NOVEL CARBON-BASED MATERIALS FOR USE IN EXTRACORPOREAL SYSTEMS

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Abstract

Activated carbons possess many of the properties desirable for use as a sorbent material in extracorporeal systems. They are physically and chemically stable, may be modified in terms of porosity or surface chemistry, thus allowing a wide range of sorbent materials to be produced. One drawback of activated carbons is their inherent hydrophobicity. Unless they are used as hydrophobic matrices, the surfaces have to be modified to produce a more hydrophilic surface, to increase interaction with the biological solution of interest.

Modification of the surface is usually performed by oxidation of the surface groups, using liquid or gaseous treatments, such as nitric acid, hydrogen peroxide or oxygen respectively, to produce surfaces with different distributions of functional groups. As the first step to producing activated carbons which have specific bioaffinity for species in the plasma or blood, the conjugation of butylamine to the surface of activated carbons was undertaken.

Activated carbons (NOVACARB) based on phenol-formaldehyde resins supplied by MAST Carbon Ltd. were oxidised using 20 % nitric acid at 50, 70 and 90 °C for 2 hours to increase the hydrophilicity of the surface and the number of groups available for functionalisation. The oxidised surfaces were further functionalised with either thionyl chloride to convert the carboxylic moieties to more reactive acyl chlorides; or 1-ethyl-3-(3-dimethyl aminopropyl) carbodiimide, to allow the attachment of a test bioligand (butylamine) to the surface via the formation of an amide bond.

To determine the distribution of surface functional groups, the activated carbons were examined using a variation of the titration method proposed by Boehm et al. (1964) and the chemical and physical properties of the starting carbons and functionalised activated carbons were investigated using mass titrations, SEM, EDS, SIMS, FTIR, SAXS and nitrogen gas adsorption.

Oxidation at different temperatures was shown to have a temperature dependent effect on the distribution of functional groups, allowing for tailoring of the surface for further functionalisation. An increase in oxidation temperature decreased the amount basic and phenolic groups, but increased the number of carboxylic and lactonic moieties. Conjugation of butylamine to the surface of non-oxidised and oxidised (90 °C treatment) activated carbons was shown by the decrease in the number of carboxylic groups from the Boehm titration results and the presence of amide peaks in the FTIR spectra.

Oxidation of activated carbons using 20 % nitric acid showed a temperature dependent distribution of surface functional groups, which allowed a specific surface chemistry to be generated. Conjugation of butylamine to the surface of activated carbon was shown to be effective using both methods. These methods could form the basis for the attachment of larger bioligands to the surface of oxidised or non-oxidised activated carbons for future applications of enhanced bioaffinity in extracorporeal systems.

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Declaration

I declare that the research contained in this thesis, unless otherwise formally indicated within the text, is the original work of the author. The thesis has not been previously submitted to this or any other university for a degree, and does not incorporate any material already submitted for a degree.

Signed

Dated 10/10/09
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>EDC</td>
<td>1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive Spectroscopy by X-ray</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>GBS</td>
<td>Guillain Barre Syndrome</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>LDL</td>
<td>Low Density Lipoprotein</td>
</tr>
<tr>
<td>HDL</td>
<td>High Density Lipoprotein</td>
</tr>
<tr>
<td>MS</td>
<td>Myasthenia Gravis</td>
</tr>
<tr>
<td>NHS</td>
<td>N-hydroxysuccinimide</td>
</tr>
<tr>
<td>PZC</td>
<td>Point of Zero Charge</td>
</tr>
<tr>
<td>RA</td>
<td>Rheumatoid Arthritis</td>
</tr>
<tr>
<td>SAXS</td>
<td>Small Angle X-ray Scattering</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>SLE</td>
<td>Systemic Lupus Erythematosus</td>
</tr>
</tbody>
</table>
Chapter 1  Introduction
1.0 Extracorporeal Therapies

Treatment of autoimmune disorders, sepsis and support for failing livers and kidneys using extracorporeal therapies are effective but costly as long term modes of treatment especially as the number of sufferer’s increases with both an ageing and expanding population. Therefore there is a need to:

(i) reduce costs to the healthcare provider and patient
(ii) produce a more effective or specific material/device for use in extracorporeal therapies

Treatment involves the purification of the blood or plasma of the patient using extracorporeal modalities, based on the removal of the toxic species either by physical or physico-chemical methods. They can in some cases provide a greater therapeutic benefit than drug based therapies, as they treat the cause of the disorder rather than the symptoms.

Figure 1.0 Typical circuit used in arterial-venous or venous-venous extracorporeal therapies
A typical model of an extracorporeal circuit is shown in Figure 1.0. The direction of the blood (or plasma) flow is indicated by the arrow. The blood removed via an artery or vein and is pumped round an extracorporeal circuit containing a filter, an arterial pressure manometer, and an oxygenator with filter then through a blood purification device after which the treated blood is returned to the patient via their venous system. Examples of the different extracorporeal modalities which are available are detailed in Table 1.0.

These modalities may be placed into the broad categories of dialysis, filtration, perfusion (adsorption) and apheresis. Each of the different modalities can be used with either blood or plasma.

<table>
<thead>
<tr>
<th>Therapy</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hemodialysis</strong></td>
<td>Diffusion of dissolved species through the pores of a membrane from the region of higher concentration to the region of low concentration in the dialysate outside the membrane.</td>
</tr>
<tr>
<td><strong>Hemofiltration</strong></td>
<td>Removal of excess water and toxic species from blood using filtration</td>
</tr>
<tr>
<td><strong>Hemoperfusion</strong></td>
<td>The passage of blood through columns of adsorptive material to remove toxic substances from the blood and returned to the patient</td>
</tr>
<tr>
<td><strong>Plasmaperfusion</strong></td>
<td>Whole blood is filtered to separate cells and plasma, then the plasma is perfused over a column to remove the toxic species and returned to patient or a plasma substitute is returned to the patient</td>
</tr>
<tr>
<td><strong>Apheresis</strong></td>
<td>Whole blood is removed and is continuously separated into its components which are collected and the remaining fluid returned to the patient.</td>
</tr>
</tbody>
</table>

Table 1.0  Extracorporeal modalities (Stegmayr (2005))

1.1  Autoimmune Disorders

There are approximately 80 autoimmune disorders which affect the body; they are caused by environmental or hereditary factors, they can affect all the tissues in the body and result in the body’s immune system not recognizing its own cells, tissues or organs as its own
and begins to attack them, resulting in inflammation and tissue damage. The most prevalent types of autoimmune disorders are shown in Table 1.1.

### 1.1.1 Current Treatment Methods

The current methods of treatment for autoimmune disorders include the administration of drugs e.g. corticosteroids and immunosuppressants (Fireman, Dimartini, Armstrong and Cozza, 2004), intravenously administered immunoglobulins (IVIG’s) (Stangel, 2008) or extracorporeal therapies (Stegmayr, 2005).

<table>
<thead>
<tr>
<th>Disorder Description</th>
<th>Disorder</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rheumatoid Arthritis (RA),</td>
<td>Inflammation and swelling of tissues surrounding joints</td>
<td></td>
</tr>
<tr>
<td>Guillain Barre Syndrome (GBS)</td>
<td>Progressive destruction of the myelin sheathes between nerve cells, triggered by an immune response to a viral infection</td>
<td></td>
</tr>
<tr>
<td>Myasthenia Gravis (MG)</td>
<td>Muscle weakness caused by a reduction in receptor sites on the cell membrane of muscle cells</td>
<td></td>
</tr>
<tr>
<td>Multiple Sclerosis (MS)</td>
<td>Progressive destruction of the myelin sheath surrounding nerves</td>
<td></td>
</tr>
<tr>
<td>Systemic Lupus Erythematosus (SLE)</td>
<td>Breakdown in the antigen production leading to production of antibodies that destroy healthy tissue</td>
<td></td>
</tr>
<tr>
<td>Cardiomyopathy (CM)</td>
<td>Progressive irreversible degeneration of the muscle tissue of the heart</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1 More prevalent autoimmune disorders

### 1.1.1.1 Drug Therapy

Administration of immunosuppressants is usually a long term treatment and they suppress not only the autoimmune reaction of the body, but also the body’s ability to defend itself
against infection, thereby leading to an increased risk of infection and to some forms of cancer (Karagas, Cushing Jr, Greenberg, Mott, Spencer and Nierenberg, 2001). The use of drugs such as corticosteroids to relieve the patient of inflammation and to suppress the immune system, are ideally administered only over the short term, as long term use may result in a number of side effects.

1.1.1.2 Intravenously Administered Immunoglobulins

Non-drug treatments such as IVIG’s have been used to treat many neurological autoimmune disorders such as Guillain Barre Syndrome (GBS), MG and immunological disorders such as SLE and many others (Stangel, 2008). The immunoglobulins used are prepared from the serum pooled from up to 15,000 donors, and can either be administered at low doses of 0.2 to 0.4 mg/kg (three times per week) or at high doses of up to 2 g/kg/month.

1.2 Adverse Effects of Treatment

Each of the aforementioned types of treatment may cause a number of adverse effects to the patient during and post treatment as outlined below.

One of the major problems associated with the use of extracorporeal therapies is the non-selective removal of plasma components, whereby species which are essential or non-inflammatory are removed with the pro-inflammatory or toxic agents.

To improve the selectivity of such processes, devices which contain a ligand that is specific for the removal of the circulating immune species, are now often being used in the treatment of autoimmune disorders. These devices are commonly referred to as immunosorbents.
### Table 1.2 Adverse effects of autoimmune disorder treatments
*(Choy, Hoogendijk, Lecky, Winer, 2005 and Dalakas, 2004)*

<table>
<thead>
<tr>
<th>Drug Based Therapies</th>
<th>Non-drug Based Therapies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Increased risk of infection</td>
<td>IVIG’s</td>
</tr>
<tr>
<td>Glucose intolerance</td>
<td><em>Mild</em> – Backache, chills, headaches, muscular pain and nausea</td>
</tr>
<tr>
<td>Hyperlipidemia</td>
<td><em>Severe</em> – Anaphylaxis, Hepatitis C, prions, reversible renal impairment, acute renal failure, thrombosis, acute haemolyis, neutropia, acute asceptic meningitis, eczema</td>
</tr>
<tr>
<td>Osteoporosis</td>
<td></td>
</tr>
<tr>
<td>Depression</td>
<td></td>
</tr>
<tr>
<td>Psychosis</td>
<td></td>
</tr>
<tr>
<td>Increased drug-drug interactions</td>
<td>Blood Purification</td>
</tr>
<tr>
<td></td>
<td>Chills, head ache</td>
</tr>
<tr>
<td></td>
<td>Hypotension</td>
</tr>
<tr>
<td></td>
<td>Drop in platelet levels</td>
</tr>
</tbody>
</table>

#### 1.3 Immunosorbents

Immunosorbents are materials composed of a matrix onto which is conjugated a biologically active moiety (e.g. antigen) which is specific for the removal of a species present in the blood or plasma (e.g. antibody).

The immunosorbent column (See Figure 1.1) is composed of a solid support matrix (A) and a biologically active group (B) (e.g. antigen). This biologically active group is capable of binding to specific molecules (C) (e.g. antibodies) from blood or plasma.

The process of immunoadsorption involves the removal of arterial whole blood from the patient, which is then separated into blood and plasma using a filter. The plasma is then passed over an immunosorbent material, usually packed in a column and the inflammatory species contained in the plasma are removed and the filtered plasma re-combined with the blood before being returned to the patient via the venous system.
1.3.1 Design of an Immunosorbent

The design of an immunosorbent system can be broken down into four steps:-

(i) Selection of suitable matrix
(ii) Activation or derivatisation of matrix
(iii) Attachment of spacer group to matrix
(iv) Attachment of ligand to spacer group.

Typical matrices which have been used are cellulose, dextran sulfate, poly (vinyl alcohol) (Organic) and silica (Inorganic), see Table 1.3.

Many of the columns that currently exist are not ideal for use as immunosorbents but have continued to be used. Ideally an immunosorbent should posses a range of predetermined characteristics, which dictate the materials' suitability for use as an immunosorbent.
## 1.3.1.1 Matrix Properties

The optimal matrix for an immunosorbent should be porous, to allow greater interaction between the matrix and the biological solution, thereby increasing removal of relevant species. The material should also possess good flow properties to allow the biological solution to pass through column without a significant increase in the pressure head. To allow greater interaction with solution the matrix should also be hydrophilic and mechanically strong to withstand pressure build up in column.

In terms of chemical properties, a matrix should be chemically stable to withstand acidic or basic treatment to add or de-protect a biologically active moiety on the surface and it should not participate in any additional reactions with the bioligand.

However, the most important factors are that the matrix should be relatively cheap, as it will only be used for one treatment session, before being disposed of and most importantly be biocompatible and non-toxic. As the “cleaned” plasma or blood will be returned to the patient (see Figure 1.0), there can be no leaching from or degradation of the matrix. There should also be no leakage of the bioligand attached to the matrix. The types of materials on which the matrices have been based are carbohydrate polymers, synthetic polymers, mixed gels and inorganic matrices. Examples of the matrix materials used include agarose, dextran, cellulose, trisacryl or polyacrylamide.
<table>
<thead>
<tr>
<th>Matrix Material</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Agarose</strong></td>
<td>▪ Readily available</td>
<td>▪ Variable physicochemical properties</td>
</tr>
<tr>
<td></td>
<td>▪ Good flow characteristics</td>
<td>▪ Ion exchange interactions</td>
</tr>
<tr>
<td></td>
<td>▪ Hydrophilic</td>
<td>▪ Lack of thermal stability</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ Swelling or shrinkage depending on ionic strength of medium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ Difficulty in freezing/drying</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ Soluble in presence of chaotropic salts</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ Gel structure irreversibly changed in organic solvents</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ Activates complement system (Getland et al. 1990)</td>
</tr>
<tr>
<td><strong>Dextran Highly Crosslinked</strong></td>
<td>▪ More hydrophilic than agarose</td>
<td>▪ Prolonged exposure to oxidising groups will increase carboxyl groups</td>
</tr>
<tr>
<td></td>
<td>▪ Very stable chemically</td>
<td>▪ Less porous than dextran with low degree of crosslinking</td>
</tr>
<tr>
<td></td>
<td>▪ May be autoclaved</td>
<td></td>
</tr>
<tr>
<td></td>
<td>▪ Higher mechanical strength than Low</td>
<td></td>
</tr>
<tr>
<td><strong>Dextran Low amount of Crosslinking</strong></td>
<td>▪ More hydrophilic than agarose</td>
<td>▪ Prolonged exposure to oxidising groups will increase carboxyl groups</td>
</tr>
<tr>
<td></td>
<td>▪ Very stable chemically</td>
<td>▪ Low mechanical strength</td>
</tr>
<tr>
<td></td>
<td>▪ May be autoclaved</td>
<td></td>
</tr>
<tr>
<td><strong>Polyacrylamide (Villems and Toomik, 1993)</strong></td>
<td>▪ Stable over wide pH range 1-10</td>
<td>▪ Have to use silanised glassware</td>
</tr>
<tr>
<td></td>
<td>▪ Few charged groups</td>
<td>▪ Lack of mechanical stability</td>
</tr>
<tr>
<td></td>
<td>▪ Biologically inert</td>
<td>▪ Derivatised matrix can only adsorb small proteins</td>
</tr>
<tr>
<td></td>
<td>▪ Hydrophilic</td>
<td></td>
</tr>
<tr>
<td></td>
<td>▪ Easily derivatised</td>
<td></td>
</tr>
<tr>
<td><strong>Beaded Cellulose</strong></td>
<td>▪ More reactive than some synthetic polymers</td>
<td>▪ Lack of porosity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>▪ Non-uniform pore distribution</td>
</tr>
<tr>
<td>Crosslinked Beaded Cellulose</td>
<td>Improved porosity over cellulose</td>
<td>Lack of porosity</td>
</tr>
<tr>
<td>-----------------------------</td>
<td>---------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td></td>
<td>Can alter porous by solvent replacement</td>
<td>Non-uniform pore distribution</td>
</tr>
<tr>
<td></td>
<td>Good mechanical properties</td>
<td>Not good for large species</td>
</tr>
<tr>
<td></td>
<td>Hydrophilic</td>
<td>Easily clogged by particulate matter</td>
</tr>
</tbody>
</table>

| Trisacryl (Boschetti E, in Dean, Johnson and Middle, 1985) | Very hydrophilic | Unstable at high pH due to slow hydrolysis of amide linkage |
|                                                            | Resistant to moderate pressure (up to 3 bar) | |
|                                                            | Non-biodegradable | |
|                                                            | Stable at low temperature (-20°C) | |
|                                                            | Stable at high temperature (121°C) | |
|                                                            | Stable at low pH | |
|                                                            | Macroporous | |

<table>
<thead>
<tr>
<th>Polyacrylamide-Agarose</th>
<th>Two types of groups for immobilisation hydroxyl and amide</th>
<th>See disadvantages from both polyacrylamide and agarose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rigid</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Easy to activate with glutaraldehyde</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Better resolution due to narrow size distribution</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Hydroxyalkyl Methacrylamide (Dean, Johnson)</th>
<th>Can alter properties of matrix depending on reaction ratios</th>
<th>Ion exchange interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Hydroxyl groups posses the same disadvantages as agarose gels</td>
<td></td>
</tr>
</tbody>
</table>
### Polymeric materials used in extracorporeal therapies

*Adapted from Cutler, 1999, Dean, Johnson and Middle, 1985, Scouten, 1981, Lowe and Dean 1974 and Cuatrecasas 1971*

| and Middle, 1985) | - Biologically inert  
| - Can withstand high temperature (150°C)  
| - Can withstand high pressure  
| - Can be used with organic solvents  
| - Chemically more stable than polyacrylamide  
| - Hydrophilic  |

### 1.3.1.2 Immobilisation of Bioligands

There are a number of methods for the conjugation of bioligands to a surface which have been reviewed (Nistevtich and Firer 2001, Turkova 1999, Lowe and Dean 1974). These include physical adsorption or covalent attachment. The more appropriate of these methods is covalent attachment, which will provide greater stability for binding the bioligand to the surface.

Covalent attachment may be achieved by the use of soluble activators (e.g. carbodiimide and succinimide), photoactive agents (e.g. benzophenones or diazirines), or solid phase bound activators which allow covalent binding to the amine, hydroxyl or thiol groups of the bioligand.

The functional groups on the surface of the matrix will dictate which strategies may be employed. The methods of activation are shown in Table 1.4.
### Target Group Method of Activation

<table>
<thead>
<tr>
<th>Target Group</th>
<th>Method of Activation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxylic</td>
<td>Carbodiimides</td>
</tr>
<tr>
<td>Carboxylic/Phenolic</td>
<td>N,N'-Carbonyldiimadazole</td>
</tr>
<tr>
<td>Phenolic</td>
<td>2,4,6-Trichloro-1,3,5-triazide, Epichlorohydrin</td>
</tr>
<tr>
<td>Amine</td>
<td>Anyhydride, Glutaraldehyde, Hydrazine, Epoxide</td>
</tr>
<tr>
<td>Vicinal Diol</td>
<td>Cyanogen Bromide</td>
</tr>
<tr>
<td>Cis Diol</td>
<td>Sodium Periodate</td>
</tr>
<tr>
<td>Hydroxyl</td>
<td>Sulfonyl Halide, Epoxide, Divinylsulfone</td>
</tr>
</tbody>
</table>

#### Table 1.4 Immobilisation methods

#### 1.3.1.3 Spacer Groups

Spacer groups are usually required to attach the bioligand to the matrix surface to allow the bioligand to interact with the species in blood/plasma to be removed without the disadvantage of steric hindrance of the matrix. This is crucial when either small, low affinity ligands or high molecular weight proteins are used or if interactions involve a multitude of binding sites (Lowe and Dean, 1974). However, care is required in selecting the spacer group to be used as if the group is too short then the binding site of the species in solution may not be readily accessible, by contrast if the spacer group is very long, the binding is usually available, but there could be a risk of the spacer group folding back on itself therefore hiding the bioligand. There may also be a strong possibility that if the spacer group is too long then there could be non-specific adsorption of the species for removal to the spacer arm via hydrophobic interactions.

Therefore, the use of a spacer group to attach a bioligand to the matrix requires careful consideration with regards to not only the type of spacer group and length employed, but also whether a spacer group could be incorporated into the bioligand prior to conjugation.

Compounds used are of the form NH$_2$(CH$_2$)$_n$R, with R a carboxyl or amino group. The value of $n$ is commonly between 2 and 12. One disadvantage of using these types of spacer groups is that if used in aqueous conditions they can fold back on themselves due to interaction between the hydrophobic sites and therefore reduce the effective length of the
spacer (Lowe, Harvey, Craven and Dean, 1973). This problem may be partially alleviated by the use of hydrophilic spacers. These could be peptide sequences attached to the matrix.

1.3.1.4 **Ligand Properties**

The bioligand to be attached to the matrix or spacer group should bind strongly to the matrix by covalent bonding, under conditions which will not adversely affect the separation properties of the matrix. In addition, the ligand should be stable and have a high degree of specificity for the target to be removed from blood or plasma (Kadar, Parusel, and Spaeth, 1998).

Bioligands that are commonly used may be either of natural or synthetic origin. Several issues have to be addressed upon deciding which ligand to use:-

(i) Specificity of the ligand
(ii) Optimal immobilisation site
(iii) Instability of bioligand
(iv) Inadequate binding of ligand to matrix
(v) Cost
(vi) Availability

High performance liquid chromatography (HPLC) has previously been used to determine the dissociation constant ($K_d$) and shown that ligands with $K_d$ as low as $10^{-2}$ to $5 \times 10^{-3}$ may be used (Zopf and Ohlson, 1990).

Natural ligands isolated from genetically modified bacteria that produce proteins which are capable of binding to immunoglobulins have previously been used (Gjorstrup and May, 1990). One such ligand is Protein A which is isolated from the outer membrane of *Staphylococcus aureus*, is specific for IgG.

Synthetic ligands are usually peptide derivatives or small molecular analogues of the specific binding sites of proteins. The peptide derivatives are produced by solid phase synthesis techniques. However, they are limited to about 100 amino acid residues.
1.4 Currently Used Immunosorbents

There are currently a few manufacturers of clinically approved products for use in plasma perfusion (see Tables 1.5 and 1.6).

<table>
<thead>
<tr>
<th>Device Name (Manufacturer)</th>
<th>Matrix Material</th>
<th>Ligand</th>
<th>Removal Method</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Immusorba PH</em> (Asahi Medical)</td>
<td>PVA gel</td>
<td>Phenylalanine</td>
<td>Hydrophobic + Electrostatic</td>
<td>MG, GBS</td>
</tr>
<tr>
<td><em>Immusorba TR</em> (Asahi Medical)</td>
<td>PVA gel</td>
<td>Tryptophan</td>
<td>Hydrophobic + Electrostatic</td>
<td>MG, GBS</td>
</tr>
<tr>
<td><em>Selesorb</em> (Kareda)</td>
<td>Cellulose Beads</td>
<td>Dextran Sulfate</td>
<td>Electrostatic</td>
<td>SLE</td>
</tr>
<tr>
<td><em>Prosorba</em> (Cypress Bioscience)</td>
<td>Silica beads</td>
<td>Protein A</td>
<td>Affinity</td>
<td>RA</td>
</tr>
<tr>
<td><em>Immunosorba</em> (Exocrim)</td>
<td>Agarose beads</td>
<td>Protein A</td>
<td>Affinity</td>
<td>MG</td>
</tr>
<tr>
<td><em>Medisorba MG</em> (Kuraray)</td>
<td>Cellulose beads</td>
<td>AChR peptide</td>
<td>Ag-Ab</td>
<td>MG</td>
</tr>
<tr>
<td><em>Ig-Therasorb</em> (Therasorb Medical Systems)</td>
<td>Cellulose beads</td>
<td>Sheep pAb</td>
<td>Ag-Ab</td>
<td>MG, GBS</td>
</tr>
</tbody>
</table>

Table 1.5 Currently used immunosorbents in plasmaperfusion (Nakaji, 2001)

(Key: GBS: Guillain Barre Syndrome, MG: Myasthenia Gravis, MS: Multiple Sclerosis, RA: Rheumatoid Arthritis, SLE: Systemic Lupus Erythematosus, Ag-Ab: Antigen-Antibody Binding)
### A. Hemoperfusion

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Adsorptive</th>
<th>Disease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacrylic acid</td>
<td>LDL</td>
<td>Hyperlipidemia</td>
</tr>
<tr>
<td>Hexadecyl</td>
<td>$\beta_2$ microglobulin</td>
<td>Amyloidosis</td>
</tr>
<tr>
<td>Petroleum derived activated carbon</td>
<td>Drug, bilirubin, bile acid, creatine, amino acid</td>
<td>Toxipathy, hepatic coma, Acute renal failure</td>
</tr>
<tr>
<td>Polymyxin B</td>
<td>Endotoxin</td>
<td>Sepsis, endotoxemia</td>
</tr>
</tbody>
</table>

### B. Plasma Perfusion

<table>
<thead>
<tr>
<th>Ligand/Matrix</th>
<th>Adsorptive</th>
<th>Disease</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blood type Antigen</td>
<td>Anti –A antibody</td>
<td>ABO-incompatible</td>
</tr>
<tr>
<td></td>
<td>Anti –B antibody</td>
<td>transplantation</td>
</tr>
<tr>
<td>Torpedo $\alpha$ 183-200</td>
<td>$\alpha$ AChR Ab</td>
<td>MG</td>
</tr>
<tr>
<td>Anti-LDL ab</td>
<td>LDL</td>
<td>Hyperlipidemia</td>
</tr>
<tr>
<td>Anti-Immunoglobulin ab</td>
<td>Immunoglobulins</td>
<td>Lack of coagulation factor</td>
</tr>
<tr>
<td>Protein A</td>
<td>IgG</td>
<td>ITP, RA</td>
</tr>
<tr>
<td>Dextran sulphate</td>
<td>LDL, anticardiolipin antibody immune complex</td>
<td>Hyperlipidemia, SLE</td>
</tr>
<tr>
<td></td>
<td>Anti-DNA antibody</td>
<td>APS</td>
</tr>
<tr>
<td>Styrene-di-vinyl-benzene polymer</td>
<td>Bilirubin, bile acid</td>
<td>FH</td>
</tr>
<tr>
<td>Tryptophan</td>
<td>$\alpha$ AChR Ab immune complex</td>
<td>MG, GBS, MS</td>
</tr>
<tr>
<td>Phenylalanine</td>
<td>Rheumatoid factor immune complex</td>
<td>RA with vasculitis</td>
</tr>
<tr>
<td></td>
<td>Anti –DNA Antibody</td>
<td>SLE, GBS, MS</td>
</tr>
</tbody>
</table>

**Table 1.6** Perfusion columns for A. Hemoperfusion and B. Plasma perfusion

(Adapted from Yang, Kenpe, Tsuda, and Hashimoto, 2002)

**APS:** Autoimmune Polyglandular Syndrome, **FH:** Familial Hypercholesteremia, **GBS:** Guillain Barre Syndrome, **ITP:** Idiopathic Thrombocytopenic Purpura, **LDL:** Low density lipoproteins, **MG:** Myasthenia Gravis, **MS:** Multiple Sclerosis, **RA:** Rheumatoid Arthritis, **SLE:** Systemic Lupus Erythematosus
<table>
<thead>
<tr>
<th>Matrix (Manufacturer)</th>
<th>Ligand</th>
<th>Treatment</th>
<th>Species Removed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Collodion coated</td>
<td>None</td>
<td>Neoplastic Diseases</td>
<td>Blocking Factor</td>
</tr>
<tr>
<td>activated carbon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Terman, 1980)</td>
<td>ssDNA</td>
<td>SLE</td>
<td>Anti-DNA</td>
</tr>
<tr>
<td>Collodion coated</td>
<td>None</td>
<td>Atherosclerosis</td>
<td>LDL</td>
</tr>
<tr>
<td>activated carbon</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Terman et al., 1977)</td>
<td>ssDNA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyacrylate coated</td>
<td>None</td>
<td></td>
<td></td>
</tr>
<tr>
<td>polyacrylamide(DALI)</td>
<td>ssDNA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>Phenylalanine</td>
<td>Autoimmune Diseases</td>
<td>Rheumatoid Factor</td>
</tr>
<tr>
<td>(Immunosorba PH-350)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyvinyl alcohol</td>
<td>Tryptophan</td>
<td>Rheumatoid Arthritis</td>
<td>IgE, CIC, anti-DNA</td>
</tr>
<tr>
<td>(Immunosorba TR-350)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Porous Cellulose</td>
<td>Dextran</td>
<td>Familial</td>
<td>LDL</td>
</tr>
<tr>
<td>(Liposorber LA-40, LA-15)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica (Proisorba)</td>
<td>Protein A</td>
<td>Autoimmune diseases</td>
<td>IgG, CIC</td>
</tr>
<tr>
<td>Sepharose CL-4B</td>
<td>Anti –IgG</td>
<td>Neoplastic diseases</td>
<td>IgG</td>
</tr>
<tr>
<td>(Ig-Therasorb)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sepharose CL-4B</td>
<td>Anti-LDL</td>
<td>Atherosclerosis</td>
<td>LDL</td>
</tr>
<tr>
<td>(LDL-Therasorb)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(LDL-Lipopak-P)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sepharose CL-4B</td>
<td>Protein A</td>
<td>Autoimmune diseases/ hyperimmune response</td>
<td>IgG, CIC</td>
</tr>
<tr>
<td>(Immunosorba)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1.7 Immunosorbents in extracorporeal therapy
(Adapted from Mikhalovsky, 1999)

CIC: Circulating immune complexes, LDL: Low Density Lipoproteins
1.5 Problems Associated With Immunosorbents

There are a number of problems associated with the use of immunosorbents which have been reported including antibody leakage from matrix (Bessos et al., 1991, Goldberg et al., 1991, Sato et al., 1987, Beer et al., 1995).

These include the leakage of the bioligand from the matrix, leaching of impurities from the matrix material (Yatzidis, 1964) into the patients’ blood system during treatment, the temporary reduction in the level of antibodies which rise back to pre-treatment levels within 7-14 days (Rebound Effect), whereby the patient requires subsequent treatments every 10-14 days. The repeat treatments also raise the question of problems associated with the use of immunosorbents in the short term (more than 2 treatments) or long term treatment (Nose, 2002).

Therefore a more cost effective material on to which to base an immunosorbent is sought and activated carbon could be the material of choice for the reasons described below.

1.6 Activated Carbon

Activated carbon is the general term given to any naturally occurring or synthetically derived porous carbon material (a char), which has been subjected to reaction with gases (sometimes with the addition of chemicals e.g. ZnCl₂) before, during or after carbonisation in order to increase its adsorptive properties (Fitzer, Köchling, Boehm and Marsh, 1995).

These materials typically contain upwards of 90 % by weight of carbon, with the remaining 10 % composed of heteroatoms (hydrogen, oxygen, nitrogen and/or sulphur) or inorganic ash, the proportions of each depending on the raw materials used in the manufacturing process.

1.6.1 Production of Activated Carbon

The production of activated carbon is carried out over a number of steps but the two main stages are the carbonisation (or pyrolysis) step and the activation step.
The process of carbonisation (or pyrolysis) involves heating the raw material to over a 1000 °C to remove non-carbon groups from the surface thus creating defects in the surface, once the carbon material has been carbonised, activation may take place either by chemical or physical treatment to (i) develop the porous structure of the carbon by degradation and (ii) increase the number of surface functional groups.

Activation of the carbon leads to the development of a porous network which may by divided into three size categories: - macropores, mesopores and micropores (Gregg and Sing, 1982). Macropores are found at the surface and may be defined as pores with width of more than 50 nm, mesopores have a pore width of between 2 and 50 nm and finally, micropores are the narrowest of the three pore types, and may be defined as pores with width of approximately 2 nm or less. The borders between the pore type limits are not fixed and most activated carbons will display a pore size distribution with approximately 90 - 95 % or more of the total surface area made up of micropores (Biniak, Swiatkowski and Pakula, 2001).

Macropores account for a very small proportion of the active surface area (approximately 0.5 m²/g) and are therefore of less interest than the mesopores and micropores when adsorption is involved.

1.6.1.1 Chemical Activation

Chemical activation involves the use of reagents such as acids (e.g. H₂SO₄ or H₃PO₄), bases (e.g. KOH or NaOH) or metal halides (ZnCl₂), which are mixed with the ground raw material and heated to 600-900 °C. The final step in chemical activation process is the removal of the degrading agent by washing with HCl and water (and saline for biomedical applications).

1.6.1.2 Physical Activation

The physical activation of activated carbon relies on carbonisation of the raw material at 400-900 °C in an inert atmosphere e.g. Ar, N₂ or CO₂, followed by the introduction of a gas usually CO₂, steam, or a mixture of steam and CO₂ at 800-1000 °C. These gases react with
the active and edge sites of the carbon sheet structure becoming incorporated within the structure, forming oxygen containing functional groups.

Each type of activated carbon produced has different chemical and physical properties which are dependent on the raw materials, method of activation and reaction conditions used to activate them.

1.6.2 Surface Chemistry of Activated Carbon

The surface of activated carbons is thought to contain a variety of surface groups either of an acidic, basic or neutral nature, as first postulated by Bartell and Miller (1922). However, the exact nature of the surface groups is still the subject of much debate (Zawadzki, 1989). The reason for such debate is the difference in the reactivity of the activated carbon surface groups in comparison to similar analogues in organic chemistry (Puri, 1970).

Of the functional groups which are found on the activated carbon surface, those containing oxygen are the most important, as oxygen is the primary heteroatom adsorbed from the air and incorporated upon activation (Jankowska, Swiatkowski, and Choma, 1991).

Many of the functional groups found in organic chemistry have been proposed to exist on the surface of activated carbons such as carboxylic, lactonic and phenolic type groups and a host of others (Figure 1.2). Basic functional groups on the carbon surface have been known longer than those of an acidic nature (Bartell and Miller, 1922), although the analysis of these groups has received less attention than the acidic functional groups.

The proposed existence of basic surface groups such as pyrone, chromene, quinone and hydroquinone and a multitude of others have been used to explain the adsorption of acids and some of the electrochemical results seen, when using activated carbon. The properties of these basic groups may be similar to those of the organic analogues, however, given the availability of electrons from the basal planes of the carbon (Leon y Leon, Solar, Calemma and Radovic, 1992), determination of which groups are responsible for each effect is made all the more difficult, due to electron donating, withdrawing groups and the effects of resonance stabilisation.
The use of molecular modelling and *ab initio* calculations as employed by Suarez, Menendez, Fuente and Montes-Moran (1999 and 2000) and Fuente, Menédez, Suárez and Montes-Morán (2003) have provided some information on pK values of pyrone type structures, where the oxygen groups are spread over two or more aromatic rings.

The introduction of other heteroatoms, such as nitrogen or sulphur, in the raw material or during the activation step, will result in incorporation of these species in the surface functional groups (Cuesta, Martinez-Alonso, Tascon and Bradley, 1997).

![Diagram of proposed functional groups containing oxygen on activated carbon surface](image)

**Figure 1.2 Proposed functional groups containing oxygen on activated carbon surface**  
*(Adapted from Riley, 1939, Puri, 1970, Mattson and Mark, 1971)*

(i) Phenolic (ii) Lactone (iii) Carboxylic (iv) Peroxy (v) Ether (vi) Carboxylic Anhydride (5-membered ring) (vii) Carboxylic Anhydride (6-membered ring) (viii) Carbonyl (ix) Lactol (x) Cyclic Peroxide and (xi) Quinone

### 1.6.3 Uses of Activated Carbon

The main use of activated carbon is in the removal of impurities from solutions or gases by adsorption. This is made possible due to the high surface area (in excess of 1000 m²/g in some cases) as a result of the porous nature of the material (Jankowska, Swiatkowski and Choma, 1991).
1.6.4 Medical Uses of Activated Carbons

There are also indications of the potential use of activated carbon in a variety of clinical applications. The earliest reports of activated carbon use were in the adsorption of wound exudate to remove the unpleasant smell, as described by the followers of Hippocrates. An extension of this could possibly be the use of activated carbons in the treatment of diabetic foot ulcers.

More recently activated carbons have found use in medicine where they can be swallowed to adsorb harmful substances (enterosorbits) or in the purification of blood or plasma of patients who have suffered acute poisoning (hemo- or plasmaperfusion).

The experiments of Yatzidis et al. (1964) in the development of an artificial kidney saw patients suffering from chronic renal insufficiency received hemoperfusion using a charcoal column to remove uremic toxins from the blood passing through the column. Yatzidis et al. (1965) further explored the possibility of using a charcoal column in hemoperfusion treatment of patients suffering from barbiturate poisoning.

