ANALYSIS OF ACCELERANTS IN FIRE DEBRIS BY CAPILLARY GAS LIQUID CHROMATOGRAPHY

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ABSTRACT:

The experimental work involved in this project has been aimed at developing an understanding of the problems likely to be encountered during the routine analysis of fire debris where the analytical technique is capable of detecting approximately one–microlitre of an accelerant. This high sensitivity is achieved by analysing with Capillary Gas Liquid Chromatography a dynamic headspace extract of the fire debris.

Capillary columns are being used more extensively in G.L.C. analysis because of their greater resolving power as compared to packed columns. They have been slowly accepted in routine fire debris analysis but were used exclusively throughout the project and were found to give more information in the chromatograms to aid their interpretation. There has also been reservations about using techniques that are capable of detecting 1 μL of accelerant because of the questions of the normal background levels of the accelerants, the possibility of contamination and the interpretation of the chromatograms and these three areas were investigated. Background levels of accelerants on various materials were monitored, areas where the accidental contamination of the sample is possible were identified and alternative techniques proposed and chromatograms using capillary columns of various accelerants, synthetic and household materials are presented which would aid the interpretation of a samples' chromatogram. The chemical

characteristics of these materials were also investigated using specific ion monitoring of the chromatographic analysis.

The efforts of the forensic laboratory are reliant on the quality of the samples provided so the suitability of a sampling aid the "Sniffer" was evaluated and the instrument's shortcomings are discussed.

Techniques of identifying gas odourants utilising the equipment used for fire debris analysis are also presented which would assist the investigation of explosions.

The project also investigated the problems of the analytical discrimination of accelerants when using dynamic headspace analysis which would aid the interpretation of the chromatograms. Static headspace analysis was also examined using Tenax absorption tubes and the method could also be used in the laboratory to enable greater flexibility of operation.

III

"Our acts are attached to us
As its glimmer is to phosphorous.

They consume us, it is true,
But they make our splendour."

Andre Gide

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TABLE OF CONTENTS:

LIST OF FIGURES:

LIST OF TABLES:

CHAPTER 1. INTRODUCTION:

1.1 ARSON INVESTIGATION

The cost of arson to the Australian community was estimated at $120 million per annum in 1980/81 [1]. This figure was expected to increase and concern about the problem has resulted in a number of steps being taken to reduce the cost.

In N.S.W recently, a Standing Committee on Arson and a local chapter of the International Association of Arson Investigators have been formed, with members from the Police and Fire Fighting Authorities, Forensic Scientists, Insurance Personnel, Private Fire Investigators, Loss Assessors, Solicitors, Barristers and Academics.

The lack of a dedicated forensic fire analysis laboratory in N.S.W., caused the G.I.O. and NRMA to jointly fund a facility which was to be established at the University of Technology, Sydney. A research program was designed to establish procedures for fire debris analysis based on gas chromatography and to research the variations in the analytical results which might be found in fire debris.

The motives to commit arson are numerous and include revenge,

sabotage, pyromania, vandalism and fraud. Because there is normally little first hand eyewitness evidence, the findings of a scientific investigation are considered important pieces of evidence in criminal and civil court actions.

Internationally, the insurance industry and the public authorities have financed the scientific research of fire investigation methods and procedures. Fire cause determination is fundamental in the prevention of further fires and proof of arson is essential in negating fraudulent insurance claims and assisting criminal investigations.

Fire investigators are educated through on site training and formal courses that are designed to draw on the appropriate scientific principles from Engineering, Physics, Chemistry and Materials Science which assist the investigators' interpretation of fire origin and propagation.

1.2 DETERMINING THE FIRE CAUSE

The aim of the on– site investigation is to establish beyond reasonable doubt the cause of the fire by locating the fire origin from an investigation of the fire debris and remaining building structure and obtaining physical evidence pertinent to the ignition source.

Incendiary fires generally involve the utilisation of an agent to accelerate the intensity of the ignition phase and the rate of spread of the fire. Such an agent is normally a material which is easily ignited and highly flammable. Hydrocarbon liquids such as petrol or kerosene are generally used to ensure that the fire will be major. Such agents are called accelerants.

A fire of long duration with plenty of fuel and oxygen will leave little evidence to determine the cause of the fire and any accelerant that may have been used will be readily consumed. If the basic structure still remains then the investigator follows the progress of the fire through his interpretation of the burn patterns and locates the point of origin. A fire will burn upwards and outwards, therefore low areas of burning are of special interest to the investigator. The investigator should attempt to reconstruct the area, so that burn patterns on furniture and surfaces can be interpreted. Once the area of origin has been determined the overall degree of the burning may be used to predict the presence of an accelerant. A rapid and intense fire progress that is inconsistent with the natural fuel loading present is indicative of an accelerated fire. Multiple areas of origin generally preclude an accidental cause of the fire.[2]

The result of any investigation will be greatly enhanced if residual accelerant can be identified at positions in the fire damaged

structure at which the natural or normal presence of such a material is unlikely, e.g., petrol on the floor in the lounge room or hallway.

Therefore, a major objective in forensic fire cause determination would be to locate, sample and analyse residual accelerants.

1.3 THE NATURE OF ACCELERANTS

The accelerants most commonly used because of their availability and flammability are petrol, kerosene, diesel, mineral turps and methylated spirits. Exotic accelerants such as industrial solvents are rarely used and if so are readily identified by chemical analysis because of their similar chemical characteristics to the common accelerants.

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

The amount of accelerant remaining at the fire scene available for sampling is governed by the following:

- the initial loading of the accelerant
- the volatility of the accelerant
- the severity of the fire
- the water solubility of the accelerant
- the porosity of the substrate material
- the dryness of the area after the fire
- the elapsed time between the fire and sampling.

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

The chemical components of the common accelerants are aliphatic and aromatic hydrocarbons and oxygenated hydrocarbons such as alcohols. The oxygenated hydrocarbons are to a degree water soluble and are therefore washed away during the extinguishing of the blaze, so that little trace remains.

1.4 SAMPLING AT THE FIRE SCENE.

The investigator samples material and fire debris where he determines a quantity of accelerant will remain. These are generally areas of high initial accelerant loadings or low oxygen availability during and after the fire. The most frequently sampled item is flooring material such as carpet, underlay and linoleum. Other areas sampled include interior pot plants or the soil underneath the structure, where the accelerant may drip through the floor and be preserved in the cold, damp earth. The area behind skirting boards are sampled if the accelerant has been splashed on to the wall. Severely charred timbers do not make good samples because the timber supports the flame which assists in the depletion of the accelerant. Wet, spongy material such as clothing, towelling, bagging and bedding materials, furniture rubber and foam are ideal materials for sampling because the accelerant absorbs into the material and the water used to extinguish the blaze seals in the accelerant and prevents its evaporation.

1.5 CONTROL SAMPLES.

Control samples or "blanks" generally form part of the scientific method of analysis to ensure that materials other than the material being analysed do not contribute to the identification.

Control samples are sometimes taken at a fire scene away from the area where an accelerant is suspected and of the same material as that of the sample. The chromatographic analysis of a control sample will feature the material's pyrolysis products which are essentially its thermal molecular fragmentation.

The major problems associated with taking control samples are:–

(1) The amount and proportion of artefacts from pyrolysed material depends on the degree of burning and it is difficult to burn in the laboratory or sample a control with the same degree of burning as the sample.

(2) When sampling ash and debris of uncertain origin a control sample cannot be expected to be of the same composition.

(3) The investigator may use a false negative from a gas detector (Sniffer) reading to choose the control.

(4) The findings of an accelerant in a control sample through poor sample selection would reduce the validity of positive findings in other samples.

(5) Control Samples are an added expense to the investigator.

The research has shown however, that,

(i) The high resolution of capillary columns and the increasing use of mass spectrometry gives more information to the analyst for the correct interpretation of the chromatograms.

(ii) An experienced analyst equipped with a good library of chromatograms could readily identify non–accelerant peaks and fingerprints.

A material such as an unidentifiable or rare plastic may be sampled as a control but the preferred option would be to take two or more samples, where accelerant is suspected, of different background materials.

1.6 USE OF THE "SNIFFER" AT THE FIRE SCENE.

After the investigator has determined the area he feels may contain accelerant a small sample must be collected for submission to the laboratory. Portable gas detectors (Sniffers) can be used at this point to assist the investigator in selecting a sample with the highest probability of containing an accelerant. The investigator inserts the probe of the Sniffer in areas such as freshly lifted carpet or freshly dug soil and notes the instrument's response either via a meter or alarm.

The instrument monitors the ambient conditions through the absorption of oxygen on a semiconductor. Any changes in the oxygen level near the detector will be noted so that the Sniffer will respond to accelerant vapours. The instrument also responds to volatile pyrolysis products or entrapped smoke and so is not specific for accelerant vapours.

The sensitivity of the Sniffer is important and dual sensitivity instruments are the best to use. When confronted with a material such as rubber–backed carpet a very sensitive sniffer will give random positive readings that can confuse the investigator. The investigator would be better suited using the low sensitivity setting in this case. In most instances, however, the high sensitivity setting is used so that debris that contains traces of accelerant, which are readily detected in the laboratory, is sampled.

Sniffers that use a photoionisation or flame ionisation detector are generally too expensive and too sensitive for on– site work. They also suffer from the same lack of specificity as the molecular absorption detectors. The low cost and robust design of the molecular absorption detector makes it the most popular for use in on–site sampling of fire debris.

A positive Sniffer reading is not proof of the presence of an accelerant nor is a negative reading proof of the absence of an

accelerant. They cannot replace laboratory analysis, but when used with their shortcomings being understood by the operator, they should increase the sampling success rate of the investigator.

1.7 IMPORTANCE OF ACCELERANT ANALYSIS.

The presence and distribution of a flammable liquid at a fire scene indicates a deliberately lit fire unless it can be readily explained otherwise. Multiple samples should be taken so that the spread of the accelerant is ascertained. The analysis identifies the accelerant which confirms the investigator's understanding of the initiation and propagation of the fire.

The investigator must use laboratory analysis to support his argument. Opinions and theories can be readily challenged in court because of the complex and varied nature of fires, but laboratory evidence is irrefutable proof of the presence of an accelerant. The laboratory findings may dispute a suspects' statement so that further investigation would then be implemented. Prior storage of a flammable liquid could also be proven, which would contravene the conditions of some insurance contracts.

1.8 FIRE DEBRIS EXTRACTION AND ANALYSIS.

The analysis of accelerants in fire debris constitutes a significant portion of the routine work at a forensic laboratory and research has been aimed at investigating new techniques and aiding the interpretation of the chromatograms. The forensic laboratory uses techniques similar to those used in the industrial hygiene and environmental chemistry areas and modifies them because debris samples are usually of an unknown matrix and saturated with water.

Environmental and industrial hygiene research has been directed at developing increasingly sensitive quantitative methods, but mainly the qualitative aspect of their work has interested the forensic research. Using these sensitive techniques can pose problems in fire debris analysis and lead to false positive conclusions because of sample contamination through careless transport and storage and the application of unsatisfactory laboratory techniques. The interpretation of the results must be carefully made when sensitive techniques are used because of complications from pyrolysis products and the significance of detecting trace amounts of accelerant components.

Fire debris extraction and analytical techniques have been developed to improve sample turnover in the laboratory and

to reduce the number of inconclusive findings. The two main areas of research are to improve extraction techniques, where the accelerant is separated from the debris, and in the analysis, where the accelerant is detected and identified.

1.8.1 EXTRACTION TECHNIQUES.

The simplest and earliest extraction technique used was sampling a headspace of heated fire debris with a syringe and then injecting the sample into a G.L.C. for analysis [3]. Heated headspace analysis is also used for sample screening because it is a simple, rapid and easy technique to apply. A sample that gives a negative result when screened by heated headspace would then be subjected to a more sensitive extraction technique.

Headspace sampling can be made at room temperature or an elevated temperature to improve the recovery of accelerant. The technique however, discriminates against the less volatile components in the sample which will give less data from the chromatographic analysis for interpretation.

Distillation extractions are also widely used with steam distillation being the most popular [4]. Distillation involves heating the sample with an extraction medium and condensing the vapour to provide a sample of the accelerant in the extraction medium used.

The various mediums that have been used are water, ethanol and ethylene glycol and also vacuum distillation with subambient trapping of the volatiles can be used [4]. The accelerant may be further concentrated by controlled evaporation of the medium or by solvent extraction from the medium.

Steam distillation can be a lengthy technique and extraction times of up to 48 hours have been reported as being necessary for some samples [5]. The technique however, requires considerable clean up of the apparatus between samples and also considerable operator attention and so the sample turnover is low .

Solvent extraction is also used and involves soaking the fire debris in a suitable solvent and then filtering and evaporating the solvent to concentrate the sample [4]. The advantages of solvent extraction is that it readily extracts the less volatile components of an accelerant and therefore does not discriminate [6]. The technique however, requires the use of high purity solvents which are expensive and also matrix components such as monomers, plasticisers, glues and resins are co– extracted which may interfere with the subsequent analysis. Both distillation and solvent extraction require further concentration of the raw extracts to increase the sensitivity of the technique.

Dynamic headspace sampling is widely used for the extraction of fire debris and involves continuous sampling by sweeping the

headspace with an inert gas and simultaneously separating and concentrating the accelerant on to a suitable absorbent. The sample can be heated on a hotplate or in an oven to increase the concentration of accelerant vapour in the headspace.

Dynamic headspace sampling's recovery of accelerant is many times that of a static headspace sample and is a function of the extraction gas flow rate and the time of extraction. For example, when extracting using dynamic headspace with 500mls/minute of nitrogen for 1 hour, 30 litres of headspace will be sampled by the charcoal. The maximum static headspace sample that can be taken for analysis by packed column G.L.C. is approximately 10mls so dynamic headspace effectively samples 3000 times more headspace.

Dynamic headspace extraction also has the advantage that the can is always vented so pressure will not build up in the sample container when it is heated. Water in the sample will volatilise and effectively this steam distills the sample. Steam distillation allows high boiling point compounds to distill at a much lower temperature. Therefore extracting wet samples at 150^0C using dynamic headspace will result in compounds being recovered that have a boiling point well in excess of 150^0C. This allows for a shorter extraction time and high temperatures that could pyrolyse some samples are therefore not required.

Activated charcoal is the most commonly used absorbent because of its affinity for the compounds found in the common accelerants. It does not absorb air, nitrogen or water vapour so the accelerant is readily separated from the extraction medium used [7], [8].

The transfer gas used to sweep the headspace to the absorbent is usually nitrogen or the headspace can be drawn through the absorbent with a vacuum [9]. The sample can be heated in an oven or the nitrogen can be preheated before it enters the sample can [10]. Microwave ovens have also been used to heat the sample and the steam generated sweeps the headspace to the absorbent. This technique is reported to heat the sample fifty times faster than conventional oven heating with extraction times reduced by a factor of three [11].

A major problem of dynamic headspace extraction techniques is the carry over of contaminants from previous samples through the gas transfer lines. It was found that by removing the outward gas transfer line and connecting the charcoal tube directly to the sample container the contamination problem was reduced [12]. No loss of accelerant from the heated charcoal tube was reported.

Other absorbents that have been used successfully are Tenax G.C., and Porapak Q [13], [14]. As well as successfully absorbing accelerant components, they do not absorb water or nitrogen and allow the recovery of the accelerant with thermal dessorption.

Absorbents are also used to concentrate the accelerant vapours through passive diffusion of the accelerant vapour through the headspace to the absorbent [15], [16], [17]. The absorbent is mounted on to a suitable support and placed in the sealed fire debris container and the accelerant vapours in the headspace are concentrated for a fixed time period on to the absorbent. Charcoal is again the most popular absorbent and can be mounted to a ferromagnetic wire with a slurry of soda ash, or a piece of granular charcoal can be mounted at the end of the wire in a flattened loop. After the absorption time is completed the wire is removed and placed into a Curie Point Pyrometer, where rapid heating thermally desorbs the accelerant vapours which are then swept onto a chromatographic column for analysis. The sensitivity of the technique can be increased by increasing the absorption time in the sample container. Charcoal is the only absorbent that has been successfully used because other absorbents are difficult to attach to a support. Also the high temperature needed for rapid thermal transfer to the absorbent to give successful thermal desorption, breaks down some polymeric absorbents to give peaks in the blank analysis.

Tenax is a widely used absorbent and can sustain temperatures of up to 350^0C which makes it ideal for rapid thermal desorption [18]. It can be used to absorb a static headspace sample from a syringe or it can be mounted on the sample outlet to absorb a

dynamic headspace sample [14]. Tenax has also been used at the fire scene to absorb multiple air samples so a profile of accelerant spread at the fire scene can be ascertained later from laboratory analysis [18].

The qualities that enable an absorbent to be used successfully for accelerant extraction and analysis are its selectivity for the accelerant components which separates and concentrates the accelerant from the headspace to yield a sample that is suitable for introduction to a Capillary Gas Liquid Chromatograph. The analyst needs to understand the properties of absorbents so that a suitable absorbent can be selected and the most efficient desorption technique chosen.

1.8.2 PROPERTIES OF ABSORBENTS.

Absorption columns are essentially a gas chromatography column packed with a suitable absorbent and operated at ambient temperature. The carrier gas and means of sample introduction is the atmosphere being sampled. Commonly used absorbents are charcoal, silica gel, alumina and molecular sieves as well as the commercial porous polymers such as the Chromosorbs, XAD and PAR resins, Tenax and the Porapaks [19].

The interactions responsible for absorption are essentially Van der Waals forces [20]. The chemical nature of the absorbent, its pore size distribution, surface activity and micropore volume affect the absorption process [21]. Other factors that affect absorption are the chemical nature and concentration of the absorbate, other compounds present and the surface area of the absorbent [20].

The porous polymers are manufactured so that the surface is a collection of microspheres with diameters of approximately 10^{-4}mm. Between the microspheres are pores where molecules become trapped thereby being effectively absorbed. The size and packing factor of the microspheres determines the surface area and porosity of the absorbent [22]. As the surface area increases, the pore diameter decreases so that the larger molecules are difficult to trap in the pores because of poor diffusion in the limited pore space [23].

Absorbents such as charcoal and silica gel have a constant pore size that cannot be altered. Porous polymers however, can have a variety of pore sizes which are controlled in their manufacture by suspension and polymerisation means [22]. Their chemical nature can be altered to absorb polar and non–polar compounds whereas charcoal is unsuitable for trapping very polar compounds in the presence of water [27].

The porous polymers are manufactured from unsaturated aromatics such as styrene or divinyl benzene which have a hydrophobic nature or from acrylic esters which are hydrophilic due to the carbonyl group in the resin matrix. Alkyl derivatives of benzene, styrene, naphthalene and biphenyl have been found to come from some of the XAD resins during desorption which would interfere during the analysis of some accelerants [24]. The absorbent therefore must be chosen so that possible impurities are not compounds of interest.

Charcoal is the most common absorbent used in environmental and industrial hygiene analysis and absorbs both polar and non–polar compounds. Higher molecular weight compounds will displace absorbed lower molecular weight compounds and polar organic compounds are displaced by non–polar organics [25], [26]. Water vapour can also strip polar compounds such as ethanol from charcoal [27].

The collection efficiency of an absorbent for a particular compound is defined as:

$$\frac{\text{inlet concentration} - \text{outlet concentration}}{\text{inlet concentration}}$$

During continued sampling the absorbent capacity will be exceeded and breakthrough will occur. The volume that has passed through the collection tube is termed the breakthrough

volume and is related to the retention volume used in conventional gas chromatography [19].

Breakthrough may be capacitive (weight) or volumetric depending on the nature of the absorbent. For atmospheres containing a high concentration of organic vapours the pores of the absorbent will become filled and capacitive breakthrough will occur due to saturation. For low concentrations the compound will progress through the collection tube by virtue of its equilibrium between the absorbent and gas phase and breakthrough is termed volumetric. Activated charcoal has an extremely high collection efficiency and breakthrough is entirely capacitive for most organic compounds.

Breakthrough is affected by the geometry of the packing tube, temperature, humidity, flow rate, concentration and other compounds present [28], [29], [30]. Breakthrough volumes are of considerable importance to designers of respiratory filters and industrial absorbent equipment [31].

1.8.3 DESORPTION TECHNIQUES.

After absorption the compounds can be recovered by either thermal or solvent desorption. Desorption efficiencies are

evaluated by injecting or absorbing a known amount of compound and then desorbing and measuring the recovery.

Thermal desorption is achieved by rapidly heating the absorbent and then sweeping the compounds into a G.L.C. for analysis. The adsorbent can be heated in the injection port of the G.L.C. or in a separate oven. For use with capillary G.L.C. the sample must be introduced rapidly so efficient heat transfer is essential otherwise secondary trapping with cyrogenics is necessary.

The desorption efficiency for thermal desorption is directly related to the collection efficiency and the desorption temperature. Absorbents with extremely high collection efficiencies such as charcoal will not rapidly desorb and require secondary on–column trapping. For thermal desorption the absorbent should be chosen so that the pore size is not too large, otherwise, absorbed species penetrate too far making desorption slow. The choice of an absorbent is often a compromise between the collection and desorption properties of the absorbent and it must also sustain high temperatures to give rapid desorption for Capillary G.L.C. [32].

Microwave heating has been used successfully to thermally desorb accelerants from charcoal. The charcoal can be mounted on to ferromagnetic wires [15] or packed in tubes [33]. Other

absorbents packed in tubes can also be thermally desorbed with microwaves [34].

Thermal desorption transfers all of the sample to the G.L.C. and so is extremely sensitive. For capillary analysis the column could be easily overloaded and a second analysis would require another headspace absorption.

Solvent desorption gives a liquid sample that can be reanalysed many times but only a small amount of the sample is analysed so that the sensitivity is much less than that for thermal desorption. However, liquid samples are easily injected into a G.L.C. and reanalysis enables the operator to optimise the analytical conditions to improve resolution and the retention time reproducibility.

Solvent desorption is accomplished by adding a small amount of solvent to the absorbent and collecting the solvent through decanting, filtering or centrifuging. For solvent desorption the Van der Waals forces of absorption must be overcome and the absorbed compounds must be readily soluble after the solvent diffuses to the absorption site.

The desired properties of a desorption solvent are:

- the desorption efficiency is high.
- the solvent peak does not obscure areas of interest in the chromatogram

- the solvent is volatile so that further concentration of the sample by evaporation is possible.
- the solvent is relatively cheap, pure and has a low toxicity.
- the sample is stable on storage.

Solvent desorption efficiency is related to the temperature of desorption, the solubility of the absorbed species in the solvent, the collection efficiency and the solvent's ability to displace the absorbed species at the absorption site.

Carbon disulphide is the most commonly used solvent for the desorption of charcoal because of its low detector response and high desorption efficiency. Other solvents that are used are diethyl ether, pentane, dodecane, the freons and esters. Water, ethanol and acetone can be used to desorb polar compounds from silica gel. Very polar compounds such as ethanol have low desorption efficiencies from charcoal using carbon disulphide because they are more readily soluble in water if present. Desorption efficiency of polar compounds can be increased by adding methanol to the carbon disulphide, however, samples should be analysed within 4 hours because reactions between methanol and carbon disulphide are possible [34]. Modification of the carbon disulphide is also possible using other alcohols to increase the recovery of polar compounds [38]. Polar and non–polar compounds can be recovered from charcoal simultaneously using carbon disulphide and water and analysing both layers separately [35].

1.8.4 ANALYTICAL TECHNIQUES:

After the sample has been extracted, the extract is analysed to detect and identify possible accelerants. Gas Liquid Chromatography is the most widely used technique but others have been tried.

Infra Red Spectroscopy has been used but is unsuitable for analysing complex mixtures such as those recovered from fire debris samples. When using I.R. solely, the probability of a false positive result is high [36], [37]. Nuclear Magnetic Resonance has also been used but the interpretation is difficult for complex mixtures [38].

Gas Liquid Chromatography is widely used because of its ability to separate and detect trace amounts of volatile hydrocarbons in complex mixtures. The analysis gives a reproducible chromatographic fingerprint for each of the common accelerants which is used to positively identify accelerants in fire debris.

During the early 1960's when G.L.C. was first used to analyse fire debris extracts, packed columns and thermal conductivity detectors were used. With the introduction of Flame Ionisation Detectors (F.I.D.) an increased sensitivity of the analysis by a factor of 1000 was possible.

The FID uses a hydrogen/oxygen flame to reduce and ionise the components as they emerge from the column. The ions are measured by amplifying the current that will pass if a voltage is applied across the flame. The detector response and time of elution are registered on a graph to give a chromatogram of the analysis [32].

Capillary columns are rapidly replacing packed columns for accelerant analysis. Greater column efficiency is obtainable using capillary columns because the more permeable open bore allows the use of longer columns therefore giving greater resolution. The time of analysis is also much shorter and new manufacturing techniques have meant more robust and reproducible columns are available. Injection of a headspace sample on to a capillary column cannot be made directly because the sudden injection of a large volume of air (1– 5mls) disturbs the small carrier flow rate through the column (1– 2mls/minute) and the resolution is significantly affected. However, no problems are encountered with liquid sample injections or thermal desorption provided the absorbent is suitable and the temperature and heat transfer of the desorber is high. The higher resolving power of capillary columns gives more peaks in the chromatogram for interpretation. Interferent peaks that may obscure an accelerant peak in the chromatogram are less of a problem with the increased resolution of capillary columns. Capillary columns were first used for

accelerant analysis in 1977 and were approximately 30 metres long and the analysis of diesel required approximately 1 hour [39]. Recent advances in column phase bonding has reduced this time by one–third because the operating temperatures of the column can be increased.

As well as F.I.D. detectors, mass spectrometers have also been used to detect and qualitatively identify accelerant peaks in the chromatogram [40]. As the compounds emerge from the column the molecules are fragmented and the mass and quantity of each fragment are measured and used to positively identify the compound. Aliphatic hydrocarbons are sometimes difficult to identify because of their simple fragmentation patterns and chromatographic retention time data must also be used. Accelerant components such as the aromatic hydrocarbons or oxygenated solvents are readily identified [37].

1.8.4.(i) Principle of Gas Liquid Chromatography

Gas Liquid Chromatography is essentially a separation technique where a sample is injected onto a column and the individual volatile components are then separated in the column and detected. It was originally used for the separation of gas sample components but can be equally efficient for liquid sample separation provided the sample is vapourised first in the heated injection port at the start of the column.

Gas chromatography uses a stream of carrier gas to move the volatile components along a column. Components that are readily absorbed in the column are slow to move through and so emerge from the column later than less absorbed species. On emerging from the column the components reach a detector that produces an electrical signal which is amplified and fed to a chart recorder. The detector signals of the components versus their time of elution are recorded to give a chromatogram of the separation. By carefully controlling the gas flow rate through the column and the temperature of the column, a pure compound injected into the column will always emerge at the same time. The time after injection the compound emerges from the column is called the retention time and is used to qualitatively identify the component.

The chromatograms obtained can be quite complex depending on the number of components present in the sample. A short or inefficient column will not separate or resolve components so longer columns may be needed. As the resolving power of a column increases more components are separated from a complex mixture and more components can be identified by their retention time. Good resolution is important in fire debris analysis because accelerants are usually complex mixtures of hydrocarbons obtained from crude oil and the pyrolysis products obtained from various background materials found in samples are also complex and may obscure accelerant peaks in the chromatogram.

Capillary columns are very long and have a much greater resolving power than packed columns and therefore, separate complex mixtures more efficiently. For the analysis of petrol a chromatogram using a packed column may give only 8–10 distinct peaks whilst a capillary column will give at least 60 distinct peaks which will readily enable its identification.

CHAPTER 2. THE EXPERIMENTAL WORK OBJECTIVE

The use and adaptation of techniques from the environmental and industrial hygiene analytical chemistry fields cannot be made without a thorough investigation because of the nature of fire debris samples. Fire debris samples could be considered to be the most complex and dirty samples encountered by an analytical chemist. Samples injected into a Capillary G.L.C. for analysis should be as clean as possible to prevent contamination of the extremely sensitive and expensive equipment. The interpretation of the chromatographic results must be made carefully, due to the consequences of making a false positive finding.

The experimental work involved in this project has been aimed at developing an understanding of the problems likely to be encountered during routine fire debris analysis. In all analyses, the laboratory's efforts are dependent on the quality of the samples provided, therefore sample collection and storage procedures need to be investigated. The question of the possible contamination of a sample can easily reduce the validity of a positive analytical result. Therefore, the areas where contamination could be a problem were identified and alternative techniques were proposed.

After the chromatogram is obtained an interpretation of the results is required. The chromatogram is compared with those from a

library of chromatograms of various accelerants. If a particular accelerant is suspected, a sample of the accelerant is analysed using the same chromatographic conditions as those used for the sample. The retention times of the peaks in the samples' chromatogram are compared to those of the accelerants' and if equivalent the peak is identified. If the accelerants' components are present in the samples' chromatogram and in similar quantitative ratios then the presence of that accelerant is indicated in the sample. Chromatograms obtained from various synthetic and household materials are also required in the library so that a false positive result is not obtained. These accelerants and materials were analysed by Capillary G.L.C., and their chromatograms are discussed.

