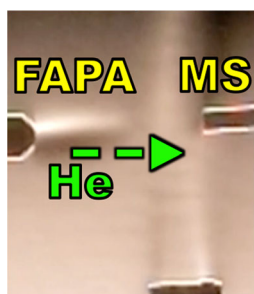


RESEARCH ARTICLE

Use of Interrupted Helium Flow in the Analysis of Vapor Samples with Flowing Atmospheric-Pressure Afterglow-Mass Spectrometry

Andrew P. Storey,¹ Offer M. Zeiri,^{1,2} Steven J. Ray,^{1,3} Gary M. Hieftje¹¹Department of Chemistry, Indiana University, Bloomington, IN 47405, USA²Nuclear Research Center Negev, Beer-Sheva, Israel³Present Address: Department of Chemistry, University at Buffalo, The State University of New York, Buffalo, NY 14260, USA

Abstract. The flowing atmospheric-pressure afterglow (FAPA) source was used for the mass-spectrometric analysis of vapor samples introduced between the source and mass spectrometer inlet. Through interrupted operation of the plasma-supporting helium flow, helium consumption is greatly reduced and dynamic gas behavior occurs that was characterized by schlieren imaging. Moreover, mass spectra acquired immediately after the onset of helium flow exhibit a signal spike before declining and ultimately reaching a steady level. This initial signal appears to be due to greater interaction of sample vapor with the afterglow of the source when helium flow resumes. In part, the initial spike in signal can be attributed to a pooling of analyte vapor in the absence of helium flow from the source. Time-resolved schlieren

imaging of the helium flow during on and off cycles provided insight into gas-flow patterns between the FAPA source and the MS inlet that were correlated with mass-spectral data.

Keywords: Ambient ionization, Ion sources, Vapor analysis, Gas-flow dynamics, Helium conservation

Received: 28 June 2016/Revised: 27 September 2016/Accepted: 2 October 2016/Published Online: 18 October 2016

Introduction

In the burgeoning field of ambient desorption-ionization mass spectrometry (ADI-MS), many sources have been introduced that enable rapid analysis, often without sample preparation. Many of these sources are plasma-based and work best when helium, a nonrenewable resource, is used as the support gas [1–3]. Recent work in our group [4] has demonstrated that the flowing atmospheric pressure afterglow (FAPA) source can be operated for the analysis of solid samples with a discontinuous flow of helium, with a consequent reduction in He consumption. Most of the samples characterized with ADI-MS have been solids or small volumes of solutions or other liquids deposited onto surfaces [1–3, 5]. Though not as widely applied, ADI-MS sources, including the FAPA, can be used also for the analysis of vapor samples

[6]. Here, vapor-phase samples are analyzed with a source operated with a discontinuous helium flow.

In the past, vapor-phase samples have often been analyzed by introducing them directly into the support-gas flow of an ionization source [7]. However, even low concentrations of vapors can severely perturb a low-power plasma, altering the ionization efficiency and the degree of molecular fragmentation [8]. Thus, sampling in the afterglow region, as done with the FAPA, is most desirable for vapor samples. In a recent study, Brüggemann and coworkers [9] devised a modified sampling apparatus for the online monitoring of volatile organic compounds in the atmosphere. In their arrangement, vapor samples were introduced into a confined sampling region along with the effluent from a continuously operating FAPA ion source. In contrast, in the work described here, as in most that employ ADI-MS, analytes are neither physically confined to a well-defined sampling region nor introduced into the source carrier gas. Rather, the sample vapor is simply allowed to interact with the source afterglow in the open atmosphere.

The primary goal of using an interrupted flow of support gas is to conserve helium; this nonrenewable resource is becoming

Electronic supplementary material The online version of this article (doi:10.1007/s13361-016-1520-z) contains supplementary material, which is available to authorized users.

Correspondence to: Gary M. Hieftje; e-mail: hieftje@indiana.edu

increasingly scarce and costly. Recently, we employed an interrupted helium flow for the analysis of solid samples with the FAPA source and demonstrated acceptable performance [4]. However, the time required to heat samples before desorption caused a delay in reaching the maximum signal and a consequent slight loss in sensitivity. A signal delay can occur for solid samples also when the source is operated with a continuous flow of helium [4].

Of course, such a delay should not exist for the analysis of vapor samples, although variations in gas composition and temperature might result from the on-off cycles of helium flow. Such changes can be directly observed with schlieren imaging, which produces images based on gradients in refractive index. This technique has proven to be powerful for visualization of gas-flow patterns when different sample types are interrogated with the FAPA source [7, 10]. Schlieren images of the FAPA have recently been compared with behavior with a commercial direct analysis in real time (DART) source [11]. In each study, the gas-flow pattern was examined when solids were interrogated, either from dried solutions deposited on a mesh or directly from a solid sample surface. Sampling of gases was not considered in those earlier studies.

