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N.M.R. STUDIES OF COAL

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ABSTRACT

Carbon-13 CP/MAS NMR was used to study a selection of fifty-seven New Zealand coals and ten Australian coals. The coal rank varied from lignite to semianthracite. A qualitative survey of the plant origins of NMR signals was followed by an EPR study of the unpaired spin-species in coal. The quantitative reliability of the NMR response of coal was analysed in relaxation and "visibility" studies. Different approaches to the problem of accounting for intensity in spinning-side-band (SSB) signals were assessed. The most successful approach was found to be the complete computer simulation of the spectrum from combinations of SSB intensity patterns broadened by a mixture of Lorentzian and Gaussian lineshapes. This method of analysis produced oxygen contents that showed a good correlation with oxygen contents (by difference) from Ultimate analysis. The resultant carbon, hydrogen and oxygen functional group analyses allowed considerable insight into the depositional influences on, and alteration of, the coal structure with increasing degree of coalification.

FRONTISPIECE

Stylised reconstruction of a New Zealand forest-swamp. The etching shows a selection of modern equivalents of plant species that are thought to have contributed to the coal-forming peats in Cretaceous and Tertiary times (Table 2.1).

Key to Etching

1. Kauri	<u>Agathis australis</u>
2. Kahikatea	<u>Podocarpus dacrydiodes</u>
3. Beech	<u>Northofagus</u> genus
4. Rimu	<u>Dacrydium cupressinum</u>
5. Manuka	<u>Myrtaceae</u> family
6. Tree Ferns	<u>Cyatheaceae</u> family
7. Cabbage Tree	<u>Liliaceae</u> family
8. Flax	<u>Phormium</u> genus
9. Sedges, Reeds, Lilies	<u>Cyperaceae</u> , <u>Sparganiaceae</u> and <u>Liliaceae</u> families

The author thanks Miss Margaret Davenport for the artwork

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1.0 INTRODUCTION

1.1 Coal Research

"Coal Research ... : it strives for knowledge as well as for utility".

D. W. Van Krevelen, 1981⁽¹⁾

Fossil fuels are the product of a small but continuous leak in the organic carbon cycle. Coal is the most heterogeneous of the fossil fuels having originated "in vast primeval swamps, where the partial decay of dead trees and plants formed thick beds of the concentrated organic matter called peat"⁽²⁾.

The plant debris was covered, compacted and chemically altered over geological periods; ie the process of coalification occurred. The variation observed in coal properties reflects; i) the nature and relative amounts of the original plant species; ii) the environmental conditions during deposition and, iii) the local geological influences such as temperature and depth of burial.

Deposits of coal are distributed throughout the world and represent approximately 90% of New Zealand's known reserves of fossil fuel⁽³⁾. The combustion process is still by far the largest consumer of coal producing energy for, for example, heating or for generating steam in industry or power stations. However, the OPEC oil embargoes of 1973 provided the impetus for the development of alternative indigenous energy sources. A resurgence in interest in synthetic liquid fuels, often with coal as the feedstock, has taken place. With the new technologies came the demand for more understanding of fundamental coal properties and their influence on particular utilisation processes⁽⁴⁾.

This new attitude is epitomized in the principal research recommendations of the 1981, American Physical Society Group on Coal Utilization and Synthetic Fuel Production⁽⁵⁾.

"We recommend that presently available and developing techniques be applied to the determination of chemical structural features of coals, including hydroaromatic and aromatic cluster configurations, functional groups and molecular weight distributions."

Of the "developing techniques", high power nuclear magnetic resonance (NMR) was then seen as⁽⁶⁾, and has now become, an extremely useful tool in the study of coal structure.

1.2 Solid State Carbon-13 NMR of Coal

1.2.1 The NMR Technique in the Solid State

The theory of NMR is well documented^(7,8). Liquid state NMR has become a routine analysis tool for many nuclei, in many areas of chemistry. However, the use of NMR to study the solid state has only recently "come of age"⁽⁹⁾ with the introduction of new techniques which have enabled the recording of high resolution spectra. Prior to this era, the NMR spectra of, for example, carbon-13 nuclei in solids were characterised by broad featureless bands. The line broadening was caused by; i) the interaction between the spin of the carbon-13 nuclei with neighbouring odd spin nuclei, eg protons, ^1H (dipolar broadening); ii) the great range in the amount of shielding felt by a particular nuclei (chemical shift anisotropy) which is caused by orientational effects in a rigid solid. Both interactions are averaged in liquids so that a single resonance is observed at the average chemical shift.

