EVALUATION OF IGNITABLE LIQUID RESIDUE ADSORPTION ON MULTIPLE ACTIVATED CARBON DEVICES FOR FORENSIC FIRE DEBRIS ANALYSIS

SYAMILAH BINTI ABDUL RAHMAN

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by

SYAMILAH BINTI ABDUL RAHMAN

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LIST OF ABBREVIATIONS

IL	Ignitable Liquid
ILR	Ignitable Liquid Residue
FRDM	Fire and Rescue Department of Malaysia
AC	Activated Carbon
GC-MS	Gas Chromatography-Mass Spectrometry
VOC	Volatile Organic Compound
UV	Ultraviolet
PID	Photo Ionisation Detector
E-Nose	Electronic Nose
NSW	New South Wales
UK	United Kingdom
ILA	Ignitable Liquid Absorbent
PHRED	Passive Headspace Residue Extraction Device
RM	Ringgit Malaysia
ACS	Activated Carbon Strip
ACP	Activated Carbon Pellet
ACC	Activated Carbon Cloth
SPME	Solid-Phase Microextraction
HS	Headspace

CNT	Carbon Nanotube-assisted
DVB	Divinylbenzene
CAR	Carboxen
PDMS	Polydimethylsiloxane
ASTM	American Society for Testing Materials
GC	Gas Chromatography
TOFMS	Time-of-Flight Mass Spectrometry
DART-MS	Direct Analysis in Real-time Mass Spectrometry
TM	Trademark
NIOSH	National Institute of Occupational Safety and Health
TIC	Total Ion Chromatogram
DCM	Dichloromethane
TCE	Tetrachloroethylene
NIST	National Institute of Standards and Technology
SEM	Scanning Electron Microscope
FESEM	Field-Emission Scanning Electron Microscopy
EDX	Energy-Dispersive X-ray Spectroscopy
C	Carbon
O	Oxygen
Al	Aluminium

Cl	Chlorine
Zn	Zinc
K	Potassium
Si	Silicon
Ca	Calcium
Ti	Titanium
Cu	Copper
BET	Brunauer-Emmett-Teller
NCFS	National Centre for Forensic Science

LIST OF SYMBOLS

ppm	part per million
ppb	part par billion
>	more than
%	percent
°C	degree Celcius
K	Kelvin
µL	microlitre
mL	millilitre
m	metre
nm	nanometre
µm	micrometre
mm	millimetre
cm	centimetre
min	minute
g	gram
m^2	square metre
cm^2	cubic centimetre

PENILAIAN PENJERAPAN SISA CECAIR MUDAH NYALA PADA PELBAGAI PERANTI KARBON AKTIF UNTUK ANALISIS BAHAN SISA KEBAKARAN FORENSIK

ABSTRAK

Penyiasatan kebakaran memainkan peranan penting dalam mengungkapkan punca dan asal-usul kejadian kebakaran, yang penting untuk pentadbiran keadilan dan pencegahan kebakaran. Pusat kepada penyiasatan ini adalah analisis serpihan kebakaran, yang melibatkan pengesanan dan pengenalan bahan cecair mudah nyala (CMN). Amalan semasa menggunakan pelbagai kaedah untuk pengumpulan CMN, termasuk swab kapas steril dan jalur karbon aktif. Walau bagaimanapun, kaedah ini mempunyai kekurangan seperti pemulihan CMN yang tidak lengkap dan kos pembelian yang tinggi. Kajian ini mengatasi cabaran ini dengan menilai secara menyeluruh pelbagai peranti karbon aktif (KA) sebagai alternatif potensi untuk penyerapan CMN. Beberapa faktor seperti masa pengambilan sampel dan permukaan pengambilan sampel dimanipulasi untuk menilai prestasi peranti KA. Dengan melakukan ini, ia bertujuan untuk mengenal pasti peranti KA yang paling efisien dan berkos rendah untuk pengumpulan sisa CMN, memberikan sumbangan kepada peningkatan analisis sisa kebakaran forensik. Dalam kalangan peranti KA yang dinilai, kain KA kelihatan menonjol dengan prestasi yang luar biasa. Pencirian fizikal mendedahkan bahawa kain KA mempunyai kawasan permukaan tertinggi, yang menghasilkan kapasiti penyerapan yang luar biasa. Selain itu, analisis GC-MS telah membuktikan keberkesanan luar biasa kain KA dalam penyerapan sisa CMN, terutamanya pada permukaan berongga seperti kayu. Selain itu, hasil analisis GC-MS menunjukkan keupayaan konsisten kain KA untuk menyerap sebatian organik meruap (SOM) petrol dalam pelbagai tempoh pengambilan sampel, bermula dari 0.5 hingga 48 jam. Penemuan ini

menggariskan kain KA sebagai calon yang berpotensi untuk penyerapan sisa CMN dalam analisis sisa kebakaran forensik, menawarkan kawasan permukaan yang besar dan kebolehan menyesuaikan diri dengan pelbagai syarat pengambilan sampel yang berbeza.

