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# Ultrasensitive Ambient Mass Spectrometric Analysis with a Pinto-Capillary Flowing Atmospheric-Pressure Afterglow Source

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# **Abstract**

The advent of ambient desorption/ionization mass spectrometry has resulted in a strong interest in ionization sources that are capable of direct analyte sampling and ionization. One source that has enjoyed increasing interest is the Flowing Atmospheric-Pressure Afterglow (FAPA). FAPA has been proven capable of directly desorbing/ionizing samples in any phase (solid, liquid, or gas) and with impressive limits of detection (<100 fmol). The FAPA was also shown to be less affected by competitive-ionization matrix effects than other plasma-based sources. However, the original FAPA design exhibited substantial background levels, cluttered background spectra in the negative-ion mode, and significant oxidation of aromatic analytes, which ultimately compromised analyte identification and quantification. In the present study, a change in the FAPA configuration from a pin-to-plate to a pin-to-capillary geometry was found to vastly improve performance. Background signals in positive- and negative-ionization modes were reduced by 89% and 99%, respectively. Additionally, the capillary anode strongly reduced the amount of atomic oxygen that could cause oxidation of analytes. Temperatures of the gas stream that interacts with the sample, which heavily influences desorption capabilities, were compared between the two sources by means of IR thermography. The performance of the new FAPA configuration is evaluated through the determination of a variety of compounds in positive- and negative-ion mode, including agrochemicals and explosives. A detection limit of 4 amol was found for the direct determination of the agrochemical ametryn, and appears to be spectrometer-limited. The ability to quickly screen for analytes in bulk liquid samples with the pin-to-capillary FAPA is also shown.

#### Introduction

Plasma sources for mass spectrometry have traditionally been viewed as tools for elemental analysis. However, plasmas operated at atmospheric pressure, such as corona and glow discharges, have been used for over 30 years for molecular analyses through soft, chemicalionization pathways. Horning et al. <sup>1</sup> first described a corona discharge sustained at atmospheric pressure for the determination of small, organic molecules; the method is commonly referred to as atmospheric-pressure chemical ionization (APCI). In APCI, just as in reduced-pressure chemical ionization, reagent ions that are generated through electron impact undergo chemical reactions to induce analyte ionization. However, because the ionization process occurs at atmospheric pressure, collisional cooling greatly reduces molecular fragmentation. Moreover, the reaction chemistry can be tuned by introducing selected solvent vapors into the plasma region. Because of these features, APCI is typically viewed as a softer and more versatile ionization method than electron impact or reduced-pressure chemical ionization.

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Because of its simplicity, the corona discharge is currently the most widely used plasma-based source for molecular mass spectrometry. However, the low operating current of the corona discharge, usually a few microamperes, leads to a relatively low density of reagent ions, which compromises detection limits and makes the ionization process more prone to matrix effects than with other plasma-based ionization sources.<sup>2–3</sup>

It was later found that APCI could be performed with increased reagent-ion densities through the use of a helium, atmospheric-pressure glow discharge (APGD).  $^{4-5}$  The higher operating currents (50 – 250  $\mu A$ ) and highly energetic states of helium formed in the APGD (>19 eV) produce a greater flux and a wider variety of reagent ions. In the original APGD configuration, samples are passed directly through the discharge, just as in corona-discharge APCI. However, the well-defined structure of a glow discharge occupies a significant volume, so this sample-introduction method leads to plasma instabilities and memory effects, which are less severe with point-source corona discharges.

To further improve on the APGD source design, Andrade et al.<sup>6</sup> developed a helium-APGD geometry that physically and electrically isolates the discharge from the sampling region. In the new geometry, the sample is introduced into the flowing afterglow, which extends into the open atmosphere; accordingly, the new ionization source was termed the Flowing Atmospheric-Pressure Afterglow (FAPA). Because the sample does not enter the active plasma region, discharge currents between 10 mA and 50 mA could be used without substantial analyte fragmentation or degradation. In fact, the base peak in the mass spectra for most analytes corresponds to either the molecular ion (M<sup>+-</sup>) or the protonated parent molecule (MH<sup>+</sup>). The FAPA source was first used for the detection of gas-phase analytes and as a detector for gas chromatography, with detection limits in the femtomole regime, even for molecules that exhibit poor sensitivity with corona-discharge APCI.<sup>6–7</sup>

