Control of the migration of gasworks pollutants in contaminated groundwater and relevant electrochemical and spectroscopic studies

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CONTROL OF THE MIGRATION OF GASWORKS
POLLUTANTS IN CONTAMINATED GROUNDWATER
AND RELEVANT ELECTROCHEMICAL AND
SPECTROSCOPIC STUDIES

by

Deborah L Hall B.Sc. (Hons)

A doctoral thesis submitted in part fulfilment of the requirements for the
award of Doctor of Philosophy of Loughborough University

August 1998

Department of Chemistry

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Abstract

ABSTRACT

The identification and subsequent treatment of contaminated land and groundwater is currently being regulated by the Environment Agency. The closure of gasworks sites during the late 1960's left areas of land contaminated with undesirable residues of the manufactured gas process, which were left to cause further pollution by leaching into surface and groundwater. The techniques available to remediate these contaminated media are numerous, but most tend to suffer from at least one major disadvantage, usually time, or cost.

The design and construction of two large rectangular cells for use in the laboratory is reported. These were designed with the intention that the flow through them would mimic the flow of contaminated groundwater. Flow rates are presented and the design faults that were identified, explained.

The design and construction of a number of small laboratory cells through which a contaminated solution was passed is reported. These were used to research the electrokinetic remediation of phenol and ammonia - two contaminants that are found at disused gasworks sites. Various parameters were altered to optimise this remediation technique, and a decrease in the concentration of the ammonia through the cell was achieved. The parameters that were varied included flow rate through the cell, voltage applied, and contaminant concentration.

The electrochemical oxidation of a selection of substituted phenols has been investigated in water and acetonitrile. In addition to this, the corresponding phenolate ions have also been investigated in water. All of the resulting data is presented and explanations are given for the resulting trends observed.

A number of these substituted phenols and phenolate ions were also studied by spectroscopic methods in water and acetonitrile. Observed relationships between substituents present on the phenol and \( \lambda_{\text{max}} \) values obtained are reported.
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To the technical staff in the Chemistry Department at Loughborough University - a large thankyou! Without the expertise of both John Spray and Alan Stevens, some of the work reported here would of proved difficult, if not impossible.

Thanks must also go to Dr Natalie Watson (nee Bell) and Dr Russ Bowman for their help and collaboration with Section 5.4.6 – Oxidation of Iodinated Phenols.

I would like to say a very big thank-you to all those who have keep me going throughout my time at Loughborough; from Kathryn and Sarah through those early days when we were all so young and naïve, to Helen, Claire and Jo to name only a few of those who were there through the last few years of my time as a student.

A special mention of course must go to my family – especially Mum and Roy – for always being encouraging and having the faith in me that I sometimes lacked.

Finally, I would like to dedicate this thesis to the two most important people that have kept me sane and made me smile throughout the research, and more importantly, the writing of this piece of work – David and Mollster. Thank-you, and I love you both very much.
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CHAPTER ONE - INTRODUCTION

1.1 - CONTAMINATED LAND AND GROUNDWATER

Contaminated land is defined as any land which appears to a local authority to be in such a condition - because of the substances it contains - that water pollution or significant harm is being, or is likely to be, caused. This interpretation is subject to guidance issued by the Secretary of State. Such land that can be classed as contaminated includes such places as abandoned industrial sites, disused manufactured gasworks sites, worked out mineral excavations, and disused waste tips. There is not at present a standard way of identifying the level of contamination at a specific site, making it difficult to ascertain the exact extent of contaminated land that needs to be reclaimed. Nor is there at present a standard to which the contaminated land needs to be remediated to. A factor governing to what extent the contamination needs to be reduced is the use of the land after reclamation. If the land were to be used as plots for houses for example, then this would need to be remediated to a greater extent than if the land were to house a large public car park.

The establishment of the Environment Agency as a result of the Environment Act 1995 has gone some way to regulate the identification and treatment of these contaminated lands. The Environment Agency was created by merging the National Rivers Authority, Her Majesty's Inspectorate of Pollution, the Waste Regulation Authorities, and several small units of the Department of the Environment. The combination of all these bodies was hoped to improve the way pollution issues were dealt with, as now only one regulator is responsible for advising and governing these issues.

The Environment Agency has the responsibility of enforcing the standards for the environment set out in UK legislation. Two of the most recent important legislation’s are The Environment Act 1995, and Water Resources Act 1991. The former is of importance as the Environment Agency was created because of it, and the latter as under the act it becomes an offence to pollute groundwater. Approximately 35% of
the public water supply in England and Wales is derived from groundwater, so it is necessary not only to remediate any existing polluted land but also to clean up any pollution that has entered the water table and caused the groundwater to become contaminated. Further problems arise when this contaminated groundwater flows off the site where the contamination first occurred, and responsibility for the clean up procedure and costs becomes ambiguous.

The Environment Agency is split into eight regions across England and Wales, each covering environmental protection, flood defence and fisheries. 1997 saw the formation of The National Groundwater and Contaminated Land Centre at Solihull, West Midlands. This brought together experts in various fields in order to create a central point within the Environment Agency. The aim of this new centre was to co-ordinate and manage research to further understand the sub-surface environment. It is hoped that the formation of this centre will also evoke the introduction of new legislation to provide a means for the Environment Agency and the concerned local government to control and rectify the problems of contaminated land.

Groundwater is defined as the subsurface water that occurs beneath the water table in soils and geological formations that are fully saturated. It accounts for two thirds of the earth's freshwater sources, which increases to almost the whole volume of the freshwater if those sources that are not able to be utilised (i.e. icecaps and glaciers) are ignored. It constitutes an important part of the hydrologic cycle, so the need to remediate contaminated groundwater is vital in order to prevent the further spread of contamination. Groundwater flow can be extremely slow in comparison with other components of the hydrologic cycle. Its residence time can extend to such lengths of time as thousands of years, in comparison to that of two weeks for rivers and ten years for lakes and reservoirs. The hydrologic cycle is depicted in Figure 1.1. With reference to this figure, it can be recognised that contamination of groundwater by industry and the general population can have serious consequences on the whole of the hydrologic cycle, so it is imperative that further contamination is prevented and remediation of contaminated groundwater is achieved.
FIGURE 1.1 - The hydrologic cycle

Addition of a small amount of magmatic water to the hydrologic cycle.
1.2 - MANUFACTURED GAS SITES

Prior to the 1960s the main source of heat and fuel was manufactured or town gas.\textsuperscript{24} The process of production used coal or oil to produce this town gas, but this also gave rise to a number of undesirable residues including polycyclic aromatic hydrocarbons (PAHs), volatile aromatic compounds, phenolics, inorganic compounds of sulphur, complex cyanides, and metals. Natural gas was discovered in the southern North Sea in the 1960s and a process of conversion from town to natural gas was undertaken in the UK, with the last gasworks site closing in 1972. The sites were decommissioned but the majority of sites are potentially contaminated by the aforementioned residues associated with town gas production.

Leachates originating from these sites have the potential to pollute surface and groundwater, so it is imperative that new methods of remediation are developed to both stop this passage of contaminants and to clean-up the original site.\textsuperscript{5}

1.3 - REMEDIATION TECHNIQUES

There have been an increasing number of remediation techniques for contaminated land under development in the last few years. A brief description of some of the methods in present use follows.

1.3.1 - Landfill

This is the process whereby the contaminated soil is physically removed from the site and disposed of at a registered disposal site.\textsuperscript{4,6,7,8} This has been the preferred option in the UK, but new legislation requires a Waste Management Licence to be held by the landfill owner until such time that the landfill no longer poses a threat to the environment. Estimates on the length of time this would relate to have been as long as five hundred years for typical domestic sites, and more for industrial sites. This has therefore led to the increasing costs of landfill, and it is anticipated that this will not be a financially viable option for much longer. There are many hazards related to this
technique - the physical removal and transport of the contaminated soil poses a threat both to the environment and to personal health, as does the fact that leaching from the landfill site often occurs which moves the problem of contamination onto other areas of land.

1.3.2 - Pump and Treat

Pump and treat requires the installation of a series of wells at either end of the contaminated area of land. The process generally involves the pumping of contaminated groundwater from its natural flow path to a treatment zone where contaminants are removed. The addition of a solvent that is pumped through the contaminated area and collected in the treatment zone is a variation on this technique but it is very specific and has not been widely investigated.

A major problem associated with the technique of pump and treat is the phenomenon that is observed when the system is turned off once the target concentrations of the contaminants have been reached. The switching off of the system causes an unexpected sharp rise in the contaminant concentration to occur. This is due to any contaminants present in small capillaries within the treatment zone diffusing out into the cleaned flow paths and thus making the contaminant level greater than the target concentration again.

A recent advancement on the pump and treat technology has been to circulate air instead of the solvent. This is known as soil vapour extraction and removes any volatile substances present within the soil.

1.3.3 - Soil Washing

The process of soil washing does not destroy the contaminants present but extracts them from the soil in order that they can be treated or disposed of at less risk. Soil washing relies on the principle that contaminants have the greatest affinity for the finer particles in the soil and gather here. Therefore the main process involved with
soil washing is particle size separation, thus reducing the volume of soil that needs to be washed and treated. The remaining fine particles after separation has occurred can either be washed with a particular solvent, which in turn then has to be disposed of, or be removed to landfill.

An *in-situ* soil washing technique that has no need for excavation has been described.\(^\text{12}\) Application of a solvent at the surface of the contaminated area ensures that the solvent flows down through the soil structure, taking any soluble contaminants with it. This contaminated liquid can then be removed from aquifers through withdrawal wells and treatment can occur above ground. The limitation set on this technique is the permeability of the soil. Those soils which are not permeable enough to allow the passage of solvent through it within the time constraint given, would not be able to use this remediation technique. This technology is similar to that of pump and treat; the main difference being that in this instance the solvent is allowed to flow down through the soil as opposed to being pumped across it. Here again, in order to prevent any further pollution from occurring, it is necessary to prevent any of the contaminated liquid from entering any ground or surface waters nearby.

### 1.3.4 - Incineration / Thermal Desorption

Organic chemicals present in the soil can be effectively removed by incineration.\(^\text{4,7,8}\) After the soil has been excavated from the land, and before incineration can occur, it has to be crushed, ground, and dried. The heating of the soil to high temperatures in an incinerator causes combustion of any organic matter present to occur. The incinerator can be located on or off site, and any aerial emissions are monitored. The ash remaining at the end of the process may still contain some undesirables so will need to be disposed of accordingly. Incineration is an effective but expensive method of remediation as the cost involved in heating the volumes of soil to the required temperature is high.
Due to the fact that the major disadvantage with incineration is the cost involved, an alternative technique which is often used is thermal desorption. This involves the heating of just the waste as opposed to the whole of the soil. The waste is heated to a temperature at which the contaminants - which are normally organic - desorb. The product can then either be burnt under controlled conditions, absorbed, or recycled.

1.3.5 - Stabilisation / Solidification

Contaminants present in the soil can either be converted into other compounds, or encased by the addition of a stabilisation, or a solidification agent. This agent can be a number of materials including cement, polymers, fly ash, and silicates. It is vital that thorough mixing occurs between the chosen agent and the contaminated soil. These new compounds can then possess altered properties that render them less harmful to the environment, which include toxicity, solubility, and mobility.

1.3.6 - Bioremediation

Bioremediation is the utilisation of micro-organisms to break down organic matter into less toxic materials. Specially selected bacteria, growth media, nutrients, and water are introduced to the contaminated area and left to reduce the contaminant concentration. The current practice for bioremediation is to promote the growth of indigenous micro-organisms. Bioremediation can be used to effectively treat both contaminated groundwater and land. This method is a cost effective remedial process and desirable in that waste products are often not produced. This is counterbalanced by the fact that it may require a substantial length of time in order to reduce concentrations to the desired level, although bio-reactors and bio-piles are relatively rapid methods of remediation and can reduce contaminant levels to the desired concentration within the time period of twenty plus weeks. The micro-organisms added to the soil can enter the natural groundwater table and cause further contamination if not monitored.
1.3.7 - Encapsulation / Isolation

These technologies are designed to be a prevention to migration as opposed to a remediation technique. They have been described as 'stand and hold' techniques which will ensure the containment of contaminants within the specified area until other, more permanent remedies can be found. Isolation involves the construction of a vertical or horizontal barrier through which the contaminants are not able to pass. The materials used include clay, soil and bentonite slurries, and bentonite / concrete mixtures. Bentonite principally comprises the minerals montmorillonite and beidellite, and is able to absorb approximately five times its own weight of water. It is a useful material for this technology because of its low permeability and it also has a small particle size distribution so is able to prevent the passage of contaminants through the smallest void. This technology is relatively cheap to employ, but it is only a prevention technique and remediation will at some point still have to be conducted.

1.3.8 - Photocatalysis

This technique has been used to remediate phenolic contaminated waters by the photocatalytic degradation of the phenolic to carbon dioxide. The light source to achieve this decrease in contaminant concentration can be either generated ultra-violet (UV) light, or natural sunlight. The addition of a catalyst such as titanium dioxide will decrease degradation times. This technique has the advantage of having little, if any hazardous waste products to dispose of. The only possible source of hazardous waste would be possible daughter products of the degradation.

1.3.9 - Electrokinetic Remediation

By applying a voltage across an area of contaminated land, the remediation can be performed electrokinetically. A voltage is directly applied across a series of electrodes installed in the ground, forcing the system to undergo physicochemical, hydrological and mechanical changes. This causes any contaminants solubilised in the groundwater to be transported across the medium towards an electrode where the
contaminants can then be flushed out. A schematic diagram of this process is shown in Figure 1.2.

**FIGURE 1.2** - A schematic diagram to show the concept of electrokinetic remediation

The application of the voltage establishes a potential difference across the electrodes which leads to electrophoresis and electroosmosis, and causes electrolysis reactions to occur at both of the electrodes. Electrophoresis is defined as the mass flux of charged particles within the system, whilst electroosmosis is concerned with the mass flux of pore fluid. Electrolysis reactions that occur at the electrodes involve those species that are in the vicinity of the electrode. These can include oxidation and reduction reactions for water, as well as secondary reactions involving metals and any products from initial reactions, if these species are present in the vicinity of the relevant electrode. Examples of these reactions include;
As the solubilised contaminants flow through the medium and towards the electrode region, secondary reactions can occur that involve those ions initially formed.

The generation of the H⁺ and OH⁻ ions at the electrodes will result in an acidic region around the anode, and an alkaline region surrounding the cathode, leading to a change in pH at both. This acid region, or front, will advance through the soil towards the cathode by means of transport mechanisms including ionic migration due to the applied electrical gradient, diffusion due to the generated concentration gradients, and pore fluid advection due to both the prevailing electroosmotic flow, and any hydraulic potential differences present. Conversely, the alkaline front generated will be advancing towards the anode due to diffusion and ionic migration, but will be hindered due to the counterflow of electroosmosis. The overall effect will therefore be a decrease in pH across the system as the acid front dominates.  

Advancement of the alkaline front will cause some contaminants to undesirably precipitate out of solution. The amount of precipitation is dependent on a number of factors including soil and pore fluid pH, and contaminant concentration. Dissolution then occurs due to the advancement of the dominant acid front. New technology places ion selective membranes in front of the cathode to prevent the advancement of the alkaline front. This will hinder the precipitation of the contaminants, and migration to the electrode and consequential removal from the medium will occur more readily. Improved removal efficiencies were noted, the disadvantage being the increased expenditure costs and processing periods.  

The advancement of this alkaline front can also be prevented by the injection of ions into the system. If a weak acid is injected at the cathode neutralising some of the hydroxide produced, the pH change will not be as great and the subsequent advancement of the front not as pronounced. Further research has been conducted on the efficiency of electrokinetic...
injection of a cation at the anode, and an anion at the cathode. The co-ions of the injected species will cause neutralisation of the products of the reactions at the electrodes, and ensure that the pH is maintained across the whole of the medium.

The effect of the pore fluid pH on electrokinetic remediation has been studied. Results showed that by increasing the pH of the pore fluid, a large decrease in energy expenditure was noted for the same number of pore volumes.

Other physicochemical medium-contaminant interactions that occur due to the application of the electric field, aside from the described precipitation, include adsorption / desorption reactions, and electrodeposition. If the medium in question is clay, attraction to and subsequent adsorption of any positively charged species onto the negatively charged clay particles is seen. Removal of said cations therefore requires desorption which is facilitated by the generation and passage of the acid front.

These interactions that occur between the media and the contaminants ensure that the latter are removed from the media. Removal is either from the media with the pore fluid, or as a precipitate at the electrodes, where removal and treatment can then be conducted. A variety of media are able to be remediated using this technique, including soils, clayey materials, rocks, groundwater, wastewater, and general hazardous waste sites. Available data has shown that this process is particularly suited to the removal of ionic contaminants, especially heavy metals and radionuclides. Most of this data has been provided by laboratory experiments although on-site research into the removal of contaminants has been reported. Anionic food dyes have also been remediated electrokinetically as the advancement of these contaminants have the advantage of being able to be visually monitored.

This process does not only have to be used as a remediation technique, it also has many other possible applications. Soils can be made more stable by de-watering using electrokinetics. The creation of an electrokinetic barrier or fence that has the ability to contain the contaminants within a set zone, is a method that can be used to prevent...
the passage of contaminants until more permanent techniques can be applied.\textsuperscript{54-57} The horizontal installation of electrodes in order to remediate groundwater beneath a building still in use has been reported.\textsuperscript{58} By combining electrokinetics with other techniques, the degree of remediation can be enhanced. One such technique is known as the 'Lasagna' process due to the layered configuration of the electrodes and treatment zones.\textsuperscript{59,60} This technique employs electrokinetics to move contaminants into the treatment zones where they are then removed by degradation, adsorption, or immobilisation. Another technique combines electrokinetics with the principle of electrodialysis to give electrodialytic remediation.\textsuperscript{61,62} Ion exchange membranes are used to separate the medium from the electrode compartments. This prevents any current carrying ions from passing into the soil from the electrode compartments, whilst ions are still able to be transported in the opposite direction. Current is therefore not wasted, thus making the process more efficient.

Another new technology has been the creation of conductive fractures within the medium, across which a potential can be applied.\textsuperscript{63} Injection of a fluid into a well at high pressure causes the well casing to crack. If conductive graphite in the form of a slurry is then injected into this fracture as it grows away from the well, a horizontal electrode has been produced. If this procedure is repeated, a series of electrodes will be produced, across which a potential can be applied.

1.3.9.1 - Coupled Flows

It is well known that the flow of a fluid through a system is dependent on the hydraulic gradient present, the flow of heat depends on the thermal gradient, the flow of electricity on the electrical gradient, and the flow of chemicals on the chemical gradient present.\textsuperscript{64-67} These flows are all related to their particular driving force by the equation:

\[ J_i = L_{ui} X_i \]
Where;

\[ J_i = \text{flow rate or flux of type } i \]
\[ L_{ii} = \text{conductivity coefficient} \]
\[ X_i = \text{gradient or driving force of type } i \]

A coupled flow is produced when two or more of these flows are occurring and cross effects are produced. A flow is driven by a potential gradient of another and can be described thus;

\[ J_i = \sum L_{ij} X_j \]

Where;

\[ J_i = \text{flow rate of type } i \]
\[ L_{ij} = \text{coupling coefficient} \]
\[ (\text{provided that } i \neq j \text{ otherwise } L = \text{conductivity coefficient}) \]
\[ X_j = \text{gradient of type } j \]

Examples of these coupled flow phenomena are presented in Table 1.1.
**TABLE 1.1** - The coupled flow phenomena when a gradient of type $j$ induces a flow of type $i$

<table>
<thead>
<tr>
<th>Flow</th>
<th>Gradient</th>
<th>HYDRAULIC</th>
<th>ELECTRICAL</th>
<th>THERMAL</th>
<th>CHEMICAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLUID</td>
<td>Hydraulic conduction</td>
<td>Electroosmosis</td>
<td>Thermoosmosis</td>
<td>Osmosis</td>
<td></td>
</tr>
<tr>
<td>ELECTRIC CURRENT</td>
<td>Streaming potential</td>
<td>Electric conduction</td>
<td>Seebeck effect</td>
<td>Diffusion &amp; membrane potentials</td>
<td></td>
</tr>
<tr>
<td>HEAT</td>
<td>Isothermal heat transfer</td>
<td>Peltier effect</td>
<td>Thermal conduction</td>
<td>Dufour effect</td>
<td></td>
</tr>
<tr>
<td>ION</td>
<td>Streaming current</td>
<td>Electrophoresis</td>
<td>Soret effect</td>
<td>Diffusion</td>
<td></td>
</tr>
</tbody>
</table>

When the flow is produced by a gradient of the same type, i.e. those in bold type in Table 1.1, a linear relationship is seen. Starting at the top left hand corner of the table, these are described by Darcy's Law, Ohm's Law, Fourier's Law, and Fick's Law respectively. From Table 1.1, it can be noted that there exists a total of four conductivity coefficients and twelve coupling coefficients. Not all of the coupled flows are relevant in soil / groundwater systems - thermoosmosis has little or no influence in those soils that are fully saturated, whilst both the Peltier and Dufour effect are not known to be of any significance. It must be taken into consideration when predicting flows through a proposed medium that some of these effects will alter the hydraulic flow. In particular to note is the streaming potential which will develop in all systems unless the ends of the sample are short circuited to prevent this from occurring.

There have been many numerical models proposed for the electrokinetic remediation of groundwater utilising these coupled flows and other parameters. Models have been both one dimensional, and two dimensional. Model predictions along with
pilot-scale tests have been reported to prove good agreement between theoretical and experimental work.

1.4 - AIMS OF RESEARCH

The aims of the research undertaken were to investigate the control of the migration of gasworks contaminants and leachates through soils. This involved the design and construction of two large rectangular cells through which the artificially contaminated water could be allowed to flow. The initial design consisted of a horizontal cell as this was believed to be more alike to the natural flow of groundwater, whilst the second modified cell utilised gravity to aid the flow through the vertical cell design.

Smaller cylindrical cells with the capability of holding only two electrodes were constructed, and these were used to investigate a number of factors influencing the efficiency of remediation. These factors under investigation included, the nature of the contaminant being introduced to the system, the potential gradient being applied between the electrodes, and the time period for which this potential gradient was applied.

Electrochemical studies concerning a particular class of contaminant found at disused gasworks sites - phenols - were carried out, in order to more clearly understand the mechanisms and reactions that were occurring at the electrode surfaces as remediation of the contaminated groundwater was progressing. The effect of various substituents on the phenol was studied, as was various other parameters including pH of the solution, alteration of the solvent itself, and the choice of electrode material.

Spectroscopic studies were also undertaken on the various phenols studied electrochemically. It was initially envisaged that this could be a method of determination of the phenolics present in the contaminated groundwater, so spectra for each were recorded and relationships between the various substituents present on the phenol and the \( \lambda_{\text{max}} \) value obtained were obtained.
CHAPTER TWO - DESIGN OF CELL A; a horizontal rectangular cell for electrokinetic remediation studies

2.1 - INTRODUCTION

As stated in CHAPTER ONE - INTRODUCTION, there is a growing need for new and innovative remediation techniques. The process of cleaning contaminated land and groundwater by means of electrokinetic remediation is a fast growing technique that is increasing in popularity due to the advantages it holds over older, more expensive methods.

The construction of a large scale laboratory cell that could closely mimic the flow of groundwater when packed with a particular medium through which a pore fluid can be passed, was undertaken. This approach, chosen in order to study electrokinetic remediation by means of a large cell, was believed to be novel in that it would enable more accurate predictions to be made with regard to 'real life' situations. Problems could then be encountered within the laboratory environment, and consequently solutions could be found before the method was used on site.

Alteration of various parameters involved in the remediation of the contaminated fluid, and the study of any changes that occur due to these alterations, would enable a greater understanding of this remediation process. Examples of the parameters that are able to be altered, include the flow rate through the packed media, the nature of the contaminant present within the pore fluid, the configuration of the electrodes, the potential difference applied between the electrodes, and the length of time for which this potential is applied.

2.2 - THEORY

Groundwater is continuously flowing in a way that is governed by established principles. These principles are expressed in the empirical Darcy's Law which can be applied to yield information on flow and direction of groundwater, and the
permeability of the medium through which it is flowing. Darcy’s Law is applicable to any fully saturated medium and is valid for groundwater flow in any direction in space. It states that:

"the flow rate through porous media is directly proportional to the head loss and inversely proportional to the length of the flow path."

This can be expressed as:

\[ v = -K (\Delta h/\Delta l) \]

Where:

- \( v \) = specific discharge \( \text{ms}^{-1} \)
- \( K \) = hydraulic conductivity \( \text{ms}^{-1} \)
- \( \Delta h \) = head loss \( \text{m} \)
- \( \Delta l \) = length of flow path \( \text{m} \)

Alternatively since \( v = Q/A \), it is possible to express Darcy’s Law as:

\[ Q = -KA (\Delta h/\Delta l) \]

Where:

- \( Q \) = flow rate \( \text{m}^3\text{s}^{-1} \)
- \( A \) = cross sectional area \( \text{m}^2 \)

The negative sign present in the equation merely indicates that the flow of fluid is in the direction of decreasing head.

It is therefore possible to determine a value of \( K \) for any specific medium. By utilising a cell of known cross sectional area \( A \), the various flow rates achieved as the head
height is altered can be noted. At each set head height, the difference between the two manometer levels also needs to be recorded (Δh), as this will then enable a plot of Q against Δh/Δl, where Δl is the length of the flow path, to be achieved. With reference to the above equation, this should lead to a straight line graph with a slope equal to KA, and since A is known, a value for the unknown hydraulic conductivity of the media can be calculated. The values of K obtained will be high for both sand and gravel, and low for clay and rocks as it is obviously easier for groundwater to flow through gravel than it is through rocks.

2.3 - DESIGN DETAILS

The basic concept of the cell design was to produce a cell that would mimic groundwater flow and real situations more effectively than a small scale laboratory test cell. A large scale cell was designed, and collaboration with BG Technology produced a basic construction as shown in Figure 2.1.

**FIGURE 2.1** - The basic design concept for Cell A
Construction was carried out at BG Technology using perspex sheets of 15mm thickness. Dimensions of the cell were 80cm x 40cm x 40cm, with the length being divided into three sections of 14cm, 49cm, and 14cm each. These three sections were separated by wire mesh membranes. A lid was machined of the same material to be attached on top of the cell so as to form a tight seal and thus create a ‘closed’ system. An array of holes were present in the lid (a set of 4 by 3) to enable the carbon rod electrodes (12mm diameter, overall length 30cm but cut to size as required) to be positioned in various configurations. When not in use these would be plugged with small pieces of cut electrode to prevent leakage.

Glass tubes were utilised as manometers and were situated at either end of the central section. A reservoir (small plastic water tank, Wilkes, Loughborough) was attached to the equipment via a rubber tube to provide a constant head of water. A hole was machined into the side of the reservoir to act as an overflow to ensure the height of the water inside could remain constant. Any fittings were made of brass (A.R. Brooks Ltd., Loughborough), O-rings were utilised (Rhondama, Loughborough), and all tubing (8mm bore, 3mm wall) and pipes (Fisons, Loughborough) reinforced to withstand any pressure.

With reference to Figure 2.1, it was intended that both of the outer sections were to be filled with gravel (Winfields Ltd., Loughborough; as bought) and the central section to be filled with sand (Winfields Ltd., Loughborough; ground down using a Glen Creston cross beater mill). By forcing water into the cell through the inlet valve, the more permeable gravel section would fill first before uniform migration of the water through the sand would occur.

In order to avoid displacement from the central section to the outside regions, the gravel was added to the cell first. The ground sand was then added in layers - each layer being compacted as much as possible before the next layer added. Displacement of the sand through the mesh was still observed, but this was unavoidable and had no detrimental effect on the permeability of the gravel.
As the sand was added to a greater and greater depth, it became apparent that the thickness of perspex chosen was not strong enough to support the weight of all the sand, and the sides of the cell began to bow. A speedclamp (132/60 24" 600/mm Record Tools Ltd., Ean Muller, Loughborough) was used to prevent further bowing and possible splitting of the sides of the cell. Due to this bowing of the sides it became impossible to fix the lid on and therefore a closed system would not be obtainable - it would stay as an ‘open’ system.

Once the central section had been completely filled, large voids were evident in the sand. A vibrating poker (Civil and Building Engineering Department, Loughborough University) was used to remove the larger of these voids. It should be noted that no amount of vibrating would get rid of all the voids.

Figure 2.2 shows a photograph of the completed Cell A - the lid is only placed on to show how the carbon rod electrodes could be configured.
FIGURE 2.2 - Photograph of the completed Cell A
2.4 - EXPERIMENTAL

Initially the cell was set-up with the reservoir providing a large head of water and the system was allowed to saturate. The reservoir height and the level of water inside the reservoir would then be altered to give different head heights, which in turn would lead to a difference in the height of the manometers (Δh), and the resulting flow (Q) through the cell measured. Once equilibrium had been established, flow into the system would be equal to flow out of the system, so measurement of the flow would be carried out at the outlet valve for simplicity. A plot of Q against Δh/Δl would, in accordance with Darcy’s Law, lead to a value for the permeability of the sand, K.

2.5 - RESULTS AND DISCUSSION

A number of experiments were conducted in which the inlet valve to Cell A was opened, and, initially, distilled water allowed to flow through the cell. Measurements of the flow were carried out at set time intervals throughout the day. This was achieved with the use of a measuring cylinder where the water from the outlet valve was collected for a set time period, and then the flow rate calculated. The results of some of these are shown in Figure 2.3. The reservoir height was constant for all runs shown - the only variant was the length of time the run was conducted for.
A design fault was noticed immediately. Once the inlet valve was opened to allow water to flow in, it became clear that the permeable gravel section was initially being filled as desired. Due to the short time taken to see the flow of water at the outlet valve, it was believed that the water was then flowing straight across the top few centimetres of the central sand. The theory was that the water would saturate the whole central section before flowing out of the cell, but this did not appear to be occurring. It is known that the preferential flow through a medium will always occur through the easiest path available, and due to the fact that this was an open system with no pressure in it, the water would naturally prefer to flow through the path of less resistance i.e. across the top few centimetres of the sand. The sand at the top of this section would be less compact due to there being no weight on top of it. The decrease in the flow throughout the length of the run can be explained by the slow saturation of the whole volume of sand. As the water flows across the sand, a portion of it will permeate down into the lower section, causing a slight decrease in the flow out the
outlet valve. Also, as the length of the run increases, the amount of water that passes from the first gravel section into the main body of the sand will increase. This will also have an effect on the flow rate measured at the outlet valve as the quantity of water available to flow across the top of the sand has decreased. This extra movement into the main body of the sand appears to have no lasting effect on the flow rate, as this increases again once the cell has been left overnight. By continual flow through the cell, it may be possible to fully saturate the whole of the sand, although it is expected that the majority of the flow would still be across the preferential top few centimetres of the sand.