EVALUATION OF IGNITABLE LIQUID RESIDUE ADSORPTION ON MULTIPLE ACTIVATED CARBON DEVICES FOR FORENSIC FIRE DEBRIS ANALYSIS

ABSTRACT

Fire investigations play a pivotal role in uncovering the causes and origins of fire incidents, vital for the administration of justice and fire prevention. Central to these investigations is the analysis of fire debris, which involves detecting and identifying ignitable liquid residues (ILRs). Current practices employ various methods for ILR collection, including sterile cotton swabs and activated carbon strips. However, these methods present limitations, such as incomplete ILR recovery and high acquisition costs. This study addresses these challenges by comprehensively evaluating multiple activated carbon (AC) devices as potential alternatives for ILR adsorption. Several factors such as sampling time and sampling surface were manipulated to assess the performance of the AC devices. By doing so, it aims to identify the most efficient and cost-effective AC device for ILR collection, contributing to the enhancement of forensic fire debris analysis. Among the evaluated AC devices, AC cloth stands out due to its remarkable performance. Physical characterization revealed that AC cloth possesses the highest surface area, which results in an exceptional adsorption capacity. Furthermore, GC-MS analysis demonstrated its remarkable efficacy in ILR adsorption, particularly on porous surfaces like wood. Additionally, the results of GC-MS analysis highlighted AC cloth's consistent ability to adsorb volatile organic compounds (VOCs) of gasoline across various sampling durations, ranging from 0.5 to 48 hours. These findings underscore AC cloth as a promising candidate for ILR adsorption in forensic fire debris analysis, offering high surface area and versatility across different sampling conditions.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Fire investigation and fire debris analysis are integral components of forensic science, working in tandem to unravel the mysteries surrounding fires. Fire investigation begins at the scene, where experts meticulously examine the aftermath to ascertain the fire's origin, cause, and other crucial details. Concurrently, fire debris analysis employs specialized techniques to identify ignitable liquid residues (ILRs) in samples collected from the scene, shedding light on whether accelerants were used and offering pivotal evidence. Together, these disciplines bridge the gap between the physical evidence left by fires and the pursuit of truth in fire-related incidents, making them indispensable in both criminal and investigative contexts.

Fire investigation involves the examination of fire-related incidents. It begins after firefighters have extinguished the fire and the location is safe to enter. To identify the fire's origin and subsequently determine the cause, the investigation will involve a thorough examination of the damaged area. However, the investigator must be well-versed in fire chemistry, behaviour, and consequences to thoroughly inspect and assess a fire scene (Daeid, 2004). Investigators can identify whether the fire was the result of an intentional act by examining the fire scenes for signs of ignitable liquids (Fabritius, et al., 2018).

In many instances of arson, fires are started or escalated using accelerants comprised of ignitable liquids (ILs), so it is crucial to find any ILR at the scene of the fire (Ferreiro-González, et al., 2016). When arson is suspected, recognising the type of accelerant is incredibly helpful information for investigators. Petroleum-based products like diesel and gasoline are the most frequently used ILs because they are accessible and easy to ignite. The detection and analysis of ILRs are highly valuable in determining both the cause and origin of a fire, helping investigators ascertain whether the fire was accidental or the result of a deliberate act.

Finding traces of ILR at fire scenes may be a helpful first step in a fire investigation, and in particular, it can help with sample collection for fire debris analysis. ILR scene detectors are presumptive in nature and are limited in their capacity to definitively identify ILR unless a proper portable gas chromatograph-mass spectrometer is carried to the scene. There will be some false negatives and false positives with any detection method employed at a fire scene since they are all presumptive testing for ILR (Stauffer, Dolan, & Newman, 2007). Nonetheless, these presumptive methods are helpful in assisting the investigator in choosing high-quality samples for the detection and identification of ILR.

In order to recover any IL used to start the fire, investigators typically search for the origin of the fire by analysing the fire debris and making a scene evaluation from fire effect and fire pattern. Before any sample is sent to the laboratory for analysis, the method of collection varies depending on the nature of the scene. Usually, the evidence collected for the determination of ILR is a sample removed from a larger object and sometimes, the entire item may be collected. It is also possible to leave the debris at the fire scene and merely collect the ILR depending on the nature of the substrate. The collection methods are categorised into two different sampling processes which are direct and indirect (Stauffer, Dolan, & Newman, 2007).

Most fire debris is collected by direct sampling and sent to the crime laboratory in its original condition such as fabric, carpet, or furniture. However, when indirect sampling becomes the only viable method, IL adsorbent devices are invaluable for collecting ILR from fire scenes, particularly when the substrate is a concrete wall or floor (Stauffer, Dolan, & Newman, 2007). Concrete walls and floors often play a crucial role in the structural integrity of buildings, and altering or damaging them during the evidence-collection process may not be advisable. Therefore, indirect sampling using IL adsorbent devices allows investigators to obtain valuable evidence without causing harm or structural disruption. The devices can be strategically placed on surfaces suspected of having come into contact with accelerants. This targeted approach minimizes the disturbance of the scene and ensures that samples are collected from areas with the highest likelihood of containing ILRs.

