# NOVEL SOLID-PHASE MICROEXTRACTION ADSORBENT FOR THE FORENSIC DETECTION OF ACCELERANTS IN ARSON SAMPLES

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*Specially dedicated*

*to my*

*beloved parents and brother…*

# ACKNOWLEDGEMENTS

# ABSTRACT

Numerous adsorbents are available commercially as coatings for solid-phase microextraction (SPME) technique. However, some analytical methodologies might demand specific properties for the extraction of selected compounds. In this study, a simple, fast, effective and environmental friendly methodology for the determination of accelerants in arson samples using headspace-SPME coupled to gas-chromatography-flame ionization detector (GC-FID) is presented. A lab-made coated fiber prepared by sol-gel method, containing 1:1 molar ratio of octyltriethoxysilane ($C_8$-TEOS): methyltrimethoxysilane (MTMOS) was employed in this technique. The fiber was tested for the headspace extraction of *n*-alkane standard hydrocarbons and common accelerants. Applicability of the fiber was demonstrated through the detection of accelerants in simulated arson samples. The $C_8$-coated fiber showed a good selectivity for accelerants. Compared with commercial PDMS/DVB fiber, the lab-made coated fiber exhibited higher extraction capability for accelerants, higher thermal stability (up to 300 $^\circ$C) and longer lifetime (~ 200 times usage). Electron microscopy experiment revealed that the surface of the fiber coating was well-distributed. A porous structure was suggested for the sol-gel derived $C_8$ coating with an approximate thickness of (3-4) μm. The underlying mechanisms of the coating process were discussed and confirmed by infra-red (IR) spectrum. HS-SPME parameters, such as extraction time, extraction temperature and desorption time were optimized. The developed headspace-SPME method using $C_8$-coated fiber showed satisfactory reproducibility (RSD < 6%), linearity (r > 0.9869) and detection limits for accelerants (0.7-1.0) μL. The lab-made SPME adsorbent was shown to be a good alternative to commercial SPME fiber for the determination of accelerants in arson cases.

# ABSTRAK

Pelbagai jenis penjerap salutan bagi teknik pengekstrakan fasa pepejal mikro (SPME) boleh didapati secara komersial. Bagaimanapun, beberapa kaedah analisis memerlukan ciri-ciri khas bagi pengekstrakan sebatian yang terpilih. Kajian ini membentangkan suatu kaedah yang mudah, pantas, efektif dan mesra alam sekitar untuk menentukan bahan penggalak kebakaran dalam sampel kebakaran yang disengajakan dengan menggunakan teknik SPME secara ruang kepala (HS) yang digabungkan dengan kromatografi gas-pengesan pengionan nyala (GC-FID). Gentian salutan buatan sendiri yang disediakan melalui kaedah "sol-gel", dengan nisbah molar oktatrietoksisilana ($C_8$-TEOS): metiltrimetoksisilana (MTMOS) 1:1 telah digunakan dalam teknik ini. Gentian tersebut telah diuji untuk pengekstrakan hidrokarbon $n$-alkana piawai dan bahan penggalak kebakaran yang lazim. Pengunaan gentian tersebut telah ditunjukkan melalui pengesanan bahan penggalak kebakaran dalam sampel simulasi kebakaran yang disengajakan. Gentian salutan $C_8$ ini menunjukkan kepilihan yang baik bagi bahan penggalak kebakaran. Berbanding dengan gentian komersil (PDMS/DVB), gentian salutan buatan sendiri menunjukkan kebolehan pengekstrakan yang lebih tinggi bagi bahan penggalak kebakaran, kestabilan terma yang lebih tinggi (sehingga 300 $^{\circ}$C) dan jangka hayat yang lebih lama (~ 200 kali penggunaan). Eksperimen mikroskopi elektron menunjukkan bahawa permukaan gentian telah disalut dengan sempurna. Struktur berliang telah dicadangkan untuk salutan $C_8$ terbitan sol-gel dengan ketebalan yang beranggaran (3-4) µm. Mekanisme proses penyalutan telah dibincangkan dan ditentukan melalui spektrum infra-merah (IR). Parameter HS-SPME, seperti masa pengekstrakan, suhu pengekstrakan dan masa penyahjerapan telah dioptimumkan. Kaedah HS-SPME yang dibangunkan menggunakan gentian salutan $C_8$ menunjukkan kebolehulangan (RSD < 6%) kelinearan(r > 0.9869) dan had pengesanan (0.7-1.0) µL yang memuaskan bagi bahan penggalak kebakaran. Penjerap SPME buatan sendiri menunjukkan suatu alternatif yang baik kepada gentian SPME komersial bagi penentuan bahan penggalak kebakaran dalam kes kebakaran yang disengajakan.

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GC   -   Gas Chromatography

FID   -   Flame ionization detector

GC-FID  -   Gas Chromatography with flame ionization detector

SPME  -   Solid phase micro extraction

HS-SPME -   Headspace solid phase micro extraction

PDMS/DVB -   Polydimethylsiloxane/Divinylbenzene

$C_8$-TEOS  -   *n*-Octyltriethoxysilane

MTMOS  -   Methyltrimethoxysilane

TMMOS  -   Trimethylmethoxysilane

LOD   -   Limit of Detection

RSD   -   Relative standard deviation

v/v   -   Volume per volume

SEM   -   Scanning Electron Microscopy

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# CHAPTER 1

# INTRODUCTION

## 1.1    Background

Arson continues to be both an urgent national problem and truly a contemporary crime. Often characterized as a clandestine tool for criminals, the true arson picture is not clearly known. The Fire and Rescue Department Malaysia reported that it has responded to 103,994 fire cases between the year 1997 to 2003 (www.bomba.gov.my, 2006). Loss of life and damage of properties are always a grave concern in fires. Economically, arson impacts insurance premium rates, removes taxable property assets and degrades communities. Historically, the inner areas of large cities often are most hard-hit and the result is that much of the cost of this destructive crime is placed on those who can least afford it (Dennett, 1980).

Arson can be defined as an intentional or attempted damaging or destruction, by means of fire or explosion, of the property of another without the consent of the owner, or of one's own property or that of another with intent to defraud (Rush, 2000). The motives to commit arson are numerous, including revenge, fraud or profit, sabotage, pyromania, vandalism, concealment of another crime and terrorism. Arsons are particularly difficult crime to investigate and prosecute. Its difficulty lies in these areas (O' Connor, 1987):

- Every fire scene need to be treated as a potential arson scene (from the standpoint of security, preservation and evidence) until clear proof of natural or accidental cause is discovered.

- The crime itself, if successful, destroys the physical evidence at its origin. In some cases, the evidence is still there but it requires careful and methodical analysis.

Arson is a crime that destroys evidence rather than creates it as it progresses and normally there is not much first hand eyewitness evidence. Therefore the findings of a scientific investigation are considered important in criminal and civil court actions.

## 1.2 Arson Crime Scene Investigation

An important aspect of an investigation of a suspected arson case involves the chemical analysis of the debris remaining after the fire. The aim of the on-site investigation is to establish beyond reasonable doubt the cause of the fire origin from an investigation of the fire debris and remaining building structure and obtaining physical evidence pertinent to the ignition source.

### 1.2.1 Arson Samples and Burn Patterns

The presence and distribution of a flammable liquid at a fire scene indicates a deliberately lit fire unless it can be readily explained otherwise. "Sniffers" or portable hydrocarbon detectors are used by many successful investigators (DeHaan, 1997).

Burn patterns are the basis of all fire investigation. It can be used to indicate the direction of fire spread observed on structural elements or wall surfaces. The typical V-pattern associated with most fires is a result of several factors, one being that the natural

plume shape of a large fire is a cone. This cone's shape depends on the size of fire with respect to a ceiling that tends to flatten and spread it horizontally. If a fire is located some distance away from the wall, a shallow U- or V-pattern may appear (O'Connor, 1987; DeHaan, 1997).

