PERFORMANCE EVALUATION OF ACTIVATED CARBON CLOTH FOR FIRE DEBRIS ANALYSIS WITH ARTIFICIAL NEURAL NETWORK APPROACH

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by

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CERTIFICATE

This is to certify that the dissertation entitled “**Performance Evaluation of Activated Carbon Cloth for Fire Debris Analysis with Artificial Neural Network Approach**” is the bona fide record of research work done by NURUL LIZAWANI BINTI SARI during the period February 2020 to September 2020 under my supervision.

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DECLARATION

I hereby declare that this thesis is the result of my own investigation, except where otherwise stated and duly acknowledge. I also declared that it has not been previously or concurrently submitted as a whole for any other degrees at Universiti Sains Malaysia or other institutions. I grant Universiti Sains Malaysia the right to use the dissertation for teaching and promotional purposes.

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Covid-19 is truly an unprecedented event; nonetheless, it has opened up many new venues, and with it, I discovered ANN experience. Lastly, I would like to give thanks and appreciation to all that were involved in making this project a success either directly or indirectly.

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LIST OF SYMBOLS

%	percent
$	Dollar
µL	microliter
µm	micrometer
°C	degree Celcius
amu	atomic mass unit
C	Carbon
CO_2	Carbon dioxide
cm	centimeter
m	meter
min	minute
m/z	mass-to-charge-ratio
mL	milliliter
ppm	part per million
vol/vol	volume per volume

LIST OF ABBREVIATIONS

ASTM	American Society for Testing Materials
ACC	Activated Carbon Cloth
ACS	Activated Carbon Strip
ANN	Artificial Neural Network
DCM	Dichloromethane
FRDM	Fire and Rescue Department of Malaysia
GC	Gas Chromatography
GCMS	Gas Chromatography Mass Spectrometry
IL	Ignitable Liquid
LOD	Limit of Detection
LOQ	Limit of Quantification
MLP	Multilayer Perceptron
NFPA	National Fire Protection Association
NCFS	National Centre for Forensic Science
RSD	Relative Standard Deviation
SAM	Standard Accelerant Mixture
SPME	Solid Phase Micro Extraction
TIC	Total Ion Chromatogram
UK	United Kingdom
US	United State

PENILAIAN PRESTASI BAGI ANALISIS RUANG TUTUP BAGI HELAIAN KARBON TERAKTIF (ACC) MENGGUNAKAN PENDEKATAN RANGKAIAN SARAF BUATAN (ANN)

ABSTRAK

Forensik kebakaran menyiasat asal dan punca kebakaran. Pengesanan dan pengenalpastian cecair mudah nyala di dalam sisa kebakaran berkemungkinan akan memberi petunjuk penting bagi mengetahui punca kebakaran dan penting bagi membuktikan bahawa berlakunya kes khianat melibatkan api. Skop kajian ini dikecilkan kepada penggunaan helaian karbon teraktif sebagai penyerap di dalam ruang tutupan pasif bagi mengesktrak sisa cecair mudah nyala. Kajian ini menyiasat pengesanan beberapa kompaun sasaran yang mewakili julat cecair mudah nyala yang besar, dari sebatian yang paling ringan (n-heksana) kepada sebatian yang lebih berat (n-eicosane) pada keadaan pengekstrakan yang berbeza terutama pada suhu serapan (60 °C hingga 120 °C) dan tempoh pengeraman (2 jam hingga 24 jam). Beberapa set data yang diperoleh dari profil kromatogram menunjukkan perbezaan yang ketara bersama parameter yang digunakan. Sebuah model computer iaitu Rangkaian Saraf Buatan telah dibangunkan dan digunakan bagi menilai kondisi optima helaian karbon teraktif sebagai bahan penyerapan dalam mengekstrak sisa cecair mudah nyala menggunakan kaedah ruang tutupan pasif. Resolusi bagi 14 kompaun terpilih dari profil kromatogram yang mewakili cecair mudah nyala telah digunakam sebagai input untuk model Rangkaian Saraf Tiruan. Rangkaian Saraf Buatan menunjukkan paparan model tindak balas (2:2-17-14:14) yang membenarkan kondisi optimum untuk berlaku pada tetapan 4 jam jangka masa dan 100 °C suhu peraman bagi pesampelan yang memerlukan waktu yang singkat. Sementara bagi pesampelan semalaman, kondisi optimum yang diperlukan adalah pada 18 jam jangka masa dan 80 °C suhu peraman.

Kondisi optimum dan tetapan yang praktikal bagi mengekstrak sebatian organik meruap menggunakan kaedah ruang tutupan pasif adalah sangat penting untuk membantu jadual kerja pegawai analisis forensik yang sibuk. Selain itu, ia juga dapat membantu dalam mengenal pasti dan mentafsir sampel sisa kebakaran yang kompleks. Penemuan ini mempunyai implikasi yang berkait untuk pegawai analisis forensik yang menjalankan siasatan bukti kebakaran.

PERFORMANCE EVALUATION OF ACTIVATED CARBON CLOTH FOR FIRE DEBRIS ANALYSIS WITH ARTIFICIAL NEURAL NETWORK APPROACH

ABSTRACT

Forensic fire investigates the origin and cause of the fire. Detection and identification of ignitable liquid (IL) residue in fire debris may provide the vital clue of the fire cause, especially important to prove incendiary fires. The scope of this study is narrowed to the usage of activated carbon cloth (ACC) as the adsorbent material by passive headspace diffusion as the extraction technique of IL residue. This study investigates the detection of selected target compounds that represent wide IL residue range from the lightest compound of n-hexane (C6) to the heavier compound of eicosane (C20) at different extraction parameters especially the temperature setting (60 °C to 120 °C) and exposure period (2 hours to 24 hours). Data sets from the chromatographic pattern vary significantly with different parameters were chosen. Computational modelling of artificial neural network (ANN) based on the pattern was developed and utilised to evaluate the extraction performance of ACC for optimisation purposed. The resolution of chromatographic behaviour of 14 selected target compounds that represent the ignitable liquid was used as input for the ANN model. The ANN display a response model of (2:2-17-14:14) allows the optimum condition with the practical setting to be 4 hours at 100 °C for urgent sampling while 18 hours at 80 °C is intended for overnight sampling. Selected optimum condition and practical settings for effective extraction of volatile compounds are important knowledge to facilitate busy laboratory operation as well as the identification and interpretation of complex fire debris samples. Thus, the finding of this research has a relevant implication for the forensic analyst who performed fire evidence investigation.