In the experiments described here, vapor-phase analytes are introduced in a carrier flow oriented perpendicular to the effluent from the FAPA. Schlieren images are coupled with corresponding mass spectra to characterize how sampling proceeds. Results indicate that sampling vapors with a discontinuous helium flow produce an initial spike in signal levels when the He flow is first started and longer periods of steady signals once the He flow has stabilized.

Experimental

Instrument and Source Conditions

All mass spectrometry experiments utilized a LECO Unique time-of-flight mass spectrometer (St. Joseph, MI, USA) operated in positive-ion mode. This instrument employs a nonlinear field for mass separation with manufacturer specifications of mass resolution >2000 and mass accuracy of <5 ppm at m/z 609. For low-mass molecules, the potential of the rf quadrupole filter was adjusted for higher sensitivity. A pin-to-capillary FAPA source was used in the configuration described elsewhere [4]. The discharge was operated in constant-current mode at 30 mA (600–1000 V) with a glow-discharge power supply (model PTV3N200X; Spellman High Voltage Electronics, Hauppauge, NY, USA) and used 1.0 L/min of helium (99.999% purity; Airgas Mid America, Bowling Green, KY, USA) when the gas flow was enabled. The FAPA source was axially positioned approximately 1.5 cm from the MS inlet, pointing directly at the inlet. A mass-flow controller was used to turn the helium flow on and off for discontinuous helium-flow experiments; periods with and without helium flow each lasted 30 s, unless otherwise noted.

Sample-Vapor Assembly

Carrier gas was passed through a gas-dispersion vessel (bubbler) that contained a sample solvent or solution to generate vapor that was carried to the MS interface, where sample vapor could interact with the afterglow from the source. The carrier-gas flow rate was adjusted between experiments within the range of 0.00 L/min to 0.75 L/min but was held steady in each experiment; only the FAPA source gas flow was operated discontinuously. Except where the use of nitrogen is specifically noted, helium was used as a carrier gas for consistency between schlieren and mass-spectrometry experiments. For schlieren imaging, it was important to use helium because it has a much lower refractive index than the surrounding atmosphere, unlike nitrogen. Tygon tubing carried sample vapor from the bubbler outlet to a position approximately 1.25 cm below the centerline between the FAPA capillary and the MS inlet. All tubing was disconnected when not in use and purged to limit the condensation or adsorption of any vapor constituents in the lines.

Reagents

All reagents, including acetonitrile (HPLC grade; EMD Chemicals Inc., Gibbstown, NJ, USA), acetone (ACS grade; EMD Chemicals Inc.), dimethyl sulfoxide (ACS grade; Fischer Chemicals, Fair Lawn, NJ, USA), ethanol (ACS grade; Fisher Scientific, Waltham, MA, USA), pyridine (ACS grade; EMD Chemicals Inc.), acetic acid (ACS grade, glacial; EMD Chemicals Inc.) were >99% pure. Acetic acid was diluted with deionized water for safety purposes. These common solvents were employed because of their relatively low toxicities at the concentrations relevant to these studies.

Schlieren Imaging of Gas Flow

Schlieren measurements take advantage of differences in refractive index among constituents in a beam of light; details of the present experimental setup have been described previously [10]. A tungsten lamp was used to illuminate a horizontal slit. The divergent beam of light was collimated by one spherical mirror (1.5 m focal length; Newport Co. Irvine, CA, USA) and refocused by another onto a horizontal razor blade. The second mirror served also to focus an image of the test zone (where the FAPA effluent intersected with the analyte-vapor stream) onto a Casio Exilim EX-F1 digital camera (for high-speed video). In the schlieren experiments, light bent down by differences in refractive index appears darker whereas light bent upward appears brighter than the rest of the illuminated portions of the working area. A capillary (35 mm long, 1.5 mm o.d., 0.25 mm i.d.) extending from a small vacuum chamber connected to a Varian TriScroll pump (Varian, Inc., Lexington, MA, USA) simulated a mass spectrometer interface. For schlieren experiments, gas flows for the source and the sampling apparatus were 1.0 and 0.75 L/min, respectively.

