Detection of odor signatures of smokeless powders using solid phase microextraction coupled to an ion mobility spectrometer

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ABSTRACT

The detection of hidden explosives through their odors is of great importance to law enforcement agencies and trained canines have traditionally been used for this purpose. This paper reports the extraction of odor signature compounds characteristic of smokeless powders, followed by their detection by ion mobility spectrometers (IMS). Such a method enables the detection of odor compounds, complementing canine detection and allows for mass calibration of IMS instruments. The smokeless powder additives reported include diphenylamine (DPA), ethyl centralite, 2-ethyl 1-hexanol and 2,4-dinitrotoluene. The pre-concentration of these volatile odor chemicals from different commercial smokeless powders onto a solid phase microextraction (SPME) device followed by IMS analysis is demonstrated in this paper. Five samples of smokeless powder samples representing double-based and single-based powders from three popular commercial brands were chosen for this study. Diphenylamine was found to be a common additive among all the powders tested. The mass of the analytes in the headspace available for detection was determined from response curves of the corresponding standards. The response curves were generated by printing precise amounts of standards onto substrates and analyzing them. The absolute detection limits were also determined from these response curves and the values ranged from 0.12 to 1.2 ng for the standards. Typical extraction times ranged between 5 and 40 min and the mass of diphenylamine and ethyl centralite extracted at the lowest extraction times was found to be greater than the LOD of the compounds.

1. Introduction

Ion mobility spectrometry (IMS) is a rapid, sensitive screening technique deployed in control points such as airports and checkpoints. IMS instruments are generally used to collect and detect trace particles of drugs and explosives from surfaces. These instruments can also be used to extract and detect volatile compounds present in the atmosphere when combined with solid phase microextraction (SPME) [1]. Such a coupling adds vapor-sampling capabilities to a bench-top instrument and thus increases the range of compounds that can be detected. Previous studies conducted in our laboratory have reported the design and efficiency of a SPME–IMS interface for the detection of explosives and taggants added to high explosives [2]. The detection of odor

signatures of illicit drugs by this interface has also been reported [3]. SPME incorporates sampling, extraction and pre-concentration into a single rapid step and when combined with the high sensitivity of IMS instruments provides an analytical approach complementary to canine detection. In the current study, we report the use of the IMS interfaced with a SPME as previously described [2] to extract and detect the odor signature compounds of smokeless powders, which are low explosives commonly used in homemade explosive devices. Traditionally, canines have been used as biological detectors of illicit drugs and explosives. The compounds that the canines alert to are reported as the odor chemicals or signatures of the compounds of interest [4,5]. However, canine trials have reported that the dogs show little or no interest in some of the volatile molecules detected by instrumental techniques in the headspace of the target compounds [6]. Our study reports the IMS detection of some of these compounds extracted from the headspace of different smokeless powders for the first time. The expected mass of the compounds extracted and the method detection limits are also reported.

Smokeless powders are a class of propellants used commonly in firearms and ammunition. Approximately 10 million pounds of smokeless powders are produced each year in the United States for

military and hunting purposes [7]. In addition, they are sold widely in sporting and hobby stores and are therefore readily available for public purchase. Since they are also used in improvised explosive devices (IEDs), smokeless powders are of forensic interest [8]. Smokeless powders are classified as single, double and triple based powders, depending on the type of the energetic material utilized. Single-based powders contain only nitrocellulose; double-based powders incorporate both nitrocellulose and nitroglycerin and triple-based powders contain nitroguanidine, nitrocellulose and nitroglycerin. Apart from the stated energetic materials, manufacturers also add stabilizers, plasticizers, flash suppressants, deterrents and opacifiers to increase stability, efficiency and the burning properties of the smokeless powders.

Detection of stabilizers such as diphenylamine (DPA), ethyl centralite (1,3-diethyl diphenyl urea), methyl centralite and deterrents such as butyl phthalate, dinitrotoluene (DNT) all play an important role in the characterization and identification of the source or origin of the smokeless powders [9]. These additives have been detected in gunshot and post-blast residues using capillary electrophoresis, HPLC and GC–MS [10,11]. Many of these methods involve solvent-based extraction procedures, which extract the additives from the powders and powder residues. Additives such as diphenylamine and 2,4-dinitrotoluene have also been shown to be present as odor compounds in the headspace of commercial powders using SPME–GC–MS. They were then used in canine trials to identify the compounds of interest to canines [4]. The above-mentioned study also provides a list of compounds that the canines did not recognize as specific to the explosives [4]. Field analytical techniques like IMS can be optimized to detect some of these compounds to complement canine detection of hidden explosives.