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Forensic fire investigates the origin and cause of fire. Fire can be categorised into three types; natural fire, accidental fire and incendiary fire (Quintiere., 2016). In the context of forensic science, an incendiary fire which is commonly called as arson is one of the most difficult crimes to investigate because almost all evidence at the scene is destroyed by the fire (Sandercock., 2008). In arson cases, the presence of ignitable liquid at the fire origin can be such an indicator. Therefore, analysis of fire debris may provide a vital clue of incendiary fire in many circumstances. Ignitable liquid is the most common material to initiate and accelerate fire due to the high availability, cheap and easy to conceal (Stauffer et al., 2008). The most common ignitable liquid available and frequently used by the arsonist are gasoline, lighter fluid, kerosene, diesel, paint thinner, lamp oil and paint thinner (Li et al., 2014; Mann and Gresham, 1990).

Contrary to general perception, the detection and identification of ignitable liquid residue are possible because it is normal for the arsonist to use a high amount of ignitable liquid to ensure total combustion. In consequence, the fire origin may contain a huge amount of ignitable liquid as it seeping down to the receiving matrix as well at the surface (Li et al., 2014). Thus, simple unburnt material can become the matrix for discarded accelerant. Fire debris residue detection from unburnt matrices have implications for crime scene investigators carrying out fire debris evidence investigation at an arson scene. However, the analysis of these residues is not always straightforward and need to consider the analytes of interest and substrate matrix (Baerncopf and Hutches, 2014). In most cases, extraction procedures have to be employed prior to instrumental analysis, to concentrate analytes and to remove extraneous matrix interference (Dhabbah et al., 2014).

In the context of applications in forensic fire investigation, activated carbon is used to recover various ignitable liquids or traces of ignitable liquid found at the fire scene. Marsh and Reinoso (2006) define activated carbon as carbon atoms enclose a space (porosity). Activated carbon is industrially used as adsorbent material. It is commonly used for purification of water and air and widely used for separation of hydrocarbon gas mixtures (Rezvani et al., 2019). Activated carbon has been acknowledged for its remarkable performance due to the high volume of micropores and mesopores. These lead to an extensive active surface area for the adsorption to happened (Marsh and Reinoso, 2006). Activated carbons can be made by various carbon-based materials such as from coals, coconut shells, hardwoods or by synthetic macromolecular systems. The specific process had been developed to produce it in the form of granular, powder, carbon strip and carbon cloth (Sandercock, 2016). Due to the differences in their origin, there are hundreds of commercial activated carbons available with different sizes of porosity with a specific application. Application of the activated carbon as adsorption material has evolved and been identified as one of the most effective technologies for the removal of volatile organic compounds (VOC) (Daifullah and Girgis, 2003).

Analysis of fire debris suggested by American Society for Testing Materials (ASTM) is Gas Chromatography coupled with Mass Spectrometry (ASTM standard E1618). According to ASTM E1618-01, the standard analysis methods to identify extracted samples of combustion residues of flammable liquids in fire scene is by Gas

Chromatography-Mass Spectrometry (GC-MS). Several studies have highlighted the effectiveness of GCMS as identification of extracted ignitable liquid from fire debris (Lentini et al., 2000; Lentini, 2001; Yang, 2016). The results show that GCMS analysis can be used to determine the presence of gasoline traces residue from different substrate. Before chromatographic separation can be done, the extraction of ignitable liquid residues from fire debris is necessary.

Several traditional and modern techniques for the extraction of ignitable liquids, such as solvent extraction, steam distillation, passive and dynamic headspace methods and solid-phase microextraction (SPME) have been developed and validated. The most recent and preferable choice of extraction method in analysing fire debris is SPME. However, SPME fibres are fragile, have a limited lifetime and need to be cleaned between analysis to avoid contamination (Martín-Alberca et al., 2016).

Thus, passive headspace diffusion is chosen as the extraction method in this study due to its effectiveness, non-destructive and simplicity (Cacho et al., 2014). ASTM standard practice E 1412 covers the procedure for removing ignitable liquid residues from fire debris by adsorption device suspended in the static headspace above the sample then desorbing the residue from the adsorbent with a solvent (Williams et al., 2012). The extraction of ignitable liquid residues from fire debris by passive headspace diffusion with activated carbon as an adsorption device is the most commonly used method. Headspace method is chosen due to its simplicity, non-destructive and low background interference.

Despite the advantages of using activated carbon headspace extraction in ignitable liquid detection and analysis, there are still challenges in the performance of the activated carbon used. Sandercock, 2016 reported ACC to be cost-effective and high practicality in term of operations to sustain forensic laboratory analysis as compared to commercial activated carbon strip (ACS). This approach offers other economic alternatives for investigators since ACS is more expensive. Thus, alternative need to be found, i.e. ACC, therefore, need to evaluate its performance. It can be influenced by various parameters during the extraction step and has been shown by several previous works. This study assesses the performance evaluation of alternative devices, i.e. activated carbon cloth (ACC) at different parameters by using Artificial Neural Network (ANN). Two parameters chosen in this study are incubation temperature and exposure time that will contribute to the absorption efficiency of the ACC devices.

1.2 Problem statement

ACS is an established ignitable liquid (IL) extraction device but expensive. Solid Phase Micro Extraction (SPME) was introduced to counter the expensive device of ACS. However, SPME is highly attentive and require the direct presence of personnel to perform the analysis. Therefore, the use of an equally efficient device is warranted. ACC was chosen as the mean for evaluation due to its low cost as compared to ACS. The unit price (1x2 cm) for ACS in the study was US$ 3.20, whereas for ACC of the same size was only US$ 0.05. Optimization study of ACC on the adsorption time, incubation temperature and compound detection of the ignitable liquid using computational modelling of ANN has never been conducted. It is laborious and time-consuming to test the optimum condition needed manually. In addition, manual interpretation and classification of IL are restricted by the skill, knowledge and subjectivity of the analyst as well as time-consuming.

