

CHAPTER 1

INTRODUCTION

1.1 FIRE, COMBUSTION AND PYROLYSIS

Fire – a single, esoteric word, evoking the very essence of primal fear in some and absolute, almost palpably carnal, fascination in others. Where does this undeniable desire to hear, learn and understand more about fire come from? The answers can be found within the ethos of each and every individual human being.

What is fire? *Fire is a chemical reaction that produces physical effects - a complex phenomenon consisting of a number of chemical reactions occurring simultaneously* [1]. Fire is an exothermic oxidation reaction proceeding at such a rapid rate that it generates heat and light [1, 2].

Combustion is the process of oxidation, heat transfer and fuel chemistry [1]. Virtually all fire processes can be reduced to simple reactions involving the oxidation of carbon, hydrogen, sulphur and nitrogen that account for the largest volume of combustion products of common fuels [1].

In order for a fire to occur, several conditions must transpire. A combustible fuel must be present, an oxidiser (*e.g.*, oxygen in air) must be available in sufficient quantity and energy must be applied as a source of ignition (*e.g.*, heat). The fuel and oxidiser must interact in a self-sustaining free-radical chain reaction [1].

Combustion (or fire) occurs as two types: flaming combustion and glowing combustion. Flaming combustion occurs when both the fuel

and the oxidiser are gases (gaseous combustion). Glowing combustion involves the surface of a solid fuel with a gaseous oxidiser. Nearly all destructive fires are flaming combustion. Many destructive flaming fires begin as small glowing fires. The differences result from the nature and condition of the fuel and the availability of oxygen [1].

The significant part of all flaming fires is the flame itself [1]. The combustion reaction is taking place entirely between liberated gases, even though the fuel feeding the flame is a solid (wood, cloth, plastic, paper, coal, etc.). A solid fuel maintains a gaseous reaction in the flames that burn around it through the phenomenon of pyrolysis. Pyrolysis occurs within the solid as a result of being strongly heated by the surrounding flames and is the decomposition of a material brought on by heat in the absence of oxygen [1].

Wood, paint, plastics and coal do not evaporate or sublime directly into fuel vapours (i.e., they do not burn). When they are heated, they decompose into smaller molecules with greater volatility and flammability and ultimately carbon, which is directly combustible. This is the process of pyrolysis and it is fundamental to nearly all fires. Pyrolysis thus describes the fact that it is the fuel vapours, generated by the solid, that are ignited to support the flames visible above the solid fuel surface and not the solid surface itself [1].

There is a zone just below the surface where pyrolysis occurs, and beneath that, is a region where no pyrolysis has yet occurred. The gaseous materials formed and liberated by the pyrolysis of the large, non-volatile molecules of the solid fuel are the materials that burn in the flame. If there were no gaseous materials present, there could be no flame [1].

The fundamental principles of combustion and pyrolysis guide our understanding and investigation of fire.

1.2 THE CRIME OF ARSON

Arson may generally be defined as the wilful and malicious burning of a person's property. It must be regarded as a possible, if not probable, cause of every fire investigated [1].

Arson is a difficult crime to investigate, solve and prosecute. One of the difficulties can be ascribed to the scene that must be carefully investigated before it can be determined whether a crime actually took place. This is unlike finding a dead body or a bloody knife at the scene, which are strong indications that a murder possibly took place. Such indicators grasp the immediate attention of investigators and they are alerted to proceed without compromising any probable evidence. This attention to detail is often lacking at a fire scene. It is vitally important that every fire scene be treated as a potential arson scene, incorporating security and preservation of evidence, until clear proof of natural or accidental cause is discovered [1, 2].

The crime itself destroys the physical evidence at its origin. *In some cases, proving the crime of arson may be compared to a homicide investigation where the victim's body has turned to dust [1].* Evidence is still there, but it requires careful and methodical analysis to prove its existence. *Arson is the one crime that destroys, rather than creates evidence as it progresses [1].*

Another complication involves the official investigation of arson. It seems to fall between the area of responsibility of the fire brigade and that of the police services. Fire brigade personnel may consider their primary responsibility to be public safety through extinguishment of the fire. Police investigators realize that the physical evidence of the crime, *i.e.*, the behaviour, diagnostic signs and charred debris, is beyond their training and may refuse to deal with it outside the obtaining of warrants, interviews and the field work necessary for a criminal investigation. This breach could result in the loss of valuable evidence and the services of a trained fire investigator are required [1].

The crime of arson is based upon certain main elements of proof that have to be present. It must be shown in court that there has been

burning and actual destruction of property, at least in part, not just scorching and soot deposition. The proof must incorporate whether the burning (fire) is incendiary (deliberately started) in origin, including the existence of an effective incendiary device, no matter how simple it may be. This can be accomplished by showing concisely how all possible natural or accidental causes have been considered and/or ruled out. It must also be adequately shown that the fire was started with the malicious intent of destroying property.

The fire investigator must keep these three elements of proof, the *corpus* (body) of the crime, in mind as the scene is examined. Although the procedural methodology of the examination is carried out in the same fashion as any thorough investigation, evidence must be constantly sought at a possible arson scene.

The detection of abnormal fire behaviour or unusual fire patterns and conditions, incendiary devices, fuels, or simply items that are out of place for no apparent reason, should sound an alarm in the mind of the fire investigator that warns of criminal activity. The circumstances of arson fires are as varied as are the characteristics of fire behaviour, method of ignition, as well as the motivation of fire starters as they relate to the detection of arson. The crime of arson is not a *specific-intent* crime, meaning that the case need only prove that the arson is meant to burn something by setting the fire. This absence of specific-intent may have an impact on the search for a motive [1, 2].

1.3 MOTIVE

DeHaan describes motive as "*some inner drive or impulse that causes a person to do something or act in a certain way*" [1]. *It is the cause, reason or incentive that induces or prompts specific behaviour* [1]. *In a legal context, motive explains why the offender committed the illegal act* [1]. Although motive is not an essential element in a criminal prosecution, it often lends support to the intent to commit the crime of arson.

The fire investigator must give due consideration to possible motives for each individual fire. The fire scene may provide clues predicting

certain behaviour patterns that can lead to identifying and intercepting the culprit, particularly in cases involving multiple acts of arson, implicating a serial arsonist.

In-depth studies have been undertaken concerning the concept of human behaviour related to various aspects of arson. Criminal analysis is one of the most interesting developments of modern crime scene investigation. It offers investigative leads based on data extracted from an analysis of the crimes and compiling offender profiles in which the age, race, sex, occupation, socio-economic status and psychological state of the offender is predicted. The primary step in developing an offender profile is the determination of an apparent motive.

A study by Leong and Silva [3] concluded that there are two groups of *"prototypical" profiles by diagnostic groups, namely "cognitive pathology" containing the psychotic and mental retardation diagnostic groups, involving impaired thinking, and an "affective pathology" containing the alcohol abuse and mood groups* [3]. The psychological motivation could be avaricious, vindictive, therapeutic, instrumental or combinations of these. The psychological mind set coincides with motives such as profit or fraud (commercial or residential), vandalism and "thrill-seeking", juvenile fire setting, revenge, retaliation, or spite directed at a person or persons, institutions, society or targeted groups, the concealment of another crime, extremism, social protest, terrorism or plain irrational fire setting, often by someone seeking attention due to vanity. Revenge remains the most common motive for intentional crimes of arson [1, 3].

The professional and, to a lesser extent, the amateur arsonist wants to produce a maximum of destruction no matter how small the first ignition and the resultant devastation, charred debris, collapsed structures, water soaked ashes, together with the smoke and stench that results from this action, makes the task of fire investigation somewhat uninviting and a seemingly impossible task.

1.4 FIRE INVESTIGATION

A fire investigator faces the often daunting challenge of carrying out a careful, methodical examination of a burnt out, water soaked, often disrupted and trampled scene in the hope of finding enough reliable indications that a cause and origin can be established. The fire investigator tries to answer the questions: "what, who, when, why, where and how?" An investigator must also fulfil the role of an expert, someone who can form an opinion and also present it in court and defend it. This defence is based on particular and/or specific information (not available to lay witnesses), the reliability of which can be established by source or comparison to other information or verified by first-hand observations of the expert. It is up to the fire investigator as an expert witness to put the pieces of the scene back together to form a logical, well-argued whole and present the case to court [4].

The fire investigator must continually ask questions: What was there to burn in the first place and what caught alight first? Who had access to the scene and who would have gained from an arson fire, financially or otherwise? When did the fire occur and when was it detected? Was there an alarm system and was it on or overridden? Where did it begin? How did it grow? Why did the fire start here? Why did it develop the way it did? Why did that particular combination of fuel, air and ignition source come together at that time? To answer the questions, the trained investigator approaches the problem much as a scientist would, by gathering some preliminary observation data and then creating a hypothesis of how the fire originated [4]. Searching for pointers (anything that serves as an indication) at the scene will also give some indication as to source and origin and goes hand-in-hand with the continual self-asked questions. Tony Café [5], an Australian fire investigator, asks the question: "*Why fire investigators get it wrong?*" One of the main reasons is because some of the information and education they have received over the years is not based on validated scientific methodology. Scientific research is based on a methodology which first makes a full review of the scientific literature, then the research work is conducted in carefully controlled tests and then the results are scientifically scrutinised before publication. The results are then

published in peer-reviewed journals or presented at conferences, where peers can question the work or make comment and should be relevant to fire investigation literature. Fire investigation is a branch of forensic science and therefore, scientific methodology should apply to fire investigation literature [5].

The second reason why fire investigators err is that they believe that fire investigation is an art. *“Art is about creativity and fire investigators are not at fire scenes to ponder creativity but are there to physically find and interpret the evidence, which will indicate the cause of the fire”* [5].

There is a Fire Investigation Handbook and pocket guide available for quick reference issued by the international insurance companies, NICB (National Insurance Crime Bureau) and FM Global, both focussing on property loss prevention [6, 7]. These guides are intended to serve the needs of the respective insurance companies, but contain very relevant data and information for all fire investigators interested in accurate, systematic and scientific fire investigation.

A wealth of information is available on the internet, covering all aspects of arson and fire investigation. The main sites are www.fire.org.uk/filinks.htm, which connects one to FireNet International, a site containing the fire site links for arson and fire investigation. This site puts one in touch with various Bulletin Boards, where information can be shared between fire investigators, loss adjusters and analysts. Another informative site is *Net-Trace*, www.nettrace.com.au/resource/investigation/fire.htm, which also provides information regarding associations and government contacts.

1.5 ANALYTICAL FIRE INVESTIGATION

There is a natural tendency to be impressed by the magnitude and destructive violence resulting from a large fire. In the case of insurance investigators, this tendency is aggravated by the fact that they are expected to assess this damage and possibly pay out against a submitted claim. Cause, not extent, should be the investigator's

concern. Too much attention to extent will obscure and complicate the search for the origin and cause. There exists a special need for fire investigators to develop a comprehensive analytical approach to the task. This analytical approach recognises the fact that, to be a successful fire investigator, numerous aspects of fire, fuels, people, and investigative procedures must be understood and mastered [1, 8].

The investigator must really understand how a fire burns, what factors control its behaviour, and that all fires do not necessarily behave predictably. It is essential to understand the fundamental properties of the fuels involved in fire, including density, thermal conductivity, heat capacity of the fuel and how to determine the ignitability and flame spread characteristics of the fuel. The investigator should therefore have a thorough knowledge of the chemistry behind fire and what is actually happening in the chemical reactions taking place. These in turn are factors that control the nature of ignition, as well as the events that follow. These properties are determined primarily by the chemistry of the fuel. Different ignition sources, whether glowing, flaming or electrical, will affect fuels differently, and so the investigator must rely on scientific data about the interaction of such sources with the first fuel ignited to help establish whether or not a particular source is even competent to accomplish ignition and what time factors may be involved. [1, 4, 8, 9, 10].

The American Society of Testing and Materials (ASTM) have established various standards via its committee system. Standard E1397-95 is classified under Forensic Sciences and sub-classified under "criminalistic" and clearly stipulates the role of the fire investigator. The ASTM standards are generally professional in content and scientifically correct, and since the minimum requirement today is that the fire investigation be able to withstand the scrutiny of science as a basis for the conclusion, such guidelines are necessary and should form a fundamental part of fire investigation training [11].

An attorney, who is involved in arson cases, whether criminal or civil, should generally be familiar with the same areas of chemistry. Any

attorney who has no understanding of what happens in chemical reactions and the results of those reactions will be seriously handicapped when questioning both lay witnesses and technical experts [1]. The book "*Chemical Analysis for the Arson Investigator and Attorney*" by Bertsch, Holzer and Sellers [2], is an excellent reference for any fire investigator or attorney.

Since most fires investigated involve either residential or industrial structures, there is a tendency to think of fires only in those terms. This error becomes apparent when a forest or "veld" (bush, wild-land) fire is under investigation. While "veld" fires involve the same basic combustion of fuel in air, the dynamics of fire spread and the analysis and interpretation of diagnostic signs of fire behaviour are quite different from that of structural fires [1].

The analytical approach to fire investigation involves careful, methodical investigation of the scene. Patient, thorough, and systematic evaluation of the debris will usually pay off and provide information critical to the case. It must be appreciated that the destruction of some scenes is so complete due to prolonged burning that virtually nothing can be ascertained from the ashes regarding the origin, cause, and development of the fire. Despite such utter destruction, even such scenes can yield information about the contents of the structure, which can in turn reveal fraud. DeHaan [1] points out a curious tendency for some investigators to show "*an inherent bias as to cause*". These investigators appear to believe that all fires have a single cause, *e.g.*, electrical appliances or smoking materials. These investigators then expend vigorous energy to prove that the fire had this cause, rather than spend the time seeking the true cause. Prejudice related to fire cause is as dangerous as prejudice ascribed to any other unexplained event or crime. It is unfortunately an apparent occupational disease in many fields of investigation, but most noticeable in fire investigations. Adhering to a systematic (*not dogmatic*) approach will minimise the unfortunate effects of such prejudicial tendencies. It is also vital not to extrapolate observations about fuels and combustion in small-scale fires to full-blown incidents without knowing whether in fact they are appropriate or accurate. It is here that data from fire engineering and fire dynamics studies can best be applied, but only if the user is

fully aware of the conditions and limitations of the information, especially if the fire investigator is an expert in these particular disciplines [1].

The complexities encountered in fire investigation are sometimes overwhelming to the investigator, but patience and adherence to fundamental scientific principles of combustion and fire behaviour will usually result in a reasonable diagnosis of the fire event [1, 10].

1.6 FIRE STATISTICS IN SOUTH AFRICA

The destructive forces involved when fire erupts are tremendous, not only as a physical phenomenon, but also financially. Fire destroys both property and human lives. The financial implication stretches beyond direct losses and human concern. Consequential losses that can amount to three or four times the direct loss, often cause greater concern, since the profitability of a company could be substantially affected, even to the point of never recovering from the financial setbacks.

In 1997, the national fire losses in South Africa amounted to R 1 196 538 618-00 (R 3.3 million per day, which amounts to R 137 000 per hour) [12]. In 1998 the national fire loss increased to R 1 319 919 750-00 (R3.6 million per day, which amounts to R150 000 per hour) [13] and in 1999 to R2 356 853 000-00 [14] – that is R 4 million per day on average (the total includes losses reported by the South African Insurance Association). The year 2000 national fire loss statistics have declined slightly to R 976 869 866-00 (an average loss of R 2.7 million each day) [15], but is still a phenomenal financial loss.

Table 1.1 below shows the total fire losses in millions of Rands from 1989 to 2000, also as a percentage of the Gross National Product (GNP). The financial losses, where the fire services were in attendance, are given in Table 1.2. With such massive losses involved, it is not surprising that fire losses are one of the most common subjects of civil litigation. Yet, for all its economic and legal importance, fire remains one of the most difficult areas of investigation.

Table 1.1: Fire Losses in South Africa: 1989-2000

Year	Total Loss	GNP	Fire Loss % GNP	No of Fires	Population
1989	339	229	0.15	34	29.91
1990	424	253	0.17	36	30.58
1991	377	253.7	0.15	40	38.01
1992	483	325.7	0.15	40	38.82
1993	625	373.6	0.17	39	39.63
1994	896	422.1	0.21	56	40.44
1995	814	475.25	0.17	43.05	41.24
1996	918.49	530.68	0.17	33.65	42.3
1997	1196.5	579.71	0.21	37.6	42.9
1998	1319.9	628.15	0.17	52.75	42.1
1999	2357.0	783.9	0.3	51.37	43.1
2000	977.0	851.1	0.11	38.4	43.7

Table Notes: Total loss measured in millions of Rands, population in millions, GNP (Gross National Product) – in thousand millions, number of fires in thousands

Courtesy of the Fire Protection Journal, Fire Protection Association of Southern Africa, [13, 14, 15].

**Table 1.2: Financial Losses in South Africa:
(fire Services in attendance)**

Description	Damage [1999]	Damage [2000]
Residential	R 258,907 756-75	R 182 190 027-00
Institutionnel	R 17 106 645-00	R 17 134 000-00
Public Assembly	R 17 531 300-00	R 7 196 600-00
Commercial	R 210 069 261-20	R 92 586 165-00
Storage	R 119 167 712-00	R 49 590 725-00
Industry	R 233 344 378-75	R 276 611 700-00
Transport	R 147 426 710-75	R 319 775 597-00
Other	R 45 006 311-50	R 31 785 053-00
Total	R1, 048 560 075-00	R 976 869 866-00

Courtesy of the Fire Protection Journal, Fire Protection Association of Southern Africa, [14, 15].

Insurance companies and re-insurers bear the brunt of this phenomenon and are suffering under the onslaught of the spiralling increases in the national fire losses. About 12% [13] of all fires are arson related, but this figure could be higher given the theory that many of the fires listed as undetermined could probably be deliberate. The overall picture is not good for the South African economy, with rumours of deteriorating emergency services throughout the country and the lack of local government funding being channelled towards such emergency services. Insurers too, will need to focus more on technical underwriting and the provision of sprinklers and other fire protection equipment and the actual fire risk involved. The implications of a weak insurance industry and the inability to secure cover are untenable and could have disastrous consequences [12].

What role does the fire investigator play in this tragedy? By accurately and efficiently identifying the causes of fires, whether they are accidental or incendiary, investigators can make a real and substantial contribution toward reducing these terrible losses.

1.7 FIRE INVESTIGATION IN SOUTH AFRICA

South Africa has a fully established National Police Service Forensic Science Laboratory situated in Silverton, Pretoria, serving all SA Police Service stations in South Africa and the SADC countries of Southern Africa. They have recently expanded their services, such that they have satellite Forensic Laboratories functional in Kwa-Zulu Natal, Eastern Cape and the Western Cape. The Chemistry Unit of the SAPS Forensic Science Laboratory has trained personnel in the discipline of arson debris analysis, both as fire investigators, assisting the South African Police Service in their criminal investigation and examination of an arson crime scene, and analytical chemists, who are trained in arson chemistry for the purpose of supporting the judicial process.

In the private sector, there are established independent fire investigators, holding various qualifications, including two with Doctorates in Science and one with a Mechanical Engineering Degree. Loss adjusters either appoint these independent fire investigators or,

as loss adjusters, they work as fire investigators in their private capacity. The independent fire investigators number in the region of six. The number of loss adjusters who act in this capacity is uncertain.

The Council for Scientific and Industrial Research, CSIR, is the only scientific and research organisation of its kind in sub-Saharan Africa [<http://www.csir.co.za>]. It is a para-Statal organisation involved in aspects of research and development of new and improved technologies. The Forensic Fire Investigation program, situated within the Division of Building and Construction Technology, provides a private, independent fire investigation service. The business area comprises four fully trained and experienced fire investigators, who are also members of the International Association of Arson Investigators (IAAI) and hold Diplomas in Fire Investigation from the British Forensic Science Society. They are certified as CFI (Certified Fire Investigator) and one holds a Chemistry Degree. In light of the need for competent, highly trained and experienced fire investigators, the CSIR has ensured that this competence is provided.

1.8 THE USE OF CANINES FOR ACCELERANT DETECTION

For centuries dogs have been used in hunting situations for their strong desire to search and their keen olfactory ability. These abilities have also been exploited in police and military situations [16]. Their work began in the early nineteen hundreds as “police dogs” or “canine (K-9) units”, assisting their trainer/handler in police situations. In 1983, a forensic analyst, Richard Strobel and explosives investigator/dog trainer, Robert Noll (Bureau of Alcohol, Tobacco and Firearms, USA), extended the concept of using dogs to detect ignitable liquid accelerants. In 1984 initial tests were performed very successfully leading to intensive training of canines for the purpose of accelerant detection [16, 17, 18, 19, 20, 21]. The training involves imprinting a known accelerant odour, nullification (exposure of the dog to pyrolysis products in order to learn to avoid alerting when no accelerant is present), discrimination (where the dog is taught to discriminate between known accelerants and pyrolysis products by alerting to appropriate samples) and

verification (to ensure that the dog and handler are working well with one another, and that the dog is alerting correctly, not due to handler influence or to receive the reward) [16, 19].

Canines have now been successfully used in actual fire investigations in South Africa. Both the South African Police Services (SAPS) and the CSIR are privileged to have fully trained, certified and verified arson detection canines. The SAPS train their own canines. The CSIR canines are owned and trained by one of the fire investigators. The canines are mostly border collies and have successfully assisted fire investigators in numerous arson related cases.

1.9 FORENSIC ARSON LABORATORY

The investigation into the cause of a fire is a multi-step procedure beginning with detection and subsequent suppression of a fire, the decision whether or not the fire is of a suspicious nature, evaluation and investigation of the fire scene (using a trained fire investigator), analysis of the evidence, and finally, prosecution and court disposition [1, 2]. The minimum expectation for fire investigation is to be able to withstand the scrutiny of science. Understanding and being able to discuss the laboratory results is required to conduct the investigation. However, the important chemical analysis of fire debris for the presence of accelerants remains only one part of the total fire investigation.

Fire investigation had escalated in South Africa and it became apparent that a dedicated arson laboratory would best serve the needs of the business sector if it functioned within the core business sector of fire investigation.

An arson laboratory was established at the CSIR in June 1996 as a result of fire investigation becoming an integral part of CSIR day-to-day business, thus continuing and improving an already experienced and established analytical arson chemistry service

By October 1996, the laboratory was fully operational and research into various aspects of arson chemistry began using the technique of gas chromatography – mass spectrometry (GC-MS) and tandem

mass spectrometry (GC-MSⁿ). Mass spectrometry was selected as the analytical technique since GC-MS is the accepted method of analysis for fire debris sample extracts and mass chromatography (ion profiling) is the preferred approach for gas chromatography - mass spectrometry data interpretation [45, 55 - 67].

1.10 THE FIRE INVESTIGATOR AND ANALYST AS A FORENSIC TEAM

How much should an analyst know about the case assigned to them for analysis and interpretation of physical evidence? – In short, as much as possible without compromising subjective opinion!

There are two reasons for having to know the case circumstances when performing an analysis. The interpretation of results is done in the context of the history of the sample prior to its collection and preservation. This will assist in distinguishing between explainable and unexplainable differences between the evidence and a reference sample and it helps to “formulate the correct question”. With access to vital samples and case information provided by the fire investigator, the analyst has a chance to retrieve analytical information from apparently irrelevant data and provide the fire investigator with supporting analytical results.

The chances of the fire investigator and the analyst being called to court to give “expert testimony” in an arson case are only too real. The following legally technical section involving “*Daubert versus Merrell Dow Pharmaceuticals*” is therefore relevant and these arguments have come up in South African court cases involving deliberation pertaining to the crime of arson and whether to apply Daubert factors to all expert testimony, without regard to practical qualifications of the expert, or limit its application to scientific evidence cases only.

In 1993, the U.S. Supreme Court delivered its opinion in the case of Daubert v. Merrell Dow Pharmaceuticals, 509 U.S. 579 (1993). In Daubert, the Supreme Court held that the trial court, as “gatekeeper”, must assess whether “scientific” testimony or evidence is both relevant and reliable. Since the Daubert decision, there has

been significant controversy over the types of expert testimony subject to scrutiny by the trial court under the *Daubert* standard. The International Association of Arson Investigators (IAAI), in an *amicus* (friendly) brief (correspondence) to the U.S. Supreme Court, argued that the *Daubert* factors should only apply to expert testimony regarding fundamental science, and should not apply to every type of opinion that could implicate or be indirectly based on scientific principles, theories, techniques, or data. The brief distinguishes experts whose specialised technical knowledge is derived from a combination of training and experience from experts whose testimony is based on fundamental scientific issues that have not been adequately tested or verified to be considered sufficiently reliable for court purposes. The IAAI also urged the Supreme Court to not only apply *Daubert* to scientific experts, but also to fire investigators whose training and experience qualify them to render an opinion. This response arose, firstly from a Supreme Court case that upheld the trial court's decision to exclude a fire investigator's expert testimony, and secondly, that the testimony of a fire investigator was barred on the basis that he had not complied with the scientific method [22, 23].

With this in mind, fire investigators should tread lightly when qualifying as experts. It may result in their testimony being considered scientific testimony requiring scientific verification of the methodology used to reach the conclusion in the case. Communication between the fire investigator and the analyst is thus vitally important to substantiate their evidence, especially if the analytical results go to court.

1.11 RESEARCH IN ARSON DEBRIS ANALYSIS

The analyst is fully aware of the contribution the analytical result will have in an arson case and the possible implication that such a result will have on the lives of the people involved. However, the analyst merely analyses for ignitable liquids and does not determine if arson has been committed.

Research was undertaken into an analytical method that would provide concise, reliable and unequivocal results, especially in cases

where the accelerant traces extracted from fire debris samples were either too weak or were prone to pyrolysis interferences from the fire debris itself.

Since the instrument used for this study included tandem mass spectrometry (MS-MS) capability, this was the method to be explored and applied to problem cases where a result was inconclusive, either to confirm a negative result or to actually determine a positive trace analytical result in a sample which gives a weak response in conventional gas chromatographic-mass spectrometric analysis. Tandem mass spectrometry was thus investigated as a second confirmatory analysis to ensure a concise, reliable and accurate result.

The following chapters deal with the various analytical techniques used for the detection of ignitable liquid accelerants in fire debris. Chapter 4 specifically details the tandem mass spectrometry technique, with emphasis on the GC-MS instrument used during this study. Chapters 5, 6 and 7 discusses the research work and actual case studies relating to the analysis of ignitable liquids in fire debris samples and Chapter 8 provides concluding remarks on the technique. The thesis as a whole is written in a comprehensive way to double as a training manual for new comers to the field of arson debris analysis by GC-ion trap mass spectrometry.

CHAPTER 2

ARSON INVESTIGATION

2.1 WHAT IS AN ACCELERANT?

A fire that has been set intentionally usually requires some substance that speeds up the burning process and gets the fire underway quickly and simultaneously at several locations. Such substances are called accelerants and often consist of ignitable (flammable) liquids such as petrol that burn readily. Fires of this type are called incendiary fires. The most popular accelerants are the petroleum-based liquids.

When a liquid is poured onto a surface (such as carpet or wood), the material of the surface behaves like a matrix or wick [2, 24]. It holds the liquid like a sponge. Carpet absorbs more readily than wood. Whenever an absorbed liquid is heated, it undergoes evaporation. Most accelerants and nearly all petroleum-based fuels consist of mixtures of up to 200 or 300 components. These components have different physical and chemical properties. Substances can generally be grouped into different categories. Some categories, such as alcohols, are more soluble in water than others, such as hydrocarbons. Some have higher volatilities than others and the most volatile components evaporate first. When petrol is left in the open, it begins to evaporate. The heat that is generated in a fire has a similar but accelerated effect. A sample exposed in such a manner has undergone weathering or partial evaporation [2].

When a lit match or other ignition source is brought into contact with material such as carpet or wood, a fire does not start readily. Additives, such as flame-retardants, are used to prevent products

from readily igniting. Solids or liquids, like diesel fuel, are not easily ignited. The reason being that carpet, wood and most other solids do not produce significant amounts of volatiles at room temperature. Elevated temperatures are required. Combustion occurs when the vapour surrounding the fuel ignites. The combustion produces heat that may break down a non-volatile matrix such as carpet into volatile substances. This process is called pyrolysis [2].

Depending on the chemical nature of these volatile pyrolysis products, they may or may not support combustion. In cases where the pyrolysis products are not combustible, the flame does not spread. Wood can be set on fire by an accelerant because the initial heat provided by the combustion of the accelerant generates pyrolysis vapours that are combustible. The heat produced in the process generates more volatiles on which the flame feeds. Concrete does not burn when exposed to an accelerant because it does not generate volatiles.

Fire debris is what is left over after a fire. Typical materials are partially burnt carpet, wood, tile, *etc.* The purpose of chemical analysis is to examine a fire debris sample for the presence of components that make up typical accelerants. It is routine practice for an analyst to collect typical accelerants and establish an accelerant library. An accelerant library contains data useful and relevant for determining the identity of accelerants. In some cases, the residual accelerant, i.e., the accelerant that is still left in a debris sample after a fire can directly be matched to a specific accelerant. In most cases, this is not possible, because of evaporation and other factors. The analyst may only be able to provide a generic description such as "medium petroleum distillate" [2].

The analyst must use methods that prove the presence of an accelerant unequivocally. There are at least three reasons why an accelerant may not be found in a fire debris sample, namely; (i) the sample may not contain an accelerant in the first place, (ii) the accelerant may have been totally consumed in the fire and (iii) not enough accelerant may have survived the fire [2].

A “negative sample” does not necessarily mean that the fire was accidental. On the other hand, finding residual accelerant does not always prove that a fire has been set deliberately.

An understanding of what constitutes a petroleum distillate and its behaviour as an accelerant becomes important when the scene of a fire is visited. Amongst others, it will influence the selection of fire debris samples taken as evidence.

2.2 ARSON INVESTIGATION METHODOLOGY

An arson investigation usually begins right after a fire has been brought under control. The appointed fire investigator, preferably someone with a background in law enforcement, electrical engineering, or some other area of science and with formal training in fire investigation, makes a preliminary determination of the cause and origin of the fire by assessing the factors that contributed to the fire's behaviour [25].

Conventional fires can be characterised as a complex interaction between fuel, oxygen (air) and heat. A source of ignition of sufficient energy is required to start the chain reaction in which a fuel is converted into gaseous products, mostly water and carbon dioxide [1, 2, 8, 9, 25].

Once the starting conditions of the fire have been established, fire behaviour can be predicted fairly accurately. The chemical reactions taking place during combustion are complex, but distinctively different for normal fires and fires that have been accelerated by an artificial source of fuel, such as petrol. In a normal fire, energy in the form of hot gasses moves upward in a room, and the fire spreads vertically if fuel is available. A room may fill with hot gases at the ceiling, which in turn may create other sources of ignition. These gases, soot and pyrolysis products ignite once the temperature increases sufficiently and the fire may spread across the top of the room and into adjacent spaces if there are no physical barriers. There the layer of hot gases may ignite further thermal decomposition products of other fuel sources, resulting in a flashover. At this point, temperatures rise rapidly and also spread downward,

distributing heat more evenly. Further pyrolysis takes place when the oxygen content in a confined space drops rapidly [1, 25].

In contrast, an accelerated fire produces a large amount of heat from the readily available fuel vapours (only the fuel vapours of the ignitable liquid are actually combusting) within a short period of time and at a specific location. In extreme cases, gases can expand so rapidly that windows or doors are blown out with explosive force. If liquid accelerants are used, the available oxygen may be rapidly consumed, leaving an excess of fuel. Most liquid fuels reach their boiling point and boil away before being subjected to pyrolytic decomposition. Even when exposed to an intense general fire, convection within a deep pool (as opposed to a thin film) helps to mix the cooler and warmer liquids. The liquid at the surface boils off into the flame with the heat absorbed from the flames being lost by evaporation. This maintains the temperature of the entire pool at or just below the boiling point of the liquid; the liquid pool protects the surface upon which it lies. The flames are intense, but the amount of heat and the rate at which it is transferred into the matrix may be insufficient to cause pyrolysis at a level necessary to sustain combustion. Liquids themselves so rarely burn that their combustion properties are of little or no interest except for their production of ignitable (flammable) vapours, a process integral with combustion [1, 2, 25].

In most arson cases, petroleum-based distillates such as petrol, paraffin, lacquer thinners, diesel and white spirits are poured along the corners of the walls and floors of a structure. Solid accelerants that involve mixtures of oxidizers (chlorates or nitrates) and combustible compounds (sugar or starch) require analysis procedures that are entirely different from those used for liquids. Combustion properties have different significance when applied to various types of fuel. The concept of flash point is essentially meaningless when applied to solid fuels, although it may apply to volatile materials derived by heating the solid fuel. Physical properties of fuels such as vapour pressure, flammability (explosive) limits, flash point, flame/fire point, ignition temperature, ignition energy, boiling points, vapour density and heat of combustion are relevant and this

knowledge is essential to the proper interpretation of an accelerated fire [1, 2, 9].

A fire that appears to have multiple origins, suspicious burn patterns, an unusually high rate of fire spread, or remnants of an ignition device is highly suspect [1, 2, 8, 9]. The fire scene is photographed, and all items removed from the scene are documented. Physical evidence, typically charred material and furnishings that may contain wood, carpet, synthetic polymers, concrete, soil, or anything else the fire investigator considers a promising source of residual accelerant, is collected and a strict chain of custody is established. The fire investigator considers all these factors and determines whether a fire originated from natural causes or appears to be of an incendiary nature [2, 25]. If the physical evidence points towards a fire that has been set deliberately, the investigator assembles as much information and photographic evidence as possible to thoroughly document the case. Indirect evidence, such as motive, opportunity, and past history of the beneficiary of the fire, is then considered to determine whether a crime has been committed and if an insurance claim should be settled or refuted [25].

2.3 PETROLEUM-BASED DISTILLATES

In fire investigation the most important fuels are the hydrocarbons. The hydrocarbons range from the light gas methane to much heavier compounds, including oils and asphalts.

Since petroleum oil normally occurs in association with natural gas, it is not uncommon for the oil in an oil well to be forced to the surface by gas pressure for a period of time. When a considerable quantity of oil has been taken, the loss of oil and the associated gas may result in a drop in pressure, necessitating further removal of oil by artificial means.

Crude oil consists of a complex mixture of predominantly hydrocarbons, and the various fractions of commercial value are separated from each other by distillation. The principle fractions are reflected in Table 2.1 and each fraction is discussed in more detail below.

2.3.1 Natural Gas

Natural gas, consisting mainly of methane, shows considerable variation in composition from different geological formations and may contain some non-combustible gases. It is typically 70-90% methane, 10-20% ethane and 1-3% nitrogen, with traces of other gases [2, 9, 25].

Table 2.1: Principle Fractions From Crude Oil

Boiling range (°C)	Fraction	Uses
Below 20	Natural gas	Fuel
20-60	Petroleum ether	Solvent
60-100	Light naphtha	Solvent
25-190	Petrol (gasoline)	Motor fuel
165-255	Paraffin (kerosene)	Heating fuel
180-340	Diesel fuel (gas oil)	Motor fuel
Vacuum Distillation	Heavy oils	Lubrication
Vacuum Distillation	Greases	Lubrication
Vacuum Distillation	Asphalt or petroleum coke	Road surfacing

Courtesy of Principles of Fire Investigation, [9].

2.3.2 Liquified Petroleum Gas

Liquified petroleum gas (LPG) is a mixture of propane and butane, with small quantities of ethane, ethylene, propylene, *iso*-butane and butylene. For the most part the fire investigator can consider LPG the same as propane in its physical and combustion properties without serious error.

2.3.3 Petroleum

Petroleum in its crude state is a viscous oil varying in colour from light brown to black, formed by the partial decomposition of prehistoric organic material. It collects in pockets of porous rocks from which it can be recovered by drilling operations [1, 9, 26, 27]. It contains a very large number of compounds and compound types that are partially separated in the manufacture of petroleum fuels. Products obtained from the distillation of

petroleum include: natural gas, petroleum ether, light naphtha, petrol (gasoline), paraffin (kerosene), medium petroleum distillate oils including paint-thinner type mixtures and solvents, diesel fuels, heavy lubricating oils, vaseline, greases, paraffin wax, asphalt and coke.

2.3.4 Petroleum Naphthas

Petroleum naphthas generally refer to unrefined, partially refined or refined petroleum products and are primarily used as industrial solvents. Naphthas are not well defined and can range from paraffinic distillates to highly aromatic types. The distillation range is approximately 171°C to 240°C. Aliphatic type naphthas are more prevalent than aromatic types [2].

2.3.5 Petrol [Gasoline]

Petrol, perhaps the most important fuel of petroleum origin and the single most important accelerant encountered in incendiary fires (arson). It is a mixture of volatile, low boiling, and midrange hydrocarbons. It contains hydrocarbon compounds that distil off between approximately 25°C and 190°C, with a flammable vapour (flash point below room temperature). The average molecular mass of petrol is usually taken to be close to that of *n*-octane, about 114. Petrol is a distillate blend of many compounds. The vast majority of all compounds in petrol fall into only one of three substance classes, namely paraffins, olefins and aromatics. As opposed to all other fuels, aromatic hydrocarbons constitute a significant fraction of petrol. Paraffins can be further divided into the categories of normal alkanes, branched alkanes and cycloalkanes also referred to as naphthenes. Other component classes are only present in trace quantities.

Petrol contains more than 200 major hydrocarbons in a complex mixture whose relative component concentrations vary little from refinery to refinery. Based on a comparison of the basic hydrocarbon “profiles” of various petrols, it is not generally possible to identify one oil company’s product from another [1, 2, 9]. Fortunately, some chemicals can be added to petrol in small

quantities to improve the ignition characteristics of relatively inferior blends. Anti-knock additives such as tetraethyl lead and tetramethyl lead [28] can also be present, as well as scavengers such as 1,2-dibromomethane and 1,2-dichloroethane. Oxygenated compounds such as alcohols, methyl *tert*-butyl ether (MTBE) and organomanganese substances are now widely used to improve the octane ratings [2].

2.3.6 Aviation Fuel

Aviation fuels (as used in light aircraft) have narrower boiling point ranges than conventional petrol. The boiling point range is reduced by approximately 30°C. For safety reasons, the specifications for aviation fuel are very stringent. They have very high octane ratings, maximum heat content per mass and good chemical stability. A typical aviation fuel consists of 50-60% isoparaffins, 20-30% naphthenes and 10% aromatics. Olefins are virtually absent. 100LL grade aviation fuels contain a blue dye [2].

2.3.7 Paraffin

Paraffin (kerosene or light fuel oil) consists of the distillation fraction having a boiling range between about 165°C and 255°C. It is less volatile than petrol and has a flash point above normal ambient temperatures (38°C). Paraffin consists predominantly of alkanes between nonane (C_9H_{20}) and pentadecane ($C_{15}H_{32}$). There can be significant differences between the ratios of component alkanes and even between different batches of paraffin of the same nominal type [9].

2.3.8 White Spirits

White Spirits is similar to paraffin except that no dye is added to it and it is a fraction with a narrower boiling point range (150°C-200°C). White spirits (also known as mineral spirits or mineral turpentine) consist predominantly of alkanes between nonane (C_9H_{20}) and dodecane ($C_{12}H_{26}$) and is found in common industrial solvents, paint thinners and charcoal lighter fluids [9].

2.3.9 Diesel Fuel

Diesel fuel (a type of fuel oil) consists of a mixture of alkanes between decane ($C_{10}H_{22}$) and pentacosane ($C_{25}H_{52}$). It is less volatile than petrol, paraffin or white spirits [9]. Diesel burns in a similar manner to paraffin but there is a tendency for the flames to be significantly more “smokey”. Pristane and phytane are usually also present when derived from crude oil.

2.3.10 Oils, Lubricants, Greases, Waxes, Asphaltenes and Resins

These petroleum distillates have a common denominator in that they all have a high molecular mass. These materials are generally not significant as accelerants, but they are sometimes used in conjunction with other fuels such as petrol. High boiling range petroleum distillates do not act as accelerants, unless heated to fairly high temperatures. Sometimes high boiling point range petroleum products or distillates are used as solvents for other lipophilic substances and may, on occasion, become part of fire debris, *e.g.*, from roof shingles or wood surfaces when these become involved in a fire.

The term oil refers to a medium viscosity distillate, usually obtained by vacuum distillation. Depending on the intended use, further processing steps are added to achieve the desired properties. After processing (oxygen, nitrogen and sulphur containing compounds are completely eliminated), “white” oil is usually odourless and colourless. Technical oils, such as lubricants, have less stringent requirements. Oils used as carriers for insecticides are highly refined and insulating oils, as used in transformers, are not as highly refined. Lubricating oils consist primarily of mixtures of branched alkanes and cycloalkanes, with minor quantities of polynuclear aromatic hydrocarbons.

Greases use feedstock similar to that of liquid lubricants. To achieve the viscosity and consistency of grease, soap type compounding agents are added. Waxes constitute solids consisting largely of high molecular mass alkanes. Two types of

petroleum waxes can be distinguished: paraffin waxes in petroleum distillates and the microcrystalline waxes in petroleum residue. Paraffin wax is generally a solid crystalline mixture of n-alkanes [C_{20} to C_{36} and beyond]. Petrolatum [petroleum jelly], on the other hand, contains both liquid and solid hydrocarbons.

Asphaltines and resins make up the high molecular mass fraction of petroleum and consist of condensed ring polycyclic aromatic structures containing nitrogen, oxygen and sulphur atoms. In normal producible crude oils, they range from 0% to 40%. In addition to bituminous materials, asphaltines and resins are the major components of commercial asphalt, used to pave roads, produce roofing shingles, battery boxes, fuel briquettes, brake linings and many other applications. Asphalt is not a candidate for an accelerant as such, but may cause interferences in an analysis [2, 9].

2.3.11 Absolute Alcohol

Absolute Alcohol (Ethanol) can be produced from a fermented mash by distillation and dehydration, or chemically, by hydration of ethylene, which differs from the ethanol produced by the fermentation of sugars by yeasts. It is by far the most commonly encountered of all the alcohols and it is the only common water-miscible liquid fire accelerant. It is easily ignited and burns with a blue, scarcely visible flame and can be difficult to detect if burnt to completion [9].

2.3.12 Methylated Spirits

Methylated Spirits, consists of a mixture of approximately 90% ethanol, 9.5% methanol and 0.5% pyridine together with traces of petroleum naphthas and methyl violet dye. This mixture has burning characteristics closely similar to that of absolute alcohol. Related mixtures include industrial methylated spirits and surgical spirits, both of which are water white and consist predominantly of ethanol with a small percentage of methanol [9].

Some refinery processes produce distillates that are very different from those already discussed and are relatively rare. They represent special process streams and are usually manufactured for specific purposes. Mixtures of petroleum distillates with components other than hydrocarbons also exist, *e.g.*, a ketone may be added to a distillate to increase solubility for polar components.

Heavy fuel oils are usually not produced by distillation and may contain substantial amounts of residuals. An example of heavy fuel oil is bunker oil, used to power ocean-going vessels. In between these extremes is stove oil, which is a straight run fraction similar to kerosene. Furnace oil usually consists of a blend of straight run gas oil and cracked gas oil. Diesel fuel is very similar to furnace oil but contains a lower portion of aromatic components [2].

Liquids such as paraffin, white spirits and diesel fuel, which have flash points above ambient temperature, cannot normally be ignited by a flame or spark without the liquid having been preheated to a temperature above its flash point (the lowest temperature at which a liquid produces a vapour that can sustain a continuous flame) [1, 2].

There are various plastics, polyethylene, polypropylene, poly(vinyl chloride), polystyrene, poly(methyl methacrylate) known as perspex, cellulose acetate, cellulose nitrate, polyurethane, rubber, synthetic rubber, carbohydrates, cellulose, proteins and fats that can contribute as fuels [9].

The list of petroleum distillates and products discussed above is somewhat arbitrary and not exhaustive. Petroleum distillates are sometimes mixed and the analyst must be aware of this and be able to recognise such mixtures. The analyst may or may not be able to deconvolute the individual fractions of the mixture. When a white spirits (mineral spirits) fraction is added to a fuel oil such as diesel fuel, it is normally possible to discern a binary distribution. When it is added to paraffin (kerosene), a distinction may not be possible [2].

There are a host of other common hydrocarbon solvent blends and pure organic solvents available on the market and therefore it is important to classify these hydrocarbons into a classification scheme

enabling identification of the type of distillate present that may have been used as an accelerant [2, 97]. Most of the hydrocarbon fuels are described with specifications in the ASTM methods (D 1945-81, D 484-76, D1655-80a, D396-79, D 975-78, D 439-79, D 910-79, *etc*) [2].

2.4 IGNITABLE LIQUID CLASSIFICATION SCHEME

Petroleum based fluids have been reported in the overwhelming majority of incendiary fires in which accelerants have been found. The reason is that petroleum accelerants are inconspicuous, widely available, inexpensive and relatively safe to handle. Petrol is the most common liquid accelerant encountered in arson related fires. Very little information is available on accelerants that are not based on petroleum distillates, such as alcohols [2].

Most products leaving the petroleum refineries do not represent true distillates either. Process streams in modern refinery operations originate from cracking and upgrading units. The blending of products from these processes clearly adds components of synthetic origin. The definition of a petroleum distillate becomes indistinct, in particular in the light of new fuel technology [29].

The discussion of refinery processes makes it clear why petroleum based distillates share common features. In some cases, boiling range differences are quite small and analytical results are very similar – virtually identical petroleum distillates may be labelled differently. The arson investigator would be best served if the analyst could clearly identify a particular distillate as being "*charcoal lighter fluid of specific brand X*", but this is unfortunately not possible [27, 29, 30].

The classification of residual accelerant is greatly complicated by changes that have taken place in the distribution of substances. Components may have been lost during a fire, at the fire scene, during storage or transit of the debris or during analysis [27, 29].

It is possible to categorise liquid accelerants according to several principles. Accelerants can be arranged according to boiling point

range, chemical composition, intended use, or a combination of these (Table 2.2).

The guidelines have been established and reconfirmed by the Scientific Advisory Committee of the International Association of Arson Investigators. Over the years, attempts have been made to refine and expand this system. The classification scheme has been criticised as incomplete and too strongly oriented toward physical rather than chemical properties. Newer types of petroleum distillates, such as "isopars" and other catalytically synthesised hydrocarbons do not fit into any of these categories [2, 31].

Nowicki has suggested further improvements to the scheme detailed below [31]. The light petroleum distillate (LPD) and heavy petroleum distillate (HPD) categories are split into additional groups and a separate category for *iso*-paraffin products is suggested.

As technology progresses and crude oil deposits dwindle, alternative sources of fuel are expected to eventually replace conventional petroleum refinery products. Several large-scale operations, based on the Fischer-Tropsch process, are already in existence. Approximately 50% of the petrol produced in South Africa is derived from coal. Alternative fuel technology is expected to play an ever-increasing role in the future [2].

Table 2.2: Ignitable Liquid Classification System

Class Number (Class Name)	"Peak spread" based on n-alkane carbon numbers (unevaporated liquid)	Examples
1 Light Petroleum Distillates (LPD)	C ₄ -C ₈ (branched alkanes)	Petroleum ethers Pocket lighter fuels Some rubber cement solvents Skelly solvents V M and P naphtha Some camping fuels

Courtesy of ASTM guide E 1618-97, [29], Analytical Chemistry News & Features, [25] and Chemical Analysis for the Arson Investigator and Attorney, [2].

Table 2.2 continued: Ignitable Liquid Classification System

Class Number (Class Name)	"Peak spread" based on n-alkane carbon numbers (unevaporated liquid)	Examples
2 Gasoline	C ₄ -C ₁₂ (branched alkanes, alkylbenzenes, naphthalenes)	All brands and grades of automotive gasoline, including gasohol
3 Medium Petroleum Distillates (MPD)	C ₈ -C _{11/12} (normal alkanes, alkylbenzenes)	Mineral spirits Some paint thinners Some charcoal starters "Dry-cleaning" solvents Some torch fuels Some solvents for insecticides and polishes Some lamp oils
4 Kerosene	C ₉ -C ₁₆ (normal alkanes, alkylbenzenes, naphthalene)	No.1 Fuel oil Jet-A (aviation) fuel Insect sprays Some charcoal starters Some torch fuels Some paint thinners Some solvents for insecticides and polishes Some lamp oils
5 Heavy Petroleum Distillates (HPD)	C ₉ -C ₂₃ (normal alkanes, alkylbenzenes, naphthalenes)	No.2 Fuel oil Diesel fuel
0 Miscellaneous (unclassified)	Variable (alkanes, alkylbenzenes, alcohols, ketones, esters, toluene, xylenes, lacquer thinners, isoparaffinic hydrocarbon mixtures)	Single compounds Turpentines Speciality mixtures which cannot be further classified into one of the categories below
0.1 Oxygenated Solvents	Variable	Alcohols, ethers, ketones

*Courtesy of ASTM guide E 1618-97, [29], Analytical Chemistry News
& Features, [25] and Chemical Analysis for the Arson Investigator
and Attorney, [2].*

Table 2.2 continued: Ignitable Liquid Classification System

Class Number (Class Name)	"Peak spread" based on n-alkane carbon numbers (unevaporated liquid)	Examples
0.2 Isoparaffins	Variable	Isoparaffin products Some charcoal starters Some copier fluids Some aviation gasolines Some lamp oils Some solvents for insecticides and polishes Some camping fuels
0.3 Normal Alkanes	Variable	Speciality products formulated from normal alkanes, insecticides and polishes
0.4 Aromatic Solvents	Variable	Light, medium and heavy "aromatic naphtha" used as solvents for paints and plastics
0.5 Naphthenic/Paraf- finic Solvents	Variable	Speciality solvent/fuel products made from Class 3 or Class 4 distillates treated to remove normal alkanes and aromatics, with higher cycloalkane content than iso- paraffin products

*Courtesy of ASTM guide E 1618-97, [29], Analytical Chemistry News
& Features, [25] and Chemical Analysis for the Arson Investigator
and Attorney, [2].*

2.5 IS IT A PETROLEUM PRODUCT?

In arson related laboratory analyses, the report or the testimony of the expert in court frequently describes the ignitable [flammable] liquid detected as "a heavy petroleum distillate", "a medium petroleum distillate" or "a petroleum distillate of the gasoline type". The validity of describing the ignitable liquid detected in arson evidence as a petroleum product is becoming questionable [26, 30]. Liquid hydrocarbon fuels (synthetic fuels) can be made from coal. With the increasing use of synthetic products in fuels and chemicals,

this could lead to problems in the analyst routinely testifying that the material detected was identified as a crude oil fraction.

The characterisation or identification of accelerant residues requires a comprehensive understanding of refining operations [32, 33] and exactly how petroleum, coal and coke are classified [26, 27, 29].

The use of gas chromatography coupled with mass spectrometry (GC-MS) provides definitive identification of components but does not provide information on whether an individual hydrocarbon or alcohol was made from coal, natural gas, oil or biomass. It has been pointed out that products derived from coal and biomass conversion may be virtually indistinguishable from those originating in petroleum refineries [2]. Laboratory reports and court testimony may need to be modified to eliminate characterization of a detected accelerant as a petroleum product unless this can be conclusively demonstrated.

When it comes to “brand identification” or rigorous comparison of a fresh petroleum product with residual material, this poses almost insurmountable problems to the analyst [30]. While there are differences in different petrol blends (gasolines) produced by different refineries, for a given type and grade of petrol these differences may be quite small and undetectable. These differences arise from the crude oil supply, the refinery process and the blending of the distillates.

Differences between petrol blends produced by competing oil companies may not be appreciably greater than the batch-to-batch variations within a single company. Further limiting any meaningful differences in petroleum products are wholesaling to private brand marketers and exchanges of petrol made among oil companies, down to the brand stations, who will buy from various producers, thus creating essentially identical petrol sold by several different brand retailers, whose petrol composition could range from pure petrol to a complex mixture, generally making brand identification impossible [30].

An analogous situation exists with a number of other petroleum-based products such as charcoal lighter fluid, paint thinners, *etc.*

These materials may be purchased in bulk and then repackaged and identical material will then be sold under several brand names, again making brand differentiation impossible.

When liquid petrol samples are submitted for examination, a number of other tests in addition to gas chromatographic examination may be conducted. This includes lead content, residues, gum, octane rating and dye type, whether the petrol is regular, premium, leaded or unleaded [30, 28, 34].

The examination of relatively fresh liquid petroleum products provides the most favourable conditions for comparison. When debris collected at a fire scene is examined, the situation for comparison with a reference sample is considerably less favourable. Volatile vapours from the debris are analysed by chromatographic techniques and the only meaningful conclusion that can be drawn from a comparative examination of the detected vapour and a reference liquid is that they are similar. During storage, volatile components of a liquid such as petrol are slowly lost, thus changing the analytical pattern as compared to that of raw petrol. In unburnt residual ignitable liquid from a fire scene, high temperatures have accelerated the loss of volatile components and the chromatographic information obtained will be quite different from that of fresh petrol. The situation is somewhat less severe with heavier petroleum products such as paraffin, diesel fuel, *etc.*

The analyst will usually have no knowledge regarding the collection or storage or the temperature exposure of the debris sample and will be unable to relate its composition to that of the original product. A rigorous comparison with a reference sample will lead to a determination that both represent the same type of petroleum distillate and not the specific brand.

2.6 AIDS USED FOR DETECTING ACCELERANTS AT FIRE SCENES

The use of various aids and techniques to detect accelerants at fire scenes has attracted controversy during the past couple of years. The use of physical indicators (such as floor burn-through patterns)

to indicate the presence of accelerants, without analytical support, continues to be debated in court.

Experts using this sort of evidence without the support of positive laboratory analysis are often heard resorting to hyperbole and analogy to support their case. The fact is that these techniques should solely be used as aids to detect the presence of accelerants and samples should be submitted to the laboratory for confirmation of the presence and identification of the accelerant [35].

The locations from which samples are taken should be based upon the physical evidence. Such indicators used to detect the presence of accelerants are localised burn patterns to floors and surfaces, "V"-patterns, "hum-throughs", "trails" and overhead damage inconsistent with the naturally available fuel [35]. Accelerants are normally found at the area of origin of the fire, in doorways where an arsonist would attempt to leave a building and in large spaces such as in the centre of a room where the arsonist can move about freely when distributing the accelerant. Reports from fire fighters and eyewitnesses of a rapid fire or of suspicious odours can also indicate the presence of an accelerant. These physical indicators, if initially present, can often be destroyed during the course of the fire [35, 36, 37].

The human sense of smell can quite correctly identify the presence of accelerants, even in trace amounts. When one smells fire debris, one is actually sampling the headspace above the debris and noting the chemical fingerprint of the headspace. This ability varies amongst investigators as it can be highly developed or impaired both temporarily and permanently. Odour perception can be very treacherous and should never be used as the sole indicator for accelerant detection. Combustion products such as styrene and other unsaturated substances may impart a smell similar to petrol [2].

Sniffer-dogs are used for the detection of drugs, explosives, corpse location, termites and contraband food, for tracking purposes and also for accelerant detection. Dogs have a sense of smell that is much more sensitive than that of humans. They also have greater discriminatory powers and can respond much more quickly to target

scents. Again, an indication by a canine has to be verified by laboratory analysis.

Portable gas detectors (sniffers) are best employed when toxic vapours are present or if the investigator's sense of smell is impaired. They do not have the same discriminatory powers as the sense of smell since they respond to a wide variety of compounds in the headspace including non-accelerant vapours, but they may be useful in determining which sites to sample. They can, however, never be used as a replacement for laboratory analysis.

Portable gas chromatographs are equipped with a flame ionization detector (FID) or a catalytic oxidation probe and a small packed column. The instrument can be used as a "sniffer" where the air sample is introduced directly into the detector or as a chromatograph where the sample is introduced into the column for separation before reaching the detector and a chromatogram produced for analysis. The major problem when using nearly all types of "sniffers", regardless of their principle operation and their price, is that they cannot always discern between accelerant vapours and pyrolysis products due to intrinsic peak overlap problems (see Chapter 3). Their use at a fire scene thus remains a continual source of controversy amongst investigators [37].

Chemical tests include the use of Draeger™ tubes [35] that are routinely used for detecting hydrocarbons in the atmosphere and hydrocarbon field test kits used for soil and water analysis. Both tests rely on a colour change as a result of the hydrocarbon reacting with a developing agent. They are generally used for the quantitative analysis of hydrocarbons and cannot discriminate between hydrocarbons originating from accelerants or those originating from pyrolysis products [35].

Accurate detection of an accelerant can help arson investigation. By using modern methods of chemical analysis, even small quantities of an accelerant from a well-trampled and weathered fire scene can be detected, recovered and identified. Regardless of the technique used to detect the presence of an accelerant, the findings must be verified by the available physical evidence and by laboratory analysis.

2.7 SUITABLE MATRICES FOR FIRE DEBRIS SAMPLES

After locating the area where an accelerant is suspected, a sample of debris is required that will have the highest probability of retaining traces of an ignitable liquid. The analyst has little or no input into the selection of matrices. The requirements of the fire investigator are not always compatible with those of the forensic analyst. The most suitable matrix for the retention of an accelerant consists of a highly adsorptive material that does not readily pyrolyze and/or generate products that can be confused with accelerant type substances. The adsorptive capacity of materials must not only be large enough to store a sufficient amount of volatiles but the matrix must also be capable of releasing the adsorbed or trapped volatiles.

Generally, the best materials to be collected for evidence are absorbent or adsorbent in nature. Porous or spongy materials such as cloth, carpet, paper, cardboard, soil and concrete (which has a porous structure) are good examples of absorbent materials. Carbon or charcoal type surfaces are good adsorbent materials and may adsorb tenaciously (adsorption is the phenomenon that depends on molecular interaction between the substances to be collected, the volatiles, and the collection medium, *i.e.*, the adsorbent). On the other hand, materials such as glass and plastic are not good adsorbents and are less likely to give positive results. Readily combustible materials such as rubber and timber are generally not good materials to sample because their combustion supports depletion of the accelerant. It is preferable to avoid plastic materials since these tend to interfere with the accelerant traces to be detected [2, 36, 37].

