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Sampling Wand for an Ion Trap Mass Spectrometer

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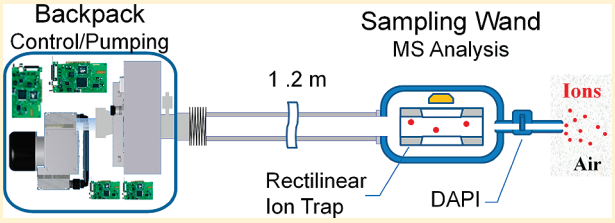
ABSTRACT: A new sampling wand concept for ion trap mass spectrometers equipped with discontinuous atmospheric pressure interfaces (DAPI) has been implemented. The ion trap/DAPI combination facilitates the operation of miniature mass spectrometers equipped with ambient ionization sources. However, in the new implementation, instead of transferring ions pneumatically from a distant source, the mass analyzer and DAPI are separated from the main body of the mass spectrometer and installed at the end of a 1.2 m long wand. During ion introduction, ions are captured in the ion trap while the gas in which they are contained passes through the probe and is pumped away. The larger vacuum volume due to the extended wand improves the mass analysis sensitivity. The wand was tested using a modified hand-held ion trap mass spectrometer without additional power or pumping being required. Improved sensitivity was obtained as demonstrated with nano-electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and low temperature plasma (LTP) probe analysis of liquid, gaseous, and solid samples, respectively.



Mass spectrometry (MS) is characterized by high sensitivity and high specificity but often involves extensive sample preparation and is almost always done in a laboratory setting. The standard paradigm is gradually being broken with the availability of miniaturized MS systems[1,2] and simplified analysis procedures.[3,4] The former involved a major effort in the miniaturization of the mass analyzers[5−10] and, more recently, the entire instruments;[11−14] the latter is currently being addressed in the fast growth of ambient ionization methods.[3,15−19] Sampling probes based on ambient ionization methods have been developed for lab-scale mass spectrometers.[20−28] Analyte ions generated in the atmosphere can be transferred into the mass analyzer using auxiliary pumping systems even over distances of some meters, but significant losses of signal occur.[20,21] Due to the restricted power and weight of miniature MS systems, these previous designs of sampling probes are not suitable for small instruments which cannot handle high flux gas flows.

Efficiency of ion transfer is currently a major limitation in the performance of miniature mass spectrometers. For these systems, ions generated in air need to be transferred into a poorly pumped manifold. Discontinuous introduction of ions (with accompanying air) is a general solution to the low pumping speed problem. The present sampling wand design takes advantage of the unique features of both the ion trap mass analyzer[29] and the discontinuous atmospheric pressure interface (DAPI).[30−32] The DAPI opens briefly (10 ms) during the ion introduction period. The gas flow rate is significantly larger than the pumping speed during that time, and the ions are trapped at elevated pressure. During the subsequent delay period (several hundred milliseconds) after the DAPI closes, the pressure decreases and then mass analysis is performed. DAPI interfaces have enabled the coupling of atmospheric pressure ionization sources to miniature ion trap mass spectrometers with extremely compromised pumping capacity.[33]

CONCEPT AND INSTRUMENTATION

In this work, we explore a sampling wand configuration for portable MS systems with ambient ionization capabilities. By analogy with the backpack vacuum cleaner, a backpack MS configuration optimizes weight distribution and ease of operation. The main weight of the instrument is in the backpack, while the sampling wand is hand-held and can easily be swept across surfaces of interest. A schematic design of the wand is shown in Figure 1. Instead of transferring neutrals and analyte ions over long distances, the ion trap mass analyzer and the DAPI are separated from the pumping system and installed close to the sample. When the DAPI is open, the ion-containing gas passes through the ion trap and the ions are trapped while the gas is pumped away. This configuration makes the ion trap act as an ion filter and as an ion concentrator.

