# The evaluation of solid phase micro-extraction fibre types for the analysis of organic components in unburned propellant powders

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## ARTICLE INFO

## ABSTRACT

This work describes the evaluation of various solid phase micro-extraction (SPME) fibre types for the detection of compounds originating from particles of unburned propellant powders. These compounds may also be found in association with organic gunshot residues (OGSR). Seven SPME fibres were assessed based on their ability to extract the compounds of interest (diphenylamine (DPA), 4-nitrodiphenylamine (4-NDPA), ethyl centralite (EC), nitroglycerin (NG) and dibutyl phthalate (DBP)) from four ammunition types across three calibres (9 mm, 5.56 mm and 7.62 mm). Extracts were analysed by gas chromatography/mass spectrometry (GC/MS). Results indicated that the 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) was the most suitable fibre type for the extraction of these compounds across the ammunition types tested. Optimal extraction time parameters were also assessed with a 35-min period determined to be suitable. A number of previously unreported considerations for extracting propellant powders and potentially OGSR related materials are discussed.

## 1. Introduction

The chemical analysis of gunshot residue can be divided into two areas; inorganic and organic. Inorganic analysis has been much more widely investigated and applied to case work. Scanning electron microscopy (SEM) combined with wavelength dispersion (WDX) or energy dispersion (EDX) X-ray analysis is the method of choice for such inorganic analyses. These techniques have the advantage of being able to provide both chemical and morphological information from a sample [1].

The analysis of the inorganic GSR by SEM can provide a great deal of information, however in recent years a number of papers have been published highlighting some potential problems with this methodology. Particles of chemical compositions and morphologies similar to or potentially indistinguishable from inorganic GSR particles have been reported, originating from fireworks [2], stud guns [3–5], and vehicle brake linings [6,7]. In some cases where inorganic residues are not present in a sample, or are only present in relatively low levels, organic gunshot residue (OGSR) components may potentially prove useful. Even when inorganic residues are present at larger levels, the analysis of OGSR may pro-

vide complementary additional information that may strengthen the probative value of a sample [8] and potentially provide an additional means of differentiating between GSR and environmentally sourced residues. However OGSR identification and characterisation methods are rarely used in laboratories at the present time [8].

Solid phase micro-extraction (SPME) has been commercially available since 1993 [9]. The technique is a variation of solid phase extraction (SPE), allowing the collection of trace and ultra-trace levels of analytes from liquid, gaseous or solid samples (via headspace) by concentrating them onto a fused-silica optical fibre coated with a layer of polymeric substances such as polydimethylsiloxane (PDMS). These coatings range in thickness between 5 and 100 μm. Coatings are attached to a supporting injection device that resembles a microsyringe. Extraction is an equilibrium process, affected by temperature, analyte, sample component concentration and the volume/thickness of the polymeric coating. A major advantage of SPME is that no solvents are required to carry out extractions; this is both economically and environmentally advantageous [10]. SPME has been applied to a number of areas within the forensic arena including fire arson investigation [11], explosives [12] and ballistic materials [13–19].

The SPME work carried out to date on ballistic materials has generally focussed on "time since discharge" back calculations based on the loss of compounds from spent cartridge cases or firearm barrels over time. These authors have applied a number of different SPME fibre types, chosen using a variety of selection criteria [18–20].

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Furton et al. [12] investigated the suitability of 6 different SPME fibre types for the recovery of explosives and ignitable liquid residues from forensic specimens. It was determined that the 65 μm polydimethylsiloxane/divinylbenzene gave the highest overall recoveries. 65 μm polydimethylsiloxane/divinylbenzene fibres were also determined to be the most suitable for recovery of nitro-aromatics by Jonsson et al. [21], while Calderara et al. [22] reported the 65 μm polydimethylsiloxane/divinylbenzene fibres to be the most appropriate for the recovery of organic explosives (some of which may be found in ammunition). However to date a comprehensive study of a large number of SPME fibre types for their ability to recover compounds present in ammunition propellant powders, and therefore potentially in OGSR, has not been published. Seven SPME fibre types have been assessed in an attempt to determine a universally applicable fibre, by assessing which type best extracted compounds present in unburned propellant (smokeless) powders.