Smokeless powders have been detected by their nitroglycerine component in IMS instruments on the recovery of particles from surfaces [12]. The particles of the smokeless powders or liquid spikes of their extracts are desorbed into the IMS from a swipe used to sample the surface and thermally desorbed to form a gas, which is then ionized using reactant ions. By coupling of a commercial IMS instrument with a mass spectrometer, Neves et al. demonstrated that solutions of some powders also produced ions of ethyl centralite in the positive ionization mode [14]. Apart from ethyl centralite, other additives such as DPA were also reported to be present in solutions of post-explosion residues by West et al [15]. The additives shown in Table 1 that are amine derivatives tend to have high proton affinities and are detected in the positive mode due to the formation of stable positive ions [16]. The plasticizer 2,4-DNT forms a negative ion by proton abstraction and is detected in the negative mode [17]. A common additive in plastic explosives, 2-ethyl hexanol, which has also been found to be an odor chemical of canine interest has not been previously reported to be detected by ^{63}Ni ionization IMS although it has been previously reported by UV ionization IMS [18]. In this paper, we report the detection of 2-ethyl hexanol in the headspace of BL C-2 using SPME–GC–MS method alone.

The detection of the nitroglycerin, by itself, is not considered confirmatory for the presence of a propellant due to its use in other types of applications such as its use as a vasodilator in heart medication [19]. As the additives readily form stable ions in the IMS, they can be used in conjunction with nitroglycerin to add more value to the detection of smokeless powders. However, these compounds have always been detected in smokeless powder extracts or by swiping the particles. This paper is the first reported extraction of these additives from the headspace of commercial powders and detection with the use of IMS. The higher vapor pressures of the additives when compared to the propellant make them possible volatile chemical markers for the smokeless powders and their detection could be indicative of the presence of the powders or of a device containing the powders.

The headspace detection of smokeless powder additives discussed above is of importance to the current study. Solid phase microextraction was used to extract and pre-concentrate the analytes present in the headspace of the powders. PDMS fibers were chosen for the entire study as they provide for efficient extractions for the analytes chosen. Previous research has also concluded that the PDMS fiber was best suited for field studies due to the shorter extraction times involved and faster desorption characteristics [20]. Generally, for quantitative analyses, analytes are extracted until equilibrium is reached between the three phases of the system—sample, headspace gas and fiber. The amount of the analyte extracted by the coating at equilibrium is determined by the partition coefficient of the volatile analyte between the entire sample and the coating. The mass transferred to the extraction phase and the time taken for efficient extraction are dependent upon the capacity of the extraction phase [21]. However, equilibrium extraction may not be practical in many cases as the time for equilibrium may be too long. For experiments where time is critical, it would be beneficial if the pre-equilibrium extractions could extract amounts significantly above the detection limit of the instrument. The mass reported in this paper is the mass extracted by the SPME fiber from the smokeless powders in conditions where equilibrium with the fiber is not yet reached in the system. The mass extracted from the fibers can be determined from a response curve of the IMS instrument for known amounts of mass extracted.

Calibration graphs generated by microdrop printing are used in this study to calculate the mass of the analytes extracted by the fibers. A drop-on-demand system enables deposition of precise amounts of analytes in solution onto a surface. Microdrops can be created in such a way that each drop generated is of a known volume and thereby of known mass loading [22]. The drops formed are generally the size of the diameter of the print head used in dispensing the solution and the drop volume can be measured by determining the diameter of the drop [22]. The microdrop printing technique is used as a precise mass delivery tool to determine the limits of detection for IMS instruments [23]. The LODs of diphenylamine and ethyl centralite in IMS were necessary to determine if the mass extracted from the headspace was sufficient for detection.

