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Assessing a novel contact heater as a new method of recovering explosives traces from porous surfaces

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Abstract

It can be very challenging to recover explosive traces from porous surfaces, such as clothing and car seats, compared to non-porous surfaces. The contact heater has been developed as a novel instrument designed to recover explosives traces from porous surfaces. Samples are taken by heating and drawing air across a surface, with the air flowing through a sampling cartridge containing adsorbent polymer beads, which act to trap any recovered explosive material. Any collected explosive can then be eluted from this cartridge using a solvent, prior to analysis. This paper outlines work performed to evaluate the usefulness of the contact heater with regards to the recovery of explosives traces from porous materials. Ethylene glycol dinitrate (EGDN) and triacetone triperoxide (TATP) were chosen as two representative explosives for this study. Quantification was performed using GC-MS for EGDN and LC-MS/MS for TATP. Different sampling temperatures, sampling times and elution solvents were investigated. Recovery was trialled from leather, carpet and denim. Reasonable recoveries of up to 71% were obtained following optimisation. It was also possible to recover TATP from fabrics exposed to TATP vapour in a vapour-laden jar up to two hours after exposure. The contact heater therefore appears to be a very useful tool for the recovery of explosives traces from porous materials.

Introduction

Forensic science can play a crucial role in identifying the cause of explosions due to illegal activity. It is widely accepted that an explosion will not consume 100% of the explosive compound involved. Traces of the explosive will remain in the form of residues and decomposition products, which will be widely scattered at an explosion scene.[1, 2] The key aim for a forensic scientist is therefore to recover traces of the unconsumed explosive. However, these may only have a short persistence in the environment, and they may be difficult to locate and recover. Triacetone triperoxide (TATP) is a common peroxide explosive. Due to its ease of synthesis and the ready availability of its precursors, it has been implicated in an increasing number of explosion incidents.[3-9] Ethylene glycol dinitrate (EGDN) is a well-recognised explosive compound which has had a high level of historical use.[10]

It is relatively rare to find traces of explosives in an everyday environment.[1, 11-13] For this reason, if explosives are detected, it is potentially a forensically significant finding, indicating contact between a surface and an explosive. Such information can be helpful for law enforcement officers investigating the cause of an explosion, for example to decide the nature of the materials involved in an event or to link a suspect to an explosive device; the findings may ultimately be used as evidence in court.[1, 14]

Chemical analysis can be used to identify the type of explosive recovered from a scene.[15] Many techniques can be employed, such as thin-layer chromatography (TLC), infra-red spectroscopy (IR), gas chromatography-mass spectrometry (GC-MS), liquid chromatography-mass spectrometry (LC-MS) and ion chromatography (IC).[16, 17] Over the last few decades, a large amount of research has been directed towards improving methods of explosives detection, leading to ever-decreasing limits of detection using a multitude of new techniques. However, comparatively less work has been performed to optimise the process of explosives recovery. Explosives residues must usually be recovered, before undergoing sample preparation and analysis, in order to detect any explosives present within the sample. For this reason, some deem the explosives recovery step the most important step in the entire examination sequence.[18]

It is known that explosives have a high persistence on fabrics, such as clothing, compared to other materials such as wood and metal.[2] This prolonged retention capability of fabrics towards explosives is thought to be due to explosives particles becoming trapped within the tightly-woven fibres of fabrics, and then being held in place by intermolecular forces such as Van der Waals forces.[19] Fabrics therefore seem to be an ideal substrate to recover explosives from – for example, following a car bomb, the fabric car seats could be examined for explosives traces, to determine the type of explosive used.

Unfortunately, porous fabrics are one of the most challenging materials to recover explosives from. Explosives traces will sit on the surface of smooth surfaces such as glass, metal and plastics, and can be easily recovered by wiping the surface using a solvent-wetted cotton swab.[15] It is much harder to recover explosives traces from fabrics using solvent-swabbing, as the explosives may become deeply embedded within the fibres. Additionally, the use of solvent on fabrics may damage the fabric in question. For this reason, vacuum sampling is routinely used to recover explosives from fabrics. Vacuum sampling uses a handheld vacuum containing a fine filter, which traps any particles of explosive pulled from the fabric.[1, 20] The main drawback of this technique is that it requires relatively large particles of explosive to be present on the fabric. If, for example, explosives had deposited on a fabric due to a process of volatilisation and re-deposition, it is likely that individual molecules of the explosive would be distributed throughout the fabric, and vacuum sampling may be unable to capture the explosives on the filter. Alternatively, sections of fabric can be cut from a larger piece and solvent extracted.[21] However, this method is destructive to the garment in question, in addition to being time-consuming and labour-intensive.

Recently, some direct sampling methods have been investigated for the detection of explosives on fabrics. These include desorption electrospray ionisation mass spectrometry (DESI-MS), direct analysis in real time mass spectrometry (DART-MS) and confocal Raman microscopy.[22-25] These techniques show great promise, with one of their main advantages being their ability to analyse fabric surfaces in real-time, without the need for any sample preparation. However, they also have several drawbacks – it is difficult to quantify the amount of explosive present on a fabric using these techniques, and for the Raman technique in particular, it is first necessary to locate an explosive particle on the piece of fabric which can be very challenging (with particles typically as small as 5 μm in diameter), before focusing the incident laser radiation on the particle. A further drawback of these direct sampling methods is that they do not allow the physical recovery of the explosive from the fabric, potentially permitting further, more detailed analysis in a laboratory.