The extraction procedure of dynamic headspace trapping with charcoal and solvent desorption was investigated in detail. The use of other adsorbents for fire debris analysis was also investigated which would enable more flexibility in the laboratory.

Gas Liquid Chromatographs have a range of detectors available. An Ion Trap Detector (I.T.D.) was used for the analysis of various samples and the results are presented which would aid interpretation when using a more common and less expensive Flame Ionisation Detector. The I.T.D. responds to specific chemical compounds and therefore identifies the class of

compounds each peak component belongs to. The I.T.D was also used to positively identify some compounds by comparing their fragmentation pattern to those of a library of standards.

The forensic laboratory needs to be flexible because complex situations that require non– routine analysis often arise. Gas explosions may require laboratory investigation and the detection of gas odourants can readily identify the gas source. An investigation was made to develop procedures to detect gas odourants using the same equipment used for fire debris analysis.

The above work was aimed at presenting an analytical scheme and an understanding of routine fire debris analysis. The basic equipment that was found to be required was a forced air oven and a Capillary G.L.C. with F.I.D. detection and chromatographic Data Processing Facilities.

2.1 THE EXTRACTION EQUIPMENT

The equipment used for dynamic headspace extraction is essentially the same as described by Lentini [7] and is shown in Figure 1. and by a schematic diagram in Figure 2. The nitrogen used was instrument grade and was regulated and prefiltered before it entered the sample can by passage through a charcoal

and then a molecular sieve filter. The gas line connections to the sample cans were made by using Swagelock fittings and 2 metal inlet and outlet lines were connected to the oven. The water traps were made using 6" glass test tubes with the lines entering and leaving via a rubber bung. Pasteur Pipettes were used for making the charcoal absorption tubes. Glass wool was used to secure the charcoal in position in the tubes at both ends.

Figure 2.1 – Extraction Equipment.

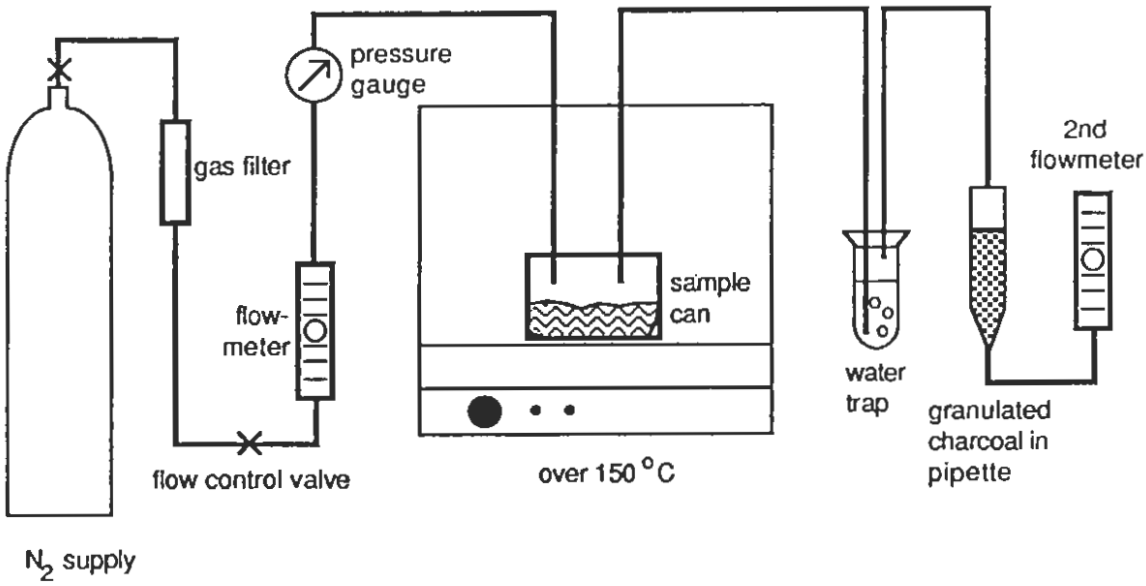

Figure 2 - Schematic Diagram of Dynamic Headspace Extraction Equipment

The nitrogen flowrate through the can was approximately 500 mls/minute and the oven was maintained at 150^{0}C for approximately one hour. The outlet flow of nitrogen from the pasteur pipette was monitored by a second flow meter to ensure there were no leaks or blockages in the system. Leaks were found mainly around the rim of the can lid because of debris accumulation. The positive pressure in the system prevented possible external contamination of the sample due to leaks or poor seals and resulted only in a reduced recovery of accelerants.

After extraction the charcoal pipette was removed and allowed to cool before approximately 1ml of A.R. grade carbon disulphide was added and allowed to percolate through the charcoal into a 2ml glass vial. The carbon disulphide was then sucked back up through the charcoal a number of times before being blown dry with a rubber teat. Water was added to the vial to seal the carbon disulphide to prevent loss of the volatile extract.

2.2 THE ANALYTICAL EQUIPMENT

The analytical instrument used for the detection and identification of possible accelerants in the extracts was a Varian 3400 Gas Liquid Chromatograph designed for use with capillary columns. The G.L.C. was fully automated and allowed the user to store up to 4 sets of operating parameters thus allowing for the rapid and versatile operation of the machine. The injector system was a Varian split/splitless capillary system and the machine was equipped with both an F.I.D. and E.C.D. detector.

As well as the Varian injector a S.G.E. Unijector was fitted to enable direct thermal desorption onto the capillary column. Small bore metal tubes packed with Tenax were used for thermal desorption and were heated by the injector heating system of the G.L.C.

The output from the detector was connected to a Varian Vista 402 Data Collection Station which stored the raw chromatographic data onto floppy disk and simultaneously plotted the chromatogram. Chromatograms that were off scale could then be replotted using a higher attenuation setting and so avoiding the need for reinjection of the sample.

The data station also produced dual plots where the samples' chromatogram is plotted alongside that from a standard accelerant so that peak retention times could be easily compared visually. The replotting allowed the chromatograms to be produced on scale so the relative ratios of the peak could also be compared during the interpretation of the results.

The operating conditions of the G.L.C. used were:–

Column	–	BP– 1 capillary (S.G.E. Australia) 25m, 0.33mm i.d., 1μm phase loading.
Oven Conditions	–	40^{0}C for 2 minute then increased at 10^{0}C/minute to 240^{0}C.
Carrier Gas	–	Hydrogen 8 p.s.i. inlet pressure.
Injector	–	Split injection (ratio 20:1) at 240^{0}C
Detector	–	F.I.D. at 240^{0}C.
Plotter	–	Vista 402 Thermal Printer.

The attenuation and chart speed were controlled by the Vista 402 and are reprinted at the start of each chromatogram.

As well as using the Varian F.I.D. detector, the capillary column was connected to a Finnigan Ion Trap Detector (I.T.D.). The molecules emerging from the column enter the I.T.D. where they are fragmented and ionised, trapped and then sequentially ejected out of the trap by changing the applied field. Ejected ions are then detected by an electron multiplier and the data collected by an I.B.M. computer. The mass and quantity of the ions are then used to positively identify the compound emerging from the column in much the same way as analysis via Mass Spectrometry.

Ions of a specific mass can be monitored so that the detector can be specific for the different classes of compounds. For example, aliphatic hydrocarbons will fragment to give ions of mass 29, 43, 57 and 71 and monitoring these ions will give a chromatogram that essentially detects only aliphatic hydrocarbons. The analysis of the various accelerants and pyrolysis products from some synthetic materials was made using the I.T.D. detector with specific ion monitoring so that the class of compound each peak component is from could be determined which would assist the interpretation of the chromatogram when using a simpler F.I.D. detector.

CHAPTER 3. EXPERIMENTAL RESULTS AND DISCUSSION.

3.1 SAMPLING WITH A SNIFFER.

112 samples of fire debris that were submitted to the laboratory over a period of six months were screened using a Sniffer before analysis and the readings evaluated as either positive or negative. The criteria used for evaluating a positive Sniffer response was the observation of the acceleration and deceleration of the meter needle as the detector probe was inserted in and out of the sample can headspace. The debris was not disturbed for fear of losing accelerant vapour. The samples were then extracted and analysed and the analytical result noted.

The fire debris samples were classified according to their overall composition and the Sniffer results are shown in Table 1, together with the number of positive analytical results shown in parenthesis.

The overall percentage of false positive results using the Sniffer was 32% and false negatives was 22%. Ash and char gave the most number of false positives. Soil gave the most number of false negatives because the accelerant is effectively sealed preventing its volatilization in the sample can at ambient

temperatures. The soil was not disturbed in the can during the Sniffer examination and the results show that soil must be disturbed when using the Sniffer on site. The carpet samples could not be classified into their various types but it has been found that burnt rubber backed carpet will normally give a positive Sniffer reading when freshly disturbed.

Material	+ve Sniffer	–ve Sniffer
Ash and Char	18(5)	10(0)
Carpet	22(18)	9(1)
Cardboard and Paper	10(10)	7(2)
Concrete	2(0)	4(0)
Soil	1(1)	12(8)
Felt and Cloth	7(7)	2(0)
Plastic	1(1)	5(0)
Timber	2(1)	0(0)
TOTAL	63(43)	49(11)

TABLE 3.1: Sniffer Responses for 112 samples.

The materials that gave the higher percentage of true positive readings were carpet, cardboard and paper, felt and cloth. The investigator should sample these materials if he has an option.

Burnt timber is not a good material to sample because the timber supports burning and the amount of accelerant remaining is significantly reduced.

3.2 CONTAMINATION OF SAMPLES

Because of the high sensitivity of dynamic headspace extraction, considerable care must be taken to avoid a false positive result through accidental contamination of the sample. Metal cans are the best sampling container to use because they are harmonious with the extraction technique used.

Contamination can occur through poor sampling techniques and carelessness during extraction. The main areas where contamination could occur are:–

- Precontamination of the container
- The transport and storage of the sample
- The extraction and analysis of the sample.

3.2.1 PRECONTAMINATION OF CONTAINERS.

Commercial grade paint cans are not guaranteed to be perfectly clean when supplied and all cans should be inspected internally

before use. Any cans that have odours, stains or traces of oil present should be immediately rejected.

Cans can be purchased in various sizes and may be either lined or unlined. Lined cans have an epoxy coating on their inside and are used for the storage of water based chemicals.

A cleaning method to prepare cans was investigated so the validity of a positive result could not be questioned as being due to the possible precontamination of the sample container.

3.2.1 (i) Analysis of Empty Cans.

Six empty lined and unlined cans were extracted in the oven for 1 hour at 150^{0}C. Chromatograms of the extracts were found to be reproducible in both cases.

The chromatogram shown in Figure 3.1 is from an unlined can and a peak at 6.301 minutes was further analysed by mass spectrometry and found to be 2– ethyl– 1– hexanol. Four new cans were baked in the oven at 200^{0}C and extracted and the amount of this compound recovered increased. 2–ethyl–1–hexanol is a decomposition product from a common plasticiser which may have been used in the manufacture of the

seal found at the base of the can. No amount of pre-- washing could prevent its recovery. Water was added to a can and the can extracted and the peak was found to be absent. The temperature inside the can did not exceed 100^{0}C which would be the case with a wet fire debris sample.

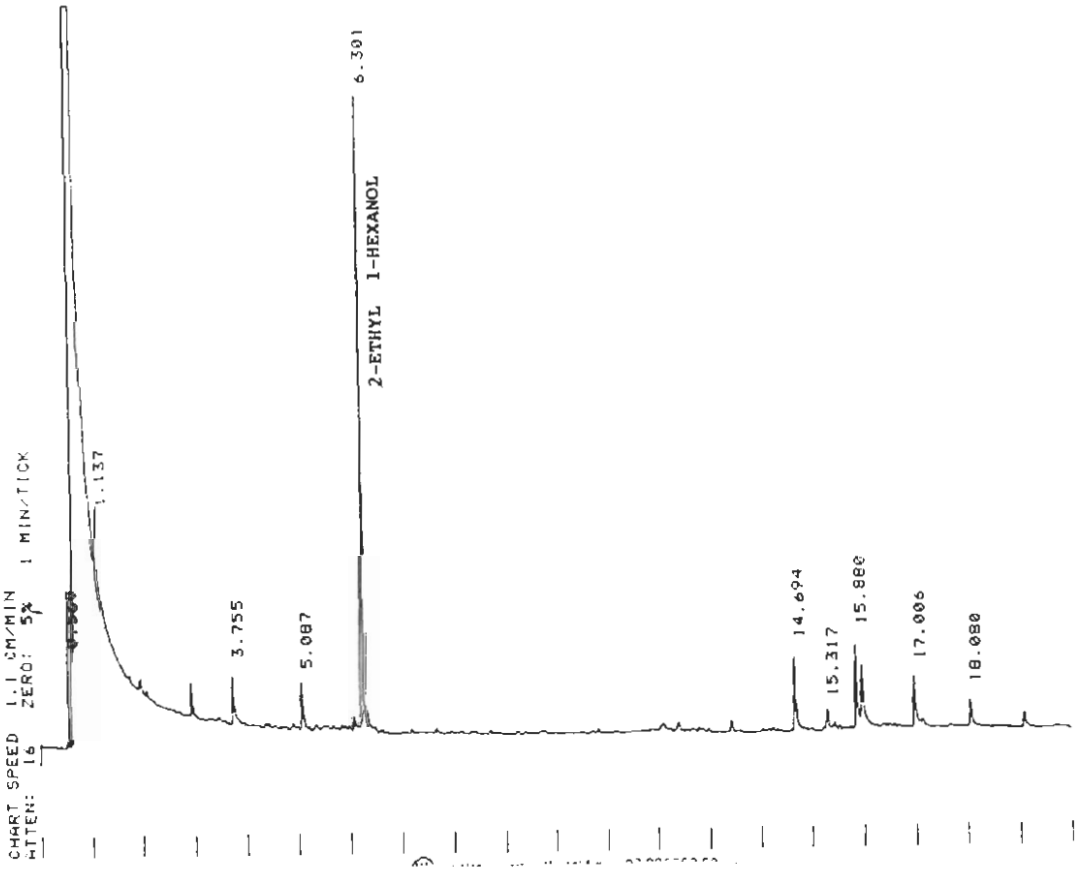

Figure 3.1 – Empty Can Chromatogram.

The analysis of the lined cans was found to be reproductible and a representative chromatogram obtained is shown in Figure 3.2. below that of a petrol standard. The compounds extracted from the can were confirmed by mass spectrometry as aromatic hydrocarbons which are found in many industrial solvents one of which may have been used in the formulation of the epoxy coating. The drying of the epoxy would trap the solvent which is then released at the extraction temperature. Lined cans should therefore never be used for sampling fire debris material because a false positive result indicating an industrial solvent or petrol being present in the fire debris could result.

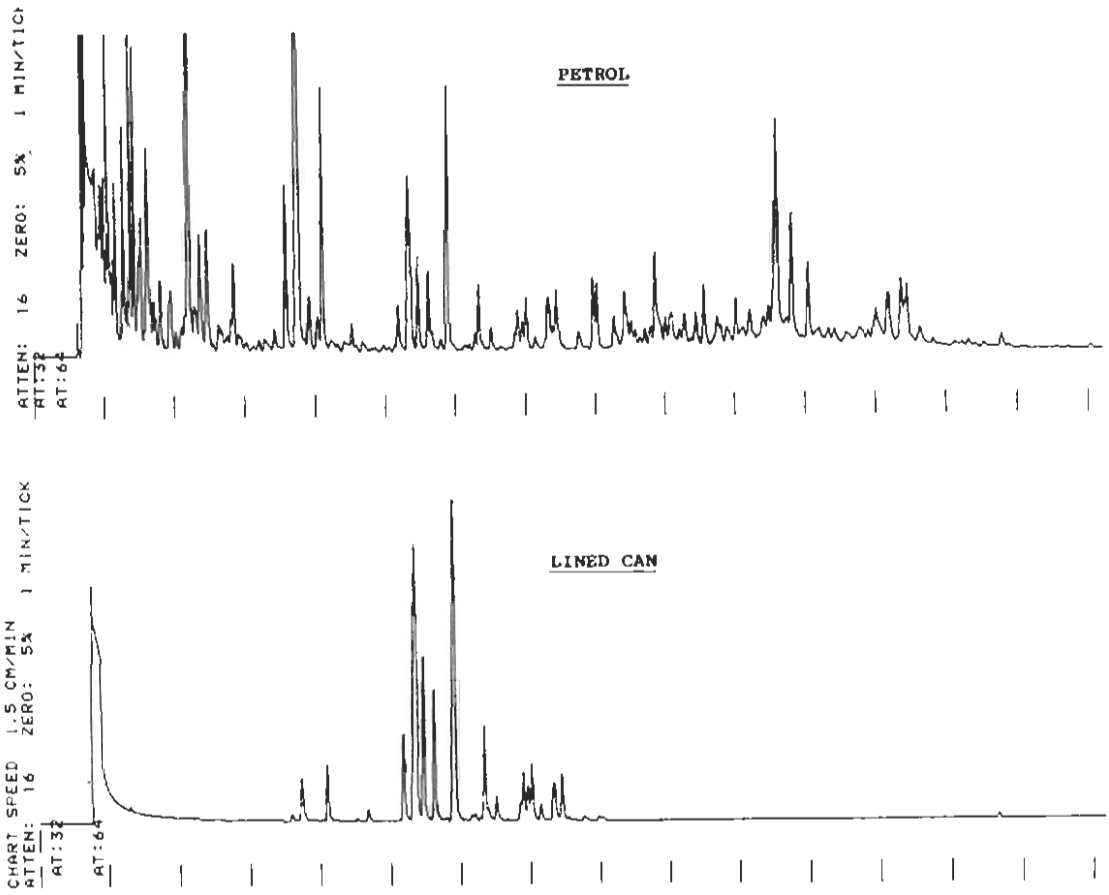

Figure 3.2 – Lined Can vrs Petrol Chromatograms.

3.2.1 (ii) Cleaning of Cans.

Cans should be inspected before use and if no odours or stains are present then the can should be cleaned and sealed before transport to the fire scene. Cans were cleaned by washing in warm, dilute detergent, rinsed and then dried in an oven for 1 hour at 150^0C, then cooled and sealed.

Two unlined cans were purposely contaminated with 1ml of petrol and then cleaned in the above manner, extracted and the extracts analysed. No traces of petrol were detected indicating the cleaning process to be satisfactory in a worse case situation. A can that was observed to be contaminated would be discarded by the investigator and the cleaning procedure is not intended to allow the recycling of previously used cans.

Eight new cans were cleaned using household washing detergent, rinsed and dried in both domestic gas and electric ovens. The cans were extracted and analysed and no extra peaks were found in the chromatograms. As investigator who does not have access to a laboratory oven could therefore prepare his cans in his home, provided the oven is reasonably clean.

3.2.2 CONTAMINATION DURING TRANSPORT AND STORAGE.

Problems of leakage and breakage can occur with samples supplied in plastic bags or glass containers and both these should not be used for sampling. Extremely wet samples have been found to cause pinholes in metal cans through rusting so samples in tins should be delivered promptly to the laboratory. Plastic bags are sometimes used inside the can to prevent rusting but these are easily pierced by fire debris.

Two cans containing polyethylene bags were extracted and the extracts analysed. The chromatogram obtained is shown in Figure 3.3. The peaks were identified as aliphatic hydrocarbons by specific ion monitoring and these compounds would distort a chromatogram obtained from a fire debris sample that contained diesel or kerosene. Therefore, a fire debris sample supplied in a tin with a plastic liner would have to be transferred back into the tin from the plastic bag thereby increasing the possibility of loss of accelerant, contamination or sample mix–up. Plastic bags offer no real advantage when used inside a metal can if the sample is delivered to the laboratory promptly.

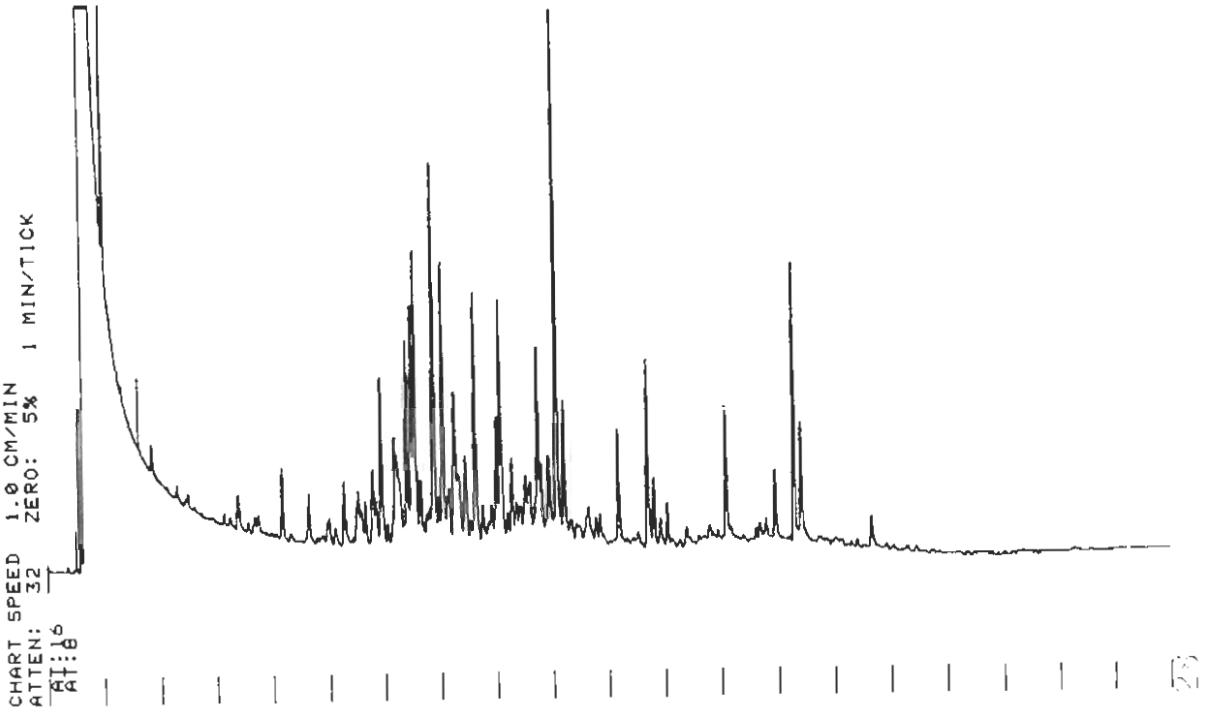

Figure 3.3 – Plastic Bag Chromatogram.

When sealing the metal cans, a poor seal is obtained if debris accumulates on the can rim. The rim should be cleaned with a screwdriver before sealing and the lid should not be trodden on to seal because a distorted lid may leak.

Cans that were sealed properly were found to hold approximately 15 p.s.i. pressure so no leakage would be expected during the storage of properly sealed fire debris samples.

3.2.3 CONTAMINATION DURING ANALYSIS.

When a sample has been received in the laboratory it should be inspected externally for possible leaks, and then opened to observe the type of debris, and smelt to estimate possible accelerant loadings. A sample that is heavily loaded with accelerant could be analysed by a simpler and less time consuming static headspace technique such as absorption onto Tenax, or extracted after other samples to prevent the contamination of the gas transfer lines.

A blank analysis should be performed before extraction to detect any contamination of the equipment. An empty can placed in the oven and extracted will reveal any contamination of the nitrogen, gas transfer lines, water trap, charcoal, carbon disulphide and the syringe. Pipettes and sample vials should be expected to be clean if they are of suitable laboratory grade and do not represent a problem of contamination unless an attempt is made to reuse them.

The gas transfer lines, water trap and syringe can be contaminated from a previous sample and must be cleaned before use. The gas transfer lines and water trap were previously cleaned by extracting a clean metal can containing water which effectively steam cleaned the lines but this was found to be inadequate after samples of high accelerant loadings were extracted. An investigation was

made to reduce the possibility of contamination during the analysis. The two areas which were investigated were the water trap and the gas transfer lines.

3.2.3 (i) Investigation of the Water Trap.

The water trap on the gas transfer line from the oven to the charcoal pipette is intended to prevent water vapour from condensing on the charcoal which reduces the surface area available for absorption. Even when using a chilled trap, water vapour is condensed in the charcoal pipette. Charcoal is used to absorb organics from water so it was felt the elimination of the water trap would not affect the recovery of accelerant.

3µl of petrol was added to two equivalent pieces of carpet and 100mls of water added to each immediately to seal the petrol. The samples were extracted, one with a chilled water trap and one without a water trap at all.

The extracts were analysed and the recovery was equivalent in both cases. The extractions were repeated using kerosene and likewise the recovery was equivalent in both cases. The large amount of water vapour condensing and passing through the charcoal did not affect the recovery of aliphatic and aromatic

hydrocarbons and so the water trap was not used in any further work.

No problems during the extraction of routine samples have been encountered since the elimination of the water trap.

3.2.3 (ii) Gas Transfer Line Material.

Contamination of the gas transfer line occurs after samples with high accelerant loadings are extracted because of condensation of the accelerant vapours on the transfer line. Heating the lines and lagging them would be expensive and result in hot steam emanating from the water in the sample contacting the charcoal which would make it difficult changing the hot pipette. An investigation was made to determine the best available material to use for the gas transfer line.

Copper, aluminium and teflon were used as the gas transfer line for the extraction under identical conditions of 0.5mls of petrol added to three empty cans. The samples were removed and empty cans were extracted and the extracts analysed. The chromatograms revealed that the aluminium line remained the most heavily contaminated whilst the copper and teflon lines were contaminated to the same degree but much less than the

aluminium. The transparent teflon line allowed the contamination to be observed as small droplets of petrol concentrated at the bends in the lines. The procedure was repeated with diesel and the same results obtained but the contamination was much heavier because of the lower volatility of diesel.

Aluminium was chosen as the best inlet gas transfer line because it was more easily manouvered in the oven and contamination was not a problem before the nitrogen gas reached the sample can. Copper was chosen as the outlet transfer line because the teflon was found to become brittle after some time and also copper was not as readily contaminated as the aluminium.

3.2.3 (iii) Cleaning of the Gas Transfer Line.

Steam cleaning of the gas transfer lines required a 1 hour extraction of a can containing water and was found to be inadequate especially when samples with high loadings of accelerant were previously extracted. Steam cleaning of the lines for a further six hours was found to still be inadequate when samples with diesel present were previously extracted. The long cleaning times significantly reduced sample turnover and a quicker cleaning method was needed.

0.5mls of petrol and diesel were extracted from wet carpet and afterwards the lines were washed with approximately 10 mls of acetone using a plastic wash bottle manually connected to the copper transfer line inlet in the oven. The acetone was collected in a residue bottle and the lines were blown dry with nitrogen for ten minutes. A blank sample was then analysed and the contamination from the petrol was found to be eliminated. The contamination from the line of which diesel was extracted was still present as the acetone did not solubilise the heavier components of diesel and continual washing with acetone was not successful. A bunsen burner was then used to heat the entire length of the copper line to red heat beginning at the inlet and a subsequent blank analysis revealed the contamination was eliminated.

Several precautions must be made when cleaning the lines using a bunsen flame because of the fire risks involved. Safety glasses and disposable gloves must be worn when washing with acetone. All traces of acetone must be blown dry from the line and the residue bottle and wash bottle removed away from the area before the burner is lit. The outlet of the transfer line must be vented to a fume cupboard when burning so vapours eminating from the line are drawn away rapidly to prevent ignition. A pressure gauge should be connected to the system and observed in case a blockage in the system causes dangerously high pressures.

Acetone was used because it solubilised both water and hydrocarbons in the transfer line, but other readily available and inexpensive solvents such as alcohol could be used. A solvent which does not solubilise the water such as hexane could not clean the water soluble contaminantes that may be present after the extraction of some fire debris samples.

3.2.3 (iv) Syringe Cleaning Procedures.

After injecting into the G.L.C. the carbon disulphide extract, the syringe is washed with acetone several times and then inserted into a heated vacuum syringe cleaner for several minutes. The cleaning unit heats the syringe needle whilst drawing air through it and no problems with contamination of the syringe have been encountered using this technique.

3.3 DISCRIMINATION DURING EXTRACTION.

When a sample is extracted in the oven, the more volatile components from the accelerant will leave the can first and become absorbed leading to possible analytical discrimination of the accelerant.

All of the accelerant's components will not be extracted in the same ratios as that of the pure accelerant and the extraction time should be as long as possible to recover the heavier components.

