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A Meticulous Review on Arson Inquest Using Gas Chromatography

Saniya Sharma

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Author Affiliation: M.Sc. Forensic Sciences, Institute of Applied Health Science, Chandigarh University, Mohali, Punjab 140413, India.

Corresponding Author: Saniya Sharma, M.Sc. Forensic Sciences, Institute of Applied Health Science, Chandigarh University, Mohali, Punjab 140413, India.

E-mail: saniyasharma4200@gmail.com

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Abstract

Arson investigation is hands down the most tedious and the robust form of investigation to go with. It is by far the multifarious and endearing type of investigation as investigating at the arson scene demands high endeavour in order to withstand from all the challenges that stood up at the scene of crime. Stringent norms have been framed by the government that defines it under section 435, 436 and 438 of IPC. In such cases, the chain of custody plays a dynamic and a crucial role as from the procurement of the most fragile samples to transporting it in the most desired form to follow the best sample preparation method before subjecting to GC analysis in order to avail the quality result. Keeping in mind the susceptibility of fire evidences American Society for Testingand Materials International has established standard guidelines for subjecting sample before GC-MS introducing solid phase micro-extraction technique linking to various GC detectors. New minds and innovation has bumped into better and more approachable forms of GC by making hybrids of it such as E-nose i.e. headspace-mass spectrometry, a strategic mass spectrometry based instrument with both qualitative and quantitative applications surpassing the bygone separation process. Revolution in the arson and analytical world is making way for non destructible techniques to serve as a better alternative to any of the GC detectors.

Keywords: Arson, Indian Penal Code, Gas Chromatography -Mass Spectrometry, Headspace-Mass Spectrometry, Electronic nose.

Introduction

With the emergence of forensic science, advancements or entailment of scientific applications in the field is the need of the hour as the scientific examination allows a forensic scientist to put forth the opinions over the evidences admissible in the court with full certainty. Over the years, due to the diversification in respect of crime and the ways of doing it has made a forensic expert to question the existence of even those exhibits that were once neglected but now serve as a corroborative one that helps in carve out a way to further proceedings.[1] There was a time when ignition of fire was considered natural or accidental, but with the time many theories have come up that doubts fire being natural, accidental or malicious i.e. Arson.[2] Deliberate fire cases were novelly grouped under violent offences but were later classed under crimes against property and public safety. New transitions and amendments with the time have now referred arson as miscellaneous IPC crime. In India, these arson cases get registered under the Section 435, 436 and 438 of Indian Penal Code (IPC).[3] Although many factors are responsible for enhancing the destruction caused by arson but

the essential and the most widely used ingredient that counts as the major cause and also serves as the major step in fire investigation is the use of accelerant.[4,5] Accelerants are basically the chemical substances knowing to initiate as well as spread the fire to a wide stretch. It can be available in all the three states i.e. either in the form of solid, liquid or gaseous.[6] Amongst the three available states, liquid accelerants especially the petroleum products like petrol, kerosene and diesel are widely abused. Other inflammable solvent accelerants that came into light are alcohol, ether, thinner and industrial solvents.[7] Identification and determination of the type of accelerant involved in arson is the key step that helps in establishing the origin as well as cause of fire. Arson investigation has always come up as a challenging one to deal with as more of the evidence usually gets destroyed due to the combustion and thermal degradation, with lot of interferences with the petroleum products that gets sum up due to abiotic factors and also sometimes many other similar accelerants in fire debris creates hurdles at the time of examination and in result of which the only existence of accelerants in fire debris cannot be considered as a definitive indicator for an arson suspected.

This review has listed the uncompensated methods showing the way to proceed in the arson inquest describing sample preparation as the key and utmost step to consider and thoroughly go with before proceeding with any analysis along with the advancements in the most indispensible tool employed for its analysis i.e. GC with its hybrid version. This review has also focused on the current needs allowing researchers to shift from destructive type of analysis to indestructive type of examination.