The contact heater is an instrument designed by the UK Forensic Explosives Laboratory (FEL) to recover explosives traces from fabrics. This present work outlines investigations into the recovery of EGDN and TATP traces from ceramic tiles, carpet, leather and denim using the contact heater. TATP was chosen as an explosive of particular interest due to its rapidly increasing use worldwide over recent years. EGDN was chosen as a 'model' explosive with which to perform initial optimisations, due to its vapour pressure being of similar magnitude to that of TATP (with vapour pressures of 6.31 x 10^{-5} atm and 1.02 x 10^{-4} atm at 25 °C for TATP and EGDN, respectively).[26] An initial assessment and optimisation of the contact heater sampling technique was performed using EGDN, with recoveries performed from a ceramic tile as a model non-porous sampling surface. The effect of different sampling variables are assessed, including sampling temperature and explosives recovery matrix. Then, recoveries of TATP are investigated from three porous surfaces spiked directly with

TATP: carpet, denim and leather. Finally, the ability of the contact heater to recover TATP from fabrics exposed to TATP vapour was assessed, and some provisional sampling window times established.

Materials and methods

The contact heater:

The contact heater is a purpose-built instrument designed by the UK Forensic Explosives Laboratory (FEL), manufactured by Plalite Ltd, Sittingbourne, Kent, UK, to recover explosives traces from fabrics. It comprises of a heated aluminium platen connected to a vacuum pump. The heated platen is placed in contact with the fabric of interest, and air is drawn over the surface of the fabric. This air passes through a cartridge containing an adsorbent polymer, where any analytes of interest are captured. The cartridge can then be eluted in the laboratory using a suitable solvent, and the extract analysed for explosives.[27, 28] A schematic of a contact heater is given in Figure 1.

Figure 1: Schematic of a contact heater.

GC-MS

EGDN detection and quantification was performed using GC-MS. The GC-MS consisted of an Agilent 6850 GC oven coupled to an Agilent 5795C VL MSD quadrupole with triple-axis detector. A 14 m silica BP5 column was used with a 0.25mm i.d., coated with bonded 5% diphenyl-dimethylsiloxane at a 0.25μm film thickness. The injector temperature was held at 175 °C and the oven temperature programme was 60 °C for 1 minute, then increased at 20 °C/minute to 200 °C for 2 minutes. The source used was electron impact, with 70 eV energy and a temperature of 230 °C. Masses were monitored between *m/z* 50-550.

LC-MS/MS

A Varian chromatography system coupled to two Varian 212-LC pumps and a Varian 460-LC autosampler was used. The analytical column was a YMC-Pack ProC18 (150 x 2.1 mm i.d., 3 μm) and the guard column was a YMC ProC18 (10 x 2.1 mm i.d., 3 μm). Isocratic elution was performed using a mobile phase comprising 65:35 methanol:water with 5 mM ammonium acetate, using a flow rate of 0.2 mL/min. This was coupled to a Varian triple quadrupole 325-MS *via* a vortex electrospray ionisation (vESI) probe assembly interface operated in positive-ion mode.

LC-MS/MS Data acquisition

Data were collected in MRM mode, monitoring the following transitions: *m/z:* 240 / 240 (a precursor ion / precursor ion transition), *m/z:* 240 / 223 and *m/z:* 240 / 74. The dwell time was 0.2 s and the amu span was 0.7.

LC-MS/MS experimental conditions

Breakdown curves were obtained to determine the optimum capillary voltage for each of the desired ions, with the following optimum values determined: *m/z* 240: 30 V, *m/z* 223: 48 V, *m/z* 74: 30 V. The collision energies for each ion were also optimised and were determined to be: *m/z* 240: 5.5 eV, *m/z* 223: 5 eV and *m/z* 74: 5 eV. The drying gas pressure was held at 19 psi as recommended in the LC-MS/MS manual, and the following optimum conditions were determined; drying gas temperature of 180 °C; vortex gas pressure and temperature of 5 psi and 50 °C respectively; shield and needle voltage of 200V and 4000V respectively and nebulising gas pressure of 30 psi. The detector was used in extended dynamic range (EDR) mode at ~1500V. The gas pressure in the collision cell was optimised at 1 mTorr, the housing was kept at 50 °C and the inside of the case was held at 46 °C and 1.6 x 10-5 Torr.

Chemicals and materials

EGDN was obtained as a 1000 μg/mL solution in acetonitrile and was Cerilliant brand (Round Rock, TX). TATP was supplied as a 0.1 mg/mL solution in acetonitrile and was AccuStandard brand (New Haven, CT). Ethyl acetate was obtained from Sigma Aldrich. HPLC grade acetonitrile was Fisher brand. XAD-7 cartridges were SKC Inc brand and were provided by Dstl. GC and LC vials were Chromacol or Agilent brand. 7 mL glass snap cap vials were Samco brand. White ceramic tiles were obtained from Homebase. 100% polypropylene carpet was obtained from Homebase. Black leather pieces were obtained from BDS Leathers. Denim pieces were cut from a pair of Denim Co jeans.

Preparation of samples – direct spiking

The material to be sampled (ceramic tile, carpet, leather or denim) was spiked using a micro syringe containing a solution of either EGDN in acetonitrile (1 mg/mL – with either 50 or 75 μL spikes used) or TATP in acetonitrile (0.1 mg/mL – 140 μL spikes used). In some instances, sampling from the surface was performed immediately after spiking, whereas in other instances, a 4-minute wait period was observed to assess the influence of solvent evaporation to allow the explosives to bind to the material.

