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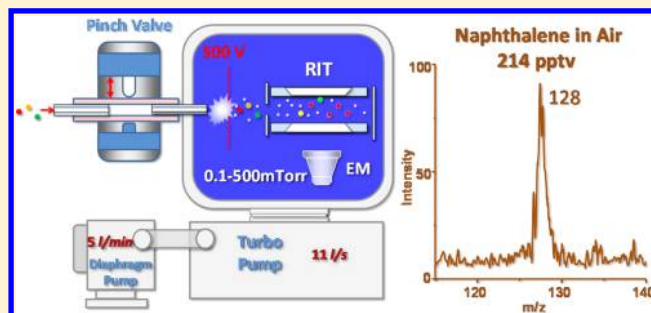
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Synchronized Discharge Ionization for Analysis of Volatile Organic Compounds Using a Hand-Held Ion Trap Mass Spectrometer

Tsung-Chi Chen[†] and Zheng Ouyang^{*,†,‡}

[†]Weldon School of Biomedical Engineering, and [‡]Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana 47907, United States

ABSTRACT: The sensitivity of mass analysis is highly dependent on the efficiencies of the sample introduction, analyte ionization, and subsequent ion transfer to the mass analyzer. For miniature mass spectrometry (MS) systems, it is highly desirable to maximize the amount of the samples that can be introduced at the pumping capability highly compromised and to have the MS analysis performed with simple electronics and robust in-vacuum components. In this study, a discharge ionization source synchronized with the sample introduction has been developed for hand-held mass spectrometers with discontinuous atmospheric pressure interfaces (DAPI). The flow rate of the sample introduced with a DAPI can be much higher than that allowed with a conventional continuous atmospheric pressure interface. The pressure variation associated with the DAPI operation was used to turn on and off the synchronized discharge ionization (SDI). For analysis of volatile organic compounds (VOCs) in air samples, the SDI has been shown to be soft and molecular ions of the VOCs have been observed as the major species. Since the ions could be transferred directly to the ion trap mass analyzer without a barrier for maintaining pressure differences, high sensitivity in chemical analysis was also achieved, with limits of detection (LODs) better than 1 ppbv obtained for PAHs (polycyclic aromatic hydrocarbons) in air.



Volatile organic compounds (VOCs) have always been a subject of concern for the environment protection^{1,2} and human health.^{3,4} Many analytical methods have been developed for the analysis of VOCs in air or on aerosols, with gas or liquid phase chromatography mass spectrometry (GC/MS or HPLC/MS) as two of the major methods.^{5–11} Although commercial MS systems at lab scales have been proven to be highly sensitive and quantitative in the chemical analysis, a major effort has also been put on the development of miniature MS systems for analysis of samples in gas and condensed phases.^{12–18} Various sample introduction methods have been used, including membrane sample introduction,^{19,20} GC capillary introduction,^{21,22} and solid-phase microextraction sample introduction.^{23,24} These methods introduce samples into the vacuum manifold, which are ionized at low pressure with an in-vacuum ionization source, typically electron impact (EI) ionization. Although EI provides demonstrated ionization efficiency for MS analysis, severe fragmentation typically occurs, which makes the spectra of complex mixtures significantly complicated. Other in-vacuum soft ionization methods, such as chemical ionization (CI),^{25–27} glow discharge ionization (GD),^{28–31} or photoionization (PI),^{32–34} in principle could all be used to produce intact molecular ions; however, they have not been widely applied for miniature MS systems. The CI and GD methods require a vacuum compartment at pressures higher than that for the mass analysis, which leads to the complication in design of the manifold and vacuum system as well as the need for additional

ion optics for transferring the ions from the source to the mass analyzer. The photoionization is of relatively low cross sections and might not provide an ion intensity high enough for a broad range of compounds with the miniature systems.³⁵

With the development of the discontinuous atmospheric pressure interface (DAPI),^{36–38} various ionization sources at ambient pressure, including electrospray ionization (ESI),^{17,39} atmospheric pressure chemical ionization (APCI),¹² desorption electrospray ionization (DESI),⁴¹ extraction electrospray ionization (EESI),¹⁵ low-temperature plasma (LTP) probe,⁴² and paper spray,⁴⁰ have been successfully coupled to the hand-held rectilinear ion trap (RIT)³⁹ MS systems.⁴¹ With the APCI source, the analysis of benzene and its derivatives in air has been achieved¹² with limits of detection (LODs) better than 1 ppb obtained. With a DAPI, the air carrying neutral analytes or ions is introduced in a pulsed mode, which is controlled using a pinch valve. When the DAPI is open, typically for 20 ms or shorter, the pressure in the vacuum increases rapidly. In our previous work, all the high voltages were turned off during the DAPI open time to avoid discharge. With a delay of several hundreds of milliseconds after the DAPI was closed, the vacuum pressure decreased back to millitorr range and the high voltages were turned on for MS analysis. In the current work, the unique feature of the pressure variation due to the DAPI