Petrol, kerosene, diesel and mineral turps were added to carpet samples in four separate cans (1ml of each) and extracted at 150^0C. The charcoal pipette was changed at 15, 30, 60 and 90 minutes and the carbon disulphide extracts analysed.

The analysis showed that all four accelerants gave the same trends in that the lower boiling point components were the first to be extracted. The four chromatograms obtained from the diesel sample are shown in Figure 3.4 with a diesel standard. The extraction time in the oven should be as long as possible to prevent discrimination especially if diesel is a suspected accelerant. Discrimination was not as much a problem with petrol because it is much more volatile than diesel, but if heavily evaporated petrol is suspected, as would be the case if the sample was very dry, then the extraction time should be slightly longer than normal. The analyst should be aware that the extraction time of one hour should be increased in the following cases:–

(1) Samples are very wet
(2) Samples are very dry
(3) Samples are char
(4) Diesel is suspected

Dry and char samples need to be extracted for a longer period of time in the oven because the amount of accelerant present would be expected to be low. Very wet samples need a longer time in the oven because the water needs to be vaporised to release the accelerants.

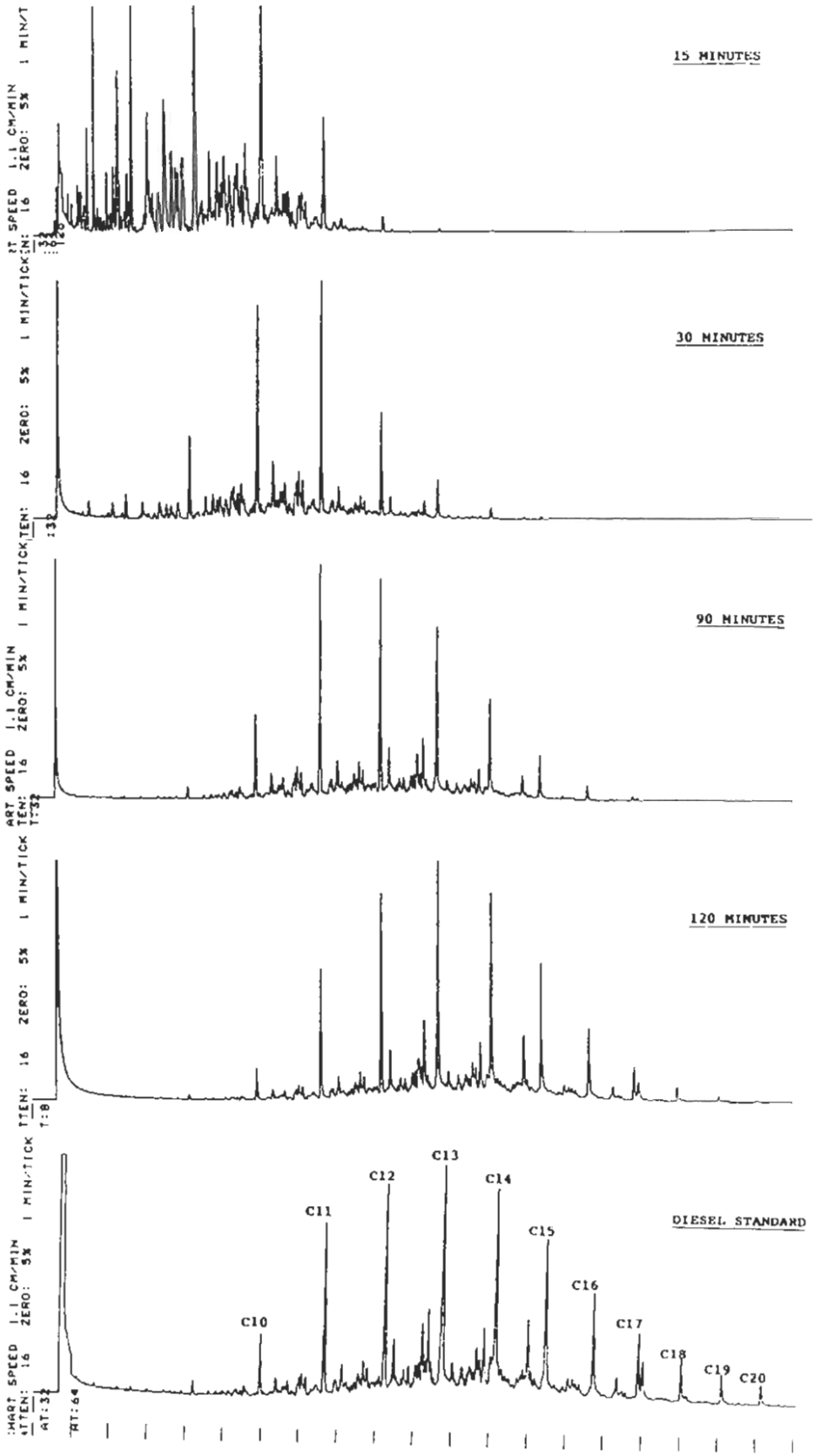

Figure 3.4 – Diesel Extracted and Sampled at 15, 30, 60 and 90 minutes vrs Diesel Chromatograms.

3.4 THERMAL DESORPTION USING TENAX:

Extraction of a sample using static headspace sampling is very rapid and easily repeated. However, the headspace sample cannot be injected directly into a Capillary G.L.C. so it must be absorbed onto an absorbent which is packed into a tube that is suitable to be thermally desorbed in the injection port of the G.L.C. The tubes are placed directly into the heated injection port and sealed and the carrier gas passes directly through the heated tube and sweeps the desorbed compounds directly onto the column.

3.4(i) Analysis of Petrol

1µL of petrol was added to some wet carpet in a can and 5 mLs of headspace was taken at room temperature and adsorbed onto Tenax, housed in an S.G.E. Unijector tube. The tube was desorbed at 280^0C with 10 p.s.i. of hydrogen in the injection port of the G.L.C. The carpet sample was then extracted using normal dynamic headspace extraction onto charcoal and desorbed with Carbon Disulphide and analysed using the same G.L.C. operating parameters as used for the thermal desorption. The chromatograms produced are shown in Figure 3.5 and show the sensitivities of the two techniques being approximately equal. The recovery of both techniques can be increased by taking larger headspace samples.

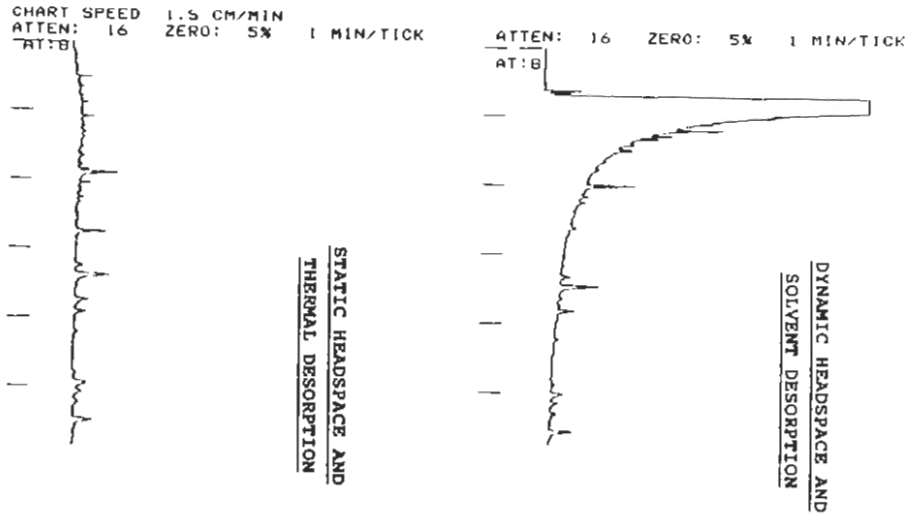

Figure 3.5 – Thermal and Solvent Desorption of Petrol Headspace.

Thermal Desorption does not give a solvent peak to obscure the volatile component of petrol. However these more volatile components will normally be absent in a fire sample. Thermal Desorption also does not give an extract that can be stored for later analysis or by mass spectroscopy and the reproducibility of the retention time is not as good as for liquid injections.

3.4(ii) Analysis of Ethanol

1μL of ethanol was added to a piece of wet carpet and a 5 mL static headspace sample was absorbed onto Tenax. The Tenax was thermally desorbed but no ethanol was detected. 8μL of ethanol

was needed to be added to the wet carpet before a peak could be detected which is shown in Figure 3.6. The retention of ethanol on the non– polar BP– 1 column was poor. The carpet sample was then extracted using dynamic headspace with charcoal absorption and carbon disulphide desorption and the chromatogram produced is also shown in Figure 3.6. Ethanol was not detected, possibly due to the following:

(i) It was obscured by the carbon disulphide peak,

(ii) It was insoluble in the carbon disulphide and

(iii) It was desorbed from the charcoal by the water in the sample.

Therefore the extraction of ethanol with carbon disulphide from a charcoal absorption tube is not possible.

Ethanol is normally recovered only in trace amounts from fire debris samples because it is water soluble and so is washed away during the extinguishing of the fire. It is a natural fermentation product from food and is also found in all alcoholic beverages.

A fire debris sample that gives an odour of or is suspected to contain ethanol should be subjected to static headspace absorption onto Tenax and the single peak should be confirmed by mass spectrometry as being ethanol because a single peak retention time can be inconclusive regarding the presence of ethanol.

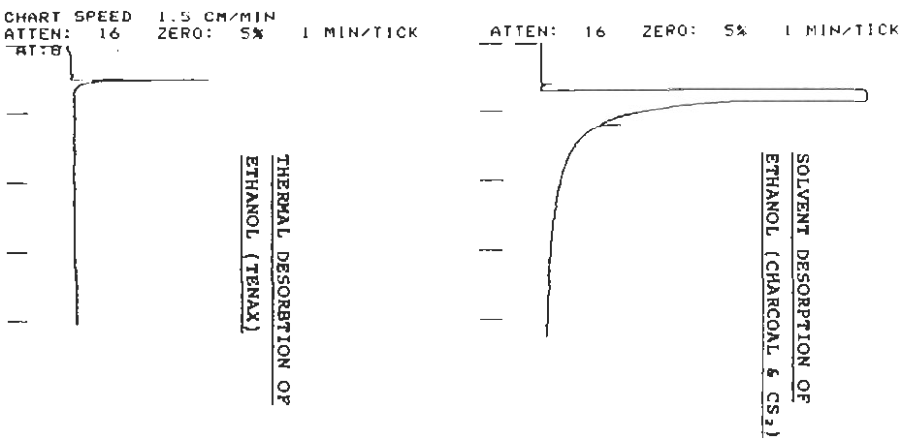

Figure 3.6 – Thermal and Solvent Desorption of Ethanol.

3.5 DETECTION OF GAS ODOURANTS.

Odourants are added to town gas and bottled gas so that leaks are detected olefactorally by the user. The odourants added to natural gas suppliers in N.S.W are Tertiary Butyl Mercaptan (T.B.M.) and Tetrahydrothiophene (T.H.T.) at a total concentration of 27 mgms/m^3.

The need of the forensic chemist to detect gas odourants was illustrated recently in Newcastle, N.S.W. during an investigation following a gas explosion. The ground where the explosion occurred had gas emerging at several locations and a gas odour was present. The three possible sources of the gas were:–

- leaking town gas
- natural gas that may have been released from the local coal seams
- sewerage gas from a redundant sewerage works nearby

All three sources were possible because the underground area contained old mine and ventilation shafts, tunnels used for military purposes during WWII and sewerage pipes. The odour detected could have been town gas odourants or hydrogen sulphide. The detection of T.B.M. or T.H.T. would identify town gas as the source and gas samples were taken for laboratory analysis. No T.B.M. or T.H.T. was detected in the samples.

The analytical results were questioned because of the possibility that the odourants had adsorbed onto the glass wall of the sample container. Also the normal method of analysing odourants in gas by packed column G.L.C. with a sulphur specific detector may not have been sensitive enough because the air samples were diluted to 5% methane and normal gas samples are analysed at 95% methane. A method of concentrating the odourants on site by using a suitable absorbent with an air sampling pump would increase the recovery of odourants. The fixing of the odourants onto an absorbent would also mean less equipment to be transported to the site. An investigation was made to develop a

suitable qualitative analytical method which uses equipment readily available at a fire investigation laboratory.

3.5.1 INVESTIGATION OF A SUITABLE ABSORBENT FOR THE ANALYSIS OF GAS.

Headspace absorption tubes packed with Tenax were tested for absorbing gas samples but were found to require at least 8 p.s.i pressure to push the air sample through the tube because of the low permeability of the packing. No portable air pump could be found to pump to 8 p.s.i. so thermal desorption tubes could not be used.

Charcoal packed in glass tubes was found to be reasonable permeable and therefore suitable for use with a portable air pump for sampling the gas. The charcoal was desorbed with carbon disulphide and the extract analysed by Capillary G.L.C. with an F.I.D. detector. The chromatogram obtained is shown in Figure 3.7 and is complex due to the absorption of hydrocarbons together with the odourants. The sample was reanalysed using an Ion Trap Detector and both aliphatic and aromatic hydrocarbons were identified by specific ion monitoring. A library search was made of the other peaks and a T.H.T. peak was identified and is marked on Figure 3.7. T.B.M. could not be identified and may have been

obscured by the carbon disulphide peak. The method was used for sampling air near a gas leak and the chromatographic fingerprint obtained was used to positively identify the gas. The sampling time and flow rate of the portable pump was approximately 1 hour and 500mls/minute.

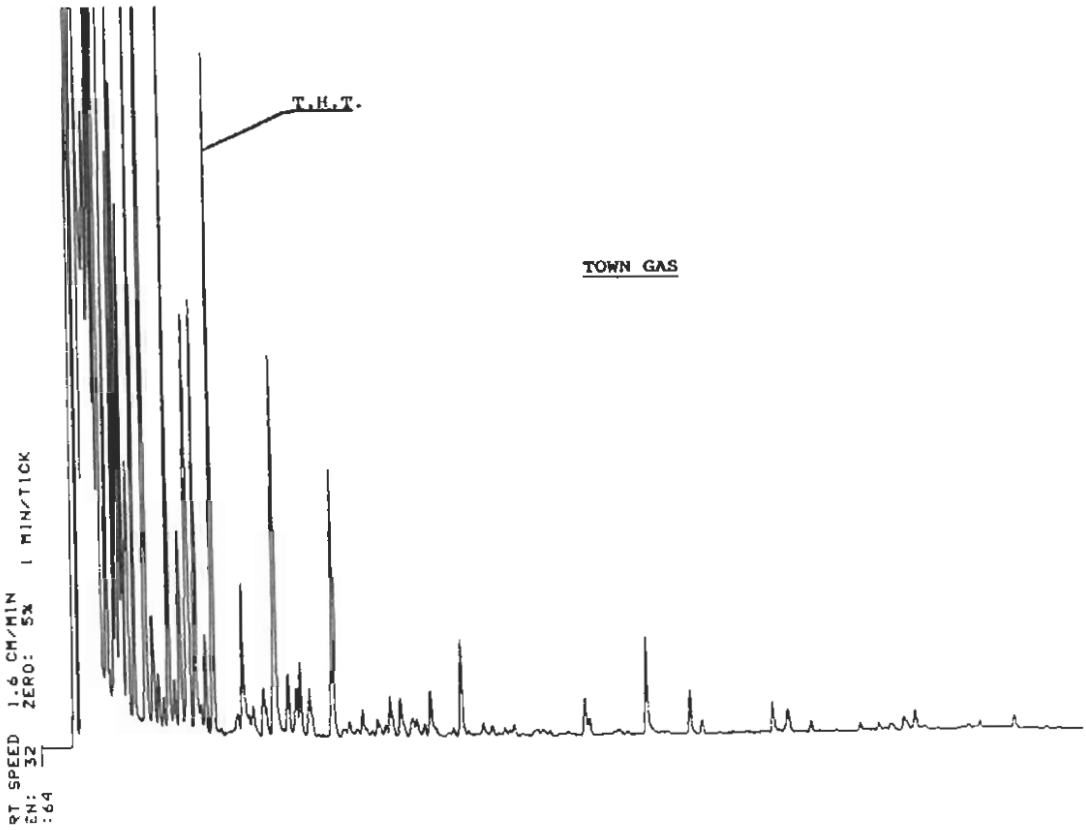

Figure 3.7 – Town Gas Chromatogram.

3.5.2 USE OF DRAGAR TUBES ON–SITE TO DETECT GAS ODOURANTS.

Commercial Drager tubes are available for the quantitative detection of T.B.M., T.H.T and hydrogen sulphide. Various samples of H_2S., T.B.M., T.H.T., and diluted town gas (10% methane) were prepared. The tubes were used in the laboratory to quantitatively analyse vapour samples of T.H.T., T.B.M. 10% town gas and H_2S, and the results are shown in Table 3.2.

Tube	Sample	Result
T.H.T	T.H.T. (12ppm)	12 ppm
T.H.T	T.B.M. (1ppm)	negative
T.H.T	H_2S (10ppm)	strong positive
T.H.T	10% gas	slight positive
T.B.M	T.H.T. (12ppm)	slight positive
T.B.M	T.B.M. (1ppm)	1 ppm
T.B.M	H_2S (10ppm)	strong positive
T.B.M	10% gas	0.33 ppm
H_2S	T.H.T. (12ppm)	negative
H_2S	T.B.M. (1ppm)	negative
H_2S	H_2S (10ppm)	10 ppm
H_2S	10% gas	negative

TABLE 3.2: Drager Tube Responses to H_2S, T.H.T., T.B.M., and Diluted Town Gas.

The results show that T.B.M. and T.H.T. could readily be identified by the appropriate tube. For diluted gas samples the amount of air sampled to detect T.H.T. and T.B.M. could be increased by increasing the number of strokes taken with the air pump. It can be seen that H_2S will give a positive result using both the T.H.T. and the T.B.M. tubes so the presence of H_2S must be checked on site with a sensitive H_2S tube before checking for T.H.T. and T.B.M.. A methane tube could also be used onsite to

determine the approximate gas concentration in the air so that the appropriate amount of air sampled for the quantitative analysis of T.H.T. and T.B.M. could be estimated.

The Drager tube results if positive for gas odourants can be verified by absorbing the gas samples onto charcoal and analysing the samples as outlined previously in section 3.5.1.

3.6 INTERPRETATION OF RESULTS:

The interpretation of the chromatogram is made to determine whether an accelerant was present in the sample and then to identify it. A library file of chromatograms obtained from the analysis of various accelerants is used to select and identify the accelerant and a standard accelerant sample is then analysed under identical chromatographic conditions to those used for the samples' analysis. The chromatograms are then compared and the retention time data of the peaks are used to confirm the presence of the accelerant' components which collectively identifies the accelerant.

The interpretation must be made by an experienced analyst with the aid of a comprehensive library that should include chromatograms from the following:–

- the common accelerants
- the industrial solvents
- burnt synthetic materials
- common household products and materials

The analyst should also be aware of the sensitivity of the extraction and analytical techniques he uses when interpreting chromatograms. Background levels of accelerant components in

various materials could present a problem when using extremely sensitive techniques and levels should be established by the analyst. Various materials and accelerants were analysed and the chromatograms obtained are presented to assist interpretation. As well as using F.I.D. detection, an I.T.D. detector was also used with specific ion monitoring.

Liquid samples were added to carbon disulphide (approximately 5µL to 1 mL of CS_2) and solid samples were burnt and extracted using dynamic headspace and desorbed with carbon disulphide.

3.6.1 BACKGROUND LEVELS OF ACCELERANTS.

The detection of 0.1µL of petrol in fire debris is readily possible when using dynamic headspace absorption with Capillary G.L.C., and less if more headspace is sampled or the extract concentrated. The question posed when these extremely small quantities of accelerants are found is what normal background levels of petrol and other possible accelerants on various materials is to be expected.

Car flooring materials were used to investigate normal background levels because of their continual exposure to an environment where petrol is stored. Twenty samples of car flooring materials

were taken from the front and back floors and the boot area of eight different cars that ranged from 5 to 20 years of age. The samples were all approximately six inch squares and were made from rubber mats, wool and synthetic carpets and underlays. Samples of soil were also taken from a motor wrecking yard where oil contamination was evident. All samples were extracted for one hour in the oven at 150^0C.

All car flooring materials analysed had no detectable traces of petrol, diesel, kerosene or mineral turps present. The chromatograms obtained from the rubber mats were complex but could not be confused with the common accelerants.

The background levels of accelerants from car flooring materials was negligible and materials from a cleaner domestic environment would be expected to be the same. The transport of fire samples in well sealed containers could therefore expected to be safely done in the boot or passenger sections of a car provided the areas are seen to be relatively clean.

The chromatogram obtained from the extraction of the soil is shown in Figure 3.8 alongside chromatograms obtained from petrol and diesel standards. Petrol is clearly evident in the sample together with a complex mixture of unresolved hydrocarbons as seen by the rising baseline which is a common feature of the analysis of oils and greases.

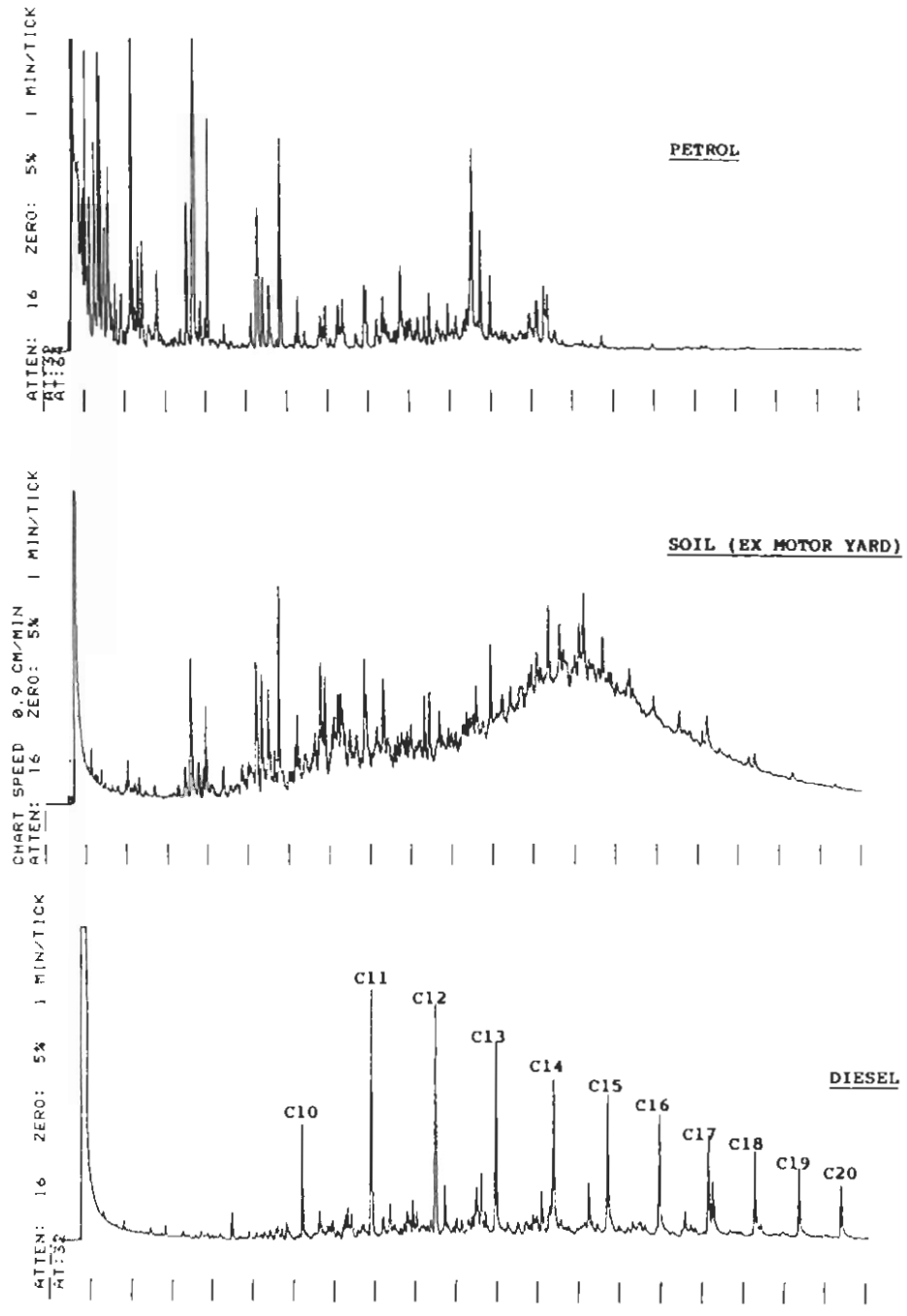

Figure 3.8 – Soil (Ex motor yard) vrs Petrol and Diesel Chromatograms.

The analysis of the soil shows that it is a good adsorbent medium for hydrocarbons and they readily persist despite the effect of rain and sun. Samples of soil or concrete taken from areas where cars have been garaged or where oil or petrol may have been previously stored may have traces of hydrocarbons present that give analysis consistent with those from the common accelerants. Samples of river sand from an environment where boat and ferry traffic were heavy have also been found during routine analysis to contain trace amounts of hydrocarbons believed to have originated from oil or diesel. Soil samples taken from under houses have been found to contain no traces of accelerants.

3.6.2 ANALYSIS OF THE COMMON ACCELERANTS.

The most common accelerants found in fire debris samples are:–

- Petrol
- Kerosene
- Mineral Turps
- Diesel

All are readily available to the fire setter and should be the first chromatograms checked when the interpretation of the samples' chromatogram is made.

3.6.2 (i) Petrol.

Petrol is produced from the reformation of crude oil where the conversion of aliphatic to aromatic hydrocarbons is made. The most basic aromatic hydrocarbon is benzene and the addition to benzene of a methyl group produces toluene. Aliphatic groups further added to the benzene ring produces the dimethylbenzenes (xylenes) and other higher molecular weight aromatic compounds.

Figure 3.9 is a chromatogram from fresh petrol and shown above is evaporated petrol. Most fire debris samples would be expected to contain petrol evaporated to a certain degree because of the high volatility of the lower molecular weight components of petrol. The complexity of the chromatogram indicates petrol is composed of a wide range of different compounds. Shown in Figure 3.10 (a and b) are the simulated ion scans from an analysis of petrol which indicates the general class of compound each peak component is from. The ion scans shown and the class of compounds they indicate are:

	TOT	Total Ion Scan
M/E	55, 69	alicyclic and olefinic hydrocarbons
	57, 71	aliphatic hydrocarbons (evaporated and fresh petrol shown)
	91, 105	aromatic hydrocarbons

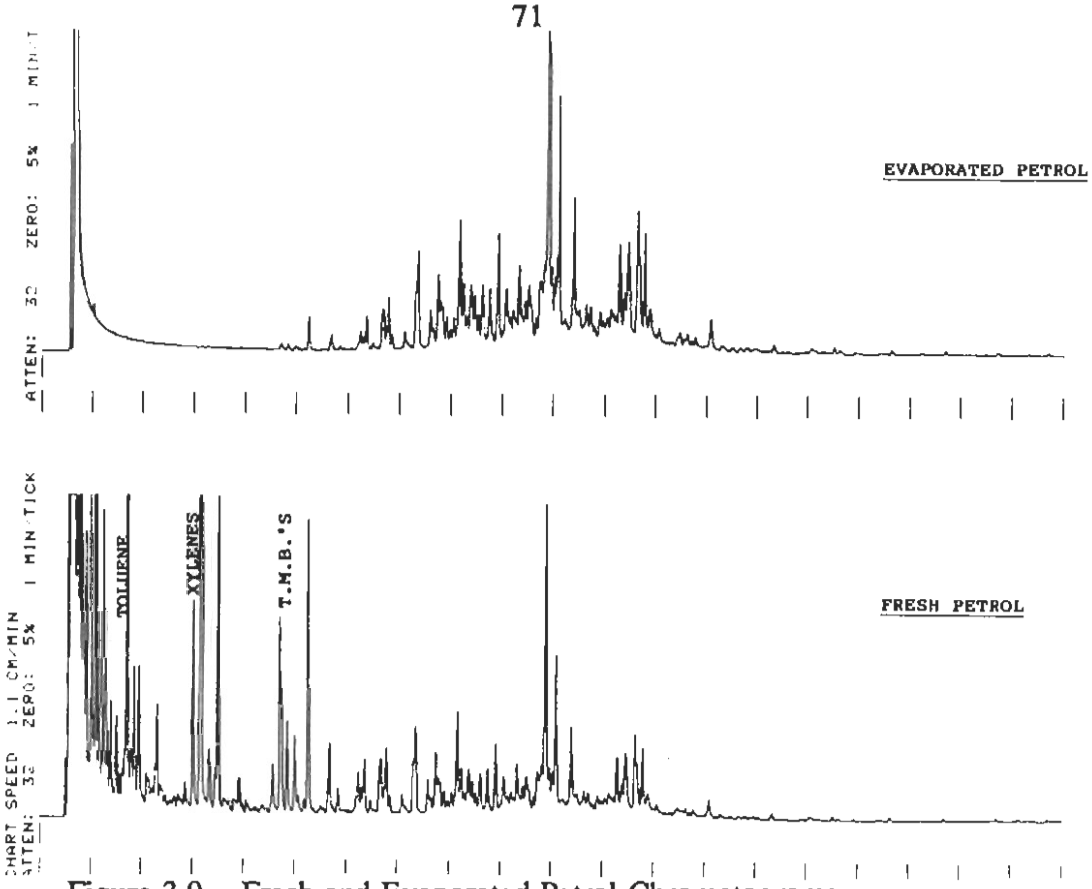

Figure 3.9 – Fresh and Evaporated Petrol Chromatograms.