Preparation of samples – vapour jars

A piece of denim, carpet or leather was cut to size in order to cover the inner base of a glass TLC jar, or half of the inner wall of a glass TLC jar (in each case, covering approximately one quarter of the

internal surface area). 140 μL of a 0.1 mg/mL TATP in acetonitrile solution was spiked onto the centre of a clean ceramic tile, and the TLC jar containing the fabric either in its base (termed the 'ceiling' condition) or the wall (termed the 'wall' condition) was immediately inverted and placed over the centre of the ceramic tile, to contain any volatilised TATP. The fabric pieces were held in place using small sticky labels. The vapour jar was left to stand for 30 minutes, 1, 2 and 24 hours to allow the acetonitrile to evaporate and the TATP to sublime and redistribute within the vapour jar. It was envisioned that some of the TATP would be caught on the surface of the fabric within the vapour jar. After the allotted time, the piece of fabric was gently removed from the jar and contact heater sampling was performed. The vapour jar experiments were all performed using acetonitrile-wetted XAD-7 cartridges. For the sampling from leather and denim, a starting platen temperature of 25 °C was used, with ramp to 105 °C – these conditions were found to be the best for TATP recovery from the direct spiking experiments. For the sampling from carpet, a constant platen temperature of 105 °C was used. Following contact heater sampling for 5 minutes at full flow, the cartridges were processed in an identical manner to those from the direct spiking experiments.

Sampling procedure – dry cartridge

The platen of the contact heater was preheated to the desired sampling temperature. The end caps were removed from a fresh XAD-7 cartridge, and the cartridge was connected into the contact heater set up using rubber tubing. The vacuum pump was switched on to the desired flow rate, and the material was sampled by moving the platen in small circles around the material for 5 min. After this time, the pump and platen heater were switched off and the XAD-7 cartridge removed. Any recovered explosives were eluted from the cartridge using 2 x 0.7 mL solvent (ethyl acetate for EGDN and acetonitrile for TATP), assisting elution using a gentle stream of nitrogen through the cartridge, and the eluent collected in a clean 7 mL glass vial. The eluent was transferred into a clean 1.5 mL autosampler vial, recording the volume of the eluent during transfer. The sample was analysed by GC-MS (for EGDN-based samples) or LC-MS/MS (for TATP-based samples). Samples were injected in triplicate for EGDN and in duplicate for TATP, and the results averaged. Quantifications were performed by determining the EGDN or TATP concentration in the measured volume of eluent and comparing this to the maximum possible concentration in the same volume of eluent, based on the quantity of EGDN or TATP spiked on the surface. In each case, a negative control of the material was taken in the same manner as taking an experimental sample, prior to spiking, to ensure no contamination was present. All negative controls tested negative for EGDN or TATP. Only one spiked sample was taken to assess recoveries for each different set of conditions, due to the limited number of XAD-7 cartridges available for this work. Ceramic tiles were cleaned between experiments by heating in an oven at 80 °C for at least 30 min, and were re-used for different experiments due to their non-porous nature. Carpet, leather and denim swatches were each used only twice – initially as a negative control followed by a corresponding experimental sample.

Sampling procedure – solvent-wetted cartridge

The platen of the contact heater was preheated to the desired sampling temperature. The end caps were removed from a fresh XAD-7 cartridge. 1 mL of solvent (ethyl acetate for the EGDN experiments; acetonitrile for the TATP experiments) was added to the top of the XAD-7 cartridge and blown through under a gentle stream of nitrogen, until all XAD-7 visible at the edge of the cartridge appeared to have absorbed solvent. The cartridge was connected into the contact heater using rubber tubing, and sampling proceeded as above.

Modified sampling procedure – no cartridge

A number of experiments were trialled in the absence of an XAD-7 cartridge, in order to assess whether recovery was possible without the use of a commercial sampling cartridge. For these experiments, sampling was performed directly into a vial of ethyl acetate. Two holes were drilled into the plastic lid of a 7mL glass snap cap vial. A fresh lid was used for each pair of samples (with each pair consisting of a negative control followed by a spiked sample). 1 mL ethyl acetate was dispensed into the vial, and two plastic micropipette tips were inserted through the holes, ensuring that the tip of one pipette tip was submerged beneath the surface of the solvent, and that there was no air gap present between the micropipette tips and the drilled holes, which would cause a loss of suction. Plastic tubing was then connected to the exposed ends of the pipette tips (with the 'submerged' pipette tip's end connecting to the platen, and the other pipette tip connected to the vacuum pump). The platen of the contact heater was preheated to the desired sampling temperature, the vacuum pump was switched on to the desired flow rate, and the material was sampled as before. After this time, the pump and platen heater were switched off and the vial of ethyl acetate removed. The contained solution was transferred into a clean 1.5 mL autosampler vial, recording the volume of the solution during transfer. The sample was analysed as above. Negative controls were performed in an analogous manner, prior to contact heater sampling of the subsequent spiked surface.

Results and discussion

The overall purpose of the contact heater is to aid the recovery of trace explosives from porous surfaces. Prior to this current study, a limited preliminary exploration of the recovery of TATP using the contact heater, in conjunction with XAD-7 cartridges, had been carried out.[28] However in this earlier work, recoveries were low, with the maximum recorded recovery only 1.1%.