IL adsorbent devices are specialized tools employed to capture and preserve volatile substances, including accelerants and ILRs, at fire scenes. These devices play a pivotal role in the meticulous examination of fire debris, helping investigators determine whether accelerants were used, the type of accelerant employed, and where it was applied. Examples of the adsorbent devices are cotton swabs, activated carbon strips and SPME fibres. Cotton swabs are frequently utilized as adsorbent devices for the collection of ILRs, especially when a surface exhibits a relatively high concentration of ignitable liquid (Burda, et al., 2016). Significant strides have been achieved in the field of IL adsorbent devices, resulting in remarkable improvements in their design, efficiency, and versatility, with particular emphasis on the utilization of activated carbon materials.

Activated carbon (AC) is a material consisting of porous carbon that has been processed to have small, low-volume pores that increase the surface area available for adsorption or chemical reaction. At the international level of forensic fire investigation, activated carbon material like activated carbon strips has been used in laboratory settings as an adsorption medium in extracting ignitable liquid residue from the fire debris sample that was obtained from the fire scene (Fabritius, et al., 2018). To explore a more cost-effective approach, tests have been conducted on both activated carbon cloth and activated carbon pellets to evaluate their effectiveness in headspace extraction of ignitable liquid residues (Carmona, et al., 2022; Ahya, 2018; Sandercock, 2016). Fortunately, both materials have demonstrated their efficacy as reliable ILR adsorbent devices.

After the ILRs have been collected by the adsorbent devices, they are carefully packaged and transported to the laboratory for in-depth analysis. Subsequently, the analysis commences at the laboratory when the samples are delivered by the scene investigator (Stauffer, Dolan, & Newman, 2007). Once the ILRs are extracted from the device and in a suitable form, instrumental analysis will be conducted. Gas chromatography-mass spectrometry (GC-MS) is primarily used as an analytical technique for the identification of IL and ILR from fire debris and the guidelines are provided by the American Society for Testing and Materials (ASTM) E1618 standard (Ferreiro-González, et al., 2016).

Based on previous studies, the performance of AC materials has been assessed primarily for its use in headspace extraction of ILR, but there has been limited evaluation of its effectiveness for sampling of ILR at fire scenes. Therefore, further research is required to explore and identify suitable AC materials for effective ILR sampling. This study assesses the performance of the selected AC materials in capturing and retaining ILR, evaluating their effectiveness across two different parameters: sampling time and sampling surface.

1.2 Problem Statement

Forensic fire debris analysis is integral to fire investigations, aiding in ascertaining fire origin, determining its cause, and identifying potential arson involvement. At the core of this analysis lies the detection and characterization of ignitable liquid residues found at fire scenes. The conventional methods currently employed in this process include cotton swabs and activated carbon strips for ILR collection.

The Fire and Rescue Department of Malaysia (FRDM), which has traditionally utilized sterile cotton swabs for collecting ILRs from fire scenes, has reported that this method has shown limited efficiency, occasionally failing to definitively identify ILR, despite yielding positive results with colourimetric tubes. While activated carbon strips have surfaced as potential alternatives for ILR sampling, their substantial procurement costs pose significant economic challenges for laboratory operations.

Consequently, an urgent need exists to explore alternative ILR adsorption materials and devices that can offer enhanced cost-effectiveness, efficiency, and improved ILR recovery rates. This pressing issue necessitates a comprehensive evaluation of multiple activated carbon devices for their potential to serve as more efficient and economically viable alternatives for ILR adsorption in forensic fire debris analysis.

1.3 Research Questions

The research questions of this study are listed below.

a) What are the physical characteristics of sterile cotton swabs and AC devices when used as adsorption materials?

b) How does the sampling time affect the effectiveness of sterile cotton swabs and AC devices in adsorbing ILRs?

c) What influence do varying sampling surfaces have on the performance of sterile cotton swabs and AC devices in capturing ILRs?

d) Which specific AC device demonstrates the highest effectiveness in adsorbing ILRs?

1.4 Research Objectives

1.4.1 General Objective

This study emphasizes the goal of enhancing the detection and identification of ignitable liquid residues in forensic fire debris analysis. This will be achieved by evaluating a range of AC materials as potential replacements for cotton swabs in ILR sampling.

1.4.2 Specific Objectives

a) To physically characterise sterile cotton swabs and AC devices as adsorption materials.

b) To assess the efficacy of sterile cotton swabs and AC devices in capturing ILRs at different sampling times and surfaces.

c) To determine which specific AC device exhibits the highest effectiveness in adsorbing ILRs.

1.5 Significance of Study

Forensic fire debris analysis is a multidisciplinary field that hinges on the synergy between chemistry, materials science, and criminal investigation methodologies. The effective analysis of ignitable liquid residues depends on robust techniques for their extraction and concentration. In this context, activated carbon, renowned for its high porosity and adsorption capabilities, has become a cornerstone of forensic science applications. Its properties make it adept at capturing trace amounts of volatile organic compounds (VOCs), including ILRs, from complex sampling matrices like concrete walls and floors. However, despite its widespread use, the optimal performance of various AC devices in extracting ILRs from these substrates remains an ongoing area of exploration.