The revolutionary techniques were termed; i) "high-power dipolar decoupling" which effectively "locks" the second spin interacting with the nuclei of interest and removes the dipolar broadening; ii) "cross polarisation" (CP) which causes a manifold enhancement of the NMR signal; iii) "magic-angle-spinning" (MAS) which simulates the molecular motion of liquids and thus averages the orientational origin of chemical shift anisotropy. The theory of the causes of line broadening, and more detailed explanations of the effectiveness of the above techniques, are given in Chapter 3.

Many organic compounds have been studied since Schaefer *et al*⁽¹⁰⁾ first applied the techniques. NMR has enabled insight into the structures of complex natural systems such as wood, soil and coal.

1.2.2 Carbon-13 NMR of Coal

With the advent of high resolution CP/MAS NMR it became possible to directly observe the unaltered coal as a complete structure. This is in contrast to other techniques which study coal either as molecular fragments separated by chemical means, or by studying the coal surface, or by measuring physical matrix properties⁽¹¹⁾ from which overall structural characteristics are inferred.

In 1971 broadline carbon-13 NMR spectra of whole coals⁽¹²⁾ were obtained but consisted of one featureless broad peak. The first high

resolution carbon-13 NMR studies of coal were performed five years later (with CP only) by VanderHart and Retcofsky⁽¹³⁾ in 1976. The initial NMR spectra of coal samples obtained with CP/MAS⁽¹⁴⁾, showed bands narrowed sufficiently for separation into aromatic and aliphatic carbon signals. Thus, an NMR estimation of aromaticity, f_a , could be made. The parameter f_a is defined as the fraction of the total signal area that is contained in aromatic carbon signals.

The early carbon-13 CP/MAS NMR spectra of coals were obtained using electromagnet spectrometers (15,16). The higher fields made possible by the introduction of superconducting magnets have greatly improved the sensitivity of carbon-13 NMR. The opportunity to compare NMR spectra of an Australian brown coal, obtained on the two types of spectrometer, is provided in the literature by Yoshida *et al*⁽¹⁷⁾, who worked at carbon-13 fields of 1.4T, and by Ohtsuka *et al*⁽¹⁸⁾ who used fields up to 7T (see Appendix 8.2). The resolution now provided by commercial superconducting spectrometers has enabled the identification of far more carbon functionalities present in the coal structures. However, the increased magnitude of the NMR field results in greater chemical shift anisotropies. The frequency of the MAS must increase in proportion to the field strength in order to effectively remove the broadening influence. For example, at 50.3 MHz the spinning rate necessary to suppress broadening effects would be 8.4 kHz⁽¹⁹⁾. In practical terms, spinning rates no greater than (and usually much less than) 4 to 5 kHz are routinely attainable⁽²⁰⁾. When spinning frequencies are less than the chemical shift anisotropy, the centreband is flanked by rotational echo signals called "spinning-side-bands" (SSB) which occur at intervals that are multiples of the spinning frequency. (The theory behind these extra signals will be discussed in Chapter 3.) The amount of intensity distributed into these signals depends on the type of carbon functionality producing the signal and also upon the deficit between the spinning frequency and chemical shift anisotropy. Thus, the advantage in resolution gained by increasing the field strength is offset, in many cases, by the complication of SSB signals.

1.3 Discussion

Several points have arisen from the survey of ^{13}C NMR studies of coal contained in the literature;

- i. With few exceptions^(18,21,22), the published NMR spectra were obtained

at low ^{13}C fields (15 to 25 MHz). Thus, the increased resolution afforded by high field spectrometers has not been utilised. The presence of SSB signals in spectra obtained at higher fields has presumably deterred many workers.

