Enhanced aerodynamic reach of vapor and aerosol sampling for real-time mass spectrometric detection using Venturi-assisted entrainment and ionization

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Abstract

Venturi-assisted ENTrainment and Ionization (VENTI) was developed, demonstrating efficient entrainment, collection, and transport of remotely sampled vapors, aerosols, and dust particulate for real-time mass spectrometry (MS) detection. Integrating the Venturi and Coandă effects at multiple locations generated flow and analyte transport from non-proximate locations and more importantly enhanced the aerodynamic reach at the point of collection. Transport through remote sampling probes up to 2.5 m in length was achieved with residence times on the order of 10⁻² s to 10⁻¹ s and Reynolds numbers on the order of 10³ to 10⁴. The Venturi-assisted entrainment successfully enhanced vapor collection and detection by greater than an order of magnitude at 20 cm stand-off (limit of simple suction). This enhancement is imperative, as simple suction

restricts sampling to the immediate vicinity, requiring close proximity to the vapor source. In addition, the overall aerodynamic reach distance was increased by approximately 3-fold over simple suction under the investigated conditions. Enhanced aerodynamic reach was corroborated and observed with laser-light sheet flow visualization and schlieren imaging. Coupled with atmospheric pressure chemical ionization (APCI), the detection of a range of volatile chemical vapors; explosive vapors; explosive, narcotic, and mustard gas surrogate (methyl salicylate) aerosols; and explosive dust particulate was demonstrated. Continuous real-time Venturi-assisted monitoring of a large room (approximately 90 m² area, 570 m³ volume) was demonstrated for a 60-minute period without the remote sampling probe, exhibiting detection of chemical vapors and methyl salicylate at approximately 3 m stand-off distances within 2 minutes of exposure.

KEYWORDS: Vapor and aerosol detection; Remote sampling; Explosives detection; Venturiassisted entrainment; Aerodynamic reach; Mass spectrometry;

1. Introduction

The need to efficiently collect, transport, and detect vapors and aerosols in real-time remains imperative to the defense, security and forensic science sectors, as well as areas including environmental and atmospheric monitoring, and biological aerosol transmission. The progression of homemade explosives, specifically nitrate ester and high volatility peroxide-based explosives, has emphasized the need for advanced vapor detection to complement the current suite of trace residue and particulate detection technologies. Similarly, the advent of synthetic narcotics has led to a rapidly increasing list of illicit compounds and the subsequent demand on law enforcement and canine units. The detection of vapors and aerosols has been demonstrated with a wide range of analytical methods [1], including colorimetric [2, 3] and fluorescence [4] detection schemes, novel nanomaterial sensors [5, 6], as well as more classical analytical techniques such as Raman spectroscopy [7], ion mobility spectrometry (IMS) and differential mobility spectrometry [8, 9], and mass spectrometry (MS) [10-13].

Traditionally, IMS and MS have been the technologies of choice for detection of trace contraband residue and particulate species using manual swipe collection. However, the detection of vapors and aerosols is often overlooked or considered of secondary importance. Advances in desorption-based ambient ionization mass spectrometry (AI-MS) have also led to a plethora of techniques for directly desorbing analytes from samples [14, 15]. However, the majority of these techniques are limited to small and relatively flat substrates that can easily be positioned near the mass spectrometer inlet. To address these limitations, research focused on the non-proximate transport of neutrals and ions has enabled remote sampling and sensitive detection of a range of compounds, eliminating the need for traditional swipe sampling/collection or well-defined substrates that can be manipulated for desorption-based AI-MS [12, 16-24]. The transport of neutrals and ions has been accomplished through a number of configurations using various vacuum pumps [18] and Venturi or ejector components [16, 17, 20-23], with glass, metal, and polymer capillaries or tubes. The Venturi effect relies on fluid dynamics principles, conservation of energy, and acceleration of a fluid through a small constriction to generate a low pressure region that induces flow [25]. Air amplifiers have been developed utilizing this phenomenon through annular constrictions that siphon and focus flow through the body of the device. These devices and principles have been implemented on a

number of occasions to improve collection and transmission of electrospray [26-30] and ultrasonic nebulization droplet/ion plumes [31, 32]. They have also been implemented in various configurations of remote sampling systems for the transport of ions and neutral species [16, 17, 22, 23, 33-36]. However, these techniques often implement simple suction at the sampling point, limiting collection to the immediate vicinity. This drastically restricts the "aerodynamic reach" of the system, requiring close proximity to the vapor source.

