

Article

A Low-Cost, Simplified Platform of Interchangeable, Ambient Ionization Sources for Rapid, Forensic Evidence Screening on Portable Mass Spectrometric Instrumentation

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Abstract: Portable mass spectrometers (MS) are becoming more prevalent due to improved instrumentation, commercialization, and the robustness of new ionization methodologies. To increase utility towards diverse field-based applications, there is an inherent need for rugged ionization source platforms that are simple, yet robust towards analytical scenarios that may arise. Ambient ionization methodologies have evolved to target specific real-world problems and fulfill requirements of the analysis at hand. Ambient ionization techniques continue to advance towards higher performance, with specific sources showing variable proficiency depending on application area. To realize the full potential and applicability of ambient ionization methods, a selection of sources may be more prudent, showing a need for a low-cost, flexible ionization source platform. This manuscript describes a centralized system that was developed for portable MS systems that incorporates modular, rapidly-interchangeable ionization sources comprised of low-cost, commercially-available parts. Herein, design considerations are reported for a suite of ambient ionization sources that can be crafted with minimal machining or customization. Representative spectral data is included to demonstrate applicability towards field processing of forensic evidence. While this platform is demonstrated on portable instrumentation, retrofitting to lab-scale MS systems is anticipated.

Keywords: ambient ionization; portable mass spectrometry; portable instrumentation; desorption electrospray ionization (DESI); paper spray ionization (PSI); paper cone spray ionization (PCSI); atmospheric pressure chemical ionization (APCI); swab touch spray ionization (STSI); modular ion sources; forensics; drug evidence; arson

1. Introduction

Portable instrumentation, such as mass spectrometry (MS), has been of increased interest to the broader scientific community due to the inherent capability of performing in-situ analyses [1,2]. Additionally, the smaller footprint of portable instrumentation compared to their laboratory-based, “benchtop” counterparts allows for transportation to locales of interest. A review of current literature shows particularly high activity in regards to portable MS instrumentation and application development amongst the environmental [3,4], forensic [5–9] and defense [10,11] communities.

Portable MS systems are of particular interest across fieldable instrumental platforms due to the sensitivity, specificity, and rich chemical information provided by the technique, particularly tandem MS analysis [12,13]. A recent review of miniaturized MS systems outlined and compared the major research directions and entities offering commercial platforms [2].

Interestingly, a major uptick in applicability of portable MS systems has been recently seen, not from major instrumental modification (e.g., vacuum system, mass analyzer), but from advances in ionization source technology, particularly ambient ionization [14]. Ambient ionization mass spectrometry, or “ambient MS,” in which analyte ions are created in the ambient environment from unprepared samples, arose with the development of desorption electrospray ionization (DESI) [15] and direct analysis in real time (DART) [16]. As ambient MS allows sample examination in its native state with little to no sample preparation, such as explosive residues on luggage [17] or fingerprints [18] or drug residues from clandestine drug lab apparatus [19], the forensic community continues to pursue adoption [20] and expansion of these techniques towards portable devices [7,21–23]. A number of recent reviews outlining forensic applications of ambient MS have been published [23–27]. Since the advent of DESI and DART, the last decade has seen an influx of new ambient MS methodologies, such as desorption atmospheric pressure chemical ionization (DAPCI) [28,29], paper spray ionization (PSI) [30], paper cone spray ionization (PCSI) [31], swab touch spray ionization (STSI) [32], low temperature plasma (LTP) probe [33], and flowing atmospheric pressure afterglow (FAPA) [34], to identify a few. Recent reviews have chronicled the development of these new ionization methods, with the number of demonstrated sources increasing every year [31,35–38].

Since the first report of ambient ionization on a portable MS system [39], researchers have sought to provide the reliability, ruggedness and usability that is required for practical in-situ analysis by non-technical operations (e.g., forensic practitioners, law enforcement officers). Subsequently, validation efforts in this realm have sought to assess competency towards adoption in the forensic sciences [20,22,40–42], for which there is an inherent need for court admissibility and method standardization. Steering committees such as the Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) [43] provide recommendations for method standardization and general classification; note that mass spectrometry (in the form of gas chromatography/mass spectrometry, or GC/MS) is considered a “Category A” technique, which is the highest ranking. Recent efforts to meet the selectivity requirement for Category A classification via ambient MS are of note, such as the coupling of PSI-MS with surface-enhanced Raman spectroscopy [44]. Forward-thinking examinations into the legality of using portable, ambient MS systems in routine law enforcement activities have also been reported [6], as well as the utility afforded by employing interchangeable, ambient ionizations sources on portable MS systems for broad chemical evidence processing [22].

The rigor and variable nature of field-borne sample processing can be burdensome, but ambient MS techniques continue to advance towards higher performance, with specific sources showing chemical and/or matrix-specific proficiency depending on the application area. To realize the full potential and applicability of ambient MS, a selection of sources may be more prudent, showing a need for a low cost, flexible ionization source platform. To this end, a centralized mounting system was developed for portable MS instrumentation that incorporates modular, rapidly interchangeable ionization sources comprised of low-cost, commercially-available parts. Herein, design considerations are reported for a suite of ambient ionization sources that can be crafted with minimal machining or customization. Representative spectral data is included to demonstrate applicability towards field processing of forensic evidence. While this platform is demonstrated on portable instrumentation, retrofitting to lab-scale MS systems is anticipated.

