

Hand-Held Portable Desorption Atmospheric Pressure Chemical Ionization Ion Source for *in Situ* Analysis of Nitroaromatic Explosives

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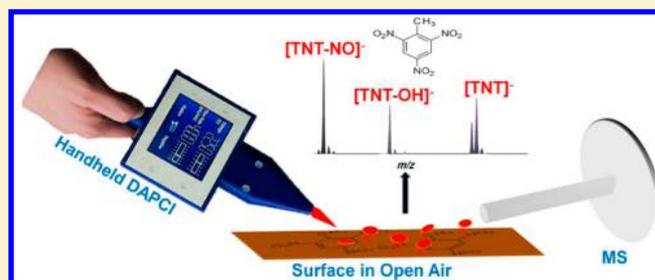
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S Supporting Information

ABSTRACT: A novel, lightweight (0.6 kg), solvent- and gas-cylinder-free, hand-held ion source based on desorption atmospheric pressure chemical ionization 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 h of continuous operation, and allowing positive- and negative-ion mass spectrometry.

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. The advantages of low carrier gas and low power consumption (<6 W), as well as zero solvent usage, have aided in developing the field-ready, hand-held device for trigger-based, “near-real-time” sampling/ionization. Individual nitroaromatic explosives (such as 2,4,6-trinitrotoluene) can be easily detected in amounts as low as 5.8 pg with a linear dynamic range of at least 10 (10–100 pg), a relative standard deviation 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 are confirmed by tandem mass spectrometry fragmentation patterns.



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 could operate *in situ* providing near instantaneous analysis would have significant implications for homeland security, border control, transportation security, national defense, and forensic investigations.¹ Condensed-phase explosives are difficult to ionize due to their wide range of volatilities, while their presence on surfaces makes direct analysis and detection difficult. *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 discharge⁸ 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

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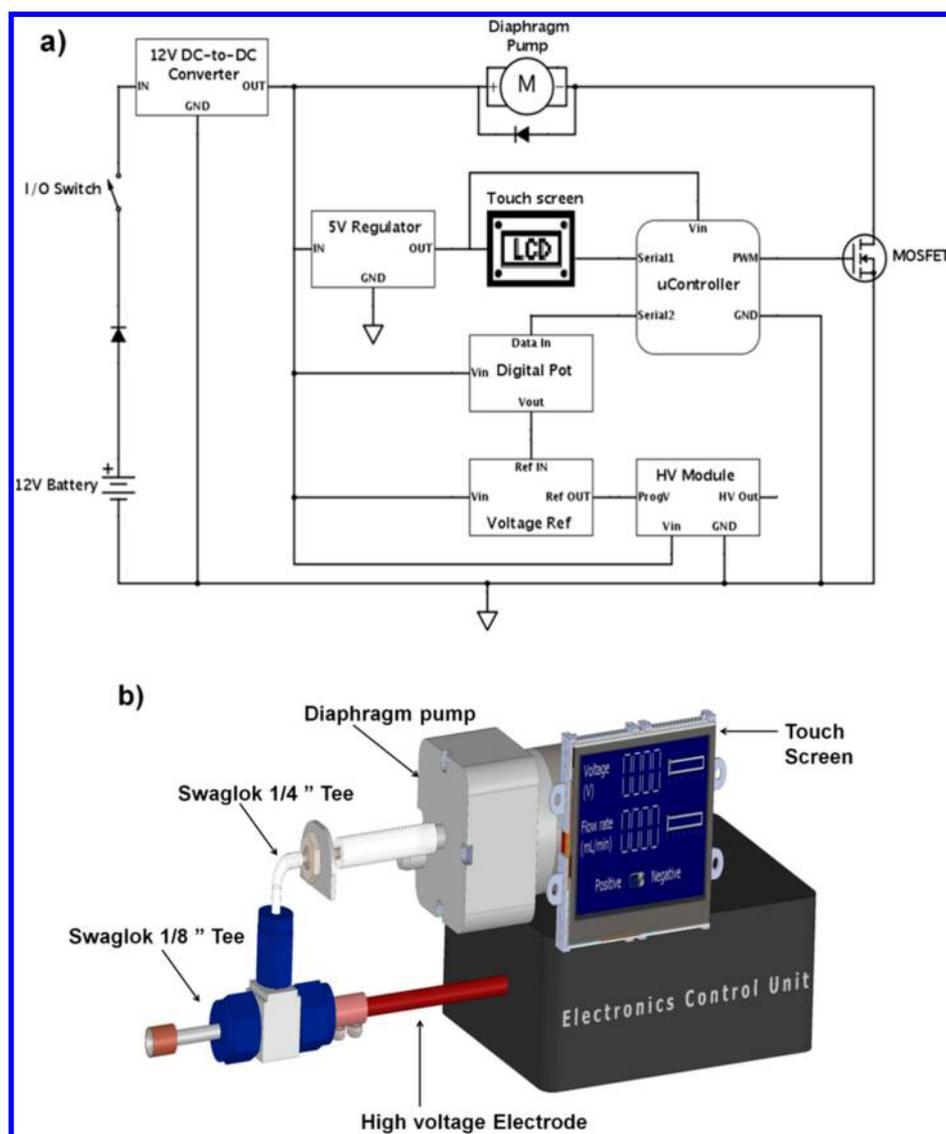


