Published in final edited form as:

J Am Soc Mass Spectrom. 2014 May ; 25(5): 800–808. doi:10.1007/s13361-014-0843-x.

Measurement and Visualization of Mass Transport for the Flowing Atmospheric Pressure Afterglow (FAPA) Ambient Mass-Spectrometry Source

Kevin P. Pfeuffer, Steven J. Ray, and Gary M. Hieftje*

Department of Chemistry, Indiana University, Bloomington, IN 47405

Abstract

Ambient desorption/ionization mass spectrometry (ADI-MS) has developed into an important analytical field over the last nine years. The ability to analyze samples under ambient conditions while retaining the sensitivity and specificity of mass spectrometry has led to numerous applications and a corresponding jump in the popularity of this field. Despite the great potential of ADI-MS, problems remain in the areas of ion identification and quantification. Difficulties with ion identification can be solved through modified instrumentation, including accurate-mass or MS/MS capabilities for analyte identification. More difficult problems include quantification due to the ambient nature of the sampling process. To characterize and improve sample volatilization, ionization, and introduction into the mass-spectrometer interface, a method of visualizing mass transport into the mass spectrometer is needed. Schlieren imaging is a well-established technique that renders small changes in refractive index visible. Here, schlieren imaging was used to visualize helium flow from a plasma-based ADI-MS source into a mass spectrometer while ion signals were recorded. Optimal sample positions for melting-point capillary and transmission-mode (stainless steel mesh) introduction were found to be near (within 1 mm of) the mass spectrometer inlet. Additionally, the orientation of the sampled surface plays a significant role. More efficient mass transport resulted for analyte deposits directly facing the MS inlet. Different surfaces (glass slide and rough surface) were also examined; for both it was found that the optimal position is immediately beneath the MS inlet.

Introduction

Since its introduction in 2004 in the form of desorption electrospray ionization (DESI) [1], ambient desorption/ionization mass spectrometry (ADI-MS) has solidified its place as an important analytical technique, with over 50 sources described in the recent literature. A compelling feature of this technique is the ability to both desorb and ionize compounds under ambient conditions, which has led to a broad range of applications, including forensics [2], high-throughput analysis [3], analysis of lithium-ion batteries [4] and numerous others. Moreover, analysis time is reduced by eliminating nearly all sample pre-treatment. Two of the most popular sources for ADI-MS are DESI and the discharge-based direct analysis in real time (DART) source [5]. For the plasma-based sources, spectra tend to be simple,

*Corresponding Author: Department of Chemistry, Indiana University, Bloomington, IN, 47405, Hieftje@indiana.edu.

resulting primarily in only the molecular ion (M^+) or protonated molecular ion ($M+H$)⁺, which enables rapid and accurate identification of compounds through exact-mass measurement or characteristic fragmentation patterns in MS/MS experiments.

The source of particular focus in the present study is the flowing atmospheric pressure afterglow (FAPA), which utilizes an atmospheric-pressure helium glow discharge operated in the flowing afterglow mode [6]. The discharge is sustained between a pin cathode and a capillary anode. A helium stream passes through the plasma and excited species and ions are swept out through a capillary, where they desorb and ionize the sample constituents. Although this manuscript will focus on the FAPA source, the findings are rather general and are likely applicable to other plasma-based ambient mass spectrometry sources such as DART [5] and the low temperature plasma (LTP) [7] probe.

As the field of ambient mass spectrometry has matured, several fundamental investigations into basic processes involved in ion formation and ionization have been performed. These studies, essential for understanding and improving the sources, have included discharge-based sources. The FAPA [8] and the low-temperature plasma (LTP) probe have been characterized optically [9]. Also, the FAPA and DART sources have been compared through current-voltage curves, thermal imaging [10] and their susceptibility to matrix effects [11]. The LTP source was also compared to ESI and APCI [12] to determine the classes of compounds that are best suited for each ionization device. A thorough comparison of DART, a dielectric barrier discharge (DBD) and a novel RF source was undertaken to elucidate water-cluster formation mechanisms [13]. This list is by no means exhaustive, but demonstrates the extensive work that is being directed into fundamental studies of ambient mass spectrometry. Despite this important progress, a gap remains in the understanding of mass transport in ADI-MS systems.