Arson

Fire – That can be unintentional i.e. either natural or accidental, basically a chemical reaction that came into existence when heat, oxygen, fuel came up and act simultaneously in an uninhibited chain reaction.[8] **Whilst**, the willful and malicious setting of fire in one's own property or of other's property because of fraudulent or criminal intent is universally termed as **Arson.**[8] **Forensically**, its investigation is considered as the most tedious and troublesome task to accomplish because of the destructive nature it possess. It not only damages the evidences and exhibits but this has the potential to destroy the scene of crime as well and left the investigator with empty handed, as some gets destroyed during burning process and rest in the extinguishing process.[9] Also many arson cases have shown a set range and a set pattern of ignition indicating towards the serial arsonist referred as pyromaniacs with major psychological issues.[10] In the American Psychiatric Association's DSM5 classification system this condition has been considered as a part of diagnosis as many case reports have revealed the fact that a true pyromaniac usually hold one thing in common in all of his criminal acts and their possible way of conviction is to identify that very possible existing evidence that they leave behind.[11] Not just pyromaniac, but they have been accompanied by people who suffer from serious schizophrenia.[10] Bradish in 1999 in one of his studies putforth the statistical data of FBI crime index that showed higher percentage of children and adolescents were held responsible for the cases of arson.[11]

Chemistry of Fire

According to Dawson Powell, six basic elements are responsible for ignition, input heat, fuel, oxygen, proportioning, mixing, ignition continuity. Fire has been categorized under different classes[9]-

- **Class 'A' Fire**- Involves setting up of fire in solid materials as in woods, paper or textiles. The commonly used fire extinguisher for this class are said to be AFF Foam, water, wet chemicals as well as dry powder.
- **Class 'B' Fire**- Involves flammable liquids such as petrol, diesel or lubricating oils. The preferred extinguishers are AFF Foam as well as carbon dioxide.
- **Class 'C' Fire**- Involves gases with the preferred extinguisher be dry powder.
- **Class 'D' Fire-** Involves metals with the preferred extinguisher be L2 and M28 powder.
- **Class 'E' Fire-** Involves live electrical apparatus with the preferred extinguisher is carbon dioxide and dry powder.

❖ **Class 'F' Fire-** Involves cooking oils such as in deep fat fryers with the preferred extinguisher be wet chemicals.

Sequential events followed by fire - Mostly in a closed apartment fire follows certain sequential levels from the beginning to the end.

❖ *Incipient stage or the growth phase* - Is the first and foremost level of fire development that begins from the moment of ignition with the flames properly localized and the fire is regulated not only by the oxygen available but also be the mass and properties of fuel as

well.[12]

- *Flash over stage* - Incipient stage is followed by flash over which is a transition stage between the growth and fully developed stage and possess collection of gases due to constant burning that will accumulate all over the room and sums up to more spread of fire. Also presence of any state of fuel will lead to form a specific characteristic "V" pattern at the fire scene.[12]
- *Fully developed or post flash over stage* – Flash over stage is followed by *fully developed or post flash over stage* that involves intense burning and also has the potential to get in contact to every inch of the apartment.
- *Smoldering or decay* - With time when the supply of oxygen become less as well as fuel and heat to keep the fire ignited falls is the stage when fire reaches to its end called as the stage of *smoldering or decay.*[12]

Various aspects of fire can be easily turned into arson and thus it became crucial to know each and every aspect that the chemistry of fire holds before actually carrying out the investigation.