The use of charcoal for hemoperfusion has several advantages over other therapies such as peritoneal dialysis and hemodialysis. The treatment is relatively simple to perform, inexpensive and the benefits of the treatment are rapidly observed.

Other investigators have used the Yatzidis experimental set-up (Dunea and Kolff, 1965) to treat uremic patients with activated carbon prepared from coconuts with very low ash content. A problem when directly contacting charcoal or activated carbon with blood is the caking which occurs. The weight gain of a 200 g carbon column as reported by Dunea and Kolff was approximately 130 g, obviously this presents a problem with returning the blood to the patient, and blood wastage was found to be of the order of 100 to 150 cm$^3$ per 200 g charcoal column. Saline used to prime the second column is then used to wash the blood from the first column. The effect of treatment by charcoal perfusion caused a decrease in the serum calcium levels, blood sugar, serum uric acid and a 50 % reduction in platelet count, although this did increase to near post perfusion levels by the next day. No significant changes in blood urea, serum electrolytes or leukocyte count were observed although a decrease in the haemoglobin was observed. Hemolysis was not observed.
As was observed by Yatzidis et al. (1965) some side effects were observed, such as nausea, vomiting, hypertension, acidosis and hyperkalemia. These last two side effects were managed with treatment with NaHCO$_3$ and resins. Some of the suggestions which were made by Dunea and Kolff (1965) to improve the treatment were to increase the length of the perfusion time, the use of a more highly activated charcoal and to change the column/s more often.

The use of activated carbon for hemoperfusion has several advantages over other therapies such as peritoneal dialysis and hemodialysis. The treatment is relatively simple to perform, inexpensive and the benefits of the treatment are rapidly observed. The assembly and sterilisation of the column are easy and the column does not have to be primed with the patients’ blood prior to use. The most commonly occurring problems of activated carbons used for hemoperfusion are microparticulate release, which causes the formation of microemboli and bioincompatibility of the carbon with blood.

As a solution to this drawback Chang (1966) developed the idea of an artificial semi-permeable membrane around carbon particles to prevent release of carbon fines while allowing the entrapment of harmful biological species. The coating of the activated carbon has to be complete to prevent release of microparticles however this coating will reduce the adsorption capacity, decrease the rate of adsorption of the activated carbon and prevent the removal of large molecular weight toxins, as they will be unable to permeate the membrane.

An alternative to coating the whole particle is the attachment of groups to the surface (i.e. antigens) that will allow the specific adsorption of species (i.e. antibodies) from blood or plasma. This method has been employed in the development of immunosorbents for the treatment of autoimmune diseases.

In the 1960’s the pioneering work by Yatzidis (1964 and 1965) saw the emergence of activated carbon as a potential material for use in the removal of toxic species from the blood. Further studies by Dunea and Kolff (1965), Hagstam, Larsson and Thysell (1966), De Myttenaere, Maher and Schreiner (1967) examined the use of activated carbons for the treatment of uraemia and poisoning (phenobarbital and glutethimide, respectively).
These techniques have been further modified and improved to allow the removal of a range of biological species from the patients’ blood or plasma as reviewed by Mikhalovsky (1999).

1.6.4.1 Enteroadsorbent (Oral Adsorption)

The use of carbon as an enteroadsorbent, or oral adsorbent dates back to the early 18th century when famously it is reported that in 1813, during a public demonstration of the efficacy of charcoal, the French chemist Bertrand swallowed a mixture of arsenic trioxide and then charcoal. In 1831, a further demonstration of the effectiveness of charcoal was shown by the French pharmacist Touéry, when he swallowed ten times the lethal dose of strychnine along with some charcoal (Holt and Holz, 1963). Both men survived the consumption of the toxic compounds due to the adsorptive powers of the charcoal.

Further studies have since shown the effectiveness of activated carbon and charcoal for the removal of toxic species such as metal halides e.g. HgCl₂ and drugs such as opiates, strychnine from liquids. Since then activated carbons have been used to treat patients who have overdosed on drugs or alcohol or to treat severe cases of poisoning (Nikolaev, 1990). The mode of action of the activated carbon is to adsorb the toxic agent before it can enter the blood stream and then pass safely out of the body bound to the toxic agent.

1.6.4.2 Uncoated Activated Carbons

Problems associated with the use of uncoated activated carbons include biocompatibility, caking of blood reducing the adsorption capacity and efficiency of the carbon, and as with any physical adsorbent the non-specific adsorption of species from the plasma or blood.

1.6.4.3 Coated Activated Carbons

Compared to uncoated activated carbons, coated activated carbons should reduce the amount of non-specific adsorption, although not significantly and also improve the biocompatibility.
1.7 Biocompatibility of Activated Carbon

Several attempts have been made to improve the biocompatibility of activated carbon for use in *ex vivo* systems. The problems that arose from the methods employed by Alwall (1952) and Yatzidis *et al.* (1964 and 1965) were the presence of fine microparticles in blood samples and microparticles in the test subjects’ organs, which caused microemboli formation. This was due to the grade of activated carbon used. Other factors which have to be considered are the ash content of the carbon used and also the ion exchange properties as these will both affect the adsorption of electrolytes from blood or plasma. The use of non-coated columns results usually in acute thrombo-and leucocytopenia, also caking of the carbon which results in pressure gradients and therefore will reduce the efficiency of clearance. Andrade *et al.* (1975) suggested the following criteria for an ideal coating system:

i) Coating should be strong enough to prevent all fragmentation and generation of microparticulates.

ii) Coating should be permeable to the toxin which is to be removed.

iii) Coating should be biocompatible with blood and its components.

iv) Coating should allow good flow characteristics and low pressure drops across the column.

v) Coating should be easily sterilised.

Chang (1966) developed the idea of an artificial semi-permeable membrane around carbon particles to prevent release of carbon fines and the entrapment of biological species. A further development was that of Andrade *et al.* (1971), who developed HEMA coated carbon particles to address such issues.
<table>
<thead>
<tr>
<th>Year</th>
<th>Coating</th>
<th>Investigator/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>1964</td>
<td>Albumin, adsorbed</td>
<td>Herbert &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
<tr>
<td>1965</td>
<td>Dextran, adsorbed</td>
<td>Herbert &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
<tr>
<td></td>
<td>Haemoglobin, adsorbed</td>
<td>Lau &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
<tr>
<td>1966</td>
<td>Nylon</td>
<td>Chang</td>
</tr>
<tr>
<td></td>
<td>Cellulose Acetate</td>
<td>Yatzidis</td>
</tr>
<tr>
<td>1967</td>
<td>Heparin complexed cellulose nitrate</td>
<td>Chang</td>
</tr>
<tr>
<td>1968</td>
<td>Cellulose nitrate (collodion)</td>
<td>Chang</td>
</tr>
<tr>
<td></td>
<td>Cellulose acetate</td>
<td>Rosenbaum &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
<tr>
<td>1969</td>
<td>Albumin, adsorbed on cellulose nitrate</td>
<td>Chang</td>
</tr>
<tr>
<td>1971</td>
<td>Albumin, crosslinked</td>
<td>Andrade &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
<tr>
<td></td>
<td>PHEMA</td>
<td>Andrade &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
<tr>
<td>1972</td>
<td>Cellulose nitrate (collodion)</td>
<td>Rietema and Van Zutphen</td>
</tr>
<tr>
<td>1973</td>
<td>PHEMA</td>
<td>Willson &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
<tr>
<td></td>
<td>Cellulose triacetate, deacetylated</td>
<td>Denti &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
<tr>
<td>1974</td>
<td>Albumin, adsorbed</td>
<td>Coleman and Andrade</td>
</tr>
<tr>
<td></td>
<td>Albumin, crosslinked</td>
<td>Coleman and Andrade</td>
</tr>
<tr>
<td></td>
<td>Hydroxyethyl cellulose</td>
<td>Davis &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
<tr>
<td></td>
<td>Methacrylate co-polymer</td>
<td>Gilchrist &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
<tr>
<td></td>
<td>Acrylic polymer</td>
<td>Fennimore &lt;i&gt;et al.&lt;/i&gt;</td>
</tr>
</tbody>
</table>

Table 1.8  Coat of activated carbon for medical applications  
(Adapted from Andrade, Coleman, Kim and Lentz, 1975)
1.7.1 Semi-permeable Membranes

Although activated carbons or charcoals are very effective at removing metabolites and toxins by hemoperfusion, there remains the issue of depletion of platelet levels (Dunea and Kolff, 1965) and release of embolizing microparticulates (Hagstam et al., 1966).

To prevent these problems there are a number of options for the treatment or encapsulation of activated carbon (Chang, 1964). The use of semi-permeable membranes containing an aqueous or suspended particulate core was first proposed by Chang (1964) and Chang et al. (1966).

The use of semi permeable membranes for coating activated carbons was proposed by Chang et al. (1968). The membranes were formed from complexes of benzalkonium/heparin/collodion by a BHC polymer coating technique. These coatings afforded an increase in the time of blood clotting (Chang et al., 1967) with the BHC collodion and BHC-collodion coated nylon having clotting times in excess of 25 hours. These coatings were shown to be nonthrombogenic (Chang, 1972) during in vivo canine studies in extracorporeal shunt chambers, but only if there were no defects in the coating. The BHC membranes cause a reduction in both the platelet and leukocyte levels however, addition of heparin-benzalkonium to the same membrane produces a surface which has no significant effect on platelet or leukocyte levels during perfusion.

In 1969 Chang performed in vivo canine studies into the effect of microencapsulated activated carbons on platelet and creatinine levels. It was found that activated carbon reduced the level of the creatinine in the blood the carbon also caused a substantial decrease in the arterial platelet levels. This decrease in platelet levels was seen for the collodion treatment also. The heparin-complexed collodion and albumin-coated collodion, both showed a less efficient reduction in the creatinine levels, however these coatings did not significantly affect the platelet levels. In the experiments involving an uncoated activated carbon fines were found at the level of 20 particles/ cm$^3$ in the effluent blood, but no particulate matter was observed with any of the microencapsulated carbons.
To elevate the problem of microparticles the use of fine mesh filters could be employed, it has also been observed that a larger particle size has been shown to reduce the incidence of microparticulates release.

In 1975 Chang published a report on the comparison of drug clearance of albumin coated activated carbon (ACAC) microcapsules. ACAC’s have been used for the treatment of patients with chronic renal failure, acute intoxication and hepatic failure. For treatment of uraemia 2 hours hemoperfusion treatment with ACAC is as effective as 6 hours treatment with an EX01 haemodialyser (Chang, 1975).

Yatzidis (1966) coated activated carbon with cellulose acetate and claimed that although the adsorptive capacity of the carbon was reduced by the order up to 6 %, no data was given as to the biocompatibility of the coating with respect to contact with blood. Other investigators have tried to coat activated carbon with cellulose acetate using a different method than that employed by Yatzidis, however, although the coated activated carbon performed better than the non-coated the reduction in platelet level of 70 %, after 6 hours perfusion were observed (Rosenbaum et al., 1968).

The use of hydrophilic polymers such as polyhydroxyethyl methacrylate (pHEMA) was proposed as a method of encapsulating activated carbon by Andrade et al. (1971) to improve biocompatibility. They showed that in vitro batch adsorption studies charcoal rapidly adsorbs uric acid and creatinine from solution, however when coated with HEMA the effect is less pronounced. Pre-polymerised HEMA shows a creatinine adsorption rate that is about half that of the non-coated activated carbon. From the in vivo experiments it was observed that non-coated activated carbon caused a significant drop in the platelet level (3 x 10^5 to 8 x 10^4 platelets/mm^3) but that coating with HEMA, 50 % weight increase, caused the platelet level to drop from 3 x 10^5 to 2 x 10^5 platelets/mm^3. From the results for a selected HEMA coated carbon, Andrade et al. concluded that the levels of calcium, phosphate, cholesterol, total protein, albumin and bilirubin were not significantly changed in the in vivo experiment. They also stated that the correct level of HEMA coating will prevent caking of the carbon surface with blood.

Further work carried out by Andrade et al. (1972) compared the adsorption rates of seven different activated carbons for in vitro adsorption of creatinine. It was shown that the
physical properties of the carbon influenced the amount of creatinine adsorbed, with the carbons possessing the greater surface area adsorbing more creatinine. The comparison of a commercially coated pHEMA coated activated carbon with a control non-coated sample from the aforementioned experiment demonstrated the effect of coating the carbon decreases the rate of adsorption and adsorption capacity. From the SEM images of the uncoated and commercially coated pHEMA carbon surface it was clear that, coating with HEMA does not totally coat the surface and therefore can not be used as a method to prevent microparticulate release from the surface. However, from \textit{in vivo} results the pHEMA coated carbon showed a drop of up to 30 \% in platelet levels, in comparison with 50-70 \% for non-coated, up to 50 \% for albumin coated and 10-15 \% for a commercially coated pHEMA carbon was observed after 1 hour of perfusion. As previously found, Andrade \textit{et al.} observed that the non-coated carbon samples became quickly caked with platelets and fibrous material, which caused a reversal of the adsorptive capacity of the coated and non-coated samples from the \textit{in vitro} results. An example of some of the coatings for activated carbons that have been used in medical applications (Table 1.8).

An alternative to the coating of the whole particle is the attachment of functional groups to the surface which have a specific affinity for the species in the plasma to be removed.

\section*{1.8 Immobilisation of Bioligands}

Chemical modification of activated carbons would allow the exploitation of the existing sorbent properties, but also allow the degree of specificity to be controlled. In the late 1970’s, Cho and Bailey (1977, 1978 and 1979) attempted the attachment of different enzymes to the surface of activated carbons. Other bioligands that have been attached to activated carbon include thymic DNA (Nikolaev \textit{et al.}, 1992). Such an application could be the use of activated carbons in affinity chromatography or in applications which use similar techniques, such as immunoadsorption.
1.9 Immunoadsorption

Immunoadsorption has been proposed for use to treat a number of autoimmune diseases and diseases of unknown aetiology as previously shown in Tables 1.5 - 1.7, by reducing the number of circulating immune complexes or antibodies. The materials upon which the immunoadsorbents have been produced are predominately based on a variety of polymer matrices (Table 1.3).

To improve the removal of circulating species materials with greater adsorptive capacity or greater specificity are sought. By utilising the greater adsorptive properties of activated carbons for the removal of circulating species in the blood or plasma, activated carbons could be used as immunosorbents, however activated carbons have to be modified prior to use.

Although coating of activated carbons is shown to improve the haemocompatibility, there is a reduction in the adsorption capacity and the issue of non-specific adsorption remains a problem. Coated activated carbons do provide an advantage over uncoated carbons, however further improvements are required and therefore a better option would be to use medical grade activated carbons and conjugate bioligands which are specific for the species which are to be removed from the blood or plasma. Using this method should provide the benefits of haemocompatibility, minimise any reduction in the adsorptive properties of the activated carbon and provide a more specific method of removal of species from the blood or plasma.
1.10 Aims

The aims of this work were to develop a carbon based immunosorbent for use in extracorporeal systems based on NOVACARB activated carbons produced by MAST Carbon Ltd. These activated carbons are produced from a phenolic resin precursor (Novolak) using the method outlined by Tennison (1998).

The main aims and objectives in this development process were:-

(i) Characterise the chemical and physical properties of two distinct NOVACARB activated carbons supplied by MAST Carbon Ltd.
(ii) Oxidise the two NOVACARBs using nitric acid to increase the number of surface functional groups to produce a range of activated carbons with different surface chemistry
(iii) Characterise the chemical and physical properties of oxidised activated carbons
(iv) Functionalise the oxidised and non-oxidised NOVACARB activated carbons with a test ligand (butylamine) using two methods:-
   a) Conjugation using a zero length crosslinker (e.g. carbodiimide)
   b) Conversion of carboxylic groups to acyl chloride groups using thionyl chloride
(v) Characterise the chemical and physical properties of the functionalised NOVACARBs
Chapter 2  Characterisation of NOVACARB
Activated Carbons
2.0 Characterisation of NOVACARB Activated Carbons

2.0.1 Introduction

The use of activated carbons produced from naturally occurring raw material is inherent with problems, none more so than the poor reproducibility of the chemical and physical properties of the activated carbons. This occurs due to the natural variation in the composition of the raw materials, the inorganic content such as silicates, aluminosilicates, also metals including calcium, magnesium, potassium and sodium and in some instances zinc, lead, tin, cobalt, boron and vanadium remains after pyrolysis. This inorganic content can account for up to 20% of the raw material (Rodriguez-Reinoso, 1997). Therefore the use of activated carbons derived from materials with a more controllable organic and inorganic content is sought. The use of polymers as the raw materials from which to produce activated carbons, results in activated carbons which are more homogeneous on the macroscale and therefore display reproducible chemical and physical properties.

The activated carbons used in this work were NOVACARB activated carbons (S-50-9/100/25-00 and S-50-9/125-00) supplied by MAST Carbon Limited.

The properties of the NOVACARB activated carbons produced are determined by the proportions of polymer (Novolak) and pore forming agent (ethylene glycol) which are added in the preparation of the activated carbon (Figure 2.0).

![Chemical structures of (a) Novolak and (b) Ethylene Glycol](image)

Figure 2.0 Chemical structures of (a) Novolak and (b) Ethylene Glycol

The chemical and physical properties of NOVACARB activated carbons are different from those displayed by activated carbons which are traditionally produced from non-polymeric starting materials e.g. coconut shells, etc., as they reportedly display a homogenous surface at the nanoscale, compared to traditionally produced activated carbons which display a heterogeneous surface chemistry.
Many different models of the porous nature of activated carbons have been proposed - from the falling card model (Dahn, Xing and Gao, 1997), the porous microtexture model of Oberlin (1989) and Stoeckli (1990), to those of glassy carbons (Peterson, Yarovsky, Snook, McCulloch and Opletal, 2003) and carbons derived from cellulosic precursors (Byrne and Marsh, 1995), to models based on virtual solids (Biggs and Agarwal, 1992 and 1994 and Archarya, Strano, Matthews, Billinge, Petkov, Subramoney and Foley, 1999), to the fractal network models of micropores (Pfeifer, Ehrburger-Dolle, Rieker, Gonzalez, Hoffman, Molina-Sabio, Rodriguez-Reinoso, Schmidt and Voss, 2002), to models based on slit like pores (Gun’ko and Mikhalovsky, 2004), and star-like pores (Py, Guillot and Cagnon, 2004).

![Figure 2.1 Representation of porous structure of activated carbons](Stoeckli, 1990)

The porous nature of NOVACARB activated carbons is different from that displayed for existing activated carbons, unlike the conventional proposed “crumpled ball of paper” structures of activated carbons as proposed by Stoeckli (1990), shown in Figure 2.1, NOVACARBs are proposed to display a “bunch of grapes” type structure as observed from scanning tunnelling microscopy (STM) (Tennison, 1998) shown diagrammatically in Figure 2.2.

The diameter of beads formed may vary from 1 to 500 µm, depending on the manufacturing conditions used. The porosity of the carbon is proposed to be formed as a
result of the spaces between the spheres (typically 4 nm) which agglomerate to form the beads.

**Figure 2.2 Porous structure of NOVACARB activated carbon**

*(Adapted from Tennison, 1998)*

The study of the porous nature of activated carbons is very important as these pores will play a significant role in how the activated carbons behave when in contact with liquids or gases, and the amount of material which may be adsorbed will be dependent not only on the surface chemistry of the material but also the porous nature of the activated carbons. The pores of activated carbons may be characterised as being of three main types defined with internal pore widths $< 2$ nm (micropores), $2 - 50$ nm (mesopores) and $> 50$ nm (macropores) in an attempt to clarify pore size (Sing, Everett, Haul, Moscou, Pierotti, Rouquerol and Siemieniewska, 1985). This characterisation however does not give any information relating to the shape of the pores.

Dependent on the size of species to be removed, the surface area and pore size distribution of the selected activated carbons should be carefully considered. For the adsorption of low molecular weight species including gases, micropores are important, however if the application of the activated carbon is the removal of larger molecular weight species (e.g.
proteins), then the meso- and macropores are of more importance. NOVACARB activated carbons are therefore ideally suited for this purpose as one of the unique properties of these activated carbons is that they contain mesopores.

In order to study the porous nature and surface area of solid materials there are a number of techniques available. Among those which are commonly used in the analysis of activated carbons are a) Gas Adsorption; b) Liquid Adsorption; c) X-ray Scattering shown in Table 2.0.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Pore Size Range</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas Adsorption</td>
<td>Up to 50 nm</td>
<td>Quadrapole effect and variations in the surface area due to the difference in size of the probe gas (N₂, He, Kr, Ar)</td>
</tr>
<tr>
<td>Liquid Adsorption</td>
<td>2 µm - 2mm or 30 nm - 30 µm</td>
<td>Can use wetting and non-wetting liquids (Organic solvents or mercury)</td>
</tr>
<tr>
<td>X-ray Scattering</td>
<td>All</td>
<td>Small angle, wide angle</td>
</tr>
</tbody>
</table>

Table 2.0  Techniques for determination of porous nature of activated carbons

Gas adsorption involves the measurement of the pressure of a gas (e.g. Kr, Ar, He, N₂) in a known volume at a known temperature. This is used to measure smaller diameter pores in the micro and mesoporous range. The use of which probe gas has to be considered given the variation in the size of probe gas molecules, which can result in different surface areas depending on the gas used.

Liquid adsorption involves the application of pressure, at a known temperature in a known volume to a liquid typically mercury, water or organic solvent in contact with a solid. The effective range of the adsorption will vary with the liquid used with mercury porosimetry giving reliable pore volume data in the 30 nm - 30 µm pore width range whereas pore width measurements with other liquids are reliable over the range of a few µm to 2 mm although deformation of pores may occur at high pressures, leading to erroneous results. The final method, X-ray scattering, can be used to determine the pore size distribution and the surface area of activated carbons. This technique can also measure the pores which are
inaccessible to the liquids or gases used in the other methods of adsorption, X-ray scattering however is the most expensive method of the three listed.

The techniques which are most commonly employed for the analysis of both the surface and bulk properties of activated carbons are listed below in Table 2.1.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Information</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titrations - Boehm</td>
<td>Oxygen containing surface groups</td>
</tr>
<tr>
<td>- Mass</td>
<td>Point of zero charge ($pH_{PZC}$)</td>
</tr>
<tr>
<td>- Potentiometric</td>
<td>$pK_a$ of surface functional groups</td>
</tr>
<tr>
<td>Spectroscopy - FTIR</td>
<td>Surface functional groups and or bulk functional groups</td>
</tr>
<tr>
<td>- Raman</td>
<td>Surface area, pore size distribution and energetics</td>
</tr>
<tr>
<td>Gas Adsorption</td>
<td></td>
</tr>
<tr>
<td>Scanning Electron Microscopy (SEM)</td>
<td>Surface topography</td>
</tr>
<tr>
<td>Transmission Electron Microscopy (TEM)</td>
<td>Structure of porous network</td>
</tr>
<tr>
<td>Electron Diffraction by X-Rays (EDX)</td>
<td>Elements present at surface</td>
</tr>
<tr>
<td>Small Angle X-ray Scattering (SAXS)</td>
<td>Total surface area, including closed pores, pore size distribution</td>
</tr>
<tr>
<td>Secondary Ion Mass Spectrometry (SIMS)</td>
<td>Surface functional groups</td>
</tr>
<tr>
<td>Bulk Density Measurements</td>
<td>Bulk density</td>
</tr>
</tbody>
</table>

Table 2.1 Techniques for the chemical and physical characterisation of activated carbons

The titration methods (Boehm, mass and potentiometric) can be used to gain information regarding the number and types of surface functional groups presents and the chemistry of the activated carbons. The surface functional groups can be further identified by SIMS, FTIR and Raman spectroscopy. Further evidence for the groups present in the top few micrometres of the surface can be provided by EDX. A range of different techniques is required if a full determination of the surface functional groups is desired, as no one technique can give both qualitative and quantitative information.
The structure of the activated carbons can be examined using microscopic methods such as SEM to examine the surface topography and TEM to view the porous structure and arrangement of the carbon sheets present.

2.1 Materials and Experimental Methods

2.1.1 Materials

Buffer solutions pH 4 (Phthalate) (Fisher Scientific)

Buffer solutions pH 7 (Phosphate) (Fisher Scientific)

Deionised water (In house, Resisitivity 15 MΩ.cm)

Electrode buffer solution (BDH)

Hydrochloric acid (HCl) (Sigma-Aldrich Company Limited)

NOVACARB S-50-9/100/125-00 (MAST Carbon Limited)

NOVACARB S-50-9/125-00 (MAST Carbon Limited)

Nitric acid (HNO₃) (Surechem Products Limited)

Potassium bromide (KBr) (Sigma-Aldrich Company Limited)

Sodium carbonate (Na₂CO₃) (Sigma-Aldrich Company Limited)

Sodium chloride (NaCl) (Sigma-Aldrich Company Limited)

Sodium hydrogen carbonate (NaHCO₃) (Sigma-Aldrich Company Limited)

Sodium hydroxide (NaOH) (Sigma-Aldrich Company Limited)

2.1.2 Equipment

Glass combination electrode (BDH)

Heating mantle (Electromantle)

pH meter Orion 410A (Thermo Electron)

Shaking orbital incubator (Bibby Stuart Scientific)

Sputter Coater (Fison Instruments)

Vacuum oven (Gallenkamp)
2.1.3 Experimental Methods

The chemical and physical properties of the activated carbons used in this work were studied using Boehm and mass titrations, Fourier Transform Infrared Spectroscopy (FTIR), secondary ion mass spectrometry (SIMS), scanning electron microscopy (SEM), energy dispersive spectroscopy by X-rays (EDX), nitrogen gas adsorption and small angle X-ray spectroscopy (SAXS). The activated carbons used were NOVACARB S-50-9/100/25-00 and S-50-9/125-00. The coding system used here is S denotes that the carbons were spherical, 50 is the average bead size (50 µm), 9/100 is a resin precursor which produces microporous carbon and 9/125 is a resin precursor which produces microporous carbon with some mesoporosity in the range 5-10 nm and 00 represents no activation burn off.

2.1.3.1 Boehm Titrations

Boehm (1964) developed a titration method to determine the different types of functional groups present on the surface of the activated carbon. This involved neutralising the acidic groups on the carbon surface by incubation of the activated carbons with bases of varying strength (NaOH, Na₂CO₃ and NaHCO₃) in aqueous solution, filtering off the carbon and from the amount of HCl required to neutralise the supernatant an equivalent number of acidic groups were calculated to exist. To determine the number of basic groups present on the surface of the activated carbon, the samples were incubated with HCl and the supernatant titrated with NaOH.

<table>
<thead>
<tr>
<th>Incubating solution</th>
<th>Functional Group Neutralised</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Basic</td>
</tr>
<tr>
<td>NaHCO₃</td>
<td>Carboxylic</td>
</tr>
<tr>
<td>Na₂CO₃</td>
<td>Carboxylic and Lactone</td>
</tr>
<tr>
<td>NaOH</td>
<td>Carboxylic, Lactone and Phenol</td>
</tr>
</tbody>
</table>

Table 2.2 Proposed functional groups neutralised by Boehm titrations
These methods are now commonly referred to as Boehm titrations (see Table 2.2). No effort was made however to distinguish between the different types of basic groups present.

All solutions used in the Boehm titration were of ACS grade. 0.05 M solutions of HCl, NaOH, NaHCO₃ and Na₂CO₃ in 0.5 M NaCl (aq) solution were prepared. The activated carbons were cleaned by placing in a conical flask filled with 400 cm³ deionised water and shaken for 24 hours. To remove the fine particulates which were found at the surface, 10 cm³ ethanol was added and the solution left to stand for 30 minutes. The fines were then decanted off. This was repeated until all fines were removed. The remaining water was then decanted off and the activated carbon slurry was then dried in a vacuum oven at 120 °C. The carbon was allowed to cool to room temperature prior to removal, and then placed in a dessicator until required. Activated carbon (0.5 g) was added to glass vials, then 20 cm³ of 0.05 M HCl or base (NaOH, NaHCO₃ or Na₂CO₃) in 0.5 M NaCl was pipetted slowly into the vial. The vials were then sealed and placed in a shaking incubator thermostatically controlled at 25 °C on a speed setting of 100 revolutions per minute (rpm), for 48 hours. Blank samples containing no carbon were also prepared. After 48 hours the samples were removed from the incubator, filtered, then 5 cm³ aliquots were removed and titrated with the respective acid (0.05 M HCl) or base (0.05 M NaOH). Titrations were performed in triplicate and measurements made using a pH meter fitted with a glass combination electrode. The results were plotted as volume vs. pH and the equivalence point determined from the 2nd derivative plot constructed from the raw data.

The number of sites neutralised upon incubation with a specific acid or base in the Boehm titration experiments were calculated using Equation 2.0 and expressed in milliequivalents of reacting groups/g of activated carbon (meq/g). The number of each type of functional group were then determined as previously shown in Table 2.2.

\[ a = \frac{(c_0 - c_1)V}{m} \quad Equation \ 2.0 \]
where \( a = \) number of surface sites (meq/g), \( c_0 = \) initial solution concentration of blank (meq/L), \( c_1 = \) solution concentration after incubation with carbon (meq/L), \( V = \) volume of solution (L) and \( m = \) mass of carbon (g).

### 2.1.3.2 Mass Titrations

The chemistry of activated carbons is very complex and is the subject of continued debate, due to the heterogeneity of the functional groups present on the surface and their interaction with the surrounding environment. The activated carbon surface in this case may be thought of as a double layer (see Figure 2.3), which can behave as either an anion or cation exchanger, depending on the solution or gas it is immersed in. The pH at which the net surface charge is zero will give information regarding the type of surface functional groups present. The point of zero charge (pH\(_{PZC}\)) may be defined as the pH at which the net surface charge density of the carbon particle is zero, it is the value of the negative logarithm of the activity in the bulk of the charge determining ions. The isoelectric point (pH\(_{IEP}\)) is defined as the pH at which the surface of the activated carbon has no net electrical charge.

![Figure 2.3 Double layer model of activated carbon surface](Adapted from Rodriguez-Reinoso 1998, Leon y Leon and Radovic 1994 and Hassler 1951)
In Figure 2.3 (A) corresponds to a carbon particle in a basic solution (pH > pH\textsubscript{IEP}), and the carbon surface is covered by deprotonated carboxyl groups and therefore the surface has a net negative charge. (B) represents the situation when the pH of the solution is the same as the pH\textsubscript{IEP}, therefore the net surface charge of the carbon is zero. Finally, (C) represents the situation when a carbon particle encounters an acidic solution (pH < pH\textsubscript{IEP}), and the overall surface charge is positive.

Solutions of pH 3, 6 and 11 were prepared from 0.1 M solutions of NaOH and HNO\textsubscript{3}. NOVACARB (0.1, 0.2, 1, 2, 5 and 10 % w/v) was added to a vial and 10 cm\textsuperscript{3} of the required pH solution added to each vial. The vials were sealed and placed in a shaking incubator at 25 °C on a speed setting of 100 rpm for 48 hours. Blank samples were prepared as above which contained no NOVACARB.

After 48 hours the samples were removed from the shaking incubator, filtered and 3 cm\textsuperscript{3} aliquots were removed and the pH of the filtered solutions measured. Measurements were performed in duplicate. The results for the three different pH solutions were plotted and the point at which the curves overlap (or plateau out) is taken as the point of zero charge (pH\textsubscript{PZC}).

2.1.3.3 Fourier Transform Infrared Spectroscopy

A Nexus FTIR spectrometer (Nicolet) equipped with a DTGS KBr detector and a XT-KBr beam splitter was setup in Transmission ESP mode. Samples were prepared as 1 mg of activated carbon in 100 mg of potassium bromide (KBr) and recorded over 32 scans at a resolution of 1 cm\textsuperscript{-1}. The spectrum of a KBr blank disc was then subtracted from the sample spectra using OMNIC ESP 5.2a Software (Nicolet). The data was transferred in the comma separated values (.csv) format to Origin version 6.0 (Microcal Software, Inc) for plotting.

2.1.3.4 Secondary Ion Mass Spectrometry (SIMS)

To examine the functional groups present at the surface of the activated carbons SIMS analysis was carried out by Millbrook Scientific Instruments PLC using a Millbrook
MiniSIMS. The activated carbon surfaces of S-50-/9/100/125-00 and S-50-9/125-00 were examined under static and dynamic conditions. The static SIMS was performed at lower energy for detection of both the negative and positive fragments. Dynamic SIMS at higher energy was performed to determine negative fragments emitted from the surface. Secondary Ion Mass Spectrometry (SIMS) is a very sensitive qualitative analytical technique for investigating the top few layers (1 nm) of the surface of a material. Materials can be examined using a low energy ion source, which allows both positive and negative secondary ions to be detected with minimal surface damage (static SIMS), or dynamic SIMS where a higher energy ion dose is used and only negative secondary ions may be detected. Dynamic mode however, causes erosion of the surface and can be used in conjunction with the results obtained with static SIMS to determine if a modification method affects only the upper surface layers.

2.1.3.5 Scanning Electron Microscopy (SEM)

Scanning electron microscopy may be used to examine the gross morphological features of the surface of the activated carbons however it is of little use in the evaluation of the porous nature of these materials as the pores are of the nanometre scale or below.

Carbon adhesive pads were fixed to aluminium stubs, then 0.5 g of each activated carbon was placed in a clean Petri dish and the stubs were carefully dipped in the carbon 10 times to coat the surface of the carbon adhesive pad. Care was taken not to crush the activated carbon. The carbon samples on the aluminium stubs were then placed in a sputter coater (Fison Instruments) and a vacuum applied. The samples were then sputter coated with palladium for 30 minutes to ensure the surface of the sample was completely coated.

The samples were removed from the sputter coater and placed on a stainless steel platform and placed into the scanning electron microscope (SEM) (JEOL 6310). The samples were examined at a working distance of 15 mm with accelerating voltage of 5 keV and images were taken at x 250 and x 15,000 magnification, to examine the topological features of the samples.
2.1.3.6 Energy Dispersive Spectroscopy by X-ray (EDX)

Energy dispersive spectroscopy by X-rays (EDX) allows the determination of elements which are present in the top 1 µm of the surface to be determined; however it provides no information with regards to the nature of the functional groups which these elements form. As it is not a true surface analysis technique it provides information about the surface and the bulk composition of the activated carbon.

The counts (intensity) of the signal can be affected by the degree of porosity of the sample, as a very porous sample will have less material from which secondary electrons can be released, when compared to a non-porous sample. The EDX was performed using the SEM (JEOL 6310), using computer package (ISIS Link, Oxford Instruments).

2.1.3.7 Low Temperature Nitrogen Gas Adsorption

Gas adsorption experiments using nitrogen were performed at MAST Carbon Ltd. This adsorption method can involve the use of noble gases such as argon or helium; however the cheaper and more commonly used gas is nitrogen. The different sizes of the gas molecules will also play a role in the different results which may be seen when the same surface is exposed to different gases. Activated carbons were added and the samples in the ampoule were then placed in a Gemini 2375 v4.01 porosimeter and immersed in liquid nitrogen and nitrogen introduced under increasing pressure.

2.1.3.8 Small Angle X-Ray Scattering (SAXS)

One of the more useful techniques for examining the porous nature of activated carbons and other porous materials is the use of X-ray scattering. The two most common types of experiments performed are wide angle X-Ray scattering and small angle X-ray scattering (WAXS and SAXS respectively). The SAXS measurements were performed at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The samples were placed in glass capillary tubes and examined at distances of 30 and 178 cm, at a temperature of 24.5 °C.
2.1.3.9 Bulk Density Measurements

Bulk density measurements allow the determination of the density of the particles, so that experiments on different activated carbons may be performed not only on a weight basis, but by comparable surface area / volume of material.

Activated carbon was added a clean pre-weighed 10 cm$^3$ glass measuring cylinder (0.1 cm$^3$ graduations) using a glass funnel and filled to approximately 5 cm$^3$. The cylinder was then gently tapped for 30 seconds, to allow the particles to pack down, then the volume was measured and the cylinder and activated carbon were weighed, to allow a bulk density to be calculated. This was repeated a further nine times to get an average bulk density for each activated carbon.

$$\rho = \frac{m}{V}$$

*Equation 2.1*

where $\rho = \text{bulk density (g/cm}^3\text{)}, m = \text{mass of carbon (g)}$ and $V = \text{volume of carbon used (cm}^3\text{)}$. However, this simplistic method does not take into account the space occupied by air in the measuring cylinder.

