

An Arson Investigation by using Comprehensive Two-dimensional Gas Chromatography-Quadrupole Mass Spectrometry

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Abstract

The aim of this investigation is to develop a new tool for the investigation of hydrocarbon accelerants. The chemical analysis of fire debris in an arson investigation has gone through several developmental stages. The nature of the analysis has been divided into three essential components due to the complexity of the samples. The first has been the extraction of the accelerants from the debris. The second has been the development of instrumental techniques for the analysis of extracted samples. The interpretation of the results is the final stage. In our investigation, we have used comprehensive two-dimensional gas chromatography-quadrupole mass spectrometry (GCXGC-qMS). GCXGC-qMS is well suited for the analysis of complex hydrocarbon accelerants. We applied the resolution and separation powers of the GCXGC with the high precision mass scanning capabilities of a quadrupole mass spectrometer to investigate these complex samples. Total and selective ion scans were performed on samples obtained from an arson investigation. By using this process, we were able to conclusively determine the presence of hydrocarbon accelerants in fire debris.

Keywords: Comprehensive two-dimensional gas chromatography-quadrupole mass spectrometry; Arson; Accelerants; Gasoline; Kerosene; Diesel

Introduction

During 2010, law enforcement agencies reported 56,825 arsons to the Federal Bureau of Investigation, at an estimated total direct cost of over \$1.5 billion in property damage. One out of every four fires is due to arson [1]. The National Fire Protection Association estimates approximately 300 to 350 civilian deaths per year due to arson. The injury rate per fire is 5.6 firefighter injuries per 100 structure fires due to arson [2]. Arson is a felony that costs heavily in human and monetary terms.

An arson investigation usually starts by looking at the four factors that must be present in order to create and sustain a fire. These four factors are known as the fire tetrahedron [3]. The tetrahedron consists of a chemical reaction, flammable substance, starting heat source and oxygen. The starting heat source needs to match the ignition temperature of the flammable substance. In order to classify a fire as arson, the investigator has to prove tampering with at least one of the factors in the fire tetrahedron.

A common arsonist's practice is the use of flammable materials and accelerants; where accelerants are ignitable fluids. Widespread accelerants used in this trade are usually hydrocarbon liquids i.e., kerosene, diesel or gasoline.

Debris from suspected arson fires are routinely analyzed for trace amounts of hydrocarbon accelerants. The samples of debris are usually sealed at the fire scene, in an airtight container, i.e., a new unlined metal paint can. Procedures for labeling the samples are given in ASTM E1459 [4]. The samples are brought to the lab for analysis. The procedures for receiving, documenting, storing and retrieving are given in ASTM E1492-11[5]. The analysis is accomplished in three stages. The first stage consists of concentration and extraction of the suspected accelerants from the debris. The second stage involves the instrumental

analysis of the concentrated extracted samples. Finally, the last stage involves the interpretation and analysis of results [6].

Much of research has gone into the first stage. Steam distillation [7] and solvent extraction [8] were historically the first methods used in the extraction and concentration of the suspected accelerants from the debris [9]. Distillation of debris samples using steam or high boiling point solvents, i.e., ethylene glycol, produces a floating layer on top of the distillate that can be used in the second stage of the investigation [10]. Distillation is a labor intensive process which can take forty eight hours or more to complete. Furthermore, the distillation rate may influence the extraction [11]. Due to the complexity of this method, the ASTM International subcommittee E30.01 withdrew this standard, ASTM E1385-00, as a procedure. On the other hand, solvent extraction is fast; however, undesirable components may be extracted from the matrixes that interfere with the analysis.

Forensic investigators have searched for better methods for the separation and concentration of the accelerants from fire debris. It involved sampling by direct [12], dynamic [13] or passive headspace with activated charcoal or solid phase microextraction [14,15].

Direct headspace sampling extracts the volatile components in the gas portion above the sample. This method turned out to be less

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sensitive and it was only useful in the detection of highly volatile accelerants, i.e. alcohol and lacquer thinners.

