# Analysis of Accelerants by Gas Chromatography-Mass Spectrometry and Cyclic Voltammetry for Biosensor Development

by

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# CERTIFICATE

I certify that the work in this thesis has not been previously submitted for a degree nor has it been submitted as part of requirements for a degree except as fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature are included in the thesis.

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# ABSTRACT

This project encompasses a detailed literature review of a variety of topics, covering fire scene examination, accelerants and present accelerant detection techniques, biosensors, the human olfactory system and electrochemical analytical techniques such as cyclic voltammetry. An overview of all these areas allows a theory to be brought together, that a biosensor could be created for the presumptive detection of accelerants at fire scenes, a sensor with a high degree of discrimination power achieved through the selectivity of specific biological agents and computerised pattern recognition fabricated into an array. As a result of the large area covered by the literature review, this project's experimental component explored the use of cyclic voltammetry as a tool to investigate the electroactive behaviour of accelerants and their extracts. Optimisation of conditions including pH, electrode type, and extraction time were also completed. The results of the research showed that no electroactive species were present in the accelerants within the detection limit of the method used. This result is important given that the future direction of this project includes the layering of an olfactory receptor onto an electrode to create a biosensor. This can be accomplished with the assurance that there will be no interference from electrode/accelerant interactions. Accelerant standards were also analysed using Gas Chromatography – Mass Spectrometry and confirmed using current fire debris sample analysis standards.

# CHAPTER 1: INTRODUCTION

Foresight....

"Did you ever try to measure a smell? Can you tell whether one smell is just twice as strong as another? Can you measure the difference between one kind of smell and another? It is obvious that we have very many kinds of smells, all the way from odour of violets and roses up to asafoetida. But until you can measure their likeness and differences you can have no science of odour. If you are ambitious to found a new science, measure smell."

(Alexander Graeme Bell, 1914) [1]

## 1.1 Fire and its Investigation

Fire is a continual public safety issue, with this destructive event having a direct impact on life and property. The calculation of the cost of a fire contains three elements: the inestimable costs of loss of human life and injury, the dollar amount of property lost, and thirdly hidden costs such as loss of business income, unemployment and reduced property values. All up, dollar amounts on loss of property alone can be estimated to cover only 10% of the total cost of a fire [2]. Fire scenes are investigated to determine origin and cause of the fire.

Incendiary fires, that is, those that are deliberately lit, represent a significant proportion of all fires [2]. This adds to the responsibility of the investigator, not only in the identification of origin and cause of the fire, but also to the identification of the person who lit the fire and the provision of evidence to courts. Evidence is often circumstantial. [3]. A significant number of fires are deliberately set with the intention of destroying property. The investigation of incendiary fires may minimise subsequent events by recognition, identification of person(s) responsible and their prosecution [2].

One problem in the investigation of fire scenes is the destruction of the scene itself, which can make the determination of origin and cause difficult. This destruction affects both accidental and incendiary cases. There is contamination by personnel, vehicles, equipment, hoses and large quantities of water from fire fighting activities. Scene security is sometimes extremely difficult and complicated by the often, large areas involved. However fires also can create evidence, such as burn patterns, post-fire indicators, heat and smoke effects, char depth and wall and floor displacement [2].

Scene examination can often take days to complete, with the wholesale destruction of the scene causing the investigator to excavate large structures. There are also delays in the examination itself, often occurring days after the incident, due to the extended efforts to put out the fires, the buildings required to be declared safe for investigation and the time it takes for the scene to cool down enough to enter. These factors all combine to make fire scene investigation an immense challenge [2]. Added to this, sampling at the fire scene is, as a result, often problematic, as it must be cost effective. This means that sampling must be accomplished selectively over a large scene to minimise time at the scene and sample numbers taken. This process, of sampling is the result of experienced crime scene investigators (fire brigade, police or private contractors) who interpret and read the scene of the fire, to determine the best possible area to take a sample that will help to determine origin and cause. This process is not random, and gives structure to the examination process, as some fires are initiated or assisted by the combustion of ignitable liquids. These ignitable liquids (or accelerants) may be deliberately introduced or distributed or may be legitimately present, but nonetheless have the effect of accelerating the fire development. It is essential for the investigator to assess whether such materials may have been involved and to identify their nature, location and distribution in order to reach a correct conclusion as to the origin and cause of the fire. To do this it is necessary to identify probable locations where residues of such liquids may be found and to take appropriate samples for laboratory examination or carry out on-site analysis. Identifying suitable samples is usually carried out by a combination of techniques that include the interpretation of the burn patterns and detection of vapours and/or odours from the residential materials.

On site volatile organic analysis techniques include both the skill and experience of the Fire Investigator, the use on an accelerant detection canine, portable sniffers, Photoionisation Detectors (PID) and Flame Ionisation Detectors (FID), portable Gas Chromatography equipment, and finally chemical detector tubes such as the Draeger tubes. The advantages and disadvantages of each will be detailed further on in this chapter.

## 1.2 Accelerants

At fires that have been determined as "suspicious" in cause, it has been a major task to establish where samples for chemical analysis should be taken. Investigators with training and experience, and the use of canines trained to detect certain types of ignitable liquids, have traditionally been used to pinpoint areas within large scenes. The term "accelerant" in this research will be used as shorthand for the term ignitable liquid, not as a descriptor for all types of potential accelerant materials. This is as ignitable liquids is now the generally preferred term for this context, as other materials can act as accelerants under certain circumstances, including solid fuels such as paper, plastics and gaseous fuels.

Ignitable liquids commonly used to start fires include:

- Petrol,
- Kerosene,
- Diesel fuel,
- Paint thinner

Hydrocarbon fuels (such as petrol, kerosene and diesel) that are made from coal tar [4] and more recently from oil, contain approximately 74% paraffins, and 22% aromatics. Historically in 1933, catalytic hydrogenation of CO from coke led to a complex mixture of hydrocarbons, with approximately 120 specific compounds [5]. This includes $C_1 - C_{12}$ paraffins and olefins, alkyl aromatics, $C_1 - C_4$ alcohols, with approximately half of the compounds boiling in the petrol range [4, 5]. The higher boiling fractions are better suited for diesel engines [5]. Currently there is a shift towards synthetic fuels, where the sources are non-petroleum based, such as solvents, coal liquification coal/plant liquids, biomass waste and natural gas [5].

Petrol and other hydrocarbon fuels have the characteristic of rarely being found in their original chemical states. This is because petrol (for example) quickly evaporates at room temperature, between 40°C and 190°C, a process that is accelerated in the presence of heat from a fire [4]. As a result, it is common to find at a fire scene only proportions of the heavier components of the petrol mixture with the lighter components having evaporated off during the fire with the residues of partially burnt petroleum products having different chemical and physical properties than the original fuel [4]. Petrol, kerosene and diesel also share many similar components having been refined in similar ways from the common natural source of crude oil. Whilst petrol, kerosene and diesel can be individually identified, it is not possible to identify individual brands within the petrol class outside of a laboratory[6-8].

The technique for the analysis of a fire debris sample in this research is Gas Chromatography – Mass Spectrometry (GC-MS), with the resulting chromatogram showing absorbance versus time. See chapter 3 for examples of these.

## 1.3 Present Accelerant Detection Techniques

At the fire scene, the location of the samples collection is of vital importance, as without giving the process some thought, the sample collected is unlikely to contain any accelerant residue [9]. Currently, the detection of ignitable liquids is carried out either presumptively at the fire scene and/or in the laboratory, for confirmatory analysis. This area will therefore be broken into two sections, Presumptive Testing on Site and Confirmation Analysis in the Laboratory.

### 1.3.1 Presumptive Testing on Site

Ignitable liquids burn well because they are volatile and can vaporize easily, therefore accelerants exposed to high temperatures in fires will evaporate quickly. The probability of collecting accelerant residues decreases when time between ignition and sampling increases [9]. Accelerant residues may also be washed away with fire suppression/overhaul and as petroleum distillates float on water, can float away with the runoff from extinguishment efforts. However both research and experience indicates that if the ignitable liquid soaks into an absorbent material such as carpet, cloth or paper, because of their hydrophobic characteristics, they resist wash-off by water unless a wetting agent is also present. Acetone and light alcohols mix with the water and are also easily washed way [9]. Therefore sampling at the scene is of critical importance, with the area the sample is taken from, the quantity of the sample taken, and the type of material taken [9]. Both amount taken and composition of the sample is crucial in the identification of the accelerant type.

At the fire scene, the portability and reliability of ignitable liquid detection has limited the techniques to the use of such aids as physical indicators, the investigators own sense of smell, portable sniffers such as the Flame-Ionising Detector (FID) and Photo-Ionising Detector (PID), sniffer dogs, portable GC's (which have been determined as not very reliable), and chemical tests such as Draeger tubes and Hydrocarbon field test kits (which rely on a colour change) [10]. It must be noted that these are aids only and all results must be backed up by laboratory analysis of the sample.

Thus far none of these techniques has shown a reliability or robustness that gives the investigator a complete "presumptive" test for accelerants at fire scenes showing a high degree of accuracy so the investigator can identify both a possible accelerant type and location before leaving the scene. Details of how a few of the many presumptive tests work, and their individual advantages and disadvantages are detailed below.

#### *1.3.1.1 Physical indicators*

Use the fire investigators own skills to identify the area best to sample by asking questions such as where do burn patterns indicate an accelerant has burnt and where does the knowledge of fire behaviour indicate an accelerant has burned. The answers to these questions are seldom the same [9]. The disadvantage with this method is that in court, opinion needs to be backed up with laboratory results and experience.

#### *1.3.1.2 The investigators sense of smell*

"The most sensitive piece of equipment to the Fire Investigator is his nose" [9]. The human nose is well engineered and can identify many accelerants, able to distinguished fresh/weathered petrol with threshold sensitivity approaching that of scientific instrumentation[9]. However the disadvantage of this sense is that different individuals have differing olfactory capabilities, with olfactory detection having problems such as bacterial/viral infections, allergies and olfactory fatigue[9] (discussed in chapter 2 in more detail). There are also problems with desensitisation to strong odours over time, so eventually they aren't detectable, and odours masking others (such as burnt plastic masking petrol) by overwhelming the senses until the olfactory system returns to its normal state [9].

#### *1.3.1.3 Sniffer dogs*

Canines have been utilized for fire investigation for many years. Advantages are that after training, canines have been successful in pinpointing areas within large scenes that could contain an accelerant for sampling and laboratory analysis. This is only possible because of the sensitive olfactory system of the canine, which is 1000 – 1 million times more sensitive than a humans nose [11]. A canine's nose also differs from humans in that they do not suffer from nose fatigue, occurring when the nose becomes overloaded with odour and loses its ability to discriminate between odours effectively. A canine's nose can serve as a direction finder, allowing scent origins to be pinpointed via minute differences in scent intensity in different nostrils [12], which is extremely important in tracking down the strongest odour at a scene.

However, disadvantages are that whilst a canine can identify areas where it senses the greatest concentration of what type of accelerant(s) it is trained on, it cannot give an indication of accelerant type (as they are often trained on more than one type). There is also the potential for a canine providing false positive indications. This can occur on compounds that the canine has been trained on but are found at the fire scene in non-accelerant sources. Hence samples must be analysed at the laboratory, firstly for confirmation that the canine indicated correctly and secondly for the type of accelerant.

#### *1.3.1.4 The use of portable sniffers such as FID and PID and the zNose*

Flame Ionising Detectors (FID's) rely on the principle of measuring an ion current in a Hydrogen flame, where current is proportional to hydrocarbon concentration introduced to the flame via a carrier gas [13]. Or more simply, air is sucked in and mixed with hydrogen, burnt in a flame at a jet causing organic vapours to become ionised. This changes the chemical conductivity across the flame, with the change detected and measured [14]. Disadvantages are that they are not as selective as the PID so are not used as often [13]. It also has relatively low sensitivity, gives false positives in the presence of burnt foam backed carpet or other sources of flammable hydrocarbon vapours and is upset by dust unless filters are used [14].

Photoionising Detectors (PID's) rely on the theory that ionisation of a species "R" with a photon from UV light/lamp which has sufficient energy to ionise the species R [15, 16] emitting electrons in proportion to the concentration of R. The relevant equation is [15]:

$$R + h\nu \Rightarrow R^{+} + e^{-}$$

PID is comparable to FID but has increased selectivity [13]. Advantages include ability to collect air directly at the scene without capturing samples, is cheap, easy to use and handle, requires little training [17]. Disadvantages include that the temperature (low) affects its usefulness, and the sample must be analysed at 15°C for accurate results [17]. The PID technique is also sensitive to methane contamination which interferes with the detection of other compounds and requires screening prior to use [18]. Methane occurs naturally in the environment quite readily so could be a significant problem [18].This is the same with other airborne contaminants, which cause variable responses to mixtures, such as partially evaporated hydrocarbon fuels and solvents [19]. PID's are also susceptible to humidity, where an increase in water vapour affects the lamp and leads to unpredictable responses with high humidity [16, 20]. Some of these humidity issues have been overcome with later models where the unit is heated slightly above ambient temperature [21]. However more research is needed to overcome problems with humidity and it's ability to be effectively used with fire debris samples. This is because many false positives as R can be molecular species such as benzene, toluene or styrene, which occur in pyrolysis of almost all modern synthetic materials, PID does not successfully differentiate between these.

The zNose utilises a single uncoated high Q surface acoustic wave (SAW) resonator to provide on-line quantitative measures for manufactured aromatic products [22]. This technique can provide a visual image of specific vapour mixtures in real time. It is also able to simultaneously identify and quantify individual chemicals [22, 23]. The SAW detector is hooked up to a portable GC, and uses a temperature controlled quartz substrate to absorb vapours as they exit the GC capillary column [23, 24]. The SAW sensors have patterned electrodes to allow a high frequency (60 – 1000MHz) surface acoustic wave to be maintained on the surfaces. The frequency of the crystal is dependent on the spacing of the electrode pattern, the temperature of the crystal and the condition of the surface [24]. The advantages with this technique are that is stable and sensitive [22, 23], the sensors do not need constant recalibration, and do not drift [25], operates over a wide range of vapour concentrations [22], response time is very fast [23, 26].

The disadvantages mostly relate to the portable GC and its use at fire scenes. Below in the next section, the disadvantages for this device become more apparent. The sensor/detection device is not as much a problem as the GC.

#### *1.3.1.5 Portable GC's*

Gas Chromatography is a method of continuous chemical separation of more than 1 individual component between two phases, a stationary phase (fixed) and a mobile phase (carrier gas) [27]. The mobile phase flows over the stationary phase. Components enter the stationary phase simultaneously at the injector, but move along the length of the phase at different rates [27]. The lower the vapour pressure (the higher the boiling point), the longer the compound remains in the stationary phase. Compounds are then detected and the end of the column with a plot of output of detector response versus time [27]. The portable GC consists of as a minimum, an injection system, a separator (or column), and a detector [28]. The device uses the laboratory model as a template for what to use in the field, allowing on-site laboratory quality data to be generated [29, 30].

Advantages include eliminating time delays and reducing the cost of testing [29, 30]. Whilst disadvantages include the nature of the complicated device being difficult to use, the internal battery is not reliable so it requires external power, requires a clean workspace to be set up on (hard at fire scene) [17], samples need to be enclosed in a bag before sampling, therefore the purpose of portability is lost, the ordinary capillary column in the stationary GC gives better separation than the portable GC [13, 17], has been described as impractical, lacking sensitivity and not cost effective [31]. The portable GC also have no provision for heating the column, injector or detector, and so the analysis of more volatile compounds is limited, with results in variation of retention time in ambient temperatures [28].

### *1.3.1.6 Chemical detector tubes tests such as Draeger tubes*

A detector tube is a tube containing a chemically impregnated packing material which indicates the concentration of a contaminant in the air by means of a chemically produced colour change [32]. Short-term detector tubes are those used for "grab tests" with a measuring time in minutes. The unit consists of a detector tube and an aspirating pump. Class A detector tubes are required to fulfil a higher accuracy measurement than B Class tubes which are used for les exacting measurements [32]. In all detector tubes, there is a degree of systematic error, which is not to exceed +/- 25% [32-36]. The chemical reactions involved in each type of tube is specific for the type of compound tested for, and can be based on oxidation/reduction, acid/base, hydrogen sulfide + lead salt reactions, the generation of water molecules or basic addition reactions [37]. The Draeger company makes specific hydrocarbon detector tubes, based on the reaction principle [38, 39] that $I_2O_5$ reacts with $C_8H_{18}$ to create a colour change with the evolution of iodine.

The Draeger 100/a and 10/a tubes both have cross sensitivity, and various petroleum hydrocarbons are indicated, but with different sensitivities. It is impossible to differentiate between them [39]. Aromatics are indicated on but only with low sensitivities [39].

Advantages are that it is simple to use, provides a direct reading, with no delaying analytical costs, it is versatile and covers many compounds, is easily portable, and can sample remotely [37]. Each tube has a 1 –2 year shelf life (dependent on manufacturer) [40]

Disadvantages are that the accuracy of the tube, scope of application and limitations of the detector tubes are also dependant on the skills and experience possessed by the manufacture and the users [41, 42]. The reliability of the tube is related to the type of gel and reaction involved in the colour change, the sample volume/flow rate, tube diameter, length and packing [41]. Inter laboratory reliability differs greatly, and both random and systematic errors are inherent in the device [37, 42, 43]. Both temperature and humidity also have an effect of results [32, 42, 44].There are also issues with its lack of specificity, the fact that short term tubes cannot give concentrations, and the results are not as accurate as other more costly test [37, 40]. The tubes also have problems with cross reactivity with other compounds and are not highly selective [40]. Also the same brand pump must be used with the same brand of tube, mixing tubes and pumps causes systematic errors in results [40, 45], which add to the inherent systematic errors in a negative way.