High-speed video was used to estimate the velocity of the interrupted helium flow as it first moved out of the source. The

usual video speed was 300 frames per second (fps, 3.33 ms between images), selected to provide adequate spatial resolution, time resolution, and field of view for the described experiments. Frames taken from these videos are shown in Figure 1a, b, and c. To study acceleration of the gas stream after flow interruption, a rotating chopper (50% duty factor, with four open sectors) was used to segment the gas flow. A variable transformer controlled the rotation rate of the chopper; the frequency of interrupted gas segments was held at 13 Hz. For videos that did not require a field of view that included the crossing analyte-vapor flow, a frame rate of 600 fps was used.

Spatial and temporal gas-flow characteristics were analyzed with tracking software (Tracker 4.92; Open Source of Physics, January 2016). The center path of gas flow was determined from schlieren images as the minimum of the first derivative of the transition from brightened areas on the top of the stream to darkened areas on the bottom of the stream.

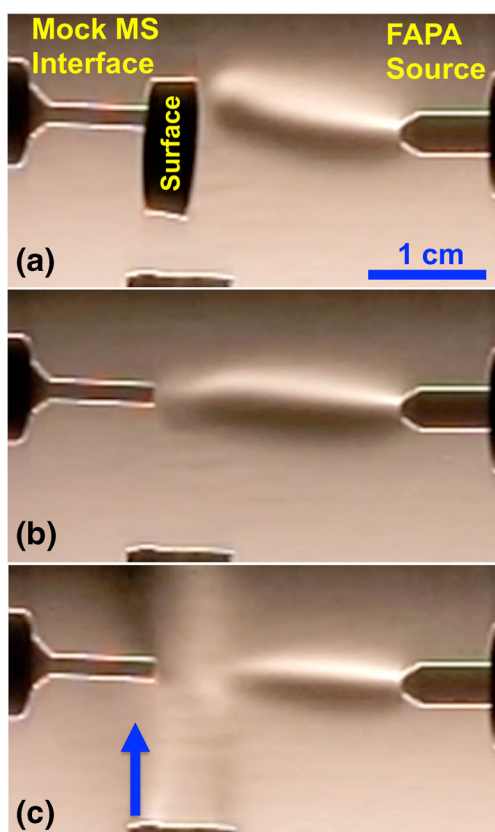


Figure 1. Schlieren images of helium flow from the FAPA source after flow is restarted and directed toward (a) a solid surface, (b) a capillary vacuum inlet (a mock mass spectrometry interface), and (c) a flowing stream of vapor (from bottom of frame as indicated by the arrow) in front of a capillary vacuum inlet. The images shown are when the interrupted stream first approaches the surface, mock interface, or carrier stream

Results and Discussion

Observations with Schlieren Imaging

Schlieren imaging was employed previously to study the interaction of a continuous FAPA stream with a solid sample [10]. This earlier work [10] described the imaging technique in detail. However, the interrupted flow used here generated dynamic gas-flow patterns as the flow through the source was turned off and restarted, and no solid sample surface was involved. Further, during periods of helium-flow interruption, atmospheric gases diffused into the cell, resulting in a temporary temperature increase [4]. These differences in gas composition and temperature could be observed visually with schlieren imaging because of their effect on refractive index. A schlieren image of the FAPA effluent approaching a solid surface is shown in Figure 1a. Deflection of the helium beam by the surface is evident. Without sample-carrier gas flow (otherwise emerging from the bottom of the frame, as in Figure 1c) or a vacuum interface, the helium rises as it passes through the air and interacts there with any gas-phase molecules in its path, both at the front and edges of the projecting gas stream. Additionally and as expected, without external forces to constrain or disperse the flow, the helium stream grows wider through diffusion as it moves farther from the source.

In contrast, Figure 1b and c show the projection of gas flow from the capillary of the source under two conditions (a mock MS interface, Figure 1b, and a crossing carrier gas, Figure 1c) that represent the sampling approaches used to study discontinuous helium flow for analyzing vapor samples. When a vacuum orifice is positioned near the carrier-gas outlet, some of the analyte-vapor flow is drawn into the mock MS inlet, as in Figure 1b. In Figure 1b, the helium flow is constrained to a narrow zone between the source and capillary vacuum inlet and becomes very stable. Regardless of the helium flow rate from the FAPA source, when a vapor-phase sample was used, the flow for this second stream was continuous for the schlieren experiments; a representative image is shown in Figure 1c. The crossing flow of sample vapor disrupts the flow profile of helium from the source dramatically, increasing the interaction between the analyte vapor and the afterglow stream. This interaction is much more direct than would be true for random diffusion into the afterglow stream. This behavior is more plainly visible in the video available in the [Electronic Supplementary Information \(ESM\)](#).