2. Experimental

2.1. Chemicals

Standards of the three of the additives studied, DPA, ethyl centralite and 2,4-DNT were obtained from Aldrich Chemical (Milwaukee, WI). 2-Ethyl-1-hexanol was obtained from Acros organics (Morris Plains, NJ). Five different types of powders were randomly chosen to represent the variety of powders available in the market. These five powders Alliant Unique, Alliant Red dot, Hodgdon H 322, Hodgdon BL C-2 and IMR 4198 were purchased from a commercial supplier.
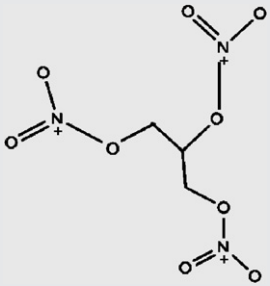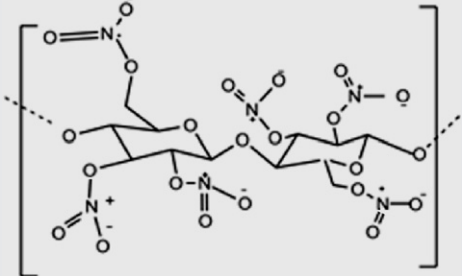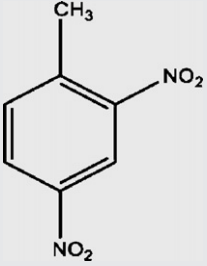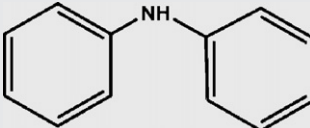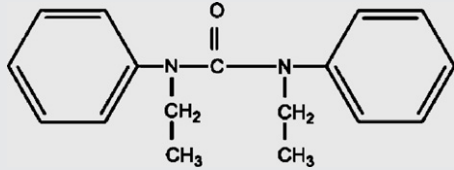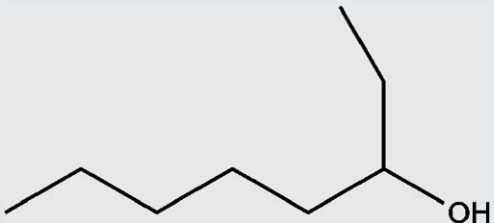
2.2. Instrumentation

A General Electric Ion Track (Wilmington, MA) Itemiser 2 Ion Mobility Spectrometer and a Smiths Detection IonScan (Mississauga, ON, Canada) 400B Ion Mobility Spectrometer were used to detect the compounds of interest. The GE Itemiser 2 front end was coupled with a SPME interface designed in our research group (patent pending) and previously described [2]. The operating parameters of the commercial instrument and the interface are detailed in Table 2. A Varian (Palo Alto, CA) CP 3800 gas chromatograph coupled to a Saturn 2000 ion trap mass spectrometer was used to determine the compounds present in the headspace of the smokeless powders. A MicroFab Technologies (Plano, TX) dispensing device with JetDrive^{TM} III controller was used as the microdrop printing system to determine the LODs of the IMS instruments and to generate the instrumental response curves.

2.3. Determination of headspace components

Solid phase microextraction–gas chromatography–mass spectrometry (SPME–GC–MS) was used to identify the compounds present in the headspace for each of the smokeless powder samples. Smokeless powders samples weighing 100 mg

Table 1
Structures and vapor pressures of volatile components found in smokeless powders.

Compound	Structure	Vapor pressure (Torr at 25 °C)
Nitroglycerin		2.4×10^{-5}
Nitrocellulose		N/A
2,4-Dinitrotoluene		2.1×10^{-4}
Diphenylamine		6.39×10^{-4}
N,N-diethyl diphenyl urea (ethyl centralite, centralite I)		NA
2-Ethyl 1-hexanol		0.136

were placed in 50 mL glass vials manufactured by Fisher Scientific (Pittsburgh, PA); the vials were then sealed and left undisturbed to equilibrate. The headspace components were extracted and pre-concentrated onto a 100 μm polydimethylsiloxane (PDMS) fiber purchased from Supelco (Bellefonte, PA). The portable SPME holders used in this study were purchased from Field Forensics (St. Petersburg, FL). Equilibrium curves for the samples were obtained by sampling the headspace at different time intervals with the SPME fibers described above and then desorbing the fibers into the GC inlet. A GC–MS method that is suitable to detect the entire range of target compounds was developed and described below. A Varian WCOT 50 m × 0.25 mm ID CP Sil-8 GC column was used for the analysis. The GC injector temperature was kept at 280 °C ensuring complete desorption of all analytes from the SPME fiber. Splitless injection mode was used and the method run time was

Table 2
Detection parameters of smokeless powder odor signatures on a commercial IMS instrument.