The Venturi-assisted ENTrainment and Ionization (VENTI) system described here builds upon this framework for the real-time detection of remotely sampled vapors, aerosols, and dust particulate. The VENTI system integrates multiple Venturi-based devices for both flow control from remote locations and more significantly, to enhance the aerodynamic reach at the point of sample collection. For sampling, a manually controlled air amplifier exploited the Venturi effect to generate a low pressure vacuum, inducing entrainment and bulk flow into the device. In conjunction with the Coandă effect, VENTI siphoned and transported the entrained vapor/gas fraction preferentially over the supply gas fraction, returning the excess supply gas back into the environment. The second Venturi-device generated continuous flow through remote sampling probes/lines up to 2.5 m long and incorporated a corona discharge component for atmospheric pressure chemical ionization (APCI) of collected vapors [37, 38]. Here we investigated the generated flow rates, aerodynamic reach, and MS response of the VENTI system for vapor detection as a function of the applied pressures, which drive analyte entrainment and transport. Enhanced aerodynamic reach and analyte collection were demonstrated with MS vapor collection experiments and observed with laser-light flow visualization and schlieren imaging. Detection of various volatile chemicals, explosive vapors, explosive and narcotic aerosols, a mustard gas chemical warfare agent (CWA) surrogate (methyl salicylate) [10], and explosive

dust particulate were demonstrated under a number of experimental conditions, including realtime remote and stand-off detection as well as continuous environmental monitoring.

2. Experimental Methods

2.1 Materials and Sample Preparation

LC-MS Chromasolv grade water, methanol and acetonitrile, 95% ethanol, and 99% methyl salicylate were purchased from Sigma-Aldrich (St. Louis, MO, USA)* and A.C.S. Reagent grade glacial acetic acid and acetone were purchased from J.T. Baker/Avantor Performance Materials (Phillipsburg, NJ, USA). Hexamethylene diperoxide diamine (HMDD), 2,4-dinitrotoluene (DNT), nitroglycerin (NG), and ethylene glycol dinitrate (EGDN) explosive standards were purchased from AccuStandard Inc. (New Haven, CT, USA) at 1 mg mL⁻¹ concentration in acetonitrile or methanol (EGDN at 0.1 mg mL⁻¹). A 2,4,6-trinitrotoluene (TNT) K9 training aid (Tripwire Operations Group, Gettysburg, PA, USA) was used as a vapor source (\approx 5 g TNT flake; safety considerations below). Methamphetamine (METH) and 3,4methylenedioxymethamphetamine (MDMA) were purchased from Cerilliant (Round Rock, TX, USA) at 1 mg mL⁻¹ concentration in methanol. Parametric investigations of the VENTI configuration were conducted on the headspace vapor of 1 mL ethanol sealed in 20 mL scintillation vials and allowed to equilibrate for 10 minutes. Each replicate experiment began by opening the vial and mass spectrometric detection was conducted for 30 s or 60 s intervals, after which the vial was closed. These sample durations (30 s & 60 s) demonstrated consistent vapor signals for ethanol equilibration times greater than one minute (Figure S-1) due to its high vapor pressure and VENTI-generated convective mass transfer to the gas phase. Four hundred

microliters (400 μ L: 40 μ g to 400 μ g depending on concentration) of explosive standards in organic solvents were deposited into 20 mL vials or 60 mL glass jars and the solvent allowed to evaporate (based on visual inspection). Following solvent evaporation, the vials were sealed for a 45-minute period and opened for detection. EGDN's high volatility led to significant evaporation of the analyte with the solvent, therefore, EGDN was sealed and detected in the presence of solvent. Aerosol detection experiments were conducted directly from compounds in organic solvent or aqueous solutions – additional details below.

