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Halo-shaped Flowing Atmospheric Pressure Afterglow – a Heavenly New Design for Simplified Sample Introduction and Improved Ionization in Ambient Mass Spectrometry

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Abstract

The flowing atmospheric pressure afterglow (FAPA) is a promising new source for atmospheric pressure, ambient desorption/ionization mass spectrometry. However, problems exist with reproducible sample introduction into the FAPA source. To overcome this limitation, a new FAPA geometry has been developed in which concentric tubular electrodes are utilized to form a halo-shaped discharge; this geometry has been termed the halo-FAPA or h-FAPA. With this new geometry, it is still possible to achieve direct desorption and ionization from a surface; however, sample introduction through the inner capillary is also possible and improves interaction between the sample material (solution, vapor, or aerosol) and the plasma to promote desorption and ionization. The h-FAPA operates with a helium gas flow of 0.60 L/min outer, 0.30 L/min inner, applied current of 30 mA at 200 V for 6 watts of power. In addition, separation of the discharge proper and sample material prevents perturbations to the plasma. Optical-emission characterization and gas rotational temperatures reveal that the temperature of the discharge is not significantly affected (< 3% change at 450K) by water vapor during solution-aerosol sample introduction. The primary mass-spectral background species are protonated water clusters, and the primary analyte ions are protonated molecular ions ($M+H^+$). Flexibility of the new ambient sampling source is demonstrated by coupling it with a laser ablation unit, a concentric nebulizer and a droplet-on-demand system for sample introduction. A novel arrangement is also presented in which the central channel of the h-FAPA is used as the inlet to a mass spectrometer.

Introduction

Ambient desorption/ionization mass spectrometry (ADI-MS) addresses the issue of sample preparation in mass spectrometry by removing it altogether. Desorption electrospray ionization (DESI)¹ and direct analysis in real time (DART)², the first sources in this new field, enabled analysis of samples under ambient conditions, while retaining the specificity and sensitivity of mass spectrometry.

Shortly afterward, the flowing atmospheric-pressure afterglow (FAPA) source, evolved from an atmospheric-pressure glow discharge (APGD),³ was described in 2006⁴ and published in 2008.⁵ The FAPA source has been coupled to several alternative sample introduction

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Supporting Information

This material is available free of charge via the Internet at <http://pubs.acs.org>.

methods, including gas chromatography,⁶ laser ablation,⁷ hydride generation,⁸ and a droplet-on-demand system;⁹ however, it was necessary in each instance to utilize a mixing tee in front of the FAPA to ensure proper alignment between the afterglow and the transport gas containing the sample. This mixing tee is problematic because it can cool the afterglow, the 90° turn is difficult for particles and droplets to navigate, and it unnecessarily complicates the design. The overall need was to balance the competing goals of strong discharge/sample interaction for efficient ionization, and discharge isolation to prevent memory effects and plasma quenching.

These downsides can be overcome with a concentric-electrode geometry, which we have dubbed the halo-FAPA (h-FAPA). It maximizes interaction between the plasma and sample by passing the sample through a toroidal plasma, but the ring shaped discharge is still physically isolated from the sample. It can be constructed entirely from commercially available parts and the two concentric electrodes offer considerable flexibility for sample introduction. Also, the concentric geometry of the gas flows in the h-FAPA eliminates any alignment problems that might arise from the use of a secondary electrode. An analogy for the h-FAPA geometry can be found in the annular inductively coupled plasma (ICP),¹⁰ which utilizes a separate gas flow to inject sample aerosol into the center of the plasma.

Here, the h-FAPA is characterized through current voltage behavior, optical emission spectrometry, and mass spectrometry. Its use as an ambient desorption/ionization source for a model pharmaceutical tablet is shown. To demonstrate the flexibility of the h-FAPA, it was combined with several alternative sample introduction techniques, including a droplet-on demand-generator, a laser ablation unit, and a concentric nebulizer. Lastly, an alternative design is presented in which the central channel of the h-FAPA is replaced with an inlet to a mass spectrometer to enable fixed geometry sampling.