Analyte	Operating mode	Mobility value (Ko)[a] (cm²/V s)	IonScan 400B		Limit of detection[b]
			Reactant gas	Drift time (ms)	
Diphenylamine	Positive	1.606	Nicotinamide	14.38	0.12 ng
Ethyl centralite	Positive	1.242	Nicotinamide	11.14	1.2 ng
2,4-Dinitrotoluene	Negative	1.566	Hexacholorethane	11.86	NA[c]

[a] Determined from analyzing standards on IonScan 400B.
[b] Values obtained on Itemiser II IMS and used for SPME–IMS studies.
[c] Value not obtained. Details given in Section 3.

18.33 min with the column oven temperatures beginning at 45 °C and going up to 300 °C. The temperature ramp was set at 20 °C/min at the lower temperatures, 15 °C/min at 200 °C, 10 °C/min at 250 °C and was increased to 50 °C/min at 300 °C where the temperature was held for 1.5 min. The mass spectrometer used an ion trap analyzer operating at 180 °C using electron impact (EI) ionization scanning from mass 40 to 400 *m/z*. The specific additives of the powders found to be in significant amounts in the headspace for the smokeless powders and those previously studied in canine trials were determined to be the volatile chemicals markers.
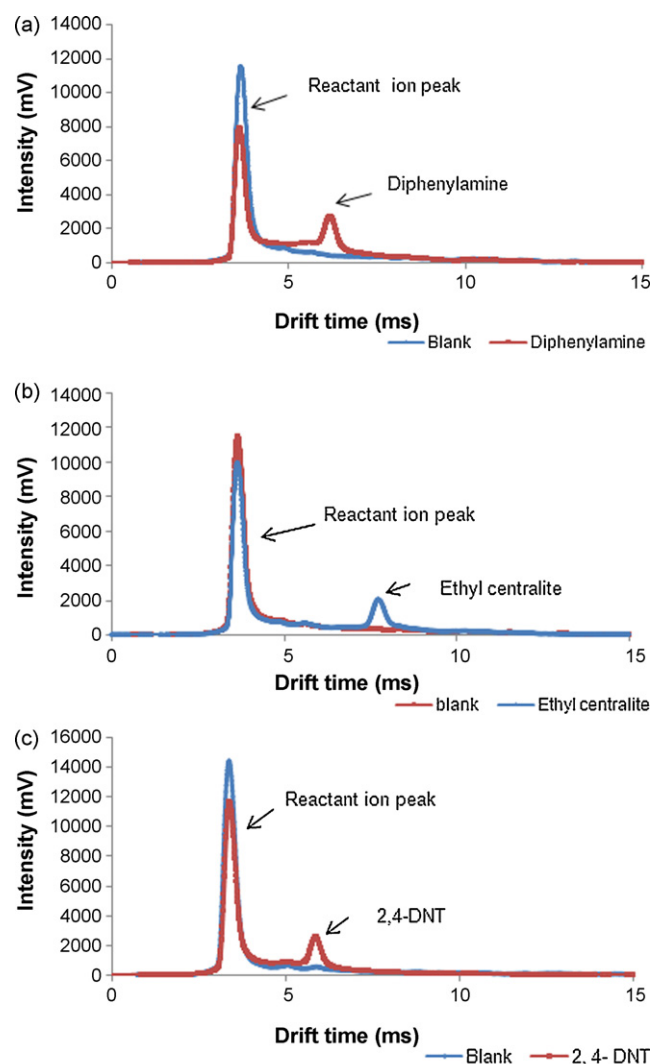
2.4. SPME–IMS studies

Standard solutions containing 50 ppm of the target compounds DPA, ethyl centralite, 2,4-DNT and 2-ethyl hexanol were spiked onto filter paper and the IMS peaks observed were confirmed for the given detection mode (positive or negative). The standard solutions were analyzed in two different IMS instruments and the mobility values of the peaks were compared to previously reported values [15]. The resulting plasmagrams for the compounds are shown in Fig. 1. The mobility values were calculated on the Smiths 400B instrument and are shown with the detection mode in Table 2. Once the location of the peaks were identified by solutions of the standards and SPME extraction of the standards, the extractions of known amount of the smokeless powder samples were carried out similarly to the GC studies described above. The SPME PDMS fiber containing the extracted analytes was introduced into the IMS interface for analysis. The SPME–IMS operating parameters are listed in Table 3. Response curves for each of the smokeless powders were generated by plotting the analyte signal versus the mass extracted.