This study plays a critical role in assessing the suitability of AC devices as adsorbents for indirect ILR sampling at fire scenes. The comparative evaluation of these devices' adsorption performance is pivotal in identifying the most effective adsorbent among them. Understanding the adsorption capabilities of AC devices as opposed to sterile cotton swabs holds the potential to offer the FRDM a cost-effective and efficient alternative for ILR sampling at fire scenes. This research can introduce a new avenue for ILR collection with optimized cost-efficiency. Furthermore, the examination of various sampling times and surfaces will provide valuable insights, suggesting the optimal conditions for the effective operation of these devices, further enhancing their applicability in forensic fire debris analysis.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Fire and Rescue Department of Malaysia (FRDM) is a government organisation in Malaysia that is in charge of technical rescue and firefighting. From 2019 to 2021, the Fire Investigation Division of FRDM recorded a total of 31,359 fire cases involving structures and vehicles across the country. This Division has also managed to record a fire-cause identification rate of 99.96 % in 2021, 99.99 % in 2020, and 99.97 % in 2019 where the cause of the fire could not be ascertained with only four, one and two cases respectively (FRDM, 2021; FRDM, 2020; FRDM, 2019). Extensive experience and knowledge in the field of fire investigation have helped and positively impacted the Department to reduce the number of fire cases whose cause cannot be proven (FRDM, 2021).

Such an example is seen in the recent fire case whereby in October 2021, a fire razed 75 houses and 11 shops in Kampung Baru Karak, Pahang. Fortunately, it was reported that about 150 victims who were occupying the premises managed to vacate in time with no deaths or injuries involved (Alagesh, 2021). There were claims that the cause of the fire might be wiring issues as the buildings were between 30 to 40 years old. However, the investigations were conducted thoroughly looking into all aspects of the scene which takes into consideration whether the fire was due to an accident, natural or incendiary. The possibility of the cause of the fire incident was determined as an accidental fire which may be due to a short circuit (Alagesh, 2021).

Fire investigations play a crucial role in preventing future catastrophes by identifying the causes and contributing factors of fires and implementing measures to mitigate the risks. By thoroughly analysing fire incidents, investigators can gather valuable information that helps identify potential hazards, improve safety protocols, and establish preventive measures to enhance fire safety (Stauffer, Dolan, & Newman, 2007). In the wake of the fire incident that occurred in 2021, fire debris analysis assumes a pivotal role in fire investigations. All collected fire debris, along with wiring evidence and other samples, underwent thorough analysis. This meticulous examination remained in progress until the conclusive determination of the fire's origin and cause.

Over the years, significant advancements have been made in the field of chemical analysis, encompassing not only improved techniques and methodologies for the analysis of fire debris but also innovations in the methods of screening, collection, extraction, and analysis of ignitable liquid residues. These advancements have collectively empowered investigators to extract more accurate and reliable information from fire scenes. These proactive measures have been undertaken to prevent arson cases where fire causes remain unidentified and unsolved.

2.2 Screening Method

A screening method for ignitable liquid residues refers to the use of specialized tools or techniques to detect the presence of ILR quickly and preliminarily at fire scenes. These methods are designed to provide initial indications or alerts to the investigators for the possible presence of accelerants or flammable substances commonly associated with arson cases. Screening methods are typically rapid and relatively simple, aiming to identify areas or materials that require further investigation or analysis. Examples include the deployment of canines trained to detect specific odours associated with ILs, the use of UV light to reveal fluorescent traces, portable ionization detectors to sense volatile compounds, and electronic noses, which analyse the chemical signatures of odours to identify the presence of ILR. The purpose of these screening methods is to quickly narrow down the areas or materials of interest, allowing investigators to focus their efforts on collecting and analysing samples that are most likely to contain crucial evidence related to the cause and origin of the fire.

2.2.1 Canines

O'Hagan and Ellis (2021) have reported the utilisation of canine detection teams in aiding the sampling process during fire investigations, as depicted in Figure 2.1. One of the key advantages of using canines is their highly developed sense of smell, which is significantly more sensitive than that of humans. They reported that canines can detect trace quantities of ignitable liquids, even as low as 0.1 parts per million (ppm) and are more efficient and faster in searching an area compared to an investigator. Thus, less manpower is required to accomplish a comprehensive examination because canines can identify samples that need to be recovered for laboratory examination, minimising the speculative process of sample collection (O'Hagan & Ellis, 2021).

However, the training process for detection canines is extensive and can be costly. It involves specialized trainers, training facilities, equipment, maintenance, and care for the canines. The cost of acquiring and training a detection canine can vary depending on factors such as the specific training program, the breed of the dog, and the desired level of proficiency. Additionally, there are ongoing expenses associated with the care, feeding, and veterinary needs of the canines throughout their operational lifespan. Ultimately, the decision to invest in training and utilizing canines will depend on the specific needs, resources, and priorities of the organization or agency involved (O'Hagan & Ellis, 2021).