#### *1.3.1.7 Conclusions*

Individually, these techniques all have points of merit. However recent research that compares three on-site accelerant detectors: the detector tube system; a photoionisation detector; and the accelerant detection canine, found that the detector tubes and photoionisation detectors were not effective on-site screening tools [46]. The accelerant detection canine team proved to be the only reliable on-site screening method, with results that compared to laboratory analysis results [46]. These findings by Casamento add to the need for a portable accelerant detection system that can provide a suitable screening test for on-site accelerants, with a large gap in the current technology for on-site fire scene investigation.

### 1.3.2 Confirmation Analysis in the Laboratory

In N.S.W., the Division of Analytical Laboratories (DAL) conducts fire debris sample analysis for the N.S.W. Police and the technique they use is one that has been developed on site by technicians. This technique is one that involves the collection of samples at scenes in either arson bags or tins by crime scene investigators. Once presented to the laboratory for analysis, the tins or bags have a tenax tube added to the containers before being heated to 60°C overnight. Once out of the oven, the tenax tube is removed from the container and placed in an auto sampler where it is then analysed using GC-FID as the technique of choice. The auto sampler is an Automated Thermal Desorber (ATD), which heats up the tenax tube with a carrier gas taking the sample through the GC to be detected by the Flame Ionising Detector (FID). Any liquid samples are run through the GC-MS, and if there are any unusual results, using the GC-FID, then the sample is retested using the GC-MS. Internal standards have been created for accelerants using fractional distillation, and every 5 years the standards are refreshed. Petrol standards have been created for 0.5, 1, 2, 5, 10, 20, 40, 60, 80 and 100% evaporated samples. Tenax tubes are re-used after being cleaned on the same auto sampler. Results are reported as containing either a specific accelerant or, for highly evaporated samples, hydrocarbon distillate.

Many other laboratories in Australia and North America commonly use similar passive headspace sampling techniques, but using activated carbon rather than tenax as the adsorbent medium. In most of Europe, the normal procedure is active headspace sampling using tenax, in which heated headspace vapours are drawn through the tube by means of a syringe or pump system.

In the laboratory, a GC-MS has been the one of standard techniques used in the United States for accelerant confirmation for many years. ASTM criteria are then used to identify the accelerant [47]. GC specifically is a separation technique used to detect components in mixtures. With petroleum hydrocarbons, the GC is configured to separate components based on the components vapour pressure over a range from butane n – $C_4H_{10}$ to n – $C_{32}H_{66}$ including products from petrol to paraffin wax [48]. The "X" axis is calibrated for hydrocarbons of known vapour pressures, and the "Y" axis is component concentrations. Peaks are components or mixtures with the same volatility. Volatility decreases to the right [48].

## 1.4 Summary

The ability to detect and analyse for accelerants at fire scenes is of growing importance as an investigative tool for intelligence led policing in a society where incendiary fires are both common and difficult to prove. If a presumptive test can be used at the scene, identifying that an accelerant was used and where, then the investigator may be able to direct their inquiry faster as well as providing a much closer link between the scene and the laboratory. This would also ultimately help in the time it takes to process the scene, and to aid in the determination of places to take samples and providing a preliminary result as to the presence and type of accelerant or the NIL presence detected at the scene. Thus far, no such device is available that completes all these functions.

## 1.5 Scope of This Project

This project encompasses a presentation of basic concepts such as: the areas of biosensors; how the human olfactory system works; and the analytical technique of cyclic voltammetry and its role in biosensor development. All are explored within the parameters of this project, with a detailed literature review is created for the initial research required to model the human olfactory system for biosensor development. This incorporates a literature investigation into the development of a suitable sensing device, together with a suitable multi-sensor array processing technique [47]. The aim of this investigation, both literature and experimental research, is to consider the idea of creating a biosensor for the presumptive testing of accelerants at fire scenes. Examining how biosensors work, which is basically a biological component attached to an electrode via an interface, whilst allowing an electrical signal to be generated when the biological component is activated, conveyed across the interface and recorded by the electrode substrate and voltammometric recording devices. Activation by smell/odour is how the olfactory system works with the literature review providing details of how this process distinctively works. By understanding the highly specific nature of human olfaction and the nature of a biosensor, additional concepts are identified that must be examined. These include the use of multiple sensors with different biological components that can provide differing specificity and sensitivity, providing different electrical activation signals for different odours. This then broadens the scope of this project to include electrochemical measurement techniques including cyclic voltammetry, using electrodes to record electrical signals generated by the addition of an odorous compound, such as petrol into an aqueous environment, thereby mimicking the mucus in the olfactory system. This could then be nano-sized and made portable, with the possibility of artificial neural network (ANN) computer processing providing pattern recognition for signals generated and odour identification in the field.

Overall this project aims to investigate both the literature and via experimental methods, consider and explore the possibility of creating a biosensor for the presumptive testing for accelerants at fire scene.

# CHAPTER 2: LITERATURE REVIEW

## 2.1 Introduction

The main aim of this research was to trial cyclic voltammetry as a method in the fabrication of a biosensor to detect accelerants from buffered aqueous solutions. This would see the field of accelerant detection develop a new material system with improved properties and expanded functionality over current techniques. Essentially creating a device that mimics both the biological process and hierarchical structure found in nature by fabricating a new "smart" material system with a unique combination of properties not possible using conventional techniques [49]. Since this has not been accomplished experimentally, one must rely on current theories of olfaction, odour detection and biosensors. However research is scattered, with no one paper covering all the topics that must be considered in this project. This chapter focuses on biosensors and their creation incorporating cyclic voltammetry and accelerant electro-activity. It is expected that by understanding these areas, that a practical method of how to make an accelerant biosensor can be postulated, with cyclic voltammetry experimentation beginning the process.

Cyclic voltammetry is the experimental method of choice in the research as it is quick, reliable electrochemical technique that has a high degree of sensitivity for detecting oxidation/reduction chemical changes in aqueous solution. It is the technique that closely mimic's the electrical signal conductance in the olfaction system, and has the scope to be nano-sized into a portable sensor. The output of an electrical signal could also be differentiated with an existing and apparently robust computer pattern recognition system of neural network processing, with little difficulty. All of these points will be detailed more thoroughly in the literature review below.

## 2.2 Basic Concepts

### 2.2.1 Biosensors

Firstly it must be noted that biological systems exemplify and provide the ultimate guide for the use of sensors, controlled regulation, actuators and smart systems of all descriptions. Like the eyes, ears, nose and taste, sensors depend on molecular interactions [50]. The spatial and temporal control needed is manifest in all levels of architecture in the biological system [50]. A smart structure/material senses the environment and responds in a purposeful way via the integrated design inclusion of a logic controller element. At present, there is a large area for research into the need for a biomimetic nose to detect, discriminate and alarm the presence of chemical explosives, illegal drugs and biological agents [50]. This could easily be expanded into the identification and sensing of accelerants in real-time. Whilst this is the direction of this research, presently there is a distinction between an electronic nose and a biosensor, with an electronic nose defined as:

"…. an instrument, which comprises an array of electronic-chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours." [51]

A biosensor is a device that combines electrochemical techniques with the specificity of biological recognition to determine the concentration of an analyte [52].

There are two approaches to the development of a biosensor: biological and biomimetic. Biological biosensors use natural biological structures attached to electronic analytical techniques. Biomimetic sensors use an electronic technique specifically to mimic a biological process or system.

This project will follow the biological approach as it provides an easier pathway for the fabrication of an electrode array for the detection of accelerants. The biomimetic approach would involve the consideration of a large number of processes that have not been fully investigated and understood. In this work the research would involve attempting to immobilize a biospecific reagent on a suitable electrode. The biospecific reagent will be an olfactory receptor, and the sensor will be tested using cyclic voltammetry and impedance techniques.

## 2.3 The Human Sense of Smell

### 2.3.1 Introduction

Humans have smell receptors, which are classed as chemoreceptors because they respond to chemicals in an aqueous solution [53]. These smell receptors are excited when chemicals dissolve in the fluid coating of the nasal membrane, or mucosa. The receptor cells are in the cilia extending from two olfactory bulbs, which is an extension of the brain [54]. Aroma molecules set off a cascade of reactions involving proteins, enzymes, cell depolarisation and second messages, culminating in an electrical impulse being sent to the brain [54]

This organ of smell is approximately a 5 $cm^2$ patch of yellow tinged psuedostratified epithelium, known as the olfactory epithelium, located in the roof of the nasal cavity [53]. Figure 1.1 [53] is an exploded view of the Human Nasal Cavity.

The olfactory system consists of three parts: the olfactory mucosa, the main olfactory bulb and the olfactory cortex [55].

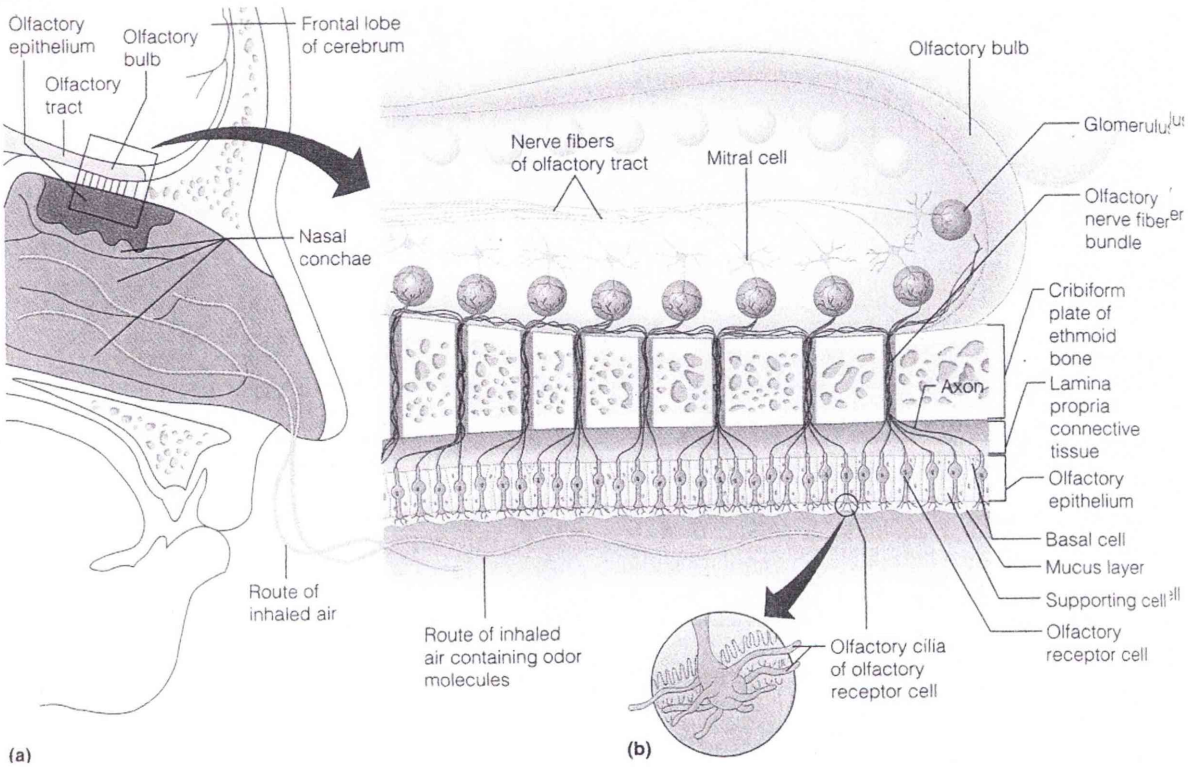



**Figure 2.1 View of the Human Nasal Cavity showing olfactory mucosa and olfactory bulb**

### 2.3.2 The Olfactory Epithelium

The olfactory epithelium is the main area of interaction between the odour and the olfactory receptors and it hosts 10 – 100 million sensory cells [56]. The Epithelial layer is approximately 75μm thick with the mucosal layer 20μm covering the epithelium [55] [57]. This mucus is secreted from the Bowmans Glands [55]. The odour is delivered to the olfactory epithelium via the nasal passage consisting of three parts, the anterial nares (through which inhalation occurs), the central chamber (consisting of the mucosa, epithelium and olfactory bulb) and the posterior nares (through which exhalation occurs). Olfaction can also occur during ingestion through the posterior nares, called olfactory respiration.

Once in the nasal cavity, odours diffuse through the mucus layer to bind with chemically sensitive membranes made up of olfactory receptor cells in the epithelium. How the odour ligands reach the olfactory receptors (OR's) is unknown. One hypothesis is that the odours diffuse through the mucus to the olfactory cilia where they access the olfactory receptor proteins (ORP's) [53]. The cilia are at one end of the olfactory neurone and connect down to nerve fibres at the other end. The olfactory neurone passes electrical signals from the olfactory epithelium to the olfactory bulb [58]. This system is housed in the olfactory epithelium (see Figure 1.1).

Below is a picture of olfactory neurone with cilia at one end and nerve fibre at the other. The cilia extend into the mucus layer (Figure 1.2), and the pathway into the olfactory bulb through the cribiform plate is also visible [59].

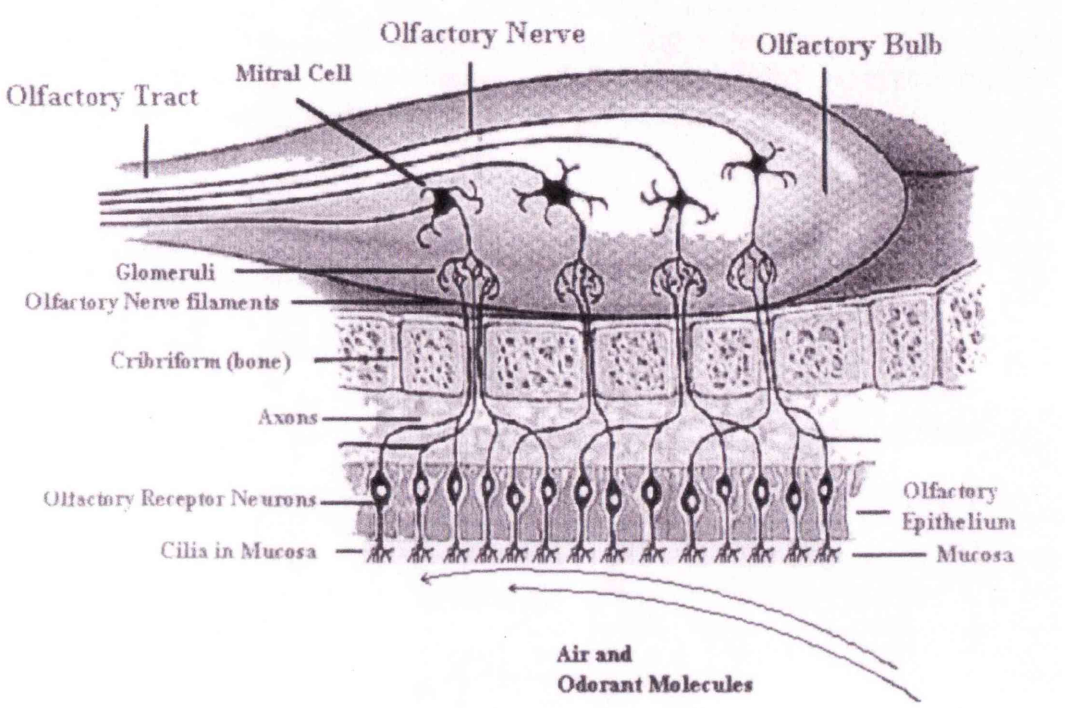



**Figure 2.2 View of an olfactory receptor neurone showing cilia and nerve fibre (at the base of the picture) extending into the mucosa**

### 2.3.3 The Olfactory Bulb

Once the olfactory neurones in the olfactory epithelium have passed on electrical signals from aromas interacting with cilia in the mucosa layer, the olfactory bulb is activated. A pattern of impulses is generated through the olfactory neurone population and transmitted to the main olfactory bulb as an array. This is called the first synaptic relay for incoming information. The original impulse from the first synaptic relay goes to form a second order electrical event, which is then sent from the olfactory bulb to the olfactory cortex [53].

### 2.3.4 The Olfactory Cortex

The second-order electrical event signal is then further processed in the central nervous system and identified by the brain as a particular smell. Perception of smell is analogous to perception of colour with receptor cells thought to be "broadly tuned" [60] [61] in which receptor cells possess a wide range of sensitivity to many odorants with an overlap between different cell classes and their subsequent responses. This means that a given cell can respond to more than one odour, and conversely a single odour can activate multiple cells [62]. The seeing colour analogy utilises the fact that colour perception relies on the adsorption of spectra of 'red', 'green' and 'blue' cones being distinctly overlapping, but tuned to particular frequencies of light [63]. Hue and intensity can be determined independently of each other. Compare this with a single receptor, such as 'blue'. Without overlapping spectra responses of receptor types, the brain could not distinguish optimal-blue at low intensity from off-blue at high intensity [55]. Therefore multiple responses from overlapping receptor types allow the visual system to discriminate hue and intensity. Such may be similar for the olfactory system where olfactory receptor responses that overlap could be exploited by neural processing within the olfactory pathway to discriminate odour quality independent of intensity [55]

Olfactory perception is thought to be holistic in nature in that the totality of the electrical signal is important in recognizing a particular odour, with the olfactory system taking a broad sample of the environment to provide meaningful information about the odour/signal [55].

### 2.3.5 Odour Recognition

It is thought that the way humans recognize an odour via the olfactory cortex is analogous to the auto associative memory system [64]. The implication is that there is a transformation of complex pattern inputs into a stable reproducible pattern, with each new odour encountered receiving an original pattern by the brain [55].

## 2.4 Initial Theories of Olfaction Incorporating Modern Odour Detection Techniques

### 2.4.1 Introduction

Before studying the individual areas of biosensors, cyclic voltammetry and accelerants electroactivity, it is worthwhile to consider the theories of olfaction and their impact on modern odour detection techniques. Olfaction in humans and animals has been researched for many years [53, 60, 64-85], with more recent literature attempting to combine theory and research into how humans identify and "smell" odours. The traditional electronic nose is an example of a system that mimics biological olfaction using electronic techniques and piezoelectric sensors and biosensors. This has then been explored further with the creation of multi sensor arrays using computational pattern recognition techniques.