1.3 Research questions

The research questions of this study are listed below:

a) What are the optimum adsorption time, incubation temperature and compound detection in the extraction of ignitable liquid by ACC using ANN?
b) What is the value of resolution factor and for compounds chosen to represent the wide range of ignitable liquid?
c) Can optimised extraction procedure give well separated, clear TIC pattern for IL identification?

1.4 Research objectives

To determine optimum response (adsorption time and incubation temperature) in relation to the resolution value of the chosen compound of activated carbon cloth headspace extraction using the ANN model in order to correctly identify chromatography pattern of IL residue from fire debris sample.

1. 5 Significance of study

This study is important to determine the ability of ACC to perform effectively as adsorbent devices in extracting IL from fire debris sample. It must be determined to obtain the reliable and clear TIC chromatogram pattern in GCMS for IL residue interpretation. Therefore, this study will help forensic science practitioner and analyst avoiding misinterpretation and wrong deduction due to poor and inadequate data. The study may also contribute knowledge for efficient sample adsorption by ACC as the alternative option to the more expensive device of ACS. It will give implications for the analyst in analysing fire debris as crucial potential evidence in forensic fire investigation. Furthermore, the utilisation of the ANN computational modelling in this study helps forensic science practitioner and analyst to correctly predict the best optimum parameters condition for the headspace sampling.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter presents a review of the literature concerning various ignitable liquid and the extraction techniques of ignitable liquids from fire debris residue. The use of activated carbon devices was discussed in particular with consideration to parameters such as incubation temperature, exposure time and volume headspace that contributes to absorption efficiency of the devices. In addition, the utilisation of ANN for correct prediction and classification on the forensic field was also reviewed.

2.2 Ignitable Liquid

Ignitable liquid is any liquid that is used to initiate and increase the growth rate of fire, including a flammable liquid and combustible liquid (NFPA,2014). It is a mixture of volatile, flammable liquid hydrocarbons derived from crude oil or raw petroleum. There are several classes of ignitable liquids that were commonly used by the arsonist to purposely initiate a fire such as gasoline, kerosene, diesel, paint thinner and turpentine (Stauffer et al., 2008) that gives such important information to forensic fire investigation on its classification.

2.2.1 Ignitable Liquid products from crude petroleum

Ignitable liquids originated from crude petroleum and made when crude petroleum is broken into various petroleum products through fractional distillation process at different temperature (Kinsara et al., 2016). This liquid contains hydrocarbons with carbon atom link together in different length of chains. The differences in length of the hydrocarbon chain come along with different properties; for example, longer hydrocarbon compound has a heavier molecular weight. As mentioned earlier that crude oil is made up of a mixture of hydrocarbon; refining process, chemical fractioning and chemical treatment process break down these hydrocarbons into different products of different uses (Anowor et al., 2014). Example of the crude oil refining process shown in Figure 2.1.

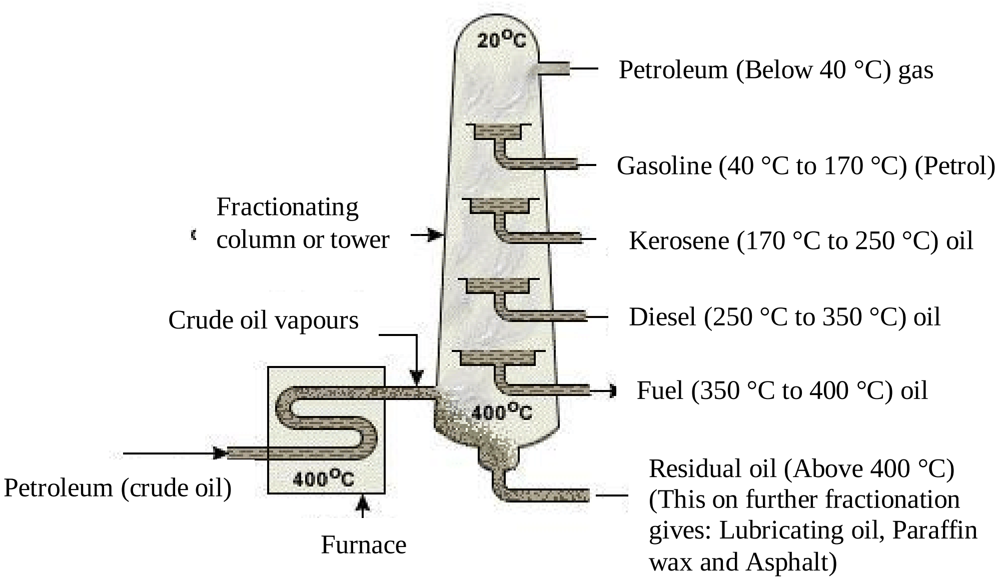

Figure 2. 1: Example of crude oil refining process (Anowor et al., 2014)

2.2.2 Classification of Ignitable Liquid for Forensic Fire

Since the ignitable liquid is widely used for automotive, commercial, daily activities as well as in initiating a fire, the classification of IL used is important in forensic fire debris analysis. American Standard Testing Material E1618 (ASTM E1618) developed a classification scheme for fire debris analysis. The classification particularly aimed to facilitate the identification and classification of recovered IL from fire debris. ASTM E1618 classify IL into seven different classes; gasoline, petroleum distillates, iso-paraffinic products, aromatic products, naphthenic-paraffinic products, normal alkenes product, oxygenated solvents and miscellaneous. Miscellaneous represent other IL that are not counted as major classes. These classes are further subdivided into three classes based on their carbon chain length; light petroleum distillates (LPD), medium petroleum distillates (MPD) and heavy petroleum distillates (HPD) (ASTM International, 2014). Overall classification with examples was tabulated in Table 2.1.