It was not possible to produce a closed system for Cell A as the sides of the cell had bowed too much. In order to overcome the problems associated with the flow, a sheet of perspex was machined to fit exactly over the top face of the sand. By placing weights onto this perspex, a slight pressure may be provided which could aid the saturation of the sand. A number of experiments were conducted with this sheet of perspex and weights in place, and some of the results are depicted in Figure 2.4. The reservoir height remained constant for all runs, as did the weight present on the perspex, the only variable once again being the length of time that the run was conducted for.
FIGURE 2.4 - To show the varying flow rates obtained for Cell A with respect to time when weights had been added to the top of the sand in an attempt to regulate the flow.

Results show that the preferential flow of water is still across the upper section of the sand, and that the presence of the weights had no stabilising effect on the flow through the cell. Again the decreases shown in the figure can be explained by the slow saturation of the volume of sand.

It is evident that due to the bowing of the sides of the cell as the sand was added, and the consequence that a 'closed' system could not be obtained, a steady flow through the cell could not be obtained. Attempts were made to fully saturate the system by covering the top face of the cell with a layer of water to allow it to permeate through, and leaving it to stand for a number of weeks. This had no effect on the flow of water through the cell, as the preferential flow was still through the less compacted upper region.
Even if a closed system had been obtainable with Cell A, another factor to consider would be the degree of compaction throughout the cell. The weight of the sand would cause the lower regions to become more compact than the upper regions of the central section. Due to the preferential flow of water being through the easiest path available the majority of the flow would still be across the less compact upper regions.

In order that further work using a new cell design could be facilitated, a particle size distribution was obtained for the sand used in Cell A. Initially, the sand had been ground and used with no prior knowledge of the particle size range present. By obtaining this knowledge now, and knowing that the size used here was probably too large for these required purposes, it would be possible to grind further batches of sand finer. A sample of sand was removed from the centre of the body of sand and the particle size distribution obtained (Coulter Laser Sizer LS130, Chemical Engineering Department, Loughborough University). Figure 2.5 shows the distribution obtained for the sand used in Cell A.
FIGURE 2.5 - Particle size analysis for the sand mixture used in Cell A (Glen Creston cross beater mill ground sand (mesh size 0.5μm))
With reference to Figure 2.5 it is noted that the majority of the sand particles lie in the size region greater than 200μm. Further grinding of the sand can be achieved to lower this value, in order for the sand to be used in a new cell which could aid the flow of the water through the whole body of the sand.

2.6 - CONCLUSIONS

In conclusion, the design of Cell A was not suitable for electrokinetic research purposes. Numerous attempts were made to ensure a steady flow through the cell, but none proved successful. The main reason that can be attributed to this is that the system is an open system and has no hydraulic head present across it to ensure a steady flow. Compaction of the sand is another important factor that will have consequences on the flow through the cell. The sand at the bottom of the cell will be more densely packed than that at the top due to the extra weight of the rest of the volume of the sand, therefore the flow of water will not preferentially travel through this.

Due to the fact that Cell A was not able to be used for investigations into the remediation of contaminated groundwater, a new cell was designed and constructed.
CHAPTER THREE - DESIGN OF CELL B: a vertical rectangular cell for electrokinetic remediation studies

3.1 - INTRODUCTION

Due to the fact that a steady flow through Cell A was not achievable, it was necessary to design a new cell. Had a steady flow been obtained, the horizontal construction of Cell A would be more comparable to the flow of groundwater in a natural state. The design of a vertical cell would lose this direct comparison to 'real' samples, but would ensure that the pore fluid would have to flow through the whole of the medium present, thus enabling electrokinetic remediation to be carried out.

3.2 - THEORY

The same theory applies to the design of this new cell as it did to the design of Cell A. By understanding the reasons that Cell A did not work, a large scale working laboratory cell could be designed. The prevailing problem encountered with the design of Cell A was that the flow of water would not pass through the whole volume of sand. This was due to the preferential path of the water being across the less compacted and therefore more permeable top portion of sand. To overcome this problem a vertical cell was designed. This would ensure that the water would have to flow from the top of the cell to the bottom by gravity flow, therefore having to pass through the whole volume of sand.

3.3 - DESIGN DETAILS

A basic design involving a square based vertical cell of dimensions 40cm x 40cm x 65cm was constructed. Nine holes were made in each of two vertical faces in a grid of 3 x 3, into which the carbon rod electrodes could be placed. This would enable the removal of electrodes and therefore the alteration of the electrode configuration to be simple and easy. The distance between the electrodes was hoped to be sufficient not to cause interference with each other, and one of the faces had the holes positioned
slightly off centre to avoid any of the electrodes from coming into contact with each other when all in position. An outlet valve was positioned at the bottom of one face, as was a glass tube acting as a manometer, with another glass tube halfway up the same face. This second manometer was positioned at a height just below where the top of the packed sand would reach (~ 40cm).

Construction was carried out at BG Technology using perspex sheets of 15mm thickness. All fittings were brass and all tubing and pipes were reinforced. Rubber bungs were used to fill any holes that did not contain electrodes. Thin membranes were placed at every outlet to prevent the overspill of sand with the flow of the water.

In order to create a closed system a lid was also made. This was to be placed on top of the sand and would be sealed in place with sanitary sealant. A volume of water present on top of the lid would give a set head height and thus control the flow of water through the cell. To achieve different head heights and therefore varying flow rates, a series of holes at increasing heights above the level of the lid were made into one face of the cell. By blocking off all these holes with rubber bungs aside from the one at the height required, water would be able to flow out at this chosen level and a constant head could be achieved. A thin layer of gravel placed on the top of the sand would prevent any disturbance of the sand, and also aid uniform flow down through the cell. To ensure uniform flow down through the lid, an array of holes of 1mm diameter were made. Handles were added to enable the lid to be removed between experiments. Figure 3.1 shows the design concept of Cell B, whilst Figure 3.2 shows a photograph of the completed cell once packed with sand.
FIGURE 3.1 - The basic design concept for Cell B

- 65cm lid
- gravel
- sand
- 40cm electrode positions
- holes to achieve various head heights

40cm outlet

Δh
FIGURE 3.2 - Photograph of the completed Cell B
3.4 - EXPERIMENTAL

With reference to CHAPTER TWO - DESIGN OF CELL A: a horizontal rectangular cell for electrokinetic remediation studies it was noted that the sand used in Cell A had been ground and used with no knowledge of the particle size range present. An analysis was obtained once it had been ascertained there was a flow problem with the particular cell design. This analysis gave a $D_{10}$ value of 188μm for this particular batch of sand (reference Figure 2.5). $D_{10}$ is the effective particle size, which refers to that grain size diameter below which 10% by weight of the sieve analysis, are finer. In order to ensure a run could be conducted within the necessary time period, the $D_{10}$ value for the sand to be used in Cell B needed to be known. Sand was ground using both a Glen Creston cross beater mill and a Fritsch Planetary mill Pulverisetic 5 four steel ball grinder. This grinding was carried out at various speeds and for different lengths of time in each grinder, and the samples were mixed together in varying quantities in order to obtain sand samples of different particle sizes. These results were analysed (Coulter Laser Sizer LS130, Chemical Engineering Department, Loughborough University) to see the particle size ranges obtainable.

In order to determine the particle size of the sand that would be preferred to be used in Cell B, the volume of sand through which the pore fluid has to travel, and the length of time it is required an experiment to last (i.e. the flow rate desired) need to be considered. A compromise needs to be reached for the flow rate to be used between being comparable to that rate for natural groundwater and time restraints. It has been stated in CHAPTER ONE - INTRODUCTION that groundwater can have residence times of up to thousands of years, which is not practical to recreate in a laboratory environment. It was considered appropriate to try to achieve a flow through time to ensure that an experiment could be conducted within the time period of a day. This would prevent the need for complicated procedures to allow the experiment to be continued overnight.

Having a knowledge of the flow through time required per experiment, enabled a value of $K$ for the sand to be estimated. Hazen developed an empirical formula that
relates the effective particle size \((D_{10})\) to the value of \(K\) for that specific media. By having an estimate of the value required for \(K\), use of the Hazen formula will also enable an estimate to be calculated for the value of \(D_{10}\). Having previously ground various batches of sand and obtained the analysis for the particle size distributions, it could then be possible to determine which mixture of ground sand would be preferred to fill Cell B. Originally, the Hazen formula was developed for the prediction of uniformly graded sands, but can also be used to obtain estimates for the whole range from fine sand up to gravel.

Hazen states that;

\[
K = A(D_{10})^2
\]

Where;

- \(K\) = hydraulic conductivity \(\text{ms}^{-1}\)
- \(A\) = constant
- \(D_{10}\) = effective particle size \(\text{mm}\)

The value of the constant \(A\) changes depending on the units of \(K\) and \(D_{10}\). If, for example \(D_{10}\) is given in mm, and \(K\) has the units of \(\text{ms}^{-1}\), then the value of \(A\) would be \(10^2\). However, if \(D_{10}\) has units of mm, and \(K\) is reported in \(\text{cmhr}^{-1}\), then the value of \(A\) would change to be 3600.

A value of \(K\) was chosen as approximately \(5\text{cmhr}^{-1}\) as this would hopefully allow an experiment to be conducted within the time period of a day. By placing this value into the Hazen formula, and letting \(A=3600\), an approximation for \(D_{10}\) in units of mm can be obtained.

\[
K = A(D_{10})^2
\]

\[5 = 3600(D_{10})^2\]

\[D_{10} = 0.037\text{mm} = 37\mu\text{m}\]
Chapter Three - Design of Cell B

Examination of the results obtained for the various mixed batches showed that the closest match to this value of $D_{10} = 37\mu m$, was a 1 : 4 mixture of four steel ball ground sand : cross beater mill ground sand, with the former being ground for five minutes at 200rpm and the latter having incorporated a mesh size of 0.5$\mu m$. Analysis of this mixture of sand gave a $D_{10}$ value of 35.95$\mu m$ (0.03595mm) and by placing this value into the Hazen formula, and again letting $A = 3600$, a value of $K$ with units of cm$hr^{-1}$ can be obtained.

\[
K = 3600 \times (D_{10})^2 \\
K = 3600 \times (0.03595)^2 \\
K = 4.6 \text{ cm}^3\text{hr}^{-1}
\]

This value was comparable to the estimate originally chosen. The remainder of the sand was ground accordingly and mixed (revolving drum mixer, Civil and Building Engineering Department, Loughborough University). Further work could involve using batches of sand with varying $D_{10}$ values, and hence different hydraulic conductivity's. However, this would probably require alteration of the cell design to enable longer time period experiments to be run. Figure 3.3 shows the sand analysis of the sand mixture chosen to be used in Cell B.
FIGURE 3.3 - Particle size analysis for the sand mixture used in Cell B (1:4 mixture of Fritsch Planetary mill Pulverisetic 5 four steel ball ground sand (5 minutes @ 200rpm) : Glen Creston cross beater mill ground sand (mesh size 0.5µm))
A set of experiments were conducted with this batch of sand to be used in Cell B in order to verify this value of K obtained. A small test cell was manufactured from a glass tube of overall length 25cm, and cross-sectional area 10.16cm$^2$ (Chemistry Department, Loughborough University). Two smaller glass tubes were fixed onto the main body of the tube to act as manometers, and the whole assembly was connected via rubber tubing to a five litre modified glass beaker that acted as a reservoir. The sand was added to the cell, compacted, and allowed to saturate before experiments were conducted. Alteration of the head height of the reservoir meant different flow rates were obtainable. Measurement of these flow rates, and the $\Delta h$ observed on the manometers enabled $Q$ to be plotted against $\Delta h/\Delta l$, and a value for the permeability of the sand to be calculated. $\Delta l$ is the distance between the manometers and was constant at 14.8cm.

Figure 3.4 shows a schematic set-up of the equipment used to obtain a value for the permeability of the sand. Table 3.1 shows the resulting $Q$, $\Delta h$, and $\Delta h/\Delta l$ values obtained at various head heights, with Figure 3.5 depicts the graph obtained from these results.

**FIGURE 3.4** - A schematic set-up to determine a value of K for a given sand sample
TABLE 3.1 - The flow rates and Δh values obtained at different head heights in order to determine a value of K for a sample of sand

<table>
<thead>
<tr>
<th>Flow rate - Q (ml/min)</th>
<th>Δh (cm)</th>
<th>Δh/Δl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>4.5</td>
<td>0.304</td>
</tr>
<tr>
<td>0.84</td>
<td>5.1</td>
<td>0.344</td>
</tr>
<tr>
<td>0.95</td>
<td>5.9</td>
<td>0.399</td>
</tr>
<tr>
<td>1.07</td>
<td>6.8</td>
<td>0.459</td>
</tr>
<tr>
<td>1.22</td>
<td>7.6</td>
<td>0.514</td>
</tr>
<tr>
<td>1.27</td>
<td>10.0</td>
<td>0.676</td>
</tr>
<tr>
<td>1.29</td>
<td>8.0</td>
<td>0.540</td>
</tr>
<tr>
<td>1.35</td>
<td>8.6</td>
<td>0.581</td>
</tr>
<tr>
<td>1.36</td>
<td>10.9</td>
<td>0.736</td>
</tr>
<tr>
<td>1.47</td>
<td>11.7</td>
<td>0.790</td>
</tr>
<tr>
<td>1.6</td>
<td>12.4</td>
<td>0.838</td>
</tr>
<tr>
<td>1.6</td>
<td>11.4</td>
<td>0.770</td>
</tr>
<tr>
<td>1.63</td>
<td>11.9</td>
<td>0.804</td>
</tr>
<tr>
<td>1.65</td>
<td>12.0</td>
<td>0.811</td>
</tr>
<tr>
<td>1.77</td>
<td>12.6</td>
<td>0.851</td>
</tr>
</tbody>
</table>
FIGURE 3.5 - A plot of Q against Δh/Δl to determine a value of K for the medium under study

With reference to Figure 3.5, a value of 0.5899 was obtained for the line produced when Q was plotted against Δh/Δl. From Darcy's Law it is stated that;

\[ Q = KA(\Delta h/\Delta l) \]
Chapter Three - Design of Cell B

It follows that,

$$KA = 0.5899$$

Since $$A = 10.16\, \text{cm}^2$$,

$$K = 0.058\, \text{cm}^3\text{min}^{-1} = 3.48\, \text{cm}^3\text{hr}^{-1}$$

This value compares favourably with the value obtained from the particle size analysis. Both methods of determination use only a small sample of sand, and are therefore probably not representative of the sand as a whole due to inadequate mixing of the two different ground batches of sand. However, an approximate value for the permeability of the sand to be placed into Cell B has been obtained. This averaged value of $$K = 4.04\pm0.56\, \text{cm}^3\text{hr}^{-1}$$ obtained from the calculated and experimental values described previously, will provide a reasonable estimate of the flow through time for Cell B.

The mixed batch of sand was added to the cell to a depth of approximately 40cm. As before, the sand was added in increments to try to achieve as compact a cell as possible. A small layer of gravel was placed on top of the sand and the lid was sealed into place. Rubber bungs were used to seal each of the holes in the faces that were not being used to house electrodes. Water was filled to the top of the cell and left to achieve saturation of the sand.

3.5 - RESULTS AND DISCUSSION

In order to verify that a steady flow through the cell could be obtained, initially experiments concentrated on the flow rate through the cell. The level of the water, and hence the head height, was kept constant by utilising one of the five holes that had been machined into one of the vertical faces for this purpose. These enabled head heights between 12cm and 16cm to be achieved. The flow rate through the cell was measured at set time intervals by recording the volume of water produced at the outlet
valve over a set period of time. This was repeated with different bungs being removed in order to alter the head height. Once it was ascertained that a steady flow was not being achieved, all five of the holes were blocked and the water level filled to the top of the cell. By forcing a larger head onto the sand, and repeating the experiment over a period of a week, it was hoped a steady flow would be obtained. The water level was now kept constant by using the reservoir from Cell A to constantly feed into the top of the cell. Figure 3.6 shows a standard set of results obtained when the middle bung is removed (~13cm head), and Figure 3.7 shows a standard set obtained when the water level was filled to the top of the cell (~25cm head).

**FIGURE 3.6** - A representative set of results showing the flow rates obtained through Cell B when the head height is approximately 13cm
FIGURE 3.7 - A representative set of results showing the flow rates obtained through Cell B when the head height is approximately 25cm

![Graph showing flow rates through Cell B](image)

With reference to Figures 3.6 and 3.7, it can be stated that it was not possible to achieve a steady flow through Cell B. This was due to the small holes present in the lid on top of the gravel which were there to aid uniform flow. These holes made the cell an open system, similar to Cell A. These holes in the lid, as well as the five holes at differing heights that were to be used to alter the head height, were filled in with sealant. The lid would now have to be sealed at a specific height in the cell in order to give a constant head. The water would be introduced into the space between the sealed lid and the gravel via an inlet tube. This pressure head created should then force the water to flow down through the sand to appear at the bottom of the cell.

A hole was machined into one side of the cell and a nozzle attached to act as an inlet valve for the water, and the lid was sealed into place at approximately 10cm above the
level of the gravel. Water was gradually introduced into this space created between the gravel and the lid, and any leaks observed were re-sealed.

Unfortunately a number of attempts to run an experiment saw that the pressure buildup in the top of the cell between the lid and the gravel was too large for this particular construction. The lid would either begin to bow upwards or the sealant would give way, before any flow through the cell was achieved. The volume of sand was too great and too compact to enable any reasonable sort of hydraulic head to force a flow through the system. If it were possible to use a hydraulic head of large proportions, a flow through the cell could be obtained. This would either mean drastic alterations to the cell design to allow space above the sand and gravel for a large volume of water to be present, or the use of a vast reservoir connected to the cell to house such a volume of water. This was ascertained to be too problematic, so work began on a new, small cell design.

3.6 - CONCLUSIONS

In conclusion, after many attempts to achieve a steady flow through Cell B, it was deemed to be unsuitable for experiments to be conducted on researching the remediation of contaminated groundwater.

Initially a similar problem was encountered as for Cell A, in so far as the cell was not a fully sealed system. Once this had been overcome by permanently fixing the lid into place, the volume of sand through which the flow needed to pass proved to be too great for the head available. Before any fluid had passed through the cell, the top of the cell began to bow, and the pressure being exerted on both the glue holding the lid in place and the lid itself was considered too great for the design of this particular cell.

The design of Cell B, once the system had been converted to a closed system, was fundamentally and theoretically correct. To ensure a flow through could be obtained in further cell designs based on Cell B, a number of factors need to be considered. A thicker perspex or stronger material would be beneficial as more pressure could then
be exerted within the cell. A larger head space above the volume of sand would create a larger hydraulic head and aid flow through the cell. Further grinding of the sand to decrease the value of K obtained would lead to a faster flow through the cell.
CHAPTER FOUR - DESIGN AND USE OF SMALL CELLS

4.1 - INTRODUCTION

For both Cell A and Cell B, the preliminary results regarding the flow through the cell had not been satisfactory and this had prevented any electrokinetic remediation work from being undertaken. In order to research this area of remediation, a smaller cell through which a flow could be observed within a short time period, was designed. By decreasing the size of the cell, the number of parameters able to be varied were also decreased i.e. the number of electrodes and their configuration, but this still left sufficient variables i.e. contaminant concentration, applied voltage, and flow rate, to be able to undertake research into electrokinetic remediation.

By designing a smaller cell, less sand would be needed to fill the body of the cell. This in turn would mean that a flow through the cell could be achieved with a relatively small hydraulic head. Changing the head height to alter the flow would be easy and more manageable.

The majority of work reported to date concentrates on the remediation of media spiked with a particular contaminant, whereas the research conducted here is concerned with contaminated fluid passing through the designed cell. This method, coupled with the specific electrode material under investigation, leads to a novel approach to electrochemical remediation.

4.2 - DESIGN DETAILS

Construction was carried out in the mechanical workshop of the Chemistry Department at Loughborough University. A cylindrical perspex tube (SBA Co. Ltd., Leicester, 60cm od, 50cm id) was utilised as the main body of the cell as this was felt to be less susceptible to stress and cracks than a rectangular counter-part. The flow through a cylindrical cell when compared to a rectangular cell should be more fluid and benefit from a decrease in any effects due to the edges and corners present in a
rectangular design. Two holes were machined in line with each other in the body of the cell where the carbon rod electrodes could be sealed into place with sanitary sealant. This would enable the removal and exchange of electrodes to be both simple and efficient. Two rectangular pieces of perspex (93mm x 93mm x 12mm) were used as the two end sections of the cell. Each had a circular groove of the same diameter as the central body machined into it, into which the central body could sit and form a seal with the aid of sanitary sealant. Nozzles were also incorporated into both end sections and these acted as either an inlet or an outlet valve depending on the orientation of the cell. Threads were placed between opposite corners of the end sections to hold the whole assembly together and screws on each end ensured as tight a seal as possible was achieved. This meant that a closed system could be obtained. Altogether six cells were made, of various lengths and electrode spacing distances. Figure 4.1 shows the basic design concept for the small cells, and Table 4.1 shows the number of each cell with their respective dimensions. Figure 4.2 shows photographs of Cells 1 – 4 once packed, and of a Cell as set-up during an experiment.

FIGURE 4.1 - The basic design concept for the small cells
**Table 4.1** - A table to show all of the small cells and their dimensions

<table>
<thead>
<tr>
<th>Cell number</th>
<th>Length of cell (mm)</th>
<th>Electrode spacing (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>210</td>
<td>115</td>
</tr>
<tr>
<td>3</td>
<td>310</td>
<td>200</td>
</tr>
<tr>
<td>4</td>
<td>355</td>
<td>250</td>
</tr>
<tr>
<td>5</td>
<td>225</td>
<td>130</td>
</tr>
<tr>
<td>6</td>
<td>225</td>
<td>130</td>
</tr>
</tbody>
</table>
FIGURE 4.2 - Photographs of a) Cells 1-4, and b) a cell in use
4.3 EXPERIMENTAL

Each of the small cells was packed and sealed in the same manner. The initial step was to cut the carbon rods down to the required size. This was achieved by scoring the surface at the place to be cut, and snapping the rod. Any rough faces that were produced were polished using a Buehler Metaserv grinder polisher and P1200 metallographic grinding paper 8"(203mm). The carbon rods were cut so that when placed in the hole, they reached almost to the other side, and sufficient was left outside the cell to enable a connection to be made to a RS Thurlby PL310 power pack (~6.7cm). This connection was made via a large sheathed crocodile clip so that at any time when the power was being supplied there were no exposed surfaces to cause a hazard. The cut carbon rods were then placed in the hole and sealed into place with sanitary sealant and left to dry. It was found that if the cell was packed before the sealant had dried, the electrodes tended to move out of position by approximately 10°. Once dry (overnight was sufficient) the bottom face of the cell was aligned into the groove of an end section and sealed into place. A small piece of damp glass wool was placed inside the cell over the nozzle to prevent the escape of any sand. The wetting of it ensured it stayed over the hole and acted as an effective filter. Before the bottom end section had dried in place, sand was packed into the main body of the cell (~400g). As with Cells A and B, the sand was added in increments and compacted down before the next increment added. This was easier and more effective in the small cells as the whole cell could be tapped to dispel any trapped air and therefore voids within the system. The cell body was then aligned into the groove in the top end section and sealed. Once again this top end section had a small damp piece of glass wool placed inside the cell and over the nozzle to prevent the sand from escaping. Once the last end section was in position, the screws on the thread were tightened to give a good seal and ensure a closed system and the cell was left to dry overnight.

Each cell was used in a vertical position and was always saturated with distilled water before each experimental run. Beakers were utilised as reservoirs for the solutions that were to be passed through the cell. Two five litre beakers had been modified by the addition of a glass tube, fitted as near to the bottom as was possible to act as an outlet
Chapter Four - Design and use of small cells

valve. Rubber tubing was used to connect each beaker to the cell. The combination of the two beakers with a T-switch enabled the eluent to be changed from contaminated solution as a run was occurring, to water in order to flush through and clean the cell ready for the next run. The beakers were able to be easily height adjusted - the level of liquid inside the beaker as well as the actual height of the beaker itself - which meant that the value of $\Delta h$ could therefore be altered easily. Variation of $\Delta h$ and therefore $Q$, as well as the voltage applied to the electrodes and the concentration of the contaminant under investigation, ensured parameters could be altered in order to achieve the best remediation results. Figure 4.3 shows the experimental set-up used for each run.
In order to determine the volume of distilled water needed to effectively flush through the cell at the end of an experiment to leave it clean and contaminant free for the next run, a simple test was designed. A glass column (30cm length, 24mm id) with a tapered end was packed with a small amount of glass wool at the end, and then filled to a depth of 20cm with sand (Fisher Scientific, as received; graded 40-100 mesh and low in iron). A known volume of phenol (Aldrich, as received - 10ml) was added to the top of the column and the solute that appeared at the bottom tested for any phenolics using a Hewlett Packard 8452 UV/vis diode array spectrophotometer.
Washings with 10ml of distilled water, followed by the testing of each washing with the spectrophotometer, proceeded until there appeared to be no traces of phenol present in the solute and the sand was therefore clean. It was ascertained that in order to wash a set volume of sand clean of contaminants, approximately the same volume of distilled water needed to be allowed to flow through.

All cells were packed with sand (Fisher Scientific, as received). By completing a series of experiments with this 'inert' sand, and establishing the parameters required to enhance remediation, it was then envisaged that 'real' sand, such as the sand used in Cell A and Cell B could be utilised as the medium, and then finally the use of samples removed off sites was envisaged. The inert sand was sent for particle size analysis (Coulter Laser Sizer LS130, Chemical Engineering Department, Loughborough University) in order that comparisons could be made between the two sets of samples. The results of this analysis are shown in Figure 4.4.
FIGURE 4.4 - Particle size analysis for sand (Fisher Scientific, as received; graded 40-100 mesh and low in iron)
With reference to Figure 4.4 and also referring back to Figures 2.5 and 3.3, it can be stated that the sand purchased from Fisons has a much narrower particle size range than either batch of the ground prepared sand. There is no presence of very fine particles of sand - the cut-off point for this sample is very definite, indicating that the sample has been sieved to remove these smaller sized particles. Ideally the sand utilised in both Cell A and Cell B would also have been sieved to remove this tail of fine particles, but time constraints prevented this from being undertaken. The $D_{10}$ and mean particle diameter values for all the three sand samples analysed are presented in Table 4.2.

**TABLE 4.2** - $D_{10}$ and mean particle diameter values for the three sand samples analysed - Fisons sand, and the sand mixtures packed into Cell A and Cell B

<table>
<thead>
<tr>
<th>Sand sample</th>
<th>Reference figure</th>
<th>$D_{10}$ ($\mu$m)</th>
<th>Mean particle diameter ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fisons sand sample</td>
<td>4.4</td>
<td>165.8</td>
<td>241.5</td>
</tr>
<tr>
<td>Sand from Cell A</td>
<td>2.5</td>
<td>188.0</td>
<td>406.6</td>
</tr>
<tr>
<td>Sand from Cell B</td>
<td>3.3</td>
<td>35.95</td>
<td>233.8</td>
</tr>
</tbody>
</table>

The mean particle size is largest for that sand that was packed in Cell A. This indicates that the purchased sand that was prepared by grinding to be used in the constructed cells, originally had a large particle size distribution and contained relatively large as well as very fine particle sizes. Further grinding of this sand to give the sand used in Cell B led to an expected decrease in the mean particle size, as well as a decrease in the $D_{10}$ value observed. Even though the Fisons sample has a similar mean particle diameter as that for the sand used in Cell B, the $D_{10}$ value observed is exceptionally larger. This can be explained by the lack of a 'tailing off' of the distribution graph, indicating the absence of very fine particles in the Fisons sand. This would make the value below which 10% of the overall volume is lower, increase.
4.3.1 - Phenol

4.3.1.1 - Introduction and Theory

Phenol was chosen as a contaminant as it is one of the major pollutants found in disused gas sites. Alteration of the concentration of phenol, and also that of sodium perchlorate (NaClO₄ Acros Organics, as received) which was to be used as a background electrolyte, as well as variation of the flow rate, the voltage applied, and the time period for which the voltage was applied, would enable the remediation of phenol by electrokinetic measures to be studied. Due to the fact that phenol absorbs at ~270nm, \((e = 2398\text{dm}^3\text{mol}^{-1}\text{cm}^{-1})\) the decrease of this peak when studied using a spectrophotometer would enable the degree of remediation to be studied.

4.3.1.2 - Experimental

Initially the cell was saturated with distilled water. The T-switch was then switched over and the phenolic solution allowed to pass through. At all times this phenolic solution was at a higher pH than 11 which was achieved by drop-wise addition of 1M sodium hydroxide solution (NaOH, Fison's, diluted in distilled water). This was to ensure that the phenolate form of the phenol was prevalent, which would then be caused to move under electrokinetic conditions. Samples were collected at set time intervals and were analysed for any phenolics between 190nm and 820nm in a quartz silica cuvette in a Hewlett Packard 8452A diode array spectrophotometer. (The theory for the UV/vis absorption spectrometry can be found in \textit{CHAPTER 6 - SPECTROSCOPIC STUDIES OF SELECTED PHENOLS}). A blank was scanned before each set of samples. Once enough time had passed to ensure the cell was saturated with the phenolic solution and the concentration of the phenol had reached a plateau, the voltage was switched on. In this instance with the phenol as a contaminant, the uppermost electrode in the configuration was made to be the anode (+ve). A Shandon Southern SAE 2761 power pack supplied this applied voltage. This initial period of sampling to achieve a concentration plateau of the phenol was normally 90 minutes long. Samples were taken as the run progressed, and
subsequently monitored to see any change in concentration of the contaminant due to this applied voltage. Sampling continued for a set period of time that was sufficient to ensure that any change that was going to occur, would. This was in the range of two to five hours depending on the flow rate chosen. Once the run had been completed, the T-switch was switched back again to allow the cell to be flushed with distilled water. The samples were disposed of accordingly. Runs were repeated - some had identical parameters to verify results, whilst others had certain conditions altered. These changeable conditions included voltage applied, concentration of both contaminant and background electrolyte, as well as changing the cell itself. The conditions under which each experiment were conducted can be found in Table 4.3. It must be noted that not all runs undertaken are tabulated - it was obvious within the first hour of an experiment being conducted whether or not the set-up was satisfactory. An unsatisfactory set up resulted in either no flow or an extremely erratic flow being observed. In some instances the cell was in need of re-packing due to improper initial packing or compaction of the sand due to excessive use of that cell. Blocked and bent tubing and blocked nozzles also prevented the equipment from functioning correctly. These such experiments are not detailed as they were abandoned prior to the voltage being applied.