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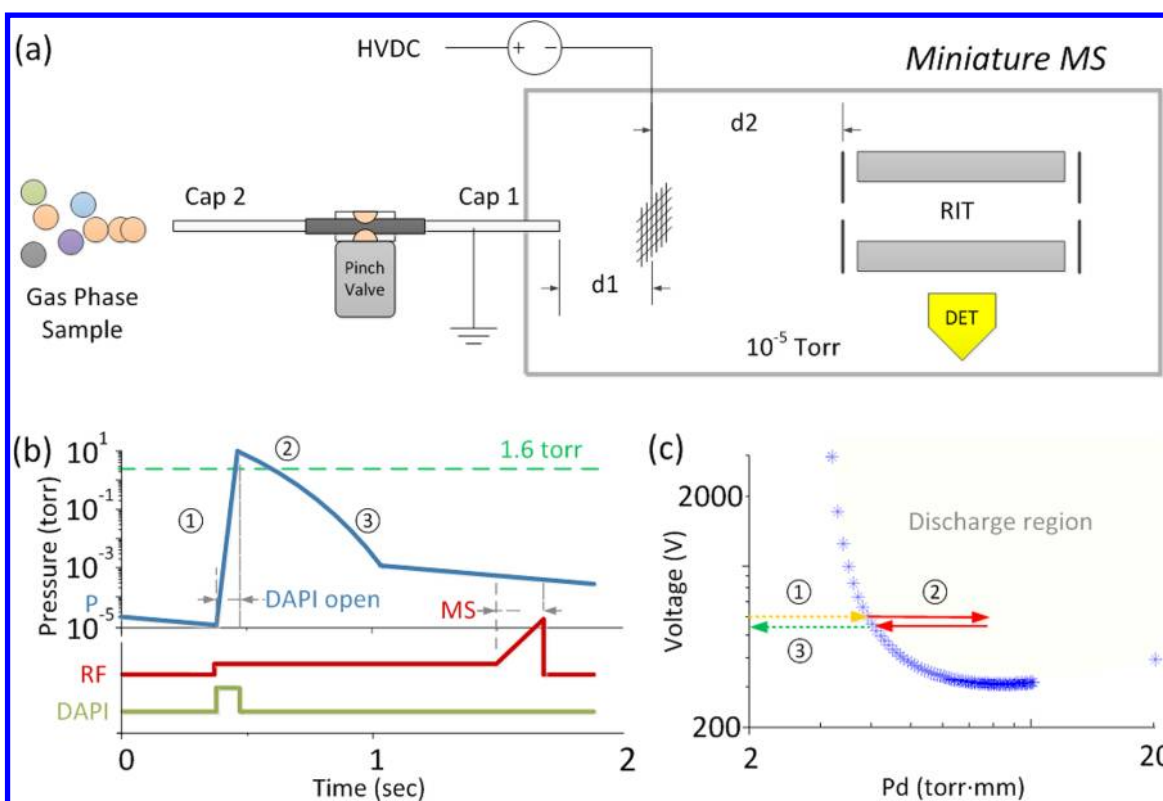


Figure 1. (a) Schematic depiction of the apparatus for an SDI-MS. (b) Control sequences for DAPI and rf and the pressure variation during the MS scan. (c) Paschen's curve for air and the discharge conditions corresponding to the pressure variation in panel b.

operation has been used to create a synchronized discharge ionization (SDI) for analyzing VOCs in gas samples.