2. Materials and Methods

2.1. Portable MS System and Ambient Ionization Sources

All ionization source development and applications were performed upon the FLIR Systems AI-MS 1.2 cylindrical ion trap (CIT) mass spectrometer (FLIR Mass Spectrometry, West Lafayette, IN USA), a fieldable, commercially-available system that has been ruggedized for in-situ analysis in harsh environments [11]. Figure S1 provides photos for scale, as well as extraneous, instrument specific information. System dimensions ($60 \times 50 \times 40$ cm, L \times W \times H) and weight (~ 45 kg), including all required peripherals for ambient ionization sources, is in line with fieldability requirements [2,45]. The AI-MS 1.2 can be operated in both positive and negative ion mode, utilizing MS/MS spectra for accurate chemical identification, which is afforded by the CIT mass analyzer. The miniaturized vacuum system of this instrument has relatively low power requirements, yet still maintains a capillary-based, atmospheric pressure inlet, which allows coupling to traditional spray-based ionization methods (e.g., electrospray ionization (ESI)) and newer ambient MS techniques. The AI-MS 1.2 platform comes with a factory-stock ESI/DESI combination ion source [46], which is detailed further in the Supplementary Materials, as it is not the focus of this work. Figure S2–S5 provide additional information, as well as sampling considerations of DESI-MS.

Development of ambient ionization sources focused on techniques that have shown high proficiency in the fields of forensic analysis, but more importantly, are noted by their simplicity of use and minimal consumable requirements. Specifically, PSI, PCSI, STSI, and atmospheric pressure chemical ionization (APCI) sources were developed, as all necessary voltages and syringe pumping requirements (for STSI) are inherent to the AI-MS 1.2 platform. No extraneous power supplies or pressurized gases are needed, enhancing overall portability. Note that the selection of ion sources developed herein, while diverse, do not represent an exhaustive list of methodologies that are or could be made inherently portable. Each constructed ionization source is described in detail below, providing design considerations, part descriptions, and representative data from samples of forensic interest and authentic evidence types. Furthermore, vendor/part information and overall cost breakdowns are delineated in Table S1 for quick reference. Consumable cost per sample (for swabs and cones) can be seen in Table S2.

For all ionization sources that employ spray solvent [ESI, DESI, PSI, PCSI, and STSI], a composition of 1:1 MeOH:H₂O with 0.1% formic acid was used; note that many solvent systems that are employed in LC-MS are typically compatible with ESI, DESI, PSI and PCSI. Spray or discharge voltage (for APCI) was set at 4 kV for all sources. All data reported herein was collected in positive ion mode.

2.2. Centralized Mounting System for Interchangeable Ion Source Modules

To allow quick interchangeability of ionization sources, akin to “plug and play” operation, a centralized, rail-based mounting/positioning system was implemented. Using stock optics parts from Thorlabs Inc. (Newton, NJ, USA), a universal base plate (CPVM) was adhered to the front fascia of the AI-MS 1.2, as depicted in Figure 1. This base plate uses a 4-rod cage assembly (ER6-P4), upon which a modular, 30 mm cage cube (C6W) can quickly slide on and off. This cage cube serves as the base for each ionization source developed, creating independent ionization “modules”. The blank cage plate (CP01) seen in Figure 1 is optional, but does serve to add structural support and vibration resistance to the overall cage assembly. This mounting system, while specifically developed for the AI-MS 1.2, could also be implemented on several other commercial (e.g., Thermo (Waltham, MA, USA), Sciex (Washington, D.C, USA), etc.) and portable (e.g., MT Explorer 50 (Masstech, Columbia, MD, USA), Acquity QDa (Waters, Milford, MA, USA), etc.) MS systems. As the overall weight of this mounting system is low (<1 lb), high performance epoxy could potentially be used in lieu of screw mounting. Note that care should be taken so any remaining warranty is not voided or internal components/electronics are damaged. Further, as with all home-built ionization source development, safety precautions could be of interest to users to avoid shock and discharge to MS instrumentation.