2.5. Mass extracted by the fibers

A series of standard solutions of each of the headspace components were prepared in acetonitrile and the solutions were injected into the GC–MS using a 20:1 split at the injector. The GC–MS temperature program used for the liquid standards was similar to the one used for SPME analysis. 2,4,6-TNT (2,4,6-trinitrotoluene) was used as an internal standard for all liquid sample analyses. Calibration graphs were generated by plotting the mass injected versus peak area for each of the analytes under investigation. The straight line equation obtained for this graph was used to re-plot the SPME–GC–MS graphs obtained from the different powders. The signal intensity for each of the extraction times was used in the equation to calculate the mass extracted. The graphs were then re-plotted as time of extraction versus the mass extracted.

For the IMS studies, similar calibration graphs were generated by using the microdrop printing technique. The SPME–IMS equilibrium curves obtained for each of the powders are re-plotted as response curves (time of extraction versus mass extracted) using the linear regression equation obtained from the calibration curves. These calibration graphs are also used to determine the limits of detection of the instruments used in this study. For IMS instruments, the LOD is different from the alert level. The mass at which the instrument alerts to the presence of the analyte is a user dependent value and therefore could be much higher than the actual limits of detection for a particular analyte.

The microdrop printing technique was used to precisely deliver known amounts of mass of the analyte onto a substrate suitable for thermal desorption into the IMS instrument. Solutions of the analytes were prepared in 2-butanol and the jetting parameters were adjusted such that a monodispersed drop(s) was generated with each trigger. The volume of the drop generated at the optimal parameters was determined by calculating the drop diameter. Varying the number of drops printed varies the mass of the analyte delivered. Therefore, known number of drops are printed onto the substrate and analyzed to generate a linear calibration graph. Seven blanks of the substrates were also obtained to determine the background signal to calculate the limit of detection. The lowest mass of the analyte deposited that is equal to three times the standard deviation of the blank signal was determined to be the limit of detection of that analyte on both the GE IonTrack Itemiser 2 and Smiths Ionscan 400B instrument.

Fig. 1. Plasmagrams of odor chemicals: (a) diphenylamine with ammonia reactant gas, (b) ethyl centralite with ammonia as reactant gas and (c) 2,4-DNT with dichloromethane as reactant gas.

Table 3
SPME–IMS operating parameters.

Detection mode	Negative/positive
Desorber temperature	215 °C
Drift tube temperature	180 °C
Sample flow	1000 mL/min
Detector flow	200 mL/min
Reagent gas in negative mode	Dichloromethane
Reagent gas in positive mode	Ammonia
Interface temperature	260 °C

Table 4
Compounds found in the headspace of the five powder samples by SPME–GC–MS studies.

Name of powder/component	Hodgdon BL-C(2)	Hodgdon H 322	IMR 4198	Alliant unique	Alliant red dot
1-Hexanol, 2-ethyl	✔				
Diphenylamine	✔	✔	✔	✔	✔
Ethyl centralite					✔
2,4-DNT		✔	✔		