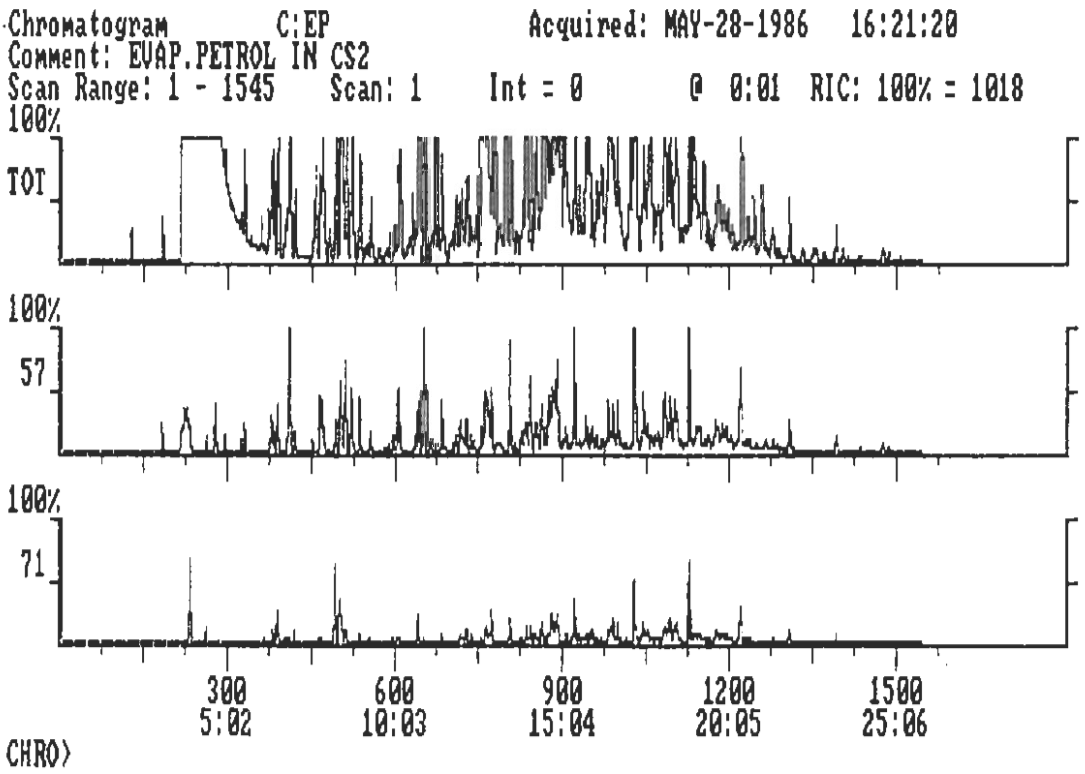

Figure 3.10 (a) Ion Scan of Evaporated Petrol.

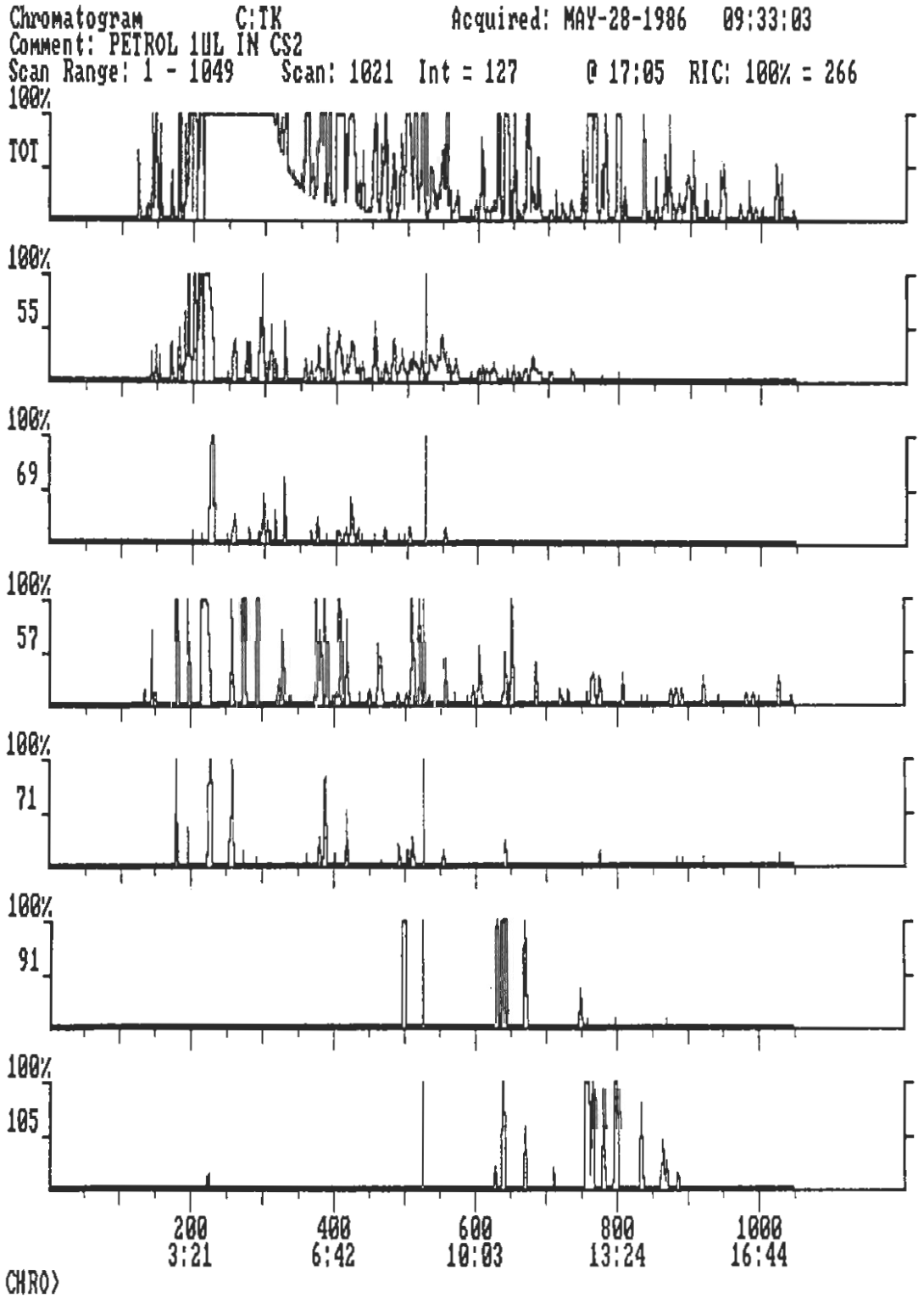

Figure 3.10 (b) – Ion Scan of Fresh Petrol.

Petrol can be seen to be composed of aliphatic and aromatic hydrocarbons, the aliphatics composing the lighter fraction of petrol and the heavier fraction of evaporated petrol.

An attempt was made to characterise two stroke petrol but the chromatogram obtained was identical to that of normal petrol. The oil added to normal petrol to produce two stroke mix is very heavy and did not elute from the column. It therefore would not be extracted from the sample in an oven at 150^0C.

3.6.2 (ii) Analysis of the Additives in Petrol.

The main additives in petrol are the organo–lead compounds tetra ethyl and tetra methyl lead. They are added to improve the octane rating of petrol, however, unleaded petrol is also available which uses various other compounds as additives to improve their octane ratings.

The lead additives are readily detected by an F.I.D. detector but they normally appear in the chromatogram obscured by other peaks and also are present only in trace amounts. An attempt was made to detect the lead compounds with an I.T.D. detector.

A chromatogram using the I.T.D. was obtained from fresh petrol

(5μL in 1ml of CS_2) is shown in Figure 3.11. Selective ion monitoring was used to eliminate any signal obtained from the aromatic compounds in petrol. The two peaks were positively identified as tetra methyl and tetra ethyl lead respectively. 20 μL of petrol was added to a can and then extracted and a chromatogram was obtained using the same analytical conditions as the petrol sample run previously. The chromatogram obtained is shown in Figure 3.12 and the lead compounds were not detected. The extraction was repeated but again the results were the same. The lead compounds were not recovered from the can having possibly decomposed at some stage during the extraction. Therefore the confirmation of petrol by identification of the lead additives in the carbon disulphide extract cannot be made successfully using dynamic headspace extraction with carbon disulphide elution. Solvent extraction would recover the lead compounds from the debris and further concentration of the solvent would be necessary before injection into the G.L.C. to increase the sensitivity of the analysis.

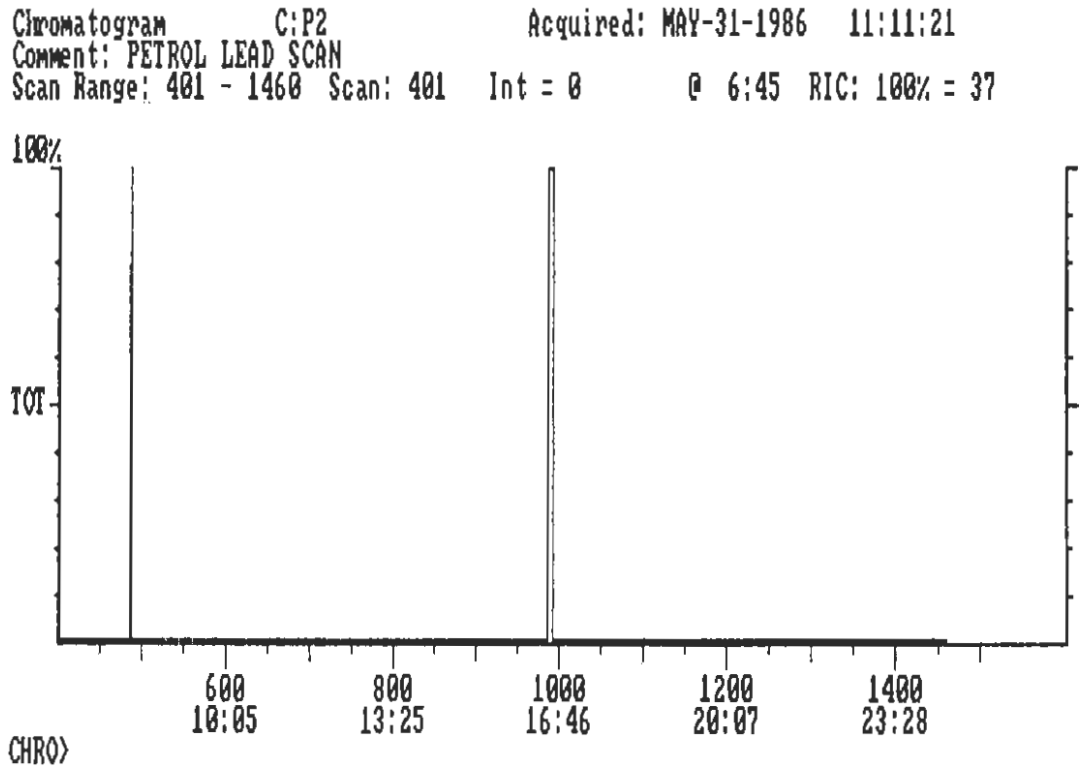

Figure 3.11 — Lead Scan of Petrol Chromatogram.

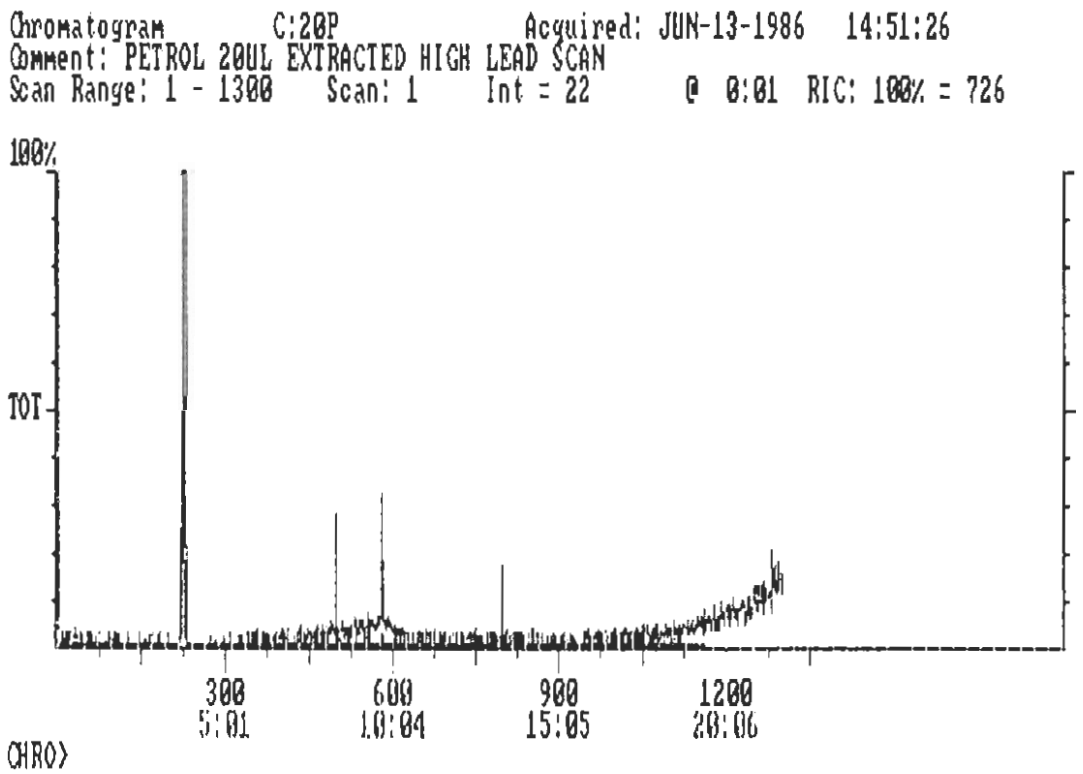

Figure 3.12 — Lead Scan of Extracted Petrol Chromatogram.

Attempts were made to detect the additives in unleaded petrol (generally ether compounds) but none were identified. Chromatograms of fresh leaded and unleaded petrol are shown in Figure 3.13 and the unleaded petrol can be seen to have greater amounts of the more volatile components. In an actual fire debris sample, however, petrol would be expected to be evaporated so that leaded and unleaded petrol could not be differentiated from the analysis.

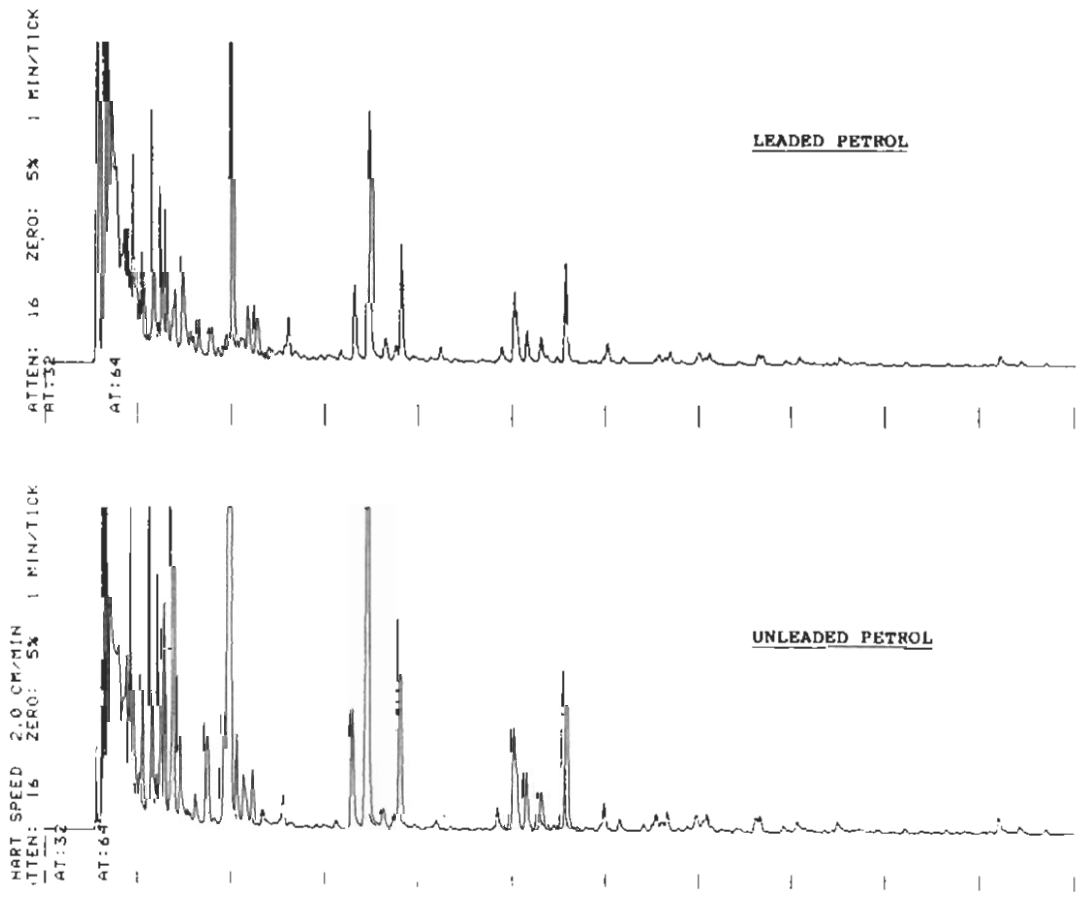

Figure 3.13 – Leaded and Unleaded Petrol Chromatograms.

3.6.2 (iii) Kerosene.

Kerosene is produced directly by distillation from crude oil which is composed mainly of aliphatic hydrocarbons.

A chromatogram from the analysis of kerosene is shown in Figure 3.14 and in Figure 3.15 are the specific ion scans of masses 57 and 71 that indicate aliphatic hydrocarbons. It can be seen that kerosene is composed mainly of aliphatic hydrocarbons. Extremely evaporated kerosene has been found to resemble diesel as shown in Figure 3.16. It is therefore difficult to distinguish evaporated kerosene and heating oil (a slightly heavier fraction) from diesel when trace amounts are recovered from a sample.

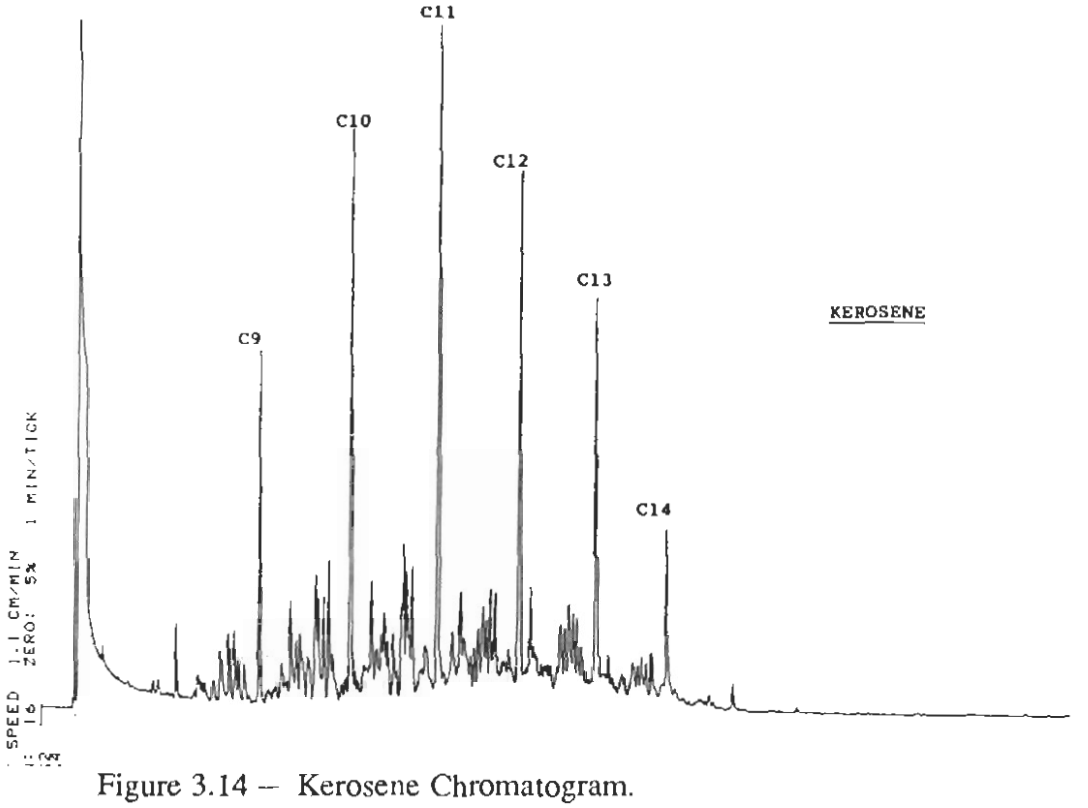

Figure 3.14 – Kerosene Chromatogram.

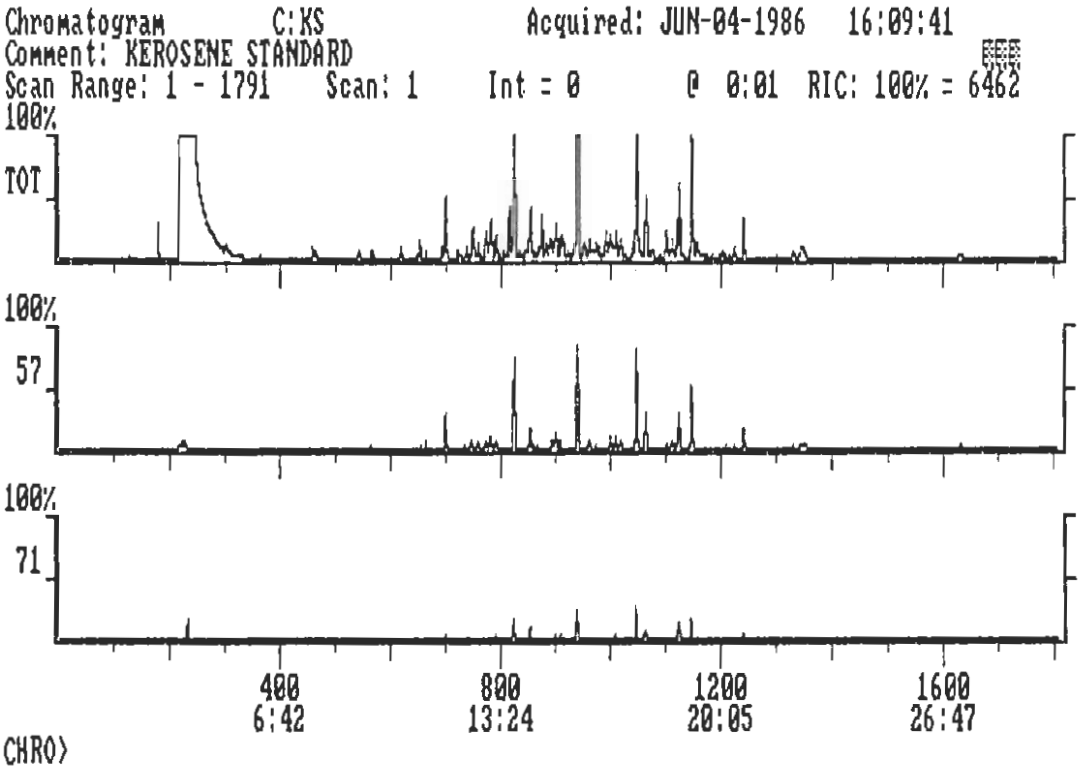

Figure 3.15 – Ion Scan of Kerosene Chromatogram.

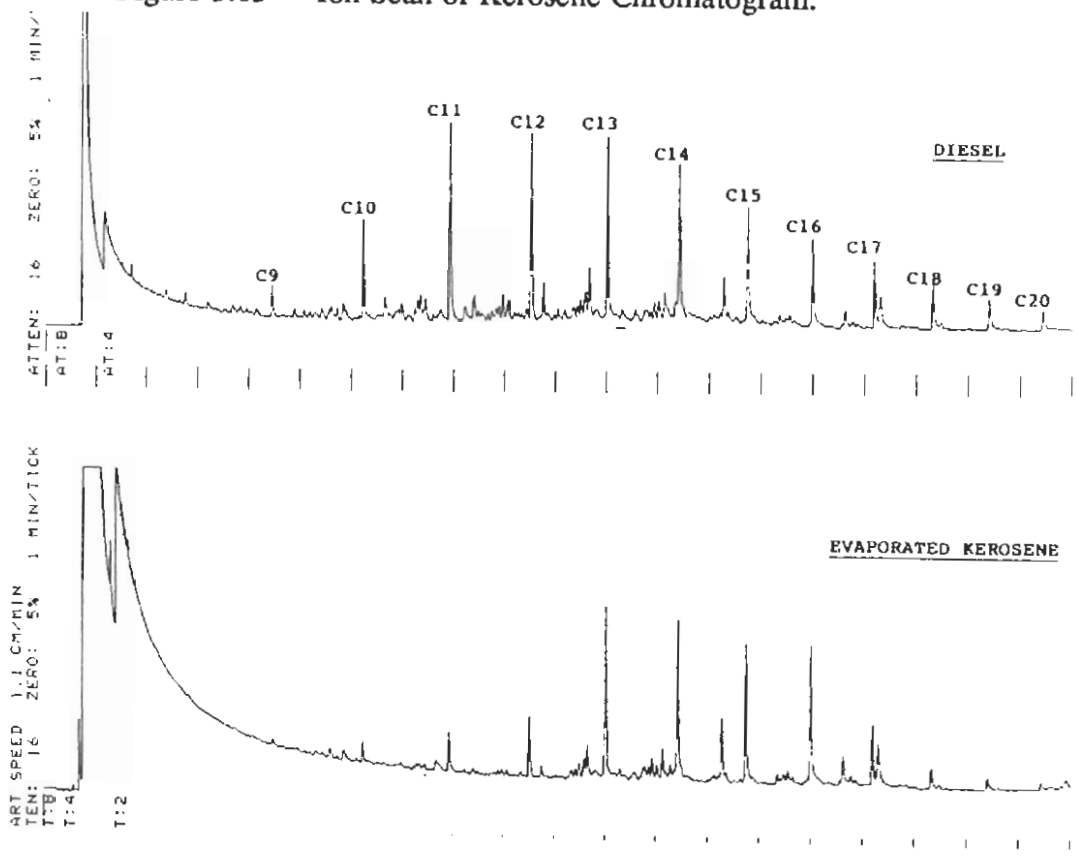

Figure 3.16 – Evaporated Kerosene and Diesel Chromatograms.

3.6.2 (iv) Mineral Turps.

A chromatogram from the analysis of fresh and evaporated mineral turps is shown in Figure 3.17 and shown below in Figure 3.18 are the specific ions scans of 57 and 71 (indicating aliphatic hydrocarbons) and 91 and 105 (indicating aromatic hydrocarbons), mineral turps being a mixture of aliphatic and aromatic hydrocarbons. The main aliphatic hydrocarbons are C11, C12 and C13, and of the aromatic hydrocarbons the xylenes and the trimethyl benzenes are prominent. No toluene in significant amounts was found in the mineral turps sample. Highly evaporated mineral turps tends to become more aliphatic in nature and resembles heating oil. To distinguish between evaporated mineral turps and an aliphatic cut, the presence of the trimethyl benzenes which are located in the chromatograpn between the C9 and C10 peaks would need to be verified in the sample.

