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# Analysis of the headspace composition of smokeless powders using GC–MS, GC– $\mu$ ECD and ion mobility spectrometry

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### ARTICLE INFO

#### Article history:

Received 24 June 2010

Received in revised form 13 October 2010

Accepted 19 October 2010

Available online xxx

#### Keywords:

Smokeless powders

Solid phase microextraction (SPME)

Ion mobility spectrometer (IMS)

Gas chromatography–mass spectrometry (GC–MS)

### ABSTRACT

Smokeless powder additives are usually detected from an extraction of post-blast residues or unburned powder particles followed by chromatographic analyses. This work presents the first comprehensive study of the detection of volatile and semi-volatile additives of smokeless powders using solid phase microextraction (SPME) as a sampling and pre-concentration technique. The goal of this study is to generate a list of compounds that can be used as target compounds for the vapor phase detection of smokeless powders. Sixty-five smokeless powders were studied using laboratory-based gas chromatography techniques and a field deployable ion mobility spectrometer (IMS). The detection of diphenylamine, ethyl and methyl centralite, 2,4-dinitrotoluene, diethyl and dibutyl phthalate by IMS is suggested as a method to indicate the presence of smokeless powders. A previously reported SPME–IMS analytical approach facilitates rapid sub-nanogram detection of the vapor phase components of smokeless powders. The analyte mass present in the vapor phase was sufficient for a SPME fiber to extract and concentrate most analytes at amounts above the detection limits of both the GC and the IMS methods. Analysis of 65 different smokeless powder samples revealed that diphenylamine was present in the headspace of 96% of the powders studied. Ethyl centralite was detected in 47% of the powders and 8% of the powders contained methyl centralite. Nitroglycerin was the dominant peak present in the headspace of the double-based powders. Another important headspace component, 2,4-dinitrotoluene, was detected in 44% of the powders comprising both double and single-based powders. Static headspace SPME of small amounts ( $\sim 100$  mg) of smokeless powder samples for  $\sim 5$  min at room temperature resulted in the successful detection of the headspace components, demonstrating the applicability of the technique for field detection of smokeless powders using IMS as a detector.

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## 1. Introduction

Smokeless powders are low explosives that are used widely in the ammunition industry. Approximately 10 million pounds of smokeless powders are produced every year in the United States and are mostly used in the manufacture of ammunition domestically or exported to international companies for making ammunition or for foreign military use [1]. A large portion of the manufactured powder is sold in containers as reloading powders. This easily available source of explosives has been used in the making of improvised explosive devices (IEDs) [2]. The pre-blast detection of bulk smokeless powders is therefore of great interest in order to prevent destructive events.

The energetic materials used in smokeless powders have not changed over many years and most powders use either nitrocellulose, nitroglycerine or nitroguanidine to provide explosive properties of the powders [3]. Depending on the combination of

the energetic components used, the smokeless powders can be classified single-based (nitrocellulose containing), double-based (nitrocellulose and nitroglycerin containing) or triple-based (all three energetics nitrocellulose, nitroglycerin and nitroguanidine). Apart from the energetic materials, the manufacturers use several other additives to control the burn rate and flash characteristics. Based on the type of smokeless powder being produced and the manufacturing process involved, the additives are incorporated at different stages of the manufacture. The different classes of additives include stabilizers, plasticizers, energetic materials, opacifiers, deterrents, flash suppressants and dyes. Several additives serve multiple purposes and therefore are added in combinations specific to the properties of the marketed powder [1,4]. Compounds such as diphenylamine and the centralites (ethyl and methyl) are added to increase the shelf life of the product by preventing the buildup of nitrous and nitric oxides formed by the decomposition of nitrocellulose and nitroglycerine (NG). Plasticizers help in making the nitrocellulose pliable and improve the gelatinizing properties and hygroscopic properties. Ethyl centralite (EC), phthalates such as dibutyl phthalate (DBP) and 2,4-dinitrotoluene (2,4-DNT) are the most commonly used plasticizers.

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Flash suppressants, deterrents and dyes are usually added as surface coatings to the smokeless powder particles. Several of these smokeless powder additives have vapor pressures that are sufficiently high for them to be emanating from a smokeless powder source as volatiles and semi-volatiles. Also of interest are the derivatives of additives such as diphenylamine (DPA) that are formed as the smokeless powder energetic materials degrade. Derivatives such as N-nitrosodiphenylamine (N-NODPA), 2-nitrodiphenylamine (2-NDPA) and 4-nitrodiphenylamine (4-NDPA) are of particular importance and are addressed in this paper.

The widespread availability of smokeless powders and the myriad number of such commercial products currently available make the analysis and detection of smokeless powders a formidable task. Several approaches have been taken by researchers worldwide for the detection of smokeless powders in pre-blast and post-blast scenarios [2,5]. Since the introduction of smokeless powders, researchers have been studying the organic components of smokeless powders using various analytical techniques. Of the chromatographic techniques, gas chromatography and liquid chromatography are the most widely used analytical separation techniques. Gas chromatography (GC) coupled to detectors like mass spectrometry, electron capture detector (ECD) and thermal energy analyzer (TEA) has been used widely for the detection of explosives [6]. However, several smokeless powder additives are thermally labile making them highly unstable in the GC–MS. Some compounds do not survive the injector temperature of the GC–MS. In the analysis of smokeless powders, components such as nitroglycerin, nitroso derivatives of diphenylamine have low thermal stabilities making their detection by GC–MS challenging [6–8]. Most of the techniques currently in use are destructive techniques and require extensive sample preparation [9–11]. These techniques do not allow for identification of questioned powders as smokeless powders or provide information that a postblast residue is that of smokeless powders on the field. However, they are excellent tools for the characterization of smokeless powders and provide valuable information that can be used for field portable techniques.