INSTRUMENTATION

As shown in Figure 1a, a previously reported hand-held RIT MS instrument with a DAPI³⁶ was modified for the development of SDI. A mesh electrode was installed between the DAPI capillary exit to vacuum and the end electrode of the RIT. In order to produce the discharge during the DAPI open time, a dc (direct current) voltage of about 500 V was applied on the mesh electrode to induce a discharge to ionize the analytes in the air. The ionization is synchronized with the pressure variation (Figure 1, parts b and c), turned on when pressure is increasing (step 1 to 2 in Figure 1, parts b and c) and turned off when the pressure is decreasing (step 2 to 3) after the DAPI is closed. The pressures for the start and end of the discharge are determined by the Paschen's curve (Figure 1c) and can be adjusted by varying the distance between the DAPI capillary exit and the mesh electrode as well as the voltage applied on the mesh electrode.

The pressure is typically elevated up to 1 Torr during the DAPI operation, and a glow discharge is expected to be produced in a pulsed mode. Previously, it has been shown that the glow discharge ionization could be soft and has been used to produce molecular ions.²⁹ In comparison with EI, this is of a significant advantage in analyzing complex mixtures. Also, the discharge ionization could be implemented without using fragile components such as a filament, which is vulnerable with pressure variation. For these reasons, the glow discharge can be greatly favored as an ionization source for miniature MS systems.³¹ For the synchronized discharge ionization implemented on a DAPI-MS system, the flux of the air sample

introduced during the DAPI open time is significantly higher than that allowed for an MS system with the same pumping capability but using a continuous sample introduction.^{36,42} In previous work,^{29,31} a separate compartment at a pressure different (higher) than that for the MS analysis region had to be used. However, with the DAPI operation, the pressure of the vacuum manifold varies from that suitable for a glow discharge to that suitable for MS analysis in a sequence; there is no need for a physical barrier between the ionization and the MS analysis regions to maintain the pressure difference. This would make the ion transfer to the mass analyzer at a significantly higher efficiency.

For a practical implementation of the SDI, a woven wired mesh (stainless steel 316, grid size of 0.0098 in., wire diameter of 0.0037 in., McMaster-Carr, Chicago, IL, U.S.A.) with a 52.7% transparency was placed between the DAPI inlet metal capillary (Cap 1 in Figure 1a) and the RIT end electrode. The metal mesh was connected to a dc power supply (model 659, Ortec, Oak Ridge, TN, U.S.A.) with an internal impedance ($\sim 2\text{M}\Omega$) that provided a constant dc voltage for discharge. The maximum allowable current was 100 μA , limited by both the internal impedance of the power supply and an in-line adjustable resistor. The distance between the mesh electrode and the DAPI capillary exit (d_1 in Figure 1a) was 2 mm, which is shorter than the distance between the DAPI capillary to any other electrically conductive surfaces. The distance between the mesh electrode and the RIT end electrode was 4 mm. The sample introduction and the subsequent SDI event were controlled by using a pinch valve (390NC24330, ASCO Valve Inc., Florham Park, NJ, U.S.A.) with a conductive silicone tube (i.d. $1/16$ in., o.d. one-eighth in., length 20 mm, Simolex Rubber Corp., Plymouth, MI, U.S.A.) connecting two stainless steel