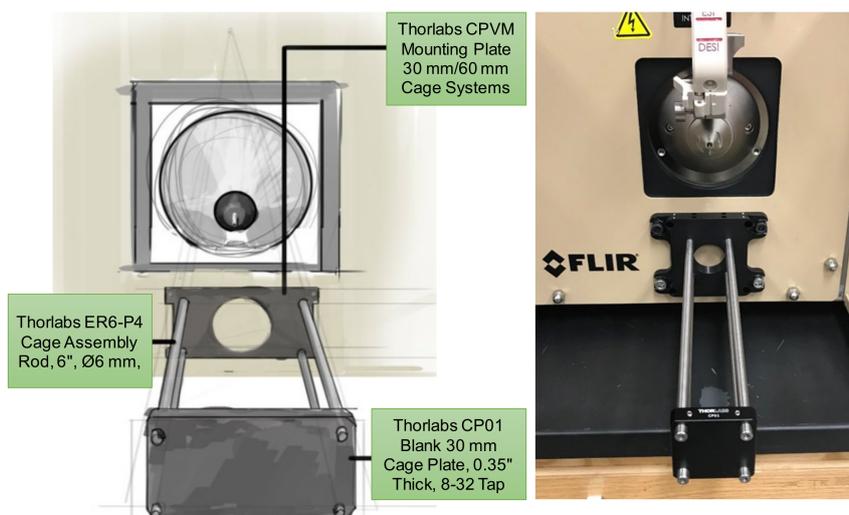


Figure 1. Centralized, rail-based mounting system to allow “plug-and-play” style operation of modular paper spray ionization (PSI), paper cone spray ionization (PCSI), atmospheric pressure chemical ionization (APCI), and swab touch spray ionization (STSI) sources, based upon stock optical consumables from Thorlabs Inc. (Newton, NJ, USA). The vertical mounting plate is attached directly with minor modification to front plate of FLIR AI-MS. The cage assembly rods are attached to the mounting plate and secured by the blank cage plate.

3. Results and Discussion

3.1. Paper Spray Ionization (PSI)

Paper spray ionization (PSI) [47], which employs mechanistic aspects of both paper chromatography and electrospray ionization, utilizes a triangularly-cut paper or porous substrate as a disposable ionization source. Analytes of interest can be investigated through a myriad of sampling strategies, such as deposition via pipetting, swabbing or dipping, and the swab itself can be used as a surface-transfer medium to investigate bound, trace residues [6,19]. Addition of a small aliquot (1–2 μL) of solution (e.g., 1:1 MeOH:H₂O with 0.1% formic acid via pipette) and high voltage allows analyte dissolution and wicking/elution to the triangular egress of the paper, from which an ESI-like spray is generated [48]. As there is no need for pneumatics or extensive sample preparation, it is one of the simplest techniques for coupling to portable MS systems. PSI has been applied broadly in the forensic community, such as quantitative determination of abused drugs in whole blood [40] and rapid detection of explosives [49] and chemical warfare agent simulants [50]. It has been shown highly proficient towards drug evidence screening on portable MS systems, as well [9,19,22,51]. Current efforts towards substrate modification are also of interest [52,53], as they offer the capability for advanced sampling strategies that should prove interesting to the forensic community.

The constructed PSI-MS module (seen in Figure 2) is built upon a ThorLabs universal base plate (UBP2) fastened to a cage cube (C6W) using four stainless steel (SS) 4-40 thread screws. High voltage application to the employed paper substrate is accomplished with a simple “alligator-style” clamping electrode that is attached to a x-y-z translational positioning system (OptoSigma, Santa Ana, CA, USA); note that there are many suppliers of similar translational stages. This allows positioning of the PSI paper substrate (Millipore MQuant blank testing strips, Fisher Scientific, Waltham, MA, USA) relative to the MS capillary. Bulk 6066 aluminum block was machined to provide adequate height of the positioning system from the universal base plate; this height will be specific to the MS system employed. For additional utility, a polytetrafluoroethylene (PTFE) tube union cross fitting (UC-F-4, iPolymer, Inc., Irvine, CA, USA) was fastened to the vertical (z) positioner of the stage. Inside the union, the HV cable terminates in a bullet-style, quick-snap connector. Soldering of the corresponding

female connector to alligator clamping electrode then allows the user to quickly switch out this part for hygiene/carryover remediation; note that this modification is not required for performing PSI-MS analysis. A side profile view of the source module can be seen in Figure S9.

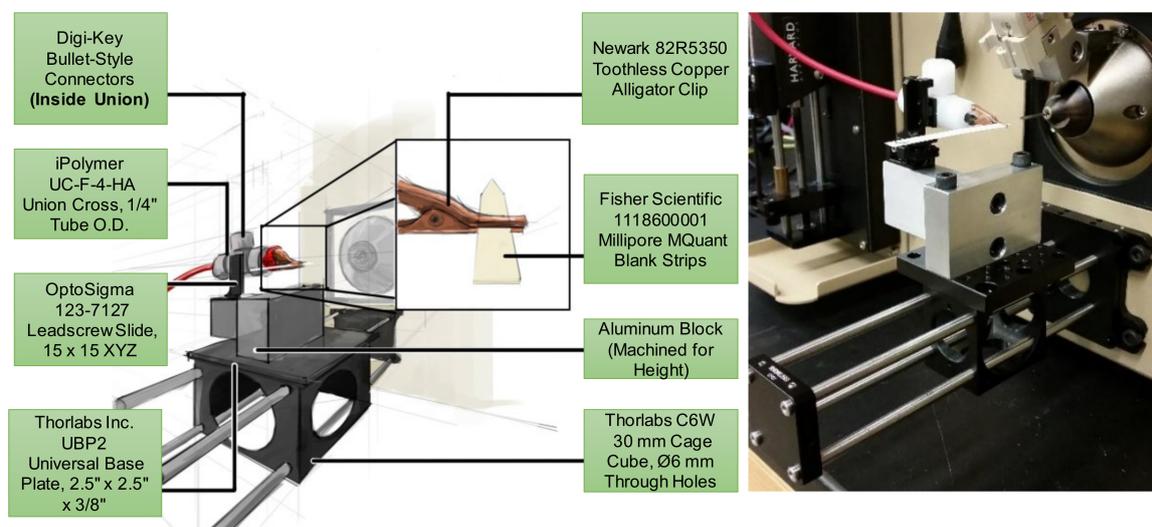


Figure 2. Simplified paper spray ionization (PSI) source module built upon the ThorLabs cage cube for the centralized mounting system. High voltage is supplied via alligator clip, which is held in place and positioned via a stock x-y-z positioner (OptoSigma). A simple Teflon union (iPolymer) is used to insulate the high voltage cable of the MS system, which terminates in a bullet-style connector that allows quick-swapping of alligator clips. Application of solvent by the user via pipette and high voltage to the paper substrate utilized produces analyte ions via electrospray-like processes. Said paper substrate can be used for dipping, spotting or physically transferring via surface swabbing chemicals of interest.