This configuration inevitably results in an expanded vacuum volume of the mass spectrometer, which is not desirable in a traditional mass spectrometer system; however, for a miniature instrument with a DAPI, the use of larger vacuum volumes can be advantageous. In a recent study,[32] we showed via a theoretical derivation that the number of ions introduced into a manifold using a DAPI is proportional to the vacuum volume (V_{vacuum}) and the maximum allowable pressure (P_{max}) (eq 1).

$$n = \frac{P_{max} V_{vacuum}}{RT} \quad (1)$$

The manifold of the mass spectrometer fitted with a DAPI serves as a vacuum capacitor, which is "recharged" with gas (n mol) containing ions each time the DAPI opens. The maximum allowable

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pressure P_{max} of the vacuum is the highest pressure at which ions can be efficiently trapped in an ion trap; this is estimated to be about 1 Torr.[34] A vacuum system of larger volume allows more gas to be introduced via the DAPI before reaching the same pressure. With the same amount of gas introduced into the vacuum, the higher the flow rate, the higher is the percentage of ions surviving the transfer step.[35] Therefore, to introduce more ions for mass analysis, it is preferable to operate the DAPI using a larger capillary instead of a longer opening time.

To test these concepts, a hand-held rectilinear ion trap mass spectrometer, Mini 11,[33] was modified with a flexible bellow tube (1.2 m long and 25 mm ID, stainless steel) added between the mass analyzer chamber and the turbo pump. The DAPI, the ion trap mass analyzer, and the electron multiplier were moved to the end of the wand, while the pumping, power, and control systems were kept in the main body of the instrument. The total vacuum volume was increased by about three times. The original flow restricting capillary (5 cm long, 250 μm ID) used in the Mini 11 was replaced with a 10 cm, 500 μm ID capillary, corresponding to an 8-fold increase in flow conductance. Remarkably, the flow conductance is comparable with that of *a commercial lab-scale* linear quadrupole ion trap (LTQ) mass spectrometer (Thermo Fisher Scientific, Inc., San Jose, CA) with an inlet capillary of 10 cm long and 500 μm ID; however, the pumping system of the Mini 11 is composed of a 10 L/s trubomolecular pump (Pfeiffer HiPace 10, Pfeiffer Vacuum Inc., Nashua, NH) and a 5 L/min diaphragm pump (1091-N84.0-8.99, KNF Neuberger Inc., Trenton, NJ), providing a pumping capacity several hundred times less than that of an LTQ. During the opening period of the DAPI, a relatively low radio frequency (RF) amplitude (700 V_{p-p}) was used for ion trapping and the high voltage applied to the electron multiplier was turned off; using a delay (ca. 1 s) after the DAPI was closed, the electron multiplier was turned on and the RF amplitude was subsequently ramped for mass analysis.

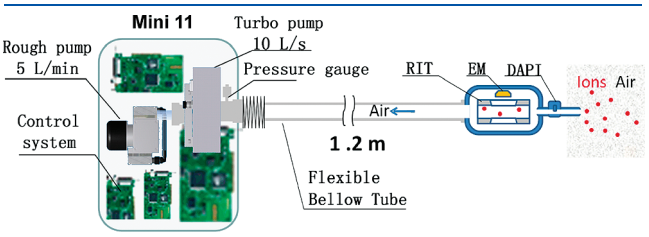

Figure 1. Schematic of the sampling wand coupled with a miniature ion trap mass spectrometer. RIT, rectilinear ion trap; EM, electron multiplier; DAPI, discontinuous atmospheric pressure interface.

EXPERIMENTAL SECTION

The sampling wand was tested using several atmospheric pressure and ambient ionization methods, including nano-electrospray ionization (ESI), atmospheric pressure chemical ionization (APCI), and a low temperature plasma (LTP) probe.[19] The nanospray tips were all pulled from borosilicate glass capillaries (1.5 mm o.d. and 0.86 mm i.d.) using a P97 Flaming/Brown micropipet puller (Sutter Instruments, Novato, CA). Spray voltages in the range of 1 to 2 kV were applied, and the distance between the nanospray tip and the mass spectrometer inlet was set as 1.5 cm. The APCI experiment was implemented by applying a 4.4 kV direct current (DC) to a stainless steel wire (0.21 mm ID, with its end 5 mm away from the DAPI inlet) to create corona discharge.[36] The LTP probe consists of a glass tube (o.d. 6.0 mm and i.d.4.0 mm) with an axial grounded electrode (stainless steel; diameter, 1.6 mm) inside and a copper tape electrode wrapped around the outside tube surface.[19] The end of the LTP probe was about 8 mm away from the DAPI inlet of the wand at a 35° angle from sample surface.

