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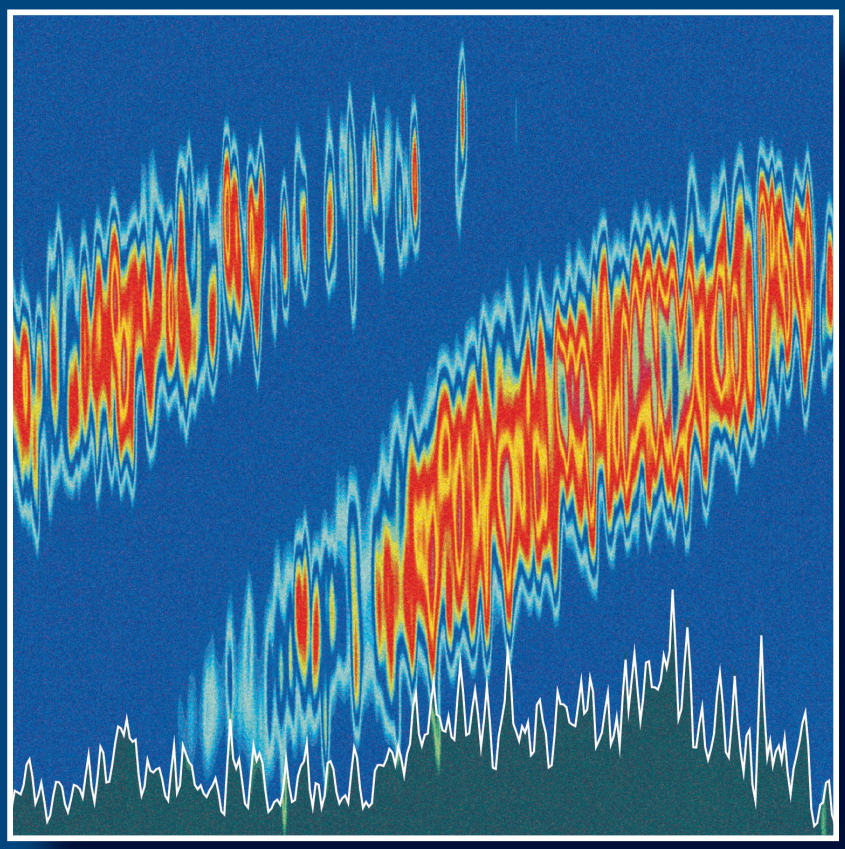

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Original Paper

Analysis of the volatile chemical markers of explosives using novel solid phase microextraction coupled to ion mobility spectrometry

Ion mobility spectrometry (IMS) is routinely used in screening checkpoints for the detection of explosives and illicit drugs but it mainly relies on the capture of particles on a swab surface for the detection. Solid phase microextraction (SPME) has been coupled to IMS for the preconcentration of explosives and their volatile chemical markers and, although it has improved the LODs over a standalone IMS, it is limited to sampling in small vessels by the fiber geometry. Novel planar geometry SPME devices coated with PDMS and sol–gel PDMS that do not require an additional interface to IMS are now reported for the first time. The explosive, 2,4,6-trinitrotoluene (TNT), is sampled with the planar SPME reaching extraction equilibrium faster than with fiber SPME, concentrating detectable levels of TNT in a matter of minutes. The surface area, capacity, extraction efficiency, and LODs are also improved over fiber SPME allowing for sampling in larger volumes. The volatile chemical markers, 2,4-dinitrotoluene, cyclohexanone, and the taggant 4-nitrotoluene have also been successfully extracted by planar SPME and detected by IMS at mass loadings below 1 ng of extracted analyte on the planar device for TNT, for example.

Keywords: Explosives / Ion mobility spectrometry / Planar geometry / Solid phase microextraction / Volatile chemical markers

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1 Introduction

Approximately 90% of the world's cargo is moved by sea and despite the presence of ion mobility spectrometry (IMS) at ports-of-entry [1], only 2% of cargo containers is actually opened and inspected upon arrival ([2], https://www.llnl.gov/str/May04/Slaughter.html). A screening technique that can detect hidden explosives and illicit drugs that is rapid, sensitive, easy-to-use, and does not require a large change in port infrastructure is needed. A novel planar solid phase microextraction (SPME) device that provides increased surface area, capacity, and extraction efficiency over fiber SPME and requires no modification to the front-end of IMS instruments is now presented. This new geometrical configuration of the SPME sampling device can effectively extract explosives and their volatile chemical markers from high-risk areas for subsequent detection by IMS.