* Certain commercial products are identified in order to adequately specify the procedure; this does not imply endorsement or recommendation by NIST, nor does it imply that such products are necessarily the best available for the purpose.

2.2 Instrumentation

2.2.1 Venturi-assisted Entrainment and Ionization

The VENTI remote sampling and ionization system comprised of a manual control air amplifier (Exair Corporation, Cincinnati, OH, USA) for discrete/pulsed Venturi-assisted entrainment; 0.5 m, 1.0 m, and 2.5 m long sampling probes (Tygon tubing: 3/16-inch inner diameter × 1/4-inch outer diameter); and a continuous Venturi-generated flow and corona discharge ionization component (Ion Air Jet, Exair Corporation). Compressed nitrogen gas, supplied through 1/4-inch polyurethane tubing at pressures of 10 psi (69 kPa) to 80 psi (552 kPa) was used to drive the entrainment and flow control components (Figure 1). The supply tubing to the entrainment air amplifier (AA1) ran parallel to the remote sampling probe/tubing (not shown in Figure 1). The Tygon sampling probe was mounted (press fit) to the exit of the entrainment air amplifier (AA1, Figure 1) by a custom 3D printed part (Supporting Information, Figure S-2), which exploiting the Coandă effect [39, 40] enabled the excess supply gas flow to be recycled back into the laboratory environment. The Coandă effect describes the tendency of a fluid flow to remain in contact with a curved surface, resulting in the supply gas flow maintaining contact with the device walls, concentric to the entrained fraction. The entrained gas, vapors, and aerosols were pulled in by the induced low pressure and transported axially through the device and collected by a second low pressure area at the end of the remote sampling probe. This low pressure area and gas flow through the remote sampling probe were similarly generated by the Venturi effect at the enclosed inlet of AA2 (Figure 1), capped with a custom machined Teflon connector. The sampling probe was press fit through the Teflon piece and held in place using a series of O-rings on either side of the Teflon wall. Volumetric flow rates through the remote sampling probes were measured with a gas flow meter (FMA 1842A, Omega Engineering, Inc., Stamford, CT, USA). Ionization was achieved by an ac 5 kV_{rms} potential applied to a needle extending into the induced flow. The ionized gas exits the device axially, 2 mm from the extended inlet of the mass spectrometer interface.

2.2.2 Mass Analyzer

A 4000 QTRAP triple quadrupole mass spectrometer (SCIEX, Redwood City, CA, USA) fitted with a 35 mm extended capillary interface was used in all experiments. The investigations demonstrated here primarily used the first quadrupole for scanning and the second and third quadrupoles as ion guides. System parameters included: 10 psi (69 kPa) curtain gas (N₂), 12 psi (83 kPa) ion source gas 1 (N₂), 0 psi (0 kPa) ion source gas 2, 100 °C interface temperature, \pm 100 V declustering potential, \pm 10 V entrance potential, and 8.3 × 10⁻³ Torr to 9.8 × 10⁻³ Torr (1.1 × 10⁻³ kPa to 1.3 × 10⁻³ kPa) operating vacuum.

2.2.3 Flow Visualization and Schlieren Imaging

Flow visualization of VENTI was conducted using both a laser light-sheet/theatrical fog setup and schlieren imaging. These experiments were used to understand the fluid flow dynamics of the VENTI system during operation and enhanced aerodynamic reach of the Venturi-assisted entrainment. The flow profile was visualized through the movement of theatrical fog, illuminated by a 2-dimensional vertical laser light-sheet, bisecting the inlet of AA1. A continuous wave 532nm laser (Coherent V7, Coherent Inc., Santa Clara, CA, USA) directed at a cylindrical glass rod produced the light sheet, while a theatrical fog machine (Mister Kool, ADJ Products LLC, Los Angeles, CA, USA) introduced neutrally-buoyant fog into the air approximately 1 m downstream of AA1. A digital camera (Handycam, Sony Corporation of America, New York, NY, USA) captured footage at 30 frames per second from an orthogonal viewing direction relative to the light-sheet. A single-mirror schlieren optical system (enabling visualization of differences in refractive index) captured footage (36 frames per second) of the VENTI system sampling acetone vapor from a polyurethane foam plug soaked in acetone. Acetone vapors were entrained against gravity and at a distance of approximately 15 cm. Details of the schlieren optical system can be found in the literature [41, 42].