2.8 SAMPLING CONTAINERS TO USE

Various containers have been used for sampling fire debris, unlined metal paint cans are, however, regarded as the most suitable because of their excellent sealing capabilities, their robust design and are suited to most analytical extraction techniques. Lined paint cans usually contain some sort of industrial solvent similar to petrol and thus are not suitable as evidence containers.

High barrier material (nylon) evidence pouches are also robust and suitable, and are often preferred, as they do not take up as much space as do metal paint cans if samples are required to be transported by air. These nylon evidence pouches are resilient, impermeable, heat sealable and suitable for packaging fire debris samples and were used in this study (KAPAK® Fire DebrisPAK pouches are obtainable from KAPAK Corporation, Minneapolis, USA – www.kapak.com).

Glass jars, especially mason jars, can be used if nothing else is readily available, but they are fragile and must be carefully pre-cleaned before use when collecting significantly weathered samples. Ordinary plastic bags are easily pierced and are prone to diffusion of vapours both into and out from the bag and are therefore not suitable [2, 25, 38].

2.9 CONTROL SAMPLES AND BLANKS

Control samples generally form part of the scientific process to ensure that background materials do not contribute to the result. These samples are often very important, especially since burnt carpeting, the glue backing of both tiles and carpet, plastics and rubber liberate a volatile signature that does interfere with trace amounts of possible accelerant residue that may be present in the sample.

Control samples must be collected at the scene along with samples taken for analysis. Control samples must not have been exposed to the fire or any incidental ignitable liquids. Both must be submitted to the laboratory for analysis. This procedure helps to eliminate potential interferences, to prove that sample contamination did not take place during transport and to prevent misinterpretation of results due to the presence of aromatic components that mimic those found in typical accelerants. The control samples are also used for expanding the chromatographic database recorded from various pyrolysate backgrounds.

Blanks are usually necessary to ensure that there are no interferences present from all potential sources other than the sample

itself. This involves not only various swabs or sample containers used in the sampling, but also solvents and adsorbants used during extraction of the sample. Every precaution is taken not to expose blanks to the actual fire scene or to any samples that have been collected at the scene. Even though the analytical approach is qualitative, it remains important to ensure that all the steps involved in the analysis are checked for possible sources of contamination.

A multi-step analytical procedure is only as strong as its weakest link and it is necessary to look at fire debris analysis in its entirety. The following stages can be defined [25]:

- Selection of samples in the field, including control samples and blanks
- Packaging and shipment of the samples to the laboratory
- Physical inspection of the sample in the laboratory
- Preparation of the sample for analysis by an instrumental method
- Instrumental analysis, usually by gas chromatography
- Interpretation of data
- Reporting and documentation.

As mentioned, the analyst has no input in sampling at the fire scene and usually has the first contact with the sample when it arrives at the laboratory. A rigorous chain of custody must be maintained that allows for tracking the sample from collection at the fire scene until the case has been legally heard in a court of law [25]. In the following chapter, the preparation of fire debris for analysis and the subsequent instrumental analysis will be discussed in more detail.

2.10 ANALYTICAL PROFICIENCY

A laboratory operating under the guidelines of Good Laboratory Practices (GLP) requires instrumentation that preserves the integrity of the analytical data according to specific mandates for legal purposes. Varian, the suppliers of the analytical instrument used for arson analysis in this study, complies with GLP and performance of the chromatographic separation can be evaluated with system suitability software. By tracking these performance criteria, the

analyst can be assured that accuracy and precision will not be compromised [39].

The Forensic Science & Engineering Committee of the International Association of Arson Investigators (IAAI) developed a set of guidelines that encourages uniformity in the reporting of analytical results [40]. These guidelines are intended to be used by analysts in the business of analysing fire debris samples for the presence of ignitable or combustible residues. The guidelines stipulate the requirements for methodical reporting of results. In this way the client can be secure in the knowledge that the analysis of the samples was carried out using recognised methods and that the identification was made according to recognised criteria [2, 25, 40].

The American Society for Testing and Materials (ASTM) has adopted a series of methods for the examination of fire debris for ignitable liquids and combustible liquid residues. Individual test methods deal with the recovery of accelerant residue from the matrix, chromatographic separation and detection, and cleanup procedures. Although minimum requirements for the identification of specific accelerants have been determined, the guidelines provide a great deal of freedom to the forensic analyst as to choice of gas chromatographic detectors (ASTM E 1618-97) [29], and that *"any column and conditions may be used provided that under the conditions of use, the test mixture can be resolved into its component peaks."*

Professional organizations, such as the American Society of Crime Laboratory Directors, have set up accreditation boards. Participation in such programs is voluntary and establishing an individual as an expert in the analysis of fire debris is done in a court of law where credentials are presented on a case-by-case basis.

Inter-laboratory testing can be done through organizations such as the Forensic Laboratory Proficiency Testing Program, a voluntary program administered by Collaborative Testing Services and affiliated with the American Society of Crime Laboratory Directors. This organization has been evaluating forensic laboratories since 1971 [25].

The selection of analytical methodology and the report format are at the discretion of the participating laboratory. Participating laboratories receive test results a few weeks after the announced deadline, and a comprehensive report describing the performance of all laboratories arrives a few months later. Although it is tempting to interpret the information from the annual reports as reflecting the state of the art in the field, this projection is probably not fully justified since the studies are intended as educational, and a cautionary note attached to each report emphasises that the summary of results is not an *"overview of the quality of work performed in the profession"*. However, shifts in the use of analytical methodology and instrumentation can easily be extracted from these reports and they provide the only comprehensive source of information available on laboratory techniques in accelerant analysis.

The degree of difficulty and rate of success varies considerably between different test rounds because each round has a different focus. In certain years, sample preparation technology was emphasized and in other years, the emphasis was on recognizing seldom-encountered accelerants. In most cases, scenarios were provided. Most laboratories have no difficulty with matrices containing relatively large quantities of accelerants, even those that underwent considerable weathering. However, high-boiling range distillates such as diesel fuel were sometimes confused with kerosene – the reason being that headspace methods often suffer from inadequate recovery of high-boiling compounds.

The most serious error made in the blind tests is the reporting of an accelerant in a sample when none was present. Between 5% and 10% of the laboratories reported an accelerant in new and charred samples when none was present. A careful evaluation of responses from the laboratories did not point to a single source of error in either sample preparation procedures or instrumentation, and the experience of the analyst did not appear to be the source of the problem. The information derived from inter-laboratory testing can assist in the prevention and ultimate elimination of such false positives, but towards this end, a concerted effort must be made [25].

CHAPTER 3

FIRE DEBRIS PREPARATION AND ANALYSIS

3.1 THE ANALYTICAL PROBLEM

The recovery, isolation and identification of residual accelerant from fire debris is a complex and often challengingly difficult task. The basic goal of chemical analysis of fire debris is to establish whether materials are present in the remnants of a fire that could have helped to start or accelerate it [2, 9, 25, 36, 37]. At first it seems that a highly volatile fuel such as petrol would burn to completion along with the structure (this is usually the expectation of the arsonist). However, traces of the fuel often remain even after an intense fire, and successful collection and analysis of these debris samples for accelerant traces remains difficult [25]. It must be borne in mind that the forensic analyst does not determine if arson has been committed, but merely analyses for the presence of ignitable liquids [2].

Two major factors make chemical analysis particularly difficult:

- 1) Pyrolysis of matrix materials generates a significant amount of volatiles that may mask and/or interfere with the accelerant components surviving a fire;
- 2) The accelerant itself may undergo changes due to extreme exposure to heat [2, 25].

Current methods of chemical analysis rely on a multi-step procedure in which the debris sample is first subjected to an accelerant recovery process. The sample extract is then determined by an instrumental

method, such as gas chromatography coupled with mass spectrometry or IR spectroscopy. In the last step, data are evaluated, usually by pattern recognition and ion profiling techniques.

There are various methods available for the recovery of volatiles from a debris sample, which is almost always followed by gas chromatography. Sample preparation methods have to be viewed in conjunction with the method to be used to characterise and identify the suspect accelerants. No single method is universally effective for all types of accelerants that are commonly encountered.

Several surface analysis techniques have been developed that allow the direct detection of organics adsorbed onto surfaces. Laser desorption mass spectrometry (LDMS) and surface enhanced Raman spectroscopy (SERS) are just two of many methods widely applied in materials science. Unfortunately, such direct surface analysis techniques cannot be readily adapted to arson analysis. An isolation method must be used for the recovery of adsorbed accelerants and these must be measured in the liquid or gas phase [2].

When choosing an isolation method, the advantages and disadvantages of each method must be considered. It is important to physically inspect the sample and carry out some preliminary investigation. Debris that gives off a strong smell of petrol will need to be treated differently from a sample that consists primarily of charcoal. Sample preparation procedures can be categorized according to the types of instruments used, or the physiological principles involved. The different types of sample preparation and extraction will be discussed briefly. Detailed explanations can be found in the literature [2, 9, 25, 44 – 48, 55 – 63, 65 - 67].

3.2 SAMPLE PREPARATION

Fire debris involves a wide variety of different matrices and the effect of these on the retention/release characteristics of accelerants and their potential for producing pyrolysates (artefact formation from pyrolysis) must also be considered. The major objective of sample preparation methods is to recover volatiles from the debris sample for subsequent introduction into an analytical instrument.

A wide variety of sample preparation methods have been introduced since about 1960 [2, 42] when sophisticated instrumental characterization methods, such as gas chromatography and various forms of spectroscopy became routinely available. Classical procedures such as distillation and solvent extraction were primarily used in the early years. More recent methods focus around the principles of heated headspace enrichment. These methods are based on adsorbents such as porous polymers and especially carbon. Two variations, the so-called dynamic (or purge-and-trap) and static (carbon strip) methods evolved. The dynamic version, the older of the two techniques, was originally adapted from environmental monitoring applications. The mechanics of each method are discussed accordingly.

3.2.1 Distillation

Distillation, including vacuum and steam distillation, was one of the first procedures to be used to extract volatiles. Distillation allows the physical isolation of accelerants, provided that a sufficient quantity is available in the sample. If the sample contains both hydrophilic and hydrophobic components, a two-layer distillate develops. Typical steam distillation using water produces two visible layers, which can be recovered individually and analysed separately. Ethylene glycol can be used instead of water in the recovery of substances with low vapour pressures. Vacuum distillation has been reported as satisfactory for petrol and paraffin, but long extraction times are required for diesel [2, 25, 41, 43, 44, 45].

Distillation procedures are effective for the recovery of polar, water-soluble substances. They are labour and time-intensive and may generate a background level of materials which could be taken as a false positive or which could interfere with the basic pattern classification. With the introduction of modern analytical techniques that only require quantities in the sub-nanogram and nanogram range, the need for physical isolation of accelerants is no longer a primary concern [2, 25, 41, 43, 45].

3.2.2 Solvent Extraction

Solvent Extraction involves soaking and rinsing or longer refluxing with a Soxhlet system. Petroleum based fuels and other non-polar liquids are highly soluble in non-polar solvents such as hexane, methylene chloride and carbon disulphide, but not in water. In the soaking method the volume of solvent must be concentrated before injection. The process is time-consuming and the concentration steps may cause loss of part of the sample. Favourable distribution coefficients ensure high enrichment factors but it also causes serious problems, especially with samples that contain synthetic polymers and other materials such as waxes which lead to significant matrix interferences, both volatile and non-volatile, which are extracted together with the accelerant, leading to unnecessary complications in chromatography. Obviously, extraction methods are not suited to the recovery of class 1-type accelerants (refer to Table 2.2).

In spite of these limitations, liquid extraction is widely used. It is unsurpassed in the recovery of high-boiling distillates. It is an inherently simple technique and requires only inexpensive glassware that is readily available [2, 25, 41, 43, 45, 46].

3.2.3 Direct Headspace

Direct Headspace is based on the equilibrium of volatiles between the solid (fire debris matrix) and the gas phase. It is a static method and no enrichment takes place with respect to the volatiles. An aliquot of the air above the sample (at either ambient or slightly elevated temperature) is simply withdrawn and introduced directly into the inlet of a gas chromatograph. Gas-tight syringes are commonly used. The composition of the headspace is a function of the vapour pressure exerted by the individual substances. The higher the molecular mass of components of the accelerant, the lower their vapour pressure will be and the less likely that these components will be at sufficient concentration to yield a response in the gas chromatograph. Condensation of the volatiles in the syringe is

also a potential problem, especially with high-boiling compounds, but it can be minimised by heating the syringe.

The major drawback of the direct heated headspace method is a general lack of sensitivity and pronounced discrimination toward low volatility components. Direct headspace analysis is most conveniently done with packed columns, but wide-bore capillary columns are a good compromise between sample size requirements, efficiency and ease of operation. It is a “clean” method, fast and simple and particularly effective for polar and highly volatile components. When sufficient accelerant is present, headspace analysis will frequently yield reproducible and meaningful results, although care must be exercised in interpretation of results because of the presence of pyrolysis products [2, 25, 41, 43, 45, 47].

3.2.4 Dynamic Headspace

Dynamic Headspace, also known as adsorbent tube, purge-and-trap and adsorption/elution, are procedures in which volatiles are continuously removed by an adsorbent from a flowing gas stream. The adsorbate is recovered, either by extraction with an appropriate solvent or by thermal desorption. Dynamic headspace sampling amounts to a continuous gas phase extraction process. Vapour is forced over or through the adsorbent and the sample is gradually depleted of the analyte, thereby stripping the volatiles from the matrix. Depending on the rate of removal, a repeat analysis may not be possible. Three principles for removal of the solute from a flowing headspace stream are cryogenic procedures (freeze-out methods), dissolution of organic vapours in a non-volatile organic matrix/stationary phase focussing in gas chromatography and adsorption onto the surface of an organic or inorganic adsorbent (conventional trapping).

Several adsorbents have been used. Most of these are either carbonaceous (charcoal) or based on synthetic polymeric substances. Charcoal is an excellent adsorbent. It has a high capacity, but bonds materials strongly. Other materials such as

Poropak Q, Tenax-GC and the Amberlite XAD resins are also suitable. Alumina and silica do not adsorb appreciable amounts of hydrocarbons [2, 25, 41, 43, 45].

3.2.5 Static Headspace

The major disadvantages of direct heated headspace (lack of sensitivity and discrimination of high molecular mass components) can be lessened with the use of an enrichment technique designed selectively to remove and trap volatiles from the headspace above a sample. The major difference between direct heated headspace and adsorption/elution is the removal of the diluting air. Static headspace exploits the high affinity of organic vapour for many adsorbents. The adsorbent is placed with the debris in a sealed, heated container for some time, usually overnight. The vapour pressure of the volatiles sets up a reversible equilibrium condition between the matrix and the adsorbent. Following adsorption, the adsorbent is removed and the volatiles are recovered by either solvent extraction or thermal elution [2, 25, 41, 43, 45, 48].

The search for better methods has lead to the adoption of concentration procedures that are comprehensive, robust and reliable. Adsorption can be done at the fire scene by drawing air through a charcoal tube or silicone rubber substrate at specific sites and the adsorbed materials are then brought to the laboratory for desorption and analysis, either with a suitable solvent or with a compatible thermal desorption technique. The classical procedures (distillation and solvent extraction), and the more recent methods which focus around the principles of heated headspace enrichment, provide relatively effective solute retention, but still require a solvent to recover the volatiles [42, 45, 102].

Passive sampling using a charcoal strip is a straightforward way of trapping volatiles. These charcoal badges have been developed for quantitative occupational exposure assessment under carefully specified sampling conditions. In this study, since the nature of the analysis is qualitative, a charcoal strip was simply placed inside an impermeable nylon evidence pouch containing the debris, sealed and

heated in an oven overnight [2, 49, 50] at 60°C and then extracted using either carbon disulphide or methylene chloride (Figure 3.1). Thermal desorption of the carbon strip is also possible, using high temperatures and suitable refocusing of the liberated volatiles before direct injection onto the column.

Solid phase micro-extraction (SPME) (Figure 3.1) has recently been introduced as another version of the static method. It differs from the conventional static method in the way the volatiles are collected and released. With SPME, the adsorbent is a thin polymer coated silica fibre, which can be extended and retracted into a syringe type needle. The major advantage of SPME over its alternatives is its simplicity. It avoids solvents altogether and can be very rapid - thermal desorption from the fibre is essentially instantaneous [42].



Figure 3.1: Examples of a Traceair® organic vapor monitor badge and solid phase-micro-extraction (SPME) holder and fibre.

It has been shown that SPME sensitivity can compare favourably to the carbon strip method [19, 42, 51]. Detection limits in the low parts per million range have been reported for some accelerants. One of the strengths of SPME based sample preparation, which is considered an equilibrium method, is that it can be applied to gas phase volatiles as well as to solutions. Accelerants can be directly recovered from water if necessary. The only serious drawback with the SPME method is that it can only be performed manually – there is

a sample size limit associated with automated SPME of solid fire debris, but then this potential drawback can be eliminated with the thermal desorption method [52, 53, 54]. Thermal desorption will develop as a routine analytical tool for arson debris analysis alongside SPME and static headspace methods.

The recovery of an ignitable liquid is strongly dependent on the properties of the analyte. Conditions that are suitable for diesel are inadequate for ethanol and vice versa. The successful outcome of an analytical procedure is critically dependant on the selection of an appropriate sample preparation method and the conditions under which the method is applied.

3.3 GAS CHROMATOGRAPHY AND SPECTROSCOPY

Modern instrumental methods for the analysis of residual accelerants are based either on the measurement of spectral properties or on chromatography.

Chromatography, in particular gas chromatography with capillary columns, is an effective method in dealing with complex mixtures at trace levels. Virtually hundreds of components can be resolved accurately and reproducibly in a very short time, typically in less than an hour [2].

A chromatogram is a representation of the distribution of components eluting from a column. Each substance produces a signal and the information that can be derived from a chromatographic peak is very limited. Spectroscopy on the other hand, is well suited for providing supporting data on molecular characteristics. Molecular structure and substance identification can often be directly deduced from spectral data. The presence or absence of specific functional groups can sometimes also be determined. Unfortunately, most spectroscopic methods are incapable of dealing with more than a single compound at a time [2].

Coupling different techniques harnesses the strengths of both chromatography and spectroscopy [2, 55]. Gas chromatography has been successfully interfaced with mass spectrometry, infrared

spectroscopy and elemental composition instrumentation, although the cost and complexity of these instruments is high and beyond the financial capability of some laboratories.

Gas chromatography (GC) coupled with Flame Ionisation Detection (FID) provides a representation of the distribution of hydrocarbon components eluting from the column and is the most widely used analysis technique for the investigation of fire debris and accelerants. There are numerous books and publications in the literature detailing gas chromatography techniques and applications [1, 2, 25, 43, 45, 51, 56]. The scope covered by gas chromatography appears to be rather limited for the analysis of unknown samples/ components. A gas chromatogram reveals only the presence of individual components. It only provides information on sample complexity, concentration, boiling point distribution, and other macroscopic properties. Unless additional information is available, little, if anything, is known about the identities of the substances. The situation changes if gas chromatography is applied to multi-component mixtures having relatively stable and predictable compound distribution. Samples that primarily consist of accelerant-type substances are more easily recognised than samples that contain only small quantities of accelerant but large amounts of interferences.

In addition to being a separation method, gas chromatography can then be used to identify components by using retention time repeatability and pattern recognition in arson debris analysis. The term pattern recognition may be used in arson analysis to describe the visual composition of chromatograms. Since data interpretation (pattern recognition) is usually carried out by visual inspection, human bias must be removed to the largest extent possible. Pattern recognition is an important aspect of data treatment and data reduction in gas chromatography [2, 57, 58, 59].

Potential interferences may be very large and also vary considerably, depending on the type of matrix from which they are derived. Compositional changes in accelerants resulting from exposure to heat also complicate chromatographic data. The low concentrations of the analytes and the high levels of interference from pyrolysis products in

many multi-component fire debris samples, lead to the use of a selective detector, namely the mass spectrometer (MS) that can selectively extract the target analytes. The switch to MS, instead of FID, eliminates most of the problems caused by pyrolysis products. Gas Chromatography - Mass Spectrometry (GC-MS) ion profiling is an effective technique whereby manipulation of the mass spectrometer software enables the identification of characteristic series of mass fragments indicative of hydrocarbon distillates [60, 61, 62].

3.4 GAS CHROMATOGRAPHY - MASS SPECTROMETRY

In the course of a fire, whether accelerated intentionally or originating from natural causes such as electrical malfunction, volatiles are produced from the thermal decomposition of the matrix. Wood, carpet, furnishings, and other materials often produce very complex patterns of volatiles [1, 2, 24, 62]. Depending on the circumstances, a fire debris extract may contain only natural matrix volatiles, or a mixture of accelerant and matrix volatiles. The relative contributions from these sources are often highly variable. Additional complications arise from changes in the composition of an accelerant that has been exposed to a fire. Depletion of the most volatile fraction is inevitable, leading to a weathered or evaporated sample. Referring to Table 2.2 (Ignitable Liquid Classification System) in Chapter 2, types "1" to "4" accelerants are made up exclusively of hydrocarbons, primarily alkanes and alkylated aromatics. Substances such as indanes, olefins, and styrenes are only present in trace quantities and are generally not useful as indicators. Some fuels may also contain traces of other substance classes, such as oxygenates, usually in the form of additives. Each accelerant type produces a chromatographically distinct pattern. The task of the analyst is thus to match the chromatographic profile of a sample to an accelerant.

Identifying an arson accelerant from the ashes of a suspicious fire has been accomplished by comparing the gas chromatograms obtained of the heated vapour extracts with those of known standards. In many real-life chemical applications, the unknown patterns often do not match any of the standard chromatograms of pure standards well enough to withstand the scrutiny of courtroom cross-examination [2, 63, 64]. Detailed discussion on the

fundamentals of mass spectrometry and mass spectral interpretation can be found in the literature [2, 68 - 78].

Gas chromatography - mass spectrometry provides universal and specific information on individual components in the debris sample, although many GC peaks remain as unresolved mixtures of two, and often more, very similar hydrocarbon components in nearly all petroleum-based accelerants. Today, mass spectrometry is perhaps the foremost tool in the identification of unknown compounds [2]. It provides information on the identity of every component in the sample by taking advantage of the common fragmentation pathways for individual substance classes, which are truly unique of a particular chemical substance, much like a fingerprint. Identifying mass spectral fragmentation patterns and recognising the molecular mass of those ions that are most characteristic for the hydrocarbons found in typical accelerants can be time consuming and does not make it easier than to just compare the chromatogram with known standards. A more effective technique, namely mass chromatography (selected ion profiling or target compound analysis) helps alleviate these problems [57, 60 - 67].

Although the usefulness of GC-MS for fire debris analysis has long been recognised, its widespread adoption by the forensic community has not been swift. This is partly due to the complexity and costs associated with GC-MS, but also with the difficulty of displaying and interpreting the resulting data. Most laboratories have adapted to the mass chromatographic approach to GC-MS data interpretation [65]. This approach is based on the realization that the numerous compounds in a petroleum liquid can be grouped into only a few classes (Table 2.2 - Ignitable Liquid Classification System) and that each of these classes can be characterised by a limited number of ions in the mass spectra. The basic principle of mass chromatography was laid out by Smith in 1983 [63], who realised that the identification of individual hydrocarbons in recovered petroleum liquids was difficult and not especially helpful, but that the overall chromatographic pattern of each group was highly characteristic. For screening accelerant residues by mass chromatography, representative diagnostic ions specific for petroleum-based accelerants are selected. Some ions correspond to

individually characteristic molecular ions (aromatic compounds), while others reflect characteristic fragment ions (aliphatics, alicyclics and alkylbenzenes) - Table 3.1.

Compared to alternative approaches, the overwhelming advantage of mass chromatography is that it preserves the complex patterns of the initial liquid and it does not require calibration for individual compounds or even the specific identification of the peaks employed. This is important since petroleum liquids contain hundreds of components and calibration for more than a small fraction of these is not practical.

Table 3.1: Representative Ions Normally Present in Mass Spectra of Common Accelerants

Compound	m/z
Saturated aliphatics (straight chain & branched)	57,71,85,99
Alicyclics and olefinics	55,69,83,97
C1 to C4-alkylbenzenes	91,105,119
Benzene and C1 to C3-alkylbenzenes	78,92,106,120
C4-alkylbenzenes	119,134
C5 and C6-alkylbenzenes	148,162
Alkyl naphthalenes	128,142,156,170
Alkylstyrenes and dihydroindenes	104,118,132,146
Alkylanthracenes	178,192,206
Alkylbiphenyls and acenaphthenes	154,168,182,196
Monoterpenes (C ₁₀ H ₁₆)	93,136

Altered data taken from R.Martin Smith [60, 63].

Petroleum liquids, especially those formulated for the automotive industry, turpentine and other common household solvents, frequently used as accelerants, are easily identified by GC-MS. Most household solvents have several main ingredients that can be identified and compared to the product label. Turpentine contains terpene compounds and lacquer thinners (painting solvents) often use toluene, xylenes and ketones in large percentages.

Automotive products have a wide range of solvent composition; gas line anti-freeze contains methanol. Xylenes account for the bulk of

many carburettor cleaners and octane boosters are composed of additives like methylcyclopentadienylmanganese tricarbonyl (MMT). Heated headspace of vapours extracted from debris and injected onto a column designed for volatiles is the best way to screen some of these products. The analyst must be careful not to rely solely on a headspace screening from debris samples suspected of containing many of the above products. The early eluting compounds are the first to evaporate in a fire, so alternative analytical procedures are necessary to detect other less volatile components in the mixture. With such a wide range of components in the various products, the analyst can be selective in choosing those compounds most easily detected by existing GC-MS system parameters and column arrangements [61].

In the course of this study, a GC-MS accelerant library was established. It is important for the analyst to become familiar with the mass chromatographic profiles for the more commonly used accelerants. Figures 3.2 to 3.5 illustrate typical, but not exhaustive, total ion chromatograms and mass chromatograms (selected ion profiles) for some of these accelerants, and similar accelerant types found in South Africa. Only the profiles for the more specific diagnostic ions are reflected. Figure 3.2 illustrates the total ion chromatograms obtained without any selected ion profiling. This is similar to the chromatogram that would be obtained from a GC-FID. Figure 3.3 illustrates the straight chain aliphatic hydrocarbon compounds, where selected ion profiling has been used to profile ion masses 57, 71 and 85. Figure 3.4 illustrates the C₂, C₃ and C₄-alkylbenzene (aromatic) hydrocarbon compounds ($m/z = 91, 105$ and 134) and figure 3.5 illustrates naphthalene and the C₁, C₂ and C₃-alkylnaphthalene compounds.

Tables 3.2.1 to 3.2.4 illustrate typical mass spectral fragments for the aromatic and polycyclic aromatic hydrocarbons. These tables illustrate just how vast and complex petroleum based accelerants can be. The mass spectrometer provides information on the identity of every component in the sample. It would be extremely time consuming to search and identify each individual component found in typical accelerants. This approach would not simplify the analysis and therefore selected ion profiling is used, which detects the mass of

those ions that are most characteristic for the hydrocarbons found in ignitable liquid accelerants.

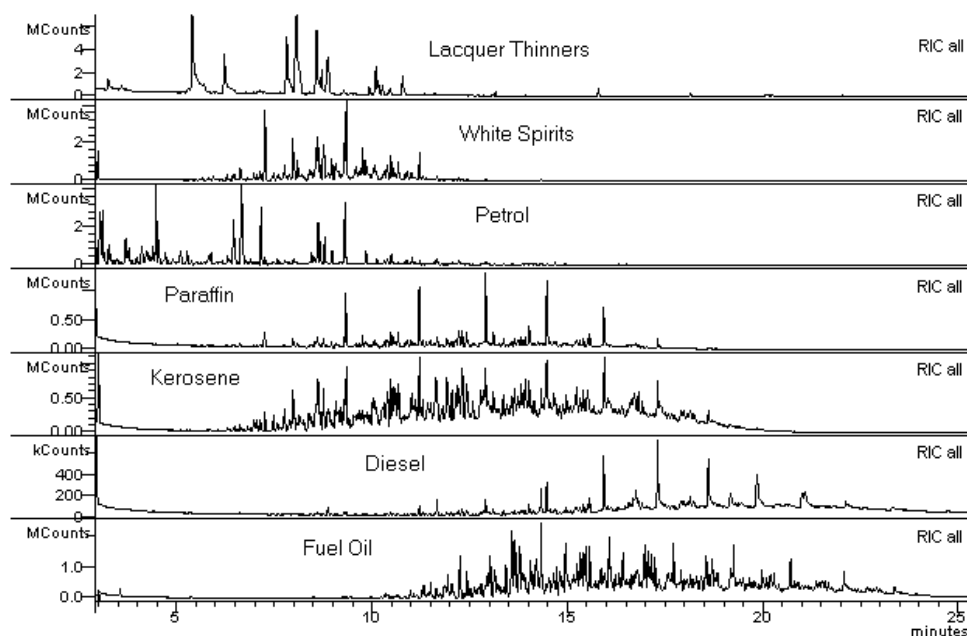


Figure 3.2: Total ion chromatograms for some of the more common ignitable liquid accelerants.

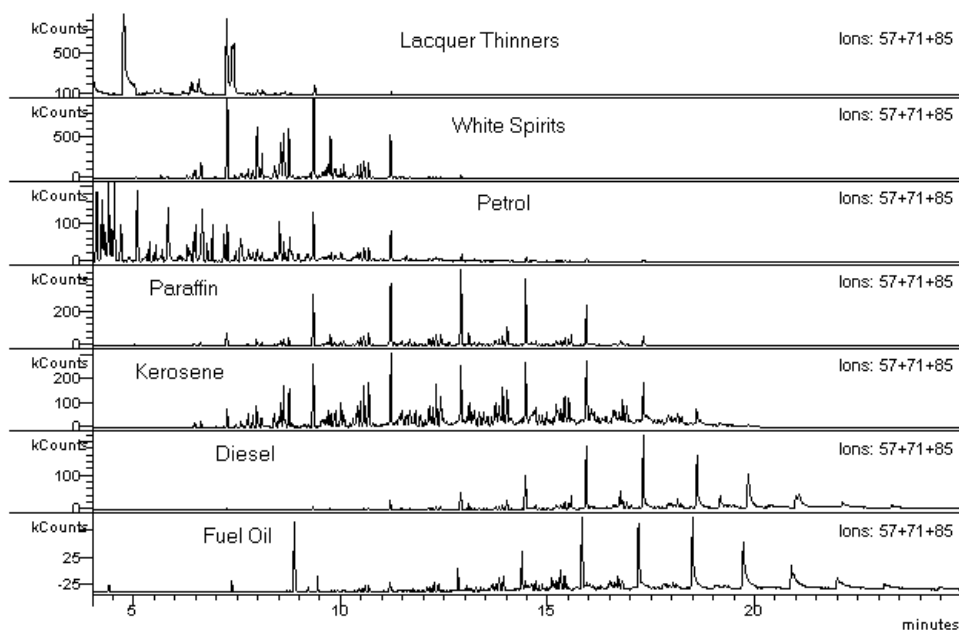


Figure 3.3: Selected ion profiles (mass chromatograms) for the aliphatic hydrocarbon compounds.

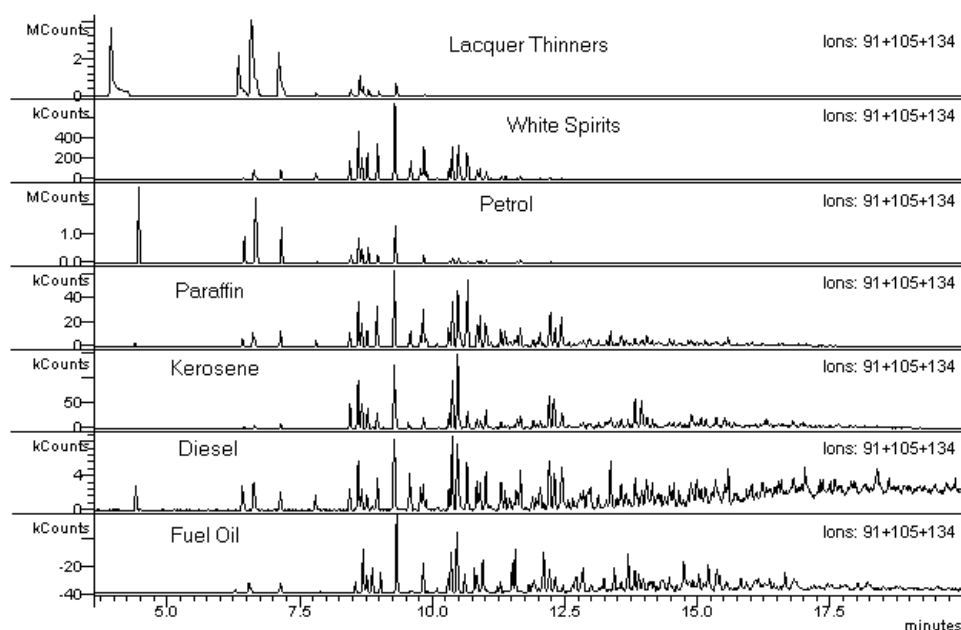


Figure 3.4: Selected ion profiles (mass chromatograms) for the C1 to C4-alkylbenzene compounds.

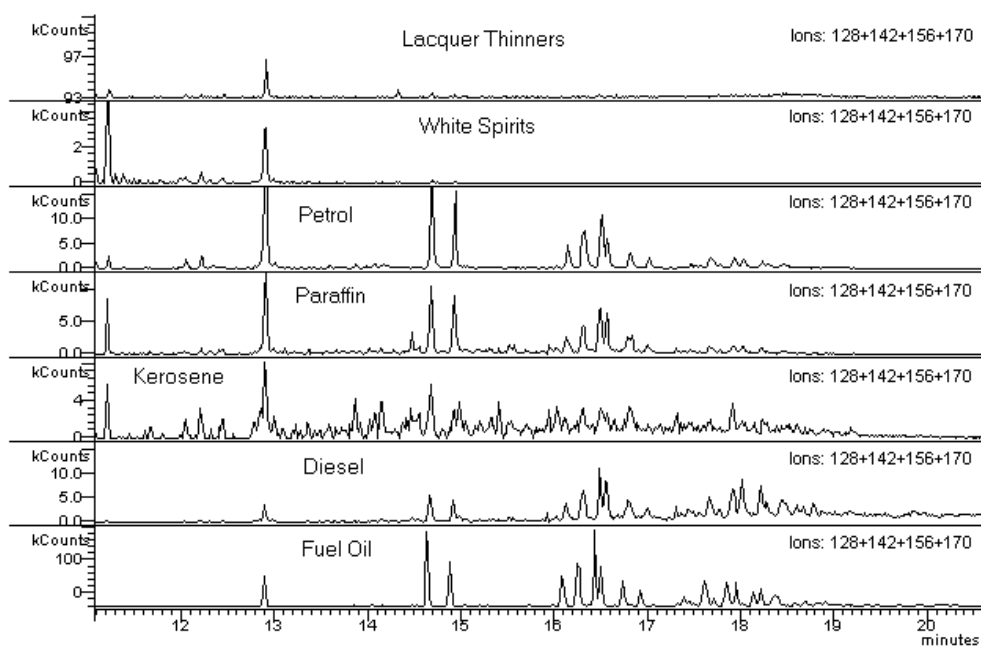


Figure 3.5: Selected ion profiles (mass chromatograms) for the C1 to C3-alkylnaphthalene compounds.

Table 3.2.1: Typical Mass Fragments for Benzene, C2 and C3-Alkylbenzene Aromatic Compounds (*own work*)

Compound	Ion (m^+)	Mass Fragment	Loss
Benzene	78*	77 (C_6H_5)	1 (H)
		51 (C_4H_3)	27 (C_2H_3)
		50 (C_4H_2)	28 (C_2H_4)
		39 (C_3H_3)	39 (C_3H_3)
Toluene	92	91 (C_7H_7)*	1 (H)
		65 (C_5H_5)	27 (C_2H_3)
		39 (C_3H_3)	53 (C_4H_5)
Ethylbenzene	106	91 (C_7H_7)*	15 (CH_3)
		65 (C_5H_5)	41 (C_3H_5)
		51 (C_4H_3)	55 (C_4H_7)
p-Xylene	106	105 (C_8H_9)	1 (H)
		91 (C_7H_7)*	15 (CH_3)
		77 (C_6H_5)	29 (C_2H_5)
		51 (C_4H_3)	55 (C_4H_7)
Isopropylbenzene	120	105 (C_8H_9)*	15 (CH_3)
		79 (C_6H_7)	41 (C_3H_5)
		77 (C_6H_5)	43 (C_3H_7)
		51 (C_4H_3)	69 (C_5H_9)
Propylbenzene	120	92 (C_7H_8)	28 (C_2H_4)
		91 (C_7H_7)*	29 (C_2H_5)
		65 (C_5H_5)	55 (C_4H_7)
		39 (C_3H_3)	81 (C_6H_9)
p-Ethyltoluene	120	105 (C_8H_9)	15 (CH_3)
		91 (C_7H_7)	29 (C_2H_5)
		77 (C_6H_5)	43 (C_3H_7)
		65 (C_5H_5)	55 (C_4H_7)
1,2,4-Trimethylbenzene	120	119 (C_9H_{11})	1 (H)
		105 (C_8H_9)*	15 (CH_3)
		91 (C_7H_7)	29 (C_2H_5)
		77 (C_6H_5)	43 (C_3H_7)

*: Indicates the base peak

Table 3.2.2: Typical Mass Fragments for C4 and C5-Alkylbenzene Aromatic Compounds (*own work*)

Compound	Ion (m^+)	Mass Fragment	Loss
Butylbenzene	134	91 (C_7H_7)*	43 (C_3H_7)
		92 (C_7H_8)	42 (C_3H_6)
		105 (C_8H_9)	29 (C_2H_5)
		65 (C_5H_5)	69 (C_5H_9)
1-Methyl-2-propylbenzene	134	105 (C_8H_9)*	29 (C_2H_5)
		106 (C_8H_{10})	28 (C_2H_4)
		77 (C_6H_5)	57 (C_4H_9)
		91 (C_7H_7)	43 (C_3H_7)
		51 (C_4H_3)	83 (C_6H_{11})
Diethylbenzene	134	105 (C_8H_9)*	29 (C_2H_5)
		119 (C_9H_{11})	15 (CH_3)
		91 (C_7H_7)	43 (C_3H_7)
		77 (C_6H_5)	57 (C_4H_9)
1,2,4,5-Tetramethylbenzene	134	119 (C_9H_{11})*	15 (CH_3)
		91 (C_7H_7)	43 (C_3H_7)
		39 (C_3H_3)	95 (C_7H_{11})
		77 (C_6H_5)	57 (C_4H_9)
		65 (C_5H_5)	69 (C_5H_9)
Pentylbenzene	148	91 (C_7H_7)*	57 (C_4H_9)
		92 (C_7H_8)	56 (C_4H_8)
		105 (C_8H_9)	43 (C_3H_7)
		65 (C_5H_5)	83 (C_6H_{11})
(1-EthylPropyl)-benzene	148	91 (C_7H_7)*	57 (C_4H_9)
		119 (C_9H_{11})	15 (CH_3)
		77 (C_6H_5)	57 (C_4H_9)
		65 (C_5H_5)	83 (C_6H_{11})
(1,1-Dimethyl-propyl)benzene	148	119 (C_9H_{11})*	15 (CH_3)
		91 (C_7H_7)	43 (C_3H_7)
		77 (C_6H_5)	57 (C_4H_9)
		120 (C_9H_{12}/C_{10})	28 (C_2H_4)

*: Indicates the base peak

Table 3.2.3: Typical Mass Fragments for C5 and C6-Alkylbenzene Aromatic Compounds (*own work*)

Compound	Ion (m^+)	Mass Fragment	Loss
1,1-Dimethyl-propylbenzene	148	119 (C_9H_{11})*	29 (C_2H_5)
		91 (C_7H_7)	57 (C_4H_9)
		77 (C_6H_5)	71 (C_5H_{11})
		120 (C_9H_{12}/C_{10})	28 (C_2H_4)
1,3-Dimethyl-5-(1-methylethyl)-benzene	148	133 ($C_{11}H/C_{10}H_{13}$)*	15 (CH_3)
		91 (C_7H_7)	57 (C_4H_9)
		105 (C_8H_9)	43 (C_3H_7)
		134 ($C_{11}H_2/C_{10}H_{14}$)	14 (CH_2)
1-Ethyl-4-(1-methylethyl)-benzene	148	133 ($C_{11}H/C_{10}H_{13}$)*	15 (CH_3)
		105 (C_8H_9)	43 (C_3H_7)
		91 (C_7H_7)	57 (C_4H_9)
		77 (C_6H_5)	71 (C_5H_{11})
1-Ethyl-2,4,5-trimethylbenzene	148	133 ($C_{11}H/C_{10}H_{13}$)*	15 (CH_3)
		119 (C_9H_{11})	29 (C_2H_5)
		105 (C_8H_9)	43 (C_3H_7)
		91 (C_7H_7)	57 (C_4H_9)
1-Methyl-4-(2-methylpropyl)-benzene	148	105 (C_8H_9)*	43 (C_3H_7)
		106 (C_8H_{10})	42 (C_3H_6)
		77 (C_6H_5)	71 (C_5H_{11})
		91 (C_7H_7)	57 (C_4H_9)
Hexylbenzene	162	91 (C_7H_7)	71 (C_5H_{11})
		92 (C_7H_8)	70 (C_5H_{10})
		105 (C_8H_9)	57 (C_4H_9)
		65 (C_5H_5)	97 (C_7H_{13}/C_8H)
1-Ethyl-1-Methylpropyl-benzene	162	133 ($C_{10}H_{13}/C_{11}H$)*	29 (C_2H_5)
		55 (C_4H_7)	107 (C_8H_{11})
		105 (C_8H_9)	57 (C_4H_9)
		91 (C_7H_7)	71 (C_5H_{11})
1- <i>tert</i> -Butyl-3-ethylbenzene	162	147 ($C_{11}H_{15}/C_{12}H_3$)*	15 (CH_3)
		119 (C_9H_{11})	43 (C_3H_7)
		91 (C_7H_7)	71 (C_5H_{11})
		148 ($C_{11}H_{16}/C_{12}H_4$)	14 (CH_2)

*: Indicates the base peak

Table 3.2.4: Typical Mass Fragments for Polycyclic Aromatic Compounds *(own work)*

Compound	Ion (m^+)	Mass Fragment	Loss
Naphthalene	128*	127 ($C_{10}H_7$)	1 (H)
		126 ($C_{10}H_6$)	2 (H_2)
		102 (C_8H_6)	26 (C_2H_2)
		77 (C_6H_5)	51 (C_4H_3)
		63 (C_5H_3)	65 (C_5H_5)
2-Methyl-naphthalene	142*	141 ($C_{11}H_9$)	1 (H)
		115 (C_9H_7)	27 (C_2H_3)
		102 (C_8H_6)	40 (C_3H_4)
		63 (C_5H_3)	79 (C_6H_7)
2-Ethyl-naphthalene	156	141 ($C_{11}H_9$)*	15 (CH_3)
		115 (C_9H_7)	41 (C_3H_5)
		128 ($C_{10}H_8$)	28 (C_2H_4)
		142 ($C_{11}H_{10}$)	14 (CH_2)
2,3-Dimethyl-naphthalene	156*	141 ($C_{11}H_9$)	15 (CH_3)
		155 ($C_{12}H_{11}$)	1 (H)
		115 (C_9H_7)	41 (C_3H_5)
		128 ($C_{10}H_8$)	28 (C_2H_4)
		77 (C_6H_5)	79 (C_6H_7)
1-Propyl-naphthalene	170	141 ($C_{11}H_9$)	29 (C_2H_5)
		115 (C_9H_7)	55 (C_4H_7)
		128 ($C_{10}H_8$)	42 (C_3H_6)
		142 ($C_{11}H_{10}$)	28 (C_2H_4)
2,3,6-Trimethyl-naphthalene	170	155 ($C_{12}H_{11}$)	15 (CH_3)
		141 ($C_{11}H_9$)	29 (C_2H_5)
		128 ($C_{10}H_8$)	42 (C_3H_6)
		115 (C_9H_7)	55 (C_4H_7)

*: Indicates the base peak

3.5 DIFFERENCES BETWEEN CONVENTIONAL GAS CHROMATOGRAPHY AND GC-MS

The purpose of a gas chromatograph (GC) is to physically resolve the volatile components in a sample. The separated components are

sensed by a detector, usually flame ionisation detection (FID), although there are many different types of detectors available. A detector can be categorized as being universal (FID) in response or specific.

A mass spectrometer (MS) can provide both universal and specific information. The sample extract, which has undergone a specific sample preparation step, is introduced into the GC injector port via a syringe. The GC separates the components and the detector is now a MS. Accelerants can consist of hundreds of substances or only a single component. All petroleum-based distillates are multi-component mixtures. The number of substances detected in a distillate such as petrol (gasoline) depends on the level of detection necessary for the problem at hand. There are perhaps a dozen components that are present at one percent concentration level or above. If one lowers the detection to a tenth or a hundredth of a percent, the number of components detected increases dramatically. Fortunately it is relatively easy to determine one part per million amounts using gas chromatography. Chromatograms can become very complex at these lower detection levels. The problem is that the matrix, *i.e.*, carpet, padding, wood, *etc.*, may generate copious amounts of volatiles that can obscure the accelerant pattern at these low levels, thus complicating the analysis. Because different accelerant types consist of distinctive compounds, different patterns are generated which are characteristic of the accelerant hydrocarbons [2, 57, 64].

A peak in a fire debris chromatogram can consist of an accelerant type hydrocarbon. It can also be derived from the thermal decomposition of the matrix. The forensic analyst uses cognitive abilities to visually establish the potential presence of an accelerant. Different people have different perceptions. Another person may not interpret a pattern that may hold all the necessary diagnostic peaks in the same way. There is an element of uncertainty in the pattern recognition process. When faced with the uncertainty of whether one peak is a constituent of an accelerant or results from the background, the mass spectrometer can help by generating individual mass spectral fragmentation patterns which are truly unique for a particular chemical substance [45, 55, 57, 58, 66].

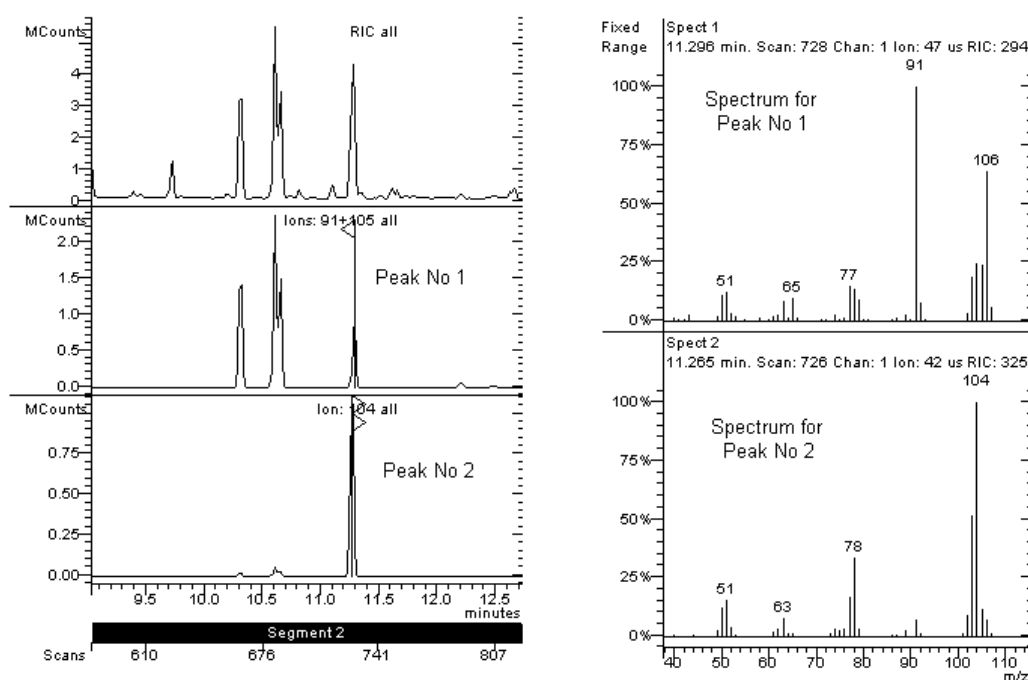


Figure 3.6: Total ion chromatogram (upper trace) and selected ion profiles for *o*-Xylene ($m/z = 91 + 105$ – middle trace) and styrene ($m/z = 104$ – lower trace). The corresponding spectra are also given for peaks no. 1 and no. 2 to differentiate between *o*-xylene and styrene.

Figure 3.6 is an example of ethylbenzene and the xylenes from a debris sample. The upper trace shows the total chromatogram, the middle trace the extracted ion profiles for ethylbenzene and the xylenes and the lower trace the extracted ion profile for styrene. The only indication that the typical isomer ratio pattern of ethylbenzene (RT = 10,3 min) : *m,p*-xylene (RT = 10,6 & 10,7 min) : *o*-xylene (RT = 11,2 min) does not conform to the expected ratio is the presence of a more significant *o*-xylene peak (RT = 11,2 min). The only way in which to distinguish whether the *o*-xylene peak is pure or whether an interfering peak is co-eluting with the *o*-xylene peak is through ion profiling whereby the $m/z = 91$ and 105 are extracted (Peak No. 1 and spectrum for Peak No. 1 at 11.296 min) and compared with the co-eluting styrene peak (Peak No. 2 and Spectrum for Peak No. 2 at 11.265 min) with $m/z = 104$. The styrene peak causes a fronting shoulder to the *o*-xylene peak. This would typically not have been

considered were it not for the resolving power and selectivity of the mass spectrometer.

In a mass spectrometer, energetic electrons impact on a neutral molecule and cause it to fragment. The analyst looks at the fragments and pieces together the original structure. The composition of petroleum-based accelerants is well known. Paraffins (kerosenes) consist almost exclusively of alkane type substances whereas petrol (gasoline) contains a more significant amount of alkylbenzenes. Unevaporated petrol contains a high proportion of both alkanes and alkylbenzenes. Highly evaporated petrol has lost most of its alkane content. It is made up almost entirely of alkylbenzenes and similar substances. Chromatographically this can clearly be seen in Figure 3.7.

Even though petrol and paraffin (kerosene) share many of the same components, the appearance of the chromatograms is very different (Figure 3.8). The ability to distinguish between different distillate groups is relatively straightforward when present in significant amounts, even partially evaporated, with gas chromatography and even more so with the resolving power of mass spectrometry. The analytical situation becomes more complicated when the level of accelerants approaches the detection limit of the instrument and matrix interferences become more significant than the accelerant traces.

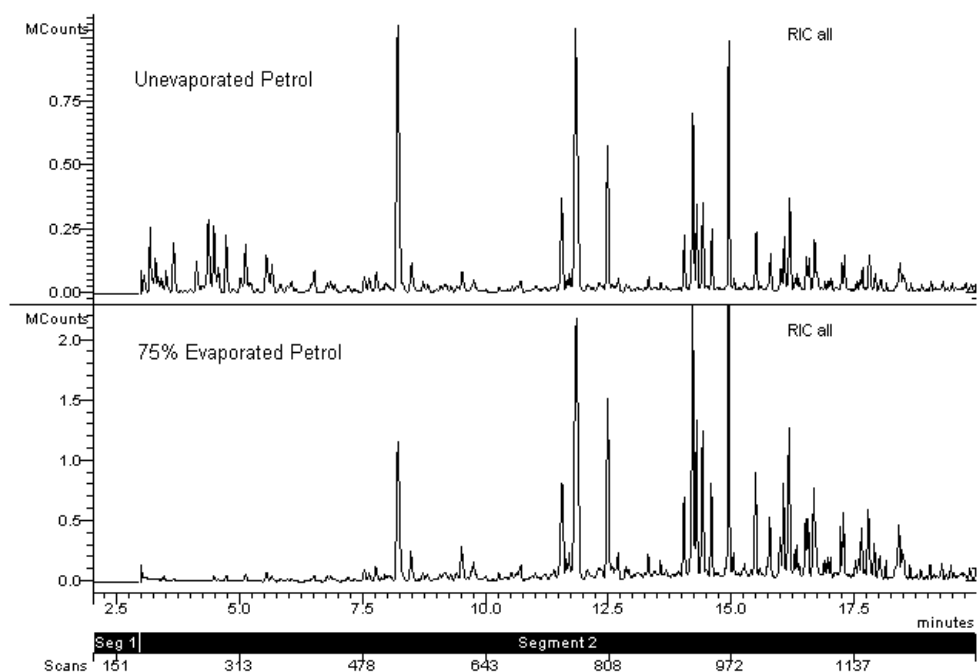


Figure 3.7: Total chromatographic ion profiles for unevaporated petrol and 75 percent evaporated petrol.

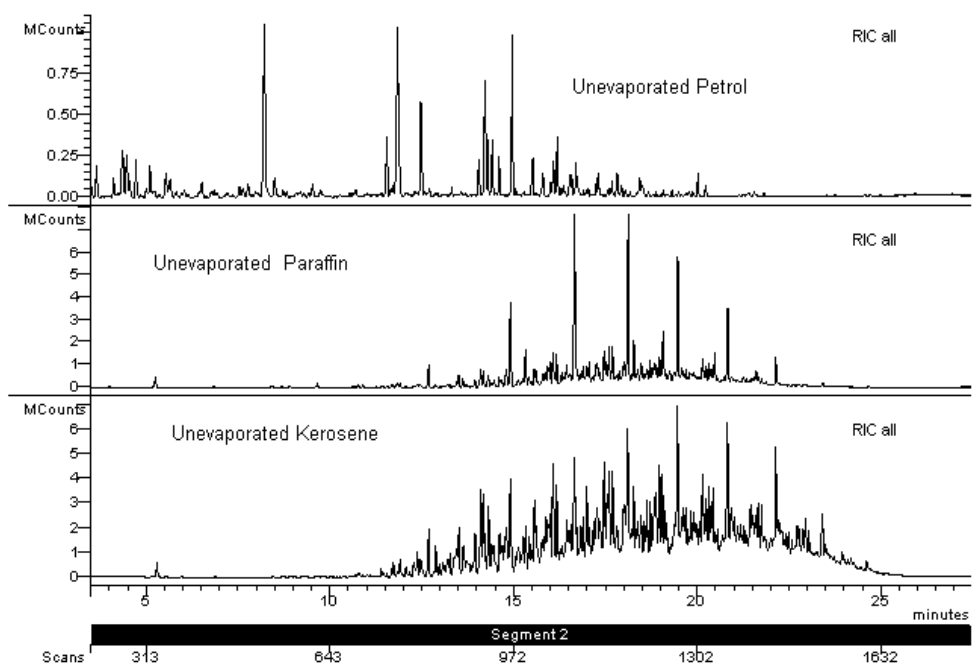


Figure 3.8: Total chromatographic ion profiles for unevaporated petrol, unevaporated paraffin and unevaporated kerosene.

3.6 HOW SPECIFIC IS THE MASS SPECTROMETER AS AN ACCELERANT DETECTOR IN THE PRESENCE OF MATRIX INTERFERENCES?

The specificity of a mass spectrometer can be defined as the degree to which the device responds to accelerant type compounds only. The question arises as to whether all accelerants are composed of substances that can be distinguished from the background? To find the answer it is necessary to compare mass spectra from accelerants to those produced from typical burnt matrices such as wood, carpet, plastics and whatever else may be found at a fire scene. Unfortunately, there is no such thing as a "representative background matrix". Combustion and pyrolysis are processes that generate a wide variety of components. The nature and quantity of the substances that make up a pyrolysate are very different for different matrices, thus the volatiles produced from vinyl tile, wood and carpet are not the same. The same matrix, *e.g.*, carpet, can produce different pyrolysates depending on the conditions of the fire [57, 79, 80 – 85, 100]. Most matrices produce a unique "volatiles" signature. Interference from background materials originate from actual liquid petroleum products that are present in the substrate material. These substrate materials pyrolyze to form interfering volatile compounds in the range of common ignitable liquids. Materials such as carpet and plastics that are manufactured from petroleum products can decompose and revert back to the small molecules from which they are made.

Carpet does generate a small number of alkylbenzene hydrocarbons but styrenes are also produced, often in large quantities [79, 86, 87, 101]. Figures 3.9 and 3.10 are examples of typical plastic and carpet backgrounds. The three carpets represent three different types of backing. The "Afghan" carpet consists of a nylon/styrene-butadiene-rubber/bitumen/hessisan-type backing; the green carpet consists of a viscose and polyurethane backing and the "Serengheti" carpet consists of a modacrylic viscose and acrylic-base backing. Looking at the selected ion profiles for the C2 and C3-alkylbenzenes, those aromatics can be seen, but it is also evident that styrene is abundant at the retention time of 12.49 minutes (o-xylene and styrene co-elute; styrene does not have strong $m/z = 91$ and 105 ions). It is

however obvious that the ratio of the peaks in the extracted ion chromatograms (selected ion profiles) for the carpet matrix and unevaporated petrol standard are very different. The patterns show very little similarity. By studying the mass spectra of the individual peaks, it becomes evident that these backgrounds do liberate aromatic volatiles. In other words, charred carpet and carpet backing produce some of the components that are diagnostic for accelerants like petrol.