Rapid field portable analytical techniques that are capable of unambiguous detection of low explosives are currently lacking. In the field, detection of hidden explosive devices is generally achieved using canine scent detection. Previous work has shown that canines use the volatile chemicals emanating from the illicit substances as scent compounds to track and detect them. Harper et al. combined SPME–GC–MS and canine trials and reported a list of compounds that are of interest in canine scent [11,12]. This study describes the pre-blast chemical detection of smokeless powders through vapor phase sampling using solid phase microextraction (SPME) where sampling and pre-concentration occurs in a single step. The chromatographic analytical methods GC–MS and GC– $\mu$ ECD were used as confirmatory techniques prior to IMS analysis of the powders. Ion mobility spectrometry (IMS) is a field portable analytical technique that has commonly been used for the detection of explosives, mostly from particles collected on swipes. Smokeless powders have previously been detected by IMS through the nitroglycerin component present in the double-based powders by the swipe method [13,14]. However, the swiping of smokeless powders primarily results in large nitro ( $\text{NO}_2^-$ ) peaks and several other interferences from the surface. The indication of the presence of the nitrates in the residue on the surface may indicate the presence of smokeless powders but does not exclude any number of nitrate sources that could be detected due to environmental cross-contamination. The swipe method is also not applicable when a concealed smokeless powder device is present and no residues are available. The use of SPME is therefore an attractive alternative to the sampling of concealed smokeless powders when the various smokeless powder additives are present

in the vapor phase. Preliminary studies describing the use of SPME coupled to IMS for the detection of volatile components were recently reported by Joshi et al. [15]. The paper described the results from the study of five smokeless powders and demonstrated the successful detection of the additives diphenylamine, ethyl centralite and 2,4-dinitrotoluene using a SPME followed by IMS detection.

This paper is the first report of an expansive study of the headspace composition of smokeless powders. The results described below are based on the information gathered from the study of 65 smokeless powders. The current detection menu of the IMS instruments includes only the nitro ( $\text{NO}_2^-$ ) peak as an alarm for smokeless powders. Nitroglycerin can produce several product ions but the characteristic peak is the nitrate peak at the temperatures used for the explosives mode of commercial IMS instruments. This peak is non-specific to smokeless powders and is prone to interferences from inorganic nitrate sources and other environmental sources. The use of additional target compounds, as reported here, allows for a better detection strategy when using IMS instruments as field detection tools for the presence of smokeless powders.

## 2. Materials and methods

### 2.1. Sample set

The smokeless powder samples were provided by a law enforcement laboratory as part of a larger study of the bulk composition of the smokeless powders. Sixty-five different samples spanning about 25 years of manufacture and representing 8 powder distributors from around the world were included in the sample set. Table 1 lists the powders by the brand name that were part of the sample set and the percentage of double and single based powders represented by each brand. The powders included in the sample set do not include all the powders of a certain brand name and each brand name has more powders available in the market. Therefore, the list is not all inclusive but represents a wide variety of powders from each brand. It is important to note that both the Alliant and Hercules brand names and the Dupont and IMR brand names are from the same distributor. Also provided by the contributor was the bulk composition of the smokeless powders based on the detection of the organic additives by solvent extraction of the powders followed by GC–MS analysis.

### 2.2. Instrumentation

Gas chromatography–mass spectrometry (GC–MS) and GC–micro electron capture detector (GC– $\mu$ -ECD) were used as confirmatory techniques for the presence of the volatile and semi-volatile compounds in the headspace when sampled by SPME. A Varian (Palo Alto, CA) CP 3800 gas chromatograph coupled to a Saturn 2000 ion trap MS was used for the detection of all the additives for smokeless powders except nitroglycerin, which was analyzed using an Agilent (Santa Clara, CA) 6890N GC with a  $\mu$ -ECD detector. A General Electric Ion Track Itemiser II IMS (Wilmington, MA) equipped with the previously reported SPME–IMS interface (patent-pending) [16] was used in this study to determine the profiles of smokeless powders by SPME–IMS analyses. The 100  $\mu\text{m}$  polydimethylsiloxane (PDMS) SPME fibers purchased from Supelco (Bellefonte, PA, USA) and fitted into portable SPME holders purchased from Field Forensics (St. Petersburg, FL, USA) were used for all extraction studies.

**Table 1**  
Smokeless powder sample set showing the number of powders per brand and the distribution of double and single-based powders in each brand.

Manufacturer	Number of powders	Double based/single based
Alliant	15	100% double-based
Hodgdon	22	64% single-based
Accurate	7	43% single-based
IMR	6	83% single-based
Vihta Vuori	3	100% single-based
Winchester	3	100% double-based
Hercules	2	100% double-based
Norma	3	33% single-based
Dupont	3	66% single-based
Scot Royal Scot	1	Double-based

