THE CHEMISTRY OF BRITISH BITUMINOUS COALS

An Assessment Of Phase Transfer Catalysed Reactions In The Determination Of Coal Structure

A THESIS SUBMITTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

BY

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THE UNIVERSITY OF ASTON IN BIRMINGHAM

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SUMMARY

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Three British bituminous coals, (Gedling, Cresswell, and Cortonwood Silkstone) were selected for study. Procedures were developed, using phase transfer catalysts (PTC's), to degrade the solvent insoluble fractions of the coals. PTC's are of interest because they have the potential to bring about selective high conversion reactions, under mild conditions, (often in the past, severe reaction conditions have had to be used to degrade the coals, this in turn resulted in the loss of much of the structural information).

We have applied a variety of physical and chemical techniques to maximise the amount of structural information, these include, elemental analysis, ^{1}H-NMR, ^{13}C–CPMAS-NMR, GPC, GC-MS, FTIR spectroscopy, DRIFT spectroscopy, and gas adsorption measurements.

The main conclusions from the work are listed below:-

(1) PTC O-methylation; This reaction removes hydrogen bonds within the coal matrix by 'capping' the phenolic groups. It was found that the polymer-like matrix could be made more flexible, but not significantly more soluble, by O-methylation. I.E. the trapped or 'mobile' phase of the coals could be removed at a faster rate after this reaction had been carried out.

(2) PTC Reductive and Acidic Ether Cleavage; The three coals were found to contain insignificant amounts of dialkyl and alkyl aryl ethers. The number of diaryl ethers could not be estimated, by reductive ether cleavage, (even though a high proportion of all three coals was solublised). The majority of the ethers present in the coals were inert to both cleavage methods, and are therefore assumed to be heterocyclic ethers.

(3) Trifluoroperacetic Acid Oxidation; This oxidant was used to study the aliphatic portions of the polymer-like macromolecular matrix of the coals. Normally this reagent will only soublise low rank coals, we however have developed a method whereby trifluoroperacetic acid can be used to degrade high rank bituminous coals.

(4) PTC/Permanganate Oxidation; This reagent has been found to be much more selective than the traditional alkaline permanganate oxidation, with a lot more structural information being retained within the various fractions. This degradative method therefore has the potential of yielding new information about the molecular structure of coals.

Key Words:- Bituminous Coals. Phase Transfer Catalysis. Degradation.
Organic Structures. Instrumental Methods Of Analysis.

DEDICATION

I would like to dedicate this thesis to my wife Diane and my two children, Michael and Holly.

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LIST OF ABBREVIATIONS

ASTM	American Standard For Testing Materials.
BET	Brunauer-Emmett-Teller Equation.
CPMAS	Cross Polarisation-Magic Angle Spinning.
DRIFT	Diffuse Reflectance Infrared Fourier Transform.
EDA	Electron-Donor-Acceptor.
ETA	Electron Transfer Agent.
f_a	Aromaticity Value.
GC-MS	Gas Chromatography-Mass Spectrometry.
GLC	Gas-Liquid Chromatography.
GPC	Gel-Permeation Chromatography.
IR	Infrared.
M_n	Number Average Molecular Weight.
M_w	Weight Average Molecular Weight.
NMR	Nuclear Magnetic Resonance.
P - D	Palonyi-Dubinin Equation.
PTC	Phase Transfer Catalysis.
Q^+	Quaternary Cation.
RT	Retention Time.
THF	Tetrahydrofuran.
TIC	Total Ion Current.
T_{CT}	Contact Time.
T_1	Spin-Lattice Relaxation Time.
$T_{1\rho}$	Proton Spin Lattice Relaxation Time.

CHAPTER 1.

INTRODUCTION

1.1 COAL CHEMISTRY

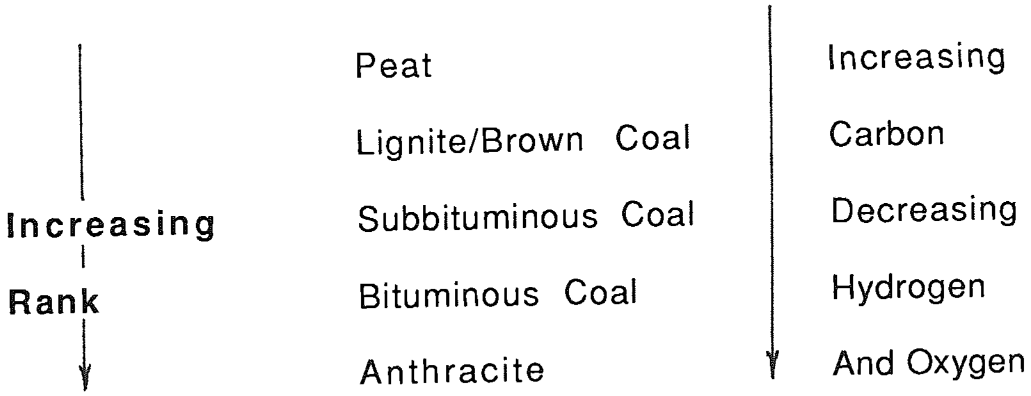
There are several good accounts in the literature of the origins, formation, and general physical properties of coal(1,2,3,4). However a brief overview is necessary here, in order to understand the problems encountered in characterising the chemical composition of the organic matter in coals and other carbonaceous materials.

Coal is a generic term for a sedimentary rock composed primarily of organic matter, but containing some inorganic materials principally in the form of clays and minerals, trapped between the layers of a coal seam. It is these inorganic substances which are responsible for the ash content of a coal, and along with the organic sulfur and nitrogen compounds, contribute to air pollution when the coals are burnt. The organic matter in coals originated from vegetation under conditions where complete biological degradation was prevented, this partially decomposed matter then became buried and over geological time further changes took place to produce a coal.

The original plants were of various types and contained differing proportions of carbohydrates, lignins, proteins, fats, waxes, etc. During diagenesis (biochemical degradation) only the most inert of these substances were retained. The degree and type of change undergone by these compounds was dependent on many factors, of which the most important were; (1) The pH prevailing at deposition. (2) The oxygen content of the bog or swamp. (3) The temperature, and (4) The rate at which the partially degraded material was covered and buried. During metamorphosis (geochemical coalification) the pressure and temperature, that these partially degraded compounds were subjected to, resulted in further compaction, so that water and simple gases such as H_2, CO_2 and CH_4 were lost, i.e the hydrogen and oxygen content of the coals decreased while the carbon content increased.

In general coalification leads to an increase in the carbon content of a coal, but this increase is largely dependent on the conditions during metamorphosis. Therefore for most purposes coals are classified according to rank, the rank of a coal being based on carbon content in conjunction with other properties, (the use of other properties is made necessary because the elemental composition of a coal may not relate directly to a coals technological properties). The ASTM rank classification of coals is shown in Table 1.1, while Table 1.2 compares some national classification systems with that of the international system. The diagram below, (Fig. 1.1) gives the progression which is believed to lead to high rank coals. (Peat, which is not normally classified as a coal is, assumed to be its precursor, and so is included in the diagram.)

Fig. 1.1 Coal Rank



If we consider the vast range of compounds present in the original vegetation and the number of variables which could have affected the final products, it is not surprising that the chemical composition of a coal varies from one mine to the next and from seam to seam. When examined on a macroscopic scale the individual seams shows banding due to the accumulation of different types of plant debris,

Table 1.1 ASTM Rank Classification Of Coals

Class	Group		Fixed Carbon		Volatile Matter		Natural Moisture	Heating Value
	Name	Symbol	Dry	Moist	Dry	Moist		Dry Basis
			%	%	%	%	%	(MJ.Kg)
1 Anthracite	meta-anthracite	ma	>98	>92	<2	<2	6	32.4
	anthracite	an	92-98	89-95	2-8	2-8	3	35.5
	semianthracite	sa	86-92	81-89	8-14	8-15	3	34.7
2 Bituminous	low-volatile	lvb	78-86	73-81	14-22	13-21	5	36.6
	medium-volatile	mvb	69-78	65-73	22-31	21-29	7	36.2
	high-volatile A	hvAb	<69	58-65	>31	>30	5	34.2
	high-volatile B	hvBb	57	53	57	40	7	28.3-34.2
	high-volatile C	hvCb	54	45	54	40	16	31.0-35.1
3 Subbituminous	subbituminous A	subA	55	45	55	38	18	28.8-31.6
	subbituminous B	subB	56	43	56	35	24	27.4-30.3
	subbituminous C	subC	53	37	53	36	30	25.1-28.7
4 Lignite	lignite A	ligA	52	32	52	35	38	20.2-26.6
	lignite B	ligB	52	26	52	32	50	<22.0

Table 1.2 International Classification Of Coal Compared With Some National Systems

Classes Of The International System			Classes Of The National System			
	Parameters					
Class No.	Volatile Matter %	Calorific Value* kJ/g	U.S.A	U.K.	Poland	Germany
0	0-3		meta-anthracite		meta-antracyt	
1A	3-6.5		anthracite	anthracite	antracyt	anthrazit
1B	6.5-10				polantracyt	
2	10-14		semianthrite	dry steam	chudy	magerkohle
3	14-20		low-volatile bituminous	coking steam	polkoksowy metakoksowy	esskohle
4	20-28		medium-volatile bituminous	medium-volatile coking	ortokoksowy	fettkohle
5	28-33		high-volatile bituminous A		gazowokoksowy	gaskohle
6	>33 (33-40)	32.4-35.4				
7	>33 (32-44)	30.1-32.4	high-volatile bituminous B	high-volatile	gazowy	flambant gras
8	>33 (34-46)	25.6-30.1	high-volatile bituminous C		gazowoplomienny	gas flammkohl
9	>33 (36-48)	<25.6	subbituminous		plomienny	

* Calculated to standard moisture content.

these bright and dull bands are known as lithotypes.

On a microscopic scale, even within the bands of a coal seam different structures can be identified. These optically different groups are known as macerals, and are analogous to minerals in rocks. There are three main types of macerals vitrinite, inertinite, and exinite (or liptinite). These main groups can be further subdivided according to their appearance under a microscope. The study of these macerals is known as coal petrography, and is dealt with in detail in a book by Stach and co-workers(5).

It is not surprising, from the above description of the origins of coal, that this fuel consists of a highly complex heterogeneous mixture of organic compounds with a highly complex physical structure. Coals therefore present many interesting and challenging problems to every type of chemist, but there are good technical and commercial as well as academic reasons for studying coals; it is hoped for example, that with a better understanding of the structures present, coal conversion technologies can be made more efficient so that this fuel can be used in the future as a chemical feed-stock.

1.2 THE ORGANIC CHEMISTRY OF COAL

Coal has been used as a fuel for thousands of years but not until the start of the industrial revolution did coal science really develop. Most of the early work was related to the determination of its technological properties, such as calorific value, ash fusibility, moisture holding capacity etc. Although useful it is difficult to relate these measurements to the coals molecular structure. Other methods however have been used to study the chemical composition of the organic matter(1,6,7,8,9,10,11,12,13), (in particular since the oil crisis in the 1970's). From the data obtained in these studies a number of conclusions have been reached which are listed below:-

1) Coal molecules include small clusters of essentially aromatic nature. The number of fused rings increasing slowly with the rank of the coal upto about 90% carbon, whereupon a rapid increase in the cluster size is observed.

2) The aromatic clusters are linked by hydroaromatic bridges, some of which are six membered rings, so that on loss of hydrogen the average size of the aromatic clusters can increase.

3) There are hetero atoms and short alkyl groups bridge between clusters forming a macromolecular network. Methylene, ethylene, ether, and disulphide groups are the common linking agents.

4) There is a significant increase in the number of aliphatic substituents as the rank of the coal increases, normally in the form of methyl groups attached to the aromatic rings.

5) As the rank increases the oxygen content of the coal decreases and a change in the functional group type is observed. Carboxylic acids and carbonyl groups decrease in number, while ether and phenolic groups increase. In anthracite coals very little oxygen remains.

6) Hetero atoms such as oxygen, sulfur, and nitrogen appear in the coals incorporated in heterocyclic fragments of the matrix.

7) Secondary bonding plays an important role in maintaining coal structure. These bonds are in the form of hydrogen bonding and $\pi-\pi$ interactions. These bonds account to some extent for the intractability of coals in organic solvents.

8) Within the matrix of a coal relatively small non-covalently bound molecules are trapped in the pores, or as part of an interpenetrating polymer-like network. These molecules are often referred to as the mobile phase of the coal.

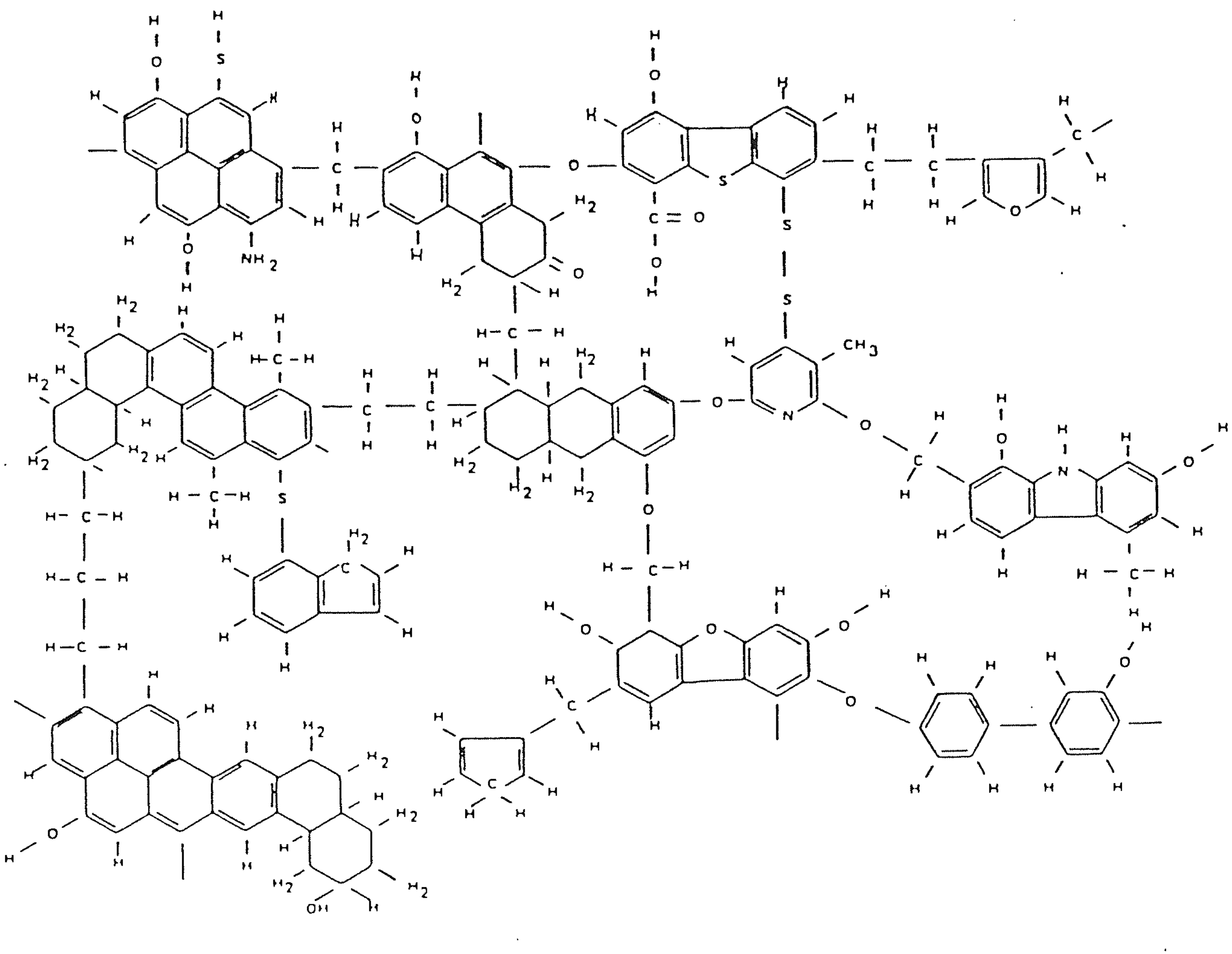
9) As the rank of the coals increases they become in general less chemically reactive, because of the decreasing number of functional groups and changes in the physical structure.

1 0) Coals are highly heterogeneous, for any given fragment it will contain many different molecules of varying molecular weights and functional group distribution, forming a three dimensional structure, with the aromatic clusters forming flat plates. In the higher rank coals these planar structures are believed to align, forming laminates.

It is impossible, because of the heterogeneous nature of coals, to represent them by a unique structure or repeat unit, but attempts have been made in the past, to outline average macromolecular structure which fit as far as possible all the available data(14,15,16,17,18). Each of these models can at best only represent a single maceral type, of a particular rank coal, with a particular elemental composition, and thus are of limited value. Such representations however do allow predictions of the chemical and physical behaviour of coals to be made, for example Fig. 1.2 shows one such representation, and is typical of the hydroaromatic/aromatic coal model now generally accepted.

It is clear from the above discussion that there are several major problems to be overcome if we are to characterise the organic constituents of a coal. These problems arise mainly because of the intractable nature of the material which means that powerful solution state techniques cannot be used, unless the coal is first degraded. The analytical methods which give information about the solid state, can only give an average picture of the whole coal, so although useful, they have to be used in combination with chemical degradation methods to yield a detailed model of a coal.

Fig.1.2 Schematic Representation Of The Structural Groups And Connecting Bridges In Bituminous Coals.[18]



Degrading the coals can however create difficulties because of the wide range of products produced, and because in the past, reagents and conditions selected to depolymerise the coals have tended to be severe and non-specific in nature, making firm identification of the parent structures impossible.

In our work we have tried to apply a large number of chemical and physical analytical techniques in order to maximise the structural information, (these methods are detailed in chapter 2). We have also attempted to evaluate and develop new milder degradative systems in order to characterise the coal more fully. In order to achieve this we have explored the use of phase transfer catalysts (PTC) to promote mild specific reactions. An introduction to PTC's is given below in section 1.3.

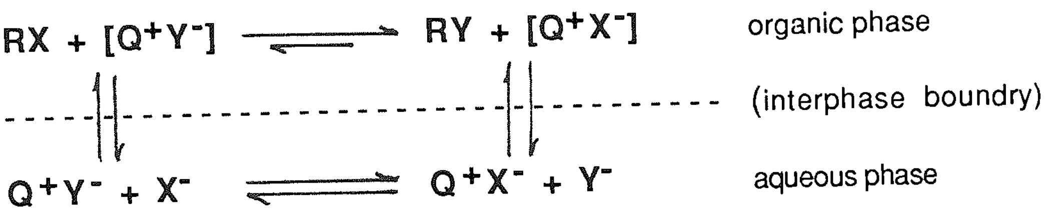
1.3 AN INTRODUCTION TO PHASE TRANSFER CATALYSTS

Reactions which occur between species in different phases, (for example between solids and liquids or organic and aqueous phases), if they occur at all, are usually very slow because the rate of reaction is limited by the area of the phase boundary. This problem of very slow reactions is customarily solved by the reactants being placed in a suitable homogeneous medium, however difficulties such as extensive solvation or solvolytic side reactions may occur. In coal chemistry this approach is only feasible for the soluble fractions, which are in general unrepresentative of the whole coal.

Phase transfer catalysts (PTC's) promote multi-phase reactions and generally show higher selectivity when compared with the uncatalysed systems. Since the 1960's when the mechanism of the PTC process was recognised by Starks(19), Makosza(20,21), and Brandstrom(22), a large volume of literature has been published. The whole area of PTC has been reviewed in three books by Weber and

Gokel(23), Starks and Liotta(24) and Dehmlow and Dehmlow(25).

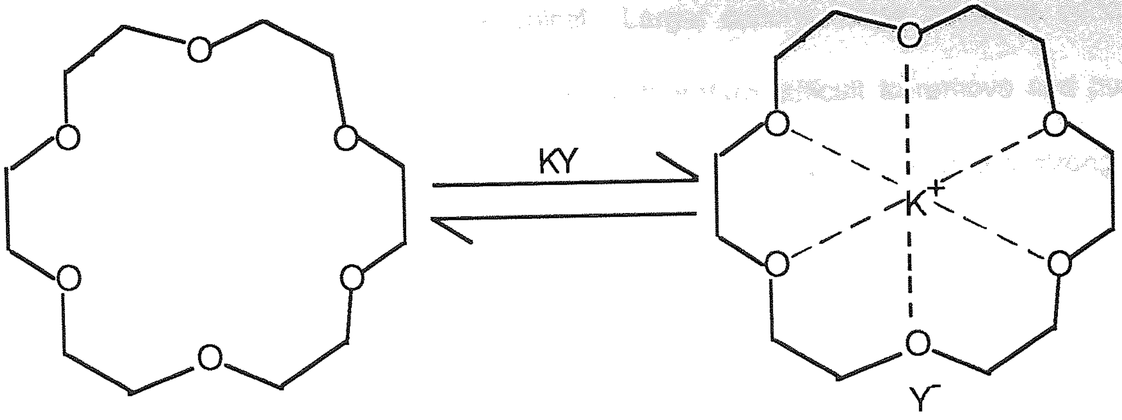
PTC's are typically onium salts or complexing agents for alkali metal cations, such as cryptates and crown ethers. The more usual PTC provides a highly organophilic cation which enables one of the reactants (in the form of an anion) to pass into the normal phase of the other reactant(s). This phase transfer allows the reagents to come into contact with each other so that a rapid reaction rate is observed. In general these reactions occur in equilibrium as shown below, and involve at least two steps, these are:- 1) the transfer of one of the reagents from its normal phase into the second phase, and 2) the reaction of the transferred reagent with the reactant in the second phase.



Where Q^+ is used to indicate a quaternary cation and [ ] indicates an ion pair.

It has been shown by Makasza(21) that PTC reactions are not micellular in nature, even though some PTC can form micelles, and that the rate of the reactions are proportional to the amount of catalyst cation in the organic phase. These results suggest that a high concentration of catalyst is desirable, except where it is expensive and/or very difficult to remove.

Crown ethers, polyethylene oxides, and cryptates work in a slightly different way to the onium salts in that they form reversible complexes with alkali metal anions so that the reactive nucleophile passes into the organic phase as a complex shown below.



Therefore in the case of the onium catalysts the reaction involves the anion transfer between two phases, but in the case of the crown ethers etc. the whole molecule is transferred.

In principle PTC can be used to transport cations, free radicals or whole molecules across phase boundaries but little work to date has been done on these systems.

When using PTC it is important to consider the following five points, all of which are dealt with in detail in the three books previously mentioned(19, 20, 21). These are :-

1) The partitioning of the PTC and its ion pair or complex between the two phases.

2) Anion transfer between the two phases.

3) The polarity of the medium.

4) The structure of the PTC, and

5) The kinetics of the PTC reaction.

Since most anions prefer an aqueous phase because the charge can be spread over the greater volume of the hydrated species, it is necessary, if the anion is to be transferred to the organic phase that it should have a large percentage of organic character. Thus the structure of the PTC needs to be such that the cation-anion pair is strongly partitioned into the organic phase, for example, onium catalysts which contain between 10 and 30 carbon atoms are typical. Larger cations cause problems because they become insoluble in polar solvents and are therefore difficult to remove and purify. The strength of the ion pair in the organic phase is important. If it is too strong the reaction with the other reactants is prevented, thus larger ions which have weaker interactions are preferred. To some extent the solvent also has a role in determining the stability of the ion pair because of the ion-dipole interactions between the solvent and the solute, for this reason PTC reactions are normally carried out in aprotic solvents of low polarity (eg. dichloromethane and chloroform). In these solvents the concentration of the free ion is very small and because there are only weak interactions between the solvent and the ion pair, reactions with the electrophilic site in the organic phase are rapid.

When considering the right PTC for coal reactions it must be taken into account that one of the reactants is a porous solid, and that for best results the coal needs to be in a swollen state to allow penetration of the reactant complex into the coal matrix. It has been found that n-tetrabutylammonium cation will swell the coal very effectively and has therefore become the cation of choice in the PTC reactions of coals(26,27). It is however known that some onium salts will undergo a Hofmann elimination reaction under relatively mild conditions, thus this particular cation will not be suitable for all applications.

CHAPTER 2.

ANALYTICAL TECHNIQUES

2.1 INTRODUCTION

Coal is primarily an insoluble organic rock, and as such does not lend itself to convenient structural analysis. As a rule most studies into the molecular structure of coals have relied on a limited number of chemical and physical techniques, this has restricted the possible structural information gained. One of our aims has been to maximise the structural data we can obtain from the coal or coal fractions, by employing a wide variety of physical and chemical analytical techniques.

This chapter introduces these analytical methods, and discusses some of the possible errors which arise when applying these techniques in coal chemistry.

2.2 SOLVENT EXTRACTION OF COAL

The removal of the mobile phase by organic solvents has been an important preliminary step in past analytical schemes. Most solvents only remove the 'trapped' or 'mobile' phase, (described in chapter 1), but some act by the breaking of covalent bonds within the coal, increasing the total amount of material solublised. Solvents which also degrade the coal are of two types;

(1) Degrading solvent, which can achieve coal solubilities of greater than 90%, and involve the thermal degradation of the coal into smaller sub-fractions. These solvents can normally be recovered from the extract solution unchanged.

(2) Reactive solvents, which achieve very high conversions to soluble products by a process of active interaction with the coal molecules. These solvents are normally hydrogen donors, and cannot be recovered unchanged from the resulting solution(s).

Although leading to high solubilities, both degrading and reactive solvents, change the structure of the coal molecules and have therefore not been used in our work.

More useful for structural characterisation are the solvents classified as 'non-specific' and 'specific', described below.

Non-specific solvents; (eg. ethanol, benzene, chloroform, and THF). Small amounts of material are usually extracted with these solvents, at temperatures of less than 100°C. The extracts consist mainly of resins waxes and other trapped materials which do not form part of the cross-linked polymer like matrix. These extracts are usually unrepresentative of the whole coal, but are more easily studied than the whole coal by conventional analytical techniques.

Specific solvents; (eg. primary amines and pyridine), extract larger amounts of material at temperatures between 100°C and 200°C. The extracts normally resemble in appearance the whole coal quite closely, and are considered to be representative of the macro-molecular matrix. These extracts are however much more difficult to analyses than the extracts produced from non-specific solvent extraction.

The choice of solvent is only one parameter which will affect the yield and composition of the extract, other factors can be of equal importance. Efficient contact between the coal and solvent is an important factor in determining the yield of extract, (good contact is achieved by reducing the particle size of the coal to increase the exposed surface area). Extraction time and temperature also appear to be critical factors. The amount of material removed by solvent can be reduced due to aggregation of the soluble coal particles, or by resorption of the extract back onto the coal surface. It is for these reasons Soxhlet extraction is the preferred method to remove the trapped material from the coals matrix, i.e. the coal is continually washed with fresh hot solvent, preventing aggregation or resorption.

The final variable which can effect the yield of extractable material and its composition, is the coal type itself. In general the higher the rank the less soluble it is, but coal solubilities often pass through a maximum as we move from low-rank to high-rank coal. It is also apparent that large variations in solubility can occur in coals of very similar rank, reflecting the heterogeneous nature of the material being studied.

A number of theories have been developed to explain changes in extract yield and composition, with the solvent used, of these the best at present is the electron-donor-acceptor theory described in section 2.2.1.

2.2.1 ELECTRON-DONOR-ACCEPTOR THEORY OF SOLVENT EXTRACTION

The variations in the ability of solvents to extract material from coal has been explained by the concept of an electron-donor-acceptor (EDA) mechanism combined with the two phase model of coal structure(28,29). In the two phase system, coal is envisaged to consist of a cross-linked polymer like matrix, (the intractable fraction), with discreet molecules 'trapped' in the pore system. These smaller molecules are held within the matrix by electron-donor-acceptor interactions between various functional groups. It is suggested that one part of the coal EDA complex is substituted by a solvent molecule, thus breaking the complex and leading to an extractable fragment. This will occur when the electron-donor or electron-acceptor strength of the coal functional group is lower than the electron-donor or acceptor capacity of the solvent. Thus the amount of extract produced in a given solvent will depend on the electron donor number of the solvent, the larger this is the greater the amount of material it will be possible to extract, because more of the EDA interactions will be broken.

Substantial evidence for this theory has come from a number of different studies(30,31,32,33).

The EDA theory provides an explanation not only for the extract yield but also for two other phenomena, these are:

(1) Solvent swelling; where intra-EDA complexes are broken during extraction leading to a loosening of the macro-molecular network.

and (2) The composition of the extracts; for example the THF soluble coal extract, (THF has a high electron donor capacity), will contain all the compounds found in the solvent soluble extract obtained using chloroform, (chloroform has a low electron donor capacity), plus more strongly complexed, material.(34)

Pyridine as expected from the above argument gives a high extract yield , but is very difficult to remove from the coals matrix after extraction, because it forms strong complexes. The pyridine extracts are also of high molecular weight and although more representative of the whole coal are more difficult to analyse.

2.3 INFRARED ANALYSIS

Coal was first studied by infrared spectroscopy in the early 1940's(35), since then many investigators have used this technique(1, 36, 37, 38, 39, 40). The results of these studies are summarised in Table 2.1 which lists the IR band assignments for coals.

Infrared spectroscopy yields valuable information about the functional components of the organic material in coal, but this information is largely qualitative, the spectra being too complex for individual compound analysis.

Table 2.1 Carbon Skeleton and Functional Group Assignment in the Infrared Analysis of Coal(41)

Wave Number (cm^{-1})	Peak Assignment
3030	Aromatic CH
2978	CH_3
2940	Aliphatic CH
2925 + 2860	CH_3, CH_2, CH
1600	Aromatic ring C=C
1575	Condensed aromatic ring C=C
1460	Aliphatic CH_2, CH_3 groups
1370	CH_3 and cyclic CH_2 groups
870 + 814 + 760	out-of-plane bending of aromatic CH
3300	Associated OH and NH
1700	non-hydrogen bonded C=O
1600	Hydrogen bonded C=O
1300 to 1000	C-O(phenol), C_{ar}-O-C_{ar}, C-O(alcohol), C_{ar}-O-C_{al}, C_{al}-O-C_{al}

(All peak assignments are stretching band unless indicated otherwise)

The infrared spectra of coals are generally very similar and poorly resolved, when compared with the spectra of pure compounds but it has been determined for example, based on the IR spectra of a large number of coals, that very few alkenes or alkynes are present(42).

The aromatic C-H absorption at 3030cm^{-1} appear, if at all, as a weak band.

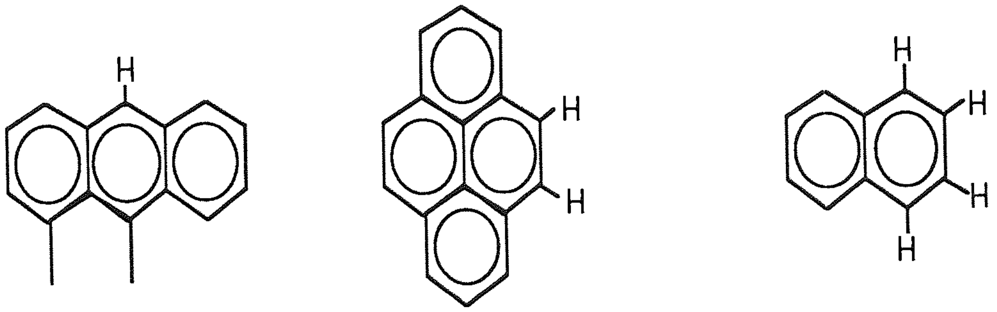
This has been taken to indicate a highly substituted and/or cross-linked system, so that there are only a few C_{ar}-H groups within the coal. The 2980cm^{-1} absorption is assigned to CH_3 and is generally a weak band in coal spectra, and thus CH_3 groups are thought to be in low concentration within the coal.

The 2925cm^{-1} and 2860cm^{-1} bands assigned to CH_3, CH_2, and CH are quite strong but it is not possible to determine if the CH_2 groups are present in the form of aliphatic chains, cycloalkanes or hydroaromatic structures(43).

The 1600cm^{-1} absorption which is often the strongest band in coal spectra has been the subject of many studies and some controversy(44,45,46), the two most probable assignments for this band are, (1) aromatic ring stretching, and (2)highly conjugated hydrogen bonded carbonyl absorptions. In recent years the former has become the more accepted assignment(47). The larger than expected intensity of this band has been ascribed to an increase in dipole of the aromatic ring because of polar substituents.

The three absorptions between 870cm^{-1} and 760cm^{-1} are due to out-of-plane bending of =C_{ar}-H groups(48, 49), (see Fig. 2.1).

Fig 2.1 A Representation of the Different Proton Locations on Condensed Aromatic Systems



760cm^{-1}
Isolated
C-H Group

814cm^{-1}
Two adjacent
C-H Group

870cm^{-1}
four adjacent
C-H Group

The most prominent of the oxygen functional groups in the infrared spectra of bituminous coal is the broad band with a maximum near 3300cm^{-1}, this is always present to some extent and is assigned to hydroxyl groups in the organic fraction of the coal(50). The majority of the hydroxyl groups have been found to be phenolic in nature(51) and hydrogen bonded(52).

In bituminous coal there appears to be very few carbonyl groups. Thus the band at 1700cm^{-1} is normally only seen as a shoulder of the 1600cm^{-1} band, if at all. Oxidised bituminous coals however, do show a prominent absorption at 1700cm^{-1} due to carbonyl groups(52).

Various other carbon-oxygen groups produce IR peaks which occur between 1300cm^{-1} and 1000cm^{-1}, but the individual absorptions cannot be separated, due to overlapping and superposition.

Mineral matter within the coal can give rise to absorptions around 1000cm^{-1}, for example silicates(53).

Quantitative studies using infrared absorption spectroscopy, have not been frequent, because of the broad overlapping bands, which along with the poor quality of the spectra result in large errors. Some attempts have been made to measure the proportions of aliphatic and aromatic C-H groups(54, 55, 56) using peak heights, for this work the ratio of the absorption coefficients were determined using a range of model compounds. Brown and Ladner(55) proposed the formula below, (equation 1), for calculating the aromaticity of coal solutions.

$$f_a = \frac{(C/H) - (H^{*}_{al}/x)}{(C/H)} \qquad (1)$$

Where C/H is the atomic ratio of carbon and hydrogen in the coal and is determined by elemental analysis.

$x = H_{al}/C_{al}$ and is assumed to be 2, i.e. the aliphatic structures are predominantly methylene groups.

$H^*_{al} = H_{al}/H$. This is determined from the IR spectra.

Brown and Ladner found good agreement between the results obtained by this method and the results obtained from ^{1}H-NMR studies of coal solutions.

Wang(56) has recently suggested that the H^*_{ar} and f_a values are better calculated using equations (2) and (3) below.

$$H^*_{ar} = \frac{[1 - (O/2H)]}{[1 + (A_{2930}/KA_{3055})]} \qquad (2)$$

$$f_a = 1 - \frac{[1 - (O/2H)] \,.\, (H/C)}{x[1 + (KA_{3055}/A_{2930})]} \qquad (3)$$

Where A is the IR absorption at the given wave number

K is the ratio of the extinction coefficients ($\sim$ 2)

x is $\sim$ 2

and C, H, and O are the carbon hydrogen and oxygen contents as determined by elemental analysis.

(Both of the above equations have been derived from an examination of coal solutions, and therefore when they are applied to solids may not give reliable quantitative results.)

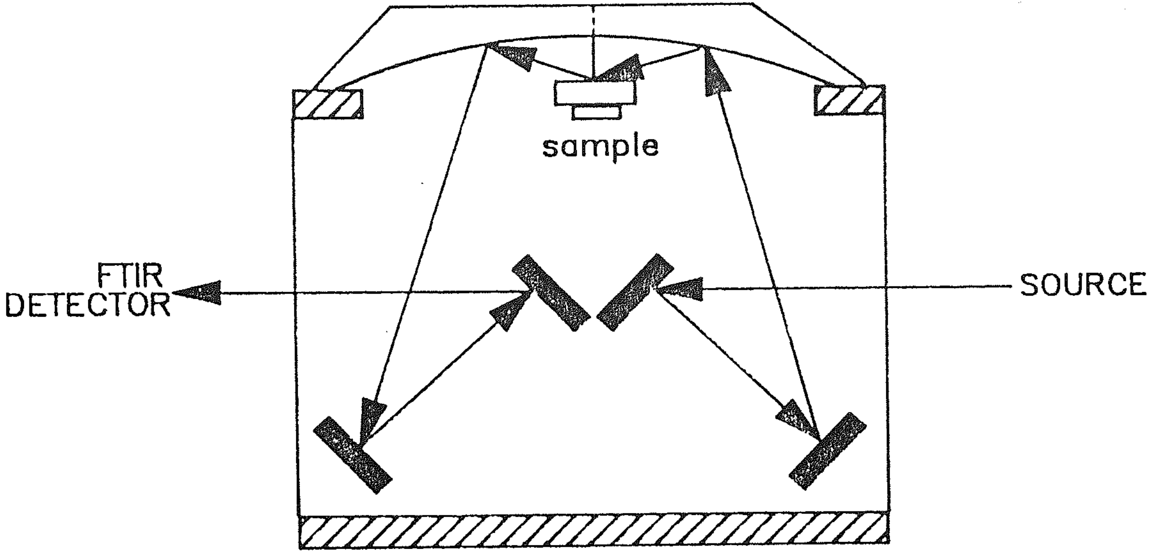
With the advent of Fourier transform infrared spectrometers and more powerful computing techniques(57) more quantitative work is now possible, for example, using factor analysis and a set of standard coals it is now possible to determine the percentage of carbon, hydrogen, nitrogen, sulfur, and ash in a coal from its infrared spectra(58). Where however a large set of standard coals are not available, diffuse reflectance infrared spectroscopy is better adapted to quantitative work. The method of diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) is described in section 2.3.1.

2.3.1 DRIFT SPECTROSCOPY

Quantitative data is difficult to obtain from KBr discs used in combination with absorption spectroscopy, due to the facts that A) background subtraction is difficult, B) the average particle size in the disc and the disc thickness needs to be determined, and C) the extensive grinding of the coal which is sometimes required to reduce scattering, may alter the organic structure. An alternative to the KBr disc method is DRIFT spectroscopy(59, 60), which measures the amount of reflected light from a mixture of ground coal (between 2% and 5%), and powdered KBr. DRIFT spectroscopy has the advantages of easy sample preparation and does not require a knowledge of the particle size or sample dimensions. Fig 2.2 shows the optical set-up of the diffuse reflectance apparatus used in this study.

The IR radiation is reflected from the sample in all directions, collected and focused so as to enter the spectrometer in the normal way. The amount of light reflected will depend on the samples depth, but the experimental conditions are chosen so that the depth of the sample holder is so large, that any further increase in the samples depth makes no difference to the amount of reflected light. This reflectance at infinite depth, is given the symbol R_∞, (approximately 5mm).

Fig. 2.2 A Schematic Representation of the Optics of the Diffuse Reflectance Apparatus.



The DRIFT spectrum obtained is then ratioed with a KBr (powdered) reference sample, and converted to the Kubelka-Munk function $F(R_\infty)$(61,62) using equation 4, before the spectrum is re-plotted in the reflectance form.

$$F(R_\infty) = (1-R)^2/2R_\infty \qquad (4)$$

where R is the reflectance due to the KBr reference.

Errors in this technique have been reported by Messerschmidt(63). These errors are due to specular reflectance from the surface of the KBr/coal mixture (such reflections were removed in the apparatus we used by a blade edge which rested on the surface of the sample). Since DRIFT spectroscopy involves reflected light, there is an implicit assumption that the surface of the coal particles are representative of the bulk coal, from the data obtained in other studies(59, 60) this assumption appears reasonable.

2.4 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Since the first use of NMR by Newman and co-workers(64) it has found increasing application in the study of coal solutions(65, 66, 67, 68). NMR is a non-destructive technique which allows the hydrogen distribution (^{1}H-NMR), and carbon distribution (^{13}C-NMR), in solublised coal fractions to be determined directly. In the case of ^{1}H-NMR the peak area resulting from a particular proton environment, is directly proportional to the number of hydrogen atoms contributing to the signal, and thus can be used quantitatively to obtain useful structural parameters(55). As stated previously most coals are largely intractable in organic solvents, therefore the data obtained by these techniques may not be representative of the bulk coal. For example the solvent soluble fractions are made up of relatively low molecular weight compounds, so that there are a large number of terminal hydrogens. The ^{1}H chemical shift commonly observed in coals are given in Table 2.2. In the case of ^{13}C-NMR spectra the peak areas are not proportional to the number of carbon atoms. This is because; (1) the range of spin-lattice relaxation times (T_1) found in coals, are such that some highly aromatic carbons are not being detected, and (2) the value of the nuclear Overhauser effects differs from carbon to carbon(69). Therefore unless the NMR experimental conditions are carefully selected, (eg. gated decoupling and the addition of relaxation agent), quantitative measurements are suspect. The ^{13}C-NMR chemical shift assignments are listed in Table 2.3.

It is now possible to examine coals in the solid state. The technique which is most widely applied is that of cross polarisation magic angle spinning ^{13}C-NMR (or ^{13}C-CPMAS-NMR). One of its main uses is in the determination of the aromaticity value of coal (f_a) as defined in equation 5.

Table 2.2 ^{1}H NMR Chemical shifts.(70)

ppm range	hydrogen type
9.0 - 8.3	hydrogen on aromatic nitrogen
9.2 - 6.2	aromatic hydrogen
9.0 - 6.0	aromatic hydrogen
9.0 - 5.0	phenolic hydroxyl
8.3 - 7.7	phenolic hydroxyl
7.15	benzene hydrogens
6.65 - 6.5	alkene hydrogens next to ring
6.0 - 4.5	alkene hydrogens
5.0 - 3.4	ring joining methylene
4.2 - 3.2	methylene α to two rings
4.4 - 1.7	aliphatic: α-CH_2, O-CH_2, α-CH_3, α,α-CH_2, β-CH_2-tetralin, β-CH_2-indanes
3.4 - 1.9	CH_3, CH_2 and CH α to aromatic rings
2.6 - 1.85	hydrogens on carbon atoms α to aromatic rings.
1.95	cyclohexane
1.90 - 1.0	β-CH_3, CH_2 and CH β from an aromatic ring, alkane CH_2 and CH
1.85 - 1.05	hydrogens on carbon atoms β to aromatic rings
1.7 - 1.0	β-CH_3, remote CH_2, γ-CH_2 alicyclics.
1.05 - 0.5	hydrogens of methyl groups of alkanes and methyl groups γ or further from an aromatic ring.

Table 2.3 NMR chemical Shifts For ^{13}C Nuclei.(70)

ppm range	Carbon type.
170 - 210	carbonyl
148 - 168	aromatic C-O eg. phenol
129.5 - 148	mainly aromatic C-H and aromatic C-NH
100 - 129.5	mainly aromatic C-H with aromatic C-H ortho to C-OH between 100 and 115 ppm
37 - 60	ring joining methylene (23-44ppm), CH in alkyl group (except iso-alkyls) and naphthenic rings: CH_2 in alkyl group adjacent to CH
27.5 - 37	CH_2 in alkyl groups not adjacent to CH (except some α-CH_3 and CH_2 adjacent to terminal CH_3 in alkyl groups > C_4). CH_2 in ring joining ethylene groups, α-CH_2 and CH, β-CH_2 in hydroaromatic rings; naphthenic CH_2.
24 - 27.5	naphthenic CH_2; shielded α-CH_2 groups; β-CH_2 in indane and propyl groups; β-CH_3 in isopropyl.
22.5 - 24	CH_2 adjacent to terminal CH_3 in alkyl groups > C_4; β-CH_2 in un-substituted tetralin structures; CH_3 on hydroaromatic and naphthenic rings (18-24 ppm).
20.5 - 22.5	α-CH_3 not shielded by any adjacent rings or groups.
18 - 20.5	α-CH_3 shielded by one adjacent ring or group.
15 - 18	β-CH_3 in ethyl groups.
11 - 15	CH_3 γ or further from an aromatic ring, α-CH_3 shielded by two adjacent rings or groups.

$$f_a = \frac{\text{number of aromatic carbon atoms}}{\text{total number of carbon atoms}} \qquad (5)$$

In the past many different methods have been used to evaluate this most important of the structural parameters(71, 72, 73, 74). All of these methods have involved one or more assumptions, and have normally produced widely differing f_a values. Retcofsky and co–workers(75), for example, found that the f_a value of a 82.6%C coal had been quoted between 0.5 and 0.9. ^{13}C-CPMAS-NMR has now largely replaced all other methods for determining f_a values, but this technique is still subject to errors. These are detailed in section 2.4.1.

2.4.1 ^{13}C-CPMAS-NMR

The ^{13}C NMR signals for solids are considerably broadened due to ^{1}H-^{13}C dipole-dipole interactions and chemical shift anisotropy, which arise from the different orientations of the molecules in the solid which are not averaged out as in solution NMR. This anisotropy also results in unsymmetrical line shapes. Another problem with solid state NMR is that the ^{13}C nuclei have very long spin lattice relaxation times, in the order of minutes for ^{13}C, and since the T_1 value determines the delay period between the NMR pulse, (normally between 3 times and 5 times T_1) this means to get a reasonable signal to noise ratio large amounts of instrument time would be required, (i.e. several days).

The dipolar interaction of the ^{1}H-^{13}C nuclei is removed by high powered decoupling at the Larmor resonance frequency, with a strong radio frequency field. This results in the ^{1}H nuclei becoming transparent to the ^{13}C nuclei. The chemical shift anisotropy is removed by the technique of magic-angle spinning (MAS), which has been dealt with in detail by Maciel(76), and involves the rapid rotation of the solid sample at an angle of 54.7° relative to the applied magnetic field. The problem of the very long T_1 values is overcome by using cross polarisation (CP). This technique which was developed by Pines and co-workers(77) and described by Miknis(78), exploits the naturally abundant ^1H system with its shorter spin-lattice relaxation times. In brief the process involves four steps: (1) The polarization of the ^1H spin system, (2) Spin-locking the rotating frame, (3) Establishing ^{13}C-^1H contact, in a time T_{TC}, and (4) Observation and recording of the free induction decay signal. The result is that much shorter pulse cycles can be used so that spectra can be obtained within an hour or so, with a good signal to noise ratio.