Under most circumstances the production of artefact peaks from matrices such as carpet does not interfere with the interpretation of diagnostic aromatic hydrocarbons characteristic for accelerants. The potential for matrices to produce extraneous volatiles by pyrolysis is difficult to evaluate, even with the resolving power of mass spectrometry. Pyrolysis interference is always a complicating factor that makes analysis difficult. When the level of accelerant approaches the detection limit of the analytical technique, the pyrolysis product may easily overwhelm the accelerant signal [86]. Volatiles from pyrolysis can be tolerated if they are sufficiently different from those in accelerants. Problems arise when the distribution of pyrolysis volatiles shows a resemblance to the distribution of volatiles in accelerants [79, 81].

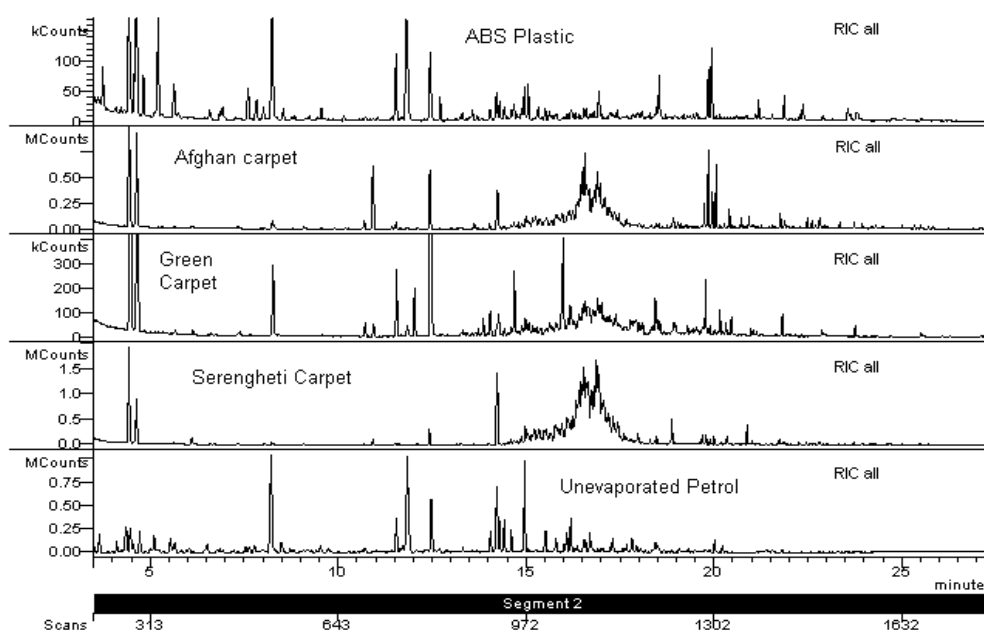


Figure 3.9: Comparison of the total chromatographic ion profiles for ABS plastic, carpet backgrounds and unevaporated petrol.

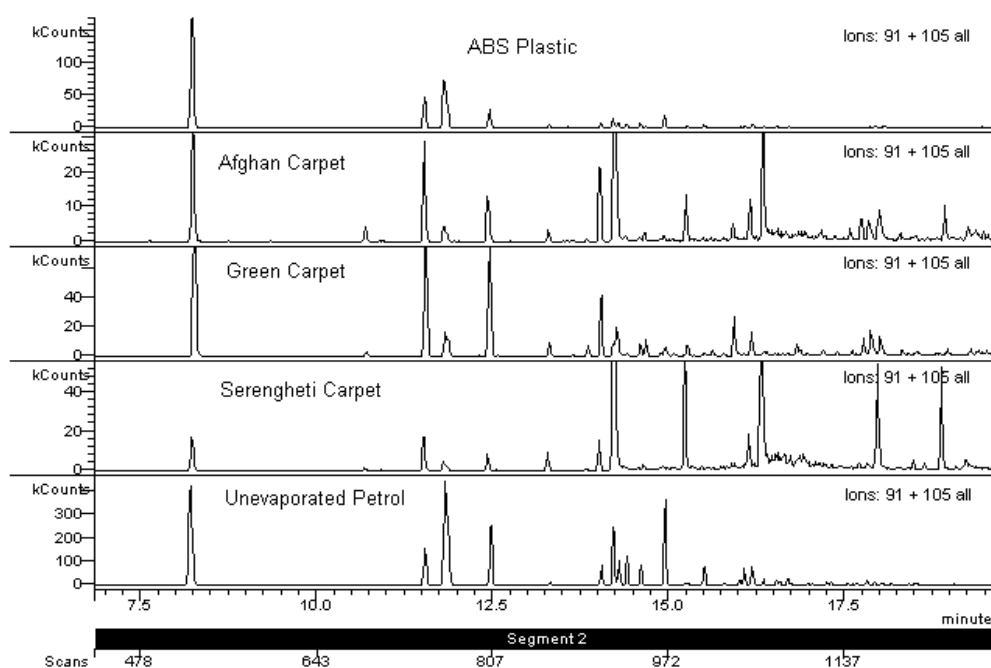


Figure 3.10: Comparison of the selected ion profiles for the C2 and C3-alkylbenzenes ($m/z = 91$ and 105) for ABS plastic, carpet backgrounds and unevaporated petrol.

Some synthetic polymers produce extremely complex patterns that directly compete with the analytes of interest. It is possible to overcome some of these problems by proper instrumental analysis techniques, such as cleanup procedures prior to instrumental analysis or by selective detection by mass spectrometry using the techniques of mass chromatography (selective ion profiling) [57, 81].

The limit of detection is another aspect that must be considered when dealing with matrix interferences. It depends on the variables of combustion time and collection delay of the debris sample. Knowledge of the relative limit of detection of different matrix background and surfaces could be valuable in the collection of proper evidence from fire scenes for subsequent accelerant detection and identification [88 - 90].

Since many arson analyses are "one-shot" injections because of extremely limited sample sizes, the generation of full mass spectra for mass chromatography gives it a distinct advantage over selected ion monitoring (SIM) [62, 63], which forces the selection of desired ions prior to the sample run, thus precluding the possibility of finding

unanticipated compounds in the sample or of more complete compound identification by spectral comparisons at a later time. But what if the GC-MS shows weak response towards accelerants and an uncertainty arises as to the origin of the traces?

Looking at a real-life example of arson debris demonstrates this type of dilemma. The debris sample was burnt paper and charcoal that was to be analysed for traces of accelerant. Figures 3.11 to 3.16 illustrate the aromatic, polycyclic aromatic and aliphatic hydrocarbon selected ion profiles that are typically examined for accelerant trace evidence.

The total ion chromatogram indicates that there is a possibility of class 2 and class 4 accelerant traces (Tables 2.2 and 3.1). Examining the profiles of the aliphatic hydrocarbon compounds more closely (Figure 3.16) indicates a possibility that there may be paraffin in the sample. Comparison of the mass spectra for the straight chain aliphatic hydrocarbons indicates that the hydrocarbon profile is that of polyethylene and not paraffin (polyethylene forms recognisable alkane doublets when burnt plastic is present). Examining the C2 and C3-alkylbenzene aromatic compounds indicates that there is styrene present, as well as excessive ethylbenzene and o-xylene. The trimethylbenzenes are tentatively similar, but do not compare favourably. There is clear evidence of aromatic comparison around the C4-alkylbenzenes. There are comparable traces around the C5 and C6-alkylbenzenes, but the GC-MS response is very weak.

Examining naphthalene and the methylnaphthalenes clearly indicates a weak response. Conclusion: Possible traces of an evaporated petrol residue? Possible traces of an evaporated aromatic product? It cannot irrefutably be shown to compare with traces of evaporated petrol, although there are similarities within specific aromatic classes. It still cannot be reported as a credible result for court purposes that this sample is truly representative of an evaporated petrol residue without additional supporting evidence.

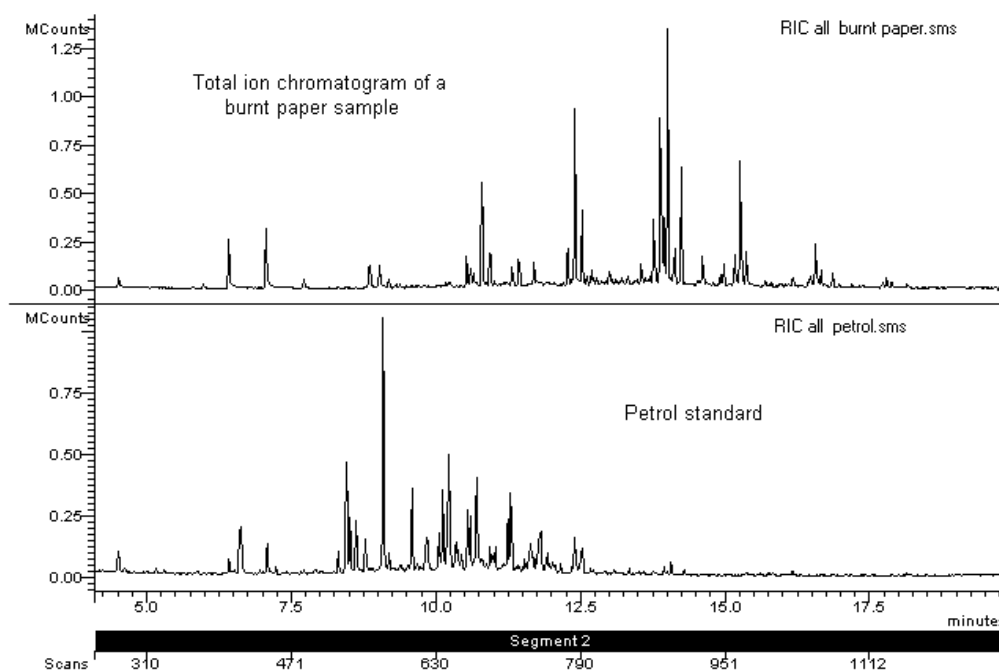


Figure 3.11: Total ion chromatograms for the burnt debris sample and a petrol standard.

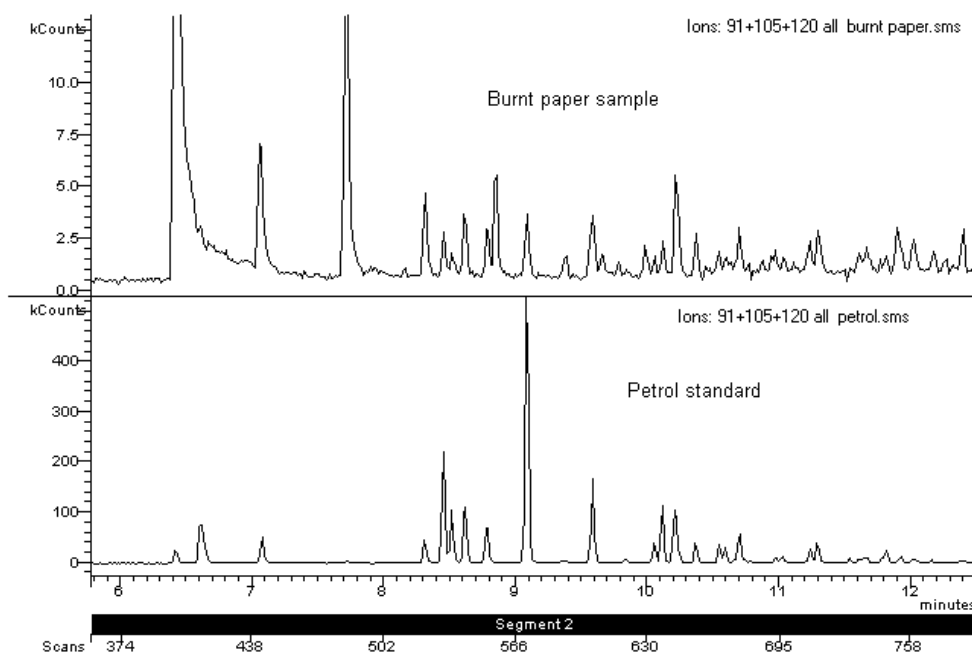


Figure 3.12: Selected ion profiles for the C2 and C3-alkylbenzene aromatic compounds for the burnt debris sample and a petrol standard.

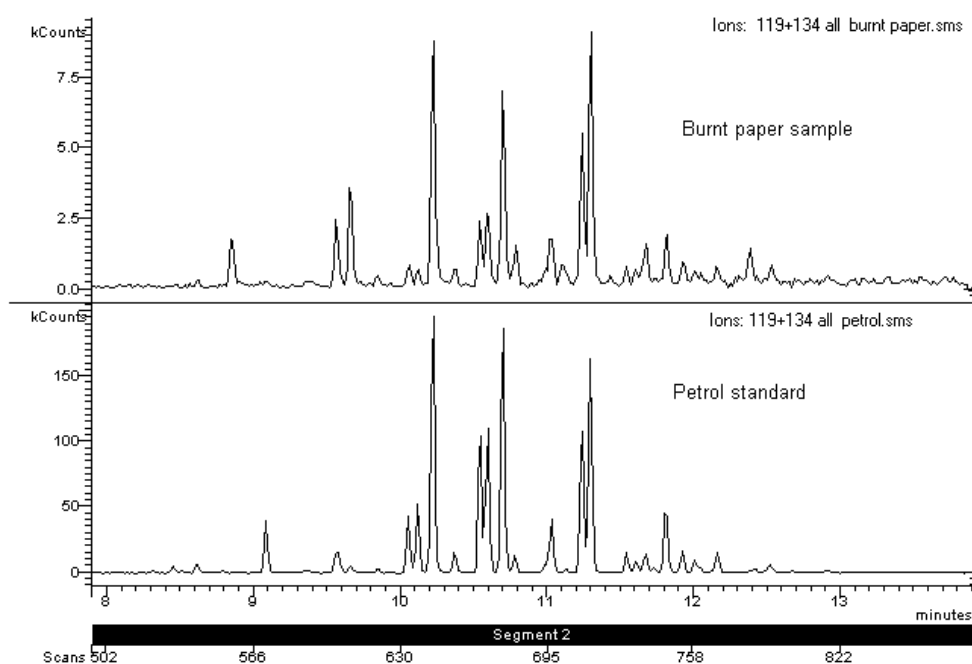


Figure 3.13: Selected ion profiles for the C4-alkylbenzene aromatic compounds for the burnt debris sample and a petrol standard.

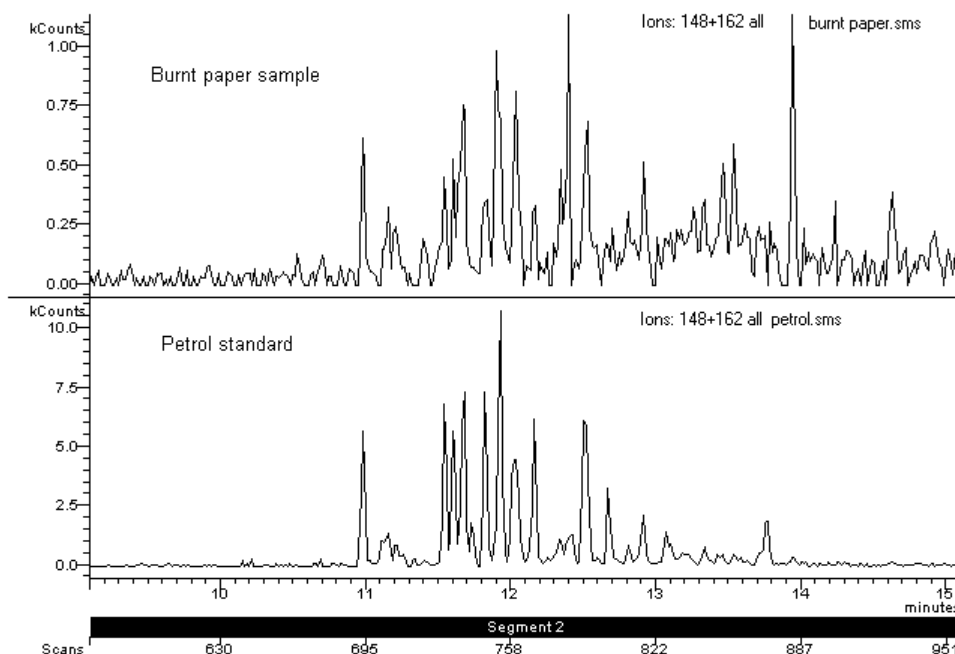


Figure 3.14: Selected ion profiles for the C5 and C6-alkylbenzene aromatic compounds for the burnt debris sample and a petrol standard.

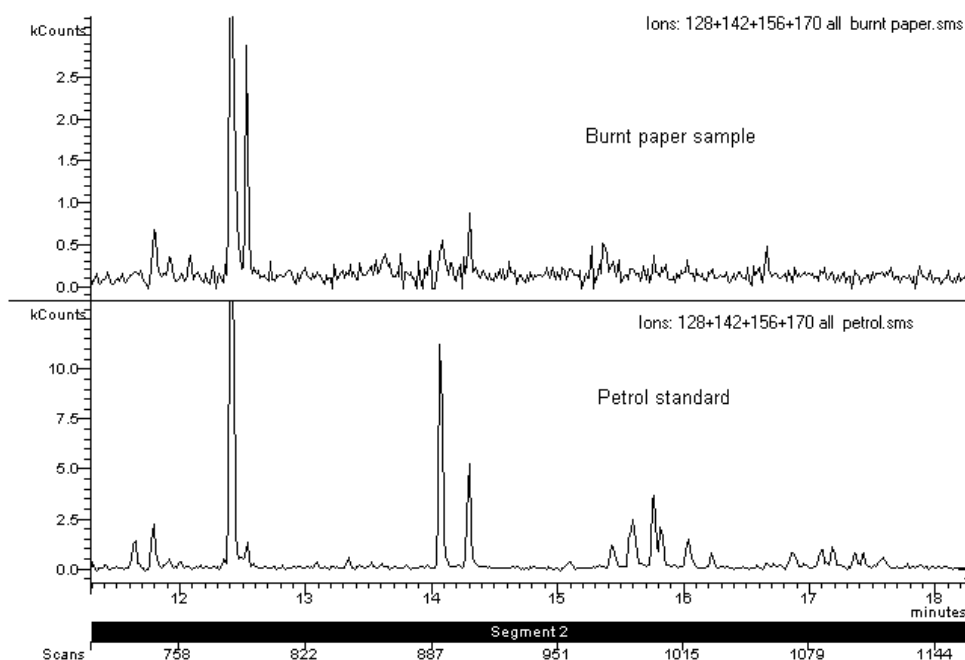


Figure 3.15: Selected ion profiles for naphthalene and the C1, C2 and C3-methylnaphthalene polycyclic aromatic compounds for the burnt debris sample and a petrol standard.

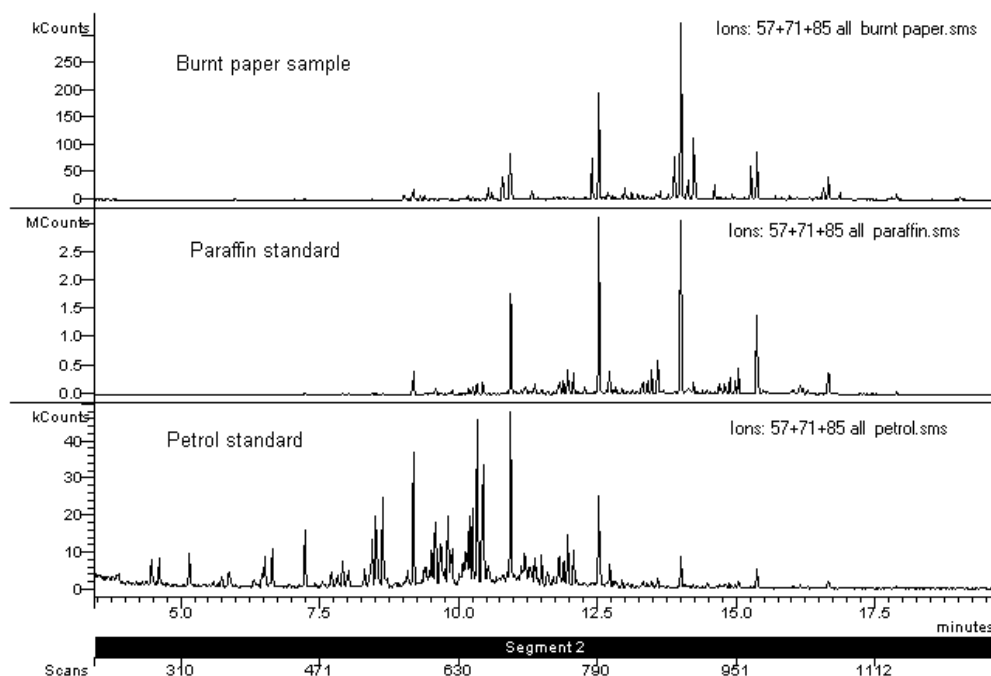


Figure 3.16: Selected ion profiles for the aliphatic hydrocarbon compounds for the burnt debris sample, a paraffin standard and a petrol standard.

A second confirmatory analysis is required. The use of GC-MS-MS (tandem mass spectrometry) on samples with a suspect response to GC-MS has been studied in detail and will be explained fully in the following chapters. Based on the analysis of pesticide residues in agricultural products by GC-MS-MS [91], the concept was adapted to the analysis of fire debris samples for the detection of ignitable liquid accelerant traces, specifically petrol, in the presence of complex matrix interferences [38, 92, 96, 103].

CHAPTER 4

TANDEM MASS SPECTROMETRY

4.1 WHAT IS TANDEM MASS SPECTROMETRY?

Gas Chromatography-Mass Spectrometry (GC-MS) is one of the most powerful analytical techniques for the characterization of mixtures of organic compounds. However, this technique is not without its limitations. Often, a target analyte cannot be quantified at a desired level because of matrix interferences, or an unknown compound cannot be identified due to a lack of conclusive fragmentation patterns. Even using the complimentary electron ionisation (EI) and chemical ionisation (CI) spectral data, the analyst's problems in these situations are often irresolvable.

The technique of isolating a single ion (precursor ion) from a mass spectral fragmentation and causing this isolated ion to undergo a collision induced dissociation (CID) in order to obtain the resulting mass spectrum (product ion spectrum) was first popularised using multiple quadrupole mass filters in tandem [68, 70 - 73]. This tandem mass spectrometry technique is called MS-MS because it can produce a secondary mass spectrum of an ion, resulting from a primary ionisation fragmentation event.

The MS-MS technique has been used with triple quadrupoles and multiple electrostatic/magnetic sector instruments as well as hybrid instruments using both sectors and quadrupoles [68, 93, 94]. Finnigan Corporation developed a novel means for using the quadrupole ion trap or Paul trap (named after its inventor Wolfgang Paul) as a mass spectrometer in the early 1980s. Since then, researchers have made many significant improvements in the ion

trap and today ion trap techniques use either the quadrupole ion trap or its relative, the ion cyclotron resonance (ICR) instrument [73].

4.2 QUADRUPOLE OPERATION

The basic principles of operation of the ion trap are best considered in relation to those of the more familiar quadrupole mass filter. The analyser for the quadrupole consists of an array of four rod-electrodes, and when connected to the power supplies these are arranged such that opposite pairs of electrodes are coupled together with radio frequency (rf) and direct current (dc) potentials applied between them. Ions emitted from a source positioned in line with the axis of the rod assembly pass into the analyser. Depending upon the combination of the mass-to-charge ratio, the amplitudes of the rf and dc potentials, the frequency of the drive potential, and the internal dimensions of the electrode array, the ions will either have "*stable*" trajectories and pass through the analyser to the detector, or "*unstable*" trajectories and collide with the electrodes. In this way, the device acts as a mass spectrometer, and a mass spectrum may be obtained by sweeping the dc and rf potentials such that the amplitudes remain at a constant ratio [68, 70, 71].

4.3 ION TRAP MASS SPECTROMETER OPERATION

Detailed theory of Ion Trap MS and MS-MS can be obtained in the literature [68, 70-73], but it is necessary to briefly discuss ion trap operation in order to fully understand MS-MS. Since this study made exclusive use of the Varian Saturn instrument, the theory discussed will largely describe the operation of this instrument [68].

The ion trap consists of three cylindrically symmetric electrodes, two end-cap electrodes and one ring electrode (Figures 4.1, 4.2 and 4.3). Each of these electrodes has accurately machined hyperbolic internal surfaces and, in normal mode of use, the end cap electrodes are connected to earth potential while a radio frequency (rf) oscillating "drive" potential, typically around 1MHz, is applied to the ring electrode.

Ions are created within the ion trap by bombarding the compound either with electrons emitted from a filament (electron impact [EI] ionization), thus destabilizing the molecular structure (or pressuring the MS with a selected reagent gas, performing EI on the gas to form reagent ions, and allowing ion-molecule reactions to occur between the compound and the reagent ion - chemical ionization (CI)).



Figure 4.1: *The Varian Saturn Ion Trap, with the exit end-cap electrode visible, courtesy of Varian Chromatography Systems.*



Figure 4.2: *The Varian Saturn Ion Trap disassembled, courtesy of Varian Chromatography Systems.*

Depending on the compound's original structure and the excess destabilizing (internal) energy present in the structure, the ionized compound breaks apart (fragmentation) and forms positively charged

ions and neutral fragments. This range of m/z values may be held in bound or so-called stable orbits, oscillating along all three axes by virtue of the rf potential (low voltage). Alternatively, a single or a range of m/z values may be stored by the superposition of an appropriate dc potential on top of the rf drive potential.

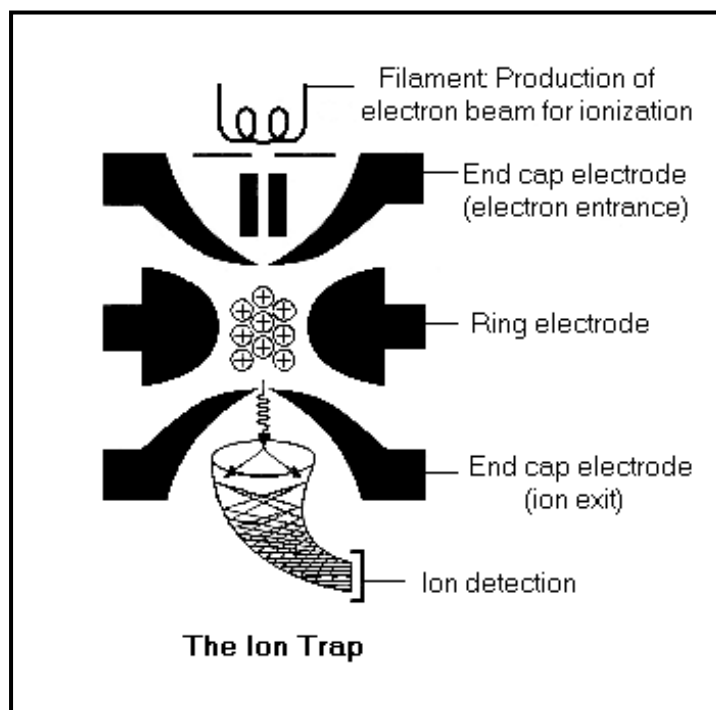


Figure 4.3: Schematic representation of the Ion Trap, courtesy of Varian Chromatography Systems.

As the amplitude of the rf potential is increased above the resonance voltage, the motion of the ions becomes progressively more energetic, such that eventually they develop unbound (unstable) trajectories along the axis of symmetry (the z -axis). Then, in order of increasing m/z values, the ions are ejected from the trap in a tightly collimated beam and exit the device through holes in one end of the end-cap electrodes and impinge on the detector. In this way, a mass spectrum is generated. The mass spectrum is a graphical representation of the ion intensities versus the mass-to-charge (m/z) ratio. A small ac voltage (axial modulation voltage) of fixed frequency and amplitude is also applied to the end-cap electrodes during the analysis to improve ion ejection and unit mass resolution.

The Saturn GC-MS has two techniques for generating sample ions in the ion trap. Consequently there are two basic scan functions, *i.e.*,

the electron ionization scan function and the chemical ionization scan function. A scan function is a representation of the timing sequence for ion trap operation. It shows the variations in time of the rf potential applied between the ring electrode and the end cap electrodes, as well as any supplementary waveforms applied to the end cap electrodes.

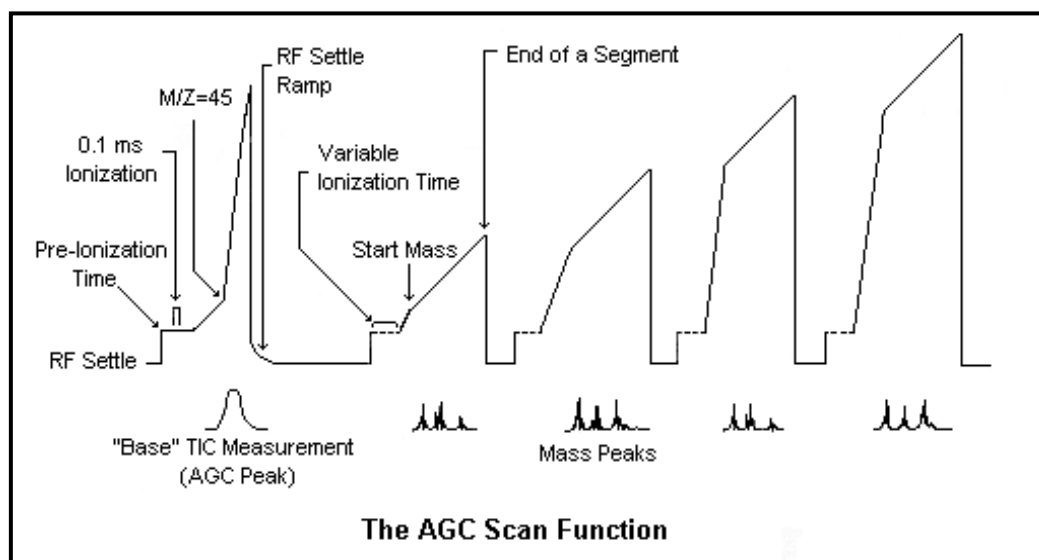


Figure 4.4: *The Automatic Gain Control (AGC) Scan Function (MS), courtesy of Varian Chromatography Systems.*

The ion trap has a maximum storage capacity, beyond which mass resolution and spectral quality deteriorate. The number of ions created is proportional to the ionization time; with more ions being produced the longer the ionization time. Automatic Gain Control (AGC) controls the ionization time in order to maintain the number of ions in the trap at the optimum level (Figure 4.4).

4.4 ION TRAP THEORY

The theory behind the operation of the ion trap is best considered by examining the equations for the electric field within the ion trap of so-called perfect quadrupolar geometry and for the resulting motion of the ions. The shape of the potential developed within the trap when the electrodes are coupled to the rf and dc potentials is described by

$$\phi = \frac{1}{2} (U - V \cos \Omega t) \left(\frac{x^2 + y^2 - 2z^2}{r_0^2} \right) + \frac{U - V \cos \Omega t}{2} \quad [4-1]$$

where U represents the maximum dc potential and V the maximum rf potential applied between the ring and the end-cap electrodes, Ω is the angular frequency of the rf drive potential, and r_0 is the internal radius of the ring electrode.

For the perfect quadrupole field the arrangement of the electrodes corresponds to the case in which $r_0^2 = 2z_0^2$, where $2z_0$ is the closest distance between the two end-cap electrodes. The oscillation of the rf potential causes the field to reverse direction periodically so that the ions are focused and defocused alternately along the z -axis and vice versa in the radial plane.

The Force, F , acting upon an ion of mass m and charge e is given by

$$\bar{F} = -e \cdot \nabla \phi = m\bar{A} \quad [4-2]$$

from which the forces acting upon the ion in each of the perpendicular directions are given by

$$\left(\frac{m}{e} \right) \frac{d^2 x}{dt^2} + (U - V \cos \Omega t) \frac{x}{r_0^2} = 0 \quad [4-3]$$

$$\left(\frac{m}{e} \right) \frac{d^2 y}{dt^2} + (U - V \cos \Omega t) \frac{y}{r_0^2} = 0 \quad [4-4]$$

$$\left(\frac{m}{e} \right) \frac{d^2 z}{dt^2} - 2(U - V \cos \Omega t) \frac{z}{r_0^2} = 0 \quad [4-5]$$

Note that none of these expressions contain cross-terms between x , y , and z , with the result that the motion may be resolved into each of the perpendicular co-ordinates, respectively. The x - and y -components are identical and may be treated independently, provided that any angular momentum, which the ions have around the z -axis, is ignored. Because of the cylindrical symmetry, the x - and y -components are often combined to give a single radial r -component using $x^2 + y^2 = r^2$.

The z -component of motion is out-of-phase by half a cycle with respect to the x - and y -motion (hence the minus sign), and the factor of 2 arises because of the asymmetry of the device brought about by the need to observe the Laplace condition $V^2\phi=0$ when applied to equation 4-1. These equations are all examples of the *Mathieu* equation, which has the generalized form

$$\frac{d^2 u}{d\xi^2} + (a_u + 2q_u \cos 2\xi) u = 0 \quad [4-6]$$

where

$$u = x, y, z \quad [4-7]$$

$$\xi = \frac{\Omega t}{2} \quad [4-8]$$

$$a_z = -2a_x = -2a_y = -\frac{16eU}{m(r_0^2 + 2z_0^2)\Omega^2} \quad [4-9]$$

and

$$q_z = -2q_x = -2q_y = -\frac{8eV}{m(r_0^2 + 2z_0^2)\Omega^2} \quad [4-10]$$

Thus, the transformations, equations 4-7 to 4-10, relate the *Mathieu* parameters a_z and q_z to the experimental variables and also to the "time" variables Ω and t . The a_u and q_u parameters are quite fundamental to the operation of the ion trap because they determine whether the ion motion is stable (i.e., the ions remain trapped) or unstable. The stability diagram (Figure 4.5) – actually only a small portion of a much larger family of curves [70] – defines the areas within which the axial (z) and radial (r) components of motion are stable; the region of overlap indicates the (a_z, q_z) co-ordinates corresponding to those ions that are held in the trap [60, 62].

The scan function for the operation of the ion trap may be seen as comprising a time period during which the (a_z, q_z) co-ordinates (Figure 4.5) for the ions remain constant at points lying on the q_z -axis close to the origin, followed by movement of the co-ordinates along the axis until they reach the right-hand boundary. Here, the ions develop unstable trajectories along the z -axis of the trap.

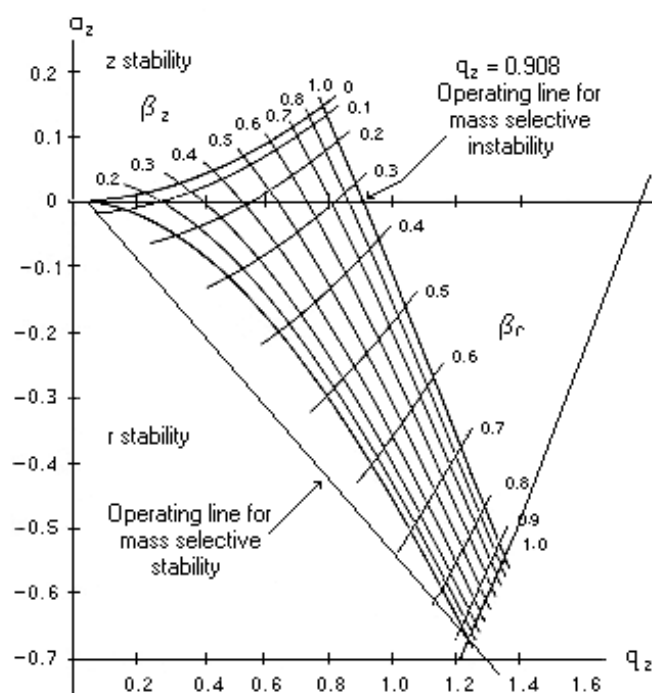


Figure 4.5: Stability diagram for the Ion Trap plotted in (a_z, q_z) space, courtesy of Todd, J.F.J. [68, 70].

The motion of ions within the ion trap may therefore be classified as being stable, when the trajectories periodically pass through zero displacement with respect to each of the three Cartesian co-ordinate directions, and unstable when the trajectories in at least one direction tend toward infinite displacement. For stability, the working (a_z, q_z) co-ordinates must lie within the boundaries of the stability diagrams.

The lines drawn across the stability region in Figure 4.5 are called iso- β lines. These lines describe the detailed trajectories of the ions at that point. The boundaries of the diagram correspond to $\beta_r, \beta_z=0$ and $\beta_r, \beta_z=1$, with the boundary $\beta_z=1$ being that at which the mass-selective ejection is normally achieved during a mass spectral scan. In addition it has been noted that the trajectories comprise low-frequency "secular" [68, 70] (rf) and high frequency components, the former being determined by the appropriate β_z value, and hence values of a_z and q_z . When the values of β_r and β_z are increased, for example, by increasing the amplitudes of the rf drive potential, then the nature of the motion becomes much more violent. This characteristic motion of the trapped ions plays an important part in the operation of the ion trap, especially in experiments in which it is

desired to pump kinetic energy into ions by resonance excitation through application of auxiliary oscillating fields applied between the end-cap electrodes.

Axial modulation, already mentioned, is one such application where performance is enhanced by employing a superimposed dc field before the lower mass ions are analysed. This adverse effect on peak shape can be reduced dramatically by applying a supplementary oscillating field of approximately 6V at a frequency of about half of the rf drive potential between the end-cap electrodes during the analytical portion of the scan function. At this point, just as the ions are being ejected, their secular motion enters into resonance with the supplementary field so that the ions are energised as they suddenly synchronise and are therefore much more tightly bunched as they are ejected.

The application of a supplementary oscillating field is also the basis of studying the collision-induced dissociation of ions in the trap, which is the fundamental basis of operation for MS-MS [68, 70, 95].

4.5 TANDEM-IN-SPACE vs TANDEM-IN-TIME

There are several types of mass spectrometers capable of tandem mass spectrometry experiments, including double quadrupoles, which have been proved to compare favorably with triple quadrupoles [93, 94]. Consider the example of a triple stage quadrupole: in a triple quad, ions are formed in the ion source and directed into the first quadrupole, which is tuned to allow a single precursor ion to pass through the quadrupole field. This isolated target ion enters the second quadrupole, which is often used as a collision cell. In this second quad, which is typically filled with argon, target ions collide with argon atoms and fragment into smaller ions. This process is called Collision Induced Dissociation (CID). The fragment or product ions produced by the collisions enter a third stage quadrupole where these ions are separated into a mass spectrum. While multi-analyser systems such as triple quads have driven the development of MS-MS technology, these systems have several major disadvantages: they are expensive, the hardware occupies a large lab space and operation is difficult for routine analysis.

The Varian Saturn 2000 Ion Trap GC-MS-MS, the instrument used for the analyses (Figure 5.1), takes advantage of the “tandem-in-time” concept, rather than “tandem-in-space”, by using a single ion trap (Figure 4.3) and a sequence of different radio frequency (rf) waveforms [68-73]. All the basic steps described for the triple quadrupole also exist within an ion trap; however, for ion trap MS-MS, these steps occur as a sequence of timed events within a single ion trap rather than across space in a series of quadrupoles.

There are three significant advantages of the ion trap approach to GC-MS-MS. The most obvious is the use of a single ion trap that does the work of three quadrupoles, each with its own vacuum system. This means that the cost of the instrumentation is significantly lower. The second advantage concerns the ease of use of a benchtop ion trap mass spectrometer against a much larger and significantly less user-friendly triple stage quadrupole. The ion trap MS-MS process has been simplified so that the majority of the method optimization can be performed by optimizing one variable – the rf amplitude during CID. The third advantage concerns the sensitivity to the product ion. Due to transmission losses in a quadrupole system, ion traps inherently recover a higher percentage of the ions produced. There is a significant sensitivity increase when one keeps the ions of interest in a single ion trap as opposed to a triple quadrupole system.

4.6 TANDEM MASS SPECTROMETRY THEORY

The two fundamental processes in mass spectrometry are ion creation and ion analysis. Tandem Mass Spectrometry (MS-MS) is a technique for isolating a single ion (precursor or parent) from a mass spectral fragmentation and causing this isolated ion to undergo a collision induced dissociation (CID) in order to obtain the resulting product or daughter ion spectrum.

The Varian Saturn 2000 Ion Trap GC-MS-MS accomplishes this by means of an Ion Preparation Method (IPM), which modifies the scan function. The ion preparation method (IPM) introduces *intermediate scan segments* (ISSs) into the basic rf scan function. This allows the

prescan and analytical scan(s) for both electron- and chemical-ionization modes of analysis to be customized.

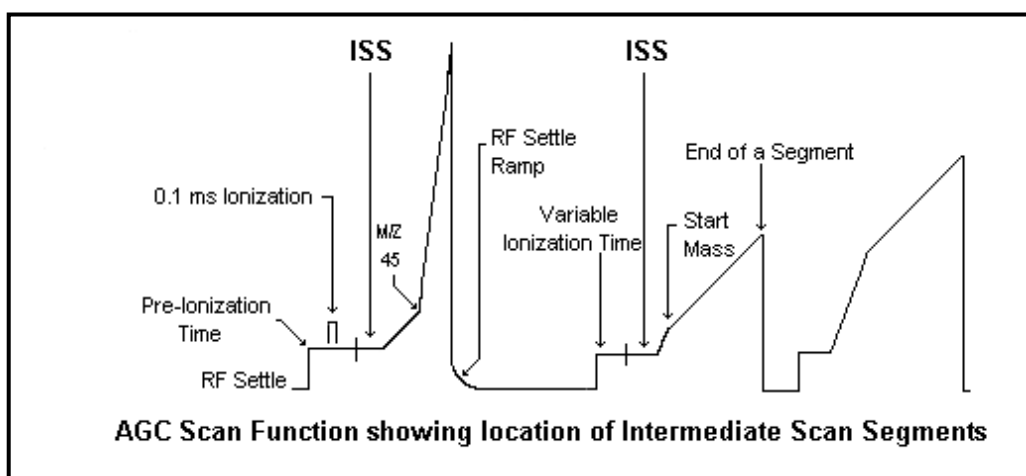


Figure 4.6: Automatic Gain Control (AGC) Scan Function showing the location of the Intermediate Scan Segments (ISS) for MS-MS, courtesy of Varian Chromatography Systems.

In the case of electron ionization (EI), ISS insertion takes place between creation of the ions (ionization) and ion analysis (Figure 4.6). Electron ionization uses the AGC scan function, which consists of a prescan and up to four analytical scans, which include ionization periods, ISSs and four voltage ramps over a user-defined range (two analytical scans are visible in figure 4.6).

There are four basic operations in Saturn ion trap tandem mass spectrometry (MS-MS) for electron ionization (Figure 4.7), namely ion formation and matrix ion ejection, parent ion isolation, product/daughter ion formation and product/daughter ion mass scanning [68].

During ion formation and matrix ion ejection, a two-step rough isolation (broadband multi-frequency) waveform is applied to the end caps to resonantly eject ions below and then above the specified parent ion mass. This two-step waveform physically removes most of the low mass ions whose space charge would otherwise affect the storage efficiency of the parent ion and most of the remaining unwanted ions from the trap [68].

Parent ion isolation uses another more accurate two-step process (fine isolation waveform), where the first step ejects the ions with masses below the parent ion mass, followed by a broadband multi-frequency waveform applied to the trap to simultaneously eject all masses above the parent ion mass [68].

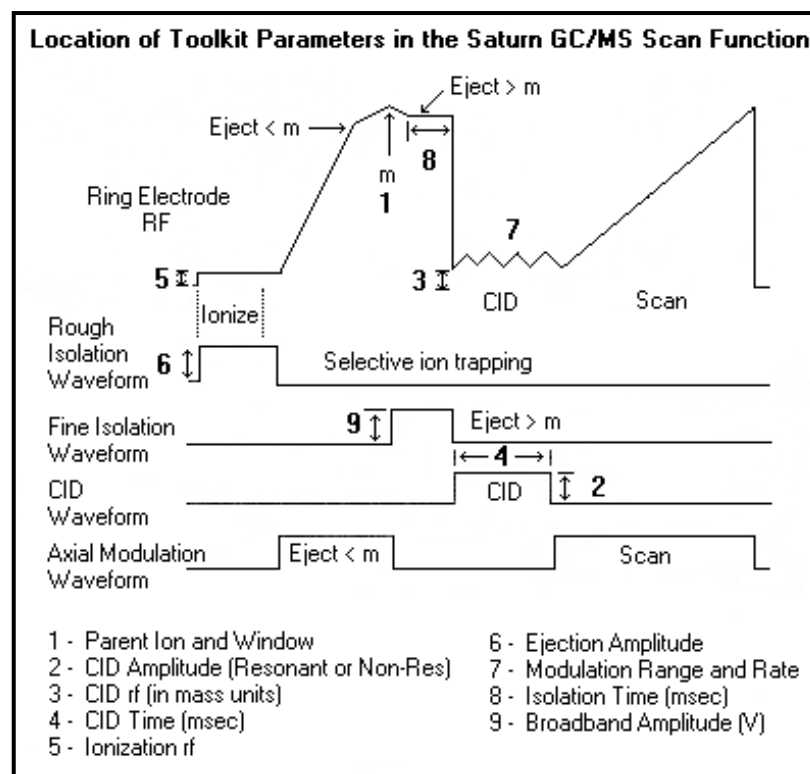


Figure 4.7: Parameters in the Saturn GC-MS-MS Scan Function, Courtesy of Varian Chromatography Systems.

Product or daughter ions are formed from the parent ions by collision induced dissociation (CID). The mass to charge distribution resulting from the CID process depends on the characteristics of the parent ion and the amount of translational kinetic energy that has been converted into internal vibrational energy. The translational kinetic energy of the parent ion can be increased using either of two methods: resonant or non-resonant excitation [68].

4.6.1 Non-Resonant Excitation

Non-resonant excitation or "boundary activation" [70] is based on the interaction of a selected ion species with the high fields derived from the rf drive potential and requires a low frequency

supplemental dipole field applied to the end-cap electrodes, resulting in an instantaneous change in the potential energy of the ion in the trapping field. The restoring force of the trapping field converts the newly increased potential energy of the ion into increased translational kinetic energy. A portion of this kinetic energy is then converted into internal vibrational energy upon subsequent collisions. It is, therefore, a mass-independent collisional process that does not require the careful tuning of the "tickle" voltage (applied potential) [68].

An advantage of using non-resonant excitation is that it is not critical to match the applied dipole frequency to that of the ion. Consequently, electronic drifts, space charge effects, or sample concentration does not affect the method. This results in reproducible product ion spectra, unaffected by changes in the trapping conditions and sample concentration. This method is often useful with parent ions that fragment by the breakage of a single weak chemical bond to form highly stable ions containing functional groups that do not undergo significant rearrangements. A disadvantage of the method is that it is not selective with respect to excitation of ions in the trap. Therefore, the method cannot be selectively tuned to excite only ions having a particular m/z . The method is also less useful with parent ions in which multiple chemical bonds are broken and with parent ions that undergo complex rearrangements following collision induced dissociation [68].

4.6.2 Resonant Excitation

Resonant excitation is achieved by applying a high frequency supplemental dipole field ("tickle" potential or applied potential – the dipole field is simply an electric field oriented along the axis of the trap) across the end cap electrodes that is tuned to the fundamental secular (oscillation) frequency of the ion. The axial component of the ion motion is thus resonantly excited. The resonant frequency of the trapped ion depends on ion mass, space charge, rf trapping field, and other instrumental factors, thus it is difficult to precisely calculate its value. The amplitude of the rf trapping field is therefore modulated over a specified range.

Since the resonant frequency of the trapped ion depends on the magnitude of the rf field, modulating the rf field amplitude results in a modulation of the resonant frequency of the ion. Modulation of this frequency causes the frequency of the ion to periodically match that of the applied supplemental dipole field. The energy coupled to the ion motion is maximized and the effects of shifts in the ion resonant frequency are minimized. The effectiveness of the resonant excitation method depends on the mass range over which the rf field is modulated and the total time spent in resonance. This increases the degree of internal energy enhancement, albeit at the expense of product ion detection efficiency [68, 70].

The resonant excitation method is selective to the mass range that is excited. It permits coupling of energy to the motion of an ion having a particular m/z value in a very controlled way. Consequently, the rate that the amplitude of the ion motion increases is just balanced by the rate that energy is removed by collisions. The ion is not ejected and energy can be deposited as internal energy by increasing the number of collisions. Increasing the excitation time does this. Thus, it is possible to fragment parent ions that require the breakage of multiple chemical bonds or that undergo significant rearrangements. Periodic modulation through ion resonance results in an averaging of the energy coupled into the ion motion and provides a reproducible product ion spectrum, even with changes in concentration. A disadvantage of this resonant method is that two parameters in addition to the excitation time and CID excitation amplitude need to be optimized; these are the modulation range and CID bandwidth [68].

To illustrate, these optimization relationships may be observed in figures 4.8 and 4.9. Changing the CID bandwidth permits simultaneous excitation of ions within a range of masses. As the CID bandwidth increases, the corresponding excited mass range also increases. At a given CID bandwidth, the mass range increases with increasing ion mass and decreases with increasing excitation rf storage level. Note that at a storage level of 48 m/z and a CID bandwidth of 4 kHz, the mass range increases from 3

to 40 m/z when the parent ion mass increases from 100 to 400 m/z . With a parent ion mass of 400 m/z and a CID bandwidth of 4 kHz, the mass range decreases from 40 m/z for a storage level of 48 m/z to a range of 12 m/z for a storage level of 143 m/z [68].

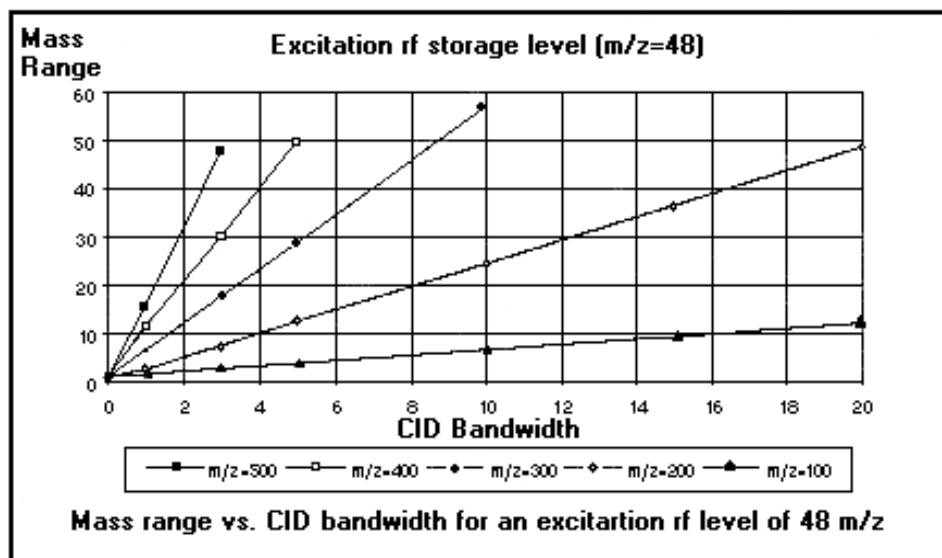


Figure 4.8: Mass range vs CID bandwidth for an excitation rf storage level of 48 m/z , courtesy of Varian chromatography Systems.

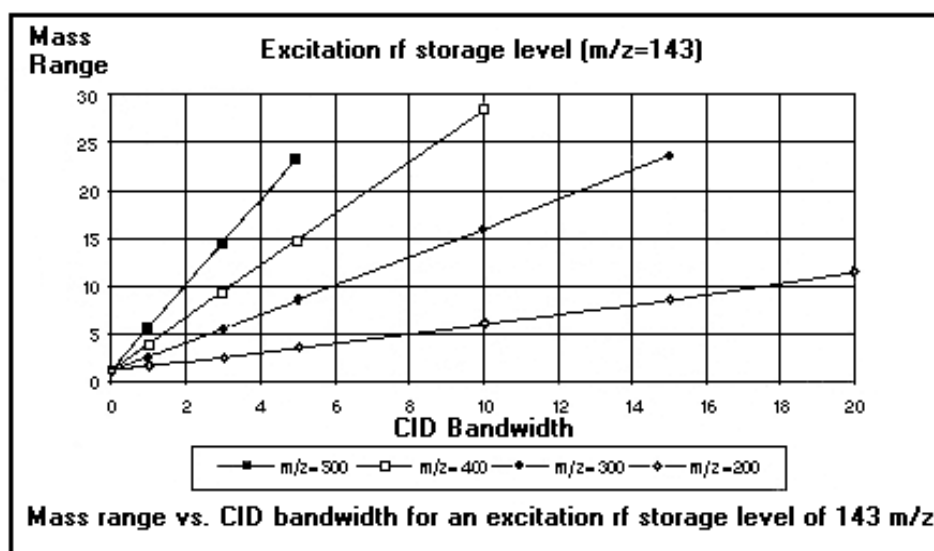


Figure 4.9: Mass range vs CID bandwidth for an excitation rf storage level of 143 m/z , courtesy of Varian Chromatography Systems.

Following formation of the product or daughter ions by CID, a single rf ramp is used along with the axial modulation field (a voltage applied at a fixed frequency and amplitude during the ramp of the rf voltage to facilitate ion ejection and improve mass resolution) to resonantly scan ions from the trap into the electron multiplier. This process generates the product or daughter ion spectrum [68].

The four operations described above, namely ionisation, parent ion isolation, product ion formation and product ion mass scanning, are used in the analytical scan. When automatic gain control (AGC) is used, either parent or product ions can be used in the prescan to determine the ionisation time required to maintain the optimum number of ions in the trap. Thus, the total ion space charge level is held constant as the sample and matrix levels change. Ensuring a constant level of parent or product ions in the analytical scan, provides consistent, reproducible product ion spectra [68].

4.7 INFORMATION CONTENT OF TANDEM MS

INFORMATION CONTENT (P_{inf})

P_{inf} = number (#) of bits of information available
in a given analytical procedure

$$P_{\text{inf}} = \sum \log_2 S_i \quad (i = 1 \text{ to } n)$$

Where n = # of different quantities to be determined
 S_i = # of measurable steps for quantity i

Figure 4.10.1: Parameters required for calculating the information content for MS and MSⁿ, courtesy of Dr Bob Brittain, Varian Chromatography Systems.

INFORMATION CONTENT IN MS

$$P_{\text{inf}} = \int_{x_a}^{x_b} R(x) \log_2 S(x) \frac{dx}{x}$$

where

P_{inf} = information content
 $x_b - x_a$ = mass range (650-10=640)
 $R(x)$ = resolution ($\delta x=1$)
 $S(x)$ = range of measurable intensity steps
 = 2^{12} (for a 12-bit ADC)

$$P_{\text{inf}} \cong MS_{\text{inf}} = 7.7 \times 10^3$$

Figure 4.10.2: Calculations showing the information content of MS, courtesy of Dr Bob Brittain, Varian Chromatography Systems.

The information that can be derived from GC-MS-MS (Figure 4.10.3) over GC-MS (Figure 4.10.2) increases almost 1000 fold and continues to increase rapidly with each additional dimension (MS^n). GC-MS-MS can be very beneficial when looking for trace quantities of accelerants in very complex pyrolysis matrices. A maximum ionisation time for the parent ion (precursor ion) can be used during the initial fragmentation step. It does not matter that the number of ions produced are beyond that required for achieving proper resolution in the ion trap because all ions, other than the parent (precursor ion), will be ejected. Maximum sensitivity is achieved with longer ionisation times, thus increasing sensitivity, enhancing selectivity and obtaining more qualitative information with the use of GC-MS-MS.

INFORMATION CONTENT IN GC-MS-MS

$$P = \iiint R(xyz) \log_2 S(xyz) dx dy dz$$

Where x is the time axis for the chromatogram
 y is the mass range for MS (10-650u)
 z is the mass range for MS/MS (50-650u)

$$\begin{aligned} P_{\text{inf}} &= (GC_{\text{inf}}) \times (MS_{\text{inf}}) \times (MS^2_{\text{inf}}) \\ &= (1.68 \times 10^3) \cdot (7.7 \times 10^3) \cdot (600) \\ &= 7.8 \times 10^9 \end{aligned}$$

Now, using the same logic, for GC-MS-MS-MS:

$$P_{\text{inf}} = (P_{\text{inf,GC-MS-MS}}) (600) = 4.7 \times 10^{12}$$

INFORMATION CONTENT INCREASES RAPIDLY WITH MSⁿ

Technique	P_{inf}	Normalized Value
MS	7.7×10^3	1
GC-MS	1.3×10^7	1680
GC-MS-MS	7.8×10^9	1.0×10^6
GC-MS-MS-MS	4.7×10^{12}	6.0×10^8

Figure 4.10.3: Calculations showing the information content of MSⁿ, courtesy of Dr Bob Brittain, Varian Chromatography Systems.

CHAPTER 5

TANDEM MS OPTIMIZATION

5.1 MS-MS AS AN ANALYTICAL TOOL

Pattern recognition of gas chromatograms is currently the method most widely used for the identification of accelerants commonly found in fire debris. Gas chromatography is used with a fair degree of confidence. With the introduction of mass spectrometry, a significantly higher degree of confidence is achieved. The mass spectrometer provides information on the identity of every component in the sample, which is time consuming and does not make it easier than to just compare the chromatogram with known standards. Differentiation of petrol, paraffin, diesel and other ignitable and combustible hydrocarbons is simplified using reconstructed ion chromatograms (RICs – also called selected ion profiling or mass chromatography) of specific mass ions unique to different types of accelerants. As discussed in chapter 3, determination of various types of gasoline, e.g., leaded or unleaded, is made possible using ion profiling (RIC) techniques [53].

Interfering pyrolysis products, particularly those of synthetic polymers, which often hinder the identification of accelerants by GC pattern recognition alone, are minimized using ion profiling techniques. As shown in the previous chapter, there are instances where it becomes necessary to look to other techniques in order to even further minimize pyrolysis interferences still prevalent in the GC-MS trace and to selectively isolate the characteristic hydrocarbons specific to flammable liquids.

Tandem mass spectrometry (GC-MS-MS) is one such technique which allows scanning of selected ion fragments specific to the aromatic hydrocarbons found in petroleum based flammable liquids. GC-MS-MS results can be very definitive resulting in an associated level of confidence with the chromatographic result [96].