2.1.3.10 Particle Size Analysis

Use of this technique allows the determination of the mean particle size the range of particle sizes in the sample examined and will allow the determination of the differences in the particle size based on the method of production. The distribution of particle sizes was determined from SEM images (x 15,000 magnification). The samples were prepared as outlined in section 2.1.3.5. The image was split into 8 sections and the diameters of intact visible particles then measured.

2.1.3.11 Small Angle X-Ray Scattering (SAXS)

SAXS involves the exposure of a sample to an x-ray source for a short period of time, from one second up to 200 seconds, depending on the scattering from the sample. X-rays are formed into a fine beam and strike the sample, with a small proportion of the beam
scattered from the sample at a certain angle \( \theta \), focused and monitored using a detector (CCD) (Figure 2.4).

![Diagram of SAXS experimental setup](image)

**Figure 2.4**  **Diagram of SAXS experimental setup**  
(Adapted from Schmidt, 1989)

SAXS measurements were performed on the BM3 beam line at the European Synchrotron Radiation Facility (ESRF) Grenoble, France. The raw data was collected and then transformed as follows. The intensity \( S \)/ number of pixels \( N \) vs. distance from the centre of the beam to the pixel being measured \( r \) was plotted. Then \( P_m \) the radial average was found. A plot \( (S/N)/P_m \) vs. \( r \) was corrected for transmission. The plots for the short and long distance were then combined to form a single plot and the plots of \( I(q) \) vs. \( q \) were constructed.

### 2.1.3.12 Statistical Analysis

For all experiments statistical treatment of the data was performed using one way analysis of variance (unstacked) and Dunnett’s comparison. The statistical methods used are described in detail in Appendix 1.

### 2.2 Results - Characterisation of NOVACARBS

#### 2.2.1 Results of Boehm Titrations

The results of the Boehm Titrations were plotted as pH vs. volume added. The equivalence points were then determined from the 2nd derivative plots and used to calculate the equivalence of each of the solutions and from this the number of surface groups of each
functional group type using Equation 2.0, where the number of samples in each case was three for each group and the mean value of $a$ was plotted. The results are shown in Figure 2.5 and tabulated in Table 2.3.

Figure 2.5  Distribution of functional groups on the surface of S-50-9/100/25-00 and S-50-9/125-00 (Mean $a$ (n=3) ± Standard Deviation)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean $a$ (meq/g) (n=3) ± Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>S-50-9/100/25-00</td>
<td>1.696</td>
</tr>
<tr>
<td></td>
<td>± 0.049</td>
</tr>
<tr>
<td>S-50-9/125-00</td>
<td>1.540</td>
</tr>
<tr>
<td></td>
<td>± 0.045</td>
</tr>
</tbody>
</table>

Table 2.3  Results of Boehm titrations for S-50-9/100/25-00 and S-50-9/125-00

From the results of the Boehm titrations, the surface chemistry of the two starting activated carbons was found to be similar, with S-50-9/100/25-00 displaying a surface with a greater phenolic character, where as the S-50-9/125-00 was more carboxylic in nature. In addition
the total number of surface groups was found to be 1.54 and 1.69 meq/g and the number of acidic (0.854 and 0.783 meq/g) and basic groups (0.842 and 0.757 meq/g) respectively. From the plots shown in Figure 2.6 and 2.7, a plot of the mean pH\(_{PZC}\) for each of the starting activated carbons was constructed (Figure 2.8). The mean values of the pH\(_{PZC}\) for both the starting activated carbons was calculated as the point when the slope of the lines was d(pH/%\(_v\)\)/d(%) = 0.

### 2.2.2 Results of Mass Titrations

From the results of the mass titrations (Figures 2.6 and 2.7) it is seen that the pH\(_{PZC}\) of the two starting activated carbons is very similar, levelling off at 9.9 and 10 respectively (Table 2.4). The mean values obtained for the incubations at the three different pH’s were then plotted to show the overall trend as the % w/v of activated carbon was increased (Figure 2.8). This shows that the pH\(_{PZC}\) of the two carbons have a basic value. From the Boehm titrations, both acidic and basic surface functional groups were found, however the surfaces were found to have a slightly greater number of basic groups present on both surfaces compared to the number of acidic groups. As the nature of the basic groups is relatively unknown this could be the reason for a high pH\(_{PZC}\).

![Figure 2.6 Plot of pH\(_{PZC}\) experiment for S-50-9/100/25-00](image)
Figure 2.7  Plot of $pH_{PZC}$ experiment for S-50-9/125-00

Figure 2.8  Plot of mean $pH_{PZC}$ for S-50-9/100/25-00 and S-50-9/125-00
Table 2.4  
<table>
<thead>
<tr>
<th>NOVACARB</th>
<th>$pH_{PZC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-50-9/100/25-00</td>
<td>9.9 ± 0.1</td>
</tr>
<tr>
<td>S-50-9/125-00</td>
<td>10.0 ± 0.1</td>
</tr>
</tbody>
</table>

Table 2.4  Mean $pH_{PZC}$ from Mass Titrations for NOVACARBs S-50-9/100/25-00 and S-50-9/125-00 (Mean (n=3) ± Standard Deviation)

2.2.3 Results of Fourier Transform Infrared Spectroscopy

The results of the transmission FTIR are shown below after re-plotting using the computer package Origin (Version 6.0)

Figure 2.9 a  Plot of FTIR Transmission Spectrum of NOVACARB S-50-9/100/25-00 and S-50-9/125-00 (4000–400 cm$^{-1}$)
Figure 2.9b  Plot of FTIR Transmission Spectrum of NOVACARB S-50-9/100/25-00 and S-50-9/125-00 (4000-2000 cm\(^{-1}\))

Figure 2.9c  Plot of FTIR Transmission Spectrum of NOVACARB S-50-9/100/25-00 and S-50-9/125-00 (2000-400 cm\(^{-1}\))
Table 2.5 FTIR peak table for NOVACARB S-50-9/100/25-00 and S-50-9/125-00

<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Functional Group</th>
<th>Wavenumber (cm⁻¹)</th>
<th>Functional Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>3627</td>
<td>-O-H str</td>
<td>3697</td>
<td>-O-H str</td>
</tr>
<tr>
<td>3417</td>
<td>-OH vib</td>
<td>3437</td>
<td>-OH vib</td>
</tr>
<tr>
<td>3297</td>
<td>Aromatic -C-H str</td>
<td>3255</td>
<td>Aromatic -C-H str</td>
</tr>
<tr>
<td>2960/2923/2877/2852</td>
<td>Aliphatic C-H str</td>
<td>3064</td>
<td>Aliphatic C-H str</td>
</tr>
<tr>
<td>1655</td>
<td>Aromatic -C=C- str</td>
<td>2956/2921/2852</td>
<td>Aliphatic C-H str</td>
</tr>
<tr>
<td>1539</td>
<td>-COO’ asym str</td>
<td>2036</td>
<td>-COO’ asym str</td>
</tr>
<tr>
<td>1521</td>
<td>Aromatic C=C</td>
<td>1740</td>
<td>Alkene -C=C- str</td>
</tr>
<tr>
<td>1458</td>
<td>Aliphatic C-H def</td>
<td>1635</td>
<td>Aromatic -C=C- str</td>
</tr>
<tr>
<td>1435</td>
<td>Alkene C-H def</td>
<td>1540</td>
<td>-COO’ asym str</td>
</tr>
<tr>
<td>1417</td>
<td>Alkene C-H def</td>
<td>1521</td>
<td>Aromatic C=C</td>
</tr>
<tr>
<td>1383</td>
<td>-COO’ sym str</td>
<td>1458</td>
<td>Aliphatic C-H def</td>
</tr>
<tr>
<td>1340</td>
<td>Aliphatic C-H def</td>
<td>1423</td>
<td>Alkene C-H def</td>
</tr>
<tr>
<td>1319</td>
<td>Aliphatic C-H def</td>
<td>1381</td>
<td>-COO’ sym str</td>
</tr>
<tr>
<td>1161</td>
<td>Aromatic C-H in plane def</td>
<td>1203/1161</td>
<td>Aromatic C-H in plane def</td>
</tr>
<tr>
<td>1115</td>
<td>Phenol C-H in plane def</td>
<td>1105</td>
<td>Phenol C-H in plane def</td>
</tr>
<tr>
<td>935</td>
<td>Alkene C-H out of plane def</td>
<td>1061</td>
<td>Lactone/ Acid Anhydride C-O str</td>
</tr>
<tr>
<td>852</td>
<td>Aromatic C-H out of plane def</td>
<td>1038</td>
<td>C-OH str</td>
</tr>
<tr>
<td>793</td>
<td>Aromatic C-H</td>
<td>958</td>
<td>Alkene C-H out of plane def</td>
</tr>
<tr>
<td>775</td>
<td>Aromatic C-H</td>
<td>908</td>
<td>Ether -C-O-C-</td>
</tr>
<tr>
<td>719</td>
<td>-CH₂- Rocking</td>
<td>798</td>
<td>Aromatic C-H</td>
</tr>
<tr>
<td>677</td>
<td>-OH out of plane bending</td>
<td>671</td>
<td>-OH out of plane bending</td>
</tr>
<tr>
<td>521/463</td>
<td>Aromatic C-H out of plane def</td>
<td>469</td>
<td>Aromatic C-H out of plane def</td>
</tr>
</tbody>
</table>

Table 2.5 FTIR peak table for NOVACARB S-50-9/100/25-00 and S-50-9/125-00

The results of the FTIR (Fig. 2.9 a-c) showed that the compositions of the two NOVACARB activated carbons were very similar. Both showed a split peak at ~2300 cm⁻¹ as a result of CO₂ adsorbed from the air. Peaks common to both carbons include O-H vib (~3470 - 3430), aliphatic C-H str (2960 - 2850 cm⁻¹), -COO’ sym str (1383 - 1381 cm⁻¹) and -COO’ asym str (1540 cm⁻¹), (1161 cm⁻¹), aromatic C-H (798 - 793 cm⁻¹) and –O-H out of plane bending (677 – 671 cm⁻¹). The expected aromatic C-H peaks (3100 - 3000 cm⁻¹) were observed only on the S-50-9/125-00 spectrum (Figure 2.9b) and were obscured due to
the wide –O-H peaks, due to either presence of water in the sample, or aliphatic or aromatic –OH peaks. There were also possible peaks in both spectra at 3851 and 3734 cm⁻¹, although both spectra were very noisy approaching 4000 cm⁻¹.

Peaks which were found only in the S-50-9/125-00 spectra include the presence at 2036 cm⁻¹ of a suspected alkyne \textit{str}. Other peaks found include lactone or acid anhydride C-O \textit{str} (1061 cm⁻¹), C-OH (1038 cm⁻¹) and a possible ether –C-O-C- (908 cm⁻¹).

The results of the FTIR of the two activated carbons supplement the information found for the Boehm titration results (Figure 2.5 and Table 2.3), with the presence of carboxyl, lactonic and phenolic surface groups.

2.2.4 Results of Secondary Ion Mass Spectrometry

From the positive SIMS data (Figures 2.10a and 2.11a, and Table 2.6) it is observed that the two surfaces had similar amounts of C⁺ and CH⁺, however there were differences observed for the other mass fragments observed, with S-50-9/100/25-00 having greater intensity peaks for CH₂⁺, CH₃⁺, C₂H₂⁺, C₂H₃⁺, C₂H₄⁺ and C₂H₅⁺. The results of the negative peak measurements showed that the two surfaces had very different intensities for the mass fragments examined. There is also a decrease in the intensities when a higher intensity ion source was used as seen in Table 2.6C, showing that for S-50-9/100/25-00 in particular, the oxygen containing functional groups are found mainly in the uppermost layers of the surface. The intensity of the C₂H₂⁺ peak which increased in comparison to the results shown for the low intensity beam (Table 2.6B) shows the increasing aromatic nature of the bulk of the activated carbons.
Figure 2.10a  Results of positive static SIMS analysis of S-50-9/100/25-00

Figure 2.10b  Results of negative static SIMS analysis of S-50-9/100/25-00
Figure 2.10c  Results of higher ion dose SIMS analysis of S-50-9/100/25-00

Figure 2.11a  Results of positive static SIMS analysis of S-50-9/125-00
Figure 2.11b  Results of negative static SIMS analysis of S-50-9/125-00

Figure 2.11c  Results of SIMS analysis of S-50-9/125-00
Table 2.6 Results of SIMS analysis of NOVACARB’s S-50-9/100/25-00 and S-50-9/125-00
2.2.5 Results of Scanning Electron Microscopy

SEM images of both the activated carbons (x 250 magnification) and their surfaces (x 15,000 magnification) were taken to determine the distribution of particle sizes and to examine the morphology of the surface.

The activated carbons S-50-9/100/25-00 and S-50-9/125-00 were shown to be spherical (Figures 2.12a and 2.13a) and the surfaces of the beads were shown to be relatively smooth (Figures 2.12b and 2.13b) at the magnifications used.

Figure 2.12 SEM Image of a) S-50-9/100/25-00 beads (x 250 Magnification) and b) Surface of S-50-9/100/25-00 bead (x 15,000 Magnification)

Figure 2.13 SEM Image of a) S-50-9/125-00 beads (x 250 Magnification) and b) Surface of S-50-9/125-00 bead (x 15,000 Magnification)
2.2.6 Results of Energy Dispersive Spectroscopy by X-Ray (EDX)

EDX analysis was performed post SEM imaging of the surfaces to determine the amount of carbon and oxygen present in the top few surface layers.

Figure 2.14 Results of EDX for NOVACARBs S-50-9/100/25-00 and S-50-9/125-00

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>Range(keV)</th>
<th>Gross</th>
<th>Net</th>
<th>% Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-50-9/100/25-00</td>
<td>C Ka</td>
<td>0.168 to 0.387</td>
<td>44887</td>
<td>40567</td>
<td>92.6</td>
</tr>
<tr>
<td></td>
<td>O Ka</td>
<td>0.407 to 0.647</td>
<td>6225</td>
<td>3222</td>
<td>7.4</td>
</tr>
<tr>
<td>S-50-9/125-00</td>
<td>C Ka</td>
<td>0.168 to 0.387</td>
<td>37866</td>
<td>33678</td>
<td>90.6</td>
</tr>
<tr>
<td></td>
<td>O Ka</td>
<td>0.407 to 0.647</td>
<td>6755</td>
<td>3492</td>
<td>9.4</td>
</tr>
</tbody>
</table>

Table 2.7 Results of EDX for NOVACARBs S-50-9/100/25-00 and S-50-9/125-00

From the EDX data (Table 2.7) the ratio of the oxygen to carbon content of the activated carbons were plotted and it was shown that the content of the top few μm were predominately carbon (> 90 %) with the remainder of the surface composed of oxygen.
Figure 2.15  Ratio of oxygen to carbon for NOVACARBs S-50-9/100/25-00 and S-50-9/125-00 as determined using EDX

From the EDX analysis the amount of oxygen groups present on the surface of both NOVACARB activated carbons was very similar. The ratio of oxygen to carbon at the surface (Fig. 2.15) was 0.079 (S-50-9/100/25-00) and 0.104 (S-50-9/125-00) respectively, showing that S-50-9/125-00 possessed a greater amount of oxygen groups at the surface as seen from the SIMS analysis (Table 2.5).

2.2.7 Results of Low Temperature Nitrogen Adsorption

The adsorption isotherm of S-50-9/100/25-00 shown in Figure 2.16 is characteristic of a Type Ia isotherm with a plateau covering a wide range of relative pressures (Gregg and Sing, 1982). This type of isotherm is typical of a material with a small external surface, where the adsorption of nitrogen is in the micropores, then some mesopores are filled when the relative pressure is increased.
Figure 2.16  \( \text{N}_2 \) Adsorption Isotherm for S-50-9/100/25-00

Figure 2.17  \( \text{N}_2 \) Adsorption Isotherm for S-50-9/125-00

The nitrogen adsorption isotherms for S-50-9/125-00 shown in Figure 2.17. This is typical of a Type IV isotherm, where the micropores are filled over a wide range of relative
pressures, then the mesopores are filled at higher pressures. To obtain an idea of the surfaces areas of the two activated carbons, the data from the low temperature nitrogen gas adsorption experiments were used to construct Brunauer, Emmett, Teller (BET) plots. However, only the data from relative pressure ($P/P_0$) in the range 0.05 to 0.35 from Figures 2.16 and 2.17 were used as this represents the filling of a monolayer of nitrogen gas molecules upon the surface. The surface areas for both the activated carbons were found to be very similar, 728 and 720 m$^2$/g for S-50-9/100/25-00 and S-50-9/125-00 from the BET plots constructed using Origin 6.0 (Microcal Software, Inc.) in Figure 2.18.

![BET Plots of S-50-9/100/25-00 and S-50-9/125-00](image)

**Figure 2.18  BET Plots of S-50-9/100/25-00 and S-50-9/125-00**

The pore size distribution of the two NOVACARBs shown in Figure 2.19, shows that both activated carbons have a bimodal distribution of pores in the micro- and mesopore range. The pore size distribution of S-50-9/125-00 as well as the contribution from the micropores, shows a significant contribution from the mesopores, which are in the range of up to approximately 30 nm in diameter. S-50-9/100/25-00 NOVACARB however was shown to have a far smaller contribution from the mesopores, with the larger mesopores of the order of 20 nm in diameter. Due to limitations in the Gemini adsorption apparatus low relative pressures are not able to be measured, therefore the more narrow micropores are not measured.
The majority of the surface area of the activated carbons is attributed to the micropores, especially for S-50-9/100/25-00, with only a small contribution from the mesopores shown in Figure 2.20. For S-50-9/125-00 however, there is a greater contribution made by the mesopores to the surface area in comparison to S-50-9/100/25-00.
2.2.8 Results of Particle Size Analysis

Analysis of the data as shown in Table 2.8 showed that the mean bead sizes of the two NOVACARB’s were found to be 35.5 and 15.9 µm for S-50-9/100/25-00 and S-50-9/125-00 respectively. The range of bead sizes was found to be similar for both activated carbons 63 and 61 µm respectively, from 5.7 – 68.8 µm for S-50-9/100/25-00 (Figure 2.21) and from 3.8 – 65 µm for S-50-9/125-00 (Figure 2.22). However, the distribution of beads was approximately normal for S-50-9/100/25-00, but the S-50-9/125-00 beads were skewed to smaller bead sizes with very few beads of more than 40 µm.

![Histogram of S-50-9/100/25-00](image)

**Figure 2.21** Plot of Bead Size Distribution of S-50-9/100/25-00
Figure 2.22  Plot of Bead Size Distribution of S-50-9/125-00
Table 2.8  Statistical analysis of the Bead Sizes of NOVACARBs
S-50-9/100/25-00 and S-50-9/125-00

<table>
<thead>
<tr>
<th></th>
<th>S-50-9/100/25-00</th>
<th>S-50-9/125-00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>35.54</td>
<td>15.93</td>
</tr>
<tr>
<td>Standard Error</td>
<td>1.311</td>
<td>0.537</td>
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<tr>
<td>Median</td>
<td>34.41</td>
<td>13.38</td>
</tr>
<tr>
<td>Mode</td>
<td>34.41</td>
<td>3.82</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>12.78</td>
<td>10.16</td>
</tr>
<tr>
<td>Sample Variance</td>
<td>163.34</td>
<td>103.27</td>
</tr>
<tr>
<td>Kurtosis</td>
<td>0.712</td>
<td>1.249</td>
</tr>
<tr>
<td>Skewness</td>
<td>-0.299</td>
<td>1.033</td>
</tr>
<tr>
<td>Range</td>
<td>63.09</td>
<td>61.18</td>
</tr>
<tr>
<td>Minimum</td>
<td>5.735</td>
<td>3.824</td>
</tr>
<tr>
<td>Maximum</td>
<td>68.82</td>
<td>65.00</td>
</tr>
<tr>
<td>Sum</td>
<td>3376.17</td>
<td>5704.71</td>
</tr>
<tr>
<td>Count</td>
<td>95</td>
<td>358</td>
</tr>
</tbody>
</table>

2.2.9  Results of Bulk Density Measurements

The bulk densities of the two NOVACARB’s (Figure 2.23) were found to be 0.675 g/cm³ and 0.609 g/cm³ for S-50-9/100/25-00 and S-50-9/125-00 respectively. The standard deviation of the S-50-9/100/25-00 was zero due to the rapid packing of the larger particulates, whereas the smaller S-50-9/125-00 beads took a longer time to pack down, resulting in a larger standard deviation.
Figure 2.23  Bulk densities of S-50-9/100/25-00 and S-50-9/125-00

(Mean n=10 ± Standard Deviation)

2.2.10 Results of SAXS Experiments

The results of the SAXS experiments revealed that the two NOVACARBs, S-50-9/100/25-00 (Figure 2.24) and S-50-9/125-00 (Figure 2.25), display a different porous nature in agreement with the previously shown results of the low temperature nitrogen adsorption experiments. The slopes of three of the four different sections of the I(q) vs. q plots found to be different, and only at q values approaching 1 were the slopes of the two plots similar.
2.3 Discussion

2.3.1 Boehm Titrations – Discussion

The two non-oxidised NOVACARBs (S-50-9/100/25-00 and S-50-9/125-00) were shown to have different distributions of surface functional groups (Fig. 2.5) with S-50-9/100/25-
having a greater total number of groups, with 0.842 and 0.854 meq/g acidic and basic groups respectively and the greatest number of phenolic groups (0.355 meq/g) compared to S-50-9/125-00 (0.215 meq/g). However, the number of carboxylic groups was greater for S-50-9/125-00 (0.364 meq/g), with a similar number of lactonic type groups (0.217 for S-50-9/100/25-00 and 0.178 meq/g for S-50-9/125-00) observed for both NOVACARBs.

Overall the total number of acidic groups appears greater than that expected for non-oxidised activated carbons. The large number of acidic groups could be as result of exposure to air after removal from the furnace, instead of cooling in an inert atmosphere.

### 2.3.2 Mass Titrations - Discussion

From the results of experiments to determine the point of zero charge (pH\textsubscript{PZC}) of S-50-9/100/25-00 and S-50-9/125-00 (Figures 2.6 and 2.7) the mean pH\textsubscript{PZC} values obtained were pH 9.91 ± 0.12 and 9.99 ± 0.08 respectively (Figure 2.8). The high pH\textsubscript{PZC} values are indicative of basic surfaces; this is observed from the number of basic groups as determined by Boehm titrations in Figure 2.5 (0.854 and 0.757 meq/g respectively). A possible reason for S-50-9/125-00 possessing a larger pH\textsubscript{PZC} value could be the ratio of basic to acidic groups is slightly higher than that for S-50-9/100/25-00, 1.034 compared to 1.014.

### 2.3.3 FTIR Spectroscopy – Discussion

The results of the FTIR (Figure 2.9 a-c) showed that the compositions of the two NOVACARB activated carbons were very similar. Determination of the functional groups present was based on the assumption that only carbon, oxygen and hydrogen were present in the activated carbon samples as determined by EDX analysis. The functional group peaks found were as expected aromatic, aliphatic peaks as well as peaks for the carboxyl, lactonic and phenolic groups as determined by Boehm titrations (Figure 2.5 and Table 2.3). The data found from the SIMS analysis of the two activated carbon surfaces (Figure 2.10a-c and Figure 2.11a-c) also agreed with FTIR and Boehm titration results with the presence of aliphatic (CH\textsubscript{x}\textsuperscript{+}) and aromatic moieties (C\textsubscript{2}H\textsubscript{2}\textsuperscript{+}), phenolic (OH\textsuperscript{-}) detected at the surface.
The presence of carboxyl groups was assumed on the basis of OH⁻ and O⁻ as no peaks of any consequence were observed at 44 m/z corresponding to CO₂⁻.

Unexpectedly a peak at 2036 cm⁻¹ was observed for S-50-9/125-00 which was assigned as an alkyne str., given that only C, O and H was present in the sample.

2.3.4 SIMS - Discussion

SIMS can be used to gain qualitative information regarding the hydrogen content of aromatic or aliphatic regions of the carbon samples studied. The main ion fragments of interest are CHₓ⁺, shown to be obtained from predominately aliphatic surfaces (Albers, Deller, Despeyroux, Schäfer, Seibold (1992) and Albers, Freund, Seibold, Wolff (1992)), and C₂H⁻ assigned to carbons in the middle of condensed ring structures with bonds to hydrogen. Graphitic type surfaces which are hydrogen deficient as known to have lower relative C₂H⁻ peak intensities, which are closely correlated to values obtained by CHN analysis (Hess et al. (1988)).

C₂⁻ assigned to carbons in the middles of condensed aromatic rings without bonds to hydrogen (Albers, Deller, Despeyroux, Schäfer, Seibold (1992), Ashida, Kanamori, Watanabe (1988), Hess, Ayala, Vegvari, Kistler (1988), Albers, Freund, Seibold, Wolff (1992)). The ratio of C₂H⁻ / C₂⁻ should be a measure of the amount of aromatic hydrogen (or the inverse average size of the aromatic system on the surface). However, this ratio can only be used as a measure of the aromatic nature of the surface if the number of aliphatic CHₓ⁺ groups is low. The ratio of C₂H₃⁺ and C₂⁺ (aliphatic) can also be used as a measure of the aliphatic nature of a surface.

The results of S-50-9/100/25-00 (Fig. 2.10a-c) and S-50-9/125-00 (Fig. 2.11a-c) seen in Table 2.5, show that the surface of S-50-9/100/25-00 is composed of aliphatic groups, predominately CHₓ⁺, as observed from the large ratio of CHₓ⁺ ion fragments (3.47), conversely the surface of S-50-9/125-00 is shown to have a lower aliphatic content (0.57). The ratio of C₂H₃⁺ /C₂⁺ was found to be 9.87 and 3.71 for S-50-9/100/25-00 and S-50-9/125-00 respectively. The aromatic nature (C₂H⁻ / C₂⁻) of the two surfaces was found to be greater for the S-50-9/100/25-00 with a greater number of edge groups however the size of the aromatic condensed ring structure was greatest for S-50-9/125-00.
Under examination using a higher intensity ion beam (Table 2.6C), the \( \text{CH}^- \) intensities decrease for both activated carbons indicating that the uppermost surface is more aliphatic and that the bulk of the activated carbon is aromatic, as observed by the intensity of the \( \text{C}_2\text{H}^- \) peak. There is also a reduction in the intensity of the \( \text{O}^- \) and \( \text{OH}^- \) peaks which suggests that the majority of the oxygen containing groups are at the outermost surface of the activated carbons.

### 2.3.5 SEM – Discussion

The SEM analysis of the two NOVACARBS, S-50-9/100/25-00 and S-50-9/125-00 shown in Figures 2.12a and b and Figure 2.13a and b respectively, show that the size distribution of the beads are different for both the carbons. The surfaces of both the carbons were found to be relatively smooth at the level of magnification used.

### 2.3.6 EDX - Discussion

The results of the EDX analysis (Figure 2.14 and 2.15) for the two NOVACARBS shows that the top 1-2 \( \text{µm} \) of the surface is composed of > 90 % carbon and oxygen. The O/C ratio was found to be greater with S-50-9/125-00 0.104 compared to 0.079 for S-50-9/100/25-00, however S-50-9/100/25-00 was found to have the greatest count for C \( \text{K}_\alpha \). This is in agreement with the SIMS results (Table 2.6) which show a far greater amount of C containing fragments when compared to S-50-9/125-00.

### 2.3.7 Low Temperature Nitrogen Adsorption Isotherms - Discussion

The nitrogen adsorption isotherms show that the two NOVACARBS have similar porous nature, displaying Type I Langmuir micropore filling for S-50-9/100/25-00 (Figure 2.16) and type IV filling for S-50-9/125-00 (Figure 2.17). The surface areas determined using BET theory were found to be 720 and 728 \( \text{m}^2/\text{g} \) for S-50-9/100/25-00 and S-50-9/125-00 respectively (Figure 2.18). The majority of the surface areas were attributed to filling of the micropores for both carbons although the contribution from the mesopores of S-50-9/125-00 was far greater than those of S-50-9/100/25-00. This difference may be attributed to the
greater number of the S-50-9/125-00 beads per gram as a result of a smaller mean bead size (15.9 µm) in comparison to S-50-9/100/25-00 (35.5 µm).

### 2.3.8 Bead Size Analysis - Discussion

The results of the bead size analysis (Table 2.8 and Figures 2.19 and 2.20) revealed that S-50-9/100/25-00 and S-50-9/125-00 have different bead size population distributions and that the mean size of these two types of NOVACARB were found to be 35.5 and 15.9 µm respectively. S-50-9/100/25-00 was found to have a normal distribution of bead sizes, however, S-50-9/125-00 was found to have a distribution skewed to bead diameter < 30 µm, with very few beads with diameters greater than 30 µm.

### 2.3.9 Bulk Density Measurements – Discussion

From the bulk density measurements it was observed that the two types of NOVACARB (Figure 2.23), possessed bulk densities of 0.675 g/cm³ (S-50-9/100/25-00) and 0.609 g/cm³ (S-50-9/125-00). The standard deviation of the 10 samples was negligible for S-50-9/100/25-00 as the larger particles were able to pack more quickly, whereas for S-50-9/125-00 due to the smaller particle size it may take a longer time to pack down in the measuring cylinder.

### 2.3.10 SAXS - Discussion

The results of the SAXS analysis revealed that the two activated carbons displayed a different range of pores as previously observed with the low temperature adsorption results. The slopes of three of the 4 sections of the plots were found to be different and it was found that only when q approaches 1 that the slopes become very similar. As scattering depends on ql, where l is the length of the structure, there is an inverse relationship between the size of the scattering structure and q. Therefore the two activated carbons have very similar microporous structures as indicated by the similar slopes -2.36 and -2.30, however as the size of the scattering structures increases the differences between the two carbons become more apparent.


2.4 Conclusions

From the chemical and physical analysis undertaken it was shown that the two NOVACARB activated carbons possess similar surface chemistries as found from the results of the Boehm and mass titrations (Figures 2.4 and Table 2.4), FTIR (Figure 2.8) and EDX (Figure 2.14 and 2.15). However, the physical properties of the two activated carbons differ with a different dispersity of bead sizes and mean bead size (Figure 2.18 and 2.19), bulk densities (Figure 2.20) and although the nitrogen isotherms are similar (Figures 2.16 and 2.17) the pore size distributions (Figure 2.18) and pore area distributions (Figure 2.19) and results of scattering of the structures as determined by SAXS (Figure 2.24 and 2.25) were found to be different.

To allow the further modification of the surface of S-50-9/100/25-00 and S-50-9/125-00 oxidation was undertaken using nitric acid to increase the number of carboxylic surface moieties as discussed in Chapter 3.
Chapter 3  Nitric Acid Oxidation of NOVACARB Activated Carbons
3.0 Nitric Acid Oxidation of NOVACARB Activated Carbons

3.0.1 Introduction

The surface of activated carbons may be considered to be hydrophobic, given the predominance of C=C, C-C and C-H groups. To increase the hydrophilicity of the surface and the number of sites available for further reaction, it is desirable to oxidise the surface. Oxidation of the surface of activated carbons leads to the formation of functional groups which are found in organic chemistry such as carboxylic, phenolic and lactonic functional groups and may be performed by either dry oxidation (involving a gas) or by wet oxidation (involving a liquid) as shown in Table 3.0.

<table>
<thead>
<tr>
<th>Oxidation Type</th>
<th>Oxidising Agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>Oxygen, ozone, air, water vapour, carbon dioxide, nitrogen oxide and halogens</td>
</tr>
<tr>
<td>Wet</td>
<td>Nitric acid, nitric/sulphuric acid, hydrogen peroxide, acidic potassium permanganate, chlorine water, sodium hypochlorite and ammonium persulfate</td>
</tr>
</tbody>
</table>

Table 3.0 Common oxidising species for activated carbons


The number and type of functional groups formed by oxidation of the surface is dependent on (i) type and concentration of oxidising agent used and (ii) reaction conditions under which the oxidation is performed (such as temperature and duration of oxidation). Of the numerous methods used to oxidise the surface of activated carbons, the most frequently used method is nitric acid (HNO₃) (Battistoni, Bompadre and Fava, 1984; Vinke, van der Eijk, Verbree, and Voskamp, 1994; Moreno-Castilla, Ferro-Garcia, Joly, Bautista-Toledo,
Nitric acid may contain a variety of nitrogen oxides such as NO, NO\textsubscript{2}, N\textsubscript{2}O\textsubscript{3}, N\textsubscript{2}O\textsubscript{4} and HNO\textsubscript{2}. Odd electron species such as NO and NO\textsubscript{2} can facilitate oxidation via extraction of a H atom (Ogata, 1978). Nitric acid may act via two methods by either nitrating aromatic groups or groups possessing π electrons with NO\textsubscript{2}\textsuperscript{+} or by oxidation of moieties possessing no π electrons. However, oxidation using nitric acid can only proceed in the presence of an initiator such as NO\textsubscript{2} (Ogata, 1978).

The use of nitric acid is however problematic as the use of a very concentrated solution may result in the degradation of the activated carbon. Nitric acid is however a relatively inexpensive method to introduce oxygen functional groups into the surface of activated carbons and carbon nanotubes and is therefore the oxidative method of choice. To circumvent the problem of degradation of the activated carbon the use of 20 % HNO\textsubscript{3} and a relatively short period of oxidation (2 hours) were employed. To achieve an increase in the number of functional groups, oxidation was performed for the same duration at three different temperatures (50, 70 and 90 °C).
3.1 Materials and Experimental Methods

3.1.1 Materials

Buffer Solutions pH 4 (Phthalate) (Fisher Scientific)
  pH 7 (Phosphate) (Fisher Scientific)
Deionised water (In house, Resisitivity 15 MΩ cm)
Electrode Buffer Solution (BDH)
Hydrochloric acid (HCl) (Sigma-Aldrich Company Limited)
Nitric Acid (HNO₃) (Surechem Products Limited)
NOVACARB S-50-9/100/125-00 (MAST Carbon)
NOVACARB S-50-9/125-00 (MAST Carbon)
Potassium Bromide (KBr) (Sigma-Aldrich Company Limited)
Sodium carbonate (Na₂CO₃) (Sigma-Aldrich Company Limited)
Sodium chloride (NaCl) (Sigma-Aldrich Company Limited)
Sodium hydrogen carbonate (NaHCO₃) (Sigma-Aldrich Company Limited)
Sodium hydroxide (NaOH) (Sigma-Aldrich Company Limited)

3.1.2 Equipment

Glass Combination Electrode (BDH)
Heating Mantle (Electromantle)
pH meter Orion 410A (Thermo Electron)
Shaking Incubator (Bibby Stuart Scientific)
Vacuum Oven (Gallenkamp)

3.1.3 Experimental Methods

The NOVACARB activated carbons were oxidised with 20 % nitric acid and then the chemical and physical properties of the activated carbons were studied using titrations (Boehm and mass), Fourier Transform Infrared Spectroscopy (FTIR), secondary ion mass spectrometry (SIMS), small angle X-ray spectroscopy (SAXS), scanning electron microscopy (SEM) and electron diffraction by X-rays (EDX).
3.1.3.1 Nitric Acid Oxidation

All glassware was washed with ethanol and dried overnight in an oven prior to use. The glassware was allowed to cool and assembled as follows. A three necked 250 cm³ round bottomed flask was fitted with a reflux condenser in the central neck. A heating mantle was placed on an adjustable stage and moved into position under the round bottomed flask. A thermometer was added to the side neck. 100 cm³ of 20 % nitric acid was added using a glass funnel, then a glass stopper was placed in the neck and the contents of the flask were heated to the desired temperature (50, 70 or 90 °C). When the temperature had stabilised the glass stopper was removed and 10 g of activated carbon added using a glass funnel and the glass stopper replaced. The reaction vessel was maintained at a constant temperature for two hours, after which time the heating mantle was lowered, to allow the contents of the reaction vessel to cool slightly. The slurry of activated carbon and nitric acid was then poured into a fritted glass column and hot water passed through the column. Washing of the activated carbon was repeated until the pH of cooled washings was > 6. The activated carbon was then poured from the column into a Petri dish and the excess of water removed. The dish was then placed in a vacuum oven at 120 °C and dried until constant weight, then when dried the carbon was placed in a tightly sealed container in a dessicator until required.