Operation of the FAPA with an interrupted helium flow produced more interesting behavior than the constant-flow mode employed in previous schlieren studies of ADI-MS sources [10]; the resumption of helium flow amounted to acceleration toward the sample from a state in which the sample vapor and its surrounding environment were previously unperturbed. Figure 2 shows the location of the gas front as the stream of

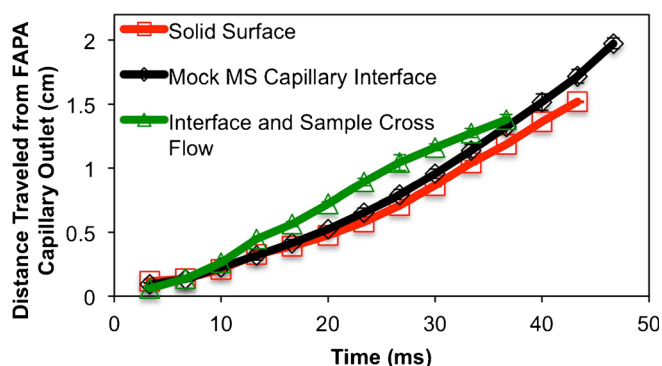


Figure 2. Observable distance traveled by helium after flow resumes, in the three configurations shown in Figure 1. Images were obtained with a 300 frame-per-second high-speed camera and points indicate the distance traversed by the helium flow in consecutive frames. Error bars (which are often too small to observe in the plot) indicate the standard deviations of three consecutive periods of resumed helium flow

helium projects from the source immediately after flow was resumed in the three configurations in Figure 1. The location of the front was gauged from the location farthest from the capillary where an objectively measurable change in the brightness of pixels (based on gray-scale of each image) was signaled by the image-tracking software. An initial acceleration of the helium flow from the FAPA source is evident in the first 10 ms for all three traces in Figure 2. This brief, initial acceleration is believed to result from a delay in reaching the maximum backing pressure inside the cell. The presence of a mock mass spectrometer interface (black trace in Figure 2) accelerates flow from the source, but the effect is small. In contrast, the green trace in Figure 2 shows that a crossing flow of the carrier He appears to expedite the advance of the gas flow from the source, likely because the carrier helium partially purged atmospheric gases from the path of the FAPA flow. The greater slope of the green trace indicates the elevated velocity beyond the first three measurement times. Later, gradual acceleration was observed for the conditions indicated by the black and red traces, as indicated by increasing slopes between points. Once the gas front advances beyond the first few millimeters of the crossing gas flow, it becomes indistinguishable in the schlieren images, so the green line is truncated in Figure 2. About 2 s after helium flow was resumed (not shown in Figure 2), the gas-flow behavior completely stabilized between the source and the mock interface. As expected, the front of the helium flow advanced and stabilized more quickly when the vacuum interface was present.

A detailed analysis of these data indicated differences between the observed and expected linear gas velocity exiting the source. The 1.6-cm gap between the capillary and the solid surface on the left in Figure 1a was filled with helium in about 42 ms. The gas front never reached a velocity greater than 2.5 m/s, although the expected mean and maximum velocity

based on the flow rate through the capillary were 12.5 and 25.0 m/s, respectively (calculated from the Hagen-Poiseuille equation and related discussion [12]). This disparity was believed to arise from the viscous drag of the surrounding atmosphere but could also be caused by a lag in the gas-flow controller.

An experiment was devised to distinguish viscous drag by the atmosphere from a turn-on delay in the mass-flow controller. A rotating mechanical chopper was used to physically interrupt the helium flow from the source to determine if the front of each flow segment moved more quickly after the mass flow controller had been turned on and stabilized. A video of these data can be found in the ESM. Even after flow from the controller had stabilized, each chopper-interrupted segment also exhibited a maximum flow velocity of about 2.5 m/s. A comparison of the segmented-flow velocity immediately after the helium has been turned on and after it already has been operating for 1 s reveals that the overall behavior becomes consistent after just three chopper cycles (0.23 s). Even during the first two chopper cycles (0.15 s), the turbulent drag of the surrounding gases developed at roughly the same location. The difference between the first and third cycle was insufficient to account for the slowing of gas flow. Clearly, turn-on delay in the flow controller was not the primary source of the slowed gas front when flow resumed.