The flow rate through the cell was approximately calculated by measuring the volume of the sample that was collected, and the time that it was collected for. It must be noted that slight fluctuations were observed throughout the day - as the reservoir continually dropped and was then replenished by hand, a slight decrease and then increase was observed. This was considered too small a difference to be of concern. The flow rates presented in Table 4.3 are therefore the approximate average over the whole period the run was conducted for.
TABLE 4.3 - Experimental parameters for the small cells with phenol as the contaminant

<table>
<thead>
<tr>
<th>Phenol concentration (M)</th>
<th>NaClO₄ concentration (M)</th>
<th>Voltage applied (V)</th>
<th>Approximate flow rate (ml/min)</th>
<th>Number of experiments conducted</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 x 10⁻³</td>
<td>0</td>
<td>30</td>
<td>3</td>
<td>1 (Cell 1)</td>
</tr>
<tr>
<td>2 x 10⁻³</td>
<td>0</td>
<td>100</td>
<td>4</td>
<td>1 (Cell 1)</td>
</tr>
<tr>
<td>2 x 10⁻³</td>
<td>2 x 10⁻⁴</td>
<td>100</td>
<td>4 / 3</td>
<td>2 (Cells 1 &amp; 2)</td>
</tr>
<tr>
<td>2 x 10⁻³</td>
<td>8 x 10⁻⁴</td>
<td>130</td>
<td>3 / 6</td>
<td>2 (Cell 2)</td>
</tr>
<tr>
<td>1.6 x 10⁻³</td>
<td>8 x 10⁻⁴</td>
<td>130</td>
<td>3</td>
<td>1 (Cell 1)</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>1 x 10⁻⁴</td>
<td>130</td>
<td>6 / 5</td>
<td>2 (Cells 1 &amp; 3)</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>1 x 10⁻⁴</td>
<td>140</td>
<td>3</td>
<td>1 (Cell 1)</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>1 x 10⁻⁴</td>
<td>160</td>
<td>6 / 8 / 8 / 2 / 6</td>
<td>5 (Cells 1 &amp; 3)</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>1 x 10⁻⁴</td>
<td>190</td>
<td>4</td>
<td>1 (Cell 3)</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>8 x 10⁻⁴</td>
<td>15</td>
<td>3 / 3</td>
<td>2 (Cell 1)</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>8 x 10⁻⁴</td>
<td>30</td>
<td>3 / 4 / 4</td>
<td>3 (Cell 1)</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>8 x 10⁻⁴</td>
<td>50</td>
<td>5 / 4 / 2</td>
<td>3 (Cell 1)</td>
</tr>
</tbody>
</table>

4.3.1.3 - Results and Discussion

It became apparent that as the voltage was applied across the two electrodes an unexpected phenomenon was occurring. As each run progressed, the solution appearing at the bottom of the cell often showed a brown tinge. On those occasions that this was not visible, it is believed that the colouration was still present but at such a low concentration as to not be visible to the naked eye. The presence of this colour meant that the phenol peak was obscured in the subsequent recorded UV/vis spectrum.

With reference to Table 4.3, the changeable parameters were varied considerably in order to prevent this brown colour from appearing. The presence of the background electrolyte and its concentration were altered, as was the applied voltage. A decrease
in the voltage did have a tendency to decrease the intensity of the colour of the solution, but this still did not allow the phenol peak to be observed on the UV/vis spectra.

The appearance of this colour was believed to be due to a reaction that was taking place between the phenol and the carbon rod electrodes as the voltage was applied. In order to ascertain whether this was a correct assumption, tests were conducted whereby approximately 50ml of solutions of various compositions were placed in a beaker, along with two carbon rod electrodes that were connected to an RS Thurlby PL310 power pack. The voltage was applied between the two electrodes for an hour and any subsequent effects studied. Table 4.4 shows the various effects observed when different solutions were placed in the beaker. The term phenolic used within the table refers to phenol and 2,6-dimethylphenol, both of which were used to conduct experiments.

**TABLE 4.4**— The varying effects observed in solutions of different compositions upon the application of a voltage between two carbon rod electrodes held in the solution

<table>
<thead>
<tr>
<th>Solution composition</th>
<th>Effects noted on application of ~110 volts for an hour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionised water</td>
<td>No visible effects</td>
</tr>
<tr>
<td>NaClO₄ only</td>
<td>Brown colouration</td>
</tr>
<tr>
<td></td>
<td>Warming of solution</td>
</tr>
<tr>
<td></td>
<td>Effervescence off electrodes</td>
</tr>
<tr>
<td>Phenolic + NaClO₄</td>
<td>Brown colouration</td>
</tr>
<tr>
<td></td>
<td>Warming of solution</td>
</tr>
<tr>
<td></td>
<td>Effervescence off electrodes</td>
</tr>
<tr>
<td>Phenolic only</td>
<td>Slight browning, warming and effervescence</td>
</tr>
</tbody>
</table>
It would appear from these results that the appearance of the brown colour, the warming effect, and the effervescence, is a cause of the current that passes through the carbon rod electrodes. The deionised and phenolic solution experiments gave no visible effects and slight effects respectively, whilst both the sodium perchlorate and phenolic, and the sodium perchlorate mixture gave considerable colour change, heat and gas evolution. These latter two solutions would both possess the ability to carry large currents between the electrodes due to the excess amount of perchlorate present. The deionised water and phenol solutions will both have reduced conductivity's, and this would cause any effects to be reduced, and possibly prevented within the set time period.

Attempts were made to prevent the solution in the beaker from changing colour in the same way as in the experiments conducted with the cell. Lower voltages were applied for shorter periods of time, and the concentration of both the phenolic and the background electrolyte were decreased. The effect of a lower voltage was to reduce the intensity of the brown colouration, and this same effect was also noted when the time period that the experiment was conducted for was decreased. However, these had no effect on the resulting spectra, as even when the solution appeared not to have changed colour, the phenol peak was obscured when the sample was placed into the spectrophotometer cell. Figure 4.5 shows this masking of the phenol peak by showing the initial UV/vis spectrum for a sample containing phenol, and also spectra of the same sample after it had been subjected to 100 volts for both 60 and 90 minutes.
FIGURE 4.5 - The masking of a phenol peak on a UV/vis spectrum due to the presence of a brown colouration

---

initial solution containing phenol and NaClO₄, prior to an experiment being conducted

---

brown coloured sample that had initially contained phenol and NaClO₄, and had been subjected to 100 volts for 60 minutes

---

brown coloured sample that had initially contained phenol and NaClO₄, and had been subjected to 100 volts for 90 minutes
The brown colouration of the solution could be due to oxidation products of the phenolic. Even though a colour change was observed with the solution containing sodium perchlorate and no phenolic, this could be attributed to the fact that the rod had previously been used in experiments and adsorption of the phenolic onto the rod had occurred. This could lead to oxidation of the adsorbed phenol once the voltage had been applied. To verify this explanation, a number of experiments were undertaken in order to achieve a brown sample so that NMR analysis could be carried out. 50ml of a solution consisting of approximately 0.02g phenolic and $7 \times 10^{-4}$ M NaClO$_4$ was placed in a beaker along with two carbon rod electrodes. 80 volts were applied between these two carbon rod electrodes for the period of an hour. This gave a light brown coloured sample. The water present in the sample was removed under reduced pressure and the dark brown viscous liquid residue taken up in CD$_3$CN. The $^1$H NMR spectrum of this sample was then carried out on a Bruker DPX-400. For reference purposes, a sample of phenol was analysed by $^1$H NMR by dissolution in CDCl$_3$. Figure 4.6 shows the $^1$H NMR spectrum of the phenol, with resonances at $\delta$6.8 - 7.2 due to the aromatic protons which appear as a multiplet, and a broad singlet at $\delta$4.2 for the hydroxyl proton. Both of these are reported with respect to TMS (tetramethylsilane) which appears at $\delta$0.0. Figure 4.7 shows the coloured sample $^1$H NMR spectrum which shows a peak at $\delta$2.19, and a triplet at $\delta$1.95 with respect to TMS. The triplet appears due to the residual proton present in the solvent CD$_3$CN, whilst the singlet appearing at $\delta$2.19 is due to the presence of residual water within the deuterated acetonitrile.
FIGURE 4.6 - $^1$H NMR spectrum of phenol (Aldrich, as received). (Solvent = CDCl$_3$)
FIGURE 4.7 - $^1$H NMR spectrum of product of 0.023g phenol in $7.8 \times 10^{-4}$M NaClO$_4$ (50ml) that has had 80 volts applied across it for one hour (Solvent = CD$_3$CN)
This test was repeated a number of times, both with phenol and 2,6-dimethylphenol (Aldrich, as received). The absence of any peaks other than those able to be assigned to the solvent, indicates that the brown colouration of the sample is not, as was thought due to any oxidation products of phenol, as these would be clearly visible as peaks on the spectrum. The colour can be accounted for by the gradual disintegration of the carbon rods into solution. This is verified by the change in morphology on the surface of the carbon rod once it has been removed from the solution at the end of the experiment. Further work in this area could involve centrifuguing the sample obtained in order to ascertain whether particles of carbon are suspended in solution.

The lack of peaks on the resulting NMR spectra leads to the conclusion that no phenol or phenol oxidation products are present in the sample. This can be attributed to adsorption of the phenol onto the electrode surface or electropolymerisation to produce a film on the electrode. Even though the initial concentration of the phenolic was substantial, it is possible that complete adsorption / electropolymerisation is occurring as the electrode area is sufficiently large to be able to feasibly account for this total loss from solution.

Another possible explanation for the loss of phenolic from solution could be distillation of the sample during the period of the application of the voltage. During this time heating of the solution did occur, and although phenol has a boiling point of 182°C (BDH Ltd: health and safety data sheet) and it would appear unlikely that this would be the case, identification of the gaseous emissions would need to be conducted before this explanation can be discounted. The boiling points of the oxidation products of the phenolic could be sufficiently lower than that of phenol, that these may be distilled, indicating that further work in this area is necessary.

An explanation for the effervescence observed upon the application of the voltage could be the production of hydrogen and / or oxygen at the cathode and anode respectively. Oxidation of the actual carbon rod to carbon dioxide is another possible explanation for the emitted gases, but further work would need to be conducted in this
area in order to be definite. This could involve the collection of the emitted gases and the subsequent analysis of them to positively identify the gases present.

The combination of these effects leads to a possible disintegration of the exterior of actual rod, as upon removal of the rods from solution when a colour change, heating and gas evolution were noted, the areas in contact with the solution showed an alteration in surface morphology. A pitted and rough surface had resulted that could be easily removed by scraping. Even though a colour change has been observed in the phenol cell experiments, it is believed that this change in morphology is not noted due to the greater electrode spacing within the cells and the decrease in voltage applied.

Further work in this area could lead to the determination of the cause of the brown colour of the sample. This could involve using solutions of higher concentrations of phenol in order to ascertain if the total loss of phenol is still occurring even when this could not be attributed to adsorption alone. The carbon rods could be ground after an experiment had been conducted, and attempts to desorb and identify any adsorbed phenol would conclude whether this is the correct assumption as to the loss of the phenol from solution. The collection and analysis of the emitted gases would give an insight into the reactions occurring at the electrode to cause effervescence. Continual monitoring of the solution with a documented technique i.e. HPLC-EC would enable the concentration profiles of the phenolic and its possible oxidation products to be monitored. It is feasible that the phenolic in question is undergoing rapid and complete oxidation through aromatic and aliphatic intermediates to produce carbon dioxide, and this would verify this theory.

Another quantitative method of phenol analysis was required in order that research could be continued. Previous studies have shown that it is possible to analyse the phenol content in an aqueous solution by using high performance liquid chromatography, with both an electrochemical detector, and an ultra-violet detector, known as HPLC-EC and HPLC-UV respectively. HPLC-EC is a well documented technique and has also been used to determine the phenol content in soils, air, and oil. Other methods of phenolic determination include a
chemiluminescent quench technique,\textsuperscript{94} capillary zone electrophoresis coupled with fluorescence detection,\textsuperscript{95} an on-line solid-phase extraction liquid chromatography method for the sorption of the phenol from the sample,\textsuperscript{96} derivatisation or extraction followed by analysis by gas chromatographic mass spectrometry (GC-MS),\textsuperscript{97,98} and electrochemical concentration modulation correlation chromatography (ECM-CC) with fluorescence detection.\textsuperscript{99}

HPLC-EC appeared to be the most documented technique to determine the phenol concentration in a given sample. BG Technology offered the use of their HPLC system that was specifically set-up for phenolics, so this seemed the most simple and efficient method to use. The system comprised a Shimadzu LC-6A pump, a Shimadzu SCL-6B system controller, an Interface Nelson Analytical 960, and a Spherisorb 5ODS 25cm x 4.5mm id column. The detector used was an ESA Coulochem II multi-electrode detector (model 5200), with an ESA Analytical cell (model 5010), and an ESA guard cell (model 5020). Four runs were carried out using Cell 6 with a phenol concentration of $1 \times 10^{-3}$ M and a NaClO$_4$ concentration of $8 \times 10^{-4}$ M. The solution was taken to pH>11 by the addition of 1M NaOH solution and the run allowed to progress. Samples were taken at set time periods ($t = 0, 15, 45, 75, 105, 135, 165, 195, 225, 255,$ and 285 mins), and at $t = 90$ mins, 80 volts were applied. Each sample was diluted with methanol (Aldrich, HPLC grade) : water (Aldrich, HPLC grade) (50 : 50) to ensure the concentration of the sample would fall within the detection limits of the detector ($<2.5$ mg/l$^1$). The samples were then labelled, and stored until all could be sent to be subjected to HPLC-EC. The cell was flushed through with distilled water between each run. All four runs gave similar results. One such set of results is shown in Table 4.5, whilst Figure 4.8 shows an example of the clean peak at a retention time of five minutes, produced by the presence of the phenol. The initial peak present on the spectrum is the injection peak, and it is after this has appeared that automatic integration of any subsequent peaks occurs. The particular peak shown represents $t = 255$ minutes from the data shown below.
### TABLE 4.5 - A set of results from a phenol run in Cell 6 analysed by HPLC-EC
(Note that at t = 90 mins, 80 volts were applied)

<table>
<thead>
<tr>
<th>Time (mins)</th>
<th>Phenol concentration (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.727</td>
</tr>
<tr>
<td>45</td>
<td>1.775</td>
</tr>
<tr>
<td>75</td>
<td>1.726</td>
</tr>
<tr>
<td>105</td>
<td>2.055</td>
</tr>
<tr>
<td>135</td>
<td>2.214</td>
</tr>
<tr>
<td>165</td>
<td>1.924</td>
</tr>
<tr>
<td>195</td>
<td>2.055</td>
</tr>
<tr>
<td>225</td>
<td>2.077</td>
</tr>
<tr>
<td>255</td>
<td>2.29</td>
</tr>
<tr>
<td>285</td>
<td>2.19</td>
</tr>
</tbody>
</table>
FIGURE 4.8 - Phenol peak observed by HPLC-EC at $t = 255$ minutes from a run using Cell 6 and with an application of 80 volts.
These results, as well as the other three runs that were measured by HPLC-EC, show no decrease once the voltage has been applied. The voltage was applied for a total of 200 minutes, which from experiments with ammonia as the contaminant (Section 4.3.2 - Ammonia) is known to be a sufficient time to see a decrease if one was going to occur. It could be possible that the brown colouration is causing the results to be obscured again, or that the carbon rod electrodes have been damaged by the phenol due to the application of the voltage. Either way, it would seem that it is not possible to tell from these parameters used whether the concentration of phenol is able to be reduced.

The work carried out on the electrokinetic remediation of phenol by using the small cells (Cell numbers 1, 2, 3 and 6) gave no conclusive results due to the appearance of the brown colour upon application of the voltage. Further work on this aspect of remediation with this particular contaminant, could involve repeating some of the same experiments but with various other electrode materials. If this proved to be successful, parameters could be varied as reported in order to optimise the remediation of phenol from contaminated water. Further work could then involve the use of substituted phenols as contaminants, and the use of groundwater samples from on site, *i.e.* 'real' samples.

4.3.2 - Ammonia

4.3.2.1 - Introduction and Theory

Contaminants at disused gasworks sites are numerous. Phenol has been studied as a contaminant in the previous section, and here the remediation of ammonia is investigated. Ammonia is a contaminant present at disused manufactured gas sites, and is able to be determined by an Ion Selective Electrode (ISE) which would ensure that samples could be analysed even if the same colour problem observed with the phenol experiments, occurred again. Ammonium chloride (NH₄Cl, Aldrich, 99.99%, as received) was used as the source of ammonia, and no other chemicals were added.
Phenol was converted to its phenolate form by the addition of 1M NaOH in order to be studied electrokinetically. The NH₄Cl was used as received, and in this way the remediation of a phenolate anion, and an ammonium cation was able to be studied and compared. The polarity of the electrodes in the small cell were altered between the change of contaminant. As stated previously, when the phenolate anion was under study, the uppermost electrode in the vertical small cell orientation was made to be the anode (+ve). Conversely, when the contaminant under investigation was the ammonium cation, the cathode (-ve) was the uppermost electrode. By having the opposite charged electrode to the contaminant nearer to the inlet valve of the cell, any effect due to the application of the voltage was hoped to be more pronounced.

As each sample was collected from the cell, a 1M solution of NaOH was added to it in a drop-wise fashion. This was in order to convert the ammonium cation to ammonia which is detectable by the ISE.

4.3.2.2 - Theory of the ISE

A Russell ISE ammonia electrode connected to a Radiometer PHM 93 reference pH meter was employed. This particular ISE utilised contains a glass electrode inner body with internal reference element, and an internal filling solution of known concentration is injected between this inner and the outer body. The ISE measures the amount of dissolved ammonia in aqueous solutions, and so subsequently is also able to measure the concentration of any ammonium once it has been converted to ammonia. Ammonia dissolves in water thus;

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- 
\]

It follows that the relative amounts of both the ammonia and ammonium will be dependent on the pH of the solution. To convert all of the ammonium to ammonia, the pH of the solution needs to be increased. This can be achieved by the drop-wise addition of 1M NaOH until the pH of the solution is above 11.
A hydrophobic gas permeable membrane present in the ISE separates the sample from an internal reference filling solution that has a set volume of 2.5ml. Dissolved ammonia in the sample diffuses through the membrane until the partial pressure \( (pp) \) on both sides is equal. This partial pressure of the ammonia is proportional to its concentration;

\[
pp \text{ NH}_3 \propto [\text{NH}_3]
\]

As the ammonia diffuses through the membrane, it dissolves in the internal solution thus;

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-
\]

Which then gives;

\[
\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \text{constant}
\]

Since the internal filling solution has such a high concentration of ammonium chloride compared with that of the sample, its concentration can be said to be fixed. It follows that;

\[
[\text{OH}^-] = [\text{NH}_3] \times \text{constant}
\]

The potential of the electrode sensing element, with respect to the internal reference element, varies in a Nernstian manner with any change in the hydroxide concentration;

\[
E = E_0 - S \log[\text{OH}^-]
\]
Where:

\[ S = \text{electrode slope} \]
\[ E_o = \text{reference potential} \]

It has already been stated that the concentration of the hydroxide ion is proportional to that of the ammonia, therefore the response of the electrode to the ammonia concentration is also Nernstian;

\[ E = E_o - S \log[\text{NH}_3] \]

Measurements of the samples were achieved with the aid of a calibration plot. Before each experiment was conducted, a set of samples of known concentration of ammonium chloride were measured. These samples were all at pH>11 to ensure total conversion of ammonium to ammonia. The graph that resulted when the log of the ammonium chloride concentration was plotted against the volts obtained from the ISE, was a straight line graph. The equation for this straight line could then be used to calculate the concentration of further samples by use of the voltage reading from the meter.

4.3.2.3 - Experimental

Initially the cell was saturated with distilled water. The T-switch was then switched over and the ammonium chloride solution allowed to pass through. Samples were collected at set time intervals and were altered to pH>11 by the drop-wise addition of 1M NaOH, before the level of ammonia present was determined using the ISE. Prior to each run a calibration with standards of known concentration was carried out and by using the equation achieved for the straight line produced, the concentration of each of the collected samples was able to be calculated. Between each sample the ISE was rinsed in distilled water and gently wiped dry.
Once enough time had passed to ensure the cell was saturated and the concentration of ammonia had reached a plateau, the voltage was switched on. This voltage was supplied by a Shandon Southern SAE 2761 power pack. It was possible to determine when the concentration of the ammonia had reached a plateau by continual sampling. By taking measurements at set time intervals for the first few runs, it became evident that an initial period of 90 minutes was substantial enough to allow the contaminated solution to flow through the cell and to reach a steady state. Samples were continually taken as the run advanced, and subsequently measured with the ISE to see the effect the application of the voltage had on the concentration of the ammonia. This sampling continued for a set period of between two and five hours. Continual measurement of the samples as they were collected enabled a plot of concentration against time to be immediately viewed. This ensured the experiment could be halted when an effect on the ammonia concentration had been observed. Once the run had been completed, the T-switch was switched back again to allow the cell to be flushed with distilled water. Once the samples had been measured, they were too numerous to be retained, so were disposed of accordingly.

Runs were repeated - some had identical parameters to verify results, whilst others had certain conditions altered. In all cases the cell was kept constant in order that comparisons could be made. Cell 6 was the cell used which had an overall length of 225mm and an electrode spacing of 130mm. The conditions altered between experiments included voltage applied, concentration of NH₄Cl, and the pH of the solution flowing through the cell. In this last case, the pH was altered by dropwise addition of either 1M HCl or 1M NaOH to change the solution to acid or alkaline accordingly. In both the acid and alkaline situations, and when nothing was added so the solution was effectively neutral, the pH of the sample was altered to pH>11 by addition of 1M NaOH prior to analysis with the ISE.

A set of experiments were also conducted whereby the above procedure was adhered to until the time where the NH₄Cl concentration had dropped and subsequently levelled off. Having carried out a number of experiments, it was possible at this stage to estimate when this time would be within the reaction period. The voltage was then
turned off and the effect monitored. After the voltage was turned off, samples were collected and monitored for on average an extra 90 minutes.

4.3.2.4 - Results and Discussion

It must be noted that some runs did not work and it was obvious within the first few hours that this would be the case. This could be due to bad packing of the cell, a blockage occurring in the tubing and/or the cell which caused the flow to stop, or merely that the cell needed to be re-packed as all the medium had gradually compacted at the bottom of the cell. These results are not presented as the experiment was stopped and the problem corrected, usually prior to the voltage being applied.

Table 4.6 shows the results for those experiments that were conducted using Cell 6, and with NH$_4$Cl as a contaminant. The last column presented in the table i.e. the average decrease in the concentration of NH$_4$Cl, was achieved by averaging all those decreases obtained for those runs undertaken under the conditions stated in the particular row in question.
### TABLE 4.6 - Results for Cell 6 when using NH₄Cl as a contaminant

<table>
<thead>
<tr>
<th>NH₄Cl concentration (M)</th>
<th>Voltage applied (V)</th>
<th>Number of runs carried out</th>
<th>Approx. flow rate (ml/min)</th>
<th>Nature of solution</th>
<th>Average decrease in concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 x 10⁻³</td>
<td>0</td>
<td>1</td>
<td>15</td>
<td>alkali</td>
<td>none</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>30</td>
<td>4</td>
<td>15</td>
<td>alkali</td>
<td>14 ± 5%</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>50</td>
<td>4</td>
<td>15</td>
<td>alkali</td>
<td>10 ± 5%</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>80</td>
<td>4</td>
<td>15</td>
<td>alkali</td>
<td>24 ± 2%</td>
</tr>
<tr>
<td>5 x 10⁻⁴</td>
<td>80</td>
<td>6</td>
<td>15</td>
<td>alkali</td>
<td>26 ± 10%</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>80</td>
<td>4</td>
<td>4-5</td>
<td>neutral</td>
<td>55 ± 10%</td>
</tr>
<tr>
<td>5 x 10⁻⁴</td>
<td>80</td>
<td>5</td>
<td>17</td>
<td>neutral</td>
<td>58 ± 8%</td>
</tr>
<tr>
<td>5 x 10⁻⁴</td>
<td>80</td>
<td>4 (turned off and monitored)</td>
<td>20</td>
<td>neutral</td>
<td>68 ± 4%</td>
</tr>
<tr>
<td>1 x 10⁻³</td>
<td>80</td>
<td>3</td>
<td>17</td>
<td>acid</td>
<td>63 ± 3%</td>
</tr>
</tbody>
</table>

Prior to each run being conducted, a calibration of the ISE with a set of standard solutions was obtained. A typical example of this calibration plot is presented in Figure 4.9, the data for which is tabulated in Table 4.7.
FIGURE 4.9 - A typical example of a calibration achieved for the ISE using standard NH₄Cl solutions

![Graph showing calibration data for ISE with NH₄Cl solutions.](image)
TABLE 4.7 - Tabulated data for the calibration of the ISE

<table>
<thead>
<tr>
<th>NH₄Cl concentration (mM)</th>
<th>log (concentration)</th>
<th>Meter reading (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.78</td>
<td>-2.750</td>
<td>29.4</td>
</tr>
<tr>
<td>2.60</td>
<td>-2.585</td>
<td>22.0</td>
</tr>
<tr>
<td>3.33</td>
<td>-2.478</td>
<td>15.2</td>
</tr>
<tr>
<td>3.79</td>
<td>-2.421</td>
<td>12.0</td>
</tr>
<tr>
<td>4.81</td>
<td>-2.318</td>
<td>6.5</td>
</tr>
<tr>
<td>5.81</td>
<td>-2.236</td>
<td>1.1</td>
</tr>
</tbody>
</table>

By assuming that extrapolation of the graph depicted in Figure 4.9 would remain linear beyond those limits shown, it would be possible to convert the measured voltage reading from the ISE for a specific sample to its concentration as required. The above data in Table 4.7 produced the following equation to allow for conversion from voltage to concentration;

\[
\log \text{concentration} = -\left[ (\text{voltage} + 0.1221) / 0.0554 \right]
\]

In order to verify the experimental method chosen, a run was conducted in alkali solution with no application of voltage (reference Table 4.6). This gave, as expected, no decrease in the concentration of NH₄Cl and produced a straight line graph when the measured concentration was plotted against time, after the initial flow through and steady state had been reached. This ensured that any decrease observed in further experiments could be said to be entirely due to the application of the voltage.

Remediation of NH₄Cl when it is present as a contaminant in the groundwater by methods of electrokinetic remediation proved successful. As each experiment was conducted a plot of the concentration of NH₃ / NH₄⁺ against time was produced in order to see any change occurring. Examples of these are shown in Figures 4.10 through 4.14.
FIGURE 4.10 - A plot of concentration of \( \text{NH}_3 / \text{NH}_4^+ \) against time for an experiment in Cell 6 and with the contaminant solution made to be alkaline by the addition of 1M NaOH. Note that between \( t = 90 \) minutes and \( t = 240 \) minutes, 30 volts were applied (Initial \( \text{NH}_4\text{Cl} \) concentration = \( 1 \times 10^{-3} \text{M} \))

- indicates application of voltage during this time period
**FIGURE 4.11** - A plot of concentration of \( \text{NH}_3 / \text{NH}_4^+ \) against time for an experiment in Cell 6 and with the contaminant solution made to be alkaline by the addition of 1M NaOH. Note that between \( t = 90 \) minutes and \( t = 240 \) minutes, 80 volts were applied (Initial \( \text{NH}_4\text{Cl} \) concentration = \( 5 \times 10^{-4} \text{M} \))

○ indicates application of voltage during this time period
**FIGURE 4.12** - A plot of concentration of NH$_3$ / NH$_4^+$ against time for an experiment in Cell 6 and with the contaminant solution made to be acidic by the addition of 1M HCl. The samples were adjusted to pH>11 prior to measurement with the ISE. Note that between $t = 180$ minutes and $t = 370$ minutes, 80 volts were applied (Initial NH$_4$Cl concentration = $1 \times 10^{-3}$M)

- indicates application of voltage during this time period
FIGURE 4.13 - A plot of concentration of NH$_3$ / NH$_4^+$ against time for an experiment in Cell 6 and with the contaminant solution used as made i.e. neutral. The samples were adjusted to pH>11 prior to measurement with the ISE. Note that between $t = 90$ minutes and $t = 250$ minutes, 80 volts were applied (Initial NH$_4$Cl concentration = $1 \times 10^{-3}$M)

• indicates application of voltage during this time period
FIGURE 4.14 - A plot of concentration of NH$_3$ / NH$_4^+$ against time for a neutral run in Cell 6 to monitor the after effects of switching the voltage off. The samples were adjusted to pH>11 prior to measurement with the ISE. Note that between $t = 90$ minutes and $t = 210$ minutes, 80 volts were applied (Initial NH$_4$Cl concentration = $1 \times 10^{-3}$M)

* indicates application of voltage during this time period
With reference to Figures 4.10 through 4.14, it can be observed that it is possible to electrokinetically remediate \( \text{NH}_3 / \text{NH}_4^+ \). An initial plateau for the concentration was commonly observed prior to the application of the voltage, and all graphs indicate a decrease in the concentration of the \( \text{NH}_3 / \text{NH}_4^+ \) at approximately 10 minutes after the voltage had been applied. This decrease continues as the voltage continues to be applied, until such a point where a limit is observed. A possible explanation for the concentration of the \( \text{NH}_3 / \text{NH}_4^+ \) not reaching zero could be edge effects present in the cylindrical cell - it is likely that the field around the two carbon rods does not extend fully to the internal wall making it possible for a portion of the contaminated water to flow through the cell without experiencing the field.

The effect of the application of different voltages is demonstrated in Figures 4.10 and 4.11, where the voltage is altered from 30 to 80 volts respectively. A greater decrease in the \( \text{NH}_3 / \text{NH}_4^+ \) concentration is observed at the higher voltage. This is simply explained by the fact that a greater field produced by the application of a larger voltage would attract more ammonium ions to the electrodes. Theoretically it may be possible to further remediate the flow through the cell i.e. decrease the concentration of the contaminant to a greater extent, but the safe use of high voltages and currents is a factor that needs to be considered.