The errors involved in ^{13}C-CPMAS-NMR have been reviewed by Davidson(70). They come about because in a highly aromatic system, not all the carbons are in close proximity to a proton, therefore there is some doubt as to whether efficient magnetisation of all the carbons can occur via the ^1H system. Davidson(70) and Dereppe(79), conclude that in general the spectra that are obtained are quantitative, however Botto and co-workers(80) suggests that cross polarisation experiments, largely discriminates against aromatic carbons in coal, and as such only provide minimum values for structural parameters such as aromaticities.

Although the quantitativeness of ^{13}C-CPMAS-NMR is still in dispute the spectra can be used to compare coals and observe trends, but some care has to be taken in the choice of pulse sequence, the contact time, the recycle time, and the type of empirical methods used to enhance the structural detail in the spectra.

2.5 GEL-PERMEATION CHROMATOGRAPHY

Gel-permeation chromatography (GPC) is a method by which soluble coal fractions can be separated according to molecular weight. This is achieved by the selective exclusion of molecules through a molecular sieve, usually a cross-linked polystyrene, so that the highest molecular weight fraction elutes first and the lowest molecular weight material last. The GPC technique allows us to obtain an insight into the molecular weight distribution of the soluble coal extracts, and also yields the number average (M_n) and weight average (M_w) molecular weights.

An alternative name for GPC is Size-exclusion chromatography, but in fact size is only one of the factors which determines the elusion volume of a particular coal molecule. It is the hydrodynamic volume of a given molecule which is important, but this is a function of, (1) The molecular weight of the compounds, (2) The solvent used to elute the sample through the column, (3) The molecules shape, and (4) The presence or absence of functional groups. For example compounds with large molecular weights will normally have a larger hydrodynamic volume, however if the solvent used allows self-association of the solute or adsorption of the molecules onto the gel, an erroneous elusion volume will result. Also condensed aromatic systems are ridged and planar and thus will have a very different volume when compared, for example, with a long-chain alkane with the same molecular weight. Because of the above mentioned problems, there is no direct relationship between the molecular weight of a compound and it's elusion volume from the GPC column. It is therefore necessary for the column to be calibrated with compounds of equivalent chemical structure to that of the fraction(s) to be examined, if reliable molecular weight data is to be obtained. Unfortunately coal solutions are not sufficiently well characterised to allow confident calibration(81), this however has not stopped the increasing use of GPC in coal chemistry(82, 83, 84, 85, 86). It appears from work done by Knudson and co-workers(87) that GPC does in fact measure some property which is a function of the molecular weight in coal solutions, and thus can be used to compare similar coal fractions qualitatively(88).

As well as calibration problems other sources of error have been noted by Larsen and co-workers(89) who showed that adsorption of some of the coal molecules occurred on the GPC column with some solvents, and by Schanne and Haenel(90) who showed that some of the high molecular weight results were due to associated aggregates of the solute. These problems can be alleviated to some extent by the correct choice of solvent and by the use of dilute solutions, but this then reduces sensitivity. A more detailed discussion of the errors involved in GPC with coal solutions is given by Bartle and co-workers(91).

It is clear from the above discussion of GPC that the actual results quoted for M_n, M_w, and the molecular weight distribution should not be taken as absolute values. It is our practice to give results in terms of polystyrene equivalent molecular weights, (as polystyrene was used to calibrate the column), and to use the results obtained for comparative purposes, to give some indication of how the molecular weight distribution changes from fraction to fraction.

2.6 SURFACE AREA MEASUREMENTS IN COAL

Coal has a complex pore structure consisting of micro-pores, which have diameters of less than 200nm, transitional-pores with diameters between 200 and 2000nm, and macro-pores that have diameters greater than 2000nm. The micro-pores have a small volume but a large surface area, acting to some extent like a molecular sieve. They have a large influence on the chemical reactivity since any reaction will occur at the surface boundary, and most of a coals surface is contained within the pores. The distribution of the various sized pores must also be considered because it is important that the 'trapped' or depolymerised material can leave the pores rapidly enough to permit access of fresh solvent/reactants, so that reasonable reaction rate can be achieved.

Two methods of estimating the pore surface area have been applied to our coals, using the adsorption of gases. When determining the surface area by these methods, the number of gas molecules necessary to cover the adsorbent in a monolayer is found. This monolayer result is then multiplied by the area occupied by a single adsorbed gas molecule to give the surface area. An introduction to the theory and methods of adsorption measurements is given by Mahajan and Walker(92), and Fuller(93).

The monolayer capacity has been calculated using the Brunauer-Emmett-Teller(94) (BET) equation, (equation 6 below).

$$\frac{p}{V(p_o-p)} = \frac{1}{V_mC} + \frac{(C-1)}{V_mC} \cdot \frac{p}{p} \qquad (6)$$

where (V) is the volume of gas adsorbed at equilibrium pressure (p).

(p_o) is the saturation vapour pressure of the adsorbate at the adsorption temperature.

(V_m) is the monolayer capacity.

(C) is a constant which represents the net heat of adsorption.

when the value of C is high, $(C-1)/C \approx 1$ and $1/V_mC \approx 0$, therefore the BET equation approximates to;

$$\frac{p}{V(p_o-p)} = \frac{1}{V_mC} \cdot \frac{p}{p_o} \qquad (7)$$

Thus a plot of $p/V(p_o-p)$ versus p/p_o passes through the origin so that only a single adsorption point is needed to calculate the monolayer capacity. The relative pressure used in the experiment appear critical, at too low a value of p/p_o, adsorption is governed by the pore size rather than the pore surface area(95,96), while at too high a value the plot may be non-linear (94).

The Palonyi-Dubinin (P-D) equation, (equation 8), has also been used to calculate the surface area of the coals from CO_2 gas adsorption measurements.

$$\log V = V_o - (0.434BT^2/\beta^2)\ [\log(p_s/p)] \qquad (8)$$

Where V_o is the micro-pore capacity.

p_s is the saturation vapour pressure of the adsorbate.

β is the affinity coefficient of the adsorbate relative to N_2.

B is a constant which is a measure of the micro-pore size.

Thus a plot of logV versus $(\log p_s/p)^2$ results in a graph whose intercept equals the micro-pore capacity. The P-D equation permits the evaluation of V_o form adsorption data obtained below 1atm pressure, and therefore conventional volumetric apparatus can be used. The equation itself is valid over a relative vapour pressure range of 1×10^{-5} to 0.2.

Gas adsorption by dinitrogen is not thought to measure the smaller micro-pores(97,98), whereas CO_2 will be adsorbed into these small pores and so measures the total surface area of the coal, by using these facts it is possible to estimate the surface area of the micropores alone (i.e. subtracting the area given by the N_2 experiment from that of the CO_2 result).

2.6.1 PARTICLE SIZE MEASUREMENTS

We have attempted to relate the pore surface area to the particle size of the coal, as measured by light scattering(99). The Brownian motion of sub-micron particles in suspension is described by a diffusion coefficient (D), which can be determined by measuring the amount of light scattered over a known period of time. An autocorrelation function $g_{(\tau)}$, showing a characteristic delay results, which is related to the diffusion coefficient by equation (9).

$$g_{(\tau)} = 1 + \alpha e^{-2DQ^2} \qquad (9)$$

Where Q is the scattering sector and is given by equation (10)

$$Q = (4\pi n/\lambda) \,.\, \sin(\theta/2) \qquad (10)$$

Where n is the refractive index of the suspending medium.

λ is the wavelength of light used.

θ is the scattering angle.

From the diffusion coefficient the Stokes diameter, or hydrodynamic size, (d), of the particles can be calculated using equation (11).

$$d = \frac{kT}{3\pi\eta D} \qquad (11)$$

Where d is the particle diameter.

k is the Boltzmann constant.

T is the absolute temperature.

η is the viscosity of the medium.

For these equations to be valid, all the particles are assumed to be spherical, this is clearly not true for coal particles. Larger particles also tend to scatter light more than smaller ones, thus the average particle size will be weighted towards the larger particles. Other assumptions include; all particles were suspended in the solvent system used, and that the coal was insoluble in such solutions. Since coals have a range of apparent densities and interact with most organic solvents in some way, the errors in the determination of particle size can be assumed to be large, so that only qualitative data resulted. It was found from a very limited study that the changes in the average partical size could not be related to changes in surface area as measured by gas adsorption, therefore the light scattering work was not continued.

2.7 GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Gas chromatography-mass spectrometry (GC-MS) is a method by which complex mixtures of organic compounds can be separated and identified quickly and accurately. Since the first attempt to couple a GC column to a mass spectrometer by Holmes and Morrell in 1957(100), there have been many advances made in both instrumentation and computer technology, so that now a GC-MS system is capable of making at least a qualitative identification of all the components in very complex mixtures containing more than a hundred compounds. Other advantages of GC-MS include trace compounds, (ie. less than 0.1% of the total) can be isolated and identified, and only a very small quantity of the original sample is required for analysis, (approximately 1μg).

The techniques, theory and applications of gas chromatography have been dealt with in many books(101, 102, 103), while mass spectrometry has been described in detail by McDowell(104), Milne(105), Merrit and McEwen(106), and Lee and co-workers(107). The combined instrumental method of GC-MS has been reviewed by McFadden(108), and Gudzinowicz and co-workers(109).

Qualitative analysis of a solution containing a mixture of compounds is carried out by analysis of the TIC (Total Ion Chromatograph) which is generated by the computer, and in many ways is similar to the chromatograph produced by a normal GC system, with each peak corresponding to a different compound. A combination of retention times (RT) and examination of the positive ion electron impact mass spectrum produced for a particular peak in the TIC is used to identify the compound. The fragmentation pattern is often suggestive of one of a number of homologues, even when a positive identification of the compound cannot be made, for example alkylbenzenes typically give fragment ions of m/e values 91, 105, 119 etc., while alkylnaphthalenes give ions of m/e values 141, 155, 169, etc., and long chain alkanes m/e's 57, 71, 85, and 99. Therefore the various homologues can be identified and placed in the correct position in the series by using the RT. Sometimes it is apparent that more than one compound is contained within the same peak envelope of the TIC, so that the resulting mass spectrum is a mixture of more than one compound. In this case it may be possible to resolve this area by the generation of a single ion fragmentogram (SIF). This is used where a single ion fragment is indicative of a particular class of compound, for example m/e 107 is usually the base peak for phenols, which often elute with other compounds and also tend to be found in low concentrations.

The quantitative analysis from the GC-MS instrument is more difficult, since the TIC is generated from the ion current measured at each scan. The magnitude of this current is not only dependent on the amount of compound present, but also on the ease with which a particular compound fragments. Thus for each type of compound there will be a different instrument sensitivity, however compounds within the same homologous series should give reasonably identical responses, and the peak area for such groups will thus be quantitative with respect to each other.

When coal solutions are examined other problems become apparent. Only compounds which are volatile i.e. boil at less than 400°C, and/or are relatively non-polar will pass through the GC column and be detected. This means that for instance the THF solvent extracts examined by this method, can at best, only be partially characterised. The problem of polar compounds being retained on the GC column can be reduced by the selection of more polar liquid phase in the column, or by derivatisation of the solutions before they are injected into the column, for example phenols and carboxylic acids can be siliylated, O-methylated, or esterified. This derivatisation also has the advantage of disrupting hydrogen bonding and thus reduces the apparent molecular weights and allows more compounds to be detected. To prevent aggregation of the solute moderately dilute solutions may have to be used, but this reduces the sensitivity of the technique.

The disadvantages listed above have not stopped the use of GC-MS in coal analysis(110, 111, 112, 113), and have shown that all coals contain within them a range of relatively simple molecules, such as alkanes, alkylbenzenes, alkylnaphthalenes, and alkyl phenols. Some of the lower molecular weight compounds identified in the soluble fractions can be used as biomarkers to indicate the conditions at the time of diagenesis and coalification, for example the ratio of pristane to phytane, (which themselves are the degradation products of the phytol side chain of chlorophyll), is used to determine if the coal was formed in a reducing or oxidising environment.

A book by Philp(114), describes in detail these fossil fuel biomarkers and their applications.

CHAPTER 3.

ANALYSIS OF UNTREATED COALS

3.1 INTRODUCTION

In chapter one it was suggested that the various components of a coal would be found in one of two distinct phases: 1) The 'mobile' or 'trapped' phase, consisting mainly of relatively simple non-covalently bound compounds, and 2) A macromolecular phase, in some respects resembling a highly cross-linked polymer.

Most of the trapped material can be removed from the coal by solvent extraction, and because of its solubility in organic solvents, it can be characterised more readily than the insoluble fractions by conventional physical and chemical techniques. The insoluble material can be examined by spectroscopic methods such as infrared or MAS-NMR, but these methods only yield an average picture of all the structures present. Therefore in order to identify the building blocks of the polymer-like matrix, the coal has to be degraded in a specific manner and the fragments (low molecular weight, solvent soluble compounds), separated and identified.

The first step in the structural characterisation of a coal is the examination of the untreated material. This initial investigation was necessary to establish if the limited number of coals selected for study, (Gedling, Cresswell, and Cortonwood Silkstone Coals), could be considered to be good representatives of the whole class of British bituminous coals. Only if the coals are found to be a representative sub-set, can any of the conclusions reached from an interpretation of the experimental data be extrapolated.

This chapter describes this initial characterisation of the whole untreated coals, plus the solvent extractable fractions, and solvent insoluble materials.

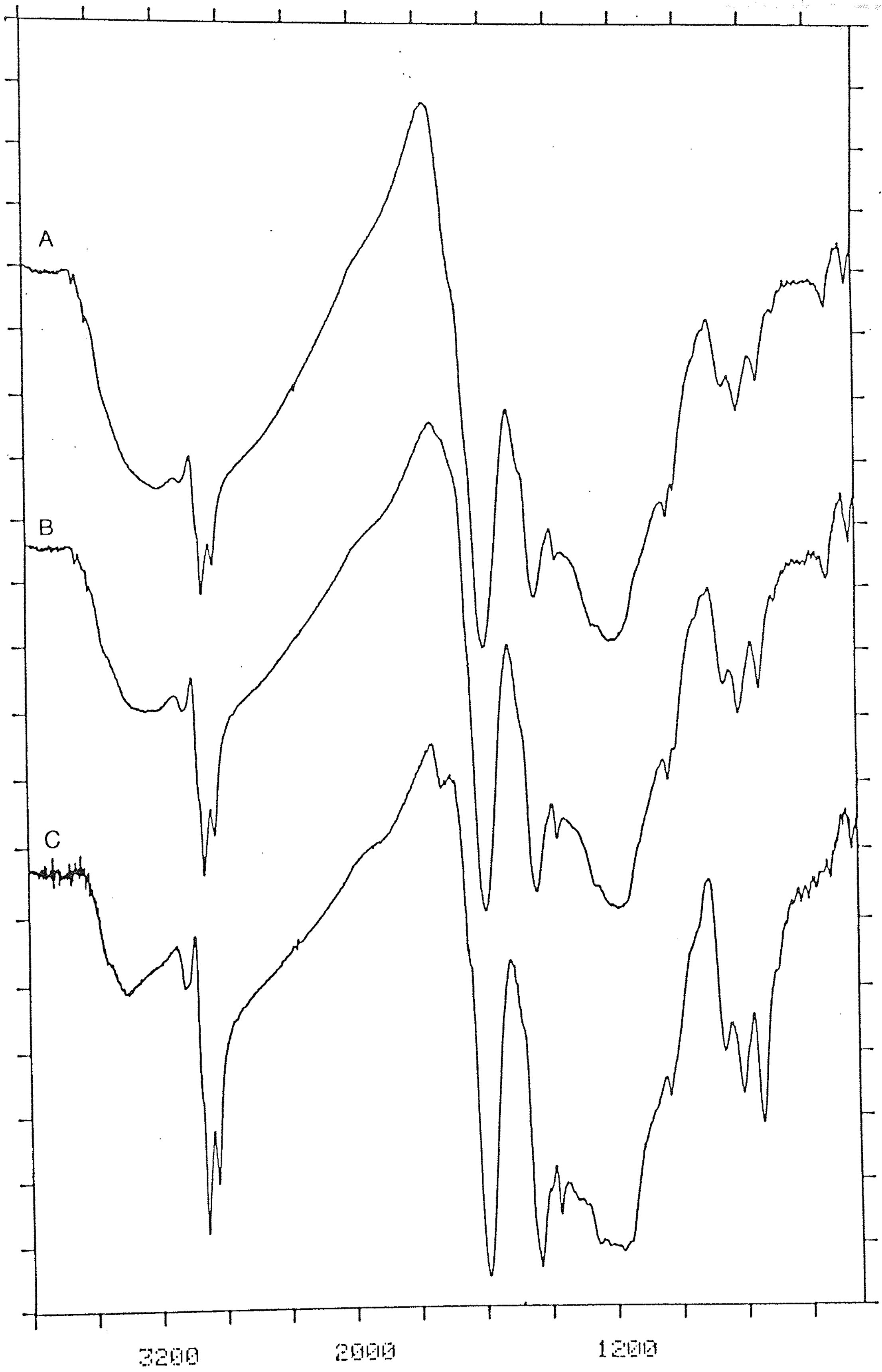
3.2 ANALYSIS OF THE WHOLE COALS

The whole coals were studied by various analytical methods which included; infrared absorption spectroscopy, DRIFT spectroscopy, ^{13}C-CPMAS-NMR, and gas adsorption measurements. The results obtained using these techniques are reported in sections 3.2.1 to 3.2.3, below.

3.2.1 INFRARED STUDIES ON WHOLE COALS

The three British bituminous coals, were examined by IR absorption spectroscopy, (Fig. 3.1 A to C) and DRIFT spectroscopy, (Figs. 3.2 to 3.4). It would be concluded from an examination of both sets of spectra that the coals are very similar to each other, since the only major differences in the spectra are in peak intensities. For example the peaks due to $C{-}H_{ar}$ stretching ($3050\text{-}3030cm^{-1}$) and $C\text{-}H_{ar}$ out-of-plane bending ($880\text{-}750cm^{-1}$), increase directly with coal rank. This shows, as expected, that the aromaticity of the three coals studied increases with coal rank. It was however noted that the intensity of the peaks due to $C\text{-}H_{al}$ stretching, ($2980\text{-}2920cm^{-1}$), and $-CH_2-$ bending, ($1450cm^{-1}$) also increased. This tends to contradict the aromaticity changes noted above. One possible explanation for this apparent increase in the aliphatic character of the coals, as determined by infrared spectroscopy, is as follows:- It is known that as the carbon content of the coals increases the oxygen content of bituminous coals falls, (see elemental analysis results, Table 3.1). This decrease in the oxygen content means that there is a reduction in the number of polar groups in higher ranked coals, i.e. the $C\text{-}H_{al}$ stretching peak is no longer hidden by the absorption due to hydroxyl functions. A similar explanation can be advanced for the apparent increase in the intensity of the $-CH_2-$ stretching absorption at $1450cm^{-1}$ with increasing coal rank, viz a change in the number of polar functions.

Fig.3.1 IR Absorption Spectra Of Untreated Coals.



A) Gedling Coal

B) Cresswell Coal

C) Cortonwood Silkstone Coal

Fig.3.2 DRIFT Spectrum Of Untreated Gedling Coal.

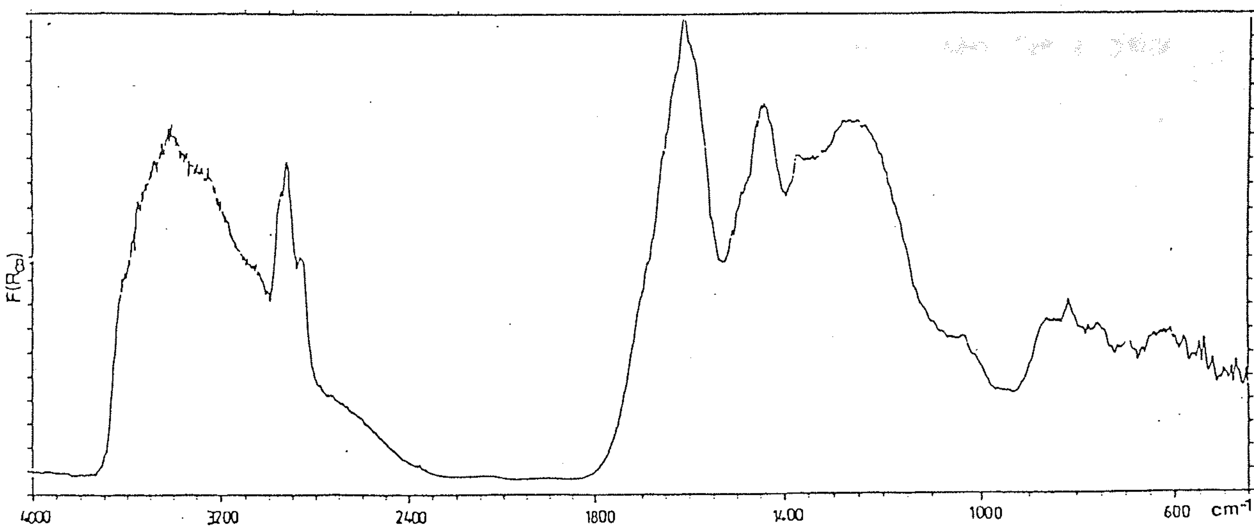


Fig.3.3 DRIFT Spectrum Of Untreated Cresswell Coal.

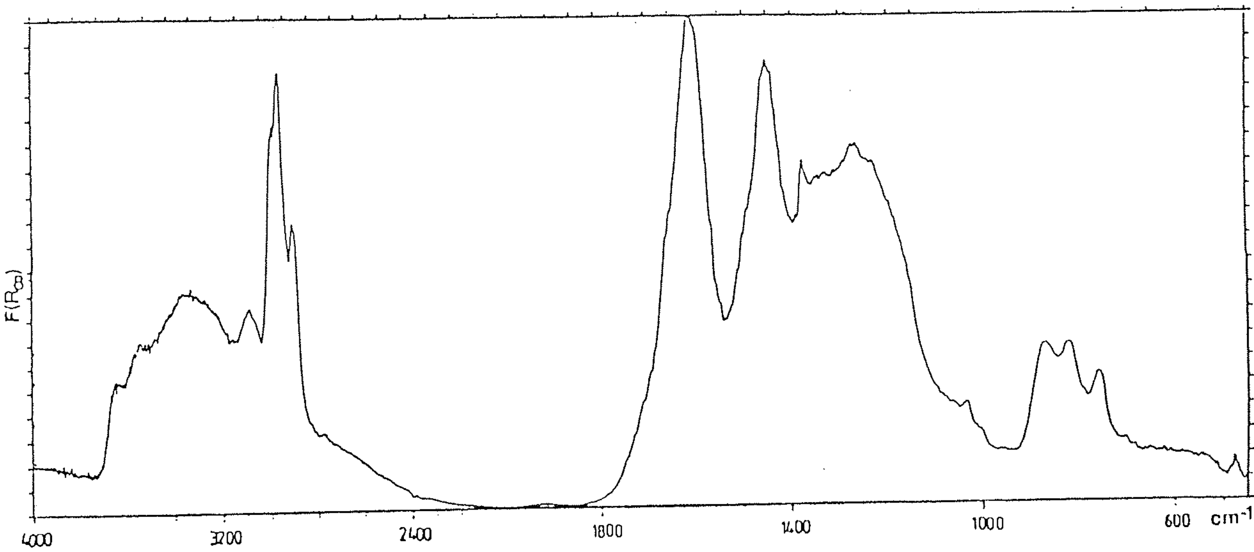
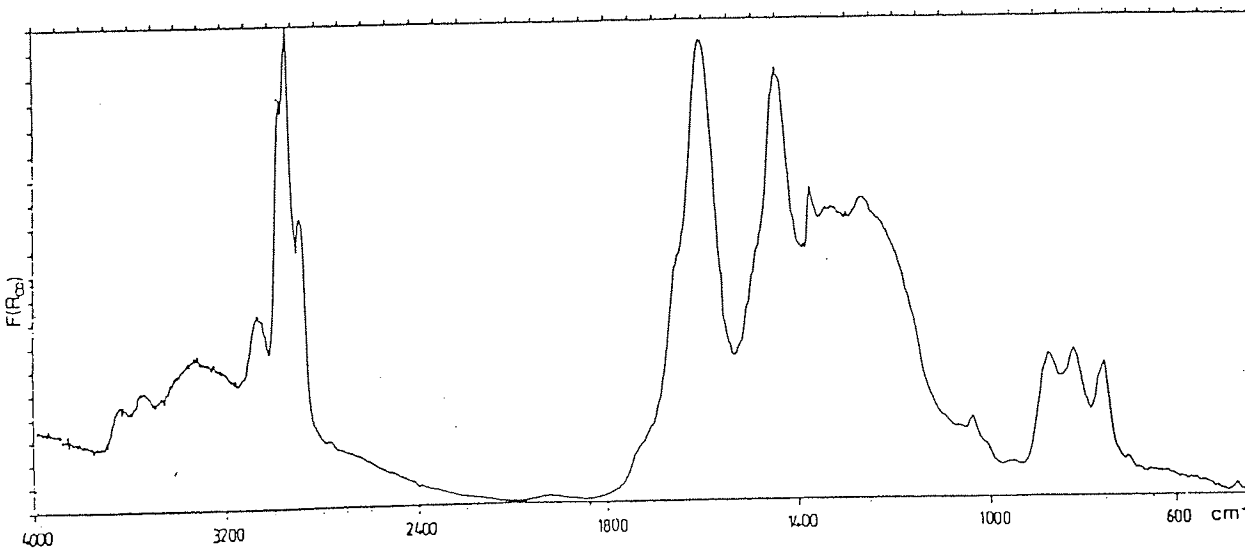


Fig.3.4 DRIFT Spectrum Of Untreated Cortonwood Silkstone Coal.



The 1450cm^{-1} peak is normally measured relative to the $-C=C-_{ar}$ absorption at 1600cm^{-1}, but it has been suggested(47) that this peak is intensified due to polar groups attached to the ring. Therefore it is possible that the apparent change in intensity of the 1450cm^{-1} peak (with increasing coal rank), is due more to a reduction in the 1600cm^{-1} band rather than to any increase in the $-CH_2-$ bending absorption.

Table 3.1 Elemental Analysis of Three British Bituminous Coals.

Coal	Elemental Analysis (% by weight)					H/C	O/C
	C	H	O	N	$S_{(T)}$		
Gedling	78.4 (.9)	5.2 (.2)	11.3 (1)	1.1 (.2)	2.0 (.5)	0.79 (.04)	0.11(.02)
Cresswell	81.2 (.6)	4.9 (.4)	9.3 (.9)	0.6 (.2)	2.0 (.2)	0.72 (.05)	0.09 (.01)
Cortonwood	85.6 (.4)	5.4 (.4)	4.1 (.6)	0.9 (.2)	2.0 (.5)	0.75 (.06)	0.04 (.01)
Silkstone							

The figures in parenthesis show the standard error (95% confidence) for each of the results. The data was obtained on, dry as received, coal samples. The oxygen content was calculated by difference assuming a 2% ash content for each coal.

If it is assumed that the aromaticity value (f_a) of the coals, calculated from the ^{13}C-CPMAS-NMR spectra are correct, (see section 3.2.2) then, it is possible to estimate the average number of hydrogens per carbon atom in the aliphatic portion of the coal, (x in equations 1 and 3 section 2.3) by using the equations derived by Brown and Ladner(55) and by Wang(56). The results of these calculations are shown in Table 3.2. The values obtained for x suggest that the average number of hydrogen atoms per aliphatic carbon atom increases with increasing rank of the coal. This in turn suggests that the alkyl substituents on the aromatic rings are tending to become shorter with increasing rank.

Table 3.2 Structural Parameters Derived from IR data*

Coal	$\frac{KA_{3055}}{A_{2930}}$	H/C	O/2H	f_a	$x^{(55)}$	$x^{(56)}$
Gedling	1.40	0.79	0.068	0.62	1.5	0.81
Cresswell	0.99	0.72	0.059	0.66	2.12	1.00
Cortonwood Silkstone	0.88	0.75	0.024	0.69	2.77	1.26

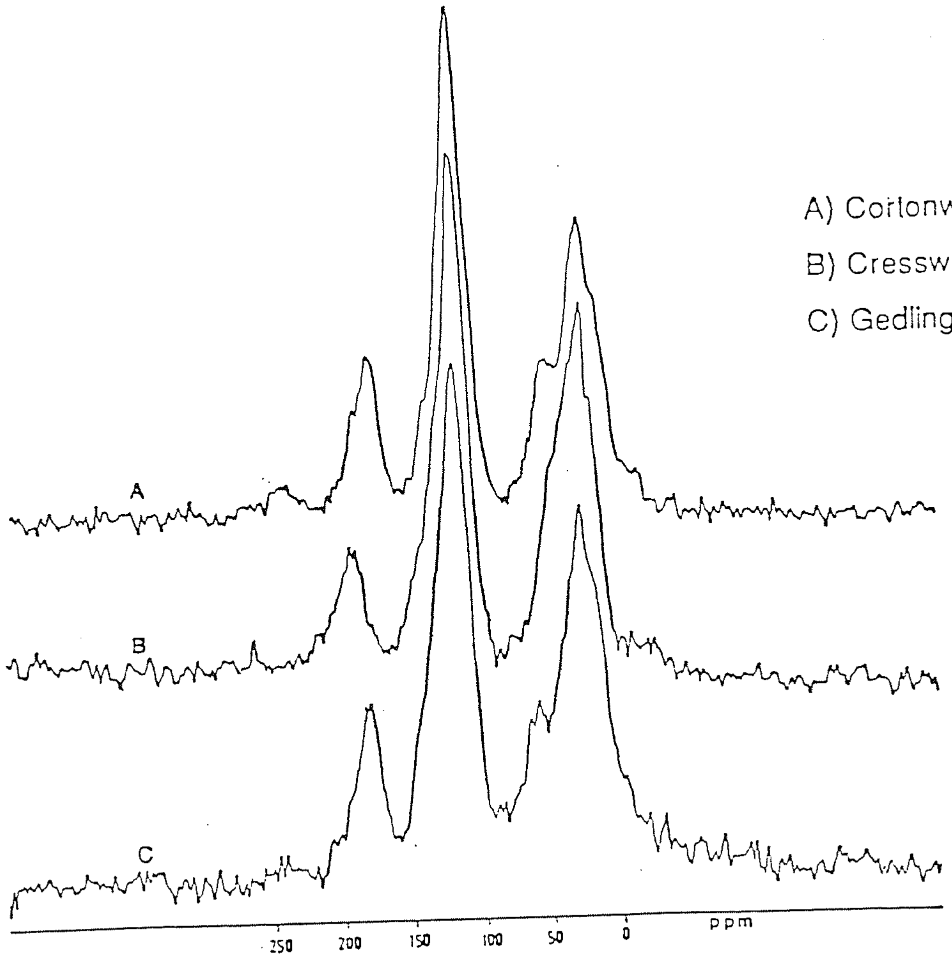
(* Data derived from DRIFT spectra Figs 3.2 to 3.4.)

When however, the Brown Ladner equation is used to calculate the f_a values, it is found that the three coals show the reverse trend to that indicated by the NMR results (cf section 3.2.2), i.e the lowest rank coal has the highest aromaticity value. This is not what would be expected for these coals suggesting that the results obtained from such equations must be treated with caution, at least when applied to solids.

3.2.2 ^{13}C-CPMAS-NMR RESULTS FOR UNTREATED COALS

The ^{13}C-CPMAS-NMR spectra obtained for each of the three coals at two different contact times (T_{CT}) are shown in Fig.3.5 A to C and Fig. 3.6 A to C.

Fig.3.5 ^{13}C-CPMAS-NMR Spectra Of Untreated Coals (T_{CT}=0.5ms).

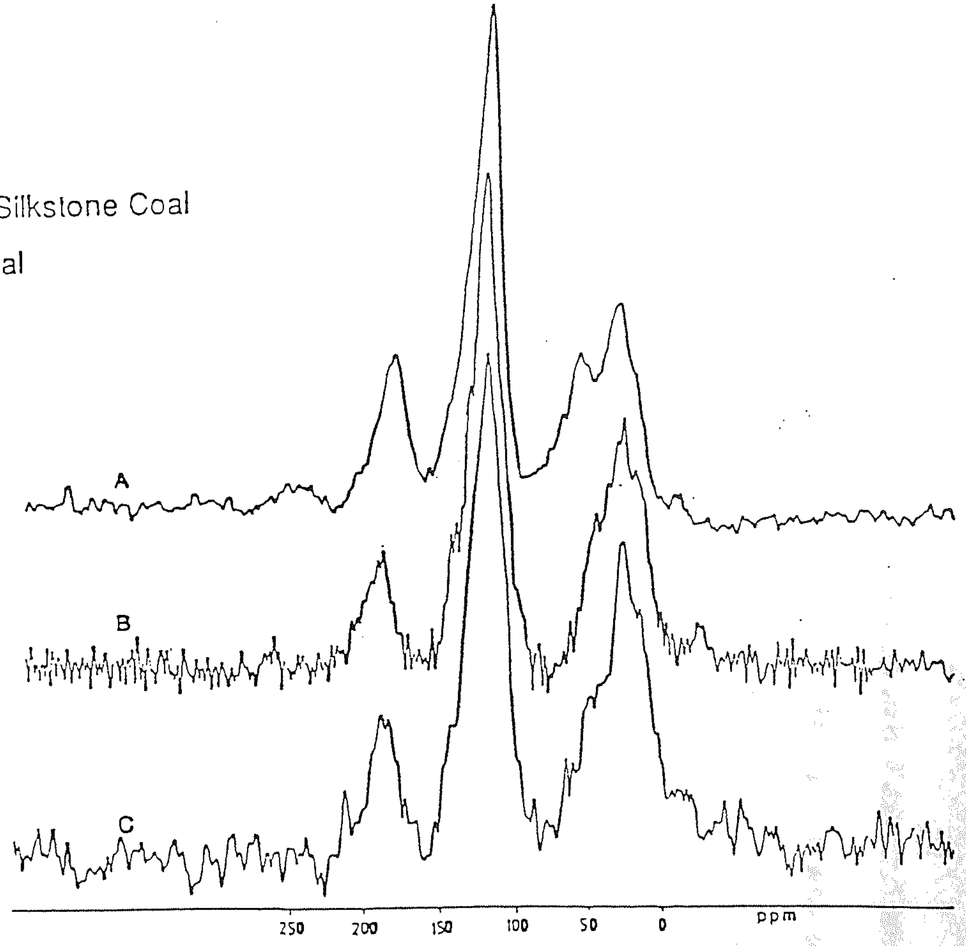


A) Cortonwood Silkstone Coal

B) Cresswell Coal

C) Gedling Coal

Fig.3.6 ^{13}C-CPMAS-NMR Spectra Of Untreated Coals (T_{CT}=2.0ms).



The proton relaxation times (T_1 and $T_{1\rho}$) are given in Table 3.3.and the f_a values calculated from the two sets of spectra are contained in Table 3.4. It was assumed in calculating the aromaticity values, that the spinning-side bands, on either side of the aromatic peak were of equal intensity. This meant that an estimation of the relative number of aliphatic carbon atoms could be made, by subtracting from the area of the aliphatic envelope (0 to 90 ppm) the area of the spinning side band between 160 and 220ppm.

Table 3.3 Proton Relaxation Times at 60MHz

Coal	**T_1/ms**		**$T_{1\rho}$/ms**	
Gedling	28%	71	44%	3.5
	72%	27	56%	0.5
Cresswell		100	50%	2.0
			50%	0.3
Cortonwood Silkstone	60%	200	40%	3.0
	40%	64	60%	0.6

Table 3.4 f_a Values For Untreated Coals At Two Different Contact Times

Sample	**f_a**	
	T_{CT} = 0.5ms	**T_{TC} = 2.0ms**
Gedling Coal	0.57	0.62
Cresswell Coal	0.59	0.66
Cortonwood Silkstone Coal	0.61	0.69

The fact that two values of $T_{1\rho}$ were obtained for each coal, (see Table 3.3), indicates, as expected, a substantial inhomogenaety in the three coal samples. The low values observed for the T_1's can be explained by the presence of paramagnetic species in the coal, which provide a means for the nuclei to rapidly relax. A visual inspection of the two sets of spectra obtained at the two contact times, (Fig. 3.5 A to C, and Fig. 3.6 A to C) shows only minor differences, but it is clear from the data contained in Table 3.4 that the contact time has a marked effect on the observed aromaticity values of the coals when determined by ^{13}C-CPMAS-NMR spectroscopy, i.e. the longer the contact time, the larger the f_a value. The aromaticity results obtained at T_{CT} = 2.0ms should be the more accurate, because the longer time that is allowed for cross polarisation, the more aromatic carbons will be detected during the NMR experiment. All the f_a values, however are still likely to be underestimates.

The three coals show the expected rank trend, i.e. Gedling coal, the lowest ranked coal of the three has the lowest f_a value, (0.62), while Cortonwood Silkstone coal has the highest f_a value, (0.69).

Little evidence of carbons bound to oxygen can be seen from the NMR spectra, (Fig. 3.5 A to C and Fig. 3.6 A to C), this is typical of all bituminous coals which have relatively small oxygen contents. Thus the study of oxygen group functionalities in coals requires the application of other analytical methods.

3.2.3 SURFACE AREA MEASUREMENTS ON WHOLE COALS

An estimate of the total, external and micropore surface areas, of the three British bituminous coals, was obtained by gas adsorption measurements using either dinitrogen or carbon dioxide, (applying both the BET and P-D equations, detailed in section 2.6). The results for the whole coals are given in Table 3.5.

Table 3.5 Gas Adsorption Results For Untreated Coals

Coal	CO_2 Adsorption P-D		N_2 Adsorption BET		Micropore area
	V_m	m^2g^{-1}	V_m	m^2g^{-1}	m^2g^{-1}
Gedling	9.33	63.45	13.48	58.7	4.75
Cresswell	7.24	49.26	6.71	26.87	22.39
Cortonwood Silkstone	6.45	43.9	4.49	19.5	24.40

The gas adsorption results for the untreated coals show a decrease in the pore volume and surface area with increasing coal rank. This is to be expected, since there is assumed to be a more ordered, closely packed, laminated type, structure for higher ranked coals where the aromatic clusters can align one on top of the other. In going from Gedling to Cortonwood Silkstone coal, the relative decrease in the surface area of the larger pores, (as measured by dinitrogen adsorption) is greater than the fall in the surface area of all the pores, (as measured by carbon dioxide adsorption). This indicates there is a change in pore size distribution (dinitrogen cannot penetrate the smaller micropores which account for a large percentage of the surface area). I.E. Cortonwood Silkstone coal has a higher proportion of micropores, (diameter less than 200nm), when compared to Cresswell coal, which in turn has a higher percentage of micropores than Gedling coal. The porosity/surface area, and pore size distribution changes, means that higher ranked coals will react more slowly in systems where mass transport is the rate limiting step, (this is the case for most coal reactions).

3.3 ANALYSIS OF COAL EXTRACTS

3.3.1 SOLVENT EXTRACTION RESULTS.

The solvent extractability result for the three coals in the specific solvent pyridine, and the non-specific solvents THF and chloroform, are shown in Table 3.6. The results in perenthesies were obtained from extraction over a 30 day period. All the other solubility results were obtained by extracting the coals for 7 days.

Table 3.6 Solvent Extractability Results

Coal	**Solvent Extractability (%)**		
	Chloroform	**THF**	**Pyridine**
Gedling	8	12 (16)	13
Cresswell	2	11 (15)	22
Cortonwood Silkstone	2	6 (10)	28

The THF and chloroform solvent extractability data are subject to an error of plus or minus 10%, due mainly to the heterogeneous nature of coals. The errors for the pyridine extraction results are larger, (19%), because not only are the coals heterogeneous, but they also combine with pyridine making this solvent very difficult to remove from the coal matrix, after solvent extraction.

The extraction results show the normal trend for bituminous coals in specific and non-specific solvents, i.e. in non-specific solvents the amount of extractable material decreases with increasing coal rank. When a specific solvent such as pyridine is used the opposite trend is observed.

The 30 day THF extracts were fractionated on a silica gel column using increasingly polar solvents. The results of this fractionation are shown in Table 3.7.

Table 3.7 Fractionation of 30 Day THF Extract by Column Chromatography

Solvent		**30 Day THF Extract Eluted (%)**		
		Gedling	**Cresswell**	**Cortonwood Silkstone**
Hexane		6	4	4
Benzene	increasing	12	10	10
Chloroform	solvent	11	35	33
Methanol	polarity	20	17	22
THF	↓	50	33	33

All the fractions were examined by IR spectroscopy, (the hexane and benzene fractions were also studied by GC-MS). The IR spectra indicated that the aromaticity of the fractions increased as the polarity of the solvent used to elute them increased. The more polar fractions also showed significant amounts of oxidation, as could be seen by the development of a carbonyl peak at 1700cm^{-1} in the IR spectra. The oxidation of the more polar fractions probably occurred during the chromatographic separation, and account for the 100% plus, recovery in the two higher ranked coals.

The GC-MS data obtained from the hexane fraction showed it to consist mainly of aliphatic material, in particular n-alkanes (C_8 to C_{31}), with some aromatic compounds. The benzene fraction contained aromatic and alkylaromatic compounds. (The compounds in the chloroform, methanol, and THF fraction were either too polar, or too high in molecular weight to give useful result from an examination by GC-MS).

Section 3.3.4 describes in more detail the GC-MS data obtained from the THF extracts, however from the results obtained on the fractionated solvent soluble extracts it is clear that the GC-MS technique is only able to analyse about 10 to 20% by weight of the extract.

The elemental analysis results for the 30 day THF extracts are given in table 3.8, along with the empirical formulas derived from these results.

Table 3.8 Elemental Analysis Results For The 30 day THF Extracts

Coal	**Elemental Analysis (% by weight)**					
	C	**H**	**O**	**N**	**S(T)**	**H/C**
Gedling	79.3 (.2)	6.1 (.3)	13.2 (.5)	0.5 (.1)	1.0 (.3)	0.92 (.04)
Cresswell	82.9 (.1)	6.2 (.3)	9.5 (.2)	0.4 (.1)	1.1 (.3)	0.89 (.02)
Cortonwood Silkstone	84.5 (.3)	5.4 (.3)	8.9 (.4)	0.2 (.1)	1.4 (.4)	0.76 (.04)

Gedling Coal	$C_{100}\ H_{91.5}\ N_{0.5}\ O_{12.5}\ S_{0.5}$
Cresswell Coal	$C_{100}\ H_{88.8}\ N_{0.4}\ O_{8.6}\ S_{0.5}$
Cortonwood Silkstone Coal	$C_{100}\ H_{75.6}\ N_{0.2}\ O_{8.0}\ S_{0.4}$

Comparing the data from table 3.8 with that for the untreated coals, (Table 3.1), it is clear that the extracts are more hydrogen rich/less aromatic. The increase in the oxygen content of these soluble fractions is probably due to oxidation, after the solvent extraction process was complete. Comparing the data, obtained for each of the three coal extracts, it appears that as coal rank increases the aromaticity of the extracts also increases, (see the H/C ratios data Table 3.8).

3.3.2 INFRARED SPECTRA OF THF EXTRACTS

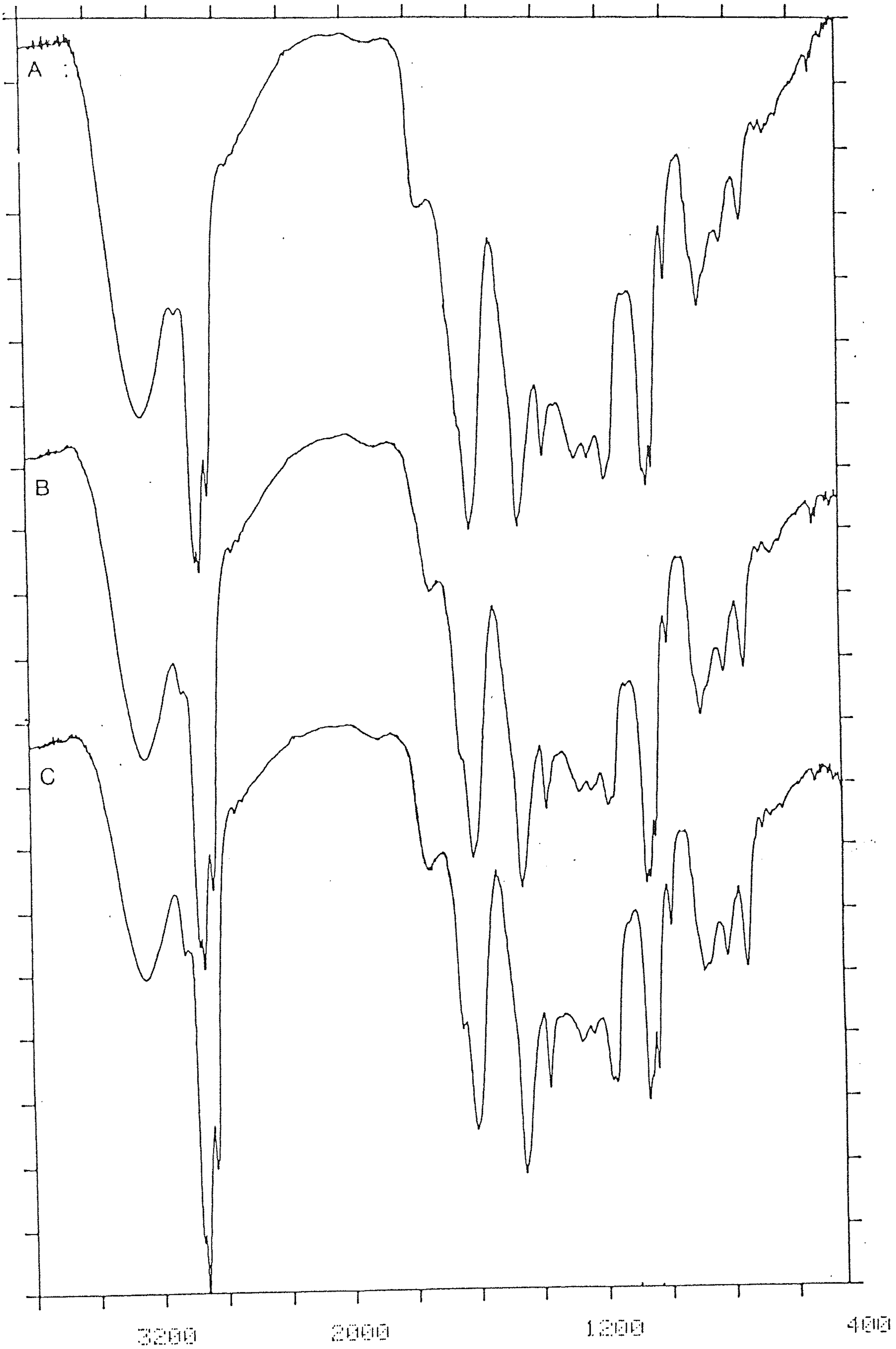
The infrared spectra of the 30 day THF extracts, (Fig. 3.7 A to C) shows the solvent soluble extracts to have a much greater aliphatic character than the whole coals, (Fig. 3.1 A to C), but the aromatic character of the three extracts does increase with increasing coal rank. A new band assigned to C-O stretching was observed for the THF soluble fractions, between 1100-1050cm^{-1}, this peak may be due to the retention of the solvent in the extract and/or to the formation of some oxidation product. As expected the three coal extracts showed reduction in the absorptions at 3300cm^{-1} and between 1300cm^{-1} and 1000cm^{-1} with increasing coal rank. This follows the trend seen for the unextracted coals, which was related to the oxygen content of the samples.