Table 2. 1: ASTM E1618 Classification Scheme for ignitable liquid (ASTM International, 2014)

Class	**Light (C4-C9)**	**Medium (C8-C18)**	**Heavy (C9-C20+)**
Gasoline-all brands, including gasohol and E85	Fresh gasoline is typically in the range C4-C12		
Petroleum Distillates (Including De-Aromatised)	Petroleum Ether Some Cigarette Lighter Fluids Some Camping Fuels	Some Charcoal Starters Some Paint Thinners Some Dry Cleaning Solvents	Kerosene Diesel Fuel Some Jet Fuels Some Charcoal Starters
Isoparaffinic Products	Aviation Gas Some Specialty Solvents	Some Charcoal Starters Some Paint Thinners Some Copier Toners	Some Commercial Specialty Solvents
Aromatic Products	Some Paint & Varnish Removers Some Automotive Parts Cleaners Xylenes, Toluene-based products	Some Automotive Parts Cleaners Specialty Cleaning Solvents Some Insecticide Vehicles Fuel Additives	Some Insecticide Vehicles Industrial Cleaning Solvents
Napththenic-Paraffinic Products	Clyclohexane based solvents/products	Some Charcoal Starters Some Insecticides Vehicles Some Lamp Oils	Some Insecticides Vehicles Some Lamp Oils Industrial Solvents
Normal-Alkanes Products	Solvents Pentane Hexane Heptane	Some Candle Oils Some Copier Toners	Some Candle Oils Carbonless Forms
Oxygenated Solvents	Alcohols Ketones Some Lacquer Thinners Fuel Additives Surface Preparation Solvents	Some Lacquer Thinners Some Industrial Solvents Metal Cleaners/Gloss Removers	
Others-Miscellaneous	Single Component Products Some Blended Products Some Enamel Reducers	Turpentine Products Some Blended Products Some Specialty Products	Some Blended Products Some Specialty Products

Each class is identified by comparison to standards or known ignitable liquid samples designated as the reference material. Database compilation of various reference materials is established by National Centre for Forensic Science (NCFS, 2006). Figures 2.2, 2.3, 2.4, and 2.5 are the TIC established by NCFS represents common IL used by arsonist such as gasoline, diesel, kerosene and paint thinner mentioned by Stauffer et al. in 2018.

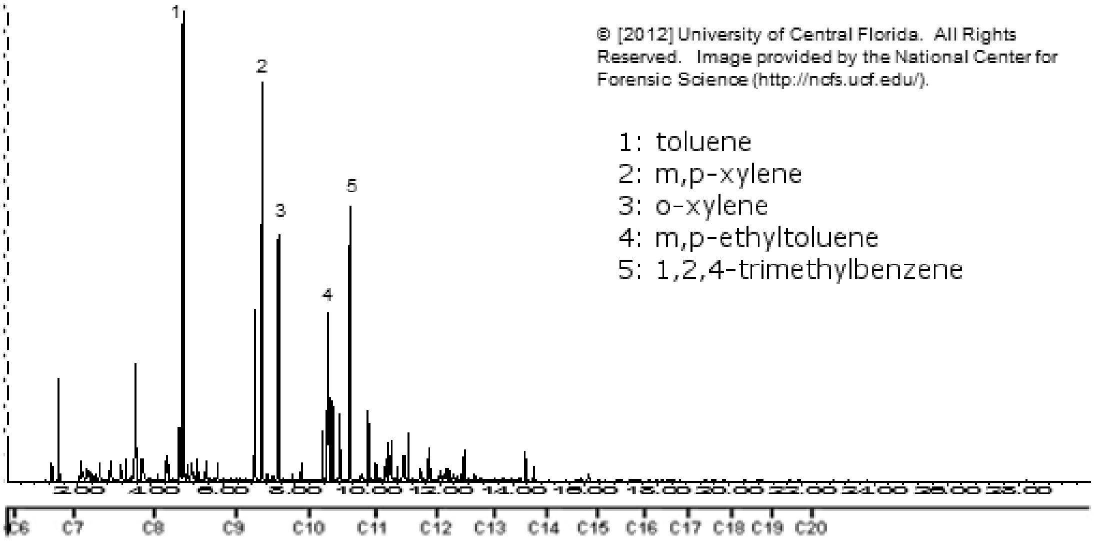

Figure 2. 2: Example of TIC of Gasoline neat liquid (NCFS, 2006)

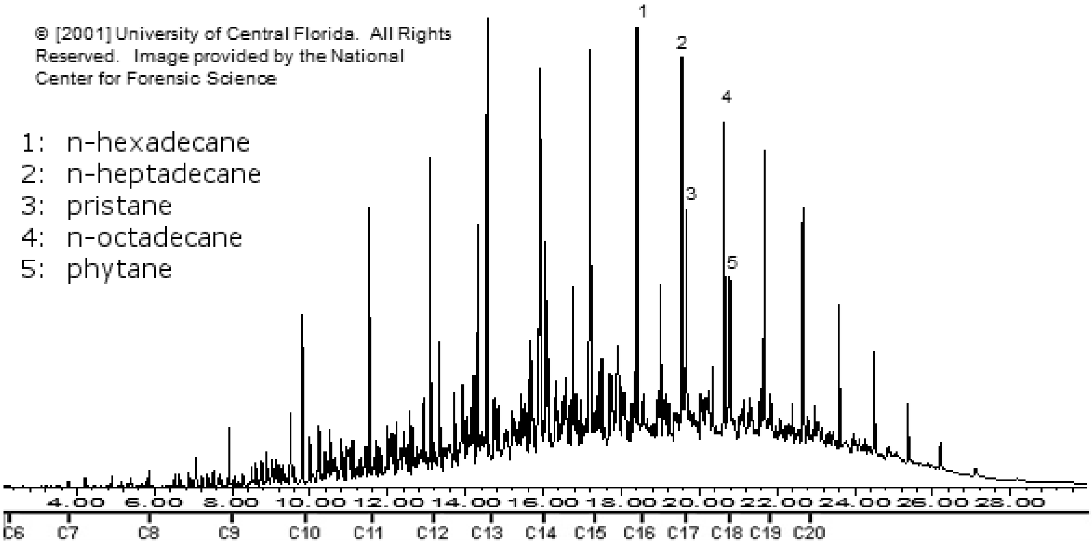

Figure 2. 3: Example of TIC of Diesel neat liquid (NCFS, 2006)