Arson samples are normally collected at the suspect crime scene and submitted to the laboratory either in new aluminium cans or forensic evidence bags. In collecting samples, investigators need to look for places where the ignitable liquids would be protected from the heat because those volatile liquids are driven off by high temperature and not likely to be found in the deepest char areas. Multiple samples should be taken so that the spread of the accelerant is ascertained (Furton *et al*., 1995).

## 1.2.2   Analysis of Fire-Scene Samples

The majority of fire-scene evidence submitted to the laboratory for analysis consist of various materials, such as wood, plastics, soil, carpet, cloth, metals, liquids and other organic and inorganic substances. Laboratory examinations of the fire debris includes (Almirall *et al*., 1996a; Harris and Wheeler, 2003; Almirall *et al*., 2004; Ma *et al*., 2004):

- Macroscopical and microscopical examination of the debris - (most fire debris consists of burned or partially burnt substances, weathering has already occurred before collection. Therefore brief visual examination of fire debris will not cause any great loss of accelerants).
- Recovery of the accelerants from the debris – [separation of analytes from the matrix (fire debris, soil and water) and concentrating them].
- Identification of the accelerants – (chemical analysis of the isolated substances and the identification of the mixture).

The difficulties with the identification of accelerants traces isolated from fire debris or environmental samples (water and soil) result mainly from the fact that the isolated traces differ qualitatively and quantitatively from the initial mixtures. These differences appear as a result of (Cavanagh *et al.*, 2002; Sandercock and Pasquier, 2003):

- Evaporation - in the isolated traces, there is a lack of volatile compounds in comparison to the high boiling ones.
- Pyrolysis - as a result of high temperature effect, the big molecules can disintegrate and the disintegration products arise.
- Microbiological decomposition.
- In the isolated traces, the additional substances appear - for example matrix components or matrix decomposition products, extinguishing medium components.

### 1.2.3    Court Presentation and Arson Evidence

The investigator must use laboratory analysis to support arguments in court. Opinion and theories can be readily challenged in court because of the complex and varied nature of fires, but laboratory evidence is irrefutable proof of the presence of an accelerant. These are the basic elements that need to be considered to prove the crime of arson (Icove and Dehaan, 2004):

- There has been a burning of property - (this must be shown to the court to be actual destruction, not just scorching or soothing).
- The burning is incendiary in origin – (proof of the existence of an effective incendiary device accomplished by showing how all reasonable natural or accidental cases have been considered and ruled out).
- The burning is shown to be started with malice – (this act of burning requires a specific intent of destroying property).

## 1.3     Nature of Accelerants

Accelerants are any type of material or substance added to the targeted materials to enhance the combustion of those materials and to accelerate the burning. Accelerants such as petrol, kerosene, diesel, mineral turpentine and methylated spirits are widely utilized in everyday life. Owing to their physico-chemical properties such as volatility and flammability, they are also used as ignitable liquids to commit arsons by offenders. Exotic accelerants such as industrial solvents are rarely used and if so are readily identified by chemical analysis because of their similar chemical characteristics to the common accelerants (Furton *et al*., 1995; Harris and Wheeler, 2003).

Accelerants can be classified as either mixtures of compounds or pure compounds. The chromatographic analysis of a pure compound will feature a single peak while a mixture will give several peaks that contribute to a fingerprint which is used to identify the accelerant. The more volatile components of an accelerant evaporate at a faster rate than the heavier components so that the overall chemical profile of the accelerant will change during the fire and before sampling (Jackowski, 1997).

The amount of accelerant remaining at the fire scene available for sampling is governed by factors such as the initial loading, volatility and water solubility of the accelerant, severity of the fire, porosity of the substrate material, dryness of the area after the fire and elapsed time between the fire and sampling. (Almirall *et al*., 1996b; Cavanagh *et al*., 2002; Almirall *et al*., 2004).

Samples of a suspected accelerant are often located at the scene in a container and are supplied for analysis. Samples of this type are usually unaffected by evaporation. It is difficult to conclusively determine if a sample of an accelerant was the same as that to initiate or propagate a fire, because of the universal composition of the common accelerants (Dennet, 1980).

The chemical components of the common accelerants are aliphatic and aromatic hydrocarbons and oxygenated hydrocarbons such as alcohols. The oxygenated hydrocarbons are somewhat water soluble and therefore washed away during the extinguishing of the blaze, so that little trace remains (Cavanagh *et al*., 2002; Sandercock and Pasquier, 2002).

The most common accelerants used by arsonists are generally low to medium boiling hydrocarbon liquids. Some common accelerants and their properties are shown in Table 1.1.

**Table 1.1**: Properties of common accelerants (Lee *et al*., 1986).

| Accelerant | Flash Point ($^{\circ}$C) | Boiling Point ($^{\circ}$C) | Self-Ignition Temperature | Explosive Limit (%) | | Flammable Range (%) |
|---|---|---|---|---|---|---|
| | | | | Low | High | |
| Gasoline | -50 | 102-230 | 495 | 1.3 | 6.0 | 1.3-6.0 |
| Kerosene | 110-165 | 400-572 | 490 | 1.16 | 6.0 | 1.2-6.0 |
| Fuel oil No.1 | 110-165 | 350-500 | 490 | 1.16 | 6.0 | 1.2-6.0 |
| Fuel oil No.2 | 110-190 | 375-650 | 494 | - | - | - |
| Turpentine | 95 | - | 488 | 0.8 | 6.0 | - |
| Petroleum benzin | 20-45 | 300-400 | 450-500 | 0.9 | 8.0 | 1.1-6.0 |

Gasoline, the most important fuel of petroleum origin, is a mixture of volatile, low-boiling and midrange hydrocarbons. The average molecular weight of gasoline is usually taken to be close to that of *n*-octane, about 114. Modern automotive gasoline contains more than 100 hydrocarbons in a complex mixture. Before being sold as a motor fuel, however, a variety of additives is added by the refinery. These additives

often include compounds to improve the burning characteristics of the fuel and dyes to identify one product from another (Almirall *et al*., 1996a; Almirall *et al*., 1996b).

Kerosene and the distillate fuels of higher boiling ranges were considered useful only for illumination until diesel motor became a common device. Although diesel fuel is similar to kerosene, it spans a wider range of less volatile components. Kerosene and heavier petroleum distillates have long been of significance in the setting of deliberate fire. Their lower volatility presents less hazard to the user than does gasoline. The liquid is more persistent so that less haste is required in its ignition and there is much less danger of explosion (Ren and Bertsch, 1999; Llyod and Edmiston, 2003).

Fuel oil No.1 (Jet Fuel A) generally contains paraffinic and olefinic hydrocarbons in the $C_{10}$-$C_{16}$ range (this range denotes hydrocarbons having 10 to 16 carbon atoms linked together). It falls in the fraction which follows gasoline in the simple distillation of crude oil. Diesel fuel contains low sulfur content and additives to improve combustion. Diesel fuel and domestic heating oil may both be described as fuel oil No. 2. The heavier stove oil used in room heaters contains hydrocarbons from a slightly higher boiling point range, usually (375-650)$^{\circ}$F. The product for home use is carefully controlled to minimize sulfur and water content which could corrode heating units having minimal service. Those fuels intended for industrial service have higher sulfur and ash content and cover a range of products and applications (O'Connor, 1987; DeHaan, 1997; Icove and Dehaan, 2004).

## 1.4    The Evolution of Accelerant Extraction Technique

The forensic discipline of ignitable liquid and fire debris analysis is rapidly changing. Refinements in existing methods as well as development of new techniques are changing the routine methods of analysis. Optimization of existing accelerant extraction, analytical techniques and research into novel methods of extraction have

improved the recovery of ignitable liquids from debris samples, sample turnover and reduced the number of inconclusive findings (Dolan, 2003).

The earliest methods of identification relied upon simple identification of the headspace odor - often referred to as a "nasal appraisal". With improvement in analytical instruments, the extraction technique used was sampling a headspace of heated fire debris with a syringe and then injecting the sample into a GC for analysis. Heated headspace analysis is also used for sample screening because it is simple, rapid and easy technique to apply. A sample that gives a negative result when screened by heated headspace would then be subjected to a more sensitive extraction technique. The technique however, discriminates against the less volatile components in the sample which will give less data from the chromatographic analysis for interpretation (Eisert and Pawliszyn, 1997; Lord and Pawliszyn, 2000).