Propellant powders contain a variety of compounds, all of which are intended to fulfil specific requirements within the powder mixture, for example as stabilisers, plasticisers and deterrents. Stabilisers (diphenylamine and ethyl centralite) are intended to increase shelf life, by removal of nitric acid formed by decomposition of the nitrated energetic. Plasticisers (nitroglycerin ethyl centralite and dibutyl phthalate) reduce the hygroscopicity of powders and deterrents (ethyl centralite and dibutyl phthalate) are used to coat powder particles in order to reduce initial burn rates and lower burn temperatures [23]. The compounds included above are common within smokeless powders, lists of other compounds that have been reported to be contained in powders maybe found elsewhere [1].

## 2. Materials and methods

### 2.1. Solvents and standards

Diethyl phthalate, carbazol, monomethyl phthalate, triacetin, resorcinol, 3,4-dinitrotoluene, 3-nitrotoluene, 2,4-dinitrotoluene, 2,6-dinitrotoluene, 2,3-dinitrotoluene, diphenylamine, N-nitrosodiphenylamine, 4-nitrodiphenylamine, 2-nitrodiphenylamine, nitroguanidine, m-cresol, o-cresol, p-cresol, dimethyl phthalate, dibutyl phthalate, 2-nitrotoluene, 4-nitrotoluene, dimethyl sebacate, 2,4-dinitrodiphenylamine, urethane, camphor, 2,3-dimethyl-2,3-dinitro butane, 2,4-dinitrotoluene were sourced from Sigma–Aldrich (St. Louis, MO, USA). Tetryl, RDX, nitroglycerin, and ethyl centralite were purchased from LGC Standards (Middlesex, UK). Working standard mixtures were prepared in analytical grade methanol purchased from Fisher Scientific (Fair Lawn, NJ).

### 2.2. Solid phase micro-extraction

Seven SPME fibre types; 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 7 μm polydimethylsiloxane (PDMS), 30 μm polydimethylsiloxane (PMDS), 100 μm polydimethylsiloxane (PDMS), 85 μm carboxen/polydimethylsiloxane (CAR/PDMS), 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) and 85 μm polyacrylate (PA) were purchased from Supelco (Bellefonte, PA, USA). Fibres were conditioned prior to use as recommended by the manufacturer. Table 1 shows the characteristics of the fibres being assessed.

### 2.3. Propellant powders

Propellant powders from four ammunition types (9 mm Magtech, 5.56 mm Magtech, 7.62 mm Lapua and 7.62 mm Federal) were supplied by Nottinghamshire Police. Cartridges had their bullets pulled and the propellant powders were collected into 8 mL headspace vials for analysis.

### 2.4. Solvent extraction of unburned propellant powders

100 mg of unburned propellant powder from three cartridges from each of the ammunition types were extracted with 2 mL of methanol, samples were placed in an ultrasonic bath for 1 h. None of the powders were completely dissolved; the 9 mm Magtech ammunition left a fine powder on the bottom of the tube, while the other three ammunitions remained as small white pellets. Samples were then placed in a centrifuge for 15 min at 13,000 rpm, the supernatant was removed and filtered through a 0.22 μm PTFE filter before being injected into the GC/MS.

### 2.5. SPME extraction of 100 mg samples of unburned propellant powders

100 mg of each of the 4 ammunition types were extracted three times by each of the 7 fibre types. Extractions were carried out in an oven at 40 °C, a temperature high enough to volatilise the compounds of interest in to the headspace of the sample vial. Nitroglycerin is also known do begin to decompose at temperatures above 50 °C and this was not desired [26]. Extracts were carried out for 35 min and the fibres introduced to the injection port of the GC/MS immediately following extraction.

Following each injection fibres were conditioned for 20 min in the GC injection linear at 250 °C in order to ensure no carryover of the compounds of interest occurred. Blank fibre runs were carried out between every extraction in order to show that the fibres were clean before each powder extraction.

### 2.6. The extraction of single particles of unburned propellant powder

The fibre determined to be the most suitable was then used to extract single particles of unburned propellant powder from the 4 ammunition types. In order to determine the most suitable extraction time for single particles of unburned powder 1 particle from each ammunition type was extracted for time periods of 5, 15, 25, 35, 45 and 55 min. Peak areas for extracted compounds were recorded.