Investigation begins with the understanding and finding of the origin of fire, causes of fire as well as finding the type of accelerants used to ignite the fire using an indispensible technique and approach.[14]

Methods

Progressive Patterns of Firsetting

Identifying the patterns formed by the fire is the first and the original physical evidence that is encountered and dealt with. These patterns are formed when number of processes such as oxidation, distortion, melting, charring takes place during and after the fire ignited and can be visually analyzed as well as measured.[16] After the fire gets extinguished, clear demarcations appear as formation of broad lines takes place that indicates the levels of heat and smoke. Formation of such demarcations are a result of a number of factors involving the surface, length of heat exposure, heat source, fire enhancing materials, fire suppression ways and ventilation as well. Studies have revealed that amongst smooth and rough surfaces, the tendency to sustain more damage rests with rough surface and also increase and decrease of damage has been attributed by materials such as paint, bricks, tiles, wallpapers and any other article. Usually, the spread of fire is upward in direction thus downward penetration is the matter of concern and needs to be examined thoroughly.[16] Penetration of fire in the downward direction is quiet unusual and can be encountered in cases like burning of furniture involving chairs, couches and mattresses. Examination of areas around a hole provides us information regarding

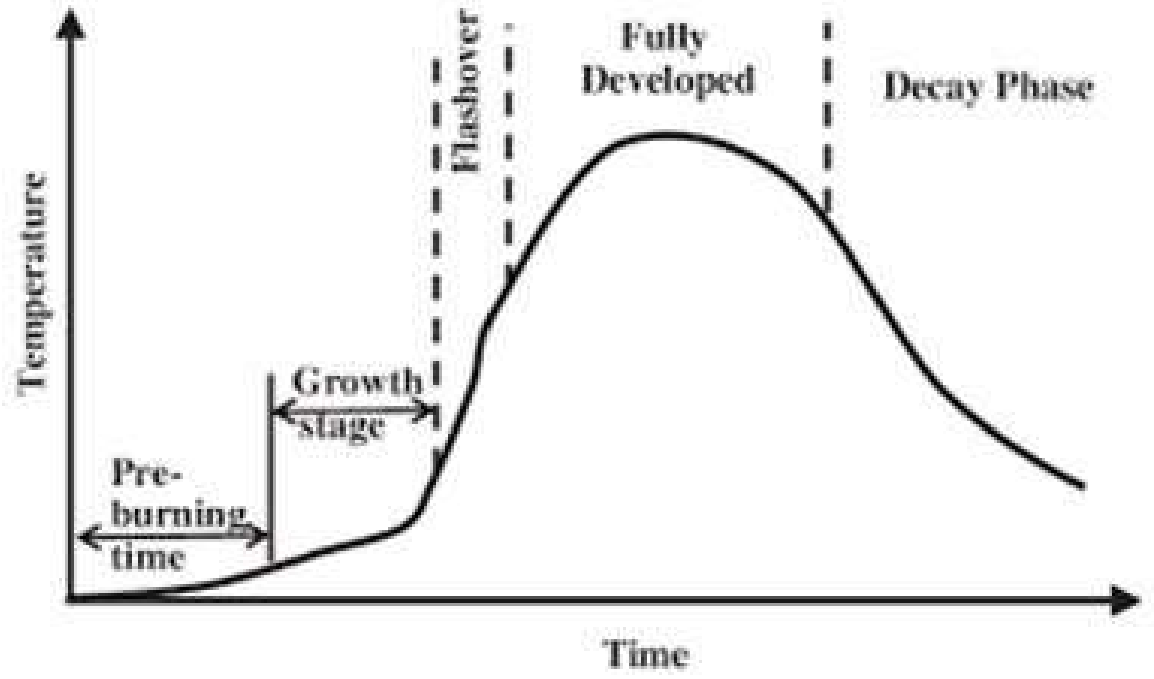

Fig. 1: Depicting Stages of fire.[13]