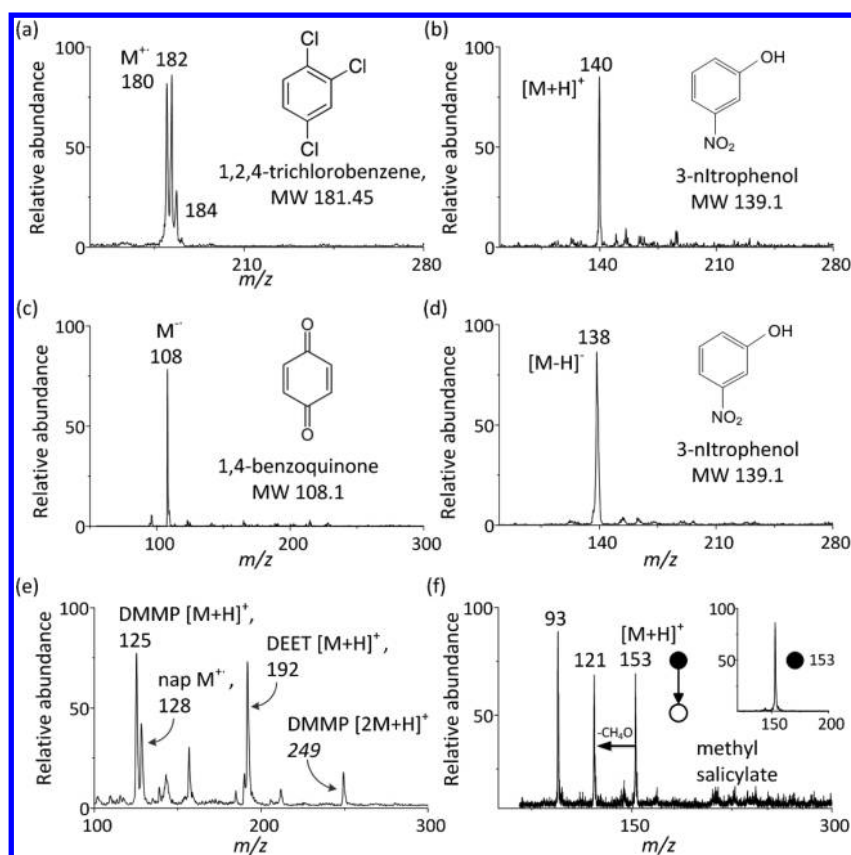


Figure 2. Mass spectra recorded using miniature SDI-MS for headspace vapors of (a) 1,2,4-trichlorobenzene (m/z 180) and (b) 3-nitrophenol (m/z 140) in positive mode, (c) 1,4-benzoquinone (m/z 108) and (d) 3-nitrophenol (m/z 138) in the negative mode, (e) mixture of DMMP, naphthalene (m/z 128), and DEET (m/z 192) in methanol solution, positive mode. (f) MS/MS spectrum of protonated methyl salicylate (m/z 153) generated by SDI.

capillaries (both 5 cm long; Cap 1, i.d. 1 mm, o.d. $1/16$ in.; Cap 2, i.d. 250 μm , unless otherwise noted, o.d. $1/16$ in.).

EXPERIMENTAL SECTION

Chemicals used to make the samples in this study included 1,2,4-trichlorobenzene (MW 181.45), 3-nitrophenol (MW 139.11), 1,4-benzoquinone (MW 108.09), dimethyl methylphosphonate (DMMP, MW 124.08), *N,N*-diethyl-3-methylbenzamide (DEET, MW 191.27), methyl salicylate (MW 152.15), toluene (MW 92.14), naphthalene (MW 128.17), acenaphthene (MW 154.21), fluorene (MW 166.22), anthracene (MW 178.23), phenanthrene (MW 178.23), pyrene (MW 202.25), benz[*a*]anthracene (MW 228.29), and chrysene (MW 228.29), all purchased from Sigma-Aldrich Chem. Co. (St. Louis, MO, U.S.A.). For the quantitation experiments, methanol solutions containing analytes of different concentrations were prepared using the method previously reported,⁴³ and the headspace air was sampled by the hand-held MS instrument through a silicon tube (10 cm long, 1.6 mm i.d.) connected to the DAPI capillary (Cap 2 in Figure 1a).

RESULTS AND DISCUSSION

With a Lexan cover used for the vacuum manifold in the instrument shown in Figure 1a, visible pulses of glow discharge were observed when the scans for MS analysis (Figure 1b) were performed repeatedly. A major ionization process for glow discharge is penning ionization,^{29,44} which could occur outside the discharge region between the DAPI capillary and the mesh electrode. In our experiments, the polarity of the discharge

voltage on the mesh electrode could be switched for positive or negative MS analysis mode. The voltage applied on the RIT end electrode was +162 or −144 V for positive or negative ions, respectively, so the ions generated between the mesh and the RIT end electrode were pushed toward the RIT.

Headspace gas samples from a series of pure chemicals were first analyzed in both positive and negative modes using SDI, and the spectra were recorded with the hand-held MS as shown in Figure 2. For all the chemicals analyzed, only the peaks for the molecular ions were observed, which confirms that the SDI is a soft ionization method. In the positive mode, radical cations m/z 180, 182, and 184 were observed for 1,2,4-trichlorobenzene (Figure 2a), whereas protonated ion m/z 140 was observed for 3-nitrophenol, which has a relatively high proton affinity (Figure 2b). In the negative mode, radical anion m/z 108 was observed for 1,4-benzoquinone (Figure 2c), which is a strong oxidizing reagent and has strong electron affinity.⁴⁵ For 3-nitrophenol of a relatively high acidity, deprotonated molecule m/z 138 was observed in the negative mode (Figure 2d). This shows that multiple ionization processes could occur during the discharge ionization, dependent on the chemical properties of the analytes. The water residue in the air could also serve as reagent during the discharge ionization to provide hydronium cations or hydroxyl anions in the reactions with 3-nitrophenol to produce the protonated or deprotonated ions, respectively.