Figure 3a shows the time-dependent behavior of gas flow from the source after He flow was restarted (designated by vertical green line in Figure 3a) and indicates that the stream

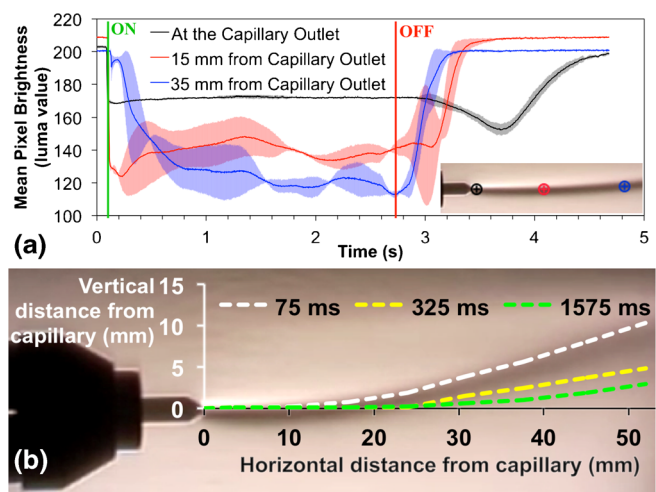


Figure 3. Schlieren characterization of helium from the FAPA source flowing into open atmosphere. (a) Refractive-index changes in the gas stream as helium flow starts and stops. The vertical green line labeled “ON” indicates when flow began and the vertical red line labeled “OFF” indicates when the flow was terminated. Shaded regions around each trace represent the standard deviation of three periods of flow interruption for each time point at the respective locations in the schlieren image. The inset photo indicates the position of the gas front corresponding to each colored trace. (b) Early spatial flow patterns when flow resumes, based on schlieren images. The shown schlieren photo is representative of the 75-ms line

required nearly a second to approach a stable state when no surface or vacuum interface was present. A decrease in the brightness of the image is related to the presence of the underside of the stream at each selected horizontal location. Only a slight delay is observed between the two regions nearest the FAPA source (represented by red and black traces in Figure 3a) due to the small distance between them. In contrast, at a distance of 35 mm from the source (blue trace), the helium flow required over a second to reach an approximately stable state. Yet, when gas flow was terminated (vertical red line in Figure 3a), the two regions farther from the source returned to their original states very quickly, whereas the location at the capillary outlet continued to be perturbed for about 1.5 s longer. These observations can be explained on the basis of the somewhat elevated gas pressure in the cell compared with the surrounding atmosphere. After He flow was terminated, positive pressure should persist in the cell for some period, during which the cell pressure would decline and helium would float upward, rather than to the farther zones tracked in Figure 3a. Presumably, only after the pressure has equilibrated would diffusion of atmospheric gases into the cell become significant.

Figure 3b displays the helium stream trajectory at selected times after He flow to the source is resumed. As time progressed, the flow projected farther forward with less buoyancy-driven upward movement. This behavior arose because of a slipstream effect: helium in front cleared a path for the following gas. This development is one of the characteristics of discontinuous helium flow for sampling vapor-phase samples. When helium flow is continuous, atmospheric gases do not significantly disrupt the flow, so the ion source samples only vapors that are present at the periphery of the helium stream. In contrast, when helium flow was restored in our new experiments, the entire He front can interact with vapors in the ambient atmosphere.

Mass-Spectrometry Signal When Helium Flow Resumes

This enhanced interaction between the FAPA stream and ambient vapors is perhaps the main reason for an observed spike in analyte signals immediately after helium flow is resumed (cf. Figure 4). This initial signal also presumably benefits from pooling of vapor molecules between the source and the MS interface when no source flow was present. When flow was resumed, the greater interaction of the gas front proceeding from the source to the interface likely ionizes and transports vapor-phase analytes to the inlet with high efficiency. However, once a steady flow profile was established, sampling was limited by diffusion of analyte vapor into the helium stream and resulted in a steadier signal. The same sort of initial signal spike was observed for all other volatile organic compounds examined, including dimethyl sulfide (DMSO), ethanol, acetonitrile, acetic acid, and pyridine.

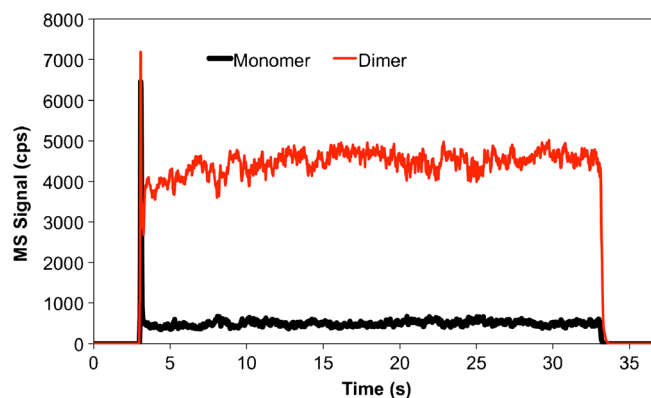


Figure 4. Chronograms of acetone signal when discontinuous helium flow is used. When helium flow is on, the flow rate through the source is 1.0 L/min. These chronograms are for the protonated monomer (m/z 59) and protonated dimer (m/z 117) over a 30-s analysis period during which helium is restored and terminated through the source. Acetone vapor is carried to the sampling region with a constant carrier-gas flow rate of 0.75 L/min

