Dynamic Planar Solid Phase Microextraction−Ion Mobility Spectrometry for Rapid Field Air Sampling and Analysis of Illicit Drugs and Explosives

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A preconcentration device that targets the volatile chemical signatures associated with illicit drugs and explosives (high and low) has been designed to fit in the inlet of an ion mobility spectrometer (IMS). This is the first reporting of a fast and sensitive method for dynamic sampling of large volumes of air using planar solid phase microextraction (PSPME) incorporating a high surface area for absorption of analytes onto a sol−gel polydimethylsiloxane (PDMS) coating for direct thermal desorption into an IMS. This device affords high extraction efficiencies due to strong retention properties at ambient temperature, resulting in the detection of analyte concentrations in the parts per trillion range when as low as 3.5 L of air are sampled over the course of 10 s (absolute mass detection of less than a nanogram). Dynamic PSPME was used to sample the headspace over the following: 3,4-methylenedioxymethamphetamine (MDMA) tablets resulting in the detection of 12−40 ng of piperonal, high explosives (Pentolite) resulting in the detection of 0.6 ng of 2,4,6-trinitrotoluene (TNT), and low explosives (several smokeless powders) resulting in the detection of 26−35 ng of 2,4-dinitrotoluene (2,4-DNT) and 11−74 ng of diphenylamine (DPA).

Ion mobility spectrometry (IMS) is one of the most successful technologies for chemical trace detection of explosives and drugs at security checkpoints.[1,2] Despite the many advantages of IMS, rapid analysis (on the order of seconds), high sensitivity, field portability, and ease of use,[2] the sample collection still relies mainly on physically trapping, by swiping or pumping trace particulates onto substrates prior to analysis,[3] and hence must be improved.[4] A tiny explosive or drug particle, either on a surface or in the air of a suspected area, may be missed while sampling or may not adhere to the collection surface.[5] Moreover, extraneous particles may overwhelm the detector's analytical response or may contaminate it through dusting. Vapor introduction is also possible by IMS by pumping air directly into the analyzer, but the volume of air it can accept is on the order of hundreds of milliliters.[2] This volume is generally insufficient to representatively sample a suspected area for trace vapor concentrations; therefore, an efficient, inexpensive, and preconcentration step can assist with the detection process.

Sampling for vapors rather than particles aims at increasing the detection sensitivities of targeted compounds in IMS, especially under closed system conditions. The solid phase microextraction (SPME) technique, first described in 1990,[6] has become a widely used preconcentration nonexhaustive static sampler employed for numerous applications and is the subject of several recent reviews.[7−9] Sampling of vapors by SPME in the headspace mode (HS-SPME), coupled to IMS analysis, was first made possible by the development of a true SPME−IMS interface.[10] The SPME−IMS method has proven to increase sensitivities in the determination of the explosive taggants, dimethyl dinitrobutane (DMNB), and the explosives 2,4,6- trinitrotoluene (TNT), 2,4-dinitrotoluene (2,4-DNT), and 2,6-dinitrotoluene (2,6-DNT) in closed containers.[10] The availability of this interface also enabled the detection of volatile chemical odor signatures known from detector dog trials and headspace analyses as being emitted from the parent drugs[11−13] and explosives.[14,15,10] Lai et. al developed a genetic algorithm (GA) optimization scheme[16] for IMS detection of the odor signatures of the illicit drugs, cocaine, marijuana, and 3,4-methylenedioxymethamphetamine (MDMA), sampled by HS-

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SPME even in the presence of interferents.[17] The SPME−IMS interface enabled the sensitive detection of smokeless powder odor signatures, 2,4-DNT, diphenylamine (DPA), and ethyl centralite (EC) from standards and unburned samples.[18]

A planar solid phase microextraction (PSPME) device was developed[19] to further increase the surface area and capacity for the extraction of these volatile and semivolatile target compounds and to eliminate the need for a SPME−IMS interface, making PSPME easily adaptable to the over 15 000 IMS instruments already installed conducting over a million analyses per year.[2] Using PSPME under static sampling conditions has increased the extraction efficiency of TNT and, as a result, has increased sensitivity, decreased the sampling time, and allowed for sampling of larger volumes.[19] More recently, PSPME−IMS enabled detection, with significant improvements over SPME−IMS, of piperonal, the odor signature of the illicit drug MDMA.[20] Thus far, PSPME has been reported only for static sampling in closed containers,[19,20] under equilibrium sampling with sampling times on the order of minutes to hours, depending on the target analyte.

Dynamic sampling is an alternate mode of SPME sampling achieved by exposing a SPME fiber to a stream of gas, typically air, containing volatile and semivolatile compounds which can be absorbed/adsorbed onto the fiber's coating. One disadvantage of this sampling is the long extraction time necessary when sampling open air,[21] as much as 1 h with the aid of an air pump.[22] Larroque et al. collected open air samples in bulbs of various volumes and sampled statically with SPME for periods of over 10 h.[23] Augusto et al. developed a rapid dynamic air SPME sampling method for detection of volatile organic compounds (VOCs) using a modified hairdryer.[24] Although sampling was possible in 30 s, the fibers likely suffered from increased fragility due to air turbulence. These previously mentioned dynamic SPME sampling methods are still limited by the surface area of the fiber geometrical configuration. A recently reported SPME device with increased surface area due to the helical carboxen/polydimethylsiloxane (CAR/PDMS) phase wound between two glass tubes has shown improvement in extraction of VOCs when compared to conventional SPME fiber dynamic sampling.[25] These dynamic sampling methods, described along with their associated advantages, cannot be coupled with the detection capabilities of IMS without appropriate interfaces.

On the basis of the effectiveness of PSPME in terms of improved recoveries, sensitivities, detection outcomes, and low cost of implementation when coupled to IMS,[19,20] the development of a PSPME device that allows dynamic sampling has been pursued. The novel dynamic PSPME device was aimed at further improving the overall sensitivity by reducing sampling time and enabling detection in open air from areas suspected of containing contraband. In this manner, the sample collection of the volatile chemical signatures of illicit compounds and subsequent IMS detection may approximate how trained detector canines alert. In the development of the novel dynamic PSPME device, a glass fiber filter substrate was coated with sol−gel PDMS nanoparticles using a unique process based on the procedure developed for the static PSPME device[19] preparation with some modification. The dynamic PSPME device presented here proved to rapidly preconcentrate target compounds during dynamic open air sampling and was followed by direct introduction into existing IMS sample desorbers for virtually real time analysis of the target compounds.

The performance of the novel device is reported for the detection of five target analytes, all volatile chemical signature compounds of illicit drugs and explosives (both high and low explosives): TNT (from standards and the explosive Pentolite), 2,4-DNT, EC, DPA (all from standards and unburned smokeless powder samples), and piperonal (from standards and seized MDMA cases).