3.3.3 NMR RESULTS

The hydrogen distribution data for the 30 day THF soluble extracts, (Table 3.9), were obtained form the ^{1}H-NMR spectra shown in Fig. 3.8 A to C. The changes in the relative amounts of protons a to the aromatic rings and those further away, indicate that as the coal rank increases there is an increasing tendency towards smaller alkyl substituents on the aromatic ring in the soluble fractions. This observation supports the conclusions reached when examining the IR spectra of the whole coals, (section 3.2.1), which showed that the number of protons on the aliphatic chains tended toward 3 as the rank of the coal increased. i.e. the number of methyl substituents increased while the number of substituents of the type $-(CH_2)_n-$ decreased.

The fine structure in the ^{1}H-NMR spectra between 2-3ppm and at 4ppm is due to THF trapped in the extract after the majority of the solvent had been removed.

Fig.3.7 Infrared Spectra Of 30 Day THF Extracts.



A) Gedling Coal

B) Cresswell Coal

C) Cortonwood Silkstone Coal

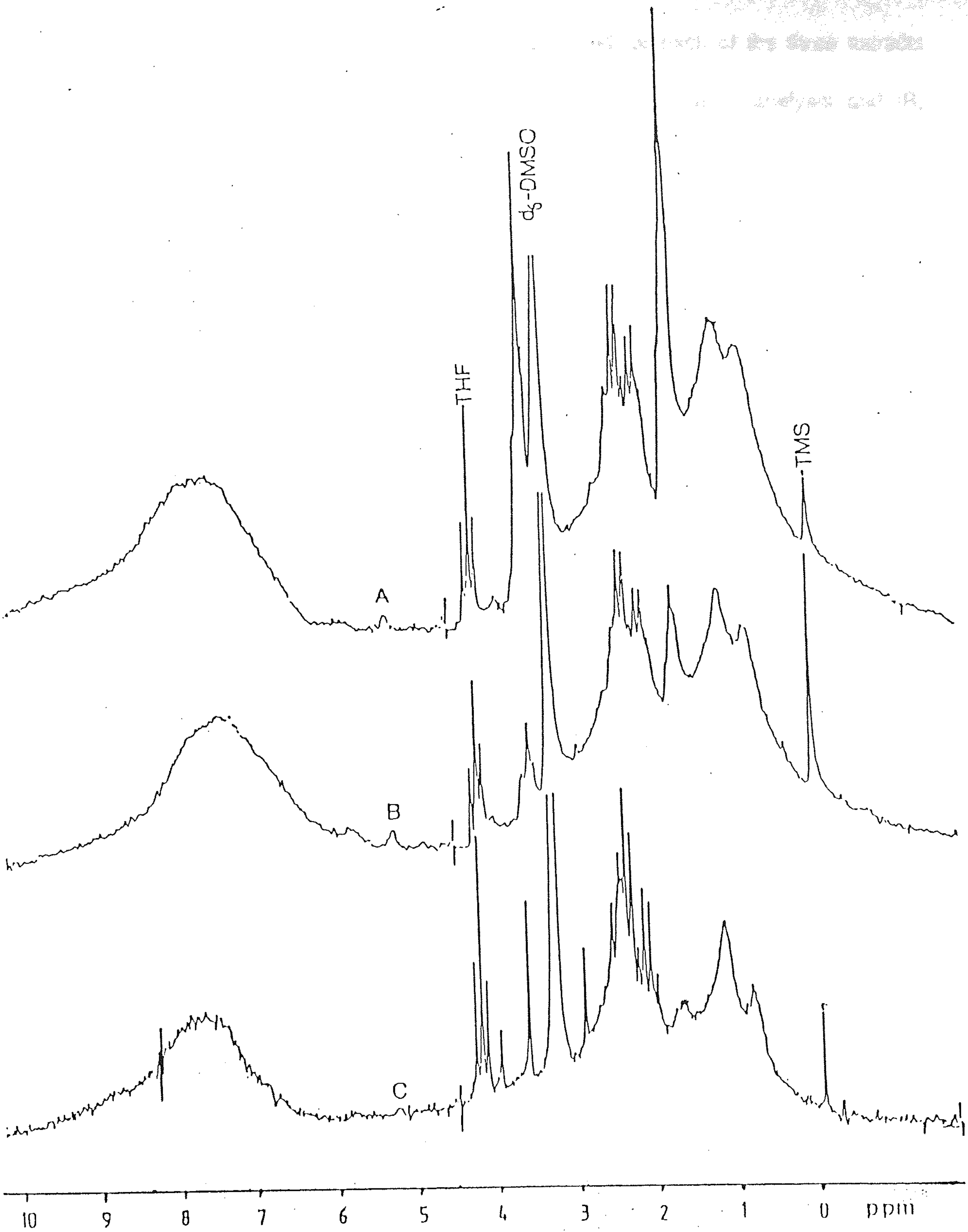


Fig.3.8 ^{1}H NMR Spectra Of THF Coal Extracts (30 Days).

A) Cortonwood Silkstone Coal

B) Cresswell Coal

C) Gedling Coal

The proportions of aromatic protons detected for each of the three extracts are very similar even though other results, particularly elemental analysis and IR, suggest that the aromaticity of the extract is increasing with increasing rank.

Table 3.9 The Hydrogen Distribution of the 30 Day THF Extracts

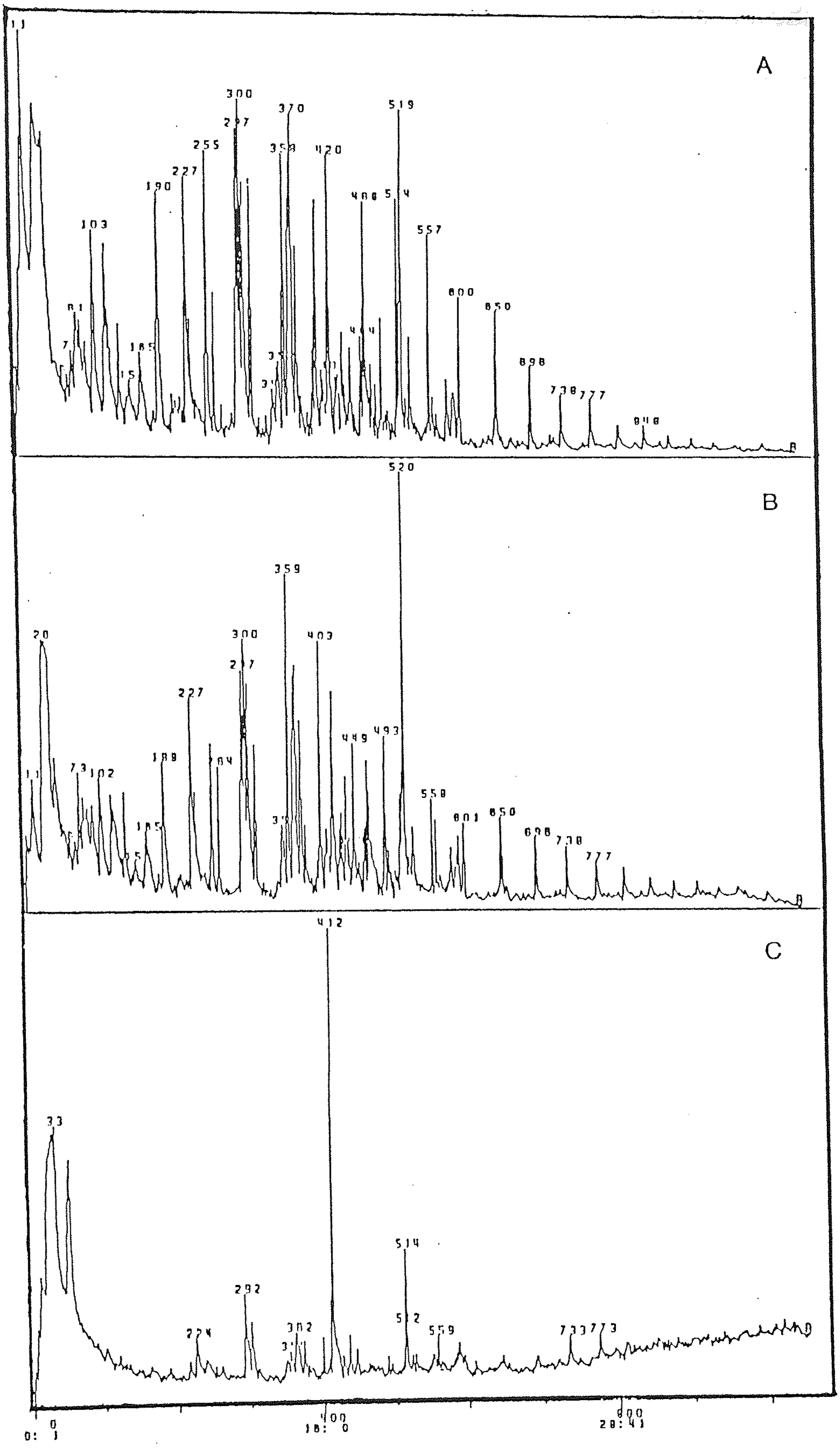
Hydrogen Type	**ppm Range**	**% Hydrogen Distribution**		
		Gedling	**Cresswell**	**Cortonwood Silkstone**
Aromatic & Phenolic hydrogen	5.0 -9.0	30.6	27.7	28.9
Ring joining hydrogens	3.4 - 5.0	7.1	3.8	8.4
Hydrogens a to aromatic rings	1.9 - 3.4	27.1	31.4	34.7
Hydrogens b to aromatic rings parafinic CH_2 and CH.	1.0 - 1.9	24.1	25.4	20.8
Hydrogens g or further from the ring system, parafinic CH_3	0.5 - 1.0	11.1	11.7	7.1

The pyridine soluble extracts failed to yield good NMR spectra, this was thought to be because the solutions were colloidal in the solvent d_5-pyridine. The colloidal nature of these extracts may also account for the very poor GC-MS data obtained from these fractions, (see section 3.3.4)

3.3.4 GC-MS RESULTS

The GC-MS chromatographs of the THF extracts, (24h extraction period) are shown in Fig. 3.9 A to C.

Fig.3.9 GC-MS TIC For THF Coal Extracts (24 h).



A) Cortonwood Silkstone Coal

B) Cresswell Coal

C) Gedling Coal

Between 40 and 80 compounds were identified for each extract, (see Table 3.10). Approximately 20% of the Gedling coal extract is made up of alkanes, this is a much smaller percentage than for the THF extracts of Cresswell and Cortonwood Silkstone coals which contain 43% and 38% alkanes respectively. The percentages of alkylbenzenes and alkylnaphthalenes in the three extracts show the same rank trend, but the difference between the three extracts is not as marked as with the alkanes.

Table 3.10 GC-MS Results obtained for the 24h THF extract

Scan No	Peak Assignment	Gedling	Cresswell	Cortonwood Silkstone	Retention Time M:S
11	1,3-dimethylbenzene	-	2.37	2.3	3:41
27	1,2-dimethylbenzene	-	2.2	2.0	4:10
42	alkane	-	1.24	1.7	4:40
60	propylcyclohexane	-	-	0.5	5:14
68	alkane	-	0.78	0.6	5:30
73	n-alkane C_9	-	1.74	-	5:39
74	propylbenzene	-	-	0.6	5:41
81	ethylmethylbenzene	-	2.13	2.3	5:52
101	ethylmethylbenzene	1.48	1.19	1.9	6:30
118	n-alkane	-	2.14	2.3	7:05
119	ethylmethylbenzene	1.11	-	-	7:06
121	isopropylbenzene	-	1.42	1.7	7:11
136	n-alkane C_{10}	-	2.11	1.9	7:39

Table 3.10 Cont... GC-MS Results obtained for the 24h THF extract

Scan No	Peak Assignment	Gedling	Cresswell	Cortonwood Silkstone	Retention Time M:S
150	alkylbenzene $C_{10}H_{14}$	-	0.42	0.4	8:06
165	alkylbenzene $C_{10}H_{14}$	-	1.0	0.8	8:34
143	alkylbenzene $C_{10}H_{14}$	-	-	0.4	8:43
181	alkylbenzene $C_{10}H_{14}$	-	0.37	0.2	9:07
189	alkyl benzene	0.93	-	-	9:19
190	n-alkane C_{11}	-	2.37	2.3	9:20
203	alkylbenzene $C_{11}H_{16}$	-	0.16	-	9:46
208	cycloalkane	-	0.28	0.4	9:56
211	alkylbenzene $C_{10}H_{14}$	-	0.52	0.3	10:02
216	furan	2.14	0.4	-	10:10
224	alkylbenzene $C_{11}H_{16}$	-	-	0.6	10:26
224	naphthalene	7.30	2.37	2.3	10:36
232	alkane	-	0.76	1.4	10:41
240	?	2.80	-	0.4	10:56
246	?	1.56	-		11:08
255	n-alkane C_{12}	-	2.37	2.3	11:25
261	?	0.56	-	-	11:36
264	alkane	-	2.37	2.2	11:42
274	$C_{12}H_{24}$	-	-	0.4	12:01
280	?	1.41	-	-	12:12
292	methylnaphthalene	8.21	2.37	2.2	12:35
296	alkane	1.09	2.37	2.3	12:43

Table 3.10 Cont... GC-MS Results obtained for the 24h THF extract

Scan No	Peak Assignment	Gedling	Cresswell	Cortonwood Silkstone	Retention Time M:S
300	methylnaphthalene	1.67	2.37	2.0	12:50
314	n-alkane C_{13}	-	2.37	2.3	13:17
343	acenaphthalene	-	-	1.2	14:12
350	dimethylnaphthalene	1.67	1.10	0.2	14:25
350	alkane	1.30	-	0.9	14:26
352	dimethylnaphthalene	-	1.1	1.0	14:29
358	dimethylnaphthalene	-	2.37	2.2	14:41
362	dimethylnaphthalene	3.91	2.37	2.3	14:48
372	dimethylnaphthalene	2.67	2.37	-	15:07
379	dimethylnaphthalene	0.81	2.37	1.0	15:20
382	dimethylnaphthalene	-	1.37	0.7	15:26
391	cycloalkane	-	-	0.3	15:43
399	?	-	-	1.3	15:59
399	n-alkane C_{15}	2.36	2.37	2.3	15:58
407	alkylnaphthalene $C_{13}H_{14}$	1.68	1.46	1.5	16:14
412	phenoxyalkyl benzene	8.54	-	-	16:23
410	trimethylnaphthalene	-	-	1.5	16:20
413	$C_{13}H_{12}$	-	2.15	-	16:26
416	?	1.44	-	-	16:31
420	trimethylnaphthalene	0.77	2.37	1.1	16:38
426	trimethylnaphthalene	1.67	0.89	0.5	16:50

Table 3.10 Cont... GC-MS Results obtained for the 24h THF extract

Scan No	Peak Assignment	Gedling	Cresswell	Cortonwood Silkstone	Retention Time M:S
435	trimethylnaphthalene	2.48	1.73	1.7	17:07
455	trimethylnaphthalene	2.62	1.25	0.3	17:23
449	trimethylnaphthalene	-	2.10	1.3	17:34
455	?	-	-	0.3	17:45
465	?	-	1.68	2.2	18:02
468	n-alkane C_{16}	-	2.24	2.3	18:11
471	?	-	2.37	1.1	18:16
475	?	-	0.79	0.3	18:23
478	?	-	-	1.0	18:29
484	?	-	-	0.7	18:40
489	alkane	0.95	2.36	1.7	18:50
494	tetramethylnaphthalene	1.16	-	-	18.50
512	tetramethylnaphthalene	4.13	-	-	19:36
498	$C_{14}H_{16}O$	-	0.69	0.3	19:07
507	pristane	-	0.31	2.3	19:30
514	n-alkane C_{17}	7.95	1.70	2.0	19:37
520	alkane	-	2.37	-	19:49
523	?	0.66	-	-	19:54
525	methylbenzophenone	-	0.96	0.9	19:58
528	phenanthrene	3.80	2.05	2.3	20:04
553	n-alkane C_{18} + ?	1.26	1.70	2.3	20:51
559	phytane	1.40	1.18	0.5	21:03

Table 3.10 Cont... GC-MS Results obtained for the 24h THF extract

Scan No	Peak Assignment	Gedling	Cresswell	Cortonwood Silkstone	Retention Time M:S
568	?	-	0.35	0.4	21:20
582	methylphenanthrene	-	0.74	0.9	21:45
587	dimethylphenanthrene	1.89	1.42	-	21:56
600	n-alkane C_{19}	-	1.51	2.0	22:21
650	n-alkane C_{20}	-	1.25	1.7	23:56
690	n-alkane C_{21}	1.09	1.26	1.2	25:12
733	n-alkane C_{22}	1.87	0.96	0.8	26:33
773	n-alkane C_{23}	2.24	0.8	0.6	27:58
814	n-alkane C_{24}	-	0.5	0.3	29:08
850	n-alkane C_{25}	-	0.3	0.3	30:13
881	n-alkane C_{26}	-	0.3	0.2	31:15
912	n-alkane C_{27}	-	0.32	0.2	32:14
941	n-alkane C_{28}	-	0.2	-	33:13
968	n-alkane C_{29}	-	0.1	-	34:12
1008	n-alkane C_{30}	-	0.1	-	35:11

(? = unidentified compound)

The TIC chromatographs obtained from the 24h THF extract of Gedling coal , (Fig. 3.9C) is obviously very different to that produced from the other two coals,(Fig. 3.9 A and B). The 30 day THF soluble extracts however, all look very similar, (see the IR, NMR, and GPC results, section 3.3.2, 3.3.3, and 3.3.5 respectively). This suggests that there is little difference in the types of compounds trapped in Gedlig coal, and those held in the matrix of the Cresswell and Cortonwood Silkstone coal samples. One possible explanation for the difference in the GC-MS chromatographs of the 24h THF extracts is that the physical structure of Gedling coal prevents the trapped material from escaping rapidly, during the early stages of solvent extraction.

The GC-MS data obtained using the chloroform soluble extracts, showed that these fractions contained fewer compounds than were present in the THF soluble samples, (also all the compounds identified in the chloroform extracts were also found in the THF soluble fractions). This is in good agreement with the arguments presented in section 2.2.1, (the electron-donor-acceptor theory of solvent extraction). The pyridine extracts could not be examined by the GC-MS method as very little of the sample passed through the column, into the mass spectrometer, (this was thought to be due to the colloidal nature of the pyridine soluble fraction).

GC-MS data from the 30 day THF extracts could not be obtained due to the large proportion of material which would not pass through the capillary column, either because of too great a polarity or too high a molecular weight.

3.3.5 GPC RESULTS FOR 30 DAY THF EXTRACTS

Gel permeation chromatography was carried out on very dilute THF solutions (<0.5% by wt) of the 30 day THF soluble extracts. The low concentrations were found necessary in order to prevent aggregation of the solute, which would cause abnormally high polystyrene equivalent molecular weights to be observed. Two types of detector were tried, a refractive index detector (RI), and a UV detector, (set to monitor the absorption at 254nm). It was found that the UV detector although more sensitive weighted the result in favor of higher molecular weight values, and it failed to detect the lower molecular weight aliphatic portions of the extracts.

The results obtained from the analysis of the chromatographs are shown in Fig. 3.10 and in Table 3.11.

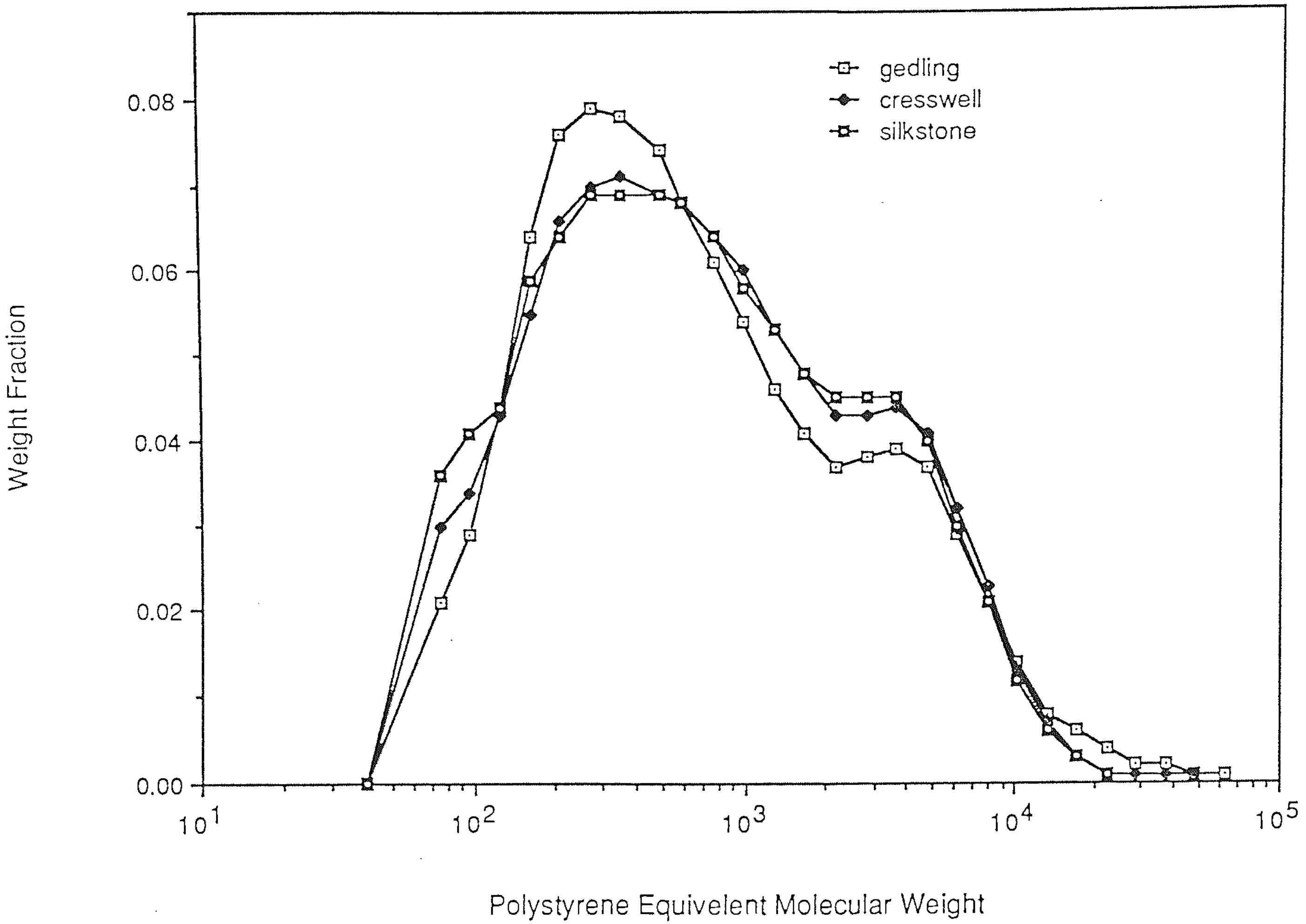
Table 3.11 GPC Results For 30 Day THF Extracts

Coal	M_w	M_n	PD
Gedling	2360	360	6.52
Cresswell	2250	360	6.23
Cortonwood Silkstone	1700	340	4.97

Note the average molecular weights quoted are polystyrene equivalent, not absolute values.

It can be seen from the weight averaged distribution curves (Fig 3.10), that all three extracts have a bimodel molecular weight distribution, and in general are very similar. The main difference in the plots being the larger amount of high molecular weight material detected for Gedling coal, when compared with the two higher ranked coals.

Fig.3.10 Weight Fraction Molecular Weight Distributions Of 30 Day THF Extracts.



3.4 ANALYSIS OF THE THF INSOLUBLE FRACTIONS

3.4.1 ELEMENTAL ANALYSIS RESULTS

Elemental analysis data for the 30 day THF extracted-insoluble fractions is given in Table 3.12.

Table 3.12 Elemental Analysis Results Of The '30 Day' THF Solvent Extracted Insoluble Fractions

Coal	Elemental Analysis (% by weight)					
	C	H	O	N	$S_{(T)}$	H/C
Gedling	77.9 (.5)	5.2 (.1)	11.8 (.6)	1.1 (.1)	2.0 (.5)	0.80 (.02)
Cresswell	81.3 (.6)	5.2 (.2)	8.3 (.4)	1.3 (.2)	2.0 (.5)	0.76 (.04)
Cortonwood Silkstone	83.9 (.9)	4.6 (.8)	5.9 (1.2)	1.6 (.9)	2.0 (1.0)	0.65 (.02)

Gedling Coal	$C_{100}\ H_{79.9}\ N_{1.3}\ O_{11.4}\ S$
Cresswell Coal	$C_{100}\ H_{76.1}\ N_{1.4}\ O_{7.6}\ S_{0.9}$
Cortonwood Silkstone Coal	$C_{100}\ H_{65.2}\ N_{1.6}\ O_{5.3}\ S_{0.9}$

Comparing these results with those for the untreated coals, (Table 3.1), it can be seen that there are no significant changes, (within experimental error), in the elemental compositions of the two lower ranked coals, during solvent extraction. The data for Cortonwood Silkstone coal, however, indicates that during extraction the insoluble fraction becomes more aromatic, (i.e. the H/C ratio for the untreated and extracted-insoluble fractions are 0.75 and 0.65 respectively).

This change in the H/C ratio is consistent with a hydrogen rich fraction being removed from the coal matrix, and supports the conclusions made in the study of the soluble fractions, (see section 3.3). The failure of the two lower ranked coals to show similar reduction in H/C ratios, during solvent extraction, is due mainly to the large errors produced when analysing small samples, (2 to 3mg) of a highly heterogeneous material, (i.e. the errors produced in the analysis are of the same order of magnitude as the changes being looked for).

3.4.2 INFRARED ANALYSIS OF THE SOLVENT INSOLUBLE COAL FRACTIONS

The insoluble residue of Cortonwood Silkstone coal after 7 days extraction using three solvents (pyridine, THF, and chloroform) are shown in Fig. 3.11 A to C. Comparing the three spectra with each other and with unextracted Cortonwood Silkstone coal (Fig. 3.1C), it can be seen that, although a hydrogen rich fraction has been removed the resulting insoluble fractions are little changed from the untreated coals.

The same observation was also noted for the solvent insoluble fractions of Gedling and Cresswell coals, and for the '30 day' THF extracted insoluble samples of the three coals, i.e. they all appeared similar to the respective unextracted coals.

3.4.3 NMR RESULT FOR THE INSOLUBLE RESIDUES

The ^{13}C-CPMAS-NMR spectra of the '30 day' THF extracted insoluble residues are shown in Fig 3.12 A to C. The f_a values calculated from the peak areas were 0.64, 0.78, and 0.70, for Gedling, Cresswell, and Cortonwood Silkstone Coals respectively. The aromaticities of the insoluble fractions have increased slightly compared with f_a values reported for the untreated coals, (section 3.2.2), as would be expected when a hydrogen rich fraction is removed.

Fig.3.11 IR Spectra Of CortonWood Silkstone Coal (Insoluble Fractions).

A) pyridine insoluble fraction B) THF Insoluble fraction C) $CHCl_3$ insoluble fraction

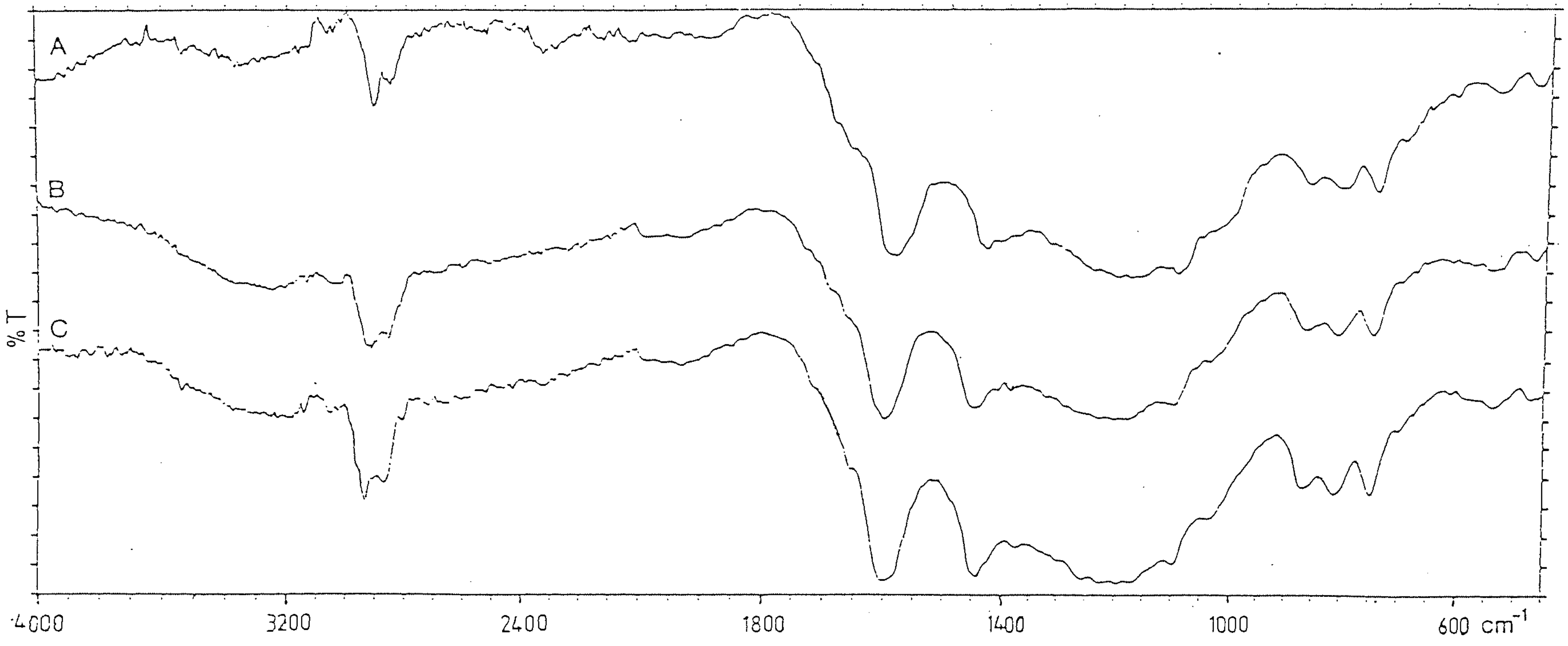
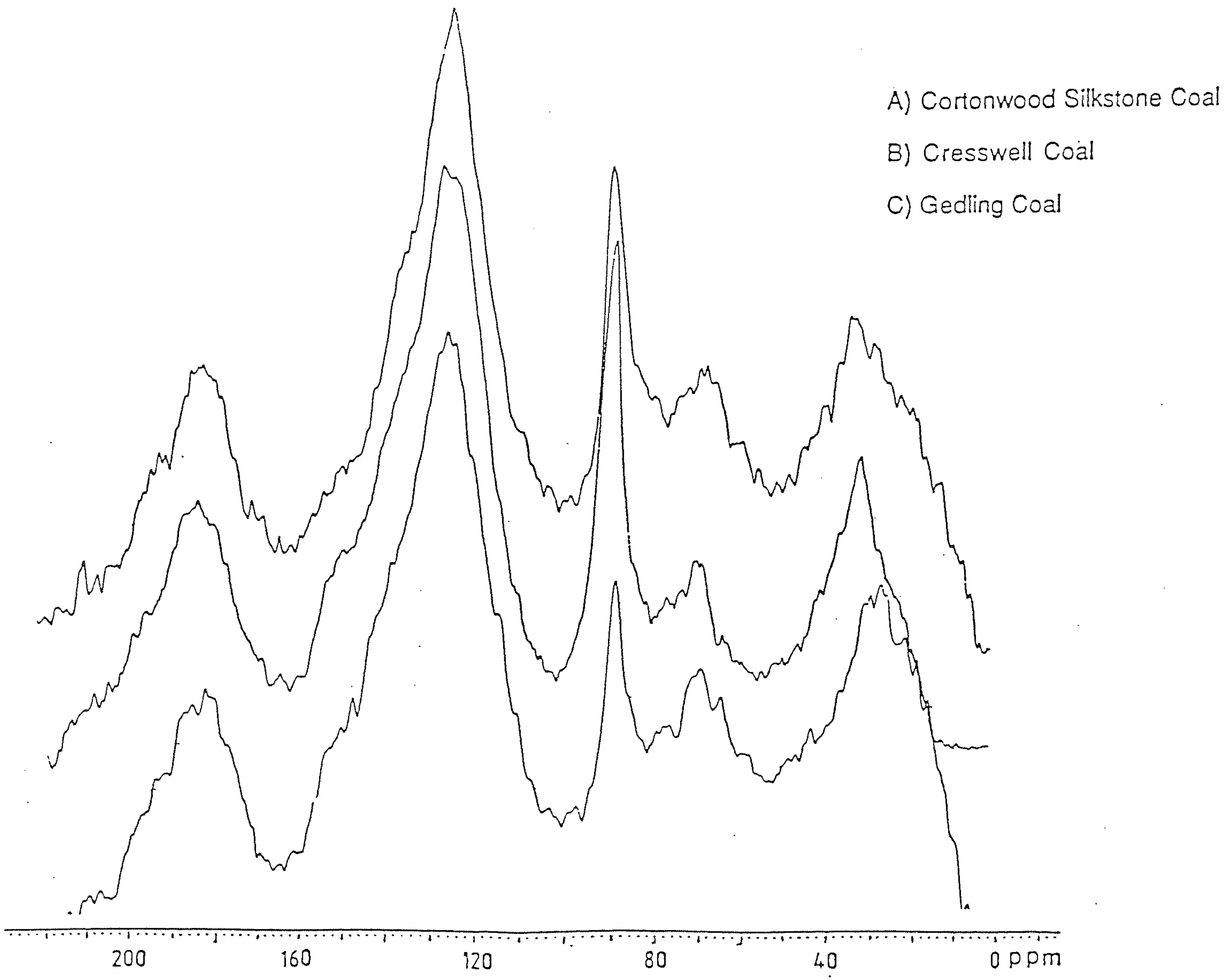


Fig.3.12 ^{13}C-CPMAS-NMR Spectra OF THF Extracted (30 Days) Coals (Insoluble Fractions).



The rank trend in aromaticity values noted for the untreated coals however appears to be lost. This may be explained by the asymmetry of the spinning side bands in the NMR spectra, which makes calculating the aliphatic/aromatic peak area ratios difficult, (this is particularly true for the Cresswell coal insoluble fraction, see Fig. 3.12 B).

3.4.4 GAS ADSORPTION DATA ON THE INSOLUBLE COAL FRACTIONS

The gas adsorption data for the '30 day' THF extracted insoluble resides (Table 3.13), shows that the surface area of all three insoluble fractions has increased during solvent extraction, (cf Table3.5). These results suggest that the voids in the coal network, left by the removal of the mobile phase, are held open by cross-links, (if this were not the case then the pores would collapse after extraction, and we would therefore expect to see an unchanged or reduced surface area in the three coals). There appears to be no correlation between the increase in surface area and the amount of material extracted from the coals, (see Table 3.6 and Table 3.13).

Table 3.13 Gas Adsorption Results For '30 Day' THF Extracted Insoluble Coal Fractions

Coal	CO_2 Adsorption P - D		N_2 Adsorption BET		Micropore area
	V_m	m^2g^{-1}	V_m	m^2g^{-1}	m^2g^{-1}
Gedling	18.19	123.73	6.02	26.20	97.53
Cresswell	11.88	80.81	8.06	35.11	45.70
Cortonwood Silkstone	19.95	135.66	6.49	28.3	107.36

A comparison of the micropore surface areas of the unextracted coals, (Table 3.5) and the THF extracted insoluble residues, (Table 3.13), suggests that Gedling coal has a greater proportion of its mobile phase located in the micropores than either of the two higher ranked coals. I.E. after extraction the micropore surface areas have increased by 92.8, 23.3, and 83.0m^2g^{-1}, for Gedling, Cresswell, and Cortonwood Silkstone coals respectively. Since the material from the micropores will be more difficult to remove by solvent extraction these results can be used to support the hypothesis proposed in section 3.3.4, which tries to explain the anomalous extraction behaviour of Gedling coal in terms of its physical structure rather than a chemical structural feature.

3.5 DISCUSSION

The three British bituminous coals, we selected for study, show all the expected rank trends, such as their solubilities in specific and non-specific solvents and the changes in aromaticity with rank. It is therefore reasonable, (based on this initial characterisation), to assume that Gedling, Cresswell, and Cortonwood Silkstone coals are good representatives of British bituminous coals, and that any conclusions arrived at from studying these samples can be extrapolated to the whole class of British bituminous coals.

As the rank of the untreated coals increases the surface area available for reaction within the coal matrix decreases. This change in physical structure will effect the apparent chemical reactivity of our coals by preventing reagents reaching any active site. Thus it is important to take into account the physical structure of the coals unless the reaction conditions are chosen so as to remove any mass transport dependence, (i.e. by using a phase transfer catalyst).

Comparing the solvent soluble extracts; we found that their aromaticities were directly related to the rank of the coals, but otherwise they were very similar, being hydrogen rich when compared to the insoluble fractions. The only time the solvent soluble extracts of the three coals appeared to behave differently from each other was when we examined the 24h THF extract of Gedling coal and compared it with the extracts from the two higher ranked coals. In this case it was thought the differences in compound distribution was due to a physical structural change, which prevented the easy removal of trapped compounds during the early stages of solvent extraction, in Gedling coal.

After solvent extraction by THF, which removed some 10%-16% of the coals, the insoluble residues appeared little changed, with only a slight increase in the aromaticities being noted (this may not be significant due to errors in calculating the f_a values from NMR data). After extraction the surface area of the insoluble coal fractions had increased, relative to the unextracted coals, suggesting that the pores of the coals are held open by some form of cross-linking.

In summary; The three coals selected for study appear to be representative of British bituminous coals.

The solvent soluble extracts appear to be made up of varying proportions of broadly similar compounds which fill the pores of the coal matrix to differing extents depending on rank.

After the mobile phase had been removed from the three coals, (i.e. by solvent extraction), the insoluble cores appeared largely unchanged. The porosity of this core material however did increase, which suggests that some form of cross-linking was holding the pores open. The type of cross links involve, (hydrogen bonding and/or covalent bonding is investigated further in chapter 4.

CHAPTER 4.

O-METHYLATION

4.1 INTRODUCTION

In chapter one, coal was described as being a highly cross-linked macromolecular solid, holding a complex mixture of organic compounds trapped within the porous three dimensional matrix. This matrix is held rigid by a combination of covalent cross links, hydrogen bonds and charge transfer interactions.

In reactions where covalent bonds are broken (eg. during oxidative degradation), changes in the secondary structure of the coal also occur. In order therefore to selectively study the weaker interactions, reactions must be selected which do not effect any covalent cross-links in the coals.

Hydrogen bonding occurs between hydrogen atoms attached to an electronegative atom and another electronegative atom or electron rich centre. The major electronegative heteroatom in the organic matter of British bituminous coals is oxygen, and since little or no carbonyl and carboxylic acid groups are to be found in the coals we selected for study, it means that most of the strong hydrogen bonds are due to interactions with phenolic sites.

There is a lot of evidence in the literature which suggests that, most of the hydroxyl groups in a coal are involved in hydrogen bonding, and that these weak interactions are to a large extent intermolecular in nature(115, 116, 117, 118). It has also been shown by many workers(119, 120, 121), that the disruption of these intermolecular forces, by capping of the hydroxyl functions using reactions such as O-methylation, O-silylation and acetylation, can be used to bring about an increase in the extractability of the coals.

Silylation is used widely, as a comparatively rapid method for the removal of hydrogen bonding(122, 123, 124). The effect of this process is to convert the hydroxyl groups to silyl ethers. Complications arise however because pyridine is often required as a solvent to facilitate the transport of the reactants into the coal, the problem then is to distinguish between the effects of the solvent (which is difficult to remove completely) and the effect of 'capping' the phenolic groups. The silyl ethers formed during the reaction also hydrolyze easily making quantitative results difficult to obtain.

Acetylation, has been used to derivatise and quantitatively determine the hydroxyl content of coals(125), but for this reaction to be selective low temperatures are required, this results in acetylation being a very slow method. Pyridine is again required in the acetylation reaction, so that as with silylation it is difficult to separate the effects of the solvent from those of the reaction.

Yohe and Blodgett(126) and Van Krevelen(1) alkylated coals using dimethyl sulphate and diazomethane respectively, it was however concluded that the O–methylation reactions were only taking place at the surface of the coal particals, where the hydroxyl groups are exposed. More recently Liotta(26,127) has reported a method for the rapid and selective O-alkylation of the weakly acidic phenolic and carboxylic acid groups in bituminous and subbituminous coals using phase transfer catalysts (PTC). This PTC reaction has been further studied by other workers(128, 129, 130, 131, 132). To date the results have shown that tetrabutylammonium hydroxide ($Bu_4N^+OH^-$) is a good PTC for the O-alkylation of hydroxyl groups, this catalyst not only swells the coal as expected(133) but also promotes the formation of the ethers and esters, (some supporting evidence for the catalytic effect of $Bu_4N^+OH^-$ comes from the observation that a very similar quaternary ammonium salt, tetraethylammonium hydroxide, swells coals but does not promote O–alkylation).

It has be found that, unlike the other O-alkylation techniques, the PTC O–methylation reaction rate is not limited by mass transport. The first step in the reaction is a rapid proton abstraction by the PTC to produce the phenoxide or carboxylate (steps 1 and 3 below). The second, rate determining step, is a nucleophilic displacement by the chosen alkyl halide (steps 2 and 4).

$$\text{Coal-Ar-OH} + \text{Bu}_4\text{N}^+\text{OH}^- \longrightarrow \text{Coal-Ar-O}^{-+}\text{NBu}_4 + \text{H}_2\text{O} \qquad (1)$$

$$\text{Coal-Ar-O}^{-+}\text{NBu}_4 + \text{RX} \longrightarrow \text{Coal-Ar-OR} + \text{Bu}_4\text{NX} \qquad (2)$$

$$\text{Coal-CO}_2\text{H} + \text{Bu}_4\text{N}^+\text{OH}^- \longrightarrow \text{Coal-COO}^{-+}\text{NBu}_4 + \text{H}_2\text{O} \qquad (3)$$

$$\text{Coal-COO}^{-+}\text{NBu}_4 + \text{RX} \longrightarrow \text{Coal-COOR} + \text{Bu}_4\text{NX} \qquad (4)$$

Steric crowding and the electronic environment about the OH groups, have effects which suggest a S_N2 type reaction is occurring. Model compound studies however have shown that some crowding around the hydroxyl group can increase o-alkylation reaction rates(128) (eg. small ortho substituents such as methyl groups), this is assumed to be due to a weakening of the ionic interaction between the phenoxide and the onium cation, if however steric crowding is very high the rate of O-alkylation is reduced, as expected.

In a competitive alkylation study(128) between cyclohexanol and phenol, it was found that the phenolic hydroxyl group reacted much faster. This strongly suggests that the rate limiting step for the O-alkylation of alcohols is the proton abstraction step, therefore when this reaction is carried out on coals it is expected that only the most acidic functions will react i.e. phenols and carboxylic acids.

Liotta(26) stated that PTC O-methylation was selective and quantitative, for the two coals he investigated, (Illinois No.6 and Rawhide coals) and although some N–alkylation occurred, this was relatively insignificant accounting for only 1 or 2% of the total methyl groups added. In contrast Martin and co-workers(129), concluded that the reaction does not go to completion. They found that just over 70% of the hydroxyl functions had reacted in a supercritical gas extract of an 82%C (dmmf) British bituminous coal.

High ranked coals, between 86% and 89%C (dmmf), with low phenolic content, were studied by Mallya and Stock(132). They noted that O-methylation only had a slight effect on the extractability of these coals. O-butylation on the other hand significantly increased the yield of coal extract of the six coals used. Since PTC O–methylation and O-butylation are equally effective in removing hydrogen bonding in coal, they concluded that the difference in extractability must have been due to other interactions being weakened. It was suggested that the bulky nature of the butyl group reduced the π-π interactions between the laminates of the high rank coal, forcing them apart. Evidence for such weak secondary bonding in coals has been put forward by Pollock and Yen(134) and Radonovich and Eyring(135). In low rank coals the lack of short range order in the aromatic systems means that there will be fewer π-π interactions.