Experimental

h-FAPA

The halo-shaped discharge was supported between two concentric stainless-steel capillaries (3.18 mm O.D., 2.67 mm I.D. and 1.59 mm O.D.; 1.07 mm I.D., Smallparts Inc., now AmazonSupply, Logansport, IN, USA) nested within each other (cf. Figure 1). An alternative design replaced the inner capillary (1.59 mm O.D., 1.07 mm I.D.) with a solid stainless steel electrode of the same dimensions. A tubular alumina insulator (Smallparts Inc, now AmazonSupply, Seattle, WA, USA) (1.59 mm I.D.) was machined down to a wall thickness of ~0.5 mm to fit outside of the small capillary, yet to leave space between the outer capillary and the insulator for the discharge gas to flow. Alternatively, polyimide tubing (100- μ m wall thickness, Smallparts Inc, now AmazonSupply, Seattle, WA, USA) was utilized as an insulating material. A 1/8" stainless-steel Swagelok® tee was used to secure both capillaries as well as to direct inner and outer gas flows, and PTFE tubing (Zeus, Orangeburg, SC) was installed around the back part of the inner capillary to ensure a gas-tight seal. The flow rate of the plasma gas, ultrahigh purity helium (99.999% purity; Airgas, Radnor, PA, USA), was regulated by mass flow controllers (MKS Instruments, Andover, MA, USA).

Current-Voltage Characterization

A high-voltage DC power supply (Model PTV3n200X2957, Spellman, Hauppauge, NY, USA) was operated in the current-regulated mode and controlled *via* LabVIEW®. Two 10-W, 2.5-k Ω ballast resistors (Vishay Dale electronics, Shelton, CT) were installed in series with the power supply and FAPA to create a stable discharge, prevent arcing, and to compensate for the negative dynamic resistance of the source. Currents ranging from 5 to 65

mA were supplied while the discharge voltage and current were monitored externally by a LabVIEW® card (PCI express 6341, National Instruments Corporation, Austin, TX) for 10 s at a 1 kHz sampling rate to record a mean and standard deviation. A white-light image of the annular plasma was taken (Casio Exilim Pro EX-F1) at each discharge current to visualize the structure of the discharge under various conditions (for an example, see the inset to Fig. 1).

Spectroscopic Characterization

Spatially resolved optical emission spectra were acquired with a commercial inductively coupled plasma (ICP) atomic emission spectrometer (ACTIVA; Horiba-Jobin Yvon, Longjumeau, France). The h-FAPA was positioned in place of the ICP for axial (end-on) measurement. Spatial profiles and spectral information were obtained from a two-dimensional CCD detector placed at the focal plane of the Czerny-Turner geometry monochromator. The concentric discharge was focused on the 10- μ m wide entrance slit of the spectrometer to obtain a profile across the halo and determine the spatial distribution of species within the discharge. Full emission spectra were taken by binning the CCD down the vertical axis of the entrance slit. The resolution of the monochromator, 8 or 16 pm, depending on the grating, was sufficient to resolve rotational fine structure of selected diatomic molecules. Rotational temperatures were determined from a Boltzmann plot from the Q1 rotational lines of OH.¹¹

Mass-Spectral Characterization

Background mass spectra for ions below 100 Th were acquired on a modified ICP-TOFMS system (Renaissance®, LECO instruments, St. Joseph, MI, USA). A detailed list of modifications can be found elsewhere,⁵ but are briefly described here. A pinhole (250 μ m) in a front plate was utilized as an ambient sampling interface and an additional rough pump was added to the first stage to handle the helium gas load, and to maintain the first stage pressure at a reasonable level (< 4 Torr).