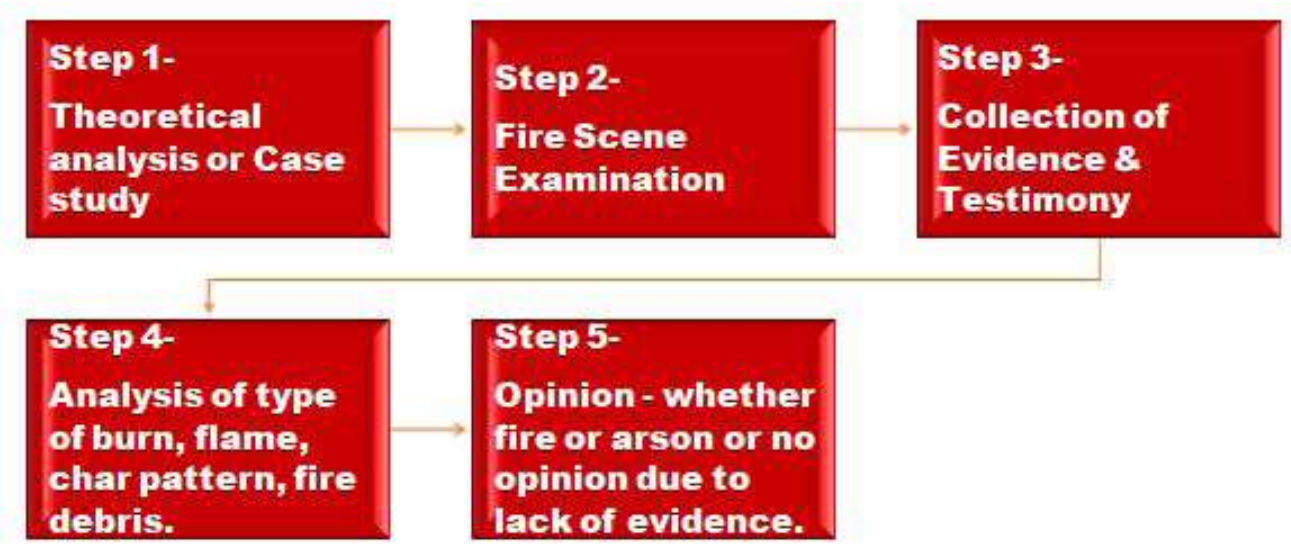

Fig. 2: Flow chart depicting series of Fire/Arson investigation.[15]

the direction of burn and its penetration. Around the hole if the sides are wider from the top along with inward slope then it indicates that the arrival of fire is from above whilst if the sides are wider from the bottom and slope upward towards the centre of hole shows that the arrival of fire is from below. The fire debris also adds up in knowing the direction that fire chooses to travel. Pattern "V" is the most common pattern encountered at the fire scene and is also referred as plume generated patterns.[16] It was claimed and believed for a while that fast burning fire usually forms narrow "V" pattern whereas a slow burning fire forms wide "V" pattern. There are other patterns as well-

1. **Confinement patterns** – When hot gas layer gets trapped beneath the ceiling and interacts with the walls give rise to pattern named as confinement patterns. Presence of these patterns at the fire scene provides investigator with a sequential data of smoke horizon and heat horizon that indicates that failure of ceiling takes place after the patterns has been formed. Such patterns are the source of information that tells about the origin in multilevel buildings and also sometimes this is the only type of pattern left at the fire scene.[17]
2. **Movement patterns** – In an apartment where the fire travels from a room to another it generally documents movement patterns at or near the doorways. These are the diagonally formed patterns tracing of which can lead to its origin.[17]
3. **Irregular patterns** – Gets formed on places particularly floors where fires have gone to flashover and remain exposed to burning for some time. Such pattern can lead to the cause of fire as it indicates the presence of ignitable liquids at the fire scene.[17]

Persistent Accelerants At The Arson Scene

The existence of liquid fuels or solvents at the fire scene is commendably a potential evidence to prove the fire scene as suspected arson.[18] Type of substrate plays a vital role in the detection and recovery of the ignitable liquid used, as from porous surface it

Table 1: Depicting comparison between widely used accelerants (7) (19).

