

Fire Chemistry and Forensic Analysis of Fire Debris

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ARTICLE INFO

Received: 23 / 05 / 2023

Accepted: 12 / 06 / 2023

Available online: 13 / 12 / 2023

DOI: [10.37652/juaps.2023.140544.1072](https://doi.org/10.37652/juaps.2023.140544.1072)

Keywords:

Fire chemistry, Fire debris, Instrumental analysis, Chromatography.

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ABSTRACT

As the combustibles are almost in contact with the oxidizers and mostly all conditions are available to start a fire, this review covers the fire scene which could be intentionally or unintentionally started using a combustible liquid. The first step in the way of investigation is identifying the starting point of the fire, followed by knowing the causes of the fire and collecting fire debris samples to determine the presence of ignitable liquid residues. The fire debris collected from the crime scene is subjected to different extractions that including solvent extraction, distillation, headspace, and solid phase micro-extraction. Among the commonly used extraction methods, headspace and solid phase micro-extraction are on top because they are fast, solvent-less, and have no loss of sample concentration. After that, the sample is analyzed by the gas chromatography technique, which is the most sensitive and effective method for detecting and characterizing ignitable liquid residues.

1. Introduction

To set a fire, some conditions must be presented. To describe the fire, there are two main models, fire triangle and fire tetrahedron as shown in **Figure 1**. Fire is an exothermic chemical reaction where the fuel is oxidized and heat is produced [1].

The theory of the fire triangle states that fire takes place when fuel (combustible substances) have the ability to interact with oxidizers when a suitable source of ignition is available. These substances are either organic substances such as petroleum, wood, and wool, or inorganic such as phosphorus. Oxygen (oxidizer) and heat (thermal energy) are also needed to interact together, where each term appears on one side of the triangle.

In other words, each side is connected to others and represents the continuous interaction between all these conditions.

The fire stops when one side of the triangle breaks. If the oxidizer or fuel is removed the triangle is not complete, the fire would not occur. When no sufficient thermal energy is presented (even if the oxidizer and fuel are present together), no fire will exist. Consequently, if the three conditions are interacting together, the fire carries out. However, in the case of the fire tetrahedron, there is an extra side corresponding to the uninhibited chemical chain reaction theory. Here, the fire triangle's basic idea is also applicable [2,3].

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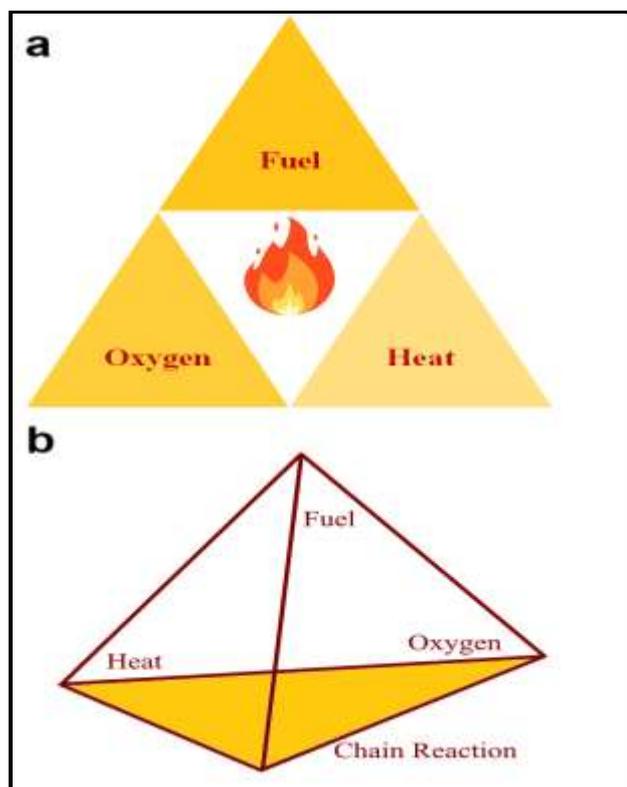


Figure 1. Models of (a) fire triangle and (b) fire tetrahedron. Fire does not spontaneously start, even though combustibles are almost always in contact with oxidizers (mainly oxygen) in the ambient atmosphere. When a substantial amount of thermal energy (ignition source) is added to combustion, the fire is carried on.