EGDN recoveries from directly-spiked ceramic tiles using dry and solvent-wetted cartridges

Initial experiments were performed using dry XAD-7 cartridges, following the protocol used by previous work with the contact heater.[28] Ceramic tiles were used as a non-porous, 'easy' sampling surface upon which to optimise the contact heater method, before moving to the more difficult porous surfaces. In all experiments, the nitrogen-assisted eluent blow-through process from the sampling cartridge tended to lead to the loss of some solvent due to evaporation, with final eluent volumes of between 400-600 μL. It was not anticipated that volatilisation of explosives would be problematic during this blow-through, as the vapour pressures of ethyl acetate and acetonitrile are much higher than those of EGDN and TATP. Calibration curves were prepared for quantification. Several variables were adjusted to determine the optimum recovery conditions: two platen temperature sequences were trialled, and a 4-minute post-spike wait period was also trialled prior to contact heater sampling, to allow any residual solvent to evaporate. In each case, the use of dry XAD-7 cartridges gave low EGDN recoveries of below 10%, as shown in Table 1.

Starting temperature (°C)	Final temperature (°C)	Time between spike and sampling (min)	% recovery
25	105	0	6.9
105	105	0	2.3
25	105	4	9.2
105	105	4	3.6

Table 1: EGDN recoveries from a ceramic tile using dry XAD-7 cartridges.

It can be seen that slightly higher EGDN recoveries were obtained when using a 25 °C to 105 °C gradual temperature ramp during sampling, compared to a constant high platen temperature of 105 °C. Additionally, the EGDN recoveries were slightly increased when sampling after all of the spiking carrier solvent had evaporated, compared to immediate sampling after spiking. Although these experiments had successfully recovered EGDN from a ceramic tile, the recoveries were very low. The sampling method was therefore modified, in an attempt to obtain higher EGDN recoveries. Douse found that explosives were more likely to transfer onto XAD-7 beads if the beads were saturated with pentane.[29] For this reason, the addition of a solvent to the XAD-7 cartridges was explored. Ethyl acetate was chosen as a compatible solvent for the subsequent GC-MS analysis, and was introduced as a wetting agent for the XAD-7 cartridges, prior to contact heater sampling, in an attempt to promote EGDN adsorption onto the XAD-7 beads. Experiments were performed using identical platen temperature sequences and post-spike wait periods as for the dry XAD-7 cartridges. These results are given in Table 2. It can be seen that significantly higher EGDN recoveries were obtained using the ethyl acetate-wetted XAD-7 cartridges, compared to the dry XAD-7 cartridges. These results are also depicted graphically in Figure 2.

Starting temperature (°C)	Final temperature (°C)	Time between spiking and sampling (min)	% recovery
25	105	0	35.1
105	105	0	63.1
25	105	4	66.5
105	105	4	3.6

Table 2: EGDN recoveries from a ceramic tile using ethyl acetate-wetted XAD-7 cartridges.
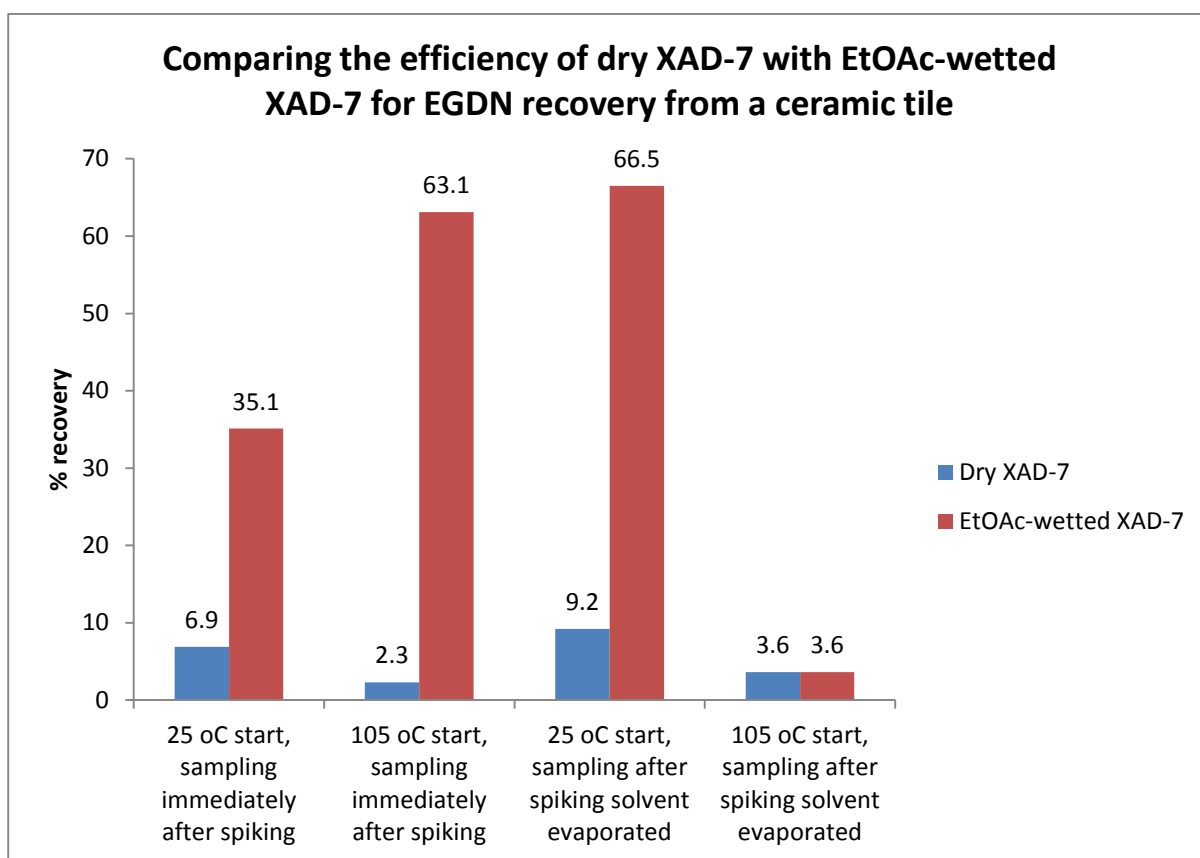

Figure 2: Comparing the efficiency of dry XAD-7 cartridges and ethyl acetate-wetted XAD-7 cartridges for EGDN recovery from a ceramic tile.