Accelerants	Petrol	Kerosene	Diesel
n-alkane hydrocarbon range	n-C4 to C12	n-C6 to C 16	n-C8 to C 21
Composition	Paraffin, isoparaffin, olefins, naphthenes and aromatics.	Saturated aliphatic and aromatic chain of alkane and cycloalkanes.	Saturated and aromatic hydrocarbons.
Boiling range	Low	Moderate	High
Application	As fuel in automotive spark ignition engine	As fuel for jets and rockets and for cooking purposes	In high speed engines, domestic burners

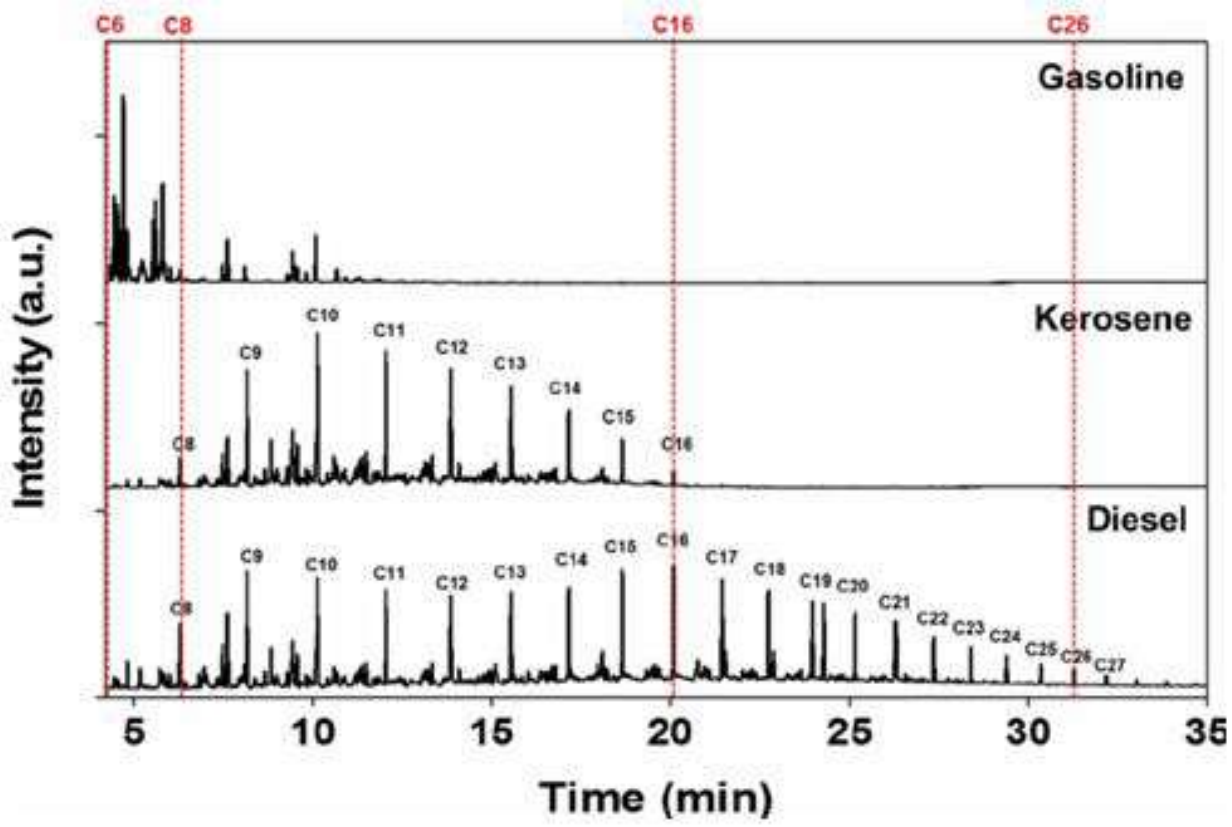

Fig. 3: Depicting difference in petrol, kerosene and diesel using chromatogram peaks.[21]

has been stated that recovery is way easier instead of procuring it from semi-porous as well as non-porous surfaces.