Figure 2.1 Accelerant detection canine

2.2.2 Ultraviolet (UV) Light

Ljungkvist and Thomsen (2019) have reported that UV light has been used for pouring pattern identification in fire investigation because of its simplicity, fast, and non-destructive nature. Figure 2.2 displays an image from their case study where the floor is illuminated with UV light that shows the presence of ILR. Fluorescence techniques are effective in fire investigations as they can complement sampling and liquid pattern analysis. The detection of fluorophores in fire investigations is dependent on the product and type of UV light used. Besides, fluorescence techniques can be used with canines in fire investigations as canines can quickly sweep the scene and indicate areas where ignitable liquids may be present. A fluorescence camera is then used to identify the exact location of potential accelerants, which fluoresce under specific light wavelengths. Then, fire debris is collected from these areas for further laboratory testing to gather evidence.

Figure 2.2 Floor illuminated with UV Light

According to Ljungkvist and Thomsen (2019), the fluorescence technique in fire investigations has limitations that investigators should be aware of. These include the need for a dark screening environment, a small distance between the detector and sample, the potential overshadowing of weak fluorescence by background materials, the possibility of misinterpretation due to reflected light, and the increase in fluorescence caused by carbon monoxide production during combustion (Ljungkvist & Thomsen, 2019). Investigators need to consider these limitations and exercise caution when using fluorescence techniques.

2.2.3 Photo Ionisation Detector

O'Hagan and Ellis (2021) reviewed the portable photo ionisation detector (PID) that has been commonly used in post-fire investigation to detect volatile organic compounds (VOCs). Its compact and portable design allows for easy field investigation. The PID works by ionizing

VOCs in the air and measuring the resulting electrical current. This allows investigators to quickly assess VOC levels in different areas of a fire scene. PIDs are non-destructive and provide valuable information for determining the extent of the fire and identifying ignitable liquids at the fire scene.

PID can be utilised to detect volatile organic molecules in soil, sediments, water, and air. Additionally, PID is capable of detecting accelerants with concentrations ranging from parts per million (ppm) to parts per billion (ppb), providing a simple and accurate detection method. It can help minimize false-positive results caused by pyrolysis, compared to canines (O'Hagan & Ellis, 2021). However, there are limitations to its application such as the PID sensitivity can be affected by high humidity levels (>70%), leading to decreased instrument sensitivity and requiring frequent re-calibration (O'Hagan & Ellis, 2021).

2.2.4 Electronic Nose (E-Nose)

E-nose may be utilised for analysing different gas components using a sensing approach comparable to the human olfactory system. The E-nose system is made up of gas sensors, signal processing components, and pattern identification software. It aims to imitate odour perception, processing, and judgement in human and animal olfactory organs. In the field of fire safety, a group of researchers have developed an E-nose that effectively identified four industrial gases: carbon dioxide, methane, ammonia, and volatile organic compounds (Li, et al., 2019). This method is reported to be more objective and reproducible than standard artificial odour recognition since it is faster, more sensitive, more accurate, and non-destructive (Li, et al., 2019). However, there are issues in using E-nose technology for industrial gas detection because of the diversity of its sensors and its inconsistent accuracy and dependability.

Wu et al. (2020) have successfully constructed a real-time electronic nose using 14 metal oxide sensors to detect five flammable liquids qualitatively and quantitatively such as ethanol, gasoline, thinner, turpentine, lacquer, and tetrahydrofuran. This effort was undertaken to prevent vehicle arson incidents, as previous E-nose technologies faced limitations when deployed in public transportation, such as buses or coaches. These limitations were particularly influenced by external factors, including temperature interference which affected the response of the sensors used (Wu, et al., 2020).

As screening methods continue to evolve, it becomes increasingly crucial to seamlessly integrate them with efficient sample collection techniques. The advancements in screening technologies, including the use of electronic noses and ionization detectors, have greatly enhanced the ability to quickly identify potential ILRs at fire scenes. However, this is only the initial step in the investigative process. In obtaining substantial evidence for thorough analysis, sample collection methods play a crucial role in ensuring the successful retrieval of the targeted samples, which are then securely transported to the laboratory for examination.

2.3 Sample Collection Method

Generally, fire debris samples are collected using sterile forceps and placed into an inert, robust, and airtight container. A lined metal paint can, for instance, need to have an airtight seal that makes it inert and capable of stopping the loss of volatile substances (O'Hagan & Ellis, 2021). For fire debris of irregular shapes such as burnt cloth or burnt carpet pieces, a nylon bag is commonly used as it retains hydrocarbons effectively. Furthermore, the storage bag must be specially designed for the study of fire debris and should be doubled for evidence gathering. Notably, nylon and polyester bags must be swan-necked and secured with thread or a cable tie.

An airtight, brand-new, and clean glass jar that allows for visual inspection before instrument analysis can be used for sample storage. It is not advisable to use rubber seals because volatile hydrocarbons might degrade the rubber closures (Low, Tyrrell, Gillespie, & Quigley, 2023).