Since petrol (gasoline) is one of the more common distillate blends used by arsonists, especially in South Africa, the identification of petrol in fire debris samples was investigated. In order to overcome pyrolysis product interference and improve detection level selectivity of the aromatic hydrocarbons in petrol residues, MS-MS was utilized as the method of detection after capillary gas chromatographic separation of petrol into its characteristic volatile hydrocarbon components [96].

5.2 INITIAL APPLICATION

Petrol is a distillate blend of complex aliphatic and aromatic hydrocarbons. When analyzed by GC-MS, the characteristic ratios of the isomers for each molecular mass ion are separated and can be identified. The most important diagnostic components for petrol are the alkylated aromatic hydrocarbons. The distribution of individual components in each group of isomers (such as the C3 and C4-alkylbenzenes) is highly characteristic and it was decided to compare only the aromatic hydrocarbons, as the extracted ion profiles of these compounds produce the most conclusive results for petrol identification by mass spectrometry. Substances such as indanes, olefins and styrenes are only present in trace quantities and are generally not used as petrol indicators [2, 45, 60, 63].

An actual petrol distillate was selected rather than a laboratory aromatic mix, since not all the components present in petrol were available in the laboratory. A standard petrol distillate was dissolved in Riedel deHaen® analytical reagent grade carbon disulphide. All analyses were qualitatively performed using a Varian Star 3400CX Gas Chromatograph coupled with a Varian Saturn 2000 GC-MS-MS Ion Trap Mass Spectrometer. Figure 5.1 depicts the 3800CX GC that is the current Varian GC used for arson analyses in this study.



Figure 5.1: *Varian Star 3800CX Gas Chromatograph coupled with a Varian Saturn 2000 GC-MS-MS Ion Trap Mass Spectrometer, courtesy of Varian Inc.*

The CID Voltage was selected as 60 and the rf excitation storage level was maintained at 48.0 m/z (as determined by the “q” calculator – see chapter 4). The CID excitation time was maintained at 20 ms and the amplitude range was maintained at 20.00 V. These values can be customised as required, but were left at their default values for the purpose of this analysis [68].

The mass spectrum is a graphical representation of the ion intensities versus the mass-to-charge ratio (x-axis - scans). When looking at the chromatograms, the ion intensities along the y-axis can be read in “kCounts” (number of counts in thousands) or “mCounts” (number of counts in millions), which are 1000 times more abundant than counts in thousands. If only “Counts” are indicated, then these are 1000 times less abundant than counts in thousands and are actually bordering on the signal-to-noise ratio of the instrument.

The mass-to-charge ratio (m/z) 91 was initially selected as the parent ion mass and was isolated throughout the chromatographic run to obtain the MS-MS product (daughter) ion chromatogram for a petrol distillate using resonant excitation. The m/z = 91 ion is the tropillium ion (C_7H_7) and is a very stable ion formed from all alkylbenzene compounds and difficult to fragment. The typical mass fragments for alkylbenzenes can be seen in Table 3.1, Chapter 3. All

the alkylbenzene compounds exhibit the formation of the tropillium ion.

In figure 5.2.1 the selected ion mass chromatogram for $m/z = 91$ has been compared with the total product ion MS-MS chromatogram obtained for $m/z = 91$ since the parent ion selected was $m/z = 91$. There is not much evidence to indicate improvement in specificity between obtaining a product ion chromatogram by MS-MS as opposed to normal ion profiling techniques by GC-MS when selecting only $m/z = 91$ as the parent ion.

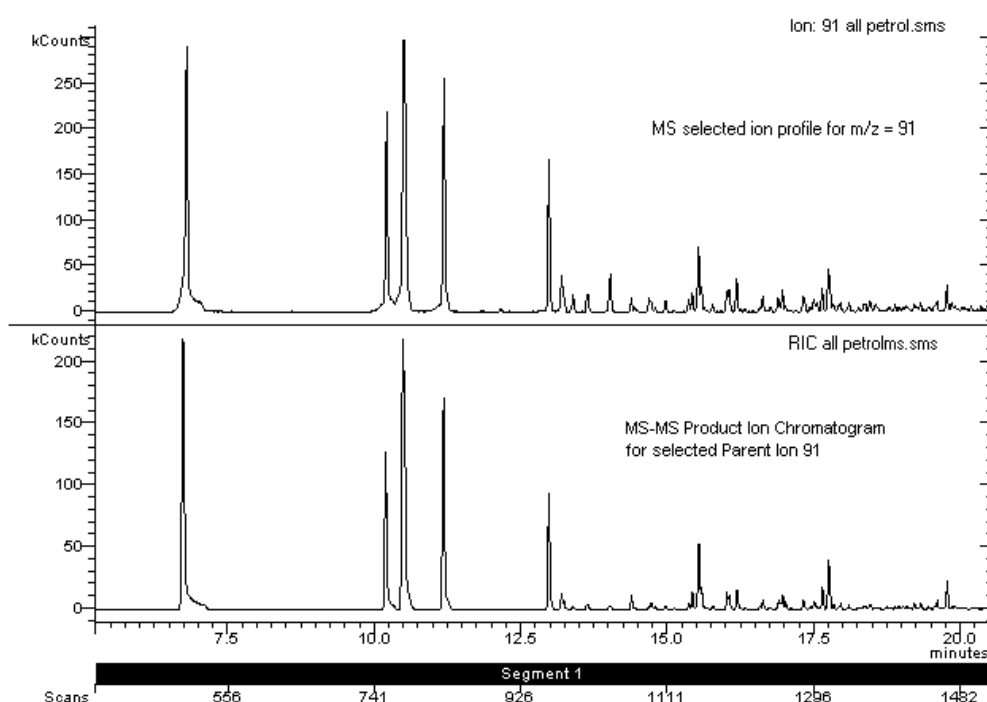


Figure 5.2.1: Comparison between the MS selected ion profile chromatogram for $m/z = 91$ and the MS-MS product ion chromatogram for selected parent ion 91.

The product ion chromatogram can be reconstructed (Figure 5.2.2) to reflect $m/z = 91$ in the same way as selected ion profiling for MS. The baseline has been enhanced to show more detail for the C3, C4 and C5-alkylbenzenes. The ratio of C1 and C2-alkylbenzenes has increased as compared with the C3 and C4-alkylbenzenes indicating improved selectivity for the $m/z = 91$ ion, but not necessarily for the higher boiling point aromatic alkylbenzenes.

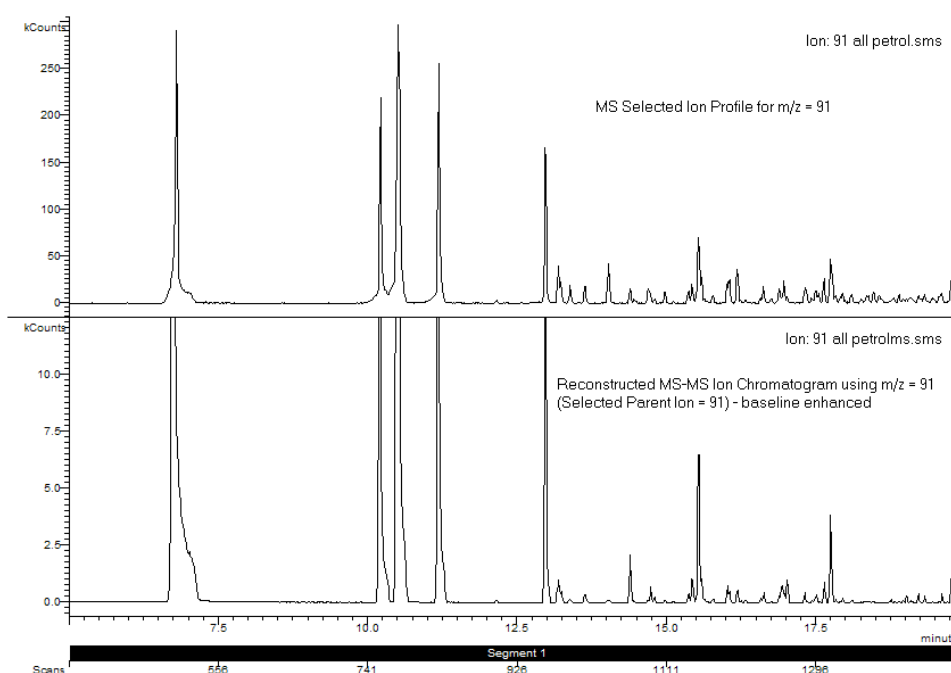


Figure 5.2.2: Comparison between the MS selected ion profile chromatogram for $m/z = 91$ and the reconstructed MS-MS product ion chromatogram for selected parent ion 91 using $m/z = 91$

When comparing the actual spectra obtained by MS and MS-MS (using propylbenzene as an example where the selected parent ion is 91 and not the molecular ion 120), it can be seen that the parent ion, $m/z = 91$, has been partially fragmented to produce more of the $m/z = 65$ ion. Fragmentation of the molecular ion ($m/z = 120$) of propylbenzene will not occur since the selected parent ion is 91. In order to form the correct ratios of the tropillium ion and $m/z = 65$, that would be typical for a propylbenzene fragment, the correct parent ion will have to be selected. The spectrum obtained for propylbenzene using $m/z = 91$ as the parent ion looks no different from what would be expected for a fragmentation of toluene (Figure 5.3).

This highlighted the fact that selecting and isolating $m/z = 91$ was too similar to SIM (selected ion monitoring). Sufficient diagnostic product ions are produced, but there is not enough specificity for the diagnostic ions required for the higher alkylbenzene compounds (C3, C4, C5 and C6-alkylbenzenes) that are characteristic for accelerant traces. The initial analysis did, however, serve to make the $m/z = 91$

aromatic isomers that are present in petrol more clearly evident in the presence of pyrolysis interference and provided a possibility for using MS-MS for the purpose of minimizing pyrolysis interference. This was then investigated further to provide product ions that correctly reflected the parent ions selected as the diagnostic ions characteristic for petroleum products.

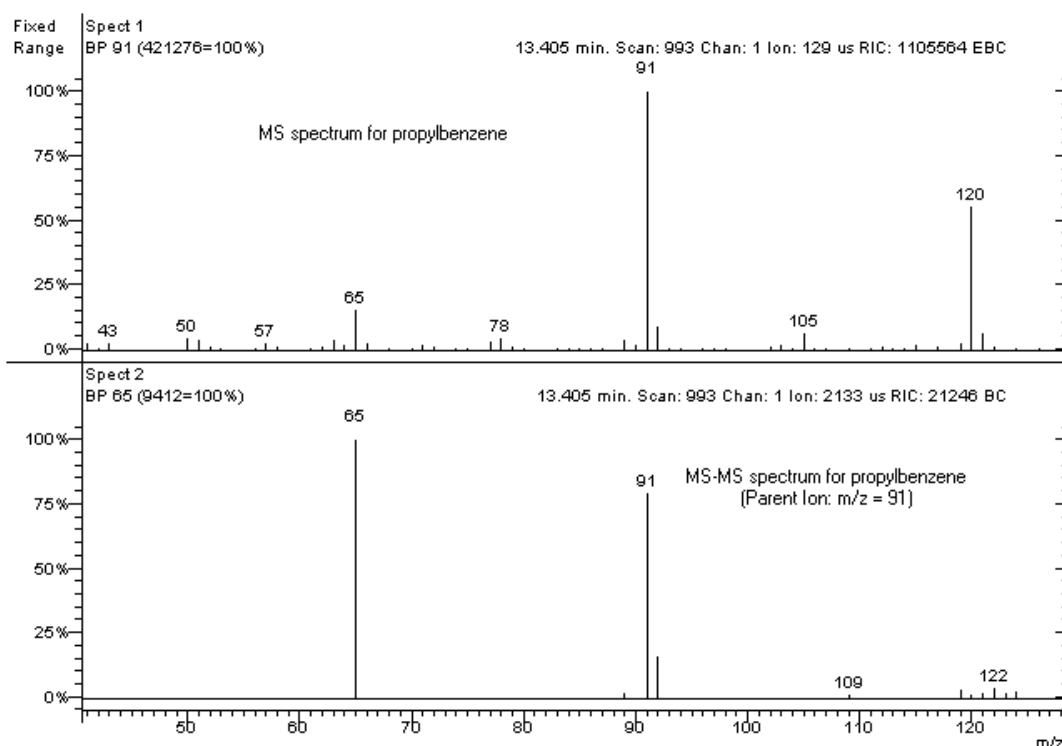


Figure 5.3: Comparison between the MS spectrum for propylbenzene and the MS-MS spectrum for propylbenzene using parent ion 91.

5.3 AUTOMATED METHOD DEVELOPMENT

The results obtained for the product ion spectra for m/z = 91 prompted the decision to use the Automated Method Development (AMD) software feature with non-resonant excitation, to optimize the amplitude of the waveform applied during CID of the parent ions (CID amplitude in volts). The parent ions selected are characteristic aromatic ions that are important in the detection and identification of petrol (Table 5.1). The AMD procedure allows the CID amplitude to be incremented on a scan-by-scan basis, which will be explained more fully in the chapter.

Table 5.1: Characteristic Aromatic Ions Selected For Petrol

Component	Molecular Ion	Base Peak	Additional Diagnostic Ions	Selected Parent Ion
Benzene	78	78	51,52,77	78
Toluene	92	91	92,65,63	91
Ethylbenzene	106	91	106,65,77	106
m,p-Xylene	106	91	106,105,77	106
o-Xylene	106	91	106,105,77	106
Isopropylbenzene	120	105	120,79,91	120
Propylbenzene	120	91	120,105,65	120
Mesitylene	120	105	120,91,79	120
1,2,4-Trimethylbenzene	120	105	120,91,79	120
1,2,3-Trimethylbenzene	120	105	120,91,79	120
Indane	118	117	118,115,91	117
Butylbenzene	134	91	92,134,105	134
C4-Alkylbenzenes	134	105,119	134,91,105	134
Pentylbenzene	148	91	92,148,105	148
C5-Alkylbenzenes	148	105,119, 133	148,133,105	148
Hexylbenzene	162	91	92,162,105	162
C6-Alkylbenzenes	162	106,119, 131,132	162,105,133	162
Naphthalene	128	128	102,127,63	128
C1-Naphthalenes	142	141	142,115,89	142
C2-Naphthalenes	156	156	141,115,128	156
C3-Naphthalenes	170	155,170	170,115,128	170

Petrol was again used as a standard to determine the common aromatic compounds in petrol. The parent ions selected were chosen (*e.g.*, the molecular ion) such that a favourable product ion spectrum could be obtained that could still be recognizably compared with the MS spectrum. Since the diagnostic ions ($m/z = 117, 133$) in the mass spectra for the methyl and dimethylindanes lie among the more important diagnostic ions ($m/z = 120, 134, 148, 162$) in the mass spectra for the alkylbenzenes and methylnaphthalenes, only the ion for indane ($m/z = 117$) has been included as a parent ion.

Table 5.2 details the settings that were used for chromatographic separation and determination of conditions required for reproducible MS-MS spectra with the AMD software.

Table 5.2: GC, MS and AMD Conditions

GC Conditions:	
Column:	Chrompack WCOT Fused Silica 30 m x 0.25 mm capillary column with CP Sil 8CB DF = 0.25 µm film coating.
Temperature program:	30 °C for 6 min, 30 °C – 70 °C @ 8 °C / min no hold, 70 °C – 270 °C @ 10 °C / min, hold at 270 °C for 4 min.
Injector temperature:	180 °C
Column flow rate:	1,2 ml / min Helium
MS and AMD Conditions:	
Scan range:	40-300 amu (atomic mass units)
Scan rate:	0.650 s (1 µScan per scan)
Background mass:	35 amu
Trap temperature:	120 °C
Manifold temperature:	45 °C (manifold has separate heater)
Transfer line temperature:	270 °C
Emission current:	50 µA (micro Amps)
AGC prescan ionization time:	100 µs (microseconds) for MS
AGC prescan ionization time:	1500 µs for AMD data collection
Target TIC:	10 000 counts

GC-MS analysis allows for the identification of the characteristic ions for the alkanes, cycloalkanes, aromatics, condensed ring aromatics and other general isomers specific to petrol. It must be emphasized that the sensitivity of the MS-MS technique also allows identification of residues of aromatic blend solvents used for coatings, paints, varnishes, adhesives and insecticides. These specialty solvents can differ from evaporated petrol only in their ratios of aromatics to aliphatics (alkanes) and therefore the GC-MS analysis must form part

of the MS-MS analysis for a total overview of the characteristic hydrocarbons actually present, especially to ensure a positive or negative identification for the presence of an ignitable liquid. In this way false negatives are prevented.

The non-resonant CID was selected so as to ensure that a dipole waveform is applied, exciting all ions in the trap simultaneously. The isolation window is selected as 3 to ensure that the parent ion mass is at the center and the duration of the CID waveform was maintained at 20 ms. The CID rf (excitation) storage level is determined using the Mathieu “q” parameter. This is the rf storage voltage in m/z units to be used during excitation of the parent ion. A higher CID rf storage level allows more energy to be imparted to an ion during excitation to form product ions. In order not to eject any desired product ions during this storage period, the excitation storage level should be set lower than the mass of the desired product ions calculated using the Mathieu “q” parameter. (See Equation 4-6 and figures 4.5, 4.8 and 4.9 in Chapter 4) [68 - 70].

Certain of the MS-MS parameters can be customized, but these parameters, namely the ionization rf (default: 48 m/z – see Chapter 4), ejection amplitude (default: 20 volts), low DAC offset (default 6 DAC), high DAC offset (default: 2 DAC), isolation time (default: 5ms) and broadband amplitude (amplitude 30 volts) were maintained at their default values. Adjustment of the high and low DAC (DAC: Digital-to-Analog Converter) offsets optimizes isolation of the stable ions and ensures efficient ejection of adjacent ions [69].

Table 5.3.1 (and Tables 5.3.2 to 5.3.13 in Annexure A) provides the initial AMD conditions required for obtaining MS-MS spectra for the selected aromatic parent ions that were considered the most characteristic for petrol identification using the AMD software. Table 5.4 indicates the actual timing sequence for MS and AMD data collection. The same GC and MS conditions that were used for the initial data collected for parent ion 91 are repeated here.

The CID amplitude was selected from 25 to 70 V (5 V increments) and the rf excitation storage level was selected as determined by the “q” calculator for each aromatic component. The CID excitation time

was maintained at 20 ms, the ejection amplitude was 20 V and the broadband amplitude range was maintained at 30 V.

Table 5.3.1: Initial AMD conditions required for CID voltage determination ($m/z = 91$ for Toluene)

Parent Ion Mass	Mass Window	CID Amplitude	Rf Excitation Storage Level	CID Time (ms)	CID Ejection Amplitude (V)	Waveform Type
91	3	25	48.0 m/z	20	20.00	Nonres
91	3	30	48.0 m/z	20	20.00	Nonres
91	3	35	48.0 m/z	20	20.00	Nonres
91	3	40	48.0 m/z	20	20.00	Nonres
91	3	45	48.0 m/z	20	20.00	Nonres
91	3	50	48.0 m/z	20	20.00	Nonres
91	3	55	48.0 m/z	20	20.00	Nonres
91	3	60	48.0 m/z	20	20.00	Nonres
91	3	65	48.0 m/z	20	20.00	Nonres
91	3	70	48.0 m/z	20	20.00	Nonres

With the AMD software ten different sets of MS-MS conditions for parent ions can be achieved involving an MS scan routine obtained over the time a chromatographic peak elutes from the GC column for a single mass spectrum. The conditions leading to the most favorable product (daughter) ion mass spectra can then be found in less time than the method of using slightly different conditions for obtaining MS-MS criteria over ten different chromatographic runs.

These results then gave the optimum conditions for obtaining MS-MS spectra. The resultant product ion spectra were comparable, although not identical, with standard MS spectra of the characteristic aromatic hydrocarbon compounds analyzed. In this manner, isomers of a particular molecular mass can be recorded at their specific retention times with little interference, if any, from pyrolysis products in the mass chromatogram.

Table 5.3 depicts the timing sequence for data collection during automated method development. Segment no 1 refers to a delay of 3:00 minutes before actual scanning begins. Segment 2 refers to the EI mode for normal MS scanning for 3:00-3:40 minutes and Segment

3 begins the MS-MS scan for benzene from 3:40 to 6:00 minutes. The segment times will vary, depending on gas flow rate. The last segment, segment 18, reverts back to EI mode for normal MS scanning.

Table 5.4: AMD Timing Sequence for Data Collection

Segment No	Segment Time (min)	Ion Mode	Mass	Mass Window	Rf Excitation Storage Level	Parent Ion
1	0:00-3:00	EI	-	-	-	-
2	3:00-3:40	EI	-	-	-	-
3	3:40-6:00	AMD	78	3	48.0 m/z	Benzene
4	6:00-10:00	AMD	91	3	48.0 m/z	C1-Benzenes
5	10:00-12:89	AMD	106	3	48.0 m/z	C2-Benzenes
6	12:89-14:14	AMD	120	3	52.7 m/z	IPB + PB
			(105)			
7	14:14-15:66	AMD	120	3	52.7 m/z	C3-Benzenes
8	15:66-15:95	AMD	117	3	51.4 m/z	Indane
9	15:95-16:82	AMD	134	3	58.9 m/z	C4-Benzenes
10	16:82-17:10	AMD	148	3	65.1 m/z	C5-Benzenes
11	17:10-17:42	AMD	134	3	58.9 m/z	C4-Benzenes
12	17:42-18:24	AMD	148	3	65.1 m/z	C5-Benzenes
13	18:24-18:60	AMD	162	3	71.3 m/z	C6-Benzenes
14	18:60-19:70	AMD	128	3	56.2 m/z	Naphthalene
15	19:70-20:80	AMD	142	3	62.4 m/z	C1-Naphthalenes
16	20:80-22:20	AMD	156	3	68.6 m/z	C2-Naphthalenes
17	22:20-24:70	AMD	170	3	74.8 m/z	C3-Naphthalenes
18	24:70-29:00	EI	-	-	-	-

All standards and samples were injected manually, which does lead to slight differences in retention time, and since the detected hydrocarbon residues from arson debris are not usually quantified, emphasis has not been placed on quantification, but rather the actual detection of trace amounts of accelerant in pyrolysis debris.

5.4 AMD MASS SPECTRA

Over the time the chromatographic peak elutes from the GC column, each product ion mass spectrum is examined under ten different sets of MS-MS conditions. Using the peak for 1, 2, 4-trimethylbenzene as an example (Table 5.3.5, [Annexure A](#)), the changing product ion mass spectrum for $m/z = 120$ is examined as the CID excitation amplitude increases from 25 V for channel 1 to 70 V for channel 10 (Figure 5.4.1 to 5.4.10). The $m/z = 120$ ion becomes fragmented, resulting in more product (daughter) ions. Keeping in mind the actual mass spectrum for 1, 2, 4-Trimethylbenzene ($m/z = 120, 105, 91, 79$), the choice of CID excitation amplitude is determined by the amount of fragmentation of the parent ion that is desired. Channel 3, 4 and 5 (Figure 5.4.3 to 5.4.5) provided the best results. The selected CID voltage was then chosen as channel 5 = 45 V.

If the CID (excitation) amplitude used is too large, the parent and product ion spectra will be absent because both ions will have been ejected from the trap and the $m/z = 120$ parent ion no longer represents a recognisable 1, 2, 4-Trimethylbenzene product ion mass spectrum (Figure 5.4.6 to 5.4.10). If the value used is too small, the parent ion spectrum will be dominant and the product ion spectrum will be weak or missing (Figure 5.4.1 and 5.4.2).

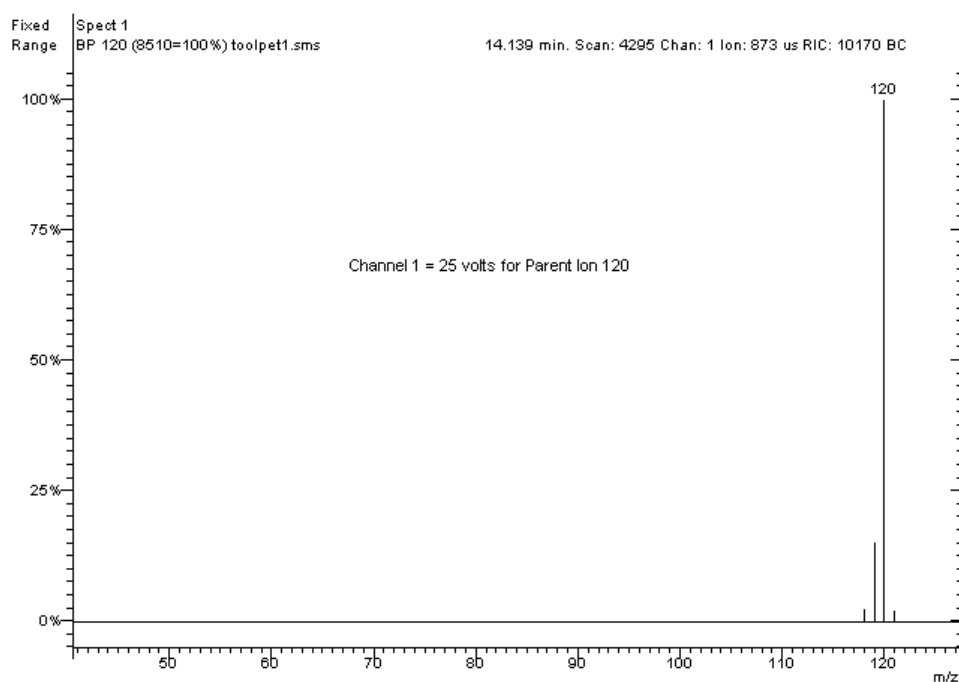


Figure 5.4.1: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 1 = 25 V CID excitation amplitude.

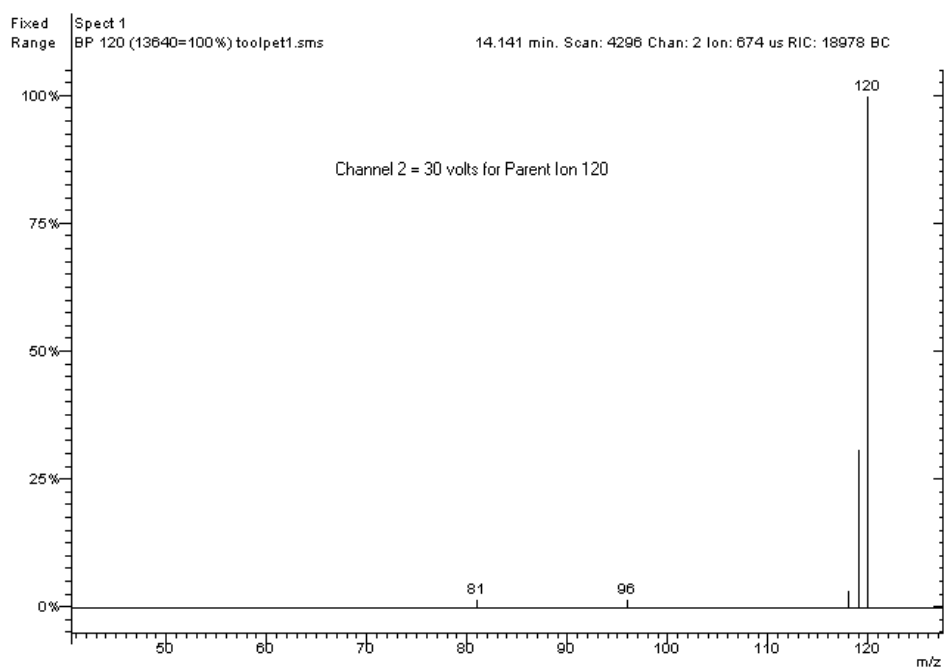


Figure 5.4.2: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 2 = 30 V CID excitation amplitude.

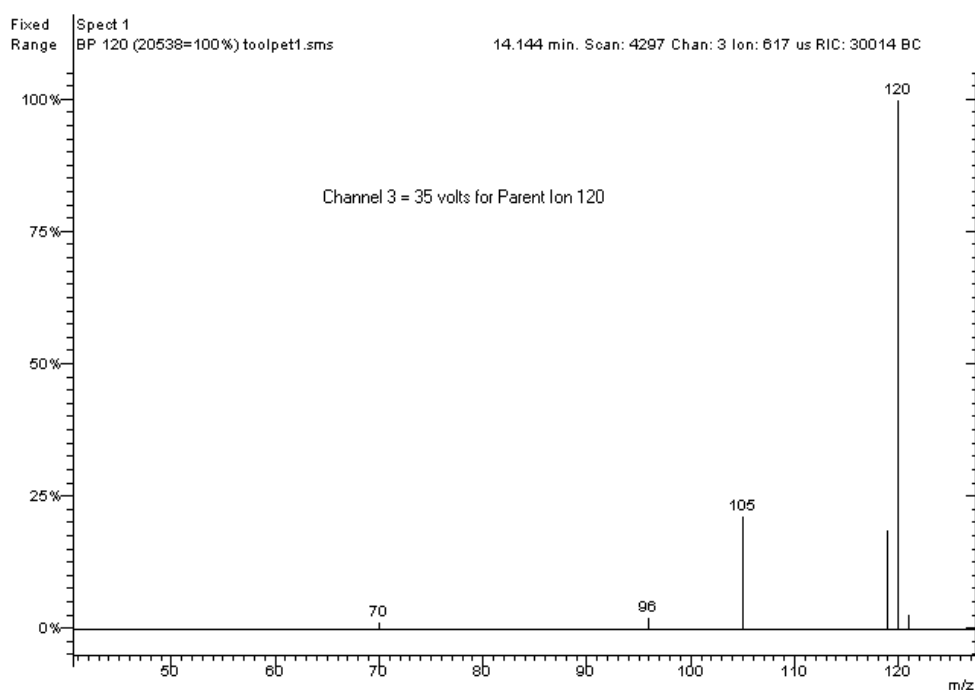


Figure 5.4.3: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 3 = 35 V CID excitation amplitude.

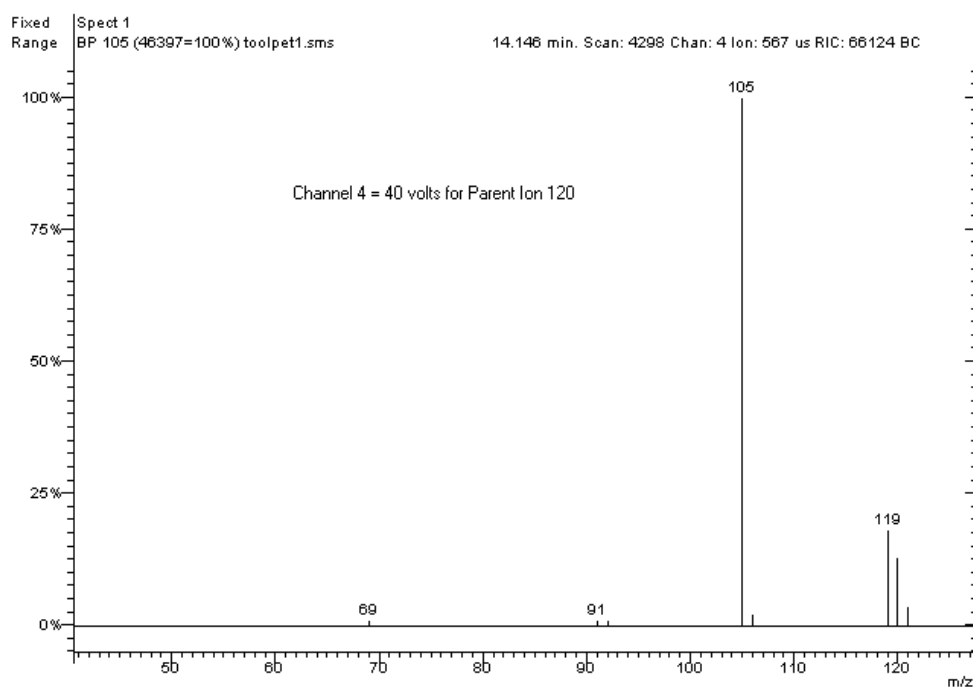


Figure 5.4.4: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 4 = 40 V CID excitation amplitude.

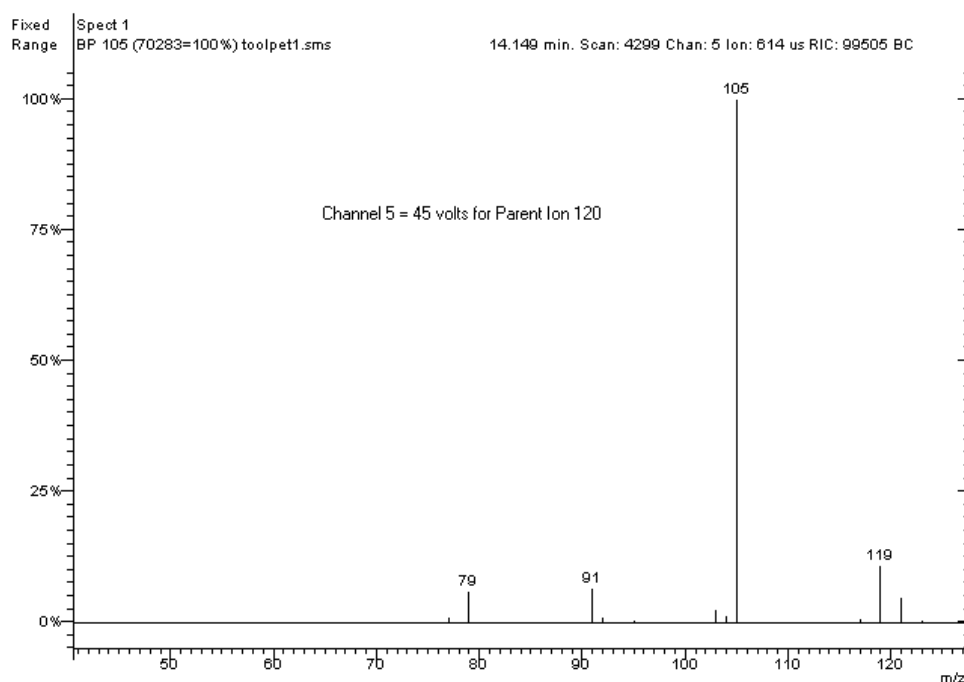


Figure 5.4.5: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 5 = 45 V CID excitation amplitude.

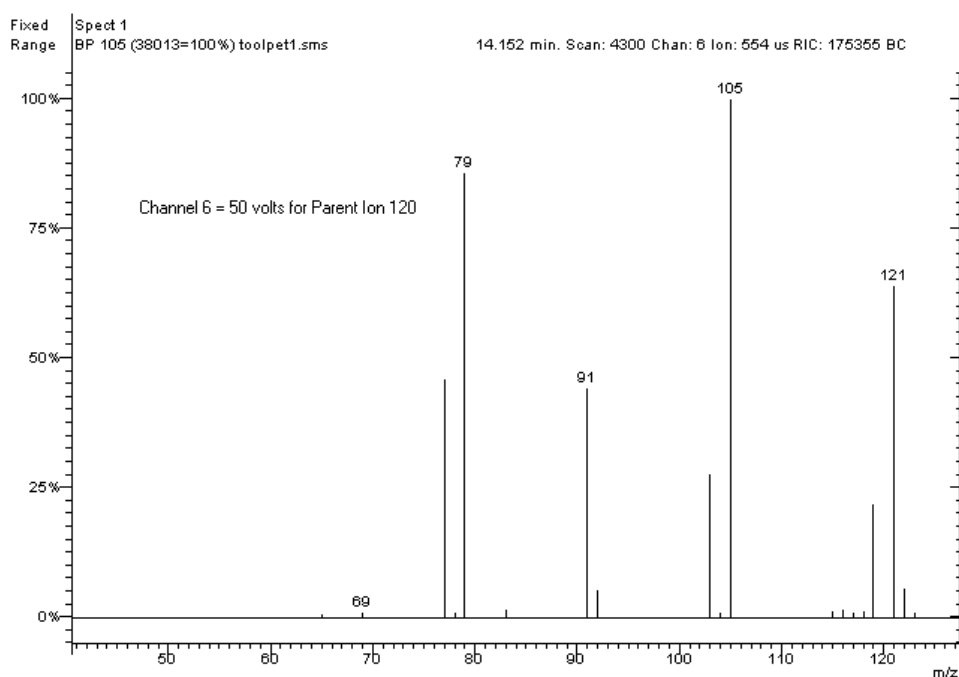


Figure 5.4.6: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 6 = 50 V CID excitation amplitude.

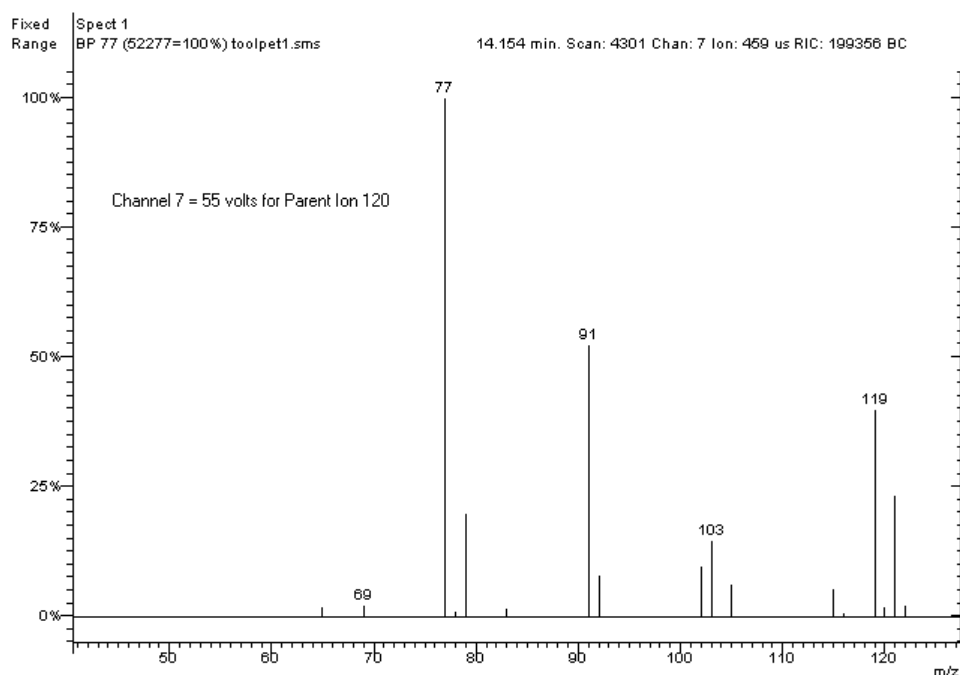


Figure 5.4.7: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 7 = 55 V CID excitation amplitude.

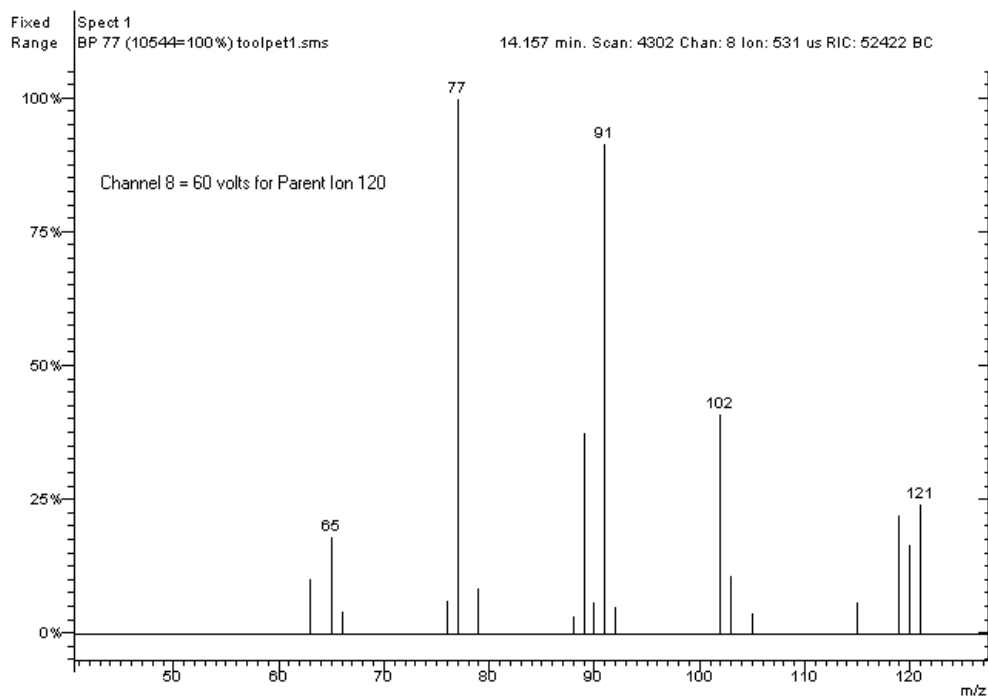


Figure 5.4.8: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 8 = 60 V CID excitation amplitude.

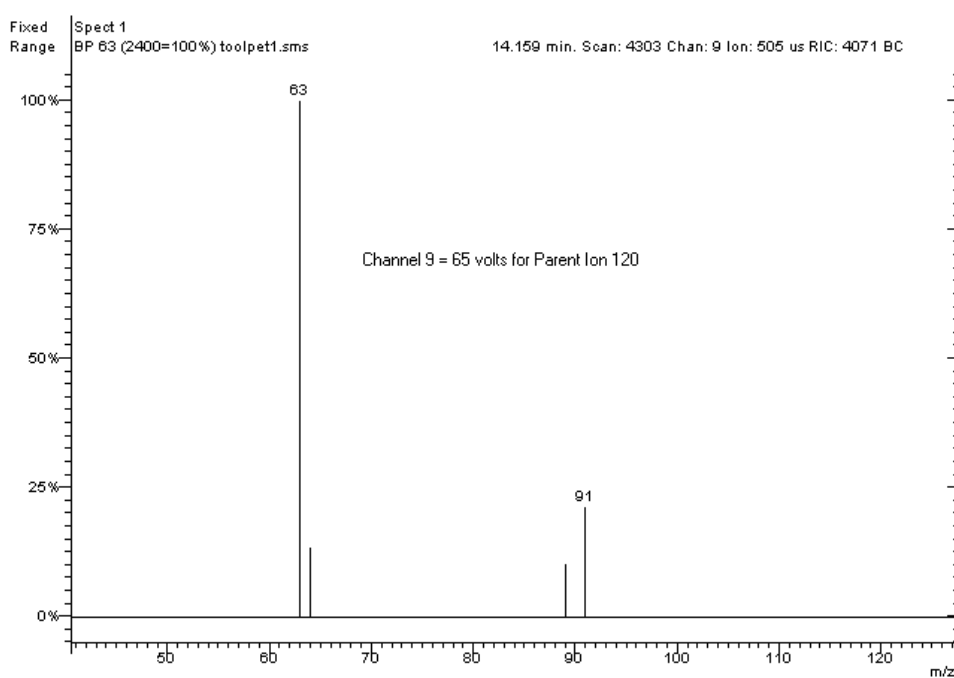


Figure 5.4.9: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 9 = 65 V CID excitation amplitude.

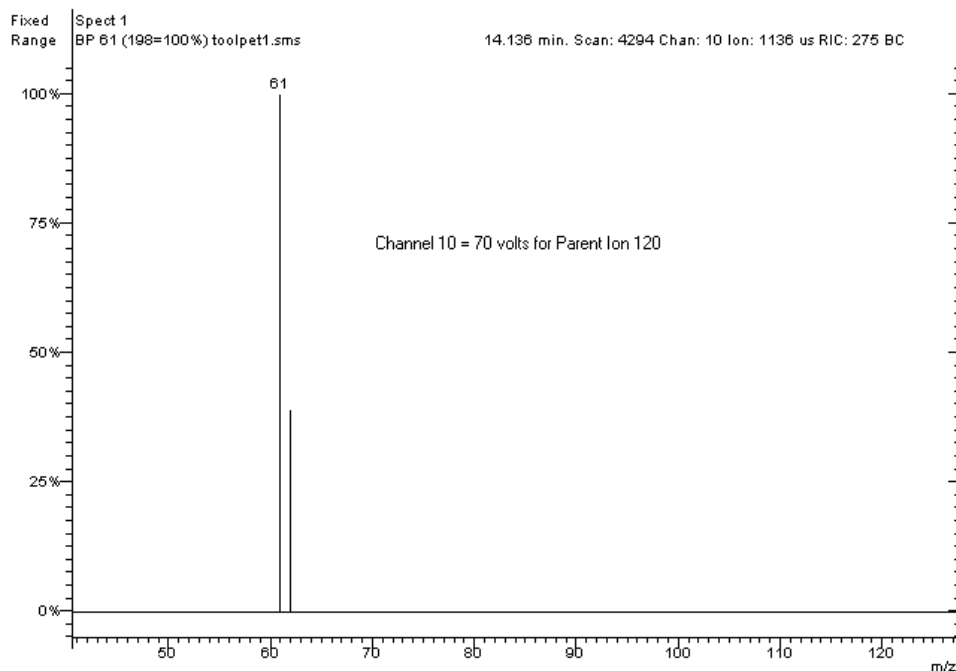


Figure 5.4.10: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 10 = 70 V CID excitation amplitude.

A second AMD is developed and run wherein the voltage increments are smaller, so as to determine the optimum CID voltage for that specific parent ion of $m/z = 120$. Since 45 V for the parent ion of $m/z = 120$ was sufficient (Figure 5.4.5), the voltages selected roughly cover this range from 43 V to 52 V. Figures 5.5.1 to 5.5.10 demonstrate the change in the product ion spectrum with single voltage increments. Notice how the $m/z = 120$ ion decreases in intensity, while the $m/z = 91$ and $m/z = 79$ ions increase in intensity. Figure 5.5.5 provides the most acceptable product ion spectrum for 1, 2, 4-trimethylbenzene ($m/z = 120$) at 47 V. This value will then be applied to the MS-MS analysis of the C3-alkylbenzene aromatics. The same principle is followed for all the selected parent ions for the characteristic aromatic hydrocarbon volatiles selected for petrol.

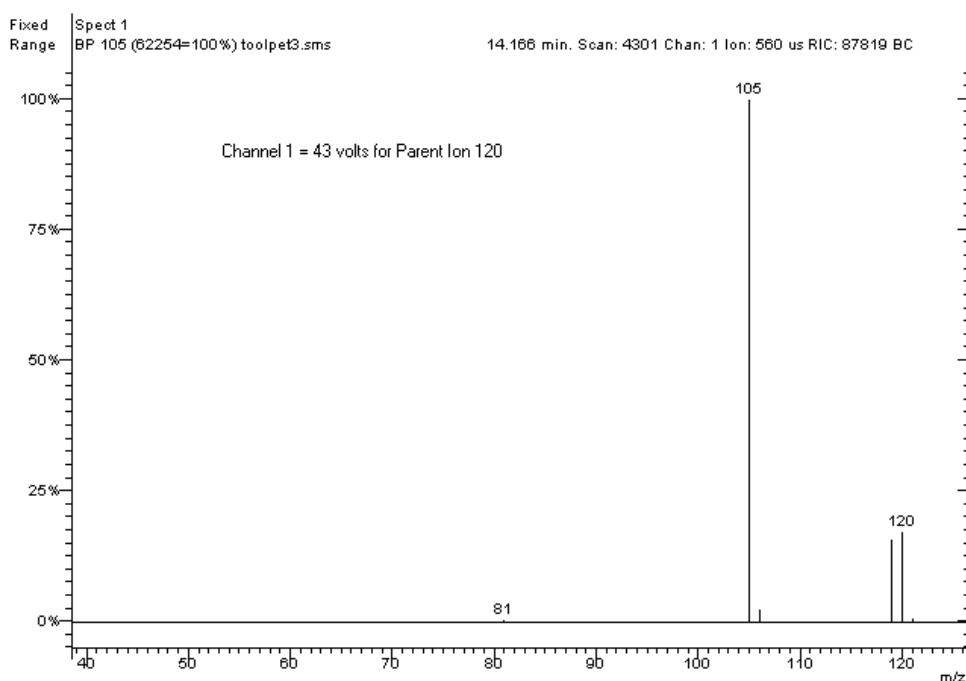


Figure 5.5.1: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 1 = 43 V CID excitation amplitude.

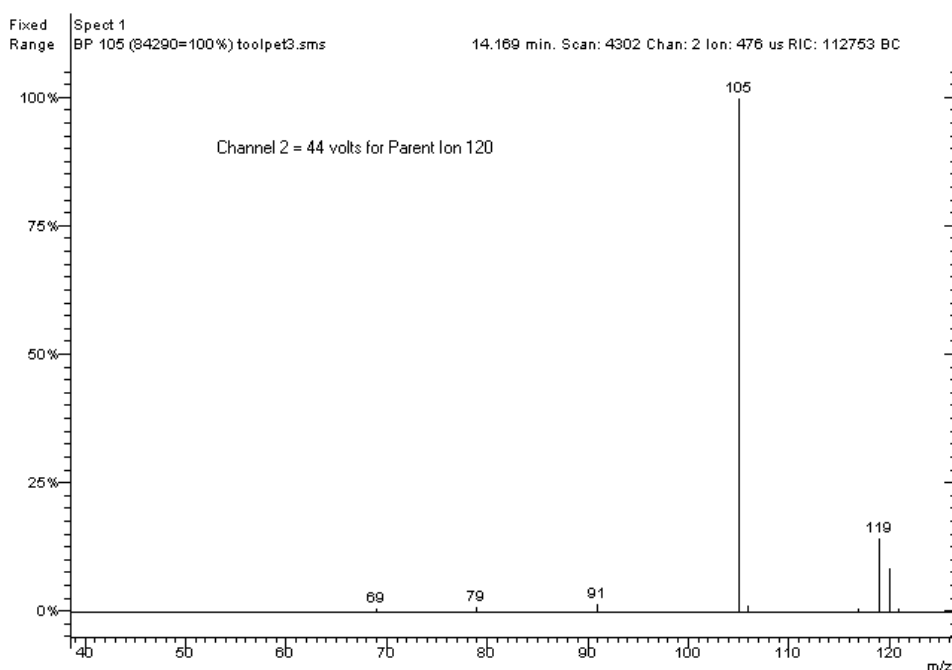


Figure 5.5.2: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 2 = 44 V CID excitation amplitude.

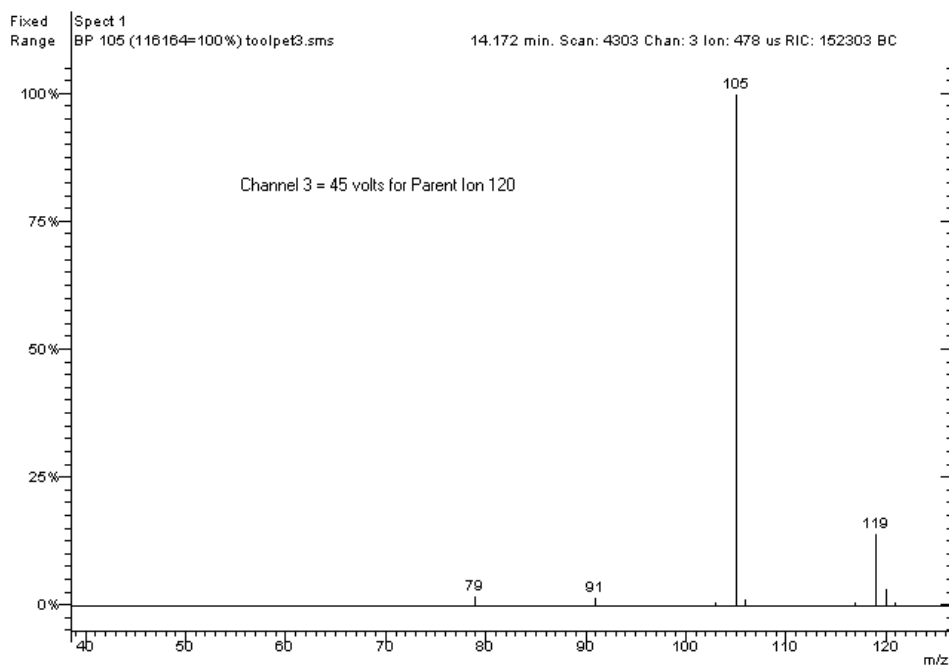


Figure 5.5.3: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 3 = 45 V CID excitation amplitude.

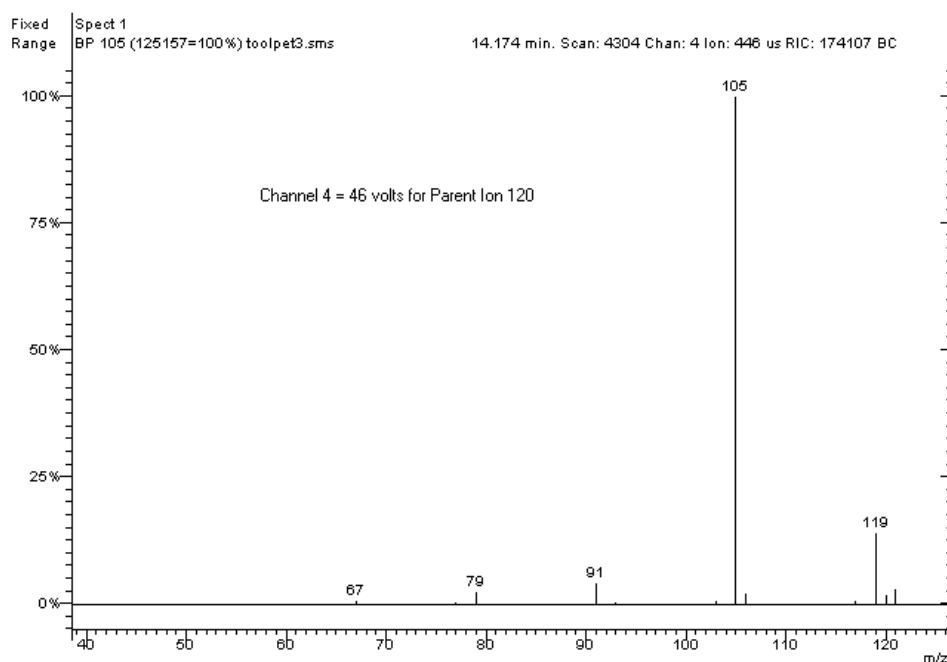


Figure 5.5.4: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 4 = 46 V CID excitation amplitude.

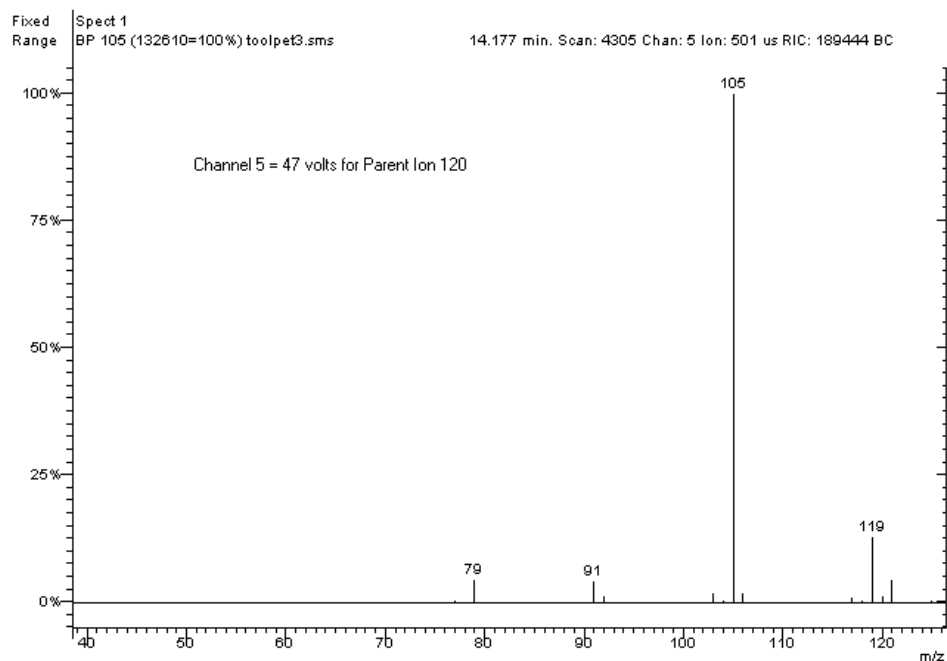


Figure 5.5.5: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 5 = 47 V CID excitation amplitude.

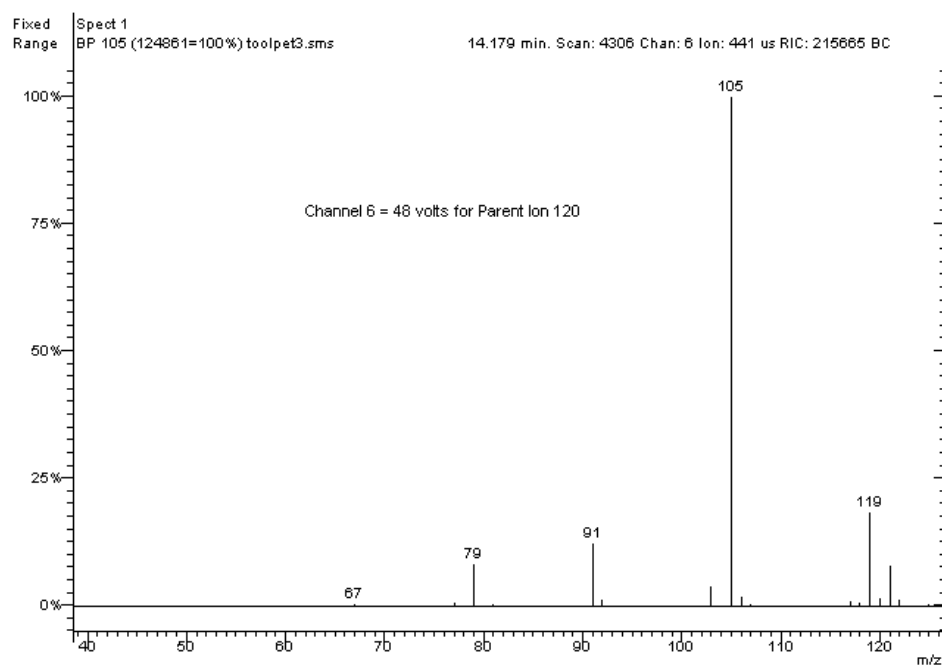


Figure 5.5.6: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 6 = 48 V CID excitation amplitude.