- ii. Most of the studies have concentrated on samples of higher rank coals from the northern hemisphere. These coals have depositional and coalification histories that are very different from those of New Zealand coals. Australian coals have been investigated more recently⁽²³⁻²⁶⁾. No New Zealand coals have been studied by NMR despite the fact that these coals have many unusual characteristics. For example, "Tertiary coals of bituminous rank are not common"⁽²⁷⁾ but are found in large quantities on the West Coast of New Zealand.
- iii. In general, NMR has only been employed as a qualitative or, at best, semi-quantitative analytical technique. There is a large amount of functional group information contained in the NMR spectra which would prove valuable if it could be retrieved.

With these points in mind, an NMR study of Australasian coals was designed with the following aims;

- i. To study a selection of coals that span the range of rank (lignite to semianthracite) that is found in New Zealand. To include several Australian coals - enabling a comparison of the New Zealand coals with others of southern hemisphere origin.
- ii. To perform a qualitative survey of the terrestrial plant origin of the signals observed in the NMR spectra.
- iii. To assess the reliability of the NMR response with respect to quantitative analysis of the spectra.
- iv. To assess current techniques for accounting for the intensity distributed into SSB signals.
- v. To develop the most promising technique into a quantitative analysis of the signal intensity observed in the NMR spectra of coals.
- vi. To characterise Australasian coals using the full functional group analyses that result from the quantitative deconvolution of the NMR spectra of coals.

The structure of the thesis follows these aims in a logical manner. The second and third chapters include general introductions to coal and solid state ^{13}C NMR, respectively. The fourth chapter outlines the sample origins and main experimental details. Chapter 5 contains a study of

signal assignments and origins, and a qualitative survey of the changes in the spectra with the increasing degree of coalification of the sample. Chapters 6, 7 and 8 contain the assessment of the quantitative reliability of the NMR response of coal. They include EPR, NMR relaxation and "visibility" studies, respectively. The survey of the different approaches to the SSB problem, and the development of a quantitative analysis method, are outlined in Chapter 9. Chapter 10 contains the structural characterisation of fifty-seven New Zealand and ten Australian coals based on carbon, hydrogen and oxygen functional group analyses.

The second part of the thesis contains the lists of data generated from the study. Publications and reports that have arisen from this research are contained in Appendix 8.

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2.0 COAL ORIGIN AND CLASSIFICATION

In order to study the chemical nature of coal it is necessary to gain an understanding of the processes involved in its formation and influences on its evolution.

2.1 Formation of Coal

2.1.1. Deposition

Coals are organic sedimentary rocks formed by the metamorphosis of plant remains which accumulated in peat swamps under conditions that inhibited decay. The properties of coals reflect the nature of the original plant material and the conditions prevailing at the onset and during coalification.

The origins and development of peat swamps are controlled by a great number of interdependent factors including the following (1):

- i. the type and variety of flora; eg whether forest or reed (or a mixture of both) plant communities dominated the contributing plant matter;
- ii. the mode of deposition; ie whether the plant debris formed the peat in situ (autochthonous) or was transported from the original site to the peat swamp (allochthonous);
- iii. the climate during deposition; eg the warmer the climate, the more tropical the plant species and the more lush the growth - but also the greater the rate of decomposition;
- iv. the type of swamp; ie whether the environment was terrestrial (telmatic), fresh water lake (limnic), brackish or marine (paralic);
- v. the behaviour of the water table. If the water table rose faster than the peat accumulated then the peat swamp was drowned. If the water table dropped then the surface of the peat rotted;
- vi. the nutrient and sulphur supply, the acidity (pH) and redox potential (Eh), all of which influenced, to a lesser or greater extent, the plant species and the bacterial activity.

