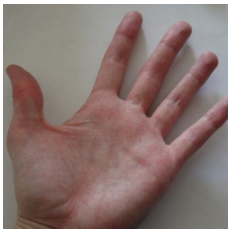
Ignitable Liquid Recovery from Hands

Burgess, K.L, Lamont, N.A and Gwinnett C*
Forensic and Crime Science Department, Staffordshire University



1. Introduction to Study

There is currently no set protocol for hand sampling during an arson investigation, although the retrieval of ignitable liquid has the potential to be a key piece of corroborative evidence; therefore, the requirement for an effective sampling technique is required. An evaluation was undertaken between Solid Phase Micro Extraction (SPME) fibres, activated charcoal, swabbing, glass beads and silly putty, a polydimethylsiloxane (PDMS). This article intends to evaluate and compare the five techniques for their capabilities in recovering four target components, benzene, toluene, p-xylene and 1,3,5-trimethylbenzene, present in ignitable liquids. The four target components are highly volatile and could be expected to easily evaporate between deposition and recovery. The ability of the methods to sufficiently recover these components, and to retain them after recovery, is a factor this article will consider when evaluating the methods.

2. Background

When a liquid is poured onto a particular area there is a possibility for the liquid to transfer onto surrounding objects. The possibility for transfer increases when the pouring of the liquid is in a disorderly manner, such as in a crime scenario. Transfer of ignitable liquids to a suspect's hands has been reported during arson investigation cases, although the persistence of the ignitable liquid is low due to the liquid's volatile nature. It is reported that approximately 90% of liquid components are lost within the first 30 minutes after transfer (Montani et al. 2010). Darrer et al (2008) undertook a study to assess the persistence of ignitable liquids on hands, gaining results that supported the expectation of a considerable loss of sample during the first 30 minutes after deposition. However, traces of ignitable liquids have been reported to remain on the surface of the hands for up to 4 hours after initial deposition. The time frame between deposition, or transfer, and sample recovery varies between individual cases, with environmental factors affecting the speed at which evaporation of the ignitable liquid occurs (Darrer et al., 2008). Other factors, for example, washing of the hands, also affects the amount of remaining ignitable liquid.

Methods utilized for the recovery of ignitable liquids from debris items, collected from crime scenes, involve the use of headspace sampling or solvent extraction; these extraction techniques allow the sample to be removed from the debris and subsequently injected into the chosen analytical equipment. The extraction techniques utilized for the recovery of ignitable liquids from hands are the same as those used for debris recovery, although additional steps are required (Williams, 2007). The headspace technique involves the ignitable liquid components vaporizing to form a headspace above the sample that should be a representation of any residues present. There is a possibility for bias in the recovered sample based on the strength of Van Der Waals (VDW) forces, where components with stronger VDW forces will displace those with weaker forces (Bogusz, 2011). Solvent extraction involves washing the recovered medium either once with a large volume of a suitable solvent, such as dichloromethane (DCM), or multiple times of lower volumes (Harris & Wheeler, 2003).

The use of different sampling methods in the area of arson investigation has been discussed in literature. Lentini (2012) and Newman et al. (1996) discuss the use of swabbing and activated charcoal in the recovery of possible ignitable liquids from abnormal surfaces and fire debris. Bernier et al (1999) determined that glass beads can be utilized for the recovery of volatile compounds present in human odour. The use of activated charcoal, glass beads and polydimethylsiloxane (PDMS) putty for ignitable liquid recovery from skin, is currently undocumented.

3. Experimental

All of the recovery methods tested in this study utilized nitrile gloves to recover the ignitable liquid petrol from; this created a safe alternative to actual skin. All methods followed the same overall process, seen in figure 1, although some methods involved the use of multiple extraction techniques, where possible, in an attempt to maximise the amount of substrate recovered. For all techniques, three repeats were carried out.