Because we wished to study the effects on hydrogen bonding alone, (ie as far as possible retain any π-π interactions), we have O–methylated the three British bituminous coals using tetrabutylammonium hydroxide as the PTC and methyliodide as the alkylating agent, (this had the added advantage that it simplifies analysis of the coal derivatives).

4.2 SOLVENT EXTRACTION RESULTS

The percentage of material extracted from the three O–methylated coals is given in Table 4.1. (cf. results obtained for the untreated coals, Table 3.6.)

Table 4.1 Solvent Extractability Results For O-Methylated Coals

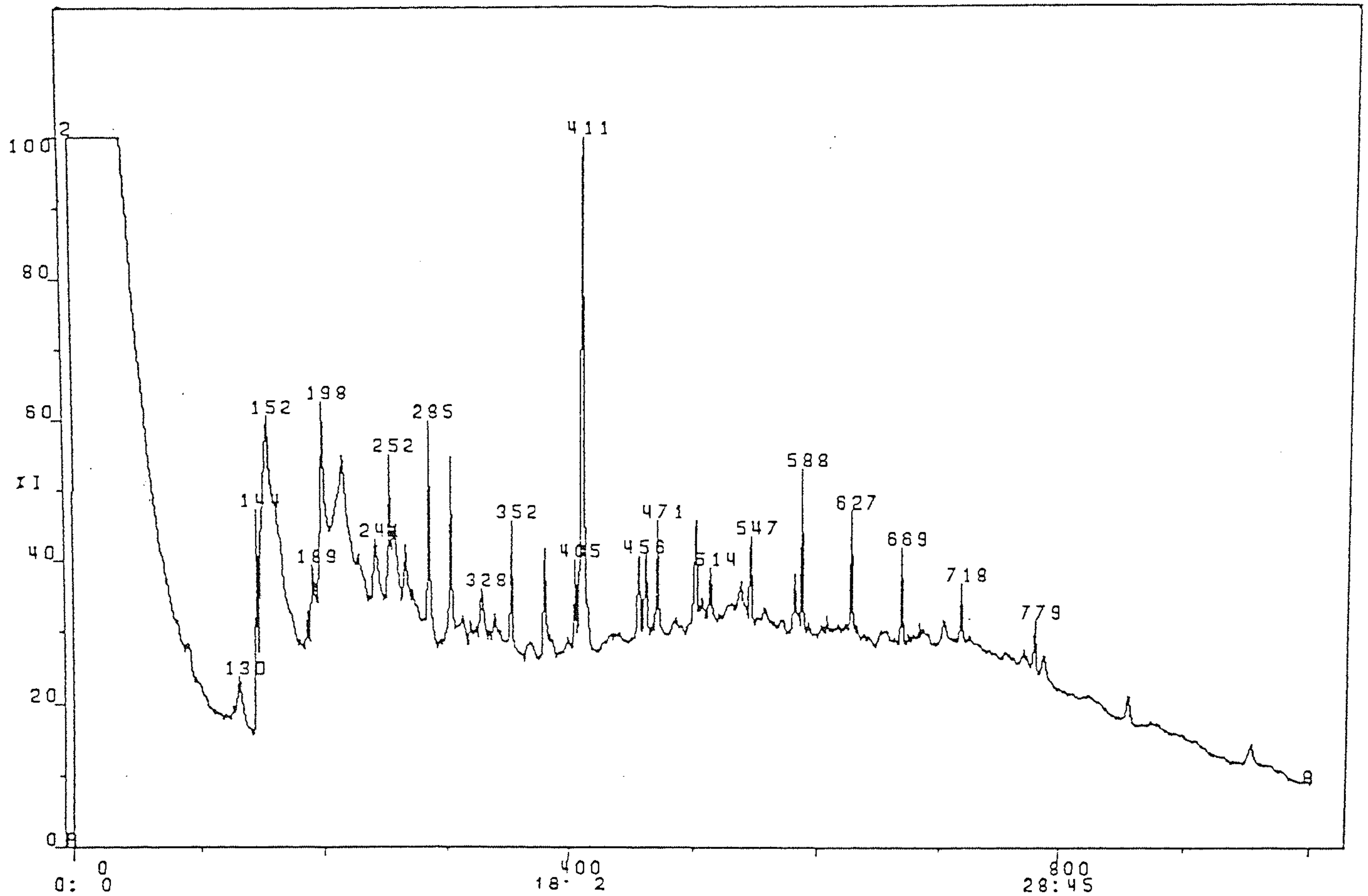
Coal	**Solvent Extractability (%)**		
	Chloroform	**THF**	**Pyridine**
Gedling	25	23	27
Cresswell	25	27	40
Cortonwood Silkstone	10	10	29

The solvent extractability results, clearly indicate that there is a significant increase in the amount of material removed from the polymer-like matrix, (over the same extraction period, 7 days), after O-methylation (compare the data in Table 4.1 with the data in Table 3.6). As the rank of the coal increases however the effectiveness of the O–methylation reaction in bringing about an increase in solubility is reduced. If the phenolic content of the three coals was directly related to the oxygen content, it would be expected that Gedling coal would show the largest solubility increase, but in fact Cresswell coal shows the largest change in solubility. This may be taken to indicate that (1) Cresswell coal contains more phenolic groups available to the reagents than either Gedling or Cortonwood Silkstone coals, and/or (2) that the phenols which are present in Cresswell coal contribute more to the hydrogen bonding than in the other two coals. (Evidence in support of this hypothesis has come from workers at Birmingham University(136), they showed that 88% of the total organic oxygen in Cresswell coal was in the form of hydroxyl groups, but only 62% and 38% for Gedling and Cortonwood Silkstone coals respectively.)

An alternative reaction sequence to that of PTC O-methylation, followed by solvent extraction, was tried in order to distinguish between the rate at which the mobile phase was being extracted from the coal matrix, and the total amount of material finally extracted: The coals were first extracted in THF for 30 days in order to remove as much as possible of the soluble material, the insoluble fractions were then O-methylated, and extracted for a further two weeks in THF. It was found that after the two week extraction period, only a small amount of the O–methylated coals had been solubilised (between 2% and 4% by weight), part of this soluble fraction being the PTC which had been trapped in the coal matrix. The remainder of the THF soluble material appeared very similar to the 30 day THF soluble fractions, (as determined by IR, GPC, and GC-MS). These results indicate that O-methylation increases the rate of extraction of the mobile phase from the coal matrix, rather than producing significant changes in the total amount of material extracted from the coals when hydrogen bonding is disrupted.

The failure to remove the PTC from the coal after O-methylation, can and does, result in difficulties in characterising the fractions, see fig 4.1 (GC-MS TIC of the O–methylated $CHCl_3$ soluble coal fraction of Gedling Coal). The high background level observed in this chromatograph is due to the tetrabutylammonium salt, and makes identification of compounds which are present in low concentrations only, very difficult, (other workers for example Hagarman and Chambers(137) have reported similar difficulties). One possible explanation for the difficulty in removing the PTC has been suggested by Liotta(127) who indicated that the retention of the tetrabutylammonium salt in the coal after washing may be due to the formation of a 1:1 adduct of the onium cation with aromatic centres.

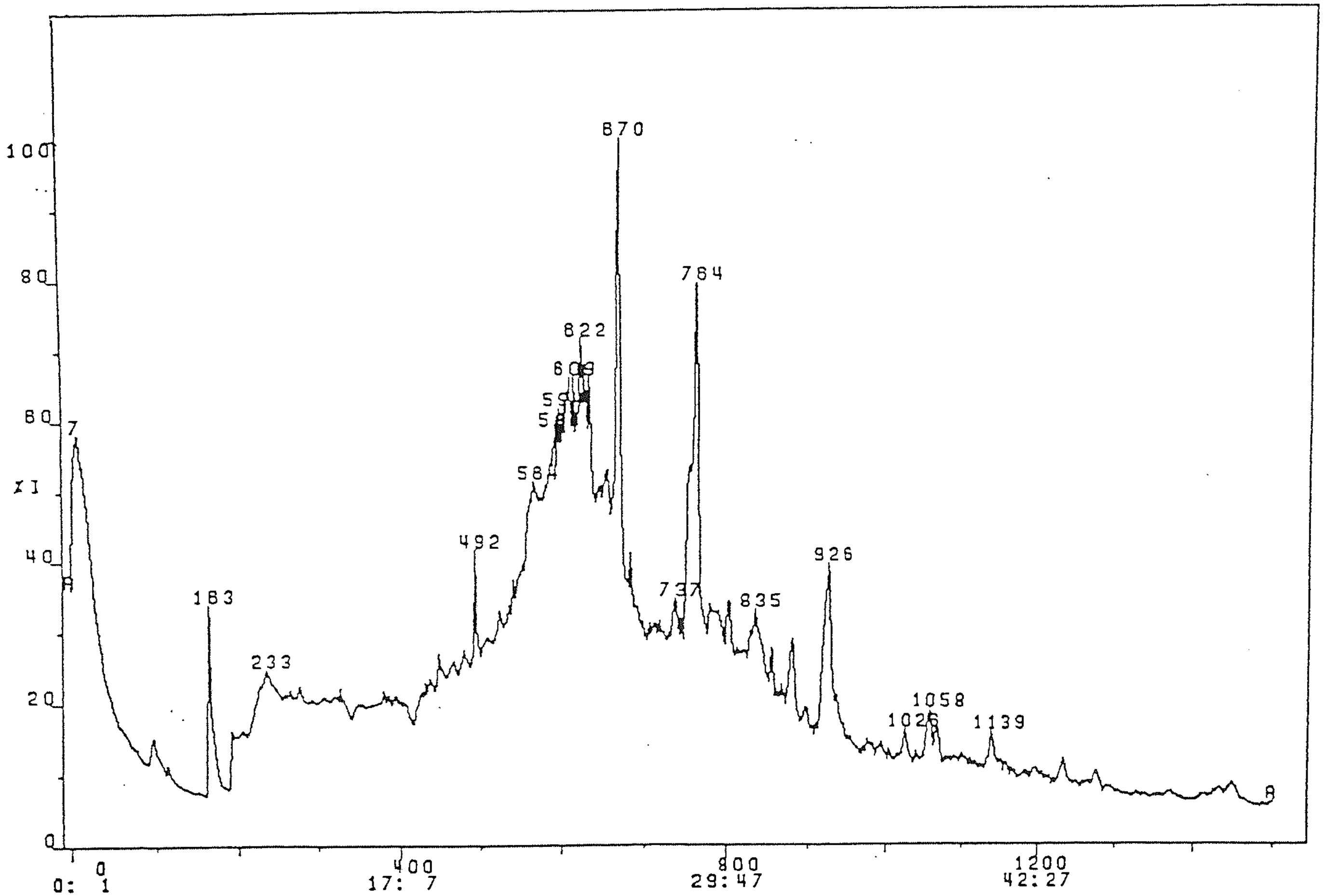
Fig 4.1 GC-MS TIC Of O-Methylated Gedling Coal Chloroform Soluble Sample.



Comparing the GC-MS chromatograph Fig. 4.1, ($CHCl_3$ extract of O-methylated Gedling coal) with that of Fig. 3.3.2 C (the THF extracts of the untreated coal), it is clear that a significant change has occurred. The distribution of compounds identified in the extracts of Gedling coal before and after O-methylation are very different, after O-methylation it ressembles the compound distribution of the two higher ranked coals before O-methylation. This observation supports the hypothesis put forward in chapter 3, which tried to explain the anomalous behaviour of the 24h THF solvent soluble extract of untreated Gedling coal, by suggesting that the mobile phase in Gedling coal is located largely in the micropores, so that the rapid release of the trapped organic matter is impaired. After O-methylation removal of the mobile phase is faster, because there are fewer cross-links to hold the matrix ridged, (i.e. the physical differences between the three coals is no longer seen).

Blank experiments have been carried out to determine the effect of the PTC alone on the three coals. These blanks showed that there was no significant increase in the solubilities of the coals when the O-methylation procedure was followed in the absence of the alkylating agent, however if the solution was filtered before acidification, a water soluble extract was obtained. This fraction could then be precipitated by the addition of a dilute acid and was found to be insoluble in a sodium hydroxide solution, or polar organic solvents such as THF. The water soluble PTC/coal extracts were highly susceptible to air oxidation. The GC-MS TIC chromatograph which resulted from the examination of the chloroform extract of a methanol insoluble PTC treated coal (Fig. 4.2), shows a very different TIC from other extracts.

Fig 4.2 GC-MS TIC Of PTC Treated Cresswell Coal Methanol insoluble, Chloroform Soluble Sample.



It was found to contain a number of compounds of quite high molecular weight, (upto 430amu), but we were not able to identify any of the material from their mass spectra. The IR spectrum of this fraction (fig. 4.3) shows the extract to be more aromatic in nature with a higher hydroxyl content than the normal solvent extracts (Fig. 3.7). The OH functionality of the remaining insoluble fraction however appeared unchanged indicating that a large amount of the phenolic groups is either unreactive to the catalyst and/or is bound to the macromolecular network of the coal. The amount of material solubilised by this method was found to be directly related to the oxygen content of the coal, but could not be quantified due to the retention of the PTC both in the soluble extract and in the insoluble fraction. The information to date is consistent with the removal of a high molecular weight phenolic containing fraction by the PTC.

4.3 INFRARED ANALYSIS OF O-METHYLATED COALS

A comparison of the IR spectra of the three O-methylated coals (Fig. 4.4 A to C) with the IR spectra of the untreated coals (fig. 3.1 A to C), suggests that if O–methylation has taken place at all, only a small amount has occurred, i.e. there is only a small decrease in the hydroxyl band centred at 3300cm^{-1}, and the C–H$_{al}$ absorptions just below 3000cm^{-1} remained unchanged. All three coals however did show signs of undergoing oxidation during the reaction, by the development of a carbonyl peak just above 1700cm^{-1}. (Liotta has suggested that this peak centred at 1720cm^{-1} is due to the methylated carboxylic ester, but since few if any carboxylic acids are found in British bituminous coals, the more likely explanation is that tetrabutylammonium hydroxide is promoting a side reaction with molecular oxygen).

Fig. 4.3 IR Spectrum Of A PTC Extract Of Cortonwood Silkstone Coal

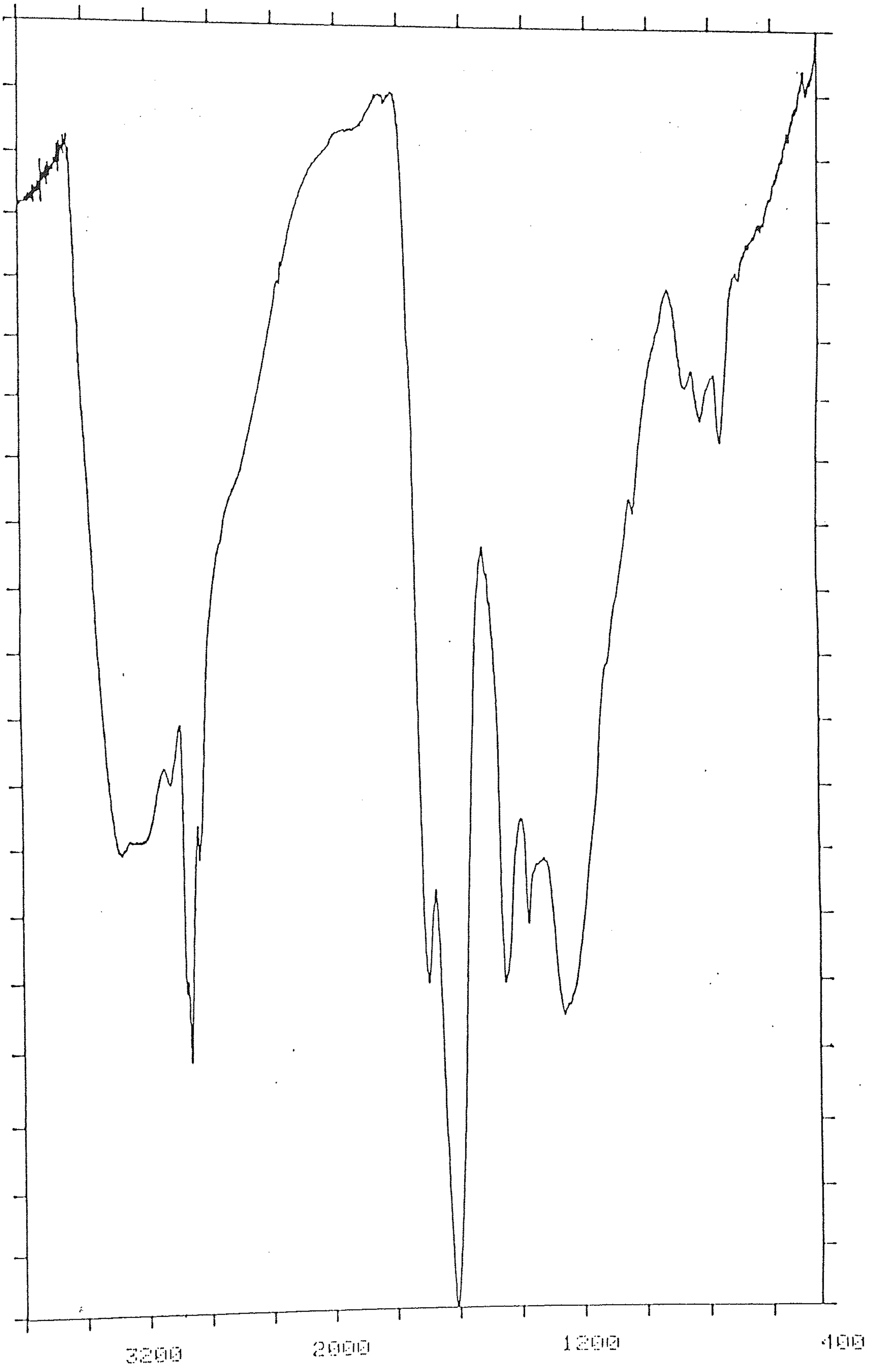
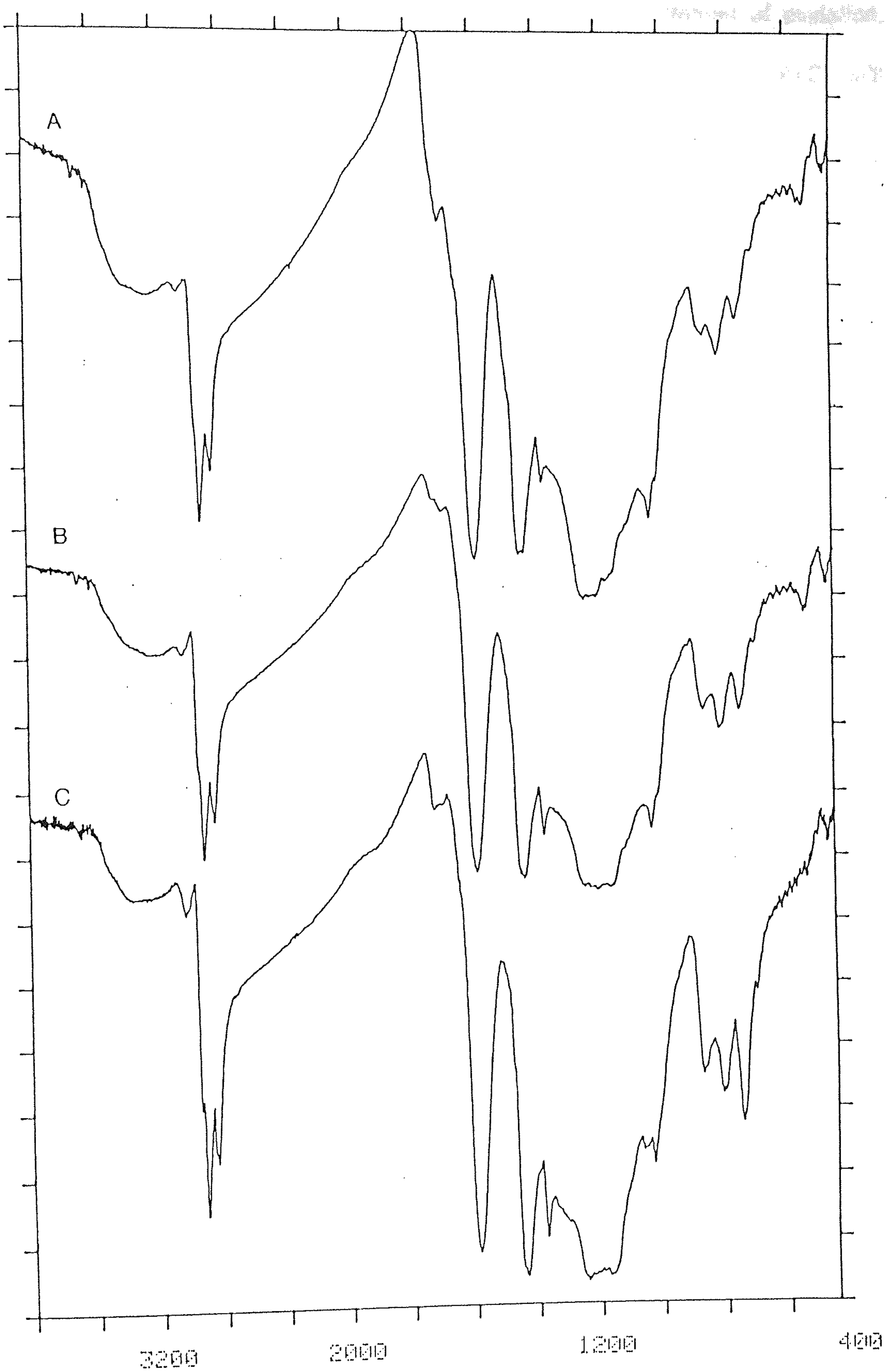


Fig. 4.4 IR Spectra Of O-Methylated Coals (CH_3I used as the alkylating agent).



A) Gedling Coal

B) Cresswell Coal

C) Cortonwood Silkstone Coal

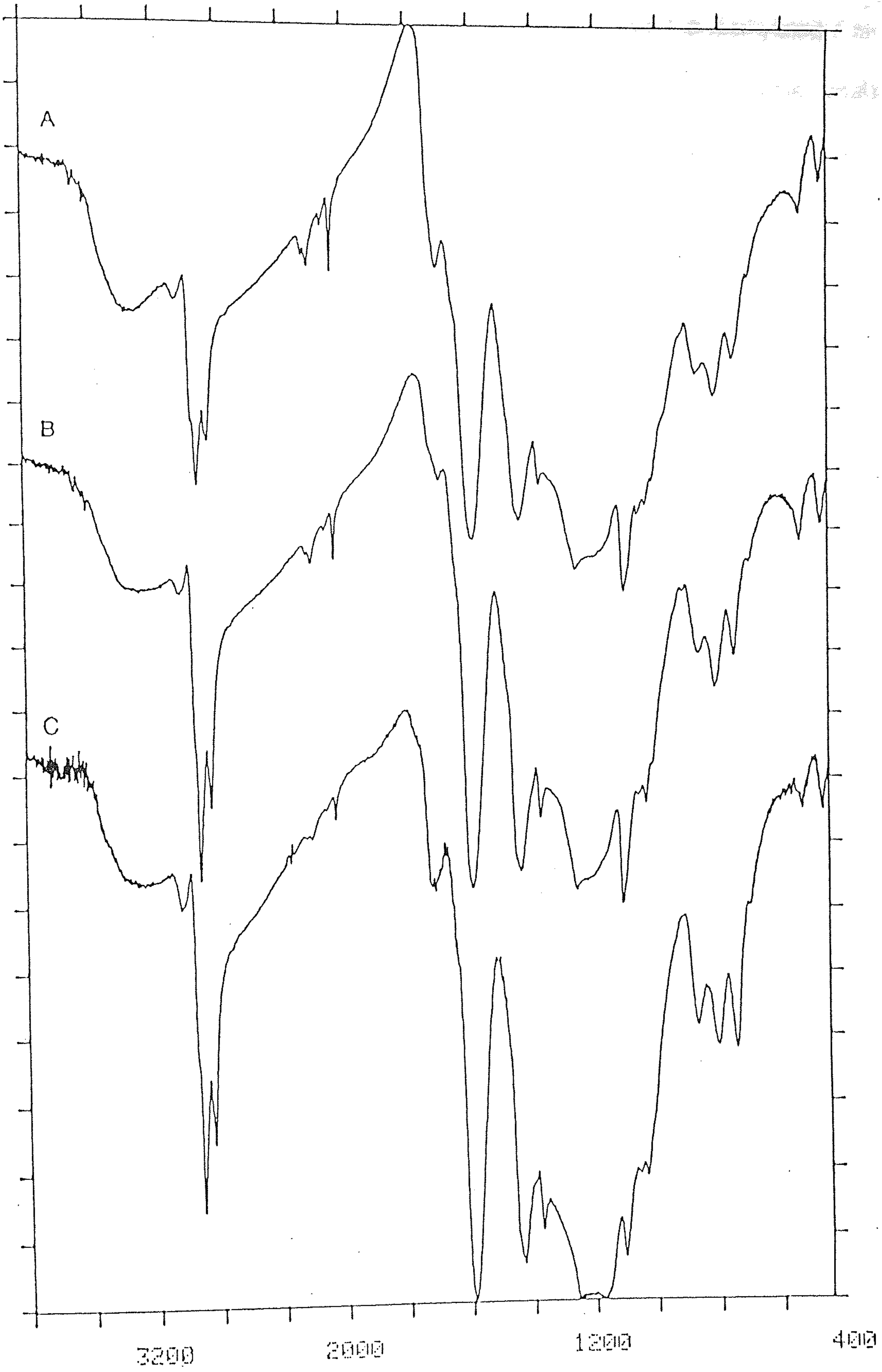
By degassing all the solutions and carrying out the reaction under an inert atmosphere (oxygen free nitrogen or argon), it was possible to reduce the amount of oxidation, however oxidation during the extensive washing, (required to remove the PTC), still occurred. The addition of oxygen during the reaction was confirmed by elemental analysis, and in consequence we were unable to quantify the number of methoxy groups added by this method.

To confirm that O-methylation had occurred, the reactions were repeated using perdeutero-iodomethane (CD_3I). The IR spectra of the three coals (Fig 4.5 A to C), showed clearly that a reaction had taken place. The peaks at 2067, 2125, 2215, and 2249cm^{-1} were assigned to the C-D stretching of the methoxy group and the peak which developed at 1107cm^{-1} was assigned to $O\text{-}CD_3$. Even though the intensities of the C-D absorptions are enhanced relative to the C-H peaks by a factor of $\sqrt{2}$, the C-D peaks are still small, it is clear therefore that the amount of methylation occurring in the three British bituminous coals is small.

Comparing the three spectra in Fig. 4.5 with each other it can be seen that the amount of O–methylation occurring decreases as the rank of the coal increases. This is the expected rank trend showing that the phenolic content of a coal falls as the rank increases. The presence of the hydroxyl absorption in the three spectra, however implies that the reaction does not go to completion, and could be due to steric hindrance at some sites and/or the presence of unreactive hydroxyl groups.

An examination of the THF soluble and insoluble fractions of the perdeutero-methylated coals showed that the majority of the methoxy groups remained in the insoluble fraction after extraction, indicating that most of the reactable phenolic groups in the coals are located on the macromolecular polymer-like phase.

Fig. 4.5 IR Spectra Of O-Methylated Coals (CD_3I used as the alkylating agent).



A) Gedling Coal

B) Cresswell Coal

C) Cortonwood Silkstone Coal

4.4 ^{13}C-CPMAS-NMR SPECTRA

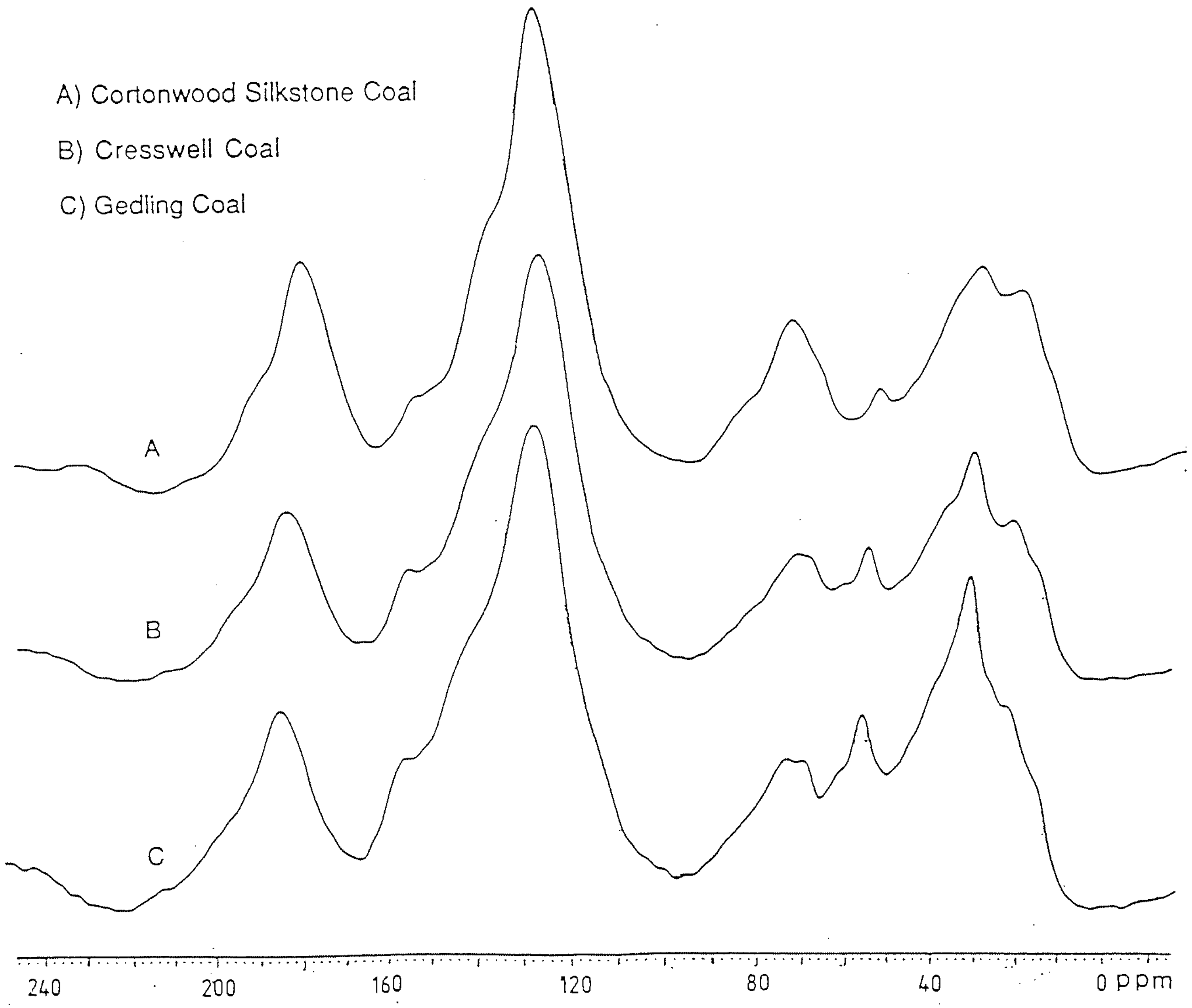
The ^{13}C-CPMAS-NMR spectra of the three extracted / O-methylated / re-extracted coals (figs. 4.6 A to C), like the IR spectra of the perdeuteromethylated coals (figs. 4.5 A to C), confirms the addition of methoxy groups in all three coals, (the peak between 54-65ppm). The semi-quantitative data obtained from the NMR spectra (Table 4.2) show that only a small number of methoxy groups were added and that the amount of O–methylation taking place was inversely related to the rank of the coal, (directly related to the oxygen content). These observations are again in agreement with those made on the IR spectra (figs 4.5 A to C), but they contradict to some extent the extractability data, which suggests that Cresswell coal should be O-methylated to the greatest extent

Table 4.2 Some Structural Parameters Derived From The NMR Spectra Of The Extracted / O-Methylated / Re-Extracted Coals.

Coal	CH_3 %	$-CH_2-$ %	OCH_3 %	Aromatic C %	f_a
Gedling	8.0	32.1	1.9	58.0	0.58
Cresswell	10.0	25.7	1.4	62.9	0.63
Cortonwood Silkstone	12.4	27.9	0.6	70.4	0.70

From the data contained in Table 4.2 it appears that the insoluble cores are becoming more aromatic, and that the amount of methyl substitution on the aromatic clusters is increasing with the rank of the coal. The data also suggests that the length of the methylene bridges are becoming shorter with increasing coal rank.

Fig. 4.6 ^{13}C-CPMAS-NMR Spectra Of Extracted / O-Methylated / Re-Extracted Coals.



The amount of O-methylation in the coals appears to be too small for the reaction to be considered quantitative. This reaction however is mild and selective, and so gives us a method of studying, (and/or protecting) the most accessible/reactive phenolic groups. PTC O–methylation also increases the rate at which the mobile phase can be extracted from the polymeric matrix.

4.5 GAS ADSORPTION DATA ON O-METHYLATED COALS

Although the number of methoxy groups added to the THF insoluble 'cores' appears small, (between 0.6 and 1.9 methoxy groups added per 100 carbon atoms), there was quite a dramatic increase in the rate of extraction of the trapped materials. This implies that there has been a significant change in the physical structure of the three coals. If this is the case it would be expected, from the the theory of O–methylation in coals (described in section 5.1), that the polymeric structures would become more open after the hydrogen bonding had been disrupted. The gas adsorption data however appears to contradict this, see Tables 4.3 and 4.4 (gas adsorption results for the THF extracted/O-methylated coals and THF extracted/O-methylated/re-THF extracted coals, respectively).

Comparing the results in Tables 4.3 and 4.4 with those in Table 3.13, (the gas adsorption results for the extracted coals) it is clear that after O-methylation the surface area of the coal has been drastically reduced . This could be a consequence of the pores filling with PTC, however after further extraction (2 weeks with THF), which should have been sufficient to remove the vast majority of the catalyst, only Gedling coal showed a significant increase in micropore surface of 20%, (as measured relative to the extracted but non-O-methylated sample), In Cresswell coal the micropore area was reduced by 23% and in Cortonwood Silkstone coal by 77%. One possible explanation for this difference between Gedling coal and the other two, could be that the hydrogen bonds in the two higher ranked coals act to keep the structure rigid but strained after solvent extraction, but once these hydrogen bonding interactions are removed the pores can collapse into the voids created by the removal of the mobile phase i.e there is a reduction in the total surface area (see fig. 4.7).

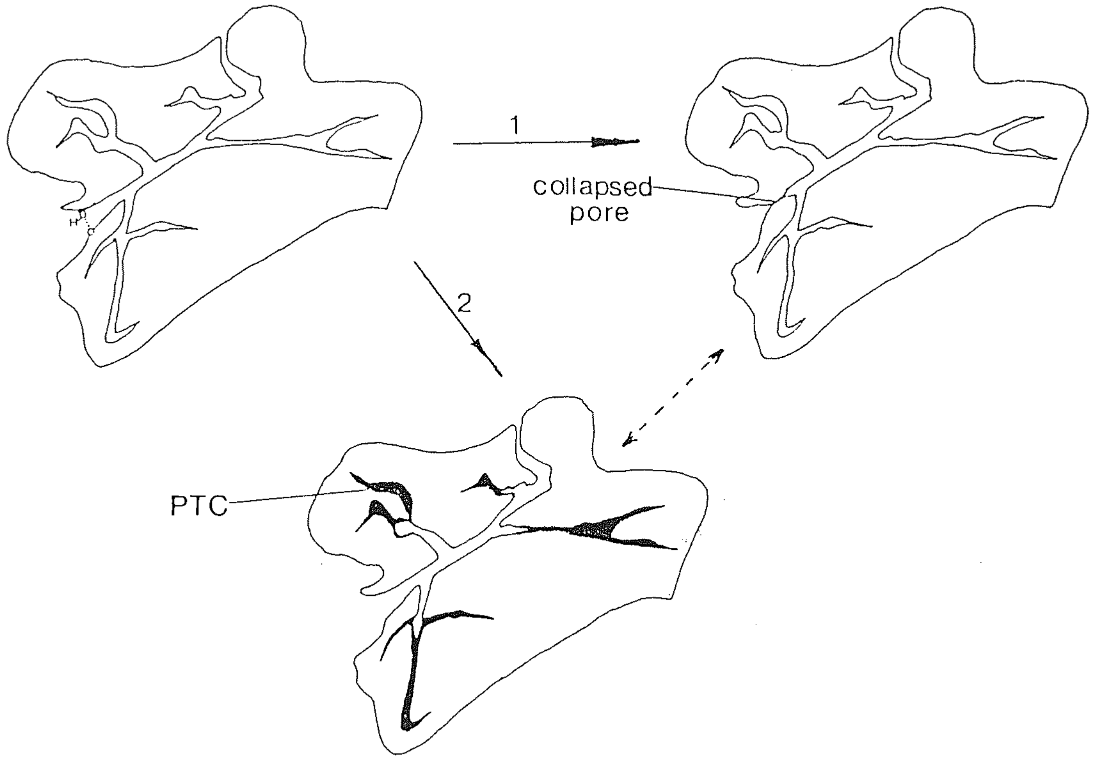
Table 4.3 Gas Adsorption Results For THF Extracted /O-Methylated Coals

Coal	**CO_2 Adsorption P - D**		**N_2 Adsorption BET**		**Micropore area**
	V_m	m^2g^{-1}	V_m	m^2g^{-1}	m^2g^{-1}
Gedling	7.50	50.99	4.40	19.18	31.81
Cresswell	8.91	60.60	6.04	24.40	36.20
Cortonwood Silkstone	8.32	56.55	4.91	21.40	35.15

Table 4.4 Gas Adsorption Results For THF Extracted /O-Methylated/Re-THF Extracted Coals

Coal	**CO_2 Adsorption P - D**		**N_2 Adsorption BET**		**Micropore area**
	V_m	m^2g^{-1}	V_m	m^2g^{-1}	m^2g^{-1}
Gedling	23.44	159.4	8.73	38.0	121.4
Cresswell	8.80	60.0	6.48	28.2	31.8
Cortonwood Silkstone	12.30	82.6	11.51	50.1	32.5

Fig. 4.7 Schematic Representation Of The Pore System Of A Solvent Extracted Coal Before And After O-Methylation



An increase in the observed extractability rate would then occur not because of a more open structure but because the physical structure of the coal would be more flexible and could therefore swell to a greater extent in a solvent allowing easier penetration and removal of material from the pores. This hypothesis however cannot explain the increase in the micro pore surface area of Gedling coal

Liotta(128) suggested that the tetrabutylammonium cation can form a one to one adduct with aromatic centres, if this occurs then, the higher the rank of the coal (i.e. the more aromatic), the more difficult it would be to remove the PTC from the pores so that even after two week further extraction with THF the pores in the higher rank coals could still remain partially blocked with PTC. This theory does fit the surface area trends seen with the three coals, but there is no evidence for the entrapment of the PTC in the coal matrix after re-extraction with THF of the O-methylated samples for two weeks.

It is clear from the above statements that no firm conclusions can be reached based on the study of only three coals. Further investigations using low and high rank coals are required to determine if the results described above are anomalous or form part of a rank trend. We were unable to do this work as the gas adsorption data was not received until after the practical work for this thesis had been completed.

4.6 DISCUSSION.

The main limiting factor in the study of coals is their general insolubility, leading to a low observed chemical reactivity and an inability to use conventional solution state instrumental techniques for the characterisation of coal fragments. O–alkylation which disrupts the secondary structure of a coal leads to a more flexible (less cross-linked) structure, bringing about an increase in the extraction rate of the trapped material by allowing the solvents to enter more readily and penetrate further into the matrix. The mobile phase can also leave more easily.

We have concluded from our studies that PTC O-methylation allows an increase in the rate the mobile phase is extracted from coals, relative to the untreated samples. Although this appears to contradict the literature(119, 120, 121), which suggests that there should be a large increase in the total amount of material made soluble, it may be that other workers have failed to extract their coals for a sufficiently long period of time before carrying out the methylation, silylation or acetylation reactions, and thus misinterpreted the results.

In support of our conclusion it should be remembered that O-methylation and the related reactions do not cleave covalent bonds, thus unless there are a significant number of hydrogen bonds between the mobile phase and the macromolecular phase, (we found no evidence of this in the three British bituminous coals examined), the reaction would not be expected to significantly increase the solubilities of the coals. It is however reasonable to expect the rate of extraction to increase since a proportion of the cross-links in the matrix are being broken, resulting in a more flexible structure after O–methylation..

O-alkylation has another important consequence, in that it protects one of the most reactive functions i.e. phenols from complete degradation by some of the reagents we used, see chapters 6 and 7.

The main conclusions which can be reached from these O-methylation studies are as follows:-

1) PTC O-methylation of British bituminous coals is a rapid and selective method of reacting some, but not all of the phenolic groups.

2) Tetrabutylammonium hydroxide promotes an oxidative side reaction, when air is not vigorously excluded from the system. After O-methylation the coals seem more resistant to oxidation by molecular oxygen.

3) It has been found very difficult to remove all the PTC from the coal matrix after the reaction and this has created problems in the analysis of the resulting soluble fractions.

4) The rate at which the mobile phase can be extracted from a coal can be increased by removing some of the hydrogen bonds in the coals polymer-like matrix.

5) The results suggest that the majority of the active hydroxyl functions are located on the macromolecular polymer-like phase.

6) The amount of O-methylation is inversely related to the rank of the coal. (It is probably more accurate to say that the number of methoxy groups added is directly related to the oxygen content of the coals) The total number of methoxy groups added per 100 carbon atoms in the core material (The insoluble coal fraction after O–methylation and extraction.) were as follows:-

Gedling Coal	1.9
Cresswell Coal	1.4
Cortonwood Silkstone Coal	0.6

these figures correlate well with the information obtained from the IR spectra of the perdeutero-methylated coal samples, before extraction.

CHAPTER 5

ETHER CLEAVAGE REACTIONS

5.1 INTRODUCTION

Ether linkages are an important feature of structural models representing typical bituminous coals, (see Fig. 1.2), and although ethers are only a minor part of the total covalently bonded cross-links, a substantial amount of the total organic oxygen content has been found to be in such groups(138). For some coals quite large solubility increases have been reported when ether functions are cleaved(139, 140, 141).

Elliott(43) and Given(140) have reviewed the literature on oxygen bridges in coals. From these reviews it appears that ether cleavage reactions fall into two groups, these are; 1) Acidic ether cleavage reactions, (e.g. the Zeisel method), which cleaves dialkyl and alkylaryl ethers.

and 2) Reductive ether cleavage reactions, (e.g. the Sternberg method), which cleave alkylaryl and diaryl ethers.

It has been concluded from various ether cleavage studies(43,139,141,142) that:- (1) Methoxy groups only account for a very small amount of the total ether groups in low rank lignites and subbituminous coals, and in higher ranked coals there are no methoxy groups. (2) There is a large variation in the amount of diaryl and alkylaryl ethers in coals, (as determined by reductive ether cleavage reactions). For example in a 87.6%C coking coal, 50% of the oxygen was found to be in the form of diaryl and/or alkylaryl ethers, while less than 5% of the oxygen was found to be in this form in an 82.2%C high volatile bituminous coal. (3) In most coals a high percentage of the oxygen bridges remain unreactive. It is assumed that most of these unreactive functions are incorporated in heterocyclic ring structures.

In order to ascertain if PTC's can be used to advantage in ether cleavage reactions, we have evaluated their use in both types of reaction (e.g. in the reductive, and acidic environment). In particular we have looked at, reductive ether cleavage using naphthalene as an electron transfer agent (ETA). Reductive ether cleavage using a crown ether as the PTC, and acidic ether cleavage using a phosphonium salt as the PTC.

5.2 REDUCTIVE ETHER CLEAVAGE REACTIONS

Three main methods, all involving an alkali metal, have been used to chemically reduce coals. The most common of these methods employs an electron transfer agent, (ETA), in an ethereal solvent. The ETA promotes the reaction between the insoluble alkali metal (usually potassium) and the insoluble coal. Stenburg and co-workers(143) were the first to use an ETA (naphthalene) which reacted with potassium in THF to form the radical anion, and dianion as below.

$$\begin{aligned}
C_{10}H_8 &+ K \longrightarrow C_{10}H_8^{-} + K^{+} \\
C_{10}H_8^{-} &+ K \longrightarrow C_{10}H_8^{2-} + K^{+} \\
2\,C_{10}H_8^{-} &+ K \longrightarrow C_{10}H_8^{2-} + C_{10}H_8
\end{aligned}$$

The naphthalene anions formed in the above sequence of reactions, can then penetrate into the organic phase where an electron transfer reaction occurs. This produces coal radical anions and dianions in the aromatic fragments of the coal matrix. It is therefore the reduction potentials of the various aromatic groups in the coal which determine the extent of the cleavage reaction. Aromatic systems which contain a heteroatom will be particularly easy to cleave(144, 145). Using naphthalene as the ETA, means that this system, (K, naphthalene, and an ether), has the potential to reduce all the aromatic structures in the coal with the exception of the less reactive phenyl derivatives. The severity of the reduction can however be controlled by altering one or more of the following parameters; (1) The metal to hydrocarbon molar ratio. (2) The reduction potential of the metal. (3) The ETA, and (4) The concentration of anions in the solution.

The initial reaction of the ETA with aromatic fraction of the coal can be summarised by the three reactions below.