Distillation technique are used with steam distillation being the most popular. Distillation involves heating the sample with an extraction medium and condensing the vapor to provide a sample of the accelerant in the extraction medium used. The various medium that have been used are water, ethanol and ethylene glycol. Vacuum distillation with sub ambient trapping of the volatiles can also be used. The accelerant may be further concentrated by controlled evaporation of the medium or by solvent extraction from the medium. Steam distillation can be a lengthy technique and extraction times of up to 48 hours have been reported as being necessary for some samples. The technique however, requires considerable clean up of the apparatus between samples and also considerable operator attention, therefore the sample turnover is low (Eisert and Pawliszyn, 1997; Lord and Pawliszyn, 2000).

Solvent extraction is also used and involves soaking the fire debris in a suitable solvent and then filtering and evaporating the solvent to concentrate the sample. The advantages of solvent extraction is that it readily extracts the less volatile components of an accelerant and therefore does not discriminate between fire debris samples. The

technique however, requires the use of high purity solvents which are expensive and also matrix components such as monomers, plasticizers, glues and resins are co-extracted which may interfere with the subsequent analysis. Both distillation and solvent extraction require further concentration of the raw extracts to increase the sensitivity of the technique (Dolan, 2003).

Dynamic headspace sampling is widely used for the extraction of accelerants. The debris is heated inside the headspace gas chromatograph and if any volatile hydrocarbons are present, they will vaporize and be present in the air or "headspace" directly above the debris. The transfer gas used to sweep the headspace to the adsorbent is usually nitrogen or the headspace can be drawn through the absorbent with a vacuum. Microwave ovens have also been used to heat the sample and the steam generated sweeps the headspace to the absorbent. A major problem of dynamic headspace extraction technique is the carry over of contaminants from previous samples through the gas transfer lines. It was found that by removing the outward gas transfer line and connecting the charcoal tube directly to the sample container, the contamination problem was reduced (Eisert and Pawliszyn, 1997; Lord and Pawliszyn, 2000; Dolan, 2003).

## 1.5    Solid-phase Microextraction (SPME)

In addition to optimizing existing extraction techniques, the field of forensic science has also introduced a new extraction technique for application to fire debris analysis: solid-phase microextraction. Much interest has been shown recently in replacing conventional accelerant residues extraction technique with headspace SPME technique ever since the technique was invented in the early 1990's by Prof. Janusz Pawliszyn. SPME is a fast, simple, time-efficient, environmental friendly and sensitive technique, which does not require the use of solvents either for sample preparation or cleanup. Analyte extraction and pre-concentration are combined in one single step

(Mester *et al*., 2001; Theodoridis *et al*., 2000). Figure 1.1 shows the dimensions and architecture of the commercially available SPME device attached with lab-made fiber.

(a)  (b)
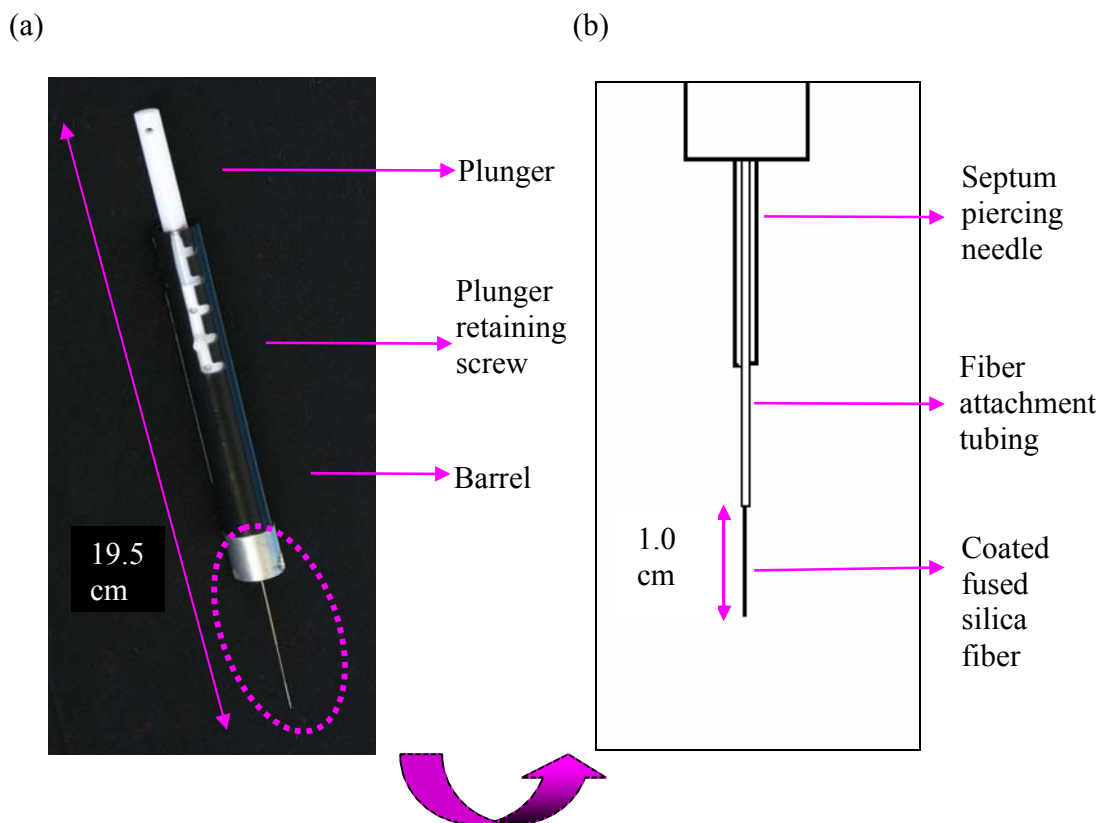


**Figure 1.1** : (a) A photograph and (b) an illustration of the commercially available SPME device attached with coated fused-silica fiber.

In SPME, the outer surface of a solid fused-silica fiber is coated with a selective stationary phase. Thermally stable polymeric materials that allow fast solute diffusion are commonly used as stationary phases. The extraction is based on the enrichment of components on a polymer or adsorbent coated fused silica fiber by exposing the fiber either directly to the sample or to its headspace. The extraction time can be considered complete when the analyte concentration has reached a distribution equilibrium between the sample matrix and the fiber coating. When using this in experimental conditions, it means that when the equilibrium is reached, the amount of the extracted analytes is

constant and independent of an increase in extraction time. This is followed by thermal desorption in a gas chromatograph (Zhang *et al.*, 1994a).

The major advantages of SPME technique are in terms of speed, sensitivity, cost effectiveness and versatility (Zhang *et al.*, 1994b). In SPME, the equilibration can be reached in only 20-30 minutes which makes it ideal for quick screening. The parts per trillion detection limits have been attained, with an ion-trap detector. The solvent purchase and disposable costs are greatly reduced in this technique. Fibers are reusable (lifetime depends on conditions of use, more than 100 uses have been achieved). SPME can be used with any GC or GC-MS with split/splitless or on-column injection.

## 1.5.1 Principles of SPME

A traditional approach to SPME involves coated fibers. The transport of analytes from the matrix into the coating begins as soon as the coated fiber has been placed in contact with the sample. Typically SPME extraction is considered to be complete when the analyte concentration has reached distribution equilibrium between the sample matrix and the fiber coating. In practice, this means that once equilibrium is reached, the extracted amount is constant within the limits of experimental error and it is dependent of further increase of extraction time. The equilibrium can be described as (Lord and Pawliszyn, 2000; Wang *et al.*, 2005):

$$n = \frac{K_{fs}V_fV_sC_o}{K_{fs}V_f + V_s} \tag{1.1}$$

where $n$ is the number of moles extracted by the coating, $K_{fs}$ is a fiber coating or sample matrix distribution constant, $V_f$ is the volume of the fiber coating, $V_s$ is the sample volume and $C_o$ is the initial concentration of a given analyte. Eq (1.1) indicates that,

after equilibrium has been reached, there is a direct proportional relationship between sample concentration and the amount of analyte extracted.