When it comes to samples such as ignitable liquid residues, the choice of an appropriate collection method is of paramount importance. Proper collection techniques are essential to effectively gather and preserve the volatile compounds for subsequent analysis. The technique used to extract the ILR also depends on the nature of the substrate. This meticulous approach plays a pivotal role in accurately identifying the cause of the fire incident.

2.3.1 On-site Extraction Method

In cases where sampling of ignitable liquid residues is required from fixated structure for example concrete wall and concrete or cement flooring, demolition of parts of the structure so it can be transported to the laboratory are rarely done. Thus, techniques and procedures were proposed for such situations. In general, porous material which is believed to have adsorbent properties would be used to sample or extract the suspected ignitable liquid residues and later packaged and sent to the laboratory for analysis. Examples of the on-site ILR extraction technique include the use of peel-off gelatine, polypropylene cloth, cat litter, passive headspace residues extraction device and ignitable liquid absorbent.

2.3.1.1 Peel-off Gelatine

Laney (2021) conducted a study into the use of peel-away polymer technology as a method for collecting IL during arson investigation. This study delved into the utilization of a peel-off gelatine material for the collection of IL from porous concrete surfaces. This method introduces a straightforward, clean, and cost-effective alternative to existing techniques in the field. Among the various polymer formulations and optimization approaches explored in this investigation, the most successful involved a simple mixture of gelatine and water (Figure 2.4) poured over sifted activated charcoal, and lightly treated with acetone.

Figure 2.3 The peel-off gelatine before the optimization process

The process involved pouring a portion of the gelatine mixture onto a surface, permitting it to dry, and subsequently peeling it off from the surface. Following the collection, the volatile compounds were extracted through passive headspace using a charcoal strip, followed by a desorption process using carbon disulfide. These extracted compounds were then subjected to analysis using GC-MS.

The peel-off gelatine, composed of only gelatine and water, produced the most favourable results compared to the other compositions. It displayed a consistent texture that was easily pourable, a relatively short drying time of approximately 5 to 10 minutes and could be peeled from both porous concrete and nonporous tile surfaces with minimal effort and without leaving a mess behind. Additionally, it was able to efficiently collect n-alkanes from both nonporous tile and porous concrete substrates.

It is crucial to emphasize that this technique is still in its early research stages. Subsequently, there is substantial scope for future investigations to validate the observed results and delve into other facets, such as sensitivity and selectivity. It is important to note that the study focused exclusively on unburnt surfaces, which limits its applicability to scenarios involving larger quantities of ignitable liquids. Furthermore, the evaluation was confined to a single class of ignitable liquid, potentially overlooking the diversity of ignitable liquids found in practical fire investigations. These considerations highlight the need for further research to broaden the technique's applicability and understanding.

2.3.1.2 Polypropylene cloth

A group of researchers in New South Wales (NSW), Australia have developed field test kits for fire scenes as an alternative to traditional swabbing methods using cotton wool and cotton tip applicators, especially for situations where direct sampling is not feasible (Burda, et al., 2016). The kit comprises a white absorbent non-woven material composed of polypropylene fibres, a sampling procedure label, a recording sample label, and a rubber band, all neatly sealed within a nylon sachet as shown in Figure 2.3.

Figure 2.4 Field test kits for fire scene

The kits have been extensively tested for collecting both burnt and unburnt petrol residues from various surfaces, such as porous or non-porous. Volatile compounds adsorbed onto the cloth were extracted through a passive adsorption method employing tubes filled with Tenax TA as the adsorbent material (Burda, et al., 2016). Subsequently, these compounds underwent thermal desorption and were subjected to analysis using GC-MS.

The research findings highlight the suitability of polypropylene cloth for inclusion in these field test kits, facilitating the collection and recovery of petroleum-based liquids and their residues from fire scenes and suspect hands. Importantly, the results demonstrate the effectiveness of these kits in absorbing residues of ignitable liquids, spanning from highly volatile methylated spirits to petrol with high aromatic content, and heavy petroleum distillates like diesel fuel. The kits are currently in widespread use by fire scene investigators across NSW due to their proven effectiveness and versatility. Their adoption has become an integral part of the standard operating procedures of the NSW Police. The sole limitation for these kits to achieve their maximum potential lies in the necessity for proper and adequate training, coupled with continuous support and guidance for fire scene investigators (Burda, et al., 2016).

2.3.1.3 Cat Litter

Smalea, Arthura, and Royds (2014) conducted research to compare techniques for extracting ILR from concrete surfaces in an open-air environment after a fire had naturally extinguished for one hour. The techniques employed included the use of absorbent matting, cotton pads, and cat litter. The results of the research indicated that cat litter was effective in extracting ILR from the concrete surface, while absorbent matting and cotton padding did not detect any of the ILR compounds (Smalea, Arthura, & Royds, 2014).