Figure 1. Hand-held, desorption atmospheric pressure chemical ionization (DAPCI) source for direct analysis of explosives: (a) circuit block diagram and (b) CAD model of internal DAPCI components.

pre-treatment. Moreover, the sample must also be transported to the laboratory for analysis.

Recently, ambient ionization (AI) methodology^{24,25} in conjunction with MS has been deployed for the trace analysis and detection of a wide range of explosives measured *in situ* at the site of interest.^{26,27} 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 electroflow 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 gas/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 $\sim 3 \mu\text{L}/\text{min}$ solvent feed and high-pressure gas flows.^{31,34} Desorption ionization sources based on photoionization, 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 exist 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, hand-held, portable AI 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, 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 a miniature mass spectrometer.⁵⁹ DAPCI, based on atmospheric pressure chemical ionization,⁶⁰ is another plasma-based AI source that is relatively under-utilized. DAPCI has been successfully utilized in the analysis of complex molecules, including detection of melamine in powdered milk,⁶¹ 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 toward 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 hand-held DAPCI ion source and its application to the direct analysis of nitroaromatic explosives from surfaces in the open environment. The complete hand-held DAPCI ion source, including the air pump, battery, and electronic circuitry, is enclosed in a 3D-printed plastic enclosure. The hand-held 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 MS/MS.^{22,65} Results obtained from the hand-held DAPCI experiments using a bench-top mass spectrometer show that the hand-held 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 $< \sim 1$ cm²). 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 (TNB), 2,4-dinitrotoluene (2,4-DNT), 1,3-dinitrobenzene (1,3-DNB), 2-amino-4,6-dinitrotoluene, and 2,4,6-trinitrophenylmethylnitramine (Tetryl) were purchased as 1 μ g/mL solutions in methanol/acetonitrile (1:1) from AccuStandards Inc. (New Haven, CT). An explosive stock solution multi-component mixture of TNT, TNB, 2,4-DNT, 1,3-DNB, 2-amino-4,6-dinitrotoluene, an Tetryl (100 μ g/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/ μ L) 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 μ L was applied onto a cellulose filter paper (Whatman, Maidstone, UK grade 1) (1 cm² total surface area) using a pipettor (Brand Gmbh, Germany). All samples were analyzed immediately in open

air using the newly developed hand-held, portable DAPCI device coupled to a commercial mass spectrometer.