EXPERIMENTAL SECTION

Materials. *Chemicals and Supplies.* Dichloromethane (DCM, 99.9%), acetonitrile (ACN, HPLC grade), concentrated sulfuric acid (96%), hydrogen peroxide (30%), and sodium hydroxide (solid) were obtained from Fisher Scientific (Fair Lawn, NJ). Hexanes (99.9%) were purchased from Pharmco-AAPER (Brookfield, CT.) Vinyl-terminated PDMS (vt-PDMS) was purchased from Gelest (Morrisville, PA), methyltrimethoxysilane (MTMOS) (>98%) from Fluka (Steinheim, Germany), poly (methylhydrosiloxane) (PMHS) from Sigma-Aldrich, and trifluoroacetic acid (TFA) 99% from Acros (St. Louis, MO). Piperonal (99%) was obtained from Sigma-Aldrich (St. Louis, MO), and drug case samples containing 3,4-methylenedioxymethamphetamine (MDMA) and/or other drugs were sampled at a local law enforcement agency. The explosive TNT was purchased as a 1000 μg mL^{-1} standard solution from Cerilliant (Round Rock, TX). The explosive, Pentolite (1:1 TNT/pentaerythritol tetranitrate (PETN)) was provided in small quantities by a local law enforcement agency. Standard solutions of the solid smokeless powder odor signatures, 2,4-DNT, EC, and DPA (Aldrich, St. Louis, MO) were prepared in ACN. Four unburned commercial smokeless powders were used in this study: H322 (Hogdon, Shawnee Mission, KS), 4198 (IMR, Shawnee Mission, KS), red dot (Alliant Powder, Radford, VA), and unique (Alliant Powder, Radford, VA).

Ion Mobility Spectrometry. An IonScan 400B (Smiths Detection, Mississauga, ON, Canada) IMS was used for analysis of TNT and the smokeless powder odor signatures, 2,4-DNT, DPA, and EC from standards and explosive samples, directly introduced by liquid spikes and following dynamic PSPME sampling. An Itemiser 2 IMS (GE Securities, Wilmington, MA) was used for analysis of the MDMA target compound, piperonal, directly introduced by liquid spikes and following extraction by the PSPME from standards and drug case samples. This instrument allowed analysis at the low drift tube temperature of 80 °C, which is necessary for piperonal detection.[16] The IMS operating conditions for both instruments, along with the targeted compounds' drift times and K_0 values are listed in Table 1.

Dynamic PSPME Device(s) Preparation. Prior to coating, glass fiber filter circles (G6, Fisherbrand, Pittsburgh, PA) were cut down to 3.1 cm in diameter. The glass fiber filter circles were prepared

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Table 1. IMS Operating Conditions

IMS operating conditions	IonScan 400B (#1)		Itemiser 2 (#2)
polarity	positive (+)	negative (−)	positive (+)
desorber temperature (°c)	250	300	215
drift tube temperature (°c)	235	115	80
sample flow (mL min^{-1})	200	300	500
drift flow (mL min^{-1})	351	351	350
reagent gas	nicotinamide	hexachloroethane	nicotinamide

analyte	piperonal	2,4-DNT	DPA	TNT	EC
IMS instrument/polarity	#2/(+)	#1/(−)	#1/(+)	#1/(−)	#1/(+)
Ko ($cm^2/V \times s$)	1.51	1.57	1.61	1.45	1.24
drift time (ms)	8.3	11.8	11.0	12.8	14.4
vapor pressure (Torr)	1.0 @ 87 °C	2.2×10^{-4} @ 25 °C	6.4×10^{-4} @ 25 °C	1.1×10^{-6} @ 25 °C	NA

for coating with a similar activation procedure described in the literature,[19] while following appropriate safety guidelines. A sol−gel PDMS solution was prepared in the following quantities: 2.060 g vt-PDMS was dissolved in 8 mL of DCM; then 1.10 mL of MTMOS and 0.535 g PMHS were added, followed by 0.875 mL of TFA (Acros) (5% water v/v). The solution was vortexed and allowed a 30 min stay. The prepared glass fiber filter circle was placed atop a cut glass slide held by vacuum on the chuck of a model WS-400B-6NPP-LITE spin-coater (Laurell Technologies, North Wales, PA). One milliliter of the coating solution was deposited on the glass fiber filter circle and the spin program, 1000 rpm for 60 s, was activated. The newly coated dynamic PSPME device was placed in the desiccator for 12 h, dipped for 1.5 h in DCM, and gelated for 12 h in an oven at 40 °C. The dynamic PSPME device was placed in a GC oven in a nitrogen atmosphere at 120 °C for 1 h, 240 °C for 1 h, and 300 °C for 3 h for final curing. Surface characterization and thickness measurements of the prepared dynamic PSPME devices and the uncoated substrates were obtained using a Philips XL30 scanning electron microscope (SEM) (FEI, Hillsboro, OR). A hand-held vacuum (DC Remote Particle Sampler, Smiths Detection), represented in Figure SA in the Supporting Information, was used as the lightweight, field portable pump for dynamic PSPME sampling and a EA-3010U hand-held anemometer (La Crosse Technology, La Crosse, WI) was used to measure the airspeeds at the nozzle.

Controlled Odor Mimic Permeation Systems (COMPS) Device Preparation. The COMPS[15,26,27] devices were used to generate a continuous emitting vapor source of the chemical signatures, thus enabling quantitation of the maximal mass of the volatile analytes in air available for dynamic PSPME extraction. They were created using piperonal (100 mg) as previously reported,[27] and for the first time, COMPS for Pentolite (3 g), 2,4-DNT (3 g), DPA (100 mg), and EC (100 mg) were also manufactured. The 7.60 cm × 7.60 cm, 50 μm thick, low-density polyethylene bags used were acquired from Uline (Waukegan, IL).

Determination of COMPS Dissipation Rates. For each of the compounds studied, COMPS devices were prepared in triplicate and were allowed to stand under ambient conditions. The mass of the bags was recorded for up to 28 consecutive days, and the average value and standard deviation for each triplicate set was determined. The average mass (in grams) was plotted vs time (days) to determine the rate of mass loss each day, derived from the best-fit lines for the linear and exponential form (for piperonal only). The dissipation rates determined for 2,4-DNT, DPA, and EC were calculated to be 15 ng s^{-1}, 7.64 ng s^{-1}, and 0.93 ng s^{-1}, respectively (Figure SB in the Supporting Information), and found to be in correlation with the analyte's relative vapor pressure (Table 1). Piperonal COMPS devices have been previously reported as a vapor source for the calibration of canine detection sensitivity for MDMA detection, and its dissipation rate was determined to be the highest, 34.7 ng s^{-1}, following the vapor pressure trend.[27] All the dissipation rates obtained represented a sufficient amount of compound released into the air after several seconds, to then be preconcentrated by the dynamic SPME device and detected by IMS. The TNT in Pentolite is an exception. Although TNT possesses an appreciable vapor pressure, the mass of Pentolite remains the same throughout the 28 days with no permeation of any component through the LDPE bag. Solid TNT (pure) was not used in the COMPS devices, since it was only available to our group in dilute standard solutions.