### 2.3. GC–MS method

A 50 m DB-5 column with 0.25 mm ID and 1  $\mu\text{m}$  film thickness was temperature programmed from 40 °C to 280 °C beginning with a 1 min hold at 40 °C and then increasing the temperature to 200 °C at 15 °C  $\text{min}^{-1}$  with a 1 min hold at 200 °C. The temperature was then increased to 240 °C at 15 °C  $\text{min}^{-1}$  and held for 6.50 min at that temperature. From 240 °C the temperature was increased at 25 °C  $\text{min}^{-1}$  to 270 °C. The final temperature of 280 °C was reached by ramping the temperature at 5 °C  $\text{min}^{-1}$  and holding there for 4 min. The injector temperature was set at 280 °C in split mode (split ratio 5:1) with a column flow of 2 mL  $\text{min}^{-1}$ . The transferline to the ion trap was set to 280 °C and the ion trap was maintained at 180 °C. Each compound of interest was studied individually using solutions made of their pure standards and identifying the resulting peak using the NIST mass spectral library. The method length of 29.3 min and the analysis method was optimized by analyzing a solution containing a mixture of all the compounds of interest. The final method chosen was the one that could resolve and produce the highest sensitivity at those conditions for a majority of the compounds of interest. Nitroglycerine (NG) could not be incorporated into the same method because of the high temperatures that were required for the other compounds and therefore a GC- $\mu$ -ECD was used to obtain sensitive detection of NG. A programmed temperature vaporizing (PTV) injector would be useful in improving the detection of the thermally labile compounds nitroglycerin and N-nitrosodiphenylamine.

### 2.4. IMS method

The Itemiser II IMS was set to temperature conditions that were optimal for both positive and negative mode detection. The heated desorber inlet was set to 250 °C and a drift tube temperature of 180 °C was used for both modes. The sample and detector flow were adjusted to 1000 mL  $\text{min}^{-1}$  and 200 mL  $\text{min}^{-1}$ . Ammonia in the positive mode and dichloromethane in the negative mode were used as dopants for the IMS reactant ion peak. The SPME–IMS interface was set at 280 °C which is the same temperature as the GC–MS injector to maintain consistency between the desorption temperatures for the fiber.

Each analyte of interest was studied in the positive and the negative mode to determine the mode that produces a well-defined product ion peak that is consistent at various concentrations. Inkjet microdroplet printing has been shown by other studies to be a superior method of determining accurate limits of detection and the methods have been described elsewhere [15,17]. The detection limits for each analyte in this study therefore were determined using microdroplet printing. The same SPME conditions as used for GC–MS studies above were used for SPME–IMS studies with desorption performed using the SPME–IMS interface.

### 2.5. Headspace analysis

Static headspace sampling was conducted by placing 100 mg of each powder in 15 mL clear glass vials (Supelco, Bellefonte, PA) with phenolic screw caps and red rubber/PTFE septa. On equilibrating for 24 h, the headspace was sampled for 60 min with a 100  $\mu\text{m}$  PDMS fiber. A 1 h extraction time was chosen since it would provide opportunity for the more volatile analytes to reach equilibrium on the fiber while extracting detectable amounts of the low volatility compounds. The SPME fibers with the extracted analytes were analyzed by the GC–MS and IMS methods described above. The 100  $\mu\text{m}$  PDMS fiber was chosen for this study due to its large extraction phase volume and its suitability for a wide range of compounds. Studies have also shown that the PDMS fiber may provide faster extraction rates than other fiber chemistries such as PDMS/DVB fibers [11]. Further studies of SPME phase chemistries that can lead to faster and more efficient extraction are necessary.

Reproducibility in the headspace extractions was determined by conducting two individual studies. In the first study, using the SPME–GC–MS technique described above, two powders were examined by conducting simultaneous extractions of the same amount of powder in three vials using three PDMS fibers. In order to study variation in the headspace of the powders between different days, a second study was conducted where five randomly chosen smokeless powders were sampled for 60 min every two days for a period of ten days.

Field screening of illicit substances such as drugs of abuse and explosives requires that the sampling time be as short as practically possible. Studies were conducted to demonstrate the variations in the headspace profiles of powders when different sampling times are used and to determine the optimal sampling time for field detection. Six powders were chosen and each powder sampled in a sealed static system with a PDMS fiber at six extraction times: 1, 5, 15, 30, 45, 60 min, and analyzed in triplicate by both GC–MS and IMS techniques. The mass extracted from the headspace of each additive at different extraction times was determined by using response graphs generated by the previously reported inkjet printing techniques [15].

## 3. Results and discussion

### 3.1. Overall distribution of volatile additives in smokeless powders

Headspace profiles were generated for all sixty-five (65) powders in the sample set by the SPME–GC–MS method described.