### 2.4.2 Olfaction Research

Duchamp and Revial's [60] research was some of the first in its field to begin an in depth experimentation into olfaction. Their article details the technique of placing a microelectrode into the nose of a frog and measuring electrical impedance responses of the olfactory receptors when vapours were passed over the receptor/micro-electrode. Earlier research in 1965 by Gesteland, Lettivin and Pitts [66] explored the methodology used. The research by Duchamp and Revial [60] achieved its aim of better understanding olfaction, however the methodology of using a dead frog with an electrode inserted into the nasal epithelium before a gas with the odour in question present, passing through the nasal passage of the frog is not universally practicable.

This research had three positive outcomes; firstly it was shown that an electrical impulse could be recorded from the olfactory receptors in the nose when an odour was passed over it. Secondly, simple data analysis techniques of clustering, factor analysis and correlation coefficients were used to determine that no two responses were identical, and finally individual receptor cells were recorded as having individual responses, either inhibitory or activatory from single or multiple odorants.

Duchamp and Revial's research however used highly purified simple odorants as the test components, some of which were common to the accelerants organic mixture, as benzene and naphthalene were tested. Other aromatic compounds such as anisole, acetophenone and nitrobenzene-benzaldehyde were also tested. The simple nature of single compounds tested is not encouraging here and is a theme carried through other research into olfaction, with mixtures not commonly tested [58, 69, 72-74, 77, 78, 85-91]. Duchamp and Revial's [60] research showed that the common aromatic nucleus caused the results to have high correlation coefficients, with aromatic components grouping in clusters when factor analysis was completed. This means that any research incorporating a mixture with common organic aromatic compounds would require a high degree of data manipulation to distinguish individual components. From this research is could be theorised that if different odours activate/inhibit receptor cells in differing ways, that a mixture would cause an overall pattern of responses that could differ from mixture to mixture.

Duchamp and Revial's method has since been replaced with the isolation of olfactory receptor cells from the nose without the use of the entire frog as described above. The isolation of receptor cells by Sicard and Holley [62] alleviated Duchamp and Revial's difficult method. Other research has also isolated olfactory receptors for various uses [58, 69, 72-74, 77, 78, 85-91], however none are as important to this project as Sicard and Holley's. Sicard and Holley were not only able to isolate receptor cells they were also able to explore more thoroughly the concept that different odours may create different receptor cell responses. Their research led to an important hypothesis covering the concept of odorant groupings and how it affects the mechanism of olfaction. Their theory is based on research that began with Duchamp and Revial [60], with Sicard and Holley's results detailing how odour stimuli are detected by several types of broadly selective receptor sites and that these receptor sites are distributed randomly amongst receptor cells.

The authors then postulated that the mechanism of olfaction could be analogous to the perception of colour, the adsorption of spectra red, green and blue, as with spectra (or in this case receptors) having overlapping sensitivities. Olfactory receptor response where there is an overlap of responses between different receptors is likely to be exploitable by neural processing within the olfactory pathway for the discrimination of odour quality, independent of intensity.

This concept is extremely important to this project because it is expected that eventually different receptor cells will be used in the fabrication of different sensors, so that when they are collectively used as an array there would be high degree of discrimination power for the detection of accelerants. The electronic nose and modern sensor arrays have also utilises this theory to create working sensors. Thus far it has not been discounted and is still the most significant theory on the process of olfaction.

Whilst Sicard and Holley were investigating the process of olfaction simultaneously there was exploration into the idea of mimicking the biological olfaction system by using gas detectors. Persuard's 1992 [92] article did not research individual gas sensors, however it did detail the many electronic gas sensing techniques available. His article correlated techniques already in use that have parts which mimic biological olfaction and then postulated a design of gas and odour sensors, with an emphasis on new conducting polymers, and information processing techniques that would be applicable. Gas sensors discussed included metal oxide gas sensors, catalytic gas sensors, and organic semi conducting gas sensors, solid electrolyte gas sensors, mass sensitive devices, fibre optic probes and Langmuir-Blodgett films. Persuard postulated that electrically conducting organic polymers based on monomers such as pyrrole, aniline and thiophene were the most promising. Previous research of his [93] showed reversible changes in conductivity when exposed to polar volatile chemicals, with rapid adsorption/desorption recorded at ambient temperatures [92].

This article whilst detailing current techniques being explored for use as odour detectors also shows that conducting polymers could be used as a thin film on electrodes to record electroactive changes when a polar volatile compound adhered to its surface. This leads to the idea of layering a reactive coating on an electrode. However given that the accelerants tested are generally non-polar, the conducting polymer films detailed would not be suitable for this project. Persuard then postulated that the use of Artificial Neural Networks (ANN's) would be the best signal-processing device for an odorant sensor, as other information processing methods such as correlation and least squares do not emulate signal processing as it occurs in the biological system. One research project has investigated the use of conducting polymer sensors in an array with neural network processing as an accelerant aroma detection device [94], as a biomimetic approach to accelerant identification. This project was shown to be feasible, but required much more investigation.

From this idea, the use of biological based sensor over conducting polymer-based sensors may offer better discrimination between samples from a fire scene, where contamination issues of fire debris can cloud the results. Humidity, temperature and equilibrium time were variable factors in this research, which needed to be precisely controlled [94]. A biological system over a biomimetic one detailed, which works in aqueous environment (like the mucus layer in the nose) would have less susceptibility to these variables. This significantly takes the idea of a modern odour detector that mimics biological olfaction a step further.

Articles by Gardner (in 1991 [95] and 1992 [96]) also details the development of current odour detectors, utilizing sensors and sensor arrays in a purely electrochemical sense, to achieve identification of vapours with different data analysis techniques. Specifically Gardner's 1991 article examines tin oxide sensors, utilising 12 sensors and exposing them to alcohols and beverages for odour discrimination. Results were analysed and the author achieved characterisation of odours via pattern recognition identifying the optimal number of sensors to achieve this as 5. Cluster analysis then improved classification of the vapours tested.

In 1992, Gardner and Hines [97] continued on with this research using the same 12 tin oxide sensors, finding that sensor saturation created a non-linear relationships between the sensor output and gas concentration. They moved on to process the data with Artificial Neural Networks (ANN's), which were demonstrated to outperform PCA or cluster analysis in vapour characterisation. This was because ANN's are able to cope with non-linear and highly correlated data.

This research by Gardner into tin-oxide sensors has two main points to be considered by this project, firstly that sensors used in an array have a higher discrimination power than the individual sensor. This goes towards confirming that olfaction processes may be able to be mimicked, as the theory of odour discrimination in biological processes uses multiple receptors with differing responses. Sensor arrays could be one way of achieving this. Secondly Gardner's research shows that ANN's are better able to cope with the highly correlated data. This is positive for this project as most of the components in the accelerants tested are organic aromatic compounds, and research by Duchamp and Revial [60] showed such compounds are highly correlated.

Tin oxide sensors have also been investigated specifically as a technique for the detection of hydrocarbons [98, 99]. The technique relies on the $O_2$ release mechanism of the reaction, where oxygen in displaced from the sensor surfaces by the adhesion of the hydrocarbon. The hydrocarbon gas is reducing in nature and adsorbs to the surface of the sensor where it is oxidised by the $O_2$ on the electrodes surface, which releases electrons into the tin oxide matrix [99]. However a problem with the technique is that the electron flow is hindered by humidity or oxygen in the atmosphere, which tends to block the adsorption sites for the hydrocarbon in this instance Liquid Petroleum Gas (LPG). Another hurdle for portability is the optimum operating temperature of the system, where adsorbed species are decomposed by oxidation, releasing electrons for conduction in the matrix. The higher the operating temperature (optimum 300°C) the higher the conductivity and the better the results [99]. This technique is one of the few electrochemical sensor techniques that have been tested not only on LPG but also on petrol, kerosene and diesel fuel. Results indicated that the sensor has some sensitivity for kerosene, but negligible sensitivity for petrol and diesel. This is a major problem and as such tin oxide sensors are not considered as a viable candidate for creating an accelerant sensor.

The idea of the electronic nose was considered in much more detail by Pearce [55] who postulated that the traditional use of electrochemical techniques for vapour/odour identification was ad hoc in its approach and that their use is limited in their ability to model the perception of chemical stimuli in humans. Problems identified with electronic noses were sensor/receptor drift, sensor/receptor poisoning, limited sensor/receptor sensitivity and the identification of odours from a complex mixture of background odours. These problems are highly relevant to this project that aims at the identification of accelerants at fire scenes where complex background mixtures of odours commonly exist.

Pearce includes a theoretical treatment concerning a new system of sensors that model the olfactory system in humans (detailing nasal morphology, olfactory receptors and signal/odour processing in the brain). Stating that odours are delivered to an array of non-specific receptors that are of vital importance to their discrimination by the brain. Pearce, in a further article [52] where he theorized on how to model machine olfaction on human olfactory processes using sensors. This second article by Pearce considers current electronic nose architecture from odour delivery to pattern recognition and odour representation. Comparisons are made between the current techniques used and new advances in understanding the processing of odours in the olfactory bulb and cortex. He then recommends how to enhance current techniques, which he admits parallel earlier attempts at understanding how the olfactory system works.

The author recommended the exploitation of the biological olfactory receptor process of non-specific receptors working as an array used to expand the electronic nose's capability of odour discrimination. Other recommendations made are too far advanced for the scope of this project, going into detail of how to create ANN programs, and what parameters to consider when setting up such a system.

These two articles have one main flaw with their application to this project. They postulate methods of biomimicry but do not have any research to aid in its application. As such detailed methodology on how to create a working biosensor must be derived from other sources. However the idea of mimicking the olfactory process via the use of a biosensor to discriminate complex odours is applicable to this project. Research into odorant recognition [88] suggests that the theory of biomimicry with receptor proteins from cilia are the way forward.

There has however been research into related areas such as the use of piezoelectric biosensors and quartz-resonators [100-105] for odour detection in an area that parallels this project. Nakamoto, Fukunishi and Mirizumi's research [102] showed that quartz-resonators coated with a sensing membrane as an array with neural network pattern recognition could be optimised, however the exact number of sensors used was not noted. Whilst membrane coating was selected from gas-chromatographic stationary phase materials and cellulosic ones, it is unknown why these coating were chosen and for what specific purpose. Results were compared with the human senses of volunteers, which is unsuitable for this project due to the issues with nose fatigue and the final goal of detecting accelerants in fire scenes where the human nose is not (as previously discussed) reliable for legal purposes.

Muramatsu, Tamiya and Karube's research [101] whilst completed before Nakamoto et al's research was more relevant to this project. Their research investigated lipid-coated piezoelectric crystal resonators that were used to detect β-ionone, citral, menthone and amyl acetate. Crystals were coated with the asolectin liposome. The authors created their biosensor by casting, where the casting material (lipid mixture) was dissolved in chloroform, and then coated on the crystal. When the chloroform was evaporated off, the coating remained on the crystal. This has some relevance to this project because of the use of a biological material to coat the crystal. However the odorants tested were quite different from the organic aromatic hydrocarbons used in this project. The method of creating the biological layer on the quartz surface is expected to be beneficial in later stage fabrication attempts.

The most relevant article to this project is that by Wu [100]. His research layered specifically ORP's from bullfrogs, onto piezoelectric crystals (6) as an array to respond to volatile compounds (n-caproic acid, isoamyl acetate, n-decyl alcohol, β-ionone, linalool and ethyl caproate) and record rapid (approximately 400s), reversible and stable responses (up to 3 months). This is a positive article for the use of ORP's used to perform olfactory evaluation of odours. The methodology of isolating a crude ORP mixture and refreshing the biosensor with a nitrogen flow to create reversibility and to allow for stability and longevity of the device could be evaluated further on. ANN's were also found to be an effective signal processing technique.

Mirmohsseni and Oladegaragoze researched chlorinated aliphatic hydrocarbons and polymer coated piezoelectric sensors, with results recorded at room temperature. A stable sensor was created, with no major atmospheric interference from compounds such as CO, $CO_2$, $NO_2$, $O_2$ and $H_2O$, and with response times between 120 and 400 seconds. This looked positive for further hydrocarbon investigation, however it is unknown if the reactions occurring on the sensor are related to the aliphatic hydrocarbon itself or the chlorinated species. This needs further examination, before such a sensor could be investigated for use at fire scenes. However there are a few problems with the piezoelectric device as a whole that preclude it from being considered useful for this project.

The piezoelectric sensor readings are affected by both humidity and temperature, with this research conducted in a dry air chamber. At the fire scene, there is much moisture in the air due to fire suppression techniques such as water and foam, and temperatures are often elevated above room temperature, even after a fire has been suppressed due to heat retained within the structure. The apparatus used is also laboratory based, and the possibility of making it portable would be difficult. Whilst this technique with crystal sensors is not applicable to use at fire scenes, it is however a positive overall result for the adhesion of an ORP to an electrode, the rapidity of analysis results, reversibility of the biosensor and stability of the ORP layer.

Other types of sensors that have been researched recently in the detection of hydrocarbons include zeolite thin film sensors [106-109], polymer film sensors including Langmuir-Blodgett thin films [51, 110-112], infrared adsorption techniques [113], fibre-optic detection devices [114, 115], thermoelectric sensors incorporating catalysts [105], bioluminescence and luminescence [116, 117] and silicon metal-oxide-semiconductors (MOS) [118]. Of these, only zeolite thin film sensors and polymer-coated sensors have a possible impact on this project.

Infrared adsorption techniques IR, fibre-optic detection techniques, thermoelectric sensors, bioluminescent and luminescent technology and silicon MOS sensors all have many advantages and disadvantages for hydrocarbon detection. However all are specifically designed for different industries that make their adaptation to portable fire scene analysis difficult, such as turbine engine fuel/air mixture monitoring using IR technology, detecting hydrocarbon leaks on large scale petroleum manufacturing sites via fibre optic cables and sensors, waste water pollutant monitoring using bioluminescent microbes, to name a few.

Zeolites are more applicable to this project. They are hydrated alumino-silicate clays that have a charged 3-Dimensional honeycomb [106]. They are known to act as electromagnetic sponges and have natural electrical conductivity. They also have an intrinsic electrical charge along with a capacity for selective ion-exchange [106]. They are temperature, pH and chemically stable with a high degree of porosity and a large surface area which can help catalyse decomposition [107]. They have been used as thin film coatings on sensors because of their ability to undergo fast and reversible gas-solid interactions between molecules with a wide range of donor properties [108].

The thickness, grain structure and orientation of the overall zeolite system determines the sensors interaction properties [108]. Research has recently been completed in utilising zeolite films for sensing methane, propane and ethanol at differing humidity levels [109]. Vilaseca et al's research found that there was an increased sensitivity for ethanol when a zeolite layer was added to the Palladium doped tin oxide sensor.

Resistance measurements were used to analyse the sensors response. Research completed into zeolites is based on the phenomena where the target compound is adsorbed onto the surface of the zeolite. And this caused problems in the analysis of accelerant based hydrocarbons. The zeolite is porous with small holes, as well as being semiconductive. Hydrocarbons commonly found in accelerants are large in size and molecular weight. This technique has problems in testing for larger molecules, with solutions tested commonly having small molecules (target compounds) dissolved in solutions of larger molecules [109]. Hydrocarbons, commonly found in accelerants, are large in size and molecular weight and are therefore expected to be difficult to detect via this method.

Polymers as a coating for microelectronic devices have also been evaluated in sensor research [51, 110-112] with advantages including potential low cost and operating power, commercial availability of coated fabrics and an expected wide dynamic range due to large surface areas, ease of measurements and stability of coated fabrics [111]. Research into stabilised zirconia sensors with a polymer coating [112] has recently been shown to be able to detect oxygen containing gases such as CO, $H_2$ and hydrocarbons. This sensor is based on the fact that oxygen is formed on the subsurface via adsorption of the test compound onto the polymer, which is then monitored by ultraviolet photoelectron spectroscopy and X-ray photoelectron spectroscopy. This technique has limitations that prevent it from being considered for this project, firstly it is laboratory based, thus making it portable would be difficult. Secondly, it is aimed at high ppm range detection of exhaust fumes, which allows sufficient signals for analysis. This means that its sensitivity is too low for operating in low ppm of ppb range hence its use at fire scene is limited. And thirdly it needs much more work into the detection of samples containing a mixture of gases. Other research into the use of zirconia based sensors [104, 105], uses a system where the test gas is heated to 600°C and the system a bench top design, which is highly impractical, and difficult to make portable.

Langmuir-Blodgett (LB) films are films (usually polymer) that have been deposited using a specific method of applying a monolayer at a time to a surface while the monolayer is maintained at a specific pressure, and as such discussion of polymer coatings is applicable here. The LB films are used to measure resistivity changes made by electroactive species engaging with the surface [119]. This type of sensor is not relevant to this project for the same reasons detailed above with polymer sensors.

### 2.4.3 Biosensors for hydrocarbons

From the literature detailed above, biosensors coupled with pattern recognition processing such as ANN's [49, 92, 95, 96, 110, 120-122] are a method that mimics biological olfaction with a high degree of discrimination for odour detection. Biosensors and electronic noses in their various forms thus far have been used and researched for the detection of odorants with differing sensitivities for many years [51, 60, 82, 84, 86, 92, 97, 100, 101, 123-142]. However from the literature, the basic structure of the biosensor does not alter dramatically, a biological material is attached to the surface of a sensor, be it a simple electrode or crystal, with responses recorded and analysed preferably by ANN's. However all the research is scattered, with only a handful using ORP's in their research [60, 86, 89, 100, 143, 144], and of these, there appears to be only one significant article incorporating ORP's in the use of a working biosensor for odours [100]. However this type of sensor, the piezoelectric crystal resonator, causes practical issues that would be difficult to overcome given the nature of the sensor itself. Hence a more robust and versatile sensor is needed, with a basic electrode structure coated with the biological material a logical place to start.