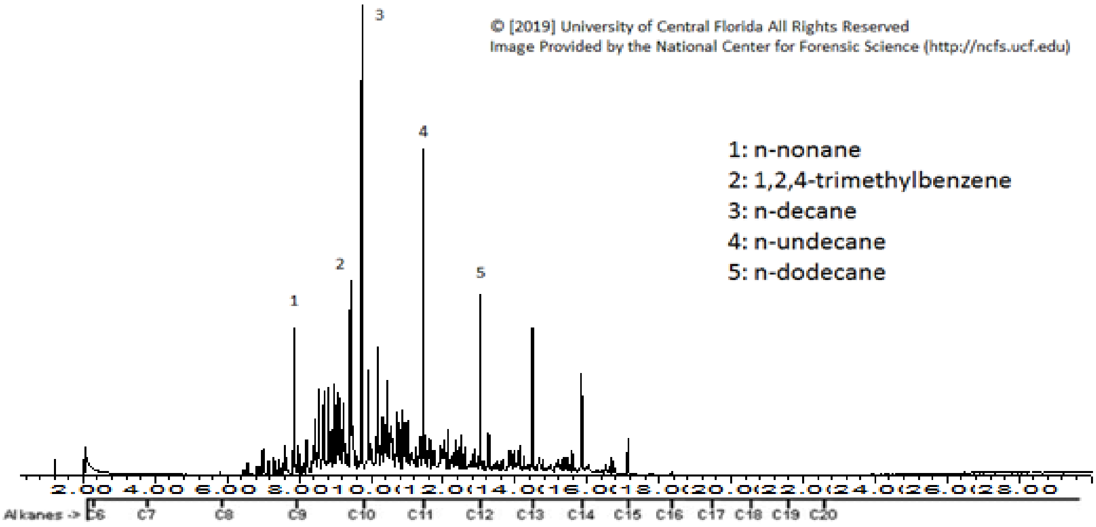

Figure 2. 4: Example of TIC of Kerosene neat liquid (NCFS, 2006)

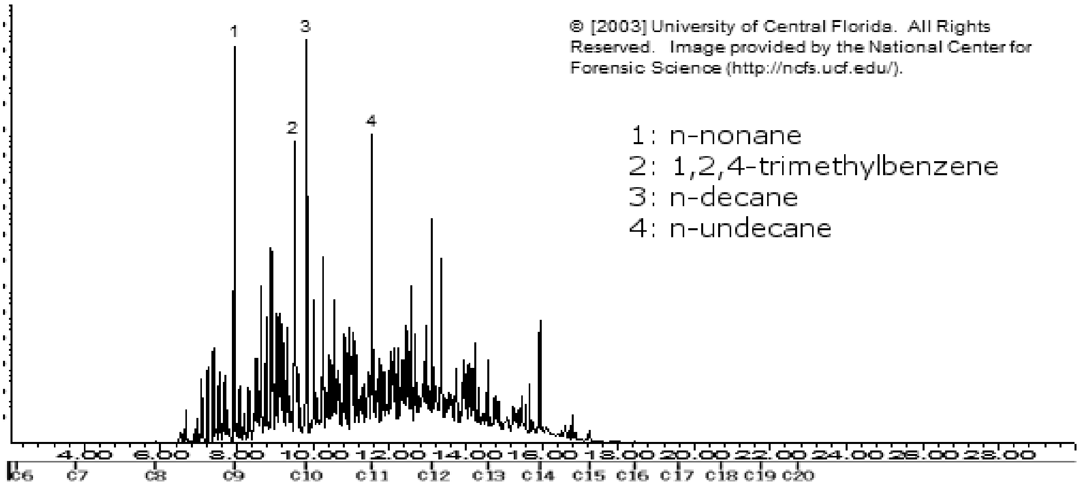

Figure 2. 5: Example of TIC of Paint thinner neat liquid (NCFS, 2006)

2.3 Headspace Extraction of IL and ILRS

Isolation of IL from fire debris has evolved over the years. Headspace technique for analysis of volatile compounds in such samples has become the preferred choice by fire forensic analyst. Direct passive headspace also knew as static headspace method was developed by Twibbel and Home in the 1970s based on vapour pressure principle and was accepted as the simplest and basic extraction method (Borusiewicz, 2002; Snow and Bullock, 2010; Soria et al., 2015; Sandercock, 2016). The operation is simple, whereby the collected fire debris sample is kept in a closed, impermeable container. After a period of time, the headspace inside the container is abstracted using a gas-tight syringe and directly injected at the GC sample port.

Li et al. (2014) used this method to extract and isolate ignitable liquids from fire debris. In previous years, Lentini (2001) used passive headspace adsorption as described in ASTM E1412 and GCMS analysis as described in ASTM E1618 to study the persistence of solvents in floor coating materials such as stain, oil finish, and polyurethane varnish. These solvents are classified under medium petroleum distillates. The experimental set up for passive headspace adsorption was by using ProTek strip (polyethene fibres strip) as adsorption material, elevated incubation temperature up to 80°C, incubation period of 16 hours and diethyl ether as a solvent. It was reported that the solvents were easily detected over a 2-year period without showing any loss of important TIC characteristic peaks using GCMS.

Lentini et al. (2000) also noted that among many types of building materials, floor coatings were common substrate materials that which may contain petroleum products. The authors found the solvents might be easily detected even after six months of application when extracted using passive headspace method followed by GCMS analysis described in ASTM E1618. The same experimental set up with Lentini (2001) was applied. These findings suggested the fire scene investigator to also collect the controlled substrate sample when collecting any sample of finished wood flooring. Passive headspace concentration is much simple and sufficient for sample extraction, especially if intended for screening purposes. It is also non-destructive, direct, safe (no chemicals involved), making it the preferred method for sample extraction. Another advantage of this method is that it provides a low level of interference. A few adjustments are made to this basic method with the application of adsorbent devices.

Similar to the previous methods, the sample is placed in a sealed container, heating them and left at a constant or elevated temperature with adsorptive material such as the carbon strip suspended in headspace until the gas phase and solid phase are in equilibrium (Kerr, 2018).

Adsorption of ignitable liquid by using a charcoal strip for the sampling of fire debris is common by many researchers (Kerr, 2018). The targeted substances which in the gas phase are adhered to the surface of adsorbent material which later is desorbed by heating or chemical means and injected into GC. Muller et al. (2011) studied the detection of gasoline on arson suspects' hand by using charcoal strip passive headspace, using dichloromethane as solvent then analysed by GCMS. However, there is no research was done using charcoal strip for sampling from human skin. This may be due to this technique requires heating of the sample at a certain amount of time. The result of this research is that the presence of gasoline residue on the palm using this method is very little amount is gasoline was detected.