As wetting the XAD-7 cartridges using solvent prior to sampling had given significantly higher EGDN recoveries in the majority of the conditions trialled, solvent-wetted cartridges were used for all subsequent experiments in an attempt to maximise recoveries.

EGDN recoveries from directly-spiked ceramic tiles using the modified sampling procedure

As increased EGDN recoveries had been obtained when collecting a contact heater sample using an ethyl acetate-wetted XAD-7 cartridge compared to a dry XAD-7 cartridge, it was considered possible that the observed increase in recoveries may be solely due to the presence of ethyl acetate, rather than the ethyl acetate acting in combination with the XAD-7 beads to increase their receptivity to EGDN. Experiments were therefore performed following the modified sampling procedure detailed earlier ('Modified sampling procedure – no cartridge' adapted from the set-up of Schulte-Ladbeck *et al* [30]) which involved sampling directly into ethyl acetate, rather than an ethyl acetate-wetted XAD-7 cartridge, to test this hypothesis. These results are detailed in Table 3.

Starting temperature (°C)	Final temperature (°C)	Time between spiking and sampling (min)	% recovery	Comments
25	105	0	23.1	Full flow, short tubing
105	105	0	5.9	Full flow, short tubing
25	105	4	26.9	Full flow, short tubing
105	105	4	27.8	Full flow, short tubing
105	105	4	9.6	Half flow, short tubing

Table 3: EGDN recoveries from sampling directly into ethyl acetate, without the use of XAD-7 cartridges.

Initial experiments involved the use of a long piece of flexible tubing (around 12") to connect the set-up however no EGDN was recovered. When a shorter piece of flexible tubing (around 5") was used EGDN recovery was observed. The longer length of tubing would have provided a larger surface area for the EGDN to come into contact with during its passage from the platen into the solvent, and the EGDN may have been adsorbed onto the tubing before it could be captured in the ethyl acetate. Previous work by Schulte-Ladbeck found that TATP adsorption could occur onto PET tubing, so it is likely that some form of analogous adsorption was occurring during these experiments.[30]

Further experiments were trialled, varying the platen temperature and vacuum flow rate. In each case, EGDN was detected in the ethyl acetate, though the quantity of EGDN recovered was generally lower than that obtained by analogous sampling into an ethyl acetate-wetted XAD-7 cartridge.

These results seem to suggest that an ethyl acetate-wetted XAD-7 cartridge is superior to ethyl acetate alone for capturing EGDN, and that ethyl acetate alone is superior to dry XAD-7 for capturing

EGDN. However, it should also be borne in mind that some EGDN adsorption is likely to have been occurring onto the length of tubing used during the direct sampling into ethyl acetate. Negative controls were performed between each experimental sample, using the same piece of tubing, and in each case, the negative controls tested negative for EGDN. This seems to suggest that once EGDN becomes adsorbed onto a piece of tubing, airflow alone of up to 1000 cc/min did not displace it readily.

EGDN recoveries from directly-spiked carpet using solvent-wetted cartridges

Following experiments giving reasonable EGDN recoveries from a ceramic tile, the focus was shifted to investigate EGDN recovery from carpet, as a representative absorbent material. These results are given in Table 4. Higher recoveries were observed with a higher starting platen temperature, so subsequent experiments used a high platen temperature of 105 °C. This result may be because the EGDN becomes tightly bound to, and entangled within, the polypropylene fibres, requiring a greater quantity of thermal energy to bring about the volatilisation of EGDN from the carpet. When sampling from a tile, the EGDN presumably remains on the surface of the tile, so differing surface-level interactions are at work.

Much higher EGDN recoveries were obtained when sampling from carpet immediately after spiking, when residual solvent would still have been present on the carpet. This may be due to the presence of solvent preventing the EGDN molecules from binding to the carpet fibres.

Starting temperature (°C)	Final temperature (°C)	Time between spiking & sampling (min)	Collection method	% recovery	Comments
25	105	0	Ethyl acetate-wetted XAD-7	3.4	
105	105	0	Ethyl acetate-wetted XAD-7	28.1	
105	105	4	Ethyl acetate-wetted XAD-7	2.7	
105	105	4	Ethyl acetate-wetted XAD-7	8.2	5 mL ethyl acetate added to carpet before applying platen
105	105	4	Ethyl acetate-wetted XAD-7	6.1	Carpet rubbed with cocktail stick, then 5 mL ethyl acetate added before applying platen
105	105	4	Ethyl acetate-wetted XAD-7	10.9	5 mL ethyl acetate added to carpet, then carpet rubbed with cocktail stick, before applying platen

Table 4: EGDN recoveries from carpet under various conditions.