<table>
<thead>
<tr>
<th>Code</th>
<th>Oxidation Temperature (°C)</th>
<th>NOVACARB</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-100-50-2</td>
<td>50</td>
<td>S-50-9/100/25-00</td>
</tr>
<tr>
<td>N-100-70-2</td>
<td>70</td>
<td>S-50-9/100/25-00</td>
</tr>
<tr>
<td>N-100-90-2</td>
<td>90</td>
<td>S-50-9/100/25-00</td>
</tr>
<tr>
<td>N-125-50-2</td>
<td>50</td>
<td>S-50-9/125-00</td>
</tr>
<tr>
<td>N-125-70-2</td>
<td>70</td>
<td>S-50-9/125-00</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>90</td>
<td>S-50-9/125-00</td>
</tr>
</tbody>
</table>

Table 3.1 Numbering codes for nitric acid oxidised NOVACARBs
Here N represents oxidation by nitric acid, 100 or 125 the NOVACARB they are derived from S-50-9/100/25-00 or S-50-9/125-00 respectively, 50, 70 or 90 represents the temperature ( °C) at which oxidation with nitric acid took place and 2 represents the duration of oxidation in hours.

3.1.3.2  **Boehm Titrations**

The nitric acid oxidised NOVACARB activated carbons were examined using Boehm titrations as outlined in section 2.1.3.1, to determine the density of surface functional groups present on the surface.

3.1.3.3  **Mass Titrations**

Mass titrations of the nitric acid oxidised NOVACARB activated carbons were performed to determine the change in the pH<sub>PZC</sub> due to oxidation, as outlined in section 2.1.3.2.

3.1.3.4  **Fourier Transform Infrared Spectroscopy**

The nitric acid oxidised NOVACARB activated carbons were examined using the method outlined in section 2.1.3.3, for the preparation of the samples for FTIR.

3.1.3.5  **Secondary Ion Mass Spectrometry (SIMS)**

SIMS analysis as outlined in section 2.1.3.4 was performed on only the samples oxidised at 90 °C, for both series of activated carbons (N-100-90-2 and N-125-90-2) at Millbrook Scientific Instruments Plc using a miniSIMS.

3.1.3.6  **Scanning Electron Microscopy (SEM)**

Scanning electron microscopy of the nitric acid oxidised NOVACARB activated carbons was performed as outlined on section 2.1.3.5.
3.1.3.7 Electron Diffraction by X-ray (EDX)

After SEM was performed, the samples were analysed using EDX as outlined in section 2.1.3.6.

3.1.3.8 Bulk Density Measurements

Bulk density measurements on the nitric acid oxidised NOVACARB activated carbons were performed as outlined in section 2.1.3.9.

3.1.3.9 Bead Size Analysis

Analysis of the effect that oxidation with nitric acid has on bead size of NOVACARB activated carbons was performed from the SEM image taken at x 15,000 magnification, as outlined in section 2.1.3.10. Mean bead size was determined and cumulative frequency bead size plots constructed. Analysis of variance and Dunnett’s comparison test were performed to determine if the nitric acid oxidation produced any statistically significant difference in the mean bead size in comparison to the non-oxidised control (S-50-9/100/25-00 or S-50-9/125-00).

3.1.3.10 Small Angle X-Ray Scattering (SAXS)

The SAXS experiments were performed on the nitric acid oxidised activated carbons as outlined in section 2.1.3.11.

3.1.3.11 Statistical Analysis

The statistical analysis performed was one way analysis of variance (ANOVA) un-stacked and Dunnett’s comparison using the statistical package Minitab 15 (Minitab Inc.). These statistical methods of analysis were used as only one factor was examined in each analysis one way ANOVA was used and as the values analysed were placed in different columns the un-stacked method was used. ANOVA was used to compare the sample values of the activated carbons which were oxidised against a control value for the corresponding non-
oxidised activated carbon S-50-9/100/25-00 or S-50-9/125-00 respectively, to determine if the value was significantly different from the control value.

Dunnett’s comparison was used to create confidence intervals for differences between the mean of each factor for the oxidised samples and mean control value of the corresponding non-oxidised activated carbon. If the confidence levels determined contained zero, there was no significant difference between the sample mean and the control mean. If the confidence intervals were all negative values the sample mean values were significantly lower than the control mean values, and the opposite applies for all positive confidence intervals. For the Dunnett’s comparison a 5 \% error rate was assumed for each family group.

3.2 Results - N-100 Series

The oxidised carbons were examined using Boehm and mass titrations, infrared spectroscopy and those oxidised at 90 °C by SIMS. N-100 Series corresponds to the activated carbons from the S-50-9/100/25-00 NOVACARB oxidised at 50, 70 and 90 °C.

3.2.1 Boehm Titrations – N-100 Series

The surface chemistry of the oxidised NOVACARBS was determined by Boehm titrations and mass titrations as outlined in Sections 2.1.3.1 and 2.1.3.2 respectively. The results of Boehm titrations for nitric acid oxidised S-50-9/100/25-00 are shown below (Figure 3.0 and Table 3.2), with the values for non-oxidised NOVACARB S-50-9/100/25-00 included for comparison.

The results of the Boehm titrations for the N-100 series (Figure 3.0 and Table 3.2) show that as the temperature of the nitric acid oxidation is increased from 50 to 90 °C, the number of acidic groups (carboxyl and lactonic) increases from 0.364 and 0.825 meq/g at 50 °C to 0.987 and 1.325 meq/g at 90 °C and the number of basic and phenolic type groups decreases from 0.455 and 0.121 meq/g at 50 °C to 0.324 and 0 meq/g at 90 °C. Statistical analysis was performed using Minitab 15 (Minitab Inc.) employing a 1-way analysis of variance (un-stacked) and Dunnett’s comparison test to determine if the changes in the
number of surface functional groups with respect to temperature were significantly different from the number of functional groups for non-oxidised S-50-9/100/25-00.

![Graph showing distribution of functional groups](image)

**Figure 3.0** Distribution of functional groups on the surface of nitric acid oxidised N-100 Series (Mean $a$ (n=3) ± Standard Deviation)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total</th>
<th>Basic</th>
<th>Acidic</th>
<th>Carboxyl</th>
<th>Lactonic</th>
<th>Phenolic</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-50-9/100/25-00</td>
<td>1.696</td>
<td>0.854</td>
<td>0.842</td>
<td>0.270</td>
<td>0.217</td>
<td>0.355</td>
</tr>
<tr>
<td></td>
<td>± 0.049</td>
<td>± 0.020</td>
<td>± 0.045</td>
<td>± 0.017</td>
<td>± 0.029</td>
<td>± 0.051</td>
</tr>
<tr>
<td>N-100-50-2</td>
<td>1.765</td>
<td>0.455</td>
<td>1.310</td>
<td>0.364</td>
<td>0.825</td>
<td>0.121</td>
</tr>
<tr>
<td></td>
<td>± 0.050</td>
<td>± 0.018</td>
<td>± 0.046</td>
<td>± 0.072</td>
<td>± 0.101</td>
<td>± 0.086</td>
</tr>
<tr>
<td>N-100-70-2</td>
<td>1.807</td>
<td>0.426</td>
<td>1.381</td>
<td>0.407</td>
<td>0.829</td>
<td>0.079</td>
</tr>
<tr>
<td></td>
<td>± 0.080</td>
<td>± 0.054</td>
<td>± 0.060</td>
<td>± 0.112</td>
<td>± 0.133</td>
<td>± 0.094</td>
</tr>
<tr>
<td>N-100-90-2</td>
<td>2.463</td>
<td>0.324</td>
<td>2.139</td>
<td>0.987</td>
<td>1.325</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>± 0.070</td>
<td>± 0.066</td>
<td>± 0.023</td>
<td>± 0.049</td>
<td>± 0.165</td>
<td>± 0.159</td>
</tr>
</tbody>
</table>

**Table 3.2** Results of Boehm Titrations for Nitric Acid Oxidised N-100 Series
3.2.1.1 Statistical Analysis of Boehm Titration Results for N-100 Series - Basic Groups

3.2.1.1.1 One Way Analysis of Variance – N-100 Series -Basic Groups

The results of the ANOVA of the number of basic surface groups found using Boehm titrations, reveals that there is a significant decrease in the number of the basic groups as the temperature of oxidation is increased (p<0.05).

3.2.1.1.2 Dunnett’s Comparison – N-100 Series -Basic Groups

The results of Dunnett’s comparison test show that there is a significant decrease as indicated by the confidence interval levels for the three activated carbons all below zero and not including zero.

3.2.1.2 Statistical Analysis of Boehm Titration Results for N-100 Series - Acidic Groups

3.2.1.2.1 One Way Analysis of Variance – N-100 Series -Acidic Groups

From the ANOVA of the Boehm titration results it is shown that oxidation of activated carbons leads to a significant increase in the number of surface functional groups as indicated by p<0.05.

3.2.1.2.2 Dunnett’s Comparison – N-100 Series -Acidic Groups

The increasing temperature of oxidation also leads to a significant increase in the number of acidic surface groups compared to the control S-50-9/100/25-00. There is also a significant difference between those oxidised at lower temperatures (50 or 70 °C) and those oxidised near reflux (90 °C) as seen from the results of Dunnett’s comparison test.
3.2.1.3  Statistical Analysis of Boehm Titration Results for N-100 Series - Carboxyl Groups

3.2.1.3.1  ANOVA– N-100 Series - Carboxyl Groups

The results of the ANOVA showed there was a significant difference (p<0.05) in the number of carboxyl groups found on the surface of the oxidised and non-oxidised control activated carbon S-50-9/100/25-00.

3.2.1.3.2  Dunnett’s Comparison – N-100 Series - Carboxyl Groups

The results of Dunnett’s comparison show that there is no significant difference between the number of carboxyl surface groups found for S-50-9/100/25-00 and N-100-50-2 and N-100-70-2 as indicated by the confidence interval levels including zero. However, there is a significant difference between S-50-9/100/25-00 and N-100-90-2 as indicated by the confidence intervals for carboxyl groups of N-100-90-2 not including zero.

3.2.1.4  Statistical Analysis of N-100 Series - Lactonic Groups

3.2.1.4.1  ANOVA – N-100 Series – Lactonic Groups

The ANOVA of the number of lactonic surface groups revealed that there was a significant increase (p<0.05) in the number of lactonic groups in the oxidised activated carbons in comparison to the non-oxidised control S-50-9/100/25-00.

3.2.1.4.2  Dunnett’s Comparison - N-100 Series – Lactonic Groups

The results of the Dunnett’s comparison agreed with the ANOVA findings, in that the number of lactonic groups after oxidation was shown to be significantly greater than the number found for the non-oxidised control S-50-9/100/25-00.
3.2.1.5 Statistical Analysis of N-100 Series - Phenolic Groups

3.2.1.5.1 ANOVA of N-100 Series – Phenolic Groups

The results of the ANOVA analysis of the number of phenolic surface groups found after oxidation at 50, 70 and 90 °C show that there is a significant decrease in the number of phenolic groups present on the activated carbons which have been oxidised with nitric acid when compared to the non-oxidised control S-50-9/100/25-00.

3.2.1.5.2 Dunnett’s Comparison – N-100 Series – Phenolic Groups

The Dunnett’s comparison results revealed that the number of phenolic groups significantly decreased as the temperature at which oxidation was performed increased when compared to the non-oxidised control S-50-9/100/25-00.

3.2.2 Results of Mass Titrations - N-100 Series

![Figure 3.2 Plot of pH PZC experiment for N-100-50-2](image-url)

Figure 3.2 Plot of pH\textsubscript{PZC} experiment for N-100-50-2
Figure 3.3  Plot of pH\textsubscript{PZC} experiment for N-100-70-2

Figure 3.4  Plot of pH\textsubscript{PZC} experiment for N-100-90-2
The results of the point of zero charge experiments for the nitric acid oxidised NOVACARBS are shown in Figures 3.2 - 3.5. As the temperature at which oxidation was performed was increased, the pH$_{PZC}$ decreased. The mean pH$_{PZC}$ values ± standard deviation for oxidised S-50-9/100/25-00 (N-100-50-2, N-100-70-2 and N-100-90-2) were found to be $5.87 \pm 0.13$, $5.80 \pm 0.10$ and $3.67 \pm 0.18$ respectively. This confirms the results of the Boehm titrations where the increase in temperature of oxidation corresponds to an increase in the total number of acidic surface functional groups and a decrease in the number of basic groups. To determine if the change in pH$_{PZC}$ were statistically significant from the non-oxidised control S-50-9/100/25-00 ANOVA and Dunnett’s comparison tests were performed on the mass titration data.
3.2.2.1 ANOVA – N-100 Series Mass Titrations

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<tr>
<td>Total</td>
<td>11</td>
<td>61.285</td>
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</table>

S = 0.1346   R-Sq = 99.76%   R-Sq(adj) = 99.67%
Pooled Standard Deviation = 0.135

From the results of the ANOVA of the mass titration results it was shown that oxidation with nitric acid caused a significant reduction in pH\textsubscript{PZC} in comparison to the non-oxidised S-50-9/100/25-00.

3.2.2.2 Dunnett's Comparisons– N-100 Series Mass Titrations

Family error rate = 0.05
Individual error rate = 0.0205
Critical value = 2.88
Control = S-50-9/100/25-00

Intervals for treatment mean minus control mean

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<tr>
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<td>N-100-50-2</td>
<td>-4.35</td>
<td>-4.04</td>
<td>-3.72</td>
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<tr>
<td>N-100-70-2</td>
<td>-4.43</td>
<td>-4.11</td>
<td>-3.79</td>
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<tr>
<td>N-100-90-2</td>
<td>-6.56</td>
<td>-6.24</td>
<td>-5.92</td>
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</table>

The results of the Dunnett’s comparison agree with the results of the ANOVA of the mass titration results, the pH\textsubscript{PZC} values were found to be significantly lower than the non-oxidised control S-50-9/100/25-00. The values for N-100-50-2 and N-100-70-2 were very similar and the values for N-100-90-2 were significantly lower which was consistent with the Boehm titration results (Table 3.2).
3.2.3 Results of FTIR Spectroscopy – N-100 Series

From Figures 3.6a and b the effect of increasing the temperature at which oxidation takes place results in a shift in the -OH peak at 3200 cm$^{-1}$ to lower wavenumber. There also
appears to be a reduction in both the peak signal and resolution associated with aliphatic C-H \textit{str} (2950 – 2850 cm$^{-1}$). This suggests that the aliphatic groups are amongst those oxidised by nitric acid. There is also the development of a broad peak at 3147 cm$^{-1}$ (aromatic C-H \textit{str}).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.6c.png}
\caption{Plot of FTIR for N-100 Series (2000-400 cm$^{-1}$)}
\end{figure}

Figure 3.6c shows that at lower wavenumbers (2000 - 450 cm$^{-1}$) the disappearance of both aliphatic and alkene C-H \textit{str} peaks (1458 and 1435 cm$^{-1}$ respectively) and aliphatic C-H \textit{def} peaks (1340 and 1319 cm$^{-1}$) again suggests that these groups are among those oxidised with nitric acid. The intensity of the –COO$^-$ \textit{sym str} at 1384 cm$^{-1}$ reduces with the emergence of a side peak at 1400 cm$^{-1}$ (carboxyl). After oxidation at 50 °C the peak at 1074 cm$^{-1}$ C-O \textit{str} becomes more pronounced and the phenol C-H \textit{oop def} found at 1115 cm$^{-1}$ disappears from the N-100-70-2 and N-100-90-2 plots. The plots of both N-100-70-2 and N-100-90-2 show an intense narrow peak at 669 cm$^{-1}$ which is indicative of -O-H and two smaller peaks at 659 and 652 cm$^{-1}$ which are proposed as O-H peaks (Lua and Yang, 2004). These peaks form as a result of the formation of more carboxylic groups upon oxidation.

The phenolic peaks O-H \textit{def} (1340 cm$^{-1}$) reduce upon oxidation in agreement with the Boehm titration results (Table 3.2).
3.2.4 Results of Secondary Ion Mass Spectrometry

From the positive static SIMS Table 3.4A the fragments emitted from the surface included alkyl fragments (CₙH₂n₊₁⁺) from CH₃⁺, to C₄H₁₇⁺, alcohols (CₙH₂n₊₁O⁻) from CH₂OH⁻ to C₇H₁₅OH⁺ and carboxylic acids (CₙH₂n-1O⁺), although it was not possible to distinguish between the alcohol and carboxylic acid fragments from 45 m/z upwards. However the presence of carboxylic acids is assumed as there is a peak at 44 m/z corresponding to CO₂⁻. C₆H₅⁺ fragment was observed at 77 m/z indicating that there were indeed 6 membered aromatic moieties at the surface. Sodium was also suspected to be present at the surface, but upon oxidation the peak ratio with C₂⁺ dramatically increased, thereby suggesting that the peak at 23 m/z may in fact be a doubly charged fragment i.e. C(OH)OH²⁺.

The results of the static SIMS of the negative ion fragments (Table 3.4B and Figure 3.7b) revealed the presence of O⁻ and OH⁻ which increased upon oxidation, indicating an increase in the number of oxygen containing surface groups, presumably carboxylic and lactonic moieties as indicated from the Boehm titrations. Fragments from the polyaromatic structure such as the edge fragments (C₂H⁻) and those from within the polyaromatic ring structure which are not bound to hydrogen (C₂⁻) were observed. The ratio of C₂H⁻/C₂⁻ was found to decrease upon oxidation indicating a possible reduction in the size of the polyaromatic networks after oxidation. This is supported by an increase in alkyl groups fragments found after oxidation at 90 °C, indicating that the aromatic structure of the surface has been oxidised and destroyed by the nitric acid.
Figure 3.7a  Results of positive static SIMS analysis of N-100-90-2

Figure 3.7b  Results of negative static SIMS analysis of N-100-90-2
Figure 3.7c  Results of higher ion dose SIMS analysis of N-100-90-2

The higher intensity analysis of the negative fragments revealed a drop in the values seen in Table 3.4C. It may be noted that the O$^-$ and OH$^-$ fragment intensities dropped dramatically from 2.44 and 1.19 to 0.45 and 0.16 respectively for N-100-90-2, indicating that the vast majority of the oxidation takes place in the top 10-20 nm of the surface.
<table>
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<tr>
<th>m/z=</th>
<th>C⁺</th>
<th>CH⁺</th>
<th>CH₂⁺</th>
<th>CH₃⁺</th>
<th>ΣCH₅⁺</th>
<th>C₂H⁺</th>
<th>C₂H₂⁺</th>
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<tr>
<td>Carbon</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>15</td>
<td>12 to 15</td>
<td>25</td>
<td>26</td>
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<tr>
<td>S-50-9/100/25-00</td>
<td>0.13</td>
<td>0.13</td>
<td>0.40</td>
<td>2.80</td>
<td>3.47</td>
<td>0.13</td>
<td>1.20</td>
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<tr>
<td>N-100-90-2</td>
<td>1.00</td>
<td>1.00</td>
<td>3.00</td>
<td>23.00</td>
<td>28.00</td>
<td>0.00</td>
<td>13.00</td>
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<table>
<thead>
<tr>
<th>m/z=</th>
<th>C₃H₃⁺</th>
<th>C₂H₄⁺</th>
<th>C₂H₅⁺</th>
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<tr>
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<td>29</td>
<td>23</td>
<td>39</td>
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<td>S-50-9/100/25-00</td>
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<td>N-100-90-2</td>
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<td>80.00</td>
<td>12.00</td>
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**A Positive SIMS Peaks (Peak Intensity Relative to C²⁺ = 1.0)**

<table>
<thead>
<tr>
<th>m/z=</th>
<th>C⁻</th>
<th>CH⁻</th>
<th>CH₂⁻</th>
<th>O⁻</th>
<th>OH⁻</th>
<th>C₂H⁻</th>
<th>C₂H₂⁻</th>
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<td>12</td>
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<td>14</td>
<td>16</td>
<td>17</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>S-50-9/100/25-00</td>
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<td>0.33</td>
<td>0.05</td>
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<td>N-100-90-2</td>
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<td>0.10</td>
<td>2.44</td>
<td>1.19</td>
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**B Negative SIMS Peaks (Peak Intensity Relative to C²⁻ = 1.0)**

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<th>CH₂⁻</th>
<th>O⁻</th>
<th>OH⁻</th>
<th>C₂H⁻</th>
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<tbody>
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<td>12</td>
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<td>14</td>
<td>16</td>
<td>17</td>
<td>25</td>
<td>26</td>
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<tr>
<td>S-50-9/100/25-00</td>
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<td>0.11</td>
<td>0.01</td>
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<td>0.10</td>
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<td>N-100-90-2</td>
<td>0.13</td>
<td>0.19</td>
<td>0.01</td>
<td>0.45</td>
<td>0.16</td>
<td>0.92</td>
<td>1.08</td>
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</table>

**C Higher Intensity Ion (Peak Intensity Relative to C₂⁻ = 1.0)**

Table 3.4 Results of SIMS experiment for S-50-9/100/25-00 and N-100-90-2
| Sample          | \(O^-\) | \(C_2^-\) | \(C_4^-\) | \(O^- / C_2^-\) | \(O^- / C_4^-\) |
|----------------|---------|-----------|-----------|----------------|----------------|---|
| S-50-9/100/25-00 | 21500   | 42300     | 2000      | 0.51           | 10.75          |
| N-100-90-2      | 19500   | 8000      | 500       | 2.44           | 39.00          |

Table 3.5 Relationship between oxidised and non-oxidised samples

Comparing the ratio of \(O^-/C_2^-\) or \(O^-/C_4^-\) (Table 3.5) the ratio of intensities for N-100-90-2 was far greater, when compared the ratio for the non-oxidised S-50-9/100/25-00. The \(C_2^-\) and \(C_4^-\) represents carbons in the polyaromatic ring structure with no hydrogen attached. This indicates that oxidation took place at the surface of the activated carbons.

3.2.5 Results of Scanning Electron Microscopy

SEM images were taken of the nitric acid oxidised activated carbon beads (x 250 magnification) and of the bead surfaces (x 15,000 magnification) to assess any changes which had occurred during the oxidation process.

3.2.5.1 N-100 Series

From the results of the scanning electron microscopy (Figures 3.8-3.10), the surfaces of the activated carbons oxidised with nitric acid show the presence of small areas of damage visible in the higher magnification images (Figure 3.8b, 3.9b and 3.10b and c) where the underlying porosity can be observed (Figure 3.10b). They also display some semblance of roughness or degradation at the surface (Figure 3.8b and 3.9b) when compared to the surface of the non-oxidised S-50-9/100/25-00 (Figure 2.12b), showing that oxidation does have an effect on the surface topography.
Figure 3.8  SEM image of a) N-100-50-2 beads (x 250 Magnification) and
b) Surface of a N-100-50-2 bead (x 15,000 Magnification)

Figure 3.9  SEM Image of a) N-100-70-2 beads (x 250 Magnification) and b)
surface of a N-100-70-2 bead (x 15,000 Magnification)
3.2.6 Results of Energy Dispersive Spectroscopy by X-ray

After analysis of the oxidised beads by SEM, EDX was performed to determine the amount of carbon and oxygen present at the surface of the activated carbons and to assess the effect of oxidation.
From the results of the EDX (Figure 3.11) only carbon and oxygen were found at the surface. The oxygen and carbon peaks reached a maximum when oxidation was performed at 70 °C. However when the percentage of each element is determined (Table 3.5) the trend is a gradual increase in the O content reaching a maximum at 90 °C. The ratio of O/C was plotted and an almost linear increase in O/C was observed as the temperature of oxidation was increased (Figure 3.12). This follows a similar trend observed for the Boehm titrations where the number of acidic groups increased with increasing oxidation temperature.
Table 3.6  Results of EDX for N-100 Series

3.2.7  Results of Bead Size Analysis

3.2.7.1  N-100 Series

To determine the mean bead size for the oxidised NOVACARBs, the results from the bead size distribution (Figure 3.13a-c and Figure 2.18) were analysed. The number of beads analysed per sample were S-50-9/100/25-00 (n = 95), N-100-50-2 (n = 122), N-100-70-2 (n = 120) and N-100-90-2 (n = 123).
Figure 3.13a  Plot of Bead Size Distribution for N-100-50-2

Figure 3.13b  Plot of Bead Size Distribution for N-100-70-2
The mean bead size was shown to decrease after oxidation at increasing temperatures however the variability in the range of particle sizes was similar throughout all the
samples. The cumulative frequency of the bead sizes was plotted to determine if there were an observable changes in the distribution of the bead particle size (Figure 3.14), however, little difference was observed.

![Cumulative frequency of N-100 Series NOVACARB bead diameter](image)

Figure 3.14 Cumulative frequency of N-100 Series NOVACARB bead diameter

The mean bead size were analysed using a one-way ANOVA and Dunnett’s comparison test to determine if there was a significant change in the bead size upon oxidation at different temperatures, using non-oxidised S-50-9/100/25-00 as a control and if there were any significant differences within the oxidised group of samples.

### 3.2.7.1.1 One-way ANOVA N-100 Series Bead Size

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<td>86487</td>
<td>190</td>
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<tr>
<td>Total</td>
<td>459</td>
<td>89469</td>
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<td></td>
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</tr>
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</table>

S = 13.77  R-Sq = 3.33%  R-Sq(adj) = 2.70%

Pooled Standard Deviation = 13.77
Unlike the mean bead size plots (Figures 3.13a-c) and the bead size distribution plot (Figure 3.14), a significant difference was observed between the oxidised and non-oxidised samples ($p < 0.05$). Therefore oxidation with 20% HNO$_3$ at temperatures up to 90°C for 2 hours was shown to decrease the mean bead size of the oxidised S-50-9/100/25-00 activated carbons.

### 3.2.7.1.2 Dunnett's Comparisons – N-100 Series Bead Size

Family error rate = 0.05  
Individual error rate = 0.0199  
Critical value = 2.34  
Control = S-50-9/100/25-00

Intervals for treatment mean minus control mean

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<th>Upper</th>
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<td>1.85</td>
</tr>
<tr>
<td>N-100-70-2</td>
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<td>-3.80</td>
<td>0.62</td>
</tr>
<tr>
<td>N-100-90-2</td>
<td>-11.62</td>
<td>-7.22</td>
<td>-2.82</td>
</tr>
</tbody>
</table>

From the results of the bead size analysis, the mean bead size is shown to decrease as the temperature of nitric acid oxidation is increased, from 35.5 µm for S-50-9/100/25-00, to 33, 32 and finally 28 µm when oxidised at 90°C (N-100-90-2). The values for N-100-50-2 and N-100-70-2 are very similar to the control S-5-90/100/25-00. However the mean bead size observed for N-100-90-2 is significantly smaller than the control S-50-9/100/25-00, as indicated by the confidence interval levels not including zero.

### 3.2.8 Results of Bulk Density Measurements

#### 3.2.8.1 N-100 Series

The bulk density of the N-100 series was shown to increase upon oxidation at increasing temperature compared to the non-oxidised S-50-9/100/25-00, reaching a maximum when
the beads were oxidised at 70 °C (Figure 3.15). This increase in bulk density can be attributed to the increase in surface groups caused by oxidation as seen in Figure 3.0. However, when oxidation is performed at 90 °C the bulk density then decreases. The reason for this decrease could be as a result of the increase in surface functional groups during oxidation however this is also accompanied by degradation of the beads at a greater rate than observed for N-100-50-2 and N-100-70-2, as observed by the decrease in mean bead size shown in (Figure 3.13c). To determine if the changes in bulk density were significantly different from the non-oxidised S-50-9/100/25-00 or between the oxidised activated carbons, ANOVA and Dunnett’s comparison were performed.

![Figure 3.15](image)

**Figure 3.15**  Plot of bulk density of N-100 series NOVACARBs
(Mean (n=10) ± Standard Deviation)

The bulk density of the nitric acid oxidised activated carbons increased to a maximum at 70 °C (0.72 g/cm³), then decreased to 0.702 g/cm³ at 90 °C.
3.2.8.1 One-way ANOVA - N-100 Series Bulk Density

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<tr>
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</tbody>
</table>

\[ S = 0.004233 \quad \text{R-Sq} = 95.83\% \quad \text{R-Sq(adj)} = 95.48\% \]

Pooled Standard Deviation = 0.004

From the ANOVA results it is observed that there is a significant difference between the non-oxidised S-50-9/100/25-00 and the oxidised activated carbons, as shown by \( p<0.05 \).

3.2.8.2 Dunnett's Comparisons - N-100 Series Bulk Density

Family error rate = 0.05
Individual error rate = 0.0192
Critical value = 2.45
Control = S-50-9/100/25-00

Intervals for treatment mean minus control mean

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<th>Upper</th>
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<td>0.037</td>
<td>0.041</td>
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<tr>
<td>N-100-70-2</td>
<td>0.048</td>
<td>0.053</td>
<td>0.057</td>
</tr>
<tr>
<td>N-100-90-2</td>
<td>0.030</td>
<td>0.035</td>
<td>0.039</td>
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</table>

From the results of Dunnett’s comparison it is observed that there is a significant increase in the bulk density caused by oxidation at 50, 70 or 90 °C from the control activated carbon S-50-9/100/25-00 as indicated by the confidence interval levels not containing zero.
3.2.9 Results of SAXS Experiments – N-100 Series

The SAXS results for the N-100 series are shown in Table 3.7, the sections 1 - 4, correspond to sections of the curve from low q (1) to large q (4). The slopes are shown to change with an increase in oxidation temperature. Section 1 representing the larger scattering structures 0.01 to 0.03 Å⁻¹ (100 to 33.3 Å) was found to increase with increasing temperature, sections 2 and 4 representing the scattering structures of 25 to 11 Å and 3.3 to 1.25 Å are shown to decrease with increasing temperature.

![SAXS plot of N-100-50-2](image)

**Figure 3.16a** SAXS plot of N-100-50-2
Figure 3.16b  SAXS plot of N-100-70-2

Figure 3.16c  SAXS plot of N-100-90-2
From the Boehm titration results for the N-125 series (Figure 3.17 and Table 3.8), it is shown that an increase in the temperature at which the nitric acid oxidation was performed shows an increase in the acidic groups (carboxyl and lactonic) from 0.329 and 0.644 at 50
°C to 0.945 and 1.291 meq/g at 90 °C, this is accompanied by a decrease in the number of
basic and phenolic type groups from 0.469 and 0.063 to 0.285 and 0 at 90 °C.

![Figure 3.17 Distribution of functional groups on the surface of nitric acid oxidised
N-125 Series (Mean a (n=3) ± Standard Deviation)](image)

**Table 3.8 Results of Boehm titrations for nitric acid oxidised N-125 series
(Mean a (n=3) ± Standard Deviation)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total</th>
<th>Basic</th>
<th>Acidic</th>
<th>Carboxyl</th>
<th>Lactonic</th>
<th>Phenolic</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-50-9/125-00</td>
<td>1.540</td>
<td>0.783</td>
<td>0.757</td>
<td>0.364</td>
<td>0.178</td>
<td>0.215</td>
</tr>
<tr>
<td></td>
<td>± 0.045</td>
<td>± 0.033</td>
<td>± 0.030</td>
<td>± 0.078</td>
<td>± 0.124</td>
<td>± 0.101</td>
</tr>
<tr>
<td>N-125-50-2</td>
<td>1.515</td>
<td>0.469</td>
<td>1.045</td>
<td>0.329</td>
<td>0.644</td>
<td>0.063</td>
</tr>
<tr>
<td></td>
<td>± 0.034</td>
<td>± 0.032</td>
<td>± 0.010</td>
<td>± 0.014</td>
<td>± 0.063</td>
<td>± 0.081</td>
</tr>
<tr>
<td>N-125-70-2</td>
<td>1.733</td>
<td>0.382</td>
<td>1.352</td>
<td>0.500</td>
<td>0.851</td>
<td>0.021</td>
</tr>
<tr>
<td></td>
<td>± 0.048</td>
<td>± 0.029</td>
<td>± 0.039</td>
<td>± 0.008</td>
<td>± 0.062</td>
<td>± 0.072</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>2.396</td>
<td>0.285</td>
<td>2.112</td>
<td>0.945</td>
<td>1.291</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>± 0.076</td>
<td>± 0.072</td>
<td>± 0.025</td>
<td>± 0.023</td>
<td>± 0.178</td>
<td>± 0.179</td>
</tr>
</tbody>
</table>
3.3.1.1 Statistical Analysis of N-125 Series – Basic Groups

3.3.1.1.1 One Way ANOVA - N-125 Series – Basic Groups

From the results of the ANOVA there is a significant decrease in the number of basic surface groups for the oxidised activated carbons compared to the control non-oxidised activated carbon (S-50-9/125-00) as indicated by the p<0.05.

3.3.1.1.2 Dunnett’s Comparison- N-125 Series – Basic Groups

The results of Dunnett’s comparison show that there is a significant reduction in the number of basic surface groups between all the oxidised activated carbons (N-125-50-2, N-125-70-2 and N-125-90-2) and the non-oxidised control S-50-9/125-00 as indicated by the confidence interval levels not including zero.

3.3.1.2 Statistical Analysis of N-125 Series – Acidic Groups

3.3.1.2.1 One Way ANOVA - N-125 Series – Acidic Groups

The results of the ANOVA revealed that there is a significant increase (p<0.05) between the number of acidic functional groups on the surface of the oxidised and non-oxidised activated carbons.

3.3.1.2.2 Dunnett’s Comparison - N-125 Series – Acidic Groups

The results of Dunnett’s comparison between S-50-9/125-00 and N-125-50-2, N-125-70-2 and N-125-90-2 revealed that there was a significant increase in the number of acidic surface groups on all the oxidised activated carbons in comparison to the number on the surface of the non-oxidised S-50-9/125-00.
3.3.1.3 Statistical Analysis of N-125 Series – Carboxyl Groups

3.3.1.3.1 One Way ANOVA - N-125 Series – Carboxyl Groups

The ANOVA results showed that there was a significant difference between the number of carboxyl groups found on the surface of N-125-50-2, N-125-70-2 and N-125-90-2 and S-50-9/125-00 as revealed by p<0.05.

3.3.1.3.2 Dunnett’s Test - N-125 Series – Carboxyl Groups

The results of Dunnett’s comparison of the carboxyl surface groups between the oxidised and non-oxidised N-125 series, revealed that there is no significant difference between the number of carboxyl surface groups on S-50-9/125-00 and N-125-50-2. However, there is a significant increase in the number of carboxyl surface groups between S-50-9/125-00 and N-125-70-2 and N-125-90-2.

3.3.1.4 Statistical Analysis of N-125 Series – Lactonic Groups

3.3.1.4.1 One Way ANOVA - N-125 Series – Lactonic Groups

The ANOVA results showed that the number of lactonic groups on the surface of the activated carbons after oxidation was significantly greater than those on the surface of the non-oxidised control S-50-9/125-00.

3.3.1.4.2 Dunnett’s Comparison – N-125 Series – Lactonic Groups

The results of the Dunnett’s comparison tally with the ANOVA results showing that as nitric acid oxidation is performed at either 50, 70 or 90 °C, there is a significant increase in the number of lactonic groups found in comparison to the non-oxidised control S-50-9/125-00.
3.3.1.5 Statistical Analysis of N-125 Series – Phenolic Groups

3.3.1.5.1 One Way ANOVA - N-125 Series – Phenolic Groups

The results of the ANOVA analysis revealed that although there is a decrease in the number of phenolic groups upon oxidation at 50, 70 or 90 ºC, the decrease was found not to be significant when compared to the non-oxidised control S-50-9/125-00.

3.3.1.5.2 Dunnett’s Comparison – N-125 Series – Phenolic Groups

The results of Dunnett’s comparison agree with the results found for the ANOVA analysis, that there is no significant decrease in the number of phenolic groups upon oxidation with nitric acid at 50, 70 or 90 ºC when compared to the non-oxidised control S-50-9/125-00.

3.3.2 Results of Mass Titrations

3.3.2.1 N-125 Series

The results of the point of zero charge experiments for the nitric acid oxidised NOVACARBs are shown in Figures 3.18 - 3.21. For oxidised S-50-9/125-00 (N-125-50-2, N-125-70-2 and N-125-90-2) the mean pH$_{PZC}$ values were found to be 6.42 ± 0.17, 5.10 ± 0.30 and 3.58 ± 0.14 respectively (Table 3.9), compared to pH$_{PZC}$ 9.99 for S-50-9/125-00. The decrease in the pH$_{PZC}$ with increasing oxidation temperature was found to follow a linear trend (Figure 3.21).
Figure 3.18  Plot of pH\textsubscript{PZC} experiment for N-125-50-2

Figure 3.19  Plot of pH\textsubscript{PZC} experiment for N-125-70-2
Figure 3.20  Plot of $pH_{PZC}$ experiment for N-125-90-2

Figure 3.21  Plot of mean $pH_{PZC}$ of nitric acid oxidised N-125 series
(Mean Value (n=6) ± Standard Deviation)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$pH_{PZC}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-125-50-2</td>
<td>6.42 ± 0.17</td>
</tr>
<tr>
<td>N-125-70-2</td>
<td>5.10 ± 0.30</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>3.58 ± 0.14</td>
</tr>
</tbody>
</table>

Table 3.9  Results of Mass Titrations for N-125 Series
These mass titration results correspond with the results previously shown for Boehm titrations, where an increase in the number of carboxyl and lactonic type groups was seen as the temperature of oxidation was increased. This was accompanied by a decrease in the number of basic and phenolic groups.