These factors are called "coal facies" and, together with the geological setting, eventually determine the structural and chemical characteristics of the coal. Teichmuller and Teichmuller⁽¹⁾ have described these coal facies in great detail but generally this, and other documentation⁽²⁾, centre the discussion on the evolution of the

Carboniferous coals of Europe and North America and the Gondwana coals of Australia, India and South Africa. These coals originated in the Permian to Mesozoic periods; ie were formed as long as 300 million years ago. Most New Zealand coals are of late Cretaceous or Tertiary age⁽³⁾, with the exception of a few thin seams of coal in Jurassic rocks in Southland⁽⁴⁾. The presence of Pleistocene lignites at North Kaipara and the peat swamps of Waikato, Southland and the Chatham Islands⁽⁵⁾ suggests that the "geological conditions that allowed coal formation, continue to the present day"⁽⁵⁾. The young age of the New Zealand coals (70 m.y.a.) infers that many of the coal facies at work during formation of the older coals of the world were completely altered by the late Cretaceous and Tertiary times. The following discussion outlines the knowledge of the depositional environments of Australasian coals.

2.1.1.1 New Zealand Coals - Geological Setting

The main coal regions of New Zealand⁽⁵⁾ are shown in Figure 2.1.

The coals of the major coalfields range in age from late Cretaceous (early Senonian) to Miocene. It is thought that the New Zealand landmass reached its maximum size in the early Cretaceous⁽⁶⁾. By the late Cretaceous most of this land had become low lying. Two processes evolved during this time which hindered the river transport of sediment to the sea and resulted in "extensive terrestrial sedimentation"⁽⁴⁾. Firstly, the onset of the general marine transgression gradually raised the river base levels and caused large coastal flats. Peat swamps developed where sediment supply and plant growth favourably balanced the water level⁽⁷⁾. Secondly, the downwarping of some inland areas allowed the local formation of very thick coal measures such as those in the Westland coal region. Thus, New Zealand coal fields originated as either extensive coastal, or shallow inland lake swamplands.

The majority of coal measures were gradually buried under marine sediments as the marine transgression continued through the late Cretaceous and early Tertiary. Most of New Zealand was covered by the sea by the mid-Oligocene, except for parts of Central Otago and the "low median ridge where the present Southern Alps are"⁽⁴⁾ found. The New Zealand landmass re-emerged during the late Oligocene and Miocene and new areas of sedimentation developed.

Figure 2.1: Coal Regions of New Zealand. Approximate positions of deposits also marked.

New Zealand's coal measures are found in two main stratigraphic positions, due to the marine transgression then later regression:

- "1. Resting on old basement rocks and overlain by (at places interfingering with) marine sediments; or
2. Close above marine beds near the base of succeeding freshwater beds."

R. P. Suggate, 1959⁽⁴⁾

The coal measures have diverse and complex structural characteristics because of the great variety in sedimentation trends and geological histories. Sherwood and Suggate⁽⁵⁾ recently published stratigraphic and structural summaries of the New Zealand coal regions.

2.1.1.2. New Zealand Coals - Climate and Vegetation

"Palynological data from Australia and New Zealand show marked vegetational changes throughout the late Cretaceous and Cenozoic in response to climatic changes, fluctuations of the Antarctic ice cap, drifting of the continents and, to a lesser extent, tectonic activity."

D. C. Mildenhall, 1980⁽⁶⁾

These vegetational changes occurred throughout the main periods of coal deposition. It is therefore likely that great variability occurred in the plant composition of the peats of different ages, different localities, and even between the base and top of large swamps.

Mildenhall⁽⁶⁾ has described the history of New Zealand's vegetation. The following is a summary of the main climatic changes and dominant vegetation between the late Cretaceous and Miocene (Table 2.1).

i. Late Cretaceous - New Zealand and Australia split apart from Antarctica. The New Zealand landmass moved to a position between 68°S and 78°S (c.f. present day latitude 36°S-46°S). The relatively low temperatures and high rainfall was reflected in temperate vegetation, particularly podocarps and ferns, throughout New Zealand and Australia. The rapid evolution of angiosperms (eg beech species) also occurred at the end of the Cretaceous.

ii. Paleocene - New Zealand and Australia moved north from Antarctica and New Zealand separated from Australia. This early isolation resulted in the development of a great amount of endemic terrestrial flora.