Methods. *IMS Response Curves.* Standard solutions of TNT were diluted from a 1000 μg mL^{-1} certified standard solution to concentrations of 0.1, 0.2, 0.5, 0.8, 1.0, 2.5, 5.0, and 10.0 μg mL^{-1} in ACN, while 2,4-DNT calibration solutions originated from a 1000 μg mL^{-1} stock and consisted of the following concentrations: 5.0, 8.0, 10.0, 25.0, 50.0, 100, 250, 500, and 750 μg mL^{-1} in hexanes. The EC solutions were prepared from a 5 μg mL^{-1} stock solution in concentrations of 0.1, 0.5, 0.9, and 1.0 μg mL^{-1} in ACN. Solutions of DPA were diluted from a 500 μg mL^{-1} stock solution to concentrations of 1.0, 5.0, 10.0, 25.0, 40.0, 50.0 μg mL^{-1} in ACN. A volume of 1 μL each of the listed concentrations was spiked onto the manufacturer provided Teflon filters (Smiths Detection, Mississauga, ON, Canada) and analyzed by the IonScan 400B IMS. Blanks of the manufacturer provided filters were taken by IMS prior to spiking and before all subsequent experiments. The filters were only used one time and stored by sealing in the metal cans supplied by the manufacturer until use.

The piperonal standard solutions were made from a stock solution of 1000 μg mL^{-1} piperonal in DCM. A volume of 2 μL each of 1, 2, 5, 8, and 10 μg mL^{-1} concentrations were spiked

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onto the manufacturer provided filters and analyzed by the Itemiser 2 IMS for piperonal monomer detection.

Triplicate analyses of each concentration for the suite of compounds were conducted and response curves were generated by plotting mass (nangram) versus the cumulative signal. From the equation of the best-fit line, the mass detected by IMS for each compound following dynamic sampling, with the novel PSPME device and the manufacturer provided filter, was calculated in the nangram range.

Dynamic PSPME Retaining Capability Studied by Analyte Solution Spiking. The dynamic PSPME device was spiked with 2 μL of standard solution, with a concentration resulting in a mass within the response curve linear range of each compound and was placed in the hand-held vacuum. The concentrations were 5, 20, 15, 1, and 0.25 μg mL^{-1} for piperonal, 2,4-DNT, DPA, TNT, and EC, respectively. The pump was turned on for various times (seconds) to determine at what point, if any, the IMS signal would diminish following desorption of the dynamic PSPME device. The same was done using the manufacturer provided filters for comparison purposes. The measurements for each analyte were performed in triplicate and IMS blanks of both the manufacturer provided filters and dynamic PSPME devices were taken before sampling.

Dynamic PSPME Retaining Capability Studied by COMPS Vapor Source for Each Analyte. Each COMPS device was placed in a particle-free hood (Labconco, Kansas City, MO) and sampled for 30 s at different heights by turning on the vacuum with the dynamic PSPME device in place (Figure SA in the Supporting Information). Once the optimum sampling height was determined, the COMPS devices were then sampled at that height for different times. Following each sampling, the dynamic PSPME device was analyzed in the appropriate IMS instrument. The manufacturer provided filter was also used at the same sampling conditions for comparison. The COMPS devices were allowed a 30 min stay in between each sampling. All the optimization measurements were performed in triplicate and with the appropriate blanks prior to sampling.

Application of Dynamic PSPME−IMS for Screening of Illicit Compounds. The dynamic PSPME device was tested on the headspace of illicit compounds with parameters designed for difficult sampling conditions in the field. The illicit compounds sealed in closed cans of quart-sized volumes were allowed to equilibrate before pumping of the open cans was performed. Table 3 summarizes the experimental conditions: the emitting source and its amount, the equilibrium time, and the pumping time applied. Following sampling, the dynamic PSPME devices were desorbed immediately into the IMS instruments for analysis of the targeted compound. Piperonal, the odor signature of the illicit drug MDMA, was sampled and analyzed at a local law enforcement agency in a blind study test of real case samples.

Lastly, four smokeless powders were sampled, targeting the analyte DPA. Additional sampling, targeting 2,4-DNT, was applied to the powders, Hodgdon H322, and IMR 4192, as these were previously reported to contain 2,4-DNT when sampled by SPME−GC/MS.[18] Sampling targeting EC was applied to the red dot powder, previously reported to contain this compound in its headspace.[18]

RESULTS AND DISCUSSION

Dynamic PSPME Device: Development and Characterization. The development of dynamic PSPME was enabled mainly by the selection of glass fiber filters as the substrate. These filters have a reported temperature limit of 500 °C by the manufacturer, well above the maximum IMS desorption temperature of 300 °C. The substrate surface withstood the corrosive activation procedure and was covalently bound to a sol−gel PDMS solution. By spin-coating the glass fiber filters, the sol−gel coating solution not only was spread by the centrifugal forces but also was absorbed throughout the thickness of the fibers. Sol−gel is defined as a colloidal suspension, gelled to form a solid, and additional details on the sol−gel reaction are described elsewhere.[28,29] The surface and the cross-section of both the uncoated glass fiber filter and the dynamic PSPME device were characterized by SEM (Figure 1). An average increase in thickness of ~44 μm for the dynamic PSPME device, corresponding to an average of ~0.16 g increase in weight, was attributed to the porous sol−gel coating. This value was obtained by subtracting the cross section thickness of the glass fiber filter substrate (~280 μm), from the dynamic PSPME device (~324 μm). The porosity of the sol−gel coating provided the PSPME device with additional surface area and more available sites for partitioning/absorption of analytes during extraction, thus affording enhanced capacity and better sensitivity. Since the dynamic PSPME device was designed and aimed for direct IMS analysis, efficient and rapid desorption was considered an essential feature. In comparison to the static PSPME device,[19,20] improved desorption profiles are expected for the dynamic PSPME since (1) the thickness of the dynamic device coating is much smaller (~44 μm) as compared to the static PSPME device (~170 μm) and (2) the dynamic PSPME device allows for flow through the sample media, which consequently takes advantage of the suction/sample flow of the IMS instruments for directing the desorbed analyte into the IMS analyzer. Figure 1c,d display surface images of the uncoated glass fiber filter and dynamic PSPME device, respectively, which demonstrate retention of the porous properties in dynamic PSPME, even after coating and final curing of the device.