Reproducibility and quantification remain problematic in ADI-MS primarily because of the ambient nature of the sampling process. Ambient air currents, sample-surface defects, and inconsistencies in sample positioning all affect signal stability and reproducibility; relative standard deviations of 35% have been reported for the FAPA source for example [14]. Acceptance volumes from atmospheric-pressure ion sources and MS inlets have been examined by Benter et. al. [15–17]. However, their experiments were concerned only with vapor-phase samples being transported into a mass-spectrometer inlet. The process of desorption from samples has not yet been considered, yet is an integral part of the ambient mass spectrometry experiment. A theoretical investigation into mass transport with the DART source was undertaken by Harris and Fernandez through finite-element simulation [18], which modeled gas flow and both conductive and convective heat flow from the DART source onto a tablet. However, these studies were computationally intensive and modeling transitional flow (into an MS inlet) is difficult.

In contrast, schlieren imaging is a relatively simple technique that renders small changes in refractive index visible. The difference in refractive index between helium (1.000036) and air at 23° C (1.0002926) [19] is sufficient for schlieren imaging. Recent work by Pfeuffer et al. proved that schlieren imaging can provide valuable insight into mass transport with the FAPA source [20]. Information about the transition from turbulent to laminar flow and how

sample placement affects helium flow was obtained. However, this previous experiment was incomplete, as no information about ion identity or abundance was obtained.

In order to correlate gas-flow patterns with ion signals, a compact schlieren imaging system was designed and constructed around a time-of-flight mass spectrometer interface. Several sample introduction configurations were examined, including a melting point capillary (MPC), a stainless steel mesh, and smooth and rough surfaces. The MPC positions close to the FAPA or close to the MS inlet were found to provide the strongest signals. In transmission mode with a mesh, only positions close to the MS inlet were found to give acceptable signals. Additionally, the direction in which the sample was oriented produced a measurable effect; better mass transport was seen when the sample faced the MS inlet for both MPC and mesh introduction modes. Finally, smooth and rough surfaces were examined and, for both, positions as close as possible to the MS inlet provided the best throughput.

Experimental

A compact double-pass schlieren system was constructed around the atmospheric-sampling inlet of a time-of-flight mass spectrometer (Leco Unique[®], St. Joseph MI, USA) (cf. Supplemental Information Figure S1). Minor modifications have been made to the mass spectrometer that were detailed previously [21] but will be briefly recapped here. An additional turbo-molecular pump and roughing pump were added to the first vacuum stage to handle the increased helium load. A heated capillary inlet (I.D. 250 μm) was utilized for all studies. The double-pass schlieren system was based on a design described by Schardin [22], and elaborated by Settles [23]. A halogen lamp (model 9006, ABS, Houston, TX, USA) was used as light source, powered at 4A and 10 V by an external supply (model 6267B Hewlett Packard, Houston, TX, USA). Light then passed through a focusing lens (5x microscope objective, Unitron, Boston, MA, USA, not shown in Figure S1) before being shaped by a slit (Oriel Instruments, Stratford, CT, USA, also not shown in Figure S1) set at 2 mm width to define the effective source dimensions. A 50/50 half-silvered mirror (Edmond Optics, Barrington, NJ, USA) was used to split the light; half fell upon a spherical mirror (15 cm diameter, 40 cm focal length), which focused the light back through the beamsplitter onto a knife edge (razor blade). A 40 cm focal length achromatic lens then focused the refracted light onto a digital camera body (Canon EOS Rebel T4i, Canon USA Inc. Melville, NY, USA) with the lens removed. The schlieren-imaging region lay just before the focusing mirror.

A prototype flowing atmospheric-pressure afterglow (FAPA) source developed by Prosolia Inc. (Indianapolis, IN, USA) was used for all studies; it is based on the pin-to-capillary FAPA source described previously [6] with minor differences described here. This FAPA version employs a 3.2-mm diameter tungsten cathode with an arrowhead shape and a tubular capillary anode (O.D. 3.14 mm, I.D. 1.0 mm, 17 mm in length). Helium flow (UHP, Airgas mid-America, Bowling Green, KY, USA) was set to 0.80 L/min by a mass flow controller (MKS instruments, Andover, MA, USA) for all studies. The discharge voltage was provided by a power supply (Model PTV200x, Spellman High Voltage, Hauppauge, NY, USA) and an offset voltage was applied to the front capillary *via* a secondary power supply (model

E3612A, Agilent Technologies, Santa Clara, CA, USA). The FAPA position was controlled by a three-dimensional translation stage (Thorlabs, Newton, NJ, USA).