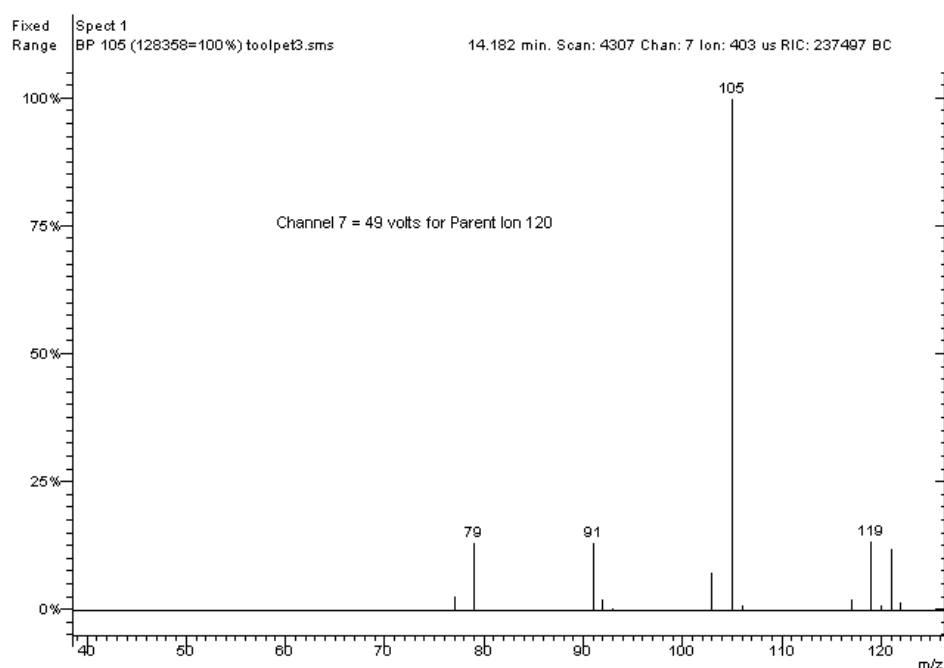


Figure 5.5.7: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 7 = 49 V CID excitation amplitude.

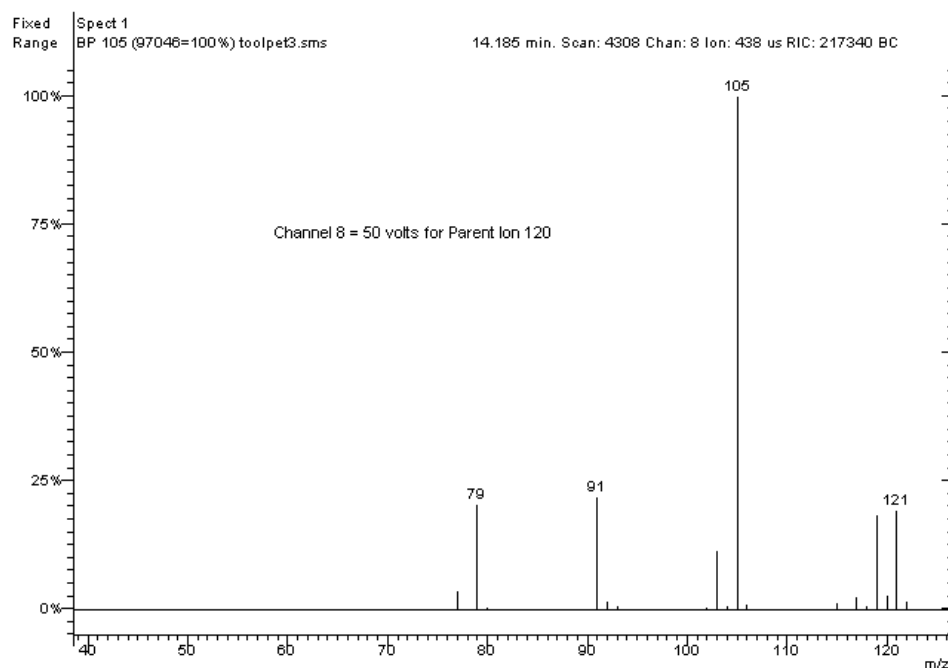


Figure 5.5.8: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 8 = 50 V CID excitation amplitude.

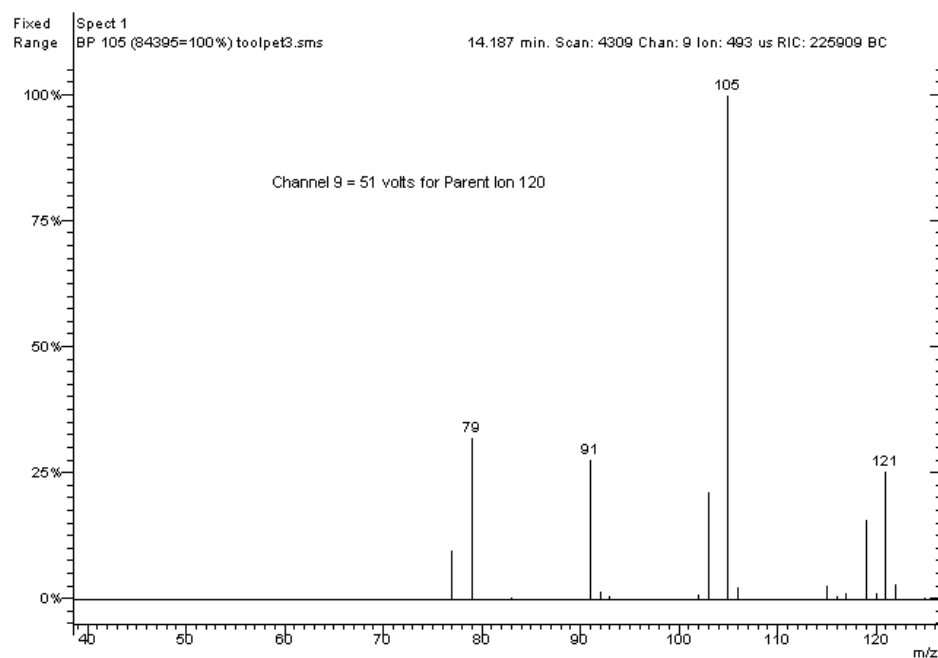


Figure 5.5.9: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 9 = 51 V CID excitation amplitude.

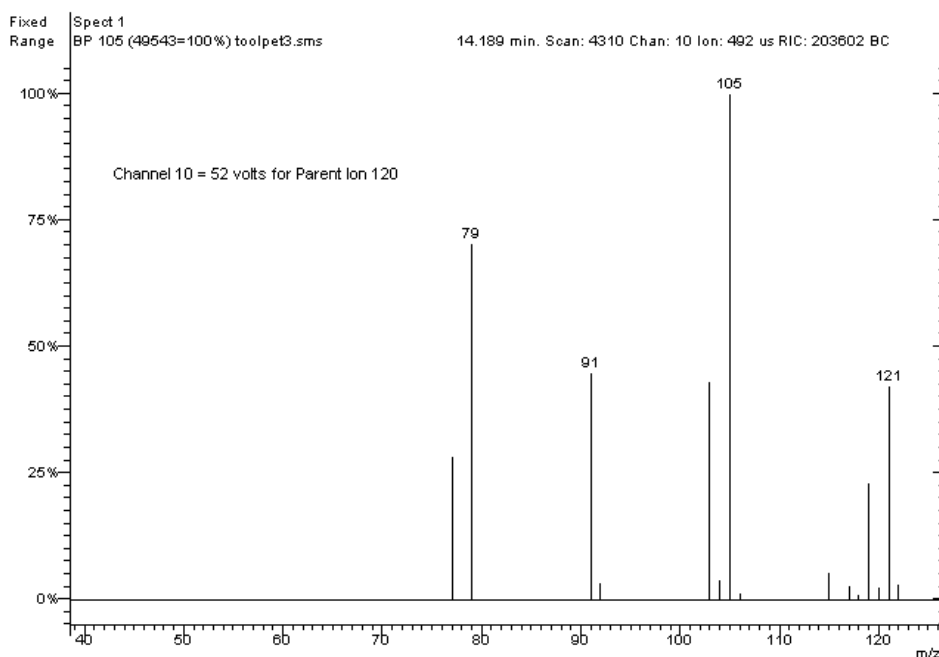


Figure 5.5.10: AMD product ion mass spectrum for 1,2,4-trimethylbenzene (parent ion mass = 120), channel 10 = 52 V CID excitation amplitude.

5.4.1 Effect of Incorrect Storage Level Selection

The CID rf excitation storage level is the storage level in m/z when the dissociation waveform is applied following the isolation. The excitation storage level range depends on the parent mass, but the storage level must be more than 2 mass units below the lowest required product ion value [69]. The default value is 48 m/z. The excitation storage level is set to avoid ejection of the lowest mass product ion to be measured. A parent ion, *e.g.*, 1, 2, 4-trimethylbenzene with $m/z = 120$, dissociates to form product ions with m/z values of 105, 91 and 79. The storage level value would not be set at 70 m/z, but rather at 50 m/z. Storage of rf values are often reported in terms of the Mathieu “q” parameter (more fully discussed in Chapter 4). The value of the “q” parameter determines the stability of the parent ion trajectory. More stable trajectories allow higher excitation voltages to be applied before ions are ejected from the trap. It has been empirically observed that a “q” value of 0.4 provides an optimum yield of product ions. The “q” calculator utility determines the

corresponding CID rf excitation storage level following user entry of a desired parent ion mass, with the minimum storage level value used of 48 m/z (Figure 4.8 and 4.9) [69].

It must be borne in mind that the value obtained from the "q" calculator is an indication of the optimum yield of product ions with a minimum storage level value of 48 m/z. The storage value obtained for a parent ion with $m/z = 120$ is 52.7 m/z. If it is necessary to observe product ions below this 52.7 m/z then a lower storage value can be used. Storage values lower than 48 m/z will then include product ions from low boiling aromatic hydrocarbons. The reason for selecting the optimum yield of product ions is so that the abundant lower masses are excluded if they are not considered diagnostic ions characteristic of accelerants.

Figure 5.6 illustrates the effect on the total ion signal of setting the excitation storage level too high (The CID amplitude voltages were the same for each component). The benzene peak (peak no 1) is completely absent. A storage level of 75 m/z is too near the molecular ion for benzene ($m/z = 78$) and when benzene fragments, the product ions are lost ($m/z = 51, 50$ and 39). Looking at the peaks for 1, 2, 4-trimethylbenzene (peak no. 7) and indane (peak no. 8), the peaks do not follow the expected abundance. The same happens for naphthalene (peak no. 9) and 2-methylnaphthalene (peak no. 10).

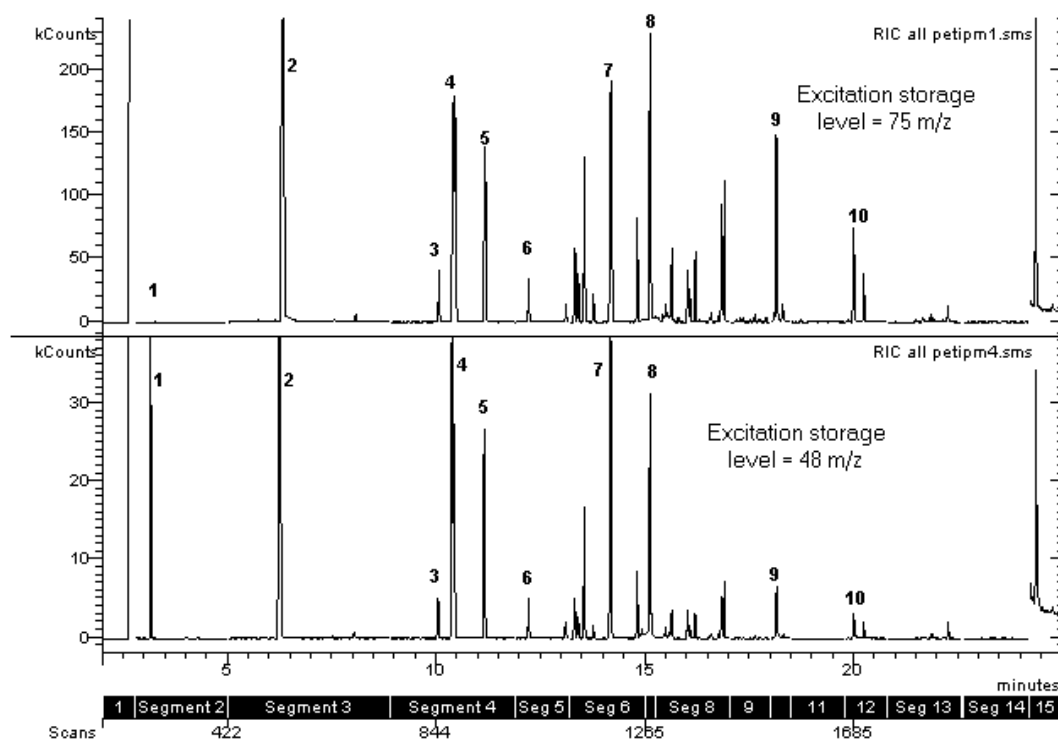


Figure 5.6: The AMD product ion chromatogram for a minimum excitation storage level incorrectly set at 75 m/z (upper trace) and correctly set at 48 m/z (lower trace). (1) benzene, (2) toluene, (3) ethylbenzene, (4) m,p-xylene, (5) o-xylene, (6) isopropylbenzene, (7) 1,2,4-trimethylbenzene, (8) indane, (9) naphthalene, (10) 2-methylnaphthalene.

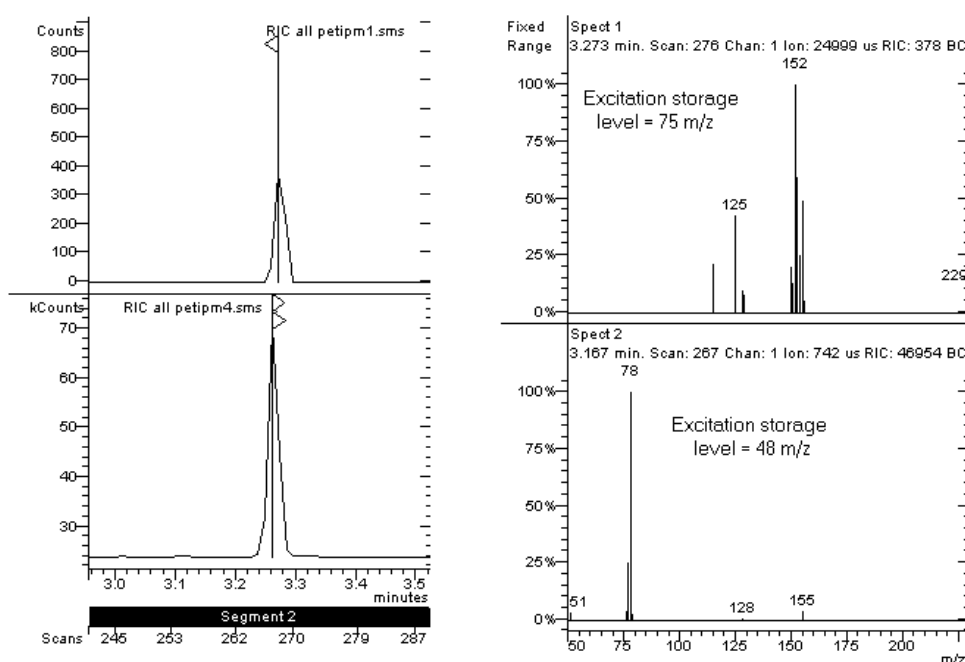


Figure 5.7.1: AMD product ion chromatographic peak and mass spectrum for benzene (78 m/z , CID voltage for channel 1 = 59). The upper trace product mass spectrum is obtained when the excitation storage level is set too high. The expected product mass spectrum is reflected in the lower trace with an excitation storage level of 48 m/z .

Figure 5.7.1 illustrates this effect more clearly. The expected product mass spectrum for benzene is $m/z = 78$, 77 and 51. This is then the spectrum for which the CID amplitude voltage would be corrected until the desired product ion mass spectrum is obtained. The upper trace reflects the product ion mass spectrum obtained when the excitation storage level is set at 75 m/z . The product ions formed are completely unrelated to benzene. The benzene peak is dissociated, but the desired product ions formed are ejected. The ions heavier than the original parent ion are clearly the result not of dissociation but of ion molecule reactions forming adducts inside the ion trap. The product ion mass spectra of selected parent ions for toluene, ethylbenzene, 1, 2, 4-trimethylbenzene and indane are also not properly dissociated. This effect can be seen in Figures 5.7.2 and 5.7.3. Compare with figures 5.14.2 – 5.14.6, Annexure B, for correct fragmentation.

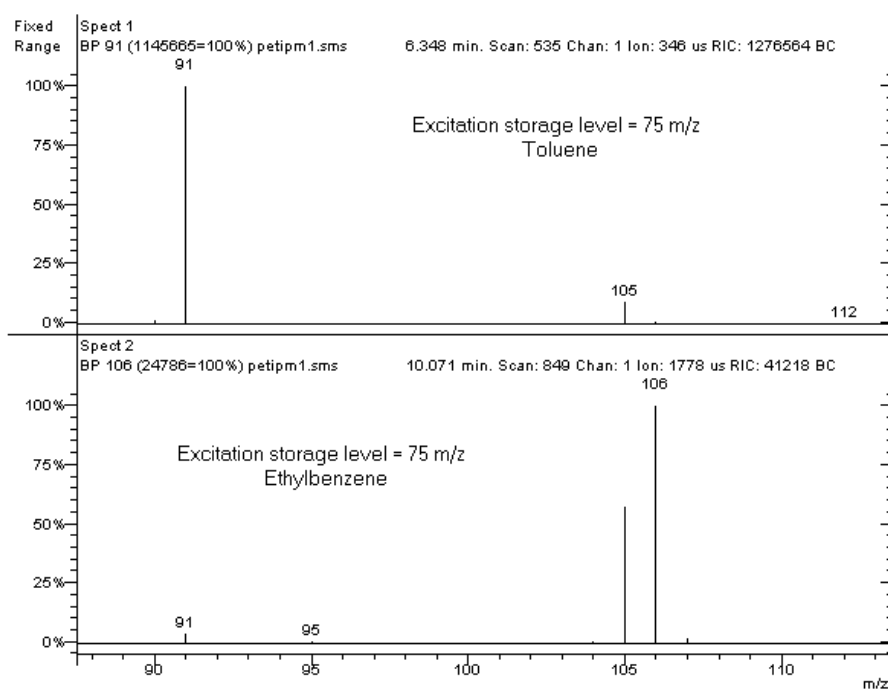


Figure 5.7.2: AMD product ion mass spectrum for toluene ($m/z = 92$, CID amplitude voltage = 57 for channel 1) and ethylbenzene ($m/z = 106$, CID voltage = 57 for channel 1).

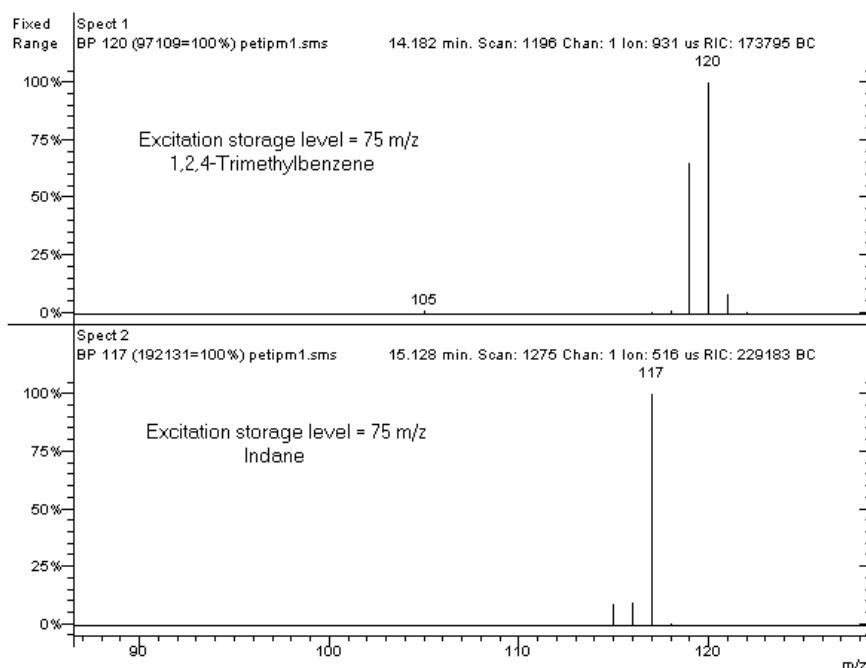


Figure 5.7.3: AMD product ion mass spectrum for 1,2,4-trimethylbenzene ($m/z = 120$, CID amplitude voltage = 53 for channel 1) and Indane ($m/z = 117$, CID amplitude voltage = 53 for channel 1).

The correct storage level for benzene should be 34.1 m/z as determined using the “q” calculator utility, but the minimum advised storage level to prevent space charge effects is 48 m/z [69]. The calculated storage level for toluene is 39.9 m/z and for ethyl benzene it is 46.5. The excitation storage level used for benzene, toluene and ethyl benzene is, therefore, m/z = 48. For 1, 2, 4-trimethylbenzene (m/z = 120) and indane (m/z = 117) it is 52.7 m/z and 51.4 m/z respectively. Figure 5.8.1 illustrates the product ion mass spectra obtained for benzene and toluene at the selected minimum excitation storage level of 48 m/z. The spectra still require additional dissociation as there are not enough product ions present, but this can be corrected by selecting the appropriate CID amplitude voltage determined by using the AMD software. Figures 5.8.2 to 5.8.4 in [Annexure B](#) are further examples of the effect of the correctly selected excitation storage levels for the diagnostic aromatic ions indicative of accelerants.

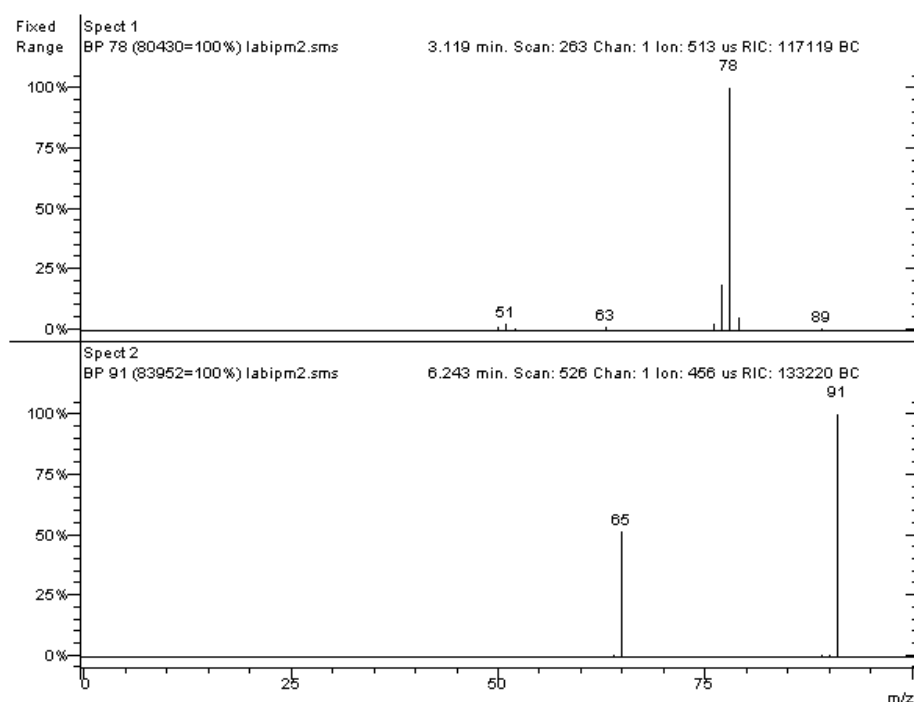


Figure 5.8.1: AMD product ion mass spectrum for benzene (m/z = 78) and toluene (m/z = 92) using the minimum advised excitation storage level of 48 m/z.

5.4.2 Initial “Toolkit” Mass Spectra

Below are some examples of the initial mass chromatographic data collected using the original “toolkit” software for automated method development. The software initially collected the raw data and after the data collection, the data had to be merged in order to create a continuum peak. Figures 5.9.1 to 5.9.4 illustrate the difference between the collected raw data, reflecting each successive CID mass spectrum and the smoothing effect of the merged data. Figure 5.9.4 shows a comparison between the GC-MS chromatogram and the GC-MS-MS toolkit product ion chromatogram of the selected C2, C3 and C4-alkylbenzenes indicative for petrol.

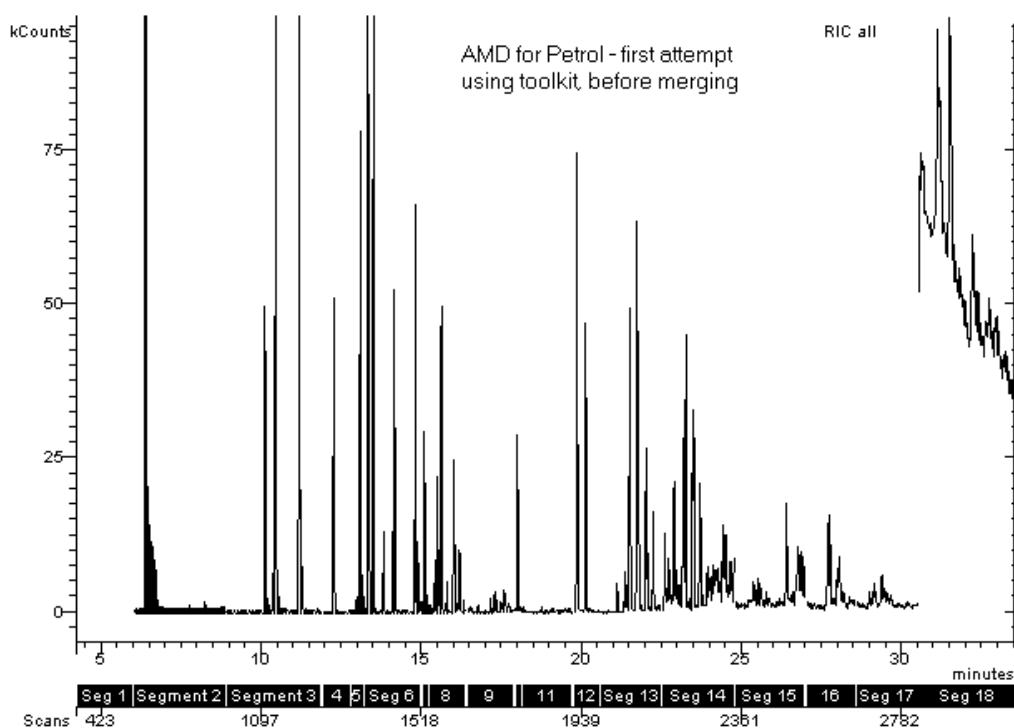


Figure 5.9.1: AMD product total ion chromatogram for petrol using “toolkit”. The data points have not been merged.

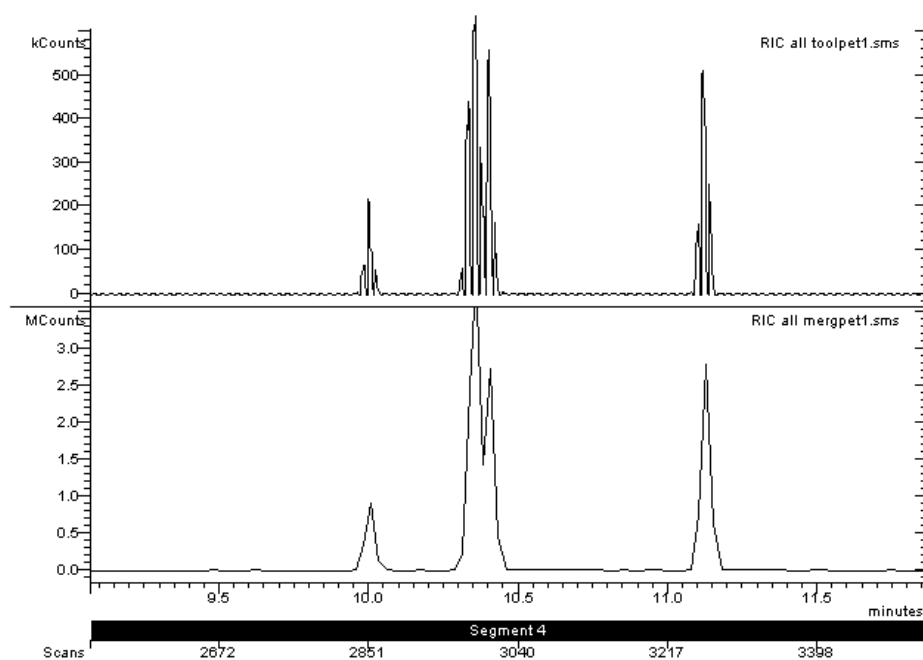


Figure 5.9.2: AMD product ion chromatogram for ethylbenzene and the xylenes. The chromatogram in the upper trace is the raw data. The chromatogram in the lower trace has been merged.

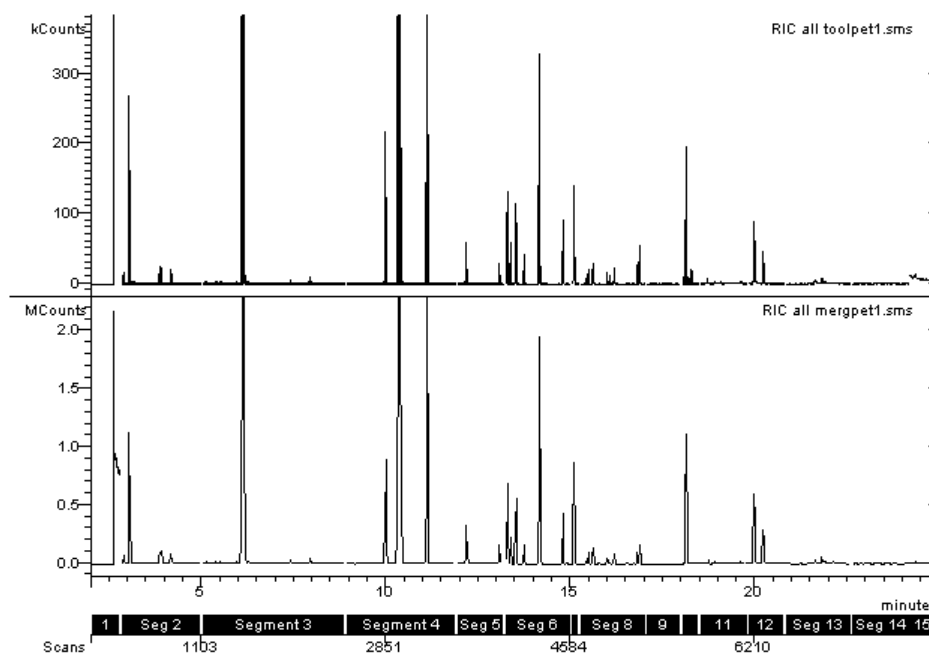


Figure 5.9.3: The total product ion chromatogram for petrol using toolkit. The chromatogram in the upper trace is the raw data. The chromatogram in the lower trace has been merged.

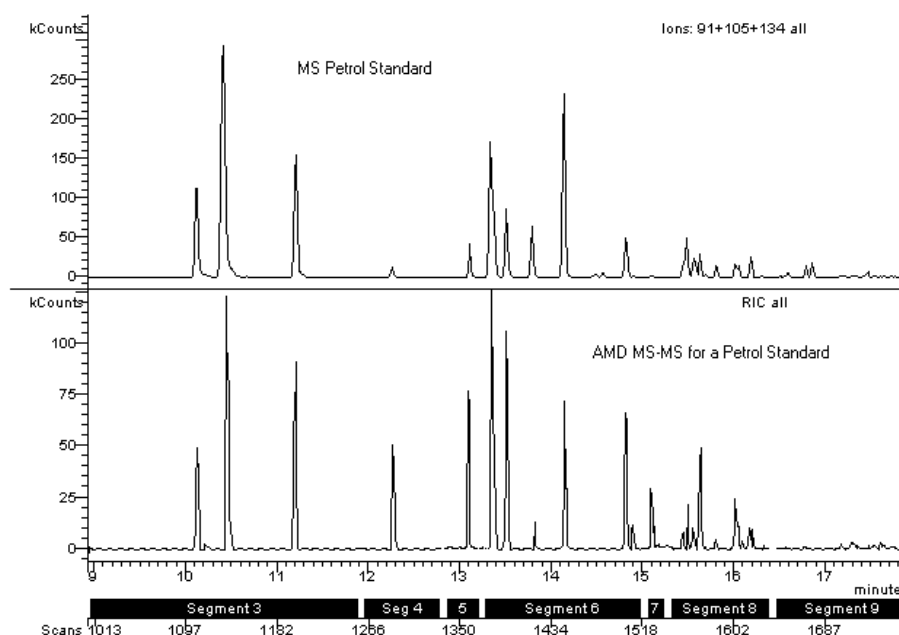


Figure 5.9.4: Comparison between the MS chromatogram for petrol and the MS-MS toolkit product ion chromatogram for petrol (merged).

Examining the product ion mass spectrum of each selected aromatic diagnostic ion led to the decision to try to obtain more information in the region of the C4 and C5-alkylbenzenes. Indane is included because the retention time for indane lies between p-isopropyltoluene and the next C4-alkylbenzene. The C3-alkylbenzene (1, 2, 3-trimethylbenzene) lies right next to the C4-alkylbenzene (p-isopropyl-toluene). This makes it tricky to select the correct retention time gap for the various timing segments for each selected parent ion. The methylindanes and dimethylindanes are not included because they are obscured by the C4, C5 and C6-alkylbenzenes and the alkylbenzenes are the preferred diagnostic ions.

Figure 5.10.1 indicates an area of C5-alkylbenzenes around RT = 16.5 min that is not very specific for the selected parent ion $m/z = 134$. This area contains C5-alkylbenzenes ($m/z = 148$) and C4-alkylbenzenes ($m/z = 134$). By isolating the $m/z = 148$ in the C4-alkylbenzene area ($m/z = 134$), the C5-alkylbenzenes are enhanced. Although it is a narrow band of $m/z = 148$ within the

$m/z = 134$ region, it allows for the verification of the presence of C5-alkylbenzenes in that region. This effect can be seen in Figure 5.10.2.

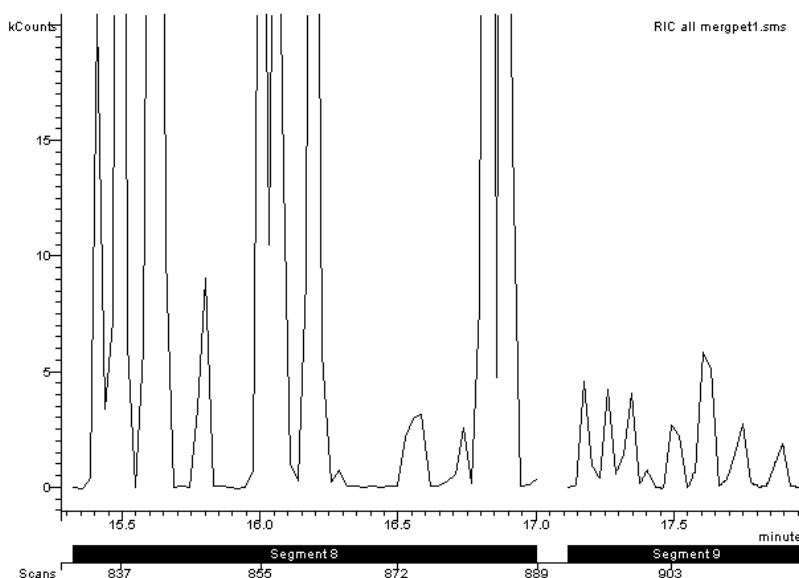


Figure 5.10.1: Selected AMD product ion mass chromatogram for the C4 and C5-alkylbenzenes.

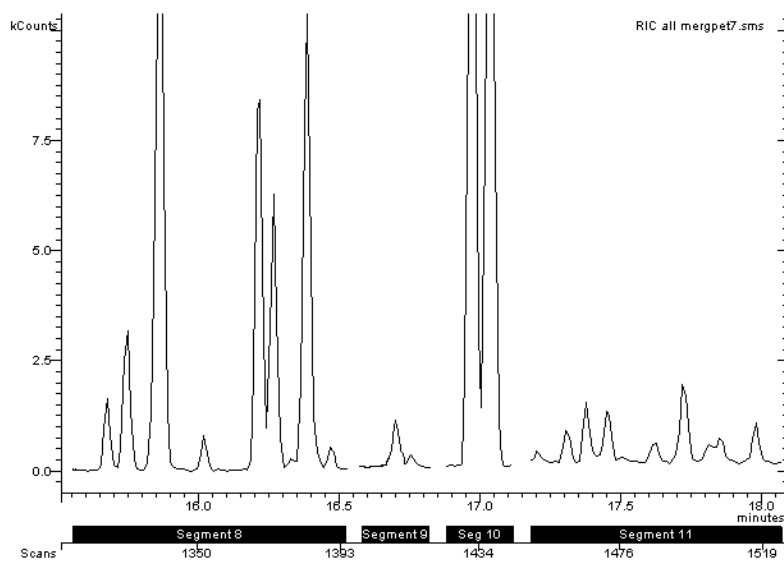


Figure 5.10.2: Selected AMD product ion mass chromatogram for the C4 and C5-alkylbenzenes.

In order to check the validity of the AMD criteria, before finalizing the CID amplitude voltages, a simulated aromatic mixture (the aromatic hydrocarbon compounds selected were those available in the laboratory) was injected and the mass spectra compared with those obtained for petrol (Figure 5.11.1 and Figures 5.11.2 to 5.11.12 in Annexure B). It was significant to notice the absence of C6-alkylbenzenes, including the hexylbenzene peak in petrol (Figure 5.11.11, Annexure B) and this enforced the reason for having to verify the choice of CID amplitude voltages against laboratory standards to ensure that the parent ions selected will form reproducible diagnostic product ions.

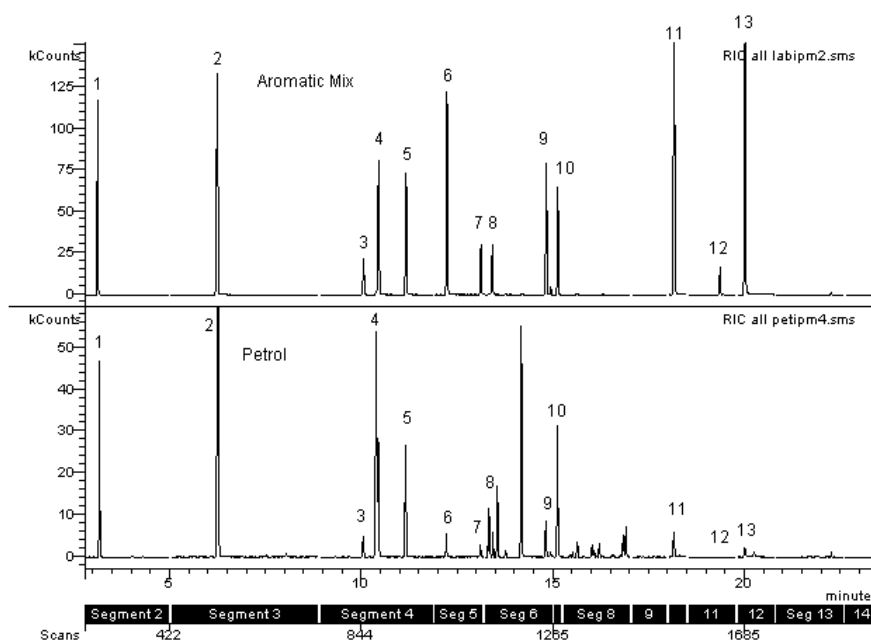


Figure 5.11.1: The AMD product ion mass chromatogram for a simulated aromatic mixture (upper trace) with the AMD product ion mass chromatogram for petrol (lower trace).

[(1) benzene, (2) toluene, (3) ethylbenzene, (4) *p*-xylene, (5) *o*-xylene, (6) isopropylbenzene, (7) propylbenzene, (8) mesitylene, (9) *p*-isopropyltoluene, (10) indane, (11) naphthalene, (12) hexyl-benzene, (13) 2-methylnaphthalene].

After the CID amplitude voltages have been established using AMD, the initial AMD product ion mass spectrum was then compared against the final AMD product ion mass spectrum for the same parent ion to ensure the correct product ion spectra are

obtained that are characteristic of the aromatic diagnostic ions for petrol and that the product ion spectra are comparable with the MS spectra for the same aromatic diagnostic ions for petrol. These comparisons can be seen for benzene in figure 5.12.1 and for the remainder of the selected parent ions in figures 5.12.2 to 5.12.13 in [Annexure B](#).

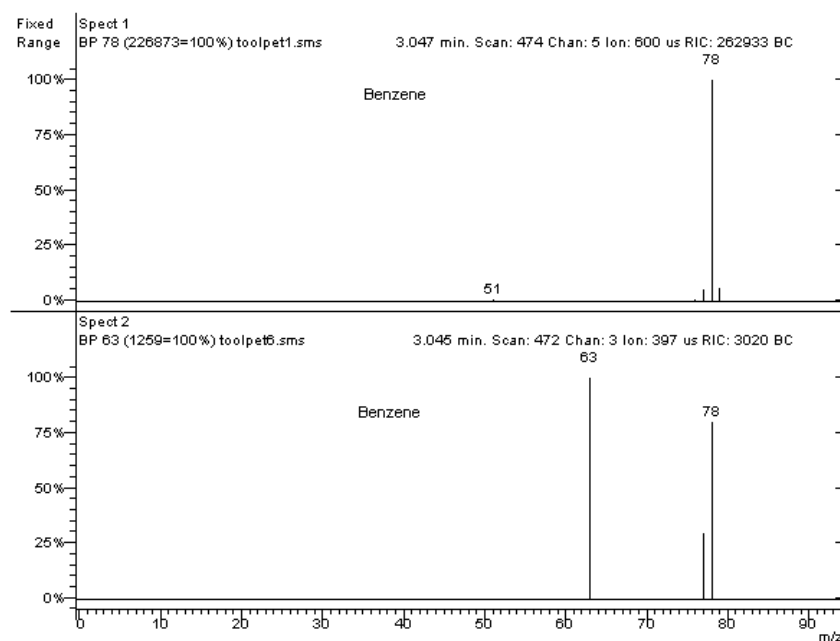


Figure 5.12.1: Comparison between the initial and final AMD product ion mass spectra for benzene.

5.5 TANDEM MASS SPECTRA

Once all the collision induced dissociation (CID) voltage parameters and the excitation CID rf storage levels for each selected parent ion have been established using the AMD software and "q"-calculator utility, the AMD parameters can then be directly transferred to the MS-MS method. Product ion mass spectra can then be generated that are characteristic of the selected diagnostic aromatic ions for a petrol standard. Table 5.6 provides the optimised conditions for obtaining MS-MS data. These are the conditions that were applied during this study to obtain reproducible MS-MS product ion spectra for petrol standards, lab standards, real-life samples and other ignitable liquid standards. The same chromatographic conditions used for component separation during the automated method development (AMD) stage, were used for the MS-MS

chromatographic separation. Non-resonant excitation was again selected so as to ensure that a dipole waveform is applied, exciting all ions in the trap simultaneously. The CID excitation time was maintained at 20 msec and the amplitude range was maintained at 20.00 V (default values). The emission current was reduced from 50 to 10 μA and 3 μscans per scan were collected instead of only 1 μscan per scan, with an isolation window of 1 instead of 3. The instrument conditions are given in Table 5.5 below:

Table 5.5: GC, MS and MS-MS Conditions

GC Conditions:

Column:	Chrompack WCOT Fused Silica 30 m x 0.25 mm capillary column with CP Sil 8CB DF = 0.25 μm film coating.
Temperature program:	30 $^{\circ}\text{C}$ for 6 min, 30 $^{\circ}\text{C}$ – 70 $^{\circ}\text{C}$ @ 8 $^{\circ}\text{C}$ / min no hold, 70 $^{\circ}\text{C}$ – 270 $^{\circ}\text{C}$ @ 10 $^{\circ}\text{C}$ / min, hold at 270 $^{\circ}\text{C}$ for 4 min.
Injector temperature:	180 $^{\circ}\text{C}$
Column flow rate:	1,2 ml / min Helium

MS and AMD Conditions:

Scan range:	40-300 amu (atomic mass units)
Scan rate:	0.910 s (3 μScans per scan)
Background mass:	35 amu
Trap temperature:	120 $^{\circ}\text{C}$
Manifold temperature:	45 $^{\circ}\text{C}$ (manifold has separate heater)
Transfer line temperature:	270 $^{\circ}\text{C}$
Emission current:	10 μA (micro Amps)
AGC prescan ionization time:	100 μs (micro seconds) for MS
AGC prescan ionization time:	1500 μs for MS-MS data collection
Target TIC:	10 000 counts

Table 5.6: CID Voltages for each Selected Mass

Segment No	Segment Time (min)	Ion Mode	Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	Parent Ion
1	0:00-3:00	EI	-	-	-	-	-
2	3:00-3:40	EI	-	-	-	-	-
3	3:40-6:00	MS-MS	78	1	67	48.0	Benzene
4	6:00-10:00	MS-MS	91	1	61	48.0	C1-Benzenes
5	10:00-12:89	MS-MS	106	1	55	48.0	C2-Benzenes
6	12:89-14:14	MS-MS	120 (105)	1	50	52.7	Isopropyl- benzene & propylbenzene
7	14:14-15:66	MS-MS	120	1	47	52.7	C3-Benzenes
8	15:66-15:95	MS-MS	117	1	55	51.4	Indane
9	15:95-16:82	MS-MS	134	1	47	58.9	C4-Benzenes
10	16:82-17:10	MS-MS	148	1	50	65.1	C5-Benzenes
11	17:10-17:42	MS-MS	134	1	47	58.9	C4-Benzenes
12	17:42-18:24	MS-MS	148	1	50	65.1	C5-Benzenes
13	18:24-18:60	MS-MS	162	1	52	71.3	C6-Benzenes
14	18:60-19:70	MS-MS	128	1	70	56.2	Naphthalene
15	19:70-20:80	MS-MS	142	1	69	62.4	C1- Naphthalenes
16	20:80-22:20	MS-MS	156	1	67	68.6	C2- Naphthalenes
17	22:20-24:70	MS-MS	170	1	69	74.8	C3- Naphthalenes
18	24:70-29:00	EI	-	-	-	-	-

There is no fixed rule that stipulates the amount of CID voltage (amplitude in V) that is required for a specific product ion mass spectrum. It depends entirely on the amount of information that is required from the product ion spectrum. If the spectrum is to be compared with that obtained by MS, then very little fragmentation is required. A low voltage would be selected. Examining the AMD fragmentation obtained for benzene in figure 5.12.1, it is clear that a low voltage was selected since the $m/z = 78$ ion, (CID amplitude voltage of 62), is still relatively intact. By increasing the voltage to

67, the product ion spectrum for benzene is altered. The $m/z = 78$ has almost disappeared and there is an entire array of product ions providing additional information. Figure 5.13.1 is an example of the final voltage selected for benzene. Figures 5.13.2 to 5.13.17 in Annexure B illustrates the product ion mass spectra for the final voltages selected for the remainder of the diagnostic aromatic parent ions characteristic for petrol.

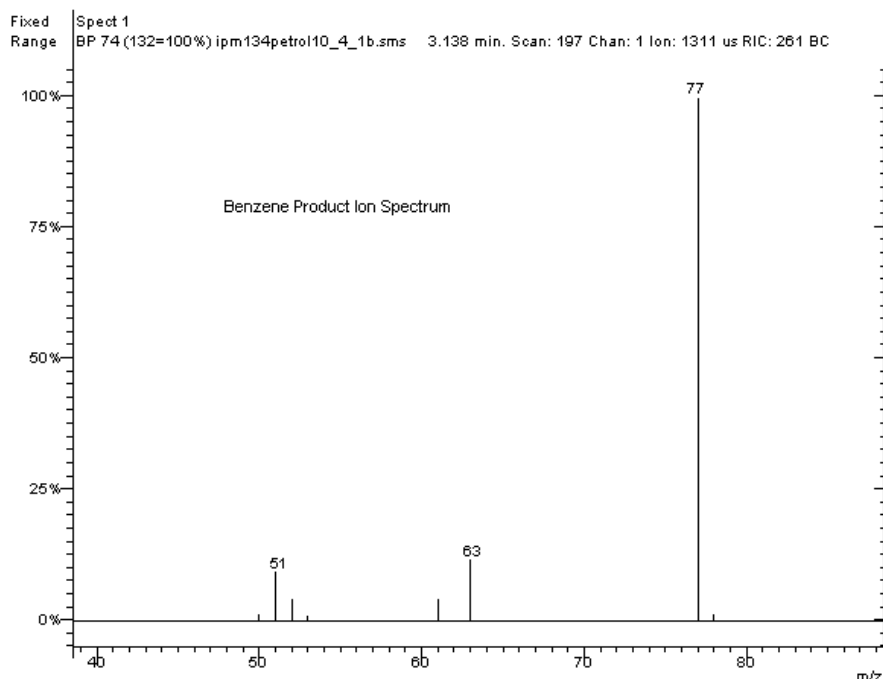


Figure 5.13.1: MS-MS product ion mass spectrum for benzene.

The question has been raised as to whether the MS-MS product ion spectra are comparable with available MS software libraries. This will entirely depend on the CID amplitude voltage selected with which the product ion mass spectra are generated. The spectra would be similar, but not entirely comparable with a known MS spectrum for a specific aromatic parent ion. Figure 5.14.1 illustrates the comparison similarities between the MS spectrum for benzene and the MS-MS product ion spectrum for benzene. Here the benzene product ion spectrum is not severely fragmented and the spectrum is recognizable as benzene, although it would not give an acceptable library match to the MS spectrum for benzene. Figures 5.14.2 to 5.14.13 in Annexure B illustrate the comparison between the

alkylbenzene and alkylnaphthalene aromatics, which have been selected as the diagnostic parent ions for petrol.

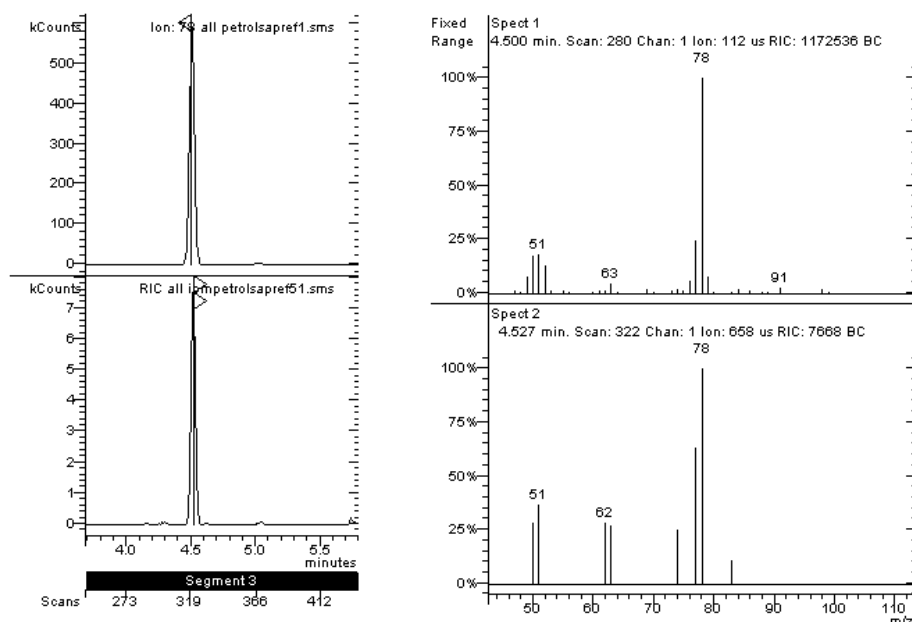


Figure 5.14.1: Comparison between the MS mass spectrum and the MS-MS product ion mass spectrum for benzene.

Intercomparison of MS-MS product ion spectra between different laboratories could prove beneficial and collaborative, if the criteria required to generate the MS-MS data can be standardized, although it must be remembered that it is the comparability of the sample and reference in the same GC-MS-MS laboratory that is important. GC-MS positives are not based on the comparability with data from another laboratory, thus it is not important to GC-MS-MS data either [96].

Different parent ions can be selected to represent the characteristic aromatic hydrocarbons under analysis from laboratory to laboratory, depending on the information required per analysis, but if a basic MS-MS method were to be set forth as an ASTM standard guide [29, 44, 46 - 48], this could then ensure conformity.

5.6 TANDEM MASS SPECTRA OF IGNITABLE LIQUIDS

MS-MS can be used for the identification of aromatic hydrocarbons in most of the commonly known ignitable liquid accelerants. It must only be decided what information is actually required. MS-MS is not useful for isolating the aliphatic hydrocarbon compounds since there are no distinguishing diagnostic ions between classes of straight chain aliphatic hydrocarbons, except for the molecular ion. The product ion spectra obtained for the aliphatic hydrocarbons do not differ significantly enough to be considered as a diagnostic tool. It has been mentioned (paragraph 5.3) that the sensitivity of the MS-MS technique also allows identification of residues of aromatic solvent blends used for coatings, paints, varnishes, adhesives and insecticides. The GC-MS analysis must, therefore, form part of the GC-MS-MS analysis for a total overview of the characteristic hydrocarbons actually present, both aromatic and aliphatic.

Figures 5.15.1 to 5.15.11 are examples of the MS-MS product ion mass chromatograms (conditions summarized in Table 5.6) for the more common ignitable liquid accelerants encountered, especially in South Africa. The chromatograms are uncomplicated and represent only the characteristic aromatic hydrocarbons selected that are important in the detection and identification of ignitable liquid accelerants. Similar chromatograms can also be obtained by selected ion monitoring in a conventional GC-MS. Tandem mass spectrometry is a two-stage process: Stage 1 involves the isolation and collision of the selected diagnostic parent ions. In this way the conditions in the ion trap are more selective for the aromatic hydrocarbons characteristic for ignitable liquids. In between the MS operations, the parent ions collide with the helium gas in the ion trap and undergo fragmentation (collision induced dissociation).

Stage 2 involves the product ion mass scanning that generates and records the new fragmentation pattern obtained as a product ion spectrum. The product ion spectrum is thus very specific for ignitable liquid components and has exceptionally little interference, if any, from other burnt components in the sample.

In the following chapter, chapter 6, specific examples will be discussed to illustrate the enhanced sensitivity and selectivity of GC-MS-MS. This enhanced sensitivity and selectivity is brought about by trapping only those selected parent ions in the ion trap and ejecting all others. This ensures a more definitive response, resulting in more defensible chromatographic evidence presented in court.

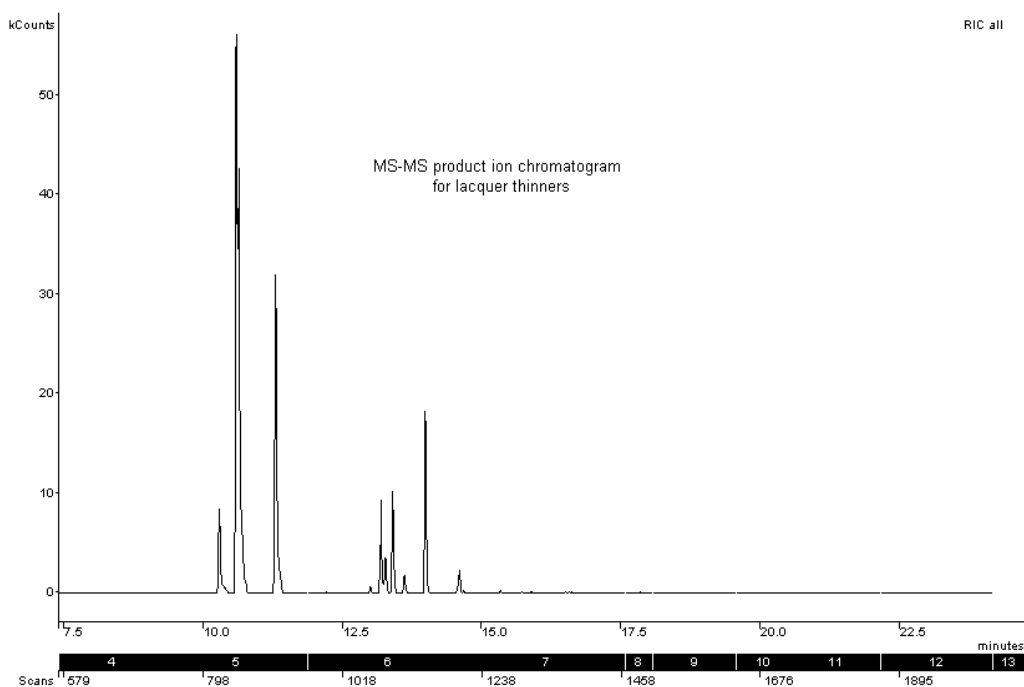


Figure 5.15.1: MS-MS product ion mass chromatogram for lacquer thinners.