Figures 4.11, 4.12, and 4.13 show the results obtained at different solution pH. In order to explain these trends it is necessary to know which form of the contaminant is dominant at which pH, and this is depicted in Figure 4.15, which shows the amounts of ammonia and ammonium ion present within a solution as a function of pH.
With reference to Figure 4.15 it is possible to explain the results obtained from the experiments conducted with Cell 6 as a consequence of the proportion of the ammonia and the ammonium ion that are present as a function of pH. At a pH > 11, i.e. in alkali solution, the majority of the solution will be comprised of ammonia. This is not ionic and will therefore not be attracted to the electrodes when the voltage is turned on. This gives rise to a small decrease in concentration of the NH$_3$ / NH$_4^+$ when the solution is treated with 1M NaOH prior to passing through the cell. Conversely at low pH i.e. in acidic solution upon the addition of 1M HCl, the ammonium ion is predominant which will experience an attraction towards the electrodes as the voltage is applied. This should lead to a large decrease, which with reference to Table 4.5 is reflected experimentally. Edge effects could account for the fact that the remediation is not 100% effective - as could the fact that the parameters used were not the most effective in this situation.
The experiments conducted in neutral solution had neither 1M NaOH nor 1M HCl added to alter the pH of the solution. The solutions were made by dissolution of the NH₄Cl in water and were used as made. The resulting pH of the solution was such that the quantity of ammonium ion present was greater than that of the ammonia, so an effect due to the application of the voltage was expected. It was noted that for the same concentration of NH₄Cl in both neutral and acidic solutions, the decrease in the neutral solution is nearing that of the acidic solution experiments. This is explained by reference to Figure 4.15 which shows that at pH values of 8 - 8.5 (i.e. the neutral solution pH), the predominant component of the mixture will be the ammonium ion.

The effect of turning off the voltage has been demonstrated in Figure 4.14. Due to the fact that the concentration returns to its original value once the application of the voltage has ceased, it can be stated that the cause of the decrease is specifically due to the voltage. The fact that the concentration does not exceed its original value once the application of the voltage has been stopped, allows it to be postulated that an actual change is occurring and the NH₃ / NH₄⁺ is not merely being held back by the application of the voltage. If this latter explanation were to be correct, an increase in the level of NH₃ / NH₄⁺ being detected would be expected once the voltage was switched off, as the NH₃ / NH₄⁺ that was being held around the lower electrode would now be able to flow freely out of the cell. With reference to Figure 4.14, it can be shown that this is not the case.

With reference to Table 4.5, a decrease in the concentration of the contaminant present appears to have the effect of increasing the amount of remediation. A two fold dilution in both the alkali and neutral solution gave a slight increase in the average percentage of contaminant remediated. Further work needs to be conducted in this area as the margins of error are significant, but it would follow that the lower the concentration of NH₃ / NH₄⁺, and therefore the fewer the number of ammonium ions present in solution, the greater the chance of those ions present have of being attracted to the electrode.
4.4 - CONCLUSIONS

In conclusion, a novel cell has been designed and constructed that allows electrokinetic remediation to be investigated.

Two of the numerous contaminants that can be found at disused gasworks sites have been used to investigate this phenomenon. The first to be studied was phenol which gave no conclusive results due to the appearance of a brown colour which obscured the phenol peak on the UV/vis spectra. The appearance of this brown colour was accompanied with effervescence from the electrodes and a warming of the solution. The brown colour was initially believed to be due to the oxidation products of the phenolic, although attempts to prove this by NMR were unsuccessful. Further work needs to be conducted in this area of the research undertaken in order to identify the emitted gases, determine the cause of the brown colouration, and to explain the disappearance of the phenol from the solution.

Further work with the phenol contaminant could involve conducting similar experiments but with various other electrode materials to try to remove this undesired colour change. If this proved to be successful, parameters could be altered to optimise the remediation. This could include phenol and background electrolyte concentration, amount of voltage applied and the length for which it was applied, and flow rate.

It has been proved to be possible to electrokinetically remediate NH₄Cl from contaminated water using the cylindrical cell with two carbon rod electrodes and a flow through of the spiked solution. Measurement of the concentration with an ISE was both effective and immediate so the concentration / time plot could be observed as the experiment was being conducted. This was advantageous in so far as timing of the application of voltage, and if a problem was observed, the experiment could be stopped without further delay.

A decrease of nearly 70% has been observed with 0.5mM NH₄Cl and the application of 80 volts. Decreasing the concentration and increasing the voltage applied could
increase this remediation value, although edge effects within the cylindrical cell may be enabling some of the contaminant to flow through the cell without experiencing the field.

Further work in this area could involve the investigation of the effect of parameters other than those reported here. By changing the shape of the cell itself, the edge effects thought to be occurring could be prevented and remediation values could be increased. The electrode size and material is another area to study, and the construction of a larger cell that enables more electrodes to be housed would enable the configuration of the electrodes to be investigated. Further alteration of the work presented i.e. the concentration of the contaminant and the voltage applied would ensure a greater understanding of electrokinetic remediation.

The study of various other amines and ammonium salts, aside from the one reported here, would also be beneficial to the understanding of the remediation of contaminated groundwater. Ammoniacal liquor, which is the by-product of the gas manufacture, can be found at the gasworks sites as either 'free' or 'fixed' ammonia. This former category consists of those salts such as the cyanide, sulphide, and carbonate, whilst the latter group contains those salts like the chloride, thiocyanate, and sulphate.

Automation of the remediation process reported is another area that could be investigated. The incorporation of an ISE into the outflow of a small cell would enable immediate results to be obtained more effectively and easily than manual measurement. By connecting the ISE to a computer, a concentration / time plot could be achieved instantaneously.
CHAPTER FIVE – MODEL ELECTROCHEMICAL STUDIES OF PHENOL

5.1 - INTRODUCTION

With regard to one particular contaminant found at disused gasworks sites, it was hoped that an electrochemical study would lead to a clearer understanding of any mechanisms and reactions that were occurring at the electrode surfaces as remediation of the contaminated groundwater was progressing. The contaminant investigated was phenol, and the effect of various substituents and their positions on the phenol were also studied. Those phenol derivatives that are likely to be found at gasworks sites include cresols and xylenols. Various other parameters were altered to determine a wider picture of the process and these included the pH of the solution, alteration of the solvent itself, and the choice of electrode material.

The electrooxidation of various phenols has previously been studied by various methods including fast voltammetric techniques, coulometry, and controlled potential electrolysis. The growth, characteristics, and the subsequent removal of an electopolymerised film from a specific surface has been reported. The research reported here initially concentrated on work involving different electrode materials and various solution pH's, before progressing to investigate a selection of phenolic compounds under specific voltammetric conditions that are believed to be novel to this research. The combination of particular substituents present on the phenol, together with the specific background electrolyte, and solvent are believed to be novel, as is the reporting of the rate of passivation of the electrode surface due to the formation of the electopolymerised film, and the subsequent comparisons between the inhibiting abilities of the films produced by different phenolics.

The section of research involving the iodinated phenols has initially been reported in a PhD thesis.109
5.2 - CYCLIC VOLTAMMETRY THEORY

The basis of voltammetry is to apply a voltage across two electrodes and to study any current that is produced. In cyclic voltammetry, an upper and a lower limit are chosen, between which the applied voltage is swept backwards and forwards for a set number of times. This results in a symmetrical 'saw-tooth' potential / time signal. Any resulting current is monitored and recorded continuously. The popularity of this technique has rapidly increased over the last few decades as it is possible to gain a great deal of knowledge about an electroactive species both quickly and simply. Such information obtainable includes the reversibility of an oxidation / reduction process, the identification of any intermediate species, and the possible determination of mechanisms involved. In order to probe the new system, experimental conditions can be varied, including potential scan rate, potential limits, and sweep direction.

The potential range needs to be chosen so as to ensure an electron transfer process will occur. Variation of the potential through this range is kept at a constant rate and this is the scan rate of the system - v. By applying this potential across the working electrode (WE) and the counter electrode (CE), a current is observed. This current, and its subsequent change as the potential is swept, is plotted as a function of the applied potential on the WE and this results in a cyclic voltammogram.

It follows that when a potential is applied across both the WE and the CE, if an electrochemical change occurs at the WE, then the converse must occur at the CE. That is to say if a species is undergoing oxidation at the WE, then reduction must be occurring at the CE. The potential at the CE is not monitored, and only those changes occurring at the WE are of interest. To prevent any of the reaction products at the CE from mixing with the rest of the bulk solution and causing interference, a separate compartment is needed to house the CE. This is achieved by the use of a sinter between the CE and the rest of the electrochemical cell.

In the past, in controlled potential experiments, the CE was also used as the reference electrode (RE). This therefore had the double function of passing current and acting as
a reference potential for controlling the potential of the WE. In present systems, three electrodes are routinely used where the current passes from the WE to the CE, and the separate RE serves purely as a reference potential and does not pass current. A potentiostat has control of the voltage across the WE / CE couple, and it adjusts said voltage to maintain the potential difference between the WE and RE (which it senses through a high-impedance feedback loop) in accordance with the programme supplied by a function generator.

The RE used is usually a saturated calomel electrode (SCE). Any readings taken off the cyclic voltammogram are quoted as being vs. the particular RE being used. Values obtained can then be compared with those stated in the literature by knowledge of the relationship between the RE used and the standard hydrogen electrode (SHE). In this instance $E_{\text{SCE}} \text{ vs. } E_{\text{SHE}} = +0.24\,\text{V}$.\textsuperscript{100}

All three electrodes are housed in a glass electrochemical cell (Chemistry Department, Loughborough University) which is shown in Figure 5.1. Gas inlet and outlet valves are used to purge nitrogen through the solution to remove any oxygen present to prevent interference from the redox process involving oxygen.
FIGURE 5.1 - A diagram of the three necked cell used in electrochemical studies

a = WE compartment
b = CE compartment
c = RE compartment
d = Purge gas inlet
e = Gas outlet
Measurements of interest on a cyclic voltammogram include peak current and peak potentials - $i_{pa}$, $i_{pc}$, $E_{pa}$, and $E_{pc}$ respectively. The subscripts a and c denote anodic and cathodic current. The peak separation on the cyclic voltammogram ($\Delta E_p = E_{pa} - E_{pc}$) is an indication of the reversibility of the system. If a value of $59/n$ mV is obtained, this indicates that the system is a reversible n-electron reaction. The greater the separation between the peaks, the greater the value of $\Delta E_p$ and the more irreversible the system.

The Randles-Sevcik equation applies to reversible systems only:

$$j_p = 2.69 \times 10^5 n^{1.5} D^{1/2} v^{1/2}$$

Where:

- $j_p$ = peak current density [Am$^{-2}$]
- $D$ = diffusion coefficient [m$^2$s$^{-1}$]
- $v$ = scan rate [Vs$^{-1}$]
- $c_i$ = concentration of electroactive species [molm$^{-3}$]

Since $j_p$ is the current density, which can be expressed as $i_p/A$, it follows that:

$$i_p = 2.69 \times 10^5 n^{1.5} A c_i D^{1/2} v^{1/2}$$

Where:

- $i_p$ = peak current [A]
- $A$ = electrode area [m$^2$]

Diagnostic tests are available in order to define the reversibility of a system, and those tests for both an n-electron reversible and an n-electron irreversible system at 298K are shown in Table 5.1.
TABLE 5.1 - Diagnostic tests for n-electron reversible and irreversible systems

<table>
<thead>
<tr>
<th>Reversible system</th>
<th>Irreversible system</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta E_p = E_{pa} - E_{pc} = 59/n \text{ mV}$</td>
<td>$\Delta E_p = E_{pa} - E_{pc} &gt; 59/n \text{ mV}$</td>
</tr>
<tr>
<td>$E_p - E_{p1/2} = 59/n \text{ mV}$</td>
<td>$E_p - E_{p2} = 48/cn \text{ mV}$</td>
</tr>
<tr>
<td>$j_p \propto \nu^q$</td>
<td>$j_p$ increases with $\nu$</td>
</tr>
<tr>
<td>$E_{pa}$ and $E_{pc}$ are independent of $\nu$</td>
<td>$E_p$ shifts with increasing $\nu$ so as to increase $\Delta E_p$</td>
</tr>
<tr>
<td>$&gt; E_{p1/2}, j^2 \propto \text{time}$</td>
<td></td>
</tr>
<tr>
<td>$- j_{pc}/j_{pa} = 1$</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5.2 shows a typical cyclic voltammogram for a simple reversible redox couple in solution, illustrating all the key measurements mentioned.
FIGURE 5.2 - Schematic diagram of the cyclic voltammogram expected for a reversible electrochemical redox system $O + e^- \leftrightarrow R$
Chapter Five – Model Electrochemical Studies of Phenol

With reference to Figure 5.2 it is possible to explain the shape of the typical cyclic voltammogram obtained for a reversible one electron transfer system thus;

reductant (R) - electron (e) ↔ oxidant (O)

On the application of the potential between the electrodes and the consequential increase of it through the region where the reaction indicated above occurs, an anodic current will be initiated. This current will continue to increase as the potential is increased until such a time when the rate at which R is being converted to O becomes so great that the rate of transfer of R from the bulk solution is not fast enough to maintain the following;

\[ [R^*] = [R]_o \]

Where;

\[ [R^*] = \text{concentration of R in the bulk solution} \]
\[ [R]_o = \text{concentration of R at the electrode surface} \]

This causes the concentration of R in the vicinity of the electrode to decrease in order that the flux of R towards the surface may be enhanced. As the potential is swept past \( E_o \) for the particular redox couple under study, this concentration of R in the vicinity of the electrode effectively drops to zero. In an unstirred solution the mass transfer will now have reached a maximum, which will now decrease as the concentration of R at greater distances from the electrode is depleted. Therefore with reference to Figure 5.2 there is a peak maximum for the current before a decrease is then observed.

It is at this instant that the peak of the 'saw-tooth' potential / time signal is reached, so a switching of the potential occurs. However the potential is sufficient enough such that it is still able to oxidise the reductant and a small anodic current will be present even though the sweep direction has been altered. Once the electrode is able to cause reduction to occur, the whole process is repeated but now the newly formed oxidant
that is predominant at the surface is reduced back to form the original solution composition.

5.3 - PHENOL OXIDATION

5.3.1 - Chemical Oxidation

It has been well documented that the oxidation of phenol will lead to dimeric and polymeric products.\textsuperscript{105-109} Oxidation mechanisms are still very much under discussion but typically involve the removal of two electrons and two protons per phenol moiety. This can involve either two one-electron steps, or one two-electron step, to give a radical or an ionic process respectively. The main mechanistic pathways for phenolic oxidations are outlined below.

5.3.1.1 - Coupling of Phenoxy Radicals

Removal of a proton and an electron from either a phenol or its respective phenolate ion, depending on the pH of the solution, will afford either a radical cation or a radical respectively. The coupling of this radical to another similar radical gives the most generally accepted mechanism for phenolic oxidation. Given a simple, non-substituted phenol, a variety of dimers, trimers, and polymers can be formed from a mixture of ortho-ortho, ortho-para, and para-para coupling. Alteration of various parameters involved i.e. pH of the solution, temperature, solvent, concentration, and oxidant will have an affect on the ratio of products formed. There are, therefore, a large variety of reaction products from the coupling of a phenolic compound.

5.3.1.2 - Radical Substitution

If the concentration of unoxidised phenol or phenolate ion is large compared to that of the radical concentration, then it is likely that a reaction will occur between the radical and the phenol or phenolate ion. This process will lead to the same reaction products
as when two phenoxy radicals couple, but will proceed via a radical ion followed by a one electron transfer.

5.3.1.3 - Heterolytic Substitution

Removal of a second electron from the phenoxy radical would require a significant amount of energy to initiate but is possible. This would lead to the formation of a cation, which in turn is able to undergo electrophilic substitution with a phenol to give a dimeric product.

5.3.1.4 - Carbon-Oxygen Coupling

It is possible for the phenoxy radical to undergo a coupling reaction with oxygen at either the ortho or the para position. This is known to occur in many natural compounds, including thyroxine, a discussion of which can be found in Section 5.4.6 - Oxidation of Iodinated Phenols.

The oxidation of phenolics with the use of an enzyme as a catalyst has also been studied.\textsuperscript{110}

5.3.2 - Electrochemical Oxidation

The electrochemical oxidation of phenolic compounds has been well documented,\textsuperscript{111-117} including cresols,\textsuperscript{118} 2,6-xylenols,\textsuperscript{119} and 2,6-diphenylphenolates.\textsuperscript{120} Here the phenolic in question undergoes an initial reaction to produce a phenoxy radical cation which in turn goes on to give reaction products. Those products obtained will be dependent on the initial concentration of the phenolic, the pH of the solution,\textsuperscript{121} the solvent chosen,\textsuperscript{122} the voltage applied, and the substituents present on the phenolic initially.\textsuperscript{123} The general oxidation pathways for phenol are shown in Figure 5.3.
FIGURE 5.3 - General oxidation pathways for phenol

OH $\rightarrow$ $\cdot$O

- $e^-$
- $H^+$

To coupling products i.e. dimers and polymers

Phenoxonium ion

Hydroquinone

OH

- $2e^-$
- $2H^+$

Catechol

p-benzoquinone

OH

O-benzoquinone

Catechol

OH
The polymeric products formed during the electrooxidation of the phenolic compounds can cause a passivating film to be deposited onto the electrode surface.\textsuperscript{124-127} The nature of this film is dependent on various parameters including phenolic type, solution pH, voltage applied, and so on. Phenol itself has been extensively studied,\textsuperscript{124-125} and the effect of various substituents on phenol derivatives has also been studied.\textsuperscript{127-129} The growth of such an electropolymerised film onto a surface has been observed,\textsuperscript{130-132} the characteristics of said film have been analysed by infra-red and scanning tunnelling microscopy,\textsuperscript{133-136} and the effective removal of the film by anodic polarisation in an acidic solution of ferric chloride has been reported.\textsuperscript{137}

By controlling the growth of these films by varying the electrochemical parameters, it is possible to obtain films of varying permeabilities.\textsuperscript{138-140} This enables effective size exclusion selective films for use in electrochemical detectors to be manufactured. These films can also be electropolymerised onto electrodes to modify them to be used as sensors,\textsuperscript{141,142} and it is also possible to entrap enzymes into the film as it grows to form reproducible enzyme sensors.\textsuperscript{143-145} Entrapment of the enzyme causes the rigidity of the molecule to increase which often improves its stability. It can also be possible to electropolymerise phenolic compounds onto electrodes to produce a protective coating that inhibits corrosion.\textsuperscript{146}

5.4 - ELECTROCHEMISTRY OF PHENOLIC COMPOUNDS

5.4.1 - Instrumentation

To record the cyclic voltammograms of a range of phenolics, a Sycopel Scientific Scanning Ministat connected to a Servogor 790 Gorez X-Y chart recorder was utilised. The three electrodes used were housed in the three necked cell (Figure 5.1). The RE and the CE remained constant throughout - SCE and platinum mesh respectively - but the nature of the WE was varied between experiments.

Prior to use the platinum WE and CE were cleaned. This had to be repeated in-between experiments due to the formation of the polymerised film which
subsequently had to be removed. In order to clean the platinum electrodes, a galvanostat and a 1M solution of sulphuric acid were used. The electrodes were placed in the acid and were held at -100mA for one minute, followed by +100mA for a further minute. This first stage oxidises any impurities off the electrode but also converts the platinum to platinum oxide, hence the need for the second stage to convert the electrode back to its original form. In the instance when the WE was a glassy carbon disc, cleaning was carried out using Buehler Alpha micropolish alumina No. 2. When the WE was the ITO (indium tin oxide, Balzers) coated glass, any polymerised film could be removed by first wiping with acetone, followed by water. Finally, in the cases when the carbon rods that were used as electrodes in the small cell experiments were utilised as the WE, removal of any polymerised film was achieved with a Buehler Metaserv grinder polisher and P1200 metallographic grinding paper 8" (203mm). This method was also used to smooth down the surface of the carbon rod prior to use.

All phenols used were commercially available (Aldrich, as received), as was the sodium perchlorate which was used as the background electrolyte in all solutions (Acros Organics, as received). Either distilled water or acetonitrile (Aldrich, HPLC grade) was used as the solvent, and a 0.2M solution of sodium hydroxide (Fisons, as received) was used to change the sample to pH>11 when the phenolate ion was to be studied.

Prior to scanning, all solutions were degassed with nitrogen for approximately five minutes to prevent interference from the reduction of any oxygen that may be present.

5.4.2 - Comparison of Different WE's

In order to ascertain if any change in the oxidation potential of phenol occurs on different electrode surfaces, four types of WE material were studied. These were platinum wire (0.32cm² surface area), carbon disc (0.20cm² surface area), ITO glass slide (55mm x 9mm, 20Ω / cm²), and one of the carbon rods that were being used as electrodes in the small cell experiments (CHAPTER FOUR - DESIGN AND USE
OF SMALL CELLS) (12mm diameter and cut to desired length - approximately 5cm.). The carbon rod was wrapped with PTFE tape so only the bottom face of the electrode was visible. This was to try to cut down on the background current as much as possible, and also to ensure that the surface area of electrode in contact with the solution under study remained constant (approximately 1.1cm² surface area in contact with the solution).

Initially the chosen electrode material was scanned in a solution containing the standard reversible redox couple hexacyanoferrate (III/II). By then transferring the electrode to the phenolic solution and scanning a set number of times, before transferring back to the hexacyanoferrate (III/II) solution and re-scanning, any decrease in peak size for the hexacyanoferrate (III/II) could be noted. Any decrease would be due to the formation of an insulating film on the electrode surface due to the polymerisation of the phenol, and it should also be possible to see whether the polymerised film is formed on different electrode materials at different rates.

5.4.2.1 - Experimental

All phenolic solutions were made in distilled water and had 0.2M NaClO₄ as background electrolyte. A standard 10mM K₃Fe(CN)₆/0.25M KNO₃ solution was used to measure the decrease in activity of the WE once the phenolic film had been polymerised onto the surface, and this was scanned between the limits of -0.2V → +0.8V. The scan rate used in all cyclic voltammograms was 0.150Vs⁻¹. The potential limits used for the phenol solution varied depending on the WE being used.

Between the phenolic and ferricyanide solution, the electrode being used was rinsed with distilled water. Fresh solutions were used for each different WE, and the electrodes were cleaned prior to use.

An initial ferricyanide cyclic voltammogram was obtained for each WE material prior to being scanned in the phenol solution in order to measure any change in peak height, and therefore any passivation of the electrode.
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Apparent oxidation potentials were measured as $E_{pa}$ values under the conditions stated.

5.4.2.2 - Results and Discussion

The potential limits and concentration of phenol used in each experiment, as well as the $E_{pa}$ values obtained from the resulting cyclic voltammograms are shown in Table 5.2. It must be noted that there are no $E_{pa}$ measurements for the carbon rod. This is due to the fact that when a cyclic voltammogram was obtained, a very large background was obtained which obscured any oxidation and reduction peaks for the phenol, so no values could be measured off the cyclic voltammogram. A few attempts were made to polymerise the phenol onto the rod by cycling in the phenolic solution for a set number of times, but this proved to be unsuccessful due to the large surface area needed to be covered. In order to verify that the phenol would still polymerise onto the carbon rod, one was placed into the phenolic solution along with a platinum mesh CE, and a constant voltage (5V) was applied for 5 minutes across the two by way of a Thurlby PL310 power pack. After this time the carbon rod was removed, rinsed, and placed in the ferricyanide solution to obtain a cyclic voltammogram. Once again the background obtained was very large, but the oxidation / reduction peaks of the ferricyanide were of a sufficient size to be evident over this background, and a decrease in peak height was evident, thus proving that electropolymerisation had occurred onto this electrode material.

**TABLE 5.2** - $E_{pa}$ values quoted as ±0.04V vs. SCE for phenol at different electrode materials

<table>
<thead>
<tr>
<th>Electrode material</th>
<th>Phenol conc$^a$ (M)</th>
<th>Potential limits (V)</th>
<th>$E_{pa}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum wire</td>
<td>$5.06 \times 10^{-3}$</td>
<td>0.0 → +1.3</td>
<td>0.95</td>
</tr>
<tr>
<td>Glassy carbon disc</td>
<td>$1.12 \times 10^{-3}$</td>
<td>0.0 → +1.3</td>
<td>0.97</td>
</tr>
<tr>
<td>ITO glass</td>
<td>$5.06 \times 10^{-3}$</td>
<td>0.0 → +2.0</td>
<td>1.77</td>
</tr>
</tbody>
</table>
The first cyclic voltammogram for a phenol solution on platinum wire and carbon disc are shown in Figures 5.4 and 5.5 respectively, whilst Figure 5.6 shows the first two cyclic voltammograms for a phenol solution on ITO glass.

**FIGURE 5.4** - The first cyclic voltammogram for a phenol solution where

$\text{WE} = \text{platinum wire}$
FIGURE 5.5 - The first cyclic voltammogram for a phenol solution where
WE = glassy carbon disc
FIGURE 5.6 - The first two cyclic voltammograms for a phenol solution where WE = ITO coated glass
It can be stated that the $E_p$ values obtained for the platinum wire and the carbon disc are very similar, whilst that value for the ITO coated glass is substantially larger. In order to ascertain if this larger $E_p$ value obtained for the ITO glass is due only to the difference in resistance of the electrode materials, a standard reversible redox couple hexacyanoferrate (III/II) was tested on both a platinum wire and an ITO WE. A shift in $E_p$ of less than +0.1 V was observed between the cyclic voltammograms produced by the platinum wire and ITO. From this we can conclude that the difference of ~0.8 V for the phenol oxidation is mainly due to this particular oxidation reaction being unfavourable on the ITO glass. The contribution to this difference from the change in resistance of the electrode material can be said to be negligible.

All the electrode materials under investigation were inhibited due to the electropolymerisation of the phenol onto the surface of the electrode, thus forming a thin film. By the method of observing any decrease in peak height for the ferricyanide cyclic voltammogram, it was noted that it took a greater number of cycles to inhibit the carbon disc electrode than the platinum wire. This can be explained by the fact that a lower concentration of phenol was used for the carbon disc experiment, and therefore there would be a smaller presence of phenol ions in the vicinity of the electrode to electropolymerise. Another factor to consider would be electrode surface area - the platinum wire has the smallest surface area, so should be the quickest to inhibit further reactions, followed by the carbon disc, with the carbon rod having the greatest surface area to cover. The results showed this to be true - the platinum wire showed almost complete shutdown after one cycle in the phenol solution by there being only a very small response to the ferricyanide solution after this one scan in the phenol solution. The carbon disc showed a marked decrease in the peak height of the ferricyanide after one scan in the phenol solution, whilst the carbon rod needed to be held at a set voltage for five minutes before any decrease was observed.

The exception to this trend was the ITO coated glass which showed no response to the ferricyanide solution after one scan in the phenol solution. This could be explained by the expanded limits used in the experiment which may have an effect on the polymerisation of the phenol.
5.4.3 - Comparison of Different Solution pH Values

With knowledge of the pKₐ value for a particular phenol, it is possible to adjust the pH of the solution to make it sufficiently basic so that the majority of the phenol present is converted to its respective phenolate form. By changing the pH of a solution of phenol to produce both a basic and an acidic solution, and then measuring the Eₒₚ values obtained, it will be possible to see if the pH of the solution has any effect on the oxidation potential of the phenol.

The effect of the pH of the solution on the speed of inhibition of the electrode surface was also studied. By recording an initial cyclic voltammogram of a simple ferricyanide solution, then recording the first cyclic voltammogram at the chosen pH, and finally re-recording the ferricyanide cyclic voltammogram, it should be possible to determine any difference between the degree of passivation for the various pH values chosen.

5.4.3.1 - Experimental

A 1.1mM phenol/0.21M NaClO₄ solution was made with distilled water. The pH of this solution was 7.07, as determined by a Radiometer PHM 93 reference pH meter. Dropwise addition of 1M sodium hydroxide to a separated third of the solution ensured a basic solution was obtained. This was followed by the dropwise addition of a 1M sulphuric acid solution to a second separated third of the solution, which led to an acidic phenol solution being obtained. The final third of the solution was left as made and was classed as the neutral sample.

A platinum wire was used as the WE, with the platinum mesh and SCE as the CE and RE respectively. Phenolic solutions were scanned at a rate of 0.150Vs⁻¹, and between the limits 0.0V → +1.3V.

A standard 10mM K₃Fe(CN)₆/0.25M KNO₃ solution was used to measure the decrease in activity of the WE once the phenolic film had been polymerised onto the surface,
and this was scanned between the limits of \(-0.2V \rightarrow +0.8V\), again with a scan rate of 
0.150Vs\(^{-1}\).

An initial ferricyanide cyclic voltammogram was obtained prior to the WE being 
scanned in the phenol solution in order to measure any change in peak height, and 
therefore any passivation of the electrode. Between the phenolic and ferricyanide 
solution, the WE was rinsed with distilled water.

Apparent oxidation potentials were measured as \(E_{pa}\) values under the conditions 
stated.

5.4.3.2 - Results and Discussion

The \(E_{pa}\) values obtained for the phenol when in basic, neutral and acidic solutions, are 
shown in Table 5.3.

**TABLE 5.3 -** \(E_{pa}\) values quoted as ±0.04V vs. SCE obtained for phenol at different 
solution pH's

<table>
<thead>
<tr>
<th>nature of solution</th>
<th>(E_{pa}) (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acidic</td>
<td>0.98</td>
</tr>
<tr>
<td>neutral</td>
<td>0.93</td>
</tr>
<tr>
<td>basic</td>
<td>0.54</td>
</tr>
</tbody>
</table>

From the \(E_{pa}\) values presented in Table 5.3, it can be stated that it is easier to oxidise 
the phenol when it is in basic solution, than when it is in neutral or acidic solution, the 
\(E_{pa}\) values for the latter being similar. The reported \(pK_a\) of phenol is given as 9.99\(^{147}\) 
which shows that in both the neutral and acidic solutions, the phenol will not have 
undergone deprotonation, so similar values for the two are expected. When the pH is 
adjusted so a basic solution is being used, the majority of the phenol will be converted
to the phenolate ion, and it is this that causes the $E_{pa}$ value observed to decrease as it becomes easier to oxidise.

At the pH below the $pK_a$ of the given phenol, the oxidation tends to proceed via an ionic process which involves the removal of two electrons in one step, and this is depicted in Figure 5.7. Conversely at a pH higher than the $pK_a$ value, i.e. when the phenolate ion is predominant, a radical mechanism is generally observed which is shown in Figure 5.8 and involves two, one-electron removal processes.

**FIGURE 5.7** - Phenol oxidation via an ionic process involving a one step, two-electron removal

\[
\text{HO} - \text{C} = \text{O} \quad \text{-}2\text{e}^- \quad \text{-}2\text{H}^+
\]

**FIGURE 5.8** - Phenol oxidation via a radical process involving two, one-electron removal processes

\[
\text{-O} - \text{C} = \text{O} \quad \text{-e}^- \quad \text{-H}^+ \quad \text{-e}^- \quad \text{-H}^+
\]

We can conclude from these results that it is easier to oxidise the phenol when it has been deprotonated, and we can postulate that this trend would be consistent with other phenolic compounds as well. Knowledge of the $pK_a$ of the particular phenol under study would mean that the pH of the solution can be adjusted accordingly to ensure complete deprotonation of all of the phenol to the phenolate ion, and therefore rapid oxidation could be achieved.
5.4.4 - Comparison of Different Concentrations of Phenolics

It has been shown that the choice of electrode material and the pH of the solution has an effect on the oxidation potential of the phenol, and its ability to inhibit the electrode. In order to ascertain what particular concentration of phenol produced the best results as far as ease of oxidising and inhibition were concerned, a range of concentrations of phenol were studied.