For sampling, the dynamic PSPME device was placed in the slot of the hand-held vacuum (Figure SB, in the Supporting Information) and the pump was turned on. The average air speed measured at the head of the nozzle's pump for the PSPME device was 0.5 m s^{-1} (0.35 L s^{-1}), while for the manufacturer provided filter, 3-fold greater velocities were obtained, 1.3 m s^{-1} (0.92 L s^{-1}). The higher resistance encountered for the PSPME device is not surprising due to the durable, heat resistant, rugged sol−gel PDMS coating of the PSPME device, allowing the expected 100 times of reuse like other PDMS SPME devices, and unlike the one-time use designation for the manufacturer provided filters. The hand-held vacuum was chosen as the pump for these experiments since it represents a common and readily available accessory for sampling particles that can typically accompany the sale of commercial IMS and the training/use by security screeners.

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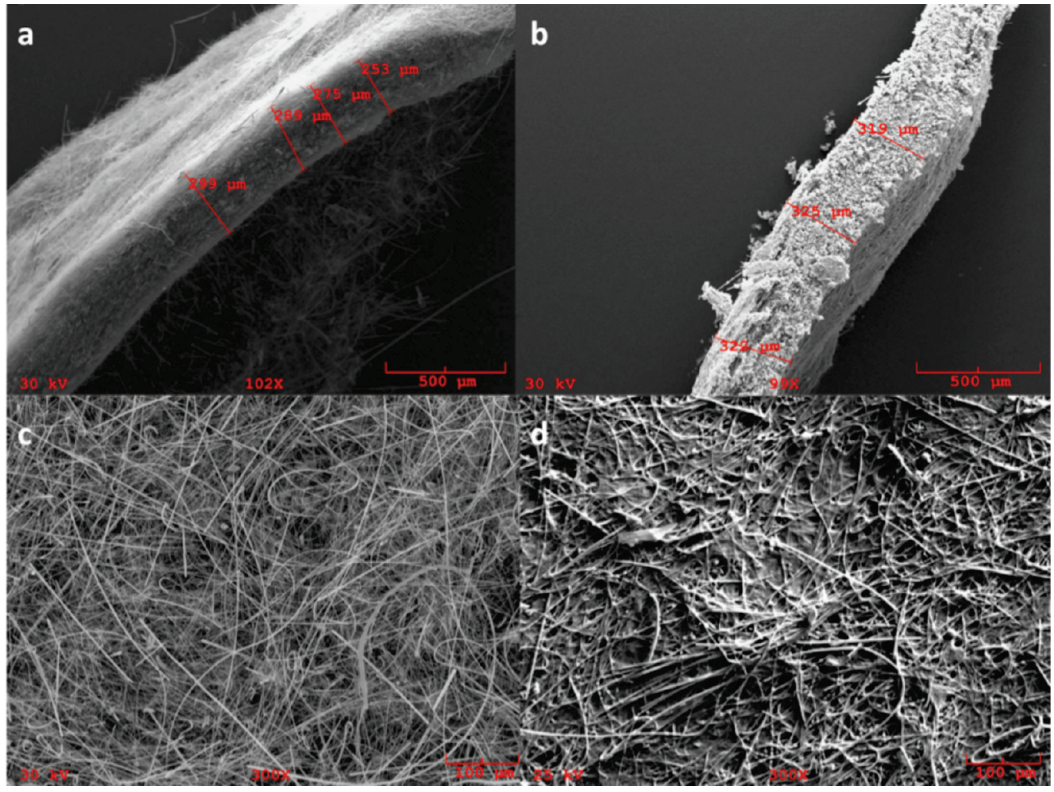

Figure 1. Scanning electron micrograph images of the cross section (a and b) and surface (c and d) of the original glass fiber filter substrate (a and c) and the coated dynamic PSPME device (b and d).

The IMS backgrounds in the IonScan 400B (± polarities) and the Itemiser 2 (+ polarity) obtained for both the dynamic PSPME device and manufacturer provided filter are shown in Figure 2a–c. Overall, relatively cleaner background plasmagrams were achieved for the novel device over the manufacturer filter at both ionization polarities. The low background signal for the sampling media used in IMS is desirable to diminish the effects of any competitive ionization between the analyte signal and that of the background signal peak(s). The clean background observed for the dynamic PSPME device was achieved by optimization of the preparation procedure and was mainly influenced by ensuring that the filter surface is washed well with deionized water (neutral pH) at the relevant stages.

Figure 2a is a plasmagram of both PSPME device and manufacturer filter blanks obtained from the IonScan 400B in the negative polarity. The peaks to the left of 11.3 ms are inherent to the negative mode plasmagram and are a result of the reactant gas, clean dry air doped with hexachloroethane, which provided the reactant ion peaks (RIP) at $K_0 = 2.60$, 2.32 $cm^2\ V^{-1}\ s^{-1}$ and $K_0 = 2.22\ cm^2\ V^{-1}\ s^{-1}$,[1 30–33]. The calibrant (cal) peak is from 4-nitrobenzyl nitrile ($K_0 = 1.65\ cm^2\ V^{-1}\ s^{-1}$). The three minor peaks (13.4, 15.6, and 17.7 ms, all with intensities below 50 d.u.) for the dynamic PSPME device do not interfere with the drift times of 2,4-DNT and TNT (Table 1). Figure 2b is a plasmagram of both the PSPME device and manufacturer filter blanks obtained from the IonScan 400B in the positive polarity, applied when targeting DPA and EC (Table 1). The reactant ion peak (RIP), also the calibrant (Cal) nicotinamide ($K_0 = 1.86\ cm^2\ V^{-1}\ s^{-1}$), has a much higher intensity for the dynamic PSPME which translates to a larger pool of reactant ions to produce product ion peaks. The depletion of the RIP evident from the plasmagram of the manufacturer provided filter is likely due to the background peaks observed in this trace. The background shown in Figure 2c resulted from IMS analysis using the Itemiser 2 optimized for piperonal detection. The RIP is nicotinamide at a drift time of 5.4 ms, and no major difference is observed between each trace.

Dynamic PSPME Device: Retention Capability. The retention capability of the novel PSPME device for the preconcentration of analytes sampled dynamically from air was studied in two consecutive steps: first, by directly spiking the standard analyte solution in a minimal solvent volume onto the substrate followed by clean air pumping, and second, by sampling the analytes in their vapor phase. For further quantitation of the analytes in this study, external standard response curves, generated by spiking standard solutions of analytes over the substrates, were determined. It is important to note that liquid spikes on a substrate do not necessarily desorb in the same fashion as absorbed vapor or swipe deposition, but this is remedied by the use of the cumulative amplitude, the sum of all the peak amplitudes that alert for the compound in IMS. Given complete desorption of the standard, meaning the signal returns to baseline before analysis ends, quantitation is possible because there is a specific instrumental response for a given mass introduced into the IMS.