Sampling for the volatile chemical markers emanating from the parent explosives and drug compounds rather than sampling for particles themselves can increase the probability of detecting contraband. This is especially true in the case of some organic explosives of interest such as hexahydro-1,3,5-trinitro-s-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and pentaerythritol tetranitrate (PETN) which have very low vapor pressures, 1.5×10^{-7}, 2.1×10^{-11}, and 5.1×10^{-8} Pa, respectively. These explosives are unavailable in the headspace making vapor sampling impossible, yet trained *Canis lupus* var. *familiaris* (the domesticated dog) can effectively detect them because canines utilize volatile components of drugs and explosive mixtures to locate the target odors even under challenging field conditions [3]. The primary odor signature for trinitrotoluene (TNT), cast explosives, and smokeless powders is 2,4-dinitrotoluene and cyclohexanone has been reported as the odor-signature of RDX [4]. It is proposed that by effectively sampling these and other volatile chemical markers in the air with the planar SPME device, rather

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Abbreviations: IMS, ion mobility spectrometry; **RDX,** hexahydro-1,3,5-trinitro-s-triazine; **SPME,** solid phase microextraction; **TNT,** 2,4,6-trinitrotoluene

than swabbing for particles, followed by IMS analysis, marked improvements in the detection of hidden explosives by IMS can be achieved.

Sampling large areas and volumes for contraband in a nonintrusive manner presents a great analytical challenge. Researchers have tried a high volume sampling method for use in cargo containers that entraps particles onto a treated filter followed by GC-IMS analysis [5]. This is a cumbersome technique requiring significant modification of IMS instruments while relying on the capture of particles rather than absorption of volatile chemical markers. SPME is a proven extraction technique for sampling volatiles and semivolatiles from air effectively, but it is limited by the fiber geometry because of the minimal surface area and capacity for analyte preconcentration. A detailed discussion of SPME analytical theory and practice can be found elsewhere [6, 7], The volatile chemical markers of TNT, 2,4-DNT, 1,3-DNB, and 2,4,6-TNT available for sampling in the air above simulated buried mines have been successfully extracted by SPME [8]. The results reported from this and other previous work [9 – 11] suggest that SPME is useful for the extraction and preconcentration of explosives and drug volatile markers. Consequently, explosives and drug analysis can be improved when a planar SPME device is used that provides a larger surface area and can be easily coupled to a field-portable IMS.

The first ever peer-reviewed SPME – IMS interface (patent pending) reported enables extraction of volatile constituent chemicals and detection taggants in explosives from a headspace for subsequent detection in a simple, rapid, sensitive, and inexpensive manner, yielding LODs of the volatile compounds 1 – 2 orders of magnitude lower than those of SPME-GC-MS [12 – 14]. Another SPME – IMS coupling has been devised that is based on the same transfer line/desorber concept as the one constructed by Almirall and coworkers [12], but is used with a handheld IMS [15]. This system has the advantage of ultra-portability but does not yet address the need for sampling of large volumes. Stir-bar sorptive SPME [16] and thin-film microextraction [17] were developed to increase capacity by increasing the surface area of the extraction phase [17], but these geometries cannot be easily coupled to current IMS instruments. The surface area and capacity can be increased further with the employment of a planar geometry SPME for direct coupling to IMS. A recent review of sample introduction systems coupled to IMS instruments concluded that "SPME – IMS coupling cannot be deemed a robust system" [18], yet with the development of this planar SPME, the need for varying fiber introduction interfaces is now eliminated providing for a more practical and effective coupling of SPME sampling/preconcentration to an IMS detector.

A study of a novel planar geometry SPME device that has a greater surface area, capacity, and extraction efficiency over fiber SPME is presented. This research addresses the urgent need for a device that can preconcentrate contraband vapors in large areas, nonintrusively, using TNT as a model compound.