5.4.4.1 - Experimental

The phenol solutions were made with distilled water with 0.02M NaClO₄ present as background electrolyte. The phenolate ion oxidation potential was studied as well as the phenol, and this was achieved by altering the pH of the solution by dropwise addition of 1M sodium hydroxide solution.

The electrodes used for this set of experiments were platinum wire, platinum mesh, and SCE, as the WE, CE, and RE respectively. The scan rate was 0.150Vs⁻¹ for all cyclic voltammograms, and the phenol solutions were scanned between the limits 0.0V → +1.3V. A standard 10mM K₃Fe(CN)₆/0.25M KCl solution was used to measure the inhibition of the WE, and this was scanned between the limits of -0.2V → +0.8V. An initial ferricyanide cyclic voltammogram was obtained prior to the WE being scanned in the phenol solution, and between the phenolic and ferricyanide solutions the WE was rinsed with distilled water.

Apparent oxidation potentials were measured as E_{pa} values under the conditions stated.

5.4.4.2 - Results and Discussion

All the E_{pa} values measured from the cyclic voltammograms, as well as the concentration of phenol used, and the form of phenol studied (i.e. phenol or phenolate ion), are presented in Table 5.4.
Chapter Five – Model Electrochemical Studies of Phenol

**TABLE 5.4** - $E_{pa}$ values quoted as ±0.04V vs. SCE for different concentrations of phenol

<table>
<thead>
<tr>
<th>Phenol conc$^a$ (M)</th>
<th>nature of phenol</th>
<th>$E_{pa}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.25 \times 10^{-3}$</td>
<td>phenolate ion</td>
<td>0.53</td>
</tr>
<tr>
<td>$3.14 \times 10^{-3}$</td>
<td>phenolate ion</td>
<td>0.56</td>
</tr>
<tr>
<td>$4.38 \times 10^{-3}$</td>
<td>phenolate ion</td>
<td>0.56</td>
</tr>
<tr>
<td>$1.10 \times 10^{-3}$</td>
<td>phenol</td>
<td>0.93</td>
</tr>
<tr>
<td>$1.32 \times 10^{-3}$</td>
<td>phenol</td>
<td>0.97</td>
</tr>
<tr>
<td>$5.06 \times 10^{-3}$</td>
<td>phenol</td>
<td>0.95</td>
</tr>
</tbody>
</table>

The values obtained for the oxidation potential of phenol and the corresponding phenolate ion compare well with those from **Section 5.4.3 - Comparison of Different Solution pH Values**.

Results show that alteration of the concentration of the phenol under study has no effect on the value of the oxidation potential. This was as expected as the addition of more of the phenol to the solution should not make it easier to oxidise. By altering the pH to produce a basic solution, and converting all the phenol to the corresponding phenolate ion, the oxidation potential decreases, indicating that oxidation is easier once deprotonation has occurred.

As the concentration of the phenol was increased, the rate at which inhibition occurs was also observed to increase. This rate of inhibition was measured by the relative decrease in peak size for the ferricyanide solutions after a set number of scans in the respective phenol solution. This trend can be simply explained as the greater the concentration, the more phenol there will be available at the surface of the electrode to be polymerised. Thus the surface will be coated with an inhibiting layer faster and more effectively at higher concentrations of phenol. This increase in passivation at increased concentrations is depicted in Figures 5.9 and 5.10. Where the phenol
solution is at a higher concentration, a larger decrease in the peak size for the ferricyanide is observed after one scan in the phenol solution when compared to that lesser concentration.

**FIGURE 5.9 -**

a) Cyclic voltammogram at 150mVs⁻¹ in an aqueous solution containing approximately 10mM K₃Fe(CN)₆/0.25M KCl. Scan initiated from -0.20V in the positive direction

b) Second cyclic voltammogram at 150mVs⁻¹ in an aqueous solution containing approximately 10mM K₃Fe(CN)₆/0.25M KCl after one scan in 1.32 x 10⁻³M phenol / 0.02M NaClO₄. Any reduction noted in the peak size is due to the passivation of the electrode by the formation of a phenolic film. Scan is initiated from -0.20V in the positive direction
FIGURE 5.10 -

a) Cyclic voltammogram at 150mVs\(^{-1}\) in an aqueous solution containing approximately 10mM K\(_3\)Fe(CN)\(_6\)/0.25M KCl. Scan initiated from -0.20V in the positive direction.

b) Second cyclic voltammogram at 150mVs\(^{-1}\) in an aqueous solution containing approximately 10mM K\(_3\)Fe(CN)\(_6\)/0.25M KCl after one scan in 5.06 x 10\(^{-3}\)M phenol/0.02M NaClO\(_4\). Any reduction noted in the peak size is due to the passivation of the electrode by the formation of a phenolic film. Scan initiated from -0.20V in the positive direction.
5.4.5 - Comparison of a Range of Phenolics with Various Solvent Systems

Previous sections have shown that the pH of the solution, the choice of electrode material, and the concentration of phenol will affect both the ability of the phenol to electropolymerise onto the electrode, and the oxidation potential observed. All experimental work in these previous sections has been on phenol itself, so a range of simple substituted phenols were chosen to study and compare the effects of the nature and position of the substituent. This will be of importance when remediation of contaminated land is being conducted, as there can be a range of phenolics present at disused gasworks sites.

5.4.5.1 - Experimental

A range of phenolics were chosen to be studied in two solvents and in both the phenol and respective phenolate form. The alkyl substituted phenols were commercially available and led to comparisons between phenols with the same number of substituted carbon atoms in various positions on the phenol ring. The rest of the phenols chosen were also commercially available and allowed direct comparison between the nitro, amino, and halogen substituents in the ortho and para positions. The list of phenols that were studied in this section are presented in Table 5.5. If the concentration of each solution is 5mM, the approximate pH of the solution when made can be calculated from the following equation, and these pH values, as well as the relevant pKₐ values are also recorded.¹⁰¹

\[
pH = \frac{1}{2} (pK_a - \log \text{ concentration})
\]

Knowledge of the pH of the solution will then enable the concentration of the respective dissociated phenolate present initially to be calculated.

\[
pH = -\log[H^+]
\]
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Since \( HA \leftrightarrow H^+ + A^- \),

\[
pH = -\log[A^-]
\]

Where \( A^- \) is the relevant phenolate ion in solution.

**TABLE 5.5** - The range of phenolics studied and their corresponding \( pK_a \) and calculated pH values

<table>
<thead>
<tr>
<th>Phenolic studied</th>
<th>( pK_a^{106,147} )</th>
<th>calculated pH</th>
<th>phenolate ion conc( ^o ) (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
<td>9.99</td>
<td>6.15</td>
<td>( 7.08 \times 10^{-7} )</td>
</tr>
<tr>
<td>2-ethylphenol</td>
<td>10.20</td>
<td>6.25</td>
<td>( 5.62 \times 10^{-7} )</td>
</tr>
<tr>
<td>4-ethylphenol</td>
<td>10.00</td>
<td>6.15</td>
<td>( 7.08 \times 10^{-7} )</td>
</tr>
<tr>
<td>2,3-dimethylphenol</td>
<td>10.54</td>
<td>6.42</td>
<td>( 3.80 \times 10^{-7} )</td>
</tr>
<tr>
<td>2,6-dimethylphenol</td>
<td>10.22</td>
<td>6.26</td>
<td>( 5.50 \times 10^{-7} )</td>
</tr>
<tr>
<td>3,5-dimethylphenol</td>
<td>10.19</td>
<td>6.24</td>
<td>( 5.75 \times 10^{-7} )</td>
</tr>
<tr>
<td>3-fluorophenol</td>
<td>9.21</td>
<td>5.75</td>
<td>( 1.78 \times 10^{-6} )</td>
</tr>
<tr>
<td>4-fluorophenol</td>
<td>9.91</td>
<td>6.10</td>
<td>( 7.94 \times 10^{-7} )</td>
</tr>
<tr>
<td>3-iodophenol</td>
<td>9.08</td>
<td>5.69</td>
<td>( 2.04 \times 10^{-6} )</td>
</tr>
<tr>
<td>4-iodophenol</td>
<td>9.21</td>
<td>5.75</td>
<td>( 1.78 \times 10^{-6} )</td>
</tr>
<tr>
<td>3-nitrophenol</td>
<td>8.36</td>
<td>5.33</td>
<td>( 4.68 \times 10^{-5} )</td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>7.08</td>
<td>4.69</td>
<td>( 2.04 \times 10^{-3} )</td>
</tr>
<tr>
<td>3-aminophenol</td>
<td>4.37</td>
<td>3.34</td>
<td>( 4.57 \times 10^{-4} )</td>
</tr>
<tr>
<td>4-aminophenol</td>
<td>5.30</td>
<td>3.80</td>
<td>( 1.58 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

The \( pK_a \) of each of the phenolics is dependent on the substituents present on the ring.\(^{107}\) With reference to Table 5.5, it can be stated that those alkyl substituted phenols do not differ greatly in \( pK_a \) value from the parent phenol. This is due to the fact that alkyl groups are neither strongly electron withdrawing or electron donating,
so will affect the acidity of the phenol to only a small degree. Those phenols with the alkyl substituent nearer to the hydroxyl group will show the greatest deviance in \( pK_\alpha \) from the parent phenol as the effect operates through bonds and through space. It follows that 2,3-dimethylphenol will show a greater difference in pH from the parent phenol than the difference between 3,5-dimethylphenol and the parent phenol, due to the two methyl groups being in closer proximity to the hydroxyl group.

The presence of both iodine and fluorine atoms causes the acidity of the phenolic to increase. A smaller \( pK_\alpha \), and hence a more acidic phenol, will be obtained for the halogenated compounds when compared to the parent phenol due to the electronegativity of the halogen substituent. The electronegative atom operates through bonds and space to withdraw electronic charge from the hydroxyl group, therefore the closer the halogen is positioned to the hydroxyl group, the greater will be the acidity of the phenol.

With reference to Table 5.5, it can be noted that the nitrophenols are more acidic than the parent phenol. The presence of the nitro substituent not only introduces an electron withdrawing effect to increase the acidity, but resonance factors are also able to contribute to the \( pK_\alpha \) of the phenol. 4-nitrophenol is the stronger acid of the two under study as this position affords resonance structures, and even though the inductive effect may be weak this is outweighed by the strong resonance effect.

The presence of an electron donating amino group causes the \( pK_\alpha \) to decrease with respect to the parent phenol. It would be expected that the presence of the amino group would cause the phenol to be basic, but the lone pair of electrons on the nitrogen stabilise the ring to such an extent that aniline itself is a very weak base, and therefore a strong acid. The presence of a hydroxyl group in the meta position on aniline (i.e. 3-aminophenol) causes an electron-withdrawing inductive effect that is not observed with the para counterpart (i.e. 4-aminophenol), therefore ensuring it is a stronger acid.
Chapter Five – Model Electrochemical Studies of Phenol

The calculation of the concentration of the phenolate ion in the initial solution enables us to state that with the majority of the phenols studied, this concentration is so small as to be insignificant. However, for both the amino substituted phenols where the concentration of the phenolate ion in solution is in the $10^{-4}$M region, this constitutes a substantial proportion of the initial composition and needs to be taken into consideration when discussing results.

The majority of the phenolic solutions were made to approximately 5mM, with a 0.2M NaClO$_4$ background electrolyte concentration. This concentration of 5mM was chosen as it would enable electropolymerisation onto the electrode to be completed within a few cycles. Both the phenolic and its corresponding phenolate ion were studied in aqueous solution, with a 1M solution of sodium hydroxide being added dropwise to alter the pH of the solution in order to obtain the phenolate ion. To compare solvent choice, the oxidation potentials of all the phenolics were also measured in acetonitrile (HPLC grade, Aldrich). All phenolics were scanned between the limits $0.0V \rightarrow +1.3V$ in aqueous solution, and $0.0V \rightarrow +1.8V$, or $0.0V \rightarrow +2.5V$ when in acetonitrile. The scan rate used for all cyclic voltammograms was 0.150Vs$^{-1}$.

The choice of WE was the platinum wire as this gave a clear cyclic voltammogram, and proved to be the easiest of the WE's from which to remove the polymerised film in preparation for the next compound. The CE and RE used were a platinum mesh and SCE respectively. When the solvent being used was acetonitrile, all electrodes were rinsed with acetonitrile before being placed in solution in order to remove any water and therefore avoid cross-contamination.

Any differences in the ability of each phenolic to electropolymerise onto the electrode and cause passivation to further reactions to occur was studied. An initial ferricyanide cyclic voltammogram (10mM K$_3$Fe(CN)$_6$/0.25M KNO$_3$) was obtained prior to the WE being scanned in the phenol solution. This was scanned between the limits $-0.2V \rightarrow +0.8V$, and the scan rate used was 0.150Vs$^{-1}$. Even when the phenolic under test was made up in acetonitrile, the ferricyanide solution remained aqueous, so
thorough rinsing of the electrodes with the solvent that they were next to be immersed in was necessary.

Apparent oxidation potentials were measured as $E_{pa}$ values under the conditions stated.

5.4.5.2 - Results and Discussion

Table 5.6 shows the oxidation potentials for the phenols and their corresponding phenolate ion in aqueous solution, and the phenol oxidation potentials in acetonitrile. Figures 5.11 through to 5.26 show examples of the cyclic voltammograms obtained from the substituted phenols. Four compounds were chosen as examples to present - 2,3-dimethylphenol, 3-nitrophenol, 3-fluorophenol, and 4-aminophenol - and the figures show the cyclic voltammograms of each phenol in aqueous and acetonitrile solution, the respective phenolate ion in aqueous solution, and the passivation capabilities of the phenol with respect to the reduction in response to a standard ferricyanide solution. These specific four sets of cyclic voltammograms were chosen to illustrate the range of substituents studied; alkyl, nitro, halogen, and amino.
**TABLE 5.6** - The oxidation potentials for a range of phenolics in aqueous and acetonitrile solutions, and their corresponding phenolate ion oxidation potentials in aqueous solution. All $E_{pa}$ values quoted as $\pm 0.04V$

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{pa}$ (V)</th>
<th>Solvent</th>
<th>Aqueous -</th>
<th>Aqueous -</th>
<th>Acetonitrile -</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>and phenol</td>
<td>phenol</td>
<td>phenolate</td>
<td>phenol</td>
</tr>
<tr>
<td>phenol</td>
<td>0.95</td>
<td>0.37 / 0.61</td>
<td>1.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-ethylphenol</td>
<td>0.88</td>
<td>0.32 / 0.80</td>
<td>1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-ethylphenol</td>
<td>0.84</td>
<td>0.32 / 0.78</td>
<td>1.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3-dimethylphenol</td>
<td>0.77</td>
<td>0.30</td>
<td>1.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,6-dimethylphenol</td>
<td>0.81</td>
<td>0.24 / 0.76</td>
<td>1.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,5-dimethylphenol</td>
<td>0.78</td>
<td>0.39</td>
<td>1.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-fluorophenol</td>
<td>0.99</td>
<td>0.69</td>
<td>1.82</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-fluorophenol</td>
<td>0.93</td>
<td>0.52</td>
<td>1.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-iodophenol</td>
<td>0.91</td>
<td>0.58</td>
<td>1.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-iodophenol</td>
<td>0.83</td>
<td>0.46</td>
<td>1.51</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-nitrophenol</td>
<td>1.14</td>
<td>1.04</td>
<td>2.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>1.22</td>
<td></td>
<td>2.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-aminophenol</td>
<td>0.68</td>
<td>0.39</td>
<td>0.79</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-aminophenol</td>
<td>0.42</td>
<td>0.24</td>
<td>0.32 / 1.76</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 5.11 - Cyclic voltammograms at 150mVs\(^{-1}\) in an aqueous solution containing 4.8mM 2,3-dimethylphenol in 0.2M NaClO\(_4\). Scans initiated from 0.0V in the positive direction

a) Scan 1

b) Scans 2 → 5
FIGURE 5.12 - Cyclic voltammograms at 150mVs⁻¹ in an aqueous solution at pH>11 containing the phenolate ion of 4.8mM 2,3-dimethylphenol in 0.2M NaClO₄. Scans initiated from 0.0V in the positive direction

a) Scan 1

b) Scans 2 → 5
Figure 5.13 - Cyclic voltammograms at 150 mVs$^{-1}$ in an acetonitrile solution containing 1.24 mM 2,3-dimethylphenol in 0.2 M NaClO$_4$. Scans initiated from 0.0 V in the positive direction.

a) Scan 1

b) Scans 2 → 5
FIGURE 5.14 -

a) Cyclic voltammogram at 150mVs\(^{-1}\) in an aqueous solution containing approximately 10mM K\(_2\)Fe(CN)\(_6\)/0.25M KCl. Scan initiated from -0.20V in the positive direction.

b) Cyclic voltammogram at 150mVs\(^{-1}\) in an aqueous solution containing approximately 10mM K\(_2\)Fe(CN)\(_6\)/0.25M KCl to show any reduction in response due to the passivation of the electrode by the formation of a phenolic film after one scan in the 4.93mM 2,3-dimethylphenol in 0.2M NaClO\(_4\) phenolic solution. Scan initiated from -0.20V in the positive direction.
**FIGURE 5.15** - Cyclic voltammograms at 150mVs\(^{-1}\) in an aqueous solution containing 4.7mM 3-nitrophenol in 0.2M NaClO\(_4\). Scans initiated from 0.0V in the positive direction

a) Scan 1

b) Scan 2 → 5
FIGURE 5.16 - Cyclic voltammograms at 150mVs$^{-1}$ in an aqueous solution at pH>11 containing the phenolate ion of 4.7mM 3-nitrophenol in 0.2M NaClO$_4$. Scans initiated from 0.0V in the positive direction

a) Scan 1
b) Scans 2 → 5
FIGURE 5.17 - Cyclic voltammograms at 150mVs\(^{-1}\) in an acetonitrile solution containing 4.97mM 3-nitrophenol in 0.2M NaClO\(_4\). Scans initiated from 0.0V in the positive direction

a) Scan 1
b) Scans 2 → 5
FIGURE 5.18 -

a) Cyclic voltammogram at 150mVs$^{-1}$ in an aqueous solution containing approximately 10mM $K_2Fe(CN)_6/0.25M$ KCl. Scan initiated from -0.20V in the positive direction.

b) Cyclic voltammogram at 150mVs$^{-1}$ in an aqueous solution containing approximately 10mM $K_2Fe(CN)_6/0.25M$ KCl to show any reduction in response due to the passivation of the electrode by the formation of a phenolic film after four scans in the 4.7mM 3-nitrophenol in 0.2M NaClO$_4$ phenolic solution. Scan initiated from -0.20V in the positive direction.
FIGURE 5.19 - Cyclic voltammograms at 150mVs\(^{-1}\) in an aqueous solution containing 5.4mM 3-fluorophenol in 0.2M NaClO\(_4\). Scans initiated from 0.0V in the positive direction

a) Scan 1
b) Scans 2 → 5
FIGURE 5.20 - Cyclic voltammograms at 150mVs⁻¹ in an aqueous solution at pH>11 containing the phenolate ion of 5.4mM 3-fluorophenol in 0.2M NaClO₄. Scans initiated from 0.0V in the positive direction

a) Scan 1
b) Scans 2 → 5
FIGURE 5.21 - Cyclic voltammograms at 150mVs\(^{-1}\) in an acetonitrile solution containing 5.09mM 3-fluorophenol in 0.2M NaClO\(_4\). Scans initiated from 0.0V in the positive direction

a) Scan 1

b) Scans 2 → 5
FIGURE 5.22 -

a) Cyclic voltammogram at 150mVs⁻¹ in an aqueous solution containing approximately 10mM K₃Fe(CN)₆/0.25M KCl. Scan initiated from -0.20V in the positive direction.

b) Cyclic voltammogram at 150mVs⁻¹ in an aqueous solution containing approximately 10mM K₃Fe(CN)₆/0.25M KCl to show any reduction in response due to the passivation of the electrode by the formation of a phenolic film after three scans in the 5.4mM 3-fluorophenol in 0.2M NaClO₄ phenolic solution. Scan initiated from -0.20V in the positive direction.
FIGURE 5.23 - Cyclic voltammograms at 150mVs⁻¹ in an aqueous solution containing 5.2mM 4-aminophenol in 0.2M NaClO₄. Scans initiated from 0.0V in the positive direction

a) Scan 1
b) Scans 2 → 5
FIGURE 5.24 - Cyclic voltammograms at 150mVs⁻¹ in an aqueous solution at pH>11 containing the phenolate ion of 5.2mM 4-aminophenol in 0.2M NaClO₄. Scans initiated from 0.0V in the positive direction

a) Scan 1
b) Scans 2 → 3
FIGURE 5.25 - Cyclic voltammograms at 150mVs$^{-1}$ in an acetonitrile solution containing 4.85mM 4-aminophenol in 0.2M NaClO$_4$. Scans initiated from 0.0V in the positive direction

a) Scan 1

b) Scans 2 → 5
FIGURE 5.26 -

a) Cyclic voltammogram at 150mVs⁻¹ in an aqueous solution containing approximately 10mM K₃Fe(CN)₆/0.25M KCl. Scan initiated from -0.20V in the positive direction.

b) Cyclic voltammogram at 150mVs⁻¹ in an aqueous solution containing approximately 10mM K₃Fe(CN)₆/0.25M KCl to show there is no reduction in response after fifteen scans in the 5.2mM 4-aminophenol in 0.2M NaClO₄ phenolic solution, indicating no phenolic film has been formed. Scan initiated from -0.20V in the positive direction.
With reference to **Section 5.4.3 - Comparison of Different Solution pH Values**, and comparison to Table 5.6, we can state that the observed trend in the previous section is also observed here. For the majority of the phenols, deprotonation to give the phenolate ion leads to a decrease in the $E_{pa}$ value.

Alteration of the solvent from an aqueous system to acetonitrile, leads to an increase in $E_{pa}$ for the phenols. Dissolution problems meant that no values were available for the phenolate ions in acetonitrile, so no comparisons are able to be made between the phenol and its respective phenolate ion in different solvent systems.

The nature of the substituent present on the phenol ring leads to different effects with regard to the $E_{pa}$ measured and the shape of the resulting voltammogram. All the alkyl substituted phenols studied gave irreversible voltammograms in aqueous solution due to the fact that either a follow up chemical reaction, or electropolymerisation onto the carbon rod electrode was taking place, thus preventing any reverse reaction from occurring and thus no peak was evident.

Comparison of the oxidation potentials measured for the alkylphenols leads to the conclusion that no great shift is observed on the addition of alkyl substituents. The reason for this is that alkyl groups have no capabilities through which further conjugation can occur, nor are they particularly strongly electron-withdrawing or electron-donating, so any changes seen are slight. When the ortho position is occupied by an alkyl group, oxidation tends to be slightly harder, possibly due to a direct interaction occurring between the hydroxyl and its neighbouring substituent. With reference to Figure 5.11, it can be noted that there is a small peak on the cyclic voltammogram of the neutral solution of 2,3-dimethylphenol. Comparison of this peak's position to that peak in Figure 5.12, the cyclic voltammogram of the alkaline solution of 2,3-dimethylphenol i.e. the phenolate form, shows that lack of buffering within the solution has probably altered the pH of the neutral solution to such an extent that a significant amount of the phenolate has been produced and a slight peak due to it is observed.
Halogenated phenols also gave rise to irreversible cyclic voltammograms, the explanation once again being the formation of the insulating film on the electrode surface. Although this film formation required more cycles for the halogenated compounds compared to the alkylphenols (Table 5.7), the formation of the 'building blocks' *i.e.* dimers and trimers, prevented the appearance of a peak due to the reverse reaction of the one that had just occurred.

The effect that the halogens have on the ease of oxidation of the compound is two fold. Halogens possess a lone pair of electrons, yet are also electronegative elements, producing a conflict of interest. When the substituent is in a position where the lone pairs are able to participate in resonance with the phenol *i.e.* the *para* position as studied here and it is possible to postulate the *ortho* position would produce similar results, an increase in the ease of oxidation, *i.e.* a smaller $E_{pa}$ will be observed. Reference to Table 5.6 shows this to be true as from phenol $\rightarrow$ 4-fluorophenol $\rightarrow$ 4-iodophenol in aqueous solution for example, the $E_{pa}$ is seen to decrease thus; $0.95V \rightarrow 0.93V \rightarrow 0.83V$. It can be postulated that the greater the electronegativity of the element, the less likely the non-bonding electrons are to interact with those electrons in the ring. This would mean that 4-fluorophenol shows the least deviance from the parent phenol as fluorine has the highest electronegativity value, whilst 4-iodophenol would be the easiest to oxidise in comparison to the parent phenol, as this is lowest in the halogen series. It could be envisaged that 4-chlorophenol and 4-bromophenol would fit into this pattern and fall between the two halogenated compounds studied to date.

When the *meta* position is occupied with a halogen substituent, the lone pair of electrons are not able to interact within the ring due to the lack of resonance structures. Instead the electronegativity of the halogen can cause the electron availability within the compound to decrease and, thus the $E_{pa}$ value increases. This will be more pronounced the higher the halogen is within the series and therefore the greater the electronegativity value.
The nitrophenols studied also gave rise to irreversible cyclic voltammograms, due to the growth of the polymeric film on the electrode surface. The ability of the nitro group to withdraw electrons away from the phenolic, leads to a decrease in electron availability, and thus the compound is harder to oxidise. This leads to the \( E_{pa} \) value being increased. Resonance factors can account for the difference in ease of oxidation between the studied 3-nitrophenol and 4-nitrophenol. In the latter case the substituent is in the para position and resonance structures are able to be drawn that leads to a larger decrease in electron availability, and thus a larger value for \( E_{pa} \), than when the meta position is occupied. It would be expected that if the nitro substituent where placed in the ortho position, oxidation would be as difficult as for 4-nitrophenol as the resonance factors are contributing again.

Differences on the cyclic voltammograms were observed between the two amino substituted phenols studied. Irreversibility was noted for 3-aminophenol whilst 4-aminophenol in an as made aqueous system gave a reversible system. An extra peak was noted on the cyclic voltammogram for the latter compound and with respect to Figure 5.23 the small peak present at \(~0.20\text{V}\) could be due to the presence of a small amount of the phenolate ion in solution. Comparison with Figure 5.24 - the cyclic voltammogram of the 4-aminophenol in aqueous solution at \( \text{pH} > 11 \) - shows that the phenolate peak here appears at \(~0.24\text{V}\) which is within the error band of \( \pm 0.04\text{V} \). With reference to Table 5.5, it is possible to see that the concentration of the phenolate ion of 4-aminophenol is appreciable in the 'as made' solution, comprising approximately 5% of the total phenol present, therefore indicating that it is probable that a small peak for this phenolate ion would be seen. The fact that 3-aminophenol produces an irreversible cyclic voltammogram is due to the formation of the insulating film, as has been the situation for the remainder of the phenols studied. However, 4-aminophenol does not appear to electropolymorise onto the electrode as no decrease in activity towards the ferricyanide couple was observed (Figure 5.26). A possible explanation for this could be the formation of a dimer which is stable enough that it goes no further in the polymerisation chain, yet is able to be reduced back to the original form to give the reversible peak on the cyclic voltammogram.
The ease of oxidation of the aminophenols when compared to the parent phenol, is increased for both of those phenols studied. This can be attributed to the presence of the lone pair of electrons on the nitrogen adjacent to the ring. The availability of the electrons within the ring is increased and therefore the ease at which one can be removed i.e. oxidation occurring, is increased. 4-aminophenol is easier to oxidise than its *meta* counterpart due to resonance contributions.

Table 5.7 presents the abilities of each of the phenolics to passivate the WE to further reaction, both in acetonitrile, in aqueous solution and for the respective phenolate form of the phenol in aqueous solution. It must be noted that when the phenols were investigated in acetonitrile, the ferricyanide solution remained aqueous, and thorough rinsing of the WE as it was transferred between solutions was employed. The number of scans indicated in the table is generally the number that the WE needed to be scanned in the phenol solution to elicit a reduction for the ferricyanide peak current to approximately a quarter of its original peak size.
**Table 5.7** - To show the number of scans needed for different phenol compounds in acetonitrile, aqueous and aqueous at pH>11, in order to elicit a reduction in response to the ferricyanide to approximately a quarter of its original peak current size.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Number of scans</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Aqueous</td>
<td>Aqueous pH&gt;11</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>2-ethylphenol</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>4-ethylphenol</td>
<td>3</td>
<td>1</td>
<td>20</td>
</tr>
<tr>
<td>2,3-dimethylphenol</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>2,6-dimethylphenol</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>3,5-dimethylphenol</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>3-fluorophenol</td>
<td>3</td>
<td>1</td>
<td>slight red&quot; noted</td>
</tr>
<tr>
<td>4-fluorophenol</td>
<td>7</td>
<td>3</td>
<td>no red&quot; noted</td>
</tr>
<tr>
<td>3-iodophenol</td>
<td>5</td>
<td>1</td>
<td>slight red&quot; noted</td>
</tr>
<tr>
<td>4-iodophenol</td>
<td>4</td>
<td>1</td>
<td>no red&quot; noted</td>
</tr>
<tr>
<td>3-nitrophenol</td>
<td>4</td>
<td>1</td>
<td>no red&quot; noted</td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>5</td>
<td>3</td>
<td>no red&quot; noted</td>
</tr>
<tr>
<td>3-aminophenol</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4-aminophenol</td>
<td>no red&quot; noted</td>
<td>no red&quot; noted</td>
<td>no red&quot; noted</td>
</tr>
</tbody>
</table>

Of all the phenolics investigated, only one compound was unable to passivate the electrode to further reaction with respect to a reduction in response to a standard ferricyanide reaction. This was 4-aminophenol, and further investigations would need to be carried out in order to ascertain the reasons why.

With reference to Table 5.7, passivation of the WE tends to occur more rapidly when the phenol is converted to its respective phenolate form. An explanation for this could be that it requires less energy for the phenolate ion to be converted to dimers, trimers and eventually a polymeric film than it does for the parent phenol. It has been shown (reference Table 5.6) that it is easier to oxidise the phenolate ion than the phenol when
in an aqueous system, so it can be postulated that the formation of the inhibiting layer would be easier for the phenolate ion, therefore requiring less scans in the phenolic solution before a peak height reduction for the ferricyanide is observed.