Figure 3 shows representative data collected with modular PSI source. Figure 3 depicts the resultant spectra obtained after using a paper substrate to gently swab the interior of a storage bag containing bulk heroin evidence. PSI-MS spectra are marked by its simplicity, here yielding the protonated molecule, $[M + H]^+$, for heroin at m/z 370. Corresponding PSI-MS/MS spectra (Figure 3B) of the protonated precursor ion produces characteristic fragmentation that can be used for accurate chemical identification. Figure 3C depicts the analysis of injectable drug evidence containing morphine sulfate via PSI-MS; here, the liquid phase drug was spotted directly on the paper substrate via the syringe paraphernalia it resided in. PSI-MS/MS collected for both heroin and morphine were highly similar to that reported in literature [54]. Photos of the authentic evidence analyzed via PSI-MS can be seen in Figures S6 and S7 for rock heroin and injectable morphine sulfate, respectively.

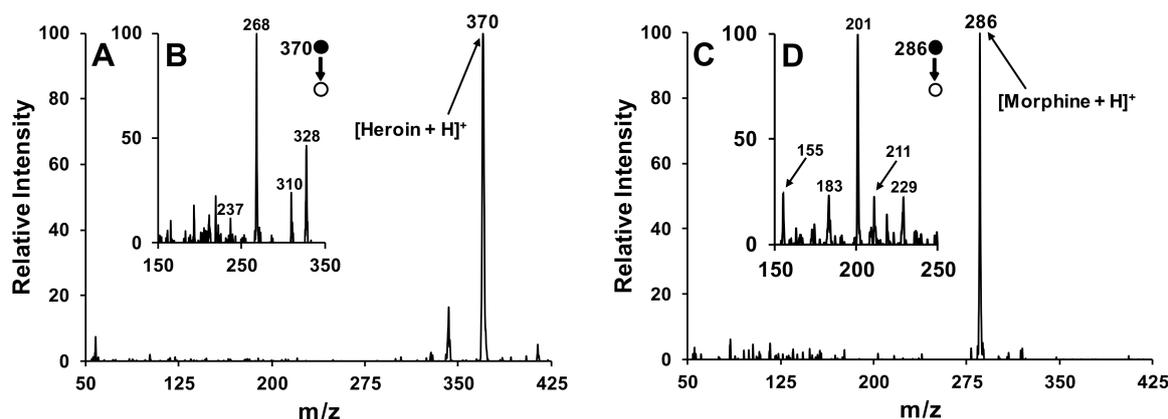


Figure 3. (A) PSI-MS spectrum from a swab used to probe heroin evidence, displaying the protonated molecule, $[M + H]^+$, at m/z 370. (B) Corresponding PSI-MS/MS spectrum of the protonated precursor ion, yielding characteristic fragmentation used for chemical identification. (C) PSI-MS spectrum collected from an injectable solution of morphine sulfate, displaying the protonated molecule at m/z 286. (D) Corresponding PSI-MS/MS spectrum of protonated morphine, yielding characteristic fragmentation.

3.2. Paper Cone Spray Ionization (PCSI)

Paper cone spray ionization (PCSI), a three-dimensional variant of PSI, employs a hydrophobic wax paper cone as both the sample holder, extraction chamber, and disposable ionization source [31]. Solid analytes (e.g., bulk powders, psychotropic plants, etc.) can be placed into the triangular pyramidal structure, in which an in-situ solid-liquid extraction occurs upon the addition of solvent (e.g., ~100 μ L of 1:1 MeOH:H₂O with 0.1% formic acid); methodologies for hand-folding these cones have been reported by Kim and Cha [31]. Similar to PSI, a high voltage is then applied to perform spray-like ionization of dissolved analytes from the pyramidal egress, with no need for pneumatic assistance. PCSI is a relatively new technique, but it has already been applied to food products such as ground beef and tea leaves [31], abused pharmaceutical tablets [22], and medicinal herbs [55]. As a majority of forensic evidence encountered in the field would be in bulk phase (e.g., powders, crystals), PCSI is a promising in-situ analysis for seized drugs for its simplicity and minimalistic preparation requirements.

The constructed PCSI-MS module (seen in Figure 4) is built upon a ThorLabs universal base plate (UBP2) fastened to a cage cube (C6W) using four SS 4-40 thread screws. To provide the proper height and angle in relation to the inlet capillary of the MS system employed, two optical construction posts (ThorLabs, TR3T) were fastened to the base plate; angular positioning of the PCSI source in relation to the MS inlet was shown to be fairly robust, with 20–60° producing relatively similar ion signal. For routing and securing the HV cable, a ThorLabs right angle clamp (RA90) and threaded adaptor (AI25E8E) was used. Using an alligator clamping electrode fashioned to the HV cable allows one to secure the conical ionization of PCSI, while also delivering the required high voltage.