2.2.4 Aerosol Generation – Ultrasonic Nebulization

Aerosols were generated in 10 μ L to 20 μ L discrete plumes with an ultrasonic nebulizer (SMM-OD10-F190, Steiner & Martins Inc., Miami, FL, USA). Details of the ultrasonic nebulizer (USN) can be found in the literature [43]. Briefly, the nebulizer consisted of a 50 μ m thick nickel-cobalt diaphragm with an array of 145 exponential acoustic horns, between two lead zirconium titanate (PZT) piezoelectric rings (250 μ m thick × 5 mm ID × 10 mm OD). The array of horns terminated in approximately 5 μ m orifices that led to droplets on the order of microns

for aqueous and organic solvent solutions operated with a 190 kHz and 20 V_{pp} (peak-to-peak voltage) to 30 V_{pp} drive signal.

2.2.5 Safety Considerations

All appropriate safety considerations related to vapor detection and explosives K9 training aids were implemented. Portable fume extractors (Sentry Air Systems Inc., Houston, TX, USA) with both HEPA and activated carbon filters were used to remove excess and expelled vapors. Aerosol generation and collection experiments were conducted in a ductless fume hood (Sentry Air Systems) with HEPA and activated carbon filters. Explosive K9 training aids, comprised of cast flakes/particulate below the detonation critical diameter for TNT, were used as directed by manufacturer/supplier and handled in accordance with best practices for the safe handling of energetic materials.

3. Results and Discussion

3.1 VENTI Remote Vapor Sampling

The main components of the VENTI system, as described above, are represented in Figure 1. The volumetric flow rates through the remote sampling probe were measured as a function of probe length and supply gas pressure. Figure 2(a) displays the probe flow rates and corresponding average velocities as a function of gas pressure for the case of simple suction driven by AA2, demonstrating an increase in flow with increasing pressure and decrease in flow with increased probe length and corresponding aerodynamic resistance. Uncertainty in the pressure reading and flow rate readings were approximately ± 2 psi (± 14 kPa) and ± 0.5 L min⁻¹ (greater than the standard deviation of replicate measurements – error bars in Figure 2 were frequently smaller than plotted data points). Under typical operating conditions investigated here, the VENTI sampling probe flow exhibited Reynolds numbers ($Re = \rho UD/\mu$, where ρ and μ are the gas density and viscosity, U is the average velocity, and D is the tube diameter) on the order of 10³ (2.5 m probe at 10 psi (69 kPa)) to 10⁴ (0.5 m probe at 50 psi (345 kPa)), yielding predominately transient and turbulent behavior.



Figure 1. Schematic representation of the Venturi-assisted entrainment and ionization (VENTI) system. Components include: a pressure driven air amplifier for enhanced aerodynamic reach of the sampling probe (AA1), a Tygon sampling probe – 0.5 m, 1.0 m, and 2.5 m – used for sample transport, a joint air amplifier corona discharge chemical ionization source for both flow control and ionization (AA2), and the mass spectrometer inlet. Schematic not drawn to scale.