It was therefore reasoned that the presence of a solvent on the carpet may be necessary to enable the loosening of the EGDN from the polypropylene fibres. Douse suggested that wetting a sampling surface using an organic solvent may lead to the more facile volatilisation of explosives.[31] Douse proposed that this was due to the solvent enabling any explosive molecules to become 'available for vaporisation'. This hypothesis was investigated more thoroughly, by trialling additional steps of vigorously rubbing the carpet with a cocktail stick prior to sampling, and adding additional solvent to the carpet prior to sampling, in various sequences. The results from these experimental variants are shown in Figure 3.
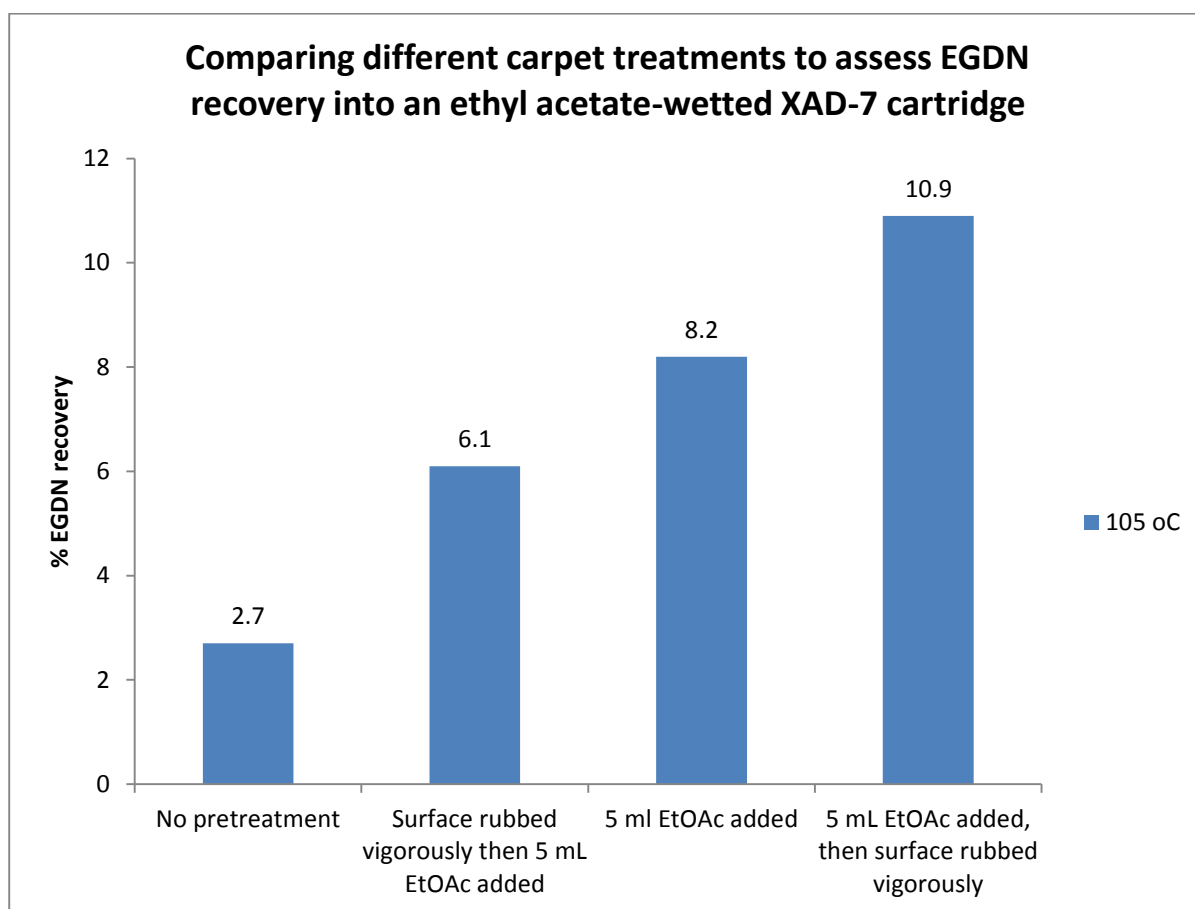

Figure 3: Comparing different carpet treatments for EGDN recoveries from carpet, sampling using an ethyl acetate-wetted XAD-7 cartridge.

It can be seen that the sequence of adding solvent to the carpet surface after spiking, followed by vigorously rubbing the surface before taking a contact heater sample, resulted in the highest EGDN recoveries. It is possible that addition of the ethyl acetate prior to rubbing resulted in any EGDN molecules bound to the carpet becoming desorbed into the ethyl acetate. The action of rubbing the surface with a cocktail stick may then act to further loosen any EGDN from the carpet, with the ethyl acetate acting as a matrix to retain the EGDN, limiting its volatilisation during the rubbing step. Volatilisation of the EGDN may then occur following the application of the heated platen. However,

one point to be borne in mind with such a sampling sequence is that it may not always be apparent exactly where explosives traces are situated on a piece of material or carpet. Therefore, in practice, it may be difficult to implement this optimisation, other than perhaps spraying/misting a large area of the surface of interest with a solvent, gradually rubbing sections of the surface just prior to sampling, and gradually sampling from the bulk of the surface in this manner. Although in principal this sounds quite laborious, it is likely that it would increase the chances of recovering any explosives from a 'difficult' sampling material such as carpet.

