionized in the open environment by application of an electric potential of -2.5 kV in the negative handheld DAPCI ion mode. Most of the nitrobenzene explosive compounds in the mixture gave intact molecular anions $[M]^-$ and deprotonated molecular peaks; 4-amino-2,6-dinitrotoluene (Mw 197), 1,3-dinitrotoluene (Mw 168), 2,6-dinitrotoluene (Mw 182), tetryl (Mw 287). 1, 3, 5-Trinitrotoluene (Mw 213), and TNT (Mw 227) both formed molecular anions $[M]^-$ (at *m/z* 277 and 213 respectively) and deprotonated peaks (at *m*/*z* 212 and 266). Inserts (i) - (iii) show the MS/MS CID data for; tetryl (*m/z* 287) molecular anion, oxidized TNT product ion at *m*/*z* 243 and 4-amino-2,6-dinitrotoluene (Mw 197) molecular anion at *m*/*z* 197 respectively.

Conclusion

The design and construction of a handheld, portable DAPCI ion source suitable for both positive and negative ion mass spectrometry has been documented. *In situ* analysis and detection of nitrobenzene explosives absorbed on surfaces using the source has been demonstrated. Through MS/MS the handheld DAPCI source has been demonstrated to be an effective method for selective analysis of condensed phase nitrobenzene explosives individually and in a mixture on surfaces under ambient conditions. From the results shown, it is evident that different nitrobenzene explosive formulations can easily be ionized and detected with the handheld ion source coupled to a mass spectrometer. If coupled to a miniaturized mass spectrometer, the ease of use of the handheld DAPCI ion source for *in-situ* experimental analysis, would make it a very attractive analytical tool for field applications such as: homeland security, border control, transportation security, national defence, and forensic investigations and other areas such as environmental monitoring where instant and direct detection of a wide range of organic compounds is desirable.[78,79] The results shown here are of interest beyond the nitrobenzene explosives studied as they demonstrate the feasibility of *in situ* analysis using the handheld DAPCI ionization source operated in ambient air for "point and shoot" applications allowing data acquisition in near real time. Future work will involve on-site analysis and quantification of these compounds in such real world scenarios using a miniature mass spectrometer.

Acknowledgements

The research leading to these results has received funding from the European Community's Seventh Framework Programme managed by REA Research Executive Agency (FP7/2007-2013) under Grant Agreement No. 285045 (www.SNIFFLES.eu) which is hereby gratefully acknowledged. Funding for this research has also been provided by the Separations and Analysis Program, Office of Basic Energy Sciences, US Department of Energy, DE-FG02-06ER15807. Fred P. M. Jjunju acknowledges a research scholarship funded by the Department of Electrical Engineering and Electronics, University of Liverpool, UK.

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