Electrochemical techniques used with the simple electrode include cyclic voltammetry and impedance incorporating linear sweep, step and pulse signal analysis. From cyclic voltammetry (CV) alone, thermodynamic, kinetic, mass transport, charge transfer and concentration details of the system can be established [145]. CV is a dynamic electrochemical method for measuring redox events and the electrochemical behaviour of species at an electrode surface, the interfacial phenomena at the electrode surface and bulk properties of materials on an electrode [146]. Hence this is an applicable technique to start the investigation of accelerants as a mixture and their interaction at electrode surfaces, as electrodes are usually the basis of modern sensors.

Literature on CV can best be encompassed by Rusling and Suib's [146] research which details the technique of CV. They determined that whilst CV did not yield direct information about the nature of the redox couple, the peak potentials gave an indication on the nature of the species. They also noted that to identify a compound or mixture, standards are necessary, which is an important aspect of this project. They also noted that sensors could be created via the coating of the electrode surface with micro-porous materials. This article makes reference to sensors with coatings of thin layers of zeolites, polymers and Langmuir-Blodgett films of surfactants. Significantly what this research does not include are thin layers of biological reagents. The parallel sensor research areas into zeolites, conducting polymers and Langmuir-Blodgett films utilising electrochemical measurement techniques have already been individually discussed, with their relevance and application to this project evaluated above.

More specifically probing accelerants with CV has no relevant literature. The closest relevant article [127] is where 8 phenols were detected on graphite modified electrodes using a thin film of peroxidase. Amperometric detection limits were recorded, with this research detailing results with the closest compound to organic accelerants tested in such a system thus far.

From all the literature surveyed, CV, in which the electrode is coated with a biological receptor, is also a technique that currently has not been investigated for the purpose of accelerant identification.

This project would then have the practical problem of how to adhere the biological reagent (and ORP) to the electrode surface via bioadhesion. This has to be completed in an aqueous environment given the natural environment where the biological reagents operate in the body (the mucus layer of the olfactory epithelium). The direct immobilization of a biological agent onto the electrode often tends to reduce the activity of the agent [147], hence two possible methods for the attachment of the agent to the electrode must be considered. The first immobilizes the agent in a membrane, and placing this membrane over the surface of the electrode, whilst the second uses a mediator to attach the enzyme to the surface [147]. This research looks at the second technique of using a mediator for the adhesion, with influence taken from nature, and bioadhesion over a synthetic process.

The earliest recorded observations of bioadhesion were recorded in the sea Mussel and its attachment to rocks in the tidal zone [148]. It has been determined that a protein from the Mytilus edulis mussel seems to solve the problem of bioadhesion. The mussel adheres to many surfaces including rock and metal in hostile aqueous environment such as our oceans [148]. The protein isolated from this mussel, which has been identified as responsible for the "adhesion" of the mussel is the Mytilus Edulis Adhesive Protein (MAP). Many experiments have been conducted on its use in adhering to both biological and metal surfaces, and it's ability to create "scaffolding" that can determine how the biological specimen will grow [149-153]. However, the article by Saby and Luong [154] is a good example how its use has now expanded to become an interface between electrodes and an enzyme layer to create a simple biosensor for the detection of glucose.

Saby and Luong's 1998 [154] research is most appropriate for this project as it details how to adhere the MAP as a thin protein layer of three electrodes, Platinum (Pt), Gold (Au) and Glassy Carbon (GC). They then immobilized glucose oxidase onto the MAP, with cyclic voltammetry used to measure electrochemical changes in the sensor when glucose was added to the system. The work included varying pH from 2 to 5. The results showed it was feasible to immobilize glucose oxidase onto various substrates (Pt, Au and GC). This research was completed as a model for the construction of an enzyme based sensor, with the conclusion reached that the MAP was a good candidate for immobilizing other enzymes onto an electrode surface.

Whilst this research is the highly applicable to this project, and the method straight forward, there is one discrepancy with the work. It was aimed at identifying a specific compound, glucose oxidase, and not a mixture. This could however be expanded with further research to incorporate a sensor array with differing ORP's on different electrodes, then coupled with pattern recognition processing (ANN's) to allow a greater degree of discrimination.

There is however one major flaw with the literature on biosensors and CV, noted throughout the reviews, all the articles researched fail to address the issue of complex mixtures and accelerants in particular. Investigations into coffee, beer and grain odours [49, 51, 155] , where specific mixtures are analysed have been the closest research completed applicable to this project. This research investigated sensor arrays such as tin-oxide for coffee analysis, conducting polymer arrays for beer and electrochemical gas sensors with use of pyrolysis over a heated catalyst for grain. Again neural network processing was preferred with the beer and grain research, whilst the coffee utilised multivariate calculations. However once again whilst these specific mixtures were tested, no aromatic compounds or their electroactivity measurements were investigated using CV. As such, electroactivity of such compounds as accelerants must be addressed so that results from CV analysis can be better understood in context.

## 2.5 Accelerant electroactivity

There is limited data on the electroactivity of accelerants. The only relevant article found involves the examination of a ruthenium incorporated tin-oxide thin film sensor where LPG gas was the test compound [99]. Positive results for LPG gas were recorded, however when petrol, kerosene and diesel were tested, only a partial sensitivity for kerosene was recorded, with petrol and diesel fuel showing negligible sensitivity. This technique used the hydrocarbons reducing ability to adsorb to the thin films surface, oxidise because of adsorbed oxygen on the surfaces and release electrons into the tin oxide matrix [98, 99, 112]. It was determined there was an optimum operating temperature with increasing conductivity of the matrix up to 300°C and a fall in conductivity above that temperature. This type of sensor has however been discounted as a method for this project due to the impractical nature of the desk top technique and that the sensor is susceptible to humidity and oxygen with conductivity falling within the tin oxide layer with water and oxygen filling the sites to which the hydrocarbon adheres.

Other literature relating to hydrocarbon electroactivity is also light in detail. Information regarding anodic and cathodic behaviour of hydrocarbons exist, with ideal conditions for their electroactivity specified [156]. Electrolytes consisting of MeCN with perchlorate salts, rotating Platinum electrodes and half wave potentials are all desired conditions for analysis. Methyl benzenes undergo an initial electron transfer followed proton loss, and cyclic voltammetry at low sweep rates in MeCN showing two irreversible oxidation peaks relating to the transfer of 2 electrons [156]. Benzenoid compounds (those most closely related to accelerant hydrocarbons) as a category in aprotic solvents are reported to be reversibly reduced to dianions, except for benzene and naphthalene [156].

From the literature discussed, it is clear that there is some electroactivity in hydrocarbons, however as no detailed research has been conducted into accelerants and their mixtures, it is difficult to theorise on the mechanism of oxidation and reduction that the accelerants will undergo with cyclic voltammetry in this project. It is also difficult before experimentation to determine whether accelerants will have any electroactivity at all, given that the method used here varies from those set out above.

The method of choice for this project uses "potentiometric sensors" with a membrane or surface sensitive to a species that then generates a potential proportional to the concentration of the active species measured relative to a reference electrode [147, 157]. This is the use of cyclic voltammetry to generate a changed potential that is altered from the reference electrodes. Whilst selectivity in many cases is not sufficient to differentiate between various electroactive species from constant applied potential, extra selectivity is often needed [146, 147]. Biological enzymes, proteins and even olfactory receptors can provide this added specificity [147], by adding a bio-recognition layer [157]. This layer is important because it interacts with the target analyte and the chemical changes resulting from the interaction are recorded as electrical signals [157].
Below is a more detailed investigation into cyclic voltammetry, the technique used in this research.

## 2.6 Cyclic Voltammetry

Initial experimentation will examine electrode interaction with accelerants without the addition of mediation layer or biological agent (ORP), and so basic electrochemical mechanisms and reactions in CV will be detailed.

Cyclic voltammetry was investigated as an electrochemical analytical technique for the determination of electrochemically active species in accelerant, measuring redox events, the study of electrochemical behaviour of species diffusing to an electrode surface as well as interfacial phenomena at the electrodes surface [146, 158]. In cyclic voltammetry, the potential of an electrode (working electrode (WE)) is changed at a known rate and the resulting current monitored. Typically a 3-electrode cell is used containing a reference electrode, working electrode and auxiliary electrode [146, 159, 160]. Different electrode surfaces (WE) have differing responses to the same electroactive species in solution, and it is necessary to optimise the electrode for a particular component. As a result electrode selection is very important [146, 160]. Metal electrodes have a general advantage in that their high conductivity results in low (usually negligible) background currents [161]. It is easy to increase sensitivity and reproducibility by forced convection, and the there is ease in the construction of the electrode assembly and polishing [161].These electrochemical processes take place at the electrode-solution interface, with the technique used in this experiment a controlled potential (potentiostatic) technique [159]. This process uses the electrode potential to drive an electron-ion transfer reaction, with the resultant current measured. This controllable parameter is viewed as "electron-pressure" [159], which forces the chemical species to lose or gain an electron (oxidation or reduction respectively). Potentiostatic techniques measure any electroactive chemical species (i.e. that can be made to reduce or oxidise) [159]. The advantages of this technique includes high sensitivity, selectivity towards electroactive species, a wide linear range, portability and low cost instrumentation, speciation capacity, and a wide range of electrodes that allow assays of unusual environments [159].

The objective of the potentiostatic technique is to obtain a current response that is related to the concentration of the target analyte (in this case accelerants). This is achieved by monitoring the transfer of electron(s) during the redox process of the analyte at the interface of the electrode and analyte [159, 160]. This consists of the application of a time-varying potential to the working electrode [162]. The result is an occurrence of oxidation or reduction reactions of electroactive species in solution, possibly by the adsorption of species according to potential. The observed current is therefore different from the steady state [162]. The faradaic current is a direct measure of the redox reaction, with the resulting current-potential plot known as the voltammogram [146, 162]. This is a display of current signal (vertical axis) vs. the applied potential (horizontal axis) [159]. The processes involved in the electrode reaction govern the shape and magnitude of the response recorded on the voltammogram. Simple reactions involve only mass transport of electroactive species to electrode surface, the electron transfer across the interface and the transport of the product back to the bulk solution [159]. More complex reactions involve additional chemical and surface processes, which precede or follow the actual electron transfer. The net rate of the reaction and hence measured current many be limited by mass transport of the reactant or by the rate of the electron transfer [159]. Mass transport can occur by diffusion, convection or migration [163]. Normally, conditions are chosen where migration effects are minimised, where the effect of the electrodes electric field are limited to a very small distance from the electrode [163]. Below in figure 2.3 is a cyclic voltammogram with simple oxidation and reduction curves [158].

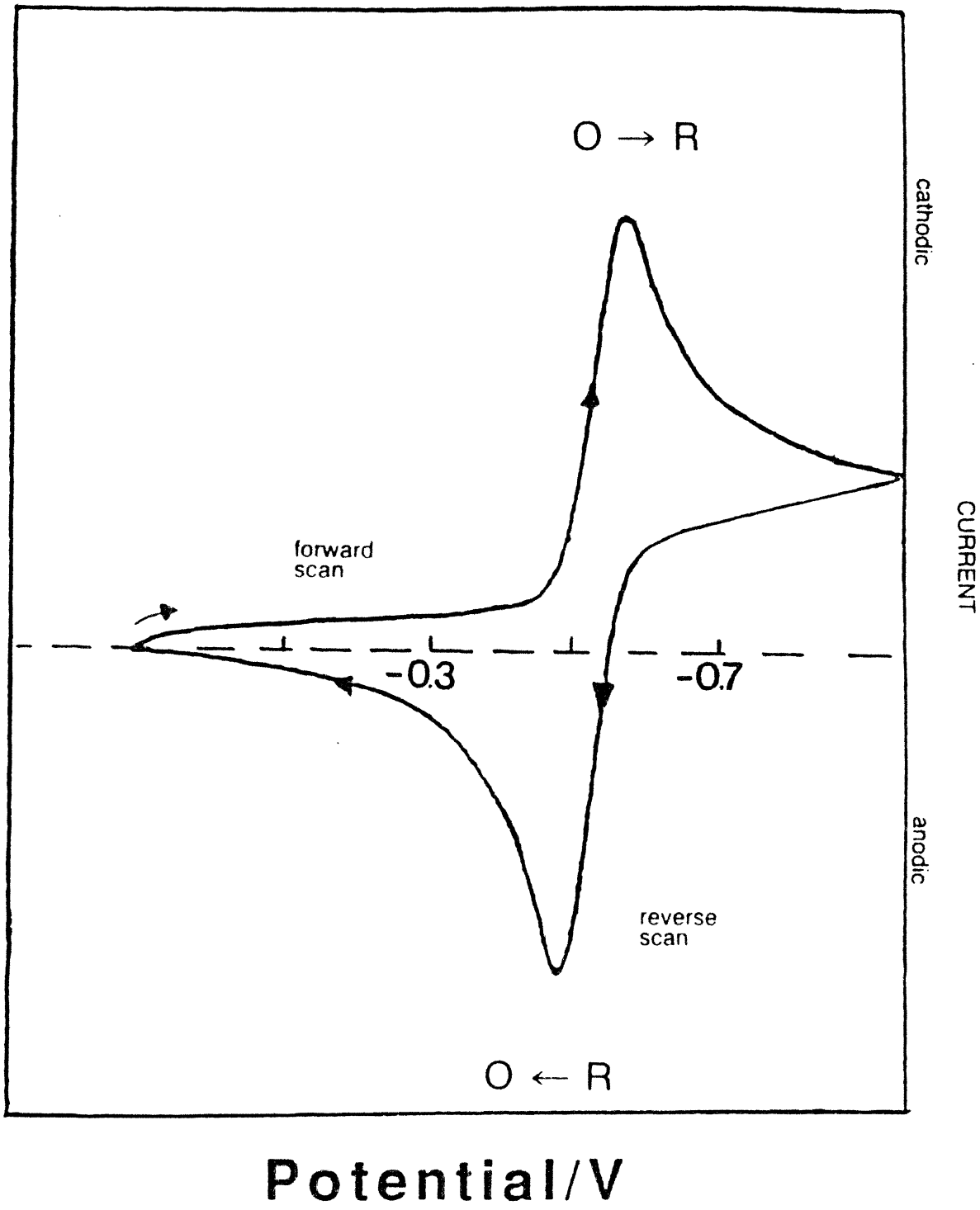



**Figure 2.3 Simple cyclic voltammogram showing reduction curve (cathodic current) and oxidation curve (aniodic current)**

The shape of the CV curve is understood in the following way, upon reaching a potential where the electrode reaction begins, the current rises as in a steady-state voltammogram [162]. The creation of a concentration gradient and consumption of electroactive species means that continuing to sweep the potential, from a certain value just before the maximum value of the current (the "peak current") the supply of electroactive species begins to fall [162]. Because of the depletion of electroactive species, the current then begins to decay, following the profile $t^{-1/2}$ [162].

This curve is modified if a reagent or product of an electrolyte reaction is adsorbed strongly or weakly onto the electrode [162]. And if the solution contains more than one electroactive species, various voltammometric waves (curves) can appear. The formation of various species in the vicinity of the electrode permits their inverse wave reaction upon reversing the sweep direction. This upon further examination and experimentation can allow the identification of species present in solution and deductions about possible mechanisms [162].

Information that cyclic voltammetry does not yield includes direct information about the nature of the redox couple, peak potentials indicate the nature of the species. To identify specific compounds, standards must be run [146].

## 2.7 Summary

From the literature presented above, the basis of the experimental part of this project is to investigate the electroactivity of accelerants such as petrol, kerosene and diesel using cyclic voltammetry. The information obtained can then be used in the future development of a simple working biosensor for accelerant detection, utilising the methodology presented above.

# CHAPTER 3: EXPERIMENTAL METHODS

## 3.1 General Experimental Overview

The use of accelerants in any research requires the generation of standards, especially when using evaporated/weathered petrol. GC-MS is the standard identification method for petroleum-based accelerants and the evaporated derivatives. As a result, GC-MS will be used in this project for the identification and validation that the petroleum based accelerants used (petrol, kerosene and diesel) correlate to known identification criteria of international standards, with all major components identified.

The second part of this research uses electrochemical analytical techniques of cyclic voltammetry (CV) to investigate and optimise any/all electrical signals created when an accelerant or its evaporated derivative is added to an aqueous solution. The aim of this is to firstly optimise the electrode type (Pt, Au or Ag), and pH (2 or 5). CV will secondly be used to identify any electrical signal that is generated by oxidation/reduction reaction with its surface. If any signal is generated at all, then it will be measured and analysed. An electrical signal is not expected in this part of the research as the non-polar nature of the accelerants being tested are not expected to undergo oxidation/reduction, as accelerants are mostly large hydrocarbon chains.

At this stage, the generation of an electrical signal due to oxidation/reduction of accelerant at the electrode surface would be considered a problem for the further fabrication of the biosensor. This is because it is expected that the accelerant will activate the olfactory receptor and not the base electrode that the olfactory receptor is attached to. The accelerant is hoped to generate an electrical signal in the OR because of its odour receptor functionality. If an electrical signal is generated with the base electrode in reaction with the accelerant, then this interaction must be compensated for in the future layering with the bio-interface and then the olfactory sensor.

Since this experiment has not been completed with accelerants in the past, the first step in the fabrication of a biosensor is narrowing down the base electrode component, solution pH, optimising the CV condition for the solution and its analysis, and most importantly, determining whether an accelerant undergoes oxidation/reduction with the electrode in solution.

## 3.2 Creation of Accelerant Standards and Analysis Using GC-MS

The technique used in this research for the analysis of a fire debris sample is Gas Chromatography – Mass Spectrometry (GC-MS), with the resulting chromatogram showing absorbance versus time.