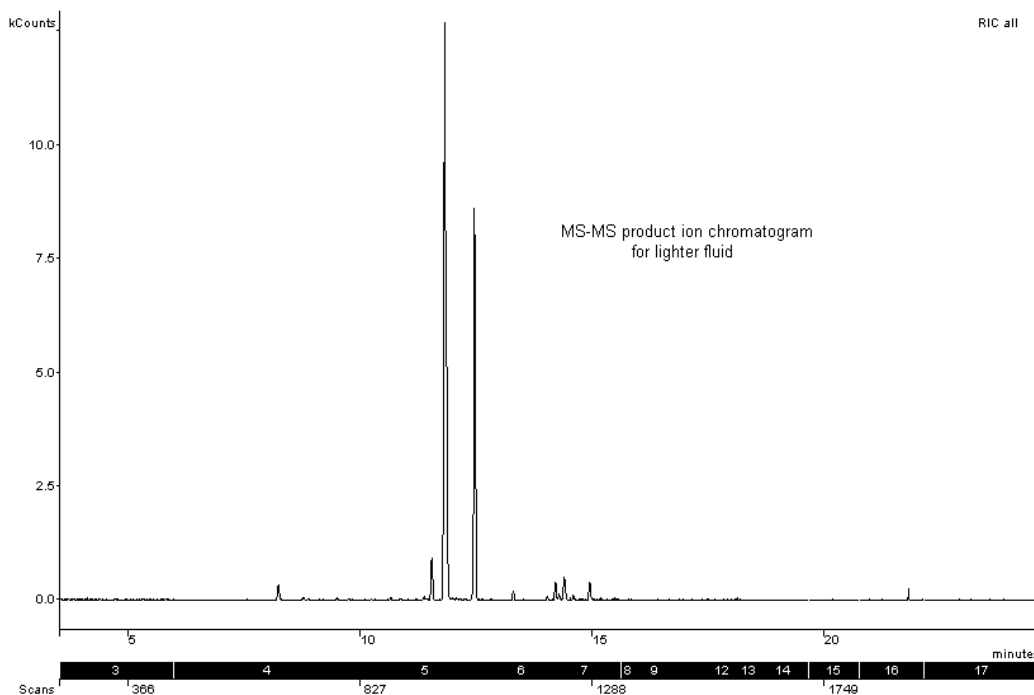


Figure 5.15.2: MS-MS product ion mass chromatogram for lighter fluid.

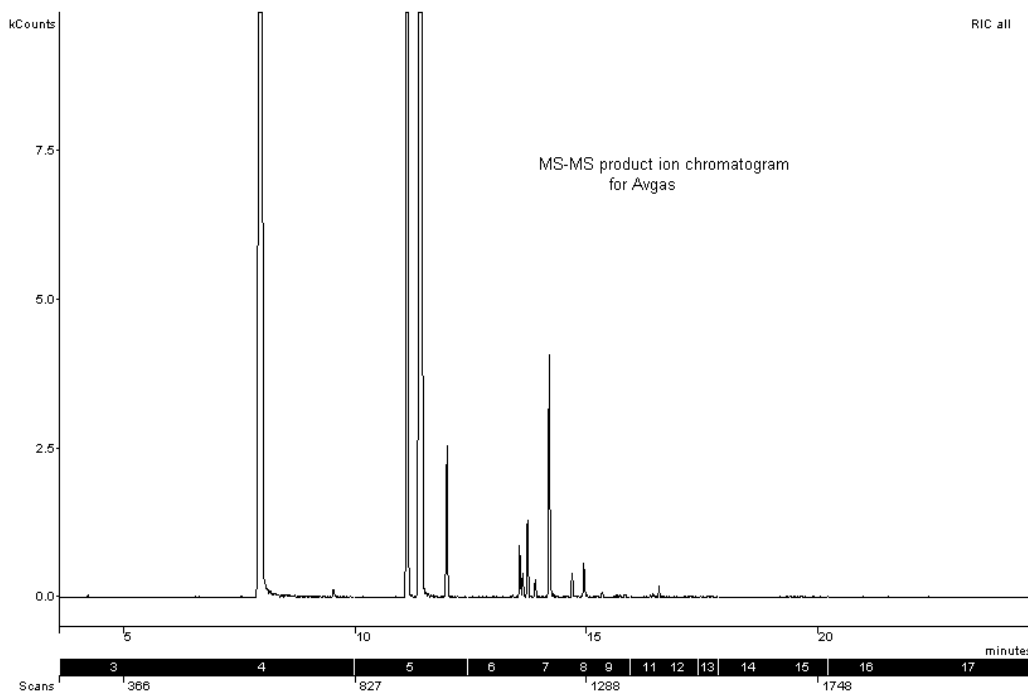


Figure 5.15.3: MS-MS product ion mass chromatogram for avgas.

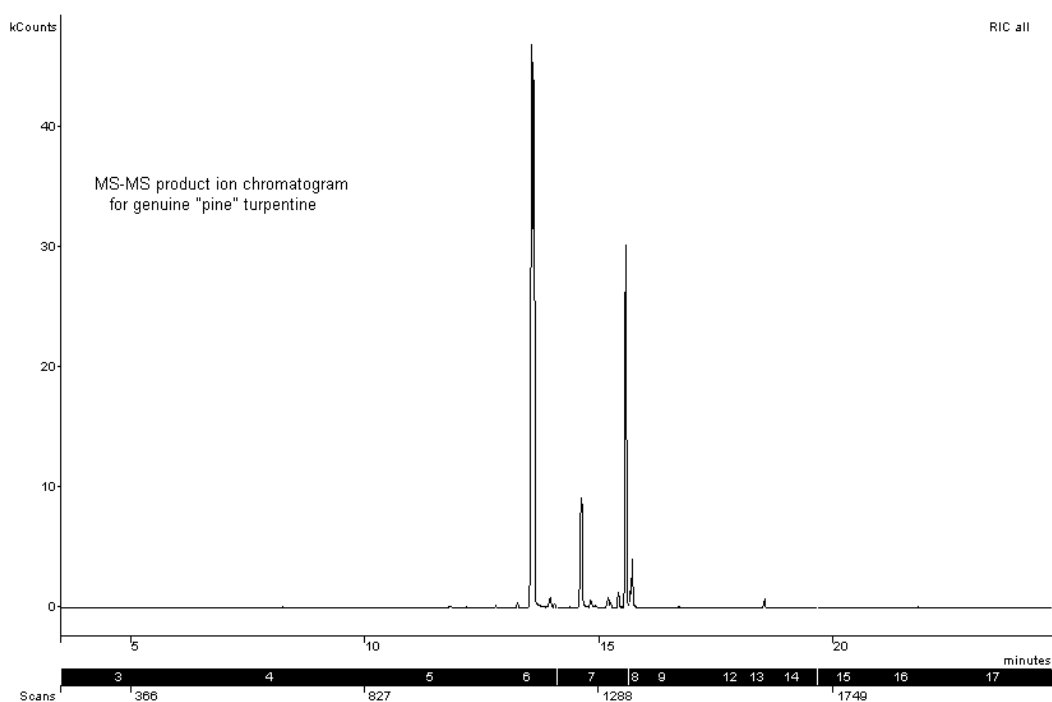


Figure 5.15.4: MS-MS product ion mass chromatogram for genuine turpentine.

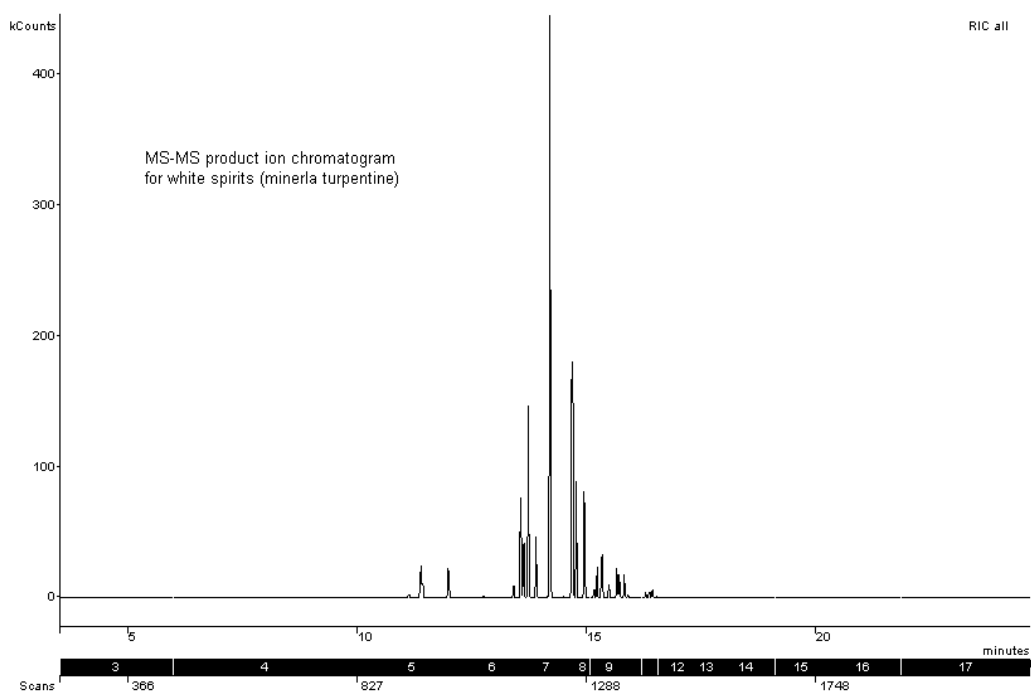


Figure 5.15.5: MS-MS product ion mass chromatogram for mineral turpentine (white spirits).

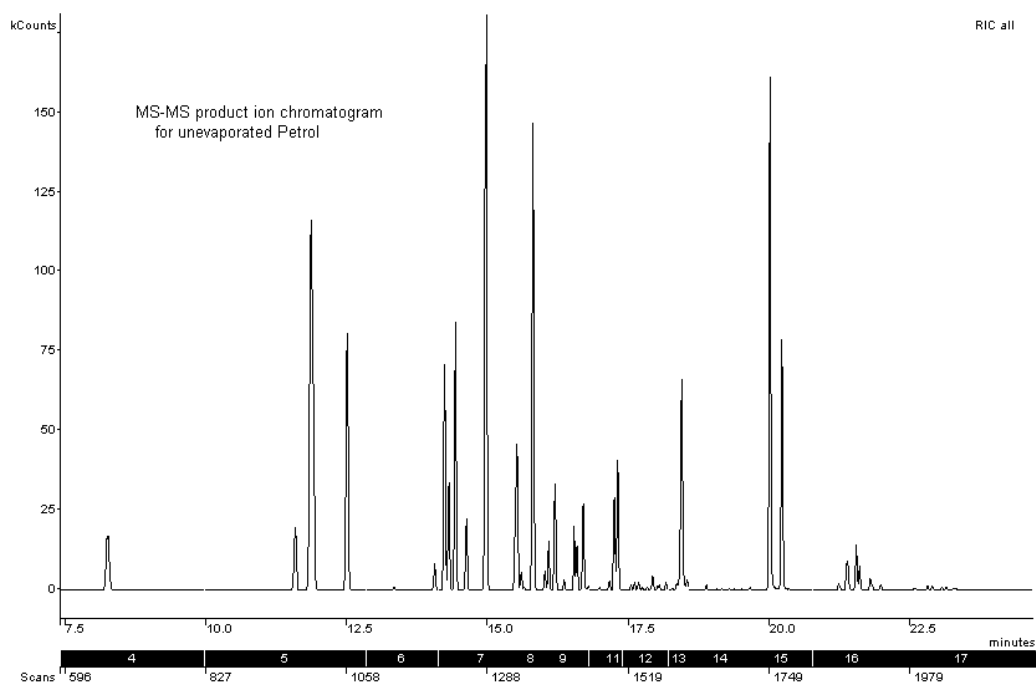


Figure 5.15.6: MS-MS product ion mass chromatogram for unevaporated petrol.

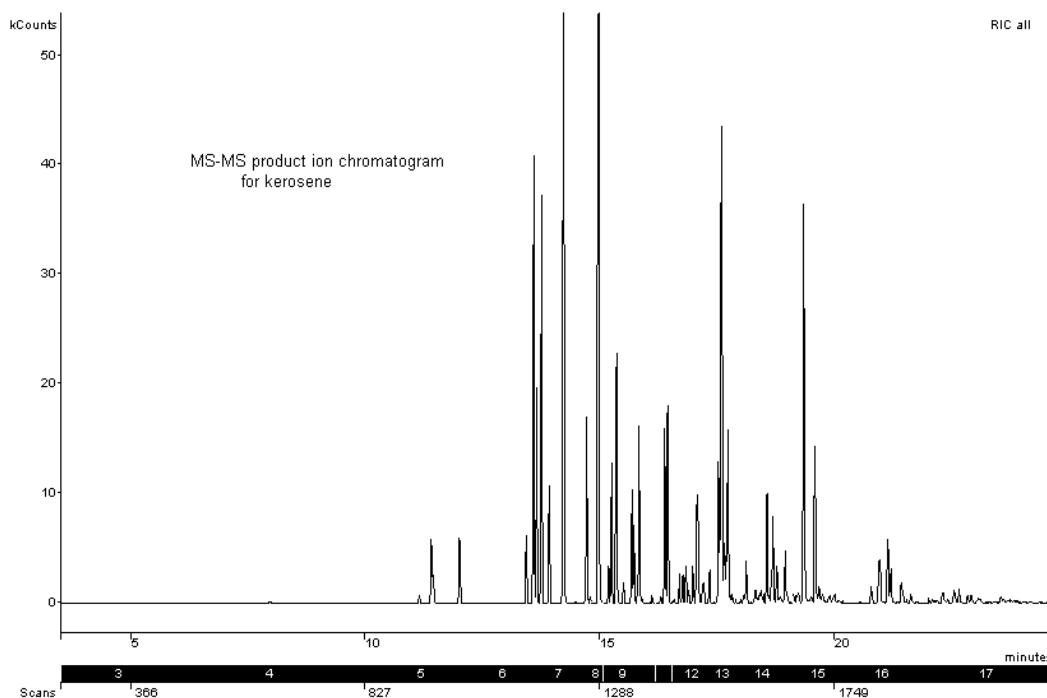


Figure 5.15.7: MS-MS product ion mass chromatogram for kerosene.

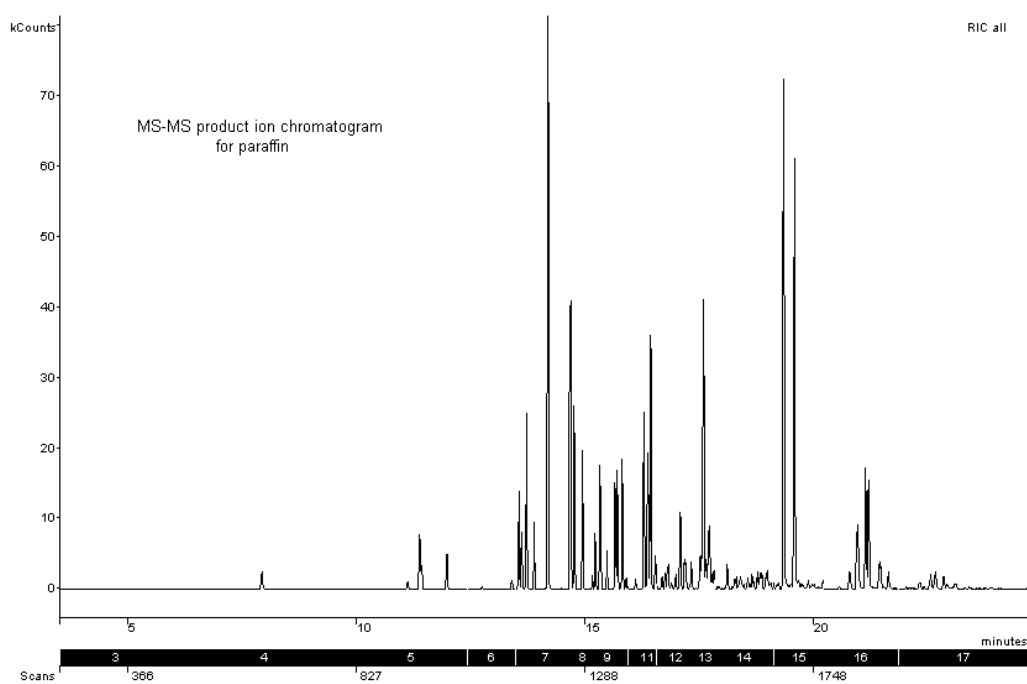


Figure 5.15.8: MS-MS product ion mass chromatogram for paraffin.

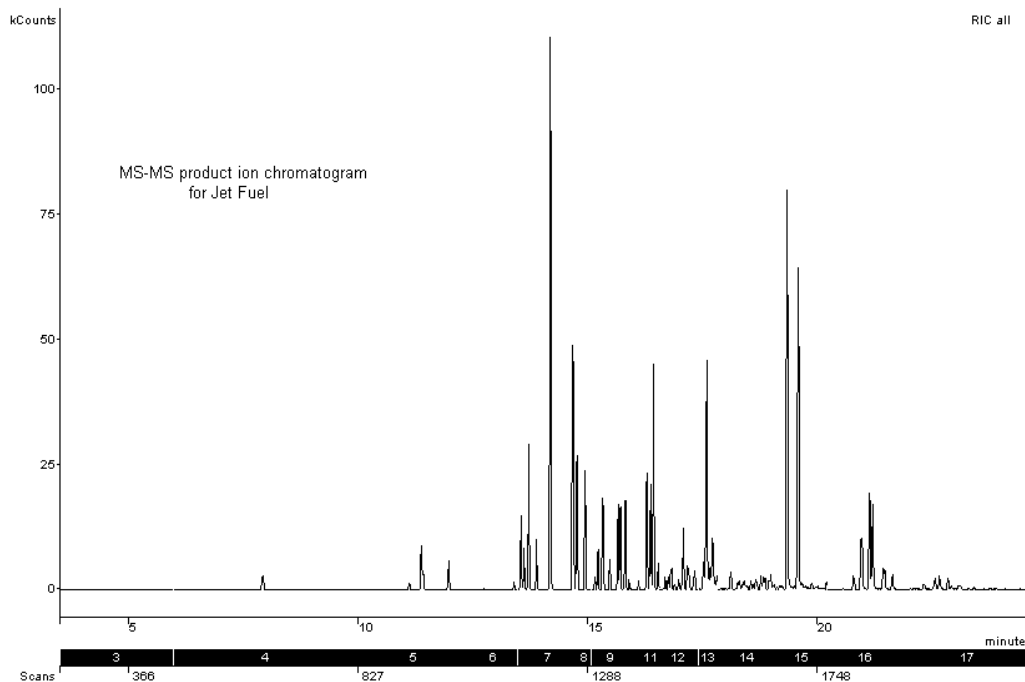


Figure 5.15.9: MS-MS product ion mass chromatogram for jet fuel.

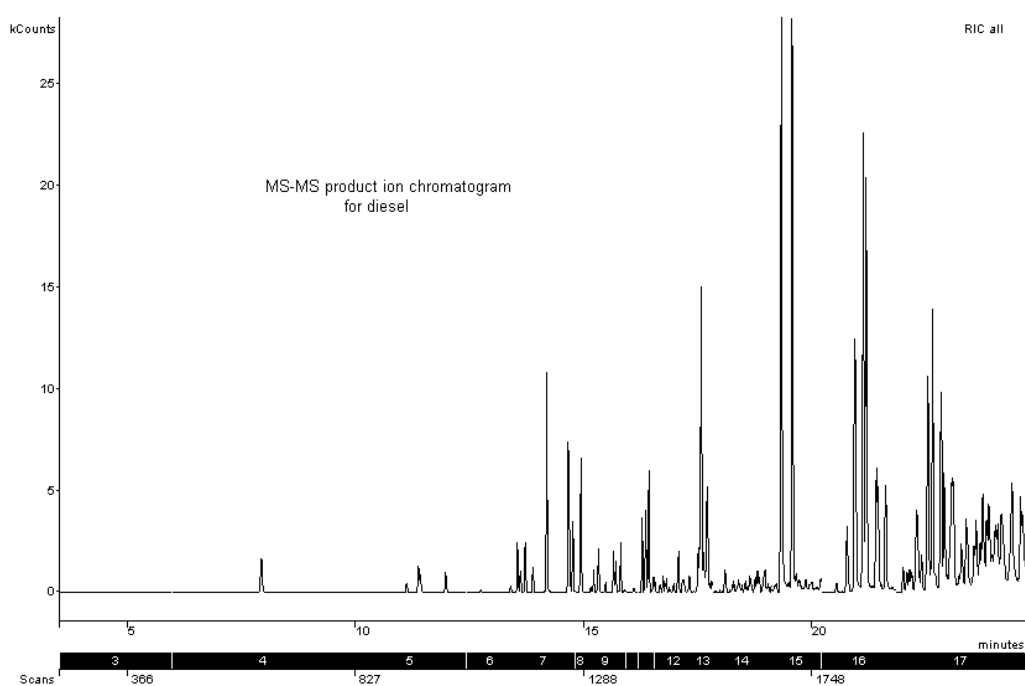


Figure 5.15.10: MS-MS product ion mass chromatogram for diesel.

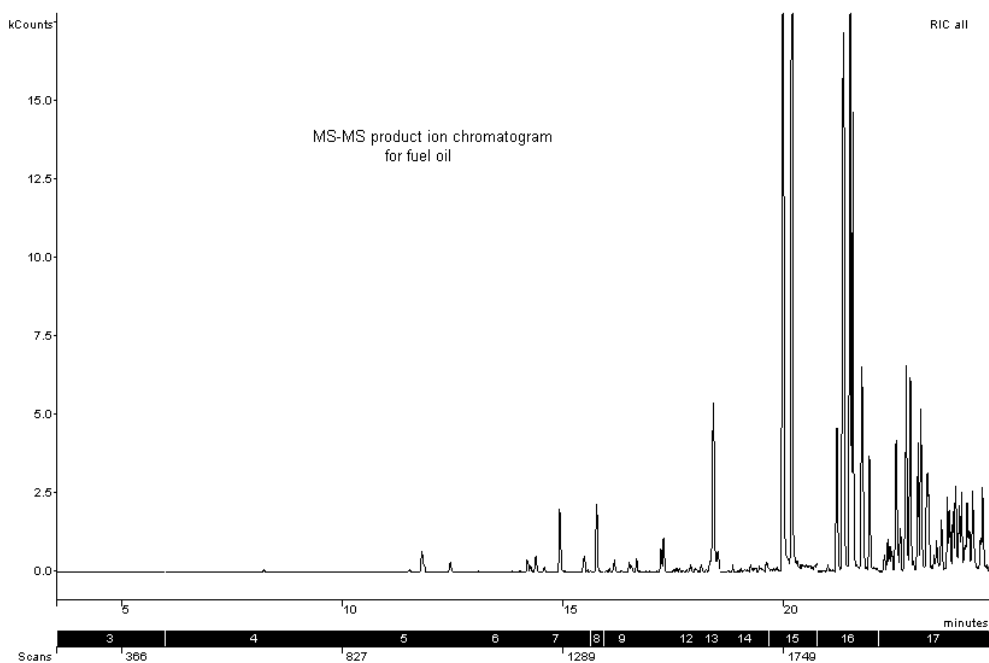


Figure 5.15.11: MS-MS product ion mass chromatogram for fuel oil.

CHAPTER 6

FIRE DEBRIS ANALYSIS BY GC-MS-MS

6.1. GC-MS-MS APPLICATION

Fire debris samples are collected at the fire scene by designated fire investigators and most of the time the samples are delivered to the laboratory by hand. If not, the samples arrive in locked toolboxes, accompanied by a chain of custody record. The laboratory does have a protocol stipulating that samples of fire debris must be properly collected and sealed at the scene using a nylon fire debris evidence pouch, roasting bag, mason-type glass jar or unlined paint tin. All samples must be clearly labelled and must be accompanied by a covering note, clearly indicating the number of samples, labelling, content and reference number. This protocol is intended to eliminate the risk of cross-contamination of samples subsequent to sample collection and incorrect labelling. The possibility of cross contamination of samples not collected and handled according to this protocol cannot be excluded. Not all debris samples submitted for analysis comply with this protocol.

There are very few really experienced fire investigators in South Africa as compared with the United States, Canada and the UK. The CSIR fire investigators ensure that their samples arrive either the same day or within a day or two of sample collection at a scene and they comply with the laboratory protocol. If the trained arson canine has been used to indicate at the scene, this is noted and the laboratory informed. Specific information pertaining to the possible presence of light petroleum distillates, *e.g.*, methylated spirits, lighter

fluid, certain industrial solvents, alcohols, acetone, *etc*, is communicated with the analyst to assist with the type of extraction selected for analysis. When these lighter boiling point distillates are suspected, the samples are extracted using solid phase micro-extraction (SPME). If medium or heavy petroleum distillates are suspected, then carbon strips are placed inside the nylon evidence pouch. The evidence pouches are heated in a calibrated oven at 60 degrees Celsius overnight. If the samples can be heated during the working day, then either a 6-hour or 8-hour period is selected at 65 degrees Celsius. The samples are extracted, either using carbon disulphide (CS_2) or methylene chloride.

The choice of analysis and extraction technique is often determined only upon receipt of the sample. Initial examination of the GC-MS chromatographic data of the sample extract will determine whether accelerant traces are present, what matrix interferences are present, resulting from the bulk of the pyrolyzed sample and whether or not the accelerant traces are clearly distinguishable from the matrix. If not, and petrol is suspected, then a second confirmatory analysis is performed by GC-MS-MS and the chromatographic data reassessed.

The analytical report issued is based only on the analysis of the debris sample(s) submitted for analysis. The analyst does not determine if arson has been committed. The fire investigator uses the analytical report to assist in his deliberations as to the cause of the fire.

The chromatograms selected for discussion are actual cases pending court procedure; therefore each case will not be discussed in detail. Only the relevance of the type of pyrolysis interference that is removed by GC-MS-MS will be discussed.

6.2. FLOOR SCREED DEBRIS SAMPLE

Pieces of chopped floor screed (or grano: a sand and cement finishing / topping / surface layer or sub-levelling layer on concrete floors prior to carpeting - usually 25 to 35 mm thick that creates a smooth surface) [96], taken from the concrete floor of a wood product factory about one month after the fire, were handed in for analysis in

a sealed nylon evidence pouch. An arson canine was used to indicate the area of sample origin. The sample was extracted using a passive charcoal strip placed inside the nylon evidence pouch and heated in a calibrated oven at 60 degrees Celsius for 16 hours. The charcoal strip was then removed from the nylon evidence pouch, extracted with carbon disulphide and analysed by GC-MS using a Varian Saturn 2000 Ion Trap Gas Chromatograph-Mass Spectrometer. ASTM Guide E1618-97 was used to determine the presence of ignitable liquids. Figures 6.1.1 and 6.1.2 depict the total chromatographic ion profile (total mass chromatogram) and typical selected (extracted) ion profiles below each total profile for a petrol standard as used by the CSIR-NML laboratory when initially examining arson chromatograms. Benzene is not usually indicated since the carbon disulphide solvent contains benzene contaminants, and unless benzene is suspected, is usually not examined. The aliphatic (alkanes and cycloalkanes) hydrocarbons are examined, as well as the alkylbenzene compounds (aromatics) and alkylnaphthalene compounds (condensed ring aromatics).

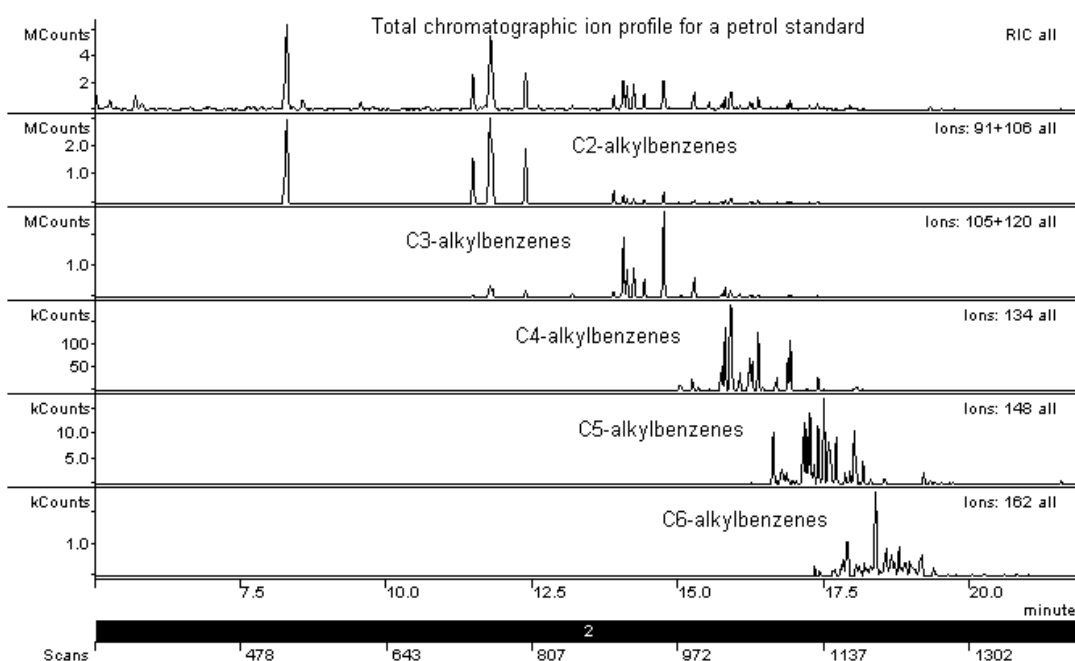


Figure 6.1.1: Total chromatographic ion profile for a petrol standard by GC-MS. The reconstructed ion profiles for the aromatic hydrocarbons are depicted below the total ion profile.

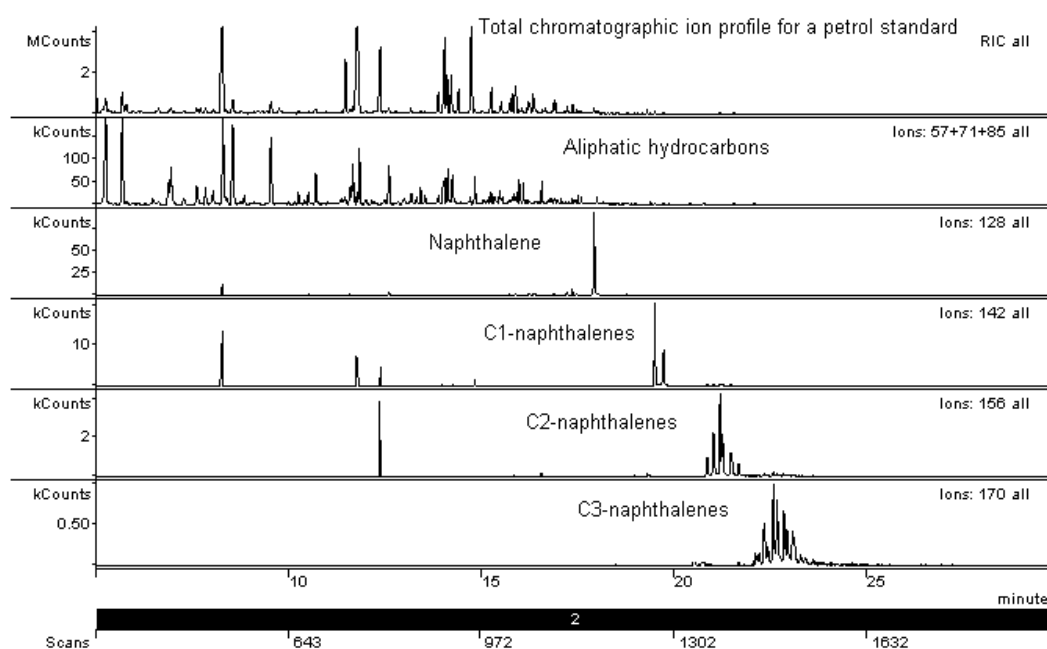


Figure 6.1.2: Total chromatographic ion profile for a petrol standard by GC-MS. The reconstructed ion profiles for the aliphatic hydrocarbons, naphthalene and the alkyl naphthalenes depicted below the total ion profile.

Figures 6.1.3 and 6.1.4 depict the same total chromatographic ion profile (mass chromatogram) and selected ion profiles for the sample of floor screed containing a reasonable amount of petrol residue and a minor amount of pyrolysis products. From these extracted GC-MS ion profiles, the aliphatic and aromatic hydrocarbons present can easily be detected and favourably compared with a GC-MS chromatographic ion profile for a petrol standard, thus giving a positive result. The presence of paraffin can also be seen from the $m/z = 57$ aliphatic hydrocarbon ion profiles. The reason why the aromatics are suspected as originating from petrol and not just paraffin is due to the abundance of both the low boiling point aromatic and aliphatic hydrocarbons at retention times below those expected for paraffin only.

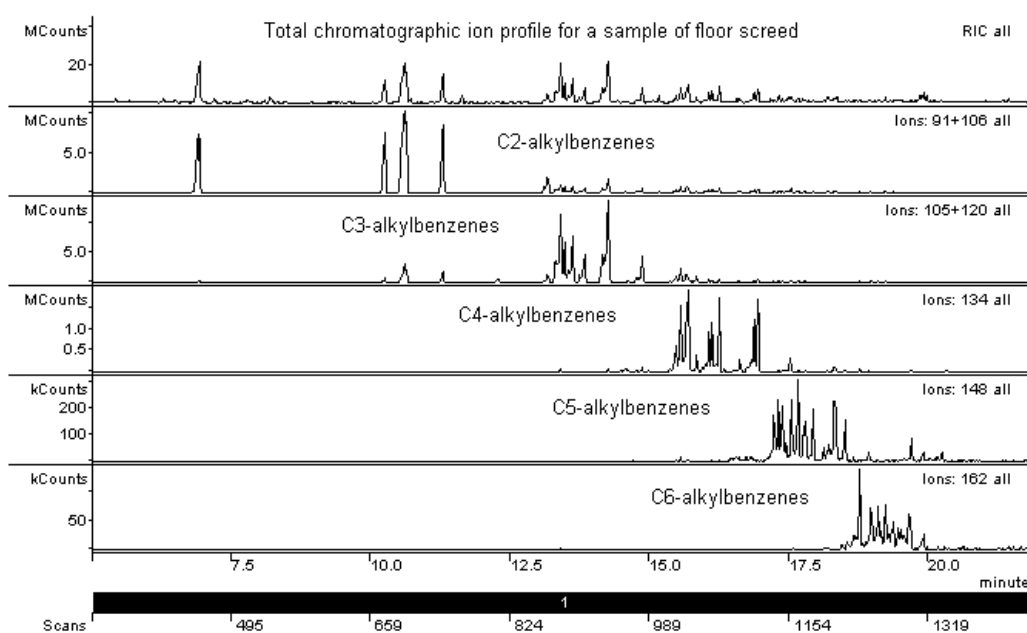


Figure 6.1.3: Total chromatographic ion profile for a debris sample of floor screed by GC-MS. The reconstructed ion profiles for the aromatic hydrocarbons are depicted below the total ion profile.

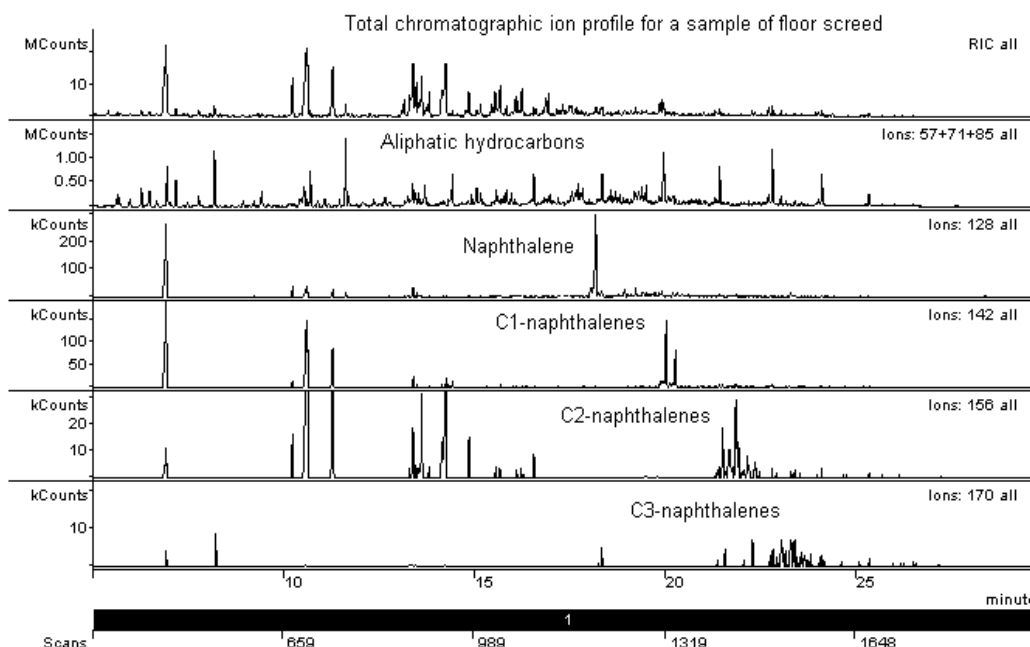


Figure 6.1.4: Total chromatographic ion profile for a debris sample of floor screed by GC-MS. The reconstructed ion profiles for the aliphatic hydrocarbons, naphthalene and the alkylnaphthalenes are depicted below the total ion profile.

In order to confirm the presence of the aromatic hydrocarbon compounds, a second confirmatory analysis by MS-MS was performed. Figure 6.1.5 depicts the MS-MS product ion chromatogram for the sample of floor screed. In this figure it can be seen that MS-MS has removed the pyrolysis products in the sample and the resultant product ion profile compares well with that of the product ion profile for a petrol standard. This is, however, a good example, where the petrol residue was easily detected and MS-MS would not really have been necessary as this data can be obtained by sequential selection of the same aromatic hydrocarbon diagnostic ions from a conventional GC-MS run. Cases where pyrolysis products have interfered with the MS chromatograms, even after examination of the extracted ion profiles, will show that MS-MS has the capability of effectively minimizing, if not entirely removing, the pyrolysis interferences.

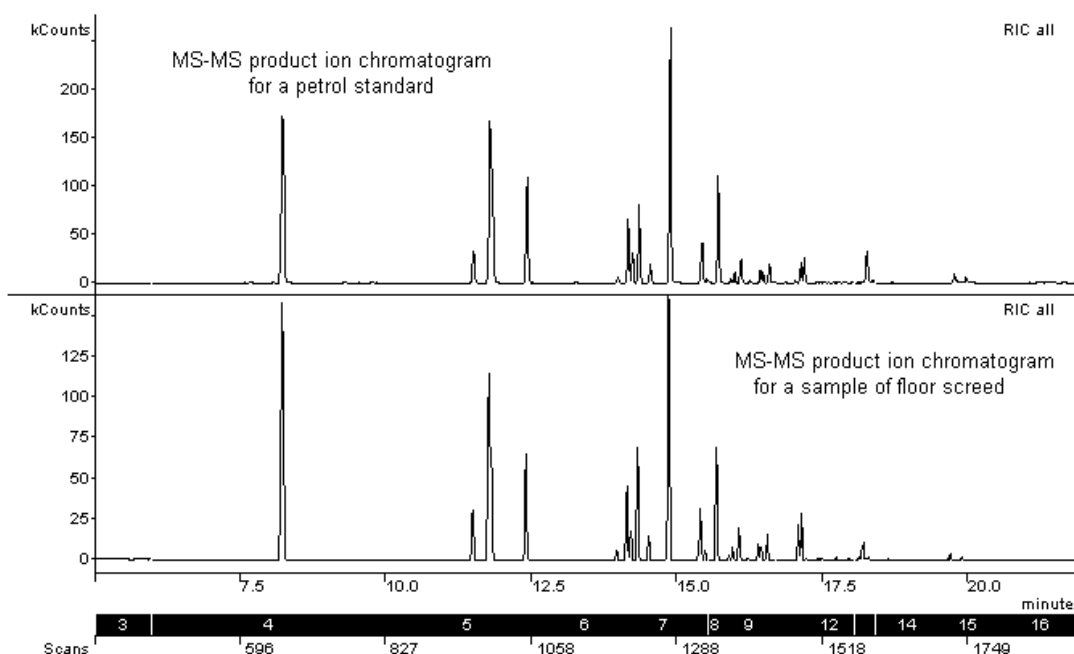


Figure 6.1.5: The MS-MS product ion chromatogram (aromatic hydrocarbon profiles – table 5.6) for a petrol standard with the MS-MS product ion chromatogram for the debris sample of floor screed below.

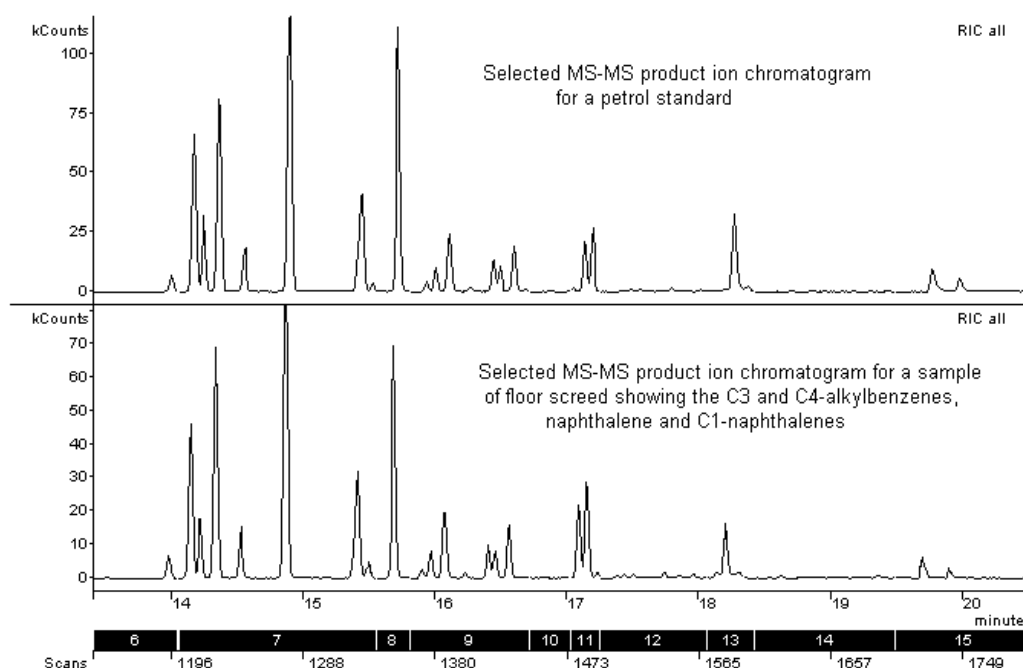


Figure 6.1.6: The selected time segment MS-MS product ion chromatogram for a petrol standard with the selected MS-MS product ion chromatogram for the debris sample of floor screed below, to illustrate more clearly the C3 and C4-alkylbenzenes, naphthalene and the C1-naphthalenes.

By reconstructing the product ion chromatogram over a specific retention time period (Figure 6.1.6), the C3 and C4-alkylbenzene compounds of the floor screed sample can be unmistakably compared with the petrol standard. Naphthalene and the C1-naphthalenes are also clearly visible.

Direct comparison of the GC-MS total chromatographic ion profile with the product ion MS-MS profile (Figure 6.1.7) gives a clear indication that the MS-MS product ion chromatographic profile provides a more definitive and less "cluttered" chromatogram than the GC-MS chromatographic profile, where pyrolysis products can obscure the characteristic isomers. The comparison between MS-MS chromatograms is more simplified and more visually understandable. The total ion chromatograms have been compared to emphasize how clearly the aromatic profile is presented by GC-MS-MS rather than by GC-MS (total ion). The aromatic profile only becomes clear with GC-MS after selected ion profiling has been performed.

When presenting evidence in court it is important that the chromatographic data be visually comprehensible the first time it is presented. This will prevent any ambiguous misunderstanding as to the exact nature of the chromatographic evidence presented for court purposes.

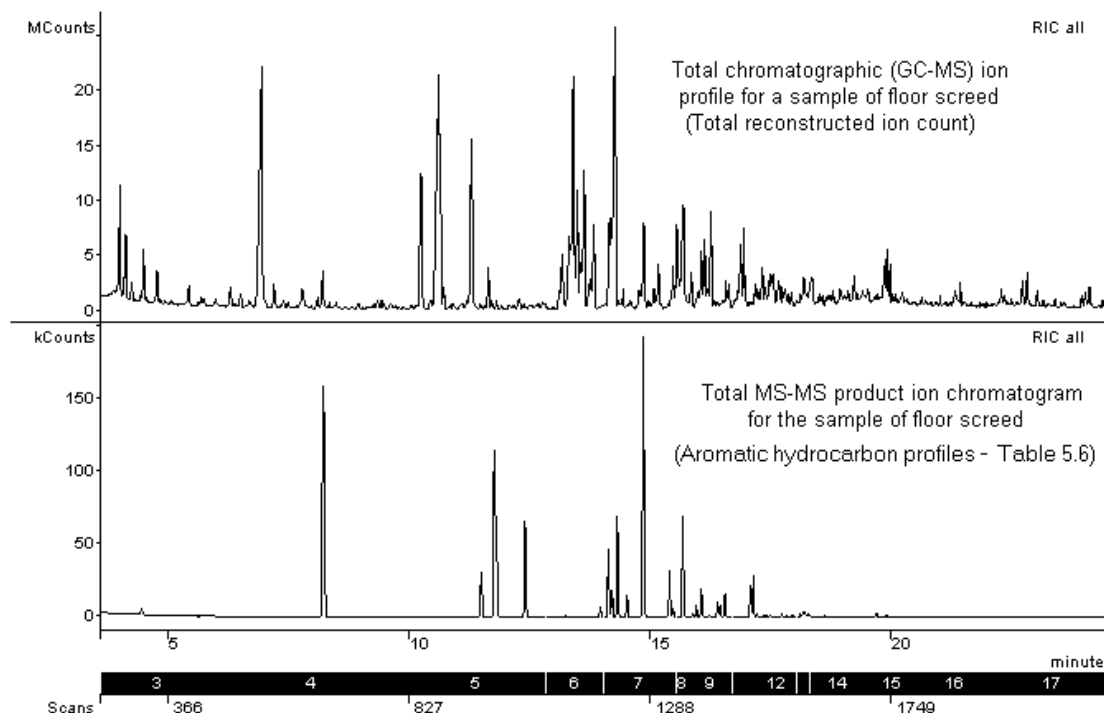


Figure 6.1.7: The GC-MS total chromatographic ion profile for the sample of floor screed with the GC-MS-MS product chromatographic ion profile below. The MS-MS aromatic hydrocarbon profile is clearly less "cluttered" than the MS total ion profile.

6.3. CHARRED PINE FLOOR PLANKING DEBRIS SAMPLE

A section of pine floor planking, which was taken in an area of "pool-mark" charring and pour-patterns, as well as where the planking had burnt through at the "tongue-and-groove joint", were handed in for analysis. The sample was extracted following the same procedure as for the floor screed sample. The total chromatographic ion profile for the sample extract of the pine floor planking is shown in figure 6.2.1 compared against the total chromatographic ion profile for a petrol

standard. Initial inspection of the RIC (reconstructed ion count) profiles would seem to indicate that the sample is not a petrol fraction, but rather a later eluting distillate fraction.

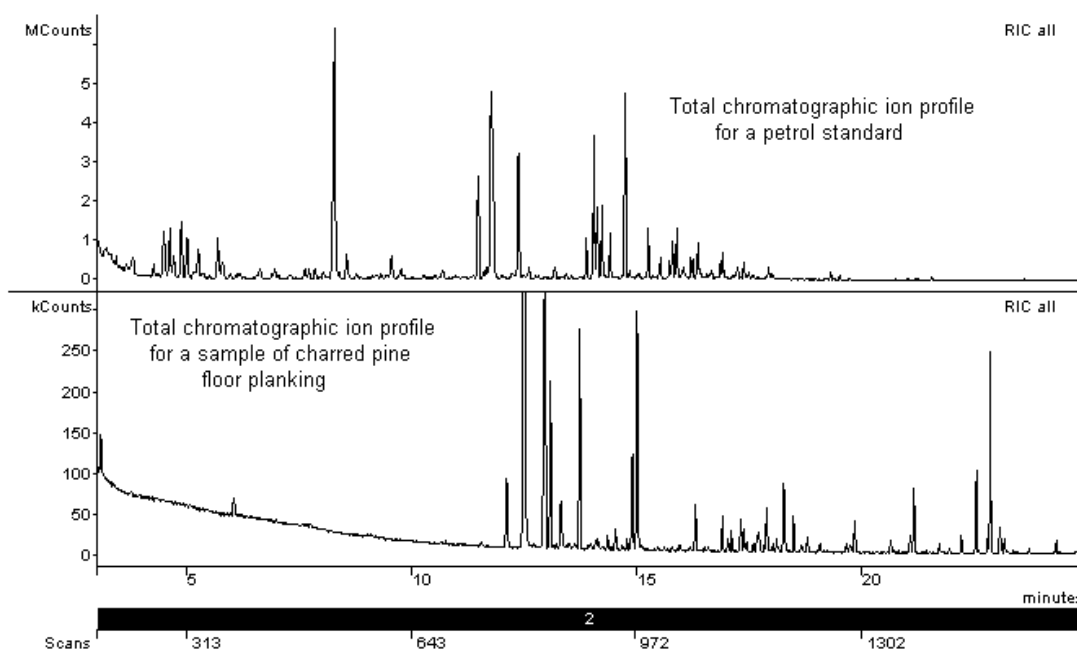


Figure 6.2.1: Total chromatographic ion profile for a petrol standard by GC-MS with the total chromatographic ion profile for a debris sample of charred pine floor planking below. The terpenoid compounds visible in the pine floor planking sample obscure the aromatic compounds.

The selected ion profiles for the charred pine floor planking sample are depicted in figure 6.2.2, with the petrol standard depicted in the upper trace and the sample traces beneath. It can be seen by the enhanced baseline, that terpenoid compounds are the main pyrolysis interference within the C3-alkylbenzene region. Since it is pinewood, these terpenoids are expected and are compared with genuine turpentine to confirm the presence or absence of genuine turpentine. This comparison is also to ensure that the terpenoids that are present are only derived from the pyrolysis of the pinewood. Next, the aromatic compounds specific for petrol are examined. The C3, C4, C5 and C6-alkylbenzene compounds are present in the sample and compare favourably with the petrol standard. The “pool-mark” charring and pour patterns verify that not only pine planking aromatics could be present. GC-MS-MS is performed on this sample

to clarify the C3-alkylbenzenes since the terpenoid compounds lie between the trimethylbenzene peaks. Only by careful mass spectrometric examination of each chromatographic peak can it be exhibited whether they represent a C3-alkylbenzene or a terpene. The third chromatogram depicted in figure 6.2.2 is a selected ion chromatogram for $m/z = 105$, 120 and 134. This chromatogram specifically illustrates that the terpene interference lies mainly within the C3-alkylbenzene region. It also allows for a clearer comparison with the petrol standard, since the Y-axis has not been expanded.

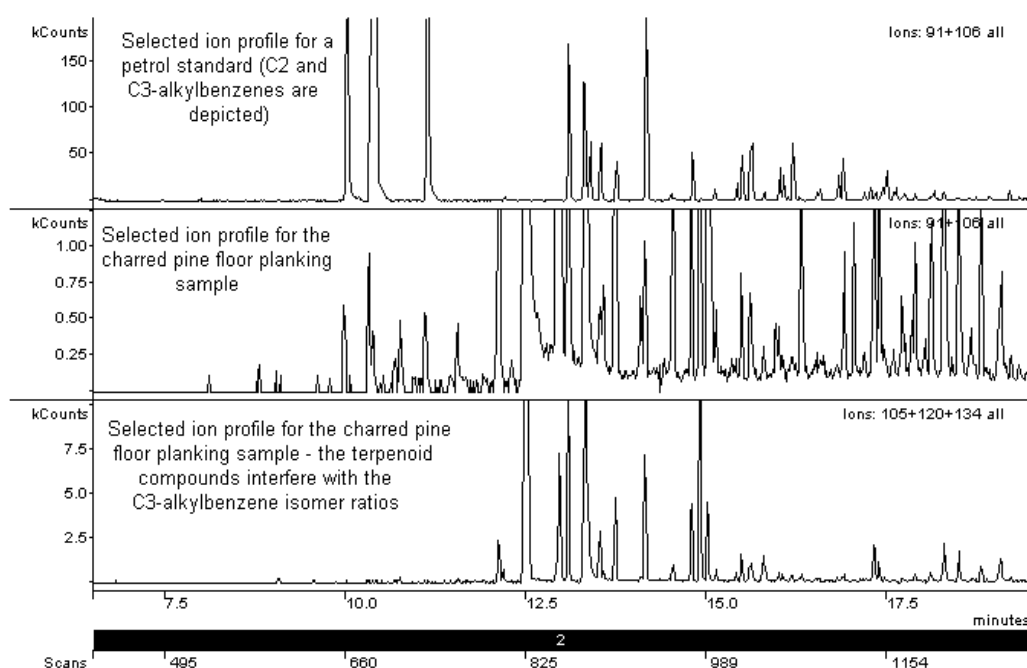


Figure 6.2.2: Reconstructed ion profile for a petrol standard showing the C2-alkylbenzenes by GC-MS (upper trace). The reconstructed ion profiles for the C2 and C3-alkylbenzenes for the charred pine floor-planking sample are depicted in the middle trace in which the Y-axis has been expanded to illustrate how the terpenoid compounds interfere with the C2 and C3-alkylbenzenes. In the lower trace the C3 and C4-alkylbenzenes have been selected to show that the terpenoid interference lies mainly within the C3-alkylbenzene region.

In figure 6.2.3 the MS-MS aromatic product ion profile for the charred pine plank sample compares favourably with petrol and upon closer examination, the C3-alkylbenzene compounds are clearly

present, confirming that petrol is part of the sample. It can be seen that there are still pyrolysate peaks present, indicating that the pyrolysates have an aromatic nature.

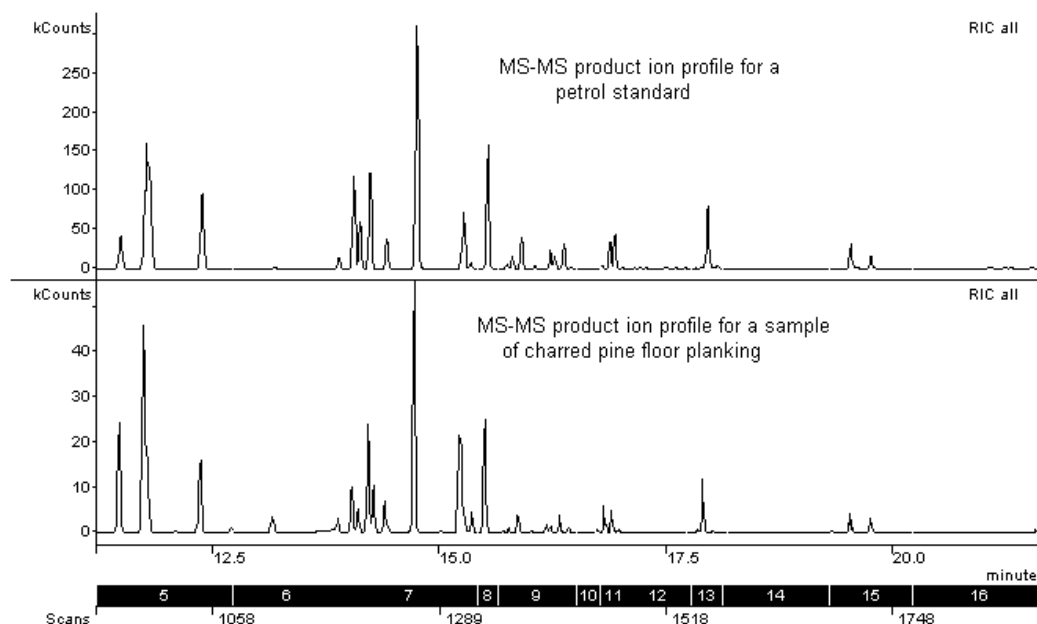


Figure 6.2.3: The MS-MS aromatic product ion profile (table 5.6) for a petrol standard (upper trace) with the MS-MS product ion profile for the debris sample of charred pine floor planking depicted in the lower trace.

Figure 6.2.4 shows the selected time segment MS-MS product ion profile for the C3-alkylbenzene compounds (diagnostic ion $m/z = 120$). When compared with a petrol standard, there is an artefact peak present as a shoulder peak adjacent to the mesitylene peak (1, 3, 5-trimethylbenzene). By reconstructing the product ion MS-MS profile (chromatogram) over the time range of the segment (segment 7) using $m/z = 105$, the artefact peak is removed. This chromatographic trace only signals peaks consisting of compounds that produce a $m/z = 120$ ion that also dissociates under collisional activation to the $m/z = 105$ fragment [single reaction monitoring (SRM) $120 \rightarrow 105$]. The artefact obviously has a $m/z = 120$ that does not produce a $m/z = 105$ under these conditions (Table 5.6, Chapter 5). The real benefit of MS-MS is the “selectivity” gain achieved through reconstruction of the chromatogram using the $m/z = 105$ ion (Figure 6.2.5). This is the first example where the real

power of MS-MS is displayed – earlier MS-MS total product ion profiles can obviously be obtained by GC-MS single ion aromatic hydrocarbon profiling using the ions selected in Table 5.6.