The performance of the VENTI remote sampling system was briefly investigated using ethanol vapor from 20 mL scintillation vials. Positive mode mass spectra were acquired continuously from m/z 30 to m/z 200 in 0.5 s scans for the duration of the experiment. The experiments presented here predominately favored the ionization and detection of the organic solvent dimer over the monomer (Figure S-3). Figure 2(b)-2(c) demonstrate the integrated signal intensity of the ethanol dimer (m/z 93, $[2M+H]^+$) across a 30 s sampling period as a function of AA1 and AA2 supply pressures and probe length. These experiments were conducted in relatively close proximity to the vapor source – approximately 2 cm. Figure 2(b) displays the

ethanol signal as a function of AA2 (component driving probe flow) pressure without the use of AA1 for increased entrainment and aerodynamic reach (AA1 = 0 psi (0 kPa)). Integrated signals from the analyte base peak were taken from extracted ion chronograms (Figure S-4). Three probe lengths and a "no probe" case – where the remote sampling probe and Teflon attachment were removed and the ethanol source placed in proximity to AA2 – were considered. Maximum MS response was achieved without the sampling probe and associated flow reductions and analyte losses. The response asymptotically increased (an order of magnitude or more) with increasing supply pressure for all probe lengths investigated. Decreased signal was demonstrated for increasing probe length, however, extending the probe from 1.0 m to 2.5 m resulted in minimal decrease in signal. All three probe lengths for the range of pressure considered, experienced high flow rates that resulted in residence times on the order of 10^{-2} s to 10^{-1} s, similar or shorter than the duration of a single mass range scan (0.5 s). Beyond the reduction in flow rate for increased probe length, phenomena such as vapor depletion, collection losses (analyte escaping the second low pressure region and returned back into environment), analyte adsorption to the probe and other losses, ionization efficiency, and ion transmission efficiency may have contributed to the observed trends. Similarly, the integrated ethanol signal was measured as a function of AA1 pressure and probe length for a constant AA2 pressure (40 psi (276 kPa)). Figure 2(c) demonstrates the minimal enhancement (1.5-fold to 2-fold) achieved for increasing AA1 pressure for samples in close proximity to the VENTI inlet (~ 2 cm). An ethanol vapor calibration curve and additional details can be found in supporting information.



Figure 2. (a) Volumetric flow rate through the remote sampling probe as a function of supply pressure (AA2) and probe length. VENTI-MS integrated signal intensity for 30 s sampling durations of the ethanol dimer (*m/z* 93) for various probe lengths as a function of (b) AA2 supply pressure (no AA1) and (c) AA1 supply pressure for AA2 at constant 40 psi (276 kPa). Data points and uncertainty expressed as the average integrated signal and standard deviations for triplicate samples – error bars often smaller than data point.

3.2 Enhanced Aerodynamic Reach

As demonstrated above (Figure 2(c)), the Venturi-assisted entrainment provided minimal improvement in the MS response at close proximity to the vapor source, however, it played a significant role in enhancing the aerodynamic reach of the system. Generally, aerodynamic reach can be defined as the distance at which the target vapors can be aerodynamically entrained into the detection system. Here, the aerodynamic reach was more specifically defined as the distance

at which vapors could be entrained/detected within the sampling period – 60 s in the following experiments. The aerodynamic reach was investigated by measuring the ethanol signal from a vapor source at increasing stand-off distances from the entrainment air amplifier collection point (uncertainty in the distance measurement was approximately 0.5 cm). Figure 3(a) displays the integrated ethanol signal (60 s sampling period) for simple suction and with Venturi-assisted entrainment. Without Venturi-assisted entrainment (i.e., simple suction: AA2 40 psi (276 kPa) and 2.5 m probe), the ethanol signal dropped by 2 orders of magnitude (100-fold) moving from a close proximity (2.5 cm), extending out to a 20 cm stand-off distance. For these experimental conditions, 20 cm was the maximum extent of aerodynamic reach for simple suction.