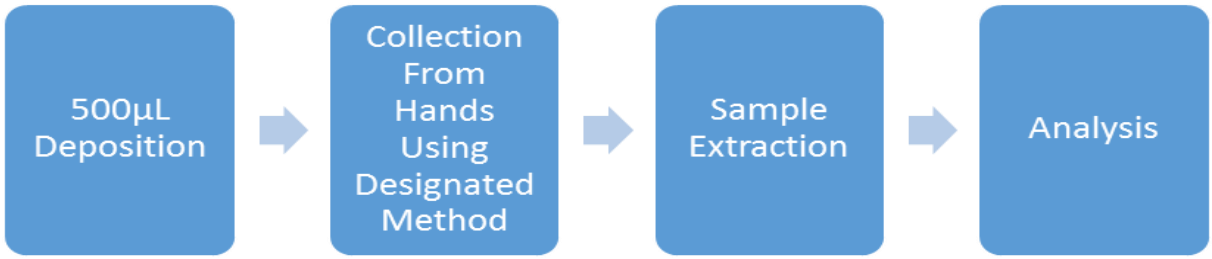


Figure 1- Outline for Each Tested Method

3.1 SPME Fibres

Solid Phase Micro Extraction (SPME) fibres were used to recover ignitable liquids from the headspace formed above two different materials; the materials tested for the SPME fibre method were filter paper and nitrile gloves. The filter paper was utilized to demonstrate the absorption likely to occur with ignitable liquids once they have been in contact with skin for a length of time; the nitrile gloves were utilized to demonstrate the evaporation likely to occur with ignitable liquids after deposition. 500µL of petrol was pipetted onto the material before being placed inside a nylon bag at room temperature for 30 minutes. The SPME fibre was secured inside the nylon bag, using string to secure the swan neck seal, and exposed to the headspace for 30 minutes prior to injection into the GC port.

3.2 Swabbing

500µL of petrol was pipetted onto gloved hands; the swab was wiped across the surface five times and the placed in a nylon bag. The headspace was allowed to form in an oven at 60°c for 30 minutes. The headspace was then sampled using a 2.5mL GC syringe and manually injected. To be as realistic as possible, three fake hands were created using Dent Stone, which were gloved during the deposition and swabbing.

An alternative approach involved 500µL of petrol being pipetted onto the gloved hands; 1mL of pentane was deposited onto the cotton swab before being rubbed across the gloved surface for approximately 30 seconds. The tip of the swab was removed and solvent extraction was utilized as the extraction method. The tip was combined with 1mL of pentane and agitated before removing the solvent. The process of applying 1mL of pentane to the swab tip, combined with the subsequent removal, was repeated a further three times to create one sample. This process was undertaken to produce a total of three samples for the wet swabbing method. A dry swabbing approach was tested by removing the pre-wetting of the swab stage; the same extraction method was then undertaken. Evaporation, using a stream of nitrogen, occurred for all of the samples to reduce the volume to below 1mL; a further 2mL of pentane was added prior to analysis.

3.3 Activated Charcoal

Samples were prepared utilizing 500µL of petrol pipetted onto gloved hands; the activated charcoal rod was rubbed across the surface, for approximately 30 seconds, before being placed into a nylon bag and heat sealed to approximately 15cm x 15cm. A headspace was allowed to form in an oven at 60°c for 30 minutes, prior to injection.

Solvent extraction, both single and multiple extractions, involved the use of 500µL of petrol pipetted onto gloved hands; the activated charcoal rod was rubbed across the surface, for approximately 30 seconds. The single extraction utilized 1mL of Dichloromethane (DCM) which was agitated in the tube; this was then followed by the same evaporation and further addition procedure that was stated in section 3.2. Multiple extractions used a volume of 200µL DCM. The wash and removal stage, utilized for swabbing, was completed five times.

A sample was also extracted using the soxhlet technique; this is where the 500µL sample was deposited directly onto the charcoal's surface, using 250 mL of pentane and a 4-hour extraction.