2 Materials and methods

The planar SPME devices used in this study were prepared by two different methods. Prior to coating, 1 mm thick, precleaned microscope slides (Chase Scientific Glass, Vineland, NJ) were cut into 3.81 cm × 2.54 cm pieces. The glass substrates were dipped individually into a 2:1 mixture of concentrated sulfuric acid (Fisher Scientific, Fair Lawn, NJ) and 30% hydrogen peroxide (Fisher Scientific) and placed in an oven at 90°C for 20 min. The solution was decanted and the substrates were rinsed with deionized water. Each substrate was dipped in 1 M NaOH for 1 h to expose the silanols on the glass surface. This was followed by thorough rinsing with deionized water to ensure wettability (no beading of water on the glass surface). The substrates were placed in an oven at 120°C for 12 h to dry. The first preparation method consisted of spin-coating a prepared glass substrate with a 3:1 mixture of chlorine-terminated PDMS (Cl-PDMS) (Sigma – Aldrich, St. Louis, MO) and dichloromethane (Acros, NJ, USA). The spin-coater used is a model WS-400B-6NPP-LITE (Laurell Technologies, North Wales, PA). One milliliter of the coating solution was deposited on the substrate and the spin program, 1000 rpm for 60 s, was activated. The PDMS planar SPME device was placed in a dessicator at room temperature for 12 h followed by dipping in deionized water to remove any excess hydrochloric acid which resulted from the reaction. The second planar SPME preparation consisted of using sol – gel technology to create a physically incorporated PDMS extraction phase as was first described by Liu *et al.* [19] for the preparation of SPME fibers. The sol solution was modified for a planar geometry and prepared as follows: 6.40 g vinyl-terminated PDMS (vt-PDMS) (Gelest, Morrisville, PA) was dissolved in 8 mL of dichloromethane; then 3.42 mL of methyltrimethoxysilane (MTMOS) (Fluka, Steinheim, Germany) and 1.67 g poly(methylhydrosiloxane) (PMHS) (Sigma – Aldrich) were added, followed by 2.73 mL of TFA (Acros) (5% water v/v). The solution was vortexed and allowed a 30 min stay. The prepared substrate was dipped in the solution for 1 h. The planar sol – gel PDMS SPME device was placed in the dessicator for 12 h, followed by a 6 h dip in dichloromethane. For both types of planar SPME, a 12 h gelation in an oven at 40°C followed the solvent rinse. Conditioning of both types of planar SPME was as follows: the planar SPME device was placed in a GC oven under nitrogen atmosphere at 120°C for 1 h, 240°C for 1 h, and 300°C for 3 h. Following conditioning, the planar SPME devices were slowly cooled to

Table 1. Experimental conditions

Smiths IonScan 400B IMS experimental conditions		
Detection mode		Explosives, taggants, and volatile chemical markers, negative ion mode (−); cyclohexanone, positive ion mode (+)
Desorber temperature	°C	225 (−); 285 (+)
Drift tube temperature	°C	115 (−); 235 (+)
Analysis time	s	10 (−); 8 (+)
Sample flow	mL/min	300 (−); 200 (+)
Drift flow	mL/min	351 (−); 300 (+)
Reagent gas		Hexachloroethane (−); nicotinamide (+)
GE Iontrack Itemiser 2 IMS experimental conditions		
Detection mode		Explosives, taggants, and volatile chemical markers, negative ion mode (−)
Desorber temperature	°C	215
Drift tube temperature	°C	180
Analysis time	s	7
Sample flow	mL/min	1000
Detector flow	mL/min	200
Reagent gas		Dichloromethane
SPME – IMS experimental conditions		
Interface temperature	°C	260 ± 1
Warm up time	h	1

room temperature to prevent cracking of the phase, especially of the sol – gel PDMS.

In this study, two ion mobility spectrometers were used for the detection of the compounds of interest: a Smiths Detection IonScan 400B (Smiths Detection, Mississauga, ON, Canada) and a General Electric Iontrack Itemiser 2 (Wilmington, MA). For SPME fiber comparisons, the front end of the GE Itemiser 2 was coupled with an SPME interface designed by the Almirall research group (patent pending) [12]. The operating conditions for both the standalone IMS instruments and the SPME – IMS interface are listed in Table 1.

Standard solutions of 2,4,6-trinitrotoluene (TNT) (Cerilliant, Round Rock, TX) were prepared from a 1000 μg/mL stock solution in concentrations of 0.1, 0.2, 0.5, 0.8, 1.0, 2.5, 5.0, 10.0, and 240 μg/mL for the experiments with ACN as the solvent (Fisher Scientific).

Response curves for each IMS instrument were generated for TNT by spiking amounts of known concentration onto swabs and introducing them into the IMS in triplicate. Sampling by the planar SPME was done by suspending the SPME device above the headspace of a can, spiking the compound of known concentration, and immediately sealing it. The same was done for the fiber except that a hole was made on the lid of the can where an 11 mm stopper sleeve (Wheaton, Millville, NJ) could fit snuggly and through which the SPME PDMS fiber (Supelco, Bellefonte, PA) was introduced and exposed for sampling immediately after the sample had been spiked and the can sealed. The determination of equilibrium time for the planar PDMS, planar sol – gel PDMS, and the PDMS fiber was determined as follows: 10 μL of 240 μg/mL TNT was spiked into quart cans and sampling at different time intervals was conducted with desorption into each IMS. For the SPME fiber sampling, only analysis by the GE Itemiser 2 was possible since there is no currently machined SPME – IMS interface for the Smiths 400B. For calculating recovery, different concentrations of TNT were spiked and sampled at the equilibrium time for each SPME device. For the comparison of extraction efficiency of the different SPME devices, different volumes of a 5 μg/mL TNT solution were spiked into quart cans and sampled at the appropriate equilibrium times with detection by the GE Itemiser 2. All extractions were conducted in triplicate.