To enhanced the aerodynamic reach, two Venturi-assisted entrainment conditions were investigated: AA1: 30 psi and 60 psi (207 kPa and 414 kPa) for a constant AA2 pressure of 40 psi (276 kPa) and 2.5 m probe. Venturi-assisted entrainment at these pressures demonstrated 7.5fold and 10-fold enhancements in the signal at a 20 cm axial stand-off distance, the limit of simple suction. In addition, incorporating Venturi-assisted entrainment improved the overall aerodynamic reach to greater than 50 cm, yielding approximately 2.5-fold to 3-fold greater reach than simple suction (Figure 3(a)). As demonstrated above, the flow within the remote sampling probe was fast, with residence times shorter than a single mass spectrum scan. However, at increasing stand-off distances, the delay for vapors to be entrained at low velocities into the VENTI system was noticeable – on the order of seconds, up to tens of seconds. It is important to note that these experiments were limited to 60 s sampling periods, indicating the possibility of larger stand-off distances with longer sampling periods, which will be addressed below.

The enhancement in aerodynamic reach of the VENTI system was also observed using flow visualization and schlieren imaging (Figure 3(b)-3(c)). With only simple suction, the pull

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from AA2 (20 psi (138 kPa)) was minimal – demonstrated by the slow pull of the ambient air and theatrical fog toward the system in Figure 3(b-ii) (Supporting Information, Video S-1: multiple on-off cycles). The application of 60 psi (414 kPa) to AA1 led to a dramatic increase in the aerodynamic entrainment seen in Figure 3(c-ii). Similarly, schlieren imaging was used to demonstrate the entrainment of acetone vapor against gravity at a distance of 15 cm from the VENTI system (Supporting Information, Video S-2: multiple on-off cycles). Figure 3(b-iii) displays a schlieren image of the acetone vapor falling (acetone is heavier than air) from a saturated foam plug substrate under simple suction conditions (AA1 off, AA2 at constant 40 psi (276 kPa)). With the application of 80 psi (552 kPa) to AA1, the VENTI system redirected the acetone plume upward, drawing it into the VENTI inlet (Figure 3(c-iii)). These flow visualization and mass spectrometry experiments demonstrated the impressive increase in aerodynamic reach of the VENTI system – a critical metric for effective remote vapor and aerosol sampling applications.



Figure 3. (a) VENTI-MS integrated signal intensity for 60 s sampling durations of the ethanol dimer (*m/z* 93) for a 2.5 m probe at 0 psi, 30 psi, and 60 psi (0 kPa, 207 kPa, and 414 kPa) AA1 pressures and constant 40 psi (276 kPa) AA2 pressure as a function of the sample stand-off distance. Data points and uncertainty expressed as the average integrated signal and standard deviations for triplicate samples. (i) Schematic, (ii) laser-sheet flow visualization, and (iii) schlieren imaging of acetone vapor from a foam plug substrate for both (b) simple suction: AA1 off and (c) Venturi-assisted entrainment: AA1 on.

3.3 VENTI-MS Vapor and Aerosol Detection

Vapor detection was demonstrated with the VENTI system for a range of chemicals,

including organic solvents, methyl salicylate, peroxide-based, nitrate ester, and nitroaromatic

explosives. These samples were collected with the 1.0 m probe for AA1/AA2 pressures of 60 psi/40 psi (414 kPa/276 kPa) at an approximately 5 cm distance. Mass spectra with clearly identifiable peaks were rapidly obtained for methanol, ethanol, acetone, acetonitrile, acetic acid, and methyl salicylate. All were detected in positive mode as protonated ions, except acetic acid, which was detected in negative mode as a deprotonated ion (Figure S-3). In addition, real-time monitoring of a large room (approximately 90 m² area and 570 m³ volume) was demonstrated without the remote sampling probe, and under these conditions, AA2 generated the Venturiassisted entrainment. During the 60-minute monitoring, an ethanol squirt-bottle was used to rinse glassware approximately 3.2 m behind the VENTI-MS system, and was readily detected (Figure S-6). Similarly, to demonstrate a CWA leak, 100 μ L (770 μ mol) of methyl salicylate was deposited 2.9 m from the instrument and detected within 2 minutes (Figure S-6). Both examples extended the measured aerodynamic reach of the system, limited in the above studies by sampling time.