The sample preparation technique used was passive headspace concentration followed by solvent extraction (adsorption/elution) with the resultant extract analysed using the GC-MS. The passive headspace adsorption/elution was carried out using DFLEX® (Diffusive Flammable Liquid Extraction) device, which is made of a charcoal impregnated polymer strip enclosed in a protective membrane, or an activated charcoal strip (ACS). The solvent used for extraction was carbon disulphide [164].

The advantages of this device are that background produced by the DFLEX at 60°C is low, the lower detection limit as set by ASTM E 1412 –95[165] can be achieved, a minimum amount of carbon disulfide is required for extraction, preservation of evidence prior to analysis is possible by storing the DFLEX® strip in the refrigerator, water does not appear to affect the function of the DFLEX® and the method is time efficient with samples being able to be heated overnight [164].

The standards for non-evaporated, petrol were obtained from a commercial Shell Service Station. A non-evaporated petrol sample was prepared as below for analysis, with non-evaporated petrol then used to make 50%, 90% and 99% evaporated petrol. For the 50% evaporated petrol sample, 900 mL was allowed to evaporate down to 450 mL in the fume cupboard over time. The 90% evaporated petrol sample was prepared with 900 mL allowed to evaporate down to 90 mL over time in the fume cupboard. A flow of nitrogen gas was used to speed up the process.

The non-evaporated and evaporated petrol, kerosene and diesel fuel were then prepared for analysis by the method below.

1L clean paint tins had a tissue placed in each, along with a drop of accelerant, administered with a Pasteur pipette. A DFLEX® device was added to the tin before it was sealed. The tin was then heated in an oven for 16 hours at 60°C. The samples were then removed from the oven. The DFLEX® device was cut open and the ACS removed and stored in a clean 2 mL vial and sealed. The ACS was stored in a freezer until analysis was to be completed. The ACS was desorbed by 800 μL of carbon disulfide, for a minimum time of 20 minutes.

Analysis of the samples for accelerants was carried out with the following equipment:
Agilent 6890 Series GC System;
Agilent 5973 Network Mass Selective Detector;
Agilent 7683 Series Injector and Auto sampler
The parameters for the GC-MS are given below in Table 3.1.

| | |
|---|---|
| Injector | Split/splitless mode (ratio14.6: 1) |
| Column | HP-5MS 5% phenyl methyl siloxane |
| | 30 m x 0.25 μm |
| | 0.25 μm film thickness |
| Detector | MS (Mass Spectrometer) |
| Temperature | Injector 250oC |
| Flow | 1.71 mL/min |
| Sample Size | 0.5 μ L |

**Table 3.1 GC/MS Parameters**

There was an initial solvent delay of 1.75 minutes. The temperature program was as follows: the initial temperature was held at 50°C for 2 min; increased at 10°/min to 230°C; increased by 70°C/min to 290°C and held for 4 minutes. The final run time was 24.86 minutes. The temperature profile used resulted from prior work, and has proved satisfactory in the identification of accelerants and their components.

Peak Analysis of the GC-MS accelerant standard results was completed utilising the MSD Chemstation (Agilent Technologies) Data Analysis Applications (product code G1701DA), with the NIST-98 library used specifically for peak identification.

## 3.3 Cyclic Voltammetry

This technique acquires electroactive reaction information whilst scanning the potential of a working electrode. The potentiostat measures the resulting current and results are obtained as a plot of current versus potential. The sweep determines oxidation and reduction of species over the cycle.

The equipment used was the eDAQ potentiostat and eCorder 401 with eChem v2 software for the analysis*. The sign convention for the results was that the negative currents could be considered anodic (oxidation currents). The compliance voltage of the potentiostat is >10 V, and the current sensitivity is 1nA to 100mA.

Experiments were conducted in order to optimise and investigate the effects of:
Types of working electrodes (Glassy Carbon (GC), Platinum (Pt) and Gold (Au))
Different pH values (5 and 2)
Scan Rates (between 0 and 200 mV/s)
Initial extraction times (0, 5 and 10 minutes)
Accelerant types (petrol, 50% EP, 90% EP, 99% EP, kerosene and diesel)

* ADInstruments Pty, Ltd
6/4 Gladstone Rd,
Castle Hill, NSW 2154
Australia

Experiments were completed using a Ag/AgCl (3M KCl) reference electrode provided by eDAQ, as was detailed in the preferred method by Saby and Luong [154]. The auxiliary electrode used was platinum, and was also provided by eDAQ.

Initial parameters considered were:
GC working electrode
pH 5 (phosphate buffer)
Scan Rates (50, 80, 100, 125 and 200 mV/s)
Initial extraction times of 0, 5 and 10 minutes
Accelerant types of petrol, 90% EP and kerosene

The pH 5 buffer (0.1M) was prepared with 85% orthophosphoric acid (Analytical Univar Reagents), with final pH adjustment to 5 completed with the addition of NaOH (1M) solution (Aldrich Chemicals). The pH was recorded daily using a calibrated pH meter, with pH measured from 5.00 – 5.13. Buffer was kept for 2 weeks in a dark cupboard before it was discarded and a fresh solution made.

The pH 2 buffer (0.1M) was made with tartaric acid (Analytical Univar Reagents), with pH recorded daily as with the pH 5 buffer. The pH was measured between 1.28 –1.31, and was also discarded after two weeks.

Amongst the experimental variables considered was the mode of cleaning the electrodes, since the working electrode and cuvette could be contaminated with adsorbed species during a given run. Three types of cleaning method were used for the working electrode:
Wiping of the electrode with a tissue after being rinsed with distilled water
The step above as well as polishing the electrode on a felt pad with alumina slurry before being rinsed for a second time with distilled water
Rinsing the electrode and wiping with a tissue before rinsing the electrode in a series of six n-hexane baths (AnalaR Chemicals), then cleaned on the felt pad with alumina slurry and a final rinse with distilled water and wiping with a tissue.

For the cuvette, rinsing with distilled water was changed to include rinsing with a mild detergent in distilled water, wiping out with a tissue, rinsing with the detergent and distilled water mix, rinsing with distilled water and finally rinsing with ethanol. The cuvette was then tapped on absorbent paper and allowed to air dry.

Buffer solution (1mL) was then added to the cuvette. After the lid was placed on the cuvette, the electrodes were inserted and connected to the potentiostat before the 100μL of accelerant was added to the system. Once the accelerant was added, the potentiostat was started (for t = 0 min runs). If the run was for t = 5 min or t = 10 min, a timer was started when the accelerant was added and when the extraction time period was over, data collection started.

Once the cleaning of the electrodes and cuvette was standardized, experimentation went further into the effects of;
Electrode (GC, Pt and Au)
pH (5 and 2)
Extraction time (5, 10, 20, 25, 40 and 50 mV/s)
Accelerant type (petrol, 50% EP, 90% EP, 99% EP, kerosene and diesel) and
Temperature control, which was achieved via an insulating jacket around the electrochemical cell, maintained at 22 – 22.5°C

# CHAPTER 4: RESULTS and DISCUSSION

## 4.1 STANDARDS ANALYSIS

### 4.1.1 Summary

GC-MS was carried out on the following samples of petrol, 50% evaporated petrol (EP) , 90% evaporated petrol, and 99% evaporated petrol, kerosene and diesel. Below are the chromatograms for the accelerants analysed: petrol (Figure 4.1); 50 %EP (Figure 4.2); 90% EP (Figure 4.3); 99%EP (Figure 4.4); kerosene (Figure 4.5); and diesel (Figure 4.6). Evaporated petrol samples are samples which have had a percentage of their volume evaporated off over time. An example would be 99% EP, where 99% of the original volume of petrol has been evaporated off, leaving 1% of the initial volume recorded.

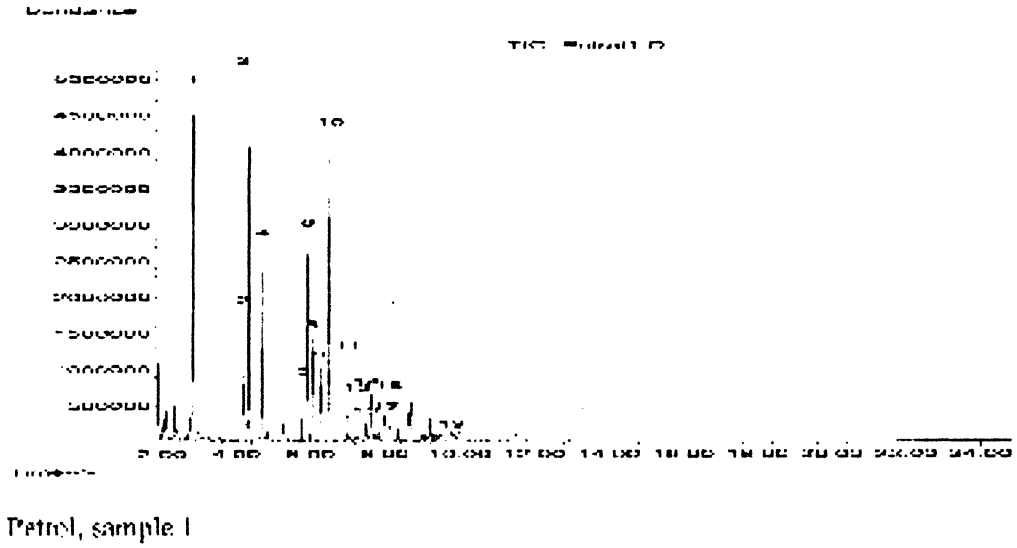



**Figure 4.1 Chromatogram of petrol with peaks of interest identified as numbers**

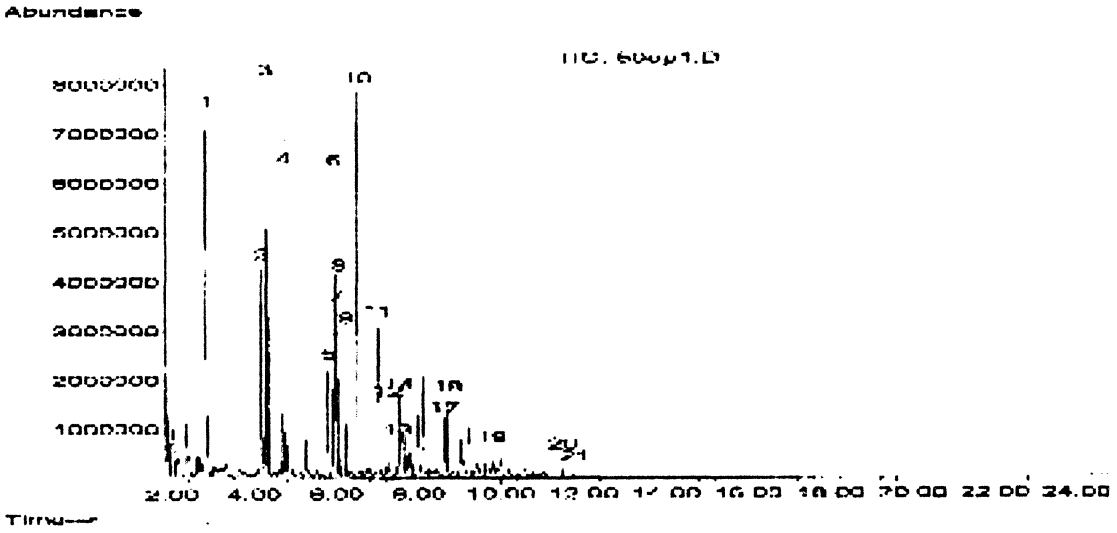



**Figure 4.2 Chromatogram of 50% EP with peaks of interest numbered**

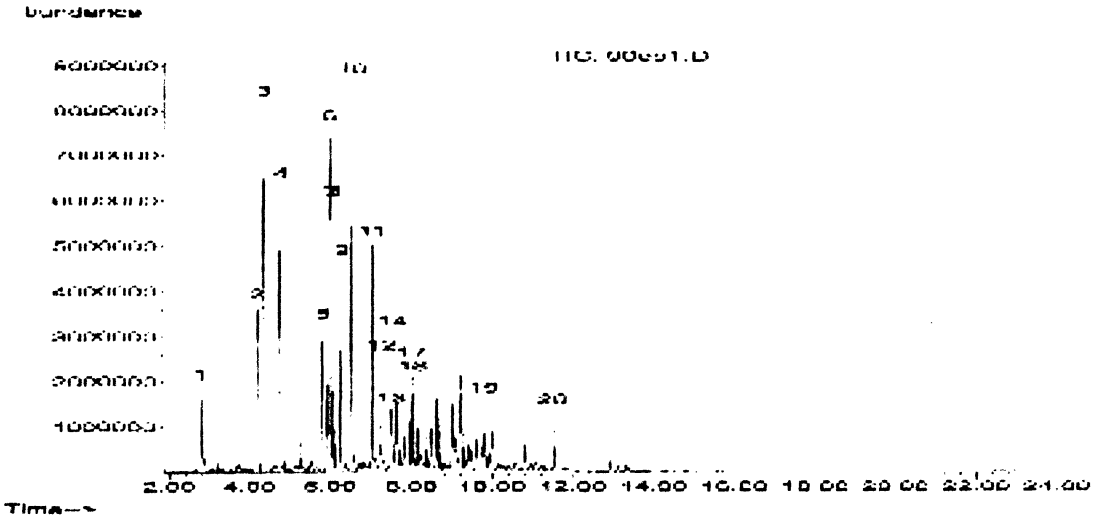
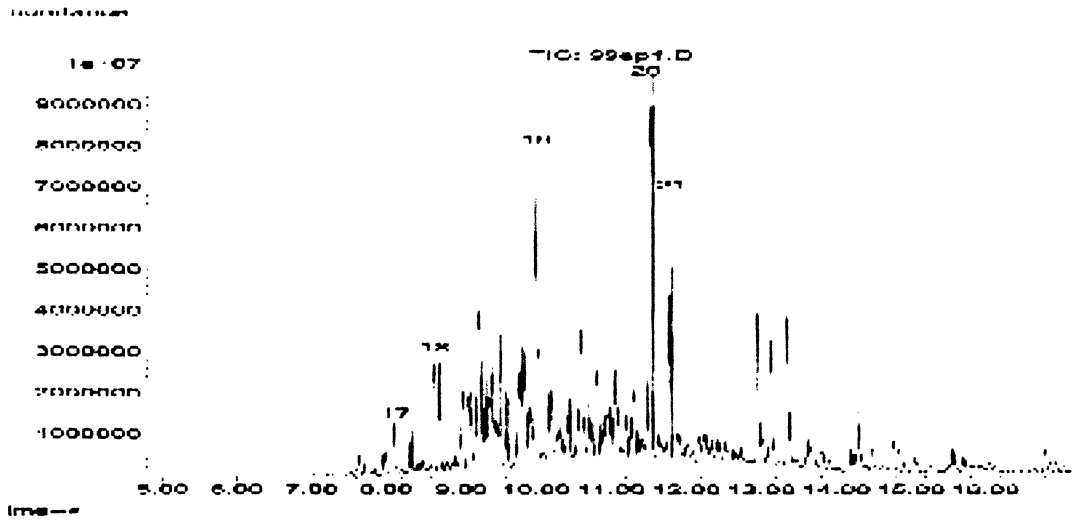
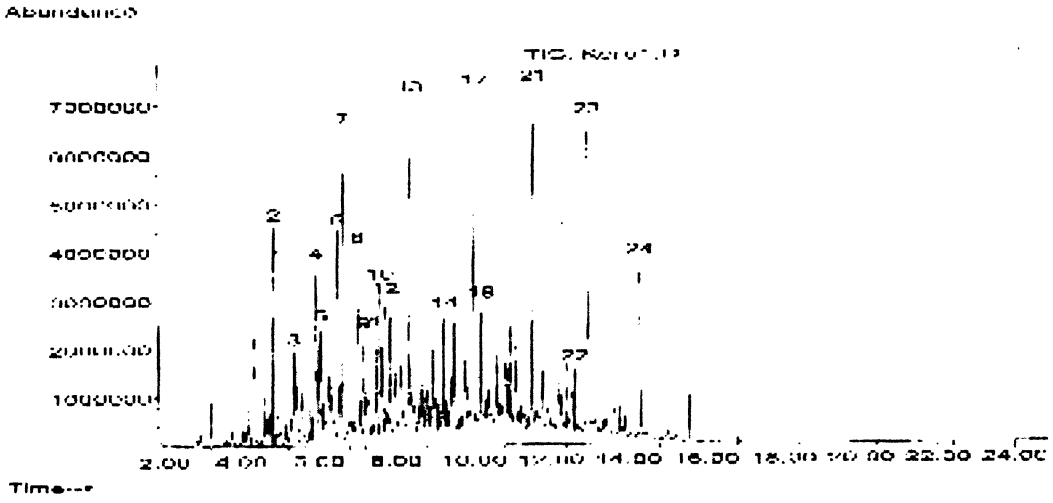



**Figure 4.3 Chromatogram of 90% EP with peaks of interest numbered**



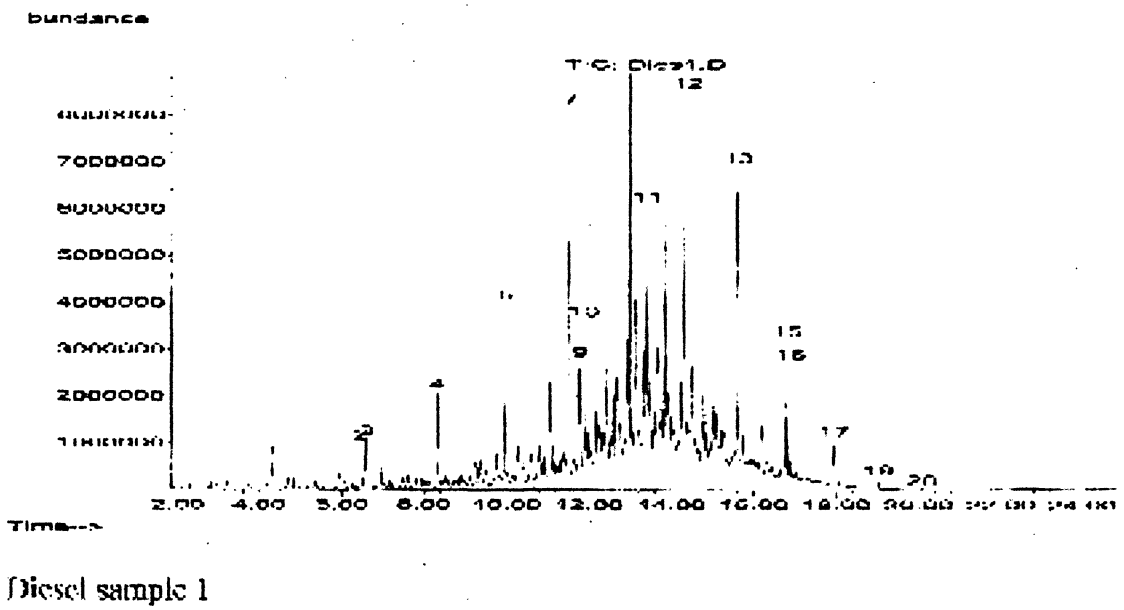

99%EP sample

**Figure 4.4 Chromatogram of 99%EP with peaks of interest numbered**




Kerosene sample

**Figure 4.5 Chromatogram of kerosene with peaks of interest numbered**




Diesel sample 1

**Figure 4.6 Chromatogram of diesel with peaks of interest numbered**

### 4.1.2 Present Accelerant Detection Techniques

At present, the detection of accelerants is carried out either at the fire scene and/or in the laboratory, for confirmatory analysis. At the fire scene, the portability and reliability of accelerant detection has limited the techniques to the use of canines and gas detectors. In the laboratory, a GC-MS is one of the standard techniques used for accelerant confirmation for many years. ASTM criteria are then used to identify the accelerant [47]. GC-FID is also used in many laboratories, with MS used if there are problems such as conflicting pyrolysis products.