Due to the multiple peaks observed, the peaks are categorized into the following ten groups to ease data presentation – diphenylamine (DPA), ethyl centralite (EC), 2,4-dinitrotoluene (2,4-DNT), the phthalate group diethyl phthalate (DEP) and dibutyl phthalate (DBP), 2-nitrodiphenylamine (2-NDPA), 4-nitrodiphenylamine (4-NDPA), nitrotoluenes (2,3-DNT, 2,5-DNT, 2,6-DNT, mononitrotoluenes and 2,4,6-trinitrotoluene), methyl centralite (MC), ethylphenylamine (EPA) and miscellaneous analytes (butyl benzoate, diphenyl sulfone, diphenyl formamide and ethyl hexanol). Of the 65 powders studied, 62 powders showed the distinct presence of DPA in their headspace. EPA was observed in the headspace of one of the powders with no DPA and could be a degradation product. The diphenylamine derivatives, 2-NDPA and 4-NDPA are sometime added to powders as stabilizers but are also degradation products. These products were generally present in very small amounts in powders with diphenylamine. 2-NDPA was more common than 4-NDPA which was observed only in the presence of 2-NDPA. Of all the powders tested, the Alliant brand of powders had the highest amounts of 2 and 4-NDPA. Of the two centralites, EC was more common and usually observed in combination with DPA. 2,4-DNT when present was extracted in large amounts from the headspace of the powders. Forty five percent of the powders showed evidence of 2,4-DNT in the headspace and these powders were comprised of both double and single-based powders. In the presence of 2,4-DNT other isomers of 2,4-DNT such as 2,6-DNT, 2,5-DNT and 2,3-DNT and mononitrotoluenes were also observed in small amounts with 2,4-DNT being the dominant peak. 2,4,6-TNT was detected as very small peaks in the headspace of the Norma powders. The phthalates, DBP and DEP were the two phthalates that were most commonly observed. The phthalates are known plasticizers which are used in several manufacturing processes and are also detected from many other sources. Their detection therefore is not specific to smokeless powders but is made significant when detected in combination with other smokeless powder additives. Compounds classified as miscellaneous compounds include compounds that do not have known specific function in smokeless powders. Ethyl hexanol is present in several powders along with other long chain hexanols. These are expected to be artifacts of the manufacture process along with butyl benzoate and other solvents. No literature sources describing their function in smokeless powder were found. In addition, these compounds are used in several other manufacturing processes and were not considered important for this study. Fig. 1 demonstrates the distribution of all the additives across the 65 powders. This graph does not include the NG distribution since the results were not obtained by the same method. The  $\mu$ -ECD results indicate that NG was present and

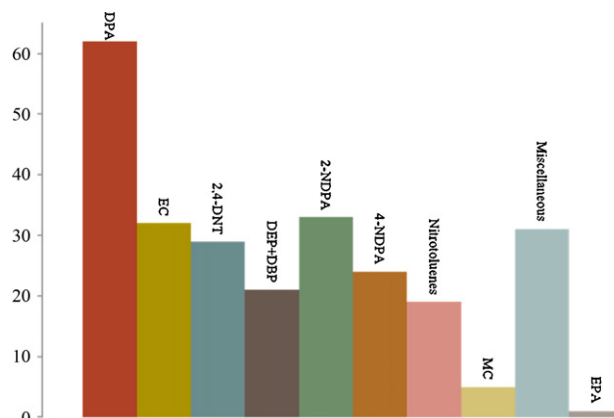


Fig. 1. Overall distribution of additives detected by headspace GC–MS analysis (N = 65 smokeless powders on the y-axis).

readily detectable in the headspace of all the double-based powders in the sample set.

### 3.2. Reproducibility studies

Overall, the reproducibility studies demonstrated that there was consistency in the headspace extractions of the powders. The average peak height of each compound detected in each of the replicates during the SPME was used as indicators of the changes in the composition of the various components of the powders. When sampled with different SPME fibers, the compounds in the headspace did not vary and the precision observed for the peak heights of the major compounds in the headspace was an average relative standard deviation of less than 25%. Therefore, the relative amount of the compounds extracted under the same conditions from three samples of the same powder did not vary with different SPME fibers. The study also indicates homogeneity of the powders since the three samples (100 mg) of the same powder had the same headspace composition as evidenced by the SPME–GC–MS studies.

The results of the second reproducibility study indicate that the headspace profiles of the five powders tested did not change significantly over the period of ten days. The two nitrated diphenylamines of interest had peak height variations that were

greater than the other compounds though this was to be expected due to the constant inter-conversions between DPA, 2-NDPA and 4-NDPA. The variation of all the compounds detected by GC–MS however fall within the method detection limits. This is useful in generating a reliable composition profile for each powder by SPME–GC–MS studies.

### 3.3. IMS studies of smokeless powder additives

The analytes specific to smokeless powders that are present in the headspace were confirmed from the GC–MS and GC– $\mu$ -ECD results. Fig. 2 shows the IMS plasmagrams generated using the pure standards of each of the smokeless powder additives that were of interest to this study. The plasmagrams for DPA, EC and 2,4-DNT which have been reported before are not shown in this figure [15]. The IMS detection mode and the drift times of all the smokeless powder additives detected by SPME–IMS are listed in Table 2. From the table, it is evident that two compounds are detected in negative mode of the IMS, NG and 2,4-DNT, whereas all others are detected in the positive mode.

Prior to this research, the nitro peak for nitroglycerin was the primary peak that was used as an indicator for the presence of