Various sample supports, including a melting point capillary (1.5–1.8 mm O.D., MPC, Chemglass Life Sciences, Vineland, NJ, USA), stainless steel mesh (100×90 and 70×70 strands per inch, McMaster Carr, Elmhurst, IL, USA) and flat surfaces (glass slides, VWR, Westchester, PA, USA and commercial sandpaper) were used to represent different sample introduction methods. Samples were reproducibly moved through the FAPA afterglow by means of an automated stage (Model Z825, Thorlabs, Newton, NJ, USA) controlled externally (Model TDC001 Thorlabs, Newton, NJ, USA). Sample material was deposited on the melting point capillary, mesh and surfaces by means of a modified commercial ink-jet printer (Epson 280, Long Beach, CA, USA). For monitoring helium flow, methyl salicylate was doped into the helium stream at an approximate concentration of 70 ppm (v/v, based on vapor pressure).

Results

Probe introduction

A melting point capillary (MPC) is a convenient vehicle for introducing liquid and solid samples into ambient desorption/ionization mass spectrometry sources. Accordingly, a MPC was used to study systematically how sample introduction affected helium flow into the mass spectrometer inlet. Methyl salicylate was doped into the helium flow to act as a tracer and the MPC was positioned vertically and moved across (perpendicular to) the afterglow in 0.25-mm increments. At the same time, the signal from the protonated molecular ion of methyl salicylate and schlieren images were both acquired. Figure 1 summarizes the results from a set of experiments in which the MPC was placed at distances of 1, 5 and 9 mm away from the FAPA source. It was found that the MPC position closest to the FAPA source (1 mm) resulted in the largest attenuation (90%) of the methyl salicylate signal. The cause of this attenuation is apparent from the schlieren images (cf. Figures 1a, b, c); a MPC position close to the FAPA deflects the majority of helium away from the MS interface and prevents the gas from being gathered by the mass spectrometer. Conversely, moving the MPC closer to the MS interface improves the amount of helium gathered by the MS. This behavior is clear from Figure 1d, which shows that more helium is gathered at a MPC position 5 mm from the FAPA than at 1 mm (only 73% reduction). Similarly, the schlieren image in Figure 1b shows deflection of helium by the MPC at a position 5 mm from the FAPA source but some is still gathered by the MS interface. With the MPC placed as close as possible (~1 mm) to the interface (9 mm from FAPA source) the attenuation of the methyl salicylate signal was lowest but still appreciable at 50%. Of course, mass transport from the FAPA to the MS is only part of the picture; at least as important is transport of analyte material from the MPC into the MS.

In order to quantify mass transport from the MPC to the mass spectrometer, a commercial ink-jet printer (Epson 380) was modified to deposit a desired solution onto the surface of a melting point capillary. Because methyl salicylate was too thermally unstable for such a study, caffeine (1 µg/mL) was substituted. Caffeine was printed on half of the longitudinal body of the MPC, and this portion of the MPC was moved through various positions

between the FAPA source and the MS inlet. The results are summarized in Figure 2. When the melting point capillary was positioned 1 mm from the FAPA source, the signal for caffeine showed a strong bimodal distribution, with analyte signals $(M+H)^+$ being strong only along the edges of the MPC (Figure 2d). This finding meshes with what has been seen previously [20] where the MPC blocks and deflects helium away from the MS inlet, so analyte could be transported from the MPC into the MS only along the edges of the MPC where the blocking effect is minimal. Moving the MPC equidistant between the FAPA source and MS inlet (Figures 2b and 2e) improves the mass transfer from the MPC, but still results in a bimodal distribution, albeit less dramatic than in the position closer to the FAPA source (Figure 2d). With the MPC located 1 mm in front of the FAPA (Figures 2c and 2f), a single peak occurred, since most of the helium was able to be drawn into the MS inlet on the other side of the probe.