Investigations are must often the next step after a fire. The fire investigator must determine the circumstances that led to its occurrence and the ignition source that initially the fire caught. The investigator must be knowledgeable about the various thermal energy sources, their transmission, and the qualities of the materials present in the region of origin. This will identify which potential sources of ignition are presented and which ones are suitable to ignite the nearby combustible. If the fire was purposefully started or, in some cases, even if it was started unintentionally, the parties' responsibility may be subject to criminal prosecution under local laws. All forensic disciplines aim to establish whether a crime has been committed, and identify the victim(s), the perpetrator(s), and the modus operandi of the offender(s) [4-6]. Two main questions should be answered "Where did the fire begin" and "What caused the fire" in order to achieve the scene's investigation. It is noteworthy that there are several techniques used to analyze blood, saliva, sweat, semen, or vaginal fluid from crime scenes including ultraviolet-visible (UV-Vis), infrared (IR), X-ray, Raman, and nuclear magnetic resonance spectroscopy

[7]. In this study, we discuss the investigation steps and analysis of fire debris.

2. Investigation Steps and Sampling

The scene of the fire is no different from any crime scene of other accidents. In the beginning, the investigator observes the fire and smoke types to identify the starting point and the source of the fire to determine the potential cause. Then, the investigator collects fire debris samples to determine the presence of ignitable liquid residues.

2.1 The Starting Point of the Fire

The fire starting point can be determined before sampling begins by one of the following methods [8]:

a. Physical Properties

The presence of containers containing flammable materials, or, for example, the presence of matches. When a fire burns up in a V-shaped pattern, the fire point would be predicted. In crime fires, flammable materials are frequently used. When fires occur, flames and hot gases rise to the top and out of the combustion area, and a shape similar to the letter V is formed as revealed in **Figure 2** [9,10].

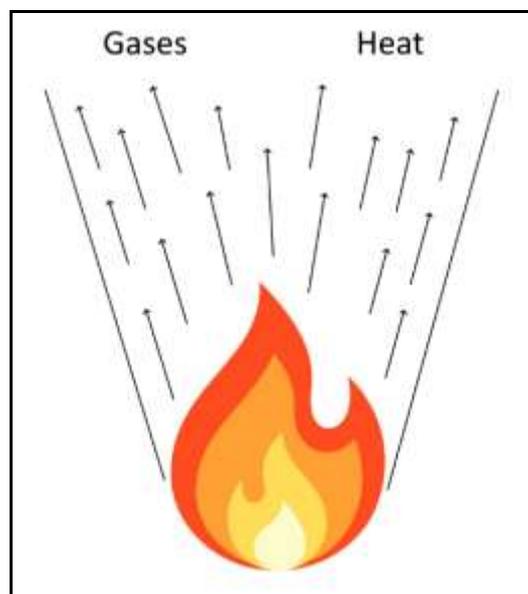


Figure 2. V-shaped pattern of fire.

b. Hydrocarbon Detector

This instrument is used to detect the petroleum materials used to ignite the fire, such as gasoline, diesel, and kerosene, even if they are in very low concentrations, as they reach 300 ppb [8].

2.2 Preparation of Samples

Sample preparation includes extraction and recovery of volatile fire-causing materials from fire

residue samples during the preparation for analysis. The extraction methods include solvent extraction, distillation, headspace, and solid phase micro-extraction (SPME). However, chromatographic analysis is one of the most important methods employed for this sake.

a. Solvent Extraction

In this method, the sample is completely immersed in a solvent and then filtered to obtain the substance. However, this method is no longer used at present because it losses part of the sample [11].

b. Distillation

It is a widely used method for separating mixtures based on the difference in evaporation degrees of the liquid mixture components. If the liquid contains many compounds that differ in boiling point, it can be heated and converted to a gas, then condensed and returned to the liquid form. Later, each sample is collected separately. In some cases, water is used as a carrier solution for the mixture components in steam distillation and extract volatiles if a sufficient sample quantity is available. However, ethylene glycol can be used instead of water as a carrier solution in high-boiling compounds such as diesel, and as a mixture of liquid ignitors [11]. The distillation technique is considered one of the first techniques used in the extraction of fire debris, where the process is shown in **Figure 3**.