The headspace vapor from a mixture of 20 μL of DMMP, 310 μL of DEET, and 0.13 mg of naphthalene in 1.8 mL of methanol solution was analyzed using SDI (Figure 2e). The

spectrum was simply dominated with peaks for molecular species including protonated DMMP at m/z 125, protonated DMMP dimer at m/z 249, radical cation of naphthalene at m/z 128, and protonated DEET at m/z 192. No fragment ions were observed, which is a significant advantage for mixture analysis. Further confirmation of the chemical structure, which is important for compound identification, could be performed with the MS/MS of the isolated molecular ions,⁴⁶ as shown in Figure 2f with an example for the protonated methyl salicylate m/z 153 generated with SDI. The collision-induced dissociation (CID) was performed using a scan function previously described^{36,47} with the residue air as the collision gas, and major fragment ions m/z 121 and m/z 93 were observed.

Though the discharge ionization was triggered and turned off by the DAPI operation, the exact pattern of the discharge during a scan cycle needed to be better understood. The discharge could not occur immediately with the opening of the DAPI since the vacuum pressure needed to be high enough to satisfy the condition for the discharge (Figure 3a). It was also

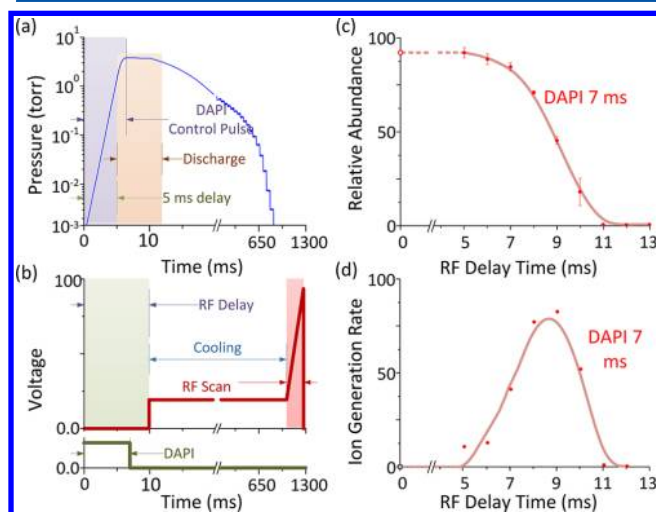


Figure 3. (a) Variation of pressure in the manifold for DAPI open time of 7 ms, 250 μm i.d. capillary. (b) Control of rf voltage with a delay from the beginning of the DAPI control pulse. (c) Normalized ion abundance monitored as a function of the DAPI-rf delay time, DAPI open time (pulse width) = 7 ms. (d) The ion generation rate as a function of DAPI-rf delay time.

known from previous studies^{36,38} that a time delay existed between the rise of the DAPI control voltage and the actual opening of the pinch valve due to a mechanical or electromagnetic delay in the valve operation (Figure 3a). Further, the vacuum pressure decreases gradually after the DAPI closes, which means the discharge might not be turned off immediately with the closing of the DAPI. In an experiment designed to characterize the SDI, a scan function as shown in Figure 3b was used. A DAPI open time (pulse width) of 7 ms was used, which was also confirmed experimentally to be long enough to produce the discharge. A delay of a varying time periods was implemented between the beginning of the DAPI operation pulse and the turn-on of the rf (at 1349 kHz) trapping voltage (from 0 to 1091 Vpp) and the end electrode dc voltage (from negative to 152 V) for trapping the positive ions (Figure 3b). The headspace vapor of 1% DMMP in methanol was analyzed, and the ion intensity of the protonated dimer m/z 249 was monitored as a function of the rf delay time before trapping, as shown in Figure 3c. The ion generation rate

R_i at the i th delay time point t_i (Figure 3d) was subsequently calculated using the following equation:

$$R_i = \frac{I_{t_i-1} - I_{t_i}}{(t_i - t_{i-1})} \quad (1)$$

where I_i is the relative abundance of m/z 249 recorded at t_i .