The FAPA can also be used as a source for ambient desorption/ionization mass spectrometry<sup>8</sup>, in which species are directly desorbed and ionized from sample surfaces, and with minimal sample preparation. 9–10 The desorption feature is presumably due to the temperature of the gas (>200 °C) and to the excited species present in the afterglow region. 11 Desorption/ionization with the FAPA source has been employed for the detection of pesticides on fruit, 12 polymer characterization, 13 and determination of active pharmaceutical ingredients. 14 The source can also be used to generate positive or negative ions and the desorption/ionization detection limits are comparable to those for gas-phase samples. 14–15 Furthermore, FAPA has been shown to be less affected by ionization matrix effects than other plasma-based ambient desorption/ionization sources. 3

These features, in conjunction with the simple source design and operation, should make the FAPA an attractive source for ambient mass spectrometric analyses. Unfortunately, some issues with the initial source design have constrained widespread use of the FAPA source. Most notably, the original FAPA design produced substantial mass-spectral background and significant oxidation of some species. These limitations ultimately led to compromised analyte identification and quantification. In the present study, a significantly improved FAPA design is presented and compared with the original FAPA. The capabilities of the improved FAPA are demonstrated through the detection of a variety of compounds, including pesticides and explosives. Lastly, detection of analytes in bulk liquid samples is shown.

# **Experimental**

#### Reagents

All reagents were analytical-grade. High-purity helium (99.995% purity helium, Indiana Oxygen, Indianapolis, IN) was used as the discharge gas in all cases. PETN, RDX, and TNT were purchased as 0.1 mg/mL standards in methanol/acetonitrile from AccuStandard Inc. (New Haven, CT). Pesticide standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) and from Riedel de Haën, Pestanal® (Seelze, Germany). The standard agrochemical solutions were the same as those used by Wiley et al. 16

## **Ionization Source Designs**

Two FAPA designs and geometries were used in these studies. The first was similar to the original one described by Andrade et al. Briefly, an APGD was sustained between a stainless-steel pin cathode and a brass-plate anode; hereafter this source will be referred to as the pin-to-plate FAPA (cf. Figure 1a). The electrodes were held in place within a Teflon discharge chamber that also served to seal the discharge region from the ambient atmosphere. A 1.6-mm hole in the plate enabled excited species, ions, and electrons formed in the discharge to flow into the open atmosphere for desorption and ionization of analytes.

The second design maintained the discharge between a pin cathode and a conductive capillary anode (1.6-mm o.d., 1.3-mm i.d., 25 mm long, McMaster-Carr, Chicago, IL); this source design will be referred to as the pin-to-capillary FAPA (cf. Figure 1b). Both electrodes were made of stainless steel and fixed in place within a machineable-ceramic discharge cell (Mykroy®, McMaster-Carr, Chicago, IL). These electrodes were also sealed to the discharge cell to limit atmospheric gases from reaching the discharge. The plasma gas entered the chamber through a port in the side and flowed into the open atmosphere through the capillary anode.

Although the two source designs were different, many of the optimal operating conditions were found to be the same between the two geometries. A negative potential was applied to the cathode through a 5 k $\Omega$  ballast resistor, from a high-voltage, DC power supply (model NO1HA60, Acopian Technical Co., Easton, PA); the anode was connected to the ground terminal of the power supply. The APGD of the FAPA was operated in a current-controlled mode at 25 mA, which resulted in a discharge voltage of ~400 V. While both versions of the FAPA could be operated with a helium discharge gas at flow rates from 0.1 to 1.5 L/min, it was found that 0.6 L/min was the optimal flow rate for detection of most analytes. This gas flow rate was adjusted with a rotameter (Key Instruments, Trevose, PA) and monitored with a mass flow meter (Fathom Technologies, Georgetown, TX). It was found that an interelectrode gap of ~7 mm yielded the strongest mass spectrometric signals, so that spacing was used for both sources throughout. Both sources were mounted onto a home-built 3D translation stage for precise alignment of the exit aperture of the source with the mass spectrometer inlet.