TATP recoveries from directly-spiked carpet, leather and denim

TATP detection and quantification was performed using LC-MS/MS, as previous research has shown that the analysis of TATP by GC-MS can cause rapid activation of a GC column.[35] Several LC-MS/MS parameters were optimised in order to enable TATP detection using the available vESI probe, as TATP is more commonly and easily detected using an APCI probe.[35] The optimised conditions were those which gave the highest peak area for the ammonium adduct of TATP. Of the masses monitored using LC-MS/MS, $m/z = 240$ is thought to correspond to the ammonium adduct of TATP ($[TATP+NH_4]^+$), $m/z = 223$ is thought to correspond to the protonated ion of TATP ($[TATP+H]^+$) and $m/z = 74$ is thought to be the monomer of TATP, monoacetone monoperoxide ($[TATP/3]^+$).[9, 35] All TATP experiments involved a 4-minute post-spike wait period, in order for the sampling material to be more representative of a real-life situation, where it is unlikely that residual solvent would be present. Acetonitrile was chosen as a suitable XAD-7 wetting solvent for the cartridges used to capture TATP, due to its compatibility with the chosen LC-MS/MS analysis method.[30, 35] TATP recoveries were trialled from carpet, denim and leather. Two platen temperature sequences were examined – a low temperature to high temperature ramp up (25 °C to 105 °C), or a constant high temperature of 105 °C, to determine the best temperature sequence for TATP recovery. The results are shown in Figure 4.
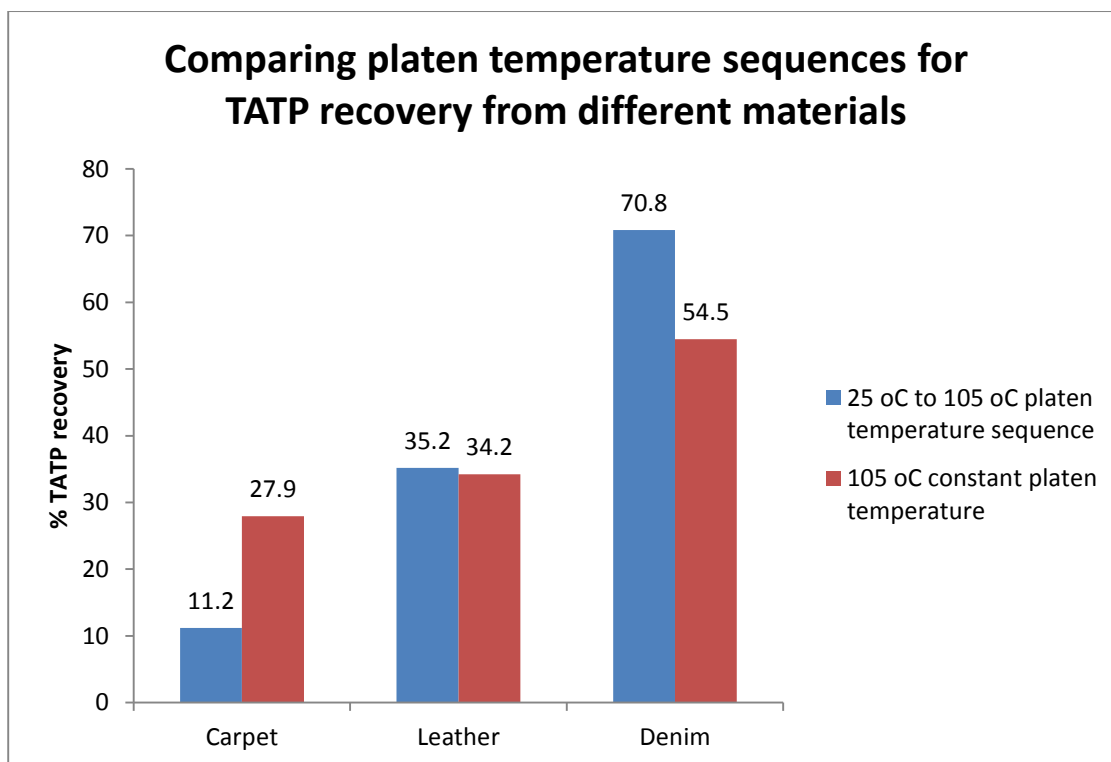
Figure 4: TATP recoveries from fabrics directly spiked with TATP, using two different platen temperature sequences

It can be seen that reasonably good TATP recoveries were obtained from carpet. A significantly higher proportion of TATP was recovered when a constant, high temperature of 105 °C was applied during sampling, rather than a gradual temperature ramp from 25 °C to 105 °C. The use of a high platen temperature for recovery from carpet was also found to be beneficial for EGDN recovery.

The TATP recovery from leather gave very similar recoveries regardless of the starting platen temperature. The recoveries were higher than the analogous TATP recoveries from carpet. Leather can be thought of as dried, treated skin, which is unlikely to have as 'rough' a surface morphology as polypropylene carpet, and as such explosive molecules may not become as deeply embedded within the presenting matrix.

TATP recovery from denim also resulted in high recoveries (71% when the platen temperature began at 25 °C and was ramped to 105 °C, and 55% when the platen was held at a constant temperature of 105 °C). These recoveries suggest that the TATP molecules sit on the surface of the upper cotton fibres, rather than become embedded or entangled to any great extent. It was also noticed that there was very little friction between the platen and the denim during the sampling process, compared to the friction between the platen and a piece of carpet or leather. The denim used was quite thin, and very flexible, which allowed for excellent contact between the platen and the material. It is strongly

suspected that the minimal friction present between the platen and the denim played a major role in the excellent recoveries of the TATP from the denim.

TATP recoveries from vapour jar experiments involving denim, carpet and leather

Vapour jar experiments were performed to explore recoveries following the airborne deposition of TATP onto fabrics. The exact dynamics of the volatilisation process were not known, and as a consequence pieces of fabric were positioned either directly above the spiked pool of TATP solution (termed the 'ceiling' condition) in the vapour jar, or to the side of the spiked pool of TATP (termed the 'wall' condition).