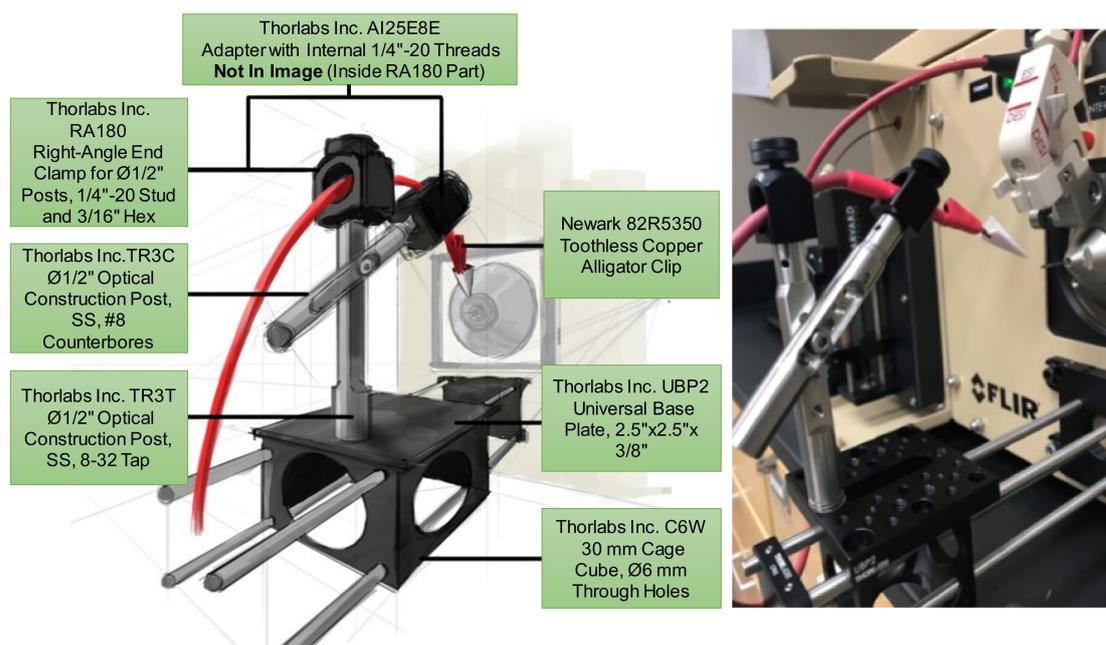


Figure 4. Simplified paper cone spray ionization (PCSI) source module built upon the ThorLabs cage cube for the centralized mounting system. Optical construction posts and adapters allow positioning of the alligator clip that serves to hold the conical ion source volume and supply high voltage. Application of spray solvent to the conical volume allows dissolution of the bulk sample placed within, followed by spray ionization at the pyramidal egress of the source.

Figure 5 shows PCSI-MS and MS/MS spectra collected directly from Suboxone[®] sublingual film, a pharmaceutical-grade opioid deterrent. By simply folding the film and placing it into the pyramidal structure, addition of spray solvent generates highly intense ion signatures for the active ingredients naloxone (m/z 328) and buprenorphine (m/z 468). A photo of this evidence can be seen in Figure S8.

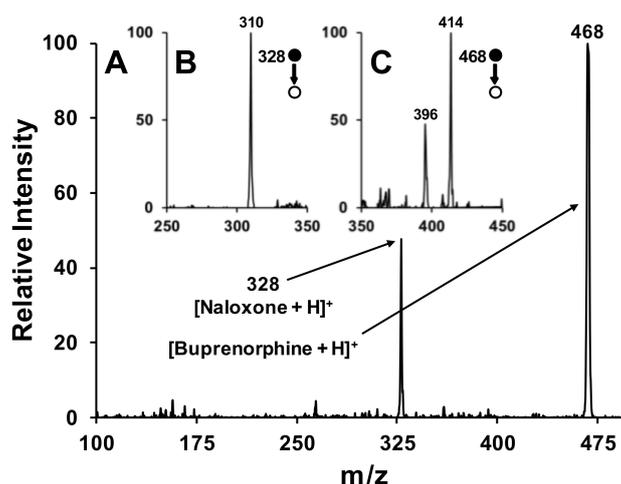


Figure 5. (A) PCSI-MS spectrum collected directly from Suboxone[®] sublingual film, a prescribed treatment for opioid addiction. Addition of the film to the conical volume of the source and spray solvent produces intense ion signatures for protonated naloxone (m/z 328) and protonated buprenorphine (m/z 468). Corresponding PCSI-MS/MS spectra from (B) naloxone and (C) buprenorphine yield fragmentation patterns similar to that reported in literature [56,57].