In previous years, Almirall et al. (2000) studied on the detection and analysis of ignitable liquid residues extracted from human skin using Solid Phase Microextraction/ Gas Chromatography (SPME/GC). This extraction method proved to be more sensitive, even a small amount of ignitable liquid can be detected. However, SPME fibres are fragile, have a limited lifetime, and need to be cleaned between analysis to avoid contamination.

Byard and Payne-James (2015) also agreed that displacement issues decrease the efficiency of the method. Conner et al. in 2006 used the method of dynamic headspace analysis technique for use in fire investigation. Basically, this method utilises the active catching of volatile compound present in the headspace container. The container containing the sample is connected with the adsorption tube that contains polymer beads as an adsorbent. It has a pump to force the headspace flow through the adsorbent filled tube. Dynamic headspace can be much more effective than passive headspace in term of isolation and concentrated analytes; however, it is complex and laborious that makes it tends to make mistakes (Kerr, 2018). To increase the analyte vapour pressure, the container was heated and thermally extracted and desorbed using a solvent. Diethyl ether was chosen as solvent desorption as suggested by the American Society for Testing and Materials (ASTM E1412, 2019). It was suggested to use Tenax GC as adsorbent material which is a porous polymer adsorbent that adsorbed and desorbed analytes easily without the use of a solvent (Conner et al., 2006). The advantages of this adsorbent are their weak affinity towards a highly volatile and polar analyte, which makes any analytes belongs to this group insufficiently concentrated.

Some researchers used the charcoal-based adsorbent as adsorbent material which void of the previous problem. Solvent desorption for these tubes can be the alternative to thermal desorption. Common solvents ignitable liquid residues are carbon disulfide, diethyl ether, pentane, Dichloromethane, and petroleum ether. Carbon disulphide and diethyl ether are naturally toxic and carcinogenic. In addition, this desorbing chemicals exposed the analyst to toxic solvents and that it appears to experience displacement due to the insufficient concentration of compounds with a high boiling point. This may lead to misclassification or misidentification of the ignitable liquid sample (Martín-Alberca et al., 2016; Alqassim et al., 2016). In later work, acetone was used as a solvent (Nichols et al., 2014). Acetone is considered to be an ignitable liquid classified as oxygenates and has never used as a desorbing solvent in the analysis. Nonetheless, it was used in the research due to safer to be used compared to carbon disulphide or diethyl ether that usually being used by other researchers.

The most recent headspace extraction technique used for the sample preparation of fire debris is SPME. Yoshida et al. (2008), used this method for residue extraction to both isolate and concentrate organic compound whereby a fibre needle is attached with chemically coated fused silica (equivalent to GC liquid phase). It will be dipped directly into a liquid sample or exposed to the headspace vapours from liquid or solid samples (Yoshida et al., 2008). SPME utilise the fact that does not use any solvents suggest that this is the direction of the next generation of analytical method should proceed (Kerr, 2018). Besides, SPME fibre can be used many times without losses of adsorbed substances save the cost. Other than that, the fibre has a limited adsorbent capacity, which prevents column overloading if analytes in the sample are present in large quantities. No further modification is needed. In addition, SPME is a preferable choice among nowadays fire analysis because it is portable and can be used directly in a fire scene during the investigation.

However, although SPME is the way forward, many researchers still conducted an experiment using activated carbon as adsorbent material due to the fact that SMPE fibre is expensive (Newman et al., 1996; Turner and Goodpaster, 2009; Sandercock, 2016). Other than that, experiment using SPME is highly attentive due to manual injection, and the syringe is easily broken if mishandled (Smith et al., 2005).

2.4 Other extraction Techniques of Ignitable Liquids from Fire Debris

Other techniques for the extraction of ignitable liquid are also practised like solvent extraction, steam distillation, passive and dynamic headspace and SPME methods, are developed and validated (Bertsch and Ren, 2000). The evolution from traditional techniques to more modern techniques with the use of sophisticated devices are documented.

2.4.1 Distillation and Solvent Wash

In modern times, vacuum distillation filtration, such as described by Willson (1977) is used for ignitable liquid isolation from fire debris. This method allows the ignitable liquid to be recovered in their pure liquid form. Distillation was carried out by placing the sample in a round bottom flask together with sufficient water to cover them together with 1 cm^3 of extraction agent. The appropriate column was attached to the flask, and distillation time was carried out for 4-6 hours (Willson, 1977). This method is suitable for the compound with a low boiling point as well as a large chain compound with a high boiling point (Bruno et al., 2011). Martín-Alberca et al. (2016) supported that this technique is efficient to extract and separate compounds of interest, especially the extraction of heavy hydrocarbons and vegetable oils.

Nonetheless, the success of ignitable liquid isolation and recovery from the fire debris also relies heavily on the sample collected at the scene, i.e. whether enough ignitable liquid can be recovered. Yang (2016) evaluate the trace residue of gasoline combustion using GCMS analysis using solvent wash as the extraction method. The solvent used was Acetone. Trace residues were transferred to 100 mL beaker containing Acetone and treated with Ultrasonic, filtered and collect the filtrate for analysis. Three different materials of the composite wooden floor, glazed tiles and concrete were analysed, and all three produced five gasoline’s characteristic peaks (4-

methyl-4-hydroxy-2-pentone, ethylbenzene, p-xylene, o-xylene and cyclic ethers) have been found in the Total Ion Chromatogram (TIC) from the database.

The most highlighted advantage of using solvent wash is that they allow separation of heavy hydrocarbon compounds with a high boiling point from the substrate matrix (Borusiewicz, 2002). This procedure is, however, laborious, time-consuming and use a lot of solvents, thus is rarely used nowadays as it seems impractical and less productive due to minute ignitable liquid residue recovery. In addition, the issue of contaminants carry over from burnt substrate is a major concern despite claimed to be more effective than adsorptive carbon strip method.