From the ASTM criteria and the GC-MS chromatograms of non-evaporated and evaporated petrol, target peaks for the identification of petrol in fire debris samples have been identified. Table 1.1 shows 21 components of which a range of organic compounds should be present in a fire debris sample to positively identify the accelerant as petrol.

| Peak | Component | Peak | Component |
|---|---|---|---|
| 1 | Toluene | 12 | Indane |
| 2 | Ethyl benzene | 13 | 1,3-diethyl benzene |
| 3 | m-xylene/p-xylene | 14 | 1-methyl-3-propyl benzene |
| 4 | o-xylene | 15 | 1,4-diethyl benzene |
| 5 | Propyl benzene | 16 | 4-ethyl-1,3-dimethyl benzene |
| 6 | 1-ethyl-3-methyl benzene | 17 | 4-ethyl-1,2-dimethyl benzene |
| 7 | 1-ethyl-4-methyl benzene | 18 | 2-ethyl-1,3-dimethyl benzene |
| 8 | 1,3,5-trimethyl benzene | 19 | Naphthalene |
| 9 | 1-ethyl-2-methyl benzene | 20 | 2-methyl naphthalene |
| 10 | 1,2,4-trimethyl benzene | 21 | 1-methyl naphthalene |
| 11 | 1,2,3-trimethyl benzene | | |

**Table 4.1 Component Results for Petrol**

Using the same ASTM criteria and analysing the kerosene GC-MS chromatogram, there are 24 components of which the majority should be present for the accelerant to be classified. The components are mainly $C_9$ to $C_{17}$ alkanes, however there are some components that are also shared with Petrol. They are m-xylene/p-xylene, 1,2,4-trimethyl benzene and 1,2,3-trimethyl benzene. Table 1.2 shows the important components for kerosene.

| Peak | Component | Peak | Component |
|---|---|---|---|
| 1 | m-xylene/p-xylene | 13 | Undecane |
| 2 | Nonane | 14 | 1,2,4,5-tetramethyl benzene |
| 3 | Propyl cyclohexane | 15 | 5,7-dimethyl undecane |
| 4 | 1-ethyl-4-methyl benzene | 16 | 3,8-dimethyl decane |
| 5 | 1,2,4-trimethyl benzene | 17 | Dodecane |
| 6 | 1,2,3-trimethyl benzene | 18 | 2,6-dimethyl undecane |
| 7 | Decane | 19 | 7-propyl tridecane |
| 8 | 4-methyl decane | 20 | 3,6-dimethyl octane |
| 90 | Butyl cyclohexane | 21 | Tridecane |
| 10 | Decahydro-trans naphthalene | 22 | 2-methyl-5-propyl nonane |
| 11 | 4-ethyl-1,2-dimethyl benzene | 23 | Tetradecane |
| 12 | 2-methyl decane | 24 | Pentadecane |

**Table 4.2 Component Results for Kerosene**

Relative results for petrol, kerosene and diesel are discernibly different and do provide more information on the nature of these accelerants, however further analysis in the area is not needed.

ASTM criteria and analysis of the diesel GC-MS chromatogram have identified 25 components for characterisation. It is in the n-alkane peak range of $C_9 - C_{23}$, and is classified as a Heavy Petroleum Distillate by the ASTM. Common components with petrol are m-xylene/p-xylene, 1,2,3-trimethyl benzene, 2-methyl naphthalene and 1-methyl naphthalene. Diesel also shares the common components m-xylene/p-xylene, 1,2,3-trimethyl benzene, decane, tridecane, pentadecane and undecane with kerosene. There are also components common to petrol, kerosene and diesel. Namely m-xylene/p-xylene and 1,2,3 –trimethyl benzene. Table 4.3 shows the component results for diesel.

| | | | |
|---|---|---|---|
| 1 | m-xylene/p-xylene | 14 | Hexadecane |
| 2 | 1,2,3-trimethyl benzene | 15 | 2,6,10-trimethyl Pentadecane |
| 3 | Decane | 16 | Heptadecane |
| 4 | Undecane | 17 | 2,6,10,14-tetramethyl Pentadecane (pristane) |
| 5 | Dodecane | 18 | Octadecane |
| 6 | 1,2,3,4-tetrahydro-5-methyl Naphthalene | 19 | Nonadecane |
| 7 | Tridecane | 20 | Eicosane |
| 8 | 2-methyl naphthalene/1-methyl naphthalene | 21 | Heneicosane |
| 9 | 2-methyl naphthalene | 22 | Docosane |
| 10 | 1,2,3,4-tetrahydro-2,7-dimethyl naphthalene | 23 | 2,6,10,14-tetramethyl hexadecane (phytane) |
| 11 | 2,6-dimethyl naphthalene | 24 | Tetracosane |
| 12 | Pentadecane | 25 | 11-decyltetracosane |
| 13 | 1,6,7-trimethyl naphthalene | | |

**Table 4.3 Component Results for Diesel**

Peak analysis using GC-MS software identified varying numbers of components in the accelerant mixtures used to classify the accelerant petrol. See table 4.4 below for a summary of the peaks not identified, and whether the accelerant was positively identified given the standards set out in table 4.1 (identified by a "yes" or "no"). Some peaks are not identified in the samples analysed for a variety of reasons including that the petrol, what companies refined from crude oils [2], come from different areas around the world. Different regions have slightly different crude oils leading to slightly different petrol compositions. Differences in final composition are also a function of different cracking/reformation regimes used by the oil companies to optimise fuel performance for local markets, irrespective of hydrocarbon source. Also the ASTM criteria provide for this disparity, with the overall chromatograms "pattern" and ratio of peaks to each other a secondary identification tool.

| Accelerant | Total Components for Identification | Component Peak Numbers NOT identified | Component Peaks | Confirmation of Accelerant |
|---|---|---|---|---|
| Petrol | 21 | 15 | 1,4-diethyl benzene | Yes |
| | | 16 | 4-ethyl-1,3-dimethyl benzene | |
| | | 20 | 2-methyl naphthalene | |
| | | 21 | 1-methyl naphthalene | |
| 50% E.P. | 21 | 15 | 1,4-diethyl benzene | Yes |
| | | 16 | 4-ethyl-1,3-dimethyl benzene | |
| 90% E.P. | 21 | 15 | 1,4-diethyl benzene | Yes |
| | | 16 | 4-ethyl-1,3-dimethyl benzene | |
| | | 21 | 1-methyl naphthalene | |
| 99% E.P. | 21 | 15 | 1,4-diethyl benzene | Yes |
| | | 16 | 4-ethyl-1,3-dimethyl benzene | |
| Kerosene | 24 | 15 | 5,7-dimethyl undecane | Yes |
| | | 16 | 3,8-dimethyl decane | |
| | | 19 | 7-propyl tridencane | Yes |
| Diesel | 25 | 6 | 1,2,3,4-tetrahydro-5-methyl naphthalene | |
| | | 8 | 2-methyl naphthalene/1-methyl naphthalene | |
| | | 14 | Hexadecane | |
| | | 18 | Octadecane | |
| | | 21 | Heneicosane | |
| | | 22 | Docosane | |
| | | 23 | 2,6,10,14-tetramethyl hexadecane | |
| | | 24 | Tetracosane | |
| | | 25 | 11-decyltetracosane | |

**Table 4.4 Summary of peaks not identified in accelerant standards**

### 4.1.3 GC Analysis Results and Review

Overall, the accelerants used in the experiments were identified with a high degree of certainty to be petrol, 50% evaporated petrol, 90% evaporated petrol, 99% evaporated petrol, kerosene and diesel. ASTM criteria were used with discrepancies identified and explained by refining techniques used by oil companies. ASTM criteria also allowed for these discrepancies.

## 4.2 CYLCIC VOLTAMMETRY

### 4.2.1 Initial Experiments

Initial experiments were completed with the first cleaning step for the working electrode and results obtained were not reliable. As a result, they have been discarded from further discussion.

pH 5 experiments

Once cleaning was standardised, the following results were recorded

### 4.2.2 Buffer plus electrodes

The following voltammogram (Figure 4.8) shows at pH 5, the 3 different working electrode signals recorded.

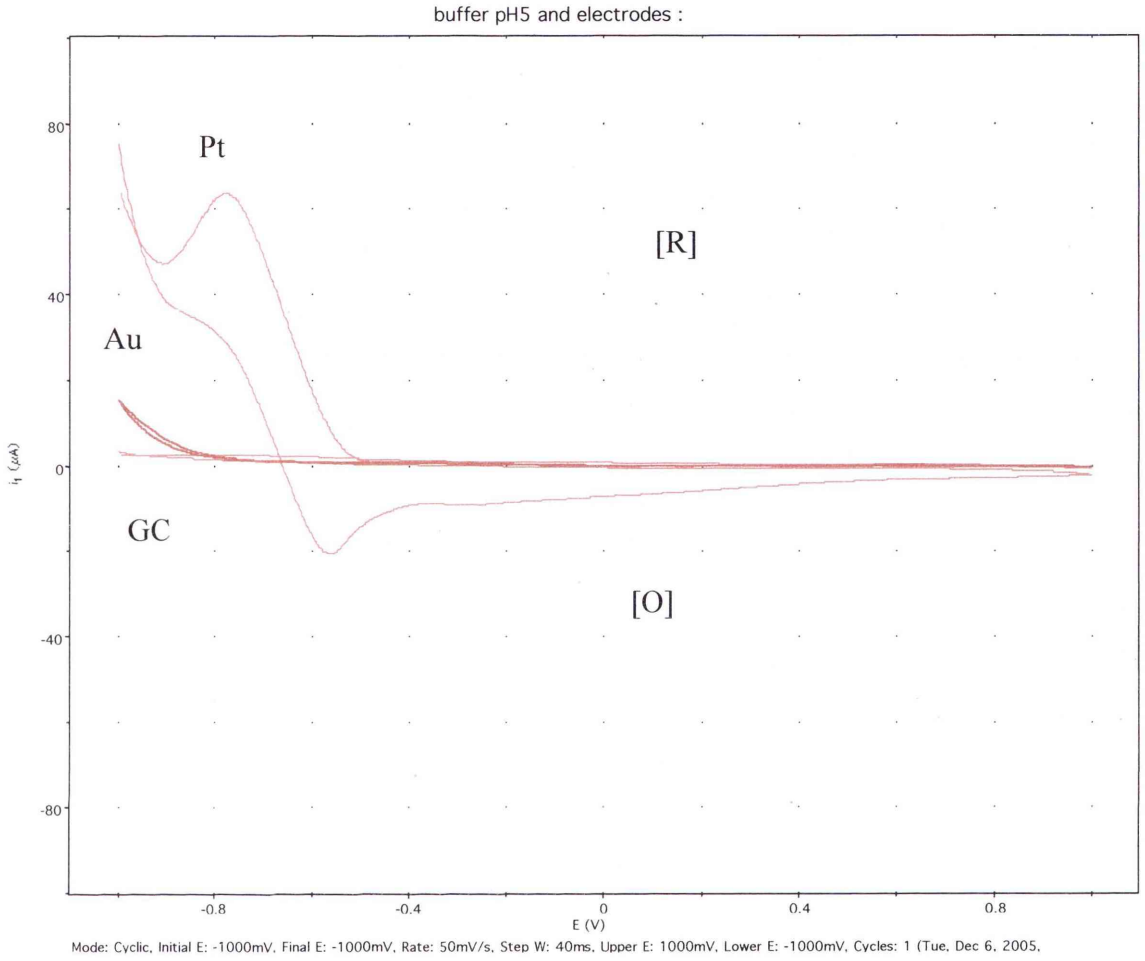



**Figure 4.7 pH 5 Buffer plus electrodes (GC, Pt and Au) voltammogram at scan rate 50 mV/s**

From the above figure (4.7) it can be seen that both GC and Au electrodes provide little oxidation and reduction information about the buffer solution. Platinum is the better performing electrode. Information on the GC and Au electrodes can only be seen by decreasing the scale dramatically, see below in figure 4.8.

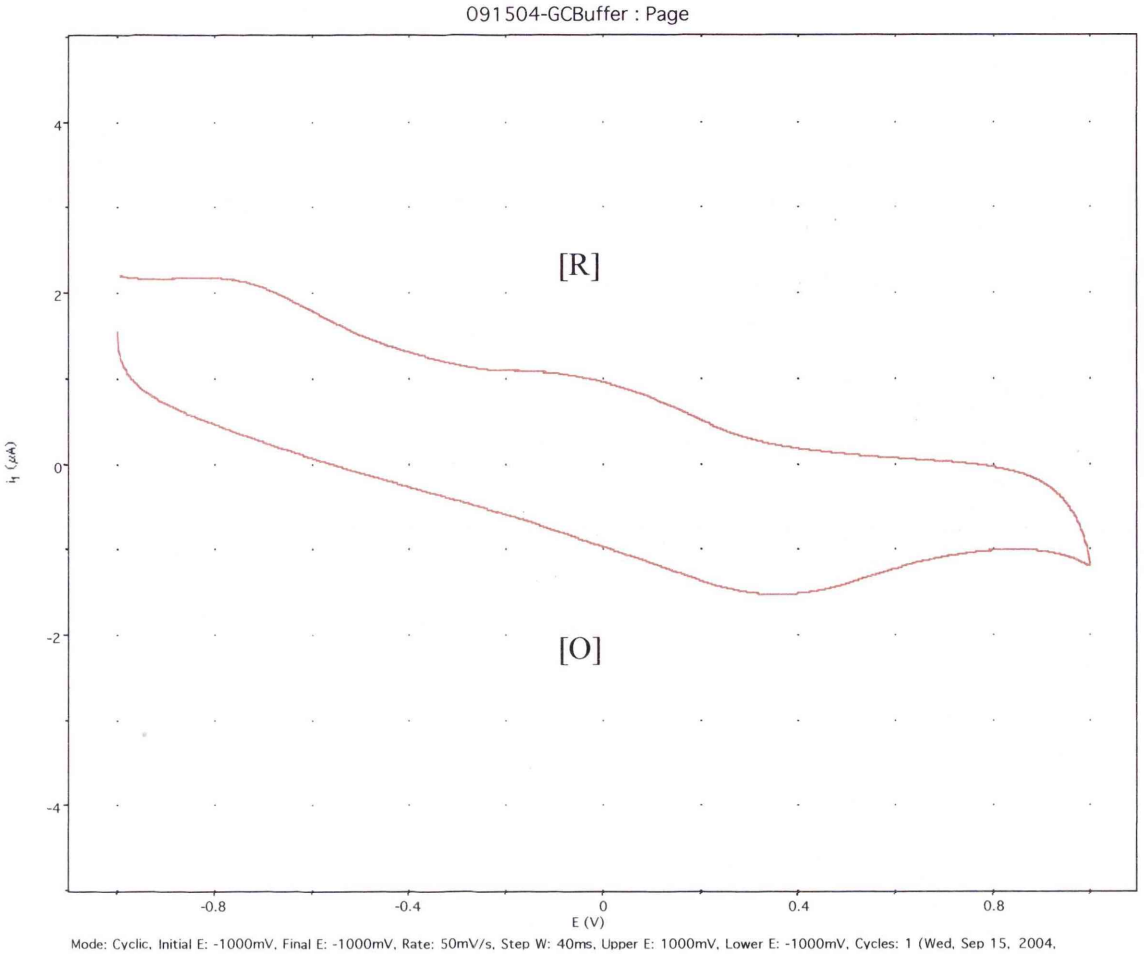



**Figure 4.8 pH 5 Buffer plus GC electrode voltammogram at scan rate 50 mV/s and enlarged scale showing peaks**

The above figure (4.8) using a glassy carbon electrode shows the oxidation (approximately +0.05V) and reduction peaks (approximately –0.7V and –0.05V) for the buffer were present, but not very distinct. Experimentation into the enhancement of the peak resolution via alteration of the scan rate from 5 to 50 mV/s was determined to be unsuccessful. The resolution above was the best of all scan rates attempted.