3.3. Swab Touch Spray Ionization (STSI)

Swab Touch Spray Ionization (STSI) utilizes a rayon swab or alternative swabbing substrate that specifically has a metallic handle. The surface-bound analytes are adsorbed via physical transfer onto said substrate after moving the swab over the surface of interest. A continual flow of solvent is applied to the swab tip along with high voltage through the metallic handle to initiate ionization [32]. Like both PSI and PCSI, there are no pneumatics or sample preparation required, barring the physical transfer event. STSI has been applied to bacterial [58] and drugs of abuse [59] detection in oral fluids, as well as the detection of organic gunshot residues from a variety of surfaces, including the hands of individuals after firearm discharge [32]. Specific benefits of STSI include the ability to collect samples from rough surfaces that can damage PSI paper substrates and the propensity for very stable spray ionization from the swab itself (e.g., extended spray durations). Of note, swab-based sampling is already used extensively by the forensic community, so there is less of a conceptual barrier [32].

The constructed STSI-MS module (seen in Figure 6) is built upon a ThorLabs universal base plate (UBP2) fastened to a cage cube (C6W) using four SS 4-40 thread screws. To provide the required height in relation to the MS inlet capillary, an optical post (ThorLabs, TR8) was used in a similar fashion as the PCSI module. Onto the optical post, a right-angle clamp (RA90) was attached to secure the HV cable, terminating with an alligator clamping electrode, in place. This electrode clamps directly to the swab handle itself, and height is adjusted so that the swab head is ~1 cm above the inlet. Solvent is flowed to the swab through fused silica capillary, which is connected to the onboard syringe pump of the AI-MS 1.2. As seen in the depiction, a slight customization was employed to protect the delicate silica capillary and secure contact to the swab head; note that this feature is not required to perform STSI-MS. A small piece of 6066 grade aluminum block was bored to the outer diameter of 1/16" SS tubing (IDEX, U-102), which is held in place by a set screw. This SS capillary sheath was bent to the appropriate angle to route the silica capillary (which is passed through the inner diameter of the capillary) to the swab head. The aluminum block was then spot-welded to the alligator clamping electrode. As all parts are conductive, HV still routes to the swab head to initiate spray ionization directly from the swab medium.

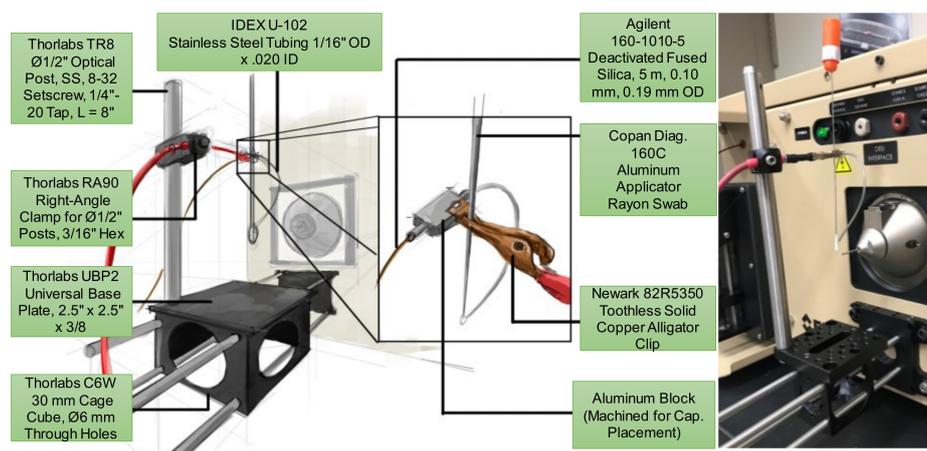


Figure 6. Simplified swab touch spray ionization (STSI) source module built upon the ThorLabs cage cube for the centralized mounting system. Similar to the PCSI source, an optical post is used to adjust positioning height of the alligator clip electrode. Depicted here is a machined clip modification, which is optional, that serves to route the fused silica, solvent delivery line running from the on-board syringe pump. A small section of stainless steel tubing, bent to an appropriate angle to maintain the position of the silica capillary in proximity to the sampling swab, is used to protect the glass-based delivery line. The high voltage applied via the alligator clip transfers directly to the wetted swab via its metallic shaft. Once adequate solvent saturates the swab, electrospray-like mechanisms produce ions from chemicals transferred to said swab during a sampling event.

Figure 7 shows representative STSI-MS spectra obtained from ethyl centralite, an organic gunshot residue commonly found on the hands and clothing of individuals who have discharged a firearm. Here, the STSI swab was used to probe a 400 ng ethyl centralite residue deposited onto the finger pad of an individual. Observed ions include the expected protonated form of ethyl centralite (m/z 269), but also a sodiated adduct at m/z 291. The propensity for alkali earth metal adducts in spray-based, ambient MS sources is commonly seen from real matrices, particularly in fingerprint oils.

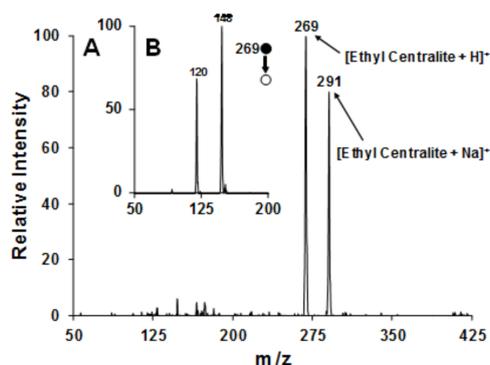


Figure 7. (A) STSI-MS spectrum collected after swabbing a trace, surface-bound residue of ethyl centralite, an organic component of gunshot residue. Both protonated (m/z 269) and sodiated (m/z 291) ethyl centralite is observed, as alkali earth metals can be abundant from authentic sample matrices and surfaces. (B) STSI-MS/MS of protonated ethyl centralite (m/z 269), yielding a simple, yet highly specific fragmentation pattern.