3.3.2.2 Statistical Analysis – N-125 Series- Mass Titrations

3.3.2.2.1 ANOVA – N-125 Series Mass Titrations

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>67.17</td>
<td>22.389</td>
<td>757.44</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>0.24</td>
<td>0.0296</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>67.41</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.1719  R-Sq = 99.65%  R-Sq(adj) = 99.52%
Pooled Standard Deviation = 0.172

From the results of ANOVA of the mass titrations for N-125 Series activated carbons, it was found that the $pH_{PZC}$ values for the oxidised carbons (N-125-50-2, N-125-70-2 and N-125-90-2) were significantly lower than that found for the non-oxidised S-50-9/125-00.

3.3.2.2.2 Dunnett's Comparisons – N-125 Series- Mass Titration

Family error rate = 0.05
Individual error rate = 0.0205
Critical value = 2.88
Control = S-50-9/125-00
Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-125-70-2</td>
<td>-5.2609</td>
<td>-4.8567</td>
<td>-4.4524</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>-6.8142</td>
<td>-6.4100</td>
<td>-6.0058</td>
</tr>
</tbody>
</table>

The results of the Dunnett’s comparison were in agreement with the ANOVA results which showed a significant decrease in the pH_{PZC} after oxidation with nitric acid. The mass titration results were similar to the Boehm titration results (Table 3.7) where an almost linear increase in acidic groups was observed (Figure 3.16).

### 3.3.3 Results of Fourier Transform Infrared Spectroscopy

#### 3.3.3.1 N-125 Series

![Figure 3.22a Plot of FTIR Results for N-125 Series (4000–400 cm⁻¹)](image_url)
The increasing temperature at which oxidation is performed on the N-125 Series activated carbons causes a broadening in the –OH peak at 3437 cm\(^{-1}\), the shoulder on the same peak is shifted to a higher wavenumber in the oxidised samples. The aliphatic C-H peaks (3000-2850 cm\(^{-1}\)) remain unaffected after oxidation (Figure 3.22b).
The region 2000-400 cm$^{-1}$ after oxidation at 50 and 70 °C reveals the presence of two or three peaks at 1734 – 1718 cm$^{-1}$, these peaks C=O from carbonyl (Lua and Yang, 2004) are also present in N-125-90-2 although the intensity is far lower. The peak at 1635 cm$^{-1}$ increased in intensity when oxidation is performed at 70 and 90 °C. The aliphatic C-H peaks at 1460 disappear at 90 °C, possibly indicating the conversion of the aliphatic groups. The alkene C-H $oop$ def remains constant throughout all the N-125 Series. The aromatic C-H double peak at 798 cm$^{-1}$ is reduced to a single peak when oxidation is performed at 70 or 90 °C.
3.3.4 Results of Secondary Ion Mass Spectrometry

From the positive static SIMS Table 3.8A the fragments emitted from the surface included alkyl fragments \((C_nH_{2n+1}^+)\) from \(CH_3^+\), to \(C_5H_{11}^+\), alcohols \((C_nH_{2n+1}O^-)\) from \(CH_2OH^-\) to \(C_4H_9OH^-\) and carboxylic acids \((C_nH_{2n-1}O^+)\), although it was not possible to distinguish the alcohol fragment and carboxylic acid fragments from 45 m/z upwards.

\(C_6H_5^+\) fragment was observed at 77 m/z indicating that there were indeed aromatic moieties at the surface. Sodium was also suspected to be present at the surface, but upon oxidation the peak ratio with \(C_2^+\) dramatically increased, thereby suggesting that the peak at 23 m/z may in fact be a doubly charged fragment i.e. \(C(OH)OH^{2+}\).

![Figure 3.23a Results of positive static SIMS analysis of N-125-90-2](image)

Figure 3.23a  Results of positive static SIMS analysis of N-125-90-2
Figure 3.23b Results of negative static SIMS analysis of N-125-90-2

Figure 3.23c Results of higher ion dose SIMS analysis of N-125-90-2
### Positive SIMS Peaks (Peak Intensity Relative to $C_2^+ = 1.0$)

<table>
<thead>
<tr>
<th>m/z=</th>
<th>$C^+$</th>
<th>$CH^+$</th>
<th>$CH_2^+$</th>
<th>$CH_3^+$</th>
<th>$\Sigma CH_y^+$</th>
<th>$C_2H^+$</th>
<th>$C_2H_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>15</td>
<td>12 to 15</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>S-50-9/125-00</td>
<td>0.14</td>
<td>0.14</td>
<td>0.00</td>
<td>0.29</td>
<td>0.57</td>
<td>0.29</td>
<td>0.71</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>1.54</td>
<td>1.54</td>
<td>3.08</td>
<td>14.62</td>
<td>20.77</td>
<td>1.34</td>
<td>6.15</td>
</tr>
</tbody>
</table>

### Negative SIMS Peaks (Peak Intensity Relative to $C_2^- = 1.0$)

<table>
<thead>
<tr>
<th>m/z=</th>
<th>$C_2H_3^+$</th>
<th>$C_2H_4^+$</th>
<th>$C_2H_5^+$</th>
<th>$Na^+$</th>
<th>$C_3H_3^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>27</td>
<td>28</td>
<td>29</td>
<td>23</td>
<td>39</td>
</tr>
<tr>
<td>S-50-9/125-00</td>
<td>3.71</td>
<td>2.14</td>
<td>3.43</td>
<td>1.14</td>
<td>5.00</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>38.56</td>
<td>12.31</td>
<td>44.62</td>
<td>40.00</td>
<td>24.62</td>
</tr>
</tbody>
</table>

### Higher Intensity Ion SIMS (Peak Intensity Relative to $C_2^- = 1.0$)

<table>
<thead>
<tr>
<th>m/z=</th>
<th>$C^+$</th>
<th>$CH^+$</th>
<th>$CH_2^+$</th>
<th>$O^+$</th>
<th>$OH^-$</th>
<th>$C_2H^+$</th>
<th>$C_2H_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>16</td>
<td>17</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>S-50-9/125-00</td>
<td>0.10</td>
<td>0.17</td>
<td>0.02</td>
<td>0.36</td>
<td>0.11</td>
<td>0.61</td>
<td>0.27</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>0.16</td>
<td>0.22</td>
<td>0.05</td>
<td>0.85</td>
<td>0.48</td>
<td>0.39</td>
<td>0.63</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>m/z=</th>
<th>$C^+$</th>
<th>$CH^+$</th>
<th>$CH_2^+$</th>
<th>$O^+$</th>
<th>$OH^-$</th>
<th>$C_2H^+$</th>
<th>$C_2H_2^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>16</td>
<td>17</td>
<td>25</td>
<td>26</td>
</tr>
<tr>
<td>S-50-9/125-00</td>
<td>0.10</td>
<td>0.11</td>
<td>0.00</td>
<td>0.24</td>
<td>0.09</td>
<td>0.72</td>
<td>0.39</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>0.09</td>
<td>0.09</td>
<td>0.01</td>
<td>0.23</td>
<td>0.08</td>
<td>0.63</td>
<td>1.23</td>
</tr>
</tbody>
</table>

Table 3.10 Results of SIMS experiment for S-50-9/125-00 and N-125-90-2
The results of the static SIMS of the negative ion fragments Table 3.10B and Figure 3.23b revealed the presence of O$^-$ and OH$^-$ which increased upon oxidation, indicating an increase in the number of oxygen containing surface groups presumably carboxylic and lactonic moieties as indicated from the Boehm titrations. Fragments from the polyaromatic structure such as the edge fragments (C$_2$H$^-$) and those from within the polyaromatic ring structure which are not bound to hydrogen (C$_2^-$) were observed. The ratio of C$_2$H$^-/C_2^-$ was found to decrease upon oxidation indicating a possible reduction in the size of the polyaromatic networks after oxidation. This is supported by the increase in alkyl groups fragments found after oxidation at 90 °C, indicating that the aromatic structure of the surface has been oxidised and disrupted by the nitric acid.

At a higher intensity the results of the negative ion fragments (Table 3.10C and Figure 3.23c) revealed that the peak intensities relative to C$_2^-$ for O-, OH- decrease dramatically from 0.85 and 0.23 to 0.48 and 0.08 respectively for N-125-90-2, indicating that oxidation only appears to be predominately occurring in the uppermost 1-2 nm of the surface.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Counts per second (cps)</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O$^-$</td>
<td>C$_2^-$</td>
</tr>
<tr>
<td>S-50-9/125-00</td>
<td>6500</td>
<td>18000</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>7000</td>
<td>8200</td>
</tr>
</tbody>
</table>

Table 3.11 Ratio of O/C$_2^-$ and O/C$_4^-$ for S-50-9/125-00 and N-125-90-2

Comparison of the peak intensity of O$^-$ relative to the C$_n^-$ fragments from within the aromatic structure (Table 3.11) revealed that when compared to S-50-9/125-00 non-oxidised sample, the N-125-90-2 sample proved that oxidation of the surface had occurred by the increased O/C$_2^-$ and O/C$_4^-$ from 0.36 to 0.85 and 8.13 to 14 respectively.
3.3.5 Results of Scanning Electron Microscopy

The nitric acid oxidised activated carbons were examined using SEM. The bead surfaces were examined to determine any changes in the surface morphology, due the oxidation process.

3.3.5.1 N-125 Series

The SEM analysis revealed that the surfaces of the N-125 Series activated carbons were similar to those of the N-100 Series, with areas of the surface where oxidation and degradation has occurred (Figure 3.24b, 3.24b and 3.26b).

Figure 3.24 SEM Image of a) N-125-50-2 beads (x 250 Magnification) and b) Surface of a N-125-50-2 bead (x 15,000 Magnification)

Figure 3.25 SEM Image of a) N-125-70-2 beads (x 250 Magnification) and b) Surface of a N-125-70-2 bead (x 15,000 Magnification)
3.3.6 Results of Energy Dispersive Spectroscopy by X-ray
- N-125 Series

As with the N-100 Series activated carbons, the N-125 Series from EDX analysis showed only the presence of oxygen and carbon on the surface of the beads. From the results of the EDX analysis of the oxygen and carbon peaks, the ratio of O/C ratio was plotted for the oxidised activated carbons.

Figure 3.27  Plot of C Kα and O Kα of N-125 Series Activated Carbons
From the plot of ratio of oxygen/carbon peak intensities as shown in Figure 3.28, as the temperature of nitric acid oxidation is increased the intensities increase for both C and O, however the ratio of O/C initially decreases from 0.104 to 0.092 for N-125-50-2, then reaches a maximum value at 70 °C (0.110). The O/C ratio then decreases to 0.099 for N-125-90-2.
3.3.7 Results of Bead Size Analysis - N-125 Series

From the results of the bead size analysis in Figures 3.29 and 3.30, it can be seen that there is no significant effect caused by the oxidation of nitric acids at 50, 70 or 90 °C. However if the cumulative frequency of the bead size is plotted versus the bead diameter, there is a clear difference in the distribution of diameters of N-125-90-2 beads compared to the other samples in the N-125 Series. Approximately 70 % of the N-125-90-2 bead population are less than 10 µm in diameter, whereas the bead populations of S-50-9/125-00, N-125-50-2 and N-125-70-2 have less than 30 % of beads with diameters less than 10 µm (Figure 3.31). The result of the bead size distributions were analysed using ANOVA and Dunnett’s comparison test to determine if there were statistically significant differences in the bead size for the nitric oxidised activated carbons, using S-50-9/125-00 as a control.

Figure 3.29a Plot of Bead Size Distribution for N-125-50-2

<table>
<thead>
<tr>
<th>Bead Diameter</th>
<th>Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>40</td>
<td>50</td>
</tr>
<tr>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>60</td>
<td>70</td>
</tr>
<tr>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>80</td>
<td>90</td>
</tr>
</tbody>
</table>

Histogram of N-125-50-2
Normal

Mean 14.51
StdDev 8.601
N 448
Figure 3.29b  Plot of Bead Size Distribution for N-125-70-2

Figure 3.29c  Plot of Bead Size Distribution for N-125-90-2
Figure 3.30  Plot of mean bead size distributions for N-125 Series activated carbons

Figure 3.31  Cumulative frequency of bead diameters of N-125 Series

NOVACARB’s
3.3.7.1 ANOVA of N-125 Series Bead Size

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>1111.1</td>
<td>370.4</td>
<td>3.99</td>
<td>0.008</td>
</tr>
<tr>
<td>Error</td>
<td>1349</td>
<td>125255.5</td>
<td>92.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>1352</td>
<td>126366.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 9.636  R-Sq = 0.88%  R-Sq(adj) = 0.66%
Pooled Standard Deviation = 9.636

From the ANOVA results of the bead size distributions of the N-125 series activated carbons, there were significant differences found between the control non-oxidised activated carbon S-50-9/125-00 and the nitric acid oxidised activated carbons as indicated by p<0.05.

3.3.7.2 Dunnett’s Comparison - N-125 Series Bead Size

Family error rate = 0.05
Individual error rate = 0.0187
Critical value = 2.35
Control = S-50-9/125-00

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-125-50-2</td>
<td>-3.030</td>
<td>-1.422</td>
<td>0.186</td>
</tr>
<tr>
<td>N-125-70-2</td>
<td>-0.874</td>
<td>0.858</td>
<td>2.591</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>-2.897</td>
<td>-0.948</td>
<td>1.001</td>
</tr>
</tbody>
</table>

The results of the bead size distribution revealed that there were no significant differences between the oxidised and non-oxidised activated carbons. This is in direct contrast to the results observed from the ANOVA results, which show that there are significant differences between the oxidised and non-oxidised activated carbons.
3.3.8 Results of Bulk Density Measurements - N-125 Series

The bulk density of the nitric acid oxidised activated carbons increased upon oxidation at 50 °C, from 0.609 to 0.64 g/ cm³. The bulk density was then observed to decrease upon oxidation at 70 and 90 °C from 0.62 to 0.614 g/ cm³. To determine if there was any significant differences in the bulk density of the activated carbons as a result of nitric acid oxidation, statistical analysis using ANOVA and Dunnett’s comparison was performed, using non-oxidised S-50-9/125-00 as the control.

![Plot of bulk densities of N-125 Series NOVACARBs](image)

**Figure 3.32** Plot of bulk densities of N-125 Series NOVACARBs
(Mean (n=10) ± Standard Deviation)

### 3.3.8.1 One-way ANOVA: N-125 Series Bulk Density

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>0.0057</td>
<td>0.0019</td>
<td>268.85</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>36</td>
<td>0.0002</td>
<td>0.000007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>39</td>
<td>0.0059</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.002652 R-Sq = 95.73% R-Sq(adj) = 95.37%

Pooled Standard Deviation = 0.00265

The results of the ANOVA analysis of the changes in bulk density caused by nitric acid oxidation at different temperatures, showed that there was a significant difference in the
bulk densities on the activated carbons which were oxidised N-125-50-2, N-125-70-2 and N-125-90-2, as indicated by \( p<0.05 \).

### 3.3.8.2 Dunnett's Comparisons - N-125 Series Bulk Density

Family error rate = 0.05  
Individual error rate = 0.0192  
Critical value = 2.45  
Control = S-50-9/125-00

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
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<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-125-50-2</td>
<td>0.028</td>
<td>0.031</td>
<td>0.034</td>
</tr>
<tr>
<td>N-125-70-2</td>
<td>0.008</td>
<td>0.011</td>
<td>0.014</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>0.002</td>
<td>0.005</td>
<td>0.008</td>
</tr>
</tbody>
</table>

From the results of the Dunnett’s comparison the oxidised activated carbons displayed bulk densities significantly greater than the non-oxidised control S-50-9/125-00 in every case.

### 3.3.9 Results of SAXS Experiments - N-125 Series

The results of the SAXS experiments are shown in Table 3.13. The sections 1 to 4 correspond to low \( q \) (1) large scattering structures to high \( q \) (4) small scattering structures. Unlike the N-100 series no clear trend was observed for the scattering of N-125 series with increasing oxidation temperature. Only the slope of section 4 for the small scattering structures was seen to increase with increasing oxidation temperature, although the slope of section 2 increased until 70 °C then decreased again as the oxidation temperature was increased.
Figure 3.33  SAXS plot of N-125-50-2

Figure 3.34  SAXS plot of N-125-70-2
Figure 3.35  SAXS plot of N-125-90-2

Figure 3.36  SAXS plot of N-125-90-2-2
Table 3.13  SAXS results for N-125 Series

<table>
<thead>
<tr>
<th>Carbon</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-50-9/125-00</td>
<td>-0.96</td>
<td>-3.61</td>
<td>-0.93</td>
<td>-2.30</td>
</tr>
<tr>
<td>N-125-50-2</td>
<td>-1.06</td>
<td>-3.75</td>
<td>-0.91</td>
<td>-2.40</td>
</tr>
<tr>
<td>N-125-70-2</td>
<td>-1.01</td>
<td>-3.79</td>
<td>-0.95</td>
<td>-2.53</td>
</tr>
<tr>
<td>N-125-90-2</td>
<td>-0.98</td>
<td>-3.76</td>
<td>-0.96</td>
<td>-2.67</td>
</tr>
<tr>
<td>N-125-90-2-2</td>
<td>-0.91</td>
<td>-3.73</td>
<td>-0.91</td>
<td>-2.62</td>
</tr>
</tbody>
</table>

3.4  Discussion

3.4.1 Boehm Titrations - Discussion

Oxidation of S-50-9/100/25-00 and S-50-9/125-00 with 20 % nitric acid at 50, 70 and 90 °C, produced a series of carbons with different distributions of surface functional groups (Figures 3.0 and 3.17). The overall trend was an increase in the total number of surface groups upon increasing oxidation temperature, as the carbon structure was oxidised to form oxygen containing functional groups. There was also a decrease in the number of basic groups and phenolic type groups which were converted to carboxyl or lactonic type groups, as a significant increase in both carboxylic and lactonic surface groups was observed.

The change in surface chemistry when S-50-9/100/25-00 was oxidised at 50 and 70 °C was very similar N-100-50-2 and N-100-70-2 (Figures 3.0). This similarity in surface chemistry can also be seen from the results of the point of zero charge experiments for nitric acid oxidised NOVACARB S-50-9/100/25-00 at different temperatures (Table 3.3) and discussed in section 3.4.2 as the temperature of oxidation increased there is only a slight decrease in the pH_{PZC} from 5.87 at 50 °C to 5.80 at 70 °C. Upon oxidation at 90 °C (N-100-90-2), the number of basic and phenolic groups continued to decrease, with a significant increase in carboxyl and lactonic groups in comparison to non-oxidised S-50-9/100/25-00. This increase in acidic functional groups was also observed as a significant decrease in the pH_{PZC} to 3.67 (Table 3.3).
From the results of the Boehm titrations and the point of zero charge measurements there appears to be different mechanisms by which nitric acid oxidation affects the surface of the S-50-9/100/25-00, depending on the temperature. At temperatures up to approximately 70 °C only the external surface groups appear to be oxidised as seen from the similar distributions of surface functional groups (Figure 3.0 and Table 3.3) however at higher temperatures (90 °C) there is a sharp rise in the number of acidic groups. The reason for this increase in acidic groups and decrease in pH\textsubscript{PZC} could be due to an increase in the rate at which nitric acid erodes the activated carbon surface, exposing new sites which were then rapidly oxidised on contact with the nitric acid. However, further work would have to be undertaken i.e. oxidation at 80 °C to provide further evidence for this relationship.

For oxidised S-50-9/125-00 as with oxidised S-50-9/100/25-00, the same trend was observed (Figure 3.17), an increase in carboxylic (0.364 meq/g for S-50-9/125-00 to 0.945 meq/g for N-125-90-2) and lactonic groups (0.178 meq/g for S-50-9/125-00 to 1.291 meq/g for N-125-90-2) accompanied by a decrease in the number of basic (0.783 meq/g for S-50-9/125-00 to 0.285 meq/g for N-125-90-2) and phenolic type groups was observed (0.215 meq/g for S-50-9/125-00 to 0 for N-125-90-2). As the temperature of oxidation increased the ratio of basic to acidic groups decreased from 1.034 for non-oxidised S-50-9/125-00, to 0.391 (N-125-50-2), then 0.282 (N-125-70-2) and finally to 0.135 for N-125-90-2.

### 3.4.2 Mass Titrations – Discussion

As mentioned in section 3.4.1, both sets of oxidised carbons displayed a different relationship between the temperature of oxidation and pH\textsubscript{PZC} as seen from Table 3.3 and 3.7. These mass titration results confirm the findings of the Boehm titrations results (Table 3.2 and 3.6). Whereby at 50 and 70 °C the N-100 series have pH\textsubscript{PZC} values which are very similar 5.87 and 5.80 respectively, there followed a significant decrease when oxidation was performed at 90 °C to a pH\textsubscript{PZC} 3.67. The response of the N-125 Series was an almost linear decrease 6.42, 5.10 to 3.58, as the temperature at which the oxidation was performed was increased from 50 to 90 °C (Figure 3.20).
This could mean that a range of nitric acid oxidised S-50-9/125-00 carbons could be produced with a tuneable pH_{PZC} simply by oxidising the carbon with 20 % nitric acid for 2 hours at different temperatures.

### 3.4.3 Fourier Transform Infrared Spectroscopy – Discussion

The two series N-100 and N-125 were shown to both be modified by oxidation with nitric acid from the FTIR results shown in Figures 3.6a-c and 3.21a-c. For the N-100 series, the phenolic peaks reduced (1340 and 1115 cm\(^{-1}\)) and the development of COO\(^-\) (1400 cm\(^{-1}\)), C-O (1074 cm\(^{-1}\)) and O-H (669, 659 and 652 cm\(^{-1}\)) was observed as the temperature at which oxidation was increased in agreement with the Boehm titration results (Table 3.2). The disappearance of both aliphatic and alkene C-H \textit{str} peaks (1458 and 1435 cm\(^{-1}\) respectively) and aliphatic C-H \textit{def} peaks (1340 and 1319 cm\(^{-1}\)) indicated their oxidation by nitric acid.

For the N-125 series oxidation at 50 and 70 °C reveals the presence of two or three peaks at 1734 – 1718 cm\(^{-1}\), these peaks C=O from carbonyl are also present in N-125-90-2 although the intensity is far lower. The peak at 1635 cm\(^{-1}\) (COO\(^-)\) increased in intensity when oxidation is performed at 70 and 90 °C. The aliphatic C-H peaks at 1460 disappear at 90 °C, possibly indicating the conversion of the aliphatic groups. The aromatic C-H double peak at 798 cm\(^{-1}\) is reduced to a single peak when oxidation is performed at 70 or 90 °C indicating degradation of the aromatic structure.

### 3.4.4 Secondary Ion Mass Spectrometry – Discussion

The SIMS results of the oxidised activated surfaces (Figures 3.7a-c and 3.22a-c) revealed the difference in the surface chemistry is clear between the N-100-90 and N-125-90 and the corresponding non-oxidised activated carbons, S-50-9/100/25-00 and S-50-9/125-00 respectively.

Although both oxidised surfaces emitted fragments of alkyl, alcohol and carboxylic acids, the size of the fragments differed dependent on the surface. For N-100-90-2 alkyl fragments (C\(_n\)H\(_{2n+1}\)\(^+\)) from CH\(_3\)\(^+\), to C\(_8\)H\(_{17}\)\(^+\), alcohols (C\(_n\)H\(_{2n+1}\)O \(^-\)) from CH\(_2\)OH\(^-\) to
C\textsubscript{7}H\textsubscript{15}OH\textsuperscript{+} were observed however for N-125-90-2 smaller fragments were observed alkyl fragments (C\textsubscript{n}H\textsubscript{2n+1} \textsuperscript{+}) from CH\textsubscript{3}\textsuperscript{+}, to C\textsubscript{5}H\textsubscript{11}\textsuperscript{+}, alcohols (C\textsubscript{n}H\textsubscript{2n+1}O \textsuperscript{+}) from CH\textsubscript{2}OH\textsuperscript{+} to C\textsubscript{4}H\textsubscript{9}OH\textsuperscript{+}.

After oxidation at 90 °C the nature of the surfaces of the activated carbons changes, as the aliphatic nature of both N-100-90-2 and N-125-90-2 were increased due to the degradation of the polyaromatic networks, as shown by the decrease in the C\textsubscript{2}H\textsuperscript{+}/C\textsubscript{2}\textsuperscript{−} for both carbons when compared to the non-oxidised controls (Table 3.4B and 3.9B). This was also shown by an increase in the intensity upon oxidation of the fragment found at 77 m/z, corresponding to C\textsubscript{6}H\textsubscript{5}\textsuperscript{+}, indicating degradation of the polyaromatic network.

Oxidation was also shown to take place predominately in the uppermost 1-2 nm of the surface as indicated by the decrease in the O\textsuperscript{−}/C\textsubscript{2}\textsuperscript{−} and OH\textsuperscript{−}/C\textsubscript{2}\textsuperscript{−} ratios when a higher intensity ion beam was used on both surfaces (Table 3.4C and 3.9C).

3.4.5 Scanning Electron Microscopy-Discussion

The topography of the surfaces of the oxidised activated carbons was shown to be rougher than those observed in Section 2.2.5 for the non-oxidised surfaces. In Figures 3.8b and Figure 3.9b, degradation of the surface is clearly visible for the N-100 series. Figure 3.10b reveals some of the underlying porous nature of the oxidised activated carbons. For the N-125 series (Figures 3.23 – 3.25) the surfaces displayed some signs of degradation and pitting of the surface, although not to the same extent as for the N-100 series.

3.4.6 Electron Diffraction by X-ray - Discussion

From the EDX analysis only oxygen and carbon were found to be present at the surface of the oxidised activated carbons of N-100 and N-125 series.

For the N-100 series an almost linear increase in the O/C ratio was observed as the temperature at which oxidation was performed was increased. This was in agreement with Boehm titration results where increases in the number of carboxyl and lactonic groups were observed by a reduction in the number of basic and phenolic groups (Figure 3.0).
For the N-125 series the trend was somewhat different than for N-100 series, where although all count values for O and C were greater than the non-oxidised control the ratio O/C showed a decrease upon oxidation at 50 °C, however this reaches a maximum at 70 °C and finally reduces again after oxidation at 90 °C. The reason for this is unclear, but it could be due to the effect of degradation of the activated carbon by the nitric acid rather than the addition of oxygen functional groups, thereby reaching a maximum of addition of groups at 70 °C followed by degradation of the matrix at 90 °C.

3.4.7 Bead Size Analysis – Discussion

The effect that oxidation had on the size of the activated carbon beads which were observed was that as the temperature of oxidation increased from 50 to 90 °C, the mean bead size found to decrease from 35.5 µm for S-50-9/100/25-00 to 32.99, 31.74 and 28.32 µm for N-100-50-2, N-100-70-2 and N-100-90-2 respectively. However for N-100 series the decrease in bead size was only significant as determined by ANOVA (Section 3.2.7.1.1) and Dunnett’s comparison (Section 3.2.7.1.2) when oxidation was performed at 90 °C. For N-125 Series there was seen to be little change in the mean bead size, form 15.93 µm for S-50-9/125-00, to 14.51, 16.79 to 14.99 µm for N-125-50-2, N-125-70-2 and N-125-90-2 respectively. The changes in bead size as a result of oxidation with nitric acid were found to be not significant for the N-125 series.

3.4.8 Bulk Density Measurements – Discussion

The bulk densities of the N-100 series were shown to increase upon oxidation with nitric acid from 0.667 g/cm³ for S-50-9/100/25-00, to 0.703 g/cm³ for N-100-50-2 reaching a maximum of 0.72 g/cm³ at 70 °C, then reducing to 0.702 g/cm³ for N-100-90-2. The reason for the maximum at 70 °C is due to the addition of surface groups as a result of oxidation with little degradation of the activated carbon, however at 90 °C, although the surface is oxidised the degradation of the activated carbon is more prevalent therefore a reduction in the bulk density is observed.

For the N-125 series the bulk density was initially 0.609 g/cm³ for S-50-9/125-00, after oxidation the bulk density rose to 0.64 g/cm³ at 50 °C (N-125-50-2), then decreased at 70
°C to 0.62 g/cm³ (N-125-70-2) then decreased further upon oxidation at 90 °C to 0.614 g/cm³ (N-125-90-2). The initial increase in bulk density is due to the addition of surface groups as a result of oxidation with little degradation. As the temperature of oxidation is increased the amount of degradation increases resulting in a decrease in the bulk density.

3.4.9 SAXS Experiments – Discussion

The results for the SAXS experiments for N-100 (Table 3.7) and N-125 series (Table 3.13) revealed that when the temperature of oxidation was increased there were changes observed in the slopes of the 4 distinct sections of each curve. N-100 Series showed for larger scattering structures as the temperature of oxidation was increased the slope of section 1 became more reduced from -1.33 to -1.26, the smaller scatters in section 2 and 4 the slopes increased however in the range of scatter structures (3) between these the slope reduced from -0.57 to -0.52. For N-125 series the changes observed for scattering structures in section 2 and 4 were the same as seen for N-100 series, with little difference seen in the slopes of scattering structures in section 1 and 3. It appears that oxidation with nitric acid causes reductions in the intensity of the scattering structures primarily in the q range of 0.03 to 0.1 Å⁻¹ and 0.12 to 1 Å⁻¹. These correspond to structures of the order of 33 to 10 Å and 8 to 1 Å, which implies that oxidation has the greatest effect on the micropores and small mesopores.

3.5 Conclusions

The oxidation of the activated carbons at three different temperatures 50, 70 or 90 °C for 2 hours was shown to cause a significant increase in the carboxyl and lactonic surface groups and a significant decrease in the basic and phenolic groups for both the N-100 (Figure 3.0) and N-125 series (Figure 3.17). The results of the mass titrations showed a linear decrease over the range of oxidation temperatures examined for the N-125 series (Figure 3.21) where as there appeared to be a stepwise decrease at 70 °C to 90 °C for N-100 series (Figure 3.5). The SIMS results for both the N-100 (Table 3.4B) and N-125 series (Table 3.9B), confirmed that oxidation had taken place as the O'/C₂⁻ and OH'/C₂⁻ were shown to increase after oxidation and that oxidation appeared to occur predominately in the
outermost 1-2 nm of the surface, as when a higher intensity ion beam was used the ratios of the O\(^7\)/C\(_2\)^{12} and OH\(^-\)/C\(_2\)^{12} fragments were reduced (Tables 3.4C and 3.9C).

FTIR of the N-100 revealed that the phenolic and aliphatic peaks reduced upon oxidation, and the COO\(^-\), C-O and O-H increased (Figure 3.6a-c), in agreement with the mass titration and Boehm titration results. The N-125 series upon oxidation revealed an increase in the intensity of C=O and COO\(^-\) peaks with a decrease in the aliphatic peaks indicating the conversion of aliphatic groups (Figure 3.21a-c).

Oxidation of the beads revealed a decrease in bead size (Figure 3.13), but this was only significant at 90 °C (N-100-90-2). The N-125 series mean bead diameter remained relatively unchanged by nitric acid oxidation (Figure 3.29). The bulk density results revealed a maximum for the N-100 series of 0.72 g/cm\(^3\) when oxidation was performed at 70 °C (Figure 3.15). For the N-125 series, a maximum of 0.64 g/cm\(^3\) was observed when oxidation was performed at 50 °C (Figure 3.31).

The results of the SAXS experiments (Tables 3.7 and 3.13) appears that to suggest that oxidation with nitric acid at increasing temperature causes reductions in the intensity of the scattering structures primarily in the q range of 0.03 to 0.1 Å\(^{-1}\) and 0.12 to 1 Å\(^{-1}\). These correspond to scattering structures of the order of 33 to 10 Å and 8 to 1 Å in size. This suggests that oxidation with nitric acid has the greatest effect on the micropores and small mesopores.
Chapter 4  Conjugation of Butylamine to the Surface of NOVACARBs Using Carbodiimide
4.0 Introduction

To test the feasibility of formation of an amide bridge on the activated carbon surface, the conjugation of a test ligand (butylamine) to the surface of the NOVACARBs was undertaken. The two methods used were (i) a water soluble carbodiimide 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) in conjunction with N-hydroxysuccinimide (NHS) in acetonitrile to attach the butylamine and (ii) formation of acyl chloride groups from the carboxylic acid moieties using thionyl chloride (SOCl2), then reaction of the acyl chloride groups with butylamine to form an amide linkage (Chapter 5).

The use of a carbodiimide such as EDC allows the reaction of the carboxylic moiety to form an active O-acylisourea intermediate to react with the test ligand (e.g. butylamine) and a urea based by-product is released into solution. The O-acylisourea intermediate formed is unstable in aqueous solutions therefore making it ineffective in a two step conjugation reaction unless a non aqueous solvent or stabilisation of the intermediate is undertaken (Figure 4.0).

Therefore the reaction is performed in a non-aqueous solvent (acetonitrile) and N-hydroxysuccinimide (NHS) used to stabilise the O-acylisourea intermediate (Figure 4.1). The intermediate reacts with the butylamine to form an amide derivative however, failure to react with an amine results in the hydrolysis of the intermediate, regeneration of the carboxylic acid moiety and release of the N-unsubstituted urea. Hydrolysis of the EDC is a competing side reaction dependent on the temperature and pH of the medium. EDC couples NHS to carboxylic groups giving an NHS activated site, and the advantage of the NHS-ester over the O-acylisourea intermediate is greater stability in slightly acidic conditions such as when a solvent such as acetonitrile is used.
Figure 4.0  Proposed reaction scheme for conjugation of butylamine to the surface of activated carbons using carbodiimide
Figure 4.1  Proposed reaction scheme for conjugation of butylamine to the surface of activated carbons using carbodiimide and N-hydroxysuccinimide
4.1 Materials and Experimental Methods

4.1.1 Materials

Acetonitrile (Fisher Scientific)
Buffer Solutions pH 4 (Phthalate) (Fisher Scientific)
    pH 7 (Phosphate) (Fisher Scientific)
Butylamine (Sigma-Aldrich Company Limited)
Deionised water
Electrode Buffer Solution (BDH)
1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) (Acros Organics)
Hydrochloric acid (HCl) (Sigma-Aldrich Company Limited)
N-hydroxysuccinimide (NHS) (Acros Organics)
NOVACARB S-50-9/100/125-00 (MAST Carbon)
NOVACARB S-50-9/125-00 (MAST Carbon)
Methanol (Fisher Scientific)
Potassium Bromide (KBr) (Sigma-Aldrich Company Limited)
Sodium carbonate (Na$_2$CO$_3$) (Sigma-Aldrich Company Limited)
Sodium chloride (NaCl) (Sigma-Aldrich Company Limited)
Sodium hydrogen carbonate (NaHCO$_3$) (Sigma-Aldrich Company Limited)
Sodium hydroxide (NaOH) (Sigma-Aldrich Company Limited)

4.1.2 Equipment

Glass Combination Electrode (BDH)
Heating Mantle (Electromantle)
pH meter Orion 410A (Thermo Electron)
Shaking Orbital Incubator (Bibby Stuart Scientific)
Vacuum Oven (Gallenkamp)
4.2 Methods

4.2.1 Conjugation of Butylamine to Activated Carbon Surface

1.5 g of S-50-9/100/25-00 or S-50-9/125-00 was placed into a 50 cm³ conical flask and 20 cm³ dried acetonitrile added. Based on the number of estimated carboxylic groups on the surface of the carbons (0.27 and 0.36 meq/g for non-oxidised S-50-9/100/25-00 and S-50-9/125-00 respectively from Table 2.3) a 10-fold molar excess of 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) and N-hydroxysuccinimide (NHS) was then added and shaken for 18 hours at room temperature on an orbital mixer set to 100 rpm. After 18 hours a 20 fold molar excess of butylamine was added to the reaction vessel and reacted for 18 hours at room temperature on an orbital mixer set to 100 rpm. Blank reactions were carried out, as above, with: no EDC (Blank 1), no butylamine (Blank 2), or EDC and NHS (Blank 3) present (Table 4.0). After 18 hours, the samples were filtered and washed with deionised water, 0.01 M and 0.10 M NaOH and in some cases methanol to dissolve precipitate. The samples were then dried in the oven at 30 °C until constant weight.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-100 Series</td>
<td></td>
</tr>
<tr>
<td>BA Conj 100</td>
<td>S-50-9/100/25-00 reacted with EDC/NHS and BA</td>
</tr>
<tr>
<td>Blank 1-100</td>
<td>S-50-9/100/25-00 reacted with EDC and BA</td>
</tr>
<tr>
<td>Blank 2-100</td>
<td>S-50-9/100/25-00 reacted with EDC/NHS</td>
</tr>
<tr>
<td>Blank 3-100</td>
<td>S-50-9/100/25-00 reacted with BA</td>
</tr>
<tr>
<td>BA-125 Series</td>
<td></td>
</tr>
<tr>
<td>BA Conj 125</td>
<td>S-50-9/125-00 reacted with EDC/NHS and BA</td>
</tr>
<tr>
<td>Blank 1-125</td>
<td>S-50-9/125-00 reacted with EDC and BA</td>
</tr>
<tr>
<td>Blank 2-125</td>
<td>S-50-9/125-00 reacted with EDC/NHS</td>
</tr>
<tr>
<td>Blank 3-125</td>
<td>S-50-9/125-00 reacted with BA</td>
</tr>
</tbody>
</table>

Table 4.0 Activated carbons prepared using carbodiimide method
4.2.2  **Boehm Titrations**

The conjugated NOVACARB activated carbons were examined using Boehm titrations as outlined in section 2.1.3.1 to determine the density of surface functional groups.