## **Mass Spectrometric Analyses**

Ions produced from each source were detected with a Thermo LTQ XL linear ion trap mass spectrometer (Thermo-Finnigan San José, CA, USA). Agrochemicals and most other compounds were detected in the positive-ion mode, while explosives were detected in negative-ion mode. To change between ionization modes, the polarity of the mass-spectrometer DC potentials was switched in the Xcalibur software. No changes to either configuration of the FAPA were needed to detect analytes in either ionization mode. Spectra were collected in automatic gain-control mode with a maximum ion trap injection time of 200 ms and 2 microscans per spectrum. The key experimental parameters for positive-ion

detection were as follows: m/z range of 50–700; capillary temperature at 200 °C; capillary voltage at 15 V; tube lens at 65 V. Tandem mass spectrometry (MS/MS) was performed via collision-induced dissociation (CID) to improve signal-to-noise ratios and to confirm the presence of the tested analytes. These MS/MS spectra were obtained with an isolation window of 1.5 Th and 25–35% relative collision energy.

# **Temperature Measurements of the Flowing Afterglow**

Temperatures of the gas stream exiting the two FAPA designs were measured by infrared thermography with a thermal imaging camera (Fluke Ti40 IR FlexCam, Everett, WA), which can register temperatures between  $-20~^{\circ}\text{C}$  and 350  $^{\circ}\text{C}$ . The method of temperature measurement was similar to that described previously. Briefly, greybody emission from a glass microscope slide placed in the flowing helium stream was recorded with the IR camera. Temperature scales in the images were corrected for the emissivity of the glass slide, 0.92, and the ambient temperature, 22  $^{\circ}\text{C}$ , in the SmartView<sup>TM</sup> software. After a source parameter was adjusted, the temperature stabilized after 2 minutes, ultimately resulting in standard deviations of less than 0.5  $^{\circ}\text{C}$  for the temperature measurements in all cases.

# **Safety Considerations**

Exposed, lethal DC high voltages were present at the FAPA source and mass spectrometer inlet. Extreme care and precaution were taken to prevent electrical shock through the use of electrically insulating gloves. Material safety data sheets for all chemicals used were consulted prior to performing experiments. Accordingly, personal protective equipment, such as safety glasses, gloves, and laboratory coats, were employed for each experiment when necessary.

#### **Results and Discussion**

# **Background Mass Spectra**

The pin-to-plate FAPA has been shown to be capable of directly desorbing/ionizing samples in any phase (solid, liquid, or gas), and with impressive power of detection (<100 fmol). <sup>8, 15</sup> Unfortunately, the original design also produces a complex background spectrum, with ions detected at nearly every m/z value. Typical pin-to-plate FAPA background mass spectra in positive- and negative-ionization modes are shown in Figures 2a and 3a, respectively. Given these background levels, detection of low-abundance or unknown species with the pin-to-plate FAPA is quite difficult without some means of removing the interfering ion signals, such as background subtraction or MS/MS. Proper background subtraction can be difficult with all ambient mass spectrometry sources, because sample shape and position are known to greatly affect detection precision<sup>14</sup> and MS/MS requires *a priori* knowledge of expected ions from a sample.

Schilling et al.  $^{14}$  noted a complex, discrete background in the low-mass range, 0 to 100 Th, for a Teflon®-bodied, pin-to-plate FAPA in negative-ionization mode. The majority of those features can be attributed to fluorinated hydrocarbons, presumably from degradation of the polymeric discharge cell. A glass discharge chamber resulted in a simpler low-mass spectrum. Schilling et al.  $^{14}$  offered no comments regarding the effect of the glass chamber on the higher-mass, quasi-continuum background or even on the positive ion background.

From these earlier findings it was clear that the discharge cell should be fabricated from a more stable material than Teflon $^{\circledR}$ . A glass-bodied, pin-to-plate FAPA was first explored to improve source performance. However, the background clutter was very similar and yielded a continuum background reduction of only  $\sim 50\%$  for the positive-ionization mode over that

shown in Figure 2a. The FAPA cell constructed from glass was also fragile and was not thermally insulating. One distinct advantage of the FAPA over other plasma-based ambient desorption/ionization sources is that the discharge directly heats the gas so no additional heat source is needed. Therefore, it is advantageous to use a source chamber that is thermally insulating to preserve the gas temperature, thus enhancing thermal desorption.