Dynamic headspace involves a flow of an inert gas through the sample vessel. The volatile accelerants are collected into a trap. The trap can be charcoal, Porapak Q, Tenax, Amberlite XAD, etc. Desorption into the analyzing instrument can be done by using a “stripping” solvents or by heating.

Dietz introduced passive headspace with activated charcoal strips in 1985 [16,17]. Charcoal strips traps and concentrate the volatiles in the headspace above the sample. A solvent, i.e. carbon disulfide, n-pentane, desorbs the volatiles absorbed by the strips [18,19]. This is a very sensitive method; which can concentrate and isolate small quantities of accelerants from fire debris.

Solid phase microextraction selectively concentrates fire debris volatiles into an absorbent fiber. This method, as the previous one, is very sensitivity; however, it has the advantage that no solvent is used [20,21]. ASTM International has formalized this method in ASTM E2154 [15].

Instrumentally, forensic investigators have used GC-FID [18,19,22,23], GC/MS [24-26], GC/MS/MS [27], FT-ICR [28], GCXGC [29,30].

ASTM International E30 committee formally withdrew the test method for analyzing fire debris ignitable liquid residues samples by gas chromatography, ASTM E1387 and recommended the use of GC/MS for this type of analysis, ASTM E1618.

Pert et al. [31] commented on the advantages of using GCXGC in the analysis of complex arson samples. It is the purpose of this study is to show that GCXGC-qMS can be used in this type of investigation.

Experimental

GC X GC/MS

The GC/MS system used was a Shimadzu QP 2010 Ultra (Shimadzu Scientific Instruments, Inc., Columbia, MD). This is a gas chromatograph-quadrupole platform. As a general rule, quadrupole mass spectrometers have a relatively slow scan speed and this has become a limiting factor for usage of quadrupoles in comprehensive

Injection	1.0 µL. Injector Temperature 325°C. Pressure 70.1 kPa. Split: 10:1.
First column	30 m X 0.25 mm X 0.50 µm, 50% Phenyl Polysilphenylene siloxane (BPX50, SGE Analytical Sc. Austin, TX).
Modulator	Period 4.0 s. Con1 330°C
Second column	2 m X 0.1 mm X 0.1 µm, 100% Polydimethylsiloxane (BPX1, SGE Analytical Sc., Austin, TX).
Oven program	40°C for 2 min. 40-325°C @ 5°C min ⁻¹ Hold at 325 °C for 30 min.

Table 1: GC Experimental Parameters.

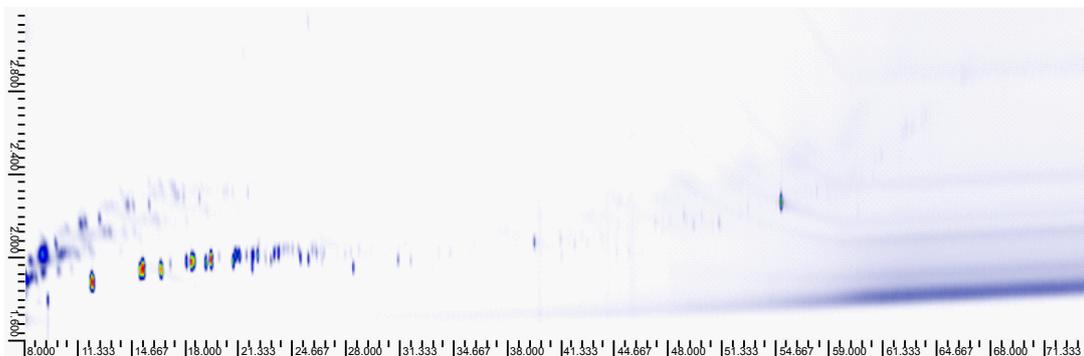


Figure 1: Comprehensive GCXGC-qMS total ion chromatogram of gasoline. X-axis: First dimension, retention time in seconds. Separation based on polarity. Y-axis: Second dimension, volatility-base separation in seconds.