Eq. (1.1), which assumes that the sample matrix can be represented as a single homogeneous phase and that no headspace is present in the system, can be modified to account for the existence of other components in the matrix by considering the volumesof the individual phases and the appropriate distribution constants. The extraction can be interrupted and the fiber analyzed prior to equilibrium. Constant convection conditions and careful timing of the extraction are necessary to obtain reproducible data (Lord and Pawliszyn, 2000).

When the sample volume is very large, Eq. (1.1) can be simplified as (Wang *et al.*, 2005) :

$$n = K_{fs}V_fC_o \tag{1.2}$$

which points to the usefulness of the technique for field applications. In this equation, the amount of extracted analyte is independent of the volume of the sample. In practice, there is no need to collect a defined sample prior to analysis as the fiber can be exposed directly to the ambient air, water or production stream. The amount of extracted analyte will correspond directly to its concentration in the matrix, without being dependent on the sample volume.

The equilibrium equation for analysis in a vial containing headspace should be expressed as shown in Eq (1.3) (Zhang and Pawliszyn, 1995; Lord and Pawliszyn, 2000):

$$n = \frac{K_{fs}V_fV_s}{K_{fs}V_f + K_{hs}V_h + V_s} C_o \tag{1.3}$$

Where $K_{hs}$ and $V_h$ represent the headspace/sample distribution coefficient and the volume of the headspace, respectively. The fact that SPME is an equilibrium rather than an exhaustive extraction technique means that even after the extraction process has been completed, a substantial portion of the analytes usually remain in the matrix. This presents an opportunity for quantification based on internal standardization, namely the standard is loaded onto the fiber prior to extraction step, instead of spiked into the sample.

## 1.5.2 Extraction Modes With Coated SPME Fibers

Generally, there are three types of extractions that can be performed using SPME: direct extraction, headspace configuration and membrane protection approach.

In the direct extraction mode, the coated fiber is inserted or immersed into the sample and the analytes are transported directly from the sample matrix to the extracting phase. In order to facilitate rapid extraction, some level of agitation is required to transport analytes from the bulk of the solution to the vicinity of the fiber. Natural convection of air is sufficient for gaseous sample to facilitate rapid equilibration (Zhang *et al*.,1994b).

In the headspace mode, the analytes need to be transported through the barrier of air before they can reach the coating. This modification serves primarily to protect the fiber coating from damage by high molecular mass and other non-volatile interferences present in the sample matrix such as proteins. This mode also allows the modification of the matrix, such as a change of the pH or temperature, without damaging the fiber (Zhang and Pawliszyn, 1993).

Another indirect SPME extraction mode is through a membrane. The main purpose of the membrane barrier is to protect the fiber against damage, similar to the use of headspace SPME when very dirty samples are analyzed. However, membrane protection is advantageous for determination of analytes having volatilities too low for the headspace approach. In addition, a membrane made from appropriate material can add a certain degree of selectivity to the extraction process. The use of thin membranes and increased extraction temperatures will result in faster extraction times (Mester *et al*., 2001; Theodoridis *et al*., 2000).

### 1.5.3    Recovery of Accelerants by Headspace-SPME (HS-SPME) Technique

The separation and recovery of accelerant residues from fire debris are essential steps for the identification of the accelerants. HS-SPME is a simple and convenient method for the recovery of accelerant vapors from fire debris. The objectives of analyzing the debris is to determine the presence of any volatile hydrocarbon compounds. Initially, therefore, the accelerant residues (volatile compounds) need to be separated from the debris (nonvolatile matrix). The technique is employed by introducing a coated SPME fiber into the headspace above the debris which is placed in an air-tight container. The volatilized hydrocarbon compounds are extracted and concentrated in the coating. After exposure to the sample headspace, the fiber is transferred to the analytical instruments for desorption of the extracted analytes (Snow and Slack, 2002.

Theoretically, any volatiles present will reach a vapor equilibrium in a sealed container. Molecules of the accelerants actually occupy the entire interior space of the container. Part of the interior is occupied by the liquid phase of the accelerant and the remainder is occupied by its vapor phase. The continuous molecular motion in liquids causes the molecules to constantly leave the liquid phase to enter the vapor phase. At the same time, molecules also continuously leave the vapor phase to reenter the liquid

phase. The molecules of a volatile compound at any given temperature have a specific average kinetic energy that is dependent upon the absolute temperature of the liquid. Some molecules at the liquid surface have energies greater than the average energy, therefore, they continuously leave and enter the gaseous phase (Snow and Slack, 2002b; Zhang and Pawliszyn, 1993).

Heating the sample to an elevated temperature provides energy for analyte molecules to overcome energy barriers which tie them to the matrix, enhances the mass transfer process and increases the vapor pressure of the analytes. However, excessive temperatures encourage the degradation of synthetics in the debris, such as carpet. These degradation products add to the complexity of the chromatogram which is used for accelerant identification. Excessive heating also lowers the level of real accelerants in debris and this does not contribute to the sensitivity of the method (Zhang and Pawliszyn, 1995).

## 1.5.4   Identification of Volatile Accelerants by SPME-Gas Chromatography Analysis

The analytical instrument used most frequently with SPME has been the gas chromatograph (GC). Standard GC injectors, such as split/splitless can be applied to SPME as long as a narrow insert with an inside diameter close to the outside diameter of the needle is used. The narrow inserts are required to increase the linear flow around the fiber, resulting in efficient removal of desorbed analytes. The split should be turned off during SPME injection. Under these conditions, the desorption of analytes from the fiber is very rapid (Lord and Pawliszyn, 2000).

GC uses a stream of gas (nitrogen or helium) as a carrier to move a mixture of gaseous materials along a column, tube filled or coated with a separating compound. The analytes interact with the separating compound by alternatively dissolving in it and then

volatilizing to be swept further along the column by the carrier. The SPME fiber is introduced onto the column at one end and at the other end is a detector (Eisert and Pawliszyn, 1997). Columns for GC analysis of suspected arson residues are usually set up to offer the best separation of components having volatilities between those of pentane ($C_5H_{12}$) and triacontane ($C_{30}H_{62}$), since that range includes all of the commonly encountered petroleum products. Packed tubular column (3 mm in diameter) were commonly used but it has now been supplanted by a very narrow capillary columns (0.1 mm in diameter). This resulted in shorter analysis time and the usage of smaller sample sizes (DeHaan, 1997).

Although the column can be selected to separate a mixture of compounds on the basis of their chemical properties, most separations in volatile accelerants analysis are made on the basis of differences in the boiling points of the various components. Almost all the components of petroleum distillates of interest are either aliphatic (straight-chain) or aromatic (ring) in structure, thus will have very similar chemical properties within those two groups. The heavier a molecule is, the less volatile it is and it will appear last on the chromatogram (Lee *et al*, 1986; Zeeuw and Luong, 2002).

Flame ionization detector (FID) has been the standard detector for analysis of hydrocarbons but now specialized detectors can be used in arson work. Electron capture detectors, which use a minute radioactive source as a monitor, are very sensitive to particular chemical species such as organometallics and halogenated hydrocarbons. They can be used to characterize a petroleum distillate more precisely than is possible with (FID) alone. There are nitrogen-phosphorus detectors that are not sensitive to common hydrocarbons but will select those compounds in a complex mixture that contain nitrogen or phosphorus. Since the crude oil feed stocks for gasoline vary considerably in their nitrogen, phosphorus and sulfur containing components, it is very likely that such techniques may allow discrimination between gasoline from different origins (DeHaan, 1997; Zeeuw and Luong, 2002).