As shown in Figure 3d, the ion generation did not start until 5 ms after the beginning of the DAPI pulse, due to both the delay in the pinch valve opening and the time necessary for the rise of the vacuum pressure (Figure 3a). At 7 ms, the DAPI control signal was off and pressure was observed to start to decrease. However, the discharge ionization did not stop and actually lasted for another 4 ms, during which the vacuum pressure gradually decreased and eventually became too low to sustain the discharge. The highest discharge ionization efficiency was observed at 9 ms, which could be due to the reach of a favorable condition for both discharge as well as gas-phase reactions for generating the protonated dimer.

The controllability of the SDI and the impact of the experimental parameters on the analytical performance were further investigated. The total charges produced during an entire SDI process in a single scan could be obtained by integrating the discharge current measured through the DAPI capillary, which is the cathode in the positive SDI mode. The total number of charges as a function of the discharge voltage applied on the mesh electrode is plotted in Figure 4a. The

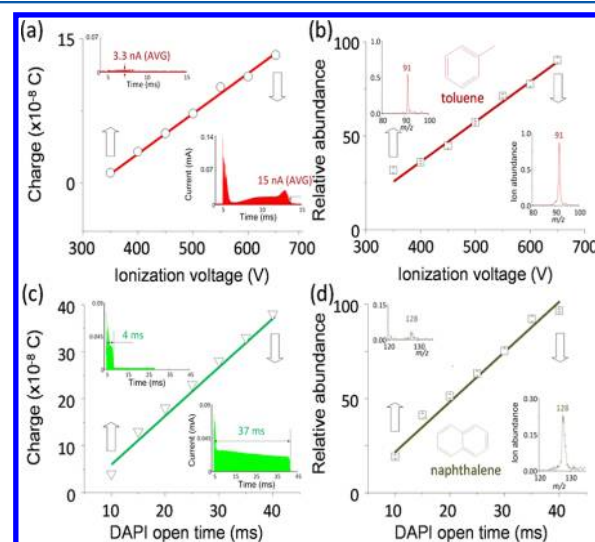


Figure 4. (a) Total number of charges generated during SDI as function of the discharge voltage, DAPI pulse time = 11 ms. (b) The relative peak abundance for toluene (m/z 91) as a function of the discharge voltage, DAPI pulse time = 11 ms. (c) The total number of charges as a function of DAPI open time, discharge voltage of 500 V. (d) The relative peak intensity of naphthalene (m/z 128) as a function of DAPI open time, discharge voltage of 500 V.

DAPI open time was set at 11 ms. As shown with the two insets in Figure 4a, the discharge current increased significantly when the discharge voltage changed from 350 to 650 V. However, overall power consumption is extremely low for SDI. For operating SDI at 500 V at a scan rate or 1/s, which is typical for a DAPI-MS system, the power consumption is only 50 μW . This is significantly lower than the operation of an EI source, normally at several watts. It is also interesting to note that the discharge pattern is not flat (Figure 4a, inset) but featured with

an initial burst at the beginning of the discharge and a variation as a function of time or pressure. For analyzing the headspace vapor of 100 ppm toluene in methanol under different discharge voltages, a 3 times increase was observed for the peak abundance when the voltage increased from 350 to 650 V. Note that the fragment peak at m/z 91 was the major peak in the SDI spectra of toluene (Figure 4b), which is identical to those obtained previously with the APCI.¹²

In another experiment to characterize the effects of DAPI open time, a capillary of a smaller i.d. at 125 μm was used as the DAPI Cap 2 (Figure 1a) to allow longer DAPI open times from 10 to 40 ms, while the variations of the discharge patterns were monitored (Figure 4c). A discharge voltage of 500 V was used here. Different from the patterns shown in Figure 4a, after the initial spike a relatively stable discharge was observed with the capillary of smaller conductance. The total number of charges produced with this capillary could actually be larger at long open times than those obtained with a 250 μm i.d. capillary. This is very different for the DAPI operation for introducing ions from atmospheric pressure ion sources, where the transfer efficiency was extremely low with a 125 μm i.d. capillary³⁶ due to the loss of the charges of the ions. For a miniature MS system using SDI, neutral analytes are introduced through the capillary and ionized inside the vacuum close by the mass analyzer. For the analysis of a headspace vapor from 50 μg of naphthalene in 1 mL of methanol, the peak intensity of the radical cation m/z 128 increased by about 5 times when the DAPI time increased from 10 to 40 ms (Figure 4d).