4.2.3  **Fourier Transform Infrared Spectroscopy**

The conjugated NOVACARB activated carbons were examined using the method outlined in section 2.1.3.3, for the preparation of the samples for FTIR.

4.2.4  **Scanning Electron Microscopy**

Scanning electron microscopy of the nitric acid oxidised NOVACARB activated carbons was performed as outlined on section 2.1.3.5.

4.2.5  **Electron Diffraction by X-ray**

After SEM was performed, the samples were analysed using EDS as outlined in section 2.1.3.6.

4.3  **Results**

4.3.1  **Results of Boehm Titrations – BA-100 Series**

The results of the Boehm titrations for the BA-100 series revealed that for BA Conj 100, Blank 1-100 and Blank 2-100 the number of carboxyl groups were found to be zero and for Blank 3-100 0.071 meq/g (Table 4.1). This would indicate that the reaction was successful between the carboxyl group and the amine moiety of the butylamine to form an amide bond, however for Blank 2-100 this is not possible as there is no addition of butylamine. There are also large reductions observed in the number of basic groups found for BA Conj 100, Blank 1-100 and Blank 2-100, however the number of basic groups for Blank 3-100 appears to be very similar to S-50-9/100/25-00. The Blank 3-100 and the non-modified S-50-9/100/25-00 show that with direct reaction of the activated carbon with butylamine the
formation of an amide bond appears to occur as only a decrease in the carboxyl groups to 0.071 meq/g is observed, whereas the other functional groups remain unchanged.

The conjugation of butylamine with EDC/NHS (BA Conj 100) shows a reduction to zero of the carboxyl groups but there is also a reduction in the basic groups and a reduction in the lactonic and phenolic groups, this reduction is accompanied with very large standard deviations. The large error bars may be due to the reaction of the titrant Na₂CO₃ with any residual EDC or urea by-product which is left after washing, as the large error bars appear only for those activated carbons treated with EDC (BA Conj 100, Blank 1-100 and Blank 2-100).

Figure 4.2  Plot of distribution of functional groups present on the surface of BA-100 Series (Mean a (n=3) ± Standard Deviation)
Table 4.1 Results of Boehm titrations for BA-100 Series

4.3.1.1 Statistical Analysis of Boehm Titrations BA-100 Series – Basic Groups

4.3.1.1.1 ANOVA - BA-100 Series – Basic Groups

The ANOVA results revealed that the number of basic surface groups on the surfaces of the carbons of the BA-100 series were significantly lower than the non-oxidised activated carbon control S-50-9/100/25-00.

4.3.1.1.2 Dunnett's Comparisons - BA-100 Series – Basic Groups

Dunnett’s comparison revealed that all the BA-100 series, had a significantly lower number of basic groups when compared to the control S-50-9/100/25-00 with the exception of Blank 3-100, which was not significantly different.
4.3.1.2  Statistical Analysis of Boehm Titrations BA-100 Series  
– Acidic Groups

4.3.1.2.1  One-way ANOVA- BA-Series – Acidic Groups

The difference in the number of acidic surface groups for the BA-100 series found after treatment with butylamine was found to be not significantly different from the number of acidic groups found on the surface of S-50-9/100/25-00.

4.3.1.2.2  Dunnett’s comparisons - BA-100 Series – Acidic Groups

From the Dunnett’s comparison of the acidic surface groups found on the butylamine conjugated surfaces, all the BA-100 series activated carbons were found not to have a significantly different number of acidic surface groups on the surface in comparison to the control sample S-50-9/100/25-00.

4.3.1.3  Statistical Analysis of Boehm Titrations BA-100 Series  
– Carboxyl Groups

4.3.1.3.1  One-way ANOVA: BA-100 Series – Carboxyl Groups

The results of the ANOVA of the number of carboxyl groups found on the butylamine conjugated surfaces were significantly different, as indicated by $p<0.05$, than the amount of carboxyl groups found on the surface of the S-50-9/100/25-00.

4.3.1.3.2  Dunnett's Comparison - BA-100 Series – Carboxyl Groups

From the results of the Dunnett’s comparison of the number of carboxyl groups, it was observed that for all the activated carbons in BA-100 series the number of carboxyl groups found were significantly lower than found on the surface of S-50-9/100/25-00.
4.3.1.4 Statistical Analysis of Boehm Titrations BA-100 Series
   – Lactonic Groups

4.3.1.4.1 One-way ANOVA - BA-100Series – Lactonic Groups

From the ANOVA results of the number of lactonic groups found for the BA-100 series, there was found to be no significant difference in the number of lactonic groups when compared to the control S-50-9/100/25-00.

4.3.1.4.2 Dunnett's Comparison - BA-100Series – Lactonic Group

As with the ANOVA results, Dunnett’s comparison revealed that the number of lactonic groups found on the surface of the BA-100 series activated carbons were not significantly different from the number of lactonic groups found on the surface of the control S-50-9/100/25-00.

4.3.1.5 Statistical Analysis of Boehm Titrations BA-100 Series
   – Phenolic Groups

4.3.1.5.1 One-way ANOVA: - BA-100Series – Phenolic Group

The number of phenolic groups was shown to be not significantly different from the number found on the surface of S-50-9/100/25-00 from the ANOVA analysis.

4.3.1.5.2 Dunnett's Comparisons - BA-100 Series – Phenolic Group

As with the ANOVA results, Dunnett’s comparison indicated that the number of phenolic surface groups were not significantly difference from the number found on the surface of S-50-9/100/25-00. A summary of the statistical analysis for BA-100 series activated carbons is shown in Table 4.2.
<table>
<thead>
<tr>
<th>Functional Group</th>
<th>ANOVA (P Value)</th>
<th>Dunnet’s Comparison</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic</td>
<td>0.000</td>
<td>Significant Decrease</td>
<td>All except Blank 3-100</td>
</tr>
<tr>
<td>Acidic</td>
<td>0.126</td>
<td>Decrease</td>
<td>All</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>0.002</td>
<td>Significant Decrease</td>
<td>All</td>
</tr>
<tr>
<td>Lactonic</td>
<td>0.336</td>
<td>Increase</td>
<td>All except Blank 3-100</td>
</tr>
<tr>
<td>Phenolic</td>
<td>0.063</td>
<td>Decrease</td>
<td>All</td>
</tr>
</tbody>
</table>

Table 4.2  Statistical analysis results for BA-100 series activated carbons

4.3.2  Boehm Titrations BA-125 Series

![Figure 4.3](image)

**Figure 4.3**  Plot of distribution of functional groups present on the surface of S-50-9/125-00 (Mean ± Standard Deviation)

The results of the Boehm titrations for all of the BA-125 series showed a reduction in the number of carboxyl groups, with all the combinations (Figure 4.2). For BA Conj 125 and Blank 3-125 the number of carboxyl groups were found to be very similar 0.068 and 0.049 meq/g respectively (Table 4.3). Again for Blank 2-125 as with Blank 2-100, this is very strange as there is no addition of butylamine. However this decrease in carboxyl groups was also accompanied by an increase in lactonic group content, suggesting that additional
lactonic moieties were generated or that the NHS not washed from the surface may react leading to an over estimation in the number of lactonic groups. Again as with BA-100 series the large error bars for the lactonic and phenolic groups, could be as a result of incomplete washing of EDC and urea by-products from the surface of activated carbons which then react with Na₂CO₃.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean $a$ (meq/g) (n=3) ± Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Total</td>
</tr>
<tr>
<td>S-50-9/125-00</td>
<td>1.540 ± 0.045</td>
</tr>
<tr>
<td>BA Conj 125.</td>
<td>0.542 ± 0.254</td>
</tr>
<tr>
<td>Blank 1-125</td>
<td>0.781 ± 0.019</td>
</tr>
<tr>
<td>Blank 2-125</td>
<td>1.339 ± 0.073</td>
</tr>
<tr>
<td>Blank 3-125</td>
<td>1.811 ± 0.094</td>
</tr>
</tbody>
</table>

Table 4.3 Results of Boehm titrations for BA-125 Series

4.3.2.1 Statistical Analysis of Boehm Titrations BA-125 Series – Basic Groups

4.3.2.1.1 ANOVA - BA-125 Series – Basic Groups

The ANOVA results revealed that the number of basic groups on the surface of the BA-125 Series activated carbons were found to be significantly different (p<0.05) from the number of basic groups found on the surface of S-50-9/125-00.
4.3.2.1.2 Dunnett's Comparisons - BA-125 Series – Basic Groups

The results of Dunnett’s comparison reveal that the number of basic groups found on the surface of BA-125 series activated carbons were not significantly different found on the surface of the control S-50-9/125-00. This is the opposite to the result found for ANOVA of the number of basic groups. This discrepancy may be as a result of the large variability found in the results.

4.3.2.2 Statistical Analysis of Boehm Titrations BA-125 Series – Acidic Groups

4.3.2.2.1 One-way ANOVA- BA-125 Series – Acidic Groups

The results of the ANOVA of the acidic groups found by Boehm titrations, revealed that the number of acidic surface groups found for the BA-125 Series were significantly different from the number found on the non-modified S-50-9/125-00.

4.3.2.2.2 Dunnett's comparisons - BA-125 Series – Acidic Groups

From the results of the Dunnett’s comparison it was observed that BA Conj 125 and Blank 1-125 had a significantly lower number of acidic groups and that Blank 2-125 and Blank 3-125 had a significantly greater number of acidic surface groups than the control S-50-9/125-00.

4.3.2.3 Statistical Analysis of Boehm Titrations BA-125 Series – Carboxyl Groups

4.3.2.3.1 One-way ANOVA: BA-125 Series – Carboxyl Groups

The number of carboxyl groups for the BA-125 series was found to be significant different from the number of carboxyl groups found for the control activated carbon S-50-9/125-00.
4.3.2.3.2 Dunnett's Comparison - BA-100 Series – Carboxyl Groups

The number of carboxyl groups was found to be significantly lower for BA Conj 125, Blank 1-125 and Blank 3-125 when compared to the control activated carbon S-50-9/125-00. The number of carboxyl groups found for Blank 2-125 was found to be not significantly different from the control activated carbon.

4.3.2.4 Statistical Analysis of Boehm Titrations BA-125 Series – Lactonic Groups

4.3.2.4.1 One-way ANOVA - BA-125 Series – Lactonic Groups

The number of lactonic groups found for the BA-125 series was found to be not significantly different from the number of groups found for the control S-50-9/125-00.

4.3.2.4.2 Dunnett's Comparison - BA-125 Series – Lactonic Group

The results of the Dunnett’s comparison agreed with the results found for the ANOVA that the number of lactonic groups found were not significantly different for the amount for the control S-50-9/125-00.

4.3.2.5 Statistical Analysis of Boehm Titrations BA-125 Series – Phenolic Groups

4.3.2.5.1 One-way ANOVA: - BA-125 Series – Phenolic Group

The number of phenolic groups was found to be significantly different to the number of phenolic groups found for the control S-50-9/125-00.
4.3.2.5.2 Dunnett's Comparisons - BA-125 Series – Phenolic Group

The results of Dunnett’s comparison reveal that only the number of phenolic groups found on the surface of Blank 3-125 were significantly different from the number found for the control surface S-50-9/125-00.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>ANOVA (P Value)</th>
<th>Dunnet’s Comparison</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic</td>
<td>0.004</td>
<td>Decrease</td>
<td>All except Blank 3-125</td>
</tr>
<tr>
<td>Acidic</td>
<td>0.000</td>
<td>Significant Decrease</td>
<td>BA-125 Conj</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Blank 1-125</td>
</tr>
<tr>
<td>Carboxyl</td>
<td>0.028</td>
<td>Significant Decrease</td>
<td>All except Blank 2-125</td>
</tr>
<tr>
<td>Lactonic</td>
<td>0.185</td>
<td>Decrease</td>
<td>BA Conj 125</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Blank 3-125</td>
</tr>
<tr>
<td>Phenolic</td>
<td>0.009</td>
<td>Significant Increase</td>
<td>Blank 3-125</td>
</tr>
</tbody>
</table>

Table 4.4 Statistical analysis results for N-125 series activated carbons

A summary of the statistical analysis for BA-100 series activated carbons is shown in Table 4.4.
4.3.3 Results of Fourier Transform Infrared Spectroscopy

4.3.3.1 BA-100 Series

The results of the FTIR analysis of BA-100 series are shown in Figures 4.4a-c with S-50-9/100/25-00 included for comparison.

Figure 4.4a FTIR Spectrum of BA-100 Series (4000-400 cm⁻¹)

Figure 4.4b FTIR Spectrum of BA-100 Series (4000-2000 cm⁻¹)
Changes in the region 4000-2000 cm\(^{-1}\) for BA-100 series are shown in Figure 4.4b. All the spectra are noisy from 4000-3500 cm\(^{-1}\), possibly due to incomplete grinding of sample during KBr disc preparation. The peaks present for BA Conj 100: -O-H (3446 cm\(^{-1}\)) N-H \textit{str} secondary amide (3336 cm\(^{-1}\)) and aliphatic C-H (2950-2850 cm\(^{-1}\)). Blank 1-100: N-H \textit{str} secondary amide (3292, 3219 cm\(^{-1}\)), aliphatic C-H \textit{str} (2964 cm\(^{-1}\)), N-H \textit{str} (2549 cm\(^{-1}\)), possible isonitrile \textit{str} (2170 cm\(^{-1}\)). Blank 2-100: aliphatic C-H \textit{str} (2964, 2922, 2850 cm\(^{-1}\)) present no evidence of N-H \textit{str}.

Figure 4.4c  FTIR Spectrum of BA-100 Series (2000-400 cm\(^{-1}\))

Changes for the BA-100 series 2000-400 cm\(^{-1}\) are shown in Figure 4.4c. BA Conj 100: amide I for a secondary amide (1684 cm\(^{-1}\)), amide II for a secondary amide (1539 cm\(^{-1}\)), aromatic C-H \textit{str} (1522 cm\(^{-1}\)), weak COO’ \textit{sym str} peak (1383 cm\(^{-1}\)) indicating conjugation of butylamine to carboxylic groups, aromatic C-H \textit{in plane def} (1168 cm\(^{-1}\)), C-O \textit{str} (1062 cm\(^{-1}\)) shifted to a lower wavenumber compared to S-50-9/100/25-00. No O-H peak was observed (~ 670 cm\(^{-1}\)).

Blank 1-100: was found to display peaks for amide I for a secondary amide (1684 cm\(^{-1}\)), amide II for a secondary amide (1539 cm\(^{-1}\)), aromatic C-H \textit{str} (1522 cm\(^{-1}\)), COO’ \textit{sym str} peak (1383 cm\(^{-1}\)) indicating conjugation of butylamine to carboxylic groups, aromatic C-H \textit{in plane def} (1151 cm\(^{-1}\)), C-O \textit{str} (1064, cm\(^{-1}\)) shifted to a lower wavenumber compared to S-50-9/100/25-00, (924 cm\(^{-1}\)), aromatic C-H \textit{oop def} (849 cm\(^{-1}\)), O-H peak was observed (677 cm\(^{-1}\)) and aromatic C-H \textit{oop def} (463 cm\(^{-1}\)).
Blank 2-100: amide I for a secondary amide (1684 cm\(^{-1}\)), amide II for a secondary amide (1539 cm\(^{-1}\)), COO' \text{sym str} peak (1383 cm\(^{-1}\)), C-O \text{str} (1082 cm\(^{-1}\)), aromatic C-H (809 cm\(^{-1}\)), no O-H peak was observed at 677 cm\(^{-1}\).

For BA Conj 100 and Blank 1-100 conjugation of butylamine appears to have been successful due to the presence of the amide I and II peaks for secondary amides and a reduction in the COO' \text{sym str} peak. N-H \text{str} for secondary amides were also found BA Conj 100 and Blank 1-100 at 3336 cm\(^{-1}\). An isonitrile peak (2170 cm\(^{-1}\)) was observed for Blank 1-100 which may indicate that this is a reaction between the acetonitrile and the surface or EDC and the activated carbon surface.

4.3.3.2 BA-125 Series

The FTIR spectra for the BA-125 series are shown in Figures 4.5a-c. The spectra are quite noisy, possibly due to the incomplete grinding of the samples.

![FTIR Spectrum of BA-125 Series (4000-400 cm\(^{-1}\))]({attachment:image.png})

**Figure 4.5a  FTIR Spectrum of BA-125 Series (4000–4000 cm\(^{-1}\))**

The region 4000-2000 cm\(^{-1}\) shown in Figure 4.5b for the BA-125 series revealed the following peaks were found for BA-Conj 125: N-H \text{str} secondary amide (3336, 3286 and 3095 cm\(^{-1}\)), aliphatic C-H \text{str} (2958 cm\(^{-1}\), 2931 cm\(^{-1}\), 2920 cm\(^{-1}\), 2872, 2864, 2850 cm\(^{-1}\)). Blank 1-125: N-H \text{str} (3336 cm\(^{-1}\)), aliphatic C-H \text{str} (2958, 2920, 2850 cm\(^{-1}\)).
Blank 2-125: N-H $\text{str}$ (3336 cm$^{-1}$), aliphatic C-H $\text{str}$ (2958, 2920, 2872, 2850 cm$^{-1}$).
Blank 3-125: N-H $\text{str}$ (3494 cm$^{-1}$), N-H $\text{str}$ secondary amide (3338 and 3319 cm$^{-1}$), aliphatic C-H $\text{str}$ (2966 cm$^{-1}$), however no aliphatic C-H peaks below 2900 cm$^{-1}$.

**Figure 4.5b**  FTIR Spectrum of BA-125 Series (4000-2000 cm$^{-1}$)

**Figure 4.5c**  FTIR Spectrum of BA-125 Series (2000-400 cm$^{-1}$)

Figure 4.5c shows the FTIR spectra in the region 2000-400 cm$^{-1}$ for the BA-125 series.
The following peaks were found for BA Conj 125: Amide I weak (1686 cm\(^{-1}\)), aromatic C=C \textit{str} (1635 cm\(^{-1}\)), amide II (1558 cm\(^{-1}\)), COO\(^{-}\) \textit{asym str} (1541 cm\(^{-1}\)), aliphatic C-H \textit{def} (1458 cm\(^{-1}\)), COO\(^{-}\) \textit{sym str} (1375 cm\(^{-1}\)), (1226 cm\(^{-1}\)), aromatic C-H \textit{in plane def} (1157 cm\(^{-1}\)), C-O \textit{str} (1074 cm\(^{-1}\)), aromatic C-H (777 cm\(^{-1}\)), 710, no O-H peak observed at 677 cm\(^{-1}\), C-H \textit{oop def} (463 cm\(^{-1}\)).

Blank 1-125: Amide I (1687 cm\(^{-1}\)), aromatic C=C \textit{str} (1643 cm\(^{-1}\)), COO\(^{-}\) \textit{asym str} (1541 cm\(^{-1}\)), aliphatic C-H \textit{def} (1458 cm\(^{-1}\)), C-O \textit{str} (1082 cm\(^{-1}\)), aromatic C-H (777 cm\(^{-1}\)), O-H peak 677 cm\(^{-1}\).

Blank 2-125: Amide I (1687 cm\(^{-1}\)), aromatic C=C \textit{str} (1655 cm\(^{-1}\)), amide II (1558 cm\(^{-1}\)), N-H \textit{str} (1541 cm\(^{-1}\)), aliphatic C-H \textit{def} (1458 cm\(^{-1}\)), COO\(^{-}\) \textit{sym str} (1385 cm\(^{-1}\)), C-O \textit{str} (1082 cm\(^{-1}\)), aromatic C-H (803 cm\(^{-1}\)), aromatic C-H (777 cm\(^{-1}\)), C-H \textit{oop def} (463 cm\(^{-1}\)).

Blank 3-125: Amide I (1687 cm\(^{-1}\)), aromatic C=C \textit{str} (1660 cm\(^{-1}\)), aromatic C=C \textit{str} (1643 cm\(^{-1}\)), ketone C=O (1632 cm\(^{-1}\)), N-H \textit{str} (1579 cm\(^{-1}\)), N-H \textit{str} (1568 cm\(^{-1}\)), amide II (1558 cm\(^{-1}\)), (1402 cm\(^{-1}\)), COO\(^{-}\) \textit{sym str} (1382 cm\(^{-1}\)), C-O \textit{str} (1090 cm\(^{-1}\)), (804 cm\(^{-1}\)).

N-H \textit{str} peaks were found in the spectra of all the samples although only BA Conj 125 and Blank 3-125 had peaks for N-H \textit{str} secondary amides, and only weak COO\(^{-}\) peaks indicating the successful conjugation of butylamine to the carboxyl groups.
4.3.4 Results of Scanning Electron Microscopy

4.3.4.1 BA-100 Series

Figures 4.6a-c revealed the surface of BA Conj 100 was very similar to that of S-50-9/100/25-00 (Figure 2.12b). There were also some small aggregates present on the surface from 0.5 to 0.1 µm. Interestingly in Figure 4.6c the internal porous structure of BA Conj 100 is visible, revealing larger pores of approximately 1 µm diameter connecting the external surface to the internal surface of the activated carbon, and a network of smaller meso and micropores.
Figure 4.7  SEM Image of a) Blank 1-100 beads (x 250 Magnification) and b) Surface of a Blank 1-100 bead (x 15,000 Magnification)

The SEM images of Blank 1-100 (Figures 4.7a and b) show that the beads and surfaces are similar to Figure 4.6 (BA Conj 100) with a sheet like structure visible in Figure 4.7b, indicating the formation of an amide coating on the surface of the beads.

Figure 4.8  SEM Image of a) Blank 2-100 beads (x 250 Magnification) and b) Surface of a Blank 2-100 bead (x 15,000 Magnification)

The surface of Blank 2-100 unlike the other surfaces in the BA-100 series were covered in what appears to be nodules of approximately 0.1 µm in diameter. The reason the surface of the Blank2-100 beads were different from the Blank1-100 beads relates to the content of the reaction mixtures (Table 4.0). The Blank 1-100 surface sheet like structure is likely to be composed of amide sheets can be formed by reaction of the butylamine with the carboxyl groups present on the activated carbon surface, however as no butylamine is present in the reactants for Blank 2-100, the sheet like structure was not observed but rather a dispersed series of nodules on the surface.
The surface of Blank 3-100 unlike Blank 1-100 displayed some aggregates approximately 0.5 μm in diameter, which were less in number than on Blank 2-100 (Figure 4.8b). These could be caused by the direct reaction of the butylamine with the surface carboxylic acid groups resulting in the formation of amide groups on the surface.

**4.3.4.2 BA-125 Series**

The surface of BA Conj 125 appeared to be covered in a sheet like structure in the high magnification image (Figure 4.10b). Similar to the sheet like structure observed previously this is probably due the coating of the surface of the carbon by reaction of the butylamine with the carboxylic acid functional groups.
The surface of Blank 1-125 (Figure 4.11b) revealed the presence of only a few sites with a sheet like structure, although not as pronounced as in Figure 4.10b.

A sheet-like structure was also found to be present on the surface of Blank 2-125 (Figure 4.12b), similar to that found on the surface of BA Conj 125 and Blank 1-125 although not as apparent.
4.3.5 Results of Energy Dispersive Spectroscopy by X-ray

4.3.5.1 BA-100 Series

The C and O Kα intensity of the BA-100 series are shown in Figure 4.14 and Table 4.5. The greatest intensity of carbon peak for the groups were found for Blank 2-100. The reason for this is for all the BA-100 series, except for Blank 2-100, butylamine was found to be conjugated to the surface. This would result in a decrease in the O counts because of loss of –OH group from carboxylic acids and an increase in the C counts due to the binding of the butylamine.
Figure 4.14  Plot of Net C Kα and O Kα for BA-100 Series

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>Range (keV)</th>
<th>Gross</th>
<th>Net</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA Conj 100</td>
<td>C Kα</td>
<td>0.168 to 0.387</td>
<td>46933</td>
<td>39307</td>
<td>98.0</td>
</tr>
<tr>
<td></td>
<td>O Kα</td>
<td>0.407 to 0.647</td>
<td>5696</td>
<td>808</td>
<td>2.0</td>
</tr>
<tr>
<td>Blank 1-100</td>
<td>C Kα</td>
<td>0.168 to 0.387</td>
<td>46100</td>
<td>37460</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>O Kα</td>
<td>0.407 to 0.647</td>
<td>7706</td>
<td>615</td>
<td>1.6</td>
</tr>
<tr>
<td>Blank 2-100</td>
<td>C Kα</td>
<td>0.168 to 0.387</td>
<td>70230</td>
<td>60900</td>
<td>97.1</td>
</tr>
<tr>
<td></td>
<td>O Kα</td>
<td>0.407 to 0.647</td>
<td>7765</td>
<td>1811</td>
<td>2.9</td>
</tr>
<tr>
<td>Blank 3-100</td>
<td>C Kα</td>
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<td>58969</td>
<td>47851</td>
<td>98.2</td>
</tr>
<tr>
<td></td>
<td>O Kα</td>
<td>0.407 to 0.647</td>
<td>9460</td>
<td>867</td>
<td>1.8</td>
</tr>
</tbody>
</table>

Table 4.5  EDX results of BA-100 series
From the results of the EDX of the O/C ratio (Figure 4.15) all the BA 100 series had a lower O/C ratio than the control carbon S-50-9/100/25-00. The O/C ratio was lowest for Blank 1-100, indicating the greatest reduction in O peak intensity in the top 1-2 µm of the surface.

4.3.5.2 BA-125 Series

The C Kα and O Kα peak intensity for the BA-125 series is shown in Figure 4.16 and Table 4.6. The greatest C Kα intensity found was for Blank 3-100 for BA-125 series (Figure 4.16)

The O/C ratio was found to be lower for all the activated carbons in the BA-125 series when compared to the control (S-50-9/125-00) in Figure 4.17. The Blank 2-125 possessed the greatest O/C ratio of the BA-125 series with BA Conj 125 shown to have the lowest O/C ratio indicating the greatest reduction in the oxygen surface functional groups.
Figure 4.16  Plot of Net C Kα and O Kα for BA-125 Series

Table 4.6  EDX Results of BA-125 Series NOVACARBs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>Range (keV)</th>
<th>Gross</th>
<th>Net</th>
<th>% Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA Conj 125</td>
<td>C Ka</td>
<td>0.168 to 0.387</td>
<td>45063</td>
<td>34557</td>
<td>98.5</td>
</tr>
<tr>
<td></td>
<td>O Ka</td>
<td>0.407 to 0.647</td>
<td>8405</td>
<td>514</td>
<td>1.5</td>
</tr>
<tr>
<td>Blank 1-125</td>
<td>C Ka</td>
<td>0.168 to 0.387</td>
<td>46016</td>
<td>38078</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>O Ka</td>
<td>0.407 to 0.647</td>
<td>6061</td>
<td>770</td>
<td>2.0</td>
</tr>
<tr>
<td>Blank 2-125</td>
<td>C Ka</td>
<td>0.168 to 0.387</td>
<td>52396</td>
<td>42544</td>
<td>97.3</td>
</tr>
<tr>
<td></td>
<td>O Ka</td>
<td>0.407 to 0.647</td>
<td>7828</td>
<td>1185</td>
<td>2.7</td>
</tr>
<tr>
<td>Blank 3-125</td>
<td>C Ka</td>
<td>0.168 to 0.387</td>
<td>92551</td>
<td>78877</td>
<td>97.8</td>
</tr>
<tr>
<td></td>
<td>O Ka</td>
<td>0.407 to 0.647</td>
<td>10629</td>
<td>1737</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The reason for this is the same given for the BA-100 series. That all the BA-125 series except for Blank 2-125, there was evidence that butylamine was found to be conjugated to the surface. This would result in a decrease in the O counts because of loss of –OH group from carboxylic acids and an increase in the C counts due to the binding of the butylamine.
Figure 4.17  Plot of ratio (oxygen/carbon) of BA-125 series

4.4 Discussion

From the results of the Boehm titrations (Figures 4.2–4.3 and Tables 4.1 and 4.3) conjugation with butylamine appears to have worked, as seen by the reduction in the number of carboxyl groups available after conjugation with butylamine for both BA 100 and BA 125 series. The results for Blank 2-100 and Blank 2-125 where the number of carboxyl groups is reduced is probably due to a competing reaction as no butylamine was added to these reactions to cause conjugation. However, these results have to be viewed with some scepticism, given the size of the errors obtained for lactonic and phenolic groups, which are calculated from the results of incubation of Na₂CO₃ - NaHCO₃ and NaOH - Na₂CO₃ respectively (Table 4.1 and 4.2). All the results which displayed very large standard deviations involved the use of the carbodiimide EDC. There may be a problem with incomplete washing of the EDC from the surface, even though EDC and urea by-products should be water soluble and removed during the sample washing. The surface of the activated carbon may have some affinity for EDC or the urea byproducts, as for Blank1-100 an isonitrile peak was observed. This may come from the reaction with the surface and acetonitrile (or EDC), possibly via formation of a π complex with the carbon surface. This reaction could proceed by a mechanism such as a Curtius Rearrangement.
Evidence of butylamine conjugation was found for BA Conj 100, BA Conj 125, Blank 3-100 and Blank 3-125 and Blank 1-100 from the FTIR spectra where peaks for amide I and II of secondary amides were found, along with N-H str for secondary amides and weak or no COO' peaks were observed.

4.5 Conclusions

From the results for BA 100 and BA 125 series it was found that conjugation of butylamine to carboxylic functional groups on the surface of activated carbons did occur for BA 100, BA 125, Blank 1-100, Blank 1-125, Blank 3-100 and Blank 3-125. However other side reactions were also found to occur which may involve the reaction of EDC or the solvent acetonitrile with the activated carbon surface, which interfered with the determination of the lactonic and phenolic groups in the Boehm titration experiments (Figure 4.2 and Figure 4.3). Therefore to minimise these side reactions the use of solvent other than acetonitrile may be a better option in the conjugation of butylamine to the activated carbon surfaces, implementation of more vigorous washing regime or possibly the use of solid phase organic chemistry techniques used in peptide assembly to attach the ligand of interest to the activated carbon surface.
Chapter 5  Conjugation of Butylamine to the Surface of NOVACARBs Using Thionyl Chloride
5.0 Introduction

The second method of conjugation undertaken was the conversion of the carboxylic acid functional groups on the surface of the activated carbons to acyl chloride moieties with thionyl chloride followed by reaction of the acyl chloride with butylamine.

![Reaction scheme for conjugation of butylamine using thionyl chloride](image)

Figure 5.0  Reaction scheme for conjugation of butylamine using thionyl chloride

The use of thionyl chloride in the transformation of carboxylic acid groups is well established in organic chemistry and this method of modification has been used recently in the transformation of carboxylic groups present on the surface of activated carbons (Tamiai et al. 2006, Silva et al. 2002, Alves et al. 2001).

5.1 Materials and Experimental Methods

5.1.1 Materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Buffer Solutions pH 4 (Phthalate)</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>pH 7 (Phosphate)</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>Butylamine</td>
<td>Sigma-Aldrich Company Limited</td>
</tr>
<tr>
<td>Deionised water</td>
<td>In house, 15 mΩ</td>
</tr>
<tr>
<td>Electrode Buffer Solution</td>
<td>BDH</td>
</tr>
<tr>
<td>Hydrochloric acid (HCl)</td>
<td>Sigma-Aldrich Company Limited</td>
</tr>
<tr>
<td>Methanol</td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>NOVACARB S-50-9/100/125-00</td>
<td>MAST Carbon</td>
</tr>
</tbody>
</table>
5.1.2 Equipment

Glass Combination Electrode     (BDH)
Heating Mantle      (Electromantle)
pH meter Orion 410A      (Thermo Electron)
Shaking Incubator       (Bibby Stuart Scientific)
Vacuum Oven       (Gallenkamp)

5.2 Experimental Methods

5.2.1 Thionyl Chloride Method

Activated carbons were dried in a vacuum oven at 120 °C to remove surface water, until constant weight, then the carbons were allowed to cool in a dessicator prior to use. Dried activated carbon (5 g) was added to a 100 cm³ round bottomed flask, to which 40 cm³ of 5 % thionyl chloride in anhydrous toluene and a boiling chip were added, a reflux condenser and a drying tube were fitted to the flask.

The contents of the flask were refluxed for 5 hours, cooled and filtered and then washed with anhydrous toluene (2 x 100 cm³) to remove any residual thionyl chloride. The washed carbon was then transferred to a Soxhlet extraction thimble and extracted with 100 cm³ anhydrous toluene for 2 hours. The thimble was removed and the carbon washed with 2 x 100 cm³ anhydrous toluene, to remove any thionyl chloride or chloride remaining. The waste solution initially had a strong yellow colour before becoming colourless. The
thimble was emptied and the activated carbon was placed in a large Petri dish and then dried at 120 °C overnight in a vacuum oven.

The carbon was added to a 100 cm³ round bottomed flask into which was added a ten fold molar excess (in relation to the number of carboxylic groups on the surface of each activated carbon) of n-butylamine in anhydrous toluene. A reflux condenser and a drying tube were then fitted to the flask and the contents refluxed for 4 hours. On addition of butylamine to the flask, white fumes were observed at the surface of the solution.

The contents of the flask were then filtered and the activated carbon washed with anhydrous toluene, then 0.1 M NaOH. The washed activated carbon was then transferred to a Soxhlet thimble and Soxhlet extracted into 100 cm³ anhydrous toluene for 7 hours. The activated carbon was then removed from the Soxhlet thimble and placed in a glass Petri dish and dried in a vacuum oven at 120 °C overnight.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC-100</td>
<td>S-50-9/100/25-00 reacted with Butylamine using SOCl₂ method</td>
</tr>
<tr>
<td>TC-125</td>
<td>S-50-9/125-00 reacted with Butylamine using SOCl₂ method</td>
</tr>
<tr>
<td>TC-100-90-2</td>
<td>N-100-90-2-2 reacted with Butylamine using SOCl₂ method</td>
</tr>
<tr>
<td>TC-125-90-2</td>
<td>N-125-90-2-2 reacted with Butylamine using SOCl₂ method</td>
</tr>
</tbody>
</table>

Table 5.1 Activated carbons prepared by thionyl chloride method

The nitric acid treated samples used in the thionyl chloride experiments (N-100-90-2-2 and N-125-90-2-2), were prepared as a second batch and are not from the previous N-100-90-2 and N-125-90-2 batches. They were however prepared using the same method of preparation as outlined in Chapter 3.

5.2.2 Boehm Titrations

Boehm titrations were performed on the thionyl chloride treated activated carbons using the experimental methods outlined in section 2.1.3.1.
5.2.3  Mass Titrations

The mass titrations of the thionyl chloride treated activated carbons were examined using the experimental methods outlined in section 2.1.3.2.

5.2.4  Fourier Transform Infrared Spectroscopy

The thionyl chloride treated activated carbons were analysed using FTIR as outlined using the method previously described in section 2.1.3.3.

5.2.5  Scanning Electron Microscopy

The thionyl chloride treated activated carbon beads were examined using the experimental methods as described in section 2.1.3.5.

5.2.6  Electron Diffraction by X-ray

The EDS of the thionyl chloride treated activated carbons were examined using the experimental methods as outlined in section 2.1.3.6.

5.2.7  Bulk Density Measurements

Bulk density measurements were performed on the thionyl chloride modified activated carbon beads, using the experimental methods as outlined in section 2.1.3.9.