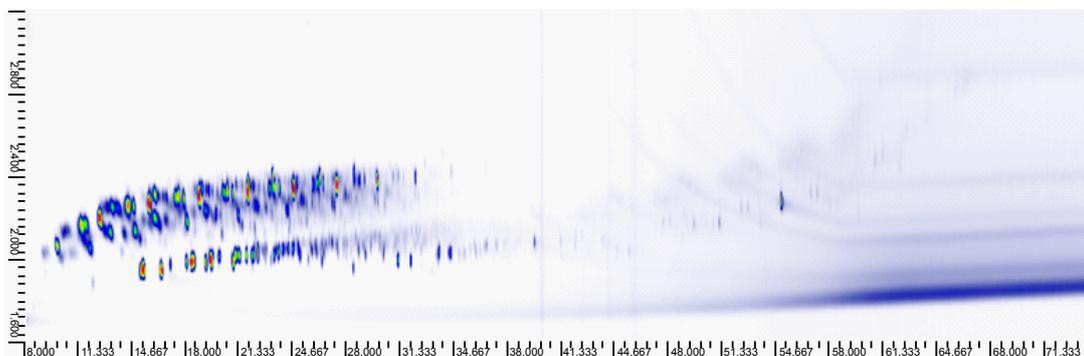


Figure 2: Comprehensive GCXGC-qMS total ion chromatogram of kerosene. X-axis: First dimension, retention time in seconds. Separation based on polarity. Y-axis: Second dimension, volatility-base separation in seconds.

GCXGC-MS. The maximum allowed data acquisition speeds have been 30 Hz. This is too slow to provide enough points for the ultra sharp

peaks generated by comprehensive GCXGC. However, this instrument is equipped with a firmware, Advanced Scanning Speed Protocol

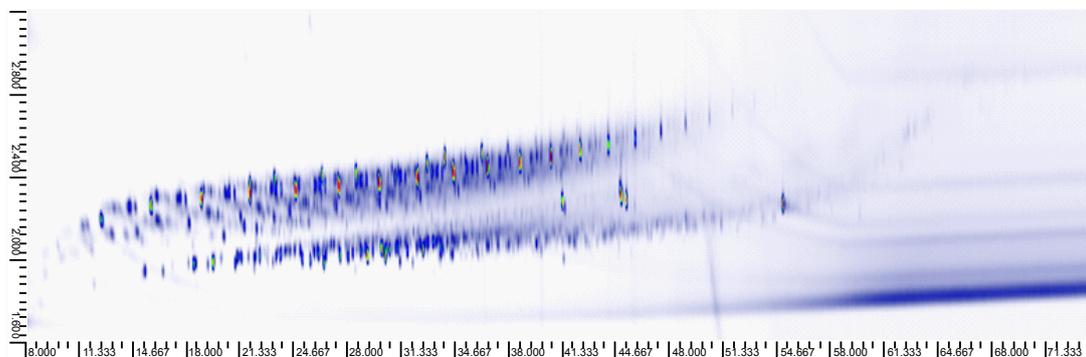


Figure 3: Comprehensive GCXGC-qMS total ion chromatogram of diesel. X-axis: First dimension, retention time in seconds. Separation based on polarity. Y-axis: Second dimension, volatility-base separation in seconds.

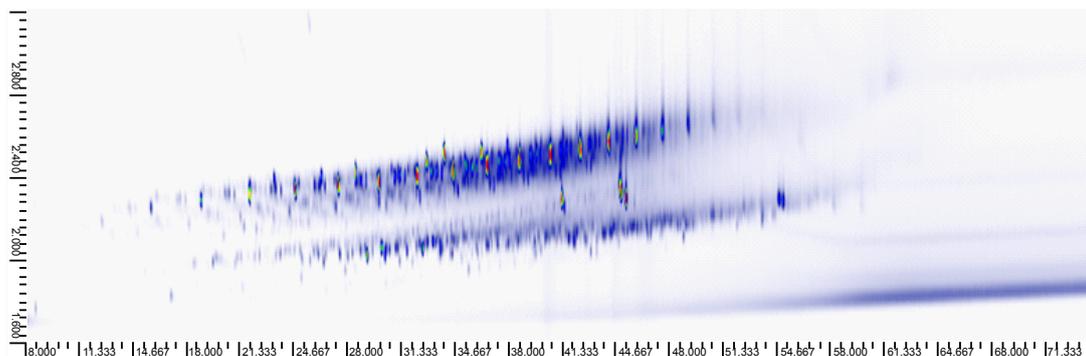


Figure 4: Comprehensive GCXGC-qMS total ion chromatogram of suspected arson sample. X-axis: First dimension, retention time in seconds. Separation based on polarity. Y-axis: Second dimension, volatility-base separation in seconds.