3.4. Atmospheric Pressure Chemical Ionization (APCI)

Direct air monitoring and headspace analysis has been demonstrated on portable MS systems by utilizing simplified atmospheric pressure chemical ionization (APCI) sources [60,61], including trace detection of toxic industrial compounds from room air [62,63] and headspace vapors of common solvents utilized in clandestine drug manufacture [19,22,64]. APCI, first reported by Horning et al., commonly employs a corona discharge to create primary reagent ions (typically a series of protonated water clusters, depending on relative humidity) via ion/molecule reactions starting with N_2^+ and O_2^+ [65]. Said protonated water clusters then go on to protonate (in positive ion mode) gas-phase analytes present in the corona region via charge exchange mechanisms, when energetically favorable [66]. Corona discharge can be produced in a minimalistic fashion, as only a discharge needle (e.g., tungsten wire) and DC HV under resistance is needed.

The constructed APCI-MS module (seen in Figure 8; photos can be found in Figures S10–S12) is built upon a ThorLabs universal base plate (UBP2) fastened to a cage cube (C6W) using four SS 4-40 thread screws. The corona discharge capillary (created from a 1 cm section of Hamilton syringe cleaning wire soldered into a 1/16" SS capillary) is housed within a PTFE body (iPolymer FRT-F-42-HA [female] and MRT-F-42-HA [male] run tees) for safety; internal views of the discharge needle and ionization volume can be seen in Figures S13 and S14. The corona discharge needle is held in close proximity (~1 cm) to the MS inlet, which serves as the counter electrode after application of 4 kV DC. Note that caution must be taken in order to prevent direct arcing to the inlet capillary, which could prove detrimental to the MS system. The exposed section of SS tubing (which extends out of the PTFE body) is where the HV cable is attached. This can be done in a variety of ways, including an alligator clip. Note that a more effective, current-controlled corona discharge is generated when resistance is applied in series to the discharge needle (100 M Ω resistor, 1.5 W, 66k6838, Newark, Inc., Chicago, IL, USA); this also offers some protection from unwanted arcing to the MS inlet. To provide the height relative to the MS inlet and rigidity of the ionization chamber, a ThorLabs optical post (TR1) was used to mount a machined aluminum plate to the universal base plate. This aluminum plate can be used to secure the ionization volume via screw clamps (CL3/M, Thorlabs) and inhibit misalignment of the

discharge needed relative to the MS inlet. The exact footprint and thickness of the aluminum plate can be matched to the instrument in question.

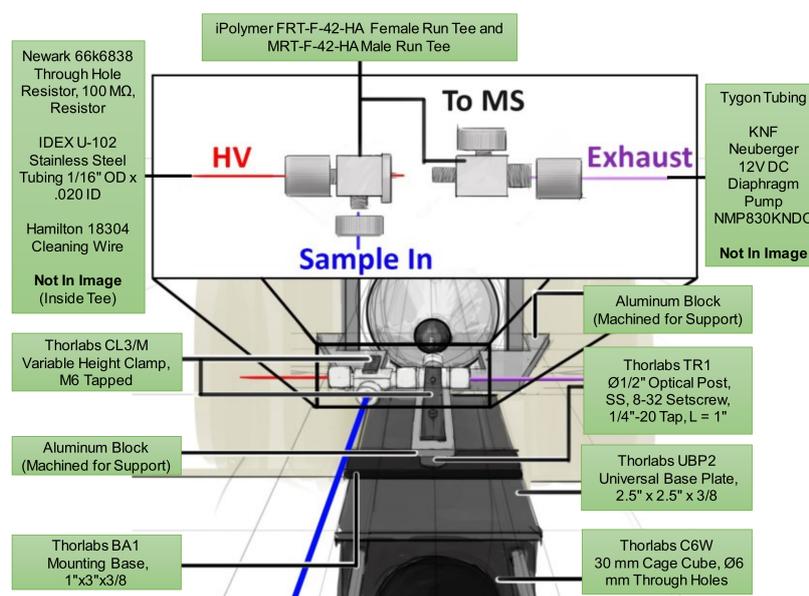


Figure 8. Simplified atmospheric pressure chemical ionization (APCI) source module built upon the ThorLabs cage cube for the centralized mounting system. A PTFE chamber is used to house a corona discharge needle and position it in proximity to the MS inlet capillary. The discharge needle is soldered to a stainless steel capillary for rigidity. High voltage is applied to the exposed portion of the discharge needle through an alligator clip electrode; a 100 MΩ resistor is soldered in series with the high voltage cable to produce a more effective corona discharge between the discharge needle and inlet capillary. The PTFE chamber is produced from tee unions, allowing an inlet for gas samples to be pulled through the source volume and exhausted via a small diaphragm pump and Tygon tubing. The PTFE chamber rests on an aluminum base that was machined to match the form factor on inlet system of the AI-MS 1.2. Overall height is controlled so that the discharge needle and inlet capillary align by an optical post.