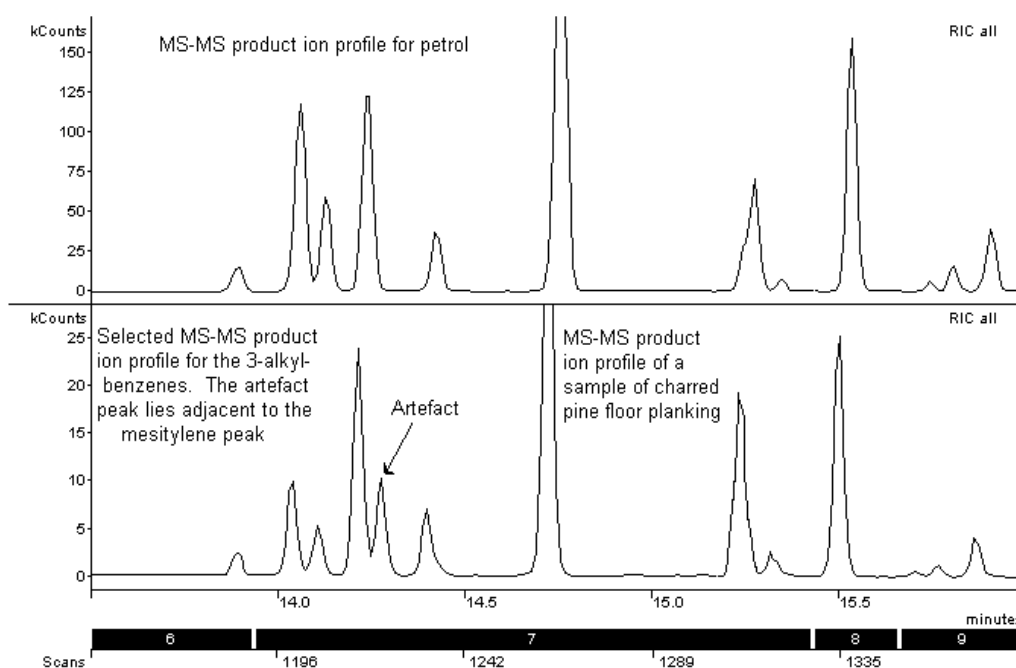


Figure 6.2.4: Selected time segment MS-MS product ion profile (all product ions of $m/z = 120$) for a petrol standard (upper trace) with the selected time segment MS-MS product ion profile for the debris sample of charred pine floor planking (lower trace). The C3-alkylbenzenes are shown with an artefact peak lying adjacent to the mesitylene peak.

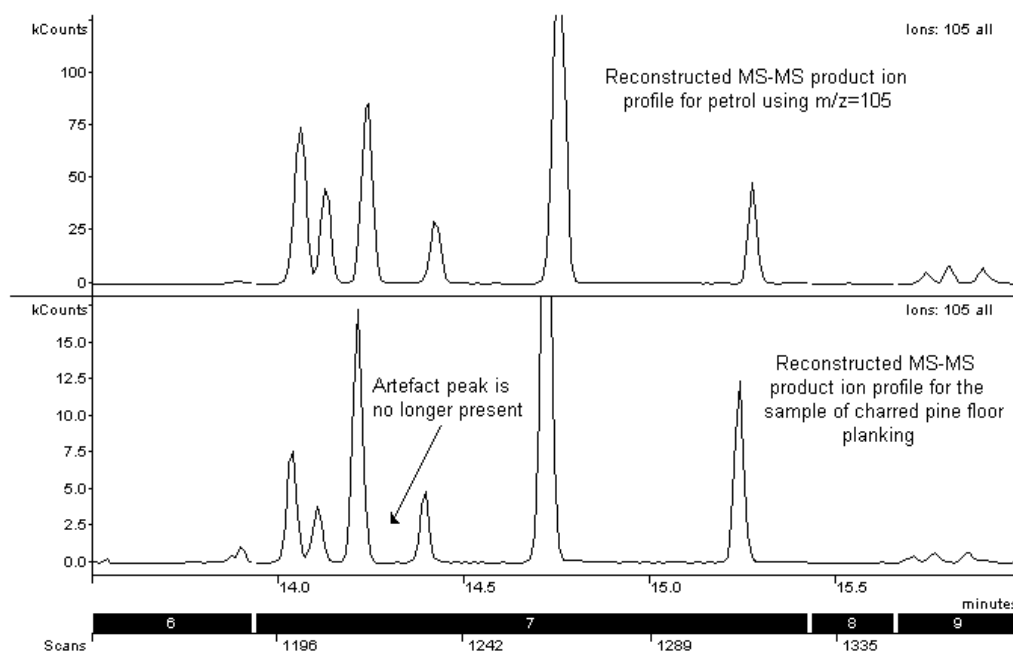


Figure 6.2.5: Reconstructed MS-MS product ion profile (SRM 120 → 105) for a petrol standard using $m/z = 105$ with the reconstructed MS-MS product ion profile for the debris sample of charred pine floor planking lower trace. The C3-alkylbenzenes are shown with the artefact peak removed.

Figure 6.2.6 shows the actual product ion spectrum for the mesitylene peak ($m/z = 120$) in a typical petrol standard as compared with the product ion spectrum of mesitylene in the charred pine planking sample. The spectra are comparable and both clearly exhibit the $m/z = 105$ product ion (including product ions of $m/z = 91$ and 79). The ability to reconstruct the MS-MS product ion chromatogram often clarifies the presence of the characteristic ignitable liquid trimethylbenzenes when interfering pyrolysis aromatics are also prevalent in the sample.

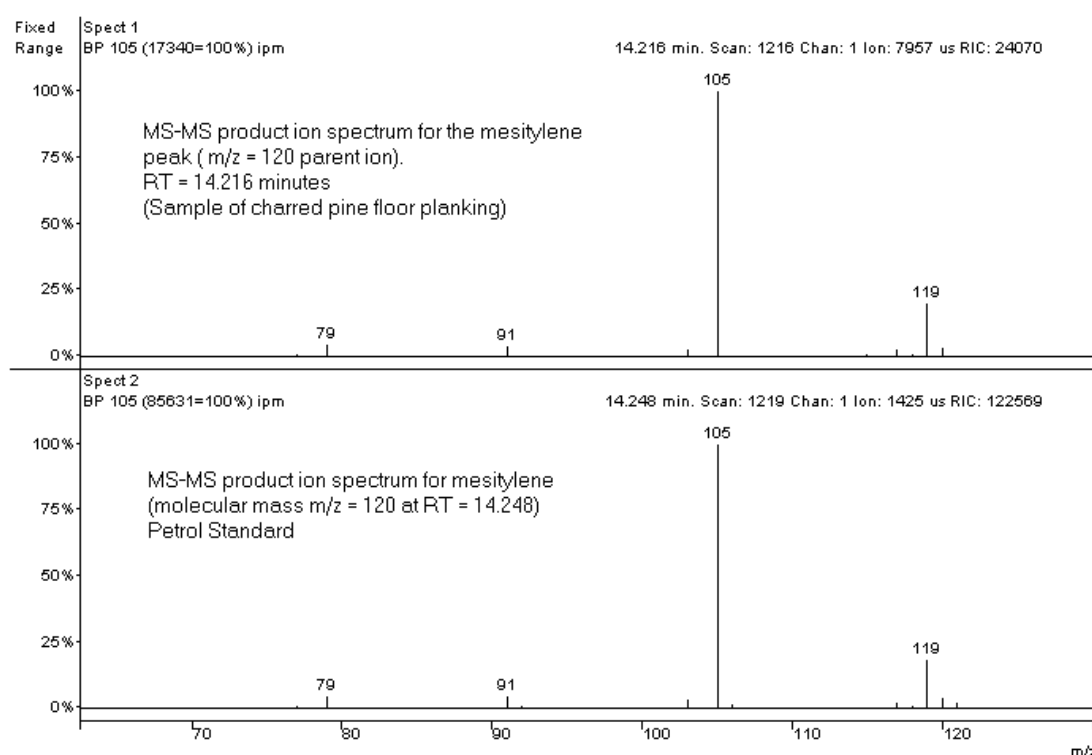


Figure 6.2.6: Product ion spectrum of parent ion $m/z = 120$ for mesitylene in a petrol standard (lower spectrum). The same parent ion was selected for the charred pine floor-planking sample and the product ion spectrum obtained is depicted in the upper spectrum.

Figure 6.2.7 shows the product ion spectrum of the artefact peak adjacent to the mesitylene peak in the charred pine floor planking sample. The sample spectrum is compared with the mesitylene product ion spectrum obtained in a petrol standard. The spectra clearly differ and the $m/z = 105$ is minimal and clearly not the base product ion formed after dissociation of $m/z = 120$ product ion with $m/z = 91$ is also stronger). The added specificity of the product ion spectra allows for added confidence in the observed chromatographic pattern. Spurious peaks are difficult to deal with in a court of law and are thus explained by reconstructing the MS-MS product ion chromatogram (SRM = 120 to 105).

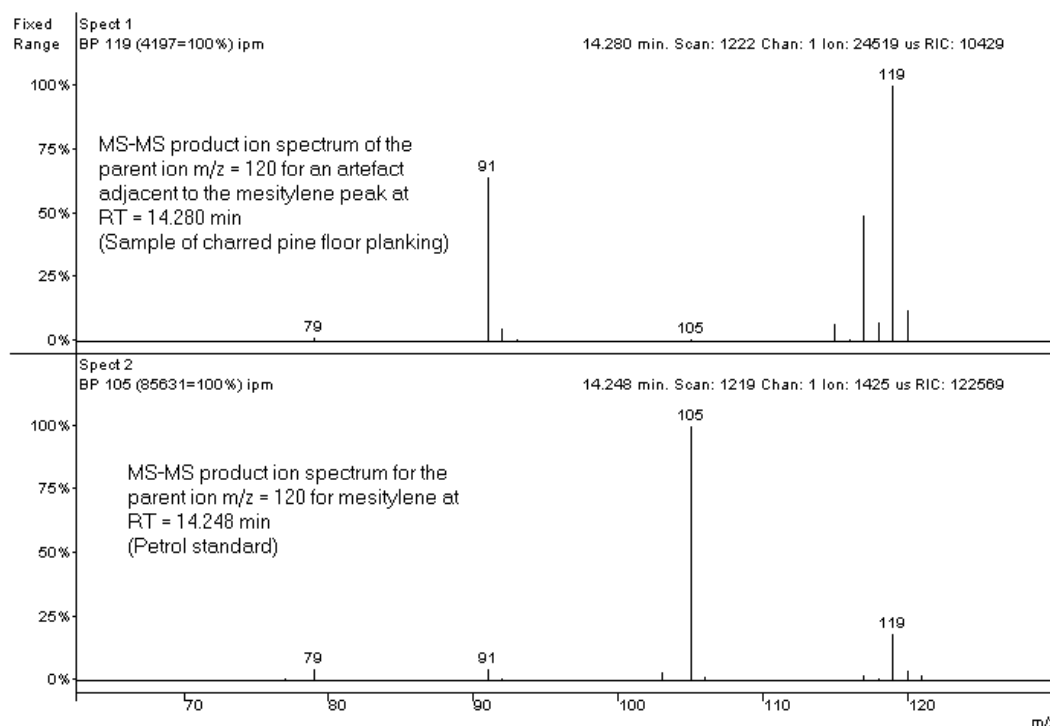


Figure 6.2.7: The unknown chromatographic peak from the charred pine planking sample adjacent to mesitylene produced the product ion spectrum of $m/z = 120$ (upper spectrum) and the product ion spectrum for the parent ion $m/z = 120$ for mesitylene in a petrol standard (lower spectrum).

6.4. SHOE STORE WAREHOUSE DEBRIS SAMPLE

A shoe-store warehouse burnt to the ground and was investigated. Suspicious pour-patterns were evident on the burnt carpeting and debris was sampled from the floor area containing the carpeting. There were polymers and glues prevalent in the area.

Figures 6.3.1 and 6.3.2 show the total chromatographic ion profile and selected ion profiles for the shoe-store floor sample, which included carpeting and shoe debris, and a petrol standard. The aliphatic hydrocarbon compounds were examined for the possible presence of paraffin or diesel, but neither profile was present.

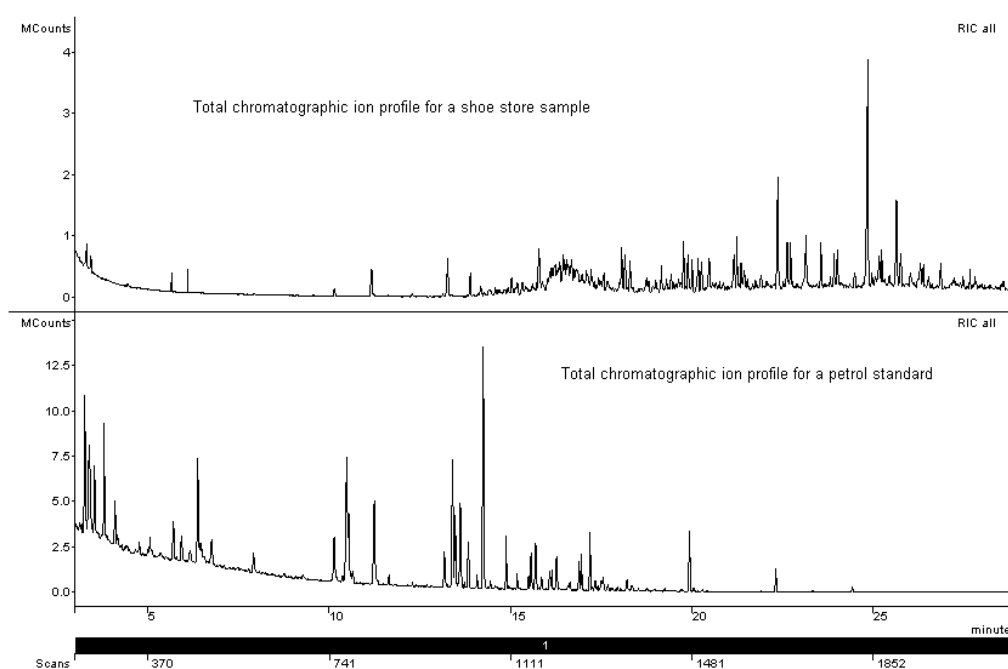


Figure 6.3.1: Total chromatographic ion profile for a debris sample of shoe debris and carpeting from a shoe store with the total chromatographic ion profile for a petrol standard depicted beneath.

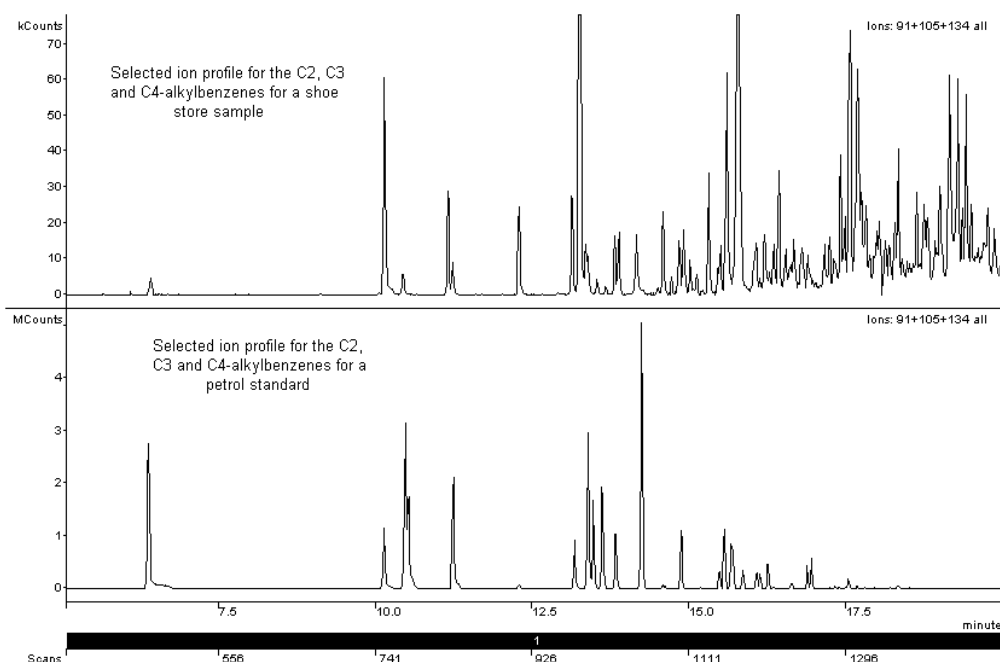


Figure 6.3.2: Selected ion profile for a debris sample of shoe debris and carpeting from a shoe store with the selected ion profile for a petrol standard depicted beneath, showing the C2, C3 and C4-alkylbenzenes.

Naphthalene and the alkylnaphthalenes were present in significant amounts, but this would not be unusual considering where the sample was taken. A number of industrial solvents are used in the making of shoes.

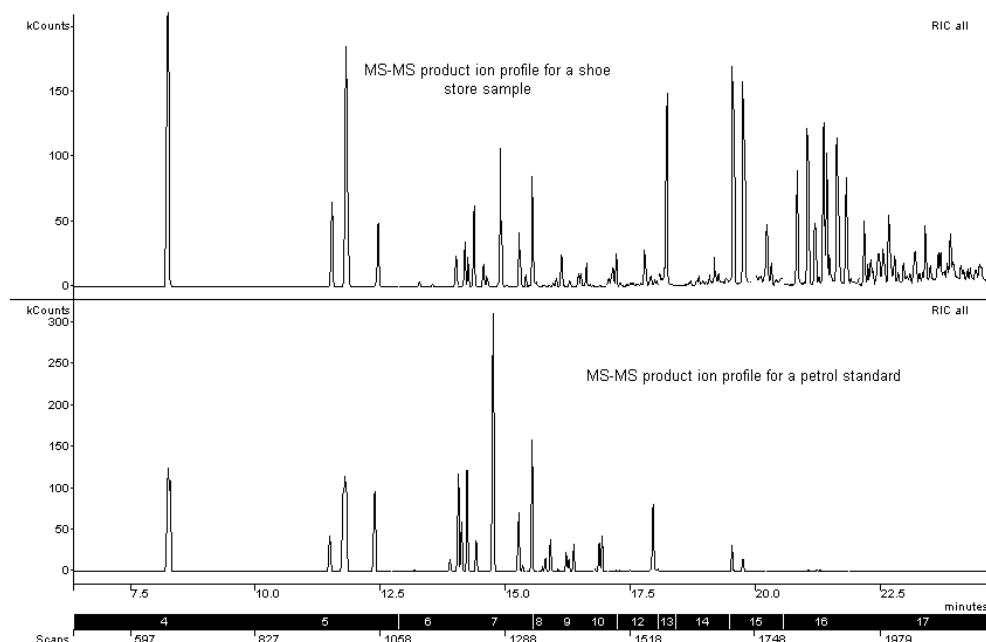


Figure 6.3.3: The MS-MS product ion profile (RT = 6-24 min, parent ions for segment 4; $m/z = 91$ – segment 17; $m/z = 170$) for a petrol standard by GC-MS (upper trace) with the product ion MS-MS profile for the debris sample of shoes and carpeting from a shoe store depicted beneath.

MS-MS was performed on the sample using the conditions stipulated in Table 5.6, Chapter 5. The MS-MS product ion profile for this sample is shown in figure 6.3.3. Note that the naphthalene compounds are very concentrated in the retention time region 17.5 minutes to 25.0 minutes (segments 13 - 17). The C3-alkylbenzenes are definitely present (approximate RT region 14 – 16 minutes; segments 7 – 8)

A closer comparison of the C3, C4 and C5-alkylbenzene compounds in figure 6.3.4 indicates the presence of petrol, which was not clearly indicated in the GC-MS selected ion profiles. This is due to additional C3-alkylbenzene and naphthalene compounds present as a result of solvents present in the shoe-store. If the alkylnaphthalenes originated from diesel, then the C3 and C4-alkylbenzene compounds

would also have been more weathered. Diesel was, however, not indicated due to the absence of aliphatic hydrocarbons.

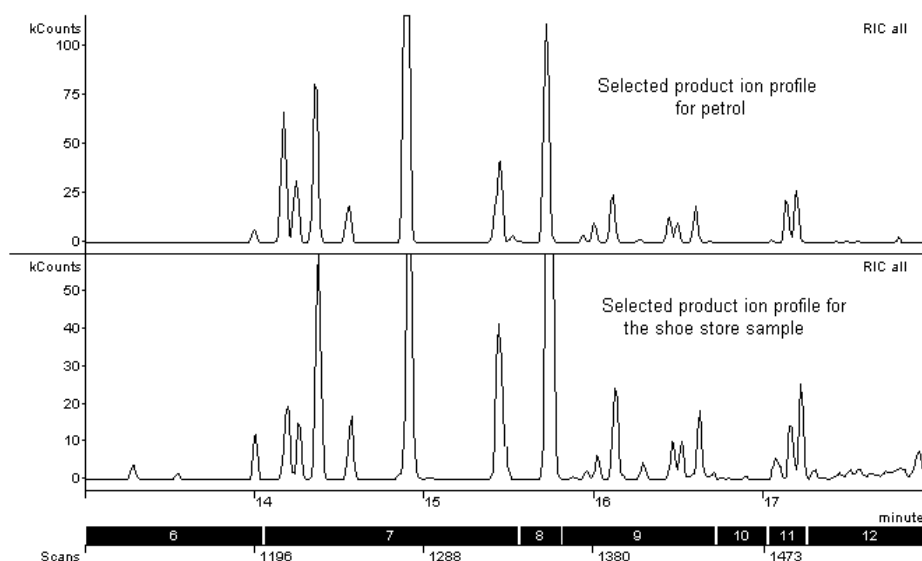


Figure 6.3.4: Selected time segment MS-MS product ion profile for a petrol standard, with the selected time segment MS-MS product ion profile for a debris sample of shoes and carpeting from a shoe store below, showing the C3 and C4-alkylbenzenes.

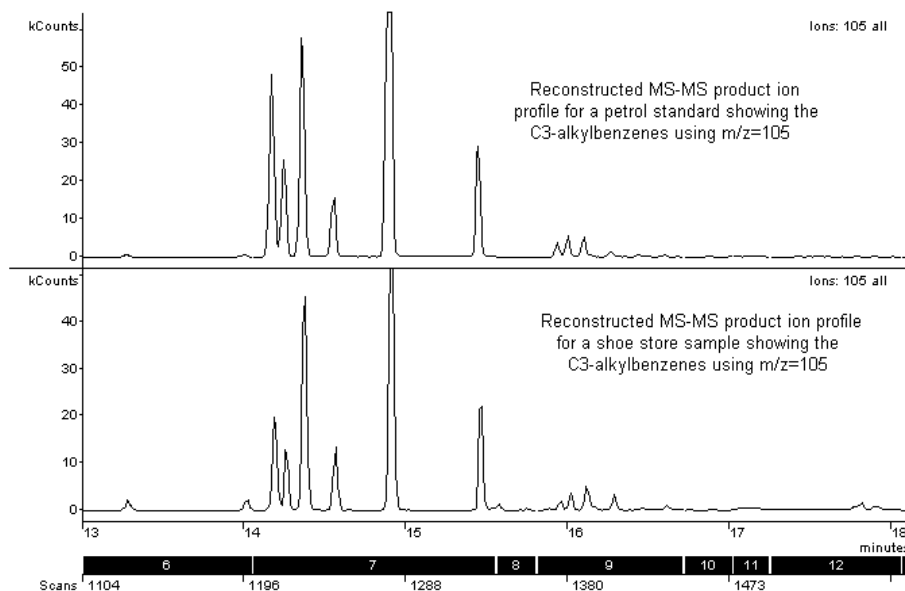


Figure 6.3.5: Reconstructed MS-MS product ion profile for a petrol standard using $m/z = 105$ with the reconstructed MS-MS product ion profile ($m/z = 105$) for the debris sample of shoes and carpeting from a shoe store below, showing the C3-alkylbenzenes more clearly.

Figure 6.3.5 is a reconstructed selected time segment MS-MS product ion profile for $m/z = 105$ (the fragmentation reaction $m/z = 120 \rightarrow 105$). Based on the GC-MS and GC-MS-MS analyses, petrol could be indicated in the sample, despite the presence of pyrolysis interferences and naphthalene compounds.

6.5. GYMNASIUM FLOOR DEBRIS SAMPLE

A gymnasium arson scene was investigated and unusual char-patterns were discovered in the centre of a huge gymnasium floor cover consisting primarily of foamed neoprene. The debris sample was collected from the region of the char-patterns and submitted to the laboratory for analysis.

Figure 6.4.1 shows the total chromatographic GC-MS ion profile for the gymnasium floor cover sample depicted in the upper trace with the total chromatographic GC-MS ion profile for a petrol standard depicted in the lower trace. Pyrolysate interferences are apparent in the sample chromatogram.

Figure 6.4.2 shows the selected ion profiles for the gymnasium floor cover sample. The C3 and C4-alkylbenzenes gave a weak response in the GC-MS chromatogram (as can be seen in the selected ion profiles for $m/z = 91 + 106$ and $m/z = 105 + 120 + 134$). MS-MS was performed using the conditions specified in Table 5.6, Chapter 5, in order to enhance and verify the possible presence of a petrol residue (Figure 6.4.3). The MS-MS product ion chromatogram of the sample compares very well with the MS-MS product ion chromatogram for a petrol standard (Table 5.6). Based on both GC-MS and GC-MS-MS analyses it could be reported that petrol was indicated in the sample. The final decision whether arson was committed or not must be decided in a court of law.

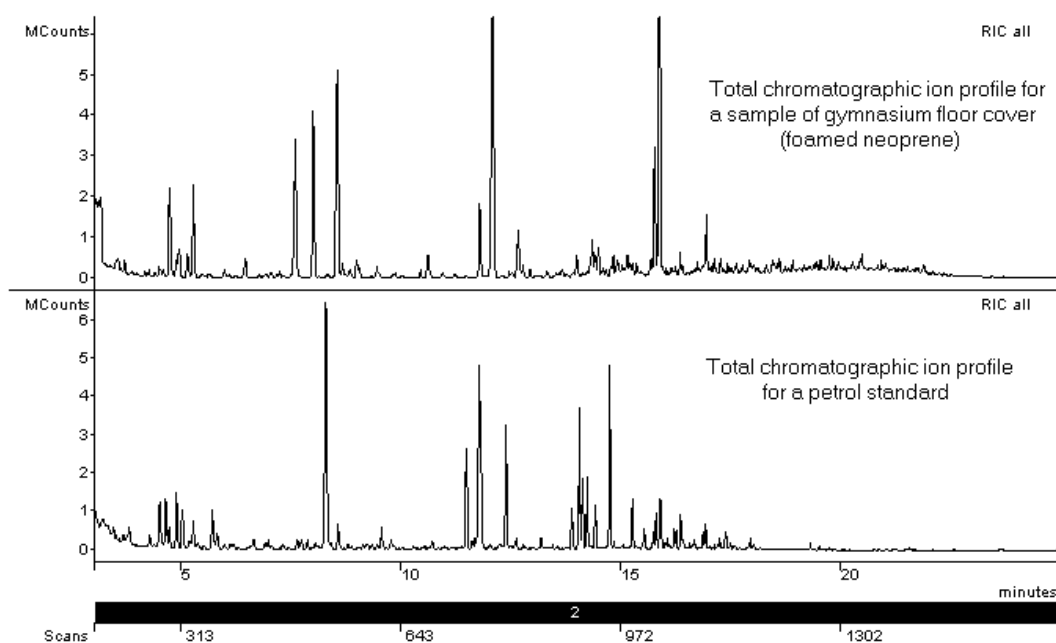


Figure 6.4.1: Total chromatographic ion profile for a debris sample of gymnasium floor cover and a petrol standard analysed by GC-MS.

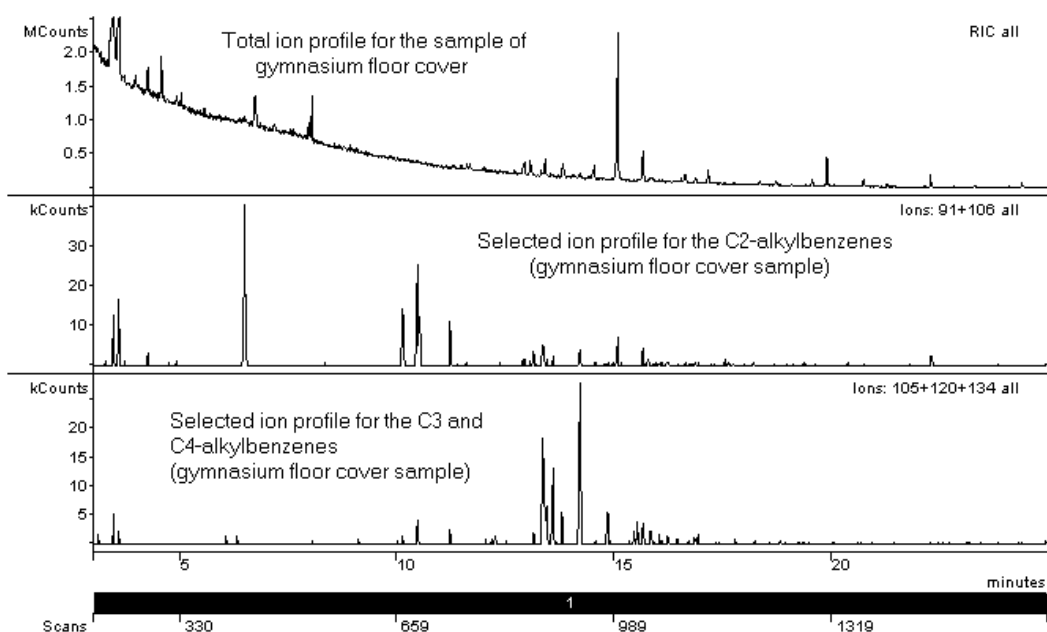


Figure 6.4.2: The total GC-MS ion profile depicted in the upper trace with the selected ion profiles for the C2 to C4-alkylbenzenes depicted beneath.

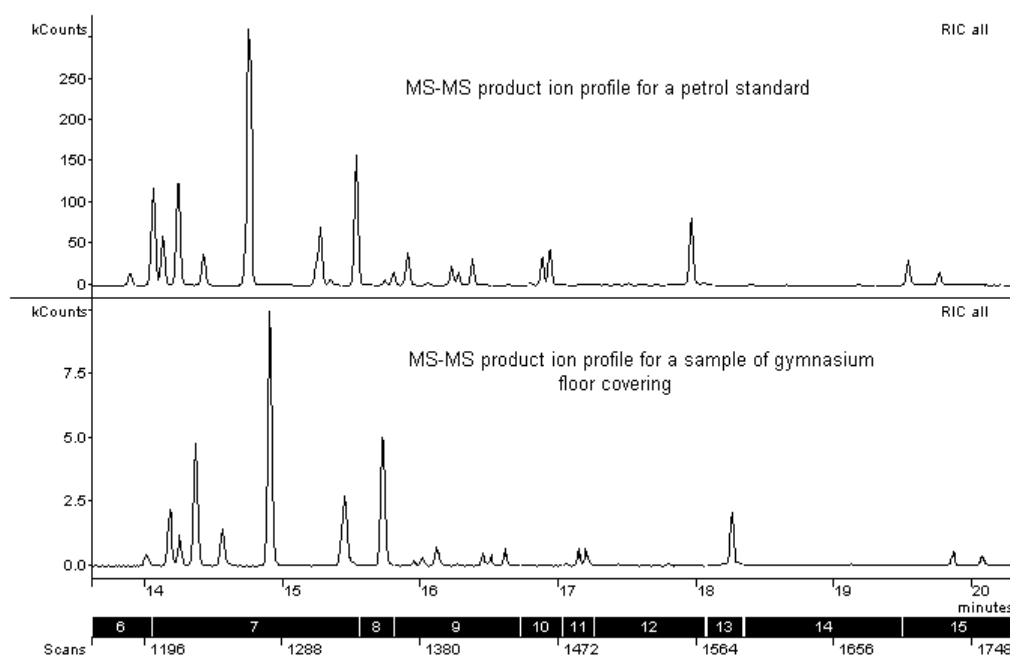


Figure 6.4.3: The MS-MS product ion profile (RT = 12 – 22 min, parent ions for segment 6; m/z = 120 – segment 15; m/z = 142) for a petrol standard, with the MS-MS product ion profile for the debris sample of gymnasium floor covering depicted beneath.

6.6 CARPET AND BEDDING DEBRIS SAMPLE FROM A PRIVATE HOME

The carpeting and bedding debris sample came from a privately owned home that had burnt under suspicious circumstances. The area of origin (spare bedroom), from which the sample had been taken, again showed evidence of accelerated char-patterns. The debris did not have a suspect odour. An arson canine indicated the area from which the debris was taken. The sample was extracted using the carbon badge method (paragraph 6.2). The GC-MS chromatogram (Figures 6.5.1 and 6.5.2) obtained from the extract did not produce very intense peaks. In the total chromatographic ion profile there was an indication of peaks in the medium petroleum distillate range, possibly accelerant traces. The aliphatic hydrocarbon compounds were checked for traces of paraffin, but none were present, not even polyethylene degradation peaks. Selected ion profiling was performed indicating the presence of traces of C3, C4

and C5-alkylbenzene aromatics in the sample, but the result is uncertain due to the weak response of the GC-MS.

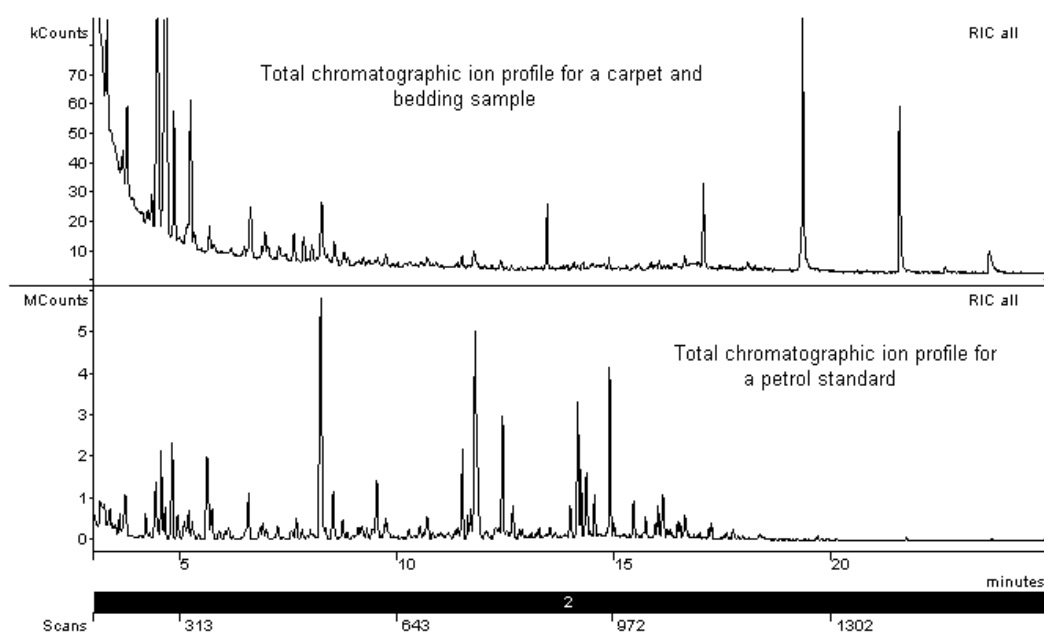


Figure 6.5.1: Total chromatographic ion profile for a sample of carpet and bedding from a home and a petrol standard.

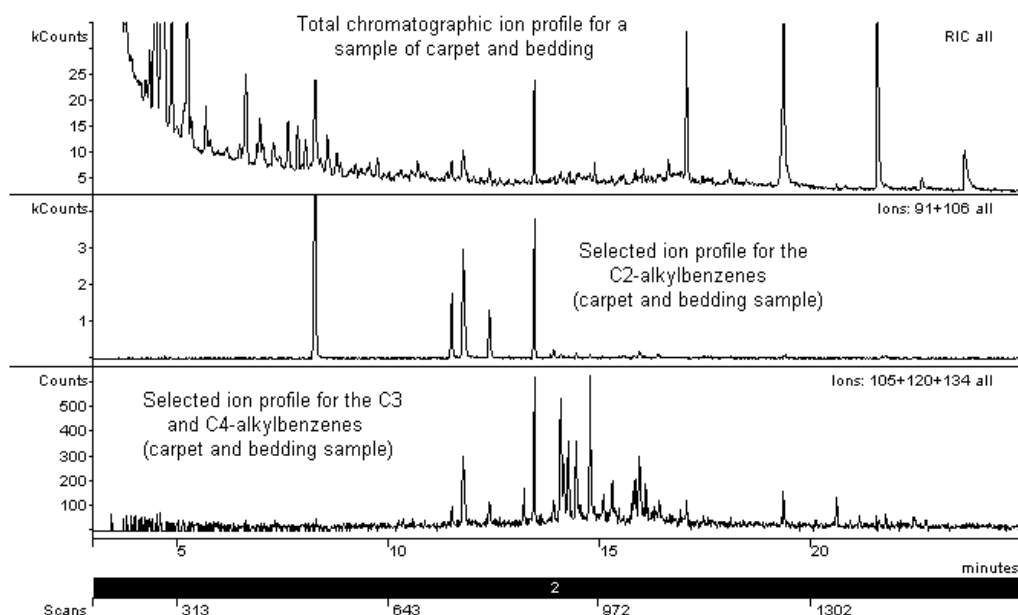


Figure 6.5.2: Total chromatographic ion profile for a debris sample of carpeting and bedding by GC-MS (upper trace). The selected ion profiles for the C2 to C4-alkylbenzenes are depicted beneath.

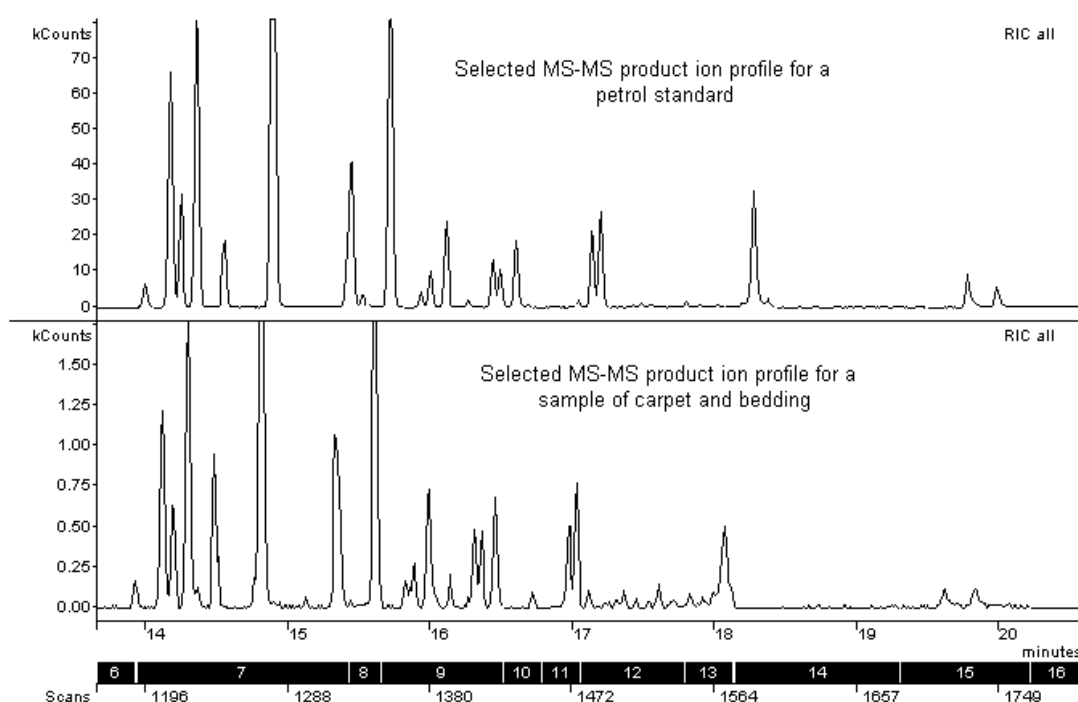


Figure 6.5.3: The MS-MS product ion profile ($RT = 12 - 22$ min, parent ions for segment 6; $m/z = 120$ – segment 15; $m/z = 142$) for a petrol standard (upper trace), with the MS-MS product ion profile for the debris sample of carpeting and bedding (lower trace), showing the C3, C4, C5-alkylbenzenes, naphthalene and the C1-naphthalenes.

A GC-MS-MS analysis was performed using the conditions specified in Table 5.6, Chapter 5. The product ion chromatographic profile clearly indicated the residual “petrol” presence (Figure 6.5.3 above). This illustrates the selectivity and sensitivity of the MS-MS method. This sample would have been reported as “negative” for the presence of accelerant traces due to the inconclusive GC-MS response, but instead was proven positive after a second, confirmational analysis by GC-MS-MS. The arson canine indication was vindicated.

6.7 BURNT PLASTIC DEBRIS SAMPLE TAKEN FROM A FACTORY

A severely burnt plastic sample, taken from the area of fire origin inside a factory office, was submitted for analysis. The sample odour was that of burnt polystyrene. The sample was extracted using a carbon badge (paragraph 6.2). The GC-MS chromatogram appeared to have some traces of petrol aromatics in the total chromatographic ion profile and toluene, ethyl benzene and styrene were predominant. This is where selected ion profiling becomes paramount since the total MS chromatographic profile could be misleading, especially if the chromatogram were generated using FID. This can be seen in figure 6.6.1. There were also traces of polyethylene degradation products present.

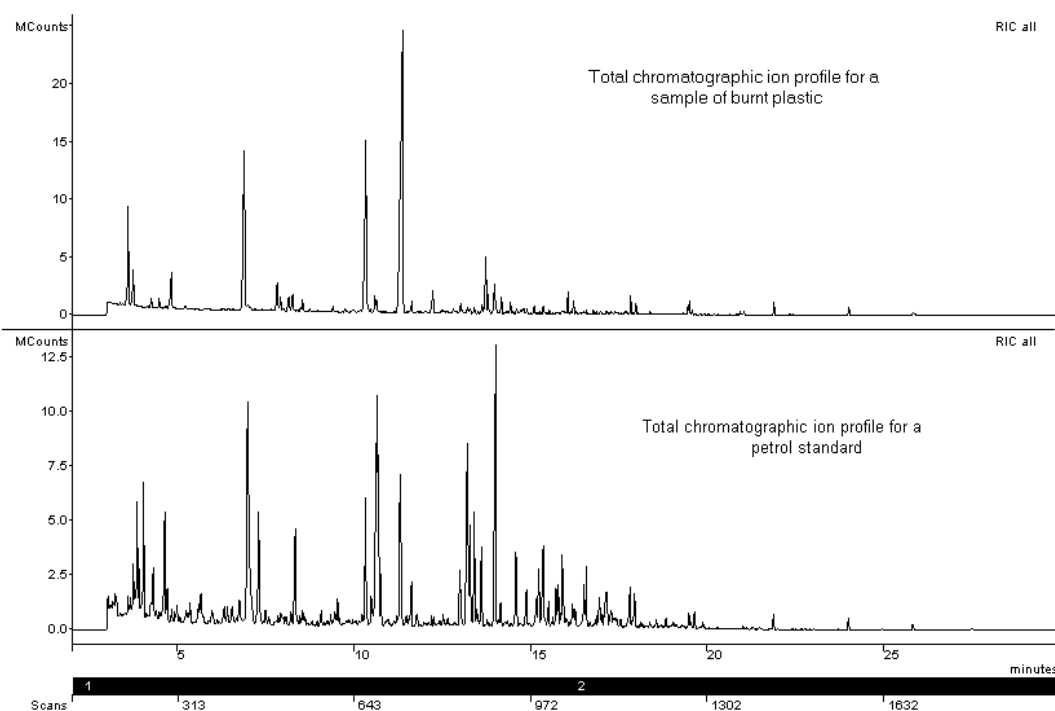


Figure 6.6.1: Total chromatographic ion profile for a sample of burnt plastic from a factory and a petrol standard.

The presence of excess toluene, ethyl benzene and styrene could clearly be seen in the selected ion profiles for the sample and petrol standard (Figure 6.6.2, RT = 6-12 minutes). Evidence of possible “petrol” aromatics is abundant, but the presence of the aromatic

pyrolysates complicates the selected ion profiles for the C2 and C3-alkylbenzenes. The mass spectra for the individual peaks clearly indicated which peaks were pyrolystates and which peaks were accelerant aromatics, but this could not be seen clearly chromatographically.

The sample was subjected to an MS-MS analysis using the conditions specified in Table 5.6, Chapter 5. The C2 and C3-alkylbenzenes can be seen more clearly looking at segments 5; $m/z = 106$ to 14; $m/z = 128$ (Figure 6.6.3).

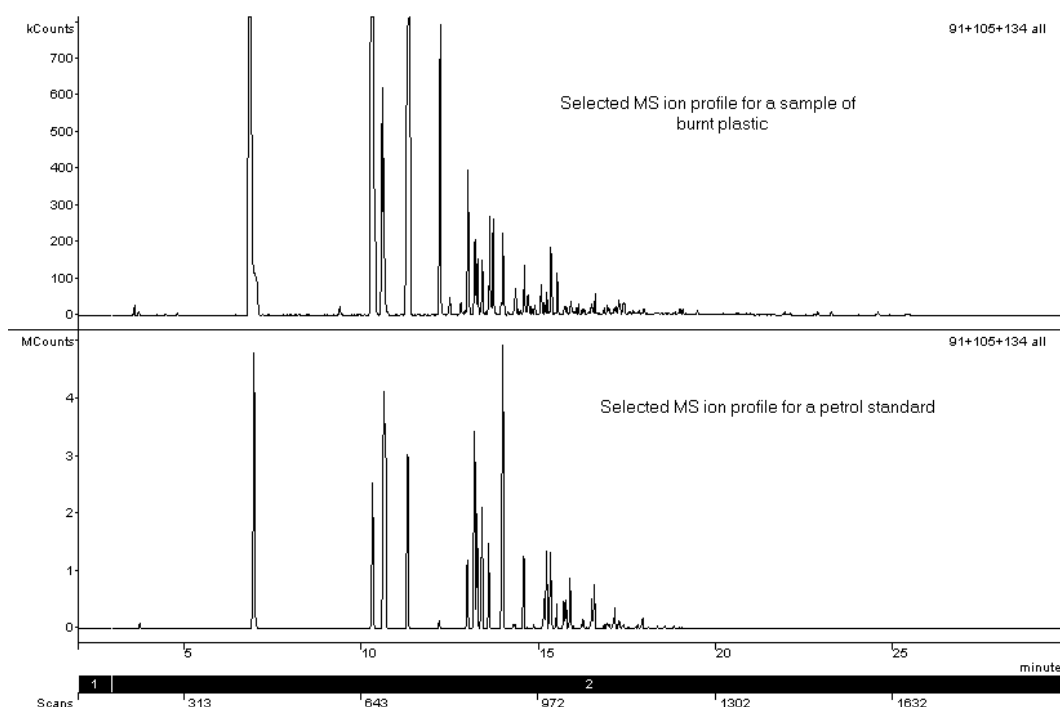


Figure 6.6.2: Selected MS ion profiles for a sample of burnt plastic from a factory and a petrol standard, showing the C2, C3 and C4-alkylbenzenes.

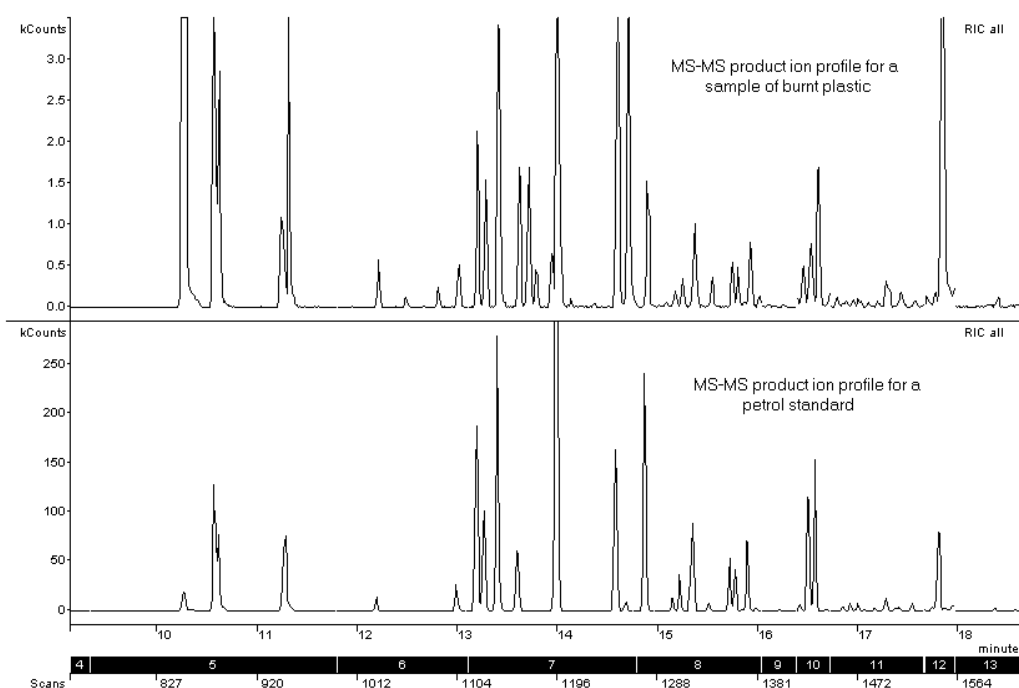


Figure 6.6.3: MS-MS product ion profiles (RT = 6 – 20 min, parent ions for segment 5; $m/z = 106$ – segment 12; $m/z = 148$) for a sample of burnt plastic from a factory and a petrol standard, showing the C2, C3, C4 and C5-alkylbenzenes. Interferences are still visible.

The ethylbenzene peak is significantly more intense than is usual for a possible petrol profile. The o-xylene peak is split in two due to the co-elution of the excess styrene that is present. There is also a more intense isopropylbenzene peak and p-isopropyltoluene peak (adjacent to the 1, 2, 3-trimethylbenzene peak at RT = 14.75 minutes). α -Methylstyrene is also evident next to the mesitylene peak (RT = 13.76 minutes).

These aromatic hydrocarbons result from the pyrolysis of polystyrene and plastic products. MS-MS does not remove these aromatic pyrolysates since they are naturally present in petroleum products, but it will remove the styrene (RT = 11.4 min) and α -Methylstyrene (RT = 14.1 min). What can be ascertained is that the ratios of ethylbenzene (RT = 10.2 min) : m, p-xylene (RT = 10.5 min) : o-xylene (RT = 11.3 min) confirm their presence as pyrolysates, and are not as constituents of a light petroleum distillate. In order to assess the C3-alkylbenzene aromatics in more detail, the MS-MS

product ion profile is reconstructed using SRM 120 \rightarrow 105. The pyrolysate aromatics are removed and the C5-alkylbenzene aromatics are clearly portrayed, confirming the presence of a petrol residue in the burnt plastic sample (Figure 6.6.4).

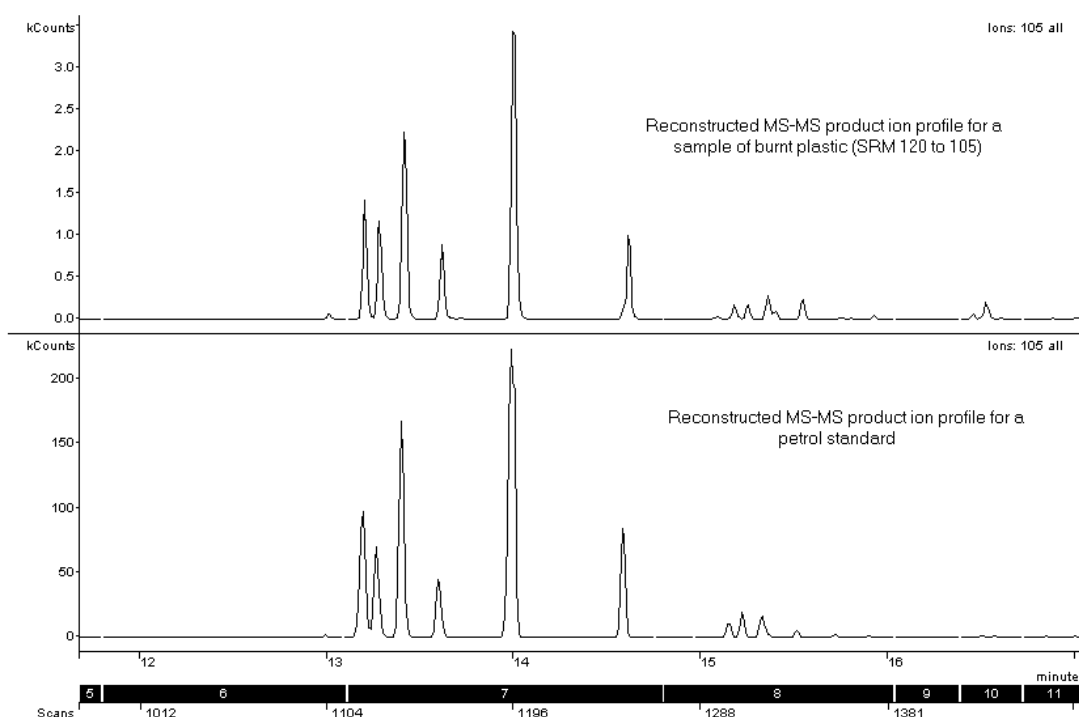


Figure 6.6.4: Reconstructed MS-MS product ion profile (SRM 120 \rightarrow 105) for a sample of burnt plastic using $m/z = 105$ with the reconstructed MS-MS product ion profile for a petrol standard below. The C3-alkylbenzenes are clearly shown with the α -methylstyrene interference removed.

6.8 CHARRED CARPET DEBRIS SAMPLE FROM A SMALL BUSINESS

A petrol can and charred carpet sample were submitted to the laboratory for analysis. The fire investigator mentioned that the fire had occurred at a small business, was very intense and that the building was in ruins. The burnt petrol can had been found at the scene. The carpet sample had been collected from an area of severe charring. The sample had no odour. The petrol can and charred

carpet samples were extracted using the passive carbon strip method (paragraph 6.2). The petrol can sample did contain petrol, but the total chromatographic ion profile for the charred carpet sample did not convey any significant aromatic component peaks (Figure 6.7.1). Had this been a GC-FID trace, the sample would have been considered negative.

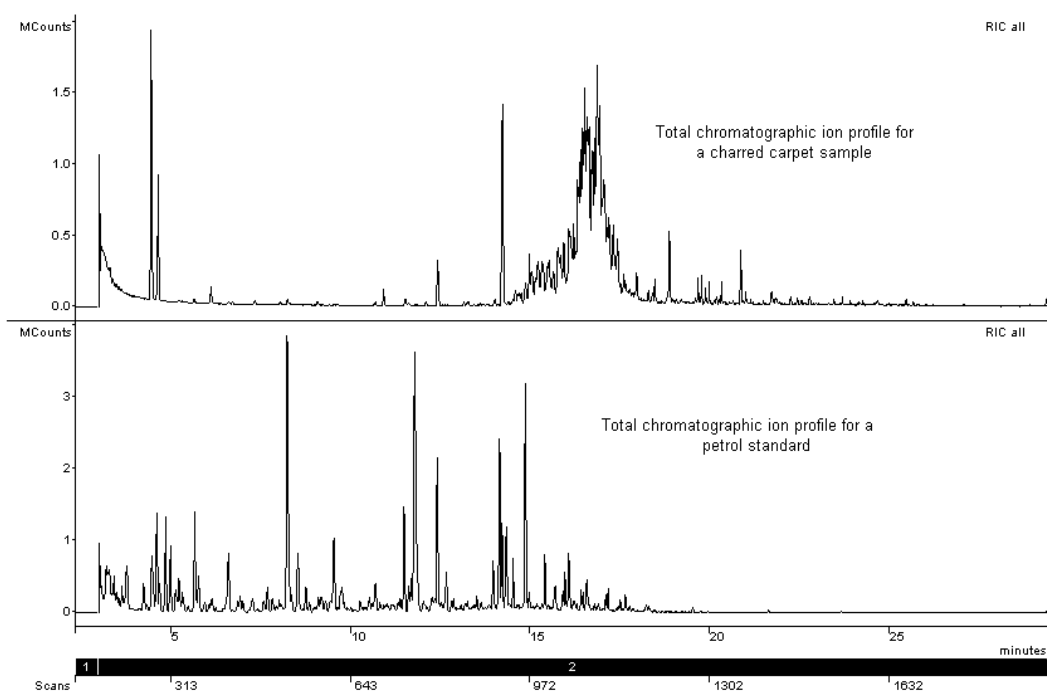


Figure 6.7.1: Total chromatographic ion profiles for a sample of charred carpet and a petrol standard, showing the C2, C3 and C4-alkylbenzenes.

Using the resolving power of the mass spectrometer, the selected ion profiles specific for aromatic hydrocarbons were examined (Figure 6.7.2).

There were aromatic hydrocarbon compounds present; typically toluene, ethylbenzene, styrene, *iso*-propylbenzene, α -methylstyrene and a host of branched aliphatic and aromatic compounds, but the isomer ratios of the C2, C3 and C4-alkylbenzene hydrocarbons (RT = 14 – 25 min) did not appear to be comparable with those found in known accelerant traces.