TABLE 2.1

FAMILY	GENUS	HABITAT	FIRST NZ APPEARANCE	MODERN EXAMPLE	
1. <u>Gymnosperms (Conifers)</u>					
Araucariaceae	Agathis	Lowland forest	Mesozoic	A. australis	Kauri
Podocarpaceae	Podocarpus	Forest (swamp forest)	Mesozoic	P. totora P. ferrugineus P. dacrydiodes ^a	Totora Miro Kahikatea
	Dacrydium	Forest	Upper Cretaceous	D. cupressinum	Rimu
	Phyllocladus	Forest	Upper Eocene	P. trichomanoides	Celery Pine or Tanekaha
2. <u>Angiosperms - Dicotyledons</u>					
Fagaceae (beech)	Northofagus	Forest	Upper Cretaceous	N. fusca N. truncata N. menziesii	Red Beech Hard Beech Silver Beech
Casuarinaceae	Casuarina ^b	Coastal forest ^c	Paleocene	C. equisetifolia ^d	She-oak
Myrtaceae	Leptospermum	Widespread	Paleocene	L. scoparium	Manuka
	Metrosideros	Forest	Paleocene	M. robusta	Nthn. Rata
3. <u>Angiosperm - Monocotyledons</u>					
Agavaceae	Phormium	Swamps/open areas	Upper Eocene (?)	P. tenax	NZ Flax
Cyperaceae (sedges)	Numerous eg	Widespread damp areas	Oligocene		
	Carex Cyperus			C. lurida C. rotundus	Sallow sedge Nut Grass
Liliaceae (lilies)	Numerous eg Astelia	Widespread	Upper Eocene	A. trinervia	Kauri Grass
Sparganiaceae	Sparganium	Wet areas	Oligocene		Maori Burr-Reed or Maru
4. <u>Spteridophytes (ferns and fern allies)</u>					
Cyatheaaceae	Cyathea (tree ferns)	Forest, lowland to sub a pine	Mesozoic	C. medullaris	Mamaku or Black Tree Fern
5. <u>Bryophytes (mosses)</u>					
Shagnaceae	Sphagnum	Widespread damp areas (acid bogs)	Late Cretaceous	S. Critatum	Sphagnum moss

(a) dacrydiodes = "resembling dacrydium"

(b) extinct taxa

(c) Merrill "Plant Life of the Pacific World" 1945

(d) Not a New Zealand native

iii. Eocene - "The Eocene was a time of widespread change in the vegetation patterns of Australia and New Zealand"⁽⁶⁾ due, in part, to the increasing distance between Australia and Antarctica. The climate became temperate but still humid. The beeches were the dominant vegetation; firstly Nothofagus fusca but then, with the cooling at the end of the Eocene, Nothofagus brassi. Many tropical and subtropical taxa disappeared.

iv. Oligocene - At the end of the Eocene and early Oligocene, New Zealand migrated northwards to between 41°S and 52°S and eventually to 35°S by the late Oligocene (about present day position). The Australian landmass moved further from Antarctica resulting in an increased influence of westerly winds on New Zealand. A great increase in new temperate plant forms occurred in the late Oligocene, although beeches and podocarps were still prominent within "high-diversity assemblages". At this stage, a differentiation was noticeable between a) South Island and North Island plant assemblages, with less diversity in species in the latter, which may indicate a change in paleoenvironment; b) between the southern and northern districts of the South Island, with the former "dominated by lake and swamp pollen", but the latter were "often coastal or near coastal and reflect dense, humid, lowland forest settings".

v. Miocene - The New Zealand landmass was positioned between 33°S and 53°S and the plant assemblages were again dominated by the "brassi" beech. "In the south of the South Island and the north of the North Island, flat low-lying swamp areas were common in which sparganium was abundant". Temperate genera were more plentiful in the southern region.

The climate was much colder in the late Miocene with a resultant change in vegetation. The "fusca" beech and podocarps were as prominent as the "brassi" beech; herbaceous species and many new taxa had developed.

These combinations of climatic changes and evolutionary trends in New Zealand flora from the late Cretaceous to the Miocene would have greatly influenced the plant communities of coal forming swamps.

Within each of the regions shown in Figure 2.1, several different coalfields are defined and detailed geological analyses have been published as Bulletins and Reports of the New Zealand Geological Survey (NZGS). With the exception of the Canterbury and Northland areas, samples from all coal regions (and most coalfields) have been included in this study.