For mass spectra of ions with m/z greater than 100 Th, a modified molecular TOF instrument (Unique®, Leco instruments, St. Joseph, MI, USA) was utilized. Modifications include the addition of auxiliary turbo and rough pumps to handle the additional helium load in the second stage.

Sample Introduction

Several alternative methods of sample introduction were explored. Discrete droplets were introduced through use of the droplet on demand system described previously.¹² A thermal inkjet process reproducibly ejects water droplets with volumes of ~17 pL at frequencies from single Hz to several kHz. An auxiliary helium flow of ~100 mL/min through a home-made glass funnel was used to transfer droplets into the central channel of the h-FAPA as was done previously.⁹

A laser ablation unit (LSX-200, Cetac technologies Inc, Omaha, NE) was employed for the introduction of solid samples into the central channel of the h-FAPA source. A 0.1% solution of caffeine in 50/50 water/methanol was deposited on a glass slide (1 μ L) and allowed to dry. Argon was utilized as the carrier gas (1.0 L/min) into the central channel of the h-FAPA, although helium or nitrogen could be used also. Single 6.5-mJ laser pulses with varying spot sizes ablated the dried material and the resulting particulates were transferred into the h-FAPA.

Solution nebulization was performed with a concentric nebulizer (Meinhard, Golden, CO) into a Wu-Hieftje vertical-rotary spray chamber (LECO, St. Joseph, MI); solution flow was

controlled by a syringe pump (Fusion 100, Chemyx Inc. Stafford, TX) optimized at 20 $\mu\text{L}/\text{min}$; the nebulizer gas was helium at 0.70 L/min.

Safety Considerations

Direct-current high voltages ($\sim 400\text{ V}$) and currents (up to 65 mA) were used in these experiments. Precautions should be taken when working with potentially lethal currents. Proper personal protective equipment should also be used when working with a class 4 laser.

Results and Discussion

h-FAPA Design

A schematic diagram of the h-FAPA source is given in Figure 1. Both end-on and side views are displayed to clarify the arrangement. In Figure 1a, an end-on diagram and corresponding white light images of the discharge and source are displayed with and without power supplied. The halo-like ring structure of the discharge can clearly be seen in the end-on, white-light image. The discharge is contained between the two electrodes and does not extend into the middle of the central channel, in an end-on view. It is currently not known whether the discharge extends into the region between the two tubes, in the side-on view, as it cannot be readily observed, but only 2 mm of the inner electrode is exposed. What is clear, however, is that a portion of the discharge covers the outer zone of the inner and outer capillaries (cf. the side view in Fig. 2b), requiring any flow carrying sample material through the inner capillary to pass through this afterglow region. Careful alignment of the central electrode (cathode) within the outer electrode (anode) is important to make them as concentric as possible. If either the anode or cathode is off-center, a discharge will preferentially form on one side or, under extreme misalignment, form an arc. Both arcing and off axis discharge formation are undesirable as they can lead to plasma instability and unstable analytical signals. A 1/8 in. Swagelok® tee was well suited to hold both the anode and the cathode in proper alignment while providing a convenient connection for the outer gas flow. If polyimide or other insulating material is used, the entire h-FAPA can be assembled from commercially available parts, with no special machining.

The inner channel can be used not only for introducing helium into the center of the h-FAPA discharge, but also for a range of other purposes, only a few of which will be explored here. The h-FAPA can desorb and ionize samples placed in front of it, in a fashion similar to that of most ADI-MS sources. In this case, a solid rather than tubular inner electrode can be used. In addition, vapor-phase samples can be introduced into the center channel directly. For example, effluent from a gas chromatograph could be passed into the center channel for simple coupling of GC to a mass spectrometer. Sample solutions can be introduced by means of a droplet introduction system, shown below, or any other nebulization device. Solid samples are accessible either through laser ablation of a surface and passing the effluent into the central channel or simply pointing the source at the surface, as shown later. Overall, gas, liquid and solid samples can all be ionized with this source without demounting it from the mass spectrometer.