To allow for the grab sampling of headspace vapors or emanating gases, a crude gas sampling system can be simply made from tygon or PTFE tubing through the available ports of the ionization chamber employed. Gaseous samples can be pulled through the discharge region for analysis (and subsequently exhausted) via a small external pump. For this source, a miniature, 12 V DC diaphragm pump (NMP830KNDC, KNF Neuberger, Trenton, NJ, USA) capable of ~3 L/min flows was employed for this purpose.

Figure 9 shows representative APCI-MS spectra obtained via grab sampling with the modular source. For Figure 9A, mock arson evidence was generated by burning pine wood in the presence of acetone as an accelerant. The charred wood sample was placed in an enclosed vessel so that headspace vapors could be formed, which were then subsequently sampled via external pumping. Headspace analysis produces rich spectra, including protonated acetone in the monomeric (m/z 59), hydrated (m/z 77), and dimeric (m/z 117) forms. The natural product pinene from the wood materials can be seen as both protonated (m/z 137) and hydrated (m/z 166) ions. Application to carpet-based arson evidence was also examined. Figure 9B shows nylon-based carpeting that was burned in the presence of ethanol as an accelerant. Headspace analysis via APCI-MS yielded the protonated ethanol dimer (m/z 93), but also interesting signatures from the carpet matrix. Spectral peaks at m/z 114 were tentatively identified as protonated caprolactam, which is a known degradation product from the nylon polymer used in construction of the carpet [67].

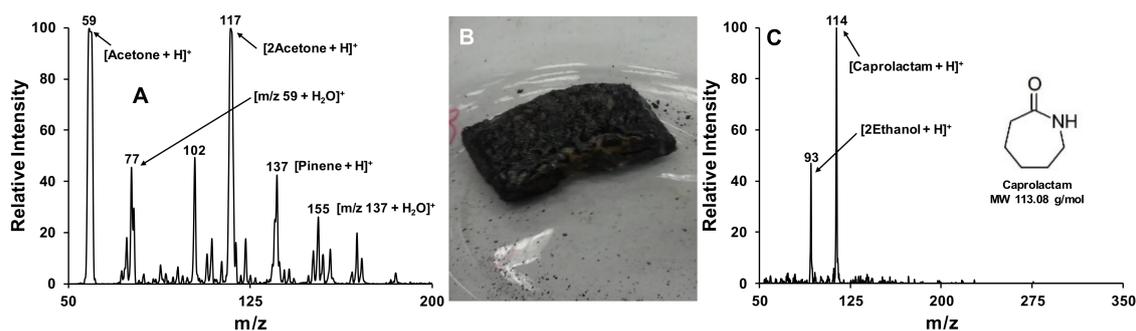


Figure 9. (A) APCI-MS spectrum collected from the gaseous headspace emanating from charred pine wood that was burned using acetone as an accelerator. Headspace analysis produces rich spectra, including the protonated acetone in the monomeric (m/z 59), hydrated (m/z 77), and dimeric (m/z 117) forms. The natural product pinene from the wood materials can be seen as both protonated (m/z 137) and hydrated (m/z 166) ions. (B) Photo showing a charred, nylon carpet sample burned in the presence of ethanol as an accelerator. (C) APCI-MS spectrum collected from the gaseous headspace emanating from the charred carpet sample, displaying the protonated ethanol dimer (m/z 93). Also seen is protonated caprolactam (m/z 114), which is a degradation product from the nylon polymer used in construction of the carpet.

4. Conclusions

In this work, design considerations are reported for a suite of ambient ionization sources that can be crafted with minimal machining or customization. The novelty of the modular, interchangeable design implemented could prove highly useful when coupled with portable MS instrumentation, particularly in application areas like forensic investigation where samples can be highly variable in nature.

As seen in Table S1, the centralized mounting system and PSI, PCSI, STSI, and APCI modules can be crafted for less than \$2000 (per current pricing) and with minimal to no machining required; minor machining of custom parts, as shown herein, can enhance the overall usability of the sources, but is not required. A majority of peripherals used are common scientific parts, and even if the specific part/items reported here become obsolete or unavailable from the specified manufacturer, an analogous, commercial solution should be easily identified. Furthermore, while this platform is demonstrated on portable instrumentation, retrofitting to lab-scale MS systems is anticipated.

As the breadth of known ambient MS techniques increases, many should prove adaptable to this modular mounting system. For instance, techniques like desorption atmospheric pressure chemical ionization (DAPCI) [68], LTP [69], atmospheric pressure photoionization (APPI) [70], and easy ambient sonic spray ionization (EASI) [71] could prove adaptable, but may necessitate external compressed gas and power requirements. Simple platforms that are both frugal and expandable, such as that reported herein, could prove to be a catalyst towards full adoption by field practitioner communities.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2410-390X/2/2/5/s1>, Table S1: Part List and Estimated Cost for Modular Ionization Sources, Table S2: Estimated Cost (per Sample) for Swab and Cone Consumables, photos of forensic evidence analyzed (Figures S6–S8), and alternate views of the modular ionization sources to guide construction (Figures S9–S14).

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spray ionization, and atmospheric pressure chemical ionization sources, respectively. Christopher C. Mulligan was primary investigator for this work, and all instrumentation development and application was conducted in his laboratory.

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