Six PAH (polycyclic aromatic hydrocarbon) compounds were selected from the EPA priority list of pollutant,^{48,49} including naphthalene, fluorine, anthracene, pyrene, benz[a]-anthracene, and chrysene. Each of the chemicals was placed in a 10 mL vial, and the headspace vapors were analyzed using the hand-held MS with SDI (Figure 5a). Naphthalene, fluorine, and anthracene, which are of relatively high volatilities, could be easily detected at room temperature (25 °C), while a heating to 70 °C helped significantly for the detection of pyrene, benz[a]-anthracene, and chrysene from their headspace vapors.

As discussed above, the SDI should provide a high sensitivity for the gas sample analysis, owing to the relatively large amount of samples introduced via DAPI and the high efficiency for ion transfer to the mass analyzer. As a demonstration for quantitative analysis, headspace vapors from methanol solutions containing naphthalene at concentrations from 2 to 250 $\mu\text{g}/\text{mL}$ were analyzed at room temperature of 25 °C. The corresponding concentrations in vapor were from 214 pptv to 27 ppbv for the vapor sample composed of about 18.9% methanol and 71.1% air. The vapor sample concentrations were determined by the static headspace sampling method⁴³ based on their vapor pressures.^{50,51} A calibration curve for trace naphthalene in vapor was obtained with the experimental data (Figure 5b), and a good linearity ($R^2 = 0.997$) was achieved. Good signal-to-noise ratio was obtained at the concentration of 214 ppbv, indicating an LOD better than this value. Headspace vapors containing low concentrations of acenaphthene, fluorine, and phenanthrene were also analyzed, and the spectra recorded (Figure 5c) showed LODs better than 148, 175, and 875 pptv, respectively, for these compounds in vapor samples.

CONCLUSIONS

A concept has been developed for utilizing the pressure variation associated with the DAPI operation to create a synchronized discharge ionization for miniature MS systems.

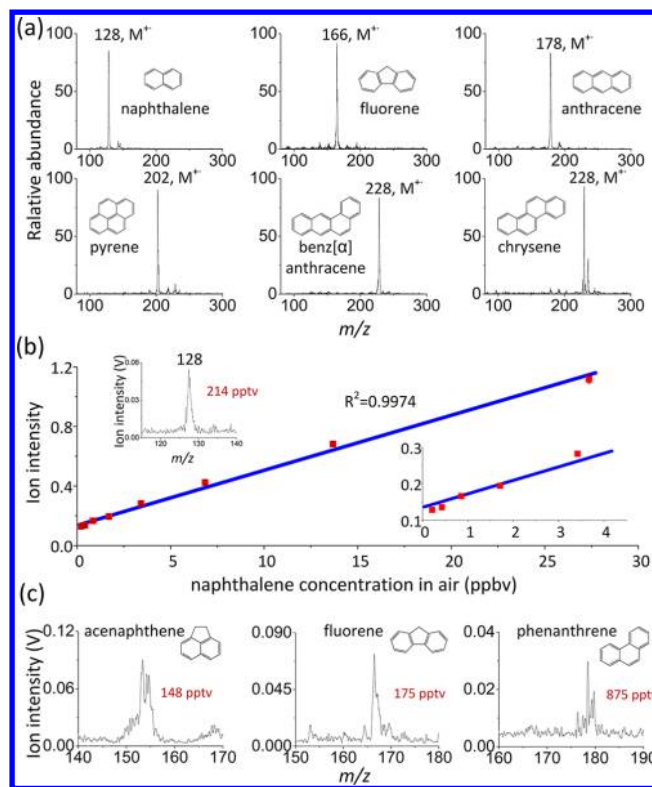


Figure 5. (a) Spectra of PAHs using SDI, including naphthalene at m/z 128, fluorine at m/z 166, anthracene at m/z 178, pyrene at m/z 202, benz[a]anthracene at m/z 228, and chrysene at m/z 228. (b) Calibration curve for naphthalene in air, 214 pptv to 27 ppbv. (c) Spectra recorded for acenaphthene (m/z 154), fluorine (m/z 166), and phenanthrene (m/z 178) at concentrations of 148, 175, and 875 pptv, respectively, in vapor samples.

The SDI is simple, robust, consumes low power, and has been demonstrated to be a soft ionization method. The experimental demonstration and characterization have been done for the analysis of volatile organic compounds in air. Limits of detection at parts-per-trillion levels have been obtained.

AUTHOR INFORMATION

Corresponding Author

*Phone: 765-494-2214. Fax: 765-496-1912. E-mail: Ouyang@purdue.edu.

Notes

The authors declare no competing financial interest.

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