Evaluation of other volatile chemical markers was achieved by extracting amounts of known concentration of the compound of interest from a quart can with the sol – gel PDMS SPME device for different sampling times. The compounds studied were: 2,4-dinitrotoluene (2,4-DNT), 4-nitrotoluene (4-NT), and cyclohexanone (Fisher Scientific). The 2,4-DNT and 4-NT were obtained in small amounts from a local law enforcement agency and diluted to the appropriate concentrations. These compounds were analyzed by the Smiths 400B IMS in the negative mode, except cyclohexanone which was detected in the positive polarity.

Surface characterization and coating thickness measurements were obtained using a Philips XL30 SEM (FEI, Hillsboro, OR).

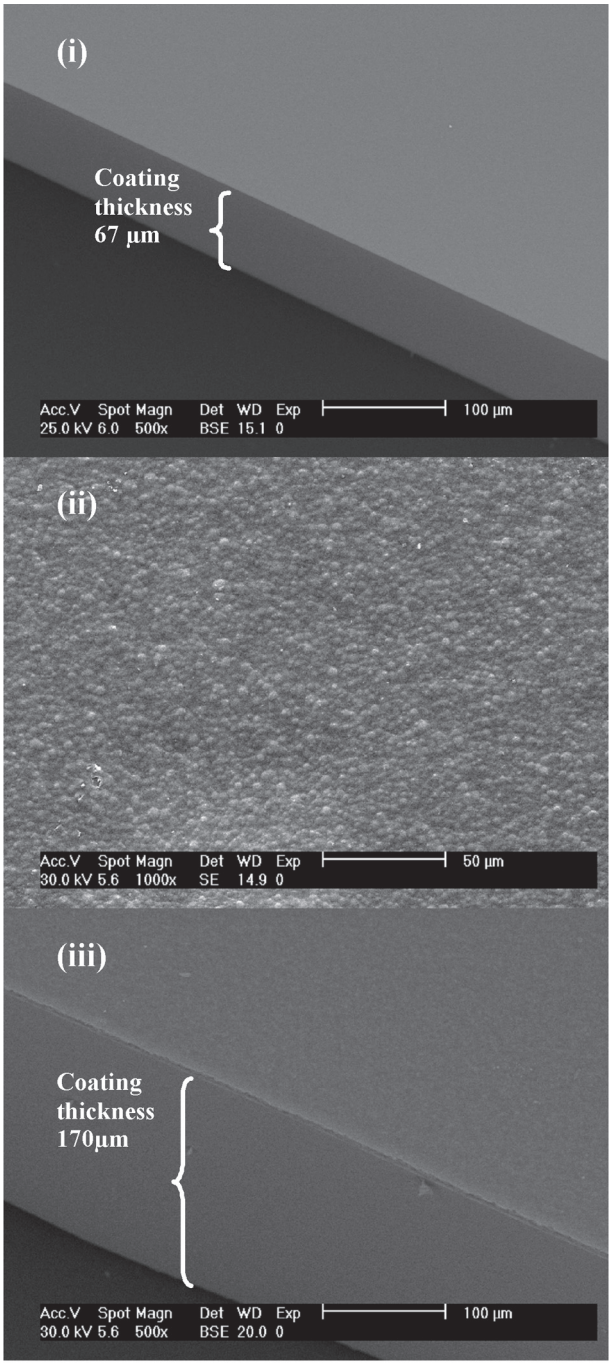

Figure 1. SEM images of the planar SPME devices. (i). SEM image of PDMS SPME device surface. The coating thickness was determined to be 67 μm. (ii). SEM image of the sol–gel PDMS SPME device surface. (iii). SEM image of the sol–gel PDMS SPME device coating thickness (170 μm).

3 Results and discussion

Coating of the planar PDMS SPME device was achieved by spin-coating chlorine-terminated PDMS onto a glass substrate with exposed silanol groups on the surface. A bimolecular nucleophilic substitution reaction (S_N2) occurs where the exposed silanol reacts with the chlorine moiety of the PDMS, liberating HCl and covalently bonding PDMS to the glass. An SEM image of the PDMS surface with its coating thickness is shown in Fig. 1(i). The coating thickness was determined to be ~67 μm.