The choice of solvent also appears to have a substantial effect on the formation of an inhibiting layer. No reduction was observed for almost half of the compounds investigated when in acetonitrile, and of those remaining it was necessary to complete at least ten cycles in the phenol solution before a reduction was observed. 3-aminophenol was the exception and gave a reduction in response after one scan in the phenol in acetonitrile solution. With reference to Table 5.6 it is noted that this is one of the compounds that gave a low $E_{pa}$ value, thereby indicating the ease at which it can be oxidised. This could be the reason why an inhibiting layer is observed for this compound, and not for the other phenols.

By comparing the values presented in Table 5.6 and Table 5.7, a possible trend can be established between the $E_{pa}$ value for each phenol and the number of scans necessary to elicit a reduction in response to a ferricyanide redox couple. Generally those compounds with a lower $E_{pa}$ value tend to require fewer scans in the phenol solution to see a decrease in peak height for the ferricyanide solution. Those phenols with para substituents have a tendency to require a greater number of scans in the phenol solution, and this can be explained by the position of the substituent hindering the coupling of the phenol to produce an inhibiting layer.

**5.4.6 - Oxidation of Iodinated Phenols**

Collaboration with an organic research student at Loughborough University led to the investigation of the oxidation of iodinated phenolics. Natalie Bell's research interests were concerned with the synthesis of thyroxine ($L$-3,5,3',5'-tetraiodothyronine) which is a naturally occurring hormone produced by the thyroid gland, and was interested to discover the effects different substituents had on the oxidation potential of thyroxine and its derivatives. This would assist the research undertaken to date as thyroxine itself is a phenol with substituents in the 2, 4, and 6 positions, and work on the
derivatives of thyroxine would lead to a clearer understanding of the effects of iodines in the ortho position, as well as alkyl and conjugated systems in the para position.

5.4.6.1 - Background to Thyroxine

The hormone thyroxine is produced by the thyroid gland in all vertebrate animals, and plays a vital role in the regulation of metabolism in the body. The diet of vertebrate animals must consist of a set intake of iodine - usually in the form of iodised salts and seafood - as iodine is essential in the biosynthesis of thyroxine from the amino acid tyrosine. Illness can result from both an excess and a deficiency of thyroxine, so the synthesis of this hormone for use as a drug is of great interest.

Most literature reports suggest that the formation of thyroxine is through the coupling of 3,5-diiodotyrosine (DIT), either with itself or with 3,5-diiodo-4-hydroxyphenylpyruvic acid (DIHPPA). This coupling takes place either through a one electron oxidation to form a radical, or a two electron process to form the corresponding ion. The synthesis under investigation was thought to involve the initial loss of one electron, and this is depicted in Figure 5.27. It was intended that the electrochemical study of this oxidation step would provide information concerning the actual oxidation step occurring in the (bio)synthesis.
Tyrosine derivatives were studied by electrochemical methods in order to determine the effect of the iodine substituents in the ortho positions. Other compounds were studied to determine the effect of the para substituent on the oxidation potential. N-acetyl-3,5-diodotyrosine ethyl ester and N-acetylthyroxine ethyl ester were obtained from Knoll Pharmaceuticals, Nottingham, and phenol and N-acetyltyrosine ethyl ester were commercial reagents and used as received. The remainder of the compounds studied - N-acetyl-3-iodotyrosine ethyl ester, 2,6-diiodo-4-methylphenol, ethyl 2-acetamido-3-(3,5-diiodo-4-hydroxyphenyl)propenate and 3,5-diiodo-4-hydroxy phenyl pyruvic acid - were prepared as described earlier. All of these compounds studied are shown in Table 5.8.
TABLE 5.8 - The synthesised iodinated phenolics studied electrochemically

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-acetyl-3,5-diiodotyrosine ethyl ester</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>N-acetyl-3-iodotyrosine ethyl ester</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>N-acetyl-tyrosine ethyl ester</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>2,6-diiodo-4-methylphenol</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>Ethyl 2-acetamido-3-(3,5-diiodo-4-hydroxyphenyl)propenate</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>N-acetylthyroxine ethyl ester</td>
<td><img src="image" alt="Structure" /></td>
</tr>
<tr>
<td>3,5-diiodo-4-hydroxyphenylpyruvic acid</td>
<td><img src="image" alt="Structure" /></td>
</tr>
</tbody>
</table>
5.4.6.2 - Experimental

The synthetic procedure under investigation used an ethanol / water mixture as the solvent system. For direct comparison, it was hoped to use this same system for electrochemical purposes, but background runs showed that masking of the phenolic oxidation peaks would occur due to the oxidation of the solvent. Acetonitrile and aqueous systems were therefore utilised instead.

The set of electrodes that were used were platinum wire as the WE, platinum mesh as the CE, and SCE as the RE. The WE and CE were cleaned electrochemically before each new compound was studied, and after any film had been formed on the surface of the electrode.

All solutions had the phenol concentration at approximately 5mM, with a 0.2M NaClO₄ background electrolyte concentration. The only exception to this was that of the N-acetylthyroxine ethyl ester which used a concentration of approximately 1.5mM in both aqueous and acetonitrile solution. The phenol and phenolate ion oxidation potentials were both measured in an acetonitrile system, and the phenolate ion oxidation was also carried out in an aqueous system. The sodium salt of the phenol was synthesised by reaction between each phenol and sodium hydroxide (1M equivalent) in anhydrous tetrahydrofuran. This resulted in the appropriate phenolate ion being present in solution when dissolution occurred.¹⁰⁹

The scan rate used for all solutions was 0.150Vs⁻¹. Limits for the cyclic voltammograms were 0.0 → +1.3V when a phenol was studied in an aqueous system, and a range of limits were utilised when the corresponding phenolate ion was studied in an aqueous system, including -0.225 → +1.225V, 0.0 → +1.2V, and 0.0 → +1.3V. In all instances the limits were set at 0.0 → +1.8V when the solvent was acetonitrile. Apparent oxidation potentials were measured as $E_{pa}$ values under the conditions stated.
5.4.6.3 - Results and Discussion

5.4.6.3.1 - Electrochemical Oxidation of Phenols

The majority of the phenols were investigated at least in duplicate, and the resulting oxidation potentials measured from the cyclic voltammograms are reported in Table 5.9. The second column of results reported in the table are the duplicate runs, and they have been presented in this manner for ease of comparison. It must be noted that dissolution difficulties prevented the phenols from being studied in an aqueous system - the only compound that successfully dissolved was phenol which is shown in the table. Figures 5.28, and 5.29 show the first five scans recorded for N-acetyl-tyrosine ethyl ester and 3,5-diiodo-4-hydroxyphenylpyruvic acid in acetonitrile, the two compounds chosen as examples to be presented.
**TABLE 5.9** - Oxidation potentials for phenol and iodo-substituted phenols in acetonitrile from the first scan at a newly cleaned electrode surface. All $E_{pa}$ values quoted as $\pm 0.04V$

<table>
<thead>
<tr>
<th>Phenol</th>
<th>Conc$^a$ (mM)</th>
<th>$E_{pa}$ (V)</th>
<th>$E_{pa}$ (V)</th>
<th>Conc$^a$ (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
<td>5.42</td>
<td>1.52</td>
<td>1.50</td>
<td>5.34</td>
</tr>
<tr>
<td>phenol (in aqueous solution)</td>
<td>5.06</td>
<td>0.95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N$-acetyl-3,5-diiodotyrosine ethyl ester</td>
<td>5.12</td>
<td>1.20</td>
<td>1.02</td>
<td>5.01</td>
</tr>
<tr>
<td>$N$-acetyl-3-iodotyrosine ethyl ester</td>
<td>5.18</td>
<td>1.28</td>
<td>1.29</td>
<td>4.73</td>
</tr>
<tr>
<td>$N$-acetyl-tyrosine ethyl ester</td>
<td>4.95</td>
<td>1.34</td>
<td>1.36</td>
<td>4.72</td>
</tr>
<tr>
<td>2,6-diiodo-4-methylphenol</td>
<td>4.99</td>
<td>1.32</td>
<td>1.31</td>
<td>4.99</td>
</tr>
<tr>
<td>&quot;</td>
<td>4.92</td>
<td>1.29</td>
<td>1.66</td>
<td></td>
</tr>
<tr>
<td>ethyl 2-acetamido-3-(3,5-diido-4-hydroxyphenyl)propenate</td>
<td>5.04</td>
<td>1.06</td>
<td>1.08</td>
<td>4.45</td>
</tr>
<tr>
<td>$N$-acetylthyroxine ethyl ester</td>
<td>1.30</td>
<td>1.24</td>
<td>1.22</td>
<td>1.06</td>
</tr>
<tr>
<td>3,5-diiodo-4-hydroxyphenylpyruvic acid</td>
<td>4.81</td>
<td>0.86</td>
<td>1.52</td>
<td></td>
</tr>
</tbody>
</table>
**FIGURE 5.28** - Cyclic voltammograms at 150mVs\(^{-1}\) in an acetonitrile solution containing 4.95mM N-acetyl-tyrosine ethyl ester in 0.2M NaClO\(_4\). Scans initiated from 0.0V in the positive direction

a) Scan 1

b) Scans 2 → 5
FIGURE 5.29 - Cyclic voltammograms at 150mVs\(^{-1}\) in an acetonitrile solution containing 4.81mM 3,5-diido-4-hydroxyphenylpyruvic acid in 0.2M NaClO\(_4\). Scans initiated from 0.0V in the positive direction

a) Scan 1

b) Scans 2 → 5
With respect to the measurements obtained for phenol itself, it can be stated that the oxidation of the compound occurs more readily in an aqueous solution than it does in acetonitrile. From this result, and with reference to Section 5.4.5 - Comparison of a Range of Phenolics with Various Solvent Systems where the same trend was observed, it can be postulated that a similar lowering of the oxidation potential, and therefore ease of oxidation would occur for the iodo-substituted phenols studied, were they able to be dissolved and subsequently measured in distilled water.

On the majority of the cyclic voltammograms for the iodo-substituted phenols, two oxidation waves were observed. The exception to this is phenol where a single wave is shown in the potential window studied, and with reference to Section 5.4.2 - Comparison of Different WE's this leads to the electropolymerisation of the phenol, which results in a passivating film being formed on the surface of the electrode. The two oxidation waves observed for the rest of the phenolics each correspond to the removal of one electron. On the reverse sweep for these phenolics a cathodic wave was observed \( (E_{pc} \approx 0.60V) \) which can be attributed to the reduction of the coupled dimer that was formed in the oxidation sweep. This of course is not the case for phenol due to the electropolymerisation of the phenol onto the electrode surface.

Comparison of the \( E_{pa} \) values obtained leads to the conclusion that the presence of the substituents on the phenol tend to increase the ease of oxidation of the compound with respect to phenol itself. Those compounds with unsaturated and conjugated substituents in the \textit{para} position (ethyl 2-acetamido-3-(3,5-diiodo-4-hydroxyphenyl) propenate, and 3,5-diiodo-4-hydroxyphenylpyruvic acid), show the greatest decrease in \( E_{pa} \) with respect to phenol. These are thus the easiest to oxidise and this can be attributed to the increased resonance and therefore stability of the intermediate radical cation produced. The resonance structures showing the increased stability available for these two compounds are illustrated in Figure 5.30, where 3,5-diiodo-4-hydroxyphenylpyruvic acid is shown as an example.
**FIGURE 5.30** - To show the resonance structures for an iodo-substituted phenol with unsaturated and conjugated substituents present in the *para* position leading to greater stability of the intermediate radical cation.

The cyclic voltammograms produced for those two compounds with unsaturated and conjugated *para* substituents, are more complex than those voltammograms produced for the remainder of the phenols. The oxidation waves are irreversible and not reproducible, although the presence of further voltammetric waves does indicate that electropolymerisation of the compound is not occurring and that the electrode is not being fouled. Instead it is possible that the side chain on the phenol may cyclise leading to the formation of a spiro compound, the result of which would be further voltammetric waves on the cyclic voltammogram due to the oxidation and reduction of these newly formed compounds. The mechanism for this possible cyclisation is shown in Figure 5.31.
FIGURE 5.31 - Mechanism for the possible cyclisation of the side chain of a conjugated phenol, leading to a spiro compound (3,5-diiodo-4-hydroxyphenylpyruvic acid is illustrated as an example)

The effect of the presence of an ortho-iodine substituent can be examined by comparison of those tyrosine derivatives with two, one and no iodines on the ring (N-acetyl-3,5-diiodotyrosine ethyl ester, N-acetyl-3-iodotyrosine ethyl ester, and N-acetyl-tyrosine ethyl ester respectively), and of 2,6-diiodo-4-methylphenol. It appears that the presence of an ortho-iodine decreases the \( E_{pa} \) value obtained, and by increasing the number of these ortho substituents the amount of decrease observed also increases. With reference to Section 5.4.5 - Comparison of a Range of Phenolics with Various Solvent Systems, the presence of an iodine substituent in both the meta and the para positions were also shown to decrease the value of \( E_{pa} \) observed. This can be explained by examination of the \( pK_a \) values of the phenols in question. As the number of iodines present on the tyrosine derivative increases from 0
Chapter Five – Model Electrochemical Studies of Phenol

→ 1 → 2, so the pKₐ of the compound decreases from 10.0 → 8.7 → 6.5.¹⁰⁷ It is conceivable that the radical cation generated by the first oxidation wave is a very short lived species and becomes even more so following the above sequence from 0 → 1 → 2 iodines present. This greater ease of oxidation can then be explained, as it is possible that the loss of the proton may be occurring simultaneously with this first oxidation.

With reference to Table 5.9, it is possible to calculate the ΔEₚₐ values for each phenolic. This is the difference between the first and second oxidation steps, and a distinctive trend was observed for those compounds studied. Table 5.10 shows the calculated ΔEₚₐ values for each phenol investigated that gave two oxidation waves.

**TABLE 5.10 - ΔEₚₐ values calculated for the iodo-substituted phenols in acetonitrile**

<table>
<thead>
<tr>
<th>Phenol</th>
<th>ΔEₚₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-acetyl-3,5-diiodotyrosine ethyl ester</td>
<td>0.36</td>
</tr>
<tr>
<td>N-acetyl-3-iodotyrosine ethyl ester</td>
<td>0.30 ± 0.01</td>
</tr>
<tr>
<td>N-acetyl-tyrosine ethyl ester</td>
<td>0.26 ± 0.02</td>
</tr>
<tr>
<td>2,6-diiodo-4-methylphenol</td>
<td>0.35 ± 0.03</td>
</tr>
<tr>
<td>ethyl 2-acetamido-3-(3,5-diiodo-4-hydroxyphenyl)propenate</td>
<td>0.70 ± 0.02</td>
</tr>
<tr>
<td>N-acetylthyroxine ethyl ester</td>
<td>0.40 ± 0.04</td>
</tr>
<tr>
<td>3,5-diiodo-4-hydroxyphenylpyruvic acid</td>
<td>0.66</td>
</tr>
</tbody>
</table>

With reference to Table 5.10, a trend is observed between those compounds with an increasing number of iodo substituents. As the number of iodines present increases from 0 (N-acetyl-tyrosine ethyl ester) → 1 (N-acetyl-1-3-iiodotyrosine ethyl ester) → 2 (N-acetyl-1-3,5-diiodotyrosine ethyl ester, 2,6-diiodo-4-methylphenol, and N-acetyl thyroxine ethyl ester), so the average ΔEₚₐ value calculated also increases. The presence of an increasing number of iodine substituents aids the stability of the phenoxy radical by electron withdrawing and mesomeric effects. Thus the removal of the first electron to achieve this radical is a more favourable process, the more iodines
there are present. Due to this extra stability of the radical cation because of the presence of the extra iodines, the removal of the second electron is made more difficult. Therefore the energy difference between the two oxidation potentials will be greater for those compounds with more iodines present in the ortho position, as the removal of the first electron is facilitated, whilst the removal of the second is made more difficult, leading to a larger ΔE\textsubscript{pa} value.

Those compounds with unsaturated and conjugated para side chains yield the greatest ΔE\textsubscript{pa} values. This can be explained by the pronounced stability of the newly formed radical cation due to the extra conjugation present within the side chain, which would ensure the removal of the second electron would be greatly unfavourable. This stable radical cation intermediate has previously been illustrated in Figure 5.30.

5.4.6.3.2 - Electrochemical Oxidation of Phenolate Ions

The phenolate ions were measured both in an aqueous system and an acetonitrile system. Again, most of the compounds were recorded in duplicate to show the reproducibility of the system - those that only have one measurement tabulated were generally those samples where initial sample size was small. Table 5.11 reports all the measured oxidation potentials for the phenolate ions. Figures 5.32, and 5.33 show the first five scans recorded for the phenolate ions of N-acetyl-tyrosine ethyl ester and 3,5-diiodo-4-hydroxyphenylpyruvic acid in an aqueous solution, the two compounds chosen as examples to be presented.
**TABLE 5.11** - Oxidation potentials for the phenolate ions of phenol and the iodo-substituted phenols in acetonitrile and aqueous solution. All $E_{pa}$ values are quoted as $\pm 0.04V$

<table>
<thead>
<tr>
<th>Phenolate</th>
<th>Acetonitrile</th>
<th>Aqueous solution</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Conc (mM)</td>
<td>$E_{pa}$ (V)</td>
<td>Conc (mM)</td>
</tr>
<tr>
<td>phenol</td>
<td>5.90</td>
<td>0.19</td>
<td>6.36</td>
</tr>
<tr>
<td></td>
<td>1.58</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“</td>
<td>11.38</td>
<td>0.14</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>1.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“</td>
<td>4.59</td>
<td>0.16</td>
<td></td>
</tr>
<tr>
<td>$N$-acetyl-3,5-diiodotyrosine ethyl ester</td>
<td>5.07</td>
<td>0.35</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td>0.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“</td>
<td>9.58</td>
<td>0.31</td>
<td>7.03</td>
</tr>
<tr>
<td></td>
<td>0.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“</td>
<td>5.30</td>
<td>0.28</td>
<td></td>
</tr>
<tr>
<td>$N$-acetyl-3-iodotyrosine ethyl ester</td>
<td>5.05</td>
<td>0.27</td>
<td>5.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N$-acetyl-tyrosine ethyl ester</td>
<td>insoluble</td>
<td></td>
<td>4.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>“</td>
<td></td>
<td></td>
<td>5.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,6-diiodo-4-methylphenol</td>
<td>4.75</td>
<td>0.20</td>
<td>3.82</td>
</tr>
<tr>
<td></td>
<td>1.34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>“</td>
<td></td>
<td></td>
<td>6.3</td>
</tr>
<tr>
<td>ethyl 2-acetamido-3-(3,5-diiodo-4-hydroxyphenyl)propenate</td>
<td>insoluble</td>
<td>3.63</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$N$-acetylthyroxine ethyl ester</td>
<td>1.03</td>
<td>0.34</td>
<td>2.43</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,5-diiodo-4-hydroxyphenylpyruvic acid</td>
<td>2.82</td>
<td>0.41</td>
<td>5.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 5.32 - Cyclic voltammograms at 150mVs\(^{-1}\) in an aqueous solution containing the phenoxide ion of 5.39mM N-acetyl-tyrosine ethyl ester in 0.2M NaClO\(_4\). Scans initiated from 0.0V in the positive direction

a) Scan 1
b) Scans 2 → 5
FIGURE 5.33 - Cyclic voltammograms at 150mVs\(^{-1}\) in an aqueous solution containing the phenoxide ion of 5.26mM 3,5-diiodo-4-hydroxyphenylpyruvic acid in 0.2M NaClO\(_4\). Scans initiated from 0.0V in the positive direction

a) Scan 1
b) Scans 2 → 5
Previous sections (5.4.3 - Comparison of Different Solution pH Values, 5.4.4 - Comparison of Different Concentrations of Phenolics, and 5.4.5 - Comparison of a Range of Phenolics with Various Solvent Systems) have shown that the oxidation potentials for the phenolate ions are significantly less positive than for the respective phenols. The results reported here comply with that trend, and comparison between Table 5.9 and Table 5.11 shows that the phenolate ions are easier to oxidise than the parent phenol.

It has been reported in Section 5.4.5 - Comparison of a Range of Phenolics with Various Solvent Systems that the oxidation of a phenol is easier in an aqueous system than it is in acetonitrile. With reference to Table 5.11, the opposite trend is observed for the phenolate ions, in so far as the obtained $E_{pa}$ values are lower in acetonitrile than in an aqueous system, thereby making them easier to oxidise in the former solvent. Further work with various other solvent systems and utilising the phenols and their respective phenolate ions is necessary in order to explain this phenomenon.

Those aqueous cyclic voltammograms of the compounds with the conjugated unsaturated side para chains show the presence of three oxidation waves. The explanation of the first wave is due to the one electron oxidation of the phenolate ion. The second wave could be due to the reaction of the formed radical with either the side chain, another radical, or a nucleophile present in the bulk solution. The resulting product would then be oxidised to a radical and this would produce the observed wave. The removal of a third electron to form the phenoxonium ion is the probable reason for the third oxidation wave. These measurements obtained were not reproducible on successive scans.

The measured $E_{pa}$ values for those iodinated tyrosine phenolate ion derivatives in both aqueous and acetonitrile systems reveal an opposite trend than was encountered for the phenols in acetonitrile. Here on progressing from the presence of 0 → 1 → 2 iodines, the oxidation potential increases whereas referring back to the results for the phenols (5.3.6.3.1 - Electrochemical oxidation of phenols), the oxidation potential was
observed to decrease. A possible explanation for this reversed trend is that the higher the $pK_a$ of the phenolate ion, the less stable it will be. This would result in a small energy difference between the ion and the radical, as the unstable ion would prefer to be converted to the more stable radical. It follows that the phenolate ion with the higher $pK_a$ should have the smaller oxidation potential, and this is what is occurring. As the $pK_a$ of the phenolate ion decreases from $10 \rightarrow 8.7 \rightarrow 6.5$, the number of iodines increases from $0 \rightarrow 1 \rightarrow 2$, and the oxidation potential increases.

Referring back to those oxidation potentials of the phenols where a decrease in $E_{pa}$ was noted as the number of iodines increased from $0 \rightarrow 1 \rightarrow 2$, this was explained by the fact that the higher the $pK_a$ of the phenol, the less stable would be the phenolate ion. Therefore the removal of this first electron to achieve this unstable ion would be unfavourable and the observed decrease in $E_{pa}$ would occur.

Comparison of the phenolate ions of phenol and $N$-acetylthyroxine ethyl ester in distilled water and acetonitrile systems reveals the same trend. The addition of iodines, along with a para substituent, to the phenol to produce the $N$-acetylthyroxine ethyl ester, causes the oxidation potential to increase. The explanation for this increase is the same as for the iodo substituted tyrosine derivatives.

Comparison of the phenolate ions of phenol and 2,6-diiodo-4-methylphenol in acetonitrile also reveals the same trend as the rest of the phenols investigated. The increase is not as great as for some phenol / phenolate ion couples, but this could be due to the presence of the slightly electron donating para methyl group. Conversely, when studied in the aqueous system, an unexpected reversal of the trend was noted. As for the phenols in solution, here an increase in the number of iodines present on the ring caused a decrease in $E_{pa}$. Again a possible explanation for this reversal could be the presence of the methyl substituent in the para position, although such a large effect is not usually expected from a single methyl group.

The presence of any second oxidation waves for those phenolate ions that have not already been discussed, can probably be attributed to the removal of a second electron
from the formed phenoxy radical. No apparent trend is observed between either the \( E_{pa} \)'s or the \( \Delta E_{pa} \)'s and reproducibility is only evident for the second scan - after this the potential shifts or, in the case of phenol, no oxidation wave is observed due to electropolymerisation onto the electrode.

5.5 - CONCLUSIONS

Different working electrodes afforded a change in \( E_{pa} \) as well as altering the shape of the cyclic voltammogram. A polymeric film was formed on each WE due to the electropolymerisation of phenol, and this was easier and more effectively removed when the WE was platinum wire. The ITO glass WE required a larger potential window in order to see the oxidation of phenols, and the carbon rod used in the small cell experiments proved to have too large a background current to be useful. Further experiments were therefore conducted using the platinum wire.

The pH of the phenol solution was an important factor to consider as at a pH above the \( pK_a \) of the phenol under study, the respective phenolate ion dominated. Deprotonating the phenol made oxidation easier, and a decrease in \( E_{pa} \) was subsequently noted.

Altering the concentration of the phenol has the effect of increasing the rate at which passivation due to electropolymerisation occurs. This is as expected as at higher concentrations there will naturally be more phenol ions in the vicinity of the electrode which are able to form the film.

The choice of solvent was observed to have an effect on the oxidation of the compound under study. Alteration from a protic solvent (i.e. distilled water) to an aprotic solvent (i.e. acetonitrile) caused different effects depending on the initial form of the phenol. The \( E_{pa} \) values measured for the phenols themselves increased on going from distilled water to acetonitrile, whilst a decrease was observed for the respective phenolate ions.
The presence of substituents on the phenol was found to have varying effects depending on the nature of said substituent. When the substituent was an alkyl group, there was no great alteration in the value of $E_{pa}$ obtained. This is attributed to the fact that alkyl groups are not capable of extending the conjugation within the phenolic compound, nor are they classed as being particularly strong electron donating or withdrawing groups. It is possible that direct interaction between substituents may occur on ortho alkylphenols, but still only a small deviation from the parent phenol will be observed. The position of a halogen substituent alters the effect it has on the oxidation potential of the compound as halogens are both able to withdraw electrons due to their high electronegativity, and donate them due to the lone pair they possess. It can be predicted that the more electronegative the halogen, the less likely it will be to donate one of its lone pairs to the phenol, and therefore it will be harder to oxidise. Nitro substituents are able to reduce the electron density present within the ring by withdrawing the electrons through its own bonds. This produces a nitrophenol that, provided the nitro substituent is in the relevant positions that resonance structures can be achieved (i.e. ortho and para), will be harder to oxidise than the relevant parent phenol. The amino substituents produced different results. 4-aminophenol gave a reversible cyclic voltammogram unlike the remainder of the phenolic compounds studied. This can be explained by the lack of film formation seen, and the possible redox situation obtained between the compound and its dimer. The lone pair of electrons present on the amino group ensure that the amino substituted compounds are easier to oxidise than the parent phenol as the electron availability within the compound is increased.

The presence of iodine substituents in the ortho position was shown to have varying effects depending on the pH of the solution. When the solution was neutral and the phenol was prevalent, the ortho iodines caused a decrease in $E_{pa}$, whilst an increase was observed when a basic solution and the phenolate ions were investigated.

The scope for continuation of the work reported in this chapter is unlimited. The further alteration of those parameters that have been varied, as well as those that were kept constant, would lead to a much wider knowledge on the electrochemical
behave of phenolic compounds. These parameters that are able to be varied include scan rate, potential limits, solvent choice, concentration of phenolic, background concentration, the nature of the background itself, electrode material, and electrode size. A larger range of phenolics is a further area that can be studied. A greater number of substituents, for example a tri-substituted phenol, as well as a variety of different natured substituents i.e. chlorine, longer alkyl chains, etc. can be investigated, in order to give a better understanding into the effect of the substituent on the electrochemical behaviour of the phenolic compound.

Continuation of this section of research could begin with an investigation of simple ortho iodophenols as this would tie together Section 5.4.5 – Comparison of a Range of Phenolics with Various Solvent Systems and Section 5.4.6 – Oxidation of Iodinated Phenols.
CHAPTER SIX - SPECTROSCOPIC STUDIES OF SELECTED PHENOLS

6.1 - INTRODUCTION

Spectroscopic studies were undertaken on those phenol compounds that had been studied electrochemically, with the exception of those synthesised and studied in Section 5.4.6 - Oxidation of Iodinated Phenols. It was initially envisaged that a spectroscopic method of determination could be used to detect the presence of the respective phenols in the contaminated groundwater. Spectra for each were thus recorded and relationships between the various substituents present on the phenol and the $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$ values obtained were determined. This area of research was not intended to be novel in the recording and consequential reporting of each of the phenolics in the various solvents. It was envisaged however, that the determination of the individual components of a mixture of phenols was a novel research idea that has begun to be investigated by spectroscopy, and that the combination of this with the use of cyclic voltammetry could enable mixtures of phenols to be positively identified.

6.2 - THEORY

Visible and ultra-violet spectra of organic molecules are associated with transitions between electronic energy levels. These spectra are recorded within the limits 190nm to 800nm - 190nm to 400nm being the UV region, and 400nm to 800nm being the visible region. The particular distance between the energy levels concerned gives rise to the specific wavelength of the absorption on the spectra - it is therefore possible to record the spectra of a sample, measure the wavelength and then calculate the energy of electronic excitation. The equation to be used is;

$$E = 1.19 \times 10^5 / \lambda$$
Where;

\[ E = \text{energy of electronic excitation} \quad \text{kJmol}^{-1} \]
\[ \lambda = \text{wavelength of absorption peak / band} \quad \text{nm} \]

The above equation used in UV/vis spectroscopy has been derived from Planck's equation which is shown below;

\[ E = h\nu \]

Where;

\[ h = \text{Planck's constant} \quad 6.62608 \times 10^{-34} \text{ Js} \]
\[ \nu = \text{frequency} \quad \text{s}^{-1} \]

Substitution of the following equation into \( E = h\nu \), and consequential alteration of the units to ensure \( E \) is given in kJmol\(^{-1}\), results in the desired relationship between wavelength and energy as shown earlier;

\[ \lambda = c / \nu \]
\[ \nu = c / \lambda \]

Hence;

\[ E = hc / \lambda \]

Where;

\[ c = \text{velocity of light} \quad 2.99792458 \times 10^8 \text{ ms}^{-1} \]
Thus;

\[ E = 1.19 \times 10^5 / \lambda \]

There are two empirical laws that need to be taken into consideration when absorption is being utilised. Lambert’s Law states that;

"the fraction of incident light absorbed is independent of the intensity of the source"\textsuperscript{149}

And also that;

"the absorption of a sample is proportional to the length of the optical path"\textsuperscript{150}

Beer’s Law states that;

"the absorption of the solution is proportional to the number of absorbing molecules present"\textsuperscript{149}

These can then be combined together to give the Beer-Lambert Law;

\[ \log_{10} \frac{I_0}{I} = \varepsilon l c \]

Where;

- \( I_0 \) = intensity of incident light \( (i.e. \) through the reference cell) \( \)
- \( I \) = intensity of transmitted light \( (i.e. \) through the sample cell) \( \)
- \( \varepsilon \) = molecular extinction coefficient \( \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1} \) (a constant for a particular molecule at a particular wavelength) \( \)
- \( l \) = pathlength of cell \( \text{cm} \)
- \( c \) = concentration of sample \( \text{mol dm}^{-3} \) \( \)
Since we can express the ratio of the intensities of the two lights in another way it is possible to derive another form of this equation;

$$\log_{10} \frac{I_0}{I} = A$$

$$A = \varepsilonlc$$

Where;

$$A = \text{absorbance}$$

By taking a sample and recording a UV/vis spectrum, a plot of $A$ against $\lambda$ will be obtained. On the spectrum there will be absorption bands, and measurements are normally taken of $\lambda_{max}$ and $\varepsilon_{max}$ - the wavelength and energy at the highest point of the absorption band respectively.