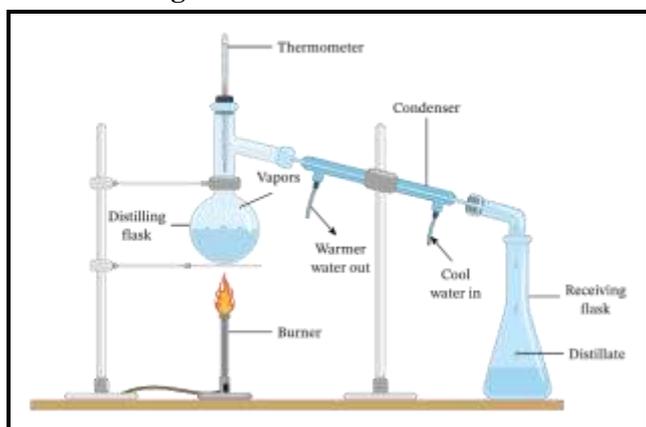


Figure 3. Distillation apparatus [12].

a. Headspace

This method is based on the evaporation of a portion of the sample by heating it in a closed system to keep it from spreading and withdrawing using a needle. Then, the sample is injected directly into the gas chromatography [13]. It is good to mention that this method is one of the preferred extraction methods for volatile material, where its concept is illustrated in **Figure 4** [14].

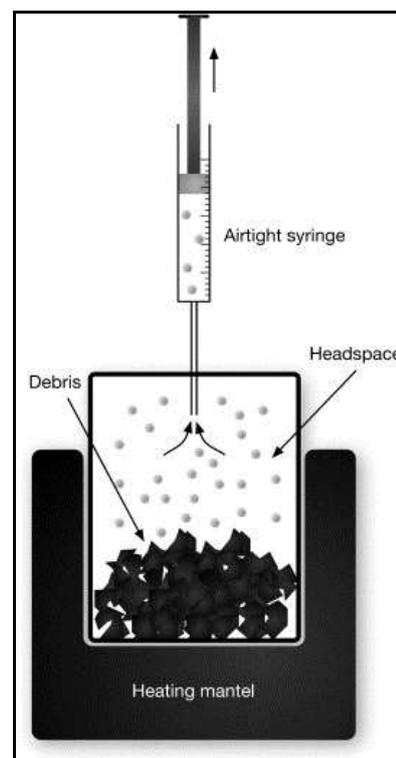


Figure 4. Concept of headspace analysis [14].

b. Solid Phase Micro-Extraction (SPME)

It is another sampling technique developed by Arthur and Pawliszyn in 1989 and used for the extraction and adsorption of volatile materials on the solid phase during heating. In this method, the volatile materials are adsorbed on the needle surface containing silica fibers as shown in **Figure 5**. Then, the fiber is inserted directly into gas chromatography injection for characterization [15].

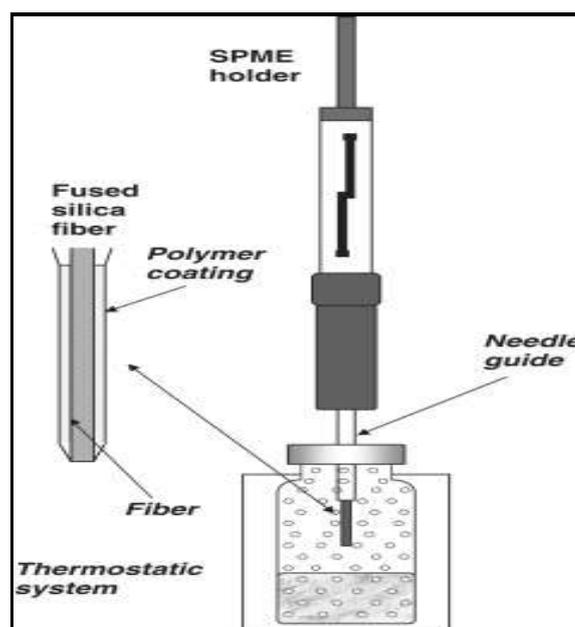


Figure 5. Diagram of Headspace-SPME holder [13].