Mass spectrometer (MS) allows each molecule to break apart into small sub molecular pieces and by counting those pieces, the chemical structure of the original molecule can be established. MS is an analytical technique that needs to be fed one compound at a time while GC is a separation technique that is good at separating a mixture of compounds. Since most of the volatile residues in fire debris involve complex mixtures, coupling the two together gives the best tool. GC/MS has the capability of displaying a mass spectrum for each peak, and scan selected ions, those that are characteristic for a particular chemical species of interest (Borusiewicz *et al*., 2004; Lennard *et al*., 1995).

## 1.6    Commercial SPME Fiber Coatings

To date, several different coating materials are available from Supelco. There are three different polydimethylsiloxane (PDMS) films of different thickness (7, 30 and 100 µm), 85 µm polyacrylate (PA), 65 µm polydimethylsiloxane/divinylbenzene (PDMS/DVB), 75 µm, Carboxen/PDMS, 65 µm Carbowax/DVB and 50 µm Carbowax template resin fibers (Dolan, 2003).

For the right selection of the polymer coating, the general principles of "like dissolves like" applies. PDMS coated fibers are typically the first choice. They are very rugged and liquid coatings are used as GC stationary phases withstanding temperatures up to 300 $^{\circ}$C. This coating is non polar showing a high affinity for non-polar compounds. Very thin fiber coatings should be used whenever the sensitivity is sufficient. The extraction time is shorter for a thinner coating and smaller distribution constants of the analytes (Lord and Pawliszyn, 2000; Dolan, 2003).

The PA fiber shows a high affinity for polar compounds such as phenols and polar pesticides. PA is a solid polymer, thus the equilibration times are higher compared to the liquid PDMS fibers. The mixed phase coatings are more suitable for volatile

compounds. The take up of these fibers is significantly higher compared to PDMS. When changing from PDMS to carbowax using the mixed phase coatings, more polar analytes can be extracted such as ketones and alcohols (Eisert and Pawliszyn, 1997; Lord and Pawliszyn, 2000; Dolan, 2003).

All the commercially available coatings can be categorized according to two types of extraction mechanism, absorption and adsorption. Both PDMS and PA extract analytes via absorption. The absorbent type fibers extract the analytes by partitioning them into a 'liquid-like" phase in which the analytes would migrate in and out of the coating. The remaining coatings, including PDMS-DVB, Carbowax-DVB, Carbowax Template Resin and Carboxen are mixed coatings, in which the primary extracting phase is a porous solid, extracts analytes via adsorption. The adsorbent type fibers extract analytes by physically interacting with the analytes and the extraction can be accomplished by trapping the analytes in the internal pores of the stationary phase (Gorecki *et al.*, 1999).

## 1.7    Novel SPME Adsorbents

Recently, researches had been carried out in developing a new SPME fiber which is more effective than commercially available fibers. Works by Gbatu *et al.* (1999) have shown that sol–gel procedure can be used to prepare SPME fibers having desired selectivity with judicious choice of precursors. These fibers are stable in different types of organic and acidic solvents and basic solutions unlike commercial SPME fibers.

Zuin *et al.* (2004) employed a novel SPME fiber coated with PDMS/PVA co-polymer to determine organochlorine and organophosphorus. The resulting procedure was shown to be a good alternative and environmentally friendly analytical method. Hou *et al.* (2004) successfully used C16-MCM-41 mesoporous materials as a novel SPME

fiber coating. The results indicated that this fiber coating has very high extraction efficiency and good selectivity towards aromatic hydrocarbons.

Yu *et al*. (2004) successfully used allyloxy bisbenzo 16-crown-5 trimethylsilane to prepare the sol–gel derived bisbenzo crown ether/hydroxyl terminated silicone oil (OH-TSO) SPME coating. The long lastingness of this novel fiber is longer than that of commercial fibers. Works by Lopes *et al*. (2004) have shown that the PDMS/PVA composite can be used as a material for SPME fiber coating. It can be synthesized by sol-gel polycondensation route. The highly microporous coating gave faster extractions and showed potentially higher analyte loadings. Several researches (Li *et al.,* 2004a; Li *et al*., 2004b) have successfully developed amide bridged-C4/OH-TSO sol-gel coated novel fiber for analysis of aliphatic amines and chlorophenols. The fiber exhibits better sensitivity, high thermal stability and satisfactory fiber-to-fiber reproducibility.

For the first time, sol-gel dendrimer coated capillaries were used for solventless microextraction and preconcentration in chemical analysis by Kabir *et al.* (2004). Due to the strong chemical bonding with capillary inner walls, sol-gel dendron coatings showed excellent thermal and solvent stability. The fiber was capable of extracting both polar and nonpolar analytes including PAHs, aldehydes, ketones, phenols and alcohols. Araanda *et al.* (2000) used two polycrystalline graphites (pencil lead and glassy carbon) as sorbents for solid phase microextraction of non-ionic alkyl phenol ethoxylate surfactant. Preliminary results showed that pencil leads and glassy carbon performed equally well as SPME fibers (PDMS/DVB and Carbowax-TPR) in terms of LOD, linear dynamic range and precision.

Works by Yun (2003) have shown that sol–gel derived diallytriethylene glycol/hydroxyl–terminated silicone oil (DATEG/ OH-TSO) coated SPME fibers have a powerful stationary phase for extraction of polar and non-polar analytes from headspace for the sample due to the selectivity of open crown and three–dimensional network provided by sol–gel process. Owing to the strong chemical binding between the coating

and surface, these fibers have high thermal and chemical stability in extraction for high–boiling point compounds.

Works by Zeng *et al*. (2001) have shown that sol–gel derived hydroxydibenzo-14-crown-4 coated fiber has good affinity for several aromatic amine derivatives. Wang *et al*. (2003) successfully developed a new sol–gel coated dihydoxy-terminated benzo-15-crown-5 (DOH-B15C5) fiber which exhibits high solvent stability, longer application lifetime, thermal stability ($\geq$ 350 $^{\circ}$C), improved selectivity and sensitivity towards different aromatic compounds (non-polar or polar). The porous structure increases the speed of extraction and desorption.

Yu *et al*. (2002) successfully developed a new porous sol–gel hydroxyfullerene (fullerol) fiber which is high temperature and solvent resistance with long durability. It shows excellent extraction characteristics for both less volatile organic compounds and polar substances, especially for planar molecules. Basheer *et al*. (2005) successfully synthesized amphiphilic and hydrophilic oligomers and coated on fused silica capillaries using sol-gel technique. The sol-gel coated fibers were successfully used for the determination of triazine herbicides in reservoir water samples. Both types of coating were stable under high temperature (up to 280 $^{\circ}$C). Compared to commercially available SPME adsorbents such as PDMS/DVB and PA, the new materials showed comparable selectivity and sensitivity towards both non-polar and polar analytes. Quantitative results obtained from these capillaries exhibited precision at LOD values comparable with commercial coating materials. The coated capillaries also exhibited longer application lifetime.

Hun *et al*. (2005) successfully prepared a novel poly(dimethylsiloxane)/$\beta$-cyclodextrin (PDMS/$\beta$-CD) coating for solid-phase microextraction (SPME) in the form of membrane instead of fiber. The fibers were capable of extracting non-polar polycyclic aromatic hydrocarbons (PAHs) and polar phenolic compounds. The membrane showed high extraction efficiency without sacrificing the analytical speed. Ugur *et al*. (2004)

described the use of SPME method with new design of functionalized stable overoxidized sulfonated polypyrrole (OSPPy) film electrode to extract metal ions (Ni (II) and Cd (II)) without derivatization from water of high silane. The extremely fast uptake and release were attained by applied potentials inducing changes in the solution pH. Fundamental results showed that (OSPPy) film offers a wide potential range for electroanalytical exploration from selective electrodes to separation and preconcentration sampling device.

Chong *et al.* (1997) and Malik *et al.* (2004) successfully developed sol-gel PDMS fibers for the extraction of PAHs. The sol-gel fiber exhibited enhanced thermal stability (up to 320 ˚C) and the coating possess a porous structure and reduced thickness which provide enhance extraction and mass transfer rate in SPME. Works by Liu *et al.* (2005) proved that sol-gel derived co-poly(butyl methacrylate/hydroxyl terminated silicone oil) (BMA/OH-TSO) has the best affinity for 2-chroethyl ethyl sulfide (CEES) in soil. The coatings proved to be stable at high temperature (350 ˚C) and have a longer lifetime (150 times).