Sol–gel PDMS has been previously used to coat SPME fibers [19] due to high thermal stability and strong bonding of the phase to the surface for longer lifetime of the extraction device. This same chemistry has been used as the extraction phase of the planar SPME device but has been modified for the difference in geometry. Sol–gel is defined as a colloidal suspension that is gelled to form a solid. The sol–gel process starts with hydrolysis of the precursor, MTMOS, which is catalyzed by TFA, and its polycondensation. This creates a polymeric network which is anchored to the glass surface since the silanol groups on the glass surface also participate in the condensation reactions. The last step is the crosslinking of the vinyl group of the PDMS during curing [19]. SEM images of the sol–gel PDMS surface and coating thickness are shown in Figs. 1(ii) and (iii), respectively. The coating thickness was determined to be ~170 μm.

The coating of the planar surface with an SPME phase greatly increases the surface area when compared to that of a fiber SPME. The thinnest SPME coating available for a fiber is 7 μm while the thickest is 100 μm. This equates to a surface area of the fiber from 0.45 to 10.47 mm^2. The planar SPME surface area ranges from 500 to 1000 mm^2. The ideal surface area for the commercial embodiment will be 792 mm^2 for a disk that is 32 mm in diameter. As a result of this increase in surface area, the capacity is also further increased since the volume of the phase is greater. The thickest SPME fiber on the market has a volume of only 1.03 mm^3 while the planar sol–gel PDMS discussed has a volume of 165 mm^3. The change from the fiber geometry to the planar geometry thus increases the surface area which greatly increases the possibility of absorbing the target compounds therefore the increase in capacity also leads to sensitivity enhancements of SPME–IMS.

Response curves of TNT for each IMS instrument were generated and the equations of the linear regression lines for the Smiths 400B (1) and the GE Itemiser2 (2) are shown below:

$$y = 1769.9x + 390.29, r^2 = 0.9678 \quad (1)$$

$$y = 1131.2x + 2517.5, r^2 = 0.9944 \quad (2)$$

From the equation for the best-fit line, the amount extracted by each SPME device can be calculated in the nanogram range.

Since SPME is an equilibrium technique, experiments were conducted to determine the minimum sampling time required to obtain the highest IMS signal for each

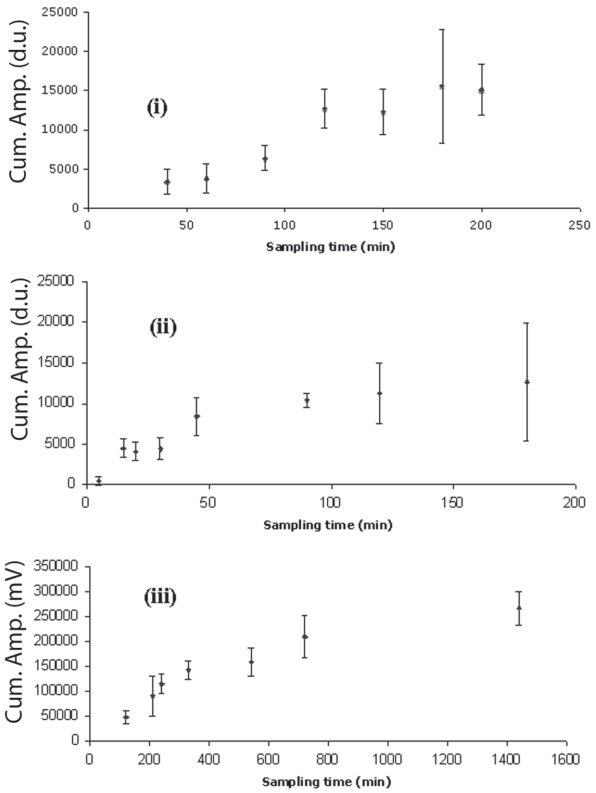

Figure 2. TNT equilibrium curves for each SPME device. (i). Planar sol – gel PDMS SPME equilibrium curve for TNT (Smiths Ion Scan 400B). (ii). Planar PDMS SPME equilibrium curve for TNT (Smiths Ion Scan 400B). (iii). PDMS SPME fiber equilibrium curve for TNT (GE Iontrack Itemiser 2).