The spatially resolved signal traces in Figure 2d through 2f indicate which position gives the strongest peak signal. The spatially integrated intensity (-3 to +3 mm) of these profiles provides the best analytical information about the different positions and conditions because ambient analyses are often performed by summing the signal as the sample moves across the ambient source. Such spatially integrated signals are shown in Table 1; within error, there is no statistical difference in signals obtained with the MPC placed near the FAPA source or immediately in front of the inlet (Figure 2d versus 2f). The high signal for the position closest to the FAPA source is likely due to the higher gas temperature there, which leads to greater sample volatilization. The temperature of the afterglow can cool by as much as 30 degrees over the 8 mm difference between capillary positions [10]. The middle position, however, produced the lowest signal, probably due to lower temperature and inefficient mass transport. Overall, MPC positions closer to the mass spectrometer inlet result in more uniform mass transport, which might be important for automated analysis (such as peak-fitting software). However, thermal desorption will play a role in determining overall signal levels.

The direction in which the deposited analyte faced was also examined. Not surprisingly, if the caffeine deposit faced the FAPA source the signal was smaller than if the deposit faced the MS inlet (cf. Table 1). Presumably, this behavior is the result of more efficient mass transport from the rear of the MPC into the MS inlet. In this experiment, the MPC was located equidistant from the MS and FAPA source (5 mm)

Transmission Mode

Transmission-mode ADI-MS experiments have recently become appealing because of the ease of sample deposition and the reduction in geometrical degrees of freedom this arrangement provides [24]. In this mode, solution samples are deposited on a mesh, with the ADI-MS source and MS inlet positioned on opposite sides. Here, two different stainless-steel mesh densities, 70×70 and 100×90 strands per inch (SPI) were examined in the same three positions used in the MPC experiments described above: 1, 5 and 9 mm from the FAPA source. The finer mesh (100×90) had a higher percentage open space (40%) than the “coarse” (70×70) mesh (30%). Although both mesh sets were evaluated, only the fine-mesh

information is shown below because it provided better analytical performance; coarse-mesh figures are available in the supplemental information (Figures S2 and S3).

The amount of helium transmitted through the mesh correlates roughly with the percent open space in the mesh, and should therefore produce the strongest signal for methyl salicylate doped into the helium stream. A mesh position closest to the FAPA source (1 mm from FAPA, Figure 3a) results in nearly total loss of the methyl salicylate signal (Figure 3d). This total attenuation is understandable from the corresponding schlieren image (Figure 3a), in which the helium flow is entirely deflected by the mesh and does not reach the mass spectrometer inlet. When the mesh is moved to an intermediate position (5 mm from FAPA source), the methyl salicylate signal rises (Figure 3d) but is still significantly lower (80%) than when the mesh is not in place. The corresponding schlieren image (Figure 3b) illustrates this point, as some helium penetrates the mesh and reaches the MS inlet, although much is still deflected. Finally, with the mesh 1 mm from the MS inlet (9 mm from FAPA source) the lowest attenuation (65%) of the methyl salicylate signal occurs. This observation, too, is supported by the corresponding schlieren image (Figure 3c).

As in the MPC experiments, mass transport from the mesh surface into the mass spectrometer was also determined. Caffeine was deposited onto 5-mm wide strips of mesh of each density (70×70 and 100×90) and positioned in the FAPA afterglow. As before, only data for the fine (100×90) mesh is shown below, but results for the coarse (70×70) mesh can be seen in the supplemental information (Figure S3). At the mesh position closest to the FAPA source (1 mm, cf. Figure 4a), the caffeine signal is seen only at the edges of the mesh (−2 mm and +2 mm in Figure 4d), which otherwise blocks most of the helium seen in Figure 4a. This edge effect was seen also in the MPC experiments. Presumably, the effect is similar here; caffeine is desorbed at the edge of the mesh and finds its way around that edge and into the MS inlet. At an intermediate position (5 mm from FAPA, Figure 4b) a similar bimodal distribution occurs, but the effect is less than in the melting point capillary experiments, as some helium passes through the mesh (cf. Figure. 4b). With the mesh even closer to the MS inlet (9 mm away from FAPA, Figure 4c) a broader, more uniform caffeine signal peak occurs, as helium was able to penetrate the mesh throughout its length (Figure 4c) and transfer more caffeine into the mass spectrometer. The local maxima for the 1 and 5 mm positions are higher than at the 9 mm position but, as with the MPC, the spatially integrated intensity across the mesh is of the greatest analytical interest. The asymmetry in the traces in Figure 4d was noted for all mesh experiments, where one side (around −2 mm) consistently yielded a much higher signal level. The reason for this behavior is currently not known; sample material was evenly distributed on the mesh.