2.1.1.3 New Zealand Coal Regions

i. The Waikato Region - The Waikato coal measures form part of the Te Kuiti group of Tertiary strata and are of Upper Eocene age⁽⁹⁾. The Lower Waikato coal measures contain two major coal seams, namely the Taupiri Upper and Lower seams. The Upper Waikato coal measures include the Kupakupa seam and, above that, the Renown seam which merges in places with the Kupakupa seam⁽⁸⁾. A seam above the Waikato coal measures, the Kamps Seam, is fully developed in the lower region of Waikato. All the coal measures lie on Mesozoic basement rocks and are overlain by a succession of marine strata of Oligocene age.

The Waikato coal measures are thought to have been deposited in a "trough"⁽⁹⁾ or wide valley made up of a series of semi-detached basins. This valley extended from north of the Maramarua coalfield (Figure 2.2) to south of the Kawhia coalfield. It was centred in the "Rotowaro Deep" where the coal measures are thickest (900 feet). Several of the coal seams are spread over very large areas and must represent very thick, laterally persistent, original peats. Different rates of river water-table rise have resulted in alternating seams of coal and mudstones.

The plant microfossils of the Lower Waikato coal measures are dominated firstly, by Haloragacidites harrisii, which is related to Casuarina (see references (11) and (17) with respect to alternative names), and secondly, to a lesser extent, by the many conifer species. In contrast, the upper coal measures contain abundant Northofagus (beech) specimens and fewer conifer species⁽¹⁰⁾.

The Kupakupa seam is the predominant seam mined in the Waikato coal region although other seams may also be included. For example, the Taupiri seams are exposed in the Rotowaro coalfield while the Kamps seam, which bears a strong marine influence, becomes important in the Kawhia and Tihiroa coalfields⁽⁸⁾. It is the only seam present in the Whatawhata coalfield.

ii. The Taranaki Region - The Taranaki coal region contains several coal measures. By far the most important are the Maryville coal measures which form part of the Miocene Mokau group. The Maryville coal measures are unusual in that they are both underlain and overlain by marine sediments⁽¹¹⁾. This implies that the peat swamps formed between marine regression and transgression. It is likely that peat deposition occurred

Figure 2.2: Waikato coalfields.

in "extensive coastal swamps separated from an open marine shore by a barrier system"⁽¹¹⁾. The higher sulphur contents of coals at the seam bases reflect the decreasing paralic influence on the peat as the marine regression occurred⁽¹¹⁾. There is also evidence for an increasing marine influence to the west of the Taranaki region.

Couper⁽¹²⁾ examined the plant assemblages of three coal samples from the Mokau coalfield and found the floras to be dominated by beech species.

The Mokau and the Waitewhena coalfields contain most of the regions coal resources⁽⁸⁾.

iii. The Westland Region - The Westland coal region includes many coalfields but most of the working mines are grouped into three main areas; Greymouth, Buller and Reefton (Figure 2.3)⁽¹³⁾.

a. The Greymouth area - The Paparoa coal measures are divided into Lower (Jay and Morgan seams), Middle (Rewanui seams) and Upper (Dunollie seams) coal horizons. The Brunner coal measures (Brunner seam) are above the Paparoa coal measures. The Paparoa measures range in age from the late Cretaceous (early Senonian), through to a Paleocene age in the upper-most Dunollie coal seams⁽¹⁵⁾. The Brunner Coal measures are of Eocene age⁽¹⁴⁾.

The geology and depositional environment of these coal measures have been described in detail by Gage⁽¹⁴⁾. The coals in the Lower and Middle Paparoa groups are believed to have accumulated during transgressions or regressions of lake waters. The mostly thin Dunollie seams, of the Upper Paparoa measures, suggest that the environment was terrestrial and accumulation of debris was slow. The Brunner coal was accumulated in "brackish swamps between low-lying land and salt-water lagoons"⁽¹⁴⁾, which are likely to have supported different vegetation from the underlying Paparoa coal measures.