**Table 1**
SPME fibres and their characteristics and applications. NP: non-polar, P: polar and BP: bipolar [24,25].

| Fibre coating type | Coating stability | Property | Polarity | Recommended analyte type |
| --- | --- | --- | --- | --- |
| PDMS 100 μm | Non bonded | Absorbant | NP | Volatiles (MW 60–275) |
| PDMS 30 μm | Non bonded | Absorbant | NP | Non-polar volatiles (MW 80–500) |
| PDMS 7 μm | Bonded | Absorbant | NP | Non-polar high MW (MW 125–600) |
| Polyacrylate 85 μm | Crosslinked | Absorbant | P | Polar semi-volatiles (MW 80–300) |
| DVB/CAR/PDMS 50/30 μm | Highly crosslinked | Adsorbant | BP | Trace compound analysis (MW 40–275) |
| PDMS/DVB 65 μm | Highly crosslinked | Adsorbant | BP | Volatiles, amines, nitro-aromatics (50–300) |
| CAR/PDMS 85 μm | Highly crosslinked | Adsorbant | BP | Gases, low molecular weight (MW 30–225) |

## 2.7. GC/MS equipment and conditions

The GC was an Agilent Technologies 6890N and the MS was an Agilent 5975MS. A J&W Scientific HP5-MS (30 m × 0.25 mm × 0.25 μm) was used. Run conditions were as follows; thermal desorption of the SPME fibres was carried out using an injector temperature of 250 °C with splitless injection. A SPME/direct inlet linear was purchased from Sigma–Aldrich in order to minimise band broadening. The initial oven temperature was 50 °C, rising to 200 °C by 6 °C/min, at 27 min the temperature was raised by 20 °C/min until 300 °C at 32 min. The total run time was 32 min. The carrier gas was Helium.

Mass spectra for recorded peaks were further evaluated using the NIST database (MS search programme Version 2.0, NIST, MSS ltd. Manchester, England).

## 3. Results and discussion

### 3.1. Analysis of standards

The developed method allowed the identification of 27 of the standard compounds (Fig. 1). *m-* and *p*-cresol were shown to co-elute but could be identified by use of mass spectral data. *N*-Nitrosodiphenylamine degraded in the injector port of the GC into DPA and was therefore seen in the DPA peak. This method was developed to allow the analysis of a much broader range of ammunitions than those used in this investigation. It should therefore be applicable to ammunitions containing any of the 27 compounds separated.

### 3.2. The comparison of solvent and SPME extractions of unburned propellant powder samples

Comparisons of solvent and SPME extracts from the same types of ammunition showed high levels of similarity. All of the compounds of interest extracted using solvents were extracted by the SPME fibre. Fig. 2 shows chromatograms from solvent and SPME extracts of 100 mg of unburned Magtech 5.56 mm calibre ammunition. In the SPME extraction of ammunitions containing DPA, 4-NDPA was also sometimes seen. The decomposition pathways of DPA in ammunition powders have been previously documented, with 4-NDPA being a degradation product of this process [27]. The
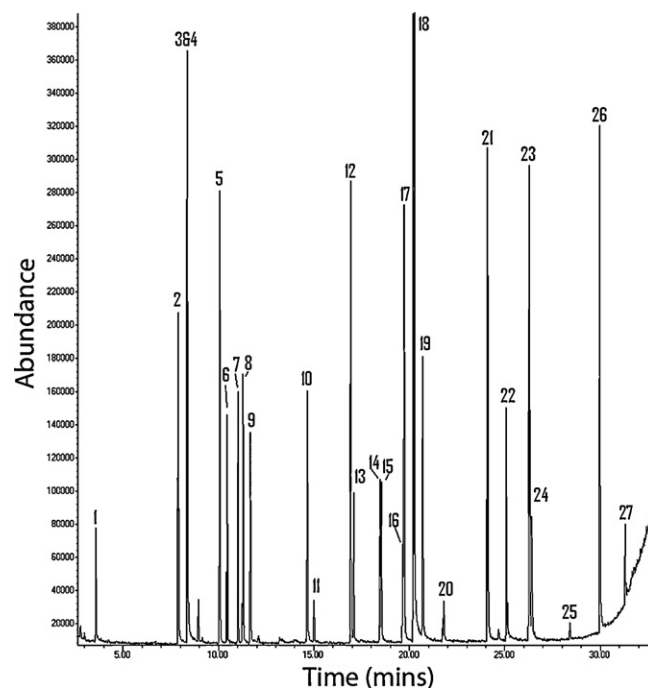