The vapor detection of select relatively volatile compounds was demonstrated in these proof-of-concept experiments, including HMDD (positive mode, Figure 4), NG (negative mode, Figure 4), EGDN (negative mode, Figure S-7), and DNT (negative mode, Figure S-7). Actual quantification of the detected amounts was not obtained for these proof-of-concept experiments and need to be investigated in the future. However, as a frame of reference, if each analyte experienced no losses during the solvent evaporation process, was in equilibrium with the surrounding air, and assumed ideal, based on their vapor pressures [44], these explosive vapor concentrations were in the range of hundreds of $\mu mol_{explosive} mol_{air}^{-1}$ (ppb) for DNT, NG, and HMDD. Again this overestimates the vapor concentration, indicating measurements likely down into the tens of nmol_{explosive} mol_{air}⁻¹

(ppb) range. Here, HMDD demonstrated strong signal in positive mode for the protonated molecule, as well as peaks associated with lingering acetonitrile solvent vapor. NG, EGDN, and DNT were all detected in negative mode, yielding adducts and ions typical of dc and ac atmospheric pressure chemical ionization [45, 46]. The nitrate esters, NG and EGDN, predominately formed adducts with available anions (m/z 46 NO₂⁻, m/z 62 NO₃⁻, m/z 61 HCO₃⁻, m/z 77 HCO₄⁻, etc.), while the nitroaromatic, DNT, formed anions through deprotonation and the loss of NO. The observed peroxymonocarbonate anion (m/z 77 HCO₄⁻) was identified in previous work using direct analysis in real time (DART) with nitrogen gas and MS/MS for confirmation, and readily formed adducts with nitrate ester explosives [47].

A TNT flake K9 training aid (5 g) was also detected with VENTI (2.5 m probe, AA1/AA2: 60 psi/40 psi (414 kPa/276 kPa)) in two experiments. The TNT flakes were on the order of several millimeters in size, however visible minute dust particulate was observed on surfaces and in the headspace of the plastic storage bag. First, VENTI was used to dislodge, aerosolize, and entrain the TNT dust particulate from the unsealed storage bag, demonstrating a significant TNT signal with expected peaks for the deprotonated and molecular anions, among others (Figure S-8). The volatilization of the solid state particle was attributed to the discharge ionization component. Similar non-equilibrium, low temperature dc and ac gas discharges (corona, glow, and dielectric barrier discharges) desorb and etch materials through energy transfer, ion impact, and interactions between the produced chemically active species (electrons, metastables, and radicals) and solid surface, in this case dust particulate [48-50]. However, further investigations are needed to fully understand the mechanisms for solid particulate aerosol vaporization and ionization, including memory effects and carryover from high concentration samples. Second, the TNT K9 training aid was placed in an open "stash tin" container in a carry-

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on suitcase (32 cm \times 48 cm \times 15 cm: 23 L) and zippered shut. Following a 2.5-hour period, VENTI was used to examine the region around the outside of the suitcase and zipper and then interrogate the interior of the suitcase (Figure 4). TNT was successfully detected from the interior of the suitcase, albeit at a much lower level than the dust particulate (approximately an order of magnitude lower). Given the lower volatility (vapor pressure) of TNT [44] and using the lossless and ideal assumptions described above, this detection was approximately 10 nmol_{explosive} mol_{air}⁻¹ (ppb), and clearly demonstrated all of the representative TNT ions observed in the particulate detection (Figure 4(f)).



Figure 4. VENTI-MS detection of HMDD and NG vapor with a 1.0 m probe and TNT from a carry on suitcase with a 2.5 m probe and AA1/AA2 of 60 psi/40 psi (414 kPa/276 kPa). (a)-(c) Extracted ion chronograms (XIC) of [HMDD+H]⁺, *m/z* 177; [NG+HCO₃]⁻, *m/z* 288; and [TNT-H]⁻, *m/z* 226. (d)-(f) Background subtracted mass spectra (orange and green boxes represent the extracted and background mass spectra, respectively). (*) denote peaks associated with remnant acetonitrile solvent. XIC data for TNT processed using a 21 point Savitsky-Golay filter (MATLAB R2015a, Mathworks Inc., Natick, MA, USA).