"The Paparoa coal measures are some of the oldest sediments which contain angiosperms in New Zealand"⁽¹⁵⁾. Raine⁽¹⁶⁾ has recently defined bio-stratigraphic units, labelled according to the dominant plant microfossil, for the West Coast which incorporate the Paparoa and Brunner coal measures. The former are included in the "Phyllocladites mawsonii" assemblage (PM) in which podocarpaceous

Figure 2.3: Westland coalfields

pollen are abundant. The "diversity and abundance of angiosperm pollen" increases through the three PM zones⁽¹⁶⁾. The Brunner coal measures are included in a separate unit characterised by the abundance of "Myricipites harrisii" (MH) (synonymous with Haloragacidites harrisii) and warm-climate taxa. In contrast to the PM zones, the pollen of gymnosperms are uncommon.

- b. The Buller area - The coal seams mined in the Buller area form part of the "Brunner coal measures" which overlie basement rocks (cf. Greymouth region) and are of Eocene age; ie of the same period as the Brunner coal measures of the Greymouth area⁽¹⁹⁾. However, the coal is considered to be "entirely of fresh-water origin"⁽¹⁸⁾. It exhibits complex splitting, with sandstone and mudstone, due to the local deposition of sediment by small streams on the deltaic environment of a shallow lake. In places the coals have very low ash contents (less than 0.5%) which is thought to represent the formation of raised bogs⁽¹⁷⁾.

The Brunner coal measures are overlain by originally very thick, "micaceous" marine siltstones, mudstones and sandy layers which make up the Kaiata Formation⁽¹⁷⁾. The distance between the coal seams and the overlying marine sediment appears to control the amount of sulphur (organic) in the coal.

- c. The Reefton area - The coal mined in the Reefton district is from the "Quartzose coal measures" which are of Eocene age⁽¹⁹⁾ and overlie basal conglomerate. Varying amounts of sandstone, siltstone and mudstone are included in the coal measures. The lower part of the Quartzose coal measures, which includes the coal seams, are fresh-water beds. The upper layers are interbedded with marine beds suggesting that the advance of the marine transgression was not uniform.

The plant microfossils of the Quartzose coal measures were studied by D. R. McQueen⁽¹⁹⁾. He concluded that the coal forming vegetation consisted of Cyperaceae, Liliaceae and Myrtaceae with some Podocarpaceae contribution.

iv. The Southland Region - The Southland coal region contains two quite separate coal areas; the coal measures of the Ohai field and the eastern Southland lignite fields (Figure 2.4).

- a. Ohai Coalfield - Coal is mined from two groups of measures; the Ohai Group and the Nightcaps Group⁽²⁰⁾. The Ohai Group of late Cretaceous sequences includes the Waimio coal measures and the Morley coal measures. The Nightcaps Group is of Eocene age and contains the Beaumont coal measures.

The deposition of coal measure sediment in the late Cretaceous initially involved a relatively short phase resulting in the thin seam of the Waimio coal measures. These measures were overlain by sand, silt and mud⁽²⁰⁾.

The formation of the many seams in the Morley coal measures is thought to have been caused by periodic but brief flooding of "poorly drained, predominantly forest swamps"⁽²¹⁾. The seams of the Morley coal measures have been divided into three paleo-botanical zones labelled according to the dominant flora; "Podocarpidites cf. ellipticus" (lower zone), "dacrydiumites" (middle zone) and "podocarpidites marwicki" (upper zone)⁽²⁰⁾.

Another period of sedimentation occurred in the middle to upper Eocene. Locally thick peat developed on lake fringing swamps. The peat was frequently flooded⁽²¹⁾ and eventually covered by the marine muds and clays of the marine transgression, forming the Beaumont coal measures. Couper⁽²⁰⁾ has also defined two floral zones, both dominated by beeches, for the Beaumont coal measures; the lower Northofagus flemingii zone and the upper Northofagus matauraensis zone. Evidence for Sphagnum and the pollen of Cyperaceae and other herbaceous plants, are also common in both sets of coal measures⁽²⁰⁾.