The platinum electrode however, allows peak trends to be identified more easily as the peaks are well resolved (see Figure 4.9 below) at a larger current scale (+/- 100 μA). Oxidation peak at –0.574V and Reduction peak at –0.784V.

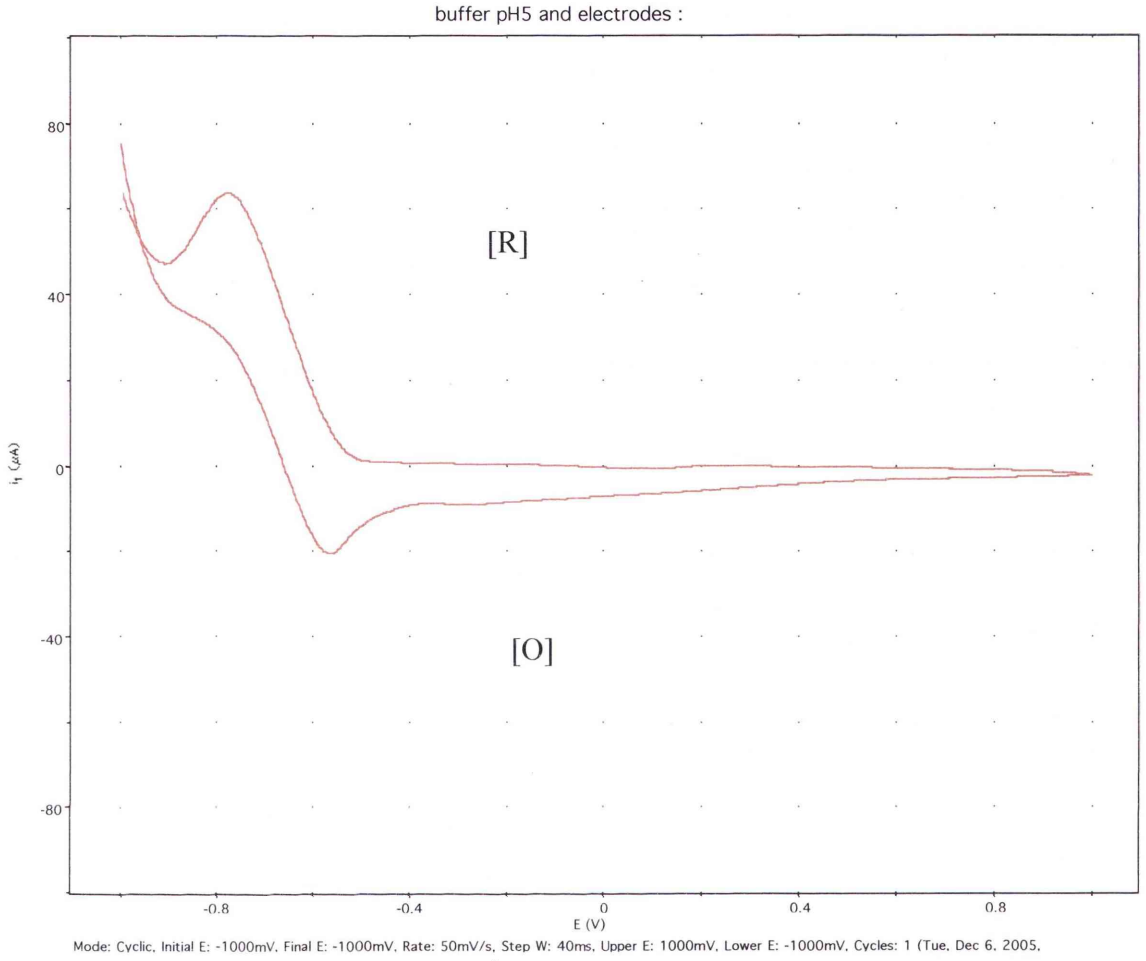



**Figure 4.9 pH 5 Buffer plus Pt electrode voltammogram at scan rate 50 mV/s**

Gold showed some unusual peaks upon closer examination (see Figure 4.10), however since the current scale had to be decreased to +/- 5 μA to see any resolution, it was not examined further at this pH because the scale reduction provided difficulties in overall signal detection, which would not transfer well for future experimentation.

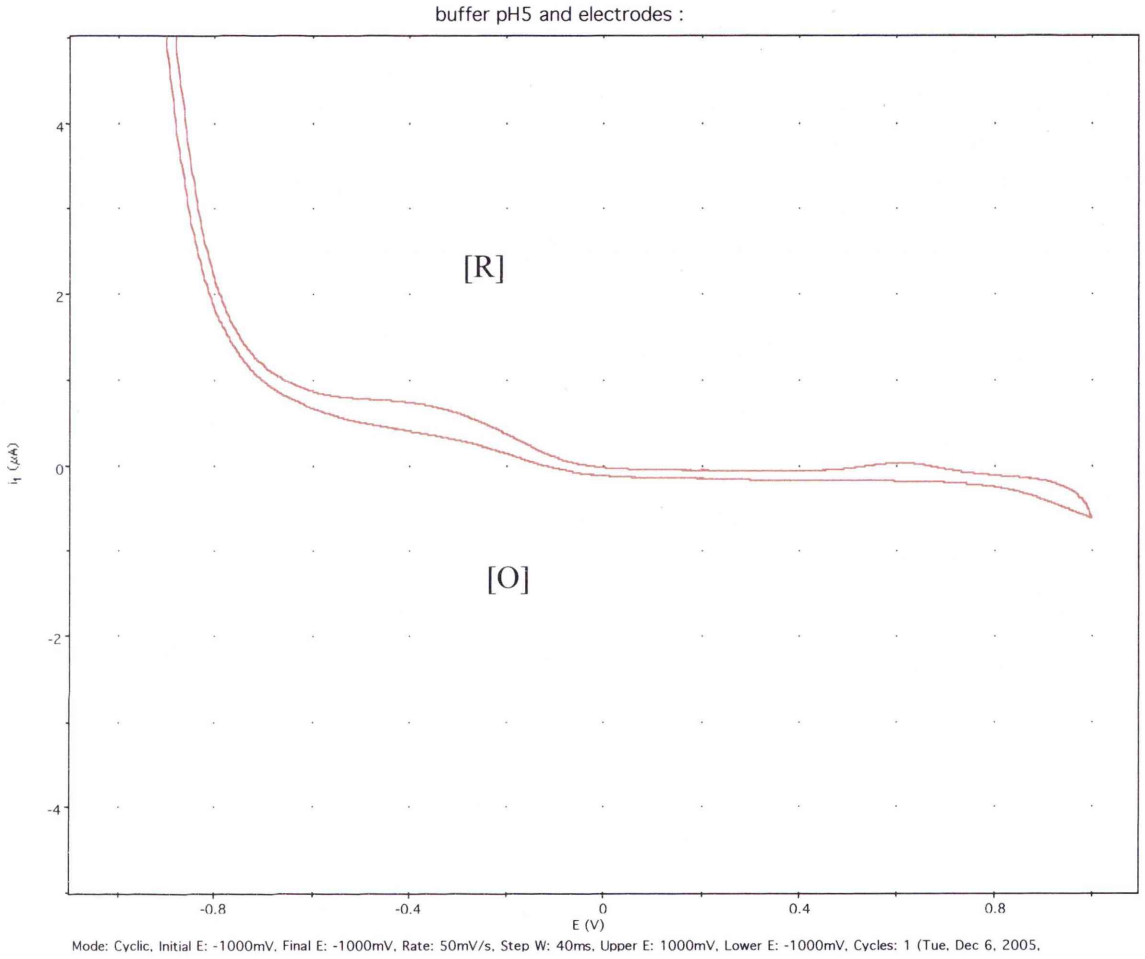



**Figure 4.10 pH 5 Buffer plus Au electrode voltammogram at scan rate 50 mV/s and scale 5 μA.**

Overall the platinum electrode provided the best peak resolution at an easy identifiable level.

### 4.2.3 Buffer plus electrodes and accelerants

#### *4.2.3.1 Glassy carbon electrode and accelerants*

This combination of experimental parameters provided little information. Optimal scan rate was determined to be 50 mV/s and extraction time was determined to be 0 minutes. There was no change in buffer signal when the accelerants petrol, 50% EP, 90% EP and kerosene were added to the cell. 99% EP continually provided an unstable signal that was not clarified with changes to the cleaning method, whilst diesel provided a possible peak shift. However due to the unreliability of the data, much more experimentation is required to stabilise the system further. The results from the platinum electrode below provide much more distinct and reliable data hence the decision was made that at pH 5 the Glassy Carbon electrode was to be discarded from future experimentation as a viable electrode. At pH 2, experimentation would continue, but only to determine if the buffer plus accelerant trend at pH 5 continues. That is, that the accelerant has no obvious impact on the electrode and buffer interactions. If this is true, then pH 5 can be used as the pH of choice.

#### *4.2.3.2 Platinum electrode and accelerants*

Cleaning issues, especially for the accelerants 99% EP and diesel were addressed early, and results stabilised with the method change. Scale was 100 μA, showing a strong electrical response. Optimal conditions chosen were t = 0 and scan rate 50 mV/s. For the sets of buffer run with the platinum electrode, standard deviation was preferred to calculate the error for each peak at the individual scan rates (below in table 4.5). Unable to being able to collect more data on the accelerants tested over all scan rates, standard deviation error calculations were not valid given the low number of data points. As a result, probable errors have been calculated (table 4.6) for the peaks recorded.

Below in Table 4.5 are the average oxidation and reduction products peak potential values for pH 5 buffer and platinum electrode over 6 scan rates (V).

| Scan Rate (mV/s) | [O]/V | [O]/V | [R]/V |
|---|---|---|---|
| 5 | -0.827 +/- 0.004 | -0.565 +/-0.001 | -0.725 +/- 0.001 |
| 10 | -0.860 +/- 0.0007 | -0.584 +/-0.000 | -0.741 +/- 0.002 |
| 20 | -0.874 +/- 0.001 | -0.577+/- 0.002 | -0.752 +/- 0.0007 |
| 25 | -0.895 +/- 0.002 | -0.565 +/-0.003 | -0.768 +/- 0.002 |
| 40 | -0.895 +/- 0.002 | -0.570 +/- 0.0007 | -0.774 +/- 0.002 |
| 50 | -0.896 +/-0.002 | -0.574 +/-0.01 | -0.784 +/- 0.009 |

**Table 4.5 pH 5 Buffer and Pt electrode average peak values (V) over variable scan rates (mV/s)**

Table 4.6 shows optimised oxidation and reduction peak potential results at 50 mV/s scan rate, for all the accelerants tested, except 99% EP, which was been discarded from testing due to the unreliable data recorded.

| Compound | [O]/V | [O]/V | [R]/V |
|---|---|---|---|
| Buffer | -0.896 +/-0.002 | -0.574 +/-0.01 | -0.784 +/- 0.009 |
| Petrol | - | -0.558 +/- 0.02 | -0.823 +/- 0.02 |
| 50% EP | - | -0.546 +/- 0.02 | -0.849 +/- 0.03 |
| 90% EP | - | -0.533 +/- 0.02 | -0.820 +/- 0.02 |
| Kerosene | - | -0.536 +/- 0.006 | -0.790 +/- 0.006 |
| Diesel | - | -0.522 +/- 0.01 | -0.891 +/- 0.04 |

**Table 4.6 pH 5, Pt electrode with all peak values (V) of the accelerants at scan rate 50mV/s**

For all accelerants, all probable error calculations were completed on 50mV/s scan rate, over the three times to allow for a more accurate calculation. As there was determined to be no significant change in the peak values over time, this is a valid correlation.

From the above set of results, it is seen that the first oxidation peak, found from the buffer solution, is not apparent in any of the accelerants tested. This could be due to the accelerants suppressing the peak or, more likely, the indistinct nature of the peak in buffer making its identification difficult when accelerants are added.

The data from the diesel accelerant show a shift in the reduction peak from –0.78 to –0.89 V (see Figure 4.11 below). This shifting in the peaks is thought to be due to the adsorption on the electrode surface of a diesel contaminant, which is interfering with the electroactive reaction taking place of the buffered solution.

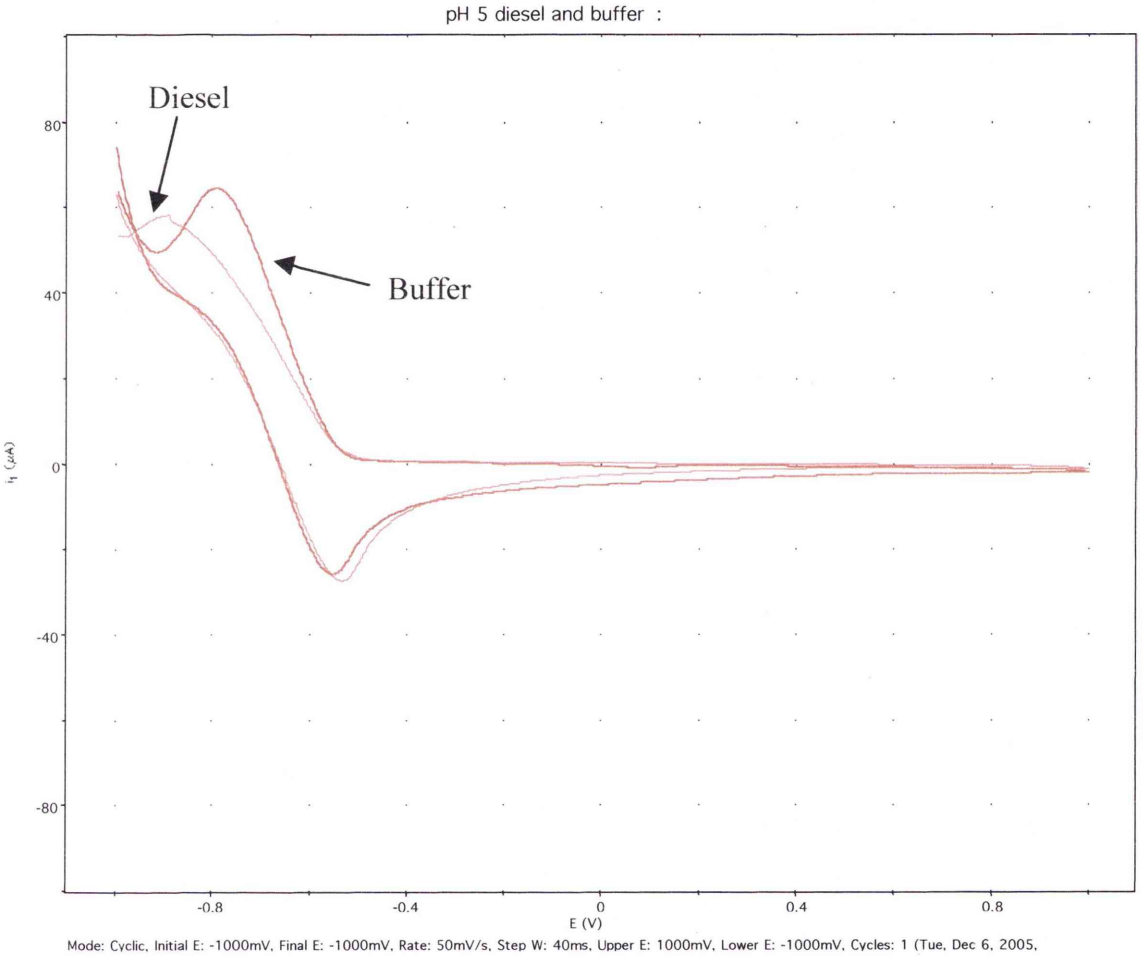



**Figure 4.11 pH 5 buffer plus Pt and diesel plus Pt voltammogram overlay at scan rate 50 mV/s**

#### *4.2.3.3 Gold electrode and accelerants*

Only preliminary experiments were completed with this electrode, with initial findings not encouraging further investigation. Although peaks were identifiable on a smaller scale analysis, compared with platinum, the results were not highly discernable. Accelerants added to the cell did not change this result. Some information was obtained and mirrored the GC findings, that there was no change in results between extraction times and that the scan rate of 50mV/s was optimal.

### 4.2.4 Summary pH 5 results

It was determined that after a comparison of the three electrodes abilities to determine oxidation and reduction peak potentials from the solutions tested, platinum was the preferred choice. There was no discernable difference in oxidation and reduction peak potentials between the extraction times of 0, 5 and 10 minutes. Hence optimal extraction time was determined as t = 0 minutes. Scan rate was optimised at 50 mV/s, showing all peaks of interest across the pHs and accelerants. 99% EP was discarded as a test accelerant given the unreliable results it provided; even after additional cleaning steps to the electrode a clean signal could not be measured. This could be due to the fact that the 99%EP sample has most of its lighter components evaporated off. The remainder of the sample is heavy high chain carbon products that could be classified as very "dirty" when added to a buffer solution, sticking to the electrode and causing interference with the buffered reaction. In appendix 1, the average scan rate results for platinum electrode and buffer, a platinum electrode and petrol voltammogram (at scan rate 50mV/s) and the average accelerant scan rate results with the platinum electrodes can be found. These results help to highlight the optimisation of 50mV/s as the best scan rate at pH 5 for the platinum electrode.

### 4.2.5 pH 2 experiments

#### *4.2.5.1 Buffer plus electrodes*

The voltammogram (figure 4.12) given below, which shows all three electrodes with pH 2 buffer, identifies no significant peaks except for the platinum electrode. The single peak at –0.29V can be attributed to the evolution of hydrogen at the electrode surface at sufficiently low potentials. This potential lay with respect to the Ag/AgCl electrode, which is very close to the reversible thermodynamic potential for hydrogen evolution, indicating that the charge transfer process on the platinum electrode is very fast.