The analytical performance of different meshes, positions and densities in Figures 4 and S3 is best compared by means of spatially integrated signal levels. Summed intensities from −4 to +4 mm for both mesh densities at all three tested positions, and for sample deposits facing both directions are compiled in Table 2. A mesh position closest to the MS inlet (labeled MS inlet) results in a higher signal than do positions in the middle (5 mm from FAPA) and close to the FAPA source (1 mm from FAPA). The finer mesh (100×90) always results in a higher signal than the coarse mesh (70×70), regardless of position, although the difference is not always statistically significant. The more important variable is that the mesh should be

placed close to the MS inlet. In MPC experiments (cf. Figure 2), positions closest to the FAPA and the MS inlet gave equivalent signals; this trend is not seen with the mesh sample introduction. This difference is because the mesh blocks helium flow more effectively than the MPC, which is able to redirect some flow around its smooth surface. The distinction between levels is not large, but is consistent for both mesh densities.

Akin to what was seen for MPCs, a higher signal level was seen when the printed analyte surface faced the MS inlet for the fine mesh (100×90 SPI). This higher signal is most likely due to easier mass transport from the mesh into the mass spectrometer. Interestingly, the coarse mesh (70×70) showed no discernible difference between positions facing the MS inlet or away; the reason is for this behavior is not currently known.

Surface Interrogation—Planar sample surfaces were examined to determine their optimal placement with respect to the FAPA outlet and the mass-spectrometer inlet. The effect of surface roughness was also evaluated. An automated stage was arranged to move a surface vertically in 0.25-mm increments into the FAPA stream, which was positioned at a 30° angle with respect to the horizontal sample surface, approximately 10 mm away from and 5 mm above the capillary inlet.

Methyl salicylate vapor was again doped into the helium flow and the protonated molecular ion was monitored while the surface was raised incrementally into the FAPA afterglow stream. Results for a smooth surface (glass slide) (cf. Figure 5) show that effectively no signal is seen as long as the surface is more than 2 mm below the MS interface. However, the signal rises steadily when the surface is moved above 2.5 mm below the FAPA stream, and reaches a plateau from approximately 1.0 mm below the MS interface to directly below the interface. From the corresponding schlieren images (Figures 5a, b, and c) it is clear that near 2 mm below the MS inlet (Figure 5b) is where helium first begins to interact strongly with the MS capillary. This effect is believed to be due to a boundary layer of helium that forms on the smooth surface [25]. This boundary layer is advantageous, as it provides some flexibility in surface placement. That is, the surface does not need to be positioned exactly under the MS inlet, but rather within 1 mm, and the interface still gathers the helium efficiently.

Sandpaper was used to represent a rough surface with a known particle size distribution. With 40-grit sandpaper (200 μm mean particle diameter) the same signal maximum was seen as with the glass surface, but the boundary-layer effect is eliminated (Figure S4). Specifically, the signal rises to a peak with the surface directly below the MS capillary inlet, in contrast to the smooth surface where a leveling effect was seen. This difference is either because the rough surface disrupts the boundary layer, or prevents sampling from within the uneven surface. An even rougher surface (average particle size 500 μm) was also examined and showed a similar trend to the 200 μm particle-diameter surface, but with a lower peak signal (data not shown). This lower signal is likely due to scattering of helium away from the MS interface by the rougher surface. The possibility of surface adsorption being responsible for the lower signal was dismissed due to the non-adsorbent behavior of aluminum oxide used in the abrasive material.

A similar set of experiments was performed except with caffeine printed onto the same sample surfaces. During caffeine desorption from the smooth surface (Figure 6), the protonated caffeine signal began to rise only with the surface positioned less than 1 mm below the MS inlet. This behavior is likely due to either thermal volatilization effects (the afterglow not being hot enough to desorb caffeine) or limited mass transfer of caffeine through the boundary layer of helium. Boundary layer issues are most likely the cause because of the difference in appearance of the caffeine signal in Figure 6 and that of methyl salicylate vapor interacting with the smooth surface (3 mm, Figure 5). For caffeine desorption from the rough surface (200 μm particle diameters, Figure S5), no statistically significant signal was observed until the surface was directly (0 mm) below the MS interface. This finding is in some contrast with the methyl salicylate work (Figure S4), where a significant signal was seen even with the surface located approximately 2 mm below the MS inlet. The reason for this difference is likely poor mass transport from the rough surface due to disruption of the boundary layer and scattering of helium.