- b. Eastern Southland Lignite Fields - The Southland lignite deposits are found in the Gore lignite measures which were deposited in the upper Oligocene to early Miocene⁽²²⁾ in a "prograding deltaic to fluvial sequence"⁽²³⁾. Estuarine (Pomahaka) and marine (Chatton) formations are occasionally found at the base of the measures. A delta plain formed, as the marine regression continued, upon which peat swamps

Figure 2.4: Southland coalfields.

developed over large areas. The deposits were eventually overlain by fluvial sediments. Thus, the Gore lignite measures generally follow the sequence; "a lower sand dominated unit in places including thin discontinuous lignite seams, a middle interval with two to five significant laterally persistent seams, and an upper unit with little lignite, dominated by gravels, sands and thick intervening mud stones"(23).

Pocknall and Mildenhall(23) have divided the Gore lignite measures into spore-pollen zones. The lignite seams are included in two zones which are dominated by beech species and Haloragacidites harrisii.

v. Otago Coal Region - The Otago coal region can also be divided into two areas; the coastal Kaitangata coalfield and the Central Otago lignite fields (Figure 2.5).

a. Kaitangata Coalfield - The Kaitangata coal deposits include many coal horizons that are part of the Taratu formation of late Cretaceous age(24). The numerous seams are thought to have been formed as a "series of peat swamps and coalescing flood-plain deposits in a structural depression"(24). The scarp of the Castle Hill fault caused the formation of a flood plain which merged with estuarine and marine beds. Streams periodically deposited conglomerate, either in restricted areas causing local seam splitting or, over the entire area forming at least eighteen coal horizons in the Taratu formation. With "progressive subsidence of the region ... the shoreline migrated westwards"(24) depositing the marine sediments of the Wangaloa formation.

b. Central Otago Lignites - The Central Otago lignites are contained within the Miocene Manuherika Group - a "thick widespread unit of fluvial, lacustrine and swamp deposits"(25). One major group of seams is, in general, mined throughout the area with mudstone partings between splits and thinner seams. The seams overlie either fluvial gravels and sands or lie directly on the basement rock. The Manuherika strata overlying the lignite consists predominantly of silty mudstones(24).

Couper(12) compared the abundance of three groups of flora (Northofagus brassi, Northofagus fusca and Podocarpaceae) in the

Figure 2.5: Otago coalfields.

"Central Otago" and "Mataura" (Southland) lignites. He showed that all three were common in the younger Central Otago lignites but that the "brassi" beeches dominated (almost to the exclusion of the other groups) the older "Mataura" lignite assemblages.

vi. Summary - In 1952, Suggate and Couper⁽²⁶⁾ defined three broad groupings of New Zealand coal measures divided by two widespread geological events; i) the "development of a peneplain during middle and upper Cretaceous times" and ii) the deposition of large amounts of sediment associated with the marine transgression which culminated in the lower Oligocene. Thus, the three groups are classed as the Lower (pre-peneplanation), Middle (post-peneplanation and pre-marine) and Upper (post-marine) coal measures.

The coal measures have been allocated to periods mainly on plant microfossil evidence. Figure 2.6 has been adapted from the work of Suggate and Couper to include coal measures that have since been paleobotanically studied and assigned an age.

2.1.1.4 Australian Coal Regions

The Australian coals included in this report include Victorian brown coals and "Black" coals from New South Wales and Central Queensland (Figure 2.7).

i. Victorian Brown Coals - The Victorian brown coals form part of the Latrobe Valley coal measures (Figure 2.8)⁽²⁷⁾. Following the peneplanation in Victoria, in the late Cretaceous, a period of uplift occurred in the lower Tertiary. The Latrobe Valley Depression formed upon which deposition began. The oldest sediments, the Childers formation, includes some brown coal but remnants of lava flows from a volcanic epoch overlie and interbed with this formation⁽²⁸⁾. The remaining measures are divided into three units based on their coal seams. The oldest, the Traralgon group, contains the Traralgon Seam which is mainly developed in the Loy Yang - Gormandale area where it is up to 200 feet thick. The Morwell Group is a "complex system of thick coal seams and interbedded clays and sands"⁽²⁷⁾. In the Yallourn - Morwell area, the group directly overlies the volcanic sediments. The Yallourn seam in the Yallourn Group is the youngest in the Latrobe Valley and is separated from the Morwell Group by clays and sands.

The thick and laterally