IMS Response Curves of Target Compounds. Standard solutions of piperonal, 2,4-DNT, DPA, TNT, and EC, were analyzed individually using the appropriate IMS instrument. The response

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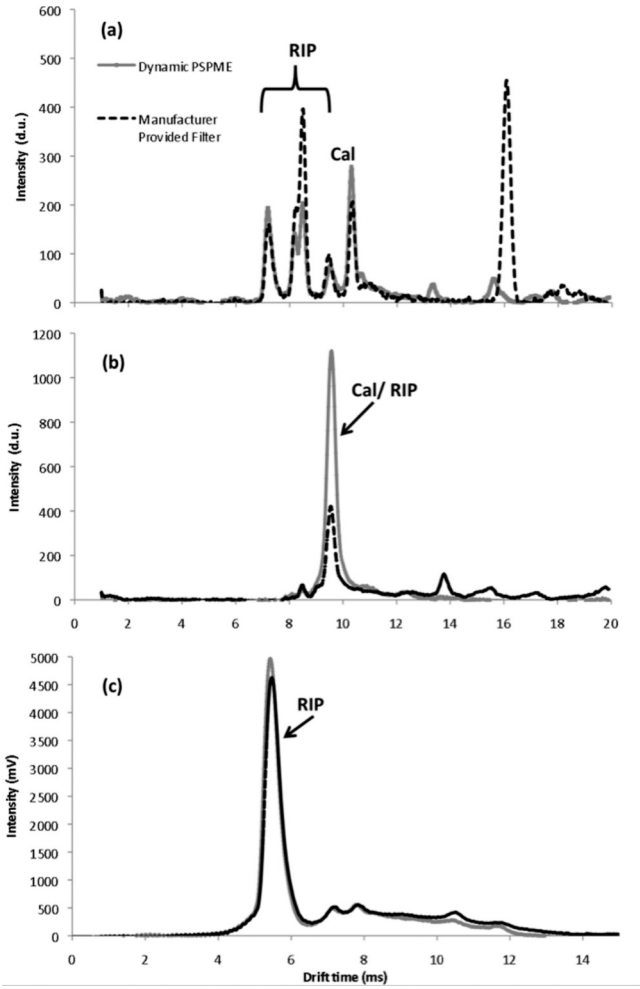

Figure 2. IMS plasmagrams of both the PSPME device and manufacturer filter blanks from IonScan 400B in negative polarity (a); IonScan 400B in positive polarity (b); Itemiser 2 in positive polarity (c).

curves exhibited a linear regression over the tested dynamic range. The results, including the r^2 values, are shown in Table 2 along with the IMS linear dynamic range (LDR) and method detection limit (MDL). Typical LDR's of 1 order of magnitude characterized these response curves. Quantitation of TNT in a broader dynamic range of 2 orders of magnitude was enabled by determining two linear dynamic ranges along the low (0.025−1 ng) and high (0.2−8 ng) concentrations, yielding for this compound the lowest LOQ and MDL of 0.025 ng. Two linear dynamic ranges can often been seen in IMS analysis since the pool of reactant ions available to yield product ions is temporally fixed. Because the kinetics of reactant ion formation are much slower than reactant ion consumption, when higher concentrations are introduced, the reactant ion pool becomes depleted much faster than it can be regenerated, resulting in product ion signals that are lower than expected.[34] The signal-to-noise ratio obtained for the LDR's lowest concentration of piperonal, TNT, and 2,4-DNT confirmed their LOQ as their MDL, while for the other analytes, lower LOD's than LOQ's are expected. Extrapolation for the lowest signal/noise ratio (S/N ≥ 3) yielded estimated MDL's of 0.05 ng and 2 ng as detected masses of EC and DPA, respectively.

(34) Young, D.; Thomas, C. L. P.; Breach, J.; Brittain, A. H.; Eiceman, G. A. *Anal. Chim. Acta* **1999**, *381*, 69–83.

Retaining Capability Studied by Analyte Solution Spiking. The ability of the dynamic PSPME device to retain compounds when subjected to the pumping of increasing air volumes was studied. The results shown in Figure 3 are arranged from the most volatile compound (Figure 3a: piperonal) down to the least (Figure 3e: EC). Equal amounts of targeted compound that resulted in a mass that fell close to the center of each analyte's LDR (Table 2) were spiked onto the surface of both the dynamic PSPME and manufacturer filters. The initial points, in immediate analyses (t = 0 s) with no pumping of air applied, originate from essentially the same signal for all compounds from both spiked substrates except for 2,4-DNT. Figure 3b shows that the 2,4-DNT spike on the dynamic PSPME filter provided a significantly greater response than that for the manufacturer provided filter. The only difference in its sample preparation was that the solvent used for 2,4-DNT standard solutions was hexane, while the other compounds, TNT, DPA, and EC were dissolved in ACN and piperonal in DCM, as described in the Methods section. Unlike those compounds which all resulted in the same cumulative signal reproducibly from both surfaces, proving the calibration with the Teflon manufacturer provided filter valid, the spikes of 2,4-DNT in hexane, a solvent with more comparable volatility to 2,4-DNT, enabled the generation of IMS response curves on manufacturer provided filters for quantitation purposes. The dynamic PSPME surface yielded a response curve (eq 1) that underestimated the mass detected following vapor sampling due to the interaction of hexane with the sol−gel PDMS phase.

$$y = 89.511x + 524.29 \qquad r^2 = 0.9846 \qquad (1)$$

This is a first indication of the affinity of the 2,4-DNT to the sol−gel PDMS extraction phase of the dynamic PSPME device. The PSPME extraction phase absorbs 2,4-DNT extremely well, retains it, and facilitates thermal desorption from the surface by aid of the IMS sample tray air flow. Taking this into account, the dynamic PSPME device developed may also serve an additional purpose as an improved sampling surface for the calibration of IMS for 2,4-DNT in hexane solutions, a compound that has proven difficult to introduce and reliably transport into the IMS reaction chamber. Another study[18] suggested the hypothesis that 2,4-DNT desorbed slowly from surfaces preventing lower mass loadings from being detectable by IMS.