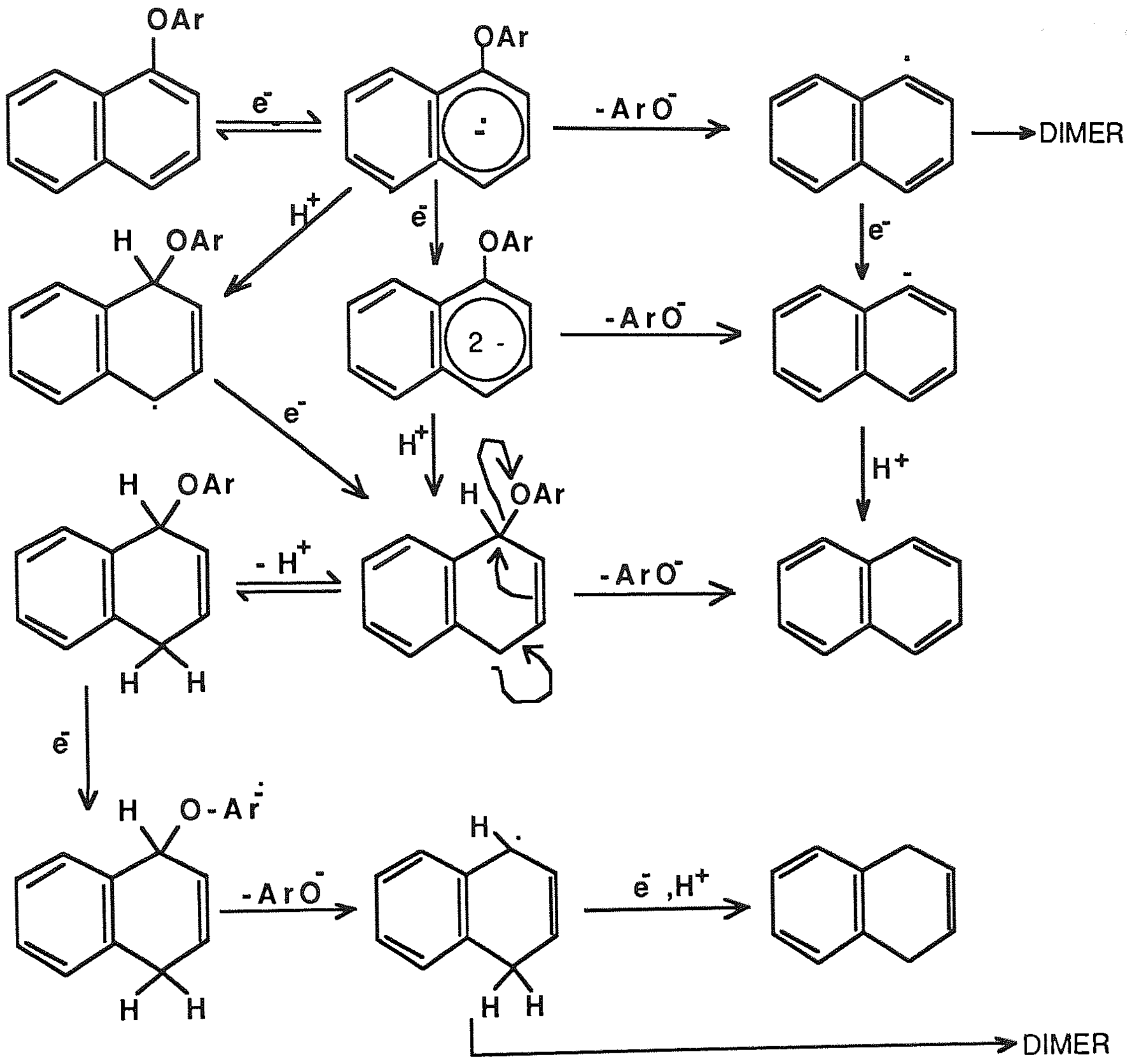
$$\begin{aligned}
&\text{Coal-ArH} + C_{10}H_8^{-} \longrightarrow \text{Coal-ArH}^{-} + C_{10}H_8 \\
&\text{Coal-ArH}^{-} + C_{10}H_8^{-} \longrightarrow \text{Coal-ArH}^{2-} + C_{10}H_8 \\
&\text{Coal-ArH}^{-} + C_{10}H_8^{2-} \longrightarrow \text{Coal-ArH}^{2-} + C_{10}H_8^{-}
\end{aligned}$$

This reaction path is, however an over simplification, dimerisation of the reduced soluble products can occur, and in concentrated solutions the ETA (naphthalene) can dimerise. It is also possible for the ETA and/or the solvent to be incorporated into the final soluble products. Since these reducing solutions are very basic a variety of proton transfer reactions can also occur(146,147), where an anion of intermediate basicity between the radical anion and the dianion can be formed(148,149), see Fig 5.1.

It is known that diaryl ethers are readily cleaved. The dianions of the ethers undergo decomposition, resulting in the formation of an aryl oxide and an aryl carbanion(151,152,153). Arylalkyl ethers are cleaved much less readily, and results in the formation of an aryloxide and an alkyl radical(152,153). Dialkyl ethers are unreactive using these reagents.

The formation of the strongly basic aryl carbanion within the coal matrix results in proton abstraction reactions, to form more stable and less basic carbanion, but other rearrangements may can also occur(150,154).

Fig. 5.1 Mechanism For The Formation Of Some Reaction Products During Reductive Ether Cleavage(150)



Other hetero atom containing functions, for example thioethers, undergo reductive cleavage reactions much more readily than the ethers, because of the more favorable reduction potentials. The result of this is that even the dialkyl thioethers are reactive under the conditions used for ether cleavage(155, 156).

Ether linkages are however not the only bond which can be cleaved during the reaction. All coals contain labile carbon-carbon bonds, which can be broken, a review of these reactions as well as the ether cleavage reactions is given by Stock(157).

Because a number of different covalent bonds are cleaved in these reductive reactions, it is difficult to estimate any particular functional group's contribution to the overall increase in coal solubility

PTC reductive ether cleavage using 18-crown-6 as the 'complexing' phase transfer agent, has been reported to give a cleaner reaction than the corresponding procedure using ETA's(158). By using a crown ether the incorporation of the ETA's anion into the coals matrix is prevented. All the other side reaction mentioned above will, however still take place.

5.3 ETHER CLEAVAGE REACTIONS USING ACIDS

Dialkyl and alkylaryl ethers are comparatively unreactive compounds, but they can be be cleaved by concentrated acids at elevated temperatures, (HI or HBr at reflux temperatures). Under these conditions dialkyl ethers initially yield an alkyl halide and an alcohol. The alcohol may then undergo a further reaction to produce more alkyl halide(159,160). Alkylaryl ethers on the other hand, because of the low reactivity of the oxygen-aromatic ring bond, always cleave between the alkyl group and the oxygen to yield a phenol and an alkyl halide(161).

$$\text{R-O-R'} + \text{HX} \longrightarrow \text{RX} + \text{R'-OH} \xrightarrow{\text{HX}} \text{R'X}$$

Where R' is larger than R.

$$\text{Ar-O-R} + \text{HX} \longrightarrow \text{Ar-OH} + \text{RX}$$

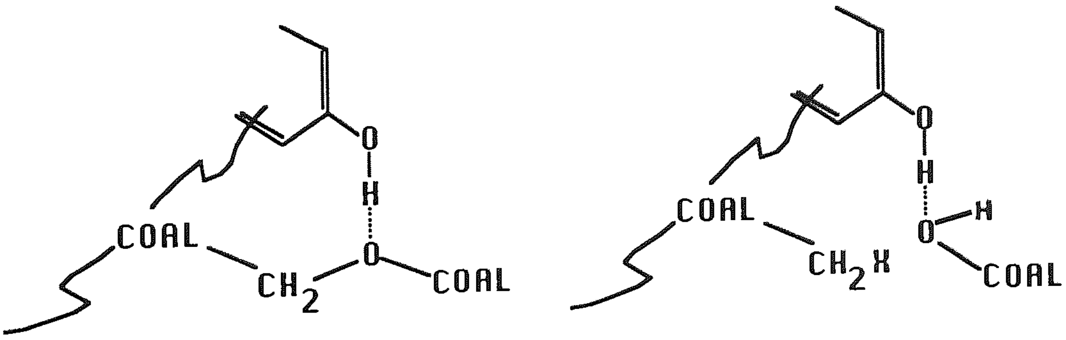
Cleavage of dialkyl and alkylaryl ethers involves the nucleophilic attack of the halide on the protonated ether, followed by the displacement of a weakly basic alcohol molecule. The order of effectiveness of the acids is as follows;

HI > HBr >> HCl.

In some cleavage reactions a strong acid, (e.g. H_2SO_4) is also used, in order to accelerate the reaction, by enhancing the protonation of the ether oxygen.

The Ziesal method (using HI) has been used to cleave ethers and estimate the methoxy content of coals(43). A modification of this method however has been reported, which facilitates the penetration of the halide ion into the coal. This is achieved by complexing HI with pyridine to form a salt which has enough organic character to enter the coal matrix(162). From studies using this and other reagents,(162, 163, 164, 165) it has been suggested that all the ether functions in a coal are hydrogen bonded, (Fig. 5.2a). If this is the case then dialkyl and alkylaryl ethers can be considered to be in an activated state, i.e. partially protonated. This means however, that after ether cleavage is complete, the hydrogen bonds may still remain, i.e. the coal network could still be held together during solvent extraction in non-specific solvents by hydrogen bonding, (see Fig.5.2b). Only when some or all of the hydrogen bonds are removed would there be an increase in the solvent extractability of the coals.

Fig.5.2 Schematic Of Hydrogen Bonded Ethers In Coals



(a)
Hydrogen bonded ethers

(b)
Coal network remains intact during ether cleavage.

PTC's were first used to promote acidic ether cleavage in heterogeneous systems by Landini and co-workers(166), but Liotta and co-workers(167) were the first to use this method to study sub-bituminous and low ranked bituminous coals. From the results of these studies they concluded that the PTC reagent would cleave most but not all alkylaryl ethers in coals.

5.4 REDUCTIVE ETHER CLEAVAGE RESULTS

PTC reductive ether cleavage using 18-crown-6 resulted in large increases in the solvent solubilities of the three coals, relative to the untreated coals, but the increases were directly related to the rank of the coal, and not as would have been expected to the oxygen content, (i.e the higher the rank of the coal, the lower the oxygen content and it is assumed the lower the ether content). Examination of the soluble and insoluble products revealed that the PTC was present in both fraction, because of this contamination, analysis of the reaction products was made very difficult. It was therefore decided to concentrate on reductive ether cleavage using the electron transfer agent (ETA), naphthalene.

ETA reductive ether cleavage gave similar extractability results to those using the PTC, (18-crown-6), (see Table 5.1), with the results again showing the reverse of the expected rank trend, i.e. a decreasing solubility with increasing coal rank. Other workers have however reported similar results for related reductions carried out in liquid ammonia(168).

Table 5.1 Extractability Results For The Reductively Ether Cleaved Coals.

Coal	ETA **Solvent Extractability (%)***	
	$CHCl_3$	**Pyridine**
Gedling	19.5	27.9
Cresswell	24.4	43.4
Cortonwood Silkstone	27.0	54.4

(* These results are only approximate since both the insoluble and soluble fractions contained trapped ETA and reaction products of the ETA)

The reversal in the expected rank trend, may indicate that the diaryl, alkylaryl, and benzylic ethers play an increasingly important role in maintaining the structural integrity of the higher ranked coals. Alternatively it may indicate that the reductive ether cleavage reaction is in competition with carbon-carbon bond cleavage, of bridging structures, these latter reactions becoming more dominant as the rank of the coal increases. Support for this latter view has come from Kuhlmann and co-workers(169).

Comparing the solubility results obtained using the two solvents, it is clear that pyridine has a larger effect on solubilities than does chloroform. One possible explanation for this is that acidic functions, (for example phenolic groups created during the reaction), are held in the coals matrix by hydrogen bonding, until a basic solvent such as pyridine is used. Pyridine, it is thought, can disrupt these secondary interactions. There is however little evidence for the creation of such functions during the reaction, see below.

The ^{13}C-CPMAS-NMR spectra of Gedling ETA reductively ether cleaved coal, (insoluble fraction) appears very similar to that of the unreacted coal with the possible exception of a slight increase in the CH_2/CH_3 ratio, (these NMR spectra were however obtained on a low resolution instrument which made quantitative measurements difficult).

The DRIFT spectra of the three ETA reductively cleaved coals, (Fig. 5.3 to 5.5), show an increased aliphatic character when compared with the untreated coals, (Fig. 3.2 to 3.4). This increase in aliphatic character may be the result of hydrogenation of aromatic centres during the reaction. The lack of a large peak due to hydroxyl groups centred at 3300cm^{-1}, suggests that few if any ethers have been converted to the phenols, and the broad peak between 1400cm^{-1} and 1200cm^{-1}, (assigned to C-O-C groups), also indicate that ethers are still present.

Examination of the GC-MS data obtained for the solvent soluble products suggests that a large amount of hydrogenation and coupling of the electron transfer agent (naphthalene) had taken place during the reaction.

Fig.5.3 DRIFT Spectrum Of Reductively Ether Cleaved Gedling Coal.

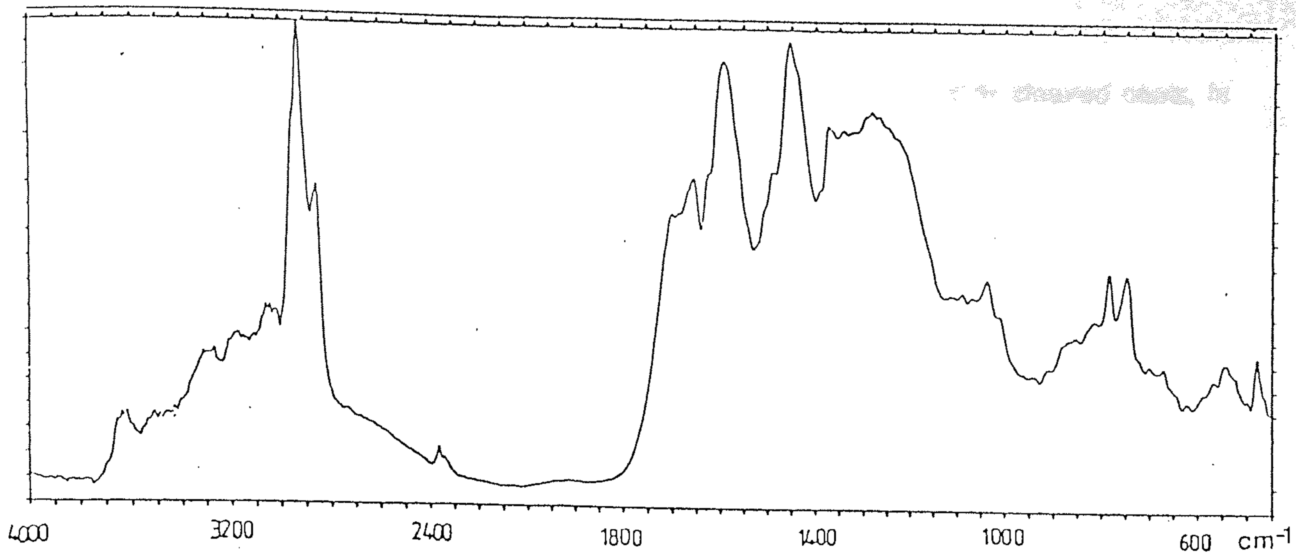


Fig.5.4 DRIFT Spectrum Of Reductively Ether Cleaved Cresswell Coal.

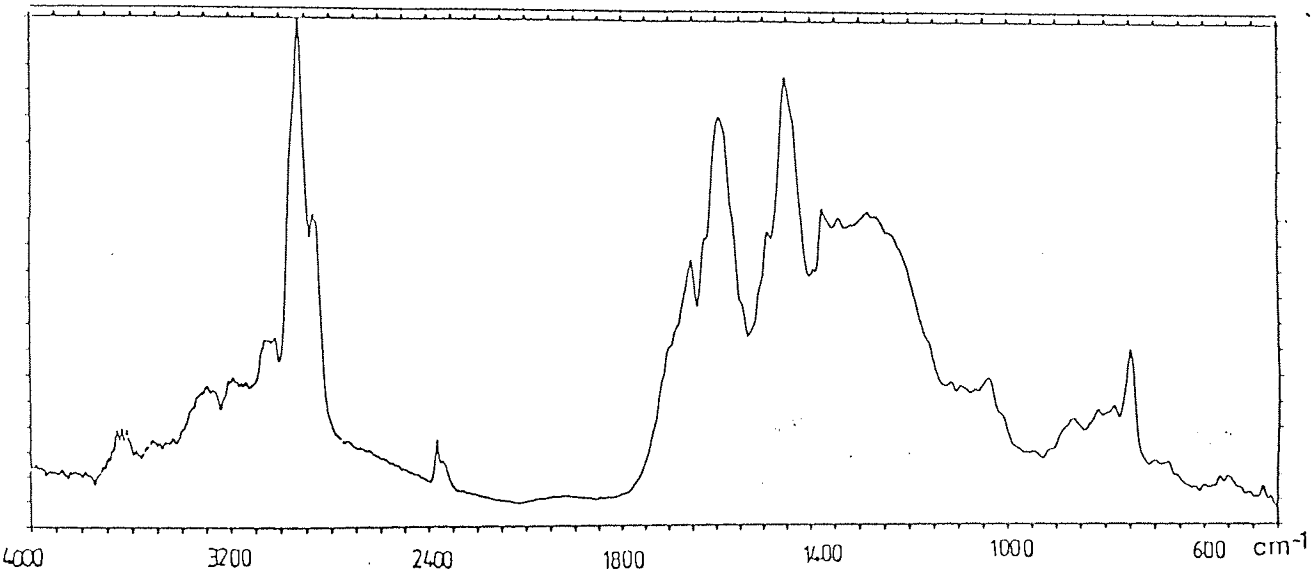
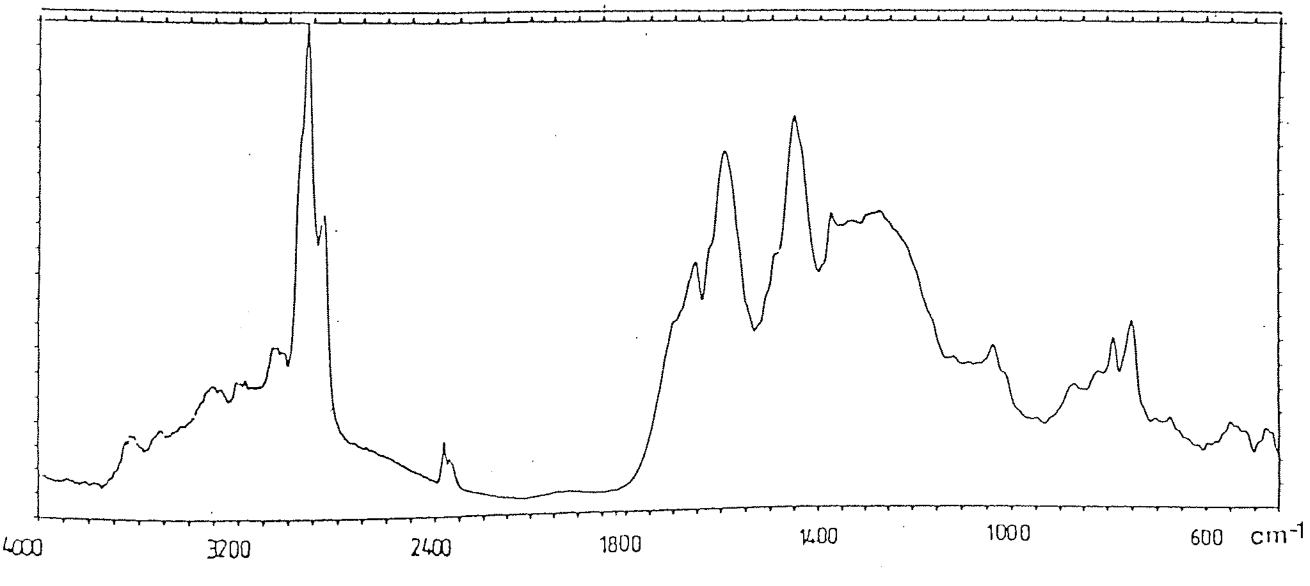


Fig.5.5 DRIFT Spectrum Of Reductively Ether Cleaved Cortonwood Silkstone Coal.



5.5 PTC/ETHER CLEAVAGE RESULTS

The extractability results obtained for the PTC acidic ether cleaved coals, in three solvents, are given in Table 5.2.

Table 5.2 Solvent Extractability Results For The PTC Acid Ether Cleaved Coals.

Coal	**Solvent Extractability (%)**		
	Chloroform	**THF**	**Pyridine**
Gedling	4.7	4.3	10.3
Cresswell	4.5	5.7	21.3
Cortonwood Silkstone	6.5	9.0	22.6

Comparing these extractability results, (Table 5.2) with those for the untreated coals, (Table 3.3.1), it can be seen that the PTC/acid ether cleavage reaction resulted in reduced solvent solubilities. When the PTC ether cleavage reaction was repeated with a small amount of concentrated sulfuric acid present as a further catalyst, no significant differences were found.

An examination of the ^{13}C-CPMAS-NMR spectra of the PTC/acid ether cleaved coal and the IR spectra of the ether cleaved coals (Fig. 5.6 to 5.8) showed no significant changes from those of the untreated samples, (cf Fig. 3.1 A to C). It was also noted that the IR spectra of the chloroform and THF soluble extracts of the PTC/acid ether cleaved coals showed very few hydroxyl groups to be present in the extracts, (this was confirmed by an examination of the soluble extracts by GC–MS), All these observations suggest that the soluble and insoluble ether cleaved coal fractions, are very similar to the original untreated coals, (see chapter 3), indicating that no ether links have been cleaved by this method.

Fig.5.6 IR Spectra Of PTC Acid Ether Cleaved Gedling Coal.

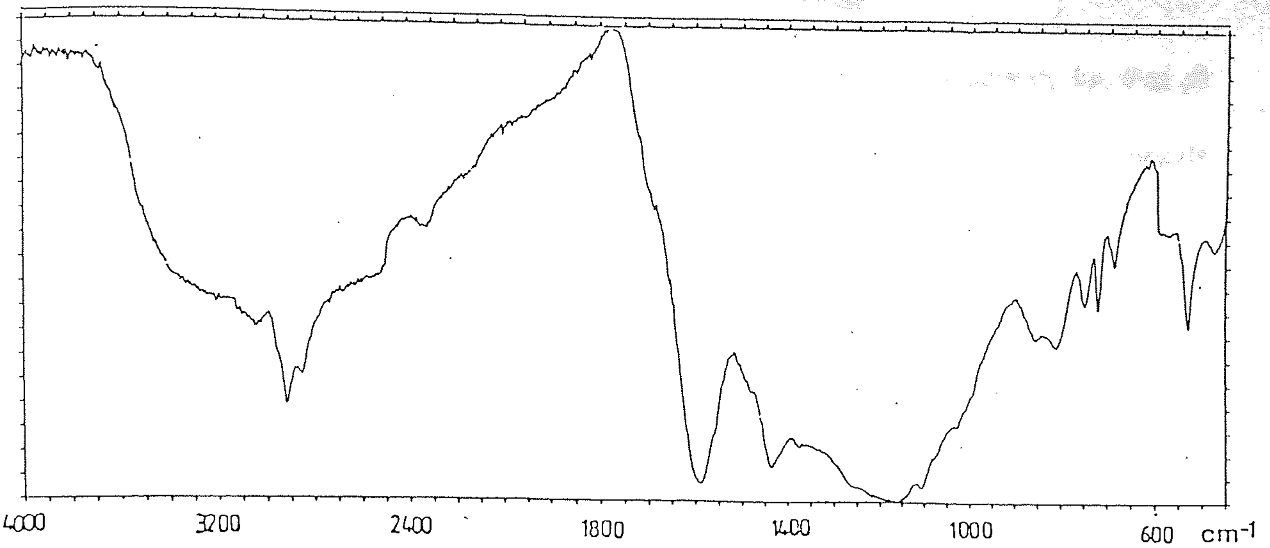


Fig.5.7 IR Spectra Of PTC Acid Ether Cleaved Cresswell Coal.

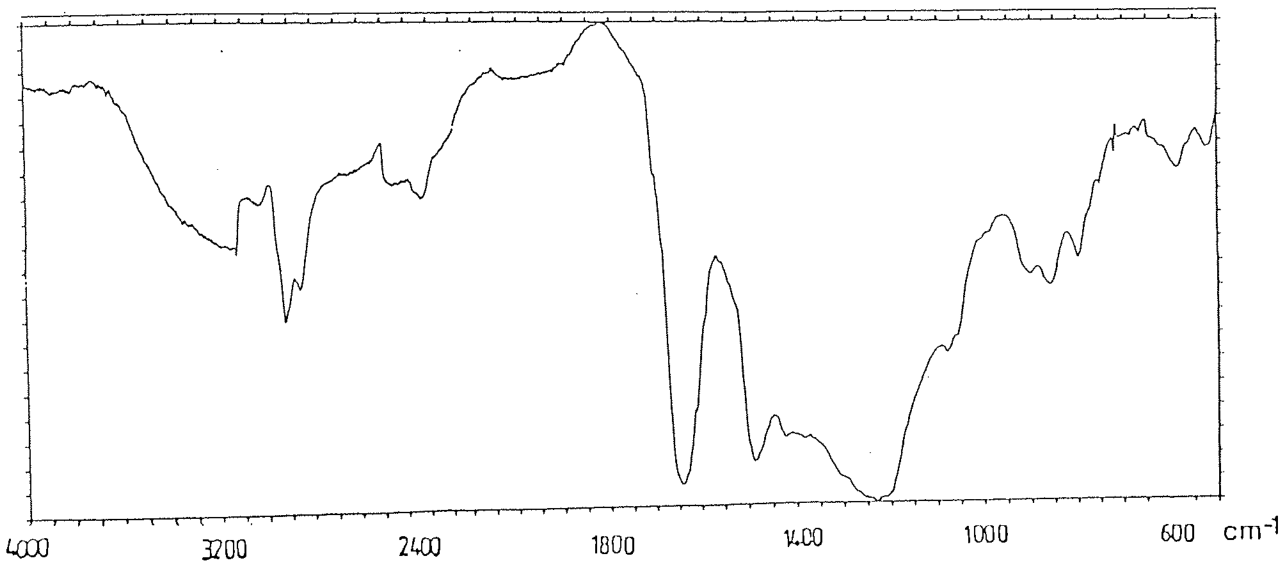
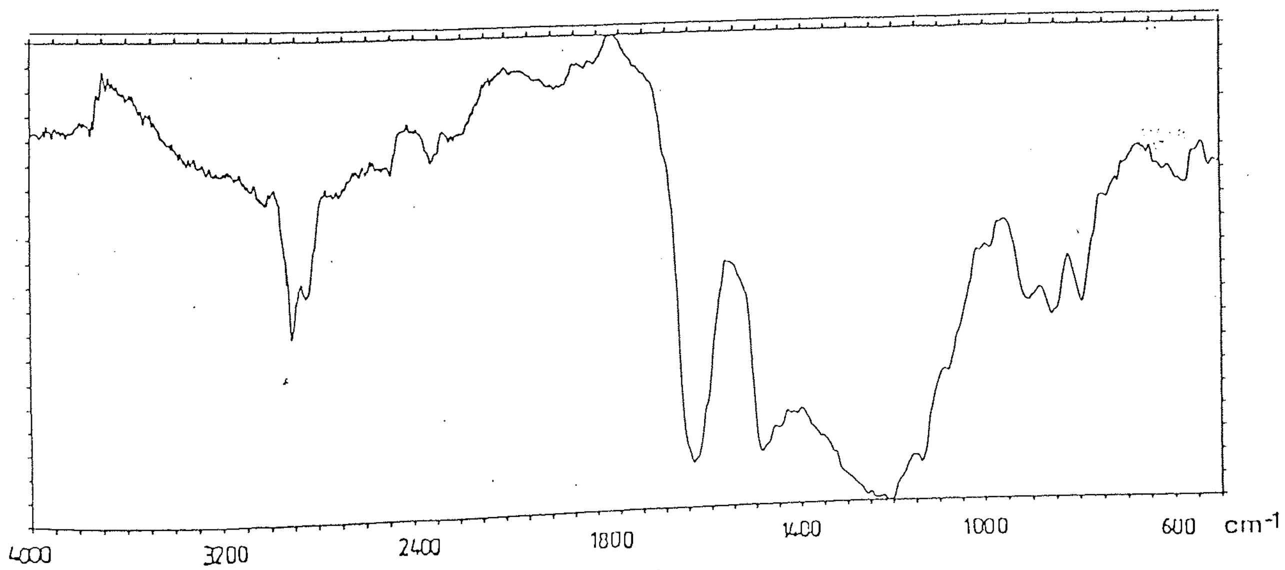


Fig.5.8 IR Spectra Of PTC Acid Ether Cleaved Cortonwood Silkstone Coal.



5.5.1 O-METHYLATION AND PTC/ETHER CLEAVAGE

Assuming that the argument put forward in section 5.3 is correct, i.e. that all the ether oxygens in a coal are involved in hydrogen bonding, then the solubility results given in Table 5.2, for the acid ether cleaved coals, can be explained, in terms of our failure to remove the hydrogen bonds which are present before and after ether cleavage. Therefore in order to ascertain whether hydrogen bonding was the cause of the reduction in coal solubility we O-methylated the PTC/acid ether cleaved coals. The solvent extraction results (Table 5.3), however showed only the increase expected of an O-methylated coal (cf Table 4.1). These results therefore indicate that if any ether cleavage was taking place it had an insignificant effect on coal solubilities.

Table 5.3 Solvent Extractability Results For The PTC Acid Ether Cleaved / O–Methylated Coals.

Coal	**Solvent Extractability (%)**		
	Chloroform	**THF**	**Pyridine**
Gedling	22.7	23.8	30.2
Cresswell	14.2	14.4	22.9
Cortonwood Silkstone	21.8	26.6	25.8

The three British bituminous coals were O-methylated prior to PTC/acid ether cleavage, in order to; (A) Prove that alkylaryl ethers, (in the form of methoxy groups), could be removed from our coals by this reagent, and (B) To facilitate the penetration of the bromide ion by removing some of the cross-links in the coal.

After ether cleavage the reaction products were O–methylated, again to break any hydrogen bonds between phenolic groups and other electronegative centres, formed during the reaction. The solvent extractability results for these fractions are given in Table 5.4 and show that, in general, the solubilities decreased when compared to the solubility results for the O-methylated samples, (Table 4.1). These observations again indicate that there are few dialkyl or alkylaryl ethers cleavable by this method in the three coals studied.

Table 5.4 Solvent Extractability Results For The O-Methylated / PTC Acid Ether Cleaved / O–Methylated Coals.

Coal	**Solvent Extractability (%)**		
	Chloroform	**THF**	**Pyridine**
Gedling	16.9	14.9	26.8
Cresswell	29.2	26.2	36.1
Cortonwood Silkstone	14.8	16.4	21.3

It was also found that PTC/acid ether cleavage failed to remove all the methoxy groups that were added during O-methylation. This means that this reaction can only be used to qualitatively estimate the alkylaryl content of bituminous coals.

5.6 DISCUSSION

Reductive ether cleavage, although solubilising a large fraction of the three British bituminous coals also appears to be cleaving carbon-carbon bonds, (in particular the more labile methylene bridges). The addition of an electron transfer agent, (naphthalene) or a PTC, (18-crown-6), appears to complicate the reaction still further by A) being incorporated into the matrix, and B) by promoting an already vigorous reaction. Methods have been devised for removing the ETA from the soluble products(170, 171), but it is doubtful that any conclusive quantitative structural information can be derived from these studies, because of the number of possible reactions, (e.g. further reactions of some of the primary products, chemical incorporation of the ETA into the coal matrix, and hydrogenation of aromatic centers).

Qualitatively, however the results do suggest that the bridging groups (diaryl ethers, alkylaryl ethers, and methylene groups) become increasingly important to the integrity of the polymer-like network as the rank of the coal increases, even though these functions become fewer in number with increasing rank.

The lack of any significant increase in coal solubilities, after ether cleavage using the PTC/acid ether cleavage method, before or after O-methylation, indicates that there are no dialkyl ethers in the three British bituminous coals. This ether cleavage method also failed to remove all the methoxy groups added during O-methylation, so that the quantitativeness of this ether cleavage technique must be in question.

Combining the results, obtained from the two types of ether cleavage reactions, it appears that:-

1) There are an insignificant number of dialkyl or alkylaryl ethers present in the three British bituminous coals.

2) The diaryl ethers, if present, cannot be quantified by the reductive ether cleavage method, since other covalent bonds are also cleaved.

3) The majority of the ethers are inert to both reagents. Therefore the majority of the ethers in the three coals, we studied, are likely to be cyclic in nature.

and 4) There appears to be no advantage in using a phase transfer catalyst or an electron transfer agent to promote ether cleavage reactions, in fact such reagents tend to hinder the analysis of both the soluble and insoluble products.

CHAPTER 6.

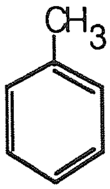
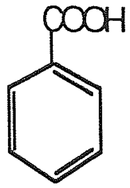
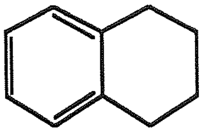
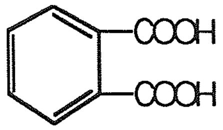
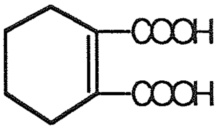
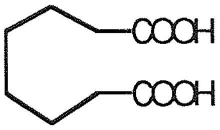
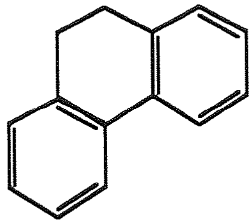
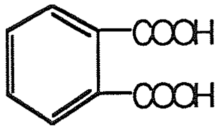
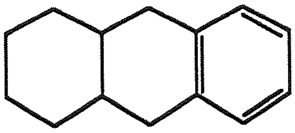
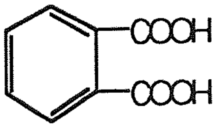
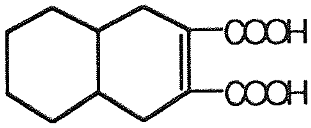
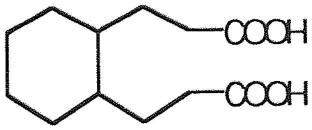
TRIFLUOROPEROXYACETIC ACID OXIDATION

6.1 INTRODUCTION

The common oxidising agents such as dichromate, permanganate, molecular oxygen, or nitric acid, degrade coal by attacking the benzylic position in alkylaromatic fragments. As a result of this mode of attack, information is lost about the aliphatic portions of the molecules. Trifluoroperoxyacetic acid (TFPA) is an alternative oxidising reagent which is reported to preserve these aliphatic structures(172, 173, 174, 175, 176) and can thus be used in conjunction with one or more of the common oxidants, to form a more complete structural picture of a coal.

TFPA was first prepared by Emmon and Ferris in 1953(177). Mechanistically it is suggested(178) that the active species in the oxidation is the hydroxyl cation (OH^+), so that the first step in the attack on coals is an electrophilic aromatic substitution. Electron withdrawing groups, (e.g. CO_2H or SO_3H), will therefore deactivate the aromatic centres and electron donating groups (e.g. hydroxyl groups), will activate the ring system to oxidation by TFPA. It has been noted for example that benzene is oxidised to carbon dioxide, and oxalic acid after several hours at room temperatures(178), but propylbenzene is converted at a faster rate to butanoic acid and propylmaleic acid(179). Anthracene also reacts at a faster rate than benzene to produce phthalic acid, plus smaller amounts of anthraquinone, and phthalide-3-carboxylic acid(180). Many studies on model compounds have now been carried out with this oxidant(181, 182, 183, 184, 185), and the products compared with those obtained from alkaline permanganate oxidation, some of this data is summarised in Fig. 6.1.

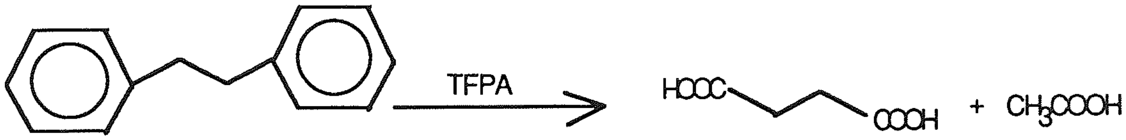
Fig. 6.1 A Comparison Of The Oxidation Products From Alkaline Permanganate Oxidation And TFPA Oxidation

Compound	**$KMnO_4$ Oxidation Products**	**TFPA Oxidation(186) Products**
		CH_3COOH
		 + 
		
		 + 

It has been shown that for branched hydrocarbons (e.g. 1-methyltetralin and 1-phenyltetralin), partial degradation of the aliphatic bridge occurred, but there is enough retention of structure in the products to allow the use of TFPA oxidation as a probe to study branched bridging groups(186).

Problems in the interpretation of the results can arise because in some TFPA oxidation experiments(185) highly substituted aromatic systems rearrange via benzene oxides, and hydrogen migration reactions. This reduces the potential of the oxidation procedure in structural investigations

Further complications in the interpretation of the results derive from more than one product being produced from the same compound during the oxidation(187). For example 1,2-diphenylethane when oxidised using TFPA yields 1,4–butandioic acid and acetic acid.



The production of acetic acid can however be reduced and in some cases eliminated by the addition of a small quantity of sulfuric acid to the reaction mixture. The presence of a strong acid such as H_2SO_4 also increases the oxidation rate which in turn has the effect of reducing the rearrangement and hydrogen migration reactions. Thus with sulfuric acid added to the reaction system most of the unwanted side reactions can be removed. Unfortunately the addition of sulfuric acid promotes the hydroxylation of long aliphatic chains(176) and eventually leads to the cleavage of the alkyl chains. As a result some information is lost about the aliphatic portion of a coal. In order to minimise this problem we have removed as much as possible of the long alkyl chains, (ie.by extracting as much of the mobile phase as possible) before TFPA oxidation was carried out.

As well as the difficulties mentioned above, it is known that different structures in the coal may yield identical oxidation products, for example compounds with the Ar–CH_2–Ar structure, produce the same acid.(1,3–propandioic acid), as some polycyclic aromatic systems(180). Thus the presence of 1,3–propandioic acid in the TFPA oxidation products cannot be related back to a single parent structure. Similarly some phenols can give rise to the same products as those resulting from the oxidation of hydroaromatic and polycyclic aromatic compounds(185).

All of the above observations have lead to questions about the value of the TFPA oxidation method for the characterisation of the aliphatic structures in coals especially when based solely on an examination of the soluble products from the TFPA reaction(176). It is for this reason that the three British bituminous coals we selected for study, were oxidised using a mild TFPA procedure (i.e. an inert solvent, 5h reaction time, conc.H_2SO_4,), and both the soluble and insoluble oxidised fractions were examined.

6.1.1 COAL TFPA OXIDATION STUDIES

TFPA was first used as an oxidant in coal studies by Deno(187). He examined coals containing between 60% and 88% carbon, and showed that most of the hydrogen in coals is located in the aliphatic structures. The majority of the aliphatic structures were in turn assumed to be incorporated in hydroaromatic rings. Deno also found the following, after oxidising the coals;

1) Greater than 50% of the aliphatic compounds with a -$(CH_2)_n$- structure were preserved when $n \geq 2$, however when $n=1$ there was almost total conversion of the methylene link to carbon dioxide and water.

2) There was no evidence of bridges between aromatic rings longer than $(CH_2)_3$.

3) Most of the bridge groups were in the form of single CH_2 linkages in hydroaromatic structures.

Examination of the products obtained from TFPA oxidation studies have provided independent evidence, that CH_3 and OCH_3 functions are the only significant alkyl and alkoxy functions attached to the aryl groups in bituminous coal.

In general it has been found that as coal rank increases the oxidant (TFPA) becomes less able to solublise the coal, (for example anthracite coals appear unreactive to the peracid oxidant, but lignite and low rank bituminous coals are almost totally solublised).

The major products from TFPA coal oxidation irrespective of rank, (excluding anthracite coals) were found to be C_3 to C_8 acyclic aliphatic diacids, acetic acid (upto 2%), oxirane tri- and tetra- carboxylic acids, benzene carboxylic acids (di-, tri-, tetra-, and penta-), acyclic aliphatic triacids and unsaturated diacids.

The severity of this peracid oxidation can and has been ameliorated by the use of an inert solvent(188,189,190). The solvent enables the reaction mixture to be maintained at the boiling point of the solvent and also dissolves the primary reaction products, preventing some over oxidation. Shadle and Given(188) reported that chloroform was the best inert solvent because of its good polar solubility characteristics and because of its boiling point of 61°C which is near the optimum temperature for the reaction quoted by Deno and co-workers(174). In consequence we adopted the modified procedure, using chloroform as the solvent. A reaction time of 5h was also adopted in order to reduce the yield of unsaturated diacids and aromatic products and optimise the yield of saturated aliphatic products and cycloalkene diacids.

TFPA oxidation of bituminous coals does not produce totally soluble organic components,nor does it totally destroy all the aromatic material, in part this is due to the formation of aromatic carboxylic acid groups which form during the reaction and have the effect of sterically hindering and/or deactivating the ring systems to further attack by the oxidant. In support of this theory it has been noted that the aromaticity of a coal has a bearing on the concentration of the aromatic oxidation products(191, 192), i.e. highly aromatic coals produce larger quantities of insoluble products and solvent soluble aromatic acids. In an attempt to explain these observations Mc Ginnis and co-workers(193), have applied Huckel molecular orbital calculations for electrophilic attack by OH+ on polycyclic aromatic compounds. The results of these calculations indicate that TFPA oxidation would only completely destroy systems consisting of three or fewer condensed rings, larger systems although attacked by the oxidant would not be solublised.

6.2 TFPA OXIDATION OF EXTRACTED AND O-METHYLATED COALS

The three British bituminous coals which had previously been exhaustively extracted in THF, O-methylated and re-extracted, were oxidised using the TFPA reagent. After oxidation the coals were further extracted with THF to remove the soluble depolymerised material still remaining within the residual matrix.

The Gedling coal was found to be 60% soluble (in THF) after a 5h oxidation period. This compares with only 20% solubilities for the two higher ranked coals, (the solubility results were not corrected for the uptake of oxygen which where 28%, 32%, and 23% by weight, for Gedling, Cresswell, and Cortonwood Silkstone coals respectively). All three insoluble residues were lustrous and hard.

The insoluble residues were examined by DRIFT spectroscopy, (Fig. 6.2 to 6.4) The spectra show that the three oxidised coals follow the typical rank trends, for example, the residues appear more aromatic as we moved from Gedling to Cortonwood Silkstone coal, (this is despite the fact that the oxidant should destroy aromatic centres), they also appear to be slightly more aromatic in nature when compared with

Fig.6.2 DRIFT Spectrum Of The TFPA Oxidised Insoluble Residues Of Gedling Coal.

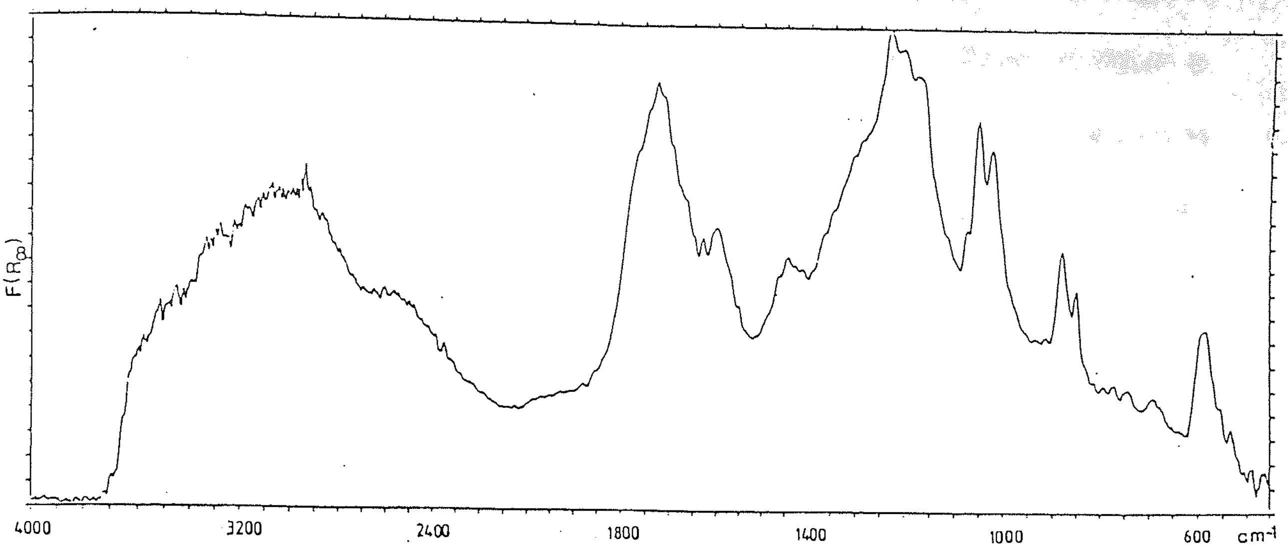


Fig.6.3 DRIFT Spectrum Of The TFPA Oxidised Insoluble Residues Of Cresswell Coal.