The relative magnitudes and consistency of the initial spike and the later, steadier signal depended on both analyte identity and carrier flow rate. In general, when the maximum of the initial spike in signals was much larger than the steady-state levels (cf. Figure 4), the repeatability of both the steady state and the spike were better (<10% RSD). At an analyte-carrier flow rate of 0.50 L/min, the initial spike was the highest observed signal throughout the measurement for ethanol, acetonitrile, and acetone, with peak levels 2–10 times greater than the steady-state signal. Ratios between the initial spike and the steady signal were also more consistent for the more volatile solvents, measured when separate periods of the sampling flow were compared (RSDs of the ratios ranged from 5% to 46%). In situations where the initial spike (followed by a clear drop then rise in signal) was lower than the steady-state level, much more variation in the spike was observed (e.g., RSD of 56% for DMSO at 0.50 L/min carrier flow). This difference in behavior cannot be attributed to analyte volatility alone; the ionization process and the tendency to form multimeric clusters also played some role. For instance, ions from acetic acid, which is very volatile but is not protonated with the FAPA source, achieved a steady-state level that was similar to the magnitude of the initial spike. Similarly, no clear trend was apparent between monomer signals and proton affinities of the analytes.

The presence of the initial signal spike makes possible the use of very short bursts of helium for analysis, perhaps even shorter than was suggested previously for solid samples [4]. In fact, the peaked signal when gas flow is initiated would permit analysis in just the 3-s periods of helium flow that was previously shown [4] to enable a stable discharge to be maintained with a discontinuous helium supply. For a source flow rate of 1.0 L/min, the total helium consumed during these first 3 s is a modest 0.05 L. Though earlier work with discontinuous helium flow was completed with the intention of lessening overall helium consumption [4], the most worthwhile aspect of

experiments with gas-phase samples might lie in the initial signal spike for rapid sampling.

Figure 4 reveals that the relatively high concentration of acetone vapor used in these experiments generates strong signals for both the monomer and dimer. The initial signal spike for both is similar in magnitude, but the subsequent lower signal is smaller but steadier for the monomer. Figure 5 shows the effect of analyte-carrier flow rate on both signal levels at higher time resolution, early after the onset of He flow. The steady-state level for the protonated acetone monomer signal was unaffected by differences in the carrier-gas flow rate, with no appreciable change in signal stability, as shown in Figure 5a. The only appreciable change in the monomer traces with different carrier-gas flow rates is in the magnitude of the initial spike, which is observed at all flow rates, including when no directed analyte-carrier flow is present (presumably some acetone vapor diffuses from the sample tubing even in the absence of a carrier flow). However, above 0.1 L/min of carrier-gas flow, the maximum of this spike declines for the acetone monomer, though the signal remains higher in all other cases than in the absence of carrier-gas flow.

In contrast, both the initial spike and steady-state level go up with carrier flow rate for the dimer signal (cf. Figure 5b). A steady-state dimer signal was achieved in 1 to 3 s, depending on the flow rate of the analyte carrier gas. Lower analyte-carrier flow rates take a longer period to reach a steady level, presumably because the carrier helium purge near the MS inlet is less effective, slowing the advance of the FAPA effluent (note behavior in the green curve in Figure 2). No dimer peak was observed without a directed carrier-gas flow, presumably because of the much lower acetone-vapor concentration.

From the monomer and dimer data in Figure 5, it appears that higher flow rates of the analyte-carrier gas through the bubbler increased the rate of vapor generation, which caused higher concentrations of vapor-phase acetone to be transported to the FAPA-MS interface. At lower carrier flow rates, the monomer dominates because of the lower acetone concentration, whereas the dimer becomes dominant when higher flow rates are used. Schlieren images in Figure 1c (cf. video in the

ESM) and the data in Figure 5 corroborate the described interaction between the continuous carrier and interrupted source flows; the shape of the carrier-gas flow is perturbed when the source flow is restarted, which affects the temporal characteristics of the MS signal.