Works by Wang *et al.* (2000) showed that polyethylene glycol coated fibers have a high thermal stability (300 ˚C). This work proves that the thickness of the polymeric layer can be controlled by varying the dipping time and the concentration of the sol solution. Zhou *et al.* (2005) successfully developed a lab-made calixarene fiber which exhibited a high affinity for the phenolic compounds and a higher extraction capability compared to commercial polyacrylate fiber. Liu *et al.* (2005b) developed sol-gel coated hydroxyl-terminated silicone oil-butyl methacrylate-divinbylbenzene (OH-TSO-BMA-DVB) and validated for the determination of volatile compounds in wine. The novel coating was found to be very effective in carrying out extraction of both polar alcohols and fatty acids and non-polar esters.

Liu *et al.* (1997) successfully prepared porous layer–coated SPME fibers by immobilizing the C-8 and C-18 bonded silica particles (5 μm diameter, typically used

for reversed-phase HPLC) onto the surface of metal wires using high-temperature epoxy. The fiber was capable of extracting aromatic hydrocarbons. Porous silica particles provide a large specific surface area, therefore, the capacity of the coating is increased. It was found that the desorption time using these fibers was less than 10 s, which provides high chromatographic efficiency without cryogenic trapping.

Xia and Leidy (2001) prepared $C_{18}$-bonded silica-coated multifibers by applying thin film of epoxy glue over the glass fiber and pressing onto a $C_{18}$-bonded silica particle bed. It was found that the absorption rate of this fiber was 10 times higher than that of a commercial PDMS fiber. It was observed that there was a 50 $^{\circ}$C difference of desorption temperature between the PDMS polymer and the $C_{18}$ bonded silica. The desorption temperature indicated that the analyte interaction with the $C_{18}$-bonded silica was stronger than that with the PDMS polymer.

Rodrigues *et al*. (2002) coated SPME fibers with modified silica particles bonded to methyl ($C_1$), hexyl ($C_6$), octyl ($C_8$), and polymeric octadecyl ($C_{18}$) groups. The fiber showed good selectivity for PAHs. The fibers could be used for up to 100 extraction cycles without a significant reduction of extraction performance. However, because the fibers were very brittle the lifetime of the fibers was mainly limited by breakage. When these porous layer fibers were subjected to GC at 300 $^{\circ}$C, some extraneous peaks were observed. This is probably due to the release of some monomers in the epoxy glue used to bond the porous layer.

Cai *et al.* (2003) have successfully prepared sol-gel dibenzo-18 crown-6 SPME fiber coating by sol-gel technology and applied for the extraction of aliphatic amines. Compared to commercial PDMS and PA fiber, the sol-gel dibenzo-18 crown-6 is more sensitive and selective for derivatized aliphatic amines. The performance of the coating is stable at high temperature (< 350 $^{\circ}$C) and it has a long lifetime (can be used < 150 times).

Djozan and Bahar (2004) have investigated the efficiency of polyaniline (PANI), coated gold wire, for use as a fiber for SPME. Aniline monomers were electropolymerized on gold wires by applying a constant current to an acetate buffer containing $NaClO_4$ as supporting electrolyte. These fibers were capable of extracting some aliphatic alcohols from gaseous samples.

Mohammadi *et al.* (2004) used the electrochemical fiber coating (EFC) technique for the preparation of dodecylsulfate-doped polypyrrole (PPy-DS), and applied it as a new fiber for SPME. PPy-Ds film was directly electrodeposited on the surface of a platinum wire from an aqueous solution containing pyrrole and sodium dodecylsulfate, using cyclic voltammetry (CV). The fiber coating can be prepared easily in a reproducible manner, it is inexpensive and has a stable performance at high temperatures (up to 300 $^{\circ}$C). The new fiber was evaluated for the extraction of PAHs from water samples.

Bagheri *et al.* (2005a) prepared three different coated fibers, polydimethylsiloxane (PDMS), polyethylenepropyleneglycol monobutyl ether (Ucon) and polyethylene glycol (PEG) based on sol-gel technology. For the first time, these fibers were evaluated for the SPME of semi-volatile drugs such as, dextromethorphan (DM) and dextrorphan (DP) in plasma. High-temperature conditioning of these fibers leads to consistent improvement in peak area reproducibility.

An aniline-based polymer was electrochemically prepared by Bagheri *et al.* (2005b). This new fiber coating was applied for solid phase microextraction of some priority phenols from water samples. The polyaniline (PANI) film was directly electrodeposited on the platinum wire surface in sulfuric acid solution using cyclic voltammetry (CV) technique. This new coating can be prepared easily in a reproducible manner and it is rather inexpensive and stable against most of organic solvents. The thickness can be precisely controlled by the number of CV cycles.

Sun *et al.* (2005) have successfully developed activated carbon fiber (ACF) for use in SPME. The fiber was used to determine benzyl chloride, benzyl dichloride and benzyl trichloride in water samples by headspace analysis. Experiments showed that ACF has a higher adsorption capacity than the commercial coated fibers except for CAR-PDMS. The compounds studied could be desorbed completely within 60 s. The fairly well-distributed surface of ACF ensures complete desorption in a short time.

3-(Trimethoxysily) propyl methacrylate (TMSPMA) was first used as precursor as well as selective stationary phase to prepare the sol-gel derived TMSPMA-hydroxyl-terminated silicone oil (TMSPMA-OH-TSO) SPME fibers for the analysis of aroma compounds in beer by Liu *et al.* (2005c). The fiber was found to be very effective in carrying out simultaneous extraction of both polar alcohols and fatty acids and non-polar esters in beer. The fiber exhibited better sensitivity to most of the investigated analytes compared to commercial PDMS, PDMS/DVB and PA fibers. High thermal stability and long lifetime are also characteristics of the new fiber.

SPME fiber coated with a novel $\gamma$-$Al_2O_3$ has been prepared and used to screen gaseous samples for traces of volatile organic compounds (VOC) by Wei *et al.* (2004). Results showed that it has good thermal stability (up to 350 $^{\circ}$C), a long life span (< 180 times), higher extraction capacity and good selectivity for alkanes and esters. Physical characteristics showed that the surface of the fiber was stacked with fine particles of $\gamma$-$Al_2O_3$ and it was porous. It was reported that the diffusion into the porous layer might be responsible for the low diffusion kinetics which prolonged the equilibration time.

Djozan *et al.* (2004) coated gold wire with polypyrrole (PPY) by electropolymerization for use in SPME. The adsorptive property of the coating was modified by doping with tetrasulfonated nickel phtalocyanine (NiPcTS). NiPcTS as a dopant enhances the sensitivity of PPY. The fiber was found to be capable of extracting BTEX compounds from water sample. Farajzadeh and Rahmani (2005) have successfully developed a new SPME fiber by electrolysis. The anode was oxidized to

copper (I) to produce copper (I) chloride as a sorbent for the studied amines on the copper wire. This fiber was capable of extracting the studied amine compounds and showed excellent fiber-to-fiber repeatability. It also exhibited lower detection limits and shorter analysis time.

A new kind of membrane used for SPME was prepared with amine compounds by Yang *et al*. (2004). The self-prepared SPME membrane was proven to be effective for analysis of forensic toxic such as dichlorvos, morphine, Phenobarbital, methyl-amphetamine, MDA, ephedrine and TNT. Tsuda *et al*. (2004) prepared a new type of fiber adsorbent attached with silica microparticles. The silica microparticles were formed by the polymerization of silica oligomers on glass fibers, which were woven into a glass filter. The surface of the silica microparticles was chemically modified by bonding $C_{18}$-ligands.