5.3  Thionyl Chloride Method – Results

The activated carbons prepared using these methods were coded as shown below in Table 5.1.
5.3.1 Results of Boehm Titrations

5.3.1.1 TC-100 Series

The results for the Boehm titrations for TC-100 (Figure 5.1) revealed that the expected reduction in carboxyl groups as a result of the reaction with butylamine to form amide moieties was not readily apparent. The reduction in the number of carboxyl groups observed in comparison to the non-conjugated surface S-50-9/100/25-00 was only 0.04 meq/g. All other surface groups were also found to have been reduced and the number of phenolic groups was found to be zero compared to 0.355 meq/g for S-50-9/100/25-00. Indicating that some other side reactions had occurred.

![Graph showing distribution of functional groups](image)

**Figure 5.1** Plot of distribution of functional groups present on the surface of S-50-9/100/125-00 and TC-100 (Mean a (n=3) ± Standard Deviation)
The results of the Boehm titrations for TC-100-90-2-2 (Figure 5.2 and Table 5.2), like the results observed for TC-100 (Figure 5.1), showed a reduction in all the surface groups. However, a large reduction in the number of carboxyl groups was observed from 0.802 for N-100-90-2-2 to 0.147 meq/g for TC-100-90-2-2, indicating the probable reaction of the acyl chloride groups with the butylamine.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total (meq/g)</th>
<th>Basic (meq/g)</th>
<th>Acidic (meq/g)</th>
<th>Carboxyl (meq/g)</th>
<th>Lactonic (meq/g)</th>
<th>Phenolic (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC-100</td>
<td>0.439±0.009</td>
<td>0.173±0.008</td>
<td>0.266±0.002</td>
<td>0.230±0.006</td>
<td>0.081±0.013</td>
<td>0±0.012</td>
</tr>
<tr>
<td>TC-100-90-2-2</td>
<td>0.470±0.011</td>
<td>0.210±0.004</td>
<td>0.260±0.010</td>
<td>0.147±0.013</td>
<td>0.199±0.016</td>
<td>0±0.024</td>
</tr>
</tbody>
</table>

Table 5.2 Results of Boehm Titrations for TC-100 Series
5.3.1.2 TC-125 Series

The Boehm titration results of TC-125 shown in Figure 5.3 and Table 5.3 revealed a reduction in the number of carboxyl groups when compared to the non-conjugated S-50-9/125-00 of 0.145 meq/g. There was also observed the disappearance in phenolic groups as observed for TC-100 (Figure 5.1), indicating the possibility of a side reaction occurring and an increase in the number of lactonic groups determined.

![Figure 5.3 Plot of distribution of functional groups present on the surface of S-50-9/125-00 and TC-125 (Mean a (n=3) ± Standard Deviation)](image)

Figure 5.3 Plot of distribution of functional groups present on the surface of S-50-9/125-00 and TC-125 (Mean a (n=3) ± Standard Deviation)

The results for conjugation of butylamine to the surface of oxidised activated carbon (TC-125-90-2-2) shown in Figure 5.4 and Table 5.3, show a reduction in the number of surface groups for all the functional groups examined. The reduction in the number of carboxylic groups was found to be 0.496 meq/g.
Figure 5.4  Plot of distribution of functional groups present on the surface of N-125-90-2-2 and TC-125-90-2-2 (Mean a (n=3) ± Standard Deviation)

Again with the TC-125 series as with the TC-100 series, the disappearance of the phenolic groups was observed. This would indicate the possible reaction of the thionyl chloride with the phenolic groups, with only a small decrease in the number of carboxyl groups observed. However, for the oxidised samples N-100-90-2-2 and N-125-90-2-2, as there are few phenolic surface groups present, a far greater decrease in the carboxyl groups is observed, indicating the reaction of the acyl chloride with the butylamine.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total</th>
<th>Basic</th>
<th>Acidic</th>
<th>Carboxyl</th>
<th>Lactonic</th>
<th>Phenolic</th>
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<tr>
<td>TC-125</td>
<td>0.832</td>
<td>0.348</td>
<td>0.483</td>
<td>0.219</td>
<td>0.337</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>± 0.027</td>
<td>± 0.015</td>
<td>± 0.023</td>
<td>± 0.012</td>
<td>± 0.034</td>
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</tr>
<tr>
<td>TC-125-90-2-2</td>
<td>0.923</td>
<td>0.208</td>
<td>0.716</td>
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<td>0.399</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>± 0.011</td>
<td>± 0.004</td>
<td>± 0.010</td>
<td>± 0.004</td>
<td>± 0.011</td>
<td>± 0.026</td>
</tr>
</tbody>
</table>

Table 5.3  Results of Boehm Titrations for TC-125 Series
5.3.2 Results of Mass Titrations

5.3.2.1 TC-100 Series

The results of the mass titrations for TC-100 shown in Figure 5.5, show that at 10 % w/v the pH_{PZC} has not been reached therefore the trendlines for the three incubation solutions were extrapolated to determine the pH_{PZC}.

![Figure 5.5 - Plot of pH_{PZC} experiment for TC-100](image)

The pH_{PZC} was determined as 6.14 for TC-100 which was lower in comparison to the pH_{PZC} of S-50-9/100/25-00 (Table 2.4) which was 9.91.

The mass titration plot for TC-100-90-2 shown in Figure 5.6 reveals that when TC-100-90-2 was incubated with the three different pH solutions there were very few surface groups with ionisable moieties to react with, as the gradient of the lines is only slight making the pH_{PZC} undeterminable. The pH_{PZC} of the non-conjugated carbon N-100-90-2-2 was 3.67.
5.3.2.2 TC-125 Series

The mass titration results for TC-125 (Figure 5.7) revealed that the pH_{PZC} was not reached when 10 % w/v activated carbon was used, therefore the pH_{PZC} was determined by extrapolated from the three trendlines. The pH_{PZC} was determined as 4.96 ± 0.24 which was considerably lower than the pH_{PZC} (9.99) as determined for S-50-9/125-00 in Table 2.4.

For TC-125-90-2-2 the mass titration results (Figure 5.8) revealed that the extrapolated pH_{PZC} was found to be 3.85±0.28. This was slightly larger than the pH_{PZC} determined for N-125-90-2-2 of 3.58.
Figure 5.7  Plot of pH\textsubscript{PZC} experiment for TC-125

Figure 5.8  Plot of pH\textsubscript{PZC} experiment for TC-125-90-2-2
5.3.3 Results of Fourier Transform Infrared Spectroscopy

5.3.3.1 TC-100 Series

The FTIR of TC-100 is shown in Figure 5.9a-c with S-50-9/100/25-00 for comparison. In the region 4000-2000 cm\(^{-1}\) (Figure 5.9b) TC-100 was found have peak at 3440 cm\(^{-1}\) (O-H), with a shoulder at 3232 cm\(^{-1}\) (N-H secondary amide). There was a broad peak representing the aliphatic C-H \textit{stretches} in the TC-100 spectra.

![FTIR Transmission spectrum of TC-100 and S-50-9/100/25-00](image)

**Figure 5.9a** Plot of FTIR Transmission spectrum of TC-100 and S-50-9/100/25-00 (4000-400 cm\(^{-1}\))
In the range 2000-400 cm\(^{-1}\) the spectra of TC-100 (Figure 5.9c) the signal to noise ratio was low, resulting in a spectra which was noisy. This could be due to incomplete grinding of the carbon during the preparation of the KBr disc. The spectra contained the aromatic C=C \(\text{str}\) at 1647 cm\(^{-1}\) and an additional peak at 1633 cm\(^{-1}\) (Amide I N-H bending). The additional aromatic C=C \(\text{str}\) peaks were weak but visible around 1500-1550 cm\(^{-1}\), however the C-H alkene \(\text{def}\) peaks at 1417 and 1435 cm\(^{-1}\) and aliphatic C-H def peaks at 1319 and
1340 cm\(^{-1}\) are not present, as the COO\(^-\) sym \textit{str} is very weak. The large peak centred at 1115 cm\(^{-1}\) for S-50-9/100/25-00 is reduced in intensity and shifted to a lower wavenumber with the emergence of two peaks at 1064 (C-O \textit{str} possibly from a lactone or acid anhydride). The reduction in the peak intensity of the peak at 1115 cm\(^{-1}\) is a consequence of the disappearance in the phenolic groups as indicated by Boehm titrations (Figure 5.1). The other peaks present from 900 to 400 cm\(^{-1}\) include aromatic C-H oop def 849 cm\(^{-1}\) and -CH\(_2\)- rocking at 714 cm\(^{-1}\) of aliphatic groups.

\textbf{Figure 5.10a}  Plot of FTIR Transmission spectrum of TC-100-90-2-2 and N-100-90-2-2 (4000-400 cm\(^{-1}\))

The FTIR spectra of TC-100-90-2-2 is shown along with the spectrum of the oxidised N-100-90-2-2 (Figures 5.10a-c) for comparison.
Figure 5.10b  Plot of FTIR Transmission spectrum of TC-100-90-2-2 and N-100-90-2-2 (4000-2000 cm\(^{-1}\))

The region 4000- 2000 cm\(^{-1}\) shown in Figure 5.10b revealed that there is a widening of the peak O-H peak and a shift to 3420 cm\(^{-1}\) from 3430 cm\(^{-1}\) and the development of a weak peak at 3340 cm\(^{-1}\) possible secondary amine N-H . The shoulder observed for N-100-90-2-2 at 3250 cm\(^{-1}\) is not visible for TC-100-90-2-2. The aliphatic C-H str at 2850 to 2950 cm\(^{-1}\) appear unchanged.

Figure 5.10c  Plot of FTIR Transmission spectrum of TC-100-90-2-2 and N-100-90-2-2 (2000-400 cm\(^{-1}\))
The 2000-400 cm\(^{-1}\) range (Figure 5.10c) reveals the presence of weak peaks for amide I and II at 1684 and 1558 cm\(^{-1}\) respectively. Peaks for COO\(^{-}\) \textit{sym} and \textit{asym str} were observed for TC-100-90-2-2 and the development of a series of peaks around 669 cm\(^{-1}\) O-H. Additional aliphatic C-H peaks were observed at 1450 cm\(^{-1}\) and 714 cm\(^{-1}\) for CH\(_2\) rocking from aliphatic groups possibly from the conjugation of the butylamine.

### 5.3.3.2 TC-125 Series

For the TC-125 series the changes as a result of the conjugation of butylamine to the surface of activated carbons TC-125 and S-50-9/125-00 are shown in Figures 5.11a-c. The spectra of TC-125 is very noisy in the range 3500 -4000 cm\(^{-1}\) possibly due to incomplete grinding of the carbon during sample preparation.

**Figure 5.11a** FTIR spectrum of TC-125-and S-50-9/125-00 (4000-400 cm\(^{-1}\))
Figure 5.11b  FTIR spectrum of TC-125-and S-50-9/125-00 (4000-2000 cm\(^{-1}\))

In the region 4000-2000 cm\(^{-1}\) shown in Figure 5.11b the O-H peak occurs at the same wavenumber for both TC-125 and S-50-9/125-00. The shoulder peak of S-50-9/125-00 is not apparent for TC-125, however a few additional peaks are found in the 2850-2950 cm\(^{-1}\) aliphatic C-H range.

Figure 5.11c  FTIR spectrum of TC-125-and S-50-9/125-00 (2000-400 cm\(^{-1}\))

In the region 2000-400 cm\(^{-1}\) (Figure 5.11c) the spectrum is noisy in the region 1700-1400
however some peaks are apparent. The amide I peak is found at 1662 cm\(^{-1}\) and amide II peak at 1560 cm\(^{-1}\). The COO\(^-\) sym str disappears in the TC-125 spectra, and aliphatic C-H def peaks at 1430 cm\(^{-1}\). The aromatic C-H def peaks are present, and a decrease in the O-H at 671 cm\(^{-1}\) is seen. There is also the emergence of a peak at 1228 cm\(^{-1}\) C-O str, possibly from lactone. A peak at 714 cm\(^{-1}\) for CH\(_2\) rocking was found from aliphatic groups possibly from the conjugation of the butylamine.

Figure 5.12a FTIR spectrum of TC-125-90-2-2 and N-125-90-2-2 (4000-400 cm\(^{-1}\))

Figure 5.12b FTIR spectrum of TC-125-90-2-2 and N-125-90-2-2 (4000-2000 cm\(^{-1}\))

The spectrum of TC-125-90-2-2 (Figure 5.12b) reveals a series of small peaks 3284, 3219,
and 3150 cm$^{-1}$ -CONH- (N-H str), 3064 and 3030 cm$^{-1}$ aromatic C-H and aliphatic C-H str peaks 2850-2950 cm$^{-1}$. The peaks from 3150 to 3284 cm$^{-1}$ indicate the successful reaction of butylamine with carboxylic groups to form amide moieties on the surface.

![FTIR Spectrum](image)

**Figure 5.12c  FTIR spectrum of TC-125-90-2-2 and N-125-90-2-2 (2000-400 cm$^{-1}$)**

The spectrum of TC-125-90-2-2 for the range 2000-400 cm$^{-1}$ (Figure 5.12c) revealed the presence of amide I and amide II peaks (1685 and 1558 cm$^{-1}$) indicating the formation of amide moieties by butylamine and carboxylic groups, aromatic C-H str (1550-1500 cm$^{-1}$), aliphatic C-H def (1458 cm$^{-1}$), COO$^-$ sym str (1385 cm$^{-1}$), at 1232 cm$^{-1}$ C-O str, possibly from lactone, C-O str (1082 cm$^{-1}$), O-H oop bending (681 and 669 cm$^{-1}$), aromatic C-H oop def (455 cm$^{-1}$).
5.3.4 Results of Scanning Electron Microscopy

5.3.4.1 TC-100 Series

Figure 5.13  SEM image of a) TC-100 beads (x 250 Magnification) and
b) Surface of a TC-100 bead (x 15,000 Magnification)

Figure 5.14  SEM image of a) TC-100-90-2-2 beads (x 250 Magnification) and
b) Surface of a TC-100-90-2-2 bead (x 15,000 Magnification)

The SEM analysis of the surfaces of TC-100 (Figures 5.13a-b) and TC-100-90-2-2 (Figure 5.14a-b), revealed that the surfaces in the higher magnification images displayed a more textured topography than those seen for the non-conjugated surfaces. This was more apparent in TC-100-90-2-2 (Figure 5.14b) which was the nitric acid oxidised surface possibly indicating a greater density of butylamine conjugated to the surface.
5.3.4.2 TC-125 Series

The results of the SEM analysis for the TC-125 series activated carbons TC-125 (Figure 5.15a-b) and TC-125-90-2-2 (Figure 5.16a-b) revealed surfaces in the higher magnification images which displayed a rougher surface possibly indicating the conjugation of butylamine to the surface. This is particularly visible in Figure 5.16b where the density of these sites is greater than the non-oxidised and TC-100 series surfaces.
5.3.5 Results of Energy Dispersive Spectroscopy by X-ray

5.3.5.1 TC-100 Series

The results of the EDX (Figure 5.17) showed the intensity of the C and O Kα signals of TC-100 possessed a greater carbon content than the control S-50-9/100/25-00, this increase was accompanied by a reduction in the oxygen surface content (Table 5.4 and Table 2.7). This indicates that the surface oxygen containing functional groups had reacted during the conjugation with butylamine. The same effect was observed for the N-100-90-2 activated carbon as the % of carbon increased from 90.2 % to 97.5 % and the oxygen content decreased to 2.5 % (Table 5.4).

Figure 5.17  Plot of net C Kα and O Kα for TC-100 series
Figure 5.18  Plot of ratio (oxygen/carbon) of TC-100 series

The ratios of the O/C shown in Figure 5.18 revealed that after conjugation with butylamine, the ratio of O/C reduced for both TC-100 and TC-100-90-2-2 when compared to the non-conjugated control, indicating that conjugation had indeed taken place by the increased carbon peak intensity and reduction in the oxygen peak intensity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>Range (keV)</th>
<th>Gross</th>
<th>Net</th>
<th>% Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC-100</td>
<td>C Ka</td>
<td>0.168 to 0.387</td>
<td>57511</td>
<td>46741</td>
<td>98.2</td>
</tr>
<tr>
<td></td>
<td>O Ka</td>
<td>0.407 to 0.647</td>
<td>7677</td>
<td>822</td>
<td>1.8</td>
</tr>
<tr>
<td>TC-100-90-2-2</td>
<td>C Ka</td>
<td>0.168 to 0.387</td>
<td>49394</td>
<td>39536</td>
<td>97.5</td>
</tr>
<tr>
<td></td>
<td>O Ka</td>
<td>0.407 to 0.647</td>
<td>8334</td>
<td>996</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 5.4  Results of EDX experiments for TC-100 series
5.3.5.2 TC-125 Series

The results of the EDX measurements on the TC-125 Series of activated carbons (Figure 5.19) revealed that the carbon peak intensities for TC-125 were only marginally greater than the control S-50-9/125-00, with the oxygen peak intensity reduced. For TC-125-90-2-2 both the carbon and oxygen peak intensities were greatly reduced in comparison to N-125-90-2-2.

![Figure 5.19 Plot of net C Kα and O Kα for TC-125 series](image)
The results of the EDX (Table 5.5) analysis for the TC-125 series revealed that after reaction with thionyl chloride and conjugation with butylamine the oxygen content of the surfaces of both TC-125 and TC-125-90-2-2 were shown to decrease from 9.4 and 9.0 to 1.6 and 2.2 % respectively (Table 5.5). This decrease was accompanied by an increase in the carbon content at the surface, which is indicative of the butylamine reacting with the functional groups of the surface to reduce the oxygen content upon formation of an amide or amine moiety.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>Range (keV)</th>
<th>Gross</th>
<th>Net</th>
<th>% Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC-125</td>
<td>C $\alpha$</td>
<td>0.168 to 0.387</td>
<td>43698</td>
<td>34836</td>
<td>97.8</td>
</tr>
<tr>
<td></td>
<td>O $\alpha$</td>
<td>0.407 to 0.647</td>
<td>7313</td>
<td>774</td>
<td>2.2</td>
</tr>
<tr>
<td>TC-125-90-2-2</td>
<td>C $\alpha$</td>
<td>0.168 to 0.387</td>
<td>47772</td>
<td>38994</td>
<td>98.4</td>
</tr>
<tr>
<td></td>
<td>O $\alpha$</td>
<td>0.407 to 0.647</td>
<td>7006</td>
<td>617</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 5.5  Results of EDX experiments for TC-125 series
5.3.6  Results of Bulk Density Measurements

5.3.6.1 TC-100 Series

The bulk densities determined for the TC-100 series activated carbons are shown in Figure 5.21. The conjugation of butylamine via the reaction of thionyl chloride with the carboxylic acid groups to form acyl chlorides caused an increase in the bulk densities of both the oxidised and non-oxidised activated carbons. The bulk density of TC-100 was shown to have increased to 0.848 g/cm$^3$ from 0.675 g/cm$^3$ for S-50-9/100/25-00 and from 0.711 g/cm$^3$ for N-100-90-2-2 to 0.886 g/cm$^3$. The difference in the bulk densities after treatment with thionyl chloride and conjugation with butylamine, is 0.173 g/cm$^3$ for TC-100 and 0.175 g/cm$^3$ for TC-100-90-2-2.

![Figure 5.21 Bulk density measurements of TC-100 series](image)

5.3.6.2 TC-125 Series

The bulk densities determined for the TC-125 series activated carbons are shown in Figure 5.22. The bulk density of TC-125 was shown to have increased to 0.803 g/cm$^3$ from 0.609 g/cm$^3$ for S-50-9/100/25-00 and from 0.643 g/cm$^3$ for N-100-90-2-2 to 0.800 g/cm$^3$. This is as a result of conjugation of butylamine to the surface, resulting in an increase in the
bulk density. The difference in the bulk densities after treatment with thionyl chloride and conjugation with butylamine, is 0.194 g/cm³ for TC-125 and 0.157 g/cm³ for TC-125-90-2-2.

Figure 5.22  Bulk density measurements of TC-125 series

5.4  Discussion

From the results of the Boehm titrations (Figures 5.1–5.4 and Tables 5.2-5.3) conjugation with butylamine appears to have worked for the oxidised surfaces TC-100-90-2-2 and TC-125-90-2-2, where a large drop in the amount of carboxylic groups was determined. There appeared to be a number of side reactions which have occurred during the conjugation, as observed by the changes in the number of lactonic and phenolic groups. Boehm titration allows the determination of carboxyl, lactonic and phenolic moieties on the surface of the activated carbons. However from the results of the SIMS (Figure 2.10a-c, 2.11a-c, 3.7a-c and 3.22a-c) where aliphatic OH fragments were found on all surfaces, these could react with the thionyl chloride to form alkyl chlorides which would then react with the butylamine to form a secondary amine. This would prevent the phenolic groups from being determined by titration. The lactonic groups which are determined may also contain lactol groups which would be chlorinated by the thionyl chloride and then react with the butylamine to form a secondary amine moiety, explaining the reduction in the
number of lactonic groups for TC-100, TC-100-90-2-2 and TC-125-90-2-2. The increase in the lactonic content of TC-125 may be explained by the positioning of phenolic (or aliphatic –OH) directly beside a carboxylic group, which upon intramolecular rearrangement with the elimination of H₂O.

As the two oxidised activated carbon surfaces were shown to have no phenolic groups present, these groups would therefore not be available to consume any butylamine and therefore the conjugation to carboxylic groups could proceed.

The FTIR of TC-100-90-2-2, TC-125 and TC-125-90-2-2 all revealed the presence of amide I and II peaks, indicating that secondary amide moieties had been formed from the reaction of the butylamine and carboxylic acid groups. TC-100 showed no evidence of amide I and II peaks, as from the Boehm titration results the reduction in the carboxyl groups found was only 0.04 meq/g (Figure 5.1). However, evidence of secondary amides were found from a weak shoulder peak at 3232 cm⁻¹.

Conjugation of butylamine to the surface groups was evident from the increases in the bulk densities for all the TC-100 and TC-125 series activated carbons (Figure 5.21 and 5.22), and the increase in carbon content and decrease in O/C peak ratio observed with EDX results (Figures 5.18 and 5.20 and Tables 5.4 and 5.5).

## 5.5 Conclusions

The conjugation of butylamine to the surface of TC-100, TC-100-90-2-2, TC-125 and TC-125-90-2-2 was shown to occur for all activated carbons, however in every case additional side reactions were also found to occur at the same time. These side reactions included the reaction of phenolic and aliphatic hydroxyl groups and lactols to form benzyl and alkyl chlorides which may then react with butylamine to form secondary amine moieties. The increase in the surface lactonic groups found for TC-125 may be a direct result of intramolecular rearrangements between carboxylic and neighbouring hydroxyl group.
The more successful conjugations were for the oxidised activated carbons TC-100-90-2-2 and TC-125-90-2-2, as the absence of hydroxyl groups (aliphatic or phenolic), saw the greatest reductions in the number of carboxyl groups.
Chapter 6  Conclusions
6.0 General Discussion

Activated carbons are generally considered to possess a hydrophobic surface due the functional groups (C=C, C-C and C-H) present on the surface. Therefore to improve their ability to interact with hydrophilic solutions in extracorporeal systems, the activated carbons have to be modified. The most common method used to increase the hydrophilicity of the surfaces is to perform oxidation. This may be either in the form of dry oxidation using a gas or wet oxidation employing an acid or oxidising solution. Of the oxidation methods used, nitric acid is one of the most common methods as it allows the rapid formation of acidic oxygen containing functional groups. To further functionalise the surfaces of the activated carbons, the conjugation of a small test bioligand (butylamine), was undertaken to examine the feasibility of modifying the surface of the activated carbons using bioligands for use in extracorporeal systems.

The activated carbons used in this work were NOVACARB activated carbons supplied by MAST Carbon Ltd. and produced from phenolic polymer based resins and are the first attempt to further modify these carbons using ligands, for use in extracorporeal systems.

The NOVACARBs were then treated with 20 % nitric acid to produce the N-100 and N-125 series respectively. Then further modification of the non-oxidised was performed by conjugation of butylamine using either a carbodiimide (BA-100 and BA-125 Series) or via conversion of the carboxylic groups to acyl chlorides using thionyl chloride (TC-100 and TC-125 series). The codes used for the activated carbons used and produced throughout this work and the modification performed are outlined in Tables 6.0 and 6.1

6.1 NOVACARB Activated Carbons

From the chemical and physical analysis undertaken it was shown that the two NOVACARB activated carbons (S-50-9/100/25-00 and S-50-9/125-00) possess similar surface chemistries, as found from the results of the Boehm and mass titrations (Figures 2.5 and Table 2.4), FTIR (Figure 2.9) and EDX (Figure 2.14 and 2.15). However, the two activated carbons have different physical properties such as a different dispersity of bead diameters and mean bead diameter (Figure 2.21 and 2.22) and bulk density (Figure 2.23).
Although the nitrogen isotherms (Figures 2.16 and 2.17) and the BET derived surface areas are similar (Figure 2.18), the pore size (Figure 2.19) and pore area distributions (Figure 2.20) also differ.

Modification of the surface of S-50-9/100/25-00 and S-50-9/125-00 was undertaken using 20 % nitric acid oxidation to increase the number of hydrophilic surface moieties at increasing temperatures.

<table>
<thead>
<tr>
<th>Code</th>
<th>Chapter/Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-50-9/100/25-00</td>
<td>Chapter 2</td>
</tr>
<tr>
<td>N-100 Series</td>
<td>Chapter 3</td>
</tr>
<tr>
<td>N-100-50-2</td>
<td>Nitric acid oxidation of S-50-9/100/25-00 at 50 °C for 2 hours</td>
</tr>
<tr>
<td>N-100-70-2</td>
<td>Nitric acid oxidation of S-50-9/100/25-00 at 70 °C for 2 hours</td>
</tr>
<tr>
<td>N-100-90-2</td>
<td>Nitric acid oxidation of S-50-9/100/25-00 at 90 °C for 2 hours</td>
</tr>
<tr>
<td>N-100-90-2-2</td>
<td>Nitric acid oxidation of S-50-9/100/25-00 at 90 °C, 2nd batch for 2 hours</td>
</tr>
<tr>
<td>BA-100 Series</td>
<td>Chapter 4</td>
</tr>
<tr>
<td>BA Conj100</td>
<td>S-50-9/100/25-00 reacted with EDC/NHS and BA</td>
</tr>
<tr>
<td>Blank 1-100</td>
<td>S-50-9/100/25-00 reacted with EDC and BA</td>
</tr>
<tr>
<td>Blank 2-100</td>
<td>S-50-9/100/25-00 reacted with EDC/NHS</td>
</tr>
<tr>
<td>Blank 3-100</td>
<td>S-50-9/100/25-00 reacted with BA</td>
</tr>
<tr>
<td>TC-100 Series</td>
<td>Chapter 5</td>
</tr>
<tr>
<td>TC-100</td>
<td>S-50-9/100/25-00 reacted with BA using SOCl₂ method</td>
</tr>
<tr>
<td>TC-100-90-2-2</td>
<td>N-100-90-2-2 reacted with BA using SOCl₂ method</td>
</tr>
</tbody>
</table>

Table 6.0 Activated carbons used and produced throughout this work derived from S-50-9/100/25-00
Table 6.1  Activated carbons used and produced throughout this work derived from S-50-9/125-00

### 6.2 Oxidation of NOVACARB Activated Carbons using Nitric Acid

The oxidation of the activated carbons at three different temperatures 50, 70 or 90 °C for 2 hours with 20 % nitric acid was shown to cause a significant increase in the carboxyl and lactonic surface groups and a significant decrease in the number of basic and phenolic groups for both the N-100 (Figure 3.0) and N-125 series (Figure 3.17). The results of the
mass titrations showed a linear decrease over the range of oxidation temperatures examined for the N-125 series (Figure 3.21) where as there appeared to be a stepwise decrease at 70 °C to 90 °C for N-100 series (Figure 3.4). The SIMS results for both the N-100 (Table 3.4) and N-125 series (Table 3.10), confirmed that oxidation had taken place as the O\(^{-}/C_2\)\(^{2-}\) and OH\(^{-}/C_2\)\(^{2-}\) were shown to increase after oxidation and that oxidation appeared to occur predominately in the outermost 1 - 2 nm of the surface, as when a higher intensity ion beam was used the ratios of the O\(^{-}/C_2\)\(^{2-}\) and OH\(^{-}/C_2\)\(^{2-}\) fragments were reduced (Tables 3.4C and 3.10C).

FTIR of the N-100 series revealed that the phenolic and aliphatic peaks reduced upon oxidation, and the COO\(^{-}\), C-O and O-H increased (Figure 3.6a-c), in agreement with the mass titration and Boehm titration results. The N-125 series upon oxidation revealed an increase in the intensity of C=O and COO\(^{-}\) peaks with a decrease in the aliphatic peaks indicating the conversion of aliphatic groups (Figure 3.22a-c).

Oxidation of the beads led to a decrease in bead size (Figure 3.13), but this was only significant at 90 °C (N-100-90-2). The N-125 series mean bead diameter remained relatively unchanged by nitric acid oxidation (Figure 3.30). The bulk density results revealed a maximum for the N-100 series of 0.72 g/cm\(^3\) when oxidation was performed at 70 °C (Figure 3.15). This could be due to an increase in the number of surface functional groups increasing the mass accompanied by a decrease in the bead size, which would allow for closer packing and therefore a greater number of beads to pack into the same volume. At 90 °C destruction of the internal structure by nitric acid may account for a loss of mass, hence the decrease in the bulk volume.

For the N-125 series, a maximum of 0.64 g/cm\(^3\) was observed when oxidation was performed at 50 °C (Figure 3.32). This is due to the initial increase in the number of surface groups before any significant destruction of the activated carbon by the nitric acid, which takes place at higher temperatures.

From the results of the SAXS experiments (Figures 3.16a-d and 3.33-3.36) it appears that oxidation with nitric acid at increasing temperatures causes reductions in the intensity of the scattering structures primarily in the q range of 0.03 to 0.1 Å\(^{-1}\) and 0.12 to 1 Å\(^{-1}\). These correspond to scattering structures of the order of 33 to 10 Å and 8 to 1 Å, which implies
that nitric acid oxidation performed at increasing temperatures has the greatest effect on the micropores and small mesopores of the activated carbons examined.

From the oxidation experiments it was shown that a series of phenolic resin based activated carbons could be produced with different ratios of acidic and basic surface functional groups, which could allow greater control over further reactions performed on the surface.

6.3 Conjugation Methods

To increase selective adsorption of biological species from the blood or plasma, the attachment of a test ligand (n-butylamine) to the surface of the activated carbons was undertaken to determine the feasibility of loading bioligands to the surface of the NOVACARB activated carbons.

The two conjugation methods employed to attach butylamine to the surface of the activated carbons were (i) use of carbodiimide and N-hydroxysuccinimide and (ii) conversion of the carboxylic acid groups to acyl chlorides to attach butylamine to the surface.

6.3.1 Conjugation of Butylamine with Carbodiimide

From the results for BA 100 (Figure 4.2) and BA 125 series (Figure 4.3) it was found that conjugation of butylamine to carboxylic functional groups on the surface of activated carbons did occur for BA 100, BA 125, Blank 1-100, Blank 1-125, Blank 3-100 and Blank 3-125. However other side reactions were also found to occur which may involve the reaction of EDC or the solvent acetonitrile with the activated carbon surface, which interfered with the determination of the lactonic and phenolic groups in the Boehm titration experiments.

Previously these effects have not been observed by researchers where only a change in the number of carboxylic groups or formation of amide bonds were reported. Therefore
greater care should be taken to investigate not only the surface group reported to be involved in the reaction but also what happens to the other surface functional groups.

Therefore to minimise these side reactions the use of solvent other than acetonitrile may be a better option in the conjugation of butylamine to the activated carbon surfaces, implementation of more vigorous washing regime or possibly the use of solid phase organic chemistry techniques used in peptide assembly to attach the bioligand of interest to the activated carbon surface.

6.3.2 Conjugation of Butylamine with Thionyl chloride

The conjugation of butylamine to the surface of TC-100, TC-100-90-2-2, TC-125 and TC-125-90-2-2 was shown to occur for all activated carbons (Figures 5.1 - 5.4) however, in every case additional side reactions were also found to occur at the same time. These side reactions included the reaction of phenolic and aliphatic hydroxyl groups and lactols to form benzyl and alkyl chlorides which may then react with butylamine to form secondary amine moieties. The increase in the surface lactonic groups found for TC-125 (Figure 5.3) may be a direct result of intramolecular rearrangements between carboxylic and neighbouring hydroxyl group.

The more successful conjugations based on the reduction in the number of carboxylic groups determined, occurred for the oxidised activated carbons TC-100-90-2-2 (Figure 5.6) and TC-125-90-2-2 (Figure 5.8) where there was an absence of hydroxyl groups (aliphatic or phenolic).

6.4 Conclusions

The results shown in chapter 3 show the successful production of activated carbons with increasing numbers of acidic functional groups as a result of nitric acid oxidation at increasing temperatures as shown by Boehm and mass titrations. The oxidised carbons produced were to shown to display an increased porosity in the micro and mesoporous range as seen from the results of the SAXS experiments and the oxidation was shown to
take place primary in the outermost layers of the surface as shown by the difference in the low and high ion negative fragments from SIMS analysis.

The results shown in chapters 4 and 5 show the successful conjugation of butylamine to the surface of the activated carbons selected using both a carbodiimide and thionyl chloride based method, however they also show that the reactions do not proceed as smoothly as would be expected and as many authors have previously suggested.

The side reactions which are proposed do offer a further insight into the reactivity of functional groups present on the surface of the activated carbons and that careful consideration has to be applied when performing both surface modifications on activated carbons and in determination of the functional groups present on the surface, not just examining a reduction in the number of carboxylic groups present.
Chapter 7  Further Work
7.0 Further Work

The direction of future work could involve the attachment of bioligands using other techniques such as (i) solid phase organic synthesis; and (ii) microwave chemistry. These techniques either singularly or in combination could be used to bind bioligands directly on to the surface on the activated carbons (Budarin, Clark, Tavener and Wilson, 2004).

This theme could be extended to use activated carbon as a solid phase support on which to assemble peptides, dendrimers, or dendrons which could have a high affinity for circulating immune complexes in the blood plasma or blood which could be removed during extracorporeal therapy, thereby improving the quality of life of patients with autoimmune disorders and reducing the economic burden to the healthcare provider.

7.1 Dendrimers

Dendrimers are hyperbranched polymers which can be based on organic molecules, amino acids or carbohydrates (or combinations thereof). They are composed of a core molecule onto which the sequential addition of monomeric units are added to build up branching generations (Gn). Depending on the dendrimer to be synthesised they may be full (e.g. G1, 2 or 3 etc.) or partial dendrimers (e.g. G0.5, 1.5, 2.5, 3.5, etc.). The assembly of dendrimers may be performed by either a convergent or divergent synthesis method.

Divergent synthesis involves assembling the dendrimer from a core molecule radially out to the final generation of branching groups, where as the convergent method of synthesis involves assembling the dendrimer from the outer branches to the core.

Theoretically generations up to 10, can be produced however their production can become prohibitively expensive in terms of purification costs, and generally only generations from G3 to G6 are used. The typical structure of a G3 dendrimer is shown in Figure 7.0

The main advantage of the use of dendrimer based strategies is that due to the increased branching as the generation increases, the number of functional groups present in the outer surface is large, compared to the number of sites required to attach the dendrimer to the
surface. The number of functional end groups is typically $2^n$ (where $n$ = generation of dendrimer). However, there are some dendrimers where this number of groups is even larger, for example those dendrimers (or dendrons) based on the amino acid lysine where the number of amine groups is $2 \times 2^n$, as there are two branching points at each generation (derived from the amine groups).

![Figure 7.0 Branching structure of a dendrimer (G3)](image)

Dendrimers have the same functional groups available on the end branches and can be attached to surfaces with conventional conjugation strategies. However, to achieve greater control of the binding the use of heterobifunctional dendrimers are required. These semi-dendrimers (or dendrons) are produced on solid phase resin, then cleaved and can be attached to the surface. They offer the advantage that the root and the outer functional groups are different e.g. carboxylic acid and amine or thiol and amine, thereby allowing greater control over attachment of the dendron to the surface.

However, the main difference between the dendrimers and or dendrons is the structure which they adopt. Dendrimers produced in solution have generally a spherical structure and dendrons produced on solid surfaces possess a hemi-spherical structure. The advantages of producing a dendron on a surface is that the dendron produced will be bifunctional, for example the outer branching groups may be –NH$_2$ and the core molecule group can be –CO$_2$H (Figure 7.1). This difference in structure is an advantage when
attempting to bind bi-functional dendritic structures to a surface as it will allow the conjugation to be directed, to maximise the amount of dendron binding to the surface.