2.4.2 Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction (SFE) for forensic fire analysis has been attempted to detect hydrocarbons soil (Lundegard et al., 2003). In some arson instances, the soil was collected as the matrix for discarded ignitable liquid. These findings have implications for crime scene investigators completing soil evidence investigation. This method is used to extract large substances in solid samples using SPE apparatus. Gases become fluid when temperature and pressure reach a critical point called the supercritical phase. The sample is placed in the extraction chamber through which the supercritical fluid is forced. The target substances are extracted from the sample. This method is a green technology. It uses gases that environmentally friendly, which is CO_2. It also uses less solvent as compared to other solvent extraction. The result of chromatography analysis gives molecular distribution with no significant bias on either low or high molecular weight component and both volatile and semi-volatile hydrocarbons.

Huang and Hsieh (2002) also assessed the used of SFE to extract unleaded gasoline, kerosene and diesel from the soil. The authors highlighted the importance of determining the optimum SFE conditions (temperature, flow rate and exposure time). They claimed that this method was faster and more efficient as compared to solvent extraction and headspace methods. The disadvantage is that it uses highly specialized and expensive equipment to perform the extraction. It also sensitive to water; thus, particular attention is needed when encountering soils with high moisture content.

However, most researchers chose headspace extraction to extract IL from the soil due to its simplicity, save cost, no need to consider the water and moisture content of the soil as compared to SFE (Harris and Wheeler, 2003; Turner and Goodpaster, 2009; Turner et al., 2014; Cacho et al., 2014). Under the experimental condition, the effects of soil water content on volatilization of gasoline from soils were not obvious using passive headspace method. However, as has been mentioned earlier, passive headspace is not suitable for hydrocarbon with high molecular weight.

2.4.3 Electric Nose for Field Detection

As fire investigations evolve due to the complexity of ignitable liquids and substrate matrixes, Conner et al. (2006) developed field sampling techniques which applied electronic noses and a dynamic headspace sampler to screen and detect ignitable liquid residues at the fire scene. Electronic noses are often used for the initial evaluation of a fire scene to detect the presence of volatile compounds. The devices examined in this study (the TLV Sniffer, the TPI Pocket combustible gas leak detector and the portable arson sampler) proved the ability to concentrate small amounts of a range of volatile ignitable liquids from burned debris. These devices are field-portable and do not require skilled operators, providing relatively simple, inexpensive methods to collect and store evidence from a suspected arson scene.

These methods have both advantages and drawbacks. As a result, sample preparation techniques still evolve for improvements because the available ignitable liquids and substrate materials also evolve. Innovations for economical and affordable methods in fire debris analysis continues.

2.5 Activated Carbon Cloth as Adsorbent Material by Passive Diffusion

One of the foremost popular extraction techniques in fire debris analysis is passive headspace adsorption using activated carbon devices. In practice, a specialised activated carbon strip (ACS) is used. In recent studies, innovations using Activated carbon cloth (ACC) were reported as a possible adsorbent material for fire debris analysis. ACC can be obtained by carbonization and activation of previously impregnated organic polymers, mostly of cellulose origin. Due to high specific surface area and microporosity, ACC shows good adsorptive properties both in the gaseous and the liquid phase (Cukierman, 2013).

Several investigators have used ACC to remove organics and inorganics from aqueous solutions (Babić et al., 1999). In 2016, Sandercock assessed the performance of ACC to recover volatile organic compound as compared to activated carbon strip (ACS) which has been commercialized and widely used. They examined whether ACC performance is comparable with the designated ACS. Both ACC and ACS were cut approximately the same size (1 x 2 cm) and weight, undergo passive diffusion extraction and GCMS analysis. It was reported that both ACC and ACS efficiently extracted a wide range of hydrocarbons from lighter ignitable liquid to heavier ignitable liquid. Both chromatogram profile did not show any significant alteration when compared with neat liquid. However, ACC extract was more consistent and concentrated than ACS extract. The result is said to be due to the more available active sites per gram of adsorbent compared to ACC. ACS has less active sites per gram resulting from the manufacturing process as ACS mixed activated carbon powder with binder which subsequently coat some of the carbon surfaces within the ACS.

This approach offers other economic alternative for investigators since ACS is more expensive. The unit price (1x2 cm) for ACS in the study was US$ 3.20, whereas for ACC of the same size was only US$0.05. ACC is a viable options and supported by Rusmaini (2018) which concurred that ACC has high adsorption and desorption rate, lower resistance to gas flow, has uniform porosity, higher surface area and flexible to any shape of sampling container and debris samples.

2.5.1 Optimisation of ACC for Fire Debris Extraction

ACC used for ignitable liquid extraction parameter's optimum condition are discussed by Newman et al., 1996; Sandercock, 2016; Rusmaini., 2018). The optimum condition is important because, in fire debris analysis, TIC pattern from GCMS comparison with appropriate abundance is crucial for classification. Parameters related to incubation parameters and container volume were focused on obtained desirable TIC pattern. The effects of incubation temperature, exposure time and container volume can lead to the finding of the most optimum condition for the extraction of ignitable liquid residues. Differences in activated carbon performance have been noted with these parameters. Newman et al. (1996) anchored the optimisation work of activated carbon device using ACS.

The work investigated the relationship between exposure time of 2, 8, 16, 24 and 48 hours and incubation temperature at ambient temperature, 60 °C, 90 °C, and 120 °C with fixed container size (Newman et al., 1996). The authors found at lower incubation temperatures; the higher molecular weight compounds were not adequately volatilised for adsorption as compared to room temperature. A good hydrocarbon compounds profile up to C14 (tetradecane) were detected. It was noted that even the incubation hour was increased to 48 hours, the component above C15 (pentadecane) were not adequately sampled at incubation temperature lower than room temperature. In contrast, at higher incubation temperature, the higher molecular weight components were adsorbed and sampled adequately. However, they found limitation that the lower molecular weight compounds were having distortion as the chromatogram shifted to the right (to higher molecular weight component) and much more pronounced over time (Newman et al., 1996).

Sandercock (2016) compared the performance of two different types of activated carbon; cloth and strips. Both ACC and ACS were examined to extract ignitable liquid at room temperature and at elevated temperature (60 °C). Incubation time and container volume were kept constant at 16 hours, and one litre of paint can. Based on the chromatogram profile, it was reported that at room temperature, heavy petroleum distillates (diesel fuel) does not show TIC pattern that matching TIC of standard accelerant mixture (SAM). In addition, the result shows at room temperature, both ACC and ACS were not able to adsorb full range of heavier compound up to C20. At elevated temperature, both ACC and ACS were able to show the pattern and a full range of TIC matching TIC pattern of SAM. Lighter petroleum distillates (lighter fluid and gasoline) were successfully extracted at both room temperature and elevated temperature.