Cessation of He flow through the FAPA cell was noted previously to result in elevated temperatures in the cell [4]. It was hypothesized that atmospheric gases that diffuse into the cell contribute to this heating; most molecular gases, which comprise the largest part of the surrounding air, have higher specific heats than helium due to their ability to store energy in their bonds. Further, these gases would result in a temporary alteration in the composition of the afterglow as it emerged from the cell. Negative consequences of this purge period were not observed in the present study; in fact, signal levels were sometimes highest during the period that included this purge within the first second of restarting helium flow (cf. Figures 4 and 5). These more thermal molecular gases have also been hypothesized to be involved as reagent ions in the afterglow [13]. In the configuration shown in Figure 1c, diffusion was not expected to cause problems with contamination or memory effects in the discharge cell from the sampled vapor because the carrier gas flow is pulled toward the MS interface. Further, the gases that diffuse into the cell when helium flow is paused are expected to be those molecules already in the surrounding environment near the source capillary outlet, which could include analytes. Variation in the composition of the gases that diffuse into the cell could affect the behavior of the discharge, as minor changes in the supporting gas have been shown to dramatically alter the behavior of the FAPA source [8]. Further study of these properties in the sampling environment could be important for the use of discontinuous flow for routine analysis of both vapors and solids.

Cluster Formation

As shown in Figures 4 and 5, some analytes form multimers when present at high concentration. Similar studies were conducted with several other volatile compounds; oligomers were

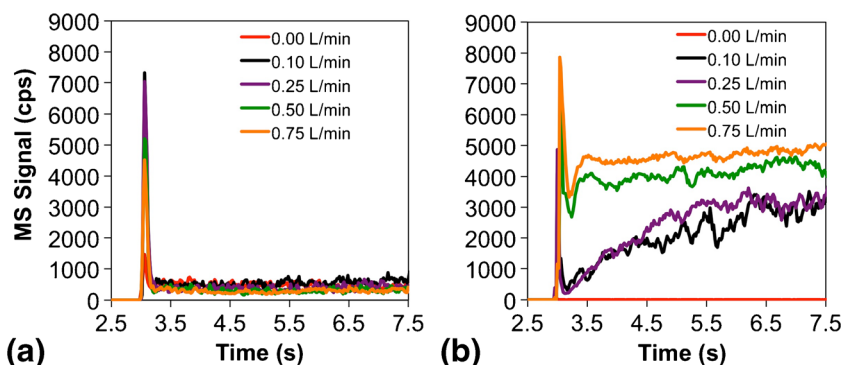


Figure 5. High temporal resolution acetone-signal chromatograms when the source helium flow is restarted at a flow rate of 1.0 L/min (at 2.75 s on the plots above). The helium carrier is flowing steadily for the entirety of each trace and the carrier flow rate is adjusted between experiments. (a) Protonated acetone monomer signal when helium flow in the FAPA source is restored, with different analyte-carrier helium flow rates denoted by color. (b) Protonated acetone dimer signal when helium flow in the FAPA source is restored with different analyte carrier-gas flow rates denoted by color

observed for all the vapor samples examined. Each mass spectrum is the sum of all spectra during a 20-s period of helium flow from the FAPA source. Acetone, DMSO, and acetonitrile all demonstrated different ratios of dimer and monomer signals. A comparison of the acetone and DMSO spectra indicates that dimer ions dominate the acetone spectrum but were the minority for DMSO. This difference for the two analogous molecules is likely due to their considerable disparity in volatility, which results in lower vapor concentrations of DMSO under the same operating conditions. Clustering of acetone and DMSO has been observed in previous studies when the solvents were sampled in their liquid form [14, 15]. In each of those cases, only the dimer was observed for pure DMSO, which is consistent with the observation that concentration in the vapor phase, solvent volatility, and the dimer-to-monomer ratio are directly related.

Acetonitrile produced even more interesting results: its spectrum exhibits peaks for trimers and tetramers. Though complete structural and stability characterization of these clusters would require further study, the current data suggest that the clusters were stable for at least the hundreds of microseconds needed for the ions to pass from the sampling region to the detector, including under elevated temperatures [4, 16] in the sampling region and reduced pressures ($<1.0 \times 10^{-6}$ kPa) in the mass spectrometer. Additional study will be required to determine the potential for use of these clusters for gas-phase chemistry applications.

Conclusion

Use of discontinuous helium flow with the FAPA source for the analysis of vapor-phase samples was explored based upon mass spectrometry data and schlieren imaging. The findings from the present study might be adapted to sample and monitor atmospheric gas composition, in addition to vapors that are intentionally introduced into the sampling region. Such an approach could enable repeatable and periodic analyses of the atmosphere with very limited helium consumption, which could be useful to industries with elevated risk of exposure to toxic vapors or for monitoring the presence of environmental contaminants in the atmosphere. Additionally, the presence of a spike in signal when the helium flow resumes could enable discrimination of peaks that arise from analytes of interest in the atmosphere from background fluctuations that originate in the source.