**Fig. 1.** Chromatogram of standard compound mixture: 1. urethane, 2. *o*-cresol, 3 and 4. *m*-cresol and *p*-cresol, 5. camphor, 6. 2-nitrotoluene, 7. 2,3-dimethyl-2,3-dinitrobutane, 8. 3-nitrotoluene, 9. 4-nitrotoluene, 10. triacetin, 11. nitroglycerin, 12. dimethyl sebacate, 13. 2,6-dinitrotoluene, 14. 2,3-dinitrotoluene, 15. 2,4-dinitrotoluene, 16. 3,4-dinitrotoluene, 17. diethylphthalate, 18. diphenylamine (including *n*-NDPA), 19. dimethylsebacate, 20. 2,4,6-trinitrotoluene, 21. carbazole, 22. ethyl centralite, 23. dibutylphthalate, 24. 2-nitrodiphenylamine, 25. tetryl, 26. 4-nitrodiphenylamine, 27. 2,4-dinitrodiphenylamine.

fact that 4-NDPA was not seen in the solvent extractions is likely to be because there was no pre-concentration performed on the samples.

Due to the selective nature of SPME fibres relative abundances of extracted compounds varied from solvent to SPME methodologies, but as it was qualitative and not quantitative analysis that was the basis of this study these differences were determined to not be detrimental to the application of SPME extraction.
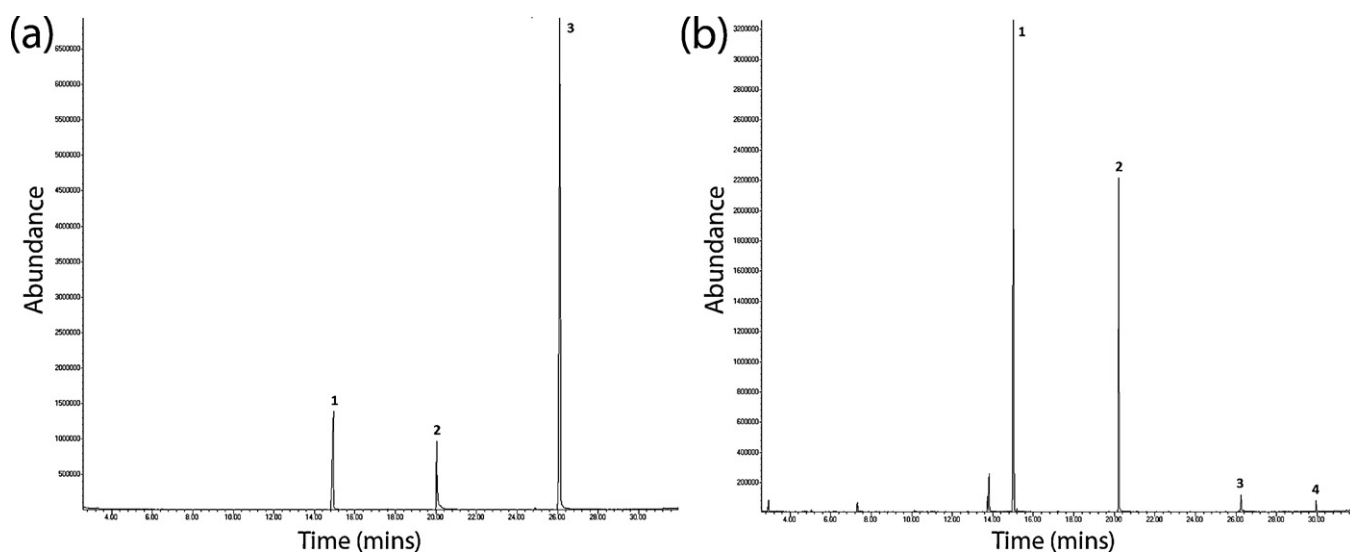


**Fig. 2.** Chromatograms from extractions of 100 mg samples of Magtech 5.56 mm propellant powders: (a) solvent extraction, (b) SPME extraction (1. nitroglycerin, 2. diphenylamine, 3. dibutyl phthalate, 4. 4-nitrodiphenylamine).