Overall, a smooth surface provides good signal level, along with flexibility in sample position. A rough surface can provide a similar signal level, but positioning becomes more important, and the possibility of signal loss due to gas scattering should be considered, primarily on an analysis by analysis situation.

Conclusions

A compact, double-pass schlieren system was installed around an atmospheric-sampling mass spectrometer to visualize mass transport and to correlate flow patterns with ion information for the FAPA ambient desorption/ionization mass spectrometry source. Three popular methods for sample introduction were explored: a probe (melting point capillary), transmission mode (stainless steel mesh), and alternative flat surfaces. It was found that a MPC position either close to the FAPA source or MS inlet (1 mm from each) provided the best throughput into the MS, despite helium flow being blocked by the MPC near the FAPA source. The higher temperature of the helium stream close to the FAPA is thought to desorb compounds more efficiently. An MPC position close to the MS inlet does, however, provide the most efficient helium flow into the mass spectrometer. Additionally, having the analyte deposit facing the MS inlet results in a stronger signal than when it is oriented away from the MS inlet and toward the FAPA outlet.

Two mesh densities (100 $\times$ 90 and 70 $\times$ 70 strands per inch) were examined in transmission-mode experiments; it was found that the greater mesh density (100 $\times$ 90) gave higher signals than the lower density, probably because of its higher transmission efficiency. The optimal position for the mesh was found to be immediately (1 mm) in front of the MS inlet; both meshes were too thick to allow helium to enter the MS inlet when they were placed close to the FAPA source. As with the MPC studies, analyte deposits facing the MS inlet generated the strongest signals.

Finally, smooth and rough planar surfaces were examined. Not surprisingly, positions as close (vertically) to the MS inlet as possible provided the highest sample throughput. For a smooth glass surface, evidence of a boundary layer was seen, where all positions $\sim$ 1 mm

below the MS inlet gave consistent signals. This boundary layer was not observed for a rough (425 μm particle size) surface.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Supported in part by the National Institute of General Medical Sciences (NIGMS) of the National Institute of Health (NIH) under award number R42GM103491 in collaboration with Prosolia, Inc (Indianapolis, IN). The content is solely the responsibility of the authors and does not necessarily represent the official views of the NIH. Salary support was provided by the Department of Energy through grant DE-FG02-98ER14890. The authors would also like to thank the Leco Corporation for the generous donation of equipment and Prosolia Inc. for loan of the prototype FAPA source.