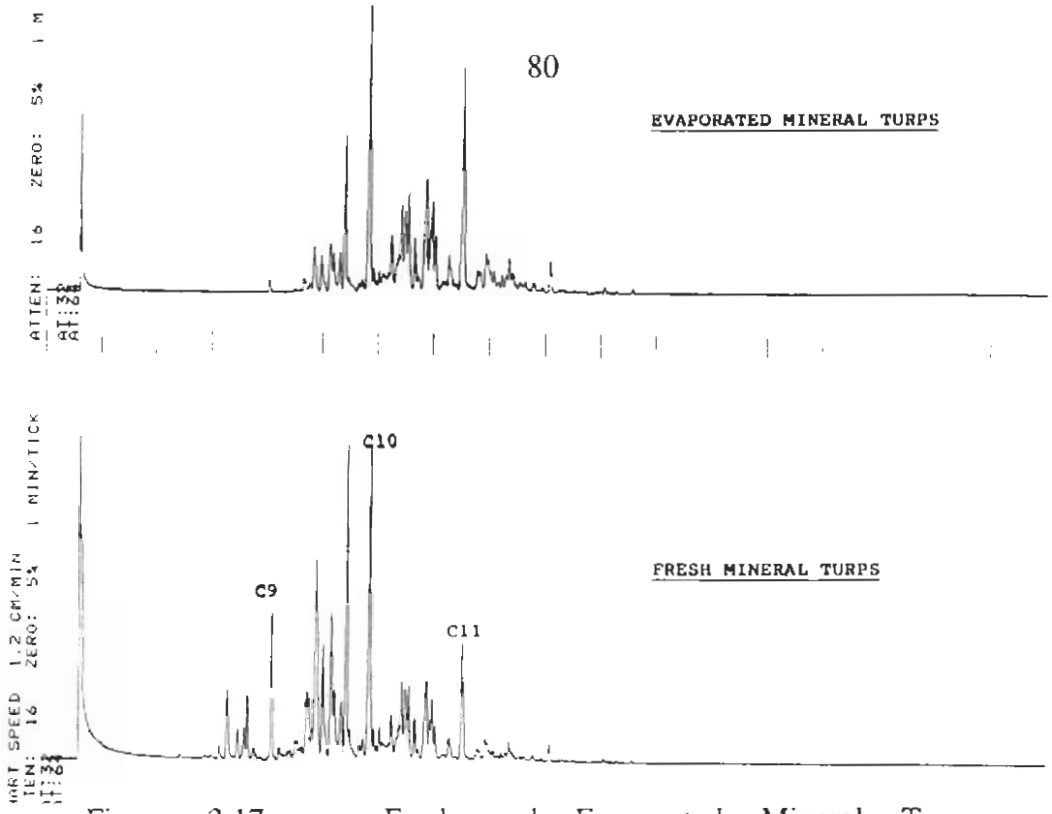

Figure 3.17: Fresh and Evaporated Mineral Turps Chromatograms.

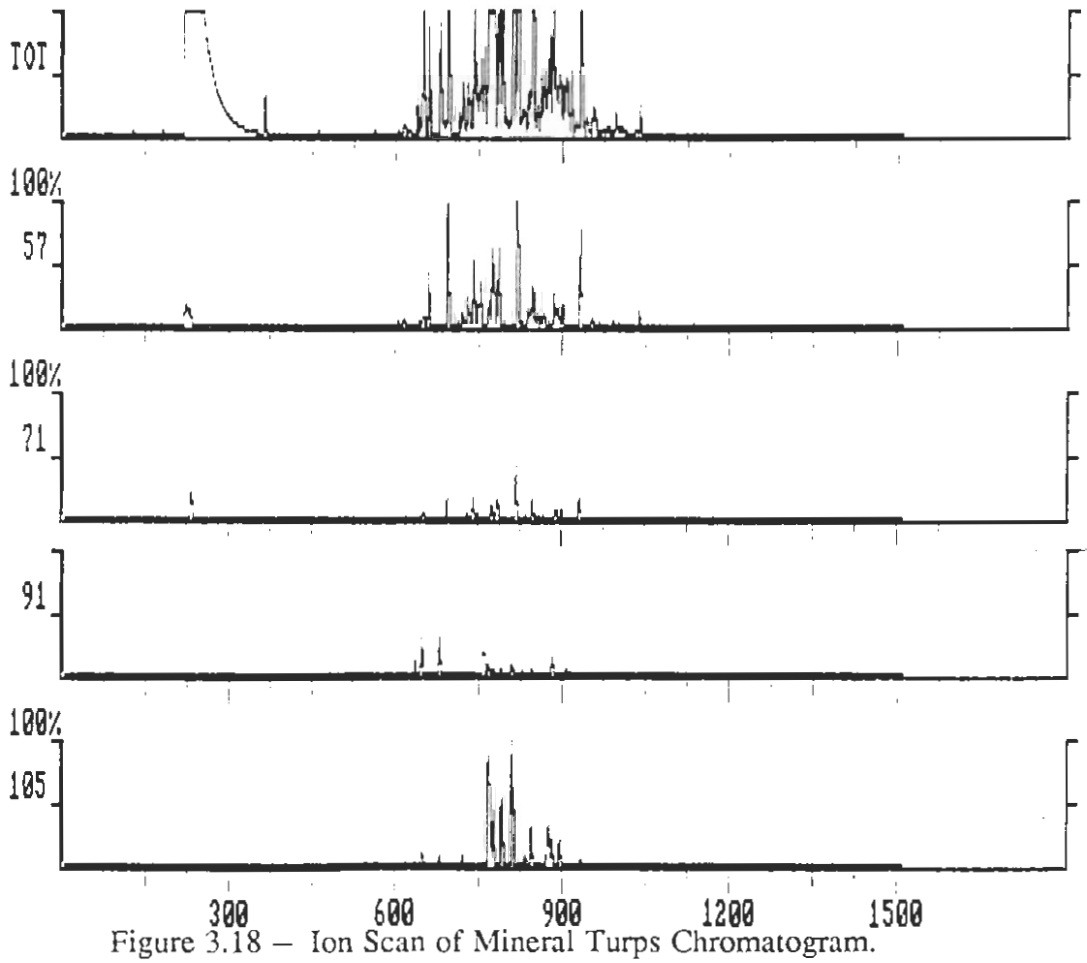

Figure 3.18 – Ion Scan of Mineral Turps Chromatogram.

3.6.2 (v) Diesel.

Diesel is similar in chemical composition to kerosene and heating oil in that it is composed of aliphatic hydrocarbons that are obtained from the fractional distillation of crude oil. Diesel is a higher boiling point fraction and the distillation range is greater than that of kerosene and heating oil being composed of essentially C10 to C25 aliphatic hydrocarbons. A chromatogram of diesel is shown in Figure 3.19 and above is a chromatogram obtained from evaporated diesel. An ion scan is shown in Figure 3.20 which reveals diesel is composed of aliphatic hydrocarbons (M/E 57 and 71). Further ion scan analysis revealed no aromatic compounds were present in diesel.

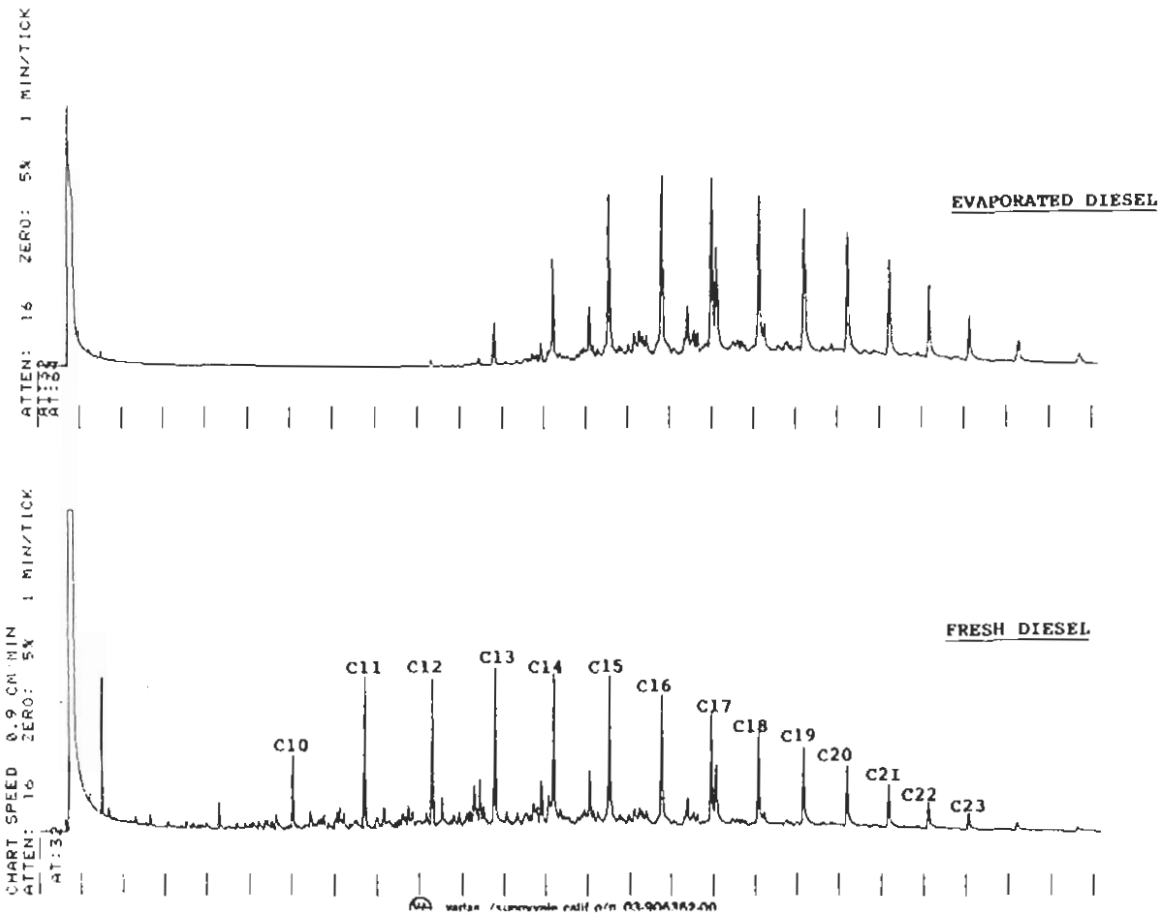

Figure 3.19 – Diesel and Evaporated Diesel Chromatograms.

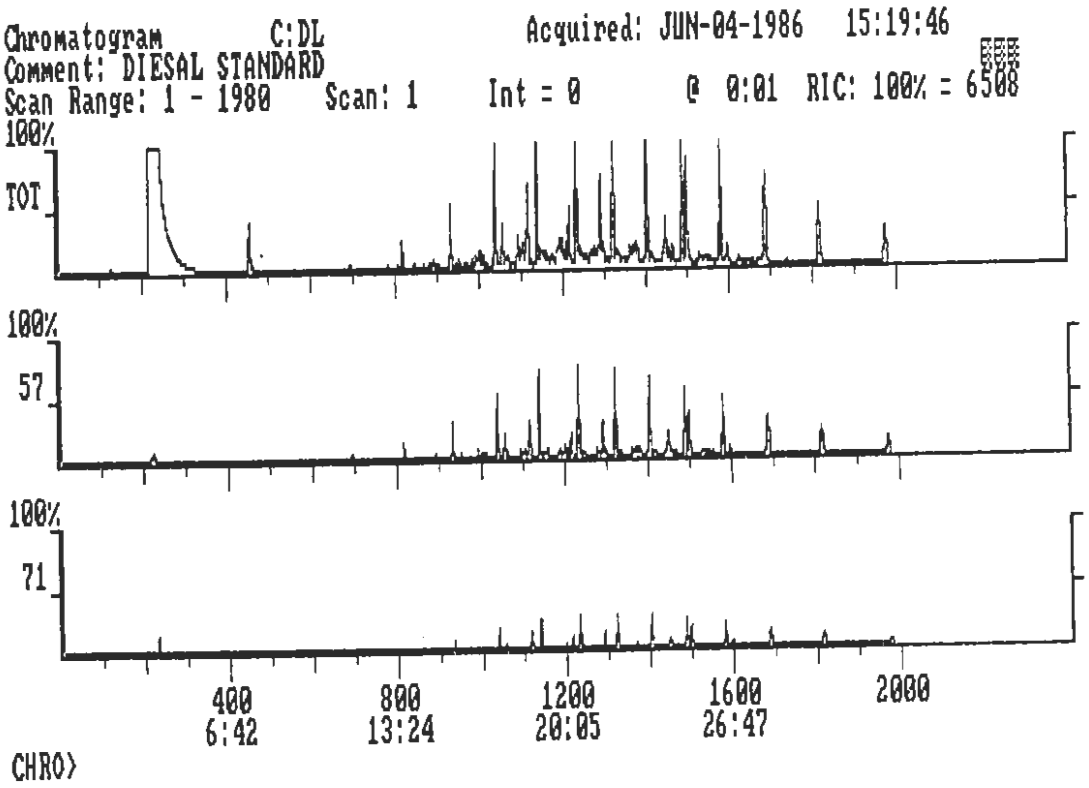

Figure 3.20 – Ion Scan of Diesel Chromatogram.

3.6.3 ANALYSIS OF THE INDUSTRIAL SOLVENTS

The industrial solvents can be used as accelerants because they have the same flammability as the common accelerants but they are not as readily available to the arsonist. The industrial solvents are usually derived from the same feedstock as the common accelerants and are similar in chemical composition in that they are composed of aliphatic or aromatic hydrocarbons. Oxygenated hydrocarbons are also available and are usually more water soluble than the common accelerants so that they can be readily washed away from the fire scene leaving little trace remaining.

Generally, solvent manufacturers duplicate each others product, the only difference being the brand name. A variety of industrial solvents were analysed as both fresh and evaporated and ion scans were also obtained to determine the general composition of each solvent.

The solvents analysed were:–

- Lacquer Thinners
- Methylated Spirits
- Shellsol A
- Shell 1552
- Shell SS926
- Shell X2
- Shell X4
- Shell X55
- Shell X95
- White Spirits
- Shell clean SS1626

The chromatograms and relevant ion scans are shown in Appendix 1.

The main features of the chromatograms are:

3.6.3 (i) Lacquer Thinners.

Lacquer thinners is a mixture of aromatic and aliphatic hydrocarbons as well as some oxygenated hydrocarbons such as ketones, acetates and alcohols. The esters give a distinctive odour to the solvent that could readily be detected olefactorally at the fire scene. The alcohols present would make lacquer thinners more water soluble than the common accelerants but traces would be expected to remain at the fire scene.

3.6.3 (ii) Methylated Spirits.

Methylated Spirits is pure ethanol with various denaturants added depending on the intended use. Methanol is added to commercial grades and MIBK, florescene and bitrex to retail methylated spirits. Various other denaturants are sometimes used.

The denaturants with the exception of methanol are present in minute quantities that would not be expected to be recovered from fire debris samples. As previously discussed Methylated Spirits cannot be detected using charcoal and carbon disulphide and headspace sampling onto Tenax with thermal desorption must be used.

Ethanol is also present in alcohol cleaning agents and is a fermentation product from many foods and products. The investigator should bear this in mind when taking samples and notify the analyst of any possible contamination of samples.

3.6.3 (iii) Shell Solvents.

The solvents were either aliphatic or aromatic hydrocarbons or a mixture of both. They could readily be confused in their analysis with some of the common accelerants if they were evaporated. White spirits, for example, is very similar to kerosene but has a narrower boiling point range. Some grades do however have aromatics present that could distinguish them from kerosene. Because some of the evaporated industrial solvents are similar in their analysis to some of the common accelerants it is difficult to positively distinguish between the two. However, a chromatogram consistant with either would indicate an accelerant present unless otherwise explained.

3.6.4 ANALYSIS OF COMMON HOUSEHOLD PRODUCTS AND MATERIALS.

Many household products and building materials use petroleum based products in their formulation and the extraction and analysis

of these materials may give chromatograms that could wrongly be interpreted as an accelerant having been present. Petroleum based solvents are used in the formulation of paints, varnishes, aerosols, cleaning chemicals, adhesives and household insecticides so all fire debris should be inspected and smelt for any evidence of these products before analysis. Taking control samples may not be possible at the fire scene so if there is any possibility of these products being present in the sample, it should be communicated by the investigator to the analyst.

A variety of household products were extracted and analysed and the chromatograms obtained. It is difficult to prepare a complete library of chromatograms of the various household and building products because of the multitude of products available and their variable formulations according to brand types. The samples analysed were:–

- floor tile glue
- varnished wood
- motor oil
- household insecticides
- vegetable oil
- brake fluid
- WD–40

3.6.4 (i) Floor Tile Glue.

The chromatogram obtained from the sample of floor tile glue is shown in Figure 3.21 alongside that of a petrol standard. Aromatic compounds are evident and were confirmed using the I.T.D. with specific ion monitoring (M/E 91,105). Although the overall fingerprint does not resemble petrol the investigator should sample another material rather than floor tiles (particularly if they are freshly laid) or supply control samples.

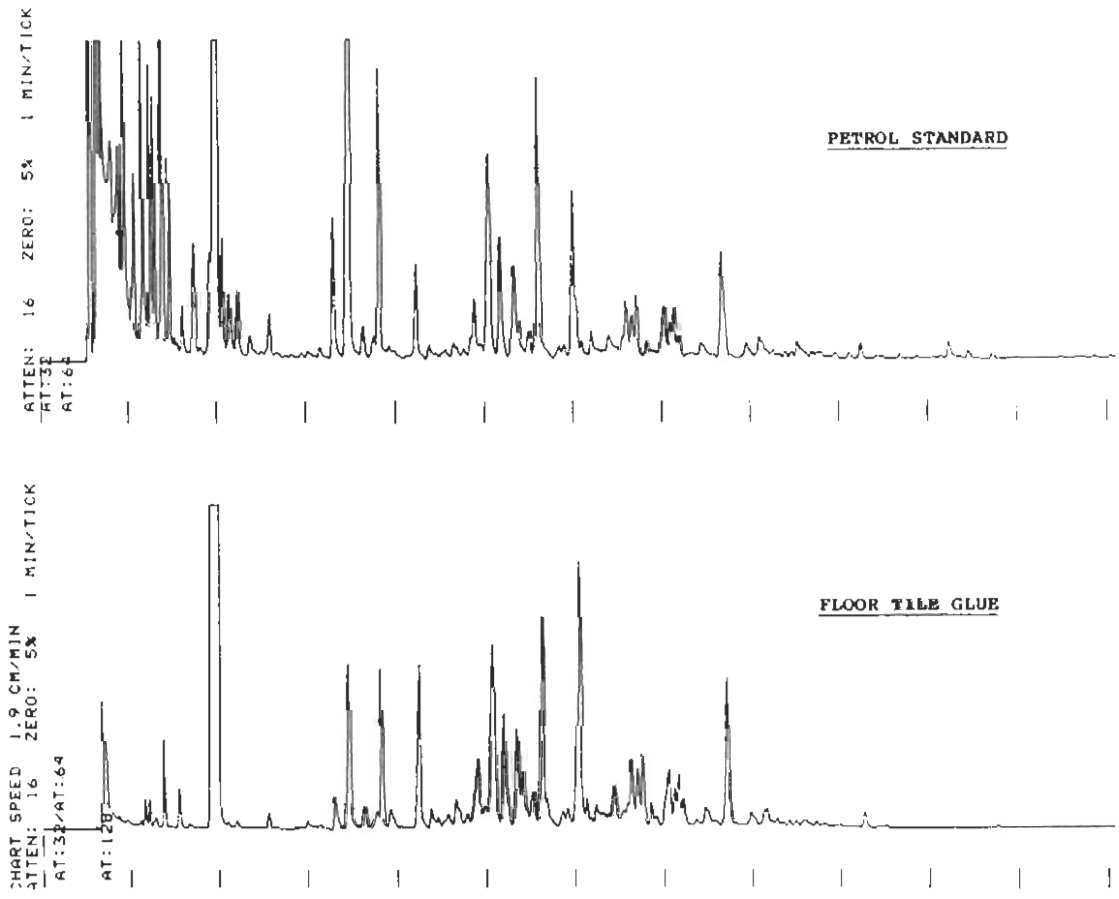

Figure 3.21 – Floor Tile Glue and Petrol Chromatograms.

3.6.4 (ii) Varnished Wood.

A sample of red cedar varnished some two months previously was extracted and analysed and the chromatogram produced is shown in Figure 3.22 below that of a petrol standard. The presence of toluene, xylenes and trimethyl benzenes in the sample can be seen from the chromatogram and were later confirmed by I.T.D. detection. These are believed to have originated from underneath the varnish film because when the wood was burnt the amount of aromatics recovered increased due to the rupturing of the film and release of the solvent. The later group of peaks were confirmed as having originated from the wood itself being wood oils that give red cedar its distinctive odour. Other types of varnishes were found to use solvents that were blends of aliphatic hydrocarbons or oxygenated hydrocarbons such as esters or alcohols.

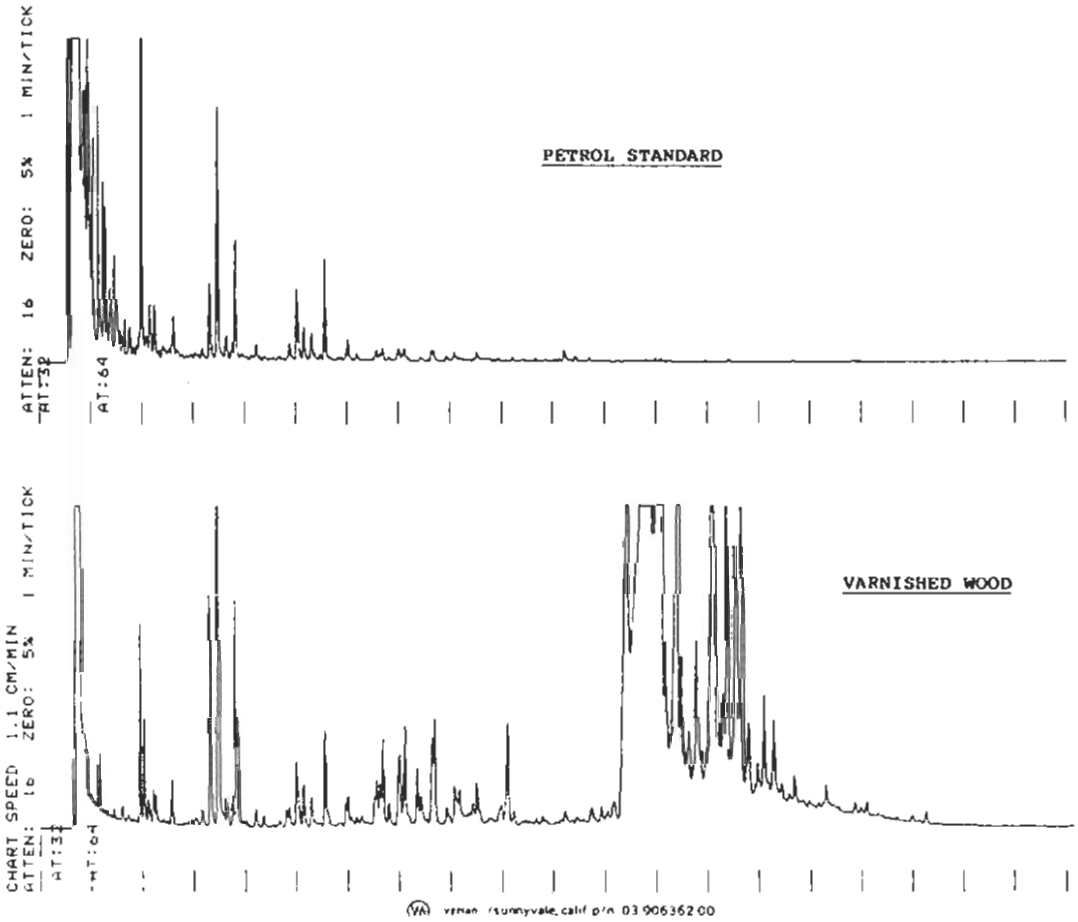

Figure 3.22 – Varnished Wood and Petrol Chromatograms.

3.6.4 (iii) Motor Oil.

Motor oil is a heavy petroleum fraction and traces of the lighter hydrocarbons are also present. These were recovered during extraction and are shown in Figure 3.23 below a chromatogram from that of a kerosene standard. A prominent "sulphorous"

odour was detected from the sample can when the lid was removed after extraction. The amount of motor oil extracted was approximately 100 grams which would be readily noticed in a fire sample.

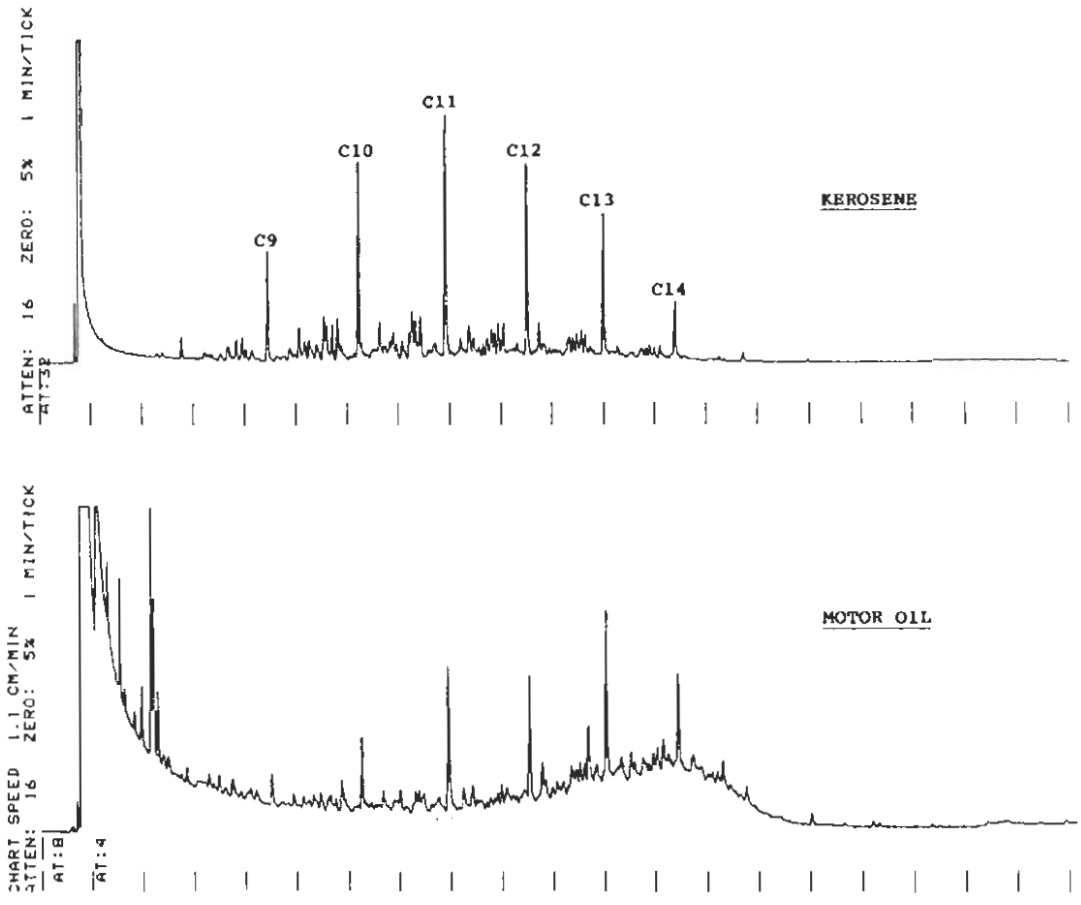

Figure 3.23 – Motor Oil vrs Kerosene Chromatograms.

3.6.4 (iv) Vegetable Oils

In the final stages of the processing of vegetable oils the oil is heated and sparged to remove odorous volatiles. The analysis of a headspace extraction of some vegetable oil is shown in Figure 3.24 and reveals that no volatiles were extracted from the oil. Rancid vegetable oil was then extracted and its chromatogram is also shown and reveals the amount of volatiles recovered increased but these peaks could not be confused with those from any of the common accelerants. Oils and fats are normally found at food outlet fires but their chromatographic analysis would be expected to resemble that of rancid oil and therefore could not be confused as being that of an accelerant.

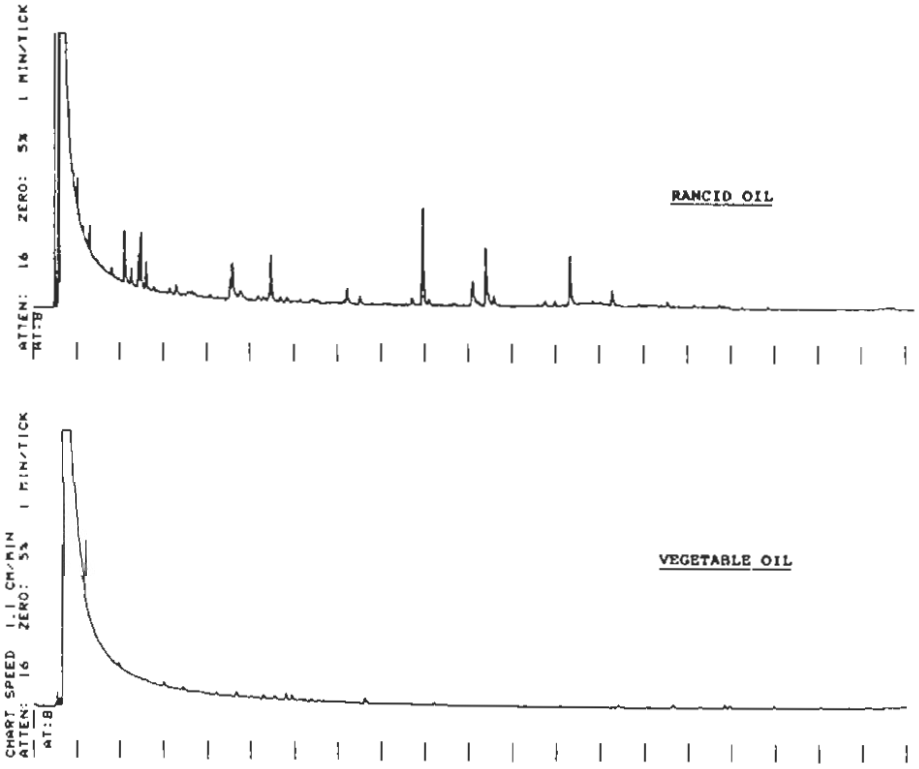

Figure 3.24 – Vegetable Oil and Rancid Oil Chromatograms.