Hand-Held DAPCI Ion Source. A custom-designed hand-held DAPCI ion source was developed; it differs from the DAPCI ion source reported previously^{60,63} in that it is battery powered and 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-in. 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 hand-held DAPCI device (see Figure 1b 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 –3 kV, generated using a high-voltage regulated 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 1a 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 hand-held 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 recharging is necessary. From a fully charged state the battery can power the device for up to 12 h 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 hand-held 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 and the diaphragm pump require a minimum 12 V 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-in. 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 hand-held DAPCI specifications is given in Table S1 (Supporting Information).

Hand-Held 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 toward a surface using a carrier gas (e.g., air, nitrogen, helium).^{38,63} The carrier gas is directed toward 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 $\pm \sim 2.5$ –3 kV so as to produce a corona discharge in close proximity at the tip of the electrode. The hand-held ion source is optimally coupled to the atmospheric pressure inlet of a commercial bench-top mass spectrometer placed at a distance of ~ 2.5 mm (Figure 2). The



Figure 2. Schematic of the hand-held DAPCI experimental setup used in the analysis of nitroaromatic explosives.

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.

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 hand-held DAPCI-MS for nitroaromatic explosives (TNT, TNB, 2,4-DNT, 1,3-DNB, 2-amino-4,6-dinitrotoluene, and 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, +3 kV; tube lens voltage, 200 V; heated capillary voltage, 25 V; capillary temperature, 200 °C; multipole rf amplitude (V_{p-p}), 400 V; multiplier voltages 1 and 2, -800 V; ion injection time, 100 ms; and three microscans. For the analysis of the same standard model compounds and the multi-component explosive mixture in negative mode the conditions were as follows: hand-held DAPCI ion source voltage applied to the tapered tip stainless steel needle, -2.5 kV; tube lens voltage, -102 V; heated capillary voltage, -20 V; capillary temperature, 200 °C; multipole rf amplitude (V_{p-p}), 400 V; multiplier voltages 1 and 2, -800 V; ion injection time, 100 ms; and five 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

Hand-Held DAPCI-MS Characterization. The hand-held 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 the Supporting Information, Figure S1). The primary reagent ions from the hand-held 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^- , and 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 Hand-Held DAPCI in Negative-Ion Mode. When air is used as the hand-held DAPCI carrier gas under the conditions in Figure S1b (Supporting Information), the ionization of oxygen gas in the presence of water clusters generates reactant anions as observed in Figure S1b at m/z 46, 32, and 60 (NO_2^- , O_2^- , and CO_3^-) which readily react with the vapors of nitroaromatic explosives.^{66,67} Such reactions are likely due to their high electron affinities, 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 hand-held 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 area of approximately 1 cm² (Figure 3).

The mass spectra recorded in the negative-ion mode for both TNT (MW 227) and TNB (MW 213) included both molecular radical cations and deprotonated molecular anions, viz. $M^{\bullet-}$ 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 MS/MS (Figure 3a, inset (i)). 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 DESI⁷⁴ and LTP⁴³ 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 $[TNB - OH]^-$ and NO at m/z 183 $[TNB - NO]^-$ is confirmed by CID MS/MS data (Figure 3b, inset (ii)).

As can be observed from Figure 3 above, the hand-held 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-DNT (MW 182), 1,3-DNB (MW 168), 2-amino-4,6-dinitrotoluene (MW 197), and Tetryl (MW 287) were analyzed, in the negative-ion mode, under conditions that favored electron capture and proton