SPME device. A 10 μL spike of a 240 μg/mL solution for each of the analytes of interest was introduced into a quart-sized can and sampled at different time intervals by each SPME device and subsequently desorbed into the Smiths IonScan 400B IMS (for the planar geometry) or the GE Iontrack Itemiser 2 IMS (for the fiber geometry) to determine the equilibrium time. All sampling time increments were repeated in triplicate, each with fresh spikes into new quart cans each time. The resulting equilibrium curves are shown in Fig. 2. In Fig. 2(i), it is evident that equilibrium is reached at about 2 h for the planar sol – gel PDMS SPME device. The equilibrium time for the planar PDMS SPME device was reached by 40 min (Fig. 2(ii)). The planar SPME devices both performed better than the fiber PDMS SPME, which required over 10 h of sampling time to reach equilibrium as shown in Fig. 2(iii). Since 10 h of sampling is not practical and in order to compare the three types of SPME devices for extraction efficiency and speed of analysis, the sampling time for the PDMS fiber was thus conservatively set at 3 h. The speed with which the planar PDMS reached equilibrium with the sample when compared to planar sol – gel can be due to the difference in coating thickness and the sol – gel network. Planar sol – gel PDMS and planar PDMS

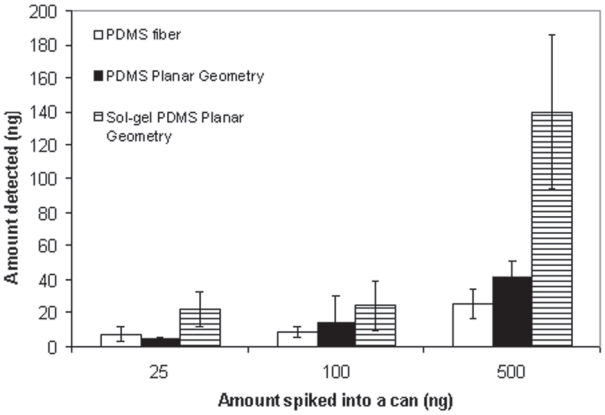

Figure 3. Comparison of extraction capabilities of the three SPME types with detection by the GE Itemiser 2.

reached equilibrium with TNT in the headspace faster than the fiber type because of the increased surface area of the planar geometry. Longer sampling times are better suited for sampling cargo containers during travel. For applications that require short sampling times, it is important to note that sufficient sampling can be achieved at pre-equilibrium conditions and still obtain an appreciable signal by IMS. For the minimum sampling times in Figs. 2(i) and (ii) for the planar sol – gel PDMS and planar PDMS SPME devices, respectively, the signals for TNT obtained are above the LODs when solving for Eq. (1). Additionally, when comparing the results displayed in Figs. 2(i) and (ii), planar PDMS is more efficient than planar sol – gel PDMS SPME at extracting in shorter times yet for planar sol – gel PDMS SPME, the signal is greater (13 000 d.u. *vs.* 8000 d.u. at their respective equilibrium times) under the same experimental conditions. As such, planar PDMS SPME would be more useful for applications that require higher throughput while the sol – gel is recommended for applications that can accommodate longer sampling times.

A comparison of the extraction efficiency of all three SPME devices at their respective equilibrium times, with detection by the GE Itemiser 2, was conducted and the results are shown in Fig. 3. The *x*-axis displays the different amounts of TNT spiked into a quart can for each extraction and the *y*-axis shows the amount detected by the IMS after desorption of the SPME device. The range of mass of TNT spiked was between 25 and 500 ng. In all cases, the planar sol – gel PDMS extracted more mass of the initially spiked sample. This can be due to the greater coating thickness and the porous sol – gel network. The planar PDMS SPME – IMS response for TNT was greater than the PDMS fiber response except at the 25 ng spike. This can be attributed to the closed nature of the sample introduction for the SPME – IMS interface as compared to the GE Itemiser 2 desorber that is used for the planar SPME devices which is open and can lead to some loss.

Table 2. Recovery of TNT calculated from response curves

	Smiths Ion Scan 400B		GE Iontrack Itemiser 2	
Sample introduction method	Amount spiked (ng)	Calculated recovery from response curve	Amount spiked (ng)	Calculated recovery from response curve
Liquid spike on paper	0.03	alert	1	alert
Planar sol – gel PDMS	5	0.34 ± 0.14 ng[a)]	8	2.21 ± 1.5 ng
Planar PDMS	8	0.18 ± 0.17 ng	25	2.54 ± 2.0 ng[b)]
Fiber SPME	N/A[c)]	N/A[c)]	25	0.32 ± 0.80 ng

a) Alarms with as low as a 2 ng spike.
b) Alarms with as low as a 10 ng spike.
c) There is no SPME – IMS interface for the Smiths Ionscan 400B.