## 3.3. The use of unburned powder samples

The use of unburned propellant powders to determine the most suitable SPME fibre type for potentially extracting compounds associated with OGSR was chosen for a number of reasons. Although it might have been preferable to use OGSR samples, the loss of materials from such samples over time has been reported to occur [17,18]. Therefore, using such samples for the selection of the most suitable fibre type would most likely yield irreproducible results. This would obviously be bias to the fibres used to carry out the initial extractions on any sample, with the compounds present for extraction diminishing with time. The amount of variability of the compounds of interest between different samples was also not known and therefore carrying out extractions across different sample was determined to be unsuitable. Secondly the use of a blown down standard mixture was decided against due to the varying amounts of each compound which are found in real samples. The levels of NG in one ammunition are unlikely to be the same in another. Furton et al. [12] reported that lower molecular weight hydrocarbons reach optimal relative recoveries much earlier than molecules of higher molecular weights. It can therefore be extrapolated that with ammunitions having variable amounts of compounds of varying molecular weights the extraction profiles are likely to be different compared to homogenous standard mixtures of compounds all at the same concentration. It was also not known whether the structures (rod, ball, flake, etc.) of different propellant powders would also affect compound recoveries, something which could not be taken into account using blown down standards. It has been reported that when a firearm is discharged both unburned and partially burned powder granules are propelled from the barrel along with the projectile [8]. Therefore it is reasonable to say that using unburned powders can justified as these unburned and partially burned residue particles will have structures identical to or similar to the non fired unburned particles. Further Newton and Booker reported that there was no difference between the chemical compositions of partially burned powders, residues taken from the barrels of fired weapons and unburned propellant powders (40 powders tested) [28].

## 3.4. Comparison of SPME fibre types

Fig. 3(a)–(d) shows the mean peak areas of compounds extracted from the four unburned propellant powders used to determine the suitability of the 7 SPME fibre types tested. It was determined that overall the most suitable fibre type for the extract of the compounds present in the unburned powders was the 65 μm PDMS/DVB type. This was based on the comparisons of the average peak areas of the compounds recovered and the relative stand deviations calculated for each fibre type. The 65 μm PDMS/DVB fibre extracted the greatest amount of NG in all powder samples. For the other compounds extracted 65 μm PDMS/DVB provided either the highest extraction amount or extracted levels very close to the leading fibre type.

Average relative standard deviations were calculated for each fibre type by taking the means of all relative standard deviations from each of the compounds extracted by each fibre. This allowed the fibres that performed the best over the entire range of compounds to be determined. The 65 μm PDMS/DVB was shown to have the third lowest relative standard deviation (Table 2). However there was only a 3% difference between the lowest average relative standard deviation and that of 65 μm PDMS/DVB. Neither 85 μm CAR/PDMS or the 100 μm PDMS fibre types performed as well as the 65 μm PDMS/DVB in terms of extracting the compounds of interest. As it was qualitative rather than quantitative information that was more important in this study the relative standard deviation figures were determined to not be as significant as the

**Table 2**
Average relative standard deviation figures for the 7 fibre SPME fibre types.

| Fibre | Average relative standard deviation |
|---|---|
| 7 μm PDMS | 26.6 |
| 30 μm PDMS | 28.9 |
| 50/30 μm DVB/CAR/PDMS | 47.2 |
| 65 μm PDMS/DVB | 20.9 |
| 85 μm carboxen/PDMS | 17.9 |
| 85 μm PA | 36.0 |
| 100 μm PDMS | 18.1 |

extraction yield data. Therefore it was concluded that the most suitable fibre type was 65 μm PDMS/DVB.