Petrol

The widely found accelerant in most of the arson cases is petrol with lesser and lighter hydrocarbon components than other petroleum products. On ignition, petrol being more volatile in nature has the tendency to form an explosive air vapor mix that led to huge destruction.[7] In order to establish a link between suspect and an arson crime scene where petrol has been detected, research have been carried out to determine whether any unique fingerprint can be obtained from petrol that belongs to different sources and analyzed that by examining more volatile components of it this can be successfully achieved.[20] But with time, this was considered to be less feasible approach to go with. As petrol exhibits a quite distinctive pattern as shown in figure 3 from other respective accelerants, many attempts were made to distinguish it from the rest of the accelerants by interpreting the chromatogram peaks present.[21] In 2003, a more promising study was carried out by Sandercock and Pasquier considering 35 random unevaporated petrol of different grades to focus on the desired poly aromatic hydrocarbons which were extracted by much advanced solid phase micro extraction process and finally analyzed under GC-MS.[7] In one study carried out by Mach, poly aromatic hydrocarbon were detected in burned exhibits of petrol and concluded that certain components are exceptional and particularly belongs to petrol.[22]

Kerosene

It is considered to be the second most widely encountered petroleum product after gasoline. Due to its lower volatility, it finds difficulty at the time of ignition but will hold longer burning duration.[5,7] Like diesel, it holds a larger proportion of lighter hydrocarbon compounds and because of its high boiling point it is more likely to leave behind traces that can be detected after a fire extinguish.[7] Similar to petrol, it also shows significant chromatogram peaks that makes it distinctive from the rest. Its chromatogram projects eight uniformly spaced peaks with its characteristic retention time. Despite of it being used for criminal act, it also has its legitimate use as it is used for cooking purposes so encountering it from places cannot directly link it with a criminal conduct and demands other factors to be analyzed before concluding.[23]

Diesel

After petrol and kerosene, the popular accelerant encountered is diesel. It is the petroleum product with heavier hydrocarbon components possess high boiling point along with low volatility and thus finds difficulty at the time of ignition i.e. consumes a long time to ignite.[7,24] Like kerosene, it also exhibit significant chromatogram pattern as it shows first eight peaks in same time interval as that of kerosene but later extends to eight more making it unique from the commonly used petrol and other accelerants.[2]

Hybrid of Gas Chromatography – for efficient analysis

From past 30 years, for the identification, characterization and analysis of accelerants from suspected arson cases the preferred instrument has been the Gas Chromatography.[25] With the gas chromatography the most apt detector employed is Mass Spectrometry known for its better separation and identification of specific type of accelerants from the fire debris.[26] For the identification and classification of ignitable liquid residues the American Society for Testing and Materials International (ASTM International) has provided standard guidelines to consider at the time of analyzing the residues under GC-MS.[27] Procured samples from fire debris cannot be directly subjected to chromatographic analysis until and unless it should be in volatile liquid form. Thus, sample preparation of fire residues is the utmost step and hence multiple ways have been stated for it and has been accepted by ASTM.

Passive Headspace Concentration with Activated Charcoal (ASTM E1412) the standard and most widely employed isolation method for ignitable liquid residues from fire debris.[28] This type of isolation has been adopted by U.S. majorly whilst isolating using solid phase micro extraction using Tenax as sorbent has been known in European countries. ASTM E1412, despite being the most sensitive, non-destructive and easier method to process with it holds a limitation of working only with the availability of solvent to extract volatile compounds from the activated charcoal strips followed by the injection of the solvent into the GC system.[6,29] Apart from the adsorbent employed earlier, St. Pierre et al in his recent study shown the use of zeolites as the most reliable adsorbent for the extraction of oxygenated ignitable liquids from fire debris samples as it demands only 4 hours of heating at 120 degree celsius which is quite rapid than the ASTM E1412.[30] Similar to ASTM E1412 it also requires a solvent (MeOH) only for oxygenated ignitable liquids.