Current-Voltage Characteristics

An i-V curve generated from the h-FAPA over the current range from 5 mA to 65 mA is shown in Figure 2. Several gas flow rates in the outer channel were tested (0.2-0.6 L/min), but the trends displayed in Fig. 2 did not change.

At currents below 11 mA, the voltage exhibits significant fluctuations. The large error bars for both voltage and current are a result of the power supply not being able to respond quickly enough to the changing plasma conditions. These fluctuations appear to be due to

discharge wander, as the plasma has not yet formed a complete halo. Imperfect alignment between the concentric electrodes is likely the ultimate cause of these instabilities. A larger ballast resistor might dampen the fluctuations; however, because such low currents are out of the useful operating range it was not deemed necessary. At currents above 12 mA, a complete halo discharge was formed, and very stable voltage and current values occur. As the current is increased from 14 to 30 mA, the number of charge carriers and excitation/emission events increases, which causes the plasma to become brighter. Over this region, the plasma has the behavior expected of a “normal” glow discharge and is the way in which the discharge is ordinarily operated. Above 43 mA, the voltage increases with current, as the halo area has been filled, suggesting the discharge transitions into the “abnormal” glow regime. At these and even higher currents, the discharge expands into the central channel of the h-FAPA.

Optical Emission Characterization

Prominent atomic lines and molecular bands emitted by the h-FAPA are labeled in Figure 3. As expected, the majority of the features are from excited helium species or atmospheric constituents. Gas flow rates of 0.60 L/min and 0.20 L/min He were chosen for the outer and inner channels, respectively, as being representative of operating conditions for the discharge as an ionization source. The current was set at 30 mA as a typical value; data were also collected at 20 and 40 mA, but showed little variation in the identity of species present in the background spectrum (cf. Figure 3).

The molecular bands of OH, N₂, and N⁺₂ are present, even though only helium is utilized in the discharge. These bands likely arise from diffusion of atmospheric gases into the discharge, or from trace contamination within gas transfer lines. Comparison of the emission spectrum of this discharge with that of the original FAPA source (then called a helium atmospheric pressure glow discharge (APGD))³ shows weaker and fewer molecular features here, primarily from the NO band (system 200–300 nm), but also from N₂ (band heads at 337 and 380 nm) and N₂⁺ (band heads at 391 and 427 nm). Weaker molecular emission from the h-FAPA here is surprising, considering that it is open to the atmosphere, whereas the original FAPA (He-APGD) was in a sealed environment. This finding suggests that the outer capillary successfully isolates the h-FAPA from atmospheric constituents, an important aspect of this geometry.

Spatially resolved emission spectra were taken across the concentric discharge as well. Full spatial patterns of OH rotational bands, N₂⁺ rotational bands, He (I) emission, and OH rotational temperatures can be seen in Supplemental Figure S2, but important findings are summarized here. A central-channel gas flow was found to be very important for preventing the influx of atmospheric gases into the discharge, and for keeping the discharge from overheating and damaging the cell. This protection and cooling are apparent from the large increase in N₂⁺ emission and OH rotational temperature (an increase from 450K to 600K) upon removal of the central channel gas flow, which suggests significant entrainment of atmospheric gases into the discharge. Addition of water vapor (~10% by volume) to simulate a heavy solvent load did not affect the rotational temperature of the discharge with less than a 3% decrease in temperature, which suggests the h-FAPA can handle a large solvent load without significant plasma quenching. The absence of a dip in the center of all end-on viewed plasma features reveals that the discharge covers the entirety of the exit of the center capillary, which in turn requires that all gases and sample material flowing from that exit pass through the discharge.