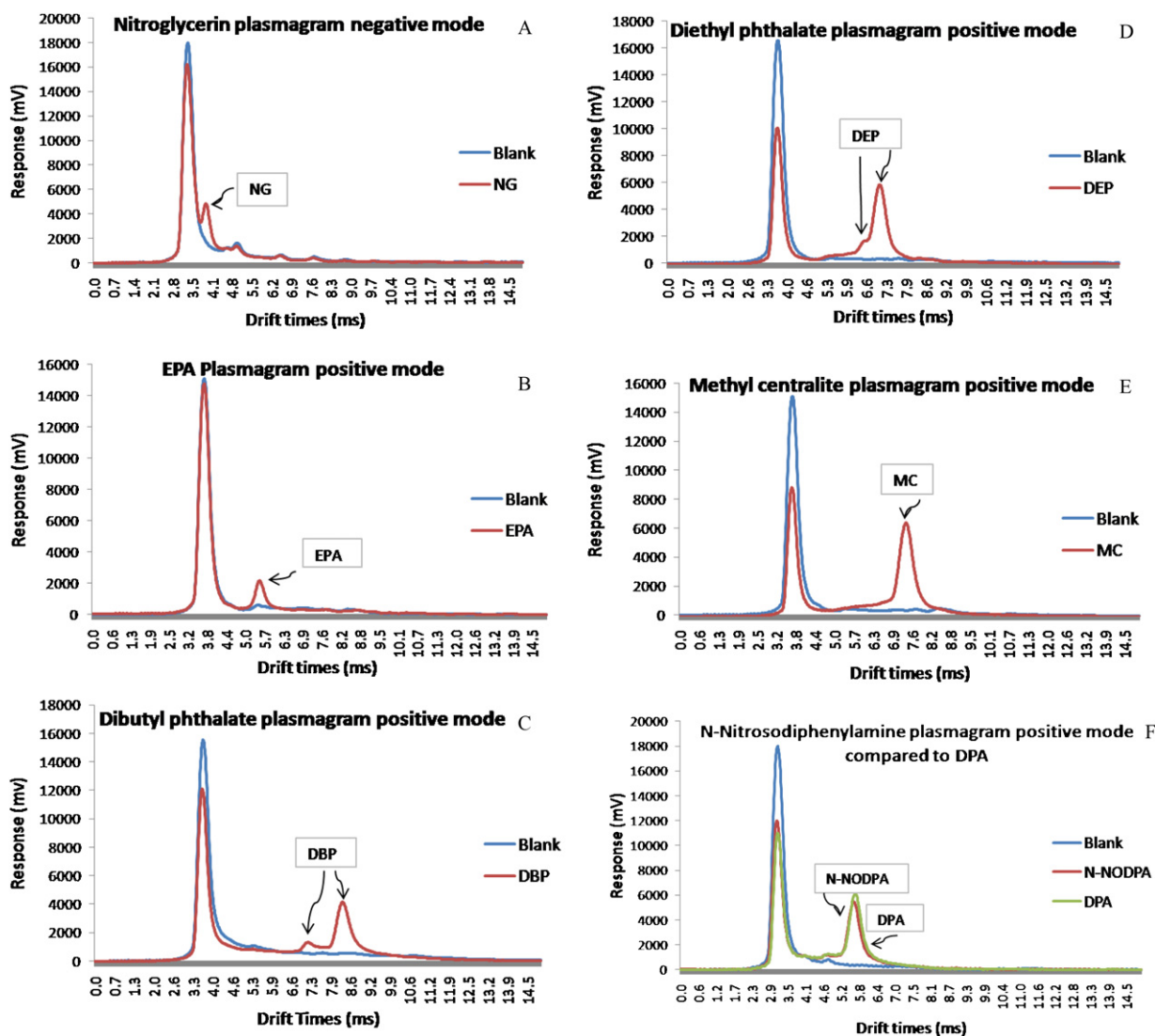


Fig. 2. Itemiser II IMS plasmagrams: (A) nitroglycerin in negative mode, (B) ethylphenylamine in positive mode, (C) dibutyl phthalate in positive mode, (D) diethyl phthalate in positive mode, (E) methyl centralite in positive mode and (F) N-nitrosodiphenylamine in positive mode.

**Table 2**  
IMS detection parameters for the Itemiser II IMS for the different smokeless powder additives.

Compound name	Detection mode	Drift time (ms)
Nitroglycerin	Negative	3.96 ± 0.030
2,4-DNT	Negative	5.83 ± 0.020
Diphenylamine	Positive	6.20 ± 0.050
Ethyl centralite	Positive	7.66 ± 0.030
Ethyl phenylamine	Positive	5.45 ± 0.030
Dibutyl phthalate	Positive	8.32 ± 0.030
		7.19 ± 0.020
Diethyl phthalate	Positive	7.03 ± 0.020
Methyl centralite	Positive	7.37 ± 0.030

smokeless powders. With the additional analytes now studied, there is a spectrum of compounds that in combination serve as indicators of the presence of smokeless powders. From the study of the each of the smokeless powders present in the sample set, it was determined that, IMS analysis of smokeless powders usually results in the detection of two or more additives with at least one being detected in the negative mode. The IMS drift times of each additive as listed in Table 2 indicates that all the peaks are sufficiently resolved from each other such that there are no overlapping peaks.

The ionization of nitroglycerin has been well studied and Ewing et al. summarize that at high temperatures, the NG molecule ionizes and forms a prominent peak for  $\text{NO}_2^-$  [18]. This single peak of  $\text{NO}_2^-$  is very close to the chloride doped reactant ion peak (RIP) in the negative mode. The line is not completely resolved from the RIP and makes quantitation difficult. In the presence of large concentrations of NG a second peak at the same drift time as 2,4,6-trinitrotoluene (2,4,6-TNT) was observed. Since it has the same drift time as 2,4,6-TNT, an alarm for the explosive is produced. This same phenomenon has been reported before with 2,4-DNT [15]. Thus both NG and 2,4-DNT may produce a second false positive alarm for TNT. The analytes that produce a single well-defined peak are diphenylamine, ethyl centralite, methyl centralite and ethylphenylamine. Diethyl phthalate and dibutyl phthalate produce more than one peak. Dibutyl phthalate gave one product ion peak at 8.32 ms which was the major peak seen in the plasmagram. A second peak that was seen at 7.19 ms was sufficiently resolved from the other peak, much smaller and appeared to be concentration dependent. Diethyl phthalate had a much more complex plasmagram. A single peak at 7.03 ms was the major product ion peak formed but the front end of the peak baseline was raised and a shoulder peak produced with a shorter drift time. The peak was also affected by concentration but not as much as the peak at 7.03 ms. Several other peaks were also formed at very high mass spikes of the diethyl phthalate. One of the analytes of interest, N-nitrosodiphenylamine that could not be detected by the gas chromatographic analyses methods employed for this study due to its thermally labile nature was also analyzed by the IMS. This product ion peak for N-nitrosodiphenylamine has the same drift time as DPA and is shown in Fig. 2F. The confirmation of the product ion identity is currently being investigated using mass spectrometry techniques in our laboratory by coupling IMS with MS. This could indicate that in the headspace extractions of smokeless powders, when DPA is detected in IMS, a small portion of the signal is contributed by the N-NODPA but the contribution cannot be quantified. The nitrated derivatives of DPA, 2-nitrodiphenylamine, and 4-nitrodiphenylamine that were detected by the GC-MS had very poor detection limits in the IMS and the peaks characteristic of these compounds could not be produced reliably in the IMS method used. The GC-MS results suggest that the mass present in the headspace of the smokeless powders is below the IMS detection limits under the current