3.6.4 (v) Aerosol Sprays – Mortein + WD– 40.

Samples of the insecticide spray "Mortein Surface Spray" and an engineering spray "WD– 40" were extracted and the analysis obtained is shown in Figure 3.25 with that from an industrial solvent "white spirits". This solvent is used in the formulation of many aerosol sprays and has an odour similar to kerosene being a similar petroleum fraction. It has been used in the formulation of WD– 40 but a heavier aliphatic hydrocarbon fraction has been used for the Mortein Surface Spray to give a slower evaporation rate which is necessary for it to function efficiently. White spirits is used in other insecticide formulations that are not surface sprays but aerial sprays.

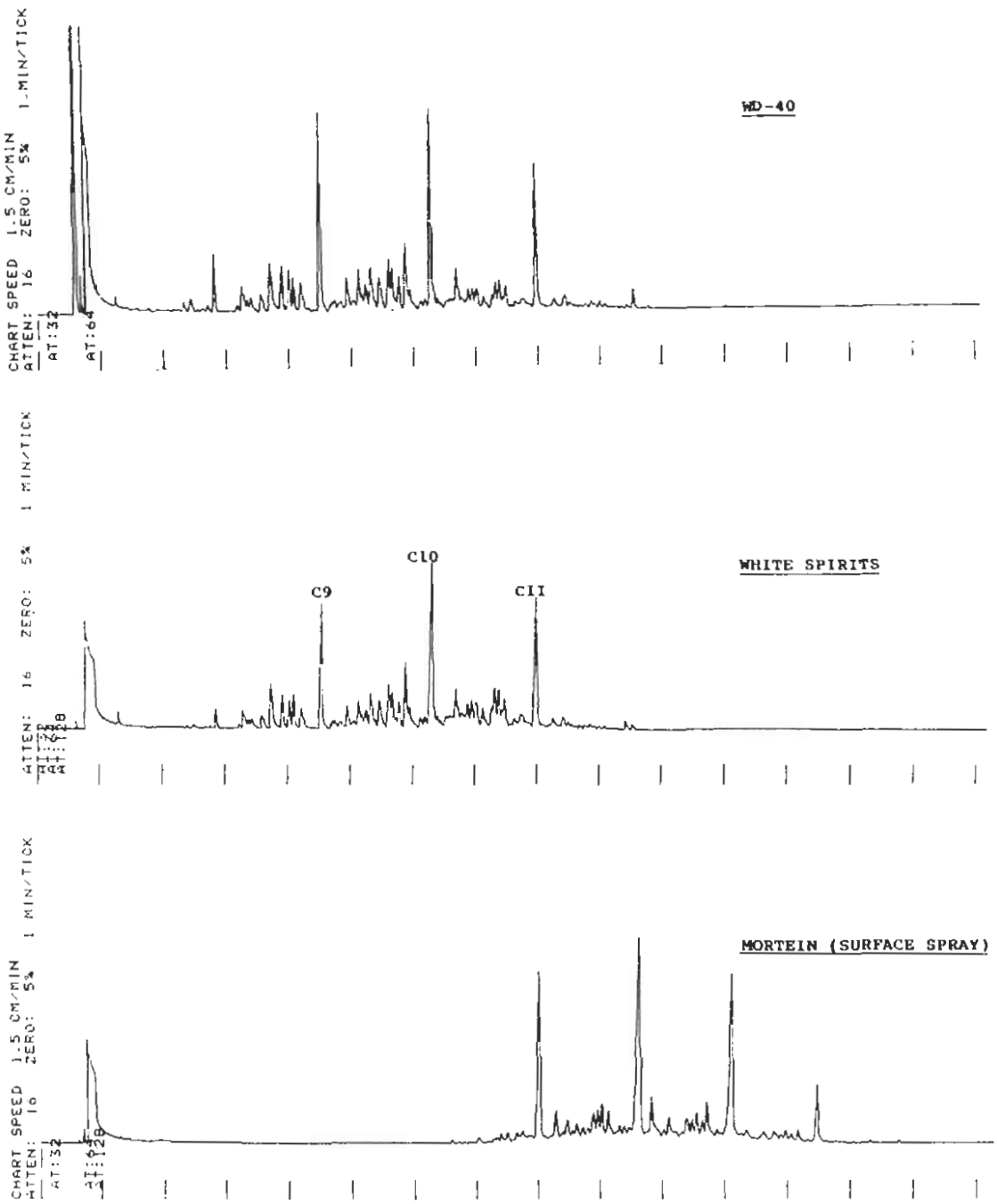

Figure 3.25 – Mortein, WD– 40 vrs White Spirits Chromatograms.

3.6.5 ANALYSIS OF BURNT SYNTHETIC MATERIALS.

Plastics are produced from the polymerisation of monomers into longer chain polymers. The burning of these plastics results in the cleavage of the molecules to yield volatile pyrolysis products that are readily extracted from fire debris containing plastics. The monomers used in the manufacture of plastics are commonly derived from petroleum products and their pyrolysis products are often aliphatic and aromatic hydrocarbons which are found in the common accelerants.

Samples of various plastics were obtained and burnt with a bunsen burner and then extracted and the chromatograms obtained. The samples were also analysed using an I.T.D. detector and specific ion mass chromatograms obtained.

The following samples were burnt and analysed.

- Nylon
- Polyvinylchloride (P.V.C.)
- Polyethylene
- Polypropylene
- Polystyrene
- Rubber carpet backing
- Rubber floor tile

3.6.5 (i) Nylon.

The chromatograph obtained from the extraction of burnt nylon is shown in Figure 3.26. The chromatogram was compared to those of the common accelerants but no possibility of peak matching was found therefore it could not be confused with any of the common accelerants.

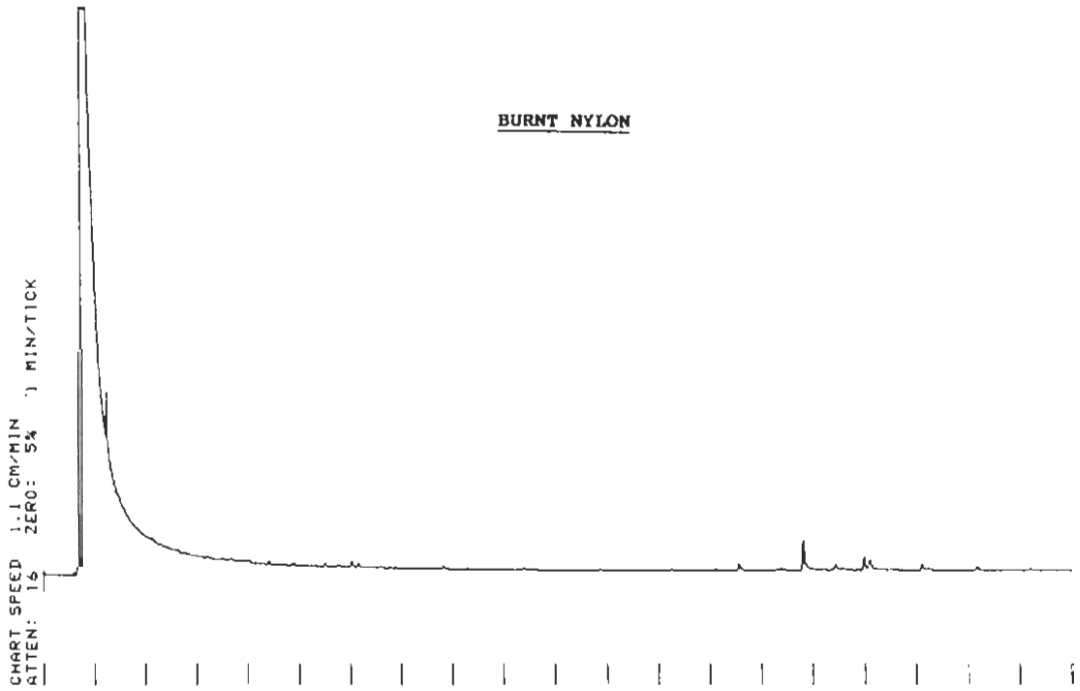

Figure 3.26 – Burnt Nylon Chromatogram.

3.6.5 (ii) Polyvinylchloride (P.V.C.).

The chromatogram obtained from burnt P.V.C. is shown in Figure 3.27 and below in Figure 3.28 is the specific ion scans of masses 57 and 71 (indicating aliphatic hydrocarbons). P.V.C. could not

be confused with any of the common accelerants and is rarely sampled because of its low flammability.

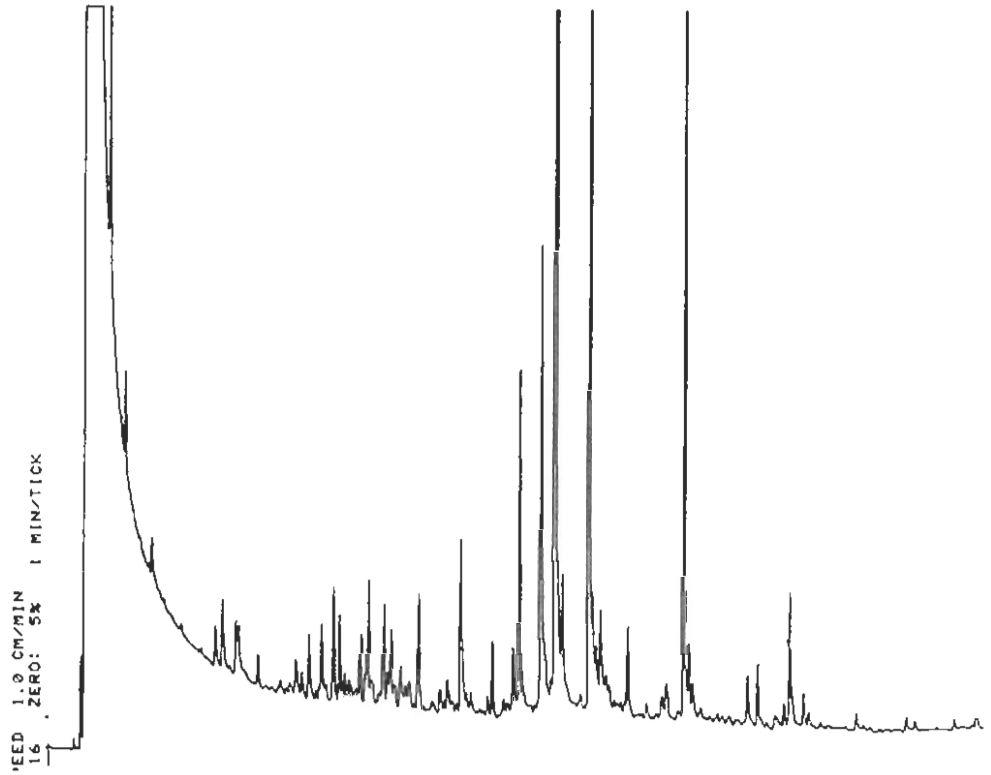

Figure 3.27 – Burnt P.V.C. Chromatogram.

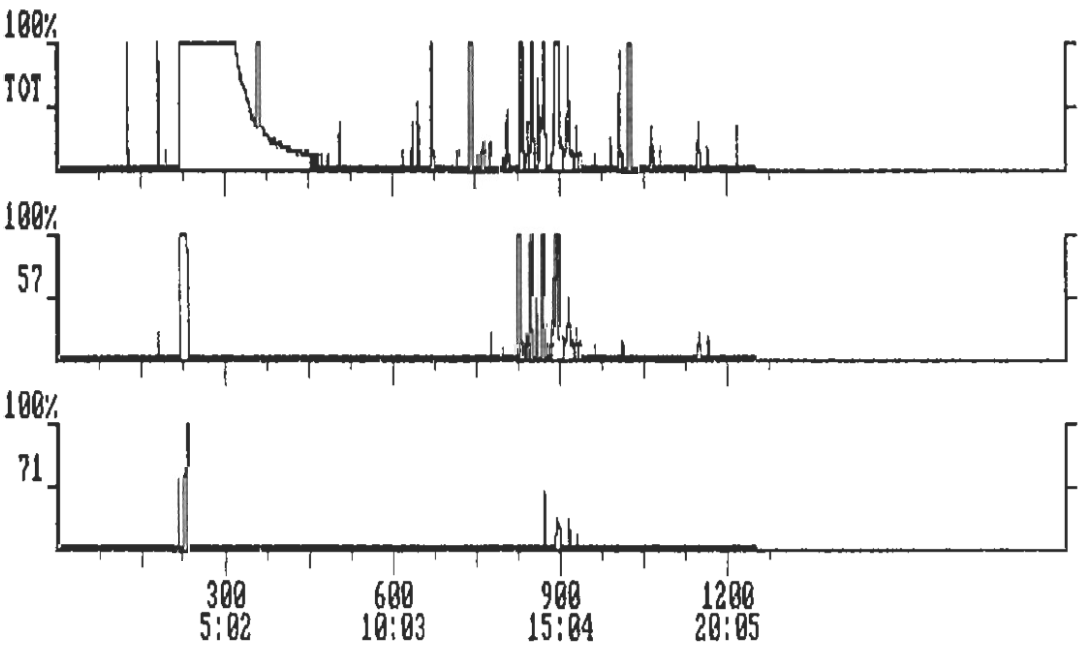

Figure 3.28 – Ion Scan of Burnt P.V.C. Chromatogram.

3.6.5 (iii) Polyethylene.

The chromatogram obtained from burnt polyethylene is shown in Figure 3.29 below that obtained from a kerosene standard. The specific ion scans of 57 and 71 (indicating aliphatic hydrocarbons) are shown below in Figure 3.30 and indicate the majority of the pyrolysis products obtained were aliphatic hydrocarbons. The majority of the hydrocarbons were branched chain because they do not have the same retention time as the prominent straight chain aliphatics found in kerosene. No aromatic compounds were found.

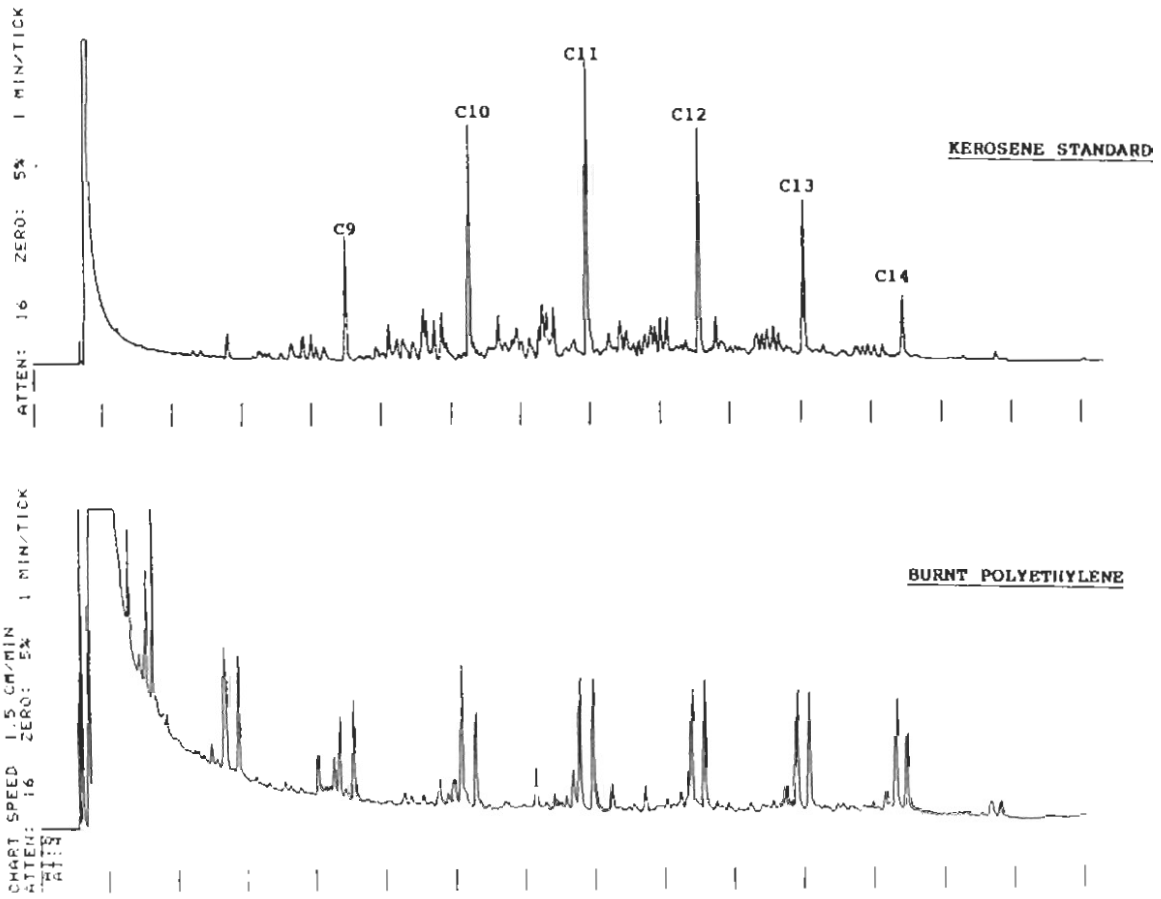

Figure 3.29 – Burnt Polyethylene vrs Kerosene Chromatograms.

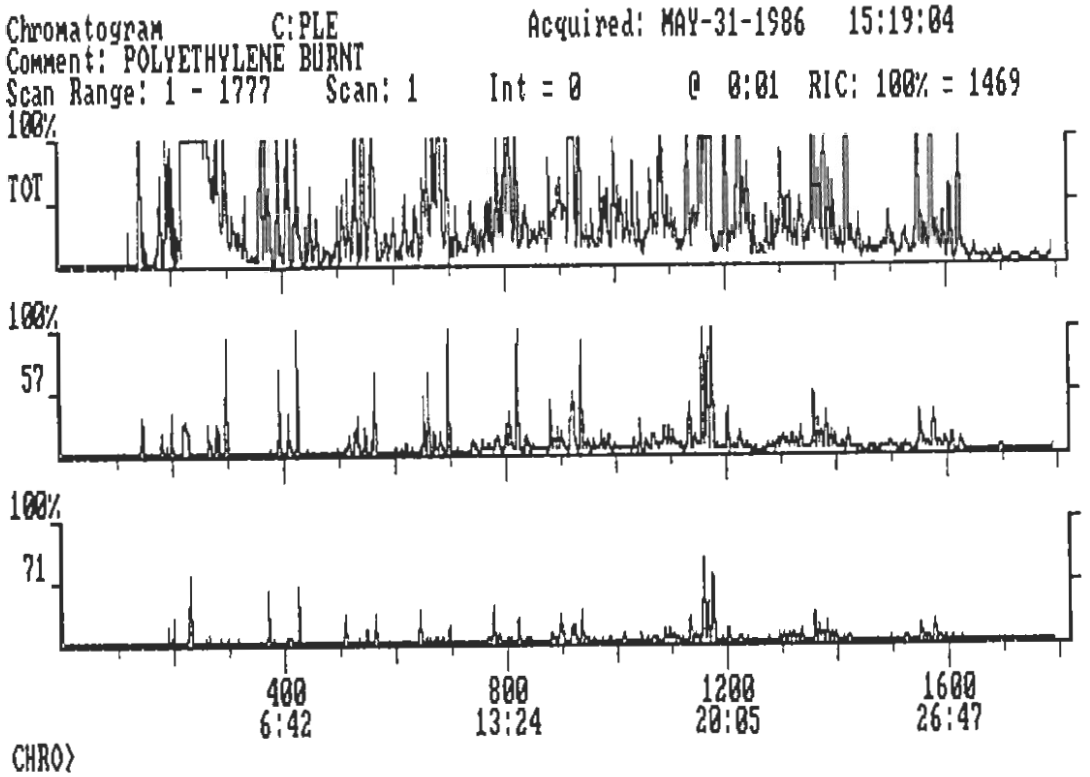

Figure 3.30 — Ion Scan of Burnt Polyethylene Chromatogram.

3.6.5 (iv) Polypropylene.

The chromatogram obtained from burnt polypropylene is shown in Figure 3.31 and specific ion monitoring revealed the majority of the compounds obtained were aliphatic hydrocarbons. No aromatics were detected in the sample.

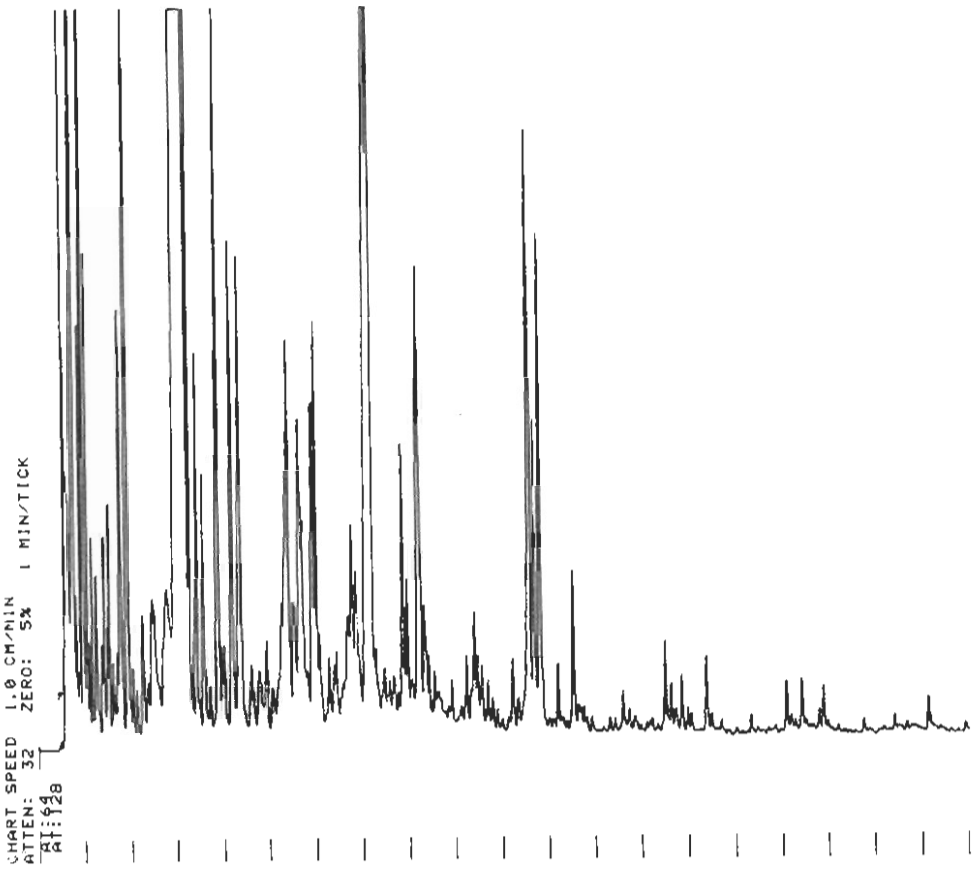

Figure 3.31 -- Burnt Polypropylene Chromatogram.

3.6.5 (v) Polystyrene.

Polystyrene is an aromatic polymer being produced from styrene monomer. The high degree of unsaturation in the molecule produces a thick black smoke when the polymer is burnt. The chromatogram obtained from burnt polystyrene is shown in Figure 3.32 below a petrol standard. The major products were found to be aromatics as shown in Figure 3.33 by the ion– scans 91 and 105 and were identified as toluene, xylenes, styrene and some trimethyl benzenes but the ratios of the components in each group was not consistent with those in petrol. No aliphatic hydrocarbons were detected using ion scans of 57 and 71.

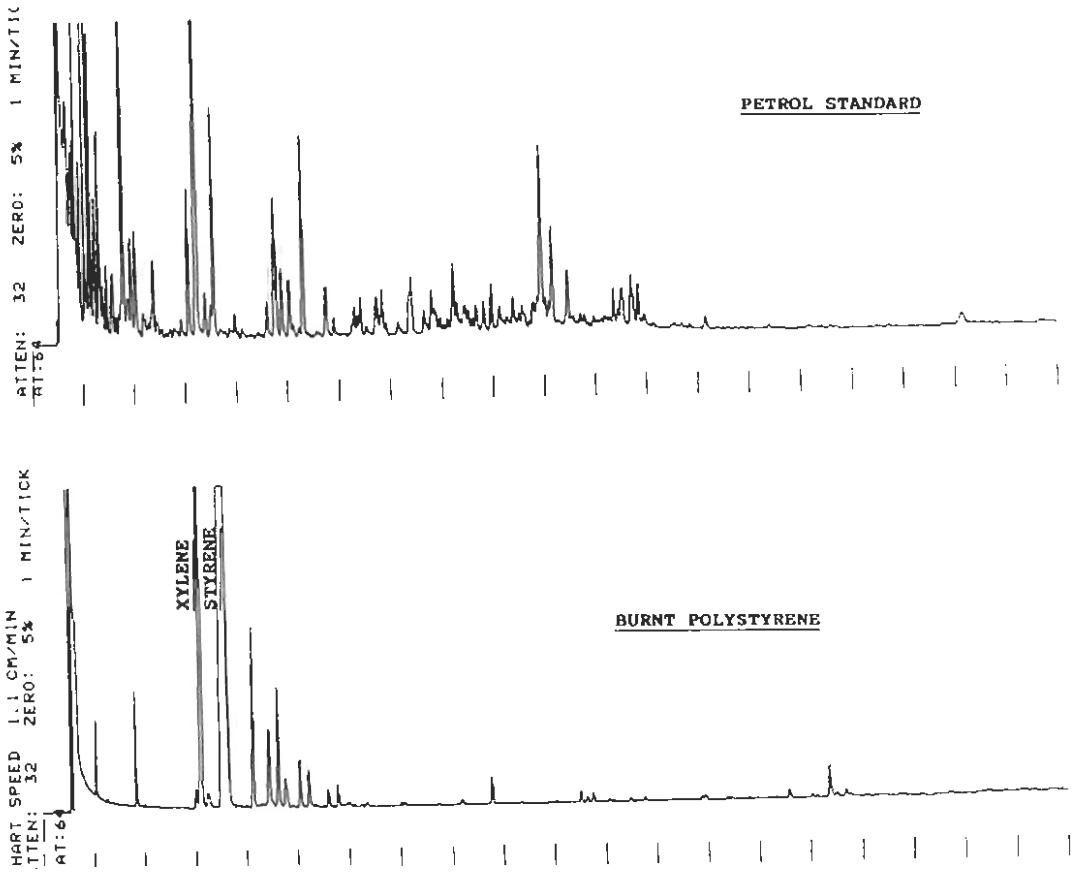

Figure 3.32 – Burnt Polystyrene vrs Petrol Chromatogram.