3. Results and discussion

The results obtained from SPME–GC–MS analyses were used to identify the various volatile compounds extracted by the fibers from the powders used in this study. Most of the compounds found in the headspace were the additives of the smokeless powders that vary between manufacturers. The compounds of interest found in the various smokeless powder samples are listed in Table 4. Diphenylamine was found to be the most common volatile odor chemical in all the powders tested. Nitrated derivatives of diphenylamine such as dinitrophenylamine were also found in the headspace of some powders. These derivates have been reported as degradation products of diphenylamine and 2,4-DNT and therefore have not been included in this study [24]. Their quantities have been reported to vary with storage conditions and age of the powders [24,25]. No significant breakdown products of ethyl centralite have been reported in the literature. 2,4-dinitrotoluene was found in large amounts in the headspace of the two single-based powders tested (IMR 4198 and Hodgdon 322). Ethyl centralite was present in the red dot powder. 2-Ethyl 1-hexanol, which is a common additive in plastic bonded explosives, was present in the double-based powder Hodgdon BL C-(2). The two Alliant powders used in this study, red dot and unique, had compounds such as toluene and guanidine in large quantities in the headspace. These compounds are used in several other applications and therefore not emphasized in this study [26,27]. 2-Ethyl hexanol is also used in several industrial applications but was considered important for this study since previous studies have reported that this is an active odor chemical for canine detection [4].

Extraction profiles of the four compounds of interest, diphenylamine, ethyl centralite, 2-ethyl hexanol and 2,4-dinitrotoluene from the different powders are obtained by SPME–GC–MS experiments. The mass of each of the above compounds extracted by the fibers was obtained by the GC–MS calibration graphs. The mass of the DPA extracted from headspace of 100 mg of the five powders tested in this study ranged from 0.15 to 6 ng. This mass was not extracted at equilibrium, typically between 5 and 120 min extractions. Pre-equilibrium extractions were carried out to simulate practical operational conditions for trace explosives detection at checkpoints. The mass range of 2,4-DNT for the IMR 4198 and H322 powders ranged from 0.72 to 41 ng for the typical 5–120 min extraction. For the red dot powder, up to 3 ng of ethyl centralite was extracted onto the fibers in 30 min. Up to 1.5 ng of 2-ethyl hexanol was extracted in 5 min onto a fiber from the BL C(2) powder.

Based on the information obtained by the SPME–GC–MS studies, the different powders were subjected to SPME–IMS analysis to detect the peaks of interest. Diphenylamine was the major peak detected in the positive mode for all powders, including the red dot powder. The peak for ethyl centralite was also present but it was significantly lower than the expected intensity. For the BL C(2) powder, 2-ethyl hexanol was not detected and only the diphenylamine peak was observed though the SPME–GC–MS results show that both diphenylamine and ethyl hexanol are extracted from the headspace of the powder by the SPME fibers. Using nicotinamide as the dopant helped in the detection of ethyl centralite at higher intensities for the red dot powder as compared to when ammonia was used as the dopant. The extraction profile for the red dot powder with nicotinamide is shown in Fig. 2. The extraction profiles of the standards of the diphenylamine and ethyl centralite are shown in Fig. 3. A summary of the compounds detected from the headspace of each of the smokeless powders is reported in Table 4.

The mass of compounds present on the fibers that was detected by the IMS was determined from the calibration graphs of IMS. These calibration graphs generated by microdrop printing are shown in Fig. 4. The mass of diphenylamine extracted from the different powders ranged between 3 and 16 ng and is shown in Fig. 5. This mass is much higher than the limit of detection for the Itemiser IMS, which was determined to be 0.12 ng by using the microdrop printed calibration graph. The mass of ethyl centralite detected from the headspace of the red dot powder was below the alarm alert level of the instrument and was not able to be quantified. The detection limit for ethyl centralite on the Itemiser IMS was determined to be 1.2 ng. The presence of two peaks in the positive mode adds more significance to the analyses.

The results from the SPME–GC–MS studies for the IMR 4198 and H 322 powders showed that a significant mass of 2,4-DNT was extracted by the fibers from the headspace of the powders. However, the peak for 2,4-DNT in the IMS was significantly lower in intensity and no quantitation was possible. It was found from
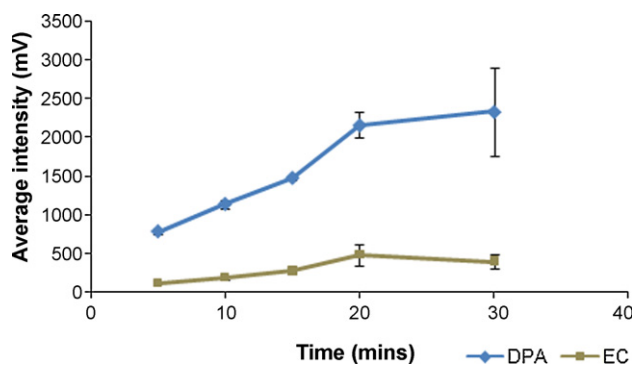