References

1. Takats Z, Wiseman JM, Gologan B, Cooks RG. Mass Spectrometry Sampling Under Ambient Conditions with Desorption Electrospray Ionization. *Science*. 2004; 306:471–473. [PubMed: 15486296]
2. Green FM, Salter TL, Stokes P, Gilmore IS, O'Connor G. Ambient mass spectrometry: advances and applications in forensics. *Surface and Interface Analysis*. 2010; 42:347–357.
3. Li LP, Feng BS, Yang JW, Chang CL, Bai Y, Liu HW. Applications of ambient mass spectrometry in high-throughput screening. *Analyst*. 2013; 138:3097–3103. [PubMed: 23549078]
4. Vortmann B, Nowak S, Engelhard C. Rapid Characterization of Lithium Ion Battery Electrolytes and Thermal Aging Products by Low-Temperature Plasma Ambient Ionization High-Resolution Mass Spectrometry. *Anal Chem*. 2013; 85:3433–3438. [PubMed: 23394434]
5. Cody RB, Laramée JA, Durst HD. Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions. *Anal Chem*. 2005; 77:2297–2302. [PubMed: 15828760]
6. Shelley JT, Wiley JS, Hieftje GM. Ultrasensitive Ambient Mass Spectrometric Analysis with a Pinto-Capillary Flowing Atmospheric-Pressure Afterglow Source. *Anal Chem*. 2011; 83:5741–5748. [PubMed: 21627097]
7. Harper JD, Charipar NA, Mulligan CC, Zhang X, Cooks RG, Ouyang Z. Low-Temperature Plasma Probe for Ambient Desorption Ionization. *Anal Chem*. 2008; 80:9097–9104. [PubMed: 19551980]
8. Shelley JT, Chan G, Hieftje G. Understanding the Flowing Atmospheric-Pressure Afterglow (FAPA) Ambient Ionization Source through Optical Means. *J Am Soc Mass Spectrom*. 2011; 1–11.
9. Chan GCY, Shelley JT, Wiley JS, Engelhard C, Jackson AU, Cooks RG, Hieftje GM. Elucidation of Reaction Mechanisms Responsible for Afterglow and Reagent-Ion Formation in the Low-Temperature Plasma Probe Ambient Ionization Source. *Anal Chem*. 2011; 83:3675–3686. [PubMed: 21526754]
10. Shelley JT, Wiley JS, Chan GCY, Schilling GD, Ray SJ, Hieftje GM. Characterization of Direct-Current Atmospheric-Pressure Discharges Useful for Ambient Desorption/Ionization Mass Spectrometry. *J Am Soc Mass Spectrom*. 2009; 20:837–844. [PubMed: 19185515]
11. Shelley JT, Hieftje GM. Ionization matrix effects in plasma-based ambient mass spectrometry sources. *Journal of Analytical Atomic Spectrometry*. 2010; 25:345–350.
12. Albert A, Engelhard C. Characteristics of Low-Temperature Plasma Ionization for Ambient Mass Spectrometry Compared to Electrospray Ionization and Atmospheric Pressure Chemical Ionization. *Anal Chem*. 2012; 84:10657–10664. [PubMed: 23134531]
13. Kratzer J, Mester Z, Sturgeon RE. Comparison of dielectric barrier discharge, atmospheric pressure radiofrequency-driven glow discharge and direct analysis in real time sources for ambient mass spectrometry of acetaminophen. *Spectrochim Acta Part B*. 2011; 66:594–603.
14. Schilling GD, Shelley JT, Barnes JH IV, Sperline RP, Denton MB, Barinaga CJ, Koppenaal DW, Hieftje GM. Detection of Positive and Negative Ions from a Flowing Atmospheric Pressure

- Afterglow Using a Mattauch-Herzog Mass Spectrograph Equipped with a Faraday-Strip Array Detector. *J Am Soc Mass Spectrom.* 2010; 21:97–103. [PubMed: 19889553]
15. Lorenz M, Schiewek R, Brockmann K, Schmitz O, Gäb S, Benter T. The distribution of ion acceptance in atmospheric pressure ion sources: Spatially resolved APLI measurements. *J Am Soc Mass Spectrom.* 2008; 19:400–410. [PubMed: 18187335]
 16. Poehler T, Kunte R, Hoenen H, Jeschke P, Wissdorf W, Brockmann K, Benter T. Numerical Simulation and Experimental Validation of the Three-Dimensional Flow Field and Relative Analyte Concentration Distribution in an Atmospheric Pressure Ion Source. *J Am Soc Mass Spectrom.* 2011:1–9.
 17. Wissdorf W, Lorenz M, Pöhler T, Hönen H, Benter T. Atmospheric Pressure Ion Source Development: Experimental Validation of Simulated Ion Trajectories within Complex Flow and Electrical Fields. *J Am Soc Mass Spectrom.* 2013; 24:1456–1466. [PubMed: 23812870]
 18. GAH. Simulations and Experimental Investigation of Atmospheric Transport in an Ambient Metastable-Induced Chemical Ionization Source. *Anal Chem.* 2008; 81:322–329.
 19. Weast, RC. *CRC Handbook of Chemistry and Physics.* CRC Press, Inc; Boca Raton, Florida: 1982.
 20. Pfeuffer KP, Shelley JT, Ray SJ, Hieftje GM. Visualization of mass transport and heat transfer in the FAPA ambient ionization source. *J Anal At Spectrom.* 2013; 28:379–387.
 21. Shelley JT, Hieftje GM. Fast transient analysis and first-stage collision-induced dissociation with the flowing atmospheric-pressure afterglow ionization source to improve analyte detection and identification. *Analyst.* 2010; 135:682–687. [PubMed: 20349535]
 22. Schardin, H. N.A.S.A. Administration. *Ergebnisse der Exakten Naturwissenschaften.* NASA; Washington, D.C: Apr. 1970
 23. Settles, GS. *Schlieren and Shadowgraph Techniques: Visualizing Phenomena in Transparent Media.* Springer-Verlag; New York: 2001.
 24. Chipuk J, Brodbelt J. Transmission mode desorption electrospray ionization. *J Am Soc Mass Spectrom.* 2008; 19:1612–1620. [PubMed: 18684639]
 25. White, FM. *Fluid Mechanics.* 2. McGraw-Hill Book Company; St. Louis: 1986.