Of a variety of discharge-cell materials that were tested, the one that exhibited the best performance was Mykroy<sup>®</sup>, a machineable ceramic. Mykroy<sup>®</sup> is a glass-bonded ceramic that exhibits low electrical and thermal conductivity, has a low thermal expansion coefficient, is stable up to 400 °C, and has high tensile strength. Also, it is not porous to oxygen or water, so outgassing or leaching of carbonaceous molecules from the chamber into the discharge, which could contribute to the background, will not occur. Lastly, Mykroy<sup>®</sup> can be easily machined or injection-molded, similar to organic thermoplastics, making it suitable for a FAPA source body.

In addition to the ceramic cell body, the discharge configuration was changed to a pin-to-capillary design (cf. Figure 1b). Positive- and negative-ion background spectra for the pin-to-capillary FAPA are shown in Figures 2b and 3b, respectively. For the positive-ion mode, the quasi-continuum background was reduced by 89% and 84% over the integrated mass ranges of 100-110 Th and 200-210 Th, respectively, compared to the pin-to-plate geometry. Although this improvement in background is quite significant, the effect is even more dramatic for the negative-ionization mode. In this case, the background was reduced by 99% or more, which ultimately improves detection limits by more than two orders of magnitude. Importantly, the signal for  $NO_3^-$ , a common reagent ion in negative mode, was nearly the same between the two geometries. This point suggests that the reagent-ion flux, and thus the ionization efficiency, was unaffected by the change in design.

## **Oxidation of Aromatic Species**

Another problem previously noted with the pin-to-plate FAPA is significant oxidation of aromatic systems, which can lead to complicated spectra. An example of the severity of this oxidation is shown by the determination of 1 ng of diphenylamine from a glass probe with the pin-to-plate FAPA (cf. Figure 4a). The parent molecular ion (MH<sup>+</sup>) of diphenylamine at m/z 170 was readily observed, but it was not the base peak in the spectrum. Rather, oxidized forms of the molecule dominated the spectrum, with the addition of up to six oxygen atoms being observed. Distributing the signal for an analyte across many m/z values, in conjunction with the quasi-continuum background, results in extremely poor signal-to-noise ratios and could make analyte identification in a complex sample difficult.

The addition of oxygen atoms is further complicated because it is not a simple, non-covalent adduct, which often occurs with water. Rather, it is a rearrangement reaction to form an alcohol. As a result, collision-induced dissociation in the first-stage of the mass spectrometer cannot be used to unravel these spectral features. While not as severe, oxidation of aromatic species is known to exist with corona-discharge APCI and has been shown to be induced by radical, atomic oxygen (O') formed in the discharge. <sup>17</sup> In addition, spatially resolved, optical emission measurements of atomic oxygen in the discharge and afterglow of another helium plasma often used for ambient mass spectrometry, the low-temperature plasma (LTP) probe, demonstrate that the major source of the radical oxygen was from molecular oxygen diffusing from the atmosphere into the discharge region. <sup>18</sup>

When the pin-to-capillary FAPA was used to desorb/ionize 1 ng of diphenylamine, significantly less oxidation occurred (cf. Figure 4b). The result was a cleaner mass spectrum, consisting of an MH<sup>+</sup> base peak and a peak corresponding to the addition of one oxygen atom at only 9% relative abundance. Also, the MH<sup>+</sup> signal with the pin-to-capillary FAPA

was more than three times that obtained with the pin-to-plate FAPA. By extending the physical distance between the discharge of the FAPA and the ambient air, via the capillary anode, atmospheric oxygen is unable to diffuse into the discharge region. Similarly, if any atomic oxygen is formed in the discharge, potentially from the gas supply, much of it is likely lost to the capillary walls before the discharge effluent enters the sampling region.

## Flowing Afterglow Temperature

While the spectral background and analyte oxidation were improved with the pin-to-capillary FAPA, it was not known how the modified source design would affect sample desorption. It has been shown that the temperature of the gas stream heavily influences analyte desorption for plasma-based ambient ionization sources. <sup>16, 19–20</sup> Accordingly, the maximum temperature of the flowing afterglow was measured for both FAPA designs.