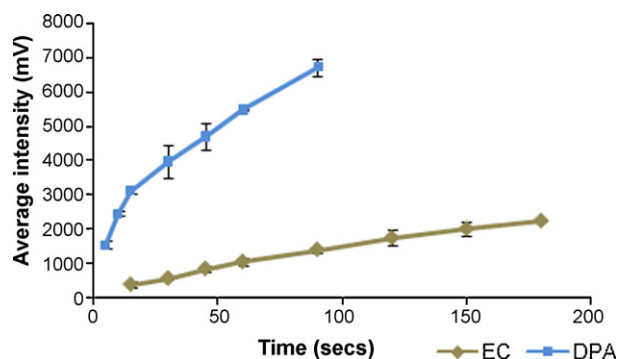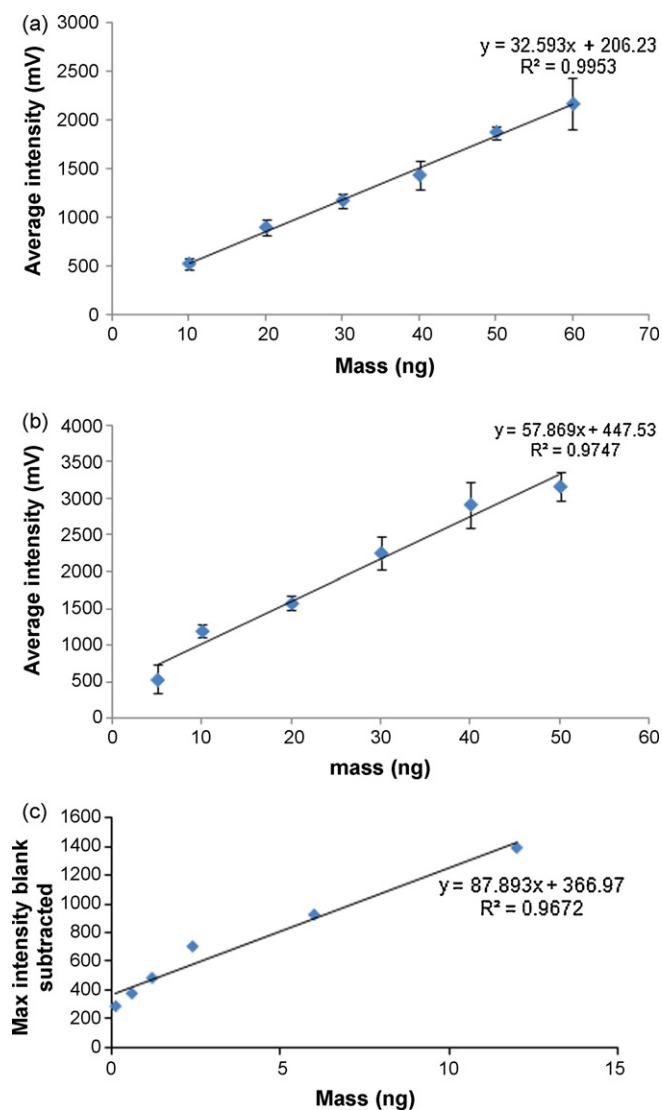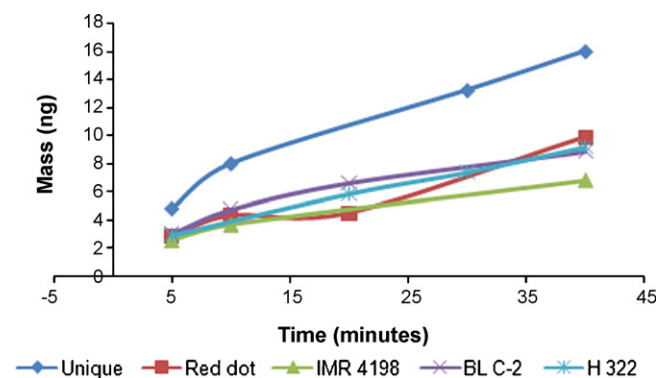**Fig. 2.** Extraction profile of red dot powder with nicotinamide as reactant gas.