Compounds	m/z ^a
Alkanes	57, 71, 85, 99
C1 to C4 alkylbenzenes	91, 105, 114
Alicyclics and olefinics hydrocarbon	55, 69, 83, 97
Benzene, C1 to C3 alkylbenzenes	78, 92, 106, 120
C4 to C5 alkylbenzenes	119, 134, 148, 162
Alkyl naphthalenes	128, 142, 156, 170

^aBoldfaced ions represent the selected ions

Table 2: Characteristic ions for accelerant pattern identification [31, 40].



Figure 5: Comprehensive GCXGC-qMS profile of selective alkanes ions for gasoline.

(ASSP), and a fast data collection algorithm, which allows for faster collection rates.

A two-stage thermal loop modulator (Zoex Corp. Lincoln, NE) was mounted on top of the GC oven in order to provide comprehensive two-dimensional gas chromatography capabilities. This system employs two gas jets, a cold and a hot jet. The single cold jet cools two different segments of the second column, entrapping the compounds in the two sections of the second column. The hot jet, positioned perpendicular to the cold one, releases the entrapped compounds. A detailed description of the two-stage loop modulator system was provided by E. B. Ledford et al. [32]

Gas chromatograph experimental parameters and columns are listed in table 1. The first column was selected with a high polarity phase and the second was non-polar. The separation occurred via a polar-by-volatile interaction with the samples. Therefore, the samples were separated by polarity in the x-axis and by boiling point y-axis retention times.

The MS data was collected with Shimadzu GC/MS Real Time Analysis. The GCXGC-q MS data was analyzed by using GC Image V 2.1 (Zoex Corp.).

Sample Preparation

Samples of gasoline, kerosene and diesel were prepared by diluting 0.09 g of each sample into 10 milliliters of methylene chloride. Arson samples were extracted with methylene chloride. Purposely, we selected solvent extraction. As previously stated, this sample extraction and concentration technique is rather sensitive, but troublesome. The solvent can extract undesirable compounds from the matrix that can interfere with the analysis.

Results and Discussion

Comprehensive GCXGC works on the principles established by J. B. Phillips [33-35]. It involves the separation by two orthogonal gas chromatographic columns. The sample is separated into fractions and each fraction is transferred and cryogenic focusing to a secondary column with different polarity than the first. The second separation is faster than the first; so, the separation obtained from the first can be maintained. Thus, chemical compounds are separated by their independent chemical properties interacting with two orthogonal column phases. [36-38]. We selected as the first column a polar column. Since the most polar compounds in the sample are aromatic, polyaromatic hydrocarbons and polyaromatic heterocycles, they are regularly spaced along the base of the two-dimensional GCXGC

chromatogram. They appear in order of increasing polarity. The first to elute are the mono-aromatic compounds followed by the two, three-ring, and heterocyclic aromatic compounds. The non-polar paraffinic components have the weakest interaction with the first column, and then the second non-polar column separates them. They emerge according to their volatility. They form the top band in the two-dimensional GCXGC chromatogram. Between these two bands, compounds with intermediated polarity and volatility will reside, i.e. alkylated mono-aromatic and polyaromatic compounds.

In order to identify the sample components, we coupled a GCXGC to a quadrupole mass spectrometer. Frysinger et al. [39] coupled a quadrupole mass spectrometer to a GCXGC system. They concluded that due to the high resolution and narrow peaks generated by the GCXGC system, a faster scanning mass spectrometer was required. Our quadrupole mass spectrometer, equipped with ASSP can scan at a faster rate than previous quadrupoles mass spectrometers and therefore, it can handle the high resolution and narrow peaks generated by GCXGC.