analysis conditions. West et al. have reported the detection of 2-NDPA in the positive mode and 4-NDPA in the negative mode using a different IMS method and solvent extraction of these analytes [19].

### 3.4. Compositional profiles

#### 3.4.1. Compositional profiles by SPME-GC-MS

These profiles are important visual information about the variety and amounts of the components in the headspace and help in determination of those that are most important for detection of smokeless powders. Fig. 3A represents the SPME-GC-MS profiles of the Hodgdon brand smokeless powders that are part of the sample set. The graph is plotted such that each of the nine categories of the compounds of interest is plotted by its peak height observed in a 60 min extraction. The detection limits of each of the compounds as determined by microdrop printing are listed in the legend of the graph. The graph excludes two other peaks of interest, nitroglycerin and the nitrosodiphenylamine both of which were not detected by GC-MS.

The graph also demonstrates that there is an abundance of information available in the smokeless powders headspace. Each powder has more than one volatile component and therefore a bouquet of compounds can be targeted as volatile signatures of smokeless powders. Overall, the major compounds available for the detection of smokeless powders by SPME sampling and using a GC-MS detector were diphenylamine, ethyl and methyl centralite, diethyl and dibutyl phthalate, and 2,4-dinitrotoluene with associated nitrotoluenes.

#### 3.4.2. Compositional profiles by SPME-IMS

Headspace profiles of smokeless powders similar to those generated by GC-MS were generated for the IMS and the Hodgdon IMS profile is shown in Fig. 3B with the limits of detection of each compound listed in the legend. Though the extraction parameters are the same as the SPME-GC-MS studies, it is important to note that the desorption time for the fiber is in the order of a few seconds for the IMS as compared to the 5 min desorption time used for the GC-MS. The analysis also occurs in a few seconds as compared to the 29.33 min method time in the GC-MS. The profiles illustrate the differences between the two analytical techniques for the same extraction parameters of the powders.

The profile shows complete absence of the 2-NDPA and 4-NDPA peaks at the front end of the graph. In the positive mode, the peaks detected were MC, DEP, DBP, DPA and EC. DPA peak is consistent with the GC-MS results and is detected in all the powders. EC was not detected in all of the powders that showed the presence of EC according to the GC-MS results due to competitive ionization. The MC peak was consistent with the GC-MS results and was detected in both the powders that have MC. The phthalates were detected in most of the powders in which they were present except in those where the amounts observed in GC-MS were very low. In the negative mode, the major peak observed was the peak indicative of nitroglycerin. It was detected in all the double-based powders where nitroglycerin is present in the headspace. The powders where 2,4-DNT is dominant in the headspace, do not show evidence of nitroglycerin in the headspace. In cases where there is a large nitro peak, a second peak was observed with the same drift time as 2,4,6-TNT producing a false alarm. This peak was also added to the profile image to demonstrate that in the negative mode, there are three possible alarms for smokeless powders and that the TNT peak for smokeless powders is associated with the presence of a large peak for the nitro group. The analysis of the explosive, 2,4,6-TNT does not produce an alarm for NG. This is important data that also supports the need for the expansion of the detection menu for smokeless powders.