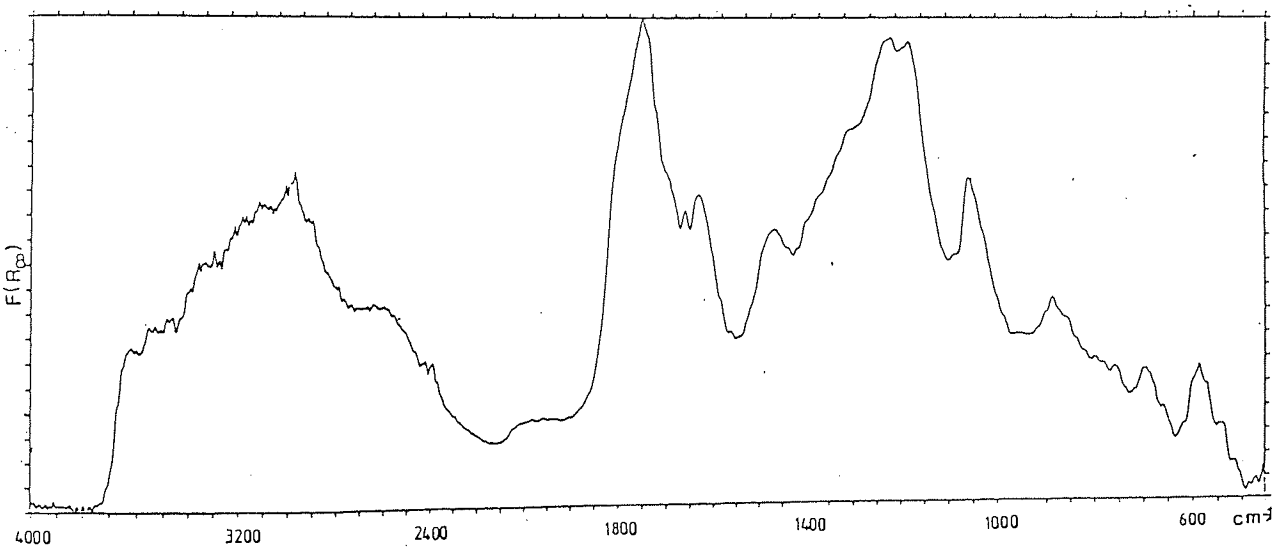
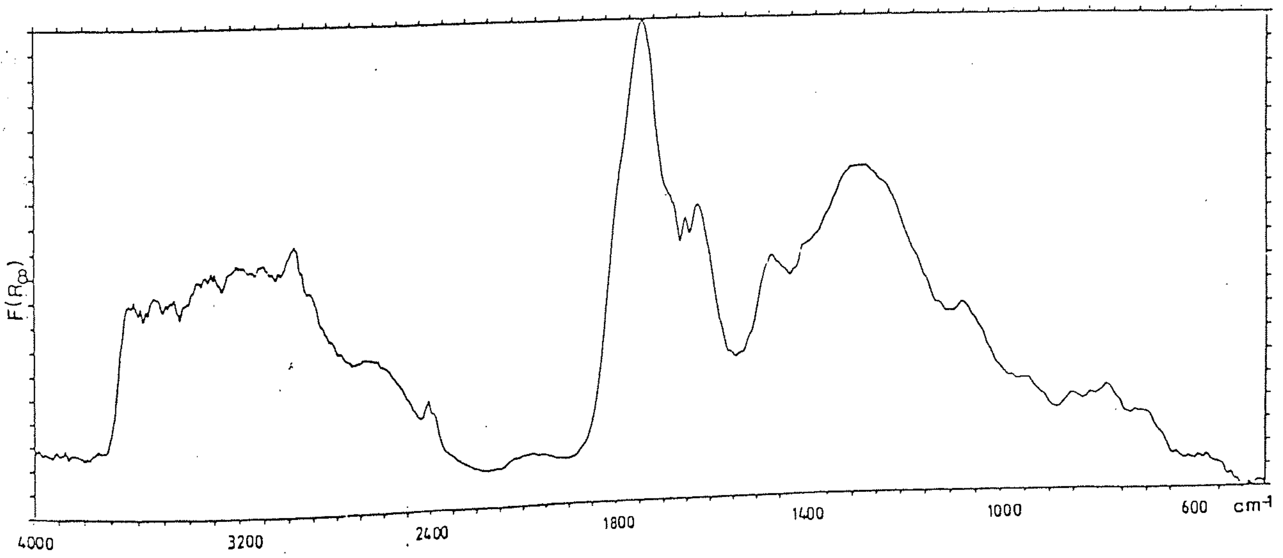


Fig.6.4 DRIFT Spectrum Of The TFPA Oxidised Insoluble Residues Of Cortonwood Silkstone Coal.

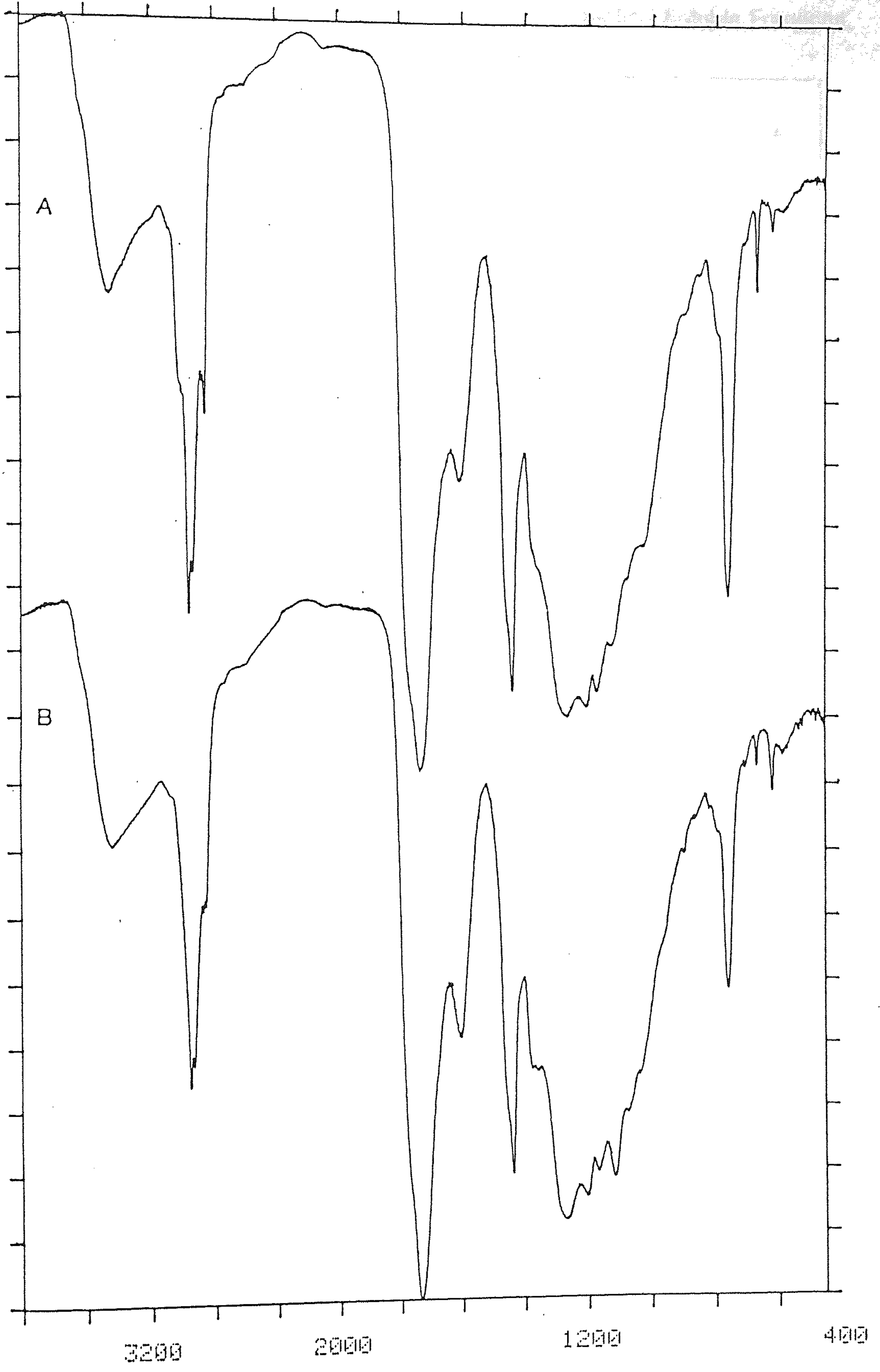


the unoxidised coals (Figs. 3.2 to 3.4) however the C–H stretching band for the oxidised coals tend to be hidden within the large hydrogen bonded OH peak making it difficult to quantify. Again this increased aromaticity is surprising since TFPA is supposed to destroy the aromatic material. The carbonyl peaks, which are very broad (between 1836cm^{-1} and 1638cm^{-1}) indicates the presence of carboxylates, carboxylic acids, and various ketone functions. If we compare the intensity of the carbonyl peaks for the three coals with that of the ether functions (1400cm^{-1} to 1095cm^{-1}) it is apparent that the carbonyl peak becomes relatively larger as the rank of the coal increases. It was also noted that the peaks at 1056, 1028, 833, 854, and 588cm^{-1} almost disappeared as the rank of the coals increased. These changes in the functional group distribution of the insoluble cores, after TFPA oxidation, may account for the large difference in solubilities between oxidised Gedling coal and the two higher ranked coals.

The IR spectra of the TFPA soluble products (after esterification with BF_3/methanol complex) are shown in Fig. 6.5 A and B. It would appear from the spectra that the soluble fractions are very similar to each other, with the lower ranked coal appearing more aliphatic, as expected. Although esterification had clearly taken place, some hydroxyl functionality remained, probably in the form of alcohol groups, since any phenols present or formed during the oxidation would have promoted the TFPA oxidation and therefore been destroyed.

The GC-MS TIC's of the soluble esterified fractions (Fig. 6.6 A to C) like the IR spectra show the soluble fractions to be very similar, but it should be noted that a large number of the peaks in the chromatographs could not be assigned to any particular compound, based on the mass spectra/retention time. From an examination of the mass spectra it is apparent that not all the aromatic material is destroyed by the modified TPFA oxidation.

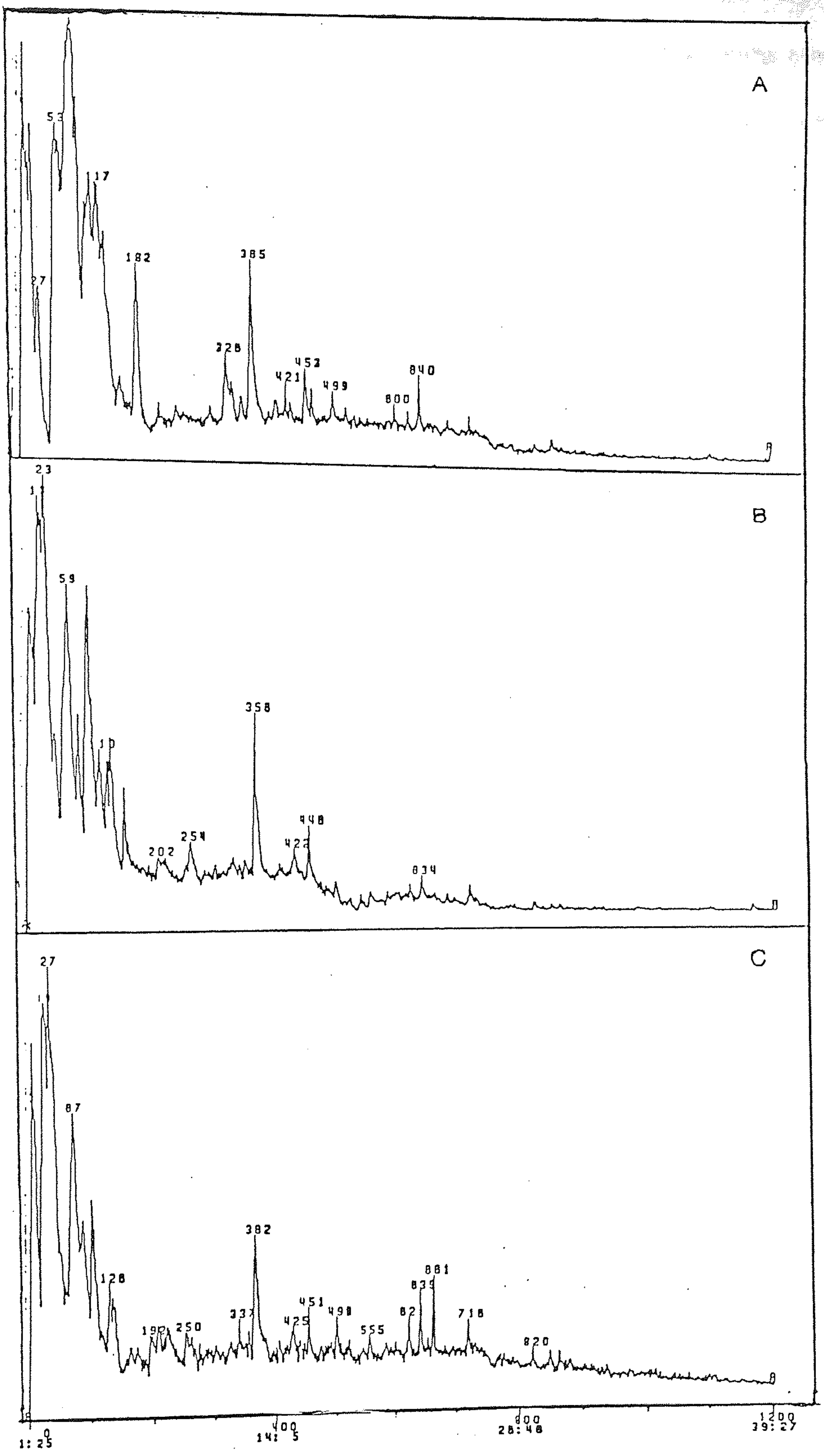
Fig.6.5 IR Spectra Of TFPA Oxidised And Esterified Soluble Fractions.



A) Gedling Coal

B) Cortonwood Silkstone Coal

Fig.6.6 GC-MS TIC's Of TFPA Oxidised And Esterified Soluble Fractions.



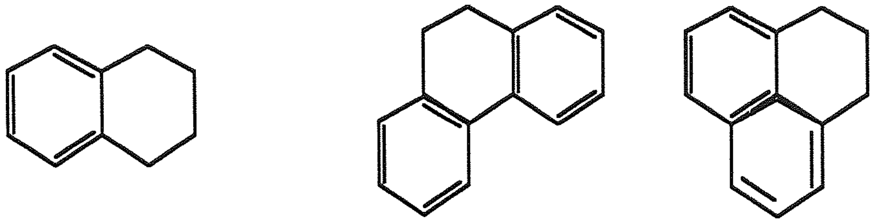
A) Cortonwood Silkstone Coal

B) Cresswell Coal

C) Gedling Coal

Compounds which were identified included the dibasic aliphatic acids,(mono-, di- and tri-) benzene carboxylic acids and naphthoic acid. Low concentrations of long chain carboxylic acids and 1,2-cyclohexenedioic acid were also found (i.e most of the products appear to come from hydroaromatic centres within the coal). Typical parent structures for three of the major products, the diacids ($HO_2C{-}(CH_2)_n{-}CO_2H$,) are shown in fig. 6.7

Fig. 6.7 Possible parent structures for the diacids identified by GC-MS



n=4 n=2 n=3

The ^{13}C-CPMAS-NMR spectra of the TFPA oxidised insoluble residues, and the data derived from them, (Fig. 6.8 A to C and Table 6.1), show even more clearly than the IR spectra (Fig. 6.2 to 6.4) the aromaticity changes on oxidation. When the NMR spectra of the TFPA oxidised insoluble fractions are compared with those of the unoxidised samples (Fig. 4.6 A to C) it is apparent that during the oxidation most of the methoxy groups are removed, i.e. PTC O–methylation is of little use in preventing the over oxidation of phenols when this reagent is used. Comparing the NMR data before and after TFPA oxidation (Tables 4.2 and 6.2) also shows that there is a general increase in the f_a values of the insoluble residues during oxidation, this increase being greater in the lowest rank coal (Gedling), indicating that the insoluble core material is aromatic in nature but deactivated toward the oxidant.

Fig.6.8 ^{13}C-CPMAS-NMR Spectra Of TFPA Oxidised Insoluble Fractions.

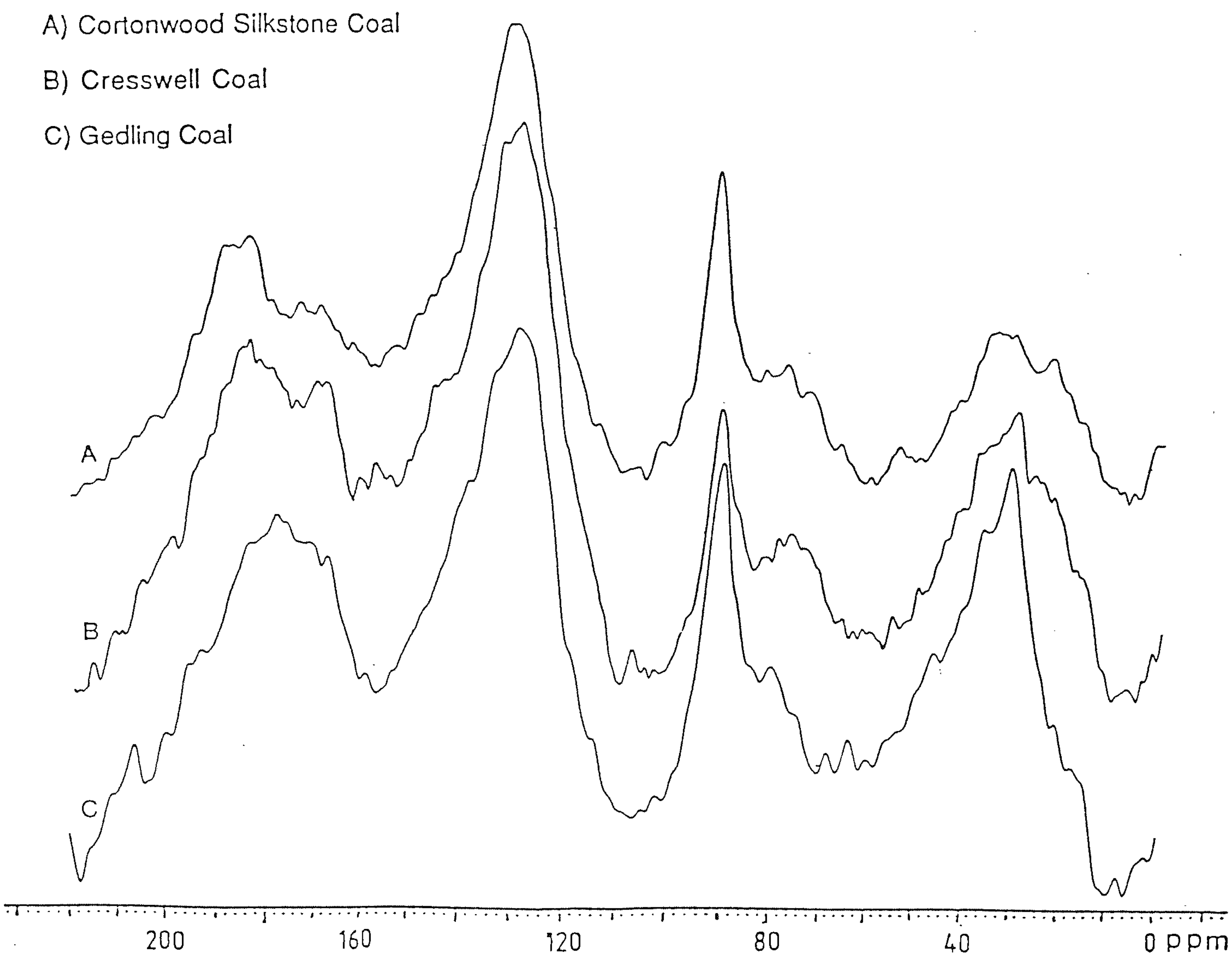


Table 6.1 Some Structural Parameters Derived From The NMR Spectra Of The Extracted / O-Methylated / Re-Extracted TFPA Oxidised Insoluble Coal Fractions.

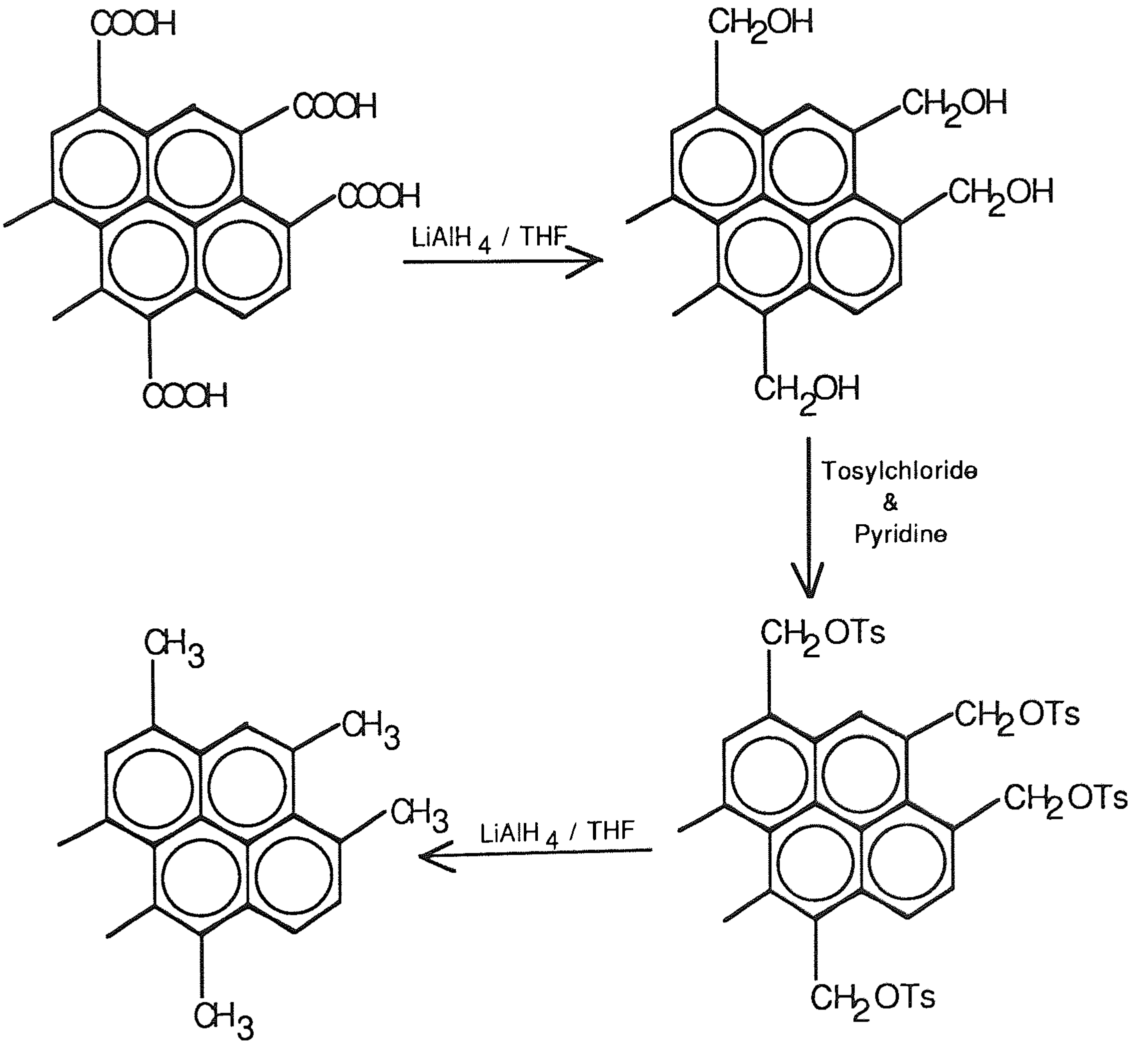
Coal	CH_3 %	$-CH_2-$ %	OCH_3 %	f_a
Gedling	2.5	32.2	0.0	0.58
Cresswell	5.0	25.6	0.0	0.63
Cortonwood Silkstone	3.3	20.0	0.2	0.70

Attack by TFPA appears to preferentially remove methyl groups, (i.e. there is a significant reduction in the CH_3/CH_2 ratios). Since TFPA destroys aromatic structures, we can conclude that most of the methyl groups in British bituminous coals are located on aromatic systems . The methyl groups which remain would be expected to be located on the larger aromatic systems, as it is only on such systems that sufficient deactivation (in the form of carboxylic acid groups) could develop to prevent the methyl groups removal or the solubilisation of the partially oxidised products.

The complex nature of the spinning side bands in the NMR spectra, around 180ppm indicates that a large number of various types of carbonyl group have been created, however because of interference from the side bands it was not possible to quantitatively estimate the amounts formed during the oxidation. Similarly structures which may be due to the creation of ethers could not be quantified because of the presence of the spinning side band at around 80ppm, and the peak at 90ppm. This latter peak is due to the delrin polymer used in the sample holder. Total Side band Suppression (TOSS) would remove the problem of the side bands, but was not available at the time the spectra were obtained, (TOSS may also introduce errors into the ^{13}C-CPMAS-NMR experiments making them less quantitative).

In order to test the hypothesis that the insoluble oxidised cores consisted of inactivated larger aromatic clusters, as suggested by Mc Ginnis and co-workers(190), we have developed a procedure to remove the acid groups, by reducing, tosylating and re-reducing the TFPA oxidised insoluble fractions (see fig. 6.9). Tosylation with the aid of a PTC (Tetrabutylammonium hydroxide) was unsuccessful probably because of the water that was present which promoted the hydrolysis of the tosyl group back to the alcohol.

Fig. 6.9 Reduction / Tosylation Reaction Sequence



It was found very difficult to remove all the hydroxyl groups from the reduced residues possibly because of steric hindrance. The ^{13}C-CPMAS-NMR spectra of Cortonwood Silkstone, TFPA oxidised per-tosylated and reduced, coal is shown in Fig. 6.10. The lower trace is an empirically enhanced spectrum where the lines are narrowed by a factor of 1/pRE (where RE = 0.00086) and multiplied by a Gaussian function e^{-t^2/AF^2} (where AF = 0.001).

Comparing the NMR spectra of the TFPA oxidised coal (Fig. 6.8C) with that of the per-tosylated and reduced sample it was clear that, (1) the tosylation/reduction reaction sequence had completely removed the carbonyl functions, (2) there was a reduction in the shoulder of the aromatic peak between 150ppm and 163ppm, (normally assigned to ArOH, $ArOCH_3$ and Ar-O-Ar functions), and (3) there was an increase in the number of methyl groups detected at around 22ppm. The peak observed at 90ppm was not due, as first thought, to Delrin (a polymer used in the sample holder), nor was it due to fluorinated carbons in our sample, since we would have expected a reduction in the size of the 90ppm peak after per-tosylation and reduction, not an increase. Ethers and diethers, however also give rise to a signal in this region and it may be possible that during the reduction, tosylation reaction sequence we condense hydroxyl functions which are in close proximity to each other. The NMR spectra suggests that a very large number of these ether groups were created during the reaction sequence. The IR spectrum of the same sample (Fig. 6.11A), however shows only a small increase in the peak intensities due to ethers but this may be because of the non-dipolar nature of the ether groups and therefore its low IR activity. The IR spectra on the other hand does show that the intended addition of methyl groups had taken place. Thus the above reaction sequence shown in Fig. 6.9, can be considered at least partially successful.

Fig.6.10 ^{13}C-CPMAS-NMR Spectra Of TFPA Oxidised Per-Tosylated And Reduced Cortonwood Silkstone Coal.

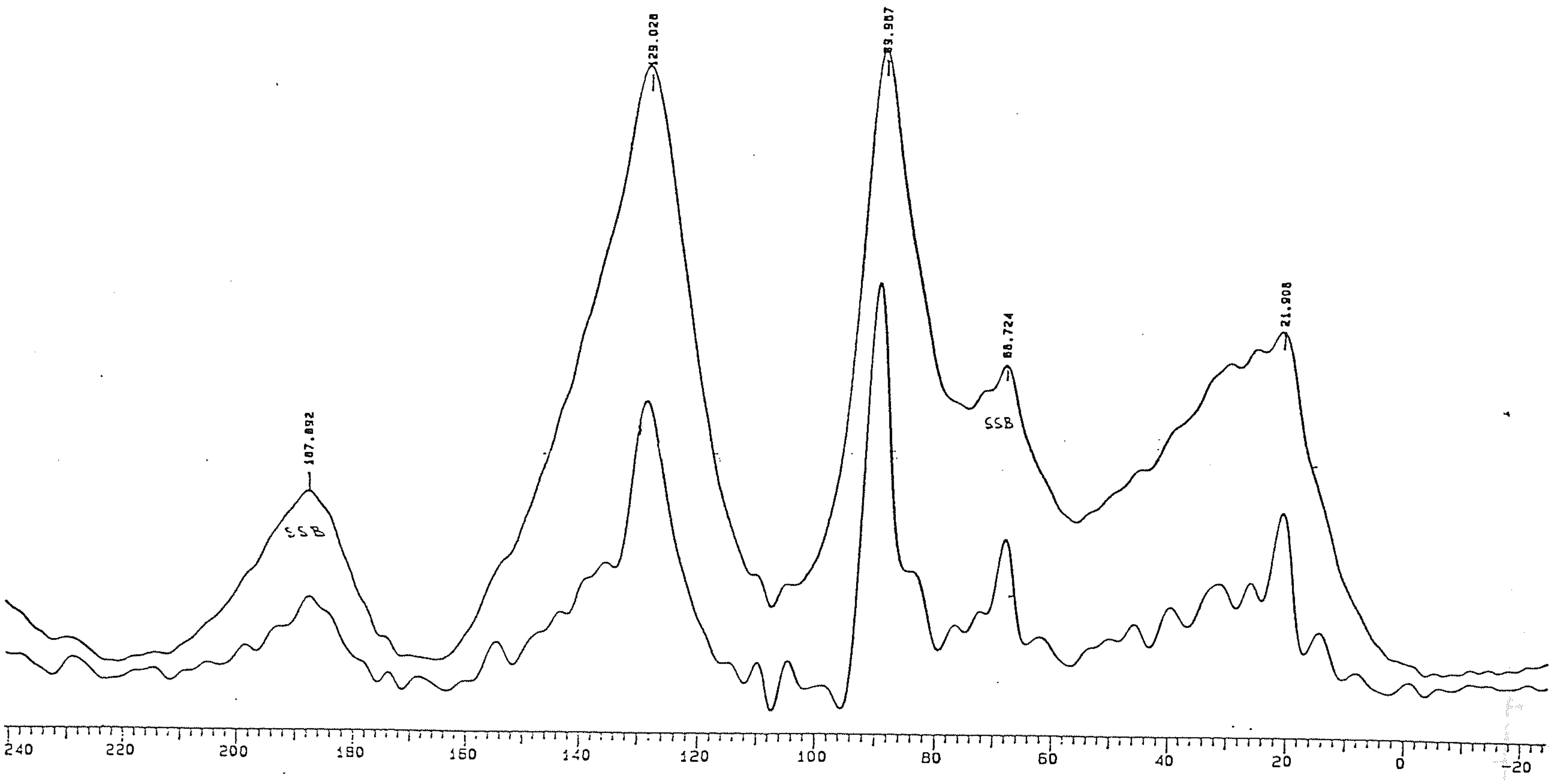
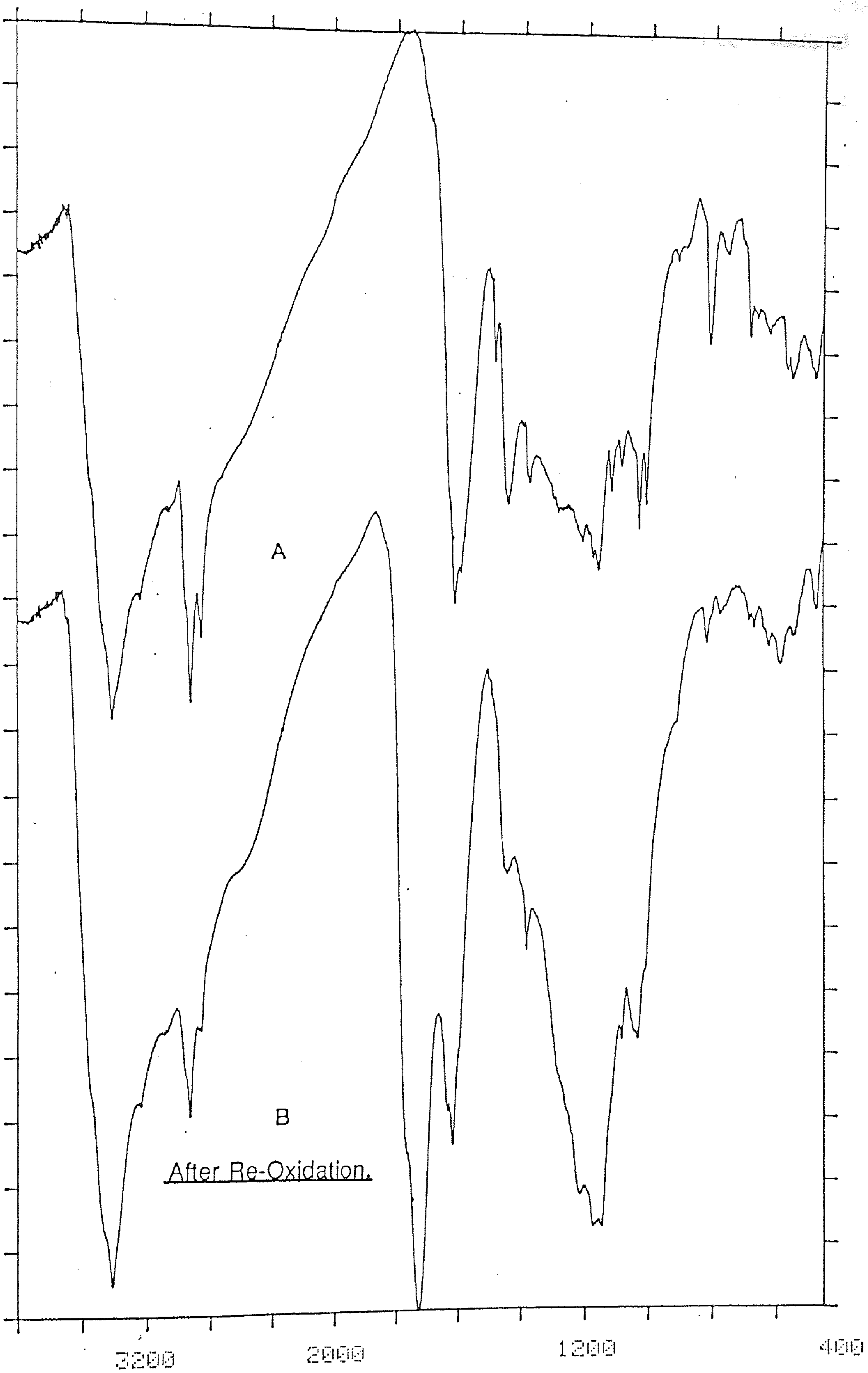


Fig.6.11 IR Spectra Of The TFPA Oxidised Tosylated And Reduced Cortonwood Silkstone Coal Before And After Re-Oxidation.

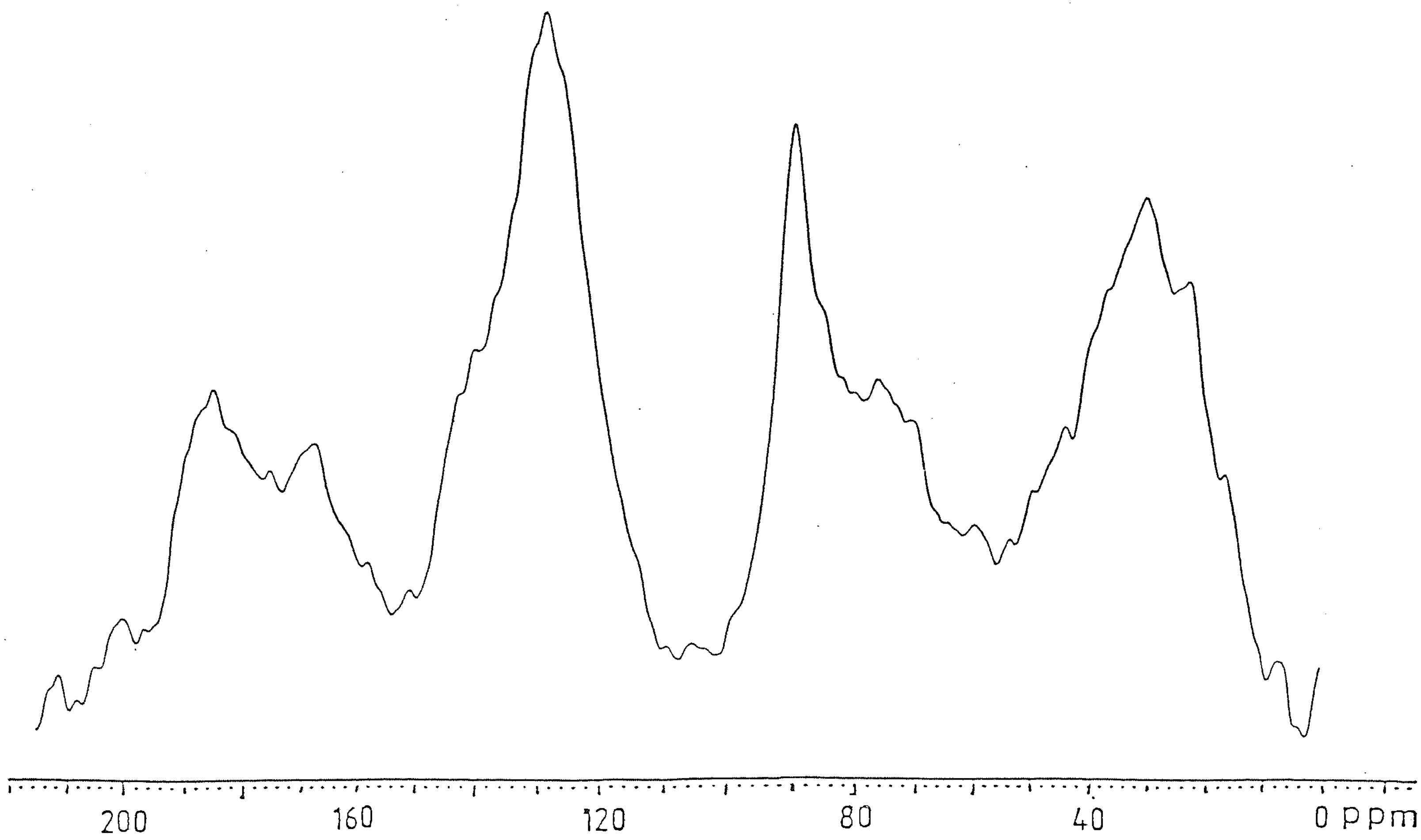


A second TFPA oxidation of the per-reduced and tosylated insoluble fraction (see Fig 6.11B for the IR spectra) was carried out to determine if it was now possible to solublise more of the coal. It was found that a further 55% of the coal core material could be taken into solution, thus it would appear that by removing the carboxylic acid groups, and replacing them with the activating methyl groups, a significant amount of a higher rank coal can be further solublised (Cortonwood Silkstone coal was only 20% soluble in the first TFPA oxidation). Thus these observations provide supporting evidence for the hypothesis of McGinnis and co-workers(193).

The reduction tosylation procedure could in principal be repeated several times resulting in more of the coal being degraded. Thus a technique has been developed whereby most of a high rank coal (normally difficult to oxidise) can be almost totally solublised by an oxidant such as TFPA.

Comparing the IR spectra of the insoluble residue after re-TFPA oxidation (Fig. 6.11B) with the per-tosylated and reduced sample (Fig. 6.11A), It is clear that after the second TFPA oxidation there has been a dramatic increase in the aromaticity of the insoluble material, (i.e. the 1450cm^{-1} absorption (due to CH_2 groups) is reduced relative to the 1600cm^{-1} peak). It is also clear from these IR spectra that the absorption peak due to ethers (centred at ~1200cm^{-1}) has a greatly increased intensity, this tends to confirm our tentative assignment of the NMR peak at 90ppm in Fig 6.8 as being due to ether groups. The ether functions would be relatively inert to the oxidant (TFPA) and would therefore be concentrated after removal by solvent extraction of all the solublised material. A substantial amount of the added methyl groups appear to survive the second oxidation intact but not all as can be seen from a comparison of the ^{13}C-CPMAS-NMR spectra of the reduced/tosylated sample (Fig. 6.10) with the re-oxidised sample (Fig 6.12), the evidence does suggest however that in the second stage

Fig.6.12 ^{13}C-CPMAS-NMR Spectra Of Re-TFPA Oxidised Cortonwood Silkstone Coal.



oxidation some of the hydroaromatic bridges which survived the first oxidation are being removed from the activated aromatic systems. Interestingly there is no evidence in the IR spectra for the formation of new carboxylic acid groups during the second oxidation, (the hydroxyl peak at 3300cm^{-1} remains sharp), oxygen however has been added apparently as carbonyl and ether functions. Given the highly aromatic nature of this insoluble oxidised fraction it is reasonable to assume that these are most likely to be quinones and diaryl or cyclic ethers.

Because of the number of steps involved in the per-reduction tosylation sequence, this method is very time consuming, so that we were unable to evaluate its applicability to the lower ranked coals, however it is reasonable to assume that they would behave similarly, since once oxidised with TFPA all the insoluble residues should be deactivated by the addition of carboxylic acid groups. The tosylation/reduction sequence of reactions, while meeting our first objective of allowing high ranked coals to be solublised to a much greater extent than would otherwise normally be possible, does appear to create other functional groups within the coal, which are largely inert to the TFPA oxidant. Therefore some form of model compound studies needs to be undertaken in order to ascertain the effects of formation of such groups on the types of products produced during the re-oxidation.

6.3 DISCUSSION

The TFPA oxidation has in the past only been applied to low and medium rank coals. This is because as the rank of the coal increases the amount of material solublised by the TFPA oxidant is reduced. We have developed a method whereby the deactivating carboxylic acid groups formed during the oxidation can be removed, and replaced with activating methyl groups. The coal can then be re-oxidised so that more soluble material is produced. By repeating the reduction, tosylation, and TFPA oxidation steps it is thought that eventually all the coal would be degraded and brought into solution for easier analysis. The problem of forming unreactive ethers during the tosylation and reduction steps will, however require further study, (in particular with model compounds), in order to determine if such groups affect our interpretation of the results.

Although most of our observations from the TFPA oxidation of British bituminous coals could be predicted from an examination of the literature. The results have established that there is a clear distinction between the Gedling coal and Cresswell and Cortonwood Silkstone coals. It was noted previously that Gedling coal had anomalous extraction properties compared with the other two coals (see chapter 3), in that case however it appeared the physical structure of the lower ranked coal was responsible and O-methylation seemed to remove the distinction in the types of material extracted (see chapter 4). In the case of the TFPA oxidation the coals were already O-methylated, so the difference in the solubilities of the three coals after oxidation is more likely to be due to changes in the chemistry of the coals, in particular the lower aromaticity of Gedling coal. The solubility changes with coal rank, during oxidation, tends to suggest that there are few large aromatic clusters (i.e greater than four fused rings) in low rank British bituminous coals. Although this is not a surprising conclusion in view of the current theories of coal structure, this result does yield independent if indirect supporting evidence.

Our work on the TFPA oxidation insoluble products has shown that there is a change in the functional group distribution in the oxidised residues, with carbonyl groups being formed in preference to ethers as the rank of the coal increases. This may indicate differences in the mode of attack of the electrophile (OH^+) in the low and high rank coals, and account for the solubility differences noted between the coals.

CHAPTER 7.

PTC / POTASSIUM PERMANGANATE OXIDATION

7.1 INTRODUCTION

Potassium permanganate is a powerful oxidant of organic compounds, but its ability to react with particular functional groups is dependent on the pH of the reaction medium(194, 195, 196, 197). In general the oxidation of organic compounds is accelerated in an alkaline solution, this is due largely to changes in the substrate. Permanganate has its lowest reactivity in neutral and weakly acidic solutions but in strongly acidic media oxidation is again rapid, (this time it is the oxidant which is altered to the much more reactive acid, $HMnO_4$). As a rule organic compounds react with permanganate in the order, anions, neutrals, cations, as below;

$$Z^{2-} > HZ^- > H_2Z > H_3Z^+$$

In order to predict which functional groups will oxidise under a particular set of conditions, it is useful to know the ionization pattern of the functional group(s) in an organic compound. At high pH values some organic functions will be in an ionised, (anionic) form. The active oxidant, under these conditions is also anionic, (MnO_4^-), we would therefore expect a reduction in the rate of oxidation because of ionic repulsions between the two anions, the oxidation rate, however increases because of the low enthalpies of activation for such systems.

The main disadvantage of using potassium permanganate as an oxidising agent, is that most non-polar organic compounds are insoluble in aqueous solutions, and potassium permanganate is insoluble in many organic solvents, therefore in many systems reactions can only occur at the phase boundary. A few organic solvents can be used because $KMnO_4$ is partially soluble in them and the solvents oxidise at a slower rate than the substrate. Examples of organic solvents which have been used in this way are acetic acid and tertiarybutyl alcohol. Alternatively, this mutual insolubility problem, between the oxidant and the substrate can be tackled by the application of PTC techniques(198, 199). The organophilicity of the phase transfer cation can be used to transport the permanganate anion into a non-polar solvent. A review of such phase transfer assisted permanganate oxidations is given by Lee(200).

Typically the quaternary ammonium, phosphonium, or arsonium permanganate, (Q^+MnO_4) is prepared insitu by anion exchange. [The PTC permanganate salt can be isolated but it has been reported that it undergoes spontaneous and explosive ignition(200)].

$$Q^+X^- + K^+MnO_4 \rightleftharpoons Q^+MnO_4 + K^+X^-$$

The PTC/permanganate complex then migrates into the organic phase (usually a solvent such as dichloromethane) where it exists as an ion pair. The anion is then free to react with the substrate in the organic phase.

Below are listed some of the major conclusions reached in past permanganate oxidation studies on various types of compounds, they are included here because the results from such work can be used to model the reactions in coals.