Mass spectra data was collected throughout the whole chromatographic runs of gasoline, kerosene, diesel and a suspected arson sample. The software identifies peaks as "blobs". A blob is a collection of the pixels that make up each peak. Each blob contains information, which identifies the two dimensional retention time and the mass spectra of the compound that makes up the collection of pixels. Furthermore, the sum of the pixels value of each blob is proportional to the quantity of the compound that composes that blob. The software allows selection of minimum area, volume and peak area for blob selection. Blob selection can also be performed by computer cursor selection of a specific blob. Total ion chromatograms for the samples (gasoline, kerosene, diesel and suspected arson sample) are shown in figures 1-4.

Total ion chromatograms can generate chromatographic patterns, which can be useful and at the same time deceiving. Pyrolysis of non-accelerant matrices may generate chromatographic patterns that may interfere in recognizing the accelerant distinctive fingerprint patterns. Individual compound identification is insignificant in an arson investigation. The overall fingerprint pattern recognition of the accelerant is the method of confirming their presence.

Fingerprint pattern of selective diagnostic ions that are associated with hydrocarbon accelerants can be used for the screening and identification of a particular accelerant. The diagnostic ions that are used for these types of identifications are given in table 2.

The sets for alkanes (57, 71, 85, 99) m/z^a , alkylbenzenes (91, 105, 119,

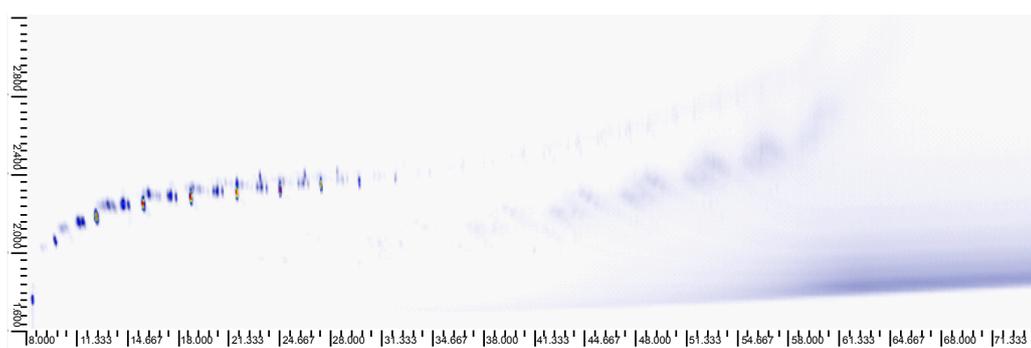


Figure 6: Comprehensive GCXGC-qMS profile of selective alkanes ions for kerosene.

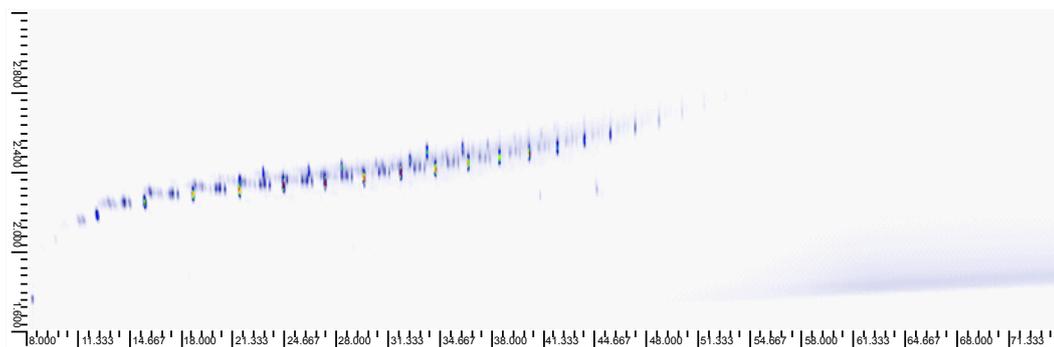


Figure 7: Comprehensive GCXGC-qMs profile of selective alkanes ions for diesel.