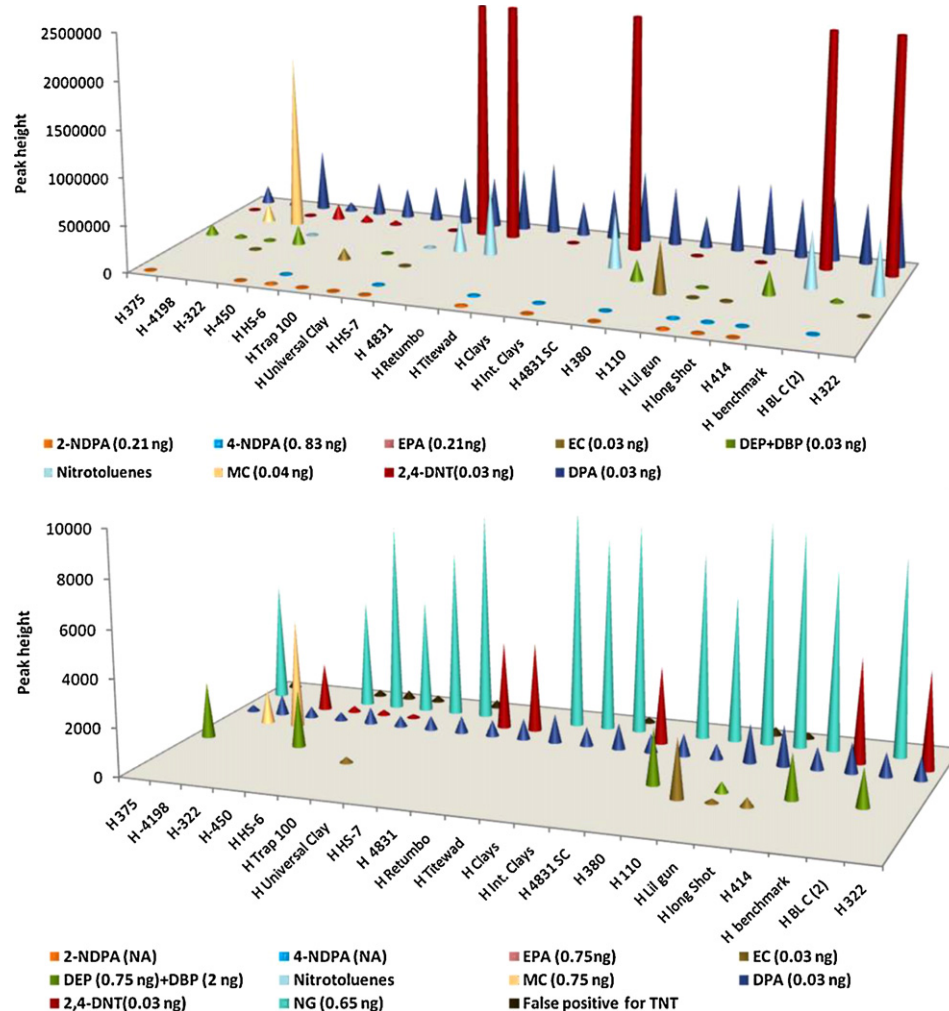


Fig. 3. Composition profiles generated by 60 min SPME depicting the variation in the headspace composition of the various Hodgdon powders studied with the limits of detection of each of the compounds listed in the legend ( $N = 22$ ). (A) SPME-GC-MS profiles and (B) SPME-IMS profiles.

Overall, the IMS profiles demonstrate that in spite of the lack of information regarding the nitrated diphenylamines, there are sufficient peaks to give conclusive detection of smokeless powders through the extraction of headspace volatiles. Most powders show evidence of at least one peak in the positive mode and one in the negative mode and this adds strength to the detection result reducing possible questions of interferences. These headspace profiles however were obtained at a 1 h SPME which is not applicable for field detection, therefore, applicability of the SPME-IMS technique is tested for field purposes by conducting extraction profile studies.

### 3.5. Extraction profiles

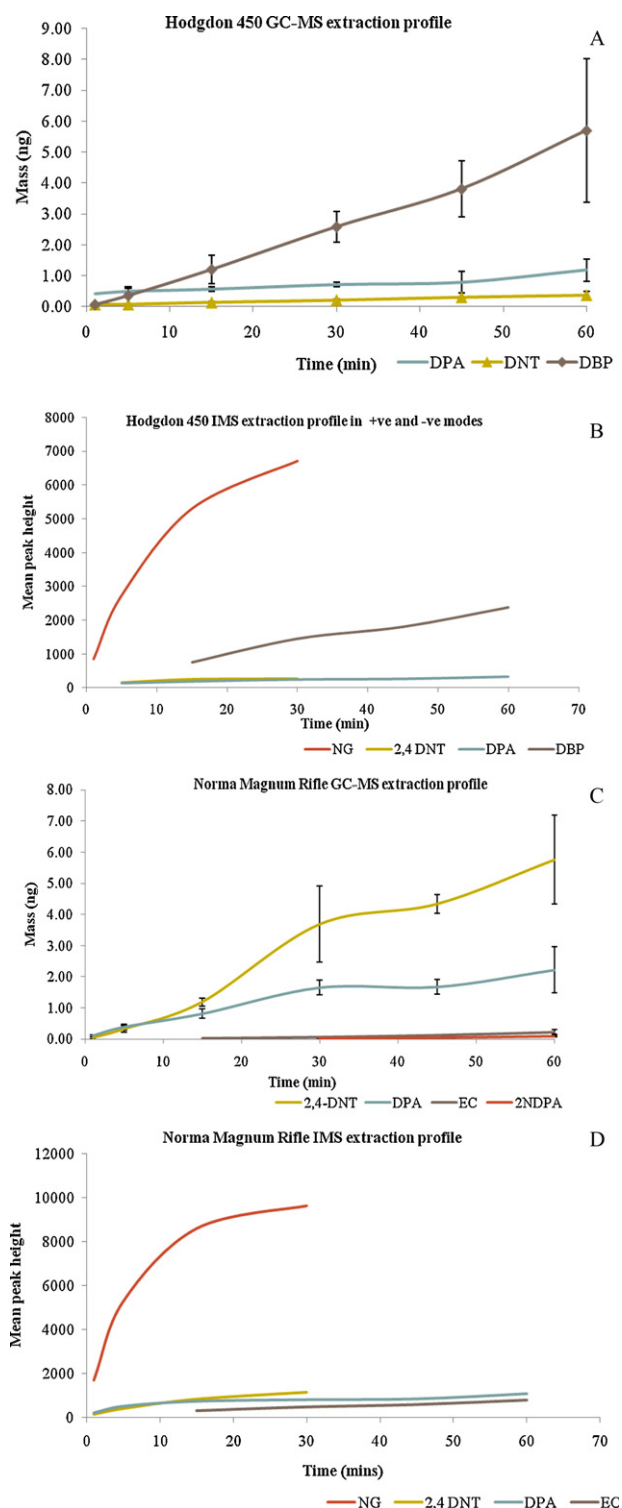
The extraction profiles demonstrate the differences between the detection of the various components in the GC-MS and the IMS and the optimal times needed for different compounds to be extracted in detectable amounts onto the fiber. The results for two of the six powders studied, H 450 and Norma Magnum Rifle are shown in Fig. 4(A)–(D).