Alkanes Prior to the advent of PTC oxidation, saturated compounds could only be oxidised with permanganate if an inert polar substituent was attached to the alkyl chain. (The enhanced reaction rate was a result of the polar group increasing the solubility of the alkane in the aqueous phase(201)). It has been suggested(202) that the first step in the oxidation of alkanes by MnO_4, is the abstraction of a hydrogen atom. The resulting radical pair,which will be trapped in a solvent cage, then recombines to form the alkyl hypomanganate ester, (see step 1 of the reaction sequence on P156). The final stage is the decomposition of the ester to form the products, (see steps 2 to 4 on P156).

$$R_3CH + MnO_4^- \longrightarrow [R_3C.MnO_4H^-] \longrightarrow R_3C\text{-}O\text{-}MnO_3H^- \qquad (1)$$

$$R_3C\text{-}O\text{-}MnO_3H^- + H_2O \longrightarrow R_3COH + H_2MnO_4^- \qquad (2)$$

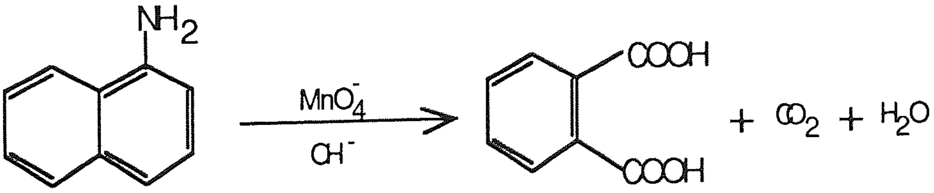
$$R_3C\text{-}O\text{-}MnO_3H^- \longrightarrow R_3C^+ + HMnO_4^{2-} \qquad (3)$$

$$R_3C^+ \longrightarrow R_3COH \qquad (4)$$

(The manganese(V) quickly disproportionates)

Schmidt and Schafer(199) studied the PTC permanganate oxidation of several alkanes. From the nature of the products they observed it appeared that tertiary C-H bonds are more easily cleaved than secondary C-H bonds. The secondary C-H bonds being 15 to 25 times less reactive towards the oxidant.

Arenes Aromatic rings are normally quite resistant to oxidation by permanganate. However if strong electron donating groups are present, such as phenolic hydroxyl groups or amines, ring rupture may occur, followed by further oxidation of the primary products. Ultimately the rings are oxidised to CO_2 and water. An example(203) of this type of vigorous oxidation is shown below.



In effect this over oxidation means the loss of structural information. Polycyclic aromatics can be degraded using alkaline permanganate without the presence of any activating substituents(203). Under PTC conditions the polycyclic arenes are often only converted to the corresponding quinones(200).

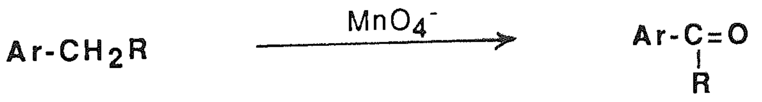
<u>Alkylarenes</u> Alkylarenes undergo oxidation more readily than arenes, because electron donating groups promote the oxidation, e.g. benzene, toluene, and xylene are progressively more reactive to permanganate.

In the non-catalysed permanganate oxidation alkyl substituents are converted to the carboxylic acid at the benzylic position,(reaction 1), except in the case where there is a tertiary hydrogen on the benzylic carbon, in this case the tertiary alcohol results, (reaction 2).

$$\mathrm{Ar\text{-}CH_2R} \xrightarrow{\mathrm{MnO_4^-}} \mathrm{ArCO_2H} \qquad (1)$$

$$\mathrm{Ar\text{-}CHR_2} \xrightarrow{\mathrm{MnO_4^-}} \mathrm{ArCR_2OH} \qquad (2)$$

Oxidation is initiated at the benzylic position by hydrogen abstraction, forming a resonance stabilized benzyl radical, this then undergoes further steps to give the product. In some cases radical coupling reactions have been noted(204). Schmidt and Schafer(199) studied some phase transfer assisted permanganate oxidations of alkyl arenes and again found that the initial attack was at the benzylic position, but when a PTC is used, the benzyl alcohols produced reacted further to give the phenyl ketones not the carboxylic acid, (reaction 3).



$$\mathrm{Ar\text{-}CH_2R} \xrightarrow{\mathrm{MnO_4^-}} \mathrm{Ar\text{-}}\underset{\substack{|\\ \mathrm{R}}}{\mathrm{C}}\mathrm{=O} \qquad (3)$$

This greater retention of the arenes structure, upon PTC/permanganate oxidation, is one of the major advantages of this technique for the elucidation of coal structures.

Ethers Under PTC conditions aliphatic ethers undergo oxidation via a hydrogen atom transfer reaction, to form the corresponding ester(199), but diaryl ethers are reported to be largely unaffected by the oxidant. Since the British bituminous coals selected for study appear to have no dialkyl ethers in them, (see chapter 5), most of the ethers present in the three coals will be unreactive towards the PTC/permanganate reagent.

7.1.1 PERMANGANATE OXIDATION OF COALS

The early work on oxidative degradation of coals using potassium permanganate was reviewed by Van Krevelen(1) and Lowry(205, 206), more recent studies have been reported by Salbut and co-workers(207), Benerjee(208, 209), and Hayatsu and co-workers(210). In the great majority of these investigations, oxidation was carried out in basic media.

It is clear from the dicussion of permanganate oxidation on relatively simple organic compounds, (section 5.1), that oxidation under alkaline conditions has some major disadvantages as a probe to characterise coal. For example, the over oxidation of phenolic rings, polynuclear aromatic systems, and heteroaromatic structures(211), will occur, producing products such as CO_2 acetic acid, and oxalic acid. These small molecules are almost useless for the purpose of investigating the structures in coal. Even in those cases where the phenolic hydroxyl groups are protected, (e.g. by O-methylation), over oxidation can still occur in basic media(212, 213).

Thus in many oxidation studies much of the structural information may have been lost. The loss of this data, inturn, could have led to a misinterpretation of results, particularly where quantitative results have been quoted. Even when the permanganate oxidation has been carried out in neutral solutions, (i.e. under milder conditions), the results are still suspect, since it has been reported that the pH of the aqueous oxidizing medium becomes basic as the reaction proceeds(210).

The PTC/permanganate oxidation of coal offers a milder and more selective degradation technique while maintaining a reasonable rate of reaction. The only example in the literature to date, applying PTC/permanganate oxidation to degrade coals was reported by Chakrabartty(27), in this case however there was no attempt to examine the reagents suitability as a probe for the investigation of the aromatic structure of coal.

7.2 MODEL COMPOUND STUDIES

When evaluating a new or modified degradation process, it is always advisable to first characterise the reaction by using model compounds. This is done so that the oxidation products can be related back to the parent structures in an unambiguous way. To this end we have oxidised sets of alkanes, arenes, alkylarenes, hydroxyl containing compounds, and ethers, under the same conditions as those used for the phase transfer catalysed permanganate oxidation of the three British bituminous coals (see section 7.3).

In order to facilitate the analysis of the oxidised fractions, the soluble products were treated with a 14% BF_3/methanol complex to esterify any carboxylic acids formed(214). A method was also developed by us, to remove the PTC, which contaminated these solutions, as it had been observed previously, (see chapters 4 and 5) that the PTC's used, would interfere with the analysis of the oxidized compounds. The method employed a strong cation exchange resin to remove any bases in the soluble fractions. It has been established, by IR, GLC, and NMR analysis, that this technique removes the last traces of the PTC from the soluble oxidised products.

The amount of CO_2 produced during the PTC/permanganate oxidation reaction was estimated by trapping the gas with barium hydroxide. It was found however that only 1,7-dihydroxynaphthalene produced CO_2 in any significant quantity.

Two different temperatures were used to oxidise the model compounds, ambient temperature, (where it was found that a number of the compounds were unreactive), and 61°C, (the solvent was changed from dichloromethane to chloroform and the mixture refluxed). In this latter case only a few of the less reactive compounds, (i.e. unreactive at room temperature) were tried.

The results obtained from the five groups of compounds are given in Table 7.1. From an examination of this data certain trends can be seen, these trends are listed below:-

1) Alkanes and arenes are for the most part unreactive to the oxidant at room temperature. At 61°C the branched alkane and phenanthrene undergo oxidation but naphthalene remains unreactive. These results are in good agreement with the literature(200).

2) Alkyl substituents on aromatic rings are much less reactive to the PTC/$KMnO_4$ oxidation than they are to the more traditional alkaline permanganate oxidation method. For high conversions to be achieved the rings must be activated as in the case of 1,3,5-trimethylbenzene. When attack by the oxidant does occur, it is at the expected benzylic position. Oxidation at the higher temperatures also results in higher yields of the oxidation products.

3) The cyclic hydroaromatic compounds yield the corresponding ketone or quinone, the exception being acenaphthene, which like 1,2-diphenylethane fails to react at all. The results for this group of compounds are again in good agreement with the literature(200).

Table 7.1 PTC/$KMnO_4$ Oxidation Of Model Compounds

Model Compounds	Oxidation Product(s)	% Conversion
Alkanes		
n-dodecane	No Reaction	0
Squalane	No Reaction	0
Arenes		
Phenanthrene	phenanthraquinone	2 - 3
Naphthalene	No Reaction	0
1-Phenylnaphthalene	No Reaction	0
9,10-Diphenylanthracene	No Reaction	0
Pyrene	No Reaction	0
Chrysene	No Reaction	0
Alkylarenes		
Toluene	No Reaction	0
Propylbenzene	benzoic acid	15
1,3,5-Trimethylbenzene	mono, di, and tri benzoic acids	100
2-Ethylnaphthalene	2-naphthoic acid	6
1,2-Diphenylethane	No Reaction	0
Acenaphthene	No Reaction	0
Indane	indanone	98
Tetrahydronaphthalene	tetralone	49
9,10-Dihydroanthracene	9,10-anthraquinone	90
Fluorene	9-fluronone	85

Table 7.1 cont. PTC/$KMnO_4$ Oxidation Of Model Compounds

Model Compounds	**Oxidation Product(s)**	**% Conversion**
Hydroxyls		
Benzyl alcohol	benzoic acid	100
1,7-Dihydroxynaphthalene	complex mixture, including some coupled products.	100
Ethers		
2-Methoxynaphthalene	?	14
Dibenzylether	benzoic acid	100
2,3-Dihydrobenzofuran	?	45
1,3-Dimethoxybenzene	Complex mixture of products	100
Diphenylether	No Reaction	0

(? = Products not identified)

4) The hydroxyl groups, as expected, reacted rapidly with the permanganate, and appeared to promote the auto-oxidation of MnO_4^- to MnO_2, (all of the permanganate being consumed within a few minutes). The oxidation of the phenolic compound gave coupling products, and many degradation products, (these were detected by GLC), but surprisingly little CO_2 was produced (<2%). The fact that a complex mixture of products were produced, shows the need to protect the OH functions in coals if structural detail is not to be lost on oxidation by permanganate.

5) Diaryl ethers appear to be inert to oxidation by the PTC/$KMnO_4$ oxidant, alkylaryl ethers are more reactive, but the most reactive appears to be dibenzyl ether. Dialkylethers in general are also reported to be reactive to this reagent(199), but are not thought to be present in any significant quantity in the coals

we selected for study.

If the ring containing the ether function is activated by an electron donating group, for example alkylaryl ethers such as 1,3-dimethoxybenzene, they will undergo rapid oxidation to produce a complex mixture of products. This result also suggests that protecting phenolic hydroxyl groups by O–methylation, will only be effective if the methoxy groups are isolated from other electron donating substituents in the coal matrix.

It is clear from the above model compound studies that the PTC/KMnO4 oxidation of coal should result in a much more selective set of cleavage reactions than conventional alkaline potassium permanganate oxidation. This fact, in conjunction with better analytical techniques should enable us to gain a better understanding of some of the structures present in coals.

7.3 INITIAL PTC/PERMANGANATE COAL OXIDATION STUDIES

Untreated coals were initially oxidised using the PTC/MnO_4^- oxidation method, but it was difficult to identify unambiguously which fragment originated from the polymer-like network and which came from the mobile phase. It was therefore decided to use the THF extracted/O-methylated/re-THF extracted coals. In these samples the majority of the mobile phase has been removed and the phenolic groups are at least partially protected from over oxidation by the PTC/oxidant.

The next set of PTC/permanganate oxidations carried out, attempted to oxidise the three extracted, O-methylated, re-extracted coals in a single step. Examination of the reaction products by IR, GC-MS, NMR, and GPC, however indicated that some oxidation of the primary products had occurred. Therefore in order to eliminate as far as possible this over oxidation, and consequent loss of structural information, it was decided to degrade the treated coals in a step-wise manner. Over oxidation is then prevented by removing the primary products at the end of each partial degradation step. The results from these experiments are detailed in section 7.4.

7.4 STEP-WISE PTC / PERMANGANATE OXIDATION OF COAL

The extensively solvent extracted and O-methylated coals were oxidised in a step–wise manner in order to reduce the possibility of re-oxidation of the primary products, because any over oxidation may confuse our interpretation of the results.

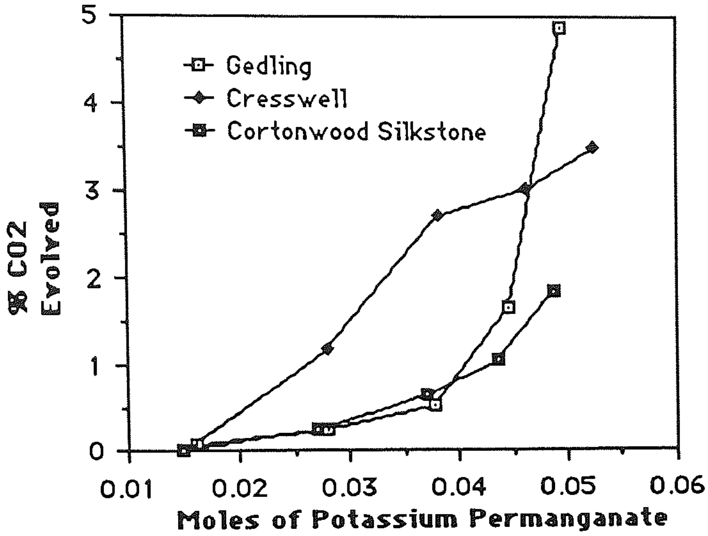
The number of oxidation steps was limited to five, because;

(1) The amount of CO_2 produced during the fifth oxidation step was quite large, at least for Gedling Coal, (see Fig.7.1), and if this was allowed to continue structural information would be lost.

and (2) A quantity of oxidised insoluble material was required to compare with the TFPA insoluble oxidised residues.

It can be seen from the graph showing CO_2 production during the step-wise oxidation, (Fig. 7.1), that the total amount of CO_2 evolved is inversely related to the rank of the coal. Since model compound studies showed that hydroxylated compound were the only substances to produce significant amounts of CO_2, it suggests that hydroxyl functions and/or other strong activating groups, are being created during the oxidation at a faster rate in lower rank coals than in higher rank coals.

Fig. 7.1 The Amount Of Carbondioxide Evolved During The Step-Wise PTC/Permanganate Oxidation Of The Coals



7.4.1 INFRARED SPECTRA OF THE OXIDISED COALS

The infrared spectra of the step-wise oxidised insoluble fractions, are shown in Fig 7.2 to 7.4. From an examination of these spectra it can be concluded that increasing amounts of oxygen were added to the insoluble cores of all three coals, as the number of oxidation steps increased. This was confirmed by elemental analysis. Apart from the increasing size of the carbonyl peak (centred at 1700cm^{-1}), with the increasing number of oxidation steps, all the spectra are remarkably similar to each other. This is despite the differences in coal rank. A plot of the carbonyl peak intensity, (as measured relative to the 1600cm^{-1} absorption), against the amount of potassium permanganate used in the oxidations, is shown in Fig 7.5. It can be seen from this graph that the two highest ranked coals behave very similarly, while Gedling coal appears to show some deviations from the trend.

Fig.7.2 Infrared Spectra Of The Insoluble Fraction Of The PTC/Permanganate Oxidised Gedling Coal.

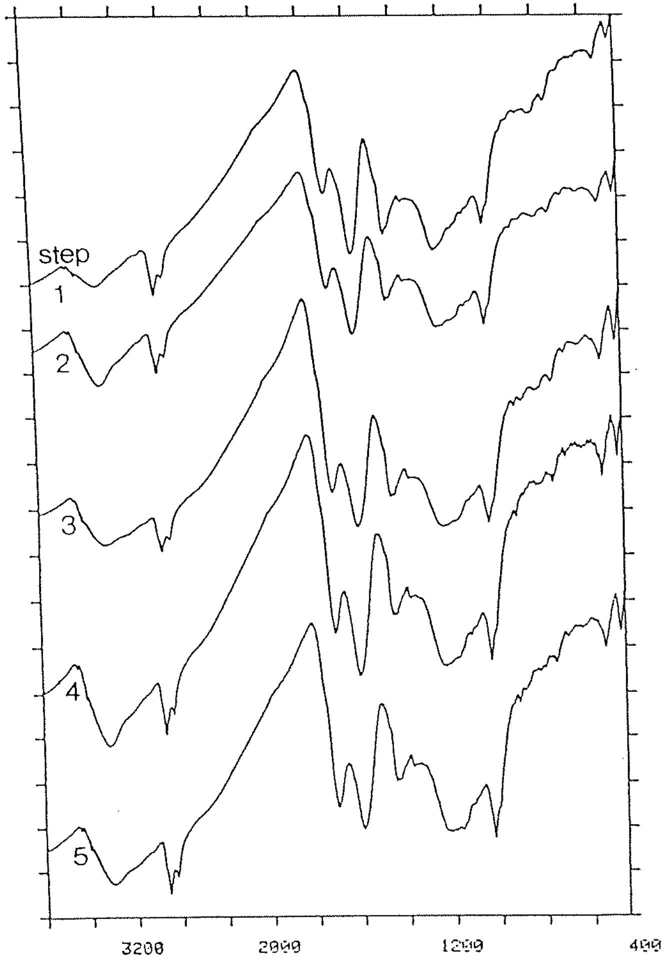


Fig.7.3 Infrared Spectra Of The Insoluble Fractions Of The PTC/Permanganate Oxidised Cresswell Coal.

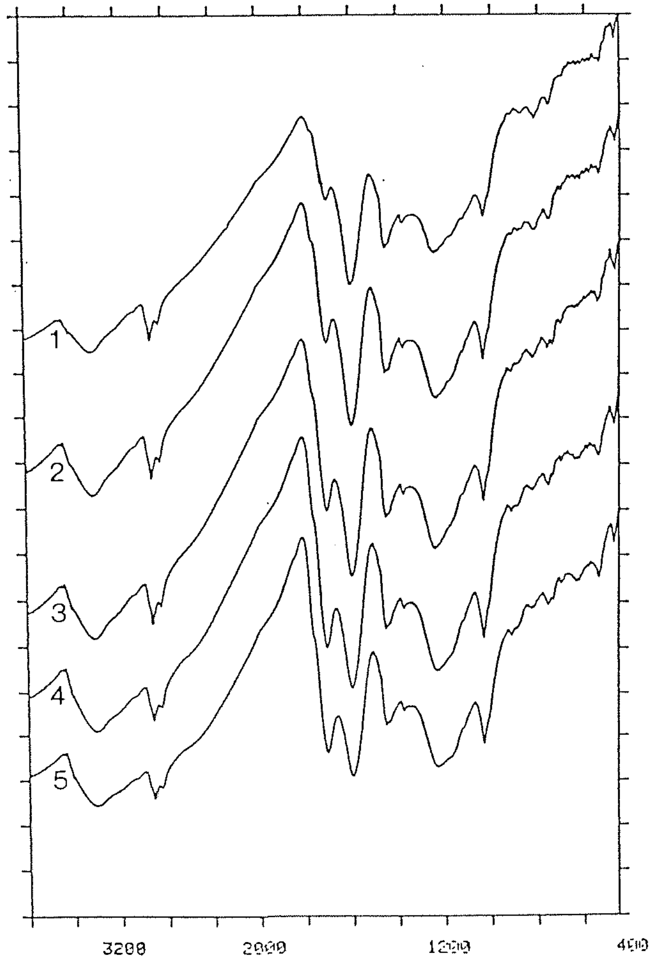


Fig.7.4 Infrared Spectra Of The Insoluble Fractions Of The PTC/Permanganate Oxidised Cortonwood Silkstone Coal.

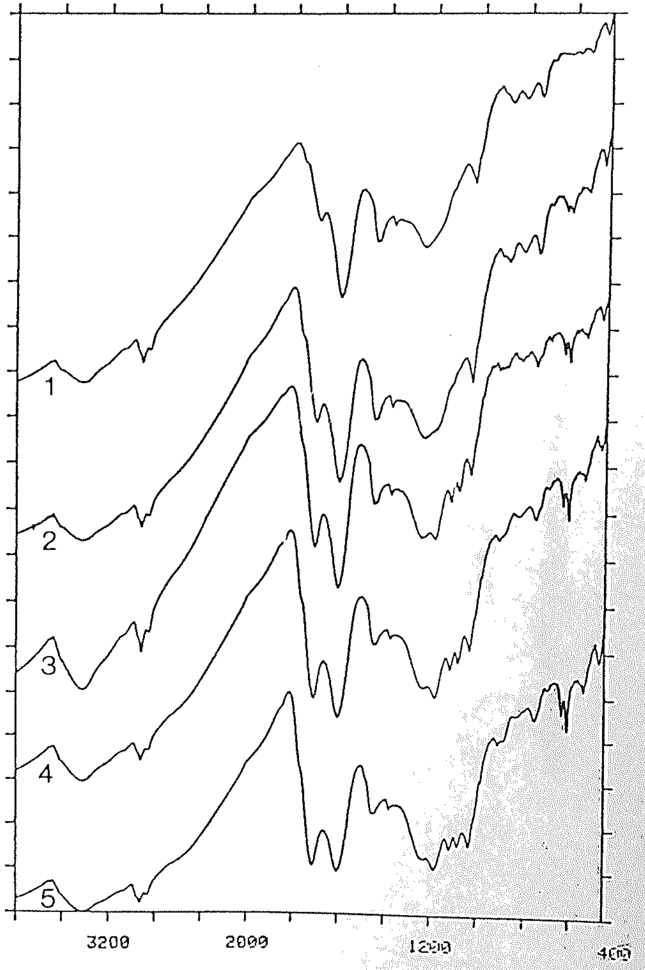
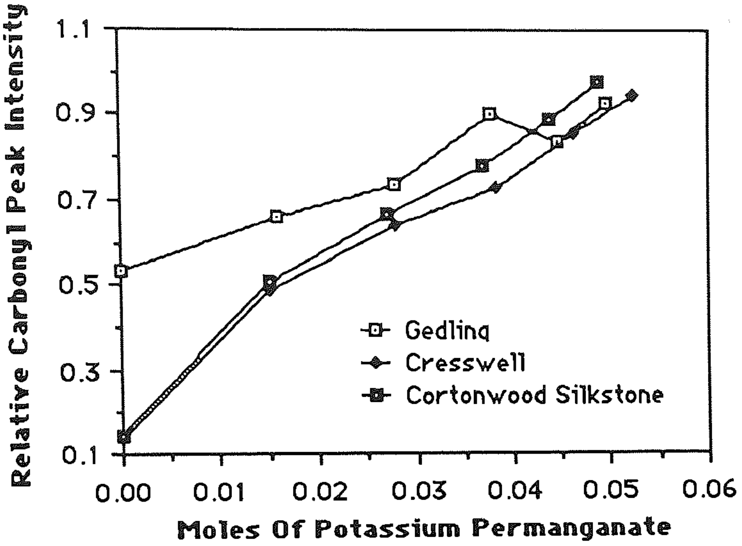


Fig. 7.5 The Increase In Carbonyl Peak Intensity During The Step-Wise PTC/Permanganate Oxidation Of The Coals



In particular Gedling coal had undergone air oxidation, and therefore produced carbonyl functions, during the preparation of the sample, i.e. before step-wise PTC/permanganate oxidation was carried out. The ease with which Gedling coal undergoes air oxidation is likely to be due to the larger number of activating polar groups in this coal compared with the two higher ranked coals.

If we assume that the growth of the carbonyl peak can be used as a measure of the ease of oxidation, then it appears from the data presented in Fig.7.5, that as the rank of the coal increases the coals become harder to oxidise with PTC/permanganate. This is not an unexpected result, since the coals increase in aromaticity with increasing rank and the aromatic rings are largely unaffected by this reagent.

The infrared spectra of the THF soluble oxidation products of the PTC/permanganate step-wise oxidised coals are given in Figs. 7.6 to 7.8. The spectra of all three coals, show a reduction in the $1600cm^{-1}$ absorption, (as measured relative to the $1450cm^{-1}$ peak), as the number of oxidation steps increases, this indicates that the solublised material contains less aromatic material as the number of oxidation steps increases. This observation also suggests that the insoluble core of the coals becomes more inert and aromatic in nature. If this is the case, we would expect to see a significant increase in the aromaticity of the insoluble fractions. The IR spectra of the oxidised insoluble residues, (Fig 7.2 to 7.4), and the ^{13}C–CPMAS-NMR spectra of the insoluble coal fractions, (Fig. 7.9 A to C, section 7.4.2), show increases in f_a values, but they are only small changes.

In a separate infrared experiment, it was observed that the carbonyl absorption at $1775cm^{-1}$, (assigned to the presence of lactones and/or anhydrides), gradually reduced in intensity, over several minutes. At the same time the 'sweet odour' of the soluble oxidised samples disappeared. The loss of this volatile component from the soluble extracts explains the erratic variation in intensity of the $1775cm^{-1}$, carbonyl peaks in Figs. 7.6 to 7.8. The volatile compound or compounds were not identified.

7.4.2 ^{13}C-CPMAS-NMR SPECTRA OF THE OXIDISED COALS

The NMR spectra of the oxidised insoluble residues (Fig. 7.9 A to C) shows that methoxy groups are not removed during the oxidation, i.e the peak at 60ppm remains, and as a fraction of the coal becomes more significant, compared with the samples before oxidation, (Fig.4.6 A to C). From this it can be concluded that the O–methylated hydroxyl groups in the coal are in general on aromatic rings with no other electron donating groups present in the rings,

Fig.7.6 Infrared Spectra Of The Soluble Esterified Fractions Of The PTC/ Permanganate Oxidised Gedling Coal.

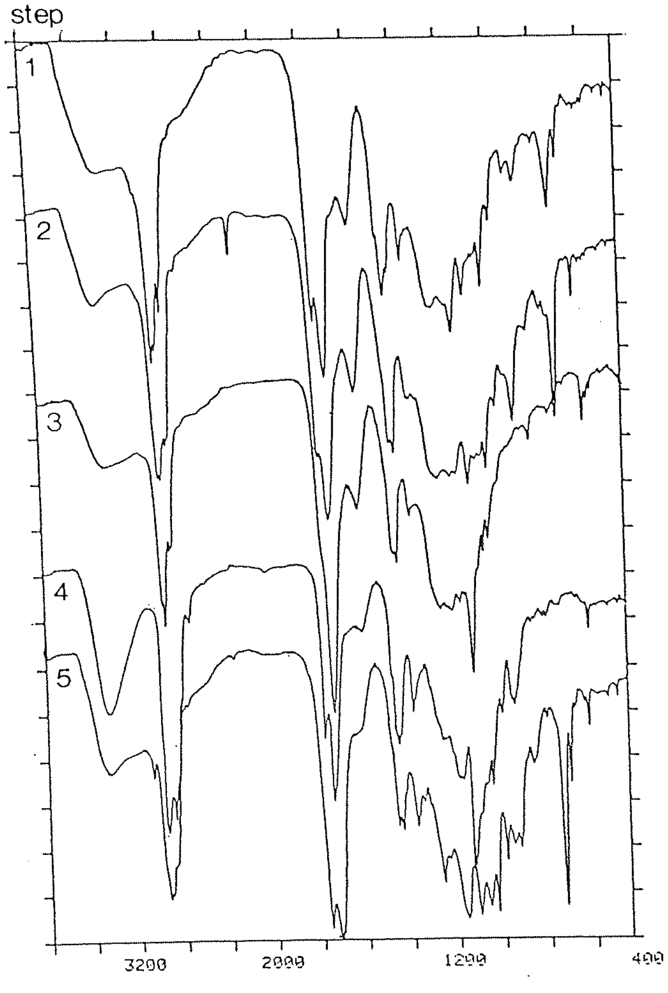


Fig.7.7 Infrared Spectra Of The Soluble Esterified Fractions Of The PTC/ Permanganate Oxidised Cresswell Coal.

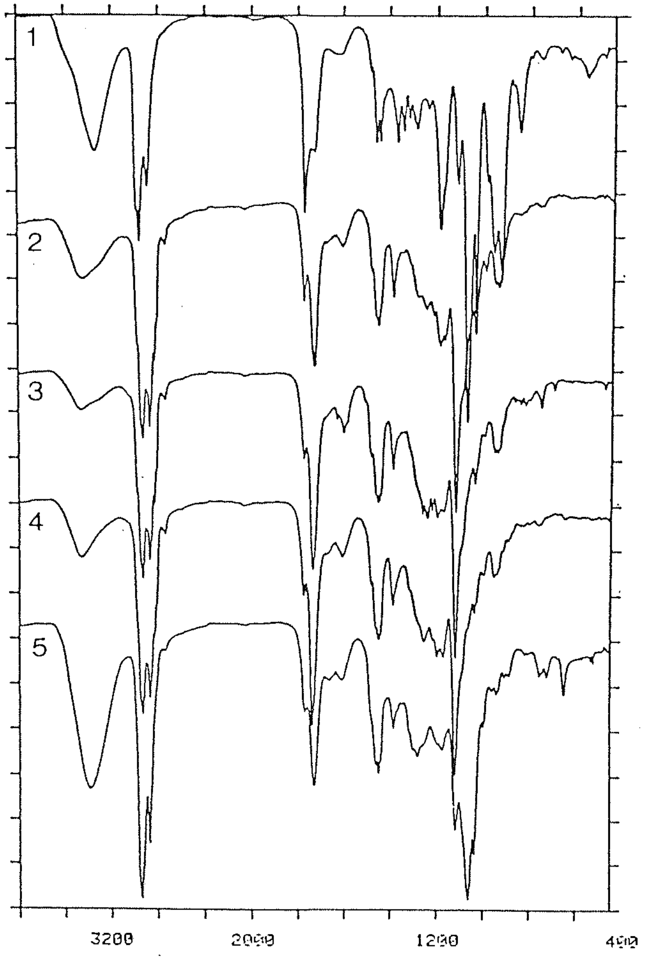


Fig.7.8 Infrared Spectra Of The Soluble Esterified Fractions Of The PTC/ Permanganate Oxidised Cortonwood Silkstone Coal.

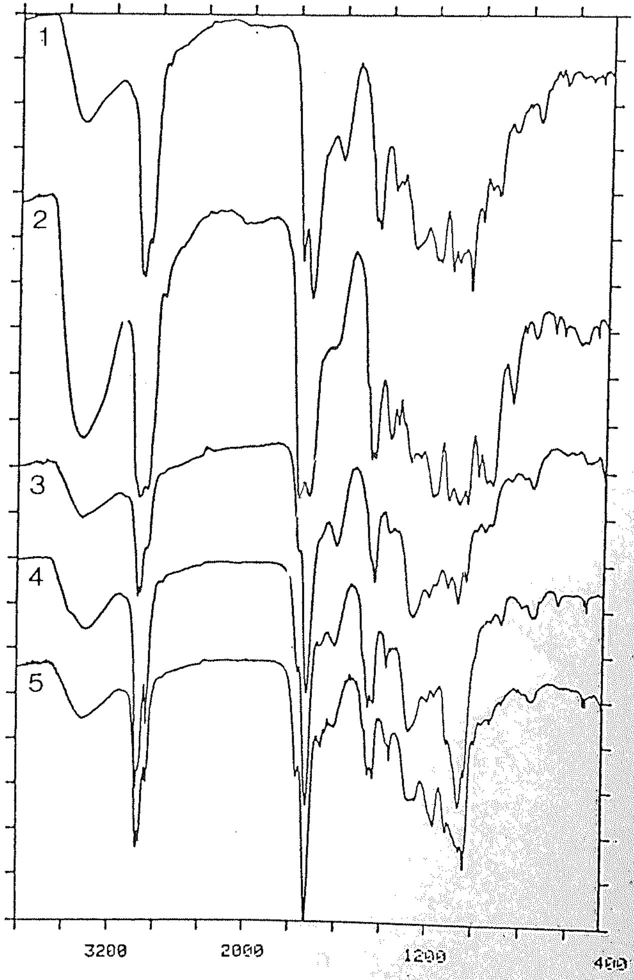
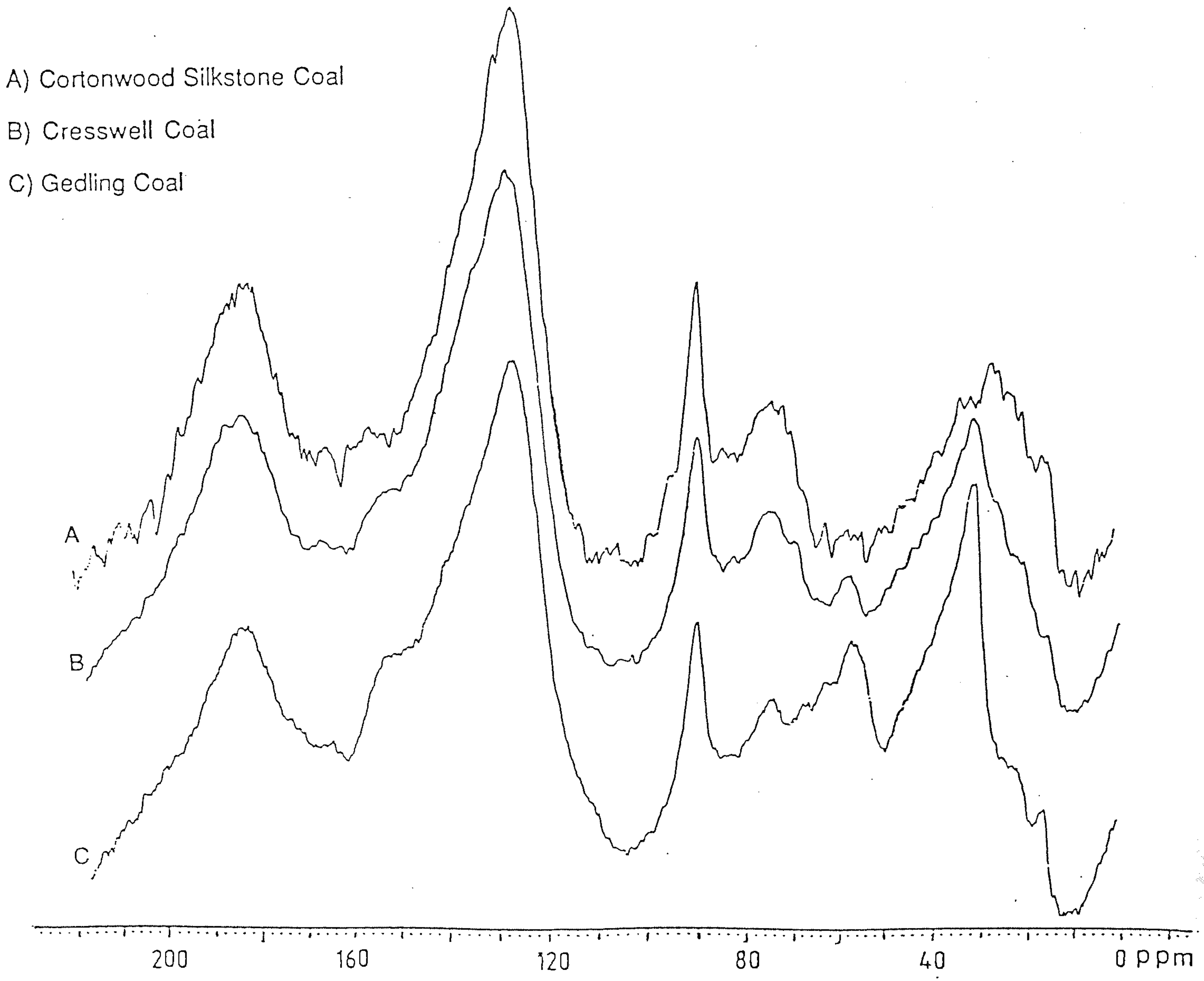


Fig.7.9 ^{13}C-CPMAS-NMR Spectra Of The PTC/Permanganate Oxidised Insoluble Residues.



(model compound studies have shown that if such activating substituents were present a complex and vigorous oxidation would take place).

The NMR spectra of the insoluble residues, (fig. 7.9 A to C), also show that carbonyl groups were added to the coal during the PTC/permanganate oxidation. The relative number of carbonyl groups added could not be quantified because of the presence of a spinning-side band (SSB) between 160 and 200ppm, which masked the carbonyl peaks occurring between 170 and 220ppm.. The area between 69 and 93ppm where we would expect to see a peak from carbons attached to ether oxygens is hidden by a peak due to the Delrin rotor used in the NMR experiment, and by a SSB between 60 and 90ppm. The shape of the peaks between 60 and 90ppm do however suggest that some ether groups were created during the step-wise PTC/ permanganate oxidation.

After the fifth oxidation step, the Gedling coal insoluble residue was O–methylated, by the PTC method described in chapter 4. This was done in order to reduce the hydrogen bonding in the sample in the hope of increasing its solubility. O–methylation, however had little effect, suggesting that the oxidised core fraction was held together by covalent bonds. The data derived from the NMR spectra, (Fig. 7.9 A to C), is given in Table 7.2.

Comparing the data contained in Table 7.2, with the data obtained from the unoxidised coals (Table 4.2), it is clear that the f_a values of all three oxidised insoluble fractions have increased,. This result was also confirmed by the decrease in the C/H ratios after each oxidation step, as measured by elemental analysis. It is also apparent from this data that there has been a reduction in the number of methyl groups during the oxidations.

Table 7.2 Some Structural Parameters Derived From The NMR Spectra Of The Step-Wise PTC / MnO_4 Oxidised Coals.

Coal	CH_3 %	$-CH_2-$ %	OCH_3 %	Aromatic C %	f_a
Gedling	3.0	24.2	11.6	60.9	0.61
Cresswell	3.0	21.2	4.9	71.3	0.71
Cortonwood Silkstone	5.2	19.3	2.0	74.2	0.74

This fall in the number of methyl groups being greatest for the lowest ranked coal. Since the model compound studies indicated that methyl groups are unreactive to the PTC/permanganate oxidant unless the aromatic system contains an activating substituent (such as another alkyl substituent or methoxy group), the above observations suggest that as the rank of a coal increases the methyl groups become isolated,in the aromatic core material, as shown in (Fig. 7.10).

Fig. 7.10 A Schematic Representation Of The Likely Positions For The Methyl Groups In British Bituminous Coals

Low Ranked Coal
activating substituents
on same ring

High Ranked Coals
isolated substituents

7.4.3 GPC RESULTS

GPC chromatographs were obtained for all the step-wise PTC/permanganate oxidised soluble esterified fractions. The polystyrene equivalent weight fraction distribution curves were then drawn, and are shown in Figs. 7.11 to 7.13. No strong trends were observed in the GPC chromatographs, however it did appear that as the number of oxidation steps increased there was a shift to lower molecular weight compounds being present in the THF soluble coal extracts, this was particularly evident for the highest rank coal examined, Cortonwood Silkstone. The shapes of the distribution curves were complex, and in general showed a high polydispersivity. No correlation could be found between the shape of the GPC chromatographs and the chemical composition of the soluble oxidised fractions. Cross-comparison of these results with other GPC data, (e.g. the results obtained from looking at the '30 day' THF soluble extracts of the untreated coals) were precluded, because the type of functional groups found in oxidised and non-oxidised fractions are very different, this means that although the compounds from the unoxidised and oxidised soluble fractions may be of similar molecular weight, they will not always elute at the same time. In general, therefore the GPC results can be considered uninformative, for PTC/permanganate oxidised soluble fractions.

Fig. 7.11 GPC Weight Fraction Distribution Curves For The Step-Wise PTC/Permanganate Oxidation Of Gedling Coal (THF Soluble Extracts)

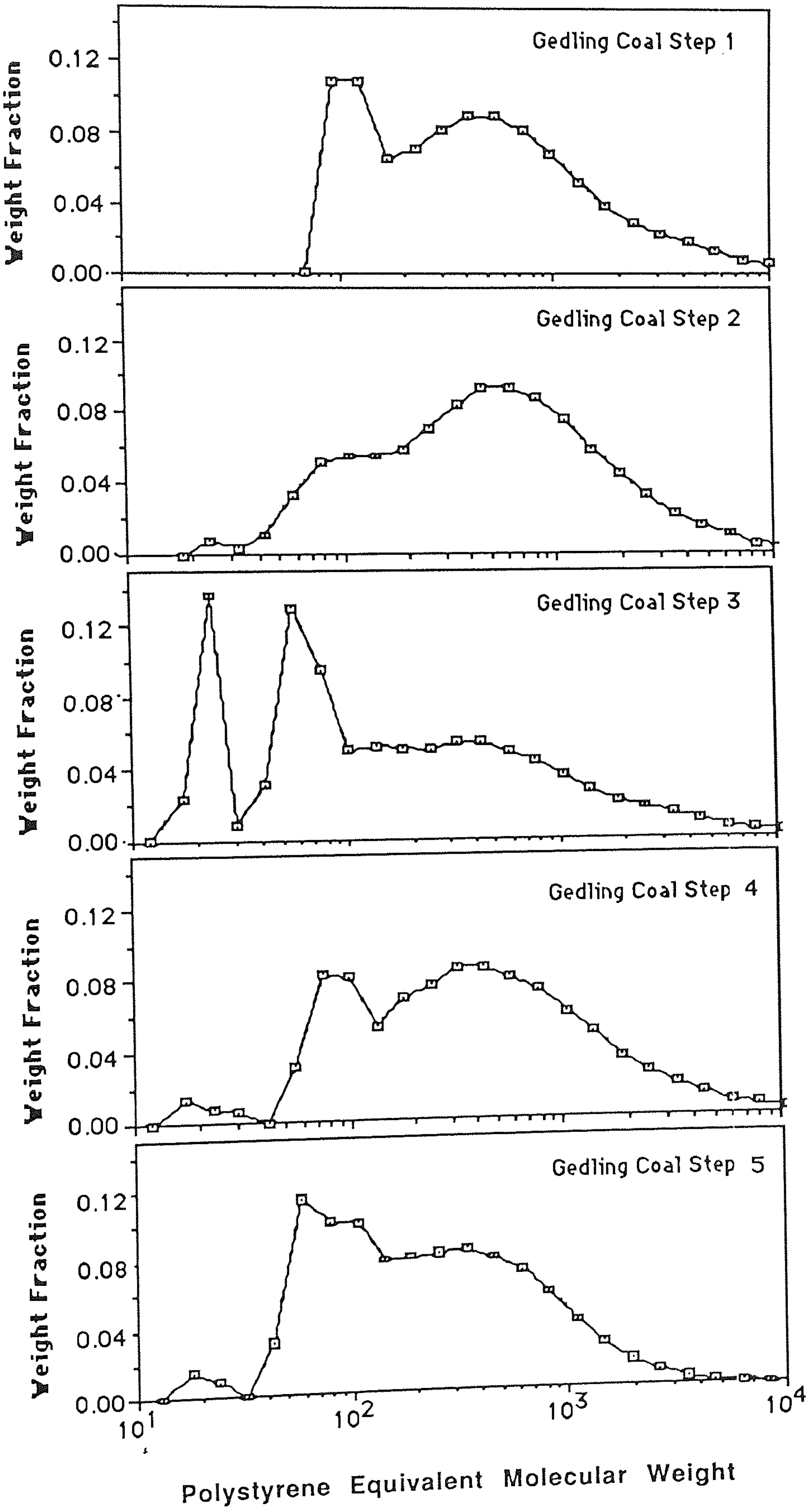


Fig. 7.12 GPC Weight Fraction Distribution Curves For The Step-Wise PTC/ Permanganate Oxidation Of Cresswell Coal (THF Soluble Extracts)

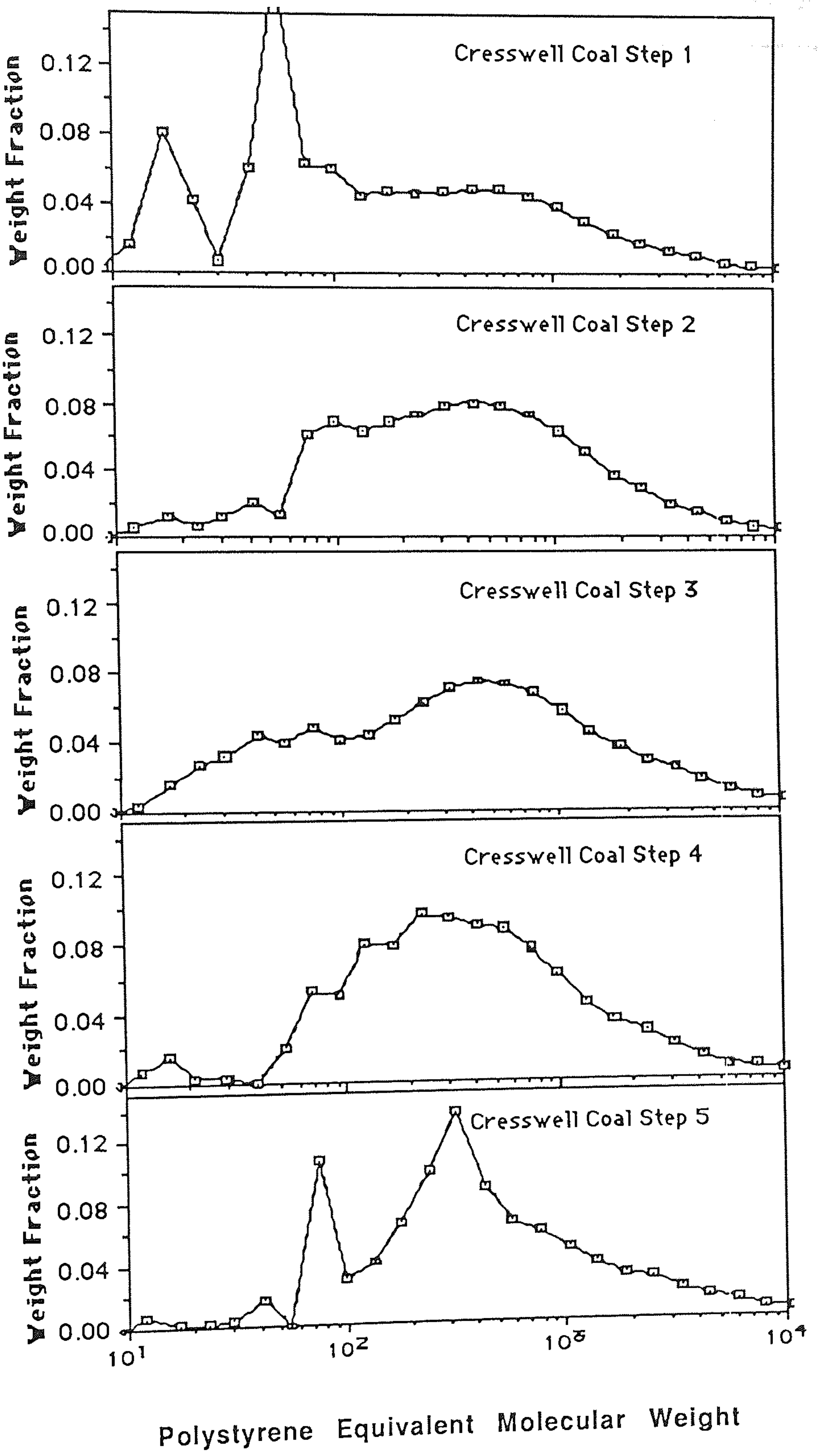
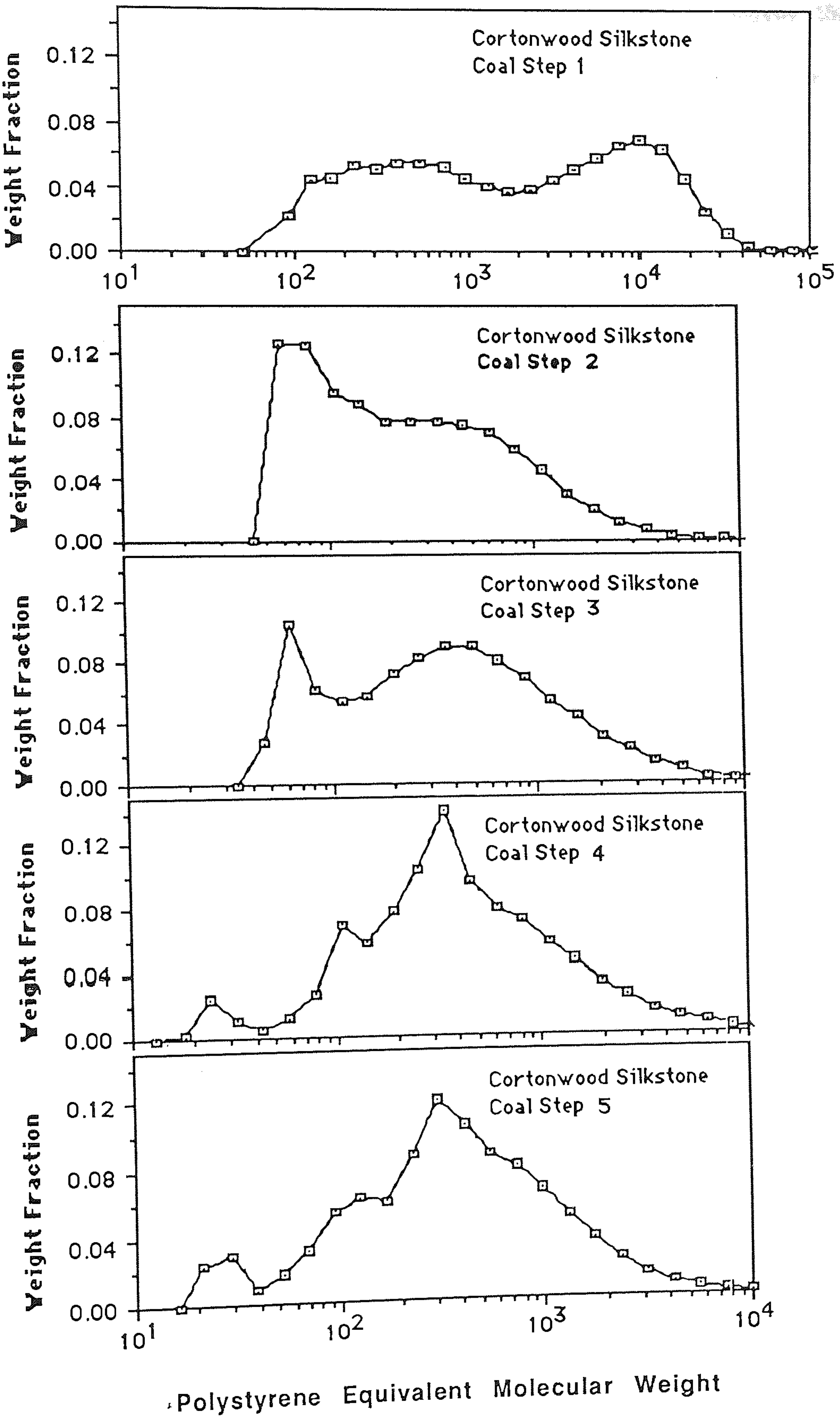


Fig. 7.13 GPC Weight Fraction Distribution Curves For The Step-Wise PTC/ Permanganate Oxidation Of Cortonwood Silkstone Coal (THF Soluble Extracts)



7.4.4 GC-MS RESULTS

GC-MS data could not be obtained for most of the step wise PTC/permanganate oxidised soluble fractions because of instrument failure, however the TIC chromatographs that were obtained showed all the fractions to be relatively similar (this was also true for the GLC chromatographs, which were obtained for all the THF soluble fractions). The number of compounds detected in the initial oxidation steps were quite small, however this increased as the number of oxidation steps increased. The fact that only low molecular weight materials were detected by the mass spectrometer when the GPC results indicated that large molecular weight compounds were present, shows the inadequacies in the GC-MS method for analysing coal products, particularly when they are likely to be polar in nature. One way of dealing with this problem would be to re-oxidise the products, this however would result in the loss of structural information. Another solution would be to use HPLC-MS but this was not available to us. The GC-MS data presented in Table 7.3 was obtained from the first step PTC/permanganate oxidation of Gedling coal. The GC-MS TIC chromatograph for this sample is shown in Fig. 7.14. Only 32 out of some 60 compounds found in the extract could be identified.