It was shown that despite 65 μm PDMS/DVB being the most appropriate fibre overall it was not always the best performer for every compound in every propellant powder. The extraction of powders using SPME is a complex process and some unexpected occurrences were observed. For example the same compound found in different propellant powders was not always extracted in the highest abundances by the same fibre. For example DPA was recovered in three of the ammunitions, with 65 μm PDMS/DVB extracting the greatest amounts in the Magtech 5.56 mm ammunition, while 100 μm PDMS performed best with the Lapua 7.62 mm ammunition, with 85 μm PA extracting the greatest levels in the Federal 7.62 mm powders. It is therefore suggested that the structural composition of different ammunitions and the ratios of compounds present may both influence the extraction process. For example the use of deterrents and other coatings such as graphite on particle surfaces may affect the levels of some compounds entering the headspace. Reference to the relative abundances of extracted compounds from the four ammunition types (Fig. 3) show variations, suggesting the partition coefficient values are different in the extraction systems for each powder analysed [28]. It has also been reported that higher concentrations of a competitive interface compound can dislodge other analytes from fibres [9]. A combination of these factors may explain this variation in which different fibres perform best for any given compound between different propellant powder samples.

The ammunitions that were used in this investigation only contained a limited number of compounds, however the inherent characteristics of the 65 μm PDMS/DVB fibre, for example its bipolar character and suitability for extracting volatiles, amines and nitro aromatics [25] suggest that it should be the most suitable fibre across most other ammunition types. Research by Furton et al. [12] into SPME extractions of explosives concluded that 65 μm PDMS/DVB was the most suitable overall for a number of additional compounds that may also be found in firearm ammunitions including nitrotoluenes, dinitrotoluenes and trinitrotoluene. Further work is being undertaken assessing this fibre type with a larger number of ammunitions and OGSR samples.

## 3.5. Evaluating the effects of extraction time on single particles of propellant powders

In OGSR samples there will obviously be variable amounts of the compounds of interest and depending on these amounts, the volume of headspace from which compounds of interest will be extracted and the volume of the sample being analysed, the optimum extraction time will vary. Although it would be impossible to account for all the potential variability from sample to sample, extracting from one particle of propellant powder was an attempt to mimic lower amounts of sample that might be found in relation to OGSR. As stated previously both unburned and partially burnt propellant powder particles may be found in association with firearm discharges [8]. Pun and Gallusser [30] showed that
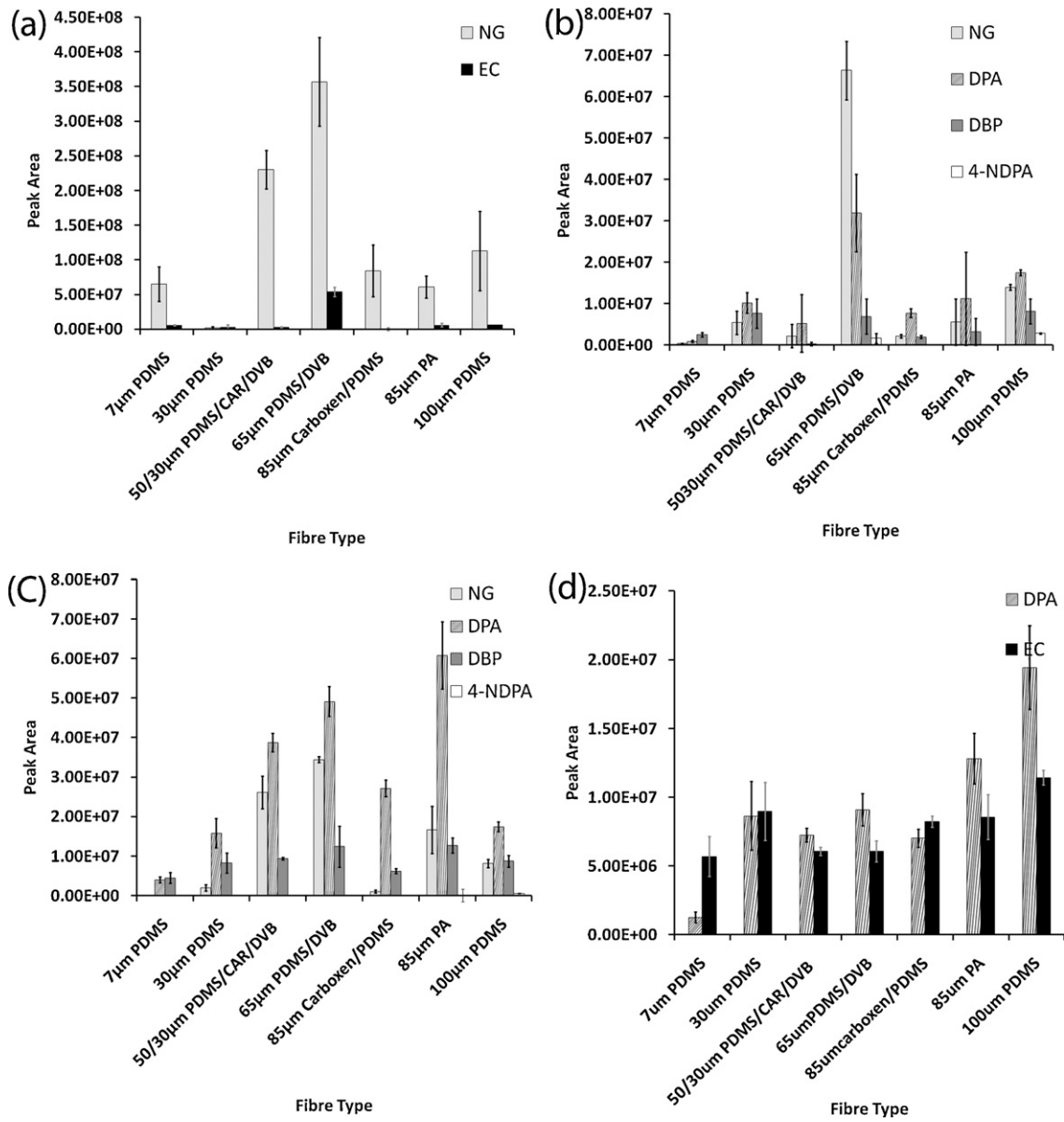
**Fig. 3.** Average peak areas for compounds extracted from 4 ammunition types by the 7 SPME fibre types: (a) Magtech 9 mm, (b) Magtech 5.56 mm, (c) Federal 7.62 mm, (d) Lapua 7.62 mm.