The planar PDMS is 1.3 times more efficient than the PDMS fiber and the sol – gel PDMS is 3.8 times more efficient than the PDMS fiber when just averaging the extraction efficiencies of each respective planar SPME device over the fiber PDMS SPME for the small masses of TNT (25 – 500 ng) spiked in the cans. There is an obvious trend for increasing extraction efficiencies for both devices over the fiber geometry when more mass is available for sampling that is a result of the 50 – 100 times surface area increase and the at least 16 times capacity increase in the planar geometry when compared to that of the fiber geometry. Thus, when sampling in real case scenarios where much more mass is available in the headspace, the improvements over fiber SPME are expected to be even more significant.

Table 2 shows the instrumental detection for TNT if introduced into the IMS instruments following a liquid spike with a known concentration. The Smiths 400B instrument can detect 30 pg and the GE Itemiser 2 can detect 1 ng, which is consistent with the manufacturer's specifications. The amount required for the instrumental detection is much higher for the GE Itemiser 2 because the desorber is a heated slot that is open to the surroundings when compared to the desorber in the Smiths 400B sample desorber, which is an enclosed heated port resulting in more efficient transfer. Table 2 also shows the minimum amounts of TNT that can be spiked in a quart can (with the associated uncertainty) and sampled at equilibrium, and detected by each IMS instrument used in this study. These values are recoveries calculated from the appropriate response curve equations. For those samples that contain mass loadings that are close to the instrumental LOD, a large uncertainty in the amount of mass recovered is expected. The planar sol – gel PDMS has a higher calculated recovery of TNT for both instruments than the planar PDMS with respect to the amount initially spiked. Since an SPME – IMS interface is available for the GE Itemiser 2 instrument, the minimum amount of sample that must be spiked in a quart can in order to be detected is 25 ng. Table 2 shows that both the fiber geometry SPME and the planar PDMS require a 25 ng TNT spike in a can, yet an alert for TNT from the GE Itemiser 2 instrument was obtained following the headspace extraction of only a 10 ng TNT spike in a quart can using the planar PDMS SPME. Since the signal obtained was less than the *y*-intercept in the equation from the GE Itemiser 2 response curve for the planar PDMS (Eq. 2), an actual recovery could not be calculated for the spiked amount. For this same reason, in order for the recovery of TNT by the planar sol – gel PDMS using the Smiths 400B to be reported, a spike greater than 2 ng in a can is required. Despite this, the instrument still reports an alert for an extraction of a 2 ng spike. Interestingly, when the same low mass (25 ng) of TNT is spiked into the quart cans for sampling with both fiber and the planar PDMS for comparison, the recovery by the planar PDMS is enhanced by almost a factor of 10 over the SPME fiber. In fact, both planar SPME devices afford the user greater recoveries than fiber SPME – IMS (a consequence of the improved extraction efficiency), an improvement since the advent of SPME – IMS, a technique which has itself greatly improved the LODs as compared to particle analysis [14].

Other volatile chemical markers that have been identified as emanating from explosives were also sampled by the planar sol – gel PDMS SPME. Of the compounds studied only cyclohexanone, an odor signature of RDX [4], was analyzed in the positive mode. The rest of the compounds: 2,4-DNT (an odor signature of TNT and cast explosives) and 4-NT (a taggant) are analyzed in the negative polarity (details are given in Table 1). Figure 4(i) – (iii) displays plasmagrams that show that the planar SPME device is capable of absorbing a sufficient amount of the analytes of interest for the detection by IMS (2,4-DNT, 4-NT, and cyclohexanone, respectively). These plasmagrams represent the segment in the analysis that shows the highest signal for the target analytes. For Figs. 4 (i) and (ii), the peak at 11.3 ms is the calibrant, 4-nitrobenzonitrile (K_0 = 1.7 cm^2 V^{-1} s^{-1}). The chloride ion peaks from the reactant hexachloroethane are at 7.1 and 8.1 ms (K_0 = 2.6 cm^2 V^{-1} s^{-1} and K_0 = 2.3 cm^2 V^{-1} s^{-1}, respectively) and the oxide ion peak is at 8.4 ms (K_0 = 2.2 cm^2 V^{-1} s^{-1}).