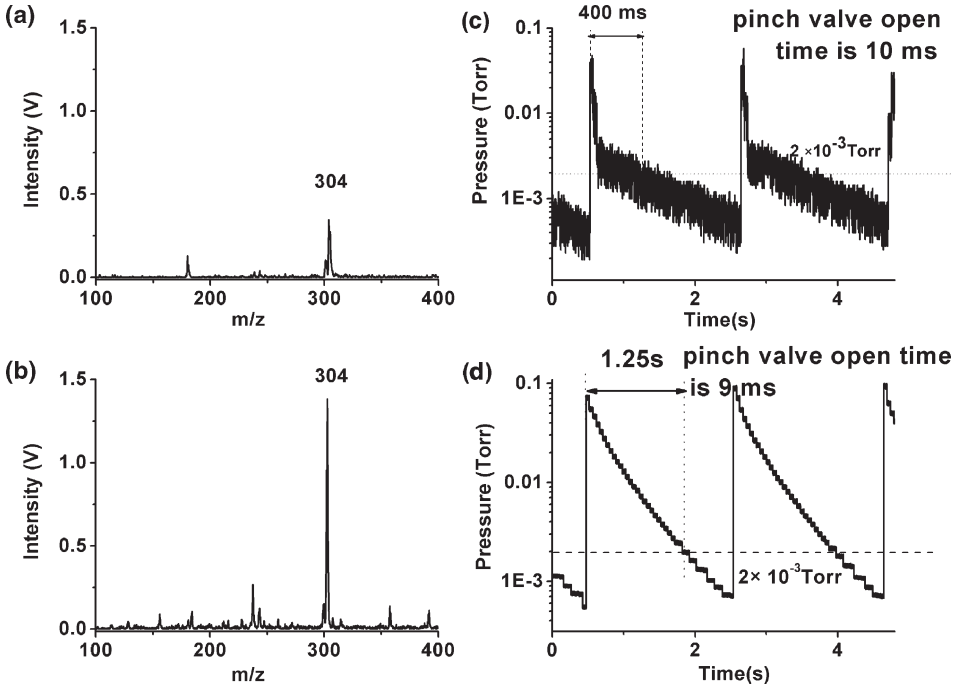

Figure 2. Mass spectra of 500 ppb cocaine solution recorded using (a) unmodified Mini 11 and (b) Mini 11 modified with the addition of a sampling wand. Both experiments using the same sample and the same nano-ESI tip for ionization. Parts (c) and (d) show corresponding manifold pressures as a function of time, recorded using an ion gauge.