partially burnt powder particles can be found in various stages of decomposition exiting the firearm barrel following discharge. The SPME extraction of partially burned particles has been shown to be possible by Burleson et al. [19].

Results for single particles extracted across the range of times (5–55 min) showed a great level of variation between individual particles from the same ammunition type and between different ammunition types.
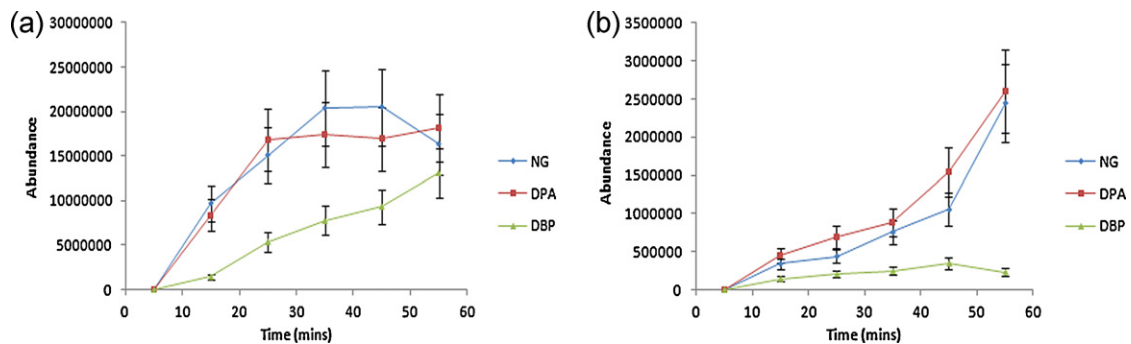