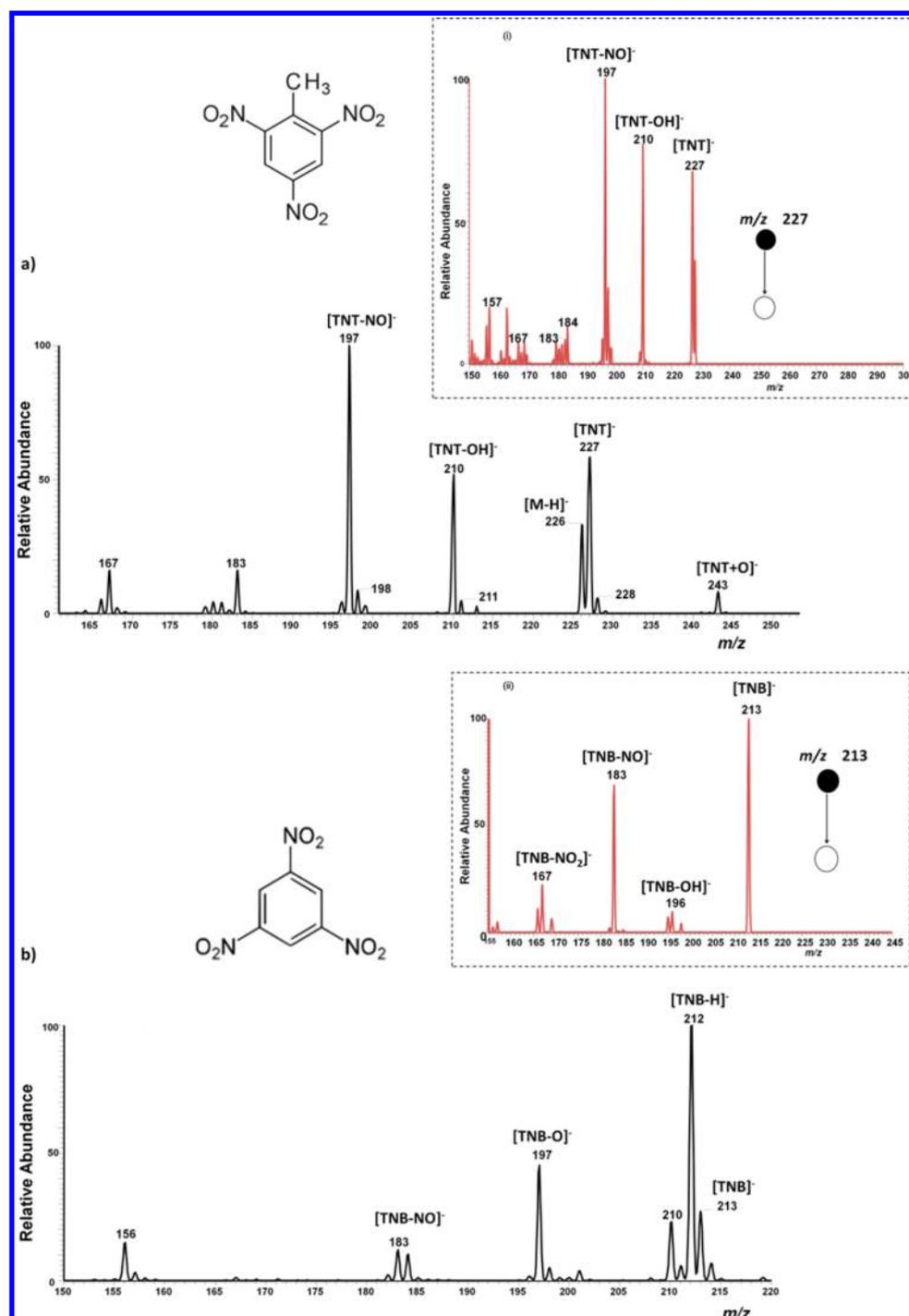


Figure 3. Typical hand-held DAPCI ion source negative mass spectra obtained using a bench-top ion trap mass spectrometer instrument. Ten picograms each of TNT (MW 227) and TNB (MW 213) model explosive compounds in methanol solution were spotted onto paper ($\sim 1 \text{ cm}^2$ surface area) surface and ionized in the open environment: (a) TNT molecular anion $[\text{M}]^-$ (m/z 227) and deprotonated ion at m/z 226; (b) TNB $[\text{M}]^-$ (m/z 213) and deprotonated ion $[\text{M} - \text{H}]^-$ at m/z 212. Insets (i) and (ii) show the CID MS/MS mass spectra of TNT (MW 227) and TNB (MW 213) radical anion $[\text{M}]^-$ at m/z 227 and 213, respectively.

abstraction as the ionization mechanisms as shown in Figure S2 (Supporting Information).