Figure 3 clearly shows opposing trends for both the PSPME device and the manufacturer filter, while simulating dynamic sampling by pumping clean air through both substrates. After only a short time of pumping (10−15 s), an increased signal was obtained for all compounds spiked on the dynamic PSPME filter, while a large drop was measured for the manufacturer provided filter. Generally, while pumping air, unavoidable evaporation of the volatile solvent involved with the delivery of the analyte, is expected for both substrates. While significant coevaporation of analyte was measured for the manufacturer provided filters, analytes were strongly retained on the absorptive phase of the dynamic PSPME filter, confirming its efficient preconcentration capability. The trend in increasing IMS signals measured for all compounds at only the shortest pumping time applied for the dynamic PSPME filters, when at least the same results as for t = 0 were expected, can be explained. At t = 0 s, since pumping is not applied, both the solvent and analyte are introduced into the

Table 2. IMS Analysis Response Curve, Linear Dynamic Range (LDR), and Method Detection Limit (MDL) for Each Analyte of Interest

analyte	slope	*y* intercept	r^2	LDR (ng)	MDL (ng)
piperonal	4039.8	12683	0.98	2−20	2
2,4-DNT	62.42	−75.28	0.97	5−50	5
DPA	23.88	579.3	0.83	5−50	2
TNT	1769.9	390.29	0.99	0.2−8	
	2531.6	36.62	0.99	0.025−1	0.025
EC	11097	−1275.1	0.90	0.1−1	0.05

IMS reaction chamber. The presence of the solvent in the reaction region can serve to cluster or solvate the reaction ions affecting both the thermodynamics and kinetics of ionization.[2] Since the available charge is shielded, the ionization of analytes becomes less favorable leading to diminished responses. Pumping for as little as 10 s aids in desolvation and maximizes interactions between the analyte and the reactant ions that lead to effective ionization. A separate study was conducted to evaluate the solvent effects encountered when attempting to quantitate extracted analytes by SPME using IMS and GC/MS response curves.[35] This study showed that by minimizing the solvent, from the microliter range to the subnanliter range, both instrumental responses were significantly enhanced.

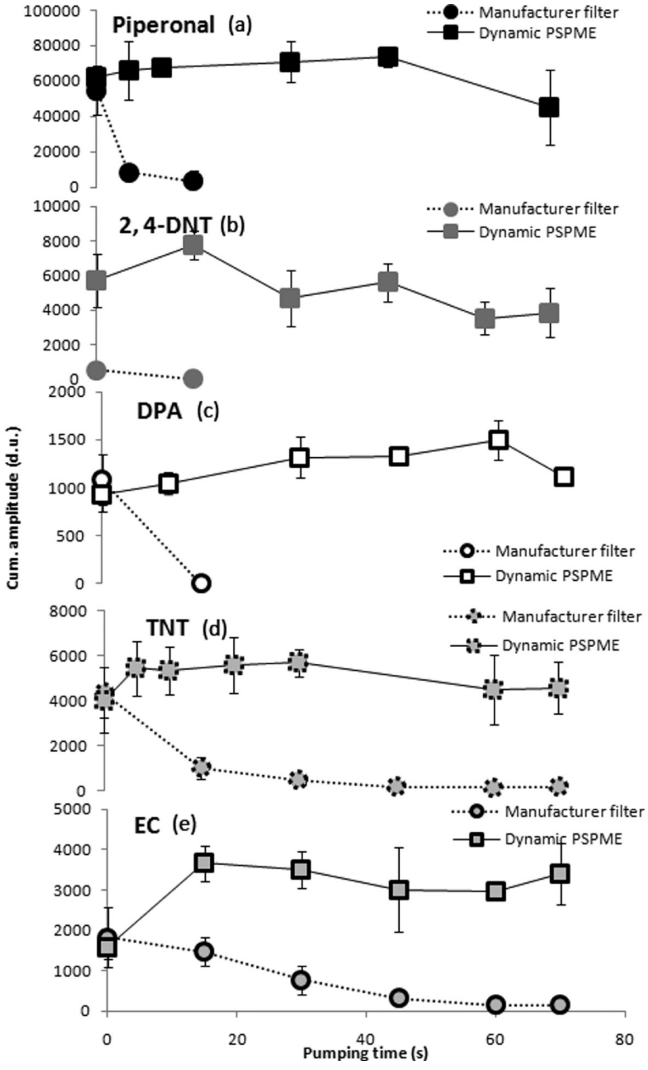

Figure 3. Retention capability study by spiking standard solution of the analytes onto the PSPME surface device and the manufacturer filter followed by clean air pumping.

The compounds, DPA, TNT, and EC are retained on the dynamic PSPME filter throughout the complete range of sampling time intervals, up to 70 s, as evidenced by the absence of signal decreases in these cases. The maximum sampling time, 70 s, was designated as a length of time that is amenable to field sampling and/or high throughput situations. Piperonal signal increased up to 45 s of sampling time (Figure 3a) after which the signal decreased 28% from the initial amount. This is not surprising due to the volatility of piperonal and its tendency to remain in the headspace.[20] Specifically, for the 2,4-DNT (Figure 3b), after 30 s of pumping, there is some signal loss (2% at 45 s), with 70 s of pumping causing the greatest signal reduction (33%).

From Figure 3, it also evident that when spiking onto the manufacturer provided filter, pumping of only 15 s caused a large drop in retention for all the compounds, with the most being retained for EC (79%) and the least for 2,4-DNT (4%). The original designation of this filter is not for preconcentration but rather for capturing particulate matter. There is no specific adsorptive/absorptive coating for collecting vapors as opposed to the dynamic PSPME device. The same would be concluded while analyzing the results taking into account total air volume sampled instead of pumping time. Even though the volume of air that was sampled is 3-fold higher for the manufacturer provided filter, when the sampling time is correlated with the appropriate sample volumes, dynamic PSPME still outperforms the manufacturer provided filter. For example, by comparing the 15 s sampling time for the manufacturer provided filter (13.8 L air sampled) with the 45 s sampling time for the dynamic PSPME device (15.75 L air sampled), the dynamic PSPME device still retains all of the starting compounds (100% or greater), except 2,4-DNT which as previously mentioned, loses a mere 2%.

Retaining Capability Studied by Analyte Vapor Source. The performance of the dynamic PSPME devices coupled to IMS analysis was estimated further by dynamic sampling of air containing the analytes. Controlled odor mimic permeation systems (COMPS)[16,26,27] devices were used to generate vapor source of the tested analytes, which enabled quantitation of their maximum mass available in air for extraction. They differ from currently available gas generating systems for SPME calibrations[36,37] in portability, since they are lightweight, do not require any power to operate, and are very inexpensive, and as opposed to a type of

(35) Gura, S.; Joshi, M.; Almirall, J. R. *Anal. Bionanal. Chem.* **2010**, submitted.
(36) Nelson, G. O. *Gas Mixtures: Preparation and Control*; CRC Press: Boca Raton, FL, 1992.
(37) Koziel, J. A.; Martos, P. A.; Pawliszyn, J. *J. Chromatogr., A* **2004**, *1025*, 3–9.

finite gas generating system,[38] they provide a continuous vapor source without encountering any solvent effects. This was an alternate manner to simulate dynamic sampling in the field for detection of vapors emitted from drugs, high and low explosives in order to test the performance of dynamic PSPME device. The optimum sampling height was determined for 30 s of pumping above the COMPS devices for each targeted compound. Sampling of piperonal, DPA, EC, and 2,4-DNT at the height of 10, 10, 5, and 5 cm, respectively, produced IMS responses within the linear dynamic range of each analyte.