**Fig. 4.** Extractions of two different single particles of Magtech 5.56 mm ammunition collected from the same cartridge.
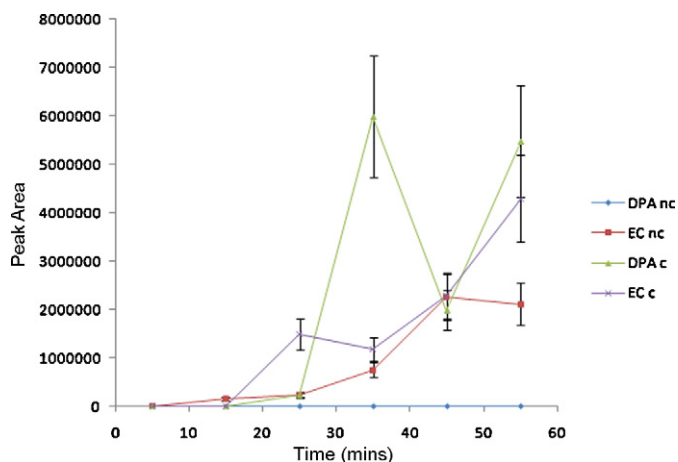
**Fig. 5.** Lapua 7.62 mm single particle extracts from cut (c) and non-cut (nc) particles.

Extractions of compounds from the same ammunition type but different individual particles showed the potential for orders of magnitude differences in extraction abundances to occur. For example two sets of extractions of 9 mm Magtech ammunition carried out consecutively on two separate particles from the same cartridge yielded abundance levels for 35 min extractions of 8,417,107 and 380,380 for NG. This suggests that on a particle to particle basis extraction efficiency may be highly variable.

The optimum extraction time for particles was also shown to vary from particle to particle within the same ammunition type. Fig. 4 shows the extractions of two different particles of the same Magtech 5.56 mm ammunition taken from the same cartridge. It can be seen that in the first set of particle extractions the levels of both NG and DPA reach an equilibrium within the extraction system at 35 min (and in the case of NG begin to drop after 45 min) and this would therefore be determined as the optimum extraction time. However in the second set of extractions the levels of DPA and NG extracted continue to increase with time up to the last extraction of 55 min suggesting this would be a more suitable time for this particle. Work is ongoing in this area.

Extractions from single particles of Magtech 9 mm and 5.56 mm ammunition types proved successful. It was determined that despite variation between particles an extraction time of 35 min was suitable. Providing good extraction and having a time similar to that of the GC/MS analysis (32 min), something stated as preferable by Wercinski [29].

Extractions from single particles of the two 7.62 mm ammunition types proved to be less effective than those of the smaller calibre ammunition types. With Lapua 7.62 mm no DPA was extracted from the individual particles, even after 55 min extractions. This compound was known to be present in this ammunition type by reference to the extracts from 100 mg samples. When this particle was subsequently cut in half, DPA was detected in extraction of 25 min and above. These findings are illustrated in Fig. 5. By exposing the inner core of the powder particle and increasing the surface area, extraction efficiency was shown to increase. However extracts from single particles of Federal 7.62 mm ammunition exhibited none of the compounds which were previously determined to be present in the ammunition (by analysis of 100 mg of the propellant powder), even at the maximum tested extraction time of 55 min. Cutting these particles into pieces had no effect and still no compounds of interest were extracted. These finding would suggest that the shape of a particle, together with the internal and external morphologies and compositions may affect the success of SPME extractions.

These results show that the specific type of ammunition being analysed can have an effect on SPME extractions. No one extraction time was shown to be universally optimal for all ammunition types, or even between individual particles of the same ammunition. However, with the exception of the Federal 7.62 mm ammunition, an extraction time of 35 min was determined to be suitable, yielding peaks for all of the OGSR compounds determined to be present in the ammunitions in this study.

## 4. Conclusions

The most suitable SPME fibre for the extraction of the compounds found in relation to unburned propellant powders and therefore potentially OGSR was determined to be the 65 μm PDMS/DVB fibre type, performing well across all of the compounds present in the ammunition investigated.

Results from extraction optimization work have shown that no one extraction time was universally optimal for all compounds being extracted. However a 35 min extraction time was determined to be suitable, allowing detection of the compounds of interest. Issues experienced with extracting compounds from the 7.62 mm ammunition types suggest that the shape of a particle, its internal and external morphologies and compositions may influence the effectiveness of SPME extractions.

Further work will be to apply these methodologies to the extraction of OGSR compounds from various media and forensic evidence types. The results of this study may also be useful to those investigating improvised explosive devises (IEDs) in which smokeless propellant powders have been used [31].

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