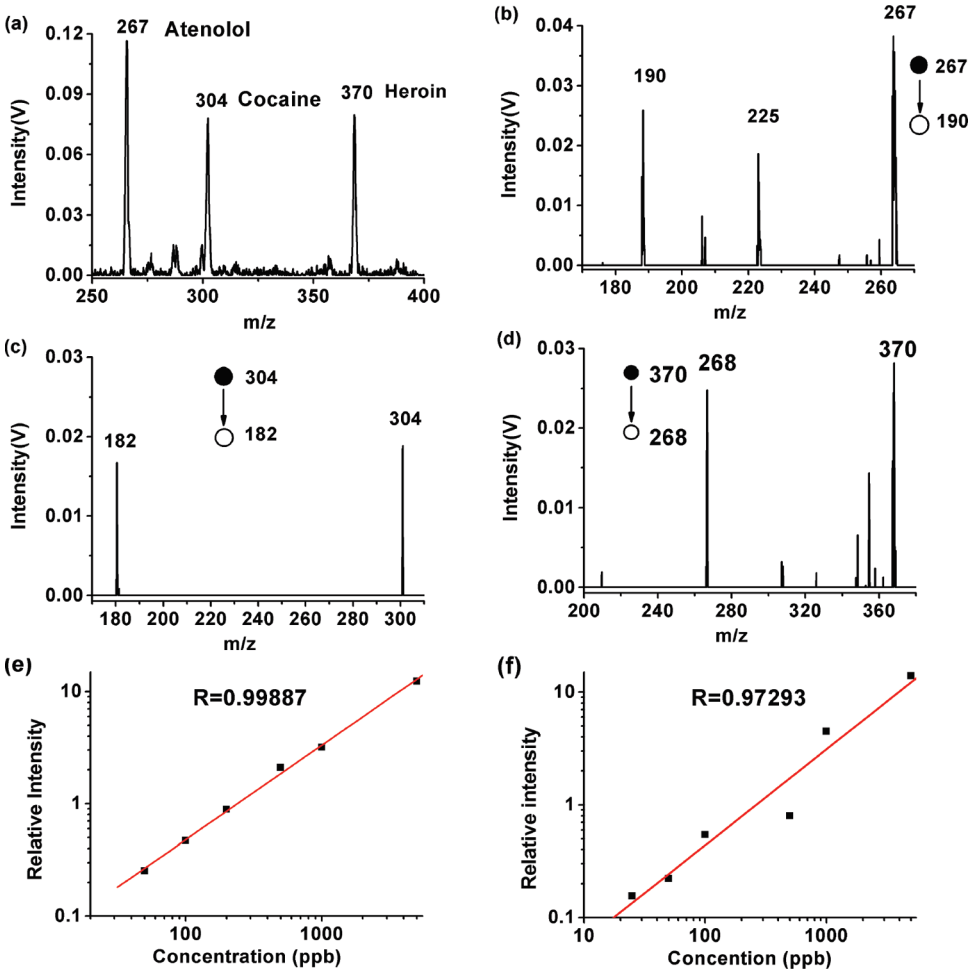

Figure 3. (a) Mass spectra of a mixture of atenolol, cocaine, and heroin, each at a concentration of 250 ppb, nano-ESI. Panels (b−d): MS/MS spectra for each analyte. Panel (e) and (f): calibration curves for cocaine and atenolol.

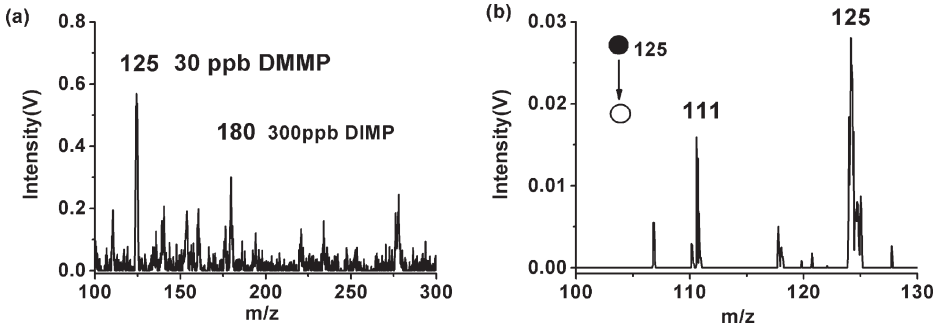

Figure 4. Mass spectra recorded using APCI for the CWA simulants DMMP and DIMP, (a) 30 ppb DMMP and 300 ppb DIMP; (b) MS/MS data for 12 ppb DMMP.