It is clear from the type of products found, that oxidation of the aromatic compounds has occurred at the benzylic position. A number of compounds which could not be identified, contained oxygen and were thought to be ethers or esters, the esters being formed from alkylethers, presumably created during the oxidation and/or esterification. It was found that quinones (eg. anthraquinone and phenanthraquinone) would not pass through the GC column. This explains why we failed to detect such compounds even though we would expect them to be present. Of the compounds identified, a large proportion were aliphatic in nature confirming the conclusions made on the basis of the IR spectra.

Fig.7.14 GC-MS TIC Of The PTC/Permanganate Oxidised Gedling Coal (Step 1).

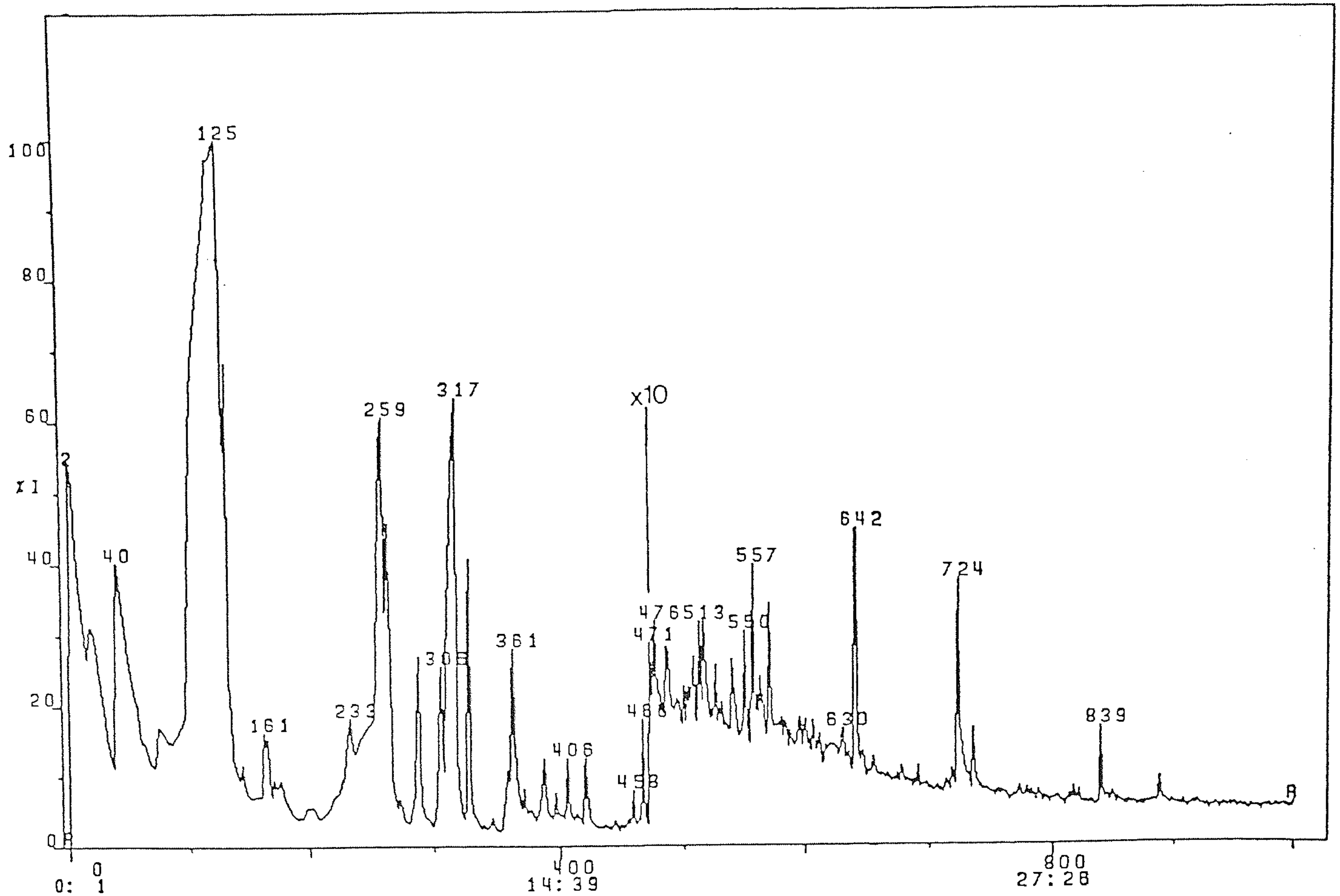


Table 7.3 GC-MS Results For The First Step Of The Oxidation Of Gedling Coal

Scan No.	Base Peak	Retention Time (m:s)	Compound
98	59	5.05	Aliphatic carboxylic acid (methylester)
125	101	5.56	" " " "
161	43	7.04	$C_7H_{10}O_2$
247	59	9.48	Aliphatic carboxylic acid (methylester)
361	71	13.25	$C_{17}H_{34}O$
364	135	13.30	Methoxybenzoic acid (methylester)
386	41	14.13	" " "
395	75	14.30	$C_9H_{20}O_2$
413	149	15.04	Benzene dicarboxylic acid (methylester)
420	163	15.18	Benzene dicarboxylic acid (dimethylester)
453	163	16.21	" " " "
466	71	16.46	$C_{12}H_{26}O_2$
476	177	17.05	Methylbenzene dicarboxylic acid (dimethyl ester)
495	135	17.41	$C_{10}H_{10}O_5$
501	178	17.53	Hydroxybenzenedicarboxylic acid (dimethylester)
508	43	18.06	Alkane (branched)
513	71	18.16	$C_{11}H_{22}O_2$
531	57	18.50	n-Alkane C_{16}

Table 7.3 Cont.. GC-MS Results For The First Step Of The Oxidation Of Gedling Coal

Scan No.	Base Peak	Retention Time (m:s)	Compound
540	193	19.08	$C_{12}H_{16}O_4$
557	74	19.40	$C_{13}H_{27}CO_2CH_3$
560	71	19.46	$C_{19}H_{34}O$
563	71	19.52	$C_{12}H_{24}O_2$
571	178	20.07	Phenanthrene
607	149	21.16	Phthalate
642	74	22.23	Hexadecenoic acid (methylester)
646	149	22.31	Phthalate
655	213	22.48	Naphthalene dicarboxylic acid (dimethylester)
678	43	23.32	Tetradecanoic acid (methylester)
691	74	23.57	Aliphatic carboxlic acid (methylester)
724	41	25.00	Octadecenoic acid (methylester)
737	74	25.25	$C_{17}H_{34}CO_2CH_3$
888	74	30.15	$C_{18}H_{36}CO_2CH_3$

The lack of any peaks due to the PTC (or the PTC's degradation products) in the GC-MS TIC chromatograph, (Fig. 7.14), shows that the ion exchange technique we developed for removing any bases in the oxidised solutions was successful.

7.5 DISCUSSION

By comparison with traditional alkaline permanganate oxidation, PTC/ permanganate oxidation using tetrabutylammoniumbromide has two distinct advantages for coal degradation, these are;

(1) Milder and more selective reactions take place.

(2) The changes in the pH of the aqueous phase, which occur during oxidation, will have little if any effect on the rate or severity of the oxidation in the organic phase.

Our model compound studies have shown that by using a PTC method, structural information, (which would have been lost if the oxidation was carried out in a basic medium), can be preserved. In particular polycyclic aromatic and alkylarenes structures are preserved. It is also easy to stop the oxidation of the primary products to simpler but less informative compounds when using a PTC to promote the reaction.

It has been found that the PTC/permanganate oxidation is only vigorous at temperatures greater than 60°C, or when the aromatic rings are activated by electron donating groups. The former is easily controlled and the latter can be diminished to some extent by the O–methylation of phenolic groups in the coals. (Note under basic conditions and at temperatures above 60°C, the PTC anion, Bu_4N^+, will undergo a Hoffmann elimination reaction.).

The ion exchange technique, developed by us, as a method for removing the last traces of a PTC from the soluble fractions avoids the problems encountered in earlier work (i.e. contamination by the PTC, preventing effective analysis of the products).

The results obtained from the PTC oxidation of the three British bituminous coals show this oxidation system to be mild and selective, gradually removing aliphatic material from the coal matrix. As the rank of the coal increases it appears harder to oxidise, as would be expected for a reaction which is attacking benzylic carbons and hetero atom functional groups.

The NMR spectra of the insoluble oxidised residues suggest that the oxidation as well as increasing the aromaticity of the insoluble core material also creates ethers and quinone type structure in the oxidised matrix, but because of the positions of the spinning side bands the number of these groups formed during the oxidation could not be quantified. The NMR data also indicates that as coal rank increases the methyl substituents on the aromatic core material become isolated on different aromatic rings.

The GPC results for the soluble oxidised fractions, while being structurally uninformative do show the products to have a large polydespersivity. The GC-MS results fail to show this.

Although the PTC/permanganate oxidation of coals should result in more structural information being retained, it is clear that, analytical techniques other than the ones used here, are required to maximise the available data. It would also be advantageous if the oxidations could be repeated at higher temperatures so that cleavage of the structures into smaller molecular weight fractions can occur, however because of time limitations we were unable to carry out these experiments.

Taking into account the qualifying statements above it should be said that the PTC / permanganate oxidation of coals as a structural probe looks promising, since the reaction severity is easily controlled, and the type of cleavage reactions which occur are quite specific in nature.

CHAPTER 8

CONCLUSIONS

8.1 CONCLUSIONS

Coals, along with other carbonaceous materials, (eg. oil shales and humic substances), are very difficult to fully characterise because of their intractable nature. This lack of solubility in organic solvents means that either; (1) Solid state analytical method must be used in isolation, and consequently only an 'average picture' of the whole coal or coal fraction can be obtained, or (2) The coals have to be degraded so that the soluble fractions produced can be examined by the more powerful solution state analytical methods, which can separate and identify individual compounds. It is the method used to degrade the coals into lower molecular weight soluble compounds which creates most of the difficulties. In the past, reagents and conditions selected to depolymerise the coals have tended to be severe and non-specific in nature, resulting in the formation of low molecular weight products such as CO_2, H_2O, benzoic acids, and oxalic acid. From such compounds it is impossible to unambiguously identify the parent structures, which in turn leads to controversy about the nature of the building block of the polymer-like coal network.

In this study we have attempted to develop and evaluate milder degradative systems, in order to solublise the coals and identify the building blocks with more certainty. In particular we have explored the use of phase transfer catalysts (PTC) to promote mild specific reactions. In tandem with this evaluation of PTC reactions we have also applied a large number of chemical and physical analytical techniques to the various coal fractions, in order to maximise the amount of structural information obtained from our studies.

The initial part of our study was chiefly concerned with establishing that the coals selected for study, (Gedling, Cresswell, and Cortonwood Silkstone) were in general representative of British bituminous coals. In the process of confirming this we also characterised as far as possible the whole untreated coal, the macro-molecular phase (after the mobile phase had been removed by solvent extraction), and examined the major components of the solvent soluble materials.

We showed that (1) The solvent soluble material or mobile phase, extracted from all three coals, were very similar to each other, but different from the macromolecular phase. The composition of the solvent extracted fractions changed with extraction time, becoming more like the macro-molecular phase. The fractions obtained even after very long extraction periods however were still hydrogen rich in comparison to the insoluble fractions. It was noted that the aromaticity of the soluble fractions followed the same trend as the whole coals, increasing with rank.

(2) The macro-molecular phase appeared to be chemically very similar to the whole untreated coals, but surface area measurements indicated that there was an increase in pore volume of the insoluble material during solvent extraction. This suggests that the pores are held open after solvent extraction by cross-linking, which is probably a combination of covalent and hydrogen bonding.

Once it was established that the three British bituminous coals were a reasonable sub-set of this class to study, we attempted to characterise the macro-molecular polymer-like phases by chemically altering their structure in a mild and selective manner. In order to accomplish this we investigated the use of phase transfer catalysis (PTC) techniques in the following reactions:-

(1) O-methylation.

(2) Reductive ether cleavage.

(3) Acid ether cleavage.

(4) Tosylation.

(5) Potassium permanganate oxidation.

PTC's have two major advantages over conventional methods used to promote coal reactions, these are;

(A) They allow milder reaction conditions to be used in heterogeneous systems. In turn this reduced severity leads to more selective reactions taking place.

(B) They remove to some extent, the effects of the coals physical structure on the apparent reactivity of the reagent(s). For example, coals which are chemically very similar can behave very differently because a reagent in one coal is unable to reach the reactive sites during the course of the reaction, while in another coal penetration into the matrix is rapid, (i.e. PTC's can to some extent remove mass transport effects, making it easier to compare the chemical differences between coals).

We found that for reactions 1) and 5), the PTC's used allowed mild and selective reaction to occur, but PTC/tosylation was unsuccessful, (this was thought to be due to the presence of water in the reaction system which hydrolysed the products back to the starting material). PTC/reductive ether cleavage was found to promote an already vigorous reaction so that there was no gain in selectivity using a PTC in this reactive system.

One major disadvantage of using PTC's to promote reactions in coals, was their tendency to become physically incorporated into the products. The PTC's then interfered with the analysis of the various coal fractions produced during the reactions. Only in the latter stages of our work was a method developed by us to remove the onium cation from the soluble oxidised products, (this involved the use of a strong cation ion exchange resin).

The first PTC reaction to be carried out on the three coals was O-methylation, (the results are reported in chapter 4). From our methylation studies we concluded that the PTC reaction did not go to completion, this is contrary to the original work reported by Liotta$^{(26)}$ and suggests that either some of the hydroxyl functions in the three coals are unreactive to this reagent, i.e alcohol OH groups, or that some of the phenolic hydroxyl group in the coal are inaccessible to the reagent. There is no evidence in the literature that British bituminous coals contain significant quantities of alcoholic hydroxyl groups so the latter explanation is the more likely. During O-methylation the solubilities of the three coals appeared to only increase slightly. It was noted however that the rate the material could be extracted from the solid matrix did increase. These observations suggests that hydrogen bonding plays an important role in maintaining the rigidity of the macro-molecular phase but does not play a significant role in bonding the mobile phase to the polymer-like matrix. The results using isotopically labeled methyliodide, (CD_3I) also supports the conclusion, that the hydrogen bonding in coals is intramolecular, (i.e. between different fractions of the macro-molecular network) and not intermolecular, (i.e. between the macro-molecular phase and the mobile phase).

Although O-methylation does not solublise large fraction of a coal, it does offer us a method by which we can accelerate the removal of the mobile phase from the coals. Providing care is taken to minimise the amount of air oxidation during O-methylation the reaction can also be useful in protecting the more reactive/accessible hydroxyl functions from over vigorous reactions with reagents such as permanganate.

The results obtained from an examination of the degradation products from the ether cleavage reactions, (see chapter 5) were largely inconclusive. There was little or no evidence for the presence of dialkyl ethers in the three coals studied, (this is in agreement with other workers), and it was impossible from the reductive ether cleavage work to quantify the number of diaryl ethers present. Most of the ether functions appeared to be unaffected by both cleavage methods (PTC/reductive or PTC/acidic). This has lead us to believe that a large proportion of the ether groups in British bituminous coals, form part of heterocyclic ring systems.

Two oxidative degradation methods have been used to solublise the macro-molecular solvent insoluble coal fractions. The first of these methods used trifluoroperacetic acid (TFPA) as the oxidant, to try and characterise the aliphatic portions, (see chapter 6). The second oxidant was PTC/permanganate which was used to study the aromatic fractions, (see chapter 7).

TFPA is normally only effective in totally solublising low rank coals, such as lignites. We have developed a method however, whereby the use of this reagent can be extended to high rank bituminous coals. During TFPA oxidation of high rank coals the aromatic centres are progressively deactivated by the formation of electron withdrawing carboxylic acid groups, this prevents the complete degradation of the coal. By reducing, tosylating and re-reducing the oxidised insoluble products the deactivating carboxylic acid groups can be converted to activating methyl groups. The insoluble fraction can then be re-oxidised using the TFPA oxidant. It was apparent from the results obtained, that this sequence of reactions produced some unexpected products, but due to lack of time we were unable to evaluate the procedure .

Examination of the TFPA oxidation products indicated that the size of the aromatic clusters, and the number of methyl groups on the aromatic rings, increased with coal rank. While TFPA can be used to convert coals into solvent soluble products, the evidence suggests that the primary oxidation products undergo further oxidation. As a result of these secondary reactions some structural information will be lost about the aliphatic portions of the coals.

PTC/permanganate model compound studies have shown this oxidant to be relatively mild and selective when compared with the more traditional permanganate oxidation in basic media. For example polycyclic aromatic, and alkylaryl compounds are preserved using this reagent unless there are electron donating groups present on the ring(s). PTC/permanganate oxidation also has the advantage that the reaction severity can be easily controlled either by changing the temperature of the reaction or the concentration of the PTC.

The PTC/permanganate oxidation of the three British bituminous coals when carried out in a step-wise manner, gradually removed aliphatic material from the coals. Examination of the soluble products showed that there were few large aliphatic substituents attached to the aromatic centres. The insoluble core material left after oxidation and solvent extraction when examined by ^{13}C-CPMAS-NMR indicated that the methyl substituents remaining were isolated on separate rings.

The various reactions studied, have shown that PTC's can be used to advantage in obtaining a better understanding of the molecular structures present in British bituminous coals, but some care must be taken in choosing the reactions where they will be beneficial. Although a lot more work is required, (especially on the analysis of the fractions produced when using PTC's), it is felt that the mild specific methods developed in this project, show significant potential for the elucidation of coal structure.

CHAPTER 9.

EXPERIMENTAL

9.1 INTRODUCTION

The techniques and reactions described in this chapter are those used throughout the work, unless otherwise stated in the relevant sections.

9.2 REAGENTS

The reagents used were of general purpose grade (GPR) unless otherwise indicated.

Reagent	**Supplier**
'Amberlite' resin IR120 (Na) (14-52 mesh)	BDH
Chloroform	May & Baker
Dichloromethane	May & Baker
Hydrogenperoxide 30% w/v Analar	BDH
Iodomethane	Aldrich/BDH
Iodomethane-D_3 99%+	Aldrich
Lithium aluminium hydride	BDH
Methanol	May & Baker
Methanol / Borontrifluride (50% complex)	Aldrich
Pyridine	BDH
Tetrabutylammonium bromide 99%+	Aldrich
Tetrabutylammonium hydroxide 40% aq sol	Aldrich
Tetrahydrofuran*	May & Baker
Tetrahydrofuran HPLC Grade	Fison
Tetraphenylphosphonium bromide	Lancaster
Trifluroacetic acid	Lancaster

*Distillation Of THF

GPR grade THF contains approximately 1% quinol as a stabiliser which had to be removed. This was done by distillation of the solvent from a flask containing lithium aluminum hydride. The THF was then stored over molecular sieve 3A until required.

9.3 SAMPLE SELECTION AND PREPARATION

Three British bituminous coals, supplied by the National Coal Board, and obtained from the Dutch Coal Bank were selected as representing the range of bituminous coals mined in this country. The coals were in order of increasing rank;

Gedling Coal 81.6% C (dmmf)

Cresswell Coal 84.5% C (dmmf)

Cortonwood Silkstone Coal 87.2% C (dmmf).

The coals, supplied in individual metal containers were thoroughly shaken before smaller portions were removed. This was done to insure a representative sample of coal was taken.

This smaller coal sample was then ground to a fine powder using a Tema (manufactured by Siebtechnik). A maximum of 15 seconds crushing between each pass through a 120 mesh sieve (0.124mm) was allowed, in order to avoid thermal degradation and oxidation of the sample. The process was repeated until all the sample had a partical size of less than 0.124mm.

Once the coal was in a finely divided state, it was placed in small air tight containers and sealed under a static dinitrogen atmosphere.

9.4 INSTRUMENTATION

The following instruments and techniques were used to investigate the organic fractions of the coals.

9.4.1 ELEMENTAL ANALYSIS

A Carlo-Erba auto analyser, model 1106 was used to determine the carbon, hydrogen, nitrogen and sulfur content of the various coal fractions. The oxygen content was calculated by difference. Vanadium pentoxide was added to the coal samples to promote the complete combustion of the organic matter. Ten sets of results were obtained for each sample and the mean values and standard error calculated, this was done in order to minimise the effects of the variation in elemental composition, which occurs because of the heterogeneous nature of these materials.

Before elemental analysis was carried out the samples were dried in a vacuum oven over night at 100°C to remove any water present. The result obtained were not corrected for mineral matter content.

9.4.2 INFRARED ANALYSIS

Two infrared instruments were used, a Perkin-Elmer 599B spectrometer fitted with a 3600 data station (running Perkin-Elmer PECDS software), and a Perkin-Elmer Fourier-Transform spectrometer model 1710 fitted with an auto-sample shuttle, (connected to a 3600 data station running Perkin-Elmer M1700 software).

Infrared spectra of solutions were obtained as thin films on KBr plates. Infrared spectra of solids were obtained either by using the KBr disk method, or by using a Barnes Analytical/Spectra-Tech diffuse reflectance accessory, centre focusing version, attached to the 1710 instrument.

9.4.3 GAS CHROMATOGRAPHY- MASS SPECTROSCOPY

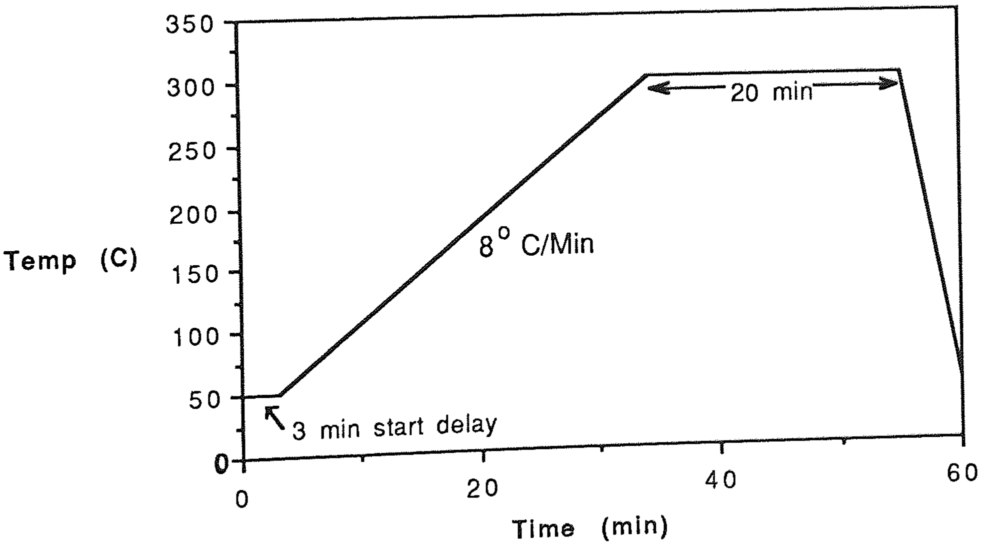
All GC-MS analysis was carried out using a VG Micromass system comprising of the following units:-

1) A Pye-Unicam series 304 gas chromatograph, fitted with an Alltech 30m fused silica capillary column (I.D. 0.32mm), containing a poly-dimethylsiloxane bonded phase, 0.25microns thick. The column temperature programme is shown if Fig 9.1, and was used for all samples unless otherwise stated.

2) A VG MM12/12 quadropole mass spectrometer, linked to a VG micro computer. The source was set at 70eV to produce positive ion electron impact spectra.

3) A Digital PDP8a data storage system fitted with twin RL02 disks, and running release 8 VG MS2000 software.

Fig. 9.1 Temperature Programme For GC-MS Column



9.4.4 NMR ANALYSIS

^1H and ^{13}C solution NMR spectra were obtained using a Joel FX90Q spectrometer. ^{13}C-CPMAS-NMR where generated on one of three instruments, a Varian 300MHz spectrometer (Durham University), a Bruker AC300MHz spectrometer (Aston University) and a 90MHz NMR spectrometer (University of East Anglia). The contact time for all CPMAS-NMR experiments was 3ms, unless indicated otherwise.

9.4.5 GEL-PERMEATION CHROMATOGRAPHY

THF soluble samples ($0.5cm^3$) were run on a gel-permeation system consisting of a Perkin Elmer series 10 liquid chromatograph fitted with a styrogel column using HPLC grade THF at a flow rate of $1cm^3min^{-1}$. The pressure limits were set to between 2MPa and 13MPa. The eluent was monitored using a duel detection system consisting of a Knauer differential refractometer and a Perkin Elmer LC65B spectrophotometric detector. The GPC column was calibrated at the low molecular weight end using a series of n-alkanes, and at the high molecular weight end using polystyrene upto $6x10^6$ a.m.u.

9.5 SOLVENT EXTRACTION

Solvent extraction was carried out using the soxhlet method. All samples were extracted using freshly distilled solvents and under a continuous flow of dinitrogen to prevent air oxidation.

9.6 METHYLATION REACTIONS

9.6.1 PTC/O-METHYLATION

A typical example of the PTC/O-methylation reaction is given below:-

120mesh ground coal (1g) was slurried in THF ($15cm^3$), to this was added a 40%

aqueous solution of tetrabutylammonium hydroxide ($1cm^3$), and a two fold excess of the alkylating agent iodomethane, (calculated on the amount of PTC). The mixture was then stirred under a static dinitrogen atmosphere for 48 h. A 1N HCl solution was then added until the mixture was just acidic. The solvent, excess alkylating agent and some of the water were then removed on a rotary evaporator. The coal was then filtered and washed with a methanol/water solution (50:50 v/v) until a negative silver nitrate test was observed for the washings. The O-methylated coal was then dried in a vacuum oven at between 95^oC and 105^oC for 24 h.

9.6.2 BF_3/MeOH METHYLATION

Soluble oxidation products were dried using sodium sulphate which is removed afterwards by vacuum filtration. The solvent is then removed on the rotary evaporator and a 14% boron trifluoride/methanol complex added (~$15cm^3$ for every 0.5g of soluble oxidised product.). The esterifying agent was made up from a BF_3/CH_3OH complex (~50%) and dried methanol.

The solution was refluxed for 48h before the esters were extracted from a saturated salt solution, into dichloromethane. The aqueous phase was re-extracted twice more with the same solvent and the organic extracts combined. The dichloromethane solution was then washed in a 10% sodium carbonate solution followed by a further washing with a saturated salt solution. The organic layer was separated, and dried using sodium sulphate. After vacuum filtration the dichloromethane was removed on the rotary evaporator.

9.7 ETHER CLEAVAGE REACTIONS

9.7.1 ETA REDUCTIVE ETHER CLEAVAGE

Carefully dried THF (82cm^3), and the ETA, naphthalene (0.6g), were mixed together before potassium (1.5g) was added, this gave a dark green solution. To this reagent was added the coal, which had previously been dried in a vacuum oven for 48 h at between 100°C and 110°C. The mixture was then stirred at ambient temperatures for 24 h, under an atmosphere of dinitrogen. The reaction was quenched by adding ammonium chloride (3g) in THF (15cm^3), followed by the addition of methanol.

The coal was then filtered and washed with pentane and water before the sample was dried in a vacuum oven.

9.7.2 PTC REDUCTIVE ETHER CLEAVAGE

18-crown-6 (9.5g), carefully dried THF (20cm^3), and potassium (1.6g) were mixed together. To this solution was added the ground coal, which had previously been dried in a vacuum oven for 48h at between 100°C and 110°C. The reaction mixture was then stirred under a dinitrogen atmosphere for 48h before the reaction was quenched, carefully, with water. The THF was removed on a rotary evaporator. The coal was then filtered and the crown ether washed from the sample by Soxhlet extraction in water for 48h.

9.7.3 PTC ACIDIC ETHER CLEAVAGE

Constant boiling hydrobromic acid (55cm^3) and tetraphenylphosphonium bromide (5g) was slurried with the ground coal (3g), and heated with stirring, under a dinitrogen atmosphere, at between 100°C and 110°C for at least 48h. The mixture was then filtered hot and the coal washed with hot water until the pH of the washings were neutral.

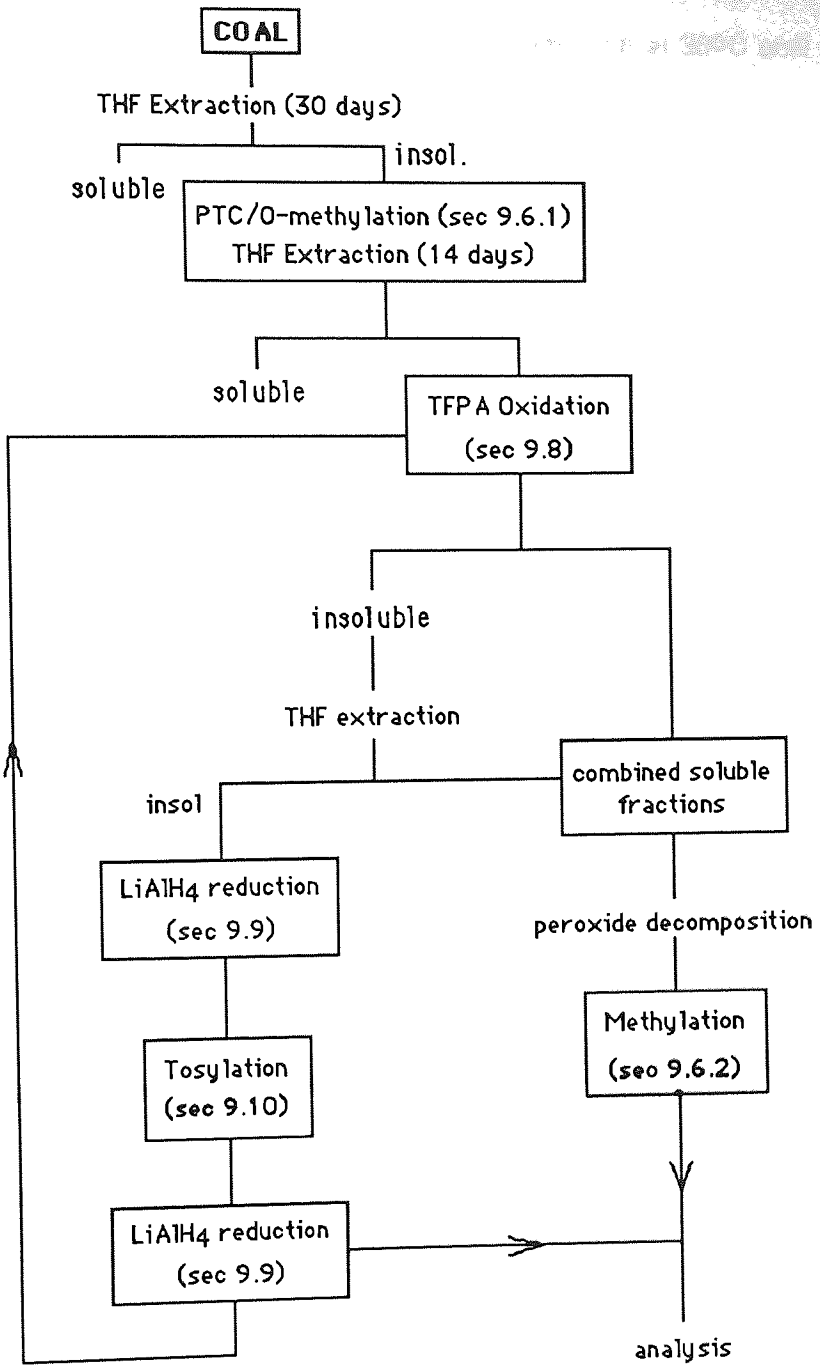
9.8 TRIFLUOROPERACETIC ACID OXIDATION

To the refluxing mixture of (THF extracted, o-methylated, and re-extracted) coal (2g), and chloroform ($80cm^3$), was added drop-wise with stirring, a mixture of trifluoroacetic acid, 30%w/v hydrogen peroxide and 98% sulfuric acid, made up in the ratio of 8:10:5 ($80cm^3$). Refluxing and stirring continued for 5h before the reaction was quenched using an ice bath. The solution was then filtered and the oxidised insoluble fraction washed with chloroform until a clear solution was obtained. The excess peroxide was then destroyed by adding to the filtrate 5% platinum on kaowool (40mg), and stirring it until a negative starch iodide test was observed. After drying the solution over magnesium sulphate the solution was filtered and the solvent removed. The soluble oxidation products were then esterified as in section 9.6.2. The insoluble fraction of the coal was dried in a vacuum oven overnight at between 100^oC and 110^oC ready for analysis or further treatment. A schematic of the procedures followed is shown in Fig. 9.2.

9.9 REDUCTION OF THE TFPA OXIDISED INSOLUBLE FRACTIONS

The insoluble TFPA oxidised coal fractions were reduced using the following method:- The insoluble coal fraction (0.6g), carefully dried THF ($25cm^3$) and lithium aluminum hydride (0.3g) were refluxed for a week under a dried dinitrogen atmosphere. The reaction was then quenched carefully with water before being filtered and washed with a 1N hydrochloric acid solution. The sample was then dried in a vacuum oven at between 100^oC and 110^oC for 24h.

Fig.9.2 Procedure Followed For The TFPA Oxidation Of Coal



9.10 TOSYLATION OF REDUCED TFPA OXIDISED COAL FRACTIONS

The reduced coal fraction (0.5g), p-toluenesulfonyl chloride (1g) and pyridine (5cm^3) were stirred at ambient temperatures for one week. The reaction mixture was then poured into water (100cm^3) to form the tosylic acid which dissolved slowly in the water. The coal was then filtered and washed with water followed by chloroform. The products were then placed in a vacuum oven at 30°C until dried. (Note tosyl derivatives are thermally unstable)

9.11 PTC/PERMANGANATE OXIDATION

9.11.1 PTC/PERMANGANATE OXIDATION OF MODEL COMPOUNDS

0.005 Moles of the model compound, 0.2M potassium permanganate solution (150cm^3), dichloromethane (100cm^3), and tetrabutylammonium bromide (1g) were stirred together at ambient temperatures for 24h, under a constant flow of dinitrogen. Any carbon dioxide produced in the reaction was trapped quantitatively using barium hydroxide.

After the 24h reaction period any excess permanganate was reduced using a saturated solution of sodium sulphite. The manganese dioxide was then removed by first acidifying the solution with concentrated hydrochloric acid followed by the addition of more sodium sulphite. The organic fraction was then separated and esterified using the procedure in section 9.6.2.

The PTC was removed from the esterified solution using the procedure in section 9.12.2.

9.11.2 ONE-STEP PTC/PERMANGANATE OXIDATION OF COAL

The THF extracted, O-methylated, and re-extracted coal (0.5g), 0.2M $KMnO_4$ (234cm^3), dichloromethane (100cm^3), and tetrabutylammonium bromide (5g) was stirred together for 24h at ambient temperatures, under a constant flow of dinitrogen. Any carbon dioxide produced in the reaction was trapped quantitatively using barium hydroxide.

After the 24h reaction period any excess permanganate was reduced using a saturated solution of sodium sulphite. The manganese dioxide was then removed by first acidifying the solution with concentrated hydrochloric acid followed by the addition of more sodium sulphite. The coal was then filtered and Soxhlet extracted for 24h using THF. Both the dichloromethane and THF fractions were then combined and esterified as in section 9.6.2, before any excess phase transfer reagent was removed using the method described in section 9.12.2.

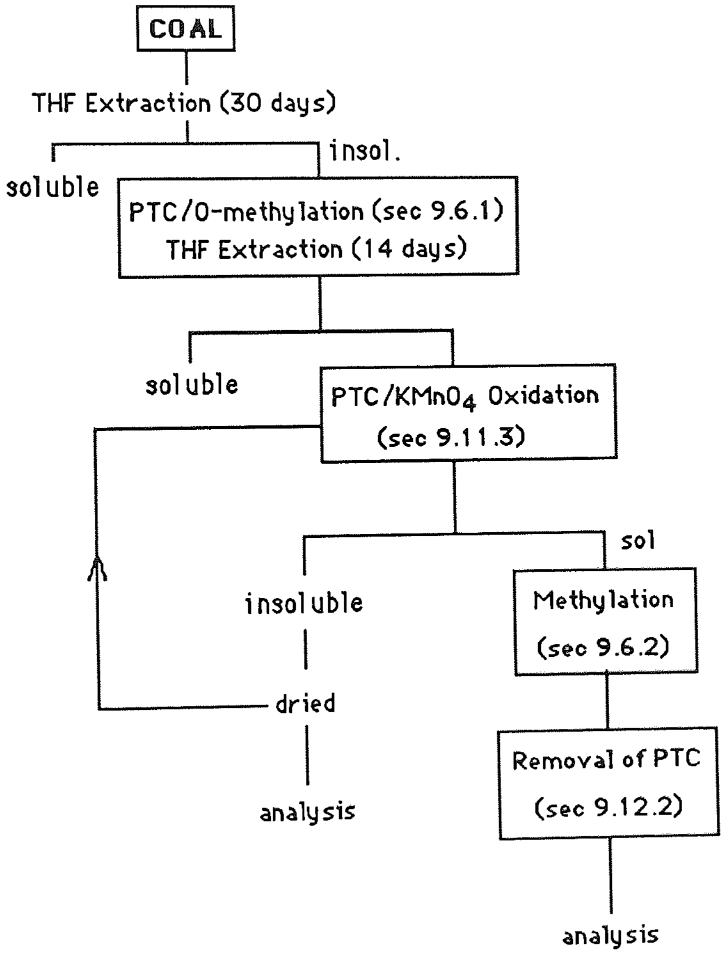
9.11.3 STEP-WISE PTC/PERMANGANATE OXIDATION OF COAL

Approximately 5g of the THF extracted, O-methylated, and re-extracted coal, was weighed out accurately. To this was added half the amount by weight of $KMnO_4$ in the form of a 0.2M solution, and an equal volume of dichloromethane, plus tetrabutylammonium bromide (1g). The slurry was stirred for 24h over a constant flow of dinitrogen. Any carbon dioxide produced in the reaction was trapped quantitatively using barium hydroxide.

After the 24h reaction period any excess permanganate was reduced using a saturated solution of sodium sulphite. The manganese dioxide was then removed by first acidifying the solution with concentrated hydrochloric acid followed by the addition of more sodium sulphite. The coal was then filtered and Soxhlet extracted for 24h using THF. Both the dichloromethane and THF fractions were then combined and esterified as in section 9.6.2, before any excess phase transfer reagent was removed using the method described in section 9.12.2.

The insoluble fraction of the coal was dried in a vacuum oven at 100°C before being weighed. This partially oxidised fraction was then further oxidised using the same method as above, the weight of potassium permanganate being reduced to compensate for the smaller amount of coal to be oxidised. The oxidation procedure was repeated a total of five times for each coal. This procedure is summerised in Fig. 9.3.

Fig.9.3 Procedure followed For The Step-Wise PTC/Permanganate Oxidation Of Coal



9.12 REMOVAL OF THE PTC FROM OXIDISED COAL SOLUTIONS

9.12.1 PREPARATION OF THE ION EXCHANGE COLUMN

An ion exchange column, 400mm long and 25mm in diameter, was made up using a strong cation exchange resin (Amberlite IR120) in the sodium salt form. The protonated form was then generated by washing through with a ~1N hydrochloric acid solution. The column was then washed with several litres of a THF/deionised water solution (75:25 v/v), until the washings, when concentrated, showed no material that could be detected by an infrared spectrometer.

9.12.2 REMOVAL OF THE PTC FROM THE OXIDISED COAL

The esterified oxidation products were taken up in a THF/deionised water solution (50:50 v/v) and passed through the column slowly. The column was then washed with a less polar solution of THF/deionised water (80:20 v/v), and the washings combined. The THF was removed on a rotary evaporator. The remaining organic fraction was then separated from the water by extracting it into dichloromethane. The organic solution was removed and dried using magnesium sulphate, before the solvent was distilled off.

9.12.3 REGENERATION OF THE ION EXCHANGE COLUMN

To regenerate the column the ion exchange resin was washed slowly in a THF/~1N HCl solution (50:50v/v). The excess acid was then removed by washing the column with a THF/deionised water solution (70:30 v/v), until the pH of the washings was neutral.

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