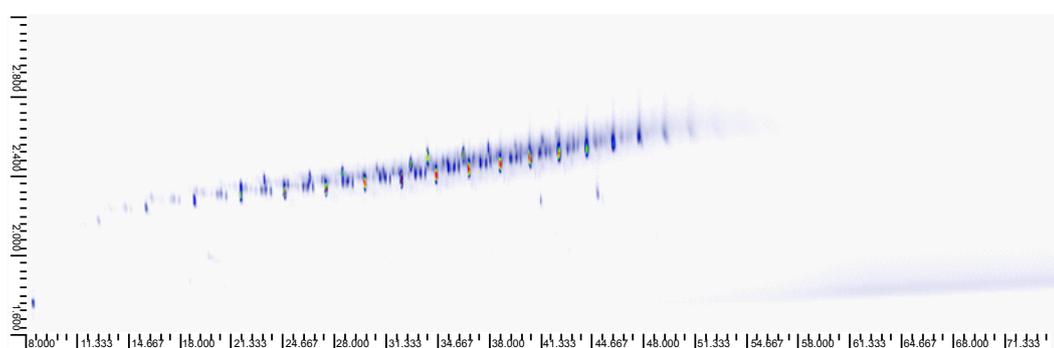


Figure 8: Comprehensive GCXGC-qMs profile of selective alkanes ions for the suspected arson sample.

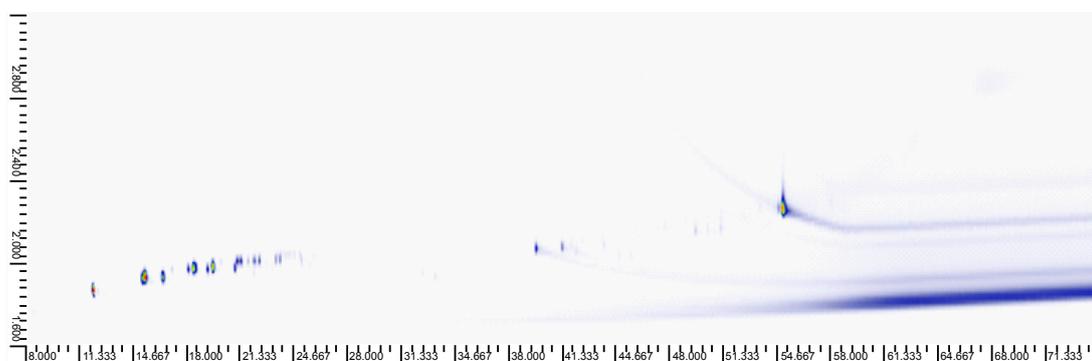


Figure 9: Comprehensive GCXGC-qMs profile of selective alkylbenzenes ions for gasoline.

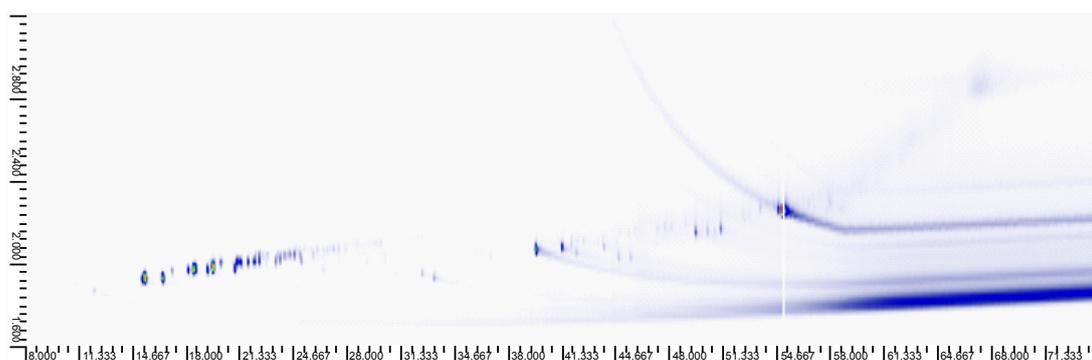


Figure 10: Comprehensive GCXGC-qMs profile of selective alkylbenzenes ions for kerosene.