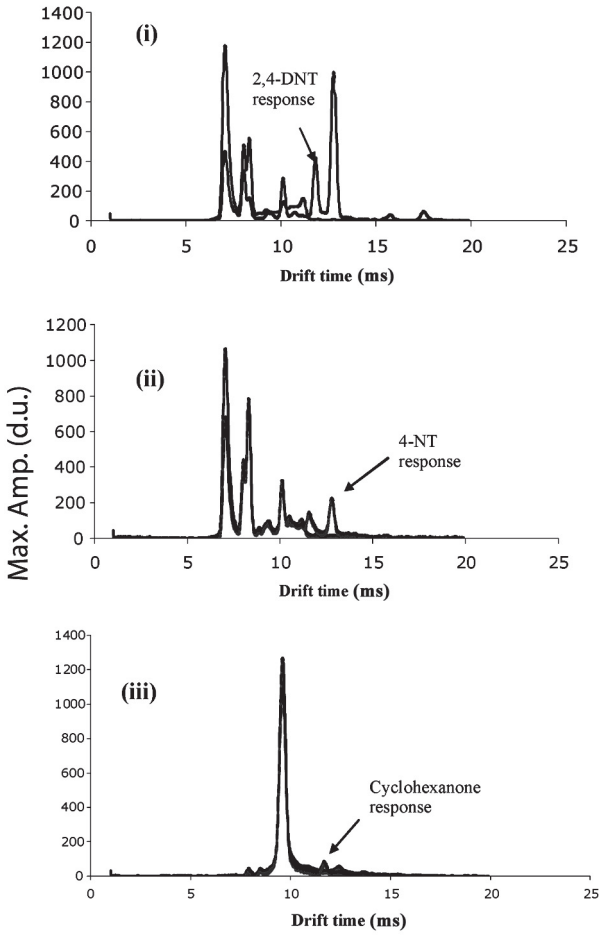

Figure 4. Plasmagrams of other volatile chemical markers with detection by the Smiths 400B. (i). Plasmagram of sol–gel PDMS SPME extraction of 2,4-DNT: 200 μg spike in a can, sampled for 24 h. (ii). Plasmagram of sol–gel PDMS SPME extraction of 4-NT: 30 μg spike in a can, sampled for 24 h. (iii). Plasmagram of sol–gel PDMS SPME extraction of cyclohexanone: 10 μg spike in a can, sampled for 1 h.

The peaks to the left of the calibrant peak are present before IMS analysis begins, but are depleted during the analysis and peak formation. In Fig. 4(i), the 2,4-DNT signal (K_0 = 1.6 $cm^2 V^{-1} s^{-1}$) has a drift time of 11.8 ms. Figure 4(ii) shows the plasmagram for the extraction of 4-NT, with a peak differing from the blank at 12.8 ms. In Fig. 4(iii), the peak at 9.6 ms in the positive polarity is the reactant ion peak nicotinamide (K_0 = 1.9 $cm^2 V^{-1} s^{-1}$). It is also interesting to note that for just a 1 h extraction of such a highly volatile compound as cyclohexanone (5.8×10^2 Pa (http://www.arb.ca.gov/db/solvents/solvent_pages/Ketones-HTML/cylclohexanone.htm) (K_0 = 1.5 $cm^2 V^{-1} s^{-1}$) for which the smallest amount (10 μg) in a can is sampled, a detectable peak is found at 11.7 ms (Fig. 4(iii)).

4 Concluding remarks

This study has shown that by altering the widely used SPME fiber type to a planar geometry SPME device, the surface area is greatly increased by a factor of 50 – 100 times. As a result, the capacity is also increased because the volume of the SPME phase is increased by a factor of at least 16 times that of the fiber geometry enhancing analyte recovery at least 10 times when extracting even trace amounts. Another advantage is the decrease in equilibrium time (from more than 10 h down to 40 min). Although sampling at equilibrium is ideal to obtain the highest signal, it has been shown that sampling at pre-equilibrium (on the order of minutes), does result in detectable signals. Due to the reduction in equilibrium time, faster on-site analyses can be conducted with this geometry when compared to fiber SPME. When comparing the two planar SPME devices, sol–gel PDMS takes longer to reach equilibrium than PDMS, yet for the same extraction times, PDMS produces a consistently higher signal. These planar SPME devices afford the higher throughput with planar PDMS SPME and higher sensitivity with planar sol–gel SPME for applications that can accommodate longer sampling times. The extraction efficiency of SPME for TNT is improved over the fiber geometry. Extraction of more volatile compounds such as taggants and odor signatures has been shown to be practical and effective when coupled with detection by IMS. Finally, it is no longer necessary to fabricate an interface between SPME and IMS since with the planar geometry coupling is readily compatible with the already large installed base of IMS instruments and no significant modification of the security infrastructure should be necessary.

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