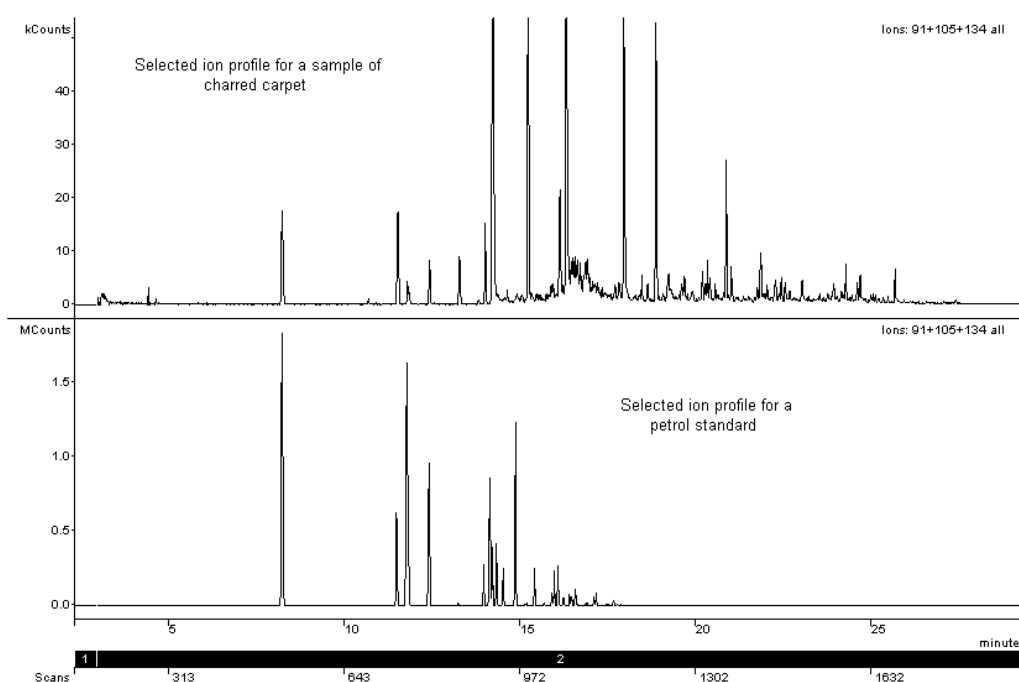


Figure 6.7.2: Selected MS chromatographic ion profiles for a sample of charred carpet and a petrol standard, showing the C2, C3 and C4-alkylbenzenes.

The GC-MS response is very weak and the sample was subjected to an MS-MS analysis using the conditions specified in Table 5.6, Chapter 5. Figure 6.7.3 illustrates the MS-MS product ion for the charred carpet sample. The C2-alkylbenzene isomer ratios are not comparable with those of a petrol standard. Excess ethylbenzene, styrene and *iso*-propylbenzene are inherently present, either due to pyrolysis or possibly the carpet itself. These C2-alkylbenzene aromatic pyrolysate compounds are not as significant as the copious amounts of matrix interference present in the sample (Figure 6.7.1; RT = 14 – 20 min), but a significant amount of these interferences have been removed (RT = 13 – 17.5 min) in the MS-MS analysis. The C3-alkylbenzenes are now more clearly discernable (RT = 14 – 15.7 min), but the ratios are not clearly comparable with the typical isomer ratios found in petrol or similar petroleum accelerants.

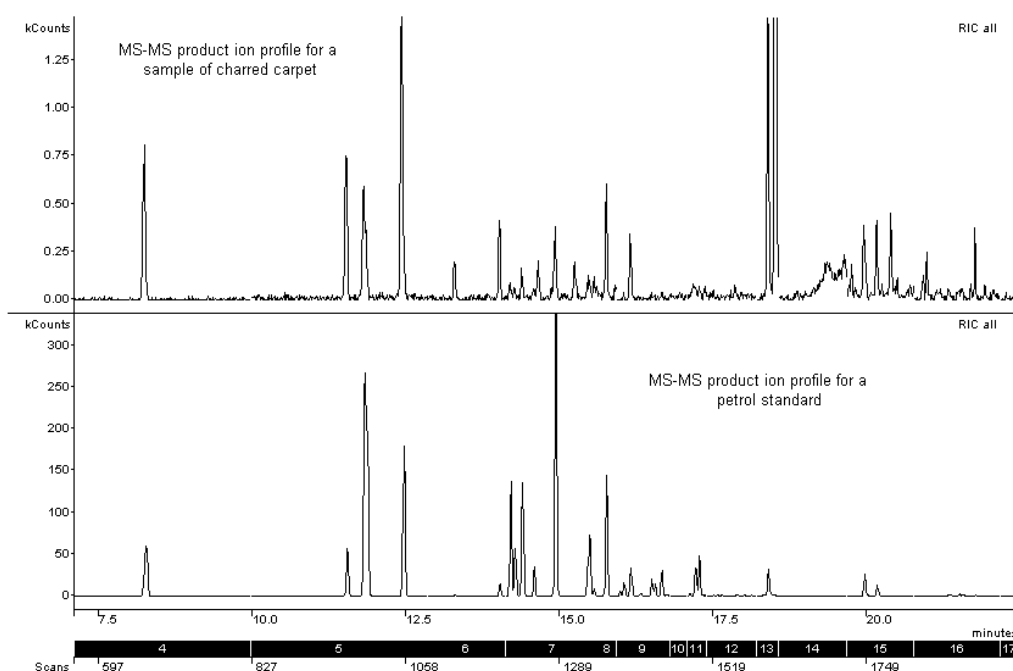


Figure 6.7.3: MS-MS product ion profiles (RT = 6 – 24 min, parent ions for segment 4; $m/z = 91$ – segment 17; $m/z = 170$) for a sample of charred carpet and a petrol standard, showing the C2, C3, C4 and C5-alkylbenzenes, naphthalene and methyl-naphthalenes.

Figure 6.7.4 shows the reconstructed MS-MS product ion profile (SRM 120 \rightarrow 105) highlights the C3-alkylbenzene region and indicates that the ratios of the C3-alkylbenzenes are similar to the ratios typically found in petrol. There are still aromatic interferences present, like the abundant *iso*-propylbenzene (RT = 13.2 min), but these do not obscure the C3-alkylbenzene region. The GC-MS chromatogram indicates the absence of possible accelerant traces, but the MS-MS chromatogram confirms that there are comparable aromatic traces. It cannot be conclusively shown that traces of evaporated petrol are present, but there is evidence of trace accelerant aromatics present. GC-MS selected ion profiling methods would not have been able to show the aromatic traces present in the charred carpet sample (see Table 2.2, Chapter 2 [29]) in the same way that the MS-MS reconstructed ion profiles can.

It would be easy to try and “find” traces of petrol aromatics in the chromatogram obtained for the charred carpet sample knowing that

petrol had been found at the scene. It is, therefore, important to examine each chromatogram independently and to ensure that the isomer ratios are verified by examining the C4, C5 and C6-alkylbenzenes and not only the C3-alkylbenzenes. This will confirm whether the aromatic traces are typical of an accelerant or not. The laboratory report must also reflect this unambiguously.

The final result as to whether or not the small business was intentionally burnt down will have to be determined by the judicial process based on the final report submitted by the fire investigator.

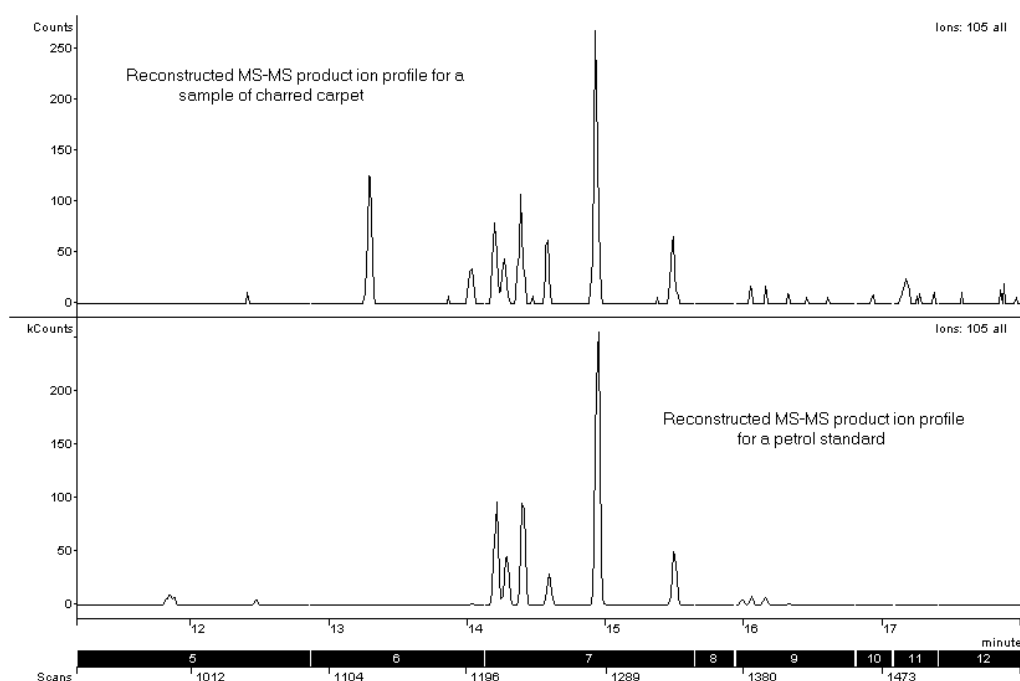


Figure 6.7.4: *Reconstructed MS-MS product ion profile (SRM 120 → 105) for a sample of charred carpet using $m/z = 105$ with the reconstructed MS-MS product ion profile for a petrol standard below. The ratios of the C3-alkylbenzenes are evident although there are still traces of interferences present.*

Since background components from carpet and plastic are often the most common sources of pyrolysis interference, the resulting chromatographic data must be carefully examined taking all aspects of the analysis into consideration (both GC-MS and GC-MS-MS). Figures 6.7.5 and 6.7.6 illustrate this point.

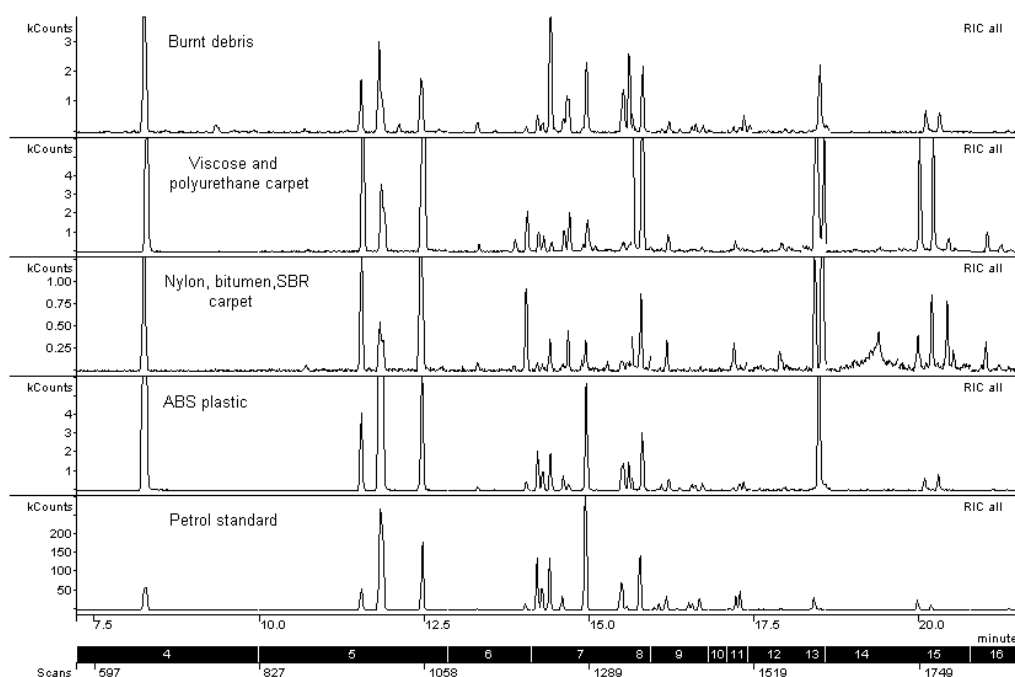


Figure 6.7.5: MS-MS product ion profiles for burnt debris, burnt carpet and burnt plastic samples and a petrol standard.

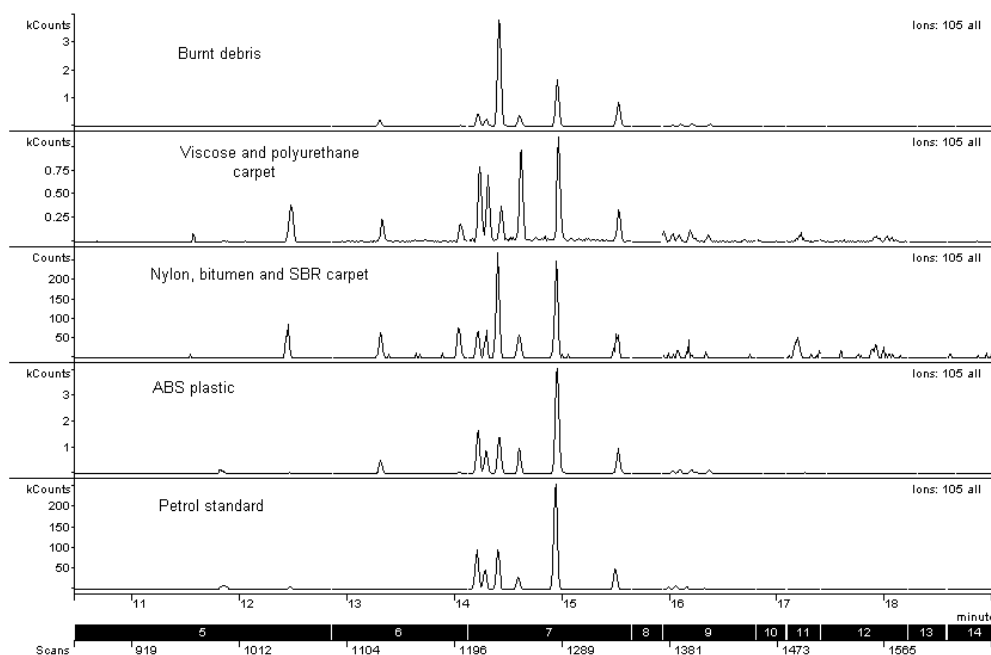


Figure 6.7.6: Reconstructed MS-MS product ion profiles (SRM 120 → 105) for burnt debris, burnt carpet and burnt plastic samples and a petrol standard, using $m/z = 105$.

The C2-alkylbenzene isomer ratios are not always skewed by excess amounts of ethylbenzene and o-xylene/styrene. The ratios could

very well mimic those encountered in ignitable liquids. The same applies to the C3-alkylbenzenes. Consider the ABS plastic sample (acrylonitrile : butadiene : styrene); the reconstructed MS-MS product ion profile could be taken for *bona fide* C3-alkylbenzenes from petrol if only this aspect of the analysis is considered. But if the abundance of the isomer ratios is considered in relation to the sample extract, the GC-MS trace and the GC-MS-MS trace, then an informed opinion and reasonable assessment can be made pertaining to the presence or absence of ignitable liquid accelerant traces. Even so, the MS-MS analysis clarifies the presence of these C3-alkylbenzenes and their isomer ratios such that an incorrect assessment is avoided as far as possible.

6.9 ROUTINE ANALYSIS BY GC-MS-MS

GC-MS-MS is a well established and understood technology that significantly improves the chances of identifying ignitable liquid traces in highly weathered samples that contain ignitable liquid traces. The use of GC-MS-MS has been tested in court [98]. Of particular note was the use of GC-MS-MS for successfully testing the validity of the blood evidence in the O.J. Simpson trial. Other experts recognize the excellent ability of GC-MS-MS to further reduce the chemical matrix interference in fire debris [92, 96, 98, 99]. It is an improved method for examining evidence from fire claims and has the enthusiastic support of a Canadian laboratory employing the technique [38, 98]. Some laboratory researchers have expressed doubts. The critique was levelled at rather improving chromatography and chromatographic processing and that the technique was considered "*overkill*" [38]. A criminalist supervisor, renowned for his knowledge and expertise in arson investigation and chemistry, was not aware that the technique was used to test anything other than drugs and explosives. He said that there was *a danger in pushing detection limits lower and lower because tiny traces of petroleum products could be found that had nothing to do with arson – we live in a hydrocarbon world where there can be chance contaminants present* [38].

Fire debris is riddled with "chance contaminants" due to the matrix interferences inherent in pyrolysates. GC-MS-MS has therefore been

tested on numerous samples and has proven reliable in not registering false positives based on naturally occurring hydrocarbons [38, 96].

The primary goal of using gas chromatography - tandem mass spectrometry is to extend the period between the fire and sampling and obtain more decisive results in the analysis of ignitable liquid residues. Often, the fire investigator does not get to the scene right away. There could be many reasons for these delays, such as, an investigation into potential motives of an arsonist prior to the expensive investigation of the scene of the fire. Between the date of the fire and the date of sampling, suspect materials may lose an appreciable fraction of the mere traces of ignitable liquids present. This additional loss is due to the exposure to precipitation, sunlight, high temperature and bacteriological degradation, which results in highly weathered samples. This is especially true in warm climates and adds to the problem of evaporation of accelerant traces due to the fire itself [98].

Nearly every fire investigator has a case where evidence of burn patterns and suspect behaviour indicate arson. Samples are taken to support these observations and are often located with the aid of electronic detectors or trained arson canines and thus should have a high probability of being positive. However, many of the results from the laboratory analyses of older or highly weathered samples come back as negative. This represents a significant loss of important high profile evidence. There is a significant probability that some of these samples are actually positive. Those samples that are falsely reported as negative, when there is actually an ignitable liquid trace present, does not necessarily indicate a faulty analysis. It is more probable that the method of analysis is not ideally suited to these highly weathered samples.

Most laboratories that specialise in the analysis of fire debris are using gas chromatography-mass spectrometry. Methods developed are often based on unevaporated or only moderately evaporated samples. Highly evaporated and additionally weathered samples are not efficiently detected by GC-MS. This is because the signal response is weak and pyrolysate interference is more serious, thus

obscuring the presence of target ions or complicating the chromatogram to the point that it becomes uncertain whether the peaks are of accelerant pyrolysate origin. The use of GC-MS-MS significantly improves the capability of detecting ignitable liquid traces in fire debris and answers commonly asked questions on potential environmental contamination of evidence. It provides an understanding of the sensitivity of today's analyses and has become a routine analytical tool in the CSIR-NML laboratory.

With the introduction of GC-MS-MS for elucidation purposes in arson analysis, clients will have access to fundamental scientific issues that have been adequately tested or verified for court [99]. The execution of this method is compliant with ASTM 1618-97 [29] and is a methodology that has been used successfully in significant courtroom proceedings. GC-MS-MS provides extra assurance that traces of ignitable liquids will not be missed and adds the highest level of confidence to the results.

CHAPTER 7

ALTERNATIVE METHODS OF ANALYSIS

7.1 CHEMICAL IONIZATION-MS-MS

Hydrocarbons were the first analytical target of organic mass spectrometry. It was in the 1940s that analytical chemists recognised the power of the technique for analysing hydrocarbon mixtures employed as fuels. At that time electron impact ionisation (EI) was the only effective ionisation method available and, in the case of long-chain alkanes and alkenes, it had severe limitations, due to the low abundance of molecular ions and to the formation of fragment ions not always related to the original structure [104]. Chemical Ionisation (CI) is a soft ionisation technique in which a reagent gas is allowed into the ion source at a pressure substantially in excess over that of the sample. This reagent gas is then ionised by conventional EI, the ions thus formed interacting to produce the reagent ions that subsequently react with the sample molecules to produce sample ions [104 - 106].

To avoid problems related to the high energy deposition occurring in EI, alternative methods of ionisation were developed; in particular positive-ion chemical ionisation, which was highly effective in the production of molecular ion species. Ion trap mass spectrometry is valuable in chemical ionisation experiments. The characteristic temporal separation of the reactant ion production followed by its reaction with the analyte, guarantees the real and exclusive nature of chemical ionisation, without any overlapping of EI-induced ionisation/decomposition phenomena. The mechanisms describing

the chemical ionisation fragmentation pathways of reagent gases and liquids selected for use are well documented [68 - 78].

Since the ion trap is ideally suited to MS-MS, CI-MS and CI-MS-MS were selected as alternative ionisation mechanisms to study the effect in possibly providing more diagnostic ions for detecting ignitable liquid accelerants. Methanol was selected as the reagent liquid. The mass spectra are inherently different since the $M+1$ and $M+2$ ions are more abundantly present than in the typical EI mass spectra for aromatic hydrocarbons (Figure 7.1 to 7.3). This is due to the fact that the amount of energy transferred into the sample molecule by CI-MS is significantly less than the energy transferred from EI, resulting in less fragmentation and a consequent improvement in the amount of information at higher masses. This method could be ideally suited to ignitable liquids that predominantly consist of aliphatic hydrocarbons if the molecular ion could be preserved intact for the identification of the characteristic alkanes and olefins.

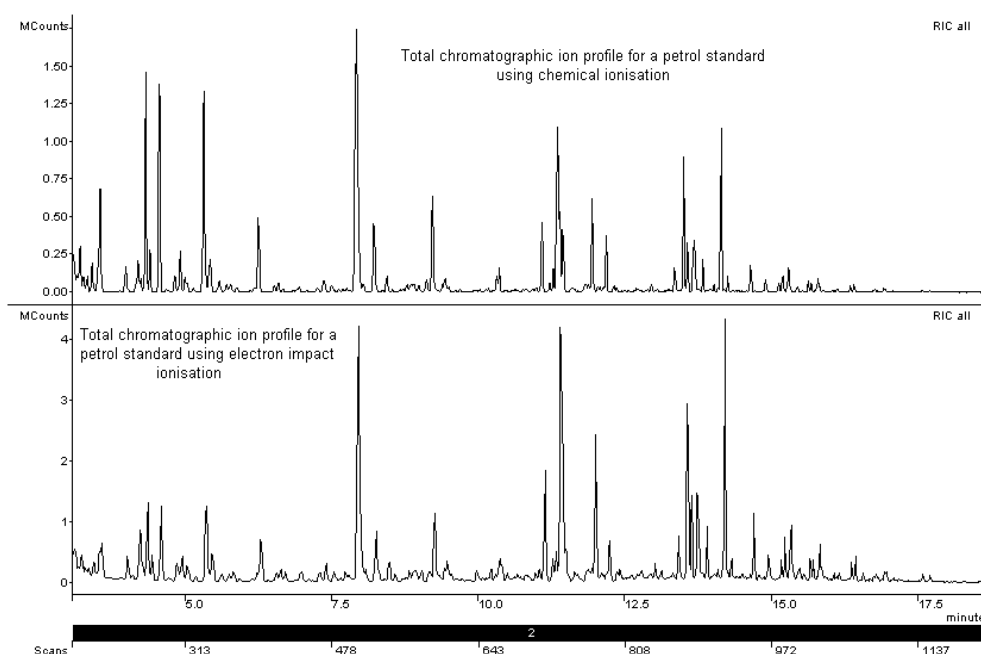


Figure 7.1: Comparison between the total chromatographic ion profile for petrol generated by chemical ionization using methanol and conventional electron impact ionisation.

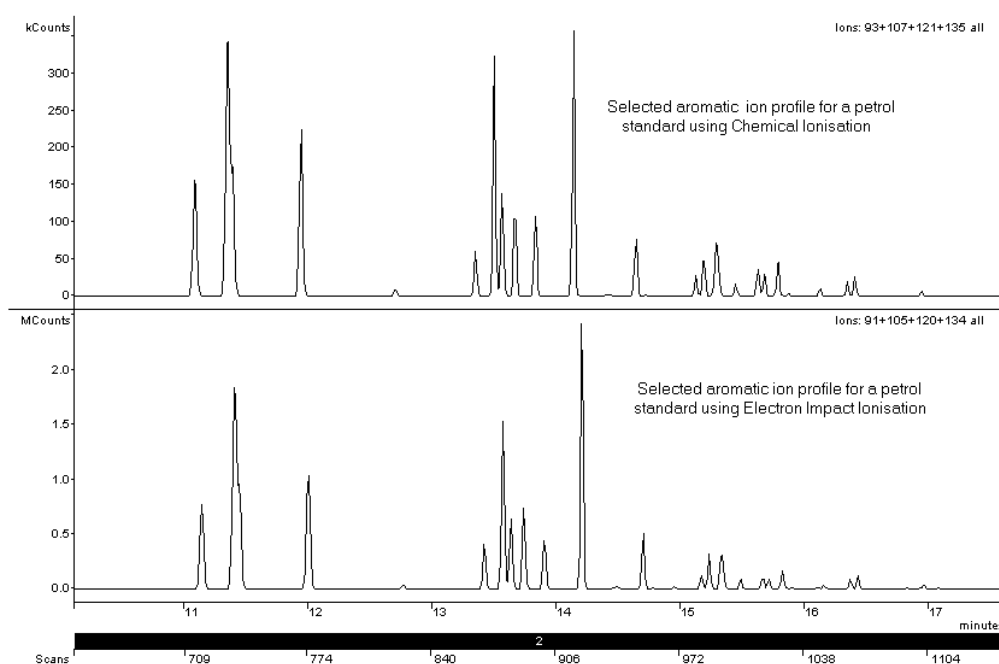


Figure 7.2: Comparison between the selected aromatic ion profile for petrol generated by CI using methanol and conventional EI.

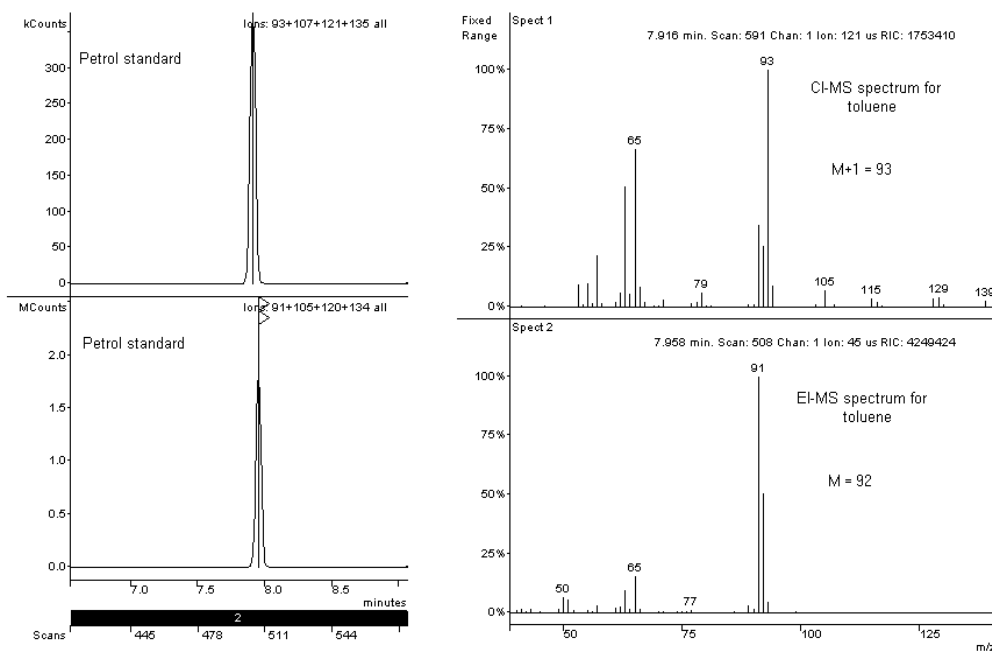


Figure 7.3: The MS spectrum for toluene from a petrol standard with the upper trace and spectrum generated by CI and the lower trace and spectrum generated with conventional EI.

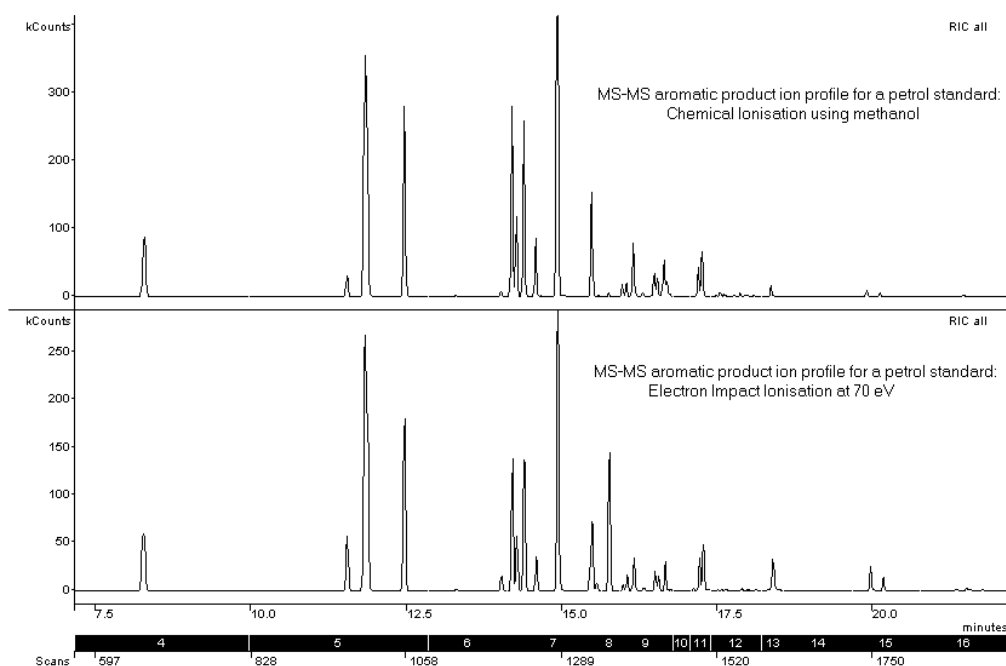


Figure 7.4: *The CI-MS-MS (Table 7.1) and EI-MS-MS (Table 5.6) product ion profiles for a petrol standard.*

Unfortunately the aliphatic hydrocarbons do not give an $M+1$ ion using CI, but the aromatic hydrocarbons do. A CI-MS-MS method was developed, based on the data obtained from EI-MS-MS [96], mainly just to compare the merits of CI as compared with EI. The CI-MS-MS aromatic product ion chromatogram generated for a petrol standard compared well with that generated for EI-MS-MS (Figure 7.4). The criteria selected for CI-MS-MS is given in Table 7.1. The CID voltages selected are similar to those selected for EI-MS-MS (Table 5.6, Chapter 5). Examining the CI-MS-MS product ion mass spectra shows a similar type of product ion to that obtained by EI-MS-MS, although there are more product ions present. This is due to the methanol present in the collision gas causing harder collisions than with only helium (a higher collision energy). This can be seen in figures 7.5 and 7.6. 1, 2, 4-trimethylbenzene exhibits an $M+1 = 121$ with CI ($M = 120$ for EI) and naphthalene exhibits an $M+1 = 129$ with CI as opposed to the $M = 128$ for conventional EI.

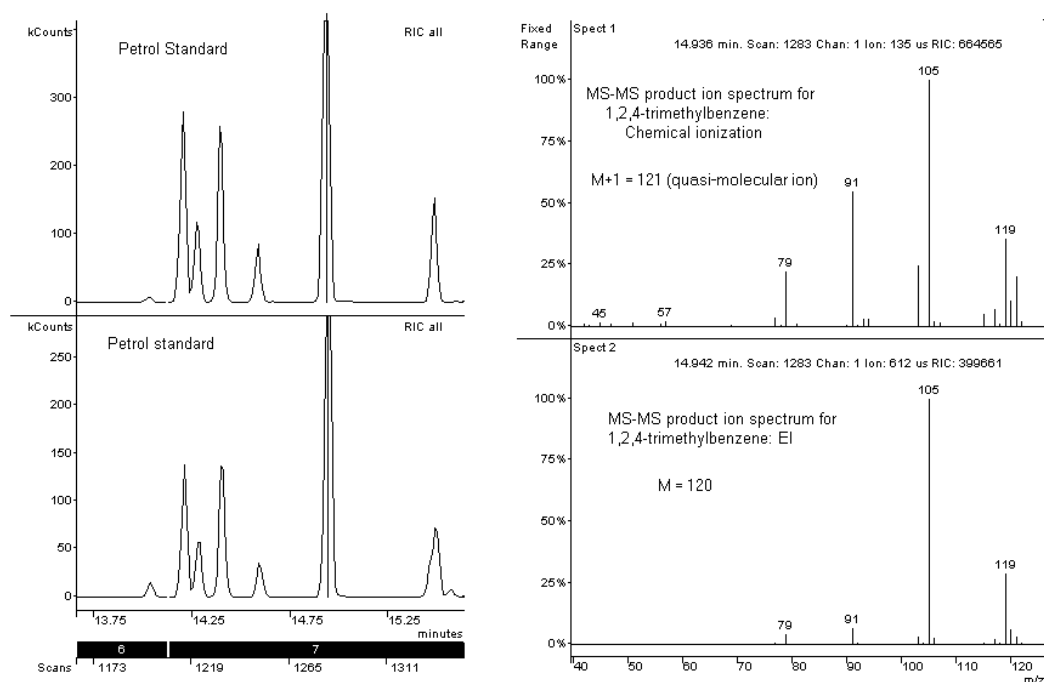


Figure 7.5: Comparison between an MS-MS product ion spectrum for 1,2,4-trimethylbenzene generated by CI (upper trace and spectrum) and conventional EI (lower trace and spectrum).

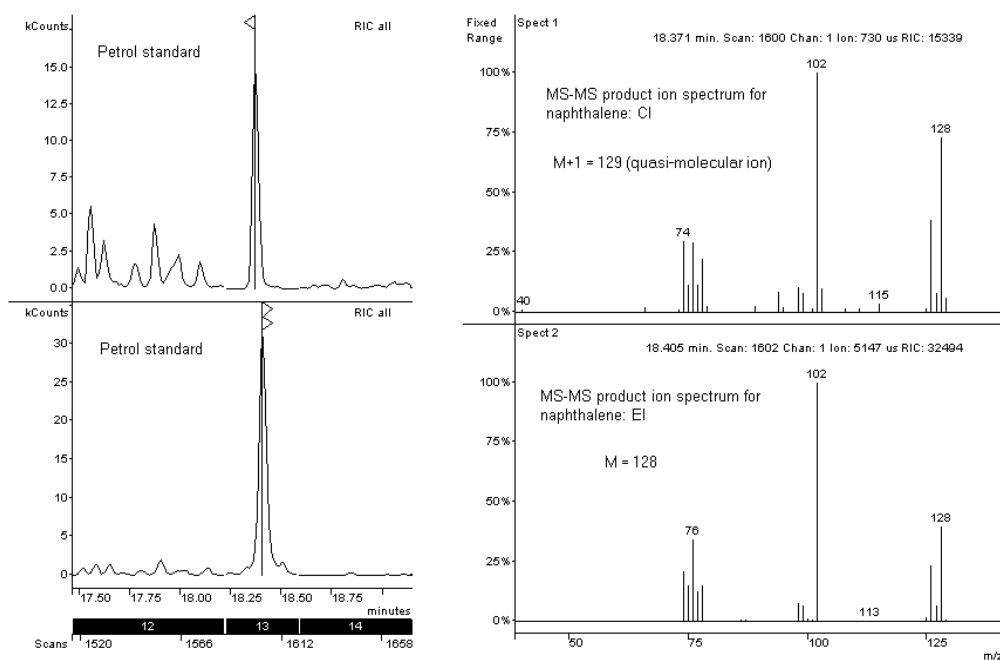


Figure 7.6: Comparison between an MS-MS product ion spectrum for naphthalene generated by CI (upper trace and spectrum) and conventional EI (lower trace and spectrum).

**Table 7.1: CID Voltages for each Selected Parent Ion Mass
(Chemical Ionization)**

Segment No	Segment Time (min)	Ion Mode	Mass	Mass Window	CID Voltage	Rf Excitation Storage Level	Parent Ion (M+1)
1	0:00-3:00	CI	-	-	-	-	-
2	3:00-3:40	CI	-	-	-	-	-
3	3:40-6:00	CI-MS-MS	79	1	59	48.0	Benzene
4	6:00-10:00	CI-MS-MS	93	1	58	48.0	C1-Benzenes
5	10:00-12:89	CI-MS-MS	107	1	55	48.0	C2-Benzenes
6	12:89-15:66	CI-MS-MS	121	1	50	53.1	IPB, PB & C3-Benzenes
7	15:66-15:95	CI-MS-MS	119	1	55	52.2	Indane
8	15:95-16:82	CI-MS-MS	135	1	54	59.3	C4-Benzenes
9	16:82-17:10	CI-MS-MS	149	1	56	65.5	C5-Benzenes
10	17:10-17:42	CI-MS-MS	135	1	54	59.3	C4-Benzenes
11	17:42-18:24	CI-MS-MS	149	1	56	65.5	C5-Benzenes
12	18:24-18:60	CI-MS-MS	163	1	50	71.7	C6-Benzenes
13	18:60-19:70	CI-MS-MS	129	1	69	56.7	Naphthalene
14	19:70-20:80	CI-MS-MS	143	1	69	62.9	C1- Naphthalenes
15	20:80-22:20	CI-MS-MS	157	1	66	69.0	C2- Naphthalenes
16	22:20-24:70	CI-MS-MS	171	1	66	75.2	C3- Naphthalenes
17	24:70-29:00	CI	-	-	-	-	-

CI-MS-MS was applied to a sample collected from a fire scene that was positive for the presence of petrol, in order to verify the use of the technique. The CI-MS-MS product ion chromatogram provided the same selectivity capability as for EI-MS-MS and pyrolysate interferences were removed. The possibility of using CI-MS-MS is well suited to arson debris analysis, but would be selected depending on ionization requirements and analysis criteria.

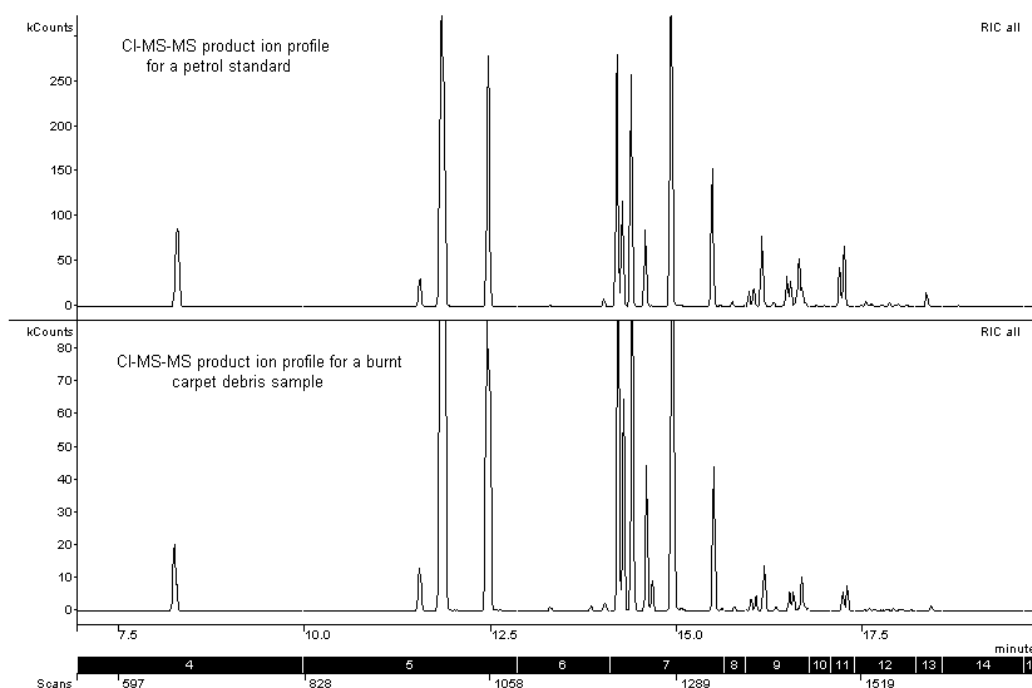


Figure 7.7: *CI-MS-MS product ion spectrum for a petrol standard and a sample of carpet debris (Table 7.1).*

7.2 AROMA DETECTION TECHNOLOGY

The analytical challenge in analysing fire debris is establishing the presence of trace accelerant residues in a background of pyrolysis interference. As an alternative to the conventional methods already discussed, the ability to classify different ignitable liquid accelerants using aroma detection technology was investigated [100].

Aromas are mixtures of volatile organic chemicals; each vapour sample may contain hundreds of volatile components. The key to aroma detection is not to monitor individual chemicals, but to have an array of sensors able to respond to a large number of different chemicals. The goal of an aroma detector is to ensure that every component in a vapour is detected by at least one sensor so that each vapour sample gives a characteristic fingerprint from the sensor array. This is the basic operating principle behind some recently developed devices called "*electronic noses*". The detection mechanism of the electronic devices mimics the main aspects of the canine olfactory system: sensing, signal processing, and recognition [19-21, 100]. Canines have been trained to detect and indicate

ignitable liquid vapours indicative of accelerants. The use of electronic devices is based on this knowledge.

The theory for scent detection is based on a “lock and key” mechanism where each scent molecule has a different shape that must fit within a receptor of the corresponding shape to be registered by the brain. After a receptor accepts a scent molecule, the impulse is sent to the brain for identification. This theory is applied to a vapour sample that is introduced across an array of sensors where each sensor within the array exhibits a characteristic change in electrical resistance upon interaction with the components of the aroma. Recognition and identification can then be achieved using an artificial neural network trained on known vapour samples. The sensors are based on the polymers of aniline, pyrrole and thiophene to which different functional groups have been added to produce unique sensing capabilities. The sensors respond to steric, ionic, hydrophobic and hydrophilic variations of a sample causing temporary changes in electrical resistance at the polymer surface. As in training canines for scent discrimination, identification by the neural network is only as good as the reference sample training set.

The use of aroma detection technology for detecting ignitable liquid accelerants in fire debris has been shown to be feasible. The humidity, temperature and equilibration time variables affecting the change in sensor response need to be precisely controlled to achieve consistent results. For standard reference samples these variables can be controlled, but the wide variations in water content on actual fire debris samples and variations in sample composition and concentration also influence the sensor response. There are a number of factors, like sampling conditions and sample composition inconsistencies, which further affect the results, but sorbent sampling prior to aroma detection can diminish these. Despite the similarities between trained police canines and the electronic noses, the forensic or law enforcement communities have not investigated aroma detection technologies seriously. Further work is necessary, but the technique definitely holds promise for the future.

7.3 MULTIDIMENSIONAL GAS CHROMATOGRAPHY

Current methodology for the identification of volatile petroleum distillates in fire debris samples involves three stages: extraction, characterisation and interpretation. The volatile components are first isolated from the debris by a sample preparation technique. The isolated sample volatiles are usually separated by gas chromatography and identified by mass spectrometry using selected ion profiling. The final stage is data evaluation and interpretation. An experienced analyst using interpretative procedures usually performs this final step manually.

Multidimensional gas chromatography is a powerful approach to improving the separation capacity in gas chromatography [107]. Although it does not seem to have been applied routinely to the analysis of fire debris samples, it offers considerable potential as a supplementary technique to improve the identification of target compounds and to reduce the influence of matrix and pyrolysis interferences.

Petroleum distillates contain mixtures of alkanes, cycloalkanes, alkenes, cycloalkenes, aromatic and polycyclic aromatic compounds. Knowledge of their relative concentration and identity is important in establishing the probability of a sample belonging to a certain accelerant class. The volatility distribution of petroleum distillates on non-polar phases is almost always required to characterise the sample origin. By multidimensional gas chromatography employing a non-polar column with the selective transfer of certain regions of the chromatogram for further resolution on a polar column, both an estimate of the volatility distribution of the sample and the isolation of the target compounds (mostly the aromatic hydrocarbons) on the second column can be made concurrently. The difference in polarity between the two columns also increases the probability that contaminants that co-elute on the first column are separated on the second column reducing the frequency of misidentification of the target compounds.

Multidimensional GC is used to speciate petrol and petrol exhaust samples providing a more complete picture of their complexity than is

possible using a single column. There are various approaches, namely enrichment (used to increase amounts of trace components), heart-cutting (grabs an unresolved portion of a sample for improved separation) and “backflushing” (reverse column flow to drive off highly retained components). Anti-knocking agents and additives are easily identified by this technique. In comprehensive multidimensional GC (GC x GC) the data is usually represented as a three-dimensional contour plot and the individual classes of compounds are clearly separated according to their characteristic physical and chemical properties.

7.4 THERMAL DESORPTION AND GC-MS FOR ARSON ANALYSIS

The extraction and concentration of residual fire accelerant components from fire residue and their introduction into a gas chromatograph is usually performed using liquid injection, purge and trap or thermal desorption by SPME. While inexpensive in terms of materials, solvent extraction is insensitive, labour intensive and subject to masking of peaks of interest by the solvent selected. Conventional equilibrium headspace systems are also limited with regard to sample size and sensitivity, particularly with higher boiling fuels such as paraffin and diesel. SPME is also an excellent extraction technique, eliminating the solvent masking, but the sensitivity achieved is sometimes inadequate. The most sensitive and readily automated approach is to use dynamic sampling/purging of a large volume of vapour from around a fire debris sample onto a sorbent tube and then to introduce these extracted volatiles directly onto the GC column by means of thermal desorption (TD).

The potential for using TD-GC in arson analysis for accelerant traces has been demonstrated [52-54]. Informative chromatography is produced with the minimum of effort and interference from preparation techniques. Coupling thermal desorption with multidimensional gas chromatography-tandem mass spectrometry could potentially lead to tremendous informative power when applied to the detection of volatiles from arson debris samples.

7.5 “DNA” TECHNOLOGY FOR FIRE INVESTIGATION

Arson is the easiest crime to commit but the most difficult to solve. The arsonist usually works under cover of darkness, chooses the time of attack to minimise contact, usually gains entry through an entrance hidden from view, concocts an inconsistent alibi that will usually stand up to a cursory investigation and relies on the fire itself to destroy any evidential link to the scene of the crime.

Trace analysis of fire debris samples for ignitable liquid residue is typically performed by gas chromatography-mass spectrometry. Using such equipment, the forensic analyst can determine a sample's compound structure and relative concentrations and then identify or “fingerprint” specific organic compounds. These fingerprints, in turn, can be identified as specific classes of petroleum products, allowing the fire investigator to identify the type of accelerant used by the arsonist to ignite a fire.

Courts of law today often demand physical and circumstantial evidence that positively links a suspect to a crime scene before they will deliver a verdict. This unequivocal level of DNA-like forensic evidence has been historically hard to come by in arson investigation cases. This situation could possibly change. Based on preliminary studies of stable carbon isotopic analyses, gas chromatography isotope-ratio mass spectrometry (GC-IRMS) technology promises to take investigation a crucial step further by positively linking the accelerant from fire debris to accelerant identified in samples of the suspected arsonist's containers or clothing. The GC-IRMS takes advantage of other types of tracers called stable isotopes contained within the same analyte compounds, which are not evaluated by structural GC-MS. The associated technique separates individual compounds by GC, combusts them into carbon dioxide and measures the isotopic composition of the resultant carbon dioxide peaks with a very precise isotope-ratio mass spectrometer. The precisely measured isotopic values can be used as “isotopic fingerprints” for a variety of purposes [108].

The original and most significant purpose for such molecular isotope data was for tracing petroleum migration between subsurface

reservoirs in the oil industry. Review of test data has convinced experts from the pharmaceutical field that this method will provide them with a way of proving the source of counterfeit drugs by showing that they cannot have come from the actual manufacturer whose set of isotopic fingerprints are already known. It promises to provide fire and arson investigators with the ability to link together the ignitable liquid accelerant residue recovered from burned flooring with partially evaporated ignitable liquid accelerant residue from the arsonists' clothing with the neat liquid remaining in the accelerant container. Linkage of a specific accelerant at a fire scene to the accelerant in a container and accelerant found on the clothing of a suspected arsonist would make an extremely strong case.

7.6 FIRE DEBRIS ANALYSIS: THE FUTURE

Fire investigators often collect samples for chemical analysis in order to identify any liquid accelerants that may have been involved in the initiation of the fire. In many cases the samples are found to be negative by the laboratory. A number of factors are important in determining whether or not fire debris analysis results will be negative. These include the fire scene conditions, the type of liquid accelerant involved, the proficiency of the fire investigator and the competency of the forensic analyst. Even though there may be some unusual burn-patterns present at the fire scene, liquid accelerants will not be detected when the fires are accidental. Many incendiary fires are started without the use of liquid accelerants. As the severity of the fire damage increases, the likelihood of obtaining a positive sample decreases. In addition, the amount of delay in securing samples will affect the result, as will the weather conditions from the time of the fire until sample collection. But even in those situations where it is clear that a liquid accelerant was used, positive results are not always obtained.

Factors to consider include volatile, water-soluble liquids (alcohols and acetone) that burn and evaporate readily and are vulnerable to dilution and washing away with water used by fire fighters to extinguish the fire. As a result, these liquids are generally not recovered, even when the fire damage is quite limited, unless they are present in significant quantities. If the severity of the fire is great

enough, even the heavier fuels (paraffin and diesel) may be completely consumed. Thus, in some arson cases it is not possible to collect positive samples because there is no trace of liquid accelerant left, even though one may have been used to start the fire.

Another factor to bear in mind involves the methods employed by the fire investigator. Even at scenes where liquid accelerants were used and residues remain, if the assessment of the scene is incorrect, samples may be collected in areas that do not contain those residues. The sample containers used for collection of debris material must also be suitable and even then accelerant traces are lost if the samples are not sealed properly or opened too often to sniff the volatile contents. If a trained arson canine alerts to a specific area, this can aid the fire investigator in obtaining more suitable samples, but again, this is no guarantee that the sample will be positive. Canines used as detectors for accelerants at actual fire scenes sometimes respond positively to burnt carpets and rubber underlays on which no accelerant liquid has been placed [19, 20].

The last factor involves the laboratory. Without proper training in chemistry and fire debris analysis, the analyst may not be able to identify the accelerants present in the samples. Even with proper training and using applicable extraction procedures, the forensic analyst may miss an accelerant if the amount present is very small or if the background matrix interference is significant. It must also be established whether the laboratory in question used GC-FID or GC-MS for the analytical identification. GC-MS is a powerful technique and is ideally suited for fire debris analysis, not only for pattern recognition, but also for identification of specific compounds by their mass spectra, and of groupings of related components by selected ion profiling. GC-MS-MS adds a second confirmatory analytical dimension to such an analysis and does help to reduce the total number of false positives and false negatives [96, 103].

Destruction of property by fire is unfortunately here to stay – the cause may differ, but the outcome remains the same. Taking into consideration that arson is a crime, then the benefits of a thorough arson investigation, including chemical analysis of the fire debris, is a necessity. Technology has advanced at a rapid pace and there really

is little excuse for inconclusive results. Many different factors are important in determining whether or not laboratory results will be positive or negative for fire debris samples collected at arson scenes. As a result, it is not unexpected that sample results will be negative in some arson cases, even though liquid accelerants were present. Fire investigators are trained and experienced, there are numerous tools at their disposal from portable "sniffers" to trained arson canines and they have the support of sophisticated instrumentation if an analysis for accelerant traces is required. Not every laboratory performing chemical analyses will have every possible technique available on the market, but the techniques that are at their disposal could most probably be utilised for ignitable liquid accelerant residues in fire debris samples. There are a number of extraction techniques that can be employed and the choice of coupled instrumental techniques used will depend on the instrumentation available for analysis. Methods for accelerant detection in fire debris analysis are constantly being refined and improved and an important requirement is that the analyst performing the analysis be trained and experienced in arson chemistry, so that he or she can correctly interpret the analytical results.

CHAPTER 8

DISCUSSION AND CONCLUSION

Understanding the chemistry behind the destructive force of fire and the motives that drive people to commit the crime of arson involves a wealth of learning, experience and insight. It is a complex science and trained fire investigators must ensure that they remain unbiased and focussed on finding the truth.

The forensic analyst relies on the fire investigator to collect relevant samples of fire debris for analysis in as much as the fire investigator relies on the trained and experienced forensic analyst to analyse the debris for the presence of ignitable liquid residual traces using the most sophisticated techniques applicable.

The procedures followed for the identification and collection of fire debris samples, the extraction procedures followed and analytical technique applied, all contribute to the successful outcome of a meaningful laboratory result that can assist the course of justice.

The arson laboratory was established at the CSIR in June 1996 as a result of the escalation of arson related fires in South Africa. This laboratory was relocated to the CSIR National Metrology Laboratory in 2002 and now offers a forensic analytical chemistry support service to the CSIR fire investigation team.

As a result of the research reported on in this thesis the number of arson related analyses increased from 46 samples in 1996 (October to December) to 421 samples last year (January to December 2001 – Table 8.1). Arson analyses are performed for support and research purposes specifically for the CSIR due to the nature of the mandate upheld by the CSIR-NML. A suitable analytical laboratory has been identified that is able to undertake the arson analyses for the private sector and plans are in place to train the staff in the fundamentals of arson analysis lending credence to the compilation of this thesis as a training manual.

Table 8.1: Arson Sample Analyses by GC-MS and GC-MS-MS

Year	No of Analyses
1996	46
1997	107
1998	187
1999	214
2000	268
2001	421

This laboratory has built up a vast library of ignitable liquid standards (accelerants), as well as various individual and combination matrix backgrounds. The library was started in 1996 and has since been expanded into a very comprehensive database.

The use of GC-MS-MS as a means of recording indicative aromatic profiles for petrol shows improvements over the use of GC-MS selected ion profiling methods. It shows a distinct improvement in the elimination of pyrolysis interference. All the information required for the positive identification of petrol in a sample of fire debris, containing large amounts of pyrolysis products, can now be obtained in a conventional MS chromatographic run, followed by a second confirmatory GC-MS-MS chromatographic run.

The molecular ions of aromatic compounds are quite stable, but fragment sufficiently to give very intense product (daughter) ions. The degree to which the selected parent molecular ions are fragmented depends on the amount of information to be derived from

the MS-MS product ion spectrum or reconstructed SRM product ion chromatogram. If a small excitation amplitude value is used, then the parent ion will fragment less and the resultant product ion spectrum will more closely resemble the GC-MS mass spectrum for that compound. If a completely different, more informative, MS-MS product ion spectrum is desired, a larger excitation amplitude value is necessary in order to almost totally fragment the parent ion and produce a unique MS-MS product ion mass spectrum. MS-MS is very specific and the method of fragmentation is thus focused on the detection of the characteristic aromatic hydrocarbons found in petroleum distillates like petrol.

The aim of the study was to select one characteristic parent ion in a given retention time segment and repetitively obtain the product ion spectrum of this ion. The diagnostic ions selected for MS-MS were based on the experience of the author. This allows for a more sensitive chromatogram, similar to that of single ion monitoring (SIM) which is an enhancement over scanning GC-MS. The advantages of MS-MS are, firstly, that the focus is trapping aromatic indicator ions, ejecting all other ions in the GC-MS mass spectrum thereby increasing the sensitivity of the ion trap which is notorious for its limited dynamic range due to ion overload and Coulomb interactions (space-charge effects).

Secondly, instead of merely looking at pre-selected single ions of aromatic indicator compounds in each retention time segment (comparable to single ion traces from a GC-MS or the less sensitive reconstructed single ion traces from a GC-MS in the scanning mode), the selected ion is simultaneously fragmented and its product ion spectrum recorded.

This provides additional information and options for data presentation and interpretation:

- (A). By summation of all the product ions for each selected ion, a trace similar to that of conventional SIM GC-MS is obtained.
- (B). In addition, a full mass spectrum is available of the product ions from the selected parent ion to confirm a peak in (A), not only by retention time, but also by its product ion mass spectrum.

- (C). Any peak of the product ion spectrum can be used to reconstruct a SRM trace (with the pre-selected parent ion fixed) of a single parent → single product (daughter) fragmentation reaction which is highly selective.

Due to its enhanced sensitivity, MS-MS also detects pyrolysates that have the same aromatic ions as the selected parent molecular ions. Again, the advantage lies in the reconstruction of both the selected parent ion and any product ions of interest. Reconstructing the single parent → single product ion chromatogram gives a totally different profile, which serves as new information for the sample case.

The choice of diagnostic ions selected as parent ions is entirely dependant on the information that is required during analysis. The characteristic aromatic ions selected do not follow a hard and fast rule, but are chosen because they are specific to the aromatic compounds found in petroleum distillates. Alkanes do not have significant diagnostic ions except weak molecular ions, which, if chosen as a parent ion, will not give any additional product ion information other than the classic aliphatic hydrocarbon spectrum. The ions ($m/z = 117, 133$) in the mass spectra of indanes can be used as diagnostic ions, but since they are obscured by the more characteristic aromatic hydrocarbons, they have not been selected for this study [96, 103].

GC-MS-MS, used in conjunction with GC-MS, provides a second confirmatory analysis and can simplify complex or weak responses seen in the GC-MS analysis due to pyrolysis interferences. Both GC-MS and GC-MS-MS are sensitive. Through the application of MS-MS for the characterization of specific ion fragments, the sensitivity and selectivity is enhanced.

Due to the high sensitivity and specificity of GC-MS-MS, the time window between the fire and sampling is extended thus allowing the fire investigator to obtain more definitive results in the analysis of ignitable liquid residues by the forensic laboratory. Since the ion trap is more sensitive for the detection of ignitable liquids, an associated level of confidence in the results is obtained for presentation in court. The chromatographic representation becomes more understandable

(less cluttered with spurious pyrolysate peaks), leading to a more defensible result.

GC-MS-MS is an established technology that has proved successful for both forensic and environmental applications. GC-MS-MS provides extra assurance that traces of ignitable liquids will not be overlooked. A significant number of samples, which do not provide enough information when analysed by GC-MS, have been confirmed and proven to be positive with an additional test using GC-MS-MS technology.

Modern ion trap mass spectrometers are robust and provide the additional selective techniques of chemical ionization, MS-MS and MSⁿ. The decision whether to use an ion trap analyzer or a triple quad analyzer is not critically significant; the significance lies with the instrument that is available in the laboratory and the implementation of MS-MS as a second confirmatory analysis for traces of ignitable liquid residues in fire debris samples.

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