The technique involved applying cat litter granules to the concrete surface and allowing them to gradually absorb any ILR over the course of an hour. Subsequently, ILR compounds were extracted from the granules using a passive headspace method employing a charcoal strip, followed by a desorption process using dichloromethane. The GC-MS analysis demonstrated the successful extraction of benzene, toluene, and xylene by cat litter. However, the chromatograms from the cat litter samples indicated a higher chance of interference compounds, which suggests that it may lack specificity for the target compounds typically found in petrol. Nevertheless, cat litter remains suitable for the extraction of ILR from concrete surfaces.

2.3.1.4 Passive Headspace Residue Extraction Device (PHRED)

During the study conducted by Smalea, Arthura, and Royds (2014), they also introduced a novel device capable of conducting ILR extraction directly at the crime scene, yielding samples ready for immediate analysis. This device, known as Passive Headspace Residue Extraction Device (PHRED) operated on the same principles of heating a container but functioned as a portable unit that can be affixed directly to the concrete surface. The PHRED facilitated the direct evaporation of ILR from the concrete onto a charcoal strip within the device. Figure 2.5 shows the schematic diagram of the device.

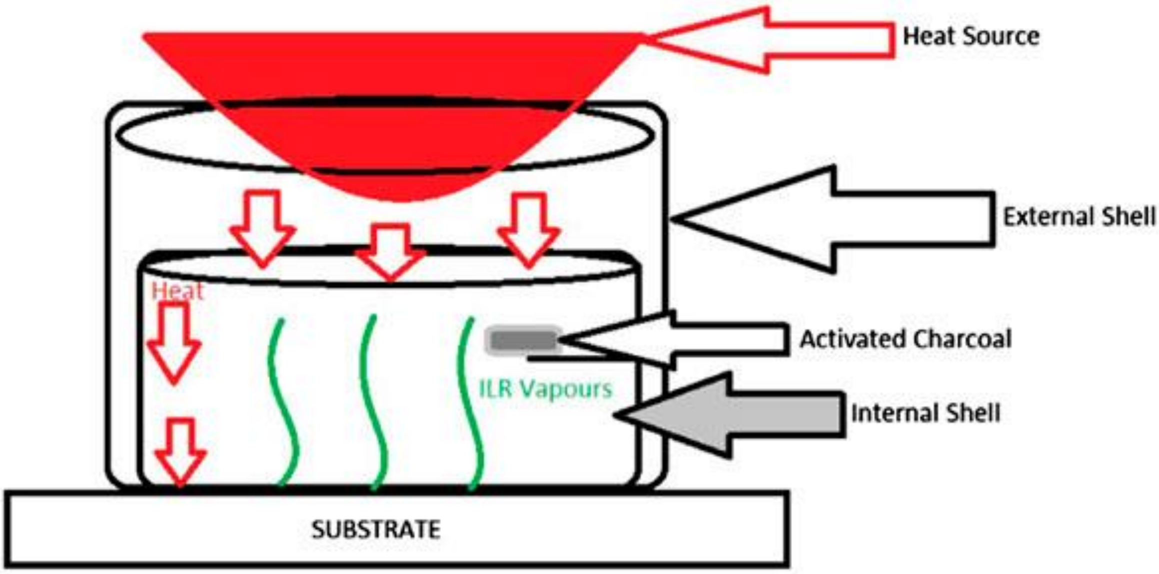

Figure 2.5 A schematic of the Passive Headspace Residue Extraction Device (PHRED).

Once the device had absorbed any ILR compounds present in the concrete substrate, the activated charcoal strip was rinsed with dichloromethane, and the resulting solution was subjected to analysis using GC-MS. The results of the analysis showed that the PHRED successfully extracted toluene, xylene and benzene, similar to the cat litter. The signal strength to the noise of the PHRED samples was higher than the cat litter samples, however, the PHRED extractions indicated the compounds in significantly higher concentrations. The main advantage of PHRED is its on-site ILR adsorption capability, reducing the necessity for material transportation to the laboratory. Despite that, further testing is required to assess its suitability for detecting ILs other than petrol.

2.3.1.5 Ignitable Liquid Absorbent^{TM} (ILA)

In a study conducted by Nowlan, et al. (2007), the use of a solid absorbent material in conjunction with an accelerant detection canine was field tested for the detection of ignitable liquids in the aftermath of structure fires. ILA, a commercially available solid absorbent, is composed of a composite material that incorporates two absorbents, a polyolefin, and a carboxylic acid, along with an indicator dye designed to change colour when exposed to hydrocarbons. The study assessed the ILA's ability to detect and absorb varying quantities of gasoline, odourless paint thinner, and camp fuel on porous surfaces following a full-scale burn.

The procedure commenced with the detector canine conducting searches on the flooring panels, and any alerts were duly recorded. Subsequently, the ILA was prepared according to the manufacturer's guidelines and evenly distributed across all flooring panels. The absorption process for the ILA ranged between 20 to 30 minutes for each panel. Once the designated absorption time had passed, the ILA was carefully brushed off from each panel into a clean metal container and securely sealed. The ILA samples were extracted onto activated charcoal strips using a passive headspace method and subsequently analyzed via GC-MS after desorption using carbon disulfide.