Figure 5 shows the maximum temperature of the helium stream issuing from the pin-to-plate and pin-to-capillary FAPA geometries under a range of operating conditions. Maximum temperatures were found to be no farther than 5 mm from the anode and had a standard error over time of less than 0.5 °C. Regardless of discharge current and helium flow rate, the pinto-plate FAPA produced higher temperatures. This finding is expected because the desorbing gas stream is located much closer to the discharge for the pin-to-plate design; for the pin-to-capillary FAPA, the anode capillary is exposed to the open air, which can act as a heat sink as the discharge-heated helium travels through the capillary. Interestingly, for both designs, the afterglow temperature increased linearly with discharge current (cf. Figure 5a). Thus, modulating the discharge current could provide a way to selectively desorb analytes with different vapor pressures, similarly to what has been done with the DART source.<sup>19</sup> However, with the FAPA there is no need for an external gas heater and the temperature changes are more rapid, less than 5 seconds. Another interesting feature of the linear fits in Figure 5a is that the slopes were identical between the two source designs, 2.6 °C/mA, indicating that the structures of the APGDs are quite similar. This similarity further supports the suggestion that the differences in afterglow temperature are almost exclusively due to heat loss as the gas travels through the capillary.

The temperature in the afterglow also was affected by changing the plasma-gas flow rate (cf. Figure 5b). The pin-to-plate geometry reached a maximum temperature at a flow rate of ~1.5 L/min and then slowly decayed at higher gas flows. It is hypothesized that the gas flow at the exit of the source becomes turbulent at higher flow rates, resulting in more rapid cooling of the afterglow. In contrast, the gas temperature of the pin-to-capillary FAPA increased monotonically with helium flow until ~3 L/min, after which a more gradual decline in temperature occurred. The anode capillary allows the plasma gas to establish a laminar flow profile prior to entering the open atmosphere, which makes the desorbing helium stream stable over a greater range of flow rates than the pin-to-plate geometry. Although the afterglow temperature is lower for the newer FAPA design, it is still comparable to gas temperatures measured for DART;<sup>21</sup> furthermore, it can be easily and rapidly adjusted by changing discharge current and flow rate

#### **Analytical Performance of Pin-to-Capillary FAPA**

To assess the sensitivity of the new pin-to-capillary FAPA, a variety of chemical substances was analyzed in positive- and negative-ionization mode. One set was commonly used agrochemicals, a list of LODs for which is compiled in Table 1. As a point of reference, the solutions and mass spectrometer were exactly the same as those used for an LTP-MS study. <sup>16</sup> Each sample was applied to a glass probe that was then reproducibly introduced (<7% RSD for analyte signals) into the FAPA source, yielding working curves with correlation coefficients of 0.99 or greater. This precision is similar to what has been

demonstrated with the pin-to-plate FAPA.<sup>7, 14</sup> MS/MS was used to improve analyte signal-to-noise ratios and thus LODs. As in a previous FAPA study,<sup>7</sup> detection limits were better than 10 fmol for all tested agrochemicals. However, the source was significantly more sensitive for some compounds. For instance, the LOD for the direct desorption/ionization of ametryn with the pin-to-capillary FAPA was approximately 4 amol, a value that appears to be instrument-limited. To the best of our knowledge, this is the best detection limit that has been reported for any plasma-based ambient mass spectrometry source. Furthermore, these LODs are more than one order of magnitude better than any previously achieved with similar helium discharge sources.<sup>12, 16</sup>

Although the linearity, precision, and accuracy of working curves obtained with the FAPA source were good, quantification of agrochemicals in complex sample matrices will no doubt not be straightforward. Indeed, this complication is endemic to all ambient mass spectrometry sources and arises from a number of factors, including desorption and ionization matrix effects, inconsistencies in sample positioning, and variances in analyte transport from the sample surface into the mass spectrometer. Consequently, direct quantification of species on or near a sample surface remains one of the most significant issues in ambient mass spectrometry. Some reports have shown that internal standardization, especially with isotopically labeled standards, can improve quantification in complex samples. However, this method necessitates *a priori* knowledge of the sample and possible analytes within it, and requires a standard that is uniformly spiked on the sample, which often is difficult or impossible to achieve. At this juncture and prior to further advances, detection limits presented for the pin-to-capillary FAPA, or any other ambient mass spectrometry source, denote the lowest possible level of analyte that can be detected in the mass-spectral screening of a sample.

Operation of the FAPA source in the negative-ionization mode was not explored in detail in earlier investigations because of the complicated background spectra arising from the polymeric discharge cell. This limitation was unfortunate, because some functional groups preclude the formation of positive ions and are more readily observed in the negative-ionization mode; nitrate-based explosives are one such group of compounds. The dramatic improvement in negative-ion background with the pin-to-capillary FAPA expands the potential utility of the source for direct analyses of such compounds.