Acknowledgments

The authors acknowledge supported in part for this work by the United States Department of Energy through grant DE-FG02-

98ER 14890. The authors are also grateful for the donation of equipment used in these studies from Prosolia, Inc. (Indianapolis, IN), which provided the FAPA source used in these experiments, and LECO Corporation (St. Joseph, MI), which provided the mass spectrometer.

References

1. Andrade, F.J., Wetzel, W.C., Chan, G.C.Y., Webb, M.R., Gamez, G., Ray, S.J., Hieftje, G.M.: A new, versatile, direct-current helium atmospheric-pressure glow discharge. *J. Anal. At. Spectrom.* **21**, 1175–1184 (2006)
2. Cody, R.B., Laramée, J.A., Durst, H.D.: Versatile new ion source for the analysis of materials in open air under ambient conditions. *Anal. Chem.* **77**, 2297–2302 (2005)
3. Harper, J.D., Charipar, N.A., Mulligan, C.C., Zhang, X., Cooks, R.G., Ouyang, Z.: Low-temperature plasma probe for ambient desorption ionization. *Anal. Chem.* **80**, 9097–9104 (2008)
4. Storey, A.P., Zeiri, O.M., Ray, S.J., Hieftje, G.M.: Helium conservation by discontinuous introduction in the flowing atmospheric-pressure afterglow source for ambient desorption-ionization mass spectrometry. *J. Anal. At. Spectrom.* **30**, 2017–2023 (2015)
5. Takáts, Z., Wiseman, J.M., Gologan, B., Cooks, R.G.: Mass spectrometry sampling under ambient conditions with desorption electrospray ionization. *Science* **306**, 471–473 (2004)
6. Pfeuffer, K.P., Schaper, J.N., Shelley, J.T., Ray, S.J., Chan, G.C.Y., Bings, N.H., Hieftje, G.M.: Halo-shaped flowing atmospheric pressure afterglow: a heavenly design for simplified sample introduction and improved ionization in ambient mass spectrometry. *Anal. Chem.* **85**, 7512–7518 (2013)
7. Pfeuffer, K.P., Ray, S.J., Hieftje, G.M.: Measurement and visualization of mass transport for the flowing atmospheric pressure afterglow (FAPA) ambient mass-spectrometry source. *J. Am. Soc. Mass Spectrom.* **25**, 800–808 (2014)
8. Wright, J.P., Heywood, M.S., Thurston, G.K., Farnsworth, P.B.: The effects of added hydrogen on a helium atmospheric-pressure plasma jet ambient desorption/ionization source. *J. Am. Soc. Mass Spectrom.* **24**, 335–340 (2013)
9. Brüggemann, M., Karu, E., Stelzer, T., Hoffmann, T.: Real-time analysis of ambient organic aerosols using aerosol flowing atmospheric-pressure afterglow mass spectrometry (AeroFAPA-MS). *Environ. Sci. Technol.* **49**, 5571–5578 (2015)
10. Pfeuffer, K.P., Shelley, J.T., Ray, S.J., Hieftje, G.M.: Visualization of mass transport and heat transfer in the FAPA ambient ionization source. *J. Anal. At. Spectrom.* **28**, 379–387 (2013)
11. Curtis, M., Keelor, J.D., Jones, C.M., Pittman, J.J., Jones, P.R., Sparkman, O.D., Fernandez, F.M.: Schlieren visualization of fluid dynamics effects in direct analysis in real time mass spectrometry. *Rapid Commun. Mass Spectrom.* **29**, 431–439 (2015)
12. Giddings, J.C.: *Unified Separation Science*. Wiley, Ann Arbor (1991)
13. Shelley, J.T., Chan, G.C.-Y., Hieftje, G.M.: Understanding the flowing atmospheric-pressure afterglow (FAPA) ambient ionization source through optical means. *J. Am. Soc. Mass Spectrom.* **23**, 407–417 (2012)
14. Song, L., Gibson, S.C., Bhandari, D., Cook, K.D., Bartmess, J.E.: Ionization mechanism of positive-ion direct analysis in real time: a transient microenvironment concept. *Anal. Chem.* **81**, 10080–10088 (2009)
15. Liu, X.-P., Wang, H.-Y., Zhang, J.-T., Wu, M.-X., Qi, W.-S., Zhu, H., Guo, Y.-L.: Direct and convenient mass spectrometry sampling with ambient flame ionization. *Sci. Rep.* **5**, 16893 (2015)
16. Shelley, J.T., Wiley, J.S., Hieftje, G.M.: Ultrasensitive ambient mass spectrometric analysis with a pin-to-capillary flowing atmospheric-pressure afterglow source. *Anal. Chem.* **83**, 5741–5748 (2011)