The abundance of the TNT molecular radical cation $[\text{TNT}]^-$ at m/z 227 was used to prepare a five point calibration curve covering the range from 10 to 100 pg. A limit of detection (LOD) of 5.8 pg (absolute) was obtained under ambient conditions in the open environment (Figure S3, Supporting Information). The analytical performance of the hand-held

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 a relative standard deviation of 7% for a 10 pg/ μL sample deposited on the paper surface (for more information, see Figure S3). The hand-held DAPCI ion source response was linear over the range 10–100 pg ($y = 2.786x + 0.0$, with $R^2 =$

0.999). Using the hand-held DAPCI ion source, the LOD for the model nitroaromatic explosive compounds studied was similar to that obtained using a hand-held LTP ion source,⁵⁹ as summarized in Table 1. Note that quantitation based on MS/MS data is also possible but was not done.

Table 1. Limit of Detection of Analyzed Nitroaromatic Explosive Model Compounds in Picograms (Absolute): Comparison between Hand-Held DAPCI Using Air and Hand-Held LTP Using Helium⁵⁹

| compound | LOD ^a using a hand-held ambient ion source (pg) | |
|-----------------------|--|------------------|
| | DAPCI using air | LTP using helium |
| 2,4,6-trinitrotoluene | 5.8 | 20 |
| 2,4-dinitrotoluene | 6.5 | nd |
| Tetryl | 1500 | 2000 |

^aLimit of detection was calculated as $LOD = 3.3(\text{standard error/slope})$, taken from a calibration curve of five points with three repetitions for each point. nd = 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 Figure S2b, inset (ii). Table S2 in the Supporting Information provides a summary of data for all the explosive compounds detected using the hand-held DAPCI including their structures, vapor pressure and CID fragmentation patterns

sampled at ambient conditions in the open environment using a cylinder and solvent-free hand-held DAPCI ion source. When air is used as the hand-held 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 details, see Figure S2d). The increased fragmentation observed from the hand-held 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 Hand-Held Portable DAPCI Ion Source. In this experiment a multi-component stock solution of the explosive mixture consisting of ~ 10 pg/ μL of each component; TNT (MW 227), TNB (MW 213), 2,4-DNT (MW 182), 1,3-DNB (MW 168), 2-amino-4,6-dinitrotoluene (MW 197), and Tetryl (MW 287) in methanol/acetonitrile solution (v/v, 1:1) was utilized. The mixture was then analyzed using the hand-held 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 hand-held DAPCI ion source. Again, as observed for the standard individual