Although many plasma-based ambient desorption/ionization MS sources have been found useful for the detection of explosives, they experience several complications. Under customary operating conditions, DART requires the introduction of an electronegative species, such as trifluoroacetic acid or chlorine from methylene chloride, to generate negative reagent ions that can undergo ion attachment with the target molecules.  $^{23-24}$  The LTP probe is capable of self-generating negative reagent ions, (e.g.  $NO_2^-$  and  $NO_3^-$ ); however, the low gas temperature of that source ( $\sim 30$  °C) limits the types of explosives that can be detected to those with relatively high vapor pressure, such as TNT.  $^{20}$ 

In contrast, the FAPA can both generate negative reagent ions directly and produce high gas temperatures, enabling direct detection of explosives without modification to the operating parameters or ionization source. Figure 6a shows an example mass spectrum of the direct determination of 66 fmol of the explosive pentraerythritol tetranitrate (PETN) from a glass surface. Both the electron and nitrate-attachment species, at m/z 316 and 378, respectively, were clearly detected, in addition to a denitration product (pentaerythritol dinitrate) at m/z 226 that occurs at temperatures greater than 100 °C. <sup>25</sup> These signals correspond to a limit of detection of approximately 500 amol. Figure 6b displays a mass spectrum of the explosive RDX detected from a latent fingerprint. Approximately 4.5 pmol of RDX was applied to a human finger. Two hours after the application, during which time the subject pursued

normal activities, the fingerprint was deposited on a glass surface and analyzed with the FAPA source. In addition to the nitrated form of RDX, lactic acid (labeled X in the spectrum), at m/z 89, and the corresponding adduct with RDX could be detected. The simple design, impressive sensitivity to explosives, and simple mass spectra obtained by the pin-to-capillary FAPA make it an attractive source for homeland security applications.

# **Analysis of Bulk Liquid Samples**

It was found that the new FAPA source was also capable of directly desorbing and ionizing analytes present in a solution. Of the numerous ambient desorption/ionization sources that have been described in the literature, only the LTP probe has been shown capable of directly analyzing bulk solutions (>100  $\mu L$ ).  $^{26}$  This method of analysis could not be performed with the pin-to-plate FAPA due to spatial considerations that often limited the size and shape of a sample that could be analyzed. In contrast, the pin-to-capillary FAPA source can be angled with respect to the MS inlet, making analysis of large or oddly shaped objects more feasible. By positioning solution samples, 2 mL contained in microcentrifuge tubes, beneath the inlet of the mass spectrometer and directing the afterglow of the FAPA onto the liquid surface, analytes were desorbed and ionized.

Figure 7a shows a mass spectrum obtained from an  $8-\mu g/mL$  solution of terbuthylazine (MH<sup>+</sup> = 230) dissolved in a 50:50 methanol-water mixture. While the protonated molecular ion can clearly be detected in the raw spectrum (cf. Figure 7a), a significant number of background species, presumably from the more volatile components in the solvent, were also observed. This spectral clutter could obviously compromise detection and identification. This problem was overcome by means of background subtraction with the blank solvent or by MS/MS of m/z 230. After background subtraction, the isotopic distribution of the chlorine-containing herbicide could be used to verify the presence of terbuthylazine; MS/MS provided structural information through the characteristic loss of the tert-butyl group.

Direct, bulk-solution analysis by FAPA-MS was found also to be quantitative by scanning solutions of varying analyte concentration underneath the FAPA source. This ability was demonstrated with the direct detection of methamphetamine in tap water. Methamphetamine was detected via MS/MS of the protonated molecular ion (m/z 150), which resulted in characteristic fragment ions at m/z 119 and 94. The chronogram of these two ions for several analyte concentrations is shown in Figure 7b. The calibration curve resulting from this analysis was found to be linear ( $r^2 = 0.999$ ) and resulted in a detection limit of 0.7 ng/ mL. This method of analysis was also applied to more complex solution matrices, such as untreated urine, with minimal loss of sensitivity. Although the mechanism of analyte desorption is not known, a correlation was found between detection limit and vapor pressure of the analyte. For example, caffeine, which has a vapor pressure seven orders of magnitude lower than that of methamphetamine, could not be detected in the bulk solution. However, caffeine is readily detected and is a model analyte for FAPA analysis of solid samples. These findings demonstrate that bulk solution analysis with FAPA-MS could prove to be a rapid and convenient screening tool for explosives detection at airports or illicit drug detection in bodily fluids.