Finally, the VENTI-MS system was demonstrated for the collection and detection of

liquid-based aerosols. Discrete 10 µL to 20 µL aerosol plumes were generated using an

ultrasonic nebulizer (190 kHz, 20 V_{pp}), yielding aerosols with diameters on the order of single microns. The efficient collection and transport of aerosols plays a significant role in safety, security, and forensics fields for the detection of explosives, chemical warfare and CBRNE agents, and illicit narcotics, which form aerosols during dispersion or thermal desorption (commonly used in trace detection platforms) [13, 51]. Here, the ultrasonic nebulizer utilized to generate artificial aerosols was placed at a 20 cm axial distance and 10 cm above the horizon of the VENTI system (Figure 5(a)). Discrete aerosol plumes of DNT, METH, MDMA, and methyl salicylate were detected using a 2.5 m probe and 60 psi (414 kPa) for both the Venturi-assisted entrainment and sampling probe flow (Figures 5, S-9, & S-10). Figure 5 displays the extracted ion chronograms and mass spectra for successive 20 µL aerosol plumes of the deprotonated DNT (negative mode) and protonated METH (positive mode) ions. Desolvation (complete or partial) of the liquid aerosol droplets was expected to occur during their transit from nebulization to the ionization region, yielding gas phase molecules. However, losses due to adsorption and condensation on the transport line walls would benefit from heating of various components or gasses, including the Venturi-assisted entrainment component, the remote probe tubing, the flow control/ionization component, or the supply gas upstream of either Venturi device [31]. Similar to the collection of vapors from increasing stand-off distances, the time scale for entrainment of the aerosols across the 20 cm distance exceeded the rapid transport through the 2.5 m remote sampling probe. These results demonstrated the capability of the VENTI system to collect vapors and aerosols from remote locations at increasing stand-off distances and transport these neutral components through a corona discharge ionization region and into the mass spectrometer.



Figure 5. VENTI-MS detection of discrete 20 μ L aerosol plumes with a 2.5 m probe and AA1/AA2 of 60 psi/60 psi (414 kPa/414 kPa). (a) Schematic representation of experimental geometry and stand-off distance between ultrasonic nebulizer and VENTI (not drawn to scale). Extracted ion chronograms (XICs) and inset background subtracted mass spectra (orange and green boxes represent the extracted and background mass spectra, respectively) for (b) the deprotonated DNT anion (*m*/*z* 181) and (c) protonated METH cation (*m*/*z* 150). The ultrasonic nebulizer (USN) was operated at 190 kHz and 20 V_{pp}.

4. Conclusions

In this proof-of-concept study, we introduced the VENTI system, demonstrating efficient and real-time entrainment, collection, transport, and mass spectrometry detection of remotely sampled vapors and aerosols – capabilities imperative to the environmental monitoring, security, and forensic science sectors. VENTI exploited the Venturi and Coandă effects in robust air amplifier components that are compact and require no moving parts or vacuum pumps. Enhanced

aerodynamic reach, efficient entrainment, and transport were generated with only pressurized gas, opening avenues for field deployable configurations with a simple air compressor and coupling to portable/miniature mass spectrometers for check-point and battlefield implementation. Here, remote sampling probes up to 2.5 m were investigated, however, results and observations clearly indicated that rapid vapor and aerosol transport through significantly longer probes could be achieved – unlocking opportunities in large area and volume scanning, e.g., cargo and other bulk commercial transportation. VENTI's large volume entrainment, and robust and efficient operation also enables long-term continuous real-time monitoring of a stationary location, e.g., large facilities, specifically applicable to CWA, high volatility explosive (peroxides), and toxic industrial chemical detection. The VENTI system and its various conceivable configurations may play an important complementary role to the highly researched and widely deployed swipe-based trace residue and particulate collection/detection techniques.

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Appendix A. Supplementary Material

Additional VENTI-MS spectra and data, flow visualization videos, and figures as noted in the text can be found in the online version.

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