Djozan and Assadii (2004) have conclusively demonstrated that pencil lead fiber modified by heating with water vapour can be used for precise analysis of PAH in water by SPME followed by GC-FID. Low cost and high temperature resistance are the main advantages of this fiber. It has characteristics required for use in routine analytical procedures. Djozan and Zehni (2003) investigated a simple and inexpensive method for the preparation of new SPME fiber consisting of copper wire coated with copper sulphide. The fibers seem very effective for extraction of aliphatic alcohols and amines from aqueous samples.

Oliveira *et al.* (2005) successfully used a glass ceramic rod as a base for the preparation of SPME fibers using sol-gel technology. The glass-ceramic rod was coated with PDMS using sol-gel reaction. The film thickness for this new base was much bigger than the fused silica base. The characteristics of this new base can be attributed to its stronger exchange capacity. The glass ceramic fiber coated with PDMS by sol-gel reaction shows good extraction characteristics for BTEX compounds.

Co-poly (hydroxy-terminated silicone divinylbenzene) coating was first prepared by sol-gel and cross-linking methods and applied to the solid-phase microextraction of phosphate and methylphosphonate from and water by Liu *et al.* (2003). The new fiber possessed high thermal (to 380 $^\circ$C) and solvent stability and a long lifetime. Compared to commercial SPME fibers, the sol-gel coated OH-TSO/DVB fiber showed better selectivity and sensitivity towards phosphate and methylphosphonate. Therefore, the novel fiber may be a good choice for analyzing warfare agents with SPME.

Silveira *et al.* (2005) developed silica-based glass fibers and modified their surfaces with $Nb_2O_5$. Fiber glass with a composition of 29 % $Li_2O$, 1 % $ZrO_2$, 5% BaO and 65 % $SiO_2$ was coated with $Nb_2O_5$ using the metallo-organic decomposition (MOD) technique. The $Nb_2O_5$-coated fibers showed excellent results both in the adsorption of phenols and in the adsorption and separation of alcohols using SPME.

A novel alumina-based hybrid organic-inorganic sol-gel coating was first developed for SPME from a highly reactive alkoxide precursor, aluminium sec-butoxide and a sol-gel active polymer hydroxyl-terminated polydimethylsiloxane (OH-TSO) by Liu *et al.* (2006a). As compared to silica based hybrid materials, the ligand exchange ability of alumina makes it structurally superior extraction sorbents for polar compounds such as, fatty acids, phenols, alcohols, aldehydes and amines. The fiber was capable of extracting volatile alcohols and fatty acids in beer.

Liu *et al.* (2006b) demonstrated a new coating technology for the preparation of SPME coating by sol-gel method. The extraction phase of PDMS containing 3 % vinyl group was physically incorporated into sol-gel network without chemical bonding. The extraction phase itself was then crosslinked at 320 $^\circ$C, forming an independent polymer network and can withstand desorption temperature of 290 $^\circ$C. Application to real life sample extraction showed that the SPME fiber is suitable for the determination of both volatile and semi-volatile compounds.

Gierak *et al.* (2006) successfully prepared new carbon fibers for SPME by the direct pyrolysis of methylene chloride on the quartz core. Owing to the high partition coefficients of the studied substances obtained on carbon fibers, it was possible to do the analysis of organic substances occurring in trace amounts in different matrices. The fiber was used for the analysis of benzene, toluene and xylene (BTX) contents in petrol.

Cai *et al.* (2006) prepared three new crown ether SPME coatings using sol-gel method. In this work, three kinds of vinyl crown ethers with different cavity and benzyl substitutions were crosslinked with vinyl triethoxysilane under radical initiator. These new coatings showed higher extraction efficiency and sensitivity for organophosphorus pesticides (OPPs) compared with commercial fibers-85 μm PA and 65 μm PDMS/DVB. The benzo-15-crown-5 (B15C5) coating with larger polarity had the best selectivity for OPPs and it was successfully used for the determination of OPPs in juice, fruit and vegetables.

Panavaite *et al.* (2006) developed a very simple method for the preparation of a new SPME fiber consisting of stainless steel wire coated with commercial silicone based high temperature resistant glue. The construction of the fiber is very simple and can be completed in a few minutes. The developed fiber was found to be mechanically stable and exhibited a relatively high thermal stability (up to 260 $^{\circ}$C). The proposed SPME fiber offers and attractive alternative to commercially available PDMS based fibers for the extraction of non-polar or less-polar compounds.

Anilinemethyltriethoxysilane (AMTEOS) was first used as precursor as well as selective stationary phase to prepare the sol-gel derived AMTEOS/PDMS SPME fibers by Hu *et al.* (2006). The novel SPME fibers exhibited higher extraction efficiency, good thermal stability, high porosity and longer lifetime compared with commercial SPME coatings. Owing to the introducing of the phenyl group in AMTEOS, the fiber offers better sensitivity towards aromatic compounds, such as monocyclic aromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAHs).

### 1.8    Sol-gel Technology


Sol-gel technology provides efficient incorporation of organic components into inorganic polymeric structures in solution under extraordinarily mild thermal conditions. In general, the sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel). Through this process, homogeneous inorganic oxide materials with desirable properties of hardness, chemical and thermal resistance, polarity and tailored porosity can be produced at room temperatures (Brinker and Scherer, 1990; Klein, 1988).


The precursors for synthesizing these colloids consist of a metal or metalloid element surrounded by various reactive ligands. A colloid is a suspension in which the dispersed phase is so small ($\sim$ 1-1000 nm) that gravitational forces are negligible and interactions are dominated by short-range forces, such as van der waals attraction and surface charges. An alkoxy is a ligand formed by removing a proton from the hydroxyl of an alcohol, as in methoxy ($\cdot OCH_3$) or ethoxy ($\cdot OC_2H_5$). Metal alkoxides are members of the family of metallorganic compounds, which have an organic ligand attached to a metal or metalloid atom. Metal alkoxides are most popular because they react readily with water.  The most widely used metal alkoxides are the alkoxysilanes, such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS). However, other alkoxides such as aluminates, titanates and borates are also commonly used in the sol-gel process, often mixed with (TEOS) (Dietz and Camara, 2005; Hofacker *et al*., 2002).


At the functional group level, three reactions are generally used to describe the sol-gel process as shown in Figure 1.2; hydrolysis (R1), alcohol condensation (R3) and water condensation (R2). The hydrolysis reaction (R1) replaces alkoxide groups (OR) with hydroxyl groups (OH) through the addition of water. Subsequent condensation reactions (R2 and R3) involving the silanol groups (Si-OH) produce siloxane bonds (Si-O-Si) plus the by-products water or alcohol. Under most conditions, condensation

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commences before hydrolysis is complete. However, conditions such as pH, H$_2$O/Si molar ratio (R) and catalyst can force completion of hydrolysis before condensation begins. Although hydrolysis can occur without addition of an external catalyst, it is most rapid and complete when they are employed. Mineral acids, for example HCl or ammonia are most generally used, however, other catalysts such as acetic acid, KOH, amines, KF and HF are also employed. It has been observed that the rate and extent of the hydrolysis reaction is most influenced by the strength and concentration of the acid or base catalyst (Brinker and Scherer, 1990; Brinker et al., 1992; Klein, 1988).
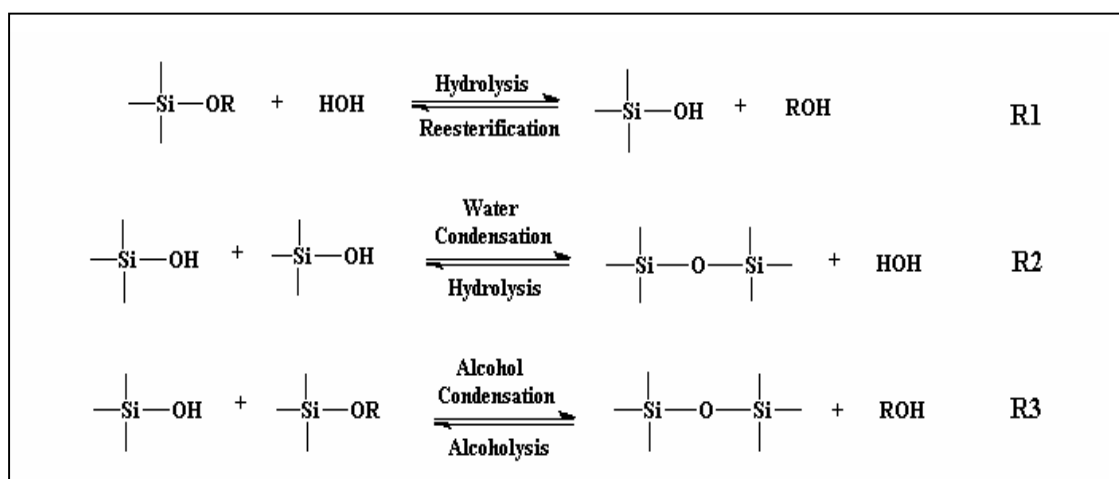