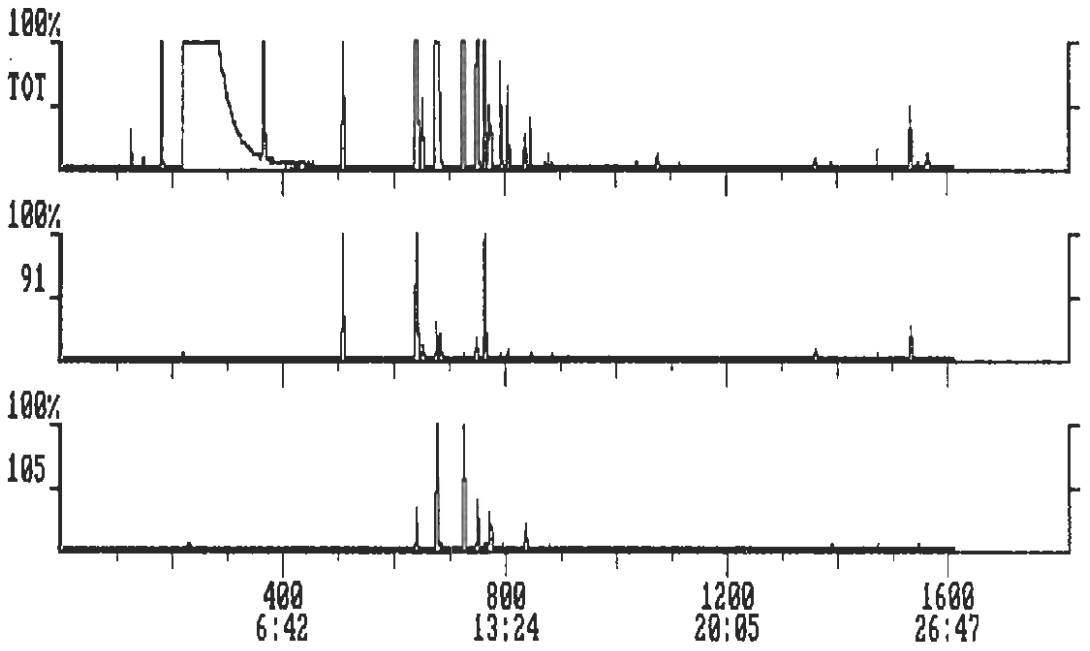

Figure 3.33 – Ion Scan of Burnt Polystyrene Chromatogram.

3.6.5 (vi) Rubber Backed Carpet.

The burning of rubber is usually accompanied by black smoke and the residue contains significant quantities of pyrolysis products as evident by the odour and Sniffer response at a fire scene. The chromatogram obtained from burnt rubber backed carpet is shown in Figure 3.34 below that of a petrol standard. Shown in Figure 3.35 are the specific ion scans of 91 and 105 that confirm the presence of the aromatic compounds and reveals toluene and the xylenes present. The xylenes are not in the same ratios as those found in petrol and the trimethyl benzenes were found to be absent. The ion scans of 57 and 71 are also shown and reveal the latter peaks to be aliphatic hydrocarbons. Other samples of rubber backed carpet were burnt to a greater degree and then extracted and the amount of pyrolysis products increased but were still in approximately the same ratios and could not be confused with petrol.

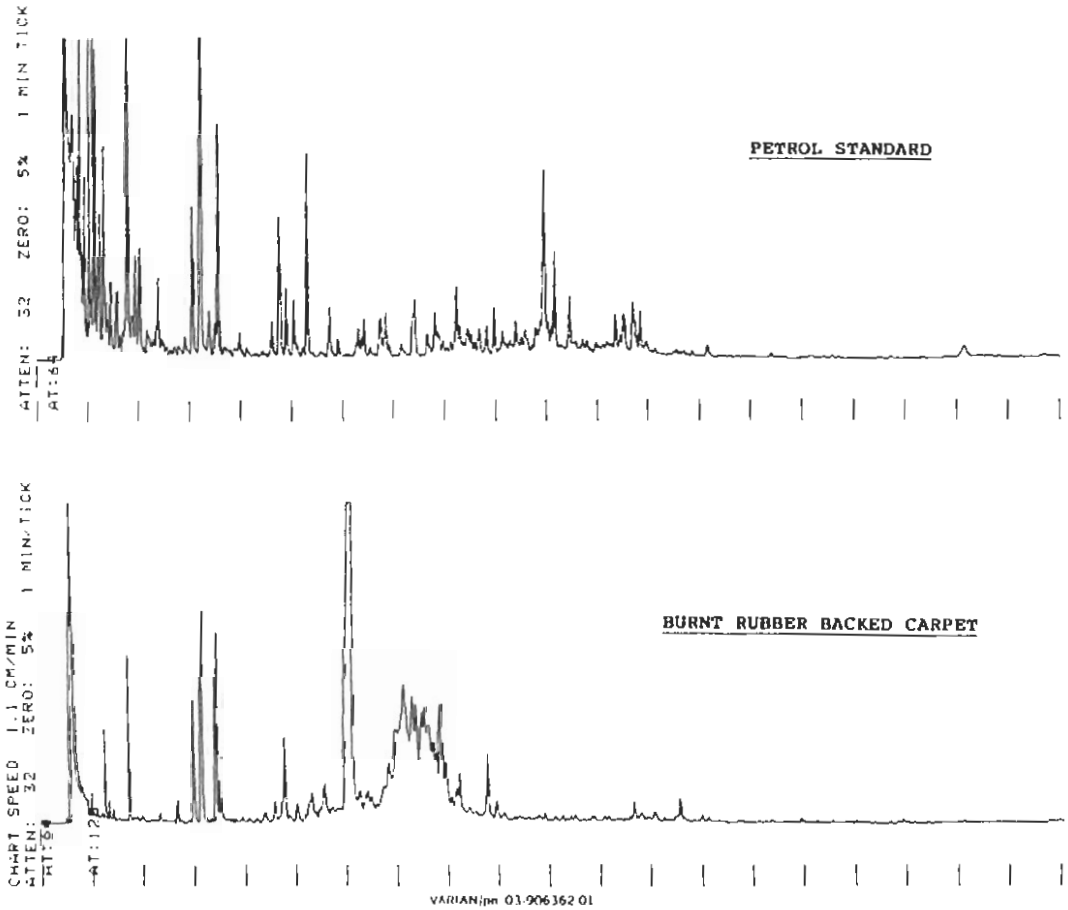

Figure 3.34 – Burnt Rubber Backed Carpet vrs Petrol Chromatograms.

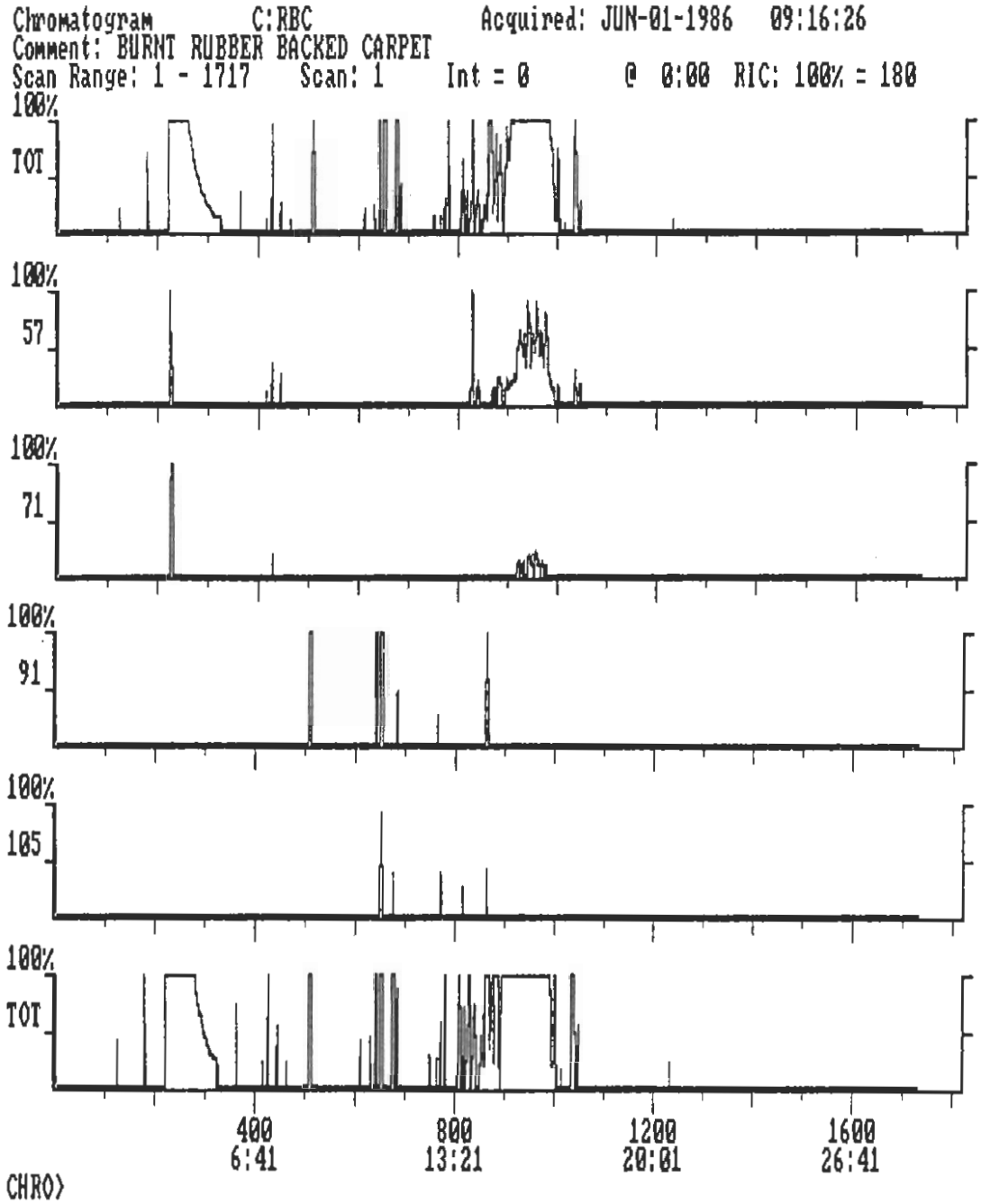

Figure 3.35 — Ion Scans of Burnt Rubber Backed Carpet Chromatograms.

3.6.5 (vii) Rubber Floor Tile.

The chromatogram obtained from a burnt floor tile is shown below in Figure 3.36 and can be seen to be quite complex. The specific ion chromatograms of 57 and 71 (aliphatic hydrocarbons) and 91 and 105 (aromatic hydrocarbons) are shown in Figure 3.37 and show that a complex mixture of hydrocarbons similar to rubber backed carpet are present, but again it could not be confused with any of the common accelerants.

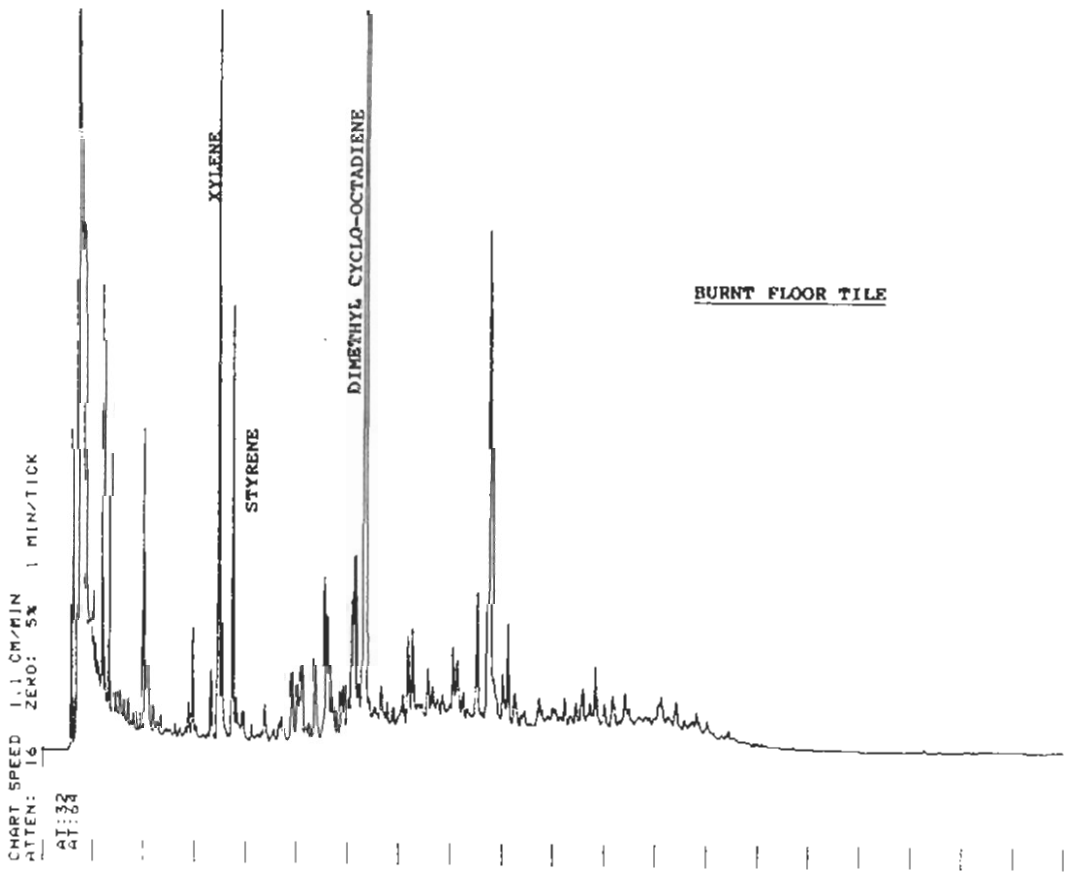

Figure 3.36 – Burnt Rubber Floor Tile Chromatograms.

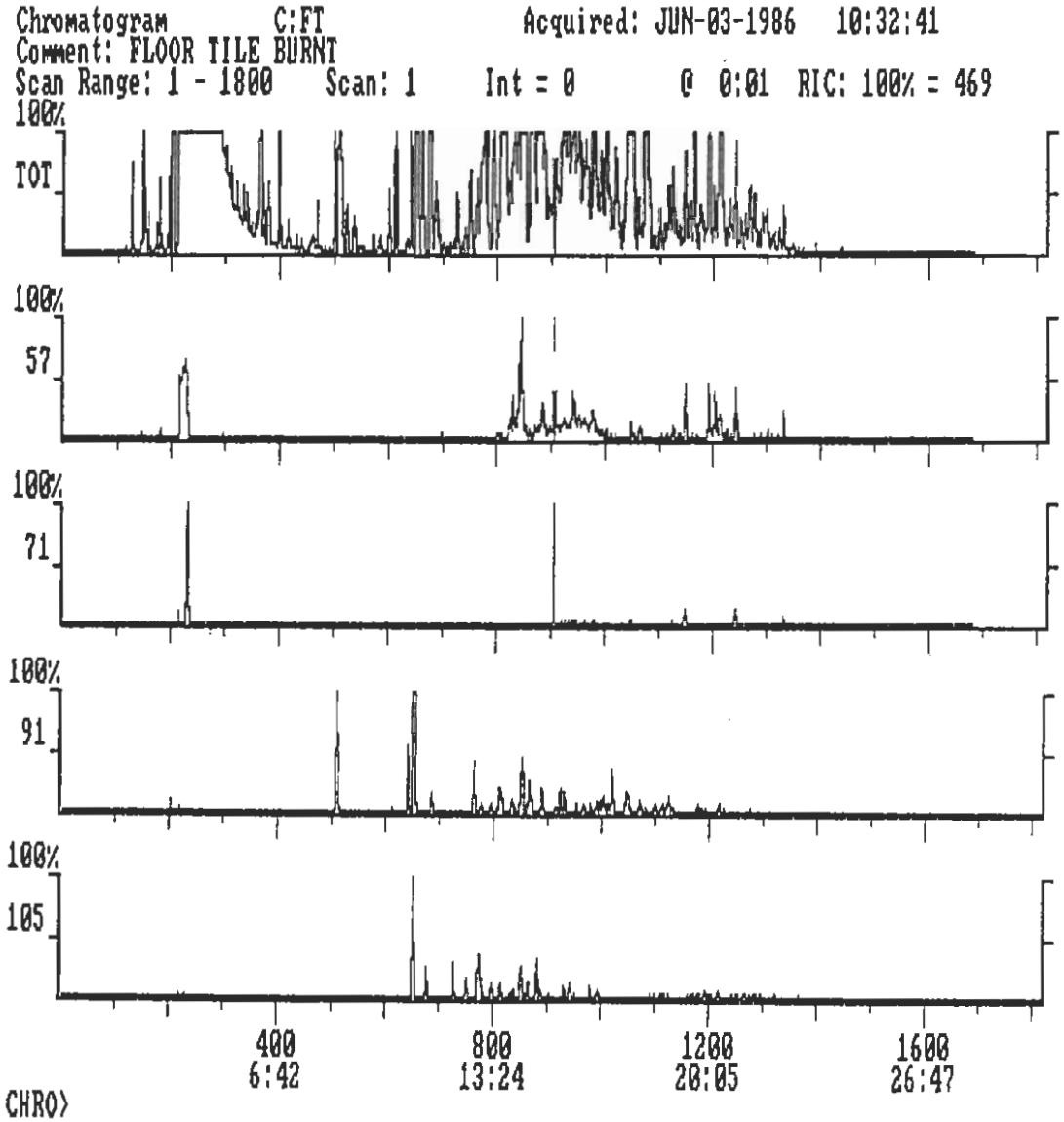

Figure 3.37 — Ion Scan of Burnt Rubber Floor Tile Chromatogram.

The analysis of the various burnt synthetic materials showed a variety of peaks present in their chromatograms of which some were found to be components of the common accelerants, but were

not in the same ratios, and hence, could not be confused with the common accelerant.

The synthetic materials tested were chosen because they are commonly found at fire scenes but new synthetic materials should be burnt and analysed to update the analyst' library.

CHAPTER 4. CONCLUSIONS

Dynamic headspace sampling with Capillary G.L.C. analysis will successfully analyse fire debris for accelerants and is capable of detecting a microlitre of accelerant.

The use of these extremely sensitive laboratory techniques must be made carefully because of the consequence of obtaining a false positive result. The possibility of the accidental contamination of a sample through poor sampling and laboratory techniques needs to be minimised. The research has shown the sample containers can be cleaned before use and should be sealed before transport to the fire scene. Samples should then be delivered to the laboratory and analysed promptly. The laboratory equipment should be cleaned before use and blank samples analysed regularly to check for any possible contamination. The extraction equipment can be cleaned by washing with acetone and heating the gas transfer lines with a bunsen burner.

The interpretation of the chromatograms must be made carefully using a library of chromatograms composed of the common accelerants, industrial solvents, common household materials and burnt synthetic materials. The analysis of numerous burnt synthetic materials was found to be distinct from the common accelerants. The common accelerants were found

to change during evaporation making it sometimes difficult to distinguish between those composed entirely of an aliphatic hydrocarbon fraction. Ethanol could not be detected in fire debris using charcoal absorption extraction techniques and alternative analytical techniques were needed.

The background level of accelerants in the environment is dependent of the history of the sample material. Traces of petrol and aliphatic hydrocarbons were found in soil from a motor wrecking yard, however, no traces were found in numerous car flooring materials indicating none would be expected from a domestic environment.

Gas odourants could also be detected using the same equipment as that used for fire debris analysis which would assist the investigation of suspected gas explosions.

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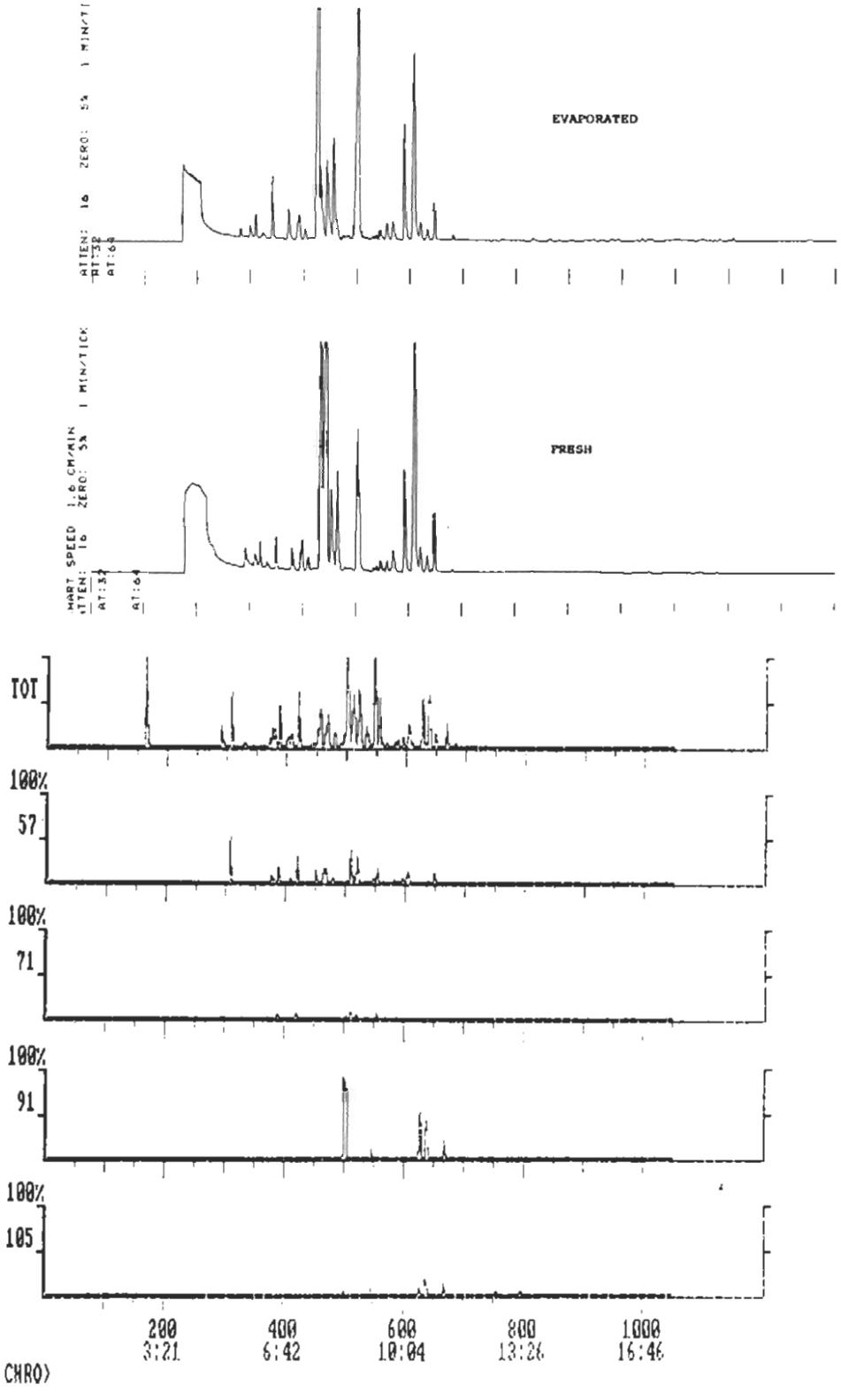
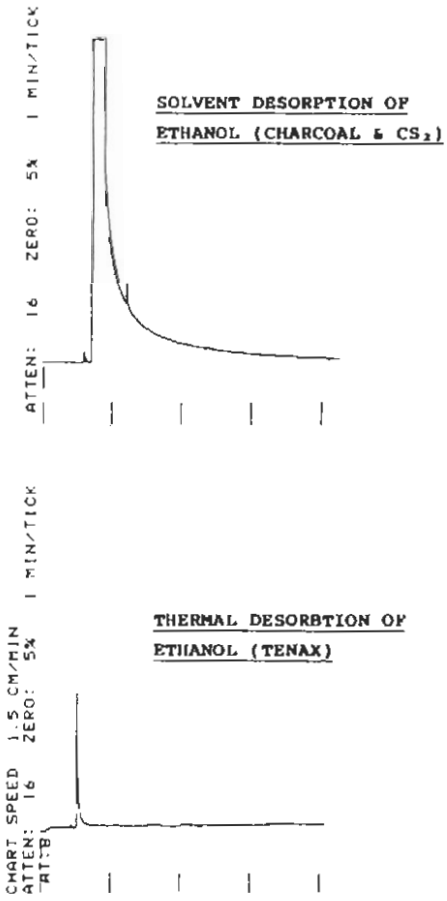
APPENDIX 1

CHROMATOGRAM OF THE INDUSTRIAL SOLVENTS



Analysis of Lacquer Thinners



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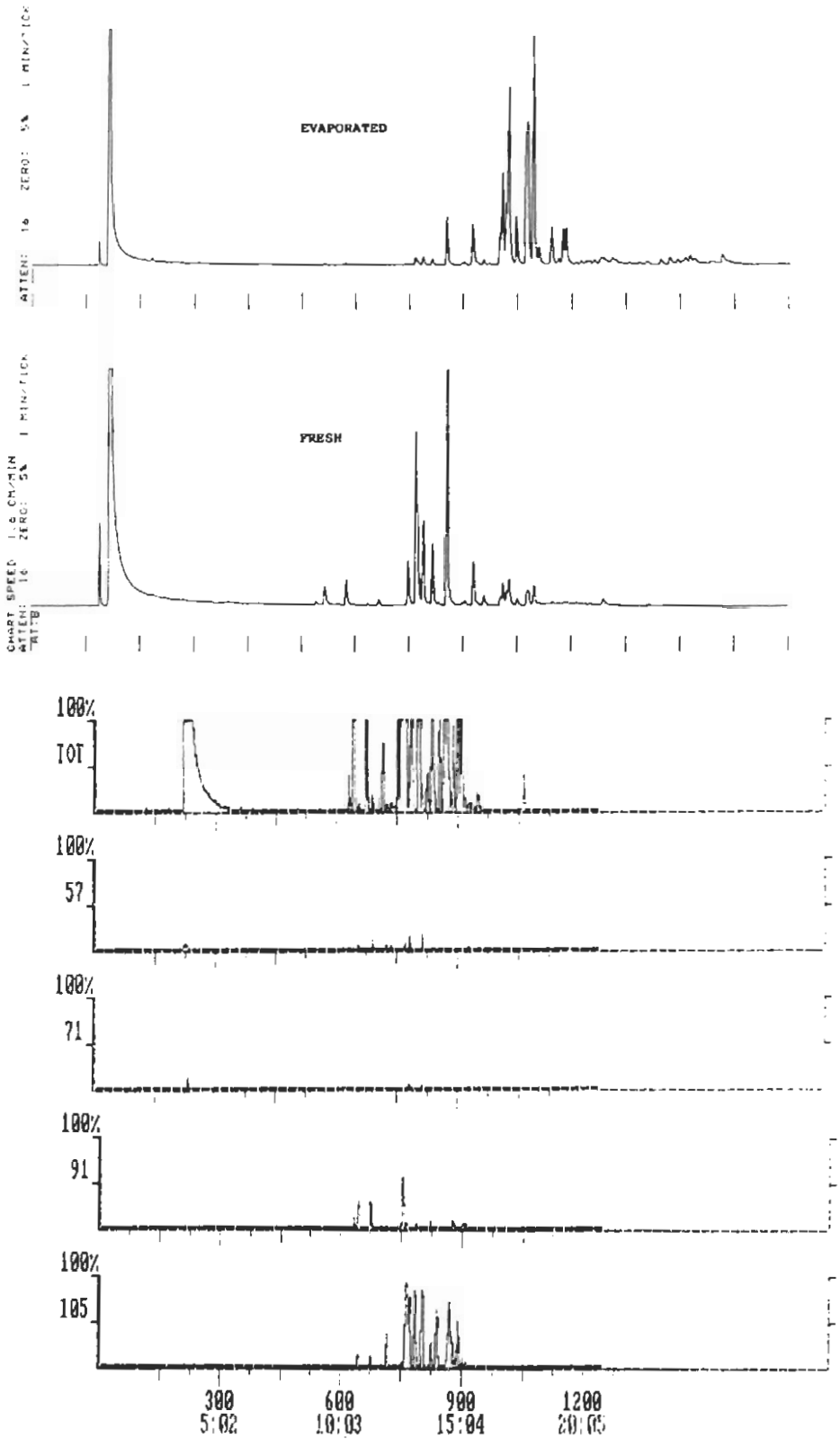