The type of cell employed to hold the sample has an effect on the shape of the spectra - glass, silica and plastic cells are available but depending on the region of interest in the spectrum, determines the choice of cell. Glass absorbs strongly at $<300\text{nm}$ so would not be the preferred choice if a full range spectrum was needed. Some chemicals and solvents react with plastic cells, so these are only suitable for certain applications. Most cells have two frosted sides by which they are to be handled and two clear sides through which the radiation must be directed. These sides must always be kept clear and free from dust, and it is important that before each spectrum is recorded the sides are wiped gently and the whole cell placed in the correct orientation within the spectrophotometer.

Choice of solvent is also important as different solvents may affect both the position and the intensity of the absorption bands. Certain solvents absorb the light below particular wavelengths, so cannot be used if the sample to be analysed absorbs in this region. Due to the solvent effect, it is important to quote the solvent used on all spectra.
The spectrum is obtained by comparing the absorption of the radiation of the sample, with that of a similar thickness of solvent. Spectrophotometers can be either single cell or double cell. The double cell variety has space for two cells, so the comparison of the sample and solvent absorption can be achieved by placing pure solvent in one of the cells. The single cell variety however only has space for one cell, so the solvent absorption or blank, must be carried out before each set of new data. This is then stored and compared with each sample as it is recorded. The double cell instruments are more advantageous as the comparison between sample and solvent is continuous, however the major advantage of the single cell instruments is lower cost.

The systems that contain the energy levels and electrons that are responsible for absorption bands and peaks seen are known as chromophores. The length of these chromophores, and the degree of conjugation present in them, affects the shifts seen on the spectra. In short, the greater the degree of conjugation, the greater the $\lambda_{\text{max}}$ value will be. Unconjugated chromophores give rise to absorption spectra but due to the fact that they are of high energy, the $\lambda_{\text{max}}$ values are generally low which means that they are not noticeable in the visible region of the spectrum.

6.3 - EXPERIMENTAL

A Hewlett Packard 8452A diode array spectrophotometer together with the HP 89531A operating software, was connected to a 486 DX2 66MHz computer and was employed to record spectra of samples. The cell was a quartz silica cell with a path length of 1cm. Solvent choice was either distilled water or HPLC grade acetonitrile (Aldrich, as received). All phenolics were of purity of at least 98+% (Aldrich, as received).

Dilute solutions were made to the desired concentration (~0.02mM phenolic and 0.2M sodium perchlorate) with the appropriate solvent. The solvent, or blank, always had to be scanned before each set of spectra as this particular instrument was the single cell variety. The cell was rinsed prior to use with the next solution to be used as this helped to ensure that there was no cross contamination of samples.
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Each of the phenolics was scanned in acetonitrile and distilled water, and in the latter solvent the corresponding phenolate was also recorded. This was achieved by drop-wise addition of 1M NaOH until the pH of the solution was above 11 and the majority of the phenol present would thus of been converted to the phenolate form. There are no spectra of the phenolate ions in acetonitrile due to dissolution difficulties encountered.

6.4 - RESULTS AND DISCUSSION

For each of the following phenols the spectra were recorded in acetonitrile, distilled water and also the respective phenolate ions were recorded in distilled water; 2-ethylphenol, 4-ethylphenol, 2,3-dimethylphenol, 2,6-dimethylphenol, 3,5-dimethylphenol, phenol, 3-fluorophenol, 4-fluorophenol, 3-iodophenol, 4-iodophenol, 3-nitrophenol, 4-nitrophenol, 3-aminophenol, and 4-aminophenol. From the resulting spectra of all the samples, the $\lambda_{\text{max}}$ values were measured. Knowledge of the concentration of the sample solution enabled $\varepsilon_{\text{max}}$ values to be calculated by the use of the equation $A = e \lambda c$. The spectra for the phenol and its respective phenolate have been grouped together in order to show more clearly any differences there are between the three spectra. Chosen as examples are 2,3-dimethylphenol, 3-iodophenol, and 4-nitrophenol which are presented as Figures 6.1 through 6.3, where both the full spectra and the expanded region of interest are depicted.
FIGURE 6.1 - The absorption spectra of ~0.02mM 2,3-dimethylphenol in aqueous solution, at pH>11 in aqueous solution, and in acetonitrile

a) full spectra

b) expanded spectra of region of interest i.e. 250 - 350nm

a)
Chapter Six - Spectroscopic Studies of Selected Phenols

b)
FIGURE 6.2 - The absorption spectra of ~0.02mM 3-iodophenol in aqueous solution, at pH > 11 in aqueous solution, and in acetonitrile

a) full spectra

b) expanded spectra of region of interest i.e. 260 - 320nm

a)
Chapter Six - Spectroscopic Studies of Selected Phenols

b)

Graph showing absorbance vs. wavelength for different conditions: Aq, Aq > 11, and Aceto.
FIGURE 6.3 - The absorption spectra of ~0.02mM 4-nitrophenol in aqueous solution, at pH>11 in aqueous solution, and in acetonitrile
   a) full spectra
   b) expanded spectra of region of interest i.e. 250 - 500nm

![Absorption Spectra Graph]
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b)

![Graph showing absorbance versus wavelength for different phenolic compounds: Aq, Aq > 11, and Aceto. The graph plots absorbance on the y-axis and wavelength on the x-axis. Peaks at specific wavelengths indicate the absorption maxima for each compound.]
6.4.1 - $\lambda_{\text{max}}$ Results

Each of the spectra for the phenols were recorded and had the respective $\lambda_{\text{max}}$ value measured. Table 6.1 shows all of these measured $\lambda_{\text{max}}$ values for the phenols in distilled water, acetonitrile and the respective phenolate ions in distilled water.

**TABLE 6.1** - $\lambda_{\text{max}}$ values quoted as ±2nm for the phenolics in distilled water and acetonitrile, and the corresponding phenolate in distilled water

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}$ in acetonitrile (nm)</th>
<th>$\lambda_{\text{max}}$ in aqueous solution (nm)</th>
<th>$\lambda_{\text{max}}$ in aqueous at pH&gt;11 i.e. phenolate (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ethylphenol</td>
<td>272</td>
<td>270</td>
<td>290</td>
</tr>
<tr>
<td>4-ethylphenol</td>
<td>280</td>
<td>276</td>
<td>292</td>
</tr>
<tr>
<td>2,3-dimethylphenol</td>
<td>274</td>
<td>270</td>
<td>282</td>
</tr>
<tr>
<td>2,6-dimethylphenol</td>
<td>272</td>
<td>268</td>
<td>286</td>
</tr>
<tr>
<td>3,5-dimethylphenol</td>
<td>274</td>
<td>272</td>
<td>290</td>
</tr>
<tr>
<td>phenol</td>
<td>272</td>
<td>270</td>
<td>286</td>
</tr>
<tr>
<td>3-fluorophenol</td>
<td>268</td>
<td>268</td>
<td>284</td>
</tr>
<tr>
<td>4-fluorophenol</td>
<td>280</td>
<td>278</td>
<td>298</td>
</tr>
<tr>
<td>3-iodophenol</td>
<td>278</td>
<td>276</td>
<td>296</td>
</tr>
<tr>
<td>4-iodophenol</td>
<td>282</td>
<td>286</td>
<td>296</td>
</tr>
<tr>
<td>3-nitrophenol</td>
<td>270</td>
<td>274</td>
<td>292</td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>310</td>
<td>318</td>
<td>398</td>
</tr>
<tr>
<td>3-aminophenol</td>
<td>288</td>
<td>282</td>
<td>290</td>
</tr>
<tr>
<td>4-aminophenol</td>
<td>310</td>
<td>296</td>
<td>398</td>
</tr>
</tbody>
</table>
With reference to Table 6.1 it can be seen that all of the phenolates have larger $\lambda_{\text{max}}$ values than their corresponding phenol form. This is due to the fact that a longer conjugated system is produced upon conversion of the phenol to its respective phenolate. This reduces the separation of energy levels, and gives rise to a longer wavelength at which the compound will absorb. This production of the longer conjugated system through the oxygen is depicted in Figure 6.4 which shows the conversion of 3,5-dimethylphenol to its phenolate form.

**FIGURE 6.4** - To show the extra stable forms available upon deprotonation of a phenol to give its respective phenolate ion

The results presented in Table 6.1 have also shown that the substituents and their position on the phenolic ring have an effect on the $\lambda_{\text{max}}$ values of the compound. The presence of an alkyl substituent on the phenol leads to a small change in $\lambda_{\text{max}}$ to higher wavelengths. This can be attributed to the minor interaction occurring between the $\sigma$ bonded electrons of the alkyl groups and the $\pi$ bond system. The absence of either a lone pair of electrons or the ability to extend the chromophore within the compound, ensures that any alteration of $\lambda_{\text{max}}$ is kept below 10nm.
The presence of halogen substituents can cause a conflict of interest regarding the electron availability within the compound. Halogens are electronegative and they also possess lone pairs. Depending on the halogen present on the compound and its position with regard to the hydroxyl group, various effects can be seen. Fluorine is the most electronegative of the halogens and when placed meta to the hydroxyl group, i.e. 3-fluorophenol, a decrease in wavelength is observed. This can be attributed to the fact that the lone pair on the fluorine is not able to contribute to stable resonance structures when in this position so the effect of the electron withdrawing is more pronounced. No decrease is observed for 3-iodophenol due to the difference in electronegativity values between the two halogens (4.0 for fluorine vs. 2.4 for iodine). When the halogen is placed in the para position, the lone pair is available and interaction can occur between these non-bonding electrons and the aromatic ring. This leads to an increase in $\lambda_{\text{max}}$ and was observed for both the para halogenated compounds studied. It can be predicted that when the halogen is in the ortho position, an increase in the wavelength will also be observed due to resonance structures available, and that this increase would be seen for those halogens not reported here. It would be expected that as the halogen changed from fluorine $\rightarrow$ chlorine $\rightarrow$ bromine $\rightarrow$ iodine, and the electronegativity decreased, so the resulting $\lambda_{\text{max}}$ value observed on the spectra for the 3-halophenol would show a smaller deviation from the parent phenol.

The presence of a nitro substituent on the phenol can have a dramatic effect on the $\lambda_{\text{max}}$ value observed on the spectra. Comparison of the values obtained for the nitro substituted phenols with the parent phenol reveals that if placed into the para position, the nitro group has the effect of increasing the $\lambda_{\text{max}}$, whilst if placed in the meta position no shift is observed. This can be explained by the extra resonance structures available through the nitro group causing an increase in conjugation when either the ortho or the para positions are occupied. When the hydroxyl and the nitro group are positioned para to each other, they complement each other electronically, leading to the large shift observed. This complementation between the two groups is illustrated in Figure 6.5.
FIGURE 6.5 - To show the complementary effect of placing the hydroxyl group and the nitro group \textit{para} to each other

![Chemical Structure](image)

Regarding those results shown for the amino substituted phenolic and comparison to the results obtained for phenol itself, it can be seen that the presence of this particular substituent produces one of the greatest shifts in the $\lambda_{\text{max}}$ value. This is due to the presence of the lone pair on the nitrogen adjacent to the ring. Interaction between the non-bonding electrons present on the nitrogen and the aromatic ring occurs which leads to the shifting of the $\lambda_{\text{max}}$ value to longer wavelengths. Comparison of amino substituents in the \textit{meta} and \textit{para} position shows that \textit{para} substitution has larger $\lambda_{\text{max}}$ values. The reason for this is that a greater number of stable resonance structures can be obtained when the amino substituent is in the \textit{para} position.

Water is a protic solvent whilst acetonitrile is a polar but aprotic solvent.\textsuperscript{107} It is this difference that causes the values for $\lambda_{\text{max}}$ to generally be slightly larger when in acetonitrile than when in aqueous solution. Protic solvents like water have the ability to hydrogen bond to sample molecules present. However, although acetonitrile is a polar solvent, it is also aprotic, which means that there are no functional groups present within the solvent that are able to serve as donors in hydrogen bonding. Comparison of the two solvents shows the degree of solvation is lower in acetonitrile due to this lack of hydrogen bonding. This in turn leads to a reduction of the energy levels for the particular sample, which in turn means larger $\lambda_{\text{max}}$ values.

Conversion of the phenol to its respective phenolate makes the oxygen available to aid conjugation. This should lead to an increase in the $\lambda_{\text{max}}$ value obtained and with reference to Table 6.1, the phenols studied do follow this trend. The effect of the substituent on the phenol also alters the $\lambda_{\text{max}}$ value on the resulting spectra. Depending
on the inductive and mesomeric effects of the substituent will depend on whether the energy level separation is decreased and the wavelength of the absorption decreased or increased.

6.4.2 - $\varepsilon_{\text{max}}$ Results

Comparison of the $\lambda_{\text{max}}$ values obtained for the various substituted phenols has revealed trends that have been explained. From the absorbance ($A$) measured at each of these $\lambda_{\text{max}}$ values it is possible to calculate the relevant $\varepsilon_{\text{max}}$ values for all the samples. The concentration ($c$) of each solution was known, so these values were able to be placed into the following equation in order to obtain $\varepsilon_{\text{max}}$ values which can be found in Table 6.2;

$$\varepsilon_{\text{max}} = \frac{A}{c}$$
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TABLE 6.2 - Calculated $\varepsilon_{\text{max}}$ and log $\varepsilon_{\text{max}}$ values for the phenolics in acetonitrile (aceto) and distilled water (aq), and the corresponding phenolate ion in distilled water (aq: pH>11). All $\varepsilon_{\text{max}}$ values are quoted in dm$^3$mol$^{-1}$cm$^{-1}$ at ±100, whilst the values for log $\varepsilon_{\text{max}}$ are quoted as ±0.01. Measurement occurred at the wavelength closest to $\lambda = 270$ nm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon_{\text{max}}$ (log $\varepsilon_{\text{max}}$)</th>
<th>aceto</th>
<th>aq</th>
<th>aq pH &gt; 11</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-ethylphenol</td>
<td>2290 (3.36)</td>
<td>2070 (3.32)</td>
<td>4083 (3.61)</td>
<td></td>
</tr>
<tr>
<td>4-ethylphenol</td>
<td>3614 (3.58)</td>
<td>2253 (3.35)</td>
<td>2692 (3.43)</td>
<td></td>
</tr>
<tr>
<td>2,3-dimethylphenol</td>
<td>2530 (3.40)</td>
<td>3221 (3.51)</td>
<td>3687 (3.57)</td>
<td></td>
</tr>
<tr>
<td>2,6-dimethylphenol</td>
<td>3043 (3.48)</td>
<td>2540 (3.40)</td>
<td>4013 (3.60)</td>
<td></td>
</tr>
<tr>
<td>3,5-dimethylphenol</td>
<td>2181 (3.39)</td>
<td>939 (2.97)</td>
<td>2406 (3.38)</td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>1731 (3.24)</td>
<td>2467 (3.39)</td>
<td>1731 (3.24)</td>
<td></td>
</tr>
<tr>
<td>3-fluorophenol</td>
<td>1696 (3.23)</td>
<td>1381 (3.14)</td>
<td>2549 (3.41)</td>
<td></td>
</tr>
<tr>
<td>4-fluorophenol</td>
<td>2747 (3.44)</td>
<td>2242 (3.35)</td>
<td>2855 (3.46)</td>
<td></td>
</tr>
<tr>
<td>3-iodophenol</td>
<td>2449 (3.39)</td>
<td>2053 (3.31)</td>
<td>3075 (3.49)</td>
<td></td>
</tr>
<tr>
<td>4-iodophenol</td>
<td>1339 (3.13)</td>
<td>837 (2.92)</td>
<td>1383 (3.14)</td>
<td></td>
</tr>
<tr>
<td>3-nitrophenol</td>
<td>5583 (3.75)</td>
<td>5162 (3.71)</td>
<td>3693 (3.57)</td>
<td></td>
</tr>
<tr>
<td>4-nitrophenol</td>
<td>7685 (3.88)</td>
<td>7064 (3.97)</td>
<td>14072 (4.14)</td>
<td></td>
</tr>
<tr>
<td>3-aminophenol</td>
<td>5776 (3.76)</td>
<td>1983 (3.30)</td>
<td>1946 (3.29)</td>
<td></td>
</tr>
<tr>
<td>4-aminophenol</td>
<td>2726 (3.44)</td>
<td>1871 (3.27)</td>
<td>1124 (3.05)</td>
<td></td>
</tr>
</tbody>
</table>

With reference to Table 6.2, it is possible to see that the results obtained for the $\varepsilon_{\text{max}}$ values for the various phenolics appear to follow a similar trend as observed with the $\lambda_{\text{max}}$ values. The majority of the phenols displayed a higher value for $\varepsilon_{\text{max}}$ when the spectrum was recorded in acetonitrile, and when in an aqueous solution, the phenolate form of the compound tended to show a higher value than the phenol itself.

In order to verify the results and the values obtained, the $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$ results were compared with literature values.151-160 Those comparable values that that were
obtained from the literature are shown in Table 6.3 along with the corresponding experimental result.

**TABLE 6.3 -** Comparison of literature and experimental $\lambda_{\text{max}}$ and log $\varepsilon_{\text{max}}$ values (experimental values quoted as $\pm 2$nm for $\lambda_{\text{max}}$, and $\pm 0.01$ for log $\varepsilon_{\text{max}}$) for phenolics in distilled water and acetonitrile

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>experimental $\lambda_{\text{max}}$ (log $\varepsilon_{\text{max}}$)</th>
<th>literature $\lambda_{\text{max}}$ (log $\varepsilon_{\text{max}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>phenol</td>
<td>distilled water</td>
<td>270 (3.39)</td>
<td>268 (3.38)$^{151}$</td>
</tr>
<tr>
<td></td>
<td>distilled water: pH&gt;11</td>
<td>286 (3.24)</td>
<td>287 (3.41)$^{158}$</td>
</tr>
<tr>
<td>2,3-dimethylphenol</td>
<td>distilled water</td>
<td>270 (3.51)</td>
<td>271 (3.09)$^{154}$</td>
</tr>
<tr>
<td></td>
<td>distilled water: pH&gt;11</td>
<td>282 (3.57)</td>
<td>289 (3.47)$^{154}$</td>
</tr>
<tr>
<td>2,6-dimethylphenol</td>
<td>distilled water</td>
<td>268 (3.40)</td>
<td>270 (3.08)$^{154}$</td>
</tr>
<tr>
<td></td>
<td>distilled water: pH&gt;11</td>
<td>286 (3.60)</td>
<td>288 (3.56)$^{154}$</td>
</tr>
<tr>
<td>3,5-dimethylphenol</td>
<td>distilled water</td>
<td>272 (2.97)</td>
<td>272 (3.08)$^{154}$</td>
</tr>
<tr>
<td></td>
<td>distilled water: pH&gt;11</td>
<td>290 (3.38)</td>
<td>290 (3.41)$^{154}$</td>
</tr>
<tr>
<td>3-fluorophenol</td>
<td>distilled water</td>
<td>268</td>
<td>268$^{155}$</td>
</tr>
<tr>
<td></td>
<td>distilled water: pH&gt;11</td>
<td>284</td>
<td>275.5$^{155}$</td>
</tr>
<tr>
<td>4-fluorophenol</td>
<td>distilled water</td>
<td>278 (3.35)</td>
<td>278 (3.35)$^{156}$</td>
</tr>
<tr>
<td></td>
<td>acetonitrile</td>
<td>280</td>
<td>a$^{159}$</td>
</tr>
<tr>
<td>3-iodophenol</td>
<td>distilled water</td>
<td>276</td>
<td>277$^{155}$</td>
</tr>
<tr>
<td></td>
<td>distilled water: pH&gt;11</td>
<td>296</td>
<td>297$^{155}$</td>
</tr>
<tr>
<td>4-iodophenol</td>
<td>distilled water</td>
<td>286 (2.92)</td>
<td>280 (3.10)$^{156}$</td>
</tr>
<tr>
<td></td>
<td>acetonitrile</td>
<td>282</td>
<td>430$^{159}$</td>
</tr>
<tr>
<td>3-nitrophenol</td>
<td>distilled water</td>
<td>274 (3.71)</td>
<td>272 (3.77)$^{151}$</td>
</tr>
<tr>
<td></td>
<td>distilled water: pH&gt;11</td>
<td>292 (3.57)</td>
<td>292 (3.62)$^{160}$</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>experimental $\lambda_{\text{max}}$ (log $\varepsilon_{\text{max}}$)</th>
<th>literature $\lambda_{\text{max}}$ (log $\varepsilon_{\text{max}}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-nitrophenol</td>
<td>distilled water</td>
<td>318 (3.97)</td>
<td>318 (4.00)$^{151}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>distilled water: pH &gt;11</td>
<td>399 (4.14)</td>
<td>390 (3.47)$^{160}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>acetonitrile</td>
<td>310 (3.88)</td>
<td>308 (3.98)$^{151}$</td>
</tr>
<tr>
<td>3-aminophenol</td>
<td>distilled water</td>
<td>282 (3.30)</td>
<td>281 (3.29)$^{151}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>acetonitrile</td>
<td>288 (3.76)</td>
<td>289 (3.42)$^{151}$</td>
</tr>
<tr>
<td>4-aminophenol</td>
<td>distilled water</td>
<td>296 (3.33)</td>
<td>296 (3.20)$^{151}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>distilled water: pH &gt;11</td>
<td>398 (4.14)</td>
<td>402.5 (4.28)$^{158}$</td>
</tr>
<tr>
<td>&quot;</td>
<td>acetonitrile</td>
<td>310 (3.44)</td>
<td>310 (3.50)$^{151}$</td>
</tr>
</tbody>
</table>

* (ref. 159) regarding 4-fluorophenol in acetonitrile – a literature value is not reported because "absorption of light by the solvent and the presence of a near lying band prevented accurate measurements".

Only those literature values obtained where the solvent and conditions were comparable with those utilised experimentally are presented and compared. With reference to Table 6.3, the log $\varepsilon_{\text{max}}$ values calculated from experiments conducted generally compare well with those obtained from the literature. Slight discrepancies are observed between experimental values and those older literature values, and it can be postulated that this is due to the samples not being as pure as can now be achieved.

### 6.4.3 - Mixtures of Phenolics

The initial intentions for part of the research undertaken was to determine the presence of a phenolic in the contaminated groundwater by the use of a UV/vis spectrophotometer. In natural situations, there would be mixtures of phenolics present as opposed to an individual phenol, therefore in order to ascertain whether an individual phenol could be recognised by UV/vis spectroscopy from a mixture of phenolics, samples were mixed together and the resulting solution scanned. All samples used were made as the phenol in aqueous solution, and various mixtures of
the phenolics were used. Figures 6.6 and 6.7 show the spectra of a mixture of 4-nitrophenol and 3-iodophenol, and 4-aminophenol and 3-iodophenol respectively.

**FIGURE 6.6** - Absorption spectra of ~0.04mM 4-nitrophenol, ~0.02mM 3-iodophenol and a mixture of the two solutions

---

4-nitrophenol + 3-iodophenol

4-nitrophenol

3-iodophenol
FIGURE 6.7 - Absorption spectra of ~0.02mM 4-aminophenol, ~0.02mM 3-iodophenol, and a mixture of the two solutions.
With reference to Figure 6.6, an additional peak has appeared on the scan of the mixture of the two phenolics. This could be attributed to the fact that the solution had not been buffered, and the pH had altered sufficiently to cause the phenolate form of 4-nitrophenol to be present. With reference to Table 6.1, it is possible to compare the $\lambda_{\text{max}}$ values of the newly formed peak with that obtained for 4-nitrophenol when in aqueous solution at pH>11, and to postulate that this is the correct explanation for this peak. Further work in this area of research would benefit from the solution being buffered in order to prevent this complication from arising.

It is evident from examination of Figures 6.5 and 6.6 that UV/vis spectroscopy is not a viable method with which to determine individual components within a phenolic mixture. The $\lambda_{\text{max}}$ values for the phenols are too close together to allow an individual peak to be resolved. However, a smoothing technique whereby the collected data is transferred to Microsoft Excel and has a smoothing programme applied, may enable individual peaks to be defined. Such a technique is in present use to aid the resolution of peaks in X-ray photoelectron spectroscopy, and further research in this area may enable such a programme to be designed.

Another method of determination that is able to be used is HPLC-EC. This is a well documented process and is capable of identifying components from a large mixture of phenolics. It is not however, as portable or as instant as a spectrophotometer, so work on the UV/vis spectroscopy coupled with a possible smoothing programme would be beneficial.

6.5 - CONCLUSIONS

In conclusion, the absorption spectra of the sample phenolics were recorded in both distilled water and acetonitrile, and the corresponding phenolate ion in distilled water only. Conversion of the phenol into its phenolate ion shifts the $\lambda_{\text{max}}$ value to higher wavelengths. This is due to the greater electron density present in the compound as the phenol undergoes deprotonation. A shift in wavelength is also seen when the solvent is changed from a protic to an aprotic solvent.
Alkyl substituents present on the phenolic afford a small change in $\lambda_{\text{max}}$ to higher wavelengths, due to the minor interaction occurring between the $\sigma$ bonded electrons of the alkyl groups and the $\pi$ bond system.

Due to the fact that halogens are electronegative as well as possessing lone pairs of electrons, a conflict between the two effects is observed when a halogen substituent is placed onto a phenolic ring. The extent of effect observed is dependent on the halogen involved (i.e. its relative electronegativity value) and its position with respect to the already present hydroxyl group. 3-fluorophenol has a lower $\lambda_{\text{max}}$ value than the parent phenol as in this particular position the lone pair is not able to contribute to stable resonance structures so the effect of the high electronegativity is more pronounced. No decrease is observed for 3-iodophenol due to the difference in electronegativity values between the two halogens. Conversely both 4-fluorophenol and 4-iodophenol showed higher $\lambda_{\text{max}}$ values than the parent phenol. This is able to be explained as in the para position, and we also postulate that the same would occur when the ortho position is occupied, a lone pair of electrons is able to interact with the electrons within the ring leading to more stable resonance. It would be expected that as the halogen group was descended, and the electronegativity value decreased, so the resulting $\lambda_{\text{max}}$ value for the 3-halophenol would show a smaller deviation from the parent phenol.

The presence of a nitro substituent in the para position of the phenol, causes an increase in $\lambda_{\text{max}}$ with respect to the parent phenol. Conversely, if the meta position is occupied no shift is observed. The extra conjugation through the nitro group when in the para and the ortho position leads to stable resonance structures which causes this increase in wavelength. This conjugation does not occur when the substituent is in the meta position, hence no great shift in wavelength is observed for the 3-halophenols.

The presence of an amino substituent produces a large shift in wavelength, due to the lone pair on the nitrogen adjacent to the ring interacting with the aromatic ring. Para substitution leads to a greater shift in wavelength due to the stable resonance structures obtainable when this position is occupied.
A trend was also observed when comparing the $e_{\text{max}}$ values obtained for the phenols. This was similar to that seen for the $\lambda_{\text{max}}$ values in so far as when the sample was recorded in acetonitrile, a larger value for $e_{\text{max}}$ was generally calculated, and on comparison of a phenol and its respective phenolate ion in distilled water, the latter tended give the larger $e_{\text{max}}$ value.

It can be concluded that UV/vis spectroscopy is not a viable method with which to determine individual components within an unknown phenolic mixture as the $\lambda_{\text{max}}$ values appear too close together to allow an individual peak to be resolved. However, a technique whereby the collected data is transferred to Microsoft Excel and has a smoothing programme applied, may enable the definition of individual peaks.

Further work in this area could include using an extended number of solvents and monitoring their effect on the $\lambda_{\text{max}}$ and $e_{\text{max}}$ values obtained. Also a larger range of phenolics could be investigated. These could include those phenolics with substituents in the ortho position and those with more than two substituents present on the ring.

A further aspect of this area of research could involve utilising the shift in wavelength observed for the phenols when the pH of the solution is adjusted to such an extent that the phenolate form is predominant. Comparison of a spectra of a mixture of, for example 4 phenolics, at a neutral buffered pH, and an alkaline pH, could afford some individual components to be positively identified. Coupled with the technique of cyclic voltammetry, again at a neutral and an alkaline pH, this could be the basis of a possible determination procedure for a mixture of phenolics.

An example of this utilisation of cyclic voltammetry and UV/vis spectroscopy at two different pH values to determine the identification of the individual components of a mixture could be a solution of 2-ethylphenol and 2,3-dimethylphenol. At a neutral buffered pH, it would not be expected to be able to identify the individual components as both of those phenols have a $\lambda_{\text{max}}$ value of 270nm. Alteration of the theoretical solution to a pH whereby the phenolate forms of the components are predominant (i.e. pH > 11), may enable the two phenols to be identified, as a greater shift for 2-ethylphenol to a $\lambda_{\text{max}}$ value of 290nm is observed, whilst 2,3-dimethylphenol...
produces an increase in $\lambda_{\text{max}}$ of only 12nm to 282nm. The postulated use of cyclic voltammetry on this mixture of phenols could confirm this identification. By scanning the solution at both a neutral and an alkaline pH, and then comparing the observed $E_{\text{pa}}$ values with the values recorded in Table 5.6, it could be possible to determine the individual components from the change in $E_{\text{pa}}$ on alteration of the solution pH. In the example chosen, a shift from 0.88V to 0.32V for 2-ethylphenol would be expected on going from a neutral to an alkaline solution, whilst a smaller shift from 0.77V to 0.30V could indicate the presence of 2,3-dimethylphenol.