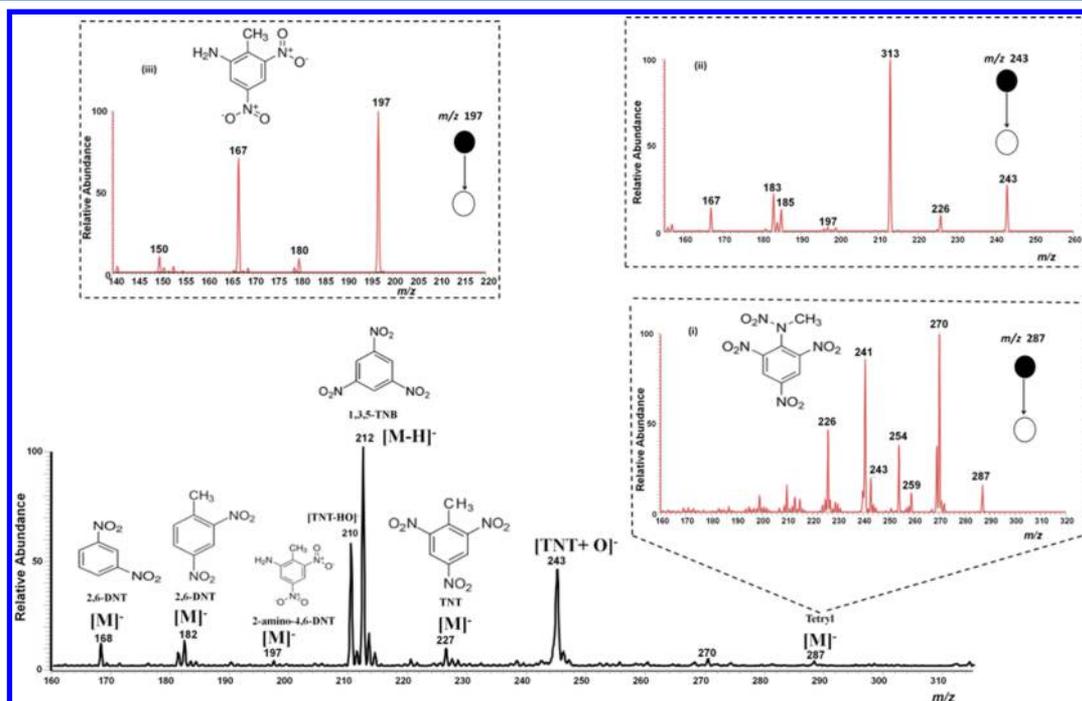


Figure 4. Negative-ion mode hand-held DAPCI mass spectrum for a mixture of several explosive model compounds analyzed using a bench-top instrument. Ten picogram absolute amounts of analytes were contained in the mixture which was deposited onto the surface and ionized in the open environment by application of an electric potential of -2.5 kV in the negative hand-held 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), and 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). Insets show the MS/MS CID data for (i) Tetryl (m/z 287) molecular anion, (ii) oxidized TNT product ion (m/z 243), and (iii) 4-amino-2,6-dinitrotoluene (MW 197) molecular anion (m/z 197).

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. Figure 4, inset (i) 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.

Figure 4, inset (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. Figure 4, inset (iii) 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 S4, Supporting Information), just as seen in the pure compound (Figure 2a, inset (i)). 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 hand-held 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 thermochemically controlled chemical sputtering as reported previously.²⁰ The results presented herein demonstrate that the hand-held DAPCI ion source allows *in situ* detection of nitroaromatic explosives from surfaces similar to other ambient ionization methods, such as DESI²⁰ and LTP.⁷⁷ The ability to form radical $[M]^-$ and deprotonated $[M - H]^-$ anions in the negative-ion 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

CONCLUSION

The design and construction of a hand-held, portable DAPCI ion source suitable for both positive- and negative-ion mass spectrometry have been documented. *In situ* analysis and detection of nitrobenzene explosives absorbed on surfaces using the source have been demonstrated. Through MS/MS, the hand-held 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 hand-held ion source

coupled to a mass spectrometer. Because of the ease of use of the hand-held DAPCI ion source for *in situ* experimental analysis, coupling it to a miniaturized mass spectrometer would make it a very attractive analytical tool for field applications such as homeland security, border control, transportation security, national defense, and forensic investigations, as well as 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 hand-held 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.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b02684.

Discussion of hand-held DAPCI background mass spectra; analysis of nitroaromatic explosives using a hand-held DAPCI ion source; semi-quantitative analysis of the aromatic benzene explosives using a hand-held DAPCI ion source; analysis of nitroaromatic explosives model compounds in a multi-component mixture using a hand-held DAPCI ion source (Figures S1–S4); summary of the hand-held DAPCI specifications and list of nitroaromatic explosive compounds analyzed using a hand-held DAPCI ion source (Tables S1 and S2) (PDF)

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Notes

The authors declare no competing financial interest.

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