The majority of the vapour jar experiments were performed using denim, as this material had previously been found to be the best surface from which to recover TATP. Recovery from the vapour jar walls and ceiling was assessed to reveal which fabric positioning gave the highest recovery. Different time periods between vapour jar preparation and contact heater sampling were also evaluated. The results are shown in Figure 5.
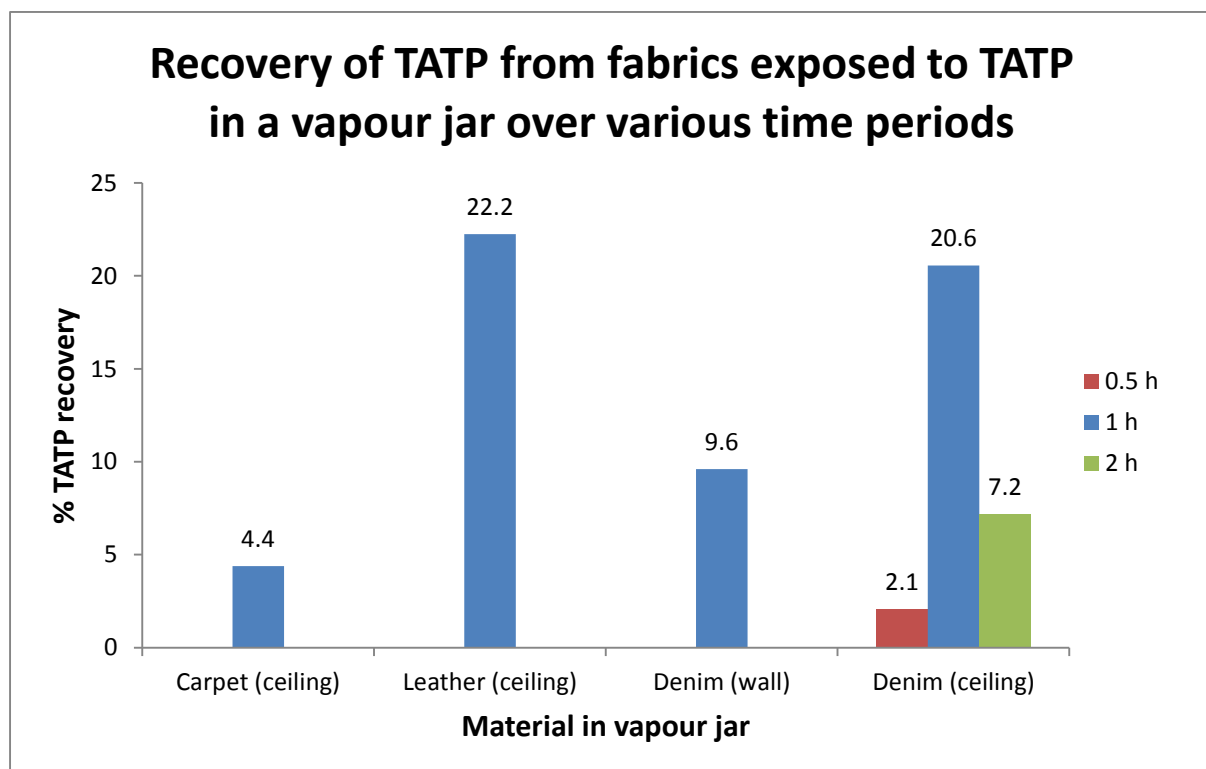

Figure 5: TATP recoveries from vapour jars involving different fabrics, fabric placements and wait times.

It can be seen in Figure 5 that TATP was recovered from the majority of the vapour jar experiments. No TATP was recovered from a denim (ceiling) condition involving a 24 hour wait period. Denim placed on the ceiling of the vapour jar was used across four different time intervals to assess the

optimum time at which contact heater sampling should be performed. This was found to be 1 hour. With this finding, an alternative denim placement was trialled – denim on the wall of the vapour jar, with a 1 hour wait interval. This gave a significantly lower TATP recovery than from the denim placed on the ceiling of the vapour jar for 1 hour. It was therefore concluded that the ceiling of the vapour jar was the best position in which to place fabric during the vapour jar experiments. Analogous vapour jar experiments were also performed using carpet and leather. Low recoveries were obtained from carpet – in agreement with previous findings from direct spiking experiments while the leather vapour jar experiment gave the highest recovery of TATP, at 22.2%.

It should be borne in mind that it is unlikely that any of the fabrics within the vapour jar would 'collect' all of the volatilised TATP as these surfaces only accounted for approximately a quarter of the inner surface area of the jar and it is likely that some of the volatilised TATP would redeposit on the bare glass and ceramic tile regions within the vapour jar, which were not sampled. Thus the recoveries shown in Figure 5 are very promising. Overall, the vapour jar experiments demonstrated that denim, carpet and leather all have surfaces suitable for trapping TATP vapour originating from volatilised TATP. Each of these surfaces should therefore be suitable for taking contact heater samples from, when surfaces suspected of being in contact with, or in close proximity to, TATP are encountered.

Conclusions

The recovery of EGDN and TATP traces was achieved from a variety of surfaces, including difficult sampling surfaces such as carpet, leather and denim. Higher recoveries were recorded using solvent-wetted sampling cartridges than dry sampling cartridges. Reasonable EGDN recoveries were also obtained by sampling directly into a vial of ethyl acetate, without the use of an XAD-7 cartridge. This may provide one avenue of reducing operating costs of the contact heater. TATP-based bell jar experiments gave promising results, with TATP being detected at 0.5 hour, 1 hour and 2 hour timescales post-spiking, from a variety of materials and in reasonable quantities. No TATP could be detected 24 hours after the preparation of a bell jar, so shorter timescales, between 2 hours and 24 hours, should be investigated to try to determine the maximum length of time between exposure and possible recovery.

Acknowledgements

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