**Figure 1.2:** Basic steps in sol-gel coating technology (Brinker and Scherer, 1990)

Additionally, because water and alkoxides are immiscible, a mutual solvent such as an alcohol is utilized. With the presence of alcohol as the homogenizing agent, hydrolysis is facilitated due to the miscibility of the alkoxide and water. As the number of siloxane bond increases, the individual molecules are bridged and jointly aggregate in the sol, which is a colloid suspension of solid particles of a diameter of hundred nanometers in a liquid phase. When the sol particles aggregate, or cross-link into a network, a micromolecular gel is formed. Upon drying, trapped volatiles are then driven off (Brinker *et al.*, 1992).

### 1.8.1    Sol-gel Method as a New Tool for SPME Fiber Coatings

Sol-gel technology offers a simple and convenient pathway for the synthesis of advanced material systems and for applying them on as surface coatings. Many different combinations of alkoxides and organoalkoxysilanes have been prepared to produce coatings with improved mechanical properties such as abrasion resistance and high chemical stability. However, the characteristics and properties of a particular sol-gel coating are strongly related to a number of factors, such as, pH, $H_2O/Si$ molar ratio (R), nature and concentration of catalyst, ageing temperature and time and drying during the synthesis of the coating (Dietz and Camara, 2005; Arkles, 2001).

Dip coating technique is commonly used in preparing sol-gel coated fibers. The substrate to be coated is immersed in sol-gel solution and withdrawn with a well defined withdrawal speed at atmospheric condition. The stages of dip coating process includes dipping of the substrate (fused silica fiber) into the coating solution, wet layer formation by withdrawing the substrate and finally gelation of the layer by solvent evaporation as shown in Figure 1.3 (Brinker and Scherer, 1990).

During the withdrawal of the substrate from the solution, the inner layer moves upward with the substrate, while the outer layer is returned to the solution. The thickness of the deposited film is related to the position of the streamline dividing the upward and downward - moving layers. The faster the substrate is withdrawn, the thicker the deposited film. Evaporation is generally relied upon to solidify the coating. The most significant factor in the rate of evaporation is the rate of diffusion of the vapor away from the film surface. The evaporation rate can be controlled by the deposition ambient. Since condensation continues to occur during sol-gel coating formation, the relative condensation and evaporation rates will dictate the extent of further cross-linking that accompanies the deposition and drainage stages (Atanacio *et al.*, 2005; Brinker *et al.*, 1992; Klein, 1988).
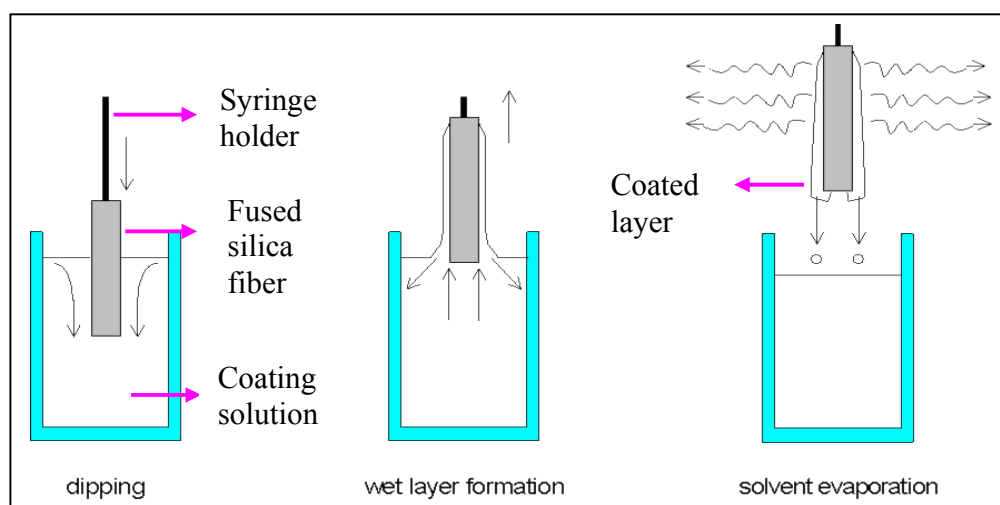
**Figure 1.3**: The stages of dip coating process (Brinker and Scherer, 1990)

Among many inherent advantages of sol-gel technology are its unique ability to achieve molecular level uniformity in the synthesis of organic-inorganic composites, strong adhesion of the coating to the substrate due to chemical bonding and high thermal stability which overcomes the sample carryover problem in SPME-GC analysis (Hofacker *et al*., 2002; Kabir *et al*., 2004; Li *et al.,* 2004a; Li *et al*., 2004b; Lopes and Augusto, 2004; Yu *et al*., 2004).

## 1.9 Problem Statements and the Needs of Study

Interpretation of forensic evidence and in particular, the ability to uniquely detect accelerant is a crucial challenge in the scientific investigation of arson. Limitations in this area are posing a significant impact on police investigations and the successful prosecution of arson cases. An improvement in accelerant extraction came with the development of SPME technique as a viable standard method in arson analysis.

The qualities that enable an SPME adsorbent to be successfully used for accelerant extraction and analysis are its selectivity towards accelerant components

which separates and concentrates the accelerant from the headspace to yield a sample that is suitable for introduction to GC-FID. Commercial SPME adsorbent have generally good extraction properties, however some aspects of their performance need to be improved to overcome the limited use of SPME in gas chromatographic applications (Dolan, 2003).

Although a number of adsorbents are commercially available for SPME but some analytical methodologies might demand specific properties for extraction of selected compounds, special coatings that have a particular volume and selectivity towards particular analytes. Commercially available fibers are rather expensive and have a short lifetime (40-100 times) (Wang *et al*., 2003; Hun *et al*., 2005; Zhou *et al*., 2005). These fibers have relatively low recommended operating temperatures and generally remain in the range of 200-270 $^\circ$C (Chong *et al*., 1997; Wang *et al*., 2000; Huo *et al*., 2004; Ugur *et al*., 2004; Yu *et al*., 2004; . Zuin *et al*., 2004; Hun *et al*., 2005; Liu *et al*., 2005a; Zhou *et al*., 2005). Poor thermal stability leads to incomplete sample desorption and sample carry-over problem (Liu *et al*., 2005b). Conventional fibers have poor solvent stability. The equilibrium and speed of the extraction process are related to physico-chemical characteristics of the sorbent, this limits the extent of selectivity obtainable using commercial fibers (Yun, 2003).

Improved mechanical and chemical resistance is in an increasing demand in coating applications such as SPME. Recently, many novel coatings have been developed using different techniques and technology for use in SPME. However, up to now, none of the novel fibers have been evaluated for the determination of accelerants in arson analysis.

## 1.10 Objectives and Scope of Study

The objectives of this study are as follows:

i. To investigate suitable SPME adsorbents for arson analysis.
ii. To evaluate the home-made SPME fiber against commercially available fibers
iii. To apply the developed fiber for detection of accelerants in fire debris.

In this study, SPME fiber coated with alternative materials was prepared by using sol-gel technology. The scope of the research is limited for the extraction of common accelerants in simulated arson samples. All the extractions in this study were performed using headspace –SPME mode.