Solid Phase Micro-Extraction (SPME) has been considered as the best alternative to the activated charcoal strip method as it is more reliable, rapid in nature, more sensitive and above all does not require any of the solvent for extraction.[6,31] American Society for Testing and Materials International has endorsed SPME as the screening test for fire residue analysis. SPME despite of the alternative developed stated unfavorable because of the low robustness of the fibers, known to be useful for shorter period and also difficult to automate when the extraction time is minimal.[6,32]

Nevertheless, of the preconcentration method described above, the major analysis of the accelerants involved remains associated with the most indispensible and versatile gas chromatography that provides visual pattern recognition of the total ion chromatogram (TIC), extracted ion chromatograms (EIC), and target compound analysis.[6] Inspite of the fact that the following stated method works well, it is laborious and also interpretation of results are totally dependent on analyst knowledge and experience as it does not holds any automation. So, this drawback seeks the employment of chemometric tools in order to help the analyst to identify and classify accelerants easily in a shorter span. With respect to chemometric tools, such as hierarchical cluster analysis (HCA), linear discriminant analysis (LDA) or soft independent modeling of class analogy (SIMCA) the combination with total ion spectrum (TIS) enables set procedures to differentiate and classify the fire debris sample and prepared an automated database search tool for fire analyst.[6, 33]

Hs-Ms As E-Nose

Studies have incorporated many forms of GC-MS making it varied number of hybrids by associating it with multiple techniques in order to acquire better efficiency and surpassing the limitations that the previously established instruments holds. Recently, researchers have brought headspace-mass spectrometry (HS-MS) also known as E-nose into existence.[6,34] In the E-nose based MS detection system, the pattern obtained is basically the summed ion spectrum quite similar to that obtained from TIS but with quick response as it does not demands chromatographic separation. Also, the E-Nose technique was optimized for the analysis of fire debris samples not even including any kind of

adsorbent to isolate the ILRs and using as the pre-concentration method where the gas syringe takes the headspace from the vial and directly injecting into the mass spectrometer without any prior chromatographic separation.[34]

Gonzalez et al. were the first to proposed direct analysis of ILRs without performing extraction and adsorption processes.[6] For his study, six different samples i.e. pine wood, cork, paper, newspaper, cardboard, and cotton sheet were initially burned without any ignitable liquid and later with the commonly available petrol, kerosene, diesel, citronella, paraffin, and ethanol. For the analysis of sample, E-Nose system composed of an HS 100 static headspace auto sampler along with Kronos quadrupole mass spectrometer (MS) was used performing different sets of burning experiments with each liquid and the burned pine wood sticks from the different sets but same ignitable liquid were used with the objective of ensuring that all of the burned samples contained the same ILRs.[6]

Results

The study carried out by Gonzalez et al. showed E-Nose as the preferred alternative because it does not require any solvent unlike the ASTM E1412 and turned to be safer for the users, eco-friendly and cheaper as well as it does not even require any absorbent.[6] Its sensitivity and selectivity is also higher as it provides different and specific fingerprints that would be beneficial for the discrimination of different Ignitable Liquid Residues.[6]

Future Perspectives

Recent studies have made arson analyst to form a different perspective for the arson inquest by evolving from the conventional, destructive gas chromatography and shifting to the non-destructive and better alternatives techniques for fire debris analysis.[26] To deal with every limitation a fire debris analysis holds, the spectroscopic techniques has came into light keeping in mind the nature of the burnt sample.