At these selected sampling heights, the effect of pumping time was studied, and as with the retention capability study, the manufacturer provided filter was also tested for comparison purposes (Figure 4). It is key to note that in Figure 4a, for the compounds piperonal, 2,4-DNT, and DPA, there is an increasing trend of amount extracted versus the sampling time, demonstrating yet again the trapping capability of the dynamic PSPME device absorbent phase.

Figure 4b depicts opposing results for the extraction of the same compounds using the manufacturer provided filter. No detectable amounts of DPA vapors were collected. Piperonal and 2,4-DNT were detected but at significantly lower masses. Moreover, those amounts collected remained constant regardless of sampling time. This demonstrates that the vapors sampled are being lost through this filter while pumping, and there is no net gain in the amount of targeted compound adsorbed, although the vapors are continuously generated.

Figure 4c shows the results for sampling EC producing the least mass detected among the suite of the target analytes. With similar masses extracted by both collection media, no advantage was observed for the PSPME device. The minimal responses obtained could be due to the low volatility of EC. The steady mass detected by the PSPME device, with no gain in mass as pumping time is increased, can be explain by the analyte's dissipation rate. The EC COMPS devices were calculated to emit only 0.93 ng s^{-1} by measuring the mass of the device each day for 28 days as described in the Methods section. However, for a compound like EC that has a relatively low vapor pressure, this method of determining the dissipation rate may not correlate directly within seconds, thus not allowing steady and continuous generation of the vapors in this time scale. Evaluation of the PSPME device in sampling TNT vapors generated by COMPS bags was not possible since solid TNT (pure) was not available, and by the use of the only available source, Pentolite, no permeation through the LDPE bag was obtained. Overall, these results demonstrate the powerful preconcentration power of dynamic PSPME device desirable for rapidly (on the order of seconds) sampling trace amounts of volatile chemical signatures of illicit compounds in the field from air.

When considering extraction efficiency or the mass detected divided by the mass available, the dynamic PSPME device performs much better than the manufacturer provided filter. The mass available is derived by the COMPS dissipation rates (nanogram per second) (Figure SB, in the Supporting Information) multiplied by the sampling time (seconds) to give a total maximal

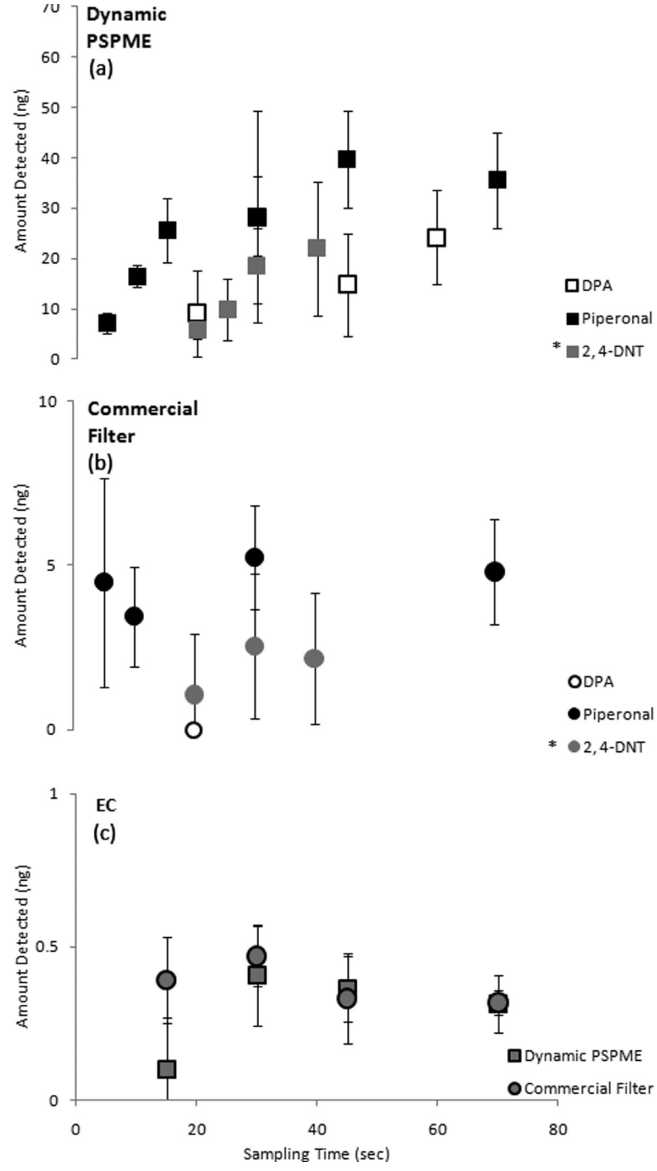

Figure 4. Retention capability study by dynamically sampling vapors of analytes emitted from COMPS bags. (*) The amount detected for 2,4-DNT was calculated using the original response curve listed in Table 1.

mass available for extraction. For piperonal (Figure 4a), 30−45 s is required to extract the highest mass when considering only the sampling time, but when taking into account the mass of piperonal in air, a sampling time of 15 s was the best, resulting in a 4.9% extraction efficiency. Averaging the extraction efficiency for all sampling times, the dynamic PSPME device resulted in 3.4% versus 1% for the manufacturer provided filter. For 2,4-DNT, the average extraction efficiency was 3.1% and 0.42% for the dynamic PSPME device and the manufacturer provided filter, respectively. For DPA, detection was only possible with the dynamic PSPME device, with an extraction efficiency of 12.4% with a 30 s extraction and an average of 6.3% extraction efficiency for all sampling times. It is important to emphasize that the amounts detected also fell within the IMS LDR's for each compound, adding to the reliability of this quantitation approach. The large recoveries obtained are evidence of the preconcentration power of the dynamic PSPME device considering that sampling was conducted in an open laboratory clean bench on the scale of seconds. By

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Table 3. Detection of Target Analytes from Real Case Samples Using the Dynamic PSPME−IMS Method

analyte	emitting source		source mass	equilibrium time (h)	pumping time (sec)	mass detected (ng)
piperonal	ecstasy tablets	case 4[20]	5 tablets (~1.5 g)	24	10	40.0 ± 2
		case 1[20]				12
2,4-DNT	smokeless powder	IMR 4198	100 mg	0.5	30	35.0 ± 11.5
		Hodgon H322				26.0 ± 14.0
DPA		Hodgon H322		24	60	38.0 ± 9.3
		IMR 4198				11.2 ± 2.5
		unique				73.9 ± 13.4
		red dot				69.1 ± 18.6
EC		red dot		24	60	N/D
TNT	pentolite		100 mg	1	30	0.60 ± 0.02

employing a dynamic sampling scenario, the extraction device's mass uptake rate is increased and the boundary layer that has to be overcome in a static sampling scenario is decreased,[24] thus allowing faster extractions. This, coupled with the large surface area of this porous dynamic PSPME device, provides greater capacity to capture a larger portion of the targeted analytes from air.