Figure 1.

A melting point capillary was oriented vertically and inserted into a helium stream doped with methyl salicylate at positions 1, 5 and 9 mm from FAPA source (images a, b and c, respectively), while schlieren images and mass-spectral signals were acquired simultaneously. Plot d shows the methyl salicylate signal as the probe is moved through the FAPA afterglow

Figure 2.

Schlieren images and ion signals for caffeine deposited on melting point capillaries positioned at the same locations within the afterglow as in Figure 2. Images a, b and c are 1, 5, and 9 mm away from the FAPA source and correspond to plots d, e and f on right.

Figure 3.

Transmission-mode experiments performed with a fine (100×90 strands/in) stainless steel mesh. Mesh positioned 1, 5 and 9 mm from the FAPA source (images a, b and c, respectively) and the corresponding methyl salicylate signal for each position, chart d. The methyl salicylate had been doped into the FAPA helium flow, so represents the efficiency with which the interface collects the afterglow gases beyond the mesh.

Figure 4.

Experiments with the fine mesh at distances of 1, 5 and 9 mm from the FAPA source with corresponding schlieren images (a, b and c) and summed signal for caffeine from mesh being moved through afterglow (d). Here, the caffeine had been deposited directly on the mesh, so signals in (d) represent the efficiency with which sample material on the mesh can reach the mass spectrometer inlet.

Figure 5.

Smooth-surface experiments with cleaned glass microscope slide at distances of 5, 2 and 0 mm below (negative) the MS inlet where 0 is touching the MS capillary, with corresponding schlieren images (a, b and c) and temporally summed signal for methyl salicylate from the helium stream for each position (d). Error bars represent plus and minus one standard deviation.

Figure 6.

Smooth-surface experiments with caffeine deposited on a glass microscope slide, which was positioned at distances of 2 and 0 mm below (negative) the MS inlet, with corresponding schlieren images (a, and b) and temporally summed signal for caffeine from the surface for each position (c). Error bars represent one standard deviation.

Table 1

Spatially summed signal (from -3 to +3 mm) for each MPC position and for both directions in which the MPC was oriented. Error represents plus/minus one standard deviation for 5 replicates. FAPA, Middle and MS inlet correspond to positions 1, 5 and 9 mm away from the FAPA source, respectively.

Position of MPC		Direction deposited surface faces	
Condition	Summed Signal (cts/10 ⁶)	Condition	Summed Signal (cts/10 ⁶)
FAPA (1 mm)	3.3±0.04	Facing MS inlet	3.7±0.4
Middle (5 mm)	2.6±0.2	Facing FAPA source	2.6±0.3
MS inlet (9mm)	3.1±0.2		

Table 2

Spatially summed signals (from -4 to $+4$ mm) for both mesh densities at all three tested positions, and for sample deposits facing both directions. Error represents plus/minus one standard deviation. MS inlet, Middle and FAPA correspond to positions 9, 5 and 1 mm away from the FAPA source, respectively.

Position of mesh		Direction deposited surface faces	
Location	Summed Signal (cts/ 10^6)	Condition	Summed Signal (cts/ 10^6)
MS inlet 100×90	3.1±0.5	70×70 mesh MS inlet	1.0±0.1
MS inlet 70×70	2.8±0.3	70×70 mesh FAPA	1.0±0.2
Middle 100×90	2.4±0.3	100×90 mesh MS inlet	1.3±0.1
Middle 70×70	2.2±0.3	100×90 mesh FAPA	0.9±0.1
FAPA 100×90	1.38±0.08		
FAPA 70×70	1.0±0.5		