# **Acknowledgments**

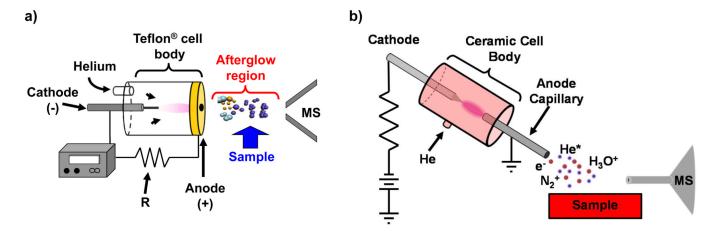
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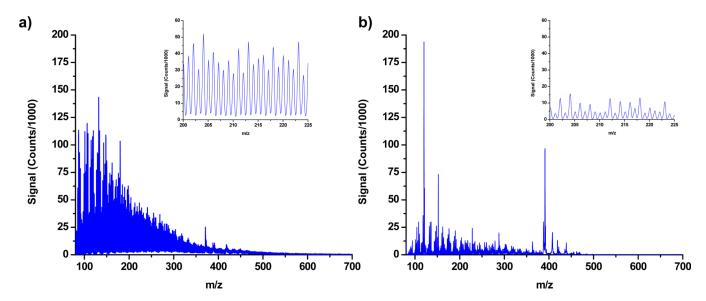
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**Figure 1.**a) Diagram of the original, pin-to-plate FAPA configuration with the discharge chamber constructed from Teflon<sup>®</sup>. A hole in the plate anode allows discharge species to flow into the sample-introduction region. b) Depiction of the new pin-to-capillary geometry FAPA with a Mykroy<sup>®</sup> ceramic discharge cell. Discharge species flow into the sampling region through the anode capillary.



**Figure 2.** Positive-ion background mass spectra for the (a) pin-to-plate and (b) pin-to-capillary FAPA sources. The insets are of the mass range between 200 and 225 m/z to emphasize the difference in background signals.

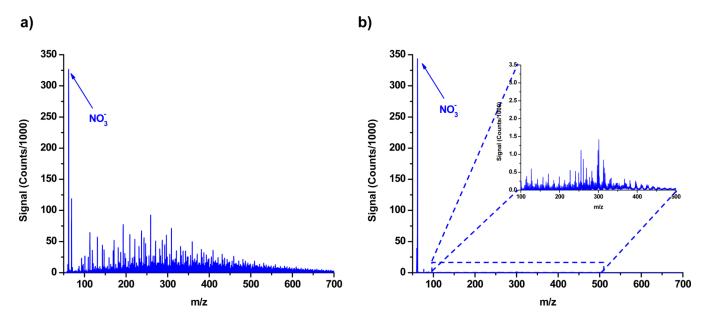
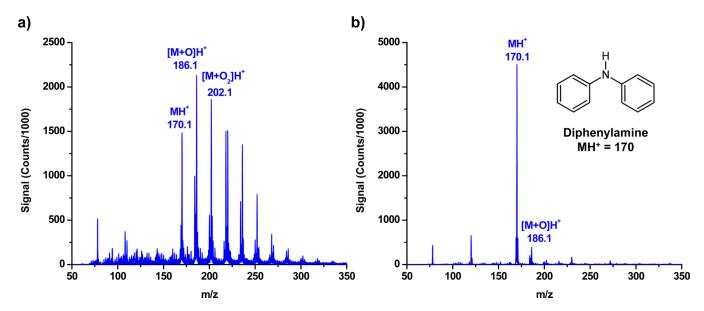
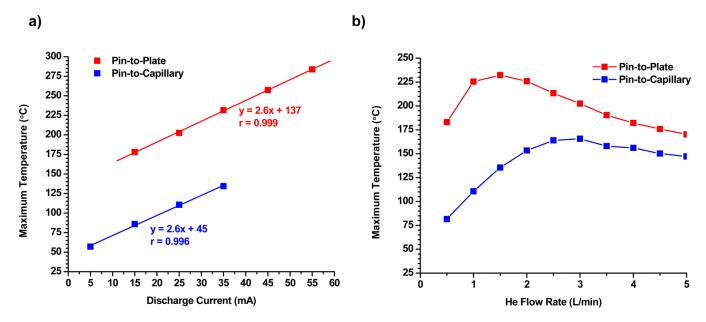