The findings of the study showed that the accelerant detection canine consistently provided accurate alerts for panels containing ignitable liquids post-fire. In contrast, the ILA indicator dye failed to indicate the presence of gasoline and camp fuel. GC-MS results revealed that the ILA successfully absorbed odourless paint thinner and camp fuel from most test panels but did not absorb gasoline from panels where its presence was confirmed (Nowlan, et al., 2007). In summary, the study indicates that ILA may not be an effective adsorbent for gasoline residues, which are frequently encountered in arson cases.

In cases where substrates such as charred fabrics and burnt furniture were suspected of containing ignitable liquid residues (ILRs) from a fire scene can be easily removed and transported to the laboratory, the extraction of ILRs is typically conducted in the laboratory. This approach allows for a controlled environment, precise equipment, and specialized techniques that facilitate the extraction and analysis of ILRs with high accuracy.

2.3.2 Laboratory Extraction Method

The laboratory extraction method for ignitable liquid residue refers to a process where fire debris suspected to contain ILR, collected from a fire scene, is transported to a controlled laboratory environment for extraction and subsequent analysis. The extraction process aims to isolate, concentrate, and prepare the ILR samples for further analysis, allowing for the identification of specific ignitable liquids used in the fire incident. Various methods have been developed and employed to effectively extract these residues while minimizing contamination and preserving the integrity of the evidence. The extraction techniques are categorised into two groups: conventional and modern.

Conventional extraction techniques include solvent extraction, steam distillation, and vacuum distillation for isolating accelerants from substrates (Low, Tyrrell, Gillespie, & Quigley, 2023). Modern extraction techniques encompass direct (heated), dynamic (purge and trap), and static (equilibrium) headspace analyses, along with methods such as the activated charcoal strip technique and the use of various adsorbents enclosed in airtight, temperature-controlled containers (Low, Tyrrell, Gillespie, & Quigley, 2023). The choice of extraction method depends on several factors, including the type of ignitable liquid suspected, the nature of the fire debris, the available equipment, and the specific requirements of the investigation.

The foundation of headspace analysis is the chemical examination of the gas phase, either in liquid or solid form, that is present above the surface of the material being examined. These procedures are regarded as quick, easy approaches that only need very little sample preparation. The devices used for the headspace extraction play important roles in adsorption and desorption ability to extract hydrocarbon vapours from fire debris samples. Examples of the reported devices are activated charcoal strips, activated charcoal pellets, activated carbon cloth and solid-phase microextraction.

2.3.2.1 Activated Charcoal Strip (ACS)

The activated charcoal strip consists of a small strip or pad made of activated charcoal enclosed in a glass or metal tube. The strip is typically exposed to the headspace above the fire debris sample for a specific period, allowing volatile compounds to adsorb onto the charcoal surface. After exposure, the strip is carefully removed from the tube and placed in a sealed container to prevent contamination. It is then sent to a laboratory for further analysis, typically using techniques such as thermal desorption or solvent extraction followed by gas chromatography-mass spectrometry (GC-MS).

The advantage of using ACS is that it provides a simple and non-destructive method for collecting volatile compounds. They can be easily transported to the laboratory for analysis, and the adsorbed compounds can be desorbed from the charcoal surface without significant loss or degradation. However, this method is expensive and time-consuming. It was reported that the concentration of volatile fractions of the ignitable liquids in the ACS required 16 hours and can cost over RM4,000 per 100 strips of the commercial ACS (Fabritius, Broillet, König, & Weinmann, 2018). Additionally, the ACS technique carries a higher risk of exposure to hazardous solvents, especially when using carbon disulfide for desorption, which is the most effective solvent. Although dichloromethane or hexane are safer options for eluting the adsorbent, they are still less effective than carbon disulfide.

2.3.2.2 Activated Charcoal Pellets (ACP)

A study conducted by a group of researchers has reported that ACPs provide a promising alternative for extracting gasoline and diesel from fire debris, allowing for efficient and reliable analysis of accelerant residues in fire investigations. In the context of fire debris analysis, ACPs can be used as an adsorbent material to collect and concentrate gasoline and diesel residues from the debris in the process such as headspace solid-phase microextraction (HS-SPME) or dynamic headspace sampling (Carmona, et al., 2022). The pellets can easily be prepared in the laboratory using inexpensive materials and only require a short period.

The use of ACPs for extracting gasoline and diesel from fire debris offers several advantages. It is a non-destructive technique that requires small sample sizes. ACPs also provide good sensitivity and selectivity for volatile compounds, making them suitable for forensic analysis. However, this method was reported to be time-consuming because it required at least 16 hours for the extraction, despite being less attentive. Additionally, this method added extra steps in the desorption process, where hexane was used and the desorption was performed by horizontal agitation at 120 rpm for 5 min, followed by a dilution process.

ACP may show that it is better in terms of cost-effectiveness and ease of preparation, however, it can be observed that the overall method is more tedious with the presence of additional steps incorporated in this method. The researchers also recommended that it is essential to conduct