In a similar experimental work, Rusmaini (2018) reported adsorption of ignitable liquid by ACC and showed that the device could produce a full range of Standard Accelerant Mixture (SAM) Total Ion Chromatogram (TIC) pattern was at the lowest temperature of 60 °C when exposed for at least 8 hours. An acceptable abundance of SAM TIC at the shortest time is at least 2 hours at temperature 120 °C with no displacement effect. The findings showed that both parameters (time and temperature) chosen must undergo careful consideration and in balance with each other.

Hypothetically, the vapour pressure of liquid increased when temperature increases (Stauffer et al., 2008). The ignitable liquid takes longer time to reach its equilibrium states at a lower temperature, and this leads to the less ignitable liquid analyte to be evaporated and adsorbed to ACC, especially higher molecular weight molecule. Generally, as molecular mass of molecule increase, the boiling point increase and hence volatility decreases which end in low vapour pressure. Therefore, lesser compounds are absorbed by ACC at a lower temperature, for example at ambient temperature. At much higher temperature as reported by the author at 60 °C and above, more compound can be absorbed by ACC because the vapour pressure increased and caused more ignitable liquid compounds evaporated to the headspace. Balanced with the incubation time, some ignitable liquid compounds were not adequately adsorbed if too short time were given to reach the equilibrium state.

Rusmaini (2018) compared the adsorption of ignitable liquid of ACC by passive diffusion at different container volume of 250 mL, 500 mL and 1000 mL tin can. The effect was evaluated from TIC obtained from GCMS. The author identified differences in peak abundance where peak height increased when the volume of container increased. The result showed that the container volume only affects peak abundance;

however, did not affect the distribution of the compounds. Headspace volume increased as the volume increased. Thus, more compounds could be evaporated to the bigger space area resulting in more compounds absorbed by the ACC. The temperature is kept constant; therefore, the vapour pressure of liquid components are equal in all containers and was not affecting the results. However, it must be noted that during headspace extraction, the container must have the minimum volume to adequately transfer the ignitable liquids compound from substrate to the adsorbent. All container volume used in the experiment exceeded the minimum volume required since the ignitable liquid compound were able to be transferred to the adsorbent. These results also reiterate that using an unlined tin can with a secured lid resulted in good TIC profile thus is applicable alternatives for nylon bag or glass jar.

2.6 Artificial Neural Network for Parameter Optimisation

TIC data sets from the chromatographic pattern (GCMS) profile of different parameters were usually examined by visual comparison of target compounds (ASTM E1618). Optimisation work of many parameters by manual comparison of TIC pattern is cumbersome and tedious. One of the drawbacks of this system is that the manual interpretation and classification of the info is restricted by the skill, knowledge and subjectivity of the analyst as well as time-consuming (Anaya et al., 2009).

Optimisation of various parameters which contains a large amount of analytical data (i.e. GC data) can be facilitated using computational mathematical modelling. Smith et al. (2005) analysed various headspace-enrichment conditions of residual petroleum distillates used by arsonist simultaneously to obtain an optimal response by simplex optimisation. The authors reported different classes of petroleum distillates volatilise at different temperature and incubation temperature. It was also emphasised that the headspace sample preparation technique is both times- and temperature-dependent. One of the limitations of this method is time-consuming and not practical since a result must be obtained in order to determine new conditions. Therefore, to overcome this problem, the big dataset obtained was introduced to a group of machine learning algorithm called Artificial Neural Network (ANN) as the means for evaluation.

ANN is able to handle many data and parameters at one time. ANN was designed to imitate the behaviour of Natural Neural Network by having neuron operation, information processing, to learn and later generalised a solution to produced desired response (Vidaki et al., 2017). In detailed, ANN contains discrete layers; the primary layer, which is the input layer that contains the dependent variables (Figure 2.2).

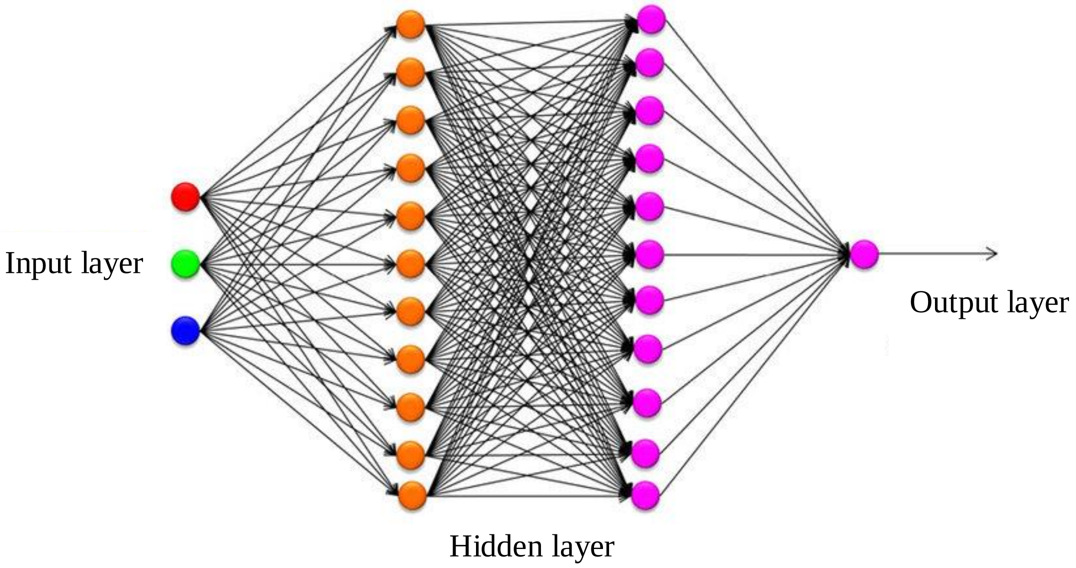

Figure 2. 6: General ANN Architecture (Bang-iam et al., 2013)

In this study, the dependent variables are the peak area of each targeted peak of different incubation temperature and adsorption time. Each of those variables is