Poly(amidoamine) (PAMAM) based dendrimers have been used previously in the delivery of DNA, RNA to cells (Tang, Redemann and Szoka, Jr., 1996) and some dendrimers have been shown to dramatically increase the antibody – antigen binding efficiency, when compared to the monomeric antigen (Baek and Roy, 2001 and 2002). The use of solid phase organic synthesis would allow the direct assembly on the surface of the activated carbons of a sequence specific for a particular cytokine or antibody in the plasma, via a peptide assembly using a Fluorenylmethyloxycarbonyl (Fmoc) based approach.

The advantages of dendrimers or dendrons produced using the solid phase organic synthesis rather than in the liquid phase are that the production times are shorter, the purification process is generally far simpler, involving a series of solvent washing steps and cleavage of the dendrimer from a resin and separation of the dendrimer using preparative HPLC, however the amount of dendrimer produced is limited by the size of the reaction vessel and typically they can only be produced on the 100’s mg scale, unless the assembly is performed in a plant scale microwave synthesiser.

Similar approaches have already been used to functionalise carbon nanotubes (Shi et al., 2009) for a variety of different purposes such as producing biosensors (Davis et al., 2003), decreasing cytotoxicity and increasing binding to cells (Wu et al., 2008) and gene delivery (Pan et al., 2007).

However the assembly of the dendrimer directly on the surface of the activated carbon may prove problematic due to blocking of the porous network as the dendrimer increases in generation. This problem could be circumvented by assembling the dendrimer (or dendron) on a polymeric resin, then cleave the dendron from the resin and attach it to the surface of the activated carbon.
This could be achieved by binding a diamine to the carboxylic acid groups to allow the carboxylic moiety at the root of the dendrimer to bind. A number synthetic routes are available for the conjugation of the dendrimer to the surface of the activated carbon, either functionalisation of a diamine, then bind a lysine based dendron to the free amine group through the carboxylic moiety at the root of the dendrimer, or add an amine containing amino acid such as arginine or histidine (Figure 7.2) at the beginning of the dendron assembly to facilitate covalent attachment to the carboxylic groups on the activated carbon surface.

This would allow the development of a range of activated carbons which could be used for treatment of specific autoimmune disorders, where the outer branches contain peptide specific sequences for the cytokine or protein to be removed.
7.2 Alternative Binding Strategies

Binding strategies that could be employed include either conversion of activated carbon surface functional groups prior to conjugation or targeting other functional groups (e.g. hydroxyl) as shown in Table 1.4.

As the surface of activated carbons and oxidised surfaces appear to possess carboxylic acid, phenolic, aliphatic alcohols and lactonic type groups. The employment of conjugation strategies which will target only one specific moiety are the ideal method for the modification of the surface chemistry of activated carbons, as has been shown in chapter 4 and 5, that unexpected side reactions can also occur when either conjugation using carbodiimide or modification of the surface moieties is performed using SOCl₂.
7.3 Conclusions

The use of activated carbons for the removal of cytokines has already been shown to be effective (Yushin et al., 2007; Sandeman et al., 2008) however the removal of specific species from the plasma based on chemistry rather than the physical adsorption to the surface of the activated carbons remains an important issue if activated carbons are to be used in the extracorporeal systems for detoxification of patients with autoimmune disorders.

The use of dendrimers bound to the surface of activated carbons would pose a novel and potentially very effective method to remove specific biomolecules from patients’ plasma, to alleviate their symptoms, reduce the duration of their stay in hospital and ultimately improve their quality of life.
References


Chang, T.M.S. (1972) *Artificial Cells*. Charles C Thomas Publisher, Springfield, USA.


Appendix A  Results of Statistical Analysis

The results of the statistical analysis performed on the activated carbon samples in chapter 3 and 4 are shown below.

A.  Results of Boehm Titrations – N-100 Series

Here DF= degrees of freedom, SS = sum of squares and MS = mean of squares (SS/DF), F = MS/Error MS.

A.1  Statistical Analysis of Boehm Titration Results
- N-100 Series - Basic Groups

A.1.1  One Way Analysis of Variance – N-100 Series -Basic Groups

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<tr>
<th>Source</th>
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<tr>
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<td>0.498</td>
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S = 0.04557   R-Sq = 96.66%   R-Sq(adj) = 95.41%
Pooled Standard Deviation = 0.046

The results of the ANOVA of the number of basic surface groups found using Boehm titrations, reveals that there is a significant decrease in the number of the basic groups as the temperature of oxidation is increased (p<0.05).
A.1.2 Dunnett’s Comparison – N-100 Series - Basic Groups

Family error rate = 0.05
Individual error rate = 0.0205
Critical value = 2.88
Control = Basic (S-50-9/100/25-00)

Intervals for treatment mean minus control mean

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<th>Level</th>
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<th>Centre</th>
<th>Upper</th>
</tr>
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<tr>
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<td>-0.288</td>
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<td>Basic90</td>
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<td>-0.526</td>
<td>-0.419</td>
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</table>

The results of Dunnett’s comparison test show that there is a significant decrease as indicated by the confidence interval levels for the three activated carbons all below zero and not including zero.

A.2 Statistical Analysis of Boehm Titration Results for N-100 Series - Acidic Groups

A.2.1 One Way Analysis of Variance – N-100 Series - Acidic Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
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<tr>
<td>Total</td>
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<td>2.57</td>
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</tbody>
</table>

S = 0.04305 R-Sq = 99.42% R-Sq(adj) = 99.21%
Pooled Standard Deviation = 0.043

From the ANOVA of the Boehm titration results it is shown that oxidation of activated carbons leads to a significant increase in the number of surface functional groups as indicated by p<0.05.
A.2.2 Dunnett’s Comparison – N-100 Series -Acidic Groups

Family error rate = 0.05
Individual error rate = 0.0205
Critical value = 2.88
Control = Acid (S-50-9/100/25-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid50</td>
<td>0.356</td>
<td>0.457</td>
<td>0.558</td>
</tr>
<tr>
<td>Acid70</td>
<td>0.427</td>
<td>0.528</td>
<td>0.629</td>
</tr>
<tr>
<td>Acid90</td>
<td>1.185</td>
<td>1.286</td>
<td>1.388</td>
</tr>
</tbody>
</table>

The increasing temperature of oxidation also leads to a significant increase in the number of acidic surface groups compared to the control S-50-9/100/25-00. There is also a significant difference between those oxidised at lower temperatures (50 or 70 °C) and those oxidised near reflux (90 °C) as seen from the results of Dunnett’s comparison test.

A.3 Statistical Analysis of Boehm Titration Results for N-100 Series - Carboxyl Groups

A.3.1 ANOVA– N-100 Series - Carboxyl Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>0.950</td>
<td>0.317</td>
<td>62.39</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>0.041</td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>0.991</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.07125  R-Sq = 95.90 %  R-Sq(adj) = 94.36 %
Pooled Standard Deviation = 0.071
The results of the ANOVA showed there was a significant difference (p<0.05) in the number of carboxyl groups found on the surface of the oxidised and non-oxidised control activated carbon S-50-9/100/25-00.

**A.3.2 Dunnett’s Comparison - N-100 Series - Carboxyl Groups**

Family error rate = 0.05
Individual error rate = 0.0205
Critical value = 2.88
Control = Carboxyl (S-50-9/100/25-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxyl50</td>
<td>-0.073</td>
<td>0.095</td>
<td>0.262</td>
</tr>
<tr>
<td>Carboxyl70</td>
<td>-0.030</td>
<td>0.137</td>
<td>0.305</td>
</tr>
<tr>
<td>Carboxyl90</td>
<td>0.550</td>
<td>0.717</td>
<td>0.885</td>
</tr>
</tbody>
</table>

The results of Dunnett’s comparison show that there is no significant difference between the number of carboxyl surface groups found for S-50-9/100/25-00 and N-100-50-2 and N-100-70-2 as indicated by the confidence interval levels including zero. However, there is a significant difference between S-50-9/100/25-00 and N-100-90-2 as indicated by the confidence intervals for carboxyl groups of N-100-90-2 not including zero.

**A.4 Statistical Analysis of N-100 Series - Lactonic Groups**

**A.4.1 ANOVA – N-100 Series – Lactonic Groups**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>1.851</td>
<td>0.617</td>
<td>44.10</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>0.112</td>
<td>0.014</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>1.963</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
S = 0.1183   R-Sq = 94.30%   R-Sq(adj) = 92.16%
Pooled Standard Deviation = 0.1183

The ANOVA of the number of lactonic surface groups revealed that there was a significant increase (p<0.05) in the number of lactonic groups in the oxidised activated carbons in comparison to the non-oxidised control S-50-9/100/25-00.

**A.4.2 Dunnett’s Comparison - N-100 Series – Lactonic Groups**

Family error rate = 0.05
Individual error rate = 0.0205
Critical value = 2.88
Control = Lactonic (S-50-9/100/25-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactonic50</td>
<td>0.330</td>
<td>0.608</td>
<td>0.886</td>
</tr>
<tr>
<td>Lactonic70</td>
<td>0.334</td>
<td>0.612</td>
<td>0.890</td>
</tr>
<tr>
<td>Lactonic90</td>
<td>0.830</td>
<td>1.108</td>
<td>1.386</td>
</tr>
</tbody>
</table>

The results of the Dunnett’s comparison agreed with the AONVA findings, in that the number of lactonic groups after oxidation was shown to be significantly greater than the number found for the non-oxidised control S-50-9/100/25-00.

**A.5 Statistical Analysis of N-100 Series - Phenolic Groups**

**A.5.1 ANOVA of N-100 Series – Phenolic Groups**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>0.160</td>
<td>0.053</td>
<td>10.01</td>
<td>0.004</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>0.043</td>
<td>0.005</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>0.203</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The results of the ANOVA analysis of the number of phenolic surface groups found after oxidation at 50, 70 and 90 °C show that there is a significant decrease in the number of phenolic groups present on the activated carbons which have been oxidised with nitric acid when compared to the non-oxidised control S-50-9/100/25-00.

**A.5.2 Dunnett’s Comparison – N-100 Series – Phenolic Groups**

Family error rate = 0.05  
Individual error rate = 0.0205  
Critical value = 2.88  
Control = Phenolic (S-50-9/100/25-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic50</td>
<td>-0.406</td>
<td>-0.234</td>
<td>-0.062</td>
</tr>
<tr>
<td>Phenolic70</td>
<td>-0.417</td>
<td>-0.245</td>
<td>-0.073</td>
</tr>
<tr>
<td>Phenolic90</td>
<td>-0.474</td>
<td>-0.302</td>
<td>-0.130</td>
</tr>
</tbody>
</table>

The Dunnett’s comparison results revealed that the number of phenolic groups significantly decreased as the temperature at which oxidation was performed increased when compared to the non-oxidised control S-50-9/100/25-00.
B. Results of Boehm Titrations – N-125 Series

B.1 Statistical Analysis of N-125 Series – Basic Groups

B.1.1 One Way ANOVA - N-125 Series – Basic Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>0.419</td>
<td>0.140</td>
<td>69.47</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>0.016</td>
<td>0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>0.435</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.04482  R-Sq = 96.30%  R-Sq(adj) = 94.92%
Pooled Standard Deviation = 0.045

From the results of the ANOVA there is a significant decrease in the number of basic surface groups for the oxidised activated carbons compared to the control non-oxidised activated carbon (S-50-9/125-00) as indicated by the p<0.05

B.1.2 Dunnett’s Comparison- N-125 Series – Basic Groups

Family error rate = 0.05
Individual error rate = 0.0205
Critical value = 2.88
Control = Basic

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic50</td>
<td>-0.419</td>
<td>-0.313</td>
<td>-0.208</td>
</tr>
<tr>
<td>Basic70</td>
<td>-0.506</td>
<td>-0.401</td>
<td>-0.296</td>
</tr>
<tr>
<td>Basic90</td>
<td>-0.603</td>
<td>-0.498</td>
<td>-0.393</td>
</tr>
</tbody>
</table>

The results of Dunnett’s comparison show that there is a significant reduction in the number of basic surface groups between all the oxidised activated carbons (N-125-50-2,
N-125-70-2 and N-125-90-2) and the non-oxidised control S-50-9/125-00 as indicated by the confidence interval levels not including zero.

**B.2 Statistical Analysis of N-125 Series – Acidic Groups**

**B.2.1 One Way ANOVA - N-125 Series – Acidic Groups**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>3.060</td>
<td>1.0201</td>
<td>1289.22</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>0.006</td>
<td>0.0008</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>3.066</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.02813  R-Sq = 99.79%  R-Sq(adj) = 99.72%

Pooled Standard Deviation = 0.0281

The results of the ANOVA revealed that there is a significant increase (p<0.05) between the number of acidic functional groups on the surface of the oxidised and non-oxidised activated carbons.

**B.2.2 Dunnett’s Comparison - N-125 Series – Acidic Groups**

Family error rate = 0.05
Individual error rate = 0.0205
Critical value = 2.88
Control = Acid (S-50-9/125-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid50</td>
<td>0.222</td>
<td>0.288</td>
<td>0.355</td>
</tr>
<tr>
<td>Acid70</td>
<td>0.529</td>
<td>0.595</td>
<td>0.661</td>
</tr>
<tr>
<td>Acid90</td>
<td>1.289</td>
<td>1.355</td>
<td>1.421</td>
</tr>
</tbody>
</table>
The results of Dunnett’s comparison between S-50-9/125-00 and N-125-50-2, N-125-70-2 and N-125-90-2 revealed that there was a significant increase in the number of acidic surface groups on all the oxidised activated carbons in comparison to the number on the surface of the non-oxidised S-50-9/125-00.

**B.3 Statistical Analysis of N-125 Series – Carboxyl Groups**

**B.3.1 One Way ANOVA - N-125 Series – Carboxyl Groups**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>0.694</td>
<td>0.231</td>
<td>128.85</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>0.014</td>
<td>0.002</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>0.708</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.04236   R-Sq = 97.97%   R-Sq(adj) = 97.21%

Pooled Standard Deviation = 0.042

The ANOVA results showed that there was a significant difference between the number of carboxyl groups found on the surface of N-125-50-2, N-125-70-2 and N-125-90-2 and S-50-9/125-00 as revealed by p<0.05.

**B.3.2 Dunnett’s Test - N-125 Series – Carboxyl Groups**

Family error rate = 0.05

Individual error rate = 0.0205

Critical value = 2.88

Control = Carboxyl

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carboxyl50</td>
<td>-0.108</td>
<td>-0.009</td>
<td>0.091</td>
</tr>
<tr>
<td>Carboxyl70</td>
<td>0.037</td>
<td>0.137</td>
<td>0.236</td>
</tr>
<tr>
<td>Carboxyl90</td>
<td>0.482</td>
<td>0.582</td>
<td>0.681</td>
</tr>
</tbody>
</table>
The results of Dunnett’s comparison of the carboxyl surface groups between the oxidised and non-oxidised N-125 series, revealed that there is no significant difference between the number of carboxyl surface groups on S-50-9/125-00 and N-125-50-2. However, there is a significant increase in the number of carboxyl surface groups between S-50-9/125-00 and N-125-70-2 and N-125-90-2.

B.4 Statistical Analysis of N-125 Series – Lactonic Groups

B.4.1 One Way ANOVA - N-125 Series – Lactonic Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>1.923</td>
<td>0.641</td>
<td>46.72</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>0.110</td>
<td>0.014</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>2.033</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.1171  R-Sq = 94.60%  R-Sq(adj) = 92.58%
Pooled Standard Deviation = 0.1171

The ANOVA results showed that the number of lactonic groups on the surface of the activated carbons after oxidation was significantly greater than those on the surface of the non-oxidised control S-50-9/125-00.

B.4.2 Dunnett’s Comparison – N-125 Series – Lactonic Groups

Family error rate = 0.05
Individual error rate = 0.0205
Critical value = 2.88
Control = Lactonic (S-50-9/125-00)
Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lactonic50</td>
<td>0.191</td>
<td>0.466</td>
<td>0.741</td>
</tr>
<tr>
<td>Lactonic70</td>
<td>0.398</td>
<td>0.673</td>
<td>0.948</td>
</tr>
<tr>
<td>Lactonic90</td>
<td>0.838</td>
<td>1.113</td>
<td>1.388</td>
</tr>
</tbody>
</table>

The results of the Dunnett’s comparison tally with the ANOVA results showing that as nitric acid oxidation is performed at either 50, 70 or 90 °C, there is a significant increase in the number of lactonic groups found in comparison to the non-oxidised control S-50-9/125-00.

B.5 Statistical Analysis of N-125 Series – Phenolic Groups

B.5.1 One Way ANOVA - N-125 Series – Phenolic Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>3</td>
<td>0.054</td>
<td>0.018</td>
<td>2.90</td>
<td>0.102</td>
</tr>
<tr>
<td>Error</td>
<td>8</td>
<td>0.050</td>
<td>0.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>11</td>
<td>0.104</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.07873  R-Sq = 52.06%  R-Sq(adj) = 34.09%

Pooled Standard Deviation = 0.07873

The results of the ANOVA analysis revealed that although there is a decrease in the number of phenolic groups upon oxidation at 50, 70 or 90 °C, the decrease was found not to be significant when compared to the non-oxidised control S-50-9/125-00.
B.5.2 Dunnett’s Comparison – N-125 Series – Phenolic Groups

Family error rate = 0.05
Individual error rate = 0.0205
Critical value = 2.88
Control = Phenolic (S-50-9/125-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolic50</td>
<td>-0.310</td>
<td>-0.125</td>
<td>0.060</td>
</tr>
<tr>
<td>Phenolic70</td>
<td>-0.355</td>
<td>-0.170</td>
<td>0.015</td>
</tr>
<tr>
<td>Phenolic90</td>
<td>-0.340</td>
<td>-0.155</td>
<td>0.030</td>
</tr>
</tbody>
</table>

The results of Dunnett’s comparison agree with the results found for the ANOVA analysis, that there is no significant decrease in the number of phenolic groups upon oxidation with nitric acid at 50, 70 or 90 °C when compared to the non-oxidised control S-50-9/125-00.
C Statistical Analysis of Boehm Titrations BA-100 Series

C.1 Statistical Analysis of Boehm Titrations BA-100 Series – Basic Groups

C.1.1 ANOVA - BA-100 Series – Basic Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>4</td>
<td>1.246695</td>
<td>0.311674</td>
<td>437.46</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
<td>0.007125</td>
<td>0.000712</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>1.253820</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.02669  R-Sq = 99.43%  R-Sq(adj) = 99.20%
Pooled Standard Deviation = 0.02669

The ANOVA results revealed that the number of basic surface groups on the surfaces of the carbons of the BA-100 series were significantly lower than the non-oxidised activated carbon control S-50-9/100/25-00.

C.1.1.2 Dunnett's Comparisons - BA-100 Series – Basic Groups

Family error rate = 0.05
Individual error rate = 0.0161
Critical value = 2.89
Control = Basic (S-50-9/100/25-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-100Basic</td>
<td>-0.633</td>
<td>-0.570</td>
<td>-0.507</td>
</tr>
<tr>
<td>1-100Basic</td>
<td>-0.552</td>
<td>-0.489</td>
<td>-0.426</td>
</tr>
<tr>
<td>2-100Basic</td>
<td>-0.675</td>
<td>-0.612</td>
<td>-0.549</td>
</tr>
<tr>
<td>3-100Basic</td>
<td>-0.013</td>
<td>0.050</td>
<td>0.113</td>
</tr>
</tbody>
</table>
Dunnett’s comparison revealed that all the BA-100 series, had a significantly lower number of basic groups when compared to the control S-50-9/100/25-00 with the exception of Blank 3-100, which was not significantly different.

C.1.2 Statistical Analysis of Boehm Titrations BA-100 Series
   – Acidic Groups

C.1.2.1 One-way ANOVA - BA-100 Series – Acidic Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>4</td>
<td>0.143</td>
<td>0.036</td>
<td>2.34</td>
<td>0.126</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
<td>0.153</td>
<td></td>
<td>0.015</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>0.296</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.1237  R-Sq = 48.33%  R-Sq(adj) = 27.67%

Pooled Standard Deviation = 0.1237

The difference in the number of acidic surface groups for the BA-100 series found after treatment with butylamine was found to be not significantly different from the number of acidic groups found on the surface of S-50-9/100/25-00.

C.1.2.2 Dunnett's comparisons - BA-100 Series – Acidic Groups

Family error rate = 0.05
Individual error rate = 0.0161
Critical value = 2.89
Control = Acidic (S-50-9/100/25-00)
Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-100Acidic</td>
<td>-0.447</td>
<td>-0.155</td>
<td>0.137</td>
</tr>
<tr>
<td>1-100Acidic</td>
<td>-0.189</td>
<td>0.103</td>
<td>0.395</td>
</tr>
<tr>
<td>2-100Acidic</td>
<td>-0.393</td>
<td>-0.101</td>
<td>0.191</td>
</tr>
<tr>
<td>3-100Acidic</td>
<td>-0.435</td>
<td>-0.143</td>
<td>0.149</td>
</tr>
</tbody>
</table>

From the Dunnett’s comparison of the acidic surface groups found on the butylamine conjugated surfaces, all the BA-100 series activated carbons were found not to have a significantly different number of acidic surface groups on the surface in comparison to the control sample S-50-9/100/25-00.

C.1.3 Statistical Analysis of Boehm Titrations BA-100 Series

– Carboxyl Groups

C.1.3.1 One-way ANOVA - BA-100 Series – Carboxyl Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>4</td>
<td>0.13019</td>
<td>0.03255</td>
<td>9.50</td>
<td>0.002</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
<td>0.03427</td>
<td>0.00343</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>0.16447</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.05854  R-Sq = 79.16%  R-Sq(adj) = 70.82%
Pooled Standard Deviation = 0.05854

The results of the ANOVA of the number of carboxyl groups found on the butylamine conjugated surfaces were significantly different, as indicated by p<0.05, than the amount of carboxyl groups found on the surface of the S-50-9/100/25-00.
C.1.3.2 Dunnett's Comparison - BA-100 Series – Carboxyl Groups

Family error rate = 0.05
Individual error rate = 0.0161
Critical value = 2.89
Control = Carboxyl (S-50-9/100/25-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-100 Carboxyl</td>
<td>-0.397</td>
<td>-0.259</td>
<td>-0.120</td>
</tr>
<tr>
<td>1-100 Carboxyl</td>
<td>-0.347</td>
<td>-0.208</td>
<td>-0.070</td>
</tr>
<tr>
<td>2-100 Carboxyl</td>
<td>-0.381</td>
<td>-0.242</td>
<td>-0.104</td>
</tr>
<tr>
<td>3-100 Carboxyl</td>
<td>-0.329</td>
<td>-0.191</td>
<td>-0.053</td>
</tr>
</tbody>
</table>

From the results of the Dunnett’s comparison of the number of carboxyl groups, it was observed that for all the activated carbons in BA-100 series the number of carboxyl groups found were significantly lower than found on the surface of S-50-9/100/25-00.

C.1.4 Statistical Analysis of Boehm Titrations BA-100 Series
– Lactonic Groups

C.1.4.1 One-way ANOVA - BA-100 Series – Lactonic Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>4</td>
<td>0.4502</td>
<td>0.1126</td>
<td>1.29</td>
<td>0.336</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
<td>0.8700</td>
<td>0.0870</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>1.3202</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.2950  R-Sq = 34.10%  R-Sq(adj) = 7.74%
Pooled Standard Deviation = 0.2950
From the ANOVA results of the number of lactonic groups found for the BA-100 series, there was found to be no significant difference in the number of lactonic groups when compared to the control S-50-9/100/25-00.

**C.1.4.2 Dunnett’s Comparison - BA-100 Series – Lactonic Group**

Family error rate = 0.05  
Individual error rate = 0.0161  
Critical value = 2.89  
Control = Lactonic (S-50-9/100/25-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-100Lactonic</td>
<td>-0.524</td>
<td>0.172</td>
<td>0.869</td>
</tr>
<tr>
<td>1-100Lactonic</td>
<td>-0.397</td>
<td>0.299</td>
<td>0.995</td>
</tr>
<tr>
<td>2-100Lactonic</td>
<td>-0.407</td>
<td>0.289</td>
<td>0.985</td>
</tr>
<tr>
<td>3-100Lactonic</td>
<td>-0.845</td>
<td>-0.149</td>
<td>0.547</td>
</tr>
</tbody>
</table>

As with the ANOVA results, Dunnett’s comparison revealed that the number of lactonic groups found on the surface of the BA-100 series activated carbons were not significantly different from the number of lactonic groups found on the surface of the control S-50-9/100/25-00.

**C.1.5 Statistical Analysis of Boehm Titrations BA-100 Series – Phenolic Groups**

**C.1.5.1 One-way ANOVA: - BA-100 Series – Phenolic Group**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>4</td>
<td>0.5771</td>
<td>0.1443</td>
<td>3.18</td>
<td>0.063</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
<td>0.4539</td>
<td>0.0454</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>1.0310</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
S = 0.2130   R-Sq = 55.98%   R-Sq(adj) = 38.37%
Pooled Standard Deviation = 0.2130

The number of phenolic groups was shown to be not significantly different from the number found on the surface of S-50-9/100/25-00 from the ANOVA analysis.

C.1.5.2 Dunnett's Comparisons - BA-100Series – Phenolic Group

Family error rate = 0.05
Individual error rate = 0.0161
Critical value = 2.89
Control = Phenolic (S-50-9/100/25-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-100Phenolic</td>
<td>-0.594</td>
<td>-0.091</td>
<td>0.412</td>
</tr>
<tr>
<td>1-100Phenolic</td>
<td>-0.679</td>
<td>-0.176</td>
<td>0.327</td>
</tr>
<tr>
<td>2-100Phenolic</td>
<td>-0.753</td>
<td>-0.250</td>
<td>0.253</td>
</tr>
<tr>
<td>3-100Phenolic</td>
<td>-0.189</td>
<td>0.314</td>
<td>0.817</td>
</tr>
</tbody>
</table>

As with the ANOVA results, Dunnett's comparison indicated that the number of phenolic surface groups were not significantly different from the number found on the surface of S-50-9/100/25-00.
D.1 Statistical Analysis of Boehm Titrations BA-125 Series

D.1.1 Statistical Analysis of Boehm Titrations BA-125 Series
– Basic Groups

D.1.1.1 ANOVA - BA-125 Series – Basic Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>4</td>
<td>0.6081</td>
<td>0.1520</td>
<td>7.75</td>
<td>0.004</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
<td>0.1961</td>
<td>0.0196</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>0.8042</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.1400  R-Sq = 75.62%  R-Sq(adj) = 65.87%
Pooled Standard Deviation = 0.1400

The ANOVA results revealed that the number of basic groups on the surface of the BA-125 Series activated carbons were found to be significantly different (p<0.05) from the number of basic groups found on the surface of S-50-9/125-00.

D.1.1.2 Dunnett's Comparisons - BA-125 Series – Basic Groups

Family error rate = 0.05
Individual error rate = 0.0161
Critical value = 2.89
Control = Basic (S-50-9/125-00)
Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-125Basic</td>
<td>-0.6301</td>
<td>-0.2996</td>
<td>0.0309</td>
</tr>
<tr>
<td>1-125Basic</td>
<td>-0.6737</td>
<td>-0.3432</td>
<td>-0.0127</td>
</tr>
<tr>
<td>2-125Basic</td>
<td>-0.6398</td>
<td>-0.3093</td>
<td>0.0211</td>
</tr>
<tr>
<td>3-125Basic</td>
<td>-0.1715</td>
<td>0.1590</td>
<td>0.4895</td>
</tr>
</tbody>
</table>
The results of Dunnett’s comparison reveal that the number of basic groups found on the surface of BA-125 series activated carbons were not significantly different found on the surface of the control S-50-9/125-00. This is the opposite to the result found for ANOVA of the number of basic groups. This discrepancy may be as a result of the large variability found in the results.

D.1.2 Statistical Analysis of Boehm Titrations BA-125 Series
– Acidic Groups

D.1.2.1 One-way ANOVA- BA-125 Series – Acidic Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>4</td>
<td>1.57639</td>
<td>0.39410</td>
<td>312.74</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
<td>0.01260</td>
<td>0.00126</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>1.58899</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.03550  R-Sq = 99.21%  R-Sq(adj) = 98.89%
Pooled Standard Deviation = 0.03550

The results of the ANOVA of the acidic groups found by Boehm titrations, revealed that the number of acidic surface groups found for the BA-125 Series were significantly different from the number found on the non-modified S-50-9/125-00.

D.1.2.2 Dunnett's comparisons - BA-125 Series – Acidic Groups

Family error rate = 0.05
Individual error rate = 0.0161
Critical value = 2.89
Control = Acidic (S-50-9/125-00)
Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-125Acidic</td>
<td>-0.78230</td>
<td>-0.69852</td>
<td>-0.61474</td>
</tr>
<tr>
<td>1-125Acidic</td>
<td>-0.49945</td>
<td>-0.41567</td>
<td>-0.33189</td>
</tr>
<tr>
<td>2-125Acidic</td>
<td>0.02502</td>
<td>0.10880</td>
<td>0.19258</td>
</tr>
<tr>
<td>3-125Acidic</td>
<td>0.02822</td>
<td>0.11200</td>
<td>0.19578</td>
</tr>
</tbody>
</table>

From the results of the Dunnett’s comparison it was observed that BA Conj 125 and Blank 1-125 had a significantly lower number of acidic groups and that Blank 2-125 and Blank 3-125 had a significantly greater number of acidic surface groups than the control S-50-9/125-00.

**D.1.3 Statistical Analysis of Boehm Titrations BA-125 Series**

– Carboxyl Groups

**D.1.3.1 One-way ANOVA - BA-125 Series – Carboxyl Groups**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>4</td>
<td>0.1894</td>
<td>0.0473</td>
<td>4.31</td>
<td>0.028</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
<td>0.1100</td>
<td>0.0110</td>
<td>0.0110</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>0.2994</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.1049  R-Sq = 63.26%  R-Sq(adj) = 48.57%
Pooled Standard Deviation = 0.1049

The number of carboxyl groups for the BA-125 series was found to be significant different from the number of carboxyl groups found for the control activated carbon S-50-9/125-00.
D.1.3.2 Dunnett's Comparison - BA-125 Series – Carboxyl Groups

Family error rate = 0.05
Individual error rate = 0.0161
Critical value = 2.89
Control = Carboxyl (S-50-9/125-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-125Carboxyl</td>
<td>-0.5230</td>
<td>-0.2755</td>
<td>-0.0280</td>
</tr>
<tr>
<td>1-125Carboxyl</td>
<td>-0.5232</td>
<td>-0.2757</td>
<td>-0.0282</td>
</tr>
<tr>
<td>2-125Carboxyl</td>
<td>-0.4468</td>
<td>-0.1993</td>
<td>0.0482</td>
</tr>
<tr>
<td>3-125Carboxyl</td>
<td>-0.5592</td>
<td>-0.3117</td>
<td>-0.0642</td>
</tr>
</tbody>
</table>

The number of carboxyl groups was found to be significantly lower for BA Conj 125, Blank 1-125 and Blank 3-125 when compared to the control activated carbon S-50-9/125-00. The number of carboxyl groups found for Blank 2-125 was found to be not significantly different from the control activated carbon.

D.1.4 Statistical Analysis of Boehm Titrations BA-125 Series – Lactonic Groups

D.1.4.1 One-way ANOVA - BA-125 Series – Lactonic Groups

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>4</td>
<td>0.3500</td>
<td>0.0875</td>
<td>1.91</td>
<td>0.185</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
<td>0.4577</td>
<td>0.0458</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>0.8076</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.2139  R-Sq = 43.33%  R-Sq(adj) = 20.67%
Pooled Standard Deviation = 0.2139
The number of lactonic groups found for the BA-125 series was found to be not significantly different from the number of groups found for the control S-50-9/125-00.

**D.1.4.2 Dunnett's Comparison - BA-125 Series – Lactonic Group**

Family error rate = 0.05  
Individual error rate = 0.0161  
Critical value = 2.89  
Control = Lactonic (S-50-9/125-00)

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-125Lactonic</td>
<td>-0.6109</td>
<td>-0.1060</td>
<td>0.3989</td>
</tr>
<tr>
<td>1-125Lactonic</td>
<td>-0.4032</td>
<td>0.1017</td>
<td>0.6066</td>
</tr>
<tr>
<td>2-125Lactonic</td>
<td>-0.1809</td>
<td>0.3240</td>
<td>0.8289</td>
</tr>
<tr>
<td>3-125Lactonic</td>
<td>-0.5649</td>
<td>-0.0600</td>
<td>0.4449</td>
</tr>
</tbody>
</table>

The results of the Dunnett’s comparison agreed with the results found for the ANOVA that the number of lactonic groups found were not significantly different for the amount for the control S-50-9/125-00.

**D.1.5 Statistical Analysis of Boehm Titrations BA-125 Series – Phenolic Groups**

**D.1.5.1 One-way ANOVA: - BA-125 Series – Phenolic Group**

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor</td>
<td>4</td>
<td>0.6572</td>
<td>0.1643</td>
<td>6.22</td>
<td>0.009</td>
</tr>
<tr>
<td>Error</td>
<td>10</td>
<td>0.2643</td>
<td>0.0264</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>14</td>
<td>0.9215</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = 0.1626  R-Sq = 71.32%  R-Sq(adj) = 59.84%  
Pooled Standard Deviation = 0.1626
The number of phenolic groups was found to be significantly different to the number of phenolic groups found for the control S-50-9/125-00.

**D.1.5.2 Dunnett's Comparisons - BA-125 Series – Phenolic Group**

Family error rate = 0.05  
Individual error rate = 0.0161  
Critical value = 2.89  
Control = Phenolic (S-50-9/125-00)

Intervals for treatment mean minus control mean

<table>
<thead>
<tr>
<th>Level</th>
<th>Lower</th>
<th>Centre</th>
<th>Upper</th>
</tr>
</thead>
<tbody>
<tr>
<td>BA-125Phenolic</td>
<td>-0.5487</td>
<td>-0.1650</td>
<td>0.2187</td>
</tr>
<tr>
<td>1-125Phenolic</td>
<td>-0.4155</td>
<td>-0.0318</td>
<td>0.3519</td>
</tr>
<tr>
<td>2-125Phenolic</td>
<td>-0.3590</td>
<td>0.0247</td>
<td>0.4084</td>
</tr>
<tr>
<td>3-125Phenolic</td>
<td>0.0703</td>
<td>0.4540</td>
<td>0.8377</td>
</tr>
</tbody>
</table>

The results of Dunnett’s comparison reveal that only the number of phenolic groups found on the surface of Blank 3-125 were significantly different from the number found for the control surface S-50-9/125-00.
Appendix B List of Suppliers

**Acros Organics**  
(supplied via Fisher Scientific)  

**BDH**  
(Supplied by VWR International)  
Hunter Boulevard  
Magna Park  
Lutterworth  
Leicestershire  
England, UK  
LE17 4XN

**Bibby Sterlin Ltd.**  
Beacon Road  
Stone  
Staffordshire  
England, UK  
ST15 0SA

**Electromantle**  
(Supplied by Thermo Fisher Scientific)  
Electrothermal House  
Unit 12A  
Purdeys Industrial Estate  
Purdeys Way  
Rochford  
Essex  
England, UK  
SS4 1ND

**Fisher Scientific UK Ltd.**  
Bishop Meadow Road  
Loughborough  
Leicestershire  
England, UK  
LE11 5RG

**JEOL (U.K.) Ltd.**  
JEOL House  
Silver Court  
Watchmead  
Welwyn Garden City  
Hertfordshire  
England, UK  
AL7 ILT

**MAST Carbon Ltd.**  
Henley Park  
Guildford  
Surrey  
England, UK  
GU3 2AF

**Nicolet**  
(Supplied by Thermo Fisher Scientific)
Riedel-de Haen
Sigma-Aldrich Laborchemikalien GmbH
PO Box 100262
30918 Seelze
Germany

Sigma-Aldrich Chemical Company Ltd.
The Old Brickyard
New Road
Gillingham
Dorset
England, UK
SP8 4XT

Surechem Products Ltd.
Units 13-14
Lion Barn Industrial Estate
Needham Market
Suffolk
England, UK
IP6 8NZ

Thermo Electron
Emerald Way
Stone Business Park
Stone
Staffordshire
England, UK
ST15 0SR

Weiss-Gallenkamp
Units 37 – 38
The Technology Centre
Epinal Way
Loughborough
England, UK
LE11 3GE