Infra-red spectroscopic techniques

It is based on the absorption of radiations by the molecules of a substance. The absorption takes place when the frequency of the radiations equals the energy difference between the two vibrational energy states of that molecule. As the frequency that get absorbed is specific for different vibrational energy states will thus helps to elucidate the structure of the molecule.[35]

Raman spectroscopic techniques

It is based on the scattering of the radiation. Around the nucleus an electron cloud exists that gets polarized by the radiation of single frequency that in turn creates an unstable excited virtual state that immediately radiates photons. Due to nuclear motion energy transfer takes place because of which the photons consist of more or less energy than the incident radiation. This difference of energy in the scattered radiations is known as Raman scattering.[35]

Discussion

Due to the destructive and less availability of the desired sample from the arson scene has made ASTM to stretch its limits and reframe the standard protocol by making sample preparation an important asset of investigation. Amongst activated charcoal strip method and solid phase micro-extraction, SPME has been preferred and used with varied GC- detectors.[31]

Almirall, *et al*, (1996) performed the recovery of accelerants in aqueous samples from fire debris using solid phase micro extraction with GC-FID and inferred that high sensitivity of solid phase micro extraction(SPME) in comparison to solvent extraction procedure for light petroleum distillate and petrol while solvent extraction of diesel did not produce identifiable chromatograms.[31]

Bodle, *et al*, 2007 performed the multivariate pattern recognition of petroleum based accelerants by solid phase micro extraction with GC-FID and inferred that soft independent modeling of class analogy (SIMCA) to be effective class predictor of accelerants.[36]

Further studies are making way to carry out the identification and classification using non-destructive techniques-

Rodriguez, *et al*, 2011 performed fire debris analysis on carpet, a DVD case, nylon, foam packaging and CD cases using Raman spectroscopy by burning them with petrol, kerosene, diesel and ethanol. The better results were obtained for the samples burnt with petrol and kerosene.[35]

Gonzalez, *et al*, 2015 on the basis of difference in research octane number discriminated two different petrol samples. Near Infra-red radiation spectrophotometry along with hierarchical cluster analysis (HCA) and linear discriminant analysis (LDA) were used to classify the gasoline samples

and found LDA as the better analysis tool than HCA.[35]

Kerr, *et al*, 2017 conducted a study using exhibits involving high density polyethylene i.e. bottle, low density polyethylene i.e. a bag, polyvinyl chloride i.e. a panel, polymethyl methacrylate i.e. flooring, cotton i.e. towel. And tried to investigate the presence of accelerants from fire debris and the results were concluded using Principle Component Analysis (PCA).[35]

Conclusion

Despite of having the best of knowledge as well as the equipments, there exist a number of other factors that unintentionally left unconsidered and sometimes leave the expert with empty handed. The Crimes like arson and its investigation itself holds a baggage of limitations and surpassing of which is a way difficult task to deal with. Despite of all the odds, a forensic expert always tries to stretch its potential by carving the most novice ways to investigate such crimes in which even traces of fire debris can tell us what the fire scene actually reflects. From stating whether the fire is natural, accidental or deliberate to stating the every specification like the origin, cause as well as the rationale behind setting up of fire by considering the psychological aspects as well, in order to exonerate the innocent. Its investigation is the most strenuous task that can be successfully executed by using gas chromatography which is the most versatile instrument that can act as an asset to the inquest. For the identification, characterization and analysis of accelerants from suspected arson cases the preferred instrument has been the Gas Chromatography. Gas chromatography has been used with varied detectors mostly FID and MS amongst which MS has always topped the list with more susceptible methods in terms of sample collection to sample preparation in order to provide the detailed study of arson debris. To maintain the standard of testing American Society for Testingand Materials International (ASTM International) has contributed by establishing set guidelines to operate and process before subjecting to GC instrument. New minds and innovation has bumped into better and more approachable forms of GC by making hybrids of it and the most talked in the recent years is E-nose i.e. headspace-mass spectrometry a strategic mass spectrometry based instrument with both qualitative and quantitative applications surpassing the bygone separation process. This technique emerges out as the most promising tool and an apt alternative hybrid GC technique to carry out the identification of ignitable liquids from the fire debris opening varied ways to conclude the arson investigation. From the beginning to till now GC has ruled in arson inquest but revolutionary ideas and implementations are making way for spectroscopic techniques such as infrared and Raman spectroscopy with an aspect of them being non-destructible in nature. Yet, more studies are required and also in queue to make it reliable and susceptible among the analytical world.

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