Mass Spectral Characterization

Figure 4a shows a background mass spectrum of the h-FAPA over the range from 10 Th to 60 Th. The two most prominent ions are protonated water clusters, which have been observed for previous geometries of the FAPA source.⁵ These water clusters are essential reagent ions in proton transfer-ionization, the most common ionization pathway hypothesized for plasma-based ADI-MS sources.⁴ The diatomic and monoatomic oxygen ions detected in the background spectrum likely arise from oxygen diffusing into the discharge or from residual impurities within the gas supply or transfer tubing. Similarly, diffusion into the discharge and residual nitrogen in the lines are the likely sources of ionized nitrogen dimer and nitric oxide observed in the spectrum.¹³ These species are important for charge-transfer ionization, so their presence in the mass spectral background is desirable.¹⁴ The background mass spectrum also reveals that the h-FAPA source has an ion distribution similar to that of other plasma based ADI-MS sources, and therefore retains their flexibility. This similarity suggests that the new source is well suited for both proton- and charge-transfer ionization.

Figure 4b displays a mass spectrum of methyl salicylate vapor that was introduced into the central channel of the h-FAPA; no attempt was made to quantify its concentration. The primary peaks are the protonated molecular ion (MH^+), and a fragment that arises from loss of a methoxy group, possibly within the first stage of the mass spectrometer.⁶ The protonated molecular ion signal was initially strong enough to saturate the detector, making it necessary to move the h-FAPA away from the sampling inlet in order to capture a full spectrum. Clearly, the h-FAPA is capable of performing proton-transfer ionization typical of plasma-based ADI-MS sources. Oxidation of analyte species, which has been reported previously¹⁵ is kept to a minimum but not eliminated, which is apparent from the small peak near 169 Th in Figure 4b. The lack of adduct formation and oxidation suggests that the h-FAPA geometry isolates the discharge sufficiently to prevent atmospheric contamination of analytes, despite some entrainment of atmospheric species into the discharge.

The low and relatively unstructured background in Figure 4b is desirable for discovery analysis, and for low limits of detection. A full background mass spectrum can be seen in the electronic supplemental material (cf. Supplemental Figure S1) but no features are detected aside from the background ions labeled in Figure 4a. The background is kept low by having the h-FAPA body made out of inert materials, such as stainless steel, alumina, and polyimide tubing, which reduce or eliminate contributions over a wide range of m/z values.

Sample Introduction Alternatives

1) To demonstrate the flexibility of this new source geometry, the device was used as a stand alone ambient ionization source and was also coupled with several sample introduction techniques. A schematic diagram illustrating both how the source is used for conventional ambient mass spectrometry and how it is coupled with sample introduction techniques is given in the electronic supplemental material (*c.f.* Figure S3). An example spectrum for use as a stand-alone ambient ionization source is given in the electronic supplemental material for the desorption/ionization of an acetaminophen tablet (*c.f.* Figure S4). The resulting spectrum is identical to that produced by the conventional FAPA source,¹⁶ with the amount of oxidized product minimal (~3%). However, the relative standard deviation is poorer (45%) than what can be achieved with the h-FAPA when sample material is introduced into the central channel (see point 3 below) or when the volatilized sample material is drawn through the central channel into a mass spectrometer interface (see point 5 below).

2) Laser ablation was utilized for introduction of aerosolized solid samples into the central channel of the h-FAPA source. Figure 5 illustrates the sensitivity of the new source for

ionization of small samples and indicates how little fragmentation results from the ablation event. A 10 μm laser spot was used to ablate a portion of 1 μg caffeine deposited on a glass microscope slide. The dominant peak in the spectrum is the protonated molecular ion of caffeine, with slight fragmentation likely caused in the first stage of the mass spectrometer. The integrated signal of protonated caffeine (m/z 195) for different laser spot diameters was plotted and a linear fit was excellent ($R^2 = 0.99$), with a slope of $4.0 \times 10^5 \pm 2.0 \times 10^4$ counts/ μm , indicating the sensitivity of this geometry for efficiently volatilizing and ionizing small amounts of sample. Regrettably, the caffeine-containing droplet dries inconsistently and the laser power varies from shot to shot, both of which lead to fluctuation in the amount of material removed. Because the thickness of the sample on the glass slide was inconsistent and unknown, an absolute detection limit cannot be estimated.