Another example of how this potential technique could be utilised would be to identify the individual components of a three phenol mixture, for example; 3-iodophenol, 3-nitrophenol, and 3-aminophenol. At a neutral buffered pH, a similar $\lambda_{\text{max}}$ value would be observed for the former two compounds at 276nm, and 274nm respectively, whilst 3-aminophenol would show a greater value of 282nm after the recommended smoothing technique had been applied. This could lead to the possible identification of one component. On the addition of a substance to alter the pH to such an extent that the phenolate form of each was predominant, a greater increase in $\lambda_{\text{max}}$ to 296nm would be noted for 3-iodophenol than for the other two components. It could be postulated that this initial identification could then be verified by the use of cyclic voltammetry. Comparison of the resulting $E_{\text{pa}}$ values obtained for the mixture at a neutral and an alkaline buffered pH with those reported in previous chapters, could theoretically identify each component. At a neutral pH, each phenol displays marked differences in the $E_{\text{pa}}$ value obtained; 0.58V for 3-iodophenol, 1.04V for 3-nitrophenol, and 0.39V for 4-aminophenol. If these peaks are able to be resolved and are clearly visible, this would prove to be a positive method of identification. Alteration of the solution to pH>11 would shift the values obtained, and consequential comparison with values reported could verify the identification. The smallest shift to 0.79V would be noted for 4-aminophenol, and the greatest shift to 2.24V for 3-nitrophenol. 3-iodophenol would lie in-between at 1.77V, and a determination of the individual components of a mixture of phenols would have been completed.
7.1 - CELLS A AND B

7.1.1. - Conclusions

Two large rectangular cells were designed and constructed. Cell A consisted of a horizontal design whilst Cell B was based on a vertical design. Cell A was the prototype design and attempts to achieve a steady flow through the cell proved to be unsuccessful. This could be attributed to the fact that the design was an open system as the lid could not be fitted due to excess pressure inside the cell causing the perspex sides to bow. A hydraulic head was therefore not obtainable to ensure a flow was observed through the sample medium.

Experiments showed that as the water was introduced to the cell through the inlet valve, a flow was observed across the top few centimetres of the central sand section. The reason for this is that the preferential flow path is through the easiest path available, and due to compaction of the sand at greater depths in the cell, the easiest path would be through this top portion of the sand. Compaction of the sand nearer the bottom of the cell had occurred due to the weight of the wet sand above it exerting a great pressure on it.

A decrease in flow rate was observed throughout an experiment and this was attributed to the fact that eventually a portion of the flow would begin to permeate into the more compact lower section, both laterally from the initial gravel section and descending from the flow across the top of the central section.

Due to a steady flow not being obtainable, another cell was designed. By changing the orientation of the cell and designing a vertical based cell, it was hoped that the problems associated with Cell A would be rectified.
Initially a similar problem was encountered with the new Cell B as for Cell A in so far as the cell was not a fully sealed system and classed as an open system. By permanently fixing the lid into place, this difficulty was overcome and a fixed head of water was achieved. Unfortunately the volume of sand present through which the flow needed to pass proved to be too great for the particular head height obtainable. Before any flow was achieved, the top of the cell began to bow, and the pressure being exerted on both the glue holding the lid in place and the lid itself was considered too great for the design of this particular cell.

In conclusion neither of the two large rectangular cells that had been designed were capable of ensuring a steady flow rate through the sample medium. Although this meant that Cells A and B were not able to be used for experiments on the remediation of pollutants, the design and construction, and consequential experiments performed on the cells have provided valuable information for further research on a scale this large to be conducted.

7.1.2 - Suggestions for Further Work

The design of Cell B, once the system had been converted to a closed system, was fundamentally and theoretically correct and it is on this design that further work could be based. Modifications to the design of Cell B would be needed to ensure a steady flow through the cell could be obtained. A thicker perspex or stronger material would be beneficial as more pressure could then be exerted within the cell. A larger head space above the volume of sand would create a larger hydraulic head and would therefore aid flow through the cell, as would decreasing the volume of sand through which the liquid had to pass. Alteration of the K value to facilitate the flow of liquid through the volume of sand present would also be beneficial.

Once a cell had been designed through which a steady flow could be obtained, the introduction of contaminants to the cell and consequential removal of them electrokinetically could be investigated. In order to optimise the remediation of the various pollutants chosen, parameters such as electrode configuration, voltage applied and contaminant concentration could be altered.
Chapter Seven - General Discussion And Further Work

7.2 - SMALL CELLS

7.2.1 - Conclusions

A small scale cylindrical cell has been designed and constructed that allows electrokinetic remediation to be investigated.

Two compounds - phenol and ammonia - were chosen to be used to investigate the phenomenon of electrokinetic remediation. These specific chemicals were chosen as they can both be found at disused gasworks sites where they are present as pollutants. The first to be studied was phenol from which no conclusions can be drawn due to the solution changing to a brown colour as the voltage was applied. This colour change was accompanied by effervescence from both of the electrodes, and a warming of the solution. This colour change was initially believed to be due to the presence of any newly formed oxidation products of the phenolic. Numerous attempts to prove this by NMR spectroscopy showed the complete removal of the phenolic from the solution as well as no identifiable peaks for any oxidation products. It was postulated that the absence of phenol in the solution could be explained by complete adsorption or electropolymerisation onto the carbon rod electrodes, and that the brown colour observed could be due to the disintegration of the actual electrodes.

Experiments were conducted and the results analysed by HPLC-EC courtesy of BG Technology. A sharp phenol peak was observed for each sample but no decrease was noted in the concentration throughout any of the runs conducted. This section of the research has plenty of scope for further work to be conducted.

It has been proved to be possible to electrokinetically remediate NH₄Cl from contaminated water using the cylindrical cell with two carbon rod electrodes and a flow through of the spiked solution. Measurement of the concentration with an ISE was both effective and immediate so the concentration / time plot could be observed as the experiment was being conducted. This was advantageous in so far as timing of the application of voltage, and if a problem was observed, the experiment could be stopped without further delay.
Experiments were carried out in alkali, neutral, and acidic environments and the applied voltage varied in order to optimise the remediation of ammonia. A decrease of nearly 70% was observed with 0.5mM NH₄Cl and the application of 80 volts. Decreasing the concentration and increasing the voltage applied could increase this remediation value, although edge effects within the cylindrical cell may be enabling some of the contaminant to flow through the cell without experiencing the field.

7.2.2. - Suggestions for Further Work

Further work involving the use of phenol as a contaminant could lead to the reason behind the colour change of the sample. This suggested work could involve using solutions of higher concentrations of phenol in order to ascertain if the total loss of phenol is still occurring even when this could not be attributed to adsorption or electropolymerisation alone. The carbon rod electrodes could be ground after an experiment had been conducted, and attempts to desorb and identify any adsorbed phenol would conclude whether this is the correct assumption as to the loss of the phenol from solution. The collection and analysis of the emitted gases would give an insight into the reactions occurring at the electrode to cause effervescence. Continual monitoring of the solution with a documented technique i.e. HPLC-EC would enable the concentration profiles of the phenolic and its possible oxidation products to be monitored. It is feasible that the phenolic in question is undergoing rapid and complete oxidation through aromatic and aliphatic intermediates to produce carbon dioxide, and this would verify this theory.

Further work could also include conducting similar experiments but with other electrodes of varying materials and size. Parameters could be altered to optimise any remediation observed if this method proved to be successful. Such parameters could include phenol and background electrolyte concentration, amount of voltage applied and the time period for which it was applied, and flow rate.

The use of a dedicated HPLC system for phenol analysis would be a more rapid and effective method of determining any decrease noted in the phenol concentration. It has
been shown that the resulting phenol peak from HPLC-EC is clear and sharp, and any reduction should be easily visible.

Once the remediation of phenol had been completed, investigations into the remediation of other phenolics could be a continuation of this work. A worthwhile suggestion for the next phenol to be studied would be 4-aminophenol as work reported in CHAPTER FIVE — MODEL ELECTROCHEMICAL STUDIES OF PHENOL has shown that this displays different properties with respect to those other phenols studied, in so far as no reduction in response was observed for the simple ferricyanide redox couple.

Further work in the area of remediation of the ammonia contaminant could involve the investigation of the effect of further parameters. By altering the shape of the cell itself, any possible edge effects could be prevented and remediation values could be increased. The electrode size and material are other areas to investigate, and further alteration of the concentration of the contaminant and the voltage applied, would all lead to a greater knowledge and understanding of the phenomenon of electrokinetic remediation.

The study of various other amines and ammonium salts, aside from the one reported here, would also be beneficial to the understanding of the remediation of contaminated groundwater. Ammoniacal liquor, which is the by-product of the gas manufacture, can be found at the gasworks sites as either 'free' or 'fixed' ammonia. This former category consists of those salts such as the cyanide, sulphide, and carbonate, whilst the latter group contains those salts like the chloride, thiocyanate, and sulphate.

Automation of the remediation process reported is another area that could be investigated. The incorporation of an ISE into the outflow of a small cell would enable immediate results to be obtained more effectively and easily than manual measurement. By connecting the ISE to a computer, a concentration / time plot could be achieved instantaneously.
The construction of a larger cylindrical cell that is able to house more electrodes would enable the electrode configuration to be investigated. Gradually increasing the size of the cell constructed, and consideration of the difficulties encountered with Cells A and B, would lead to a large scale cell being designed, and eventually trial field work could be conducted.

7.3 - ELECTROCHEMISTRY

7.3.1 - Conclusions

A change in both the value of $E_{pa}$ obtained and the shape of the cyclic voltammogram produced was observed with different WE materials. The ITO glass electrode showed the largest change in $E_{pa}$ and this was shown to be due to the particular reaction being unfavourable on this material, as the $E_{pa}$ for a standard reversible redox couple hexacyanoferrate (III/II) did not differ greatly when compared between a platinum wire and an ITO WE. A polymeric film was formed on each of the different WE's due to the electropolymerisation of phenol, and this was easier and more effectively removed when the WE was platinum wire. The ITO glass WE required an increase in the potential window used in order to see the oxidation of phenols, and the carbon rod used in the small cell experiments had too large a background to enable any decrease due to the electropolymerisation of the phenol to be observed.

Alteration of the pH of solution led to a change in the value of $E_{pa}$ for each phenol. The neutral and acidic solutions gave comparable results as in this both of these situations, the phenol form is dominant. However, altering the pH such that a basic solution is produced leads to the deprotonation of the phenol, and the relevant phenolate ion prevails. Deprotonating the phenol, i.e. ensuring a basic solution, makes it easier to oxidise, and a decrease in $E_{pa}$ is therefore observed. Knowledge of the $pK_a$ of the particular phenol under investigation will enable the pH of the solution to be altered to such an extent that the phenolate ion is predominant, and oxidation is easier.

By increasing the concentration of phenol present, the rate at which passivation of the electrode occurs is increased. This is as expected as at higher concentrations there will
naturally be more phenol ions in the vicinity of the electrode which are able to form the film.

Alteration of the solvent from a protic \textit{i.e.} aqueous system to an aprotic \textit{i.e.} acetonitrile system, led to an increase in $E_{pa}$ for the phenols. Dissolution problems meant that no values were available for the phenolate ions in acetonitrile, so no comparisons are able to be made between the phenol and its respective phenolate ion in different solvent systems.

The nature of the substituent present on the phenol led to the observation of different effects with regard to the $E_{pa}$ measured and the shape of the resulting voltammogram.

The alkyl substituted phenols studied produced irreversible voltammograms in aqueous solution. This could be attributed to either a follow up chemical reaction, or electropolymerisation onto the electrode, both preventing any reverse reaction from occurring and therefore ensuring no reverse peak visible. Comparison of the resulting $E_{pa}$ values for the alkylphenols and the parent phenol leads to the conclusion that no great shift is observed on the addition of alkyl substituents. This can be explained by the fact that alkyl groups have no capabilities through which further conjugation can occur, nor are they classed as particularly electron-withdrawing or electron-donating, so any changes that are observed are slight. When the \textit{ortho} position is occupied by an alkyl group, oxidation tends to be slightly harder and this is probably due to a direct interaction occurring between the hydroxyl group and its neighbouring substituent.

The halogenated phenols studied also gave rise to irreversible cyclic voltammograms, the explanation once again being either the formation of an insulating film on the electrode surface, or a subsequent chemical reaction. The effect that the halogen substituents have on the ease of oxidation of the compound is two fold. Halogens possess lone pairs of electrons, yet are also electronegative elements, producing a conflict of interest. When the substituent is in a position where the lone pairs are able to contribute to the resonance of the phenol \textit{i.e.} the \textit{para} position as studied here (and it is possible to postulate the \textit{ortho} position would produce similar results), an increase in the ease of oxidation was observed. This trend is illustrated as the phenol
changes from phenol \( \rightarrow \) 4-fluorophenol \( \rightarrow \) 4-iodophenol in aqueous solution, the value of \( E_{pa} \) decreases thus; 0.95V \( \rightarrow \) 0.93V \( \rightarrow \) 0.83V. It can be postulated that the greater the electronegativity of the element, the less likely the non-bonding electrons are to interact with those electrons in the ring. This would mean that 4-fluorophenol shows the least deviance from the parent phenol as fluorine has the highest electronegativity value, whilst 4-iodophenol would be the easiest to oxidise of the 4-halophenols, as iodine is lowest in the halogen series. It could be envisaged that 4-chlorophenol and 4-bromophenol would fit into this pattern and fall between the two halogenated phenolics studied to date. For the meta-halogenated phenols, the lone pair of electrons are not able to interact within the ring due to the lack of resonance structures. Instead the electronegativity of the halogen can cause the electron availability within the compound to decrease and, thus the \( E_{pa} \) value increases. It is expected that this would be more pronounced, the greater the electronegativity of the halogen.

As for the alkyl and halophenols, the nitrophenols studied also gave rise to irreversible cyclic voltammograms, again due to either the production of the film on the surface of the electrode, or because of a follow up chemical reaction had occurred. The ability of the nitro group to withdraw electrons away from the phenolic led to a decrease in electron availability, and thus the compound proved harder to oxidise. Resonance factors can account for the difference in ease of oxidation between the studied 3-nitrophenol and 4-nitrophenol. When the para position is occupied (4-nitrophenol) resonance structures are possible which leads to a larger decrease in electron availability, and thus a large value for \( E_{pa} \). This resonance is not available when the substituent is placed in the meta position (3-nitrophenol). It could be postulated that if the nitro substituent were placed in the ortho position, oxidation would be as difficult as for 4-nitrophenol as interaction with the ring is possible.

Differences on the cyclic voltammograms were observed between the two amino substituted phenols studied. For an 'as made' aqueous system, irreversibility was noted for 3-aminophenol whilst 4-aminophenol gave a reversible system. The irreversibility of the 3-aminophenol is due to either the formation of an insulating film on the electrode surface or a chemical reaction, as has been the situation for the
remainder of the phenols studied. However, 4-aminophenol does not appear to electropolymerise onto the electrode as no decrease in activity towards the ferricyanide couple was observed. A possible explanation for this could be the formation of a dimer which is stable enough that is goes no further in the polymerisation chain, yet is able to be reduced back to the original form to give the reversible peak on the cyclic voltammogram. The value of $E_{pa}$ observed for the aminophenols when compared to the parent phenol, is increased. This can be attributed to the presence of the lone pair of electrons on the nitrogen adjacent to the ring. The availability of the electrons within the ring is increased and therefore the ease at which one can be removed i.e. oxidation occurring, is increased. 4-aminophenol is easier to oxidise than its meta counterpart due to resonance contributions.

Passivation of the WE due to the formation of a polymeric film, tends to occur more rapidly when the phenol is converted to its respective phenolate form. An explanation for this could be that it requires less energy for the phenolate ion to be converted to dimers, trimers and eventually a polymeric film than it does for the parent phenol. It has been shown that it is easier to oxidise the phenolate ion than the phenol when in an aqueous system, so it can be postulated that the formation of the inhibiting layer would be easier for the phenolate ion, therefore requiring less scans in the phenolic solution before a peak height reduction for the ferricyanide is observed.

The choice of solvent also appears to have a substantial effect on the formation of an inhibiting layer. No reduction was observed for almost half of the compounds investigated when in acetonitrile, and of those remaining it was necessary to complete at least ten cycles in the phenol solution before a reduction was observed. 3-aminophenol was the exception and gave a reduction in response after one scan in the phenol in acetonitrile solution. This compound however, had a low $E_{pa}$ value and this could be the reason why an inhibiting layer is observed for this compound, and not for the other phenols.

Generally those compounds with a lower $E_{pa}$ value tended to require fewer scans in the phenol solution to see a decrease in peak height for the ferricyanide solution.
Those phenols with \textit{para} substituents had a tendency to require a greater number of scans in the phenol solution, and this can be explained by the position of the substituent hindering the coupling of the phenol to produce an inhibiting layer.

For the tyrosine derivatives studied, two oxidation waves for the phenol form were observed. Each of the two oxidation waves is believed to correspond to the removal of one electron. On the reverse sweep for these phenolics a cathodic wave was observed ($E_{pc} \sim 0.60V$) which can be attributed to the reduction of the coupled dimer that was formed in the oxidation sweep.

The presence of the various substituents on the phenol led to different effects being observed. Those compounds with unsaturated and conjugated substituents in the \textit{para} position lead to the greatest decrease in $E_{pa}$ with respect to the parent phenol. These are thus the easiest to oxidise and this can be attributed to the increased resonance, and therefore stability, of the intermediate radical cation produced. The cyclic voltammograms produced for these compounds with unsaturated and conjugated \textit{para} substituents are more complex than those voltammograms produced for the remainder of the phenols. The oxidation waves are irreversible and not reproducible, although the presence of further voltammetric waves does indicate that electropolymerisation of the compound is not occurring and that the electrode is not being fouled. Instead it is postulated that the cyclisation of the side chain is occurring, resulting in further voltammetric waves on the cyclic voltammogram due to the oxidation and reduction of these newly formed compounds. The largest $\Delta E_{pa}$ values are observed for these derivatives with the unsaturated and conjugated \textit{para} substituents. This can be explained by the pronounced stability of the newly formed radical cation due to the extra conjugation present within the side chain, which would ensure the removal of the second electron would be greatly unfavourable.

The presence of an \textit{ortho}-iodine substituent can be examined by comparison of those tyrosine derivatives with two, one and no iodines on the ring. It would appear that the presence of an \textit{ortho}-iodine causes a decrease in the value of $E_{pa}$ obtained, and by increasing the number of these \textit{ortho} substituents the amount of decrease observed also increases. This can be explained by examination of the pK$_a$ values of the phenols.
in question. As the number of iodines present on the tyrosine derivative increases from $0 \rightarrow 1 \rightarrow 2$, so the $pK_a$ of the compound decreases from $10.0 \rightarrow 8.7 \rightarrow 6.5$. It is conceivable that the radical cation generated by the first oxidation wave is a very short lived species and becomes even more so following the above sequence from $0 \rightarrow 1 \rightarrow 2$ iodines present. This greater ease of oxidation can then be explained, as it is possible that the loss of the proton may be occurring simultaneously with this first oxidation.

As the number of iodines present on the derivative increases from $0 \rightarrow 1 \rightarrow 2$, so the average $\Delta E_{pa}$ value calculated also increases. The presence of an increasing number of iodine substituents aids the stability of the phenoxy radical by electron withdrawing and mesomeric effects. Thus the removal of the first electron to achieve this radical is a more favourable process, the more iodines there are present. Due to this extra stability of the radical cation because of the presence of the extra iodines, the removal of the second electron is made more difficult. Therefore the energy difference between the two oxidation potentials will be greater for those compounds with more iodines present in the ortho position, as the removal of the first electron is facilitated, whilst the removal of the second is made more difficult, leading to a larger $\Delta E_{pa}$ value.

Alteration of the solvent from an aqueous system to acetonitrile led to an increase in $E_{pa}$ for the phenol form of the tyrosine derivatives. The opposite trend is observed for the phenolate ion form of the derivatives, in so far as the obtained $E_{pa}$ values are lower in acetonitrile than in an aqueous system, thereby making them easier to oxidise in the former solvent. Further work with various other solvent systems and utilising the phenols and their respective phenolate ions is necessary in order to explain this phenomenon.

The phenolate ions of the derivatives that posses conjugated unsaturated side para chains show three oxidation waves on their cyclic voltammograms. The first wave can be explained by the one electron oxidation of the phenolate ion. The second wave could be due to the reaction of the formed radical with either the side chain, another radical, or a nucleophile present in the bulk solution. The resulting product would then
be oxidised to a radical and this would produce the observed wave. The removal of a third electron to form the phenoxonium ion is the probable reason for the third oxidation wave. These measurements obtained were not reproducible on successive scans.

The measured $E_{pa}$ values for those iodinated tyrosine phenolate ion derivatives in both aqueous and acetonitrile systems reveal an opposite trend than was encountered for the phenol form of the derivatives in acetonitrile. For the phenolate ions, on progressing from the presence of $0 \rightarrow 1 \rightarrow 2$ iodines, the oxidation potential increases, whilst for the phenol form the oxidation potential was observed to decrease. A possible explanation for this reversed trend is that the higher the $pK_a$ of the phenolate ion, the less stable it will be. This would result in a small energy difference between the ion and the radical, as the unstable ion would prefer to be converted to the more stable radical. It follows that the phenolate ion with the higher $pK_a$ should have the smaller oxidation potential, and this is what is occurring. As the $pK_a$ of the phenolate ion decreases from $10 \rightarrow 8.7 \rightarrow 6.5$, the number of iodines increases from $0 \rightarrow 1 \rightarrow 2$, and the oxidation potential increases. The results obtained for the phenol forms where a decrease in $E_{pa}$ was noted as the number of iodines increased from $0 \rightarrow 1 \rightarrow 2$, was explained by the fact that the higher the $pK_a$ of the phenol, the less stable would be the phenolate ion. Therefore the removal of this first electron to achieve this unstable ion would be unfavourable and the observed decrease in $E_{pa}$ would occur.

The presence of any second oxidation waves for the phenolate ions of the tyrosine derivatives that have not already been discussed, can probably be attributed to the removal of a second electron from the formed phenoxy radical. No apparent trend is observed between either the $E_{pa}$s or the $\Delta E_{pa}$s and reproducibility is only evident for the second scan - after this the potential shifts or, in the case of phenol, no oxidation wave is observed due to electropolymerisation onto the electrode.
7.3.2. Suggestions for Further Work

The scope for continuation of the work reported in **CHAPTER FIVE - MODEL ELECTROCHEMICAL STUDIES OF PHENOL** is unlimited. The further alteration of those parameters that have been varied, as well as those that were kept constant, would lead to a much wider knowledge on the electrochemical behaviour of phenolic compounds. These parameters that are able to be varied include scan rate, potential limits, solvent choice, concentration of phenolic, background concentration, the nature of the background itself, electrode material, and electrode size. A larger range of phenolics is a further area that can be studied. A greater number of substituents, for example a tri-substituted phenol, as well as a variety of different natured substituents *i.e.* chlorine, longer alkyl chains, etc. can be investigated, in order to give a better understanding into the effect of the substituent on the electrochemical behaviour of the phenolic compound.

Continuation of this section of research could begin with an investigation of simple ortho iodophenols as this would tie together **Section 5.4.5 - Comparison of a Range of Phenolics with Various Solvent Systems** and **Section 5.4.6 - Oxidation of Iodinated Phenols**.

A mixture of phenols could be studied with a final analysis by HPLC-EC in order to determine whether one particular phenol electropolymerises preferentially.

7.4 - SPECTROSCOPIC STUDIES

7.4.1 - Conclusions

The absorption spectra of each of the sample phenolics were recorded in both distilled water and acetonitrile, and the corresponding phenolate ion recorded in distilled water only. By converting the phenol into its respective phenolate ion a shift in the $\lambda_{\text{max}}$ value to higher wavelengths is observed. This is due to the fact that a longer conjugated system is produced upon conversion of the phenol to its respective
phenolate. This reduces the separation of energy levels, and gives rise to a longer wavelength at which the compound will absorb.

A shift in wavelength is also observed when the solvent is changed from a protic solvent *i.e.* distilled water to acetonitrile which is a polar but aprotic solvent.\(^{107}\) It is this difference that causes the values for \(\lambda_{\text{max}}\) to generally be slightly larger when in acetonitrile than when in aqueous solution. Protic solvents like water have the ability to hydrogen bond to sample molecules present. However, although acetonitrile is a polar solvent, it is also aprotic, which means that there are no functional groups present within the solvent that are able to serve as donors in hydrogen bonding. Comparison of the two solvents shows the degree of solvation is lower in acetonitrile due to this lack of hydrogen bonding. This in turn leads to a reduction of the energy levels for the particular sample, which in turn means larger \(\lambda_{\text{max}}\) values.

The substituents and their position on the phenolic ring have an effect on the \(\lambda_{\text{max}}\) values of the compound. The inductive and mesomeric effects of the substituent will alter the energy level separation, and the wavelength of the absorption will subsequently either decrease or increase. The presence of an alkyl substituent on the phenol leads to a small change in \(\lambda_{\text{max}}\) to higher wavelengths. This can be attributed to the minor interaction occurring between the \(\sigma\) bonded electrons of the alkyl groups and the \(\pi\) bond system. The absence of either a lone pair of electrons or the ability to extend the chromophore within the compound, ensures that any alteration of \(\lambda_{\text{max}}\) is kept below 10 nm.

The presence of halogen substituents can cause a conflict of interest regarding the electron availability within the compound. Halogens are electronegative and they also possess lone pairs of electrons. Depending on the halogen present on the compound and its position with regard to the hydroxyl group, various effects can be observed. Fluorine is the most electronegative of the halogens and when placed *meta* to the hydroxyl group, *i.e.* 3-fluorophenol, a decrease in wavelength is observed. This can be attributed to the fact that the lone pair on the fluorine is not able to contribute to stable resonance structures when in this position so the effect of the electron withdrawing is
more pronounced. No decrease is observed for 3-iodophenol due to the difference in electronegativity values between iodine and fluorine. It would be expected that as the halogen changed from fluorine $\rightarrow$ chlorine $\rightarrow$ bromine $\rightarrow$ iodine, and the electronegativity decreased, so the resulting $\lambda_{\text{max}}$ value observed on the spectra for the 3-halophenol would show a smaller deviation from the parent phenol. When the halogen is placed in the para position, the lone pair is available and interaction can occur between these non-bonding electrons and the aromatic ring. This leads to an increase in $\lambda_{\text{max}}$ and this was observed for both the para halogenated compounds studied. It can be predicted that when the halogen is in the ortho position, an increase in the wavelength will also be observed due to resonance structures available, and that this increase would occur for those halogens not reported here.

The presence of a nitro substituent on the phenol can have a dramatic effect on the $\lambda_{\text{max}}$ value observed on the spectra. When placed in the para position, the nitro group has the effect of increasing the $\lambda_{\text{max}}$, whilst if placed in the meta position no shift is observed. This can be explained by the extra resonance structures available through the nitro group causing an increase in conjugation when either the ortho or the para positions are occupied. When the hydroxyl and the nitro group are positioned para to each other, they complement each other electronically, leading to the large shift observed.

An amino substituent produces one of the greatest shifts in the $\lambda_{\text{max}}$ value. This is due to the presence of the lone pair on the nitrogen adjacent to the ring. Interaction between the non-bonding electrons present on the nitrogen and the aromatic ring occurs which leads to the shift of the $\lambda_{\text{max}}$ value to longer wavelengths. Comparison of amino substituents in the meta and para position shows that para substitution has larger $\lambda_{\text{max}}$ values. The reason for this is that a greater number of stable resonance structures can be obtained when the amino substituent is in the para position.

A trend was also observed when comparing the $\varepsilon_{\text{max}}$ values that were calculated for the phenols. This was similar to that noted for the $\lambda_{\text{max}}$ values in so far as when the sample was recorded in acetonitrile, a larger value for $\varepsilon_{\text{max}}$ was generally calculated,
and on comparison of a phenol and its respective phenolate ion in distilled water, the latter tended give the larger $\varepsilon_{\text{max}}$ value.

It became evident that UV/vis spectroscopy is not a viable method with which to determine individual components within a phenolic mixture. The $\lambda_{\text{max}}$ values for the chosen phenolics are too close together to allow an individual peak to be resolved. However, a smoothing technique whereby the collected data is transferred to Excel and has a smoothing programme applied, may enable individual peaks to be defined. Such a technique is in present use to aid the resolution of peaks in X-ray photoelectron spectroscopy and further research in this area may enable such a programme to be designed.

7.4.2 - Suggestions for Further Work

Further work in this area could include using an extended number of solvents and monitoring their effect on the $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$ values obtained. A larger range of phenolics could be investigated. These could include those phenolics with substituents in the ortho position and those with two or more substituents present on the ring.

A further aspect of this area of research could involve utilising the shift in wavelength observed for the phenols when the pH of the solution is adjusted to such an extent that the phenolate form is predominant. A spectrum of a mixture of, for example 2-ethylphenol and 2,3-dimethylphenol at a neutral buffered pH, would not be expected to identify the individual components as both of those phenols have a $\lambda_{\text{max}}$ of 270nm. Alteration of the theoretical solution to a pH whereby the phenolate forms of the components are predominant (i.e. pH>11), may enable the two phenols to be identified, as a greater shift for 2-ethylphenol to a $\lambda_{\text{max}}$ value of 290nm is observed, whilst 2,3-dimethylphenol produces an increase in $\lambda_{\text{max}}$ of only 12nm to 282nm. The postulated use of cyclic voltammetry on the mixture of phenols could aid this identification. By scanning the solution mixture at both a neutral and an alkaline pH, and comparing the observed $E_{\text{pa}}$ values with the values recorded in Table 5.6, it could be possible to determine the individual components from the change in $E_{\text{pa}}$ on
alteration of the solution pH. In the example chosen, a shift from 0.88V to 0.32V for 2-ethylphenol would be expected on going from a neutral to a alkaline solution, whilst a smaller shift from 0.77V to 0.30V could indicate the presence of 2,3-dimethylphenol.

The scope for further research in this area is therefore unlimited – work could begin on a mixture of two phenols that are known to possess different $\lambda_{\text{max}}$ and $E_{\text{pa}}$ values in solutions of different pH, and then could progress onto solutions of phenols that have closer values in order to see if individual identification is still possible. Finally solutions containing three and more phenols could be utilised.
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APPENDIX I – Conferences Attended

- 'Electrokinetic Clean-up of Impregnated Soils and Clays'
  D.L. Hall and R.J. Mortimer. Poster presentation P.113 and X1.3 in the RSC Analytical Division R & D Topics Meeting, University of Hull, 10th - 11th July 1995 and SAC 95 (Poster Session X1, Sample Preparations), University of Hull, 11th - 15th July 1995, respectively

- 'Electrokinetic Clean-up of Impregnated Soils and Clays'

- Electrochemical Studies and Control of the Migration of Pollutants in Contaminated Land and Groundwater'
  D.L. Hall and R.J. Mortimer. Poster presentation in the RSC Analytical Division R & D Topics Meeting, Nottingham Trent University, 22nd - 23rd July 1996

- 'Electrochemical Studies and Control of the Migration of Pollutants in Contaminated Land and Ground Water'
  D.L. Hall and R.J. Mortimer. Poster presentation 20 at Electrochem 96, University of Bath, 16th - 19th September 1996

- 'Electrochemical Studies and Control of the Migration of Pollutants in Contaminated Land and Groundwater'
Appendix I

- East Midlands Electrochemistry Group meetings:
  University of Leicester, 30th March 1995
  Loughborough University, 24th March 1997

- BG Technology Contaminated Land Research Event
  BG Technology Centre, Loughborough, 22nd - 23rd June 1998