Methanol was obtained from Mallinckrodt Baker, INC. Methamphetamine, cocaine, atenolol, heroin, dimethyl methylphosphonate (DMMP), and diisomethyl methylphosphonate (DIMP) were purchased from Sigma Chemical Co. (Sigma-Aldrich, St. Louis, MO). Vapor-phase samples were diluted by injecting them into a flask using gastight syringes (Hamilton Company, Reno, NV,USA) and then mixing them into a gas stream using a mass flow controller (model HFC-302,Teledyne Hasting Instruments, Hampton, VA, USA). Liquid sample solutions were prepared using 1:1 methanol/water for nano-ESI and pure methanol for LTP.

RESULTS AND DISCUSSION

The Mini 11 with the new sampling wand was characterized using various ionization methods. Comparisons were made between mass spectra recorded by nano-ESI of 500 ppb cocaine solution using the original Mini 11 and the modified Mini 11 with the sampling wand (Figure 2a,b). The open time for the DAPI was 10 and 9 ms, respectively. In a significant contrast with the probes explored previously,[33] no loss in sensitivity was observed for the wand configuration, instead there was a 3-fold improvement in signal and signal/noise ratio. In addition, no extra power

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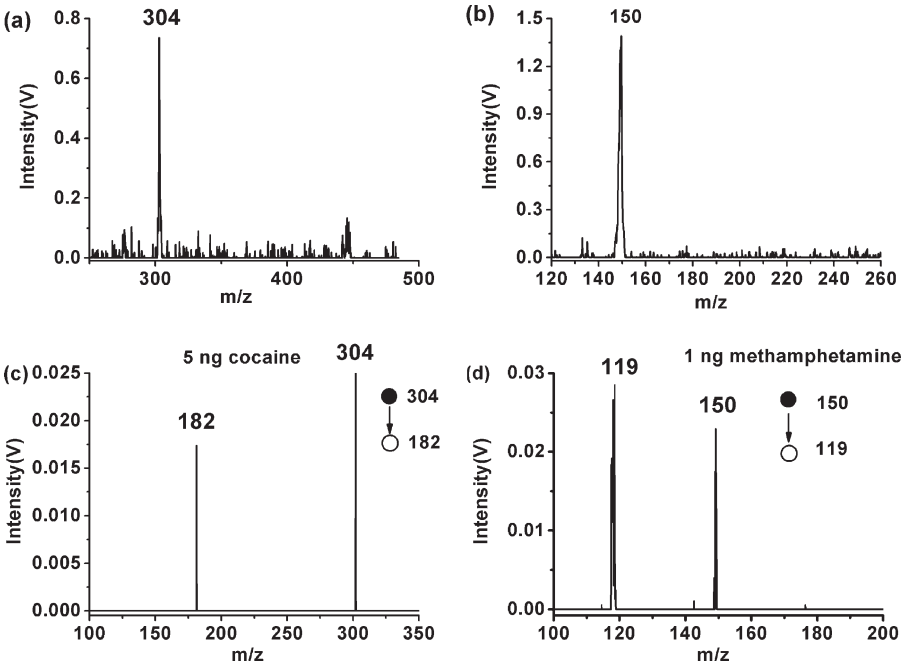

Figure 5. Mass spectra of (a) 100 ng of cocaine and (b) 100 ng of methamphetamine on glass and MS/MS spectra of (c) 5 ng of cocaine and (d) 1 ng of methamphetamine on glass, LTP used for desorption ionization.

was required as no auxiliary pumping or other devices were implemented to facilitate the improved ion transfer.

The signal improvement could be due to two factors, the enlarged vacuum system volume with the extension bellow tube and/or the increased ion transfer efficiency with a capillary of larger ID. Pressure variations during the operation were recorded, as shown in Figure 2c,d. Although the pressure varied within similar ranges for both configurations, more gas (3 times as much) containing ions was introduced into the vacuum with the wand configuration. With the 500 μm ID inlet capillary used for the wand, the mass flow rate is also much higher, which should help to improve the ion transfer through the DAPI. The observed improvement was only a factor of 3, which might be due to the negative effects associated with larger gas expansion and greater ion speed. Under these conditions, decreased efficiency for the transfer of ions into the trap as well as their trapping is expected. It has been observed that an increase in the RF voltage (e.g., 700 $V_{p\text{-}p}$ for the wand configuration vs 350 $V_{p\text{-}p}$ for original Mini 11) during ion introduction significantly helped to increase signals. This change in RF amplitude also resulted in an increased low mass cutoff (LMCO) from m/z 60 to 92.