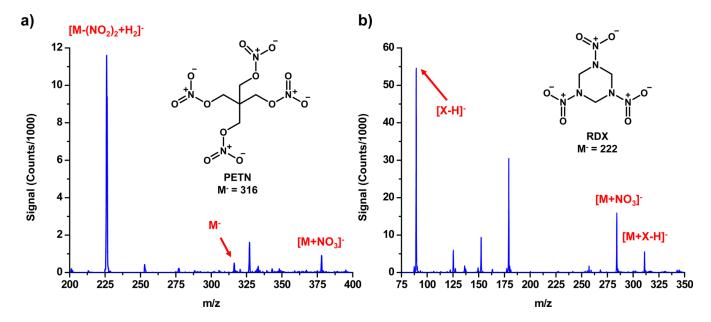
Figure 3. Negative-ion background mass spectra for (a) the Teflon®-bodied, pin-to-plate FAPA and (b) the Mykroy®-bodied, pin-to-capillary FAPA. With both sources the base peak corresponds to  $NO_3^-$  and exists at approximately the same signal strength. However, with the use of the ceramic cell body, the continuum background has been reduced by at least 99%.



**Figure 4.** Mass spectra of 1 ng of diphenylamine obtained with the (a) pin-to-plate and (b) pin-to-capillary FAPA source. The oxidation of aromatic species is attributed to O' produced in the APGD.



**Figure 5.**Maximum afterglow temperature for the pin-to-plate (red symbols) and pin-to-capillary (blue symbols) FAPA sources as a function of (a) APGD current and (b) helium flow rate. The flow rate in (a) was held at 1 L/min, while the discharge current in (b) was fixed at 25 mA. The decrease in temperature at higher He flow rates is caused by turbulent flow.



**Figure 6.**a) Mass spectrum of 66 fmol of PETN analyzed with the FAPA source. b) Mass spectrum of RDX detected from a latent fingerprint deposited on a glass slide 2 hours after exposure to the explosive. X corresponds to lactic acid present in the fingerprint.

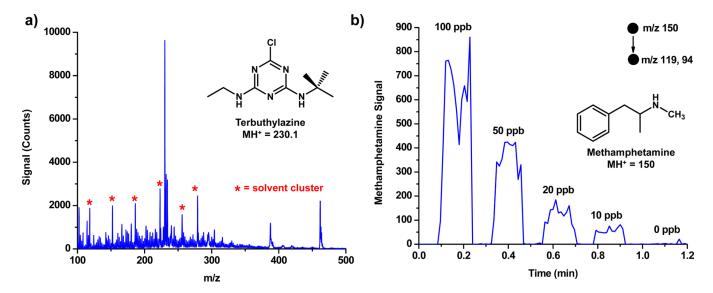


Figure 7. a) Direct analysis of a bulk solution of 8  $\mu$ g/mL terbuthylazine in methanol:water. The asterisk (\*) denotes a solvent cluster. b) Chronogram of methamphetamine MS/MS fragments for different concentrations in tap water. Resulting calibration curve has an  $r^2$  of 0.999 and a LOD of 0.7 ppb.

Table 1

Limits of detection (LOD) for selected pesticides and herbicides obtained with the pin-to-capillary FAPA ionization source

	m/z (MS/MS ions included)	LOD for FAPA (fmol)
Ametryn	228 → 186	0.004
Diphenylamine	$170 \rightarrow 92$	1.2
Ethoxyquin	$218 \rightarrow 190 + 176$	9.2
Isofenphos-methyl	$332 \rightarrow 290 + 271$	$0.9^{a}$
Isoproturon	$207 \rightarrow 165 + 72$	0.24
Malathion	$331 \rightarrow 285 + 127$	6
Parathion-ethyl	$292 \rightarrow 264$	1.7
Terbuthylazine	$230 \rightarrow 174$	0.043

 $<sup>^</sup>a\mathrm{MS/MS}$  not used for FAPA in this case.