PSPME−IMS Method Sensitivity. The detection limits for the targeted compounds using the complete dynamic PSPME−IMS method were estimated. The method, based on three consecutive steps, dynamic sampling, desorption, and detection, proved to be highly efficient in the first two stages with no virtually loss of sample, whereby determining the method's sensitivity became restricted by the third step, the IMS analysis. Accumulative extraction of a total mass of analyte onto the adsorbent phase of the novel device that is above the IMS analysis MDL is expected to alarm. The sensitivity of the PSPME−IMS method was estimated for each of the tested analytes in this study, considering a 10 s sampling time (total air volume of 3.5 L) as applicable to real case scenarios, followed by 100% efficient absorption on the substrate and complete IMS desorption. The resulting LOD's or the minimum amounts of target analyte that must be available in air for sampling are as follows: 0.6, 1.5, 0.6, 0.01, and 0.02 ng L^{-1} for piperonal, 2,4-DNT, DPA, TNT, and EC, respectively.

Application of Dynamic PSPME−IMS for Screening of Illicit Compounds. The retaining capabilities obtained for the novel dynamic PSPSME device confirm its validity in detection of the target analytes from real case scenarios. The dynamic PSPME device was tested on the headspace of illicit compounds under conditions designed to simulate difficult sampling conditions in the field. These results along with the sampling conditions are listed in Table 3. Sample plasmagrams are included in Figure SC in the Supporting Information.

Suspected MDMA tablets were sampled and analyzed, in a blind study test, on-site at a local law enforcement agency. One suspected tablet case (case 2) produced a negative response for piperonal by dynamic PSPME−IMS, and this was corroborated as negative for MDMA by GC/MS.[20] Another case (case 4) was positive for MDMA from GC/MS data, and 40 ng of piperonal were detected by IMS following only a 10 s extraction with 15 min of equilibration time. In the most difficult scenario (case 1), minimal amounts of the MDMA drug were confirmed by GC/MS data, resulting in even less amounts of piperonal being present.[20] Despite this, 11.7 ng of piperonal was detected from only a 10 s dynamic PSPME extraction in the first trial. Since 15 min was not a sufficient sealing time for such a small initial concentration of piperonal in the tablets to rebuild the headspace, no piperonal was detected for the two subsequent dynamic extractions.

A mass of 100 mg of several brands of the smokeless powders (low explosives) were sealed in a quart can, opened, and sampled by dynamic PSPME. For 2,4-DNT detection in the negative polarity, only 30 min of sealing was required followed by 30 s of sampling dynamically in order to detect 35 ng from the IMR 4198 powder and 26 ng from the Hogdon H322 powder. This is significant, since in a previous study, it was reported that although up to 41 ng of 2,4-DNT was detected by GC/MS following extraction from the headspace of 100 mg of these powders for 120 min in a 50 mL vial following equilibration, detectable amounts were not observed by SPME−IMS.[18] With dynamic PSPME, pre-equilibrium sampling of the same mass from a sample container with a volume 80-fold greater was possible in only 30 s resulting in the relatively same amount of 2,4-DNT being detected as by GC/MS.

In the positive polarity, the powders were sampled in a similar fashion except they were sealed overnight. DPA was detectable from the four powders following the dynamic PSPME−IMS method (see Table 3), with lesser amounts detected from the powders that also contained 2,4-DNT. The smokeless powder red dot is known to contain both DPA and EC,[18] but only DPA alarmed in this experimental scheme. As was shown in the COMPS sampling optimization, there was no accumulation of the EC on the dynamic PSPME even while sampling this compound alone. Additionally, the EC may in fact have been preconcentrated, but its detection was likely inhibited by competitive ionization with DPA in the IMS ionization chamber. It is expected that in a sealed static sampling system using PSPME[19,20] or if a greater mass of the smokeless powders was used as is typical for improvised explosive devices (IEDs), then this compound would be detectable. Additional research must be conducted to determine the optimal dynamic sampling parameters and IMS operating conditions to favor detection of the more discriminating compound, EC. Since smokeless powders are available in a variety of particle shapes, rods, discs, and balls, the difference in their surface area may affect the amount of the volatile chemical signature that is emitted into air. This phenomenon may inhibit an additive such as EC from being released despite that fact it is in the formulation and should be investigated. In Figure SCb in the Supporting Information, a sample plasmagram from the dynamic sampling of an EC COMPS device for 30 s from 5 cm has been included. From these results, dynamic PSPME−IMS is a rapid and sensitive

option for the detection of 2,4-DNT and DPA from a variety smokeless powders, covering both IMS ionization polarities.

The high explosive, Pentolite, was sampled by the dynamic PSPME device targeting TNT. Although the COMPS device created for Pentolite showed no measurable dissipation, it was still sampled without the barrier of an LDPE bag expecting that the semivolatile component, TNT, would still be released. After sealing a small amount, 100 mg of this powder in a can for 1 h and sampling only 30 s, an amount of 0.6 ng was detected by IMS, a value within the LDR.

CONCLUSIONS

This paper presents the first report of a SPME preconcentration device, dynamic PSPME that enables rapid air sampling of the volatile chemical signatures of drugs and explosives for direct introduction into existing IMS instruments. Dynamic PSPME is accomplished by use of a planar device that allows sampling of a large volume of air and has a high surface area for the capture and strong retention of these compounds from air. These attributes suggest dynamic PSPME as an exhaustive sampler, as opposed to the other SPME configurations that are generally considered as nonexhaustive, equilibrium-based sampling devices. This is advantageous when extracting trace amounts of volatile chemical signatures diluted in a large volume of air, as is the case when sampling in the field. This device was developed and optimized in a manner applicable to field sampling using an accessory, the hand-held vacuum, as a portable, easy-to-use pump, that is already available and in use for the collection of particles.

The results obtained for the novel device demonstrate that even with a minimal amount of emitting source present, the dynamic PSPME−IMS method performs well as a rapid and sensitive screening tool applicable for field analysis. Since there is no need for an additional interface, minimal change in security infrastructure would be necessary to employ this methodology for the open air sampling of places suspected to contain illicit drugs or explosives. It should also not restrict the flow of passenger or cargo traffic since it is a rapid, high throughput analysis method stemming from its reusability and the fact that both sampling and IMS analysis is completed in seconds.

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SUPPORTING INFORMATION AVAILABLE

Additional information as noted in text. This material is available free of charge via the Internet at http://pubs.acs.org.

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