3. Fire Debris Analysis Techniques

There are several methods to analyze samples resulting from fire debris, as there are international systematic methods used to extract and analyze samples suspected of containing petroleum materials. These methods follow the international classification number of applied standards according to the American Society for Testing and Materials (ASTM). Although forensic toxicology and other forensic sciences depend on quantitative analysis, the analysis of fire debris and explosives is essentially qualitative. The experience reveals that most arsons begin with petroleum-based accelerants. There are several analytical techniques of high sensitivity and effectivity for detecting and characterizing ignitable liquid residues, which are extracted from the fire debris that can be summarized as follows [10,16]:

- a. Gas Chromatography (GC)
- b. Gas Chromatography-Mass Spectrometry (GC-MS)
- c. Gas Chromatography Flame Ionization Detector (GC-FID)
- d. High-Performance Liquid Chromatography (HPLC)

Furthermore, in the analysis of fire debris, Raman spectroscopy [17] and thin-layer chromatography (TLC) [18] have also been employed as techniques. However, the gas chromatography with Flame Ionization Detection (FID) or Mass Spectrometry (MS) is a commonly utilized method for analyzing ignitable liquid residues from fire debris. This method plays a crucial role in providing essential information about air samples collected from the fire scene [16]. The principle of the gas chromatography techniques is based on evaporating the sample and introducing it to a capillary column with inert gas (helium or nitrogen) stream. The sample is partitioned through a tube coated with a material and this partition depends on the polarities and boiling points of the sample. In the end, each component of the mixture is separated at a different time and detected, and each component is revealed as peaks in the chromatogram [10]. **Figure 6** shows the chromatograms of kerosene and diesel fuel [19].

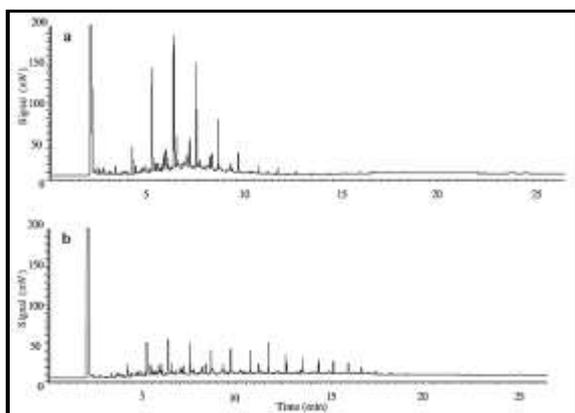


Figure 6. Chromatograms of (a) kerosene and (b) diesel fuel [16].

4. Conclusions

In this work, we presented the investigation steps and sampling of the forensic analysis of fire debris. Also, the preparation techniques for samples were listed, where the SPME method could be very dependable. The fire debris analysis techniques were also discussed, and the gas chromatography methods are dominating the analysis. Yet, the gas chromatography with FID or MS is still a reliable technique for certain cases.

Acknowledgment

The authors like to thank the Department of Chemistry at Al-Nahrain University for partially supporting this work.

Funding

None.

Conflict of Interest

There is no known conflict for the presented work.

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كيمياء الحريق وتحليل الدليل الجنائي لبقايا الحرائق

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المخلص:

نظرًا لأن المواد القابلة للاشتعال تكون عمومًا تقريبًا على اتصال مع المؤكسدات وتتوفر فيها معظم الظروف اللازمة لإشعال النار، يغطي هذا البحث دراسة النار التي يمكن أن تنشأ عن طريق استخدام سائل قابل للاشتعال في موقع الحريق، سواء كان ذلك عن قصد أو عن طريق الخطأ. يتم تحديد نقطة بدء الحريق كخطوة أولى في عملية التحقيق، تليها معرفة أسباب الحريق وجمع عينات بقايا الحريق لتحديد وجود بقايا سوائل قابلة للاشتعال. يتم تعريض بقايا الحريق التي تم جمعها من مسرح الجريمة لعمليات استخلاص مختلفة تشمل استخلاص المذيبات والتقطير والفراغ الرئيسي واستخلاص المرحلة الصلبة. من بين طرق الاستخلاص المستخدمة الشائعة، تعتبر الفراغ الرأسي واستخلاص المرحلة الصلبة هي الأكثر فاعلية لأنها سريعة ولا تحتاج إلى مذيب ولا تفقد تركيز العينة. بعد ذلك، يتم تحليل العينة باستخدام تقنية الكروماتوغرافيا الغازية، وهي الطريقة الأكثر حساسية وفعالية للكشف عن وتوصيف بقايا السوائل القابلة للاشتعال.