3.4 Glass Beads

Solvent extraction was completed with two different solvents, pentane and DCM. 500µL of petrol was pipetted onto gloved hands before ten beads, per sample, were rubbed across the gloved surface. The solvent extraction was completed as stated in section 3.2, utilizing five extractions of 500µL; this process was undertaken for both of the solvents, creating three DCM samples and one pentane sample

3.5 PDMS Putty

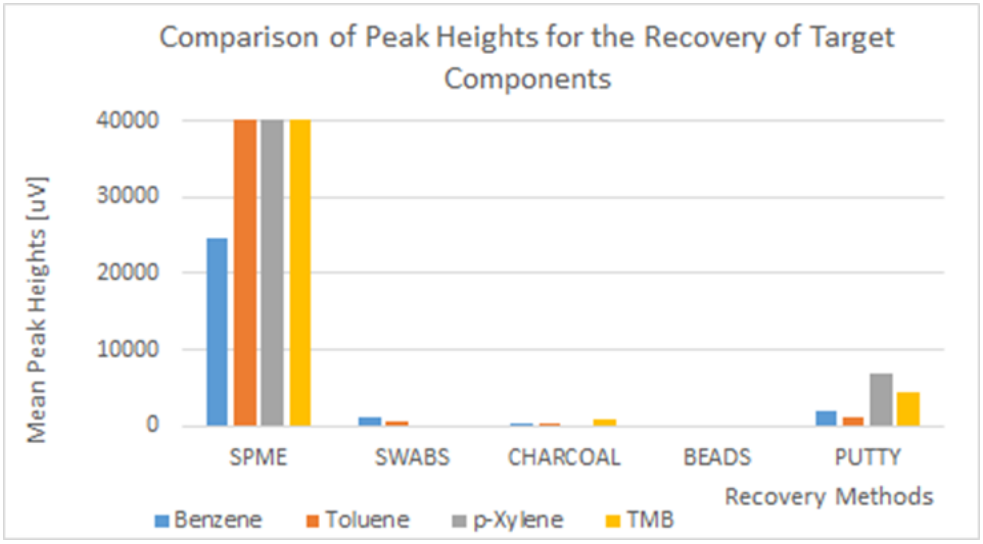
500µL of petrol was pipetted onto gloved hands; the putty was rubbed across the surface for approximately 30 seconds, placed in a nylon bag with reduced dimensions to increase the concentration of vaporised liquids in each sample, approximately 15 cm x 15 cm, and heated at 60°c for 30 minutes. Various heating times were utilized for the samples: 30 minutes, 1 hour, 2 hours and 3 hours at 60°c

4. Results and Discussion

Figure 2 displays the mean peak heights results for the following techniques: SPME fibres, swabbing using the thermal desorption technique, activated charcoal using the thermal desorption technique, glass beads and PDMS putty. The results for the alternative extraction techniques used for swabbing (use of 1mL of pentane and dry swabbing technique) and activated charcoal (soxhlet technique) contained no peaks that could be identified as any of the four target components. The chromatograms gained for these alternative techniques displayed a number of less volatile components, occurring beyond the 10 minute point. This could suggest these alternative extraction techniques were not specific to extracting highly volatile components from the swab and charcoal surfaces. Additionally, some chromatograms displayed peaks

peaks that were below the peak detection threshold for the component response, of 5.07mV; therefore, not only was there no corresponding peak height information available, but these peaks could not be eliminated as relating to baseline noise, rather than pertaining to the target components.

Figure 2- Mean Peak Heights (n=3) for the Recovered Targets Components for Each Method