For the Hodgdon 450 powder, at the shortest extraction time (1 min), all three major analytes, DPA, 2,4-DNT and DBP were detected. However, the mass extracted was close to the detection limits. DBP was the major contributor to the headspace and the mass extracted varied from 0.07 ng at 1 min to 5.70 ng at a 60 min extraction. At the 60 min extraction time DEP and 2-NDPA were

also detected but the signal was very close to the detection limit and therefore was not plotted on the graph. The negative mode of IMS shows presence of two peaks: NG and 2,4-DNT with the peak for nitroglycerin dominating. The extraction times had to be limited to 30 min for the negative mode since the NG peak depleted the reactant ion peak allowing no further detection of other components. At the 5 min extraction time, the DPA peak was detected in small amounts. It was also expected from the GC-MS results and knowledge of IMS detection limits that the mass of DBP extracted at 15 min would be detected in the IMS and this is evident from the graph.

The major compounds detected in the Norma Magnum Rifle powder in the GC-MS were 2,4-DNT, DPA, EC and 2-NDPA with a very small peak for 4-NDPA being detected at 60 min. DPA and 2,4-DNT were the major contributors to the headspace as detected by the GC-MS and were detected at all extraction times. Based on the GC-MS results the mass of EC extracted at 15 min was above the detection limits of the IMS and therefore, EC was detected at 15 min in the IMS.

Similar conclusions were drawn from the studies conducted on the other four powders. Therefore, these results clearly demonstrate that even at short extraction times (5 min), there are analytes that are extracted in detectable amounts both by the GC-MS and IMS and their detection is indicative of the presence of smokeless powders.



**Fig. 4.** Extraction profiles of smokeless powders: (A) SPME–GC–MS of Hodgdon 450 powder plotted as mass extracted vs. time, (B) Hodgdon 450 powder SPME–IMS profile in both IMS modes (positive and negative), (C) SPME–GC–MS of Norma Magnum Rifle powder plotted as mass extracted vs. time and (D) Norma Magnum Rifle SPME–IMS profile in both IMS modes.

#### 4. Conclusions and significance

There are sufficient analytes present in the headspace of smokeless powders to allow for their detection by ion mobility spectrometry. The volatile chemical components of interest for smokeless powders were determined to be diphenylamine, ethyl

centralite, methyl centralite, diethyl and dibutyl phthalate, 2-nitrodiphenylamine, 4-nitrodiphenylamine, ethylphenylamine, 2,4-dinitrotoluene and nitroglycerin. Overall, this study revealed that of the sixty five powders studied, 96% contained sufficient diphenylamine to be extracted and detected by both GC–MS and IMS. About 47% of the powders contained ethyl centralite with 2,4-DNT being detected in 44% of the powders. Half the powders contained 2-nitrodiphenylamine in their headspace with 37% containing 4-nitrodiphenylamine. Methyl centralite was present as the dominant compound in the vapor phase of 8% of the powders. Apart from these major compounds detected by GC–MS analyses, 57% of the powders were double-based and nitroglycerin was present as the dominant compound in the powders headspace as determined by SPME–GC– $\mu$ ECD studies. The study also demonstrates that a 5 min extraction using a commercially available SPME device is sufficient to extract the analytes from the headspace of smokeless powders. More than one compound of interest was extracted and detected even at such a short extraction times. The detection of these target compounds can be associated with the presence of smokeless powders. Since there is more than one analyte detected, the combination of the detected peaks adds more significance to the detection result.

This work supplements the available bulk composition data for smokeless powders and demonstrates that reliable information about smokeless powders can be obtained by using a fast analytical method such as ion mobility spectrometry with simplified sampling and sample preparation. The SPME sampling approach also avoids the extensive sample preparation methods of solvent extraction that have been used to obtain bulk composition information while providing results for the headspace composition. The differences and similarities in the compounds detected between the analytical techniques (GC–MS, GC– $\mu$ ECD and IMS) can be applied to further improve both sampling and detection by IMS. The SPME fiber was able to extract sufficient amounts of various target analytes at short (5 min) extraction times and further optimization of the SPME parameters can improve this extraction efficiency and improve sampling time in the field. A larger SPME geometry has been developed in our group and will serve to improve the efficiency of the analyte sampling and thereby increase the mass of the analyte extracted and shorten the time required for detection [20]. The overall aim of this study was to generate a list of compounds that can be targeted by those interested in improving detection and sampling methods for smokeless powders using both laboratory and field portable analytical techniques. This work therefore provides both qualitative and quantitative information on the headspace composition of various smokeless powders and the mass of the various compounds of interest extracted by the SPME fibers at different extraction times. This study of smokeless powders is part of an ongoing effort to generate a comprehensive database for the bulk and headspace composition of a wide variety of smokeless powders that are manufactured around the world and their detection by various analytical techniques.

#### Acknowledgements

The authors would like to acknowledge Forensic Examiner Ronald Kelly of the Federal Bureau of Investigation Laboratory for providing smokeless powder samples and for many useful discussions. This project was supported by Award No. 2006-DN-BX-K027 awarded by the National Institute of Justice, Office of Justice Programs, U.S. Department of Justice. The opinions, findings, and conclusions or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect those of the Department of Justice.

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