3) Nebulization of a neat solution of 10 ppm tebuthiuron into the central channel of the h-FAPA produced the spectrum in Figure 6a; the primary feature is again the protonated molecular ion ($M+H$)⁺ at m/z 229. The displayed signal was integrated for 25s and background-subtracted. A calibration performed with solutions containing 0.1, 1 and 10 ppm tebuthiuron yielded the plot in Figure 6b. Slight roll-off is seen at high concentrations and is likely due to a combination of reagent ion depletion in the h-FAPA source and solvent effects. The limit of detection based on 3 σ from a blank sample was 30 ppb. The dynamic range was 3 orders of magnitude while the relative standard deviation was 3% for a 1 ppm solution.

4) A droplet-on-demand (DOD) generator¹² was coupled with the central channel of the h-FAPA source. A null-point-like calibration¹⁷ technique recently renamed a dosing-frequency calibration (DFC)¹² was performed (c.f. Figure 7a). This technique entails ramping the frequency of droplet introduction, which changes the amount of material introduced over a fixed integration time and thereby enabling a single calibration solution to mimic a broad range of solution concentrations. Figure 7a illustrates this capability with a 1 $\mu\text{g/mL}$ solution of benzoylecgonine, cocaethylene and cocaine being introduced at frequencies ranging from 200 Hz to 2 kHz. The h-FAPA offers slightly higher sensitivity than the pin-to-plate FAPA for the introduction of droplets.⁹ In particular, the slope of the DFC lot for the pin-to-plate FAPA for benzoylecgonine was 1.9 ± 1.2 counts/Hz,⁹ while that for the h-FAPA is 3.0 ± 0.7 counts/Hz. However, the main advantage of the h-FAPA is the ease with which it can be coupled to the DOD system, here involving only the use of approximately 20 cm of tubing and a glass funnel. The precision provided by the h-FAPA is better than that of the pin to plate FAPA as well: 0.90% RSD for h-FAPA versus 2.2% RSD for the pin-to-plate FAPA at 800 Hz droplet introduction frequency.

Figure 7b again demonstrates the remarkable sensitivity of the h-FAPA geometry. Single ~ 30 pL droplets of a 5-ppm lidocaine solution were detected at a S/N ratio of 50. These droplets contain 150 fg or 640 amol of lidocaine, yielding a detection limit of 9 fg or 38 amol.

5) Finally, the central channel of the h-FAPA was replaced with an inlet capillary of an atmospheric sampling mass spectrometer. This geometry eliminates several spatial degrees of freedom typically encountered in ADI-MS systems and allows geometry independent analysis. The optimal flow rate was determined through schlieren imaging to visualize helium gas flow (c.f. ESM Fig. 5). With this arrangement, a pharmaceutical tablet containing acetaminophen (90% by weight) was moved across the entrance of the modified h-FAPA assembly, to yield the time trace at m/z 152 in Figure 8a. The first peak is slightly weaker than those that follow, likely because of the protective layer on the pill. Excluding that peak gives a peak area RSD of 5% and an average S/N ratio of 300. Also, a TLC plate was spotted with 2 μg each of three substances of interest, tebuthiuron, carbendazim and

triethylphosphate and subsequently moved through the h-FAPA setup. Three distinct peaks were observed for the three different compounds at S/N levels of 270, 240, and 870, respectively, which give detection limits based on 3 σ criterion of 22, 25 and 7 ng. This experiment shows the sensitivity of this geometry for surface sampling as well as the potential imaging capabilities of the h-FAPA with an MS inlet as the center channel.