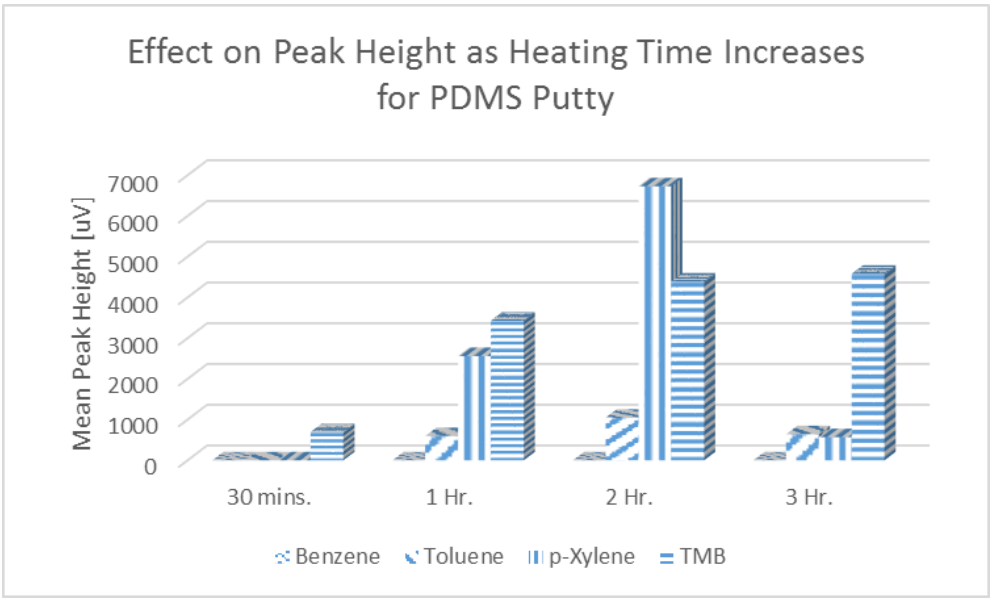


Figure 3- Mean Peak Height (n = 3) of components with different heating times for the PDMS putty method.

The results indicate that SPME fibres were the most efficient method for ignitable liquid recovery from skin alternatives, however the ability of this method to effectively recover from skin is, in this research, untested. The materials chosen for this experimentation were utilized as a replacement for human skin with the aim of testing part of the method suggested by Almirall et al. (2000); the suggested method in this study involved the hands being sealed within a nylon bag and an SPME fibre being utilized to sample the headspace formed from any residues present on the hands. This research tested the applicability of this method by depositing the petrol onto different materials, used as a replacement for human skin, and assessing the capabilities of SPME fibres to recover the target components, present in ignitable liquid residues.

PDMS putty was also successful in recovering the target components however; the peak heights for the recovered components were much lower than that achieved for SPME fibres. The putty approach identified a possible correlation between heating time and peak height. This correlation established that increasing the heating time, increased the peak heights observed for the target components. However, after the

2-hour heating time, a slight decrease in the peak heights was observed, this could be a result of the fixed temperature utilized in the experiments. Sugawara and Law (2001) recognize that for a fixed temperature there is a maximum response that can be achieved. The authors define this point, at which the maximum response is achieved, as being determined by the decrease in response following varied heating times; this characteristic trend occurred in the results obtained for the PDMS putty. Therefore, this suggests that with further investigation, a refined, effective technique may be achieved through experimentation involving varied temperatures and heating times.

Glass beads, activated charcoal and swabbing, each proved to only be able to extract small amounts of sample, concluding that these approaches are ineffective for the recovery of ignitable liquids. This in part may be due to the potential for evaporation to occur from the surface and the inability for adsorption and desorption to occur effectively on the solid surfaces.

4.1 Advantages and Disadvantages of the Recovery Techniques Tested

Although effectiveness of retrieval is paramount in deciding upon the recovery method to use, there are other factors that should be considered. Figure 5 outlines the advantages and disadvantages of each of the tested recovery methods.