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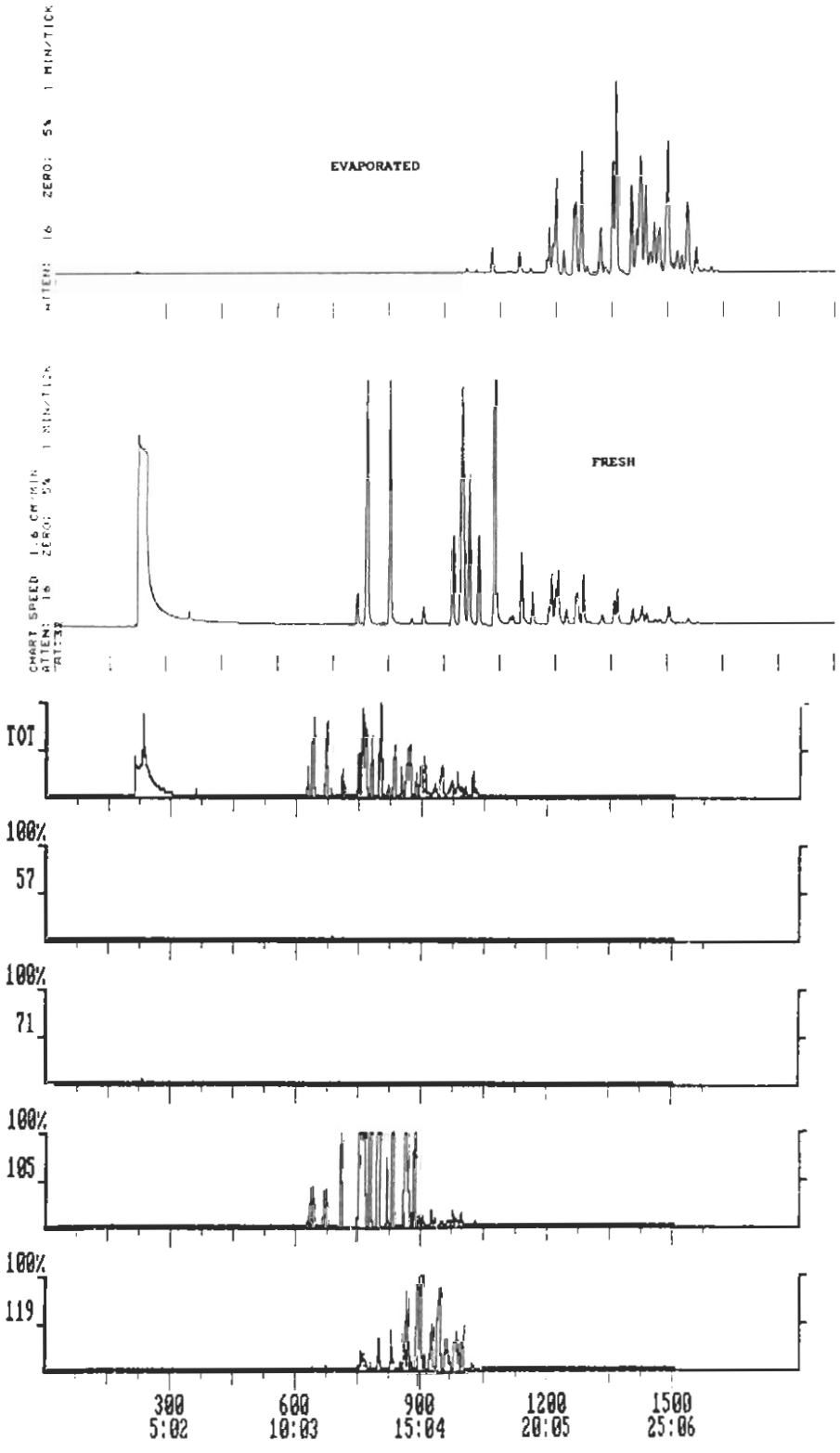

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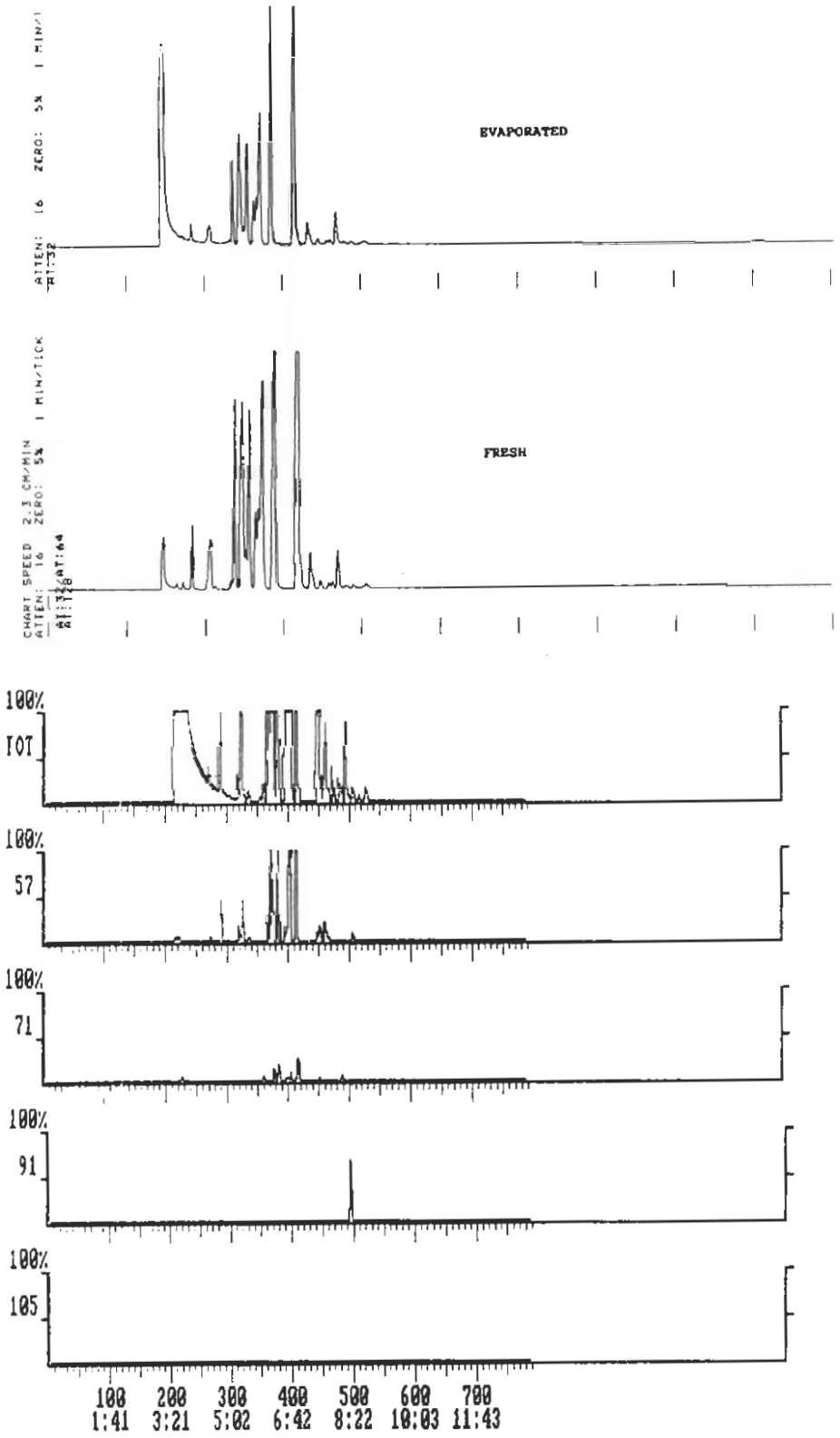

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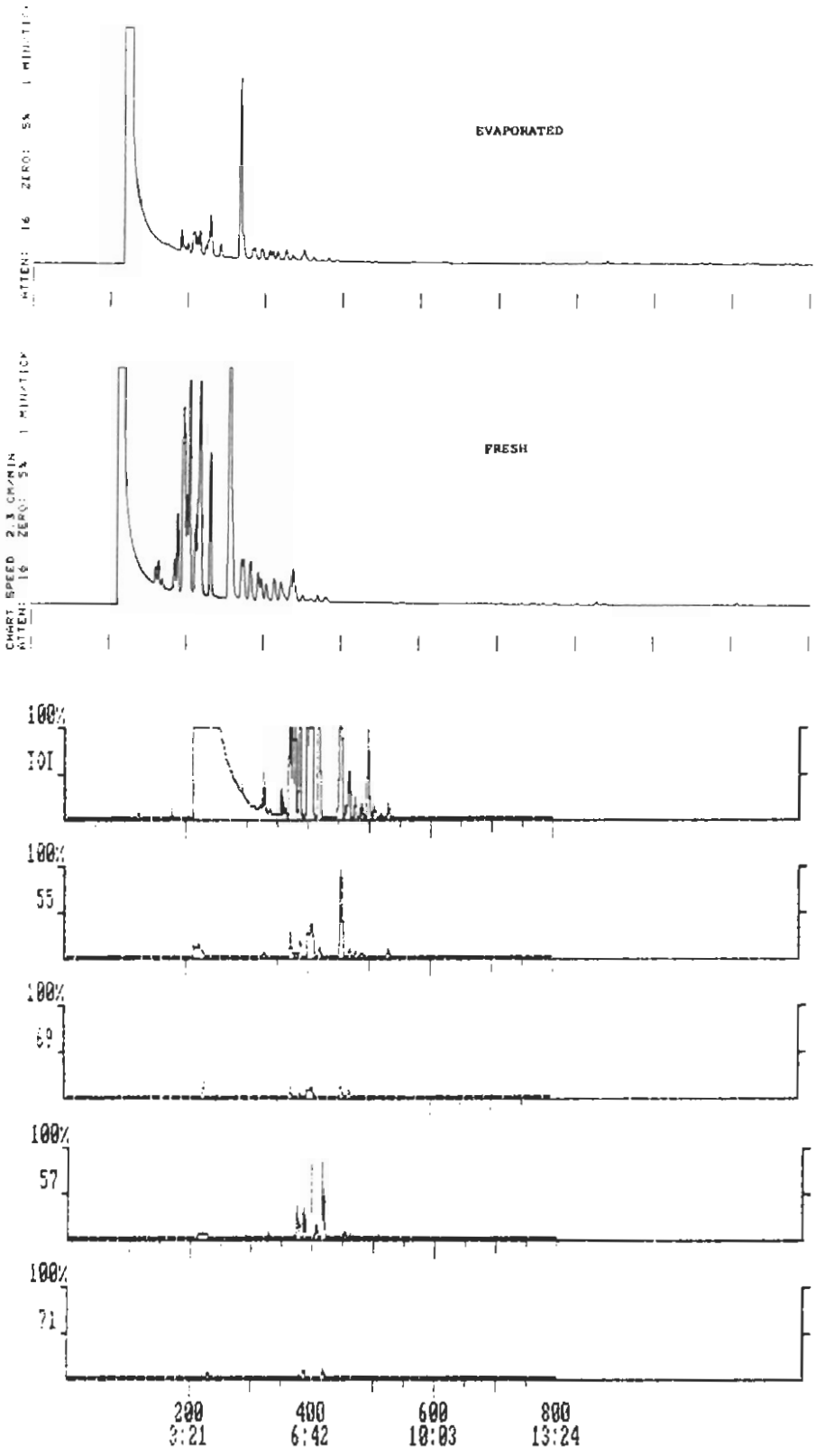

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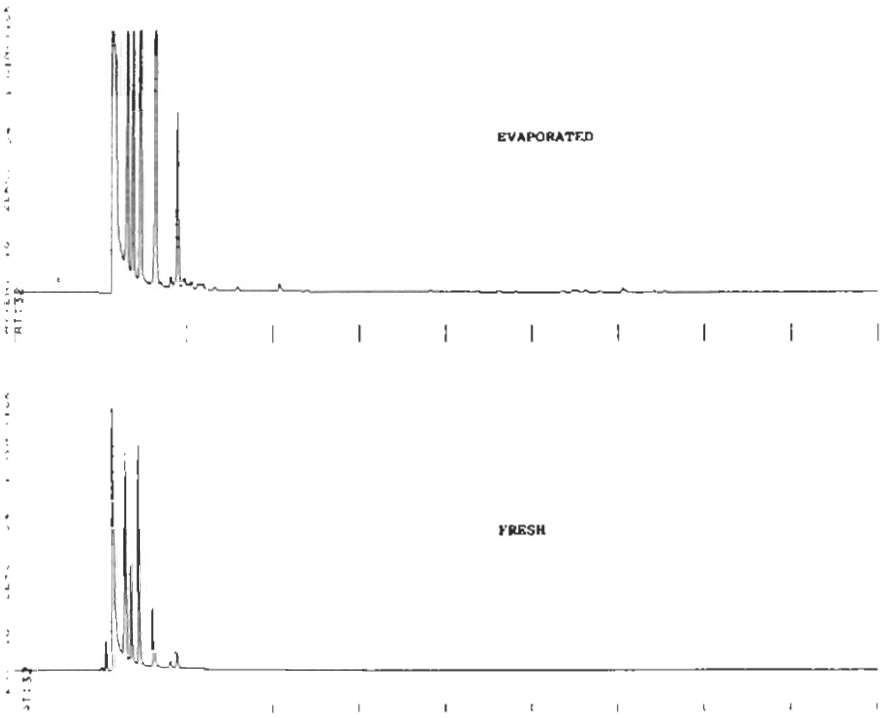

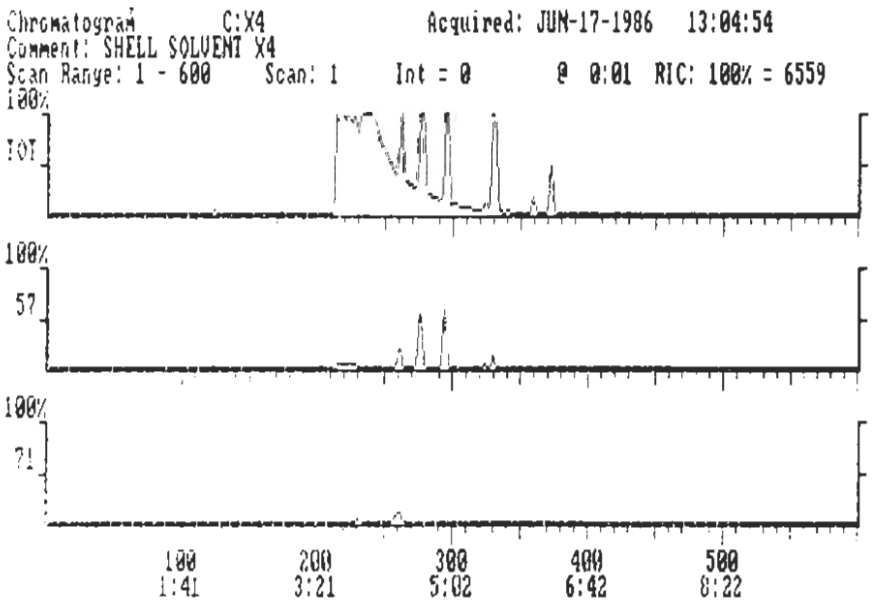

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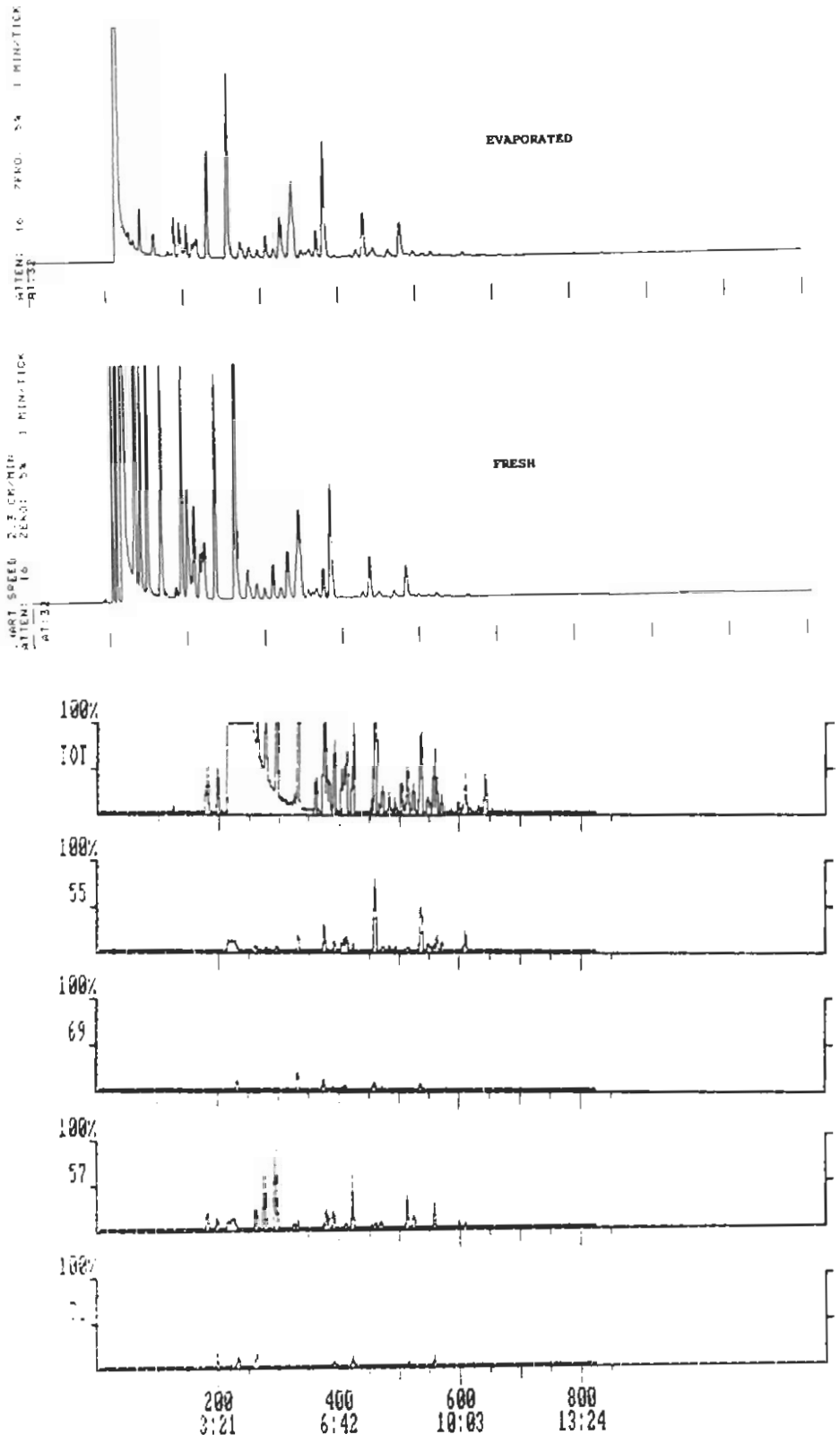

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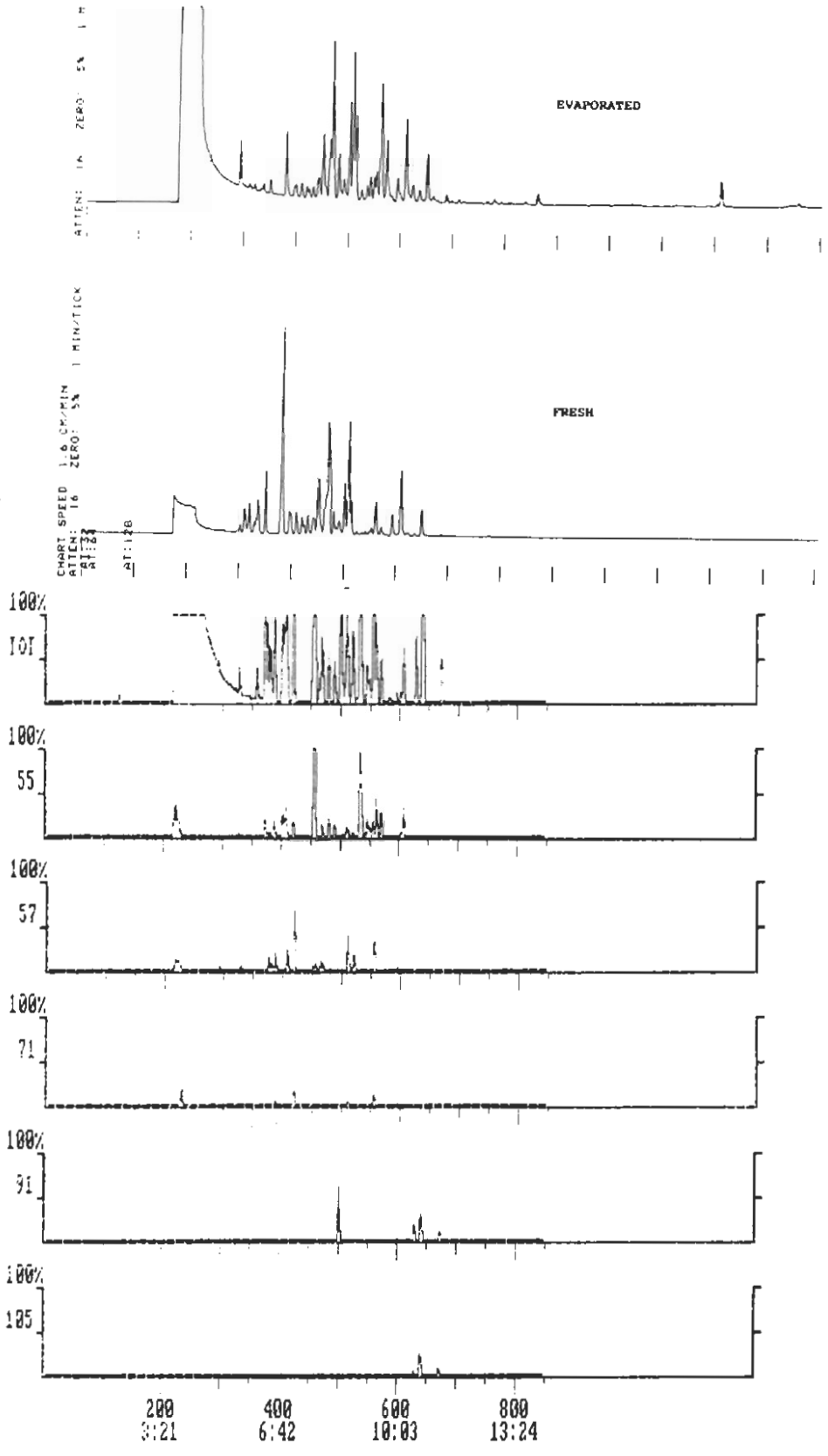

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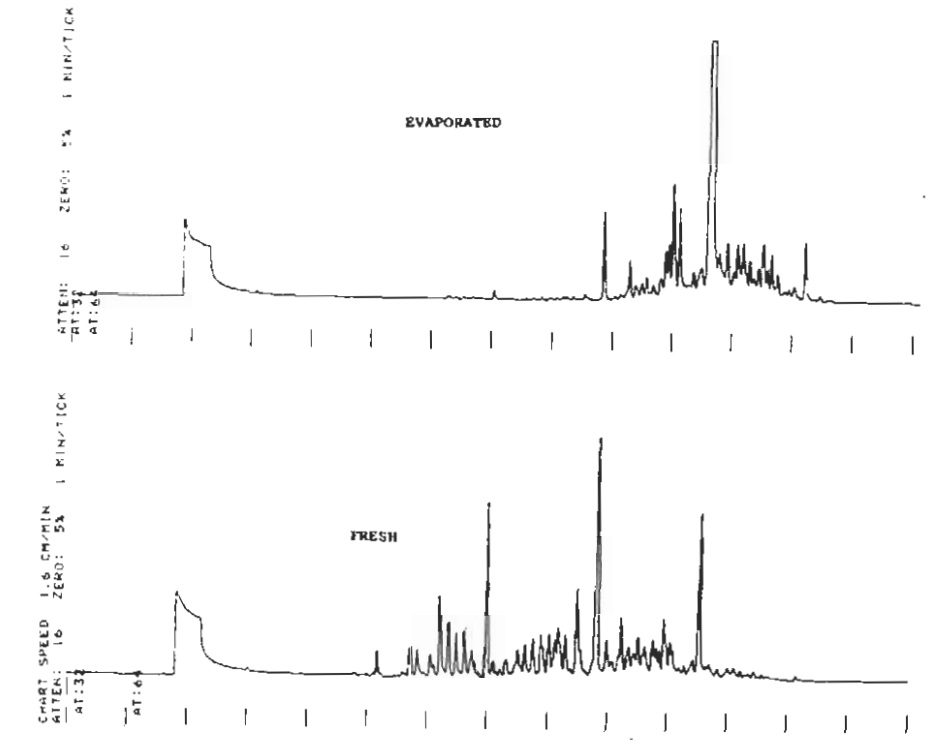

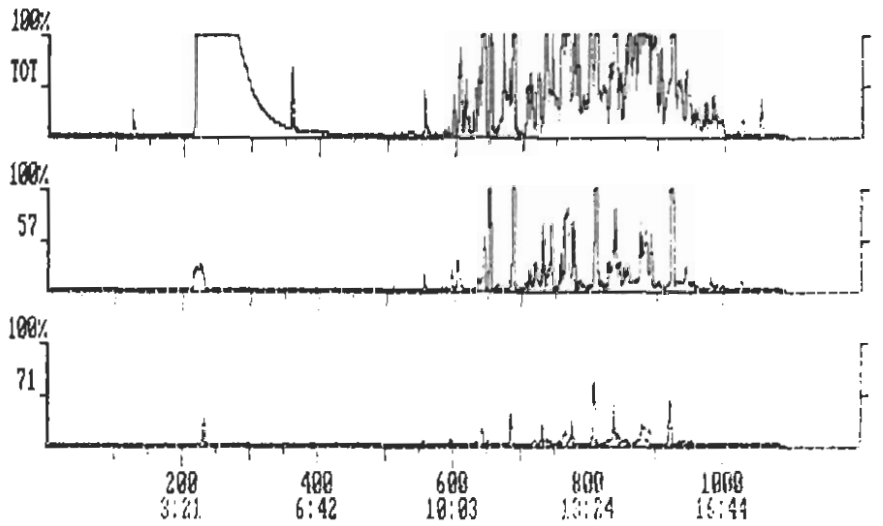

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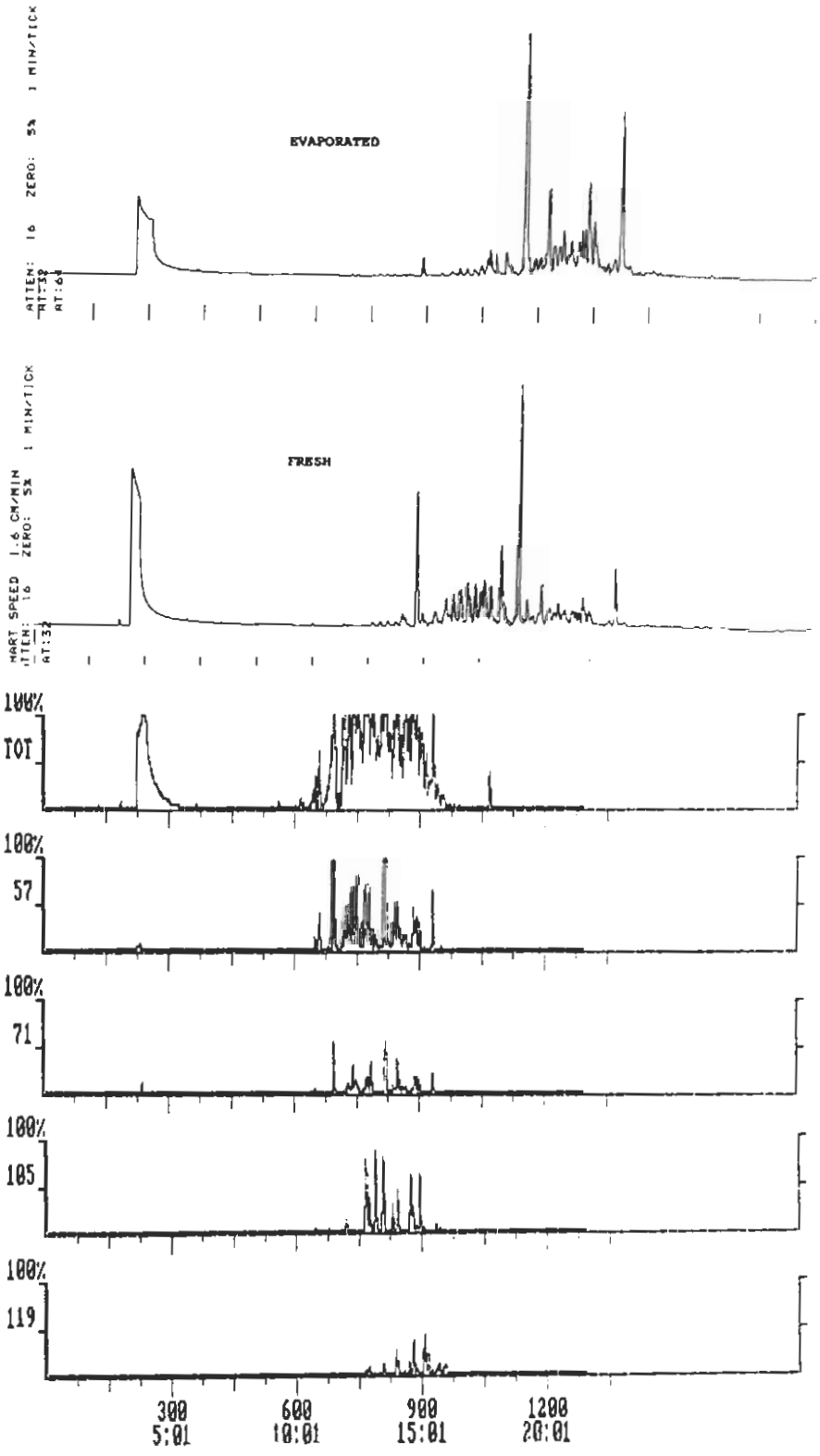

Analysis of Shell clean SS1626