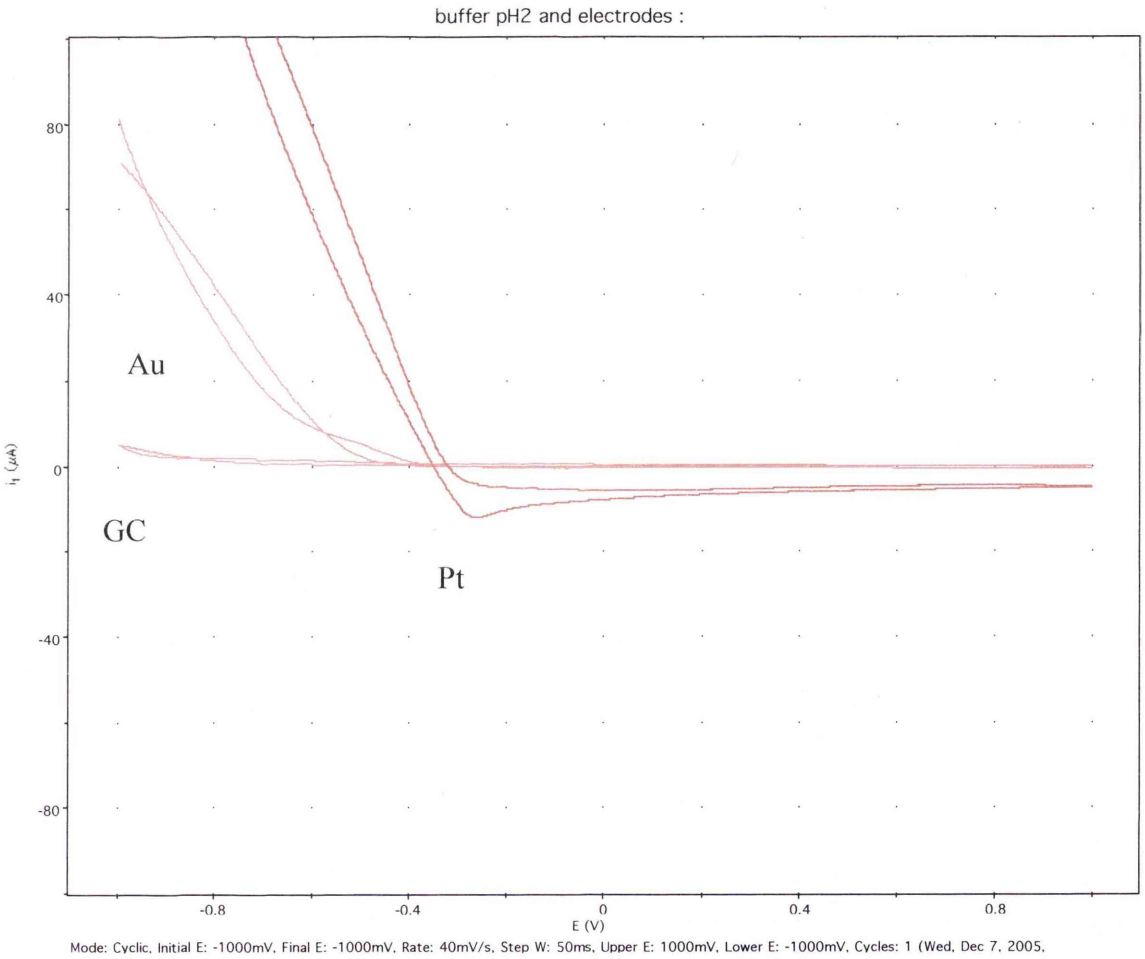



**Figure 4.12 pH 2 Buffer plus GC, Pt and Au electrodes voltammograms overlayed at scan rate 40mV/s, scale 100 µA.**

### 4.2.6 pH 2 Summary

The voltammograms for buffer with all electrodes tested and all accelerants showed no significant results, so pH 2 as a solution was discarded from future experimentation.

### 4.2.7 CV Review

From the results detailed, the platinum electrode has been identified as the best electrode base to continue the biosensors fabrication on to. pH also plays a part in the electrodes signal generation, with pH 2 showing no significant base electrical signal generation and being discarded from future experiments. pH 5 was therefore determined to be the optimal solution for future biosensor experiments. The signal generation was uneventful and attributed to the buffer solution only, NOT accelerant addition undergoing oxidation or reduction in solution. This result is also encouraging as the aqueous system in biological olfaction systems (i.e. in the mucus of the nose) is pH neutral (pH = 7). Therefore it is important to note that the CV system attempting to mimic this biological system works better when approaching biological system conditions, such as pH 7. This could also be a future avenue of research in the fabrication process.

Accelerant use in the CV system has shown, as predicted, to generate no electrical signal. This is also encouraging for the future development of the biosensor, as it has now been shown that the accelerant will not react with the electrode base of the biosensor's structure. This also means that any signal generated can be attributed to the accelerant interacting with the olfactory receptor or the biological interface used to "stick" the olfactory receptor to the electrode. More testing needs to identify interaction (if any) of the interface, and then exclude or compensate for the interface/accelerant interaction. As a result the current research however, no electrical signal needs to be accounted for between electrode and accelerant in future signal interpretation and identification.

# CHAPTER 5: CONCLUSION and FUTURE WORK

## 5.1 Conclusion

All accelerant standards were identified using GC-MS analysis and ASTM criteria for the identification of accelerant residues.

The best cyclic voltammetry reaction conditions for future development of a biosensor for the detection of accelerants were determined to be as follows:
pH 5
Platinum electrode
Extraction time of 0 minutes, and
Scan rate of 50 mV/s

Although there was determined to be no electroactive species in the accelerants, this result is very positive for future research. This result indicates that the accelerants do not undergo oxidation/reduction with the bare electrode. An electrode that does not react to an accelerant bodes well for the adhesion of an olfactory receptor that does react to the accelerants odour, giving a recordable electrical signal. This is positive for the initial stage of creating a smart biological structure that acts as a sensor for odour detection.

## 5.2 Future Work

It should be noted that some adsorption of accelerant compounds was detected and its quantification may be determined via impedance spectroscopy. Earlier work utilised impedance measurements to detect small signals from olfactory receptors when odours were passed over them. The practical examination of impedance at the electrodes is one area where research should be expanded. The amount adsorbed of a particular molecular species can be calculated from the Gibbs adsorption isotherm. From trial molecular models of the adsorbed species, the molecular orientation can be determined and whether a monolayer or bilayer etc has been formed.

There should also be further the investigation into the attachment of the olfactory receptor to the platinum electrode via a bioadhesive intermediary, such as the MAP using Saby and Luong's methodology [154] with electroactive conduction proven. This biopolymer intermediary film (MAP) attached to the platinum electrode requires morphological examination via Atomic Force Microscopy (AFM) and Environmental Scanning Electron Microscopy (ESEM) in order to determine if the film is uniformly distributed and determine the degree of porosity.

Experimentation into different olfactory receptor proteins to determine if different receptor proteins respond to the same or different accelerants should be completed. This would allow for the fabrication of a sensor array with a high odour discrimination power.

The branched areas of sensor arrays and data analysis techniques such as artificial neural networks [49, 92, 95, 96, 110, 120-122], as well as the nano-sizing of such an array, are also areas that need to be incorporated in the future.

# APPENDIX 1

## pH 5 Buffer + Pt electrode Peak Analysis Results

## Peak Averages (V) over 6 scan rates

| Scan Rate | [O] | [O] | [R] |
|---|---|---|---|
| 5 | -0.8270 | -0.5650 | -0.7240 |
| 10 | -0.8603 | -0.5840 | -0.7410 |
| 20 | -0.8740 | -0.5773 | -0.7523 |
| 25 | -0.8950 | -0.5650 | -0.7683 |
| 40 | -0.8957 | -0.5703 | -0.7747 |
| 50 | -0.8960 | -0.5743 | -0.7840 |

## Individual scan rate results

| Scan Rate | Repeat | [O] | [O] | [R] |
|---|---|---|---|---|
| 5 | 1 | -0.8240 | -0.5660 | -0.7240 |
| 5 | 2 | -0.8340 | -0.5660 | -0.7240 |
| 5 | 3 | -0.8240 | -0.5640 | -0.7260 |
| 5 | 4 | -0.8260 | -0.5660 | -0.7260 |
| 5 | 5 | -0.8320 | -0.5640 | -0.7260 |
| 5 | 6 | -0.8220 | -0.5640 | -0.7240 |
| | **Average** | **-0.8270** | **-0.5650** | **-0.7240** |

| Scan Rate | Repeat | [O] | [O] | [R] |
|---|---|---|---|---|
| 10 | 1 | -0.8600 | -0.5840 | -0.7440 |
| 10 | 2 | -0.8600 | -0.5840 | -0.7400 |
| 10 | 3 | -0.8620 | -0.5840 | -0.7420 |
| 10 | 4 | -0.8600 | -0.5840 | -0.7420 |
| 10 | 5 | -0.8600 | -0.5840 | -0.7400 |
| 10 | 6 | -0.8600 | -0.5840 | -0.7380 |
| | **Average** | **-0.8603** | **-0.5840** | **-0.7410** |

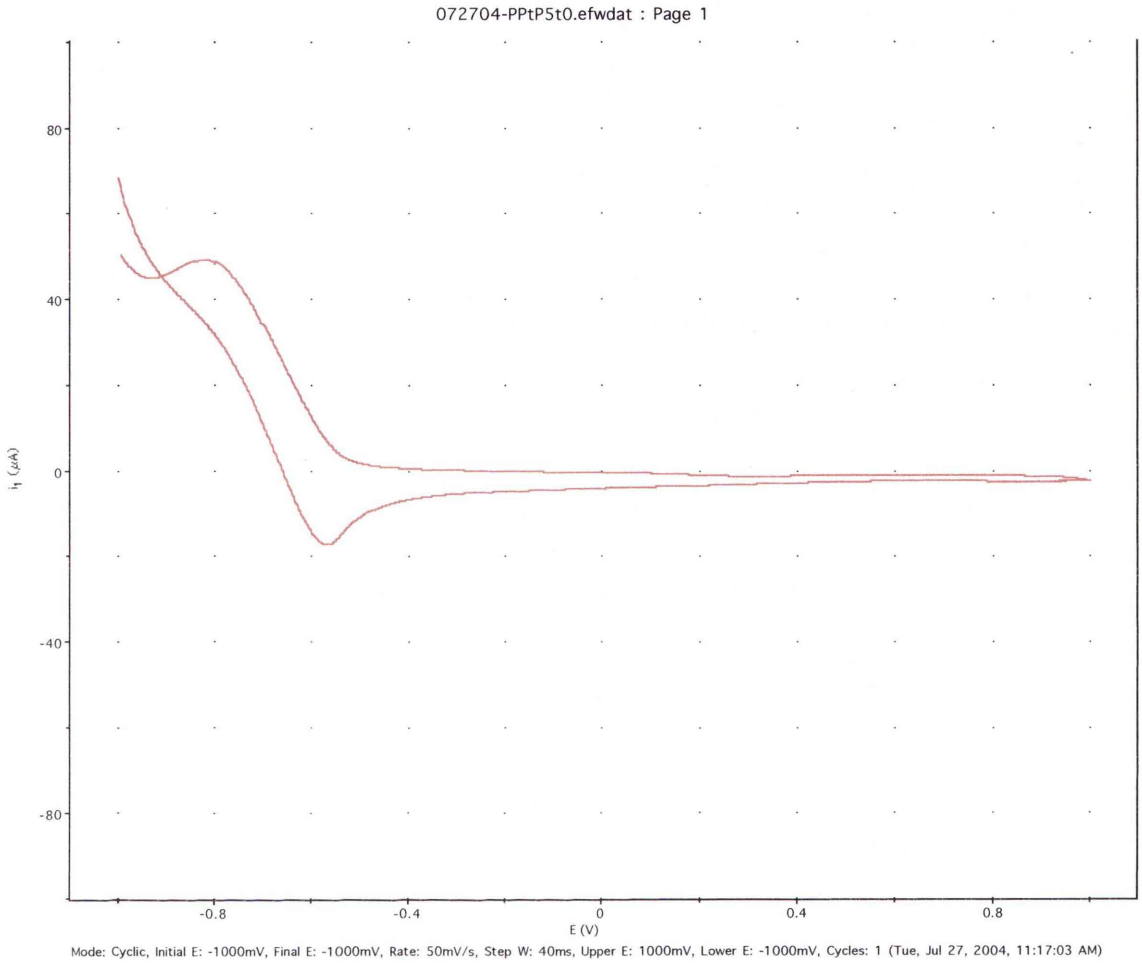
| Scan Rate | Repeat | [O] | [O] | [R] |
|---|---|---|---|---|
| 20 | 1 | -0.8720 | -0.5780 | -0.7520 |
| 20 | 2 | -0.8720 | -0.5780 | -0.7520 |
| 20 | 3 | -0.8740 | -0.5800 | -0.7520 |
| 20 | 4 | -0.8740 | -0.5780 | -0.7540 |
| 20 | 5 | -0.8740 | -0.5740 | -0.7520 |
| 20 | 6 | -0.8760 | -0.5760 | -0.7520 |
| | **Average** | **-0.8740** | **-0.5773** | **-0.7523** |

| Scan Rate | Repeat | [O] | [O] | [R] |
|---|---|---|---|---|
| 25 | 1 | -0.8920 | -0.5620 | -0.7700 |
| 25 | 2 | -0.8960 | -0.5620 | -0.7700 |
| 25 | 3 | -0.8940 | -0.5620 | -0.7700 |
| 25 | 4 | -0.8960 | -0.5680 | -0.7680 |
| 25 | 5 | -0.8980 | -0.5660 | -0.7680 |
| 25 | 6 | -0.8940 | -0.5700 | -0.7640 |
| | **Average** | **-0.8950** | **-0.5650** | **-0.7683** |

| Scan Rate | Repeat | [O] | [O] | [R] |
|---|---|---|---|---|
| 40 | 1 | -0.8980 | -0.5700 | -0.7720 |
| 40 | 2 | -0.8940 | -0.5700 | -0.7740 |
| 40 | 3 | -0.8960 | -0.5720 | -0.7780 |
| 40 | 4 | -0.8940 | -0.5700 | -0.7760 |
| 40 | 5 | -0.8980 | -0.5700 | -0.7760 |
| 40 | 6 | -0.8940 | -0.5700 | -0.7740 |
| | **Average** | **-0.8957** | **-0.5703** | **-0.7747** |

| Scan Rate | Repeat | [O] | [O] | [R] |
|---|---|---|---|---|
| 50 | 1 | -0.8940 | -0.5760 | -0.7880 |
| 50 | 2 | -0.8980 | -0.5720 | -0.7860 |
| 50 | 3 | -0.8940 | -0.5940 | -0.7880 |
| 50 | 4 | -0.8940 | -0.5720 | -0.7640 |
| 50 | 5 | -0.8980 | -0.5720 | -0.7900 |
| 50 | 6 | -0.8980 | -0.5600 | -0.7880 |
| | **Average** | **-0.8960** | **-0.5743** | **-0.7840** |

## pH 5 Buffer + Pt electrode + Petrol, scan rate 50 mV/s



# Average values for all accelerants over all scan rates

| 5 mV/s | [O] | [O] | [R] |
|---|---|---|---|
| **Buffer** | -0.887 | -0.572 | -0.734 |
| **Petrol** | - | -0.582 | -0.736 |
| **50 % EP** | - | -0.58 | -0.734 |
| **90% EP** | -0.908 | -0.59 | -0.756 |
| **99% EP** | | | |
| **Kerosene** | -0.882 | -0.572 | -0.746 |
| **Diesel** | - | -0.576 | -0.752 |

| 10 mV/s | [O] | [O] | [R] |
|---|---|---|---|
| **Buffer** | -0.883 | -0.572 | -0.751 |
| **Petrol** | - | -0.598 | -0.752 |
| **50 % EP** | - | -0.58 | -0.77 |
| **90% EP** | -0.89 | -0.592 | -0.752 |
| **99% EP** | - | - | -0.736 |
| **Kerosene** | -0.906 | -0.594 | -0.744 |
| **Diesel** | -0.888 | -0.572 | -0.778 |

| 20 mV/s | [O] | [O] | [R] |
|---|---|---|---|
| **Buffer** | -0.874 | -0.577 | -0.768 |
| **Petrol** | - | -0.586 | -0.786 |
| **50 % EP** | - | -0.572 | -0.788 |
| **90% EP** | - | -0.552 | - |
| **99% EP** | | | |
| **Kerosene** | - | -0.57 | -0.766 |
| **Diesel** | - | -0.568 | -0.772 |

| 25 mV/s | [O] | [O] | [R] |
|---|---|---|---|
| **Buffer** | -0.873 | -0.579 | -0.773 |
| **Petrol** | - | -0.574 | -0.818 |
| **50 % EP** | - | -0.562 | -0.898 |
| **90% EP** | -0.896 | -0.596 | -0.818 |
| **99% EP** | - | -0.558 | -0.82 |
| **Kerosene** | | | |
| **Diesel** | | -0.554 | -0.824 |

| 40 mV/s | [O] | [O] | [R] |
|---|---|---|---|
| **Buffer** | -0.874 | -0.573 | -0.789 |
| **Petrol** | - | | -0.79 |
| **50 % EP** | - | | -0.84 |
| **90% EP** | - | | -0.768 |
| **99% EP** | | | |
| **Kerosene** | | | |
| **Diesel** | - | | -0.844 |

| 50 mV/s | [O] | [O] | [R] |
|---|---|---|---|
| **Buffer** | -0.877 | -0.566 | -0.792 |
| **Petrol** | - | -0.5572 | -0.8828 |
| **50 % EP** | - | -0.553 | -0.819 |
| **90% EP** | - | -0.5333 | -0.820 |
| **99% EP** | -0.916 | -0.5520 | -0.7850 |
| **99% EP** | - | -0.558 | -0.77 |
| **Kerosene** | - | -0.532 | -0.786 |
| **Diesel** | - | -0.532 | -0.898 |

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