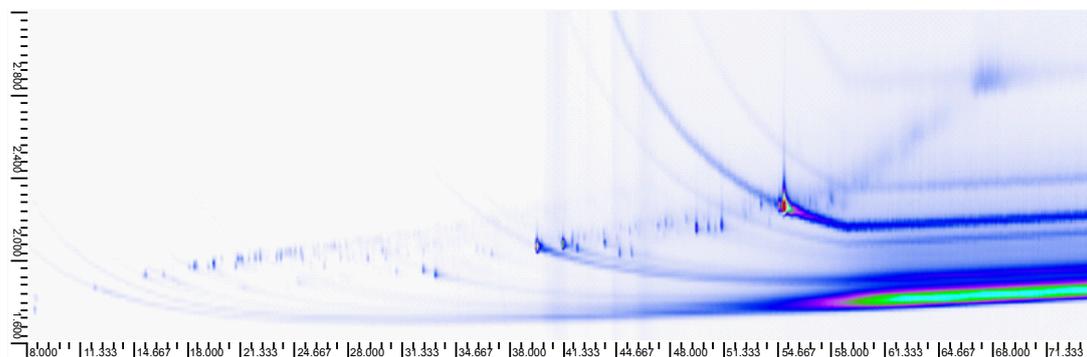


Figure 11: Comprehensive GCXGC-qMS profile of selective alkylbenzenes ions for diesel.

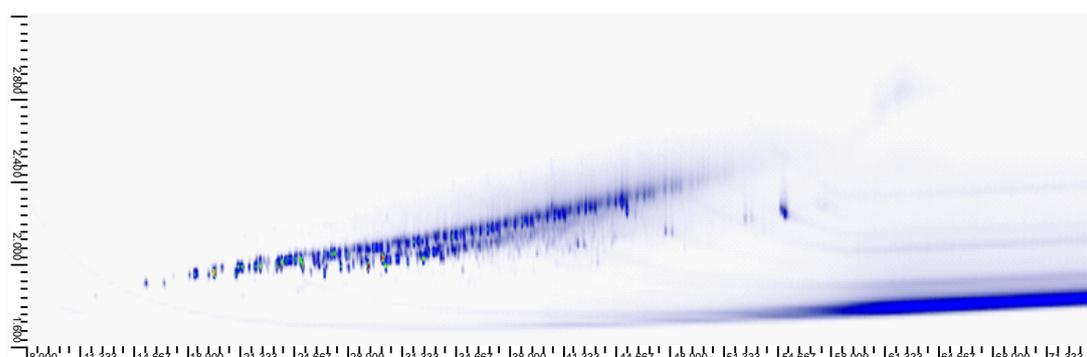


Figure 12: Comprehensive GCXGC-qMS profile of selective alkylbenzenes ions for the suspected arson sample.



Figure 13: Comprehensive GCXGC-qMS profile of selective alkylnaphthalenes ions for gasoline.

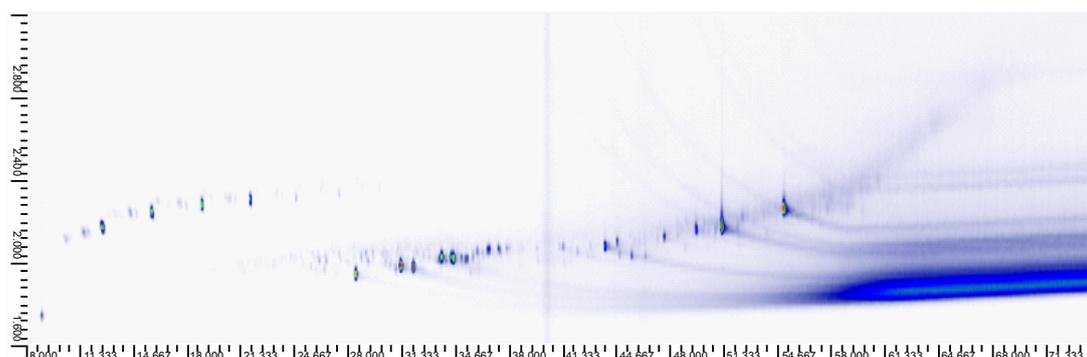


Figure 14: Comprehensive GCXGC-qMS profile of selective alkylnaphthalene ions for kerosene.