Fig. 3. Extraction profiles of standards of diphenylamine, ethyl centralite with nicotinamide reactant gas.

Fig. 4. Calibration graphs for diphenylamine and ethyl centralite on Itemiser II IMS: (a) calibration graph of ethyl centralite with nicotinamide as reactant gas, (b) calibration graph of diphenylamine with nicotinamide as reactant gas and (c) calibration graph of diphenylamine with ammonia as reactant gas.

the liquid spike studies that 2,4-DNT desorbed very slowly from surfaces for both IMS instruments used in this study. This is a possible reason for the low intensities observed for the SPME–IMS studies. The addition of a flow of helium gas (1 mL/min) to the

Fig. 5. Response curves of diphenylamine from different powders—ammonia as reactant gas.

sample injection port of the SPME–IMS interface also did not appear to improve desorption. From various liquid spike experiments conducted of standard 2,4-DNT solutions, it was observed that the detection of the compound was concentration dependent. The product ion for the peak of 2,4-DNT was formed at low mass loadings of 2,4-DNT and as the mass of 2,4-DNT analyzed increased (above 20 ng), a second peak was observed to be forming with a decrease in the first ion intensity. The product ion formed for 2,4-DNT at the conditions used in the IMS has been reported to be the $(M–H)^-$ ion [13]. By observing the baseline of the plasmagram and the locations of the peaks, one can conclude that there is a conversion of the ions in the drift tube to a secondary form. The peak for the second ion was similar to the peak obtained for 2,4,6-TNT. Spangler and Lawless observed this same phenomenon, and demonstrated that the second peak for 2,4-DNT observed at high concentrations and the peak for 2,4,6-TNT were due to the presence of different ions. They also speculated that this peak may be due to the formation of a dinitrobenzyl anion at high concentrations of 2,4-DNT [28]. However, since the peak is at the same position as the TNT peak, which is another explosive, it may cause some confusion in the detection of 2,4-DNT. The mass extracted by the fibers as observed from the SPME–GC–MS studies is much higher than 20 ng for both the IMR 4198 and H 322 powders. It is anticipated that with greater surface area of desorption and longer IMS sampling times, complete desorption of the 2,4-DNT from the SPME phase can occur [29]. In such a case, the 2,4-DNT may be detected at very low extraction times.

4. Summary and significance

The chemical characterization of odor signature compounds sampled from illicit substances by trace particle detectors expands the range of compounds detected by these instruments and increases the number of parameters that can be used to detect the presence of an explosive. In this study, we have shown that smokeless powders can be detected using an IMS through their odor chemicals. We have also shown that the limits of detection of commercial IMS instruments for these odor chemicals are very low and that there is sufficient mass present in the headspace of the powders for extraction by a SPME fiber. This study used small amounts (100 mg) of smokeless powders to extract the headspace, however, most IEDs contain larger amounts of smokeless powders and therefore there would be higher mass of the odor chemicals available for extraction and detection. An unknown material, or hidden explosive can be presumptively identified by the detection of either diphenylamine or ethyl centralite in the positive mode and 2,4-DNT in the negative mode. The instrument used in this study was limited by the ability to detect only in one mode at a time; however, dual mode detection instruments are currently commercially available and would add more information. The detection of diphenylamine, by itself, does not confirm the presence of low explosives due to its widespread use [30]. The presence of ethyl centralite along with diphenylamine adds more significance to the detection of smokeless powders. More studies are now being conducted in our lab to improve the efficiency of the extraction phase. This would improve the extraction of all four odor signature compounds simultaneously from the trace amounts present in the headspace and thereby increase the sensitivity. Of the four odor compounds important to this study, 2-ethyl hexanol and 2,4-DNT were found to be active odor chemicals for canines whereas diphenylamine and ethyl centralite were not of interest to canines. Therefore, the results presented in this paper complement canine detection by detecting these odors by instrumental techniques. The SPME–IMS technique can potentially change the way pre-blast samples of smokeless powders and other low explosive devices are detected. There is currently a large number of

IMS instruments deployed to detect trace illicit substances and with the use of SPME–IMS technique, a number of volatile chemical markers can also be included in the detection scheme to improve the detection of explosives and devices containing explosives.

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