One disadvantage of the new wand configuration is the longer time (1.25 s vs 0.4 s) required for the pressure to decrease to a value low enough (2 mTorr in this study) to record mass spectra. The minimum time for each scan was increased from about 0.7 to 1.5 s, which should still be acceptable for most in-field chemical analysis applications.

MS/MS represents an important capability for identifying target analytes in complex mixtures, especially for in situ work where chromatographic separation is not available. It not only provides a higher level of confirmation of particular chemicals, but also it helps to improve the signal-to-noise ratio significantly by removing interfering ions before fragmentation of precursor ion.[37,38] In this study, precursor ions were isolated using a forward scan and reverse scan with resonance ejection of the ions in the lower and higher m/z ranges, respectively;[39,40] then, collision-induced dissociation was implemented for fragmentation. The fragment ions were then mass analyzed by resonance ejection using a dipolar excitation at a q of 0.75 (AC = 370 kHz, 1−2.0 $V_{0\text{-}p}$).[41] The MS and MS/MS spectra recorded for a mixture of cocaine, heroin, and atenolol are shown in Figure 3. All these three analytes were present at a concentration of 250 ppb, and nano-ESI was used as the ionization method. Characteristic fragment ions were observed for each of these analytes.

The linear dynamic range of this system, coupled with nano-ESI, was also characterized for the mixture of cocaine and atenolol within a concentration range from 10 ppb to 5 ppm. As shown in Figure 3e,f, good linearity was obtained between 50 ppb to 5 ppm for cocaine and 20 ppb to 5 ppm for atenolol.

The feasibility of the use of the wand system for in-field chemical analysis was tested using APCI for gaseous samples and LTP for solid samples. Air samples containing the chemical warfare simulants DMMP (dimethyl methylphosphonate) and DIMP (diisomethyl methylphosphonate) were analyzed using the wand with APCI. The MS spectrum of a mixture containing 30 ppb DMMP and 300 ppb DIMP is shown in Figure 4a. A mass spectrum (not shown) recorded with 12 ppb DMMP has a signal/noise ratio of ca. 3, and the corresponding MS/MS spectrum (Figure 4b) shows better signal-to-noise ratio for the protonated molecular ion m/z 125 and the product ion $[CH_3P(O)OCH_3 + H_2O]^+$ at m/z 111.

The direct analysis of solid samples using the wand system was tested using an LTP probe for desorption and ionization of cocaine and methamphetamine from a glass surface. The analytes were first dissolved in pure methanol, and a selected amount was pipetted onto a glass slide and allowed to dry. Mass spectra were recorded for 100 ng of cocaine and methamphetamine (Figure 5a,b, respectively), with good signal-to-noise ratios for the protonated molecular ions m/z 304 and m/z 150. Product ion MS/MS spectra with similar signal-to-noise ratios could be obtained with much smaller amounts of samples, as shown in Figure 5c (5 ng of cocaine) and Figure 5d (1 ng of methamphetamine).

CONCLUSION

A sampling wand for a mass spectrometer system was developed. The design of the wand has particular advantages when used with miniature mass spectrometers, the performance of which is limited by low power and low pumping capacity. The design leverages a unique feature of the DAPI system, viz., that improved sensitivity is obtainable with enlarged vacuum volume. The improved performance of the system was demonstrated with the analysis of liquid, gas, and solid samples using nano-ESI, APCI, and LTP, in direct comparisons with data taken from an unmodified hand-held mass spectrometer. A 1.2 m long sampling wand was utilized without any additional pumping or power demands, and a 3-fold improvement in sensitivity was achieved for the modified hand-held instrument, in comparison with the original Mini 11.

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