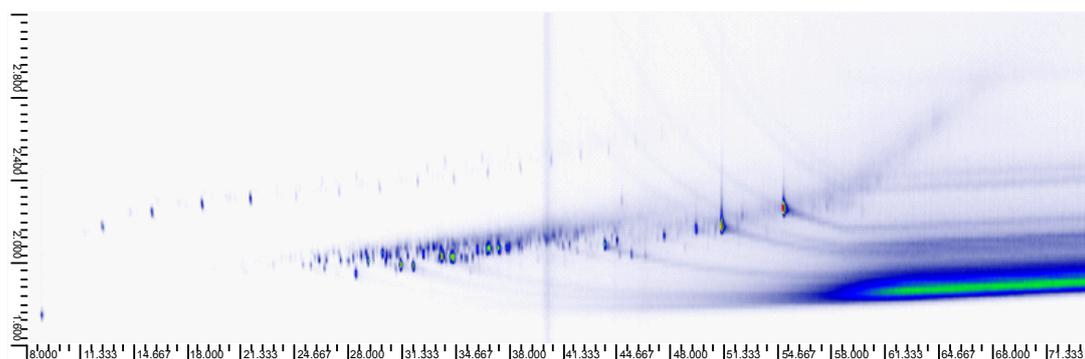


Figure 15: Comprehensive GCXGC-qMS profile of selective alkylnaphthalenes ions for diesel.

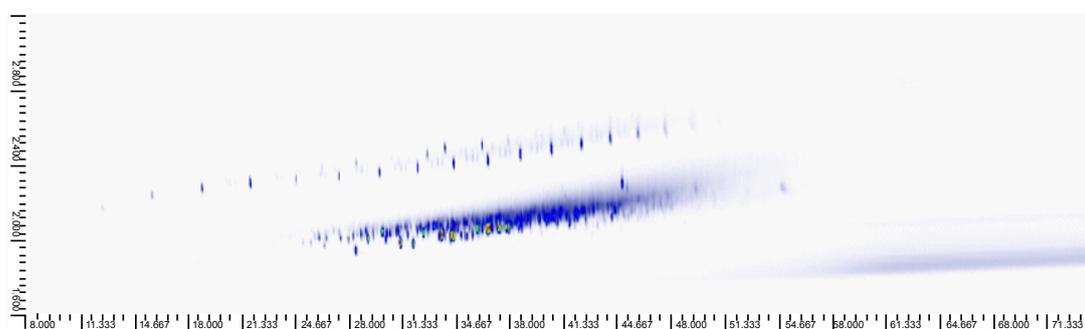


Figure 16: Comprehensive GCXGC-qMS profile of elective alkylnaphthalene ions for suspected arson sample.

134) m/z^2 and alkylnaphthalenes (128, 142, 156, 170) m/z^2 were used in this investigation. The selective ion chromatograms for these ions sets for gasoline, kerosene, diesel and the suspected arson sample are given in figures 5-16. From the selective ion chromatograms, it was possible to visualize the fingerprint pattern of an accelerant in the suspected arson sample. A fairly close match was observed between the diesel and the suspected arson sample. The light portions of the chromatographs are slightly different. The low boiling components of the accelerants are usually the first to be consumed by the fire. Therefore, it was possible to positively confirm the presence of accelerant (possibly diesel) in the suspected arson sample.

Conclusions

Hydrocarbon accelerants and a suspected arson sample were analyzed by comprehensive two-dimensional gas chromatography–quadrupole mass spectrometry (GCXGC-qMS). GCXGC-qMS has the advantage of using two orthogonal gas chromatographic columns. The first being a polar column and the second being a non-polar column, the detector was a fast scanning quadrupole mass spectrometer. By using SIM, a two dimensional separation of the samples was achieved. Clearly by using SIM of selective target ions, we can generate fingerprint patterns that can be useful in identifying accelerants in fire debris samples.

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