Conclusions

A novel concentric-electrode geometry has been developed and tested for the flowing atmospheric-pressure afterglow that allows sample introduction into a discharge without adversely affecting it. In addition to simplifying the coupling with alternative sample-introduction techniques, the central channel might be used to introduce desired reactant species into the afterglow to alter the ion chemistry. These reactive species could foster selective ionization, such as is exploited in atmospheric pressure chemical ionization (APCI)¹⁸ and atmospheric pressure photoionization (APPI).¹⁹ Mass-spectral characterization of the discharge shows the typical background ions of protonated water clusters, positive molecular ions from atmospheric gases, and formation of protonated analyte ions. Spectroscopic characterization reveals many of the same spectral features as are found with the conventional pin-to-plate FAPA and the h-FAPA sources. Addition of water vapor to the central channel does not diminish the gas rotational temperature. However, removal of the central channel gas flow causes the gas rotational temperature to increase by 150 K. Finally, applications are shown in which a laser ablation unit, concentric nebulizer and a droplet-on-demand system are successfully coupled to the h-FAPA; high ionization efficiency is demonstrated.

In addition to coupling with several sample introduction methods, the h-FAPA can also be aimed at the surface of a solid sample in the conventional way to desorb and ionize species before introduction into a mass spectrometer. An alternative mode of operation is also being explored which simplifies sampling. In this alternative mode, the central capillary is used not for sample introduction but rather for extraction of volatilized and ionized sample species into a mass spectrometer. Proof of principle of this alternative mode is given here while a fuller evaluation of the capabilities and optimization of its operating parameters (e.g. gas flows, capillary dimensions and orientation, distance from sample) is the subject of ongoing study.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.

Diagram of the h-FAPA source. **a)** end-on view of cell, with schematic diagram and photographs (on and off) of the discharge. Conditions: 25 mA, 300V 0.4 L/min He (outer) 0.20 L/min He (inner) flows. **b)** Side on view illustrating how the concentric tubes are arranged and the placement of the insulator.

Figure 2.

Current-voltage curve for the h-FAPA. Images were taken for each point on the curve, with selected images shown above. Arrows indicate the regime where the image was taken, and exact current values are given to the right of each image.

Figure 3. Optical emission background spectrum of the h-FAPA discharge with key features labeled. The number after each label is the emission wavelength in nm. Outer channel and central channel flow rates were 0.6 and 0.20 L/min helium, respectively. Applied current was 30 mA and voltage was -300V

Figure 4.

Mass spectra from the h-FAPA source. **a)** Background mass spectrum showing reagent ions.

b) Mass spectrum of methyl salicylate showing protonated molecular ion and fragment.

Frames a and b are on different scales.

Figure 5.

Background subtracted mass spectrum from a single laser ablation event. A 1 μg aliquot of caffeine (from a solution) was spotted onto a glass microscope slide, and a 10 μm laser spot was utilized. Protonated caffeine (m/z 195) was detected at a S/N level of 30.

Figure 6.

a) Mass spectrum from 1 ppm tebuthiuron nebulized into the central channel of the h-FAPA source. **b)** Semi-logarithmic calibration curve for tebuthiuron; LOD is 30 ppb, RSD at 1 ppm is 3%.

Figure 7.

a) A null-point-like calibration for cocaine and two cocaine metabolites obtained with a droplet-on-demand sample introduction system. **b)** Selected ion chromatogram for protonated molecular ion of lidocaine (235 m/z); single droplets (30 pL) of 5 ppm lidocaine were introduced into the h-FAPA discharge. Each spike corresponds to 150 fg or 640 amol of analyte

Figure 8.

a.) An aspirin tablet was moved six times through the h-FAPA with the central h-FAPA channel serving as the MS capillary inlet; a spike of protonated paracetamol was detected with each pass with an average S/N of 300. **b.)** A TLC plate was spotted with 2 μ g each of tebuthiuron, triethyl phosphate and carbendazim at 4 mm intervals. The TLC plate was then moved through the h-FAPA and compounds were detected with a S/N of 270, 240 and 870, respectively, which give theoretical LODs of 22, 25 and 7 ng, respectively.