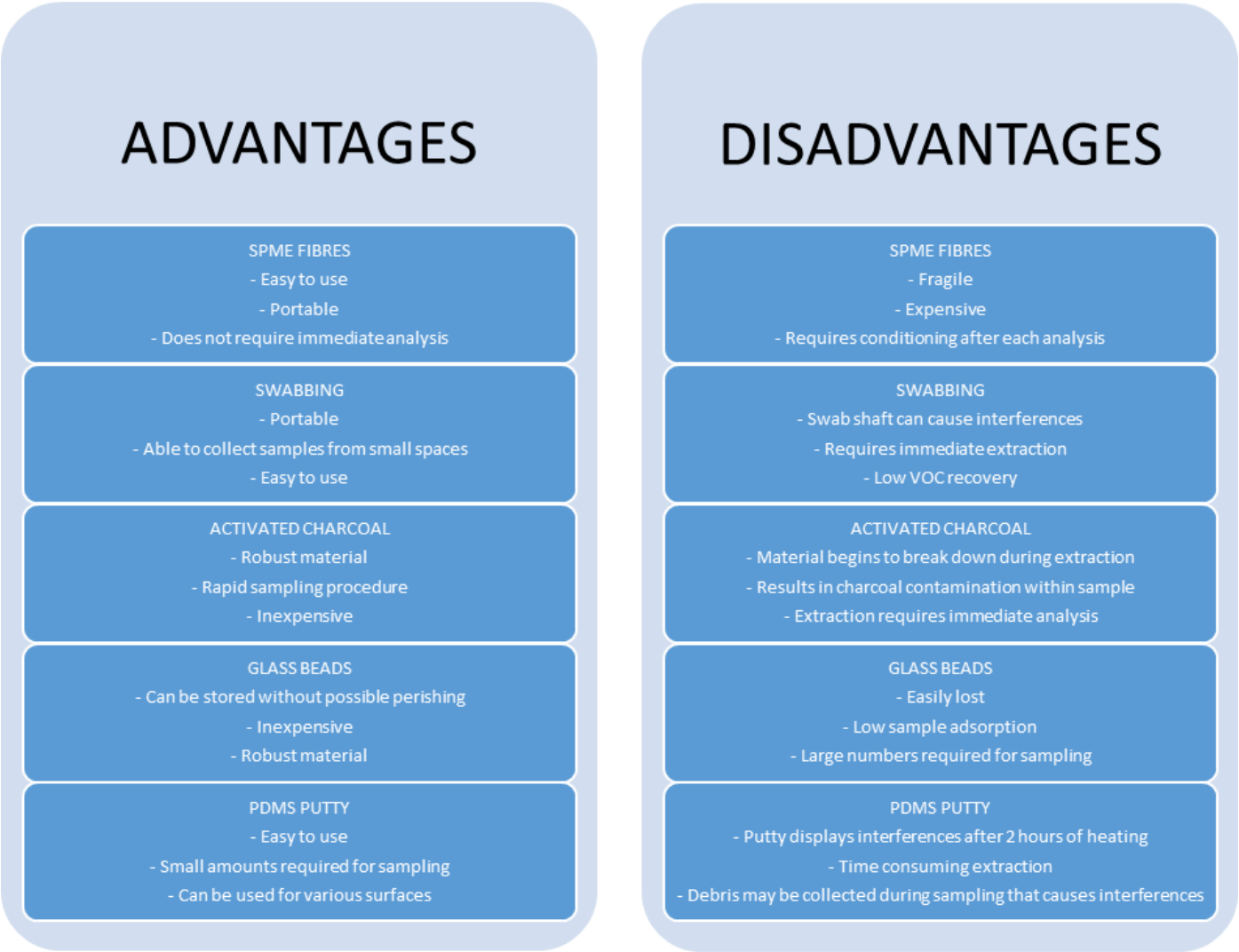


Figure 4- Advantages and Disadvantages of the Tested Recovery Methods

5. Conclusion

The aim of this research was to evaluate different recovery methods for the retrieval of ignitable liquids from simulated hands, using both known and previously unused methods. Solid Phase Micro Extraction (SPME) fibres concluded to be the most efficient recovery technique for retrieving the four target components in this study, albeit the most expensive method in comparison to the other four tested. Polydimethylsiloxane (PDMS) putty retrieved less of the four components than SPME fibres, but exceeded the recovery of target components when compared to swabbing, activated charcoal and glass beads techniques. Although PDMS putty is a previously unused method for arson investigation the capabilities of the method, with adaption and optimization, are applicable to this field. PDMS putty is considerably cheaper than SPME fibres, costing approximately £4 in comparison to £150-300 for a pack of 3 SPME fibres. Swabbing, activated charcoal and glass beads can be concluded as being ineffective in the recovery of ignitable liquids and therefore should not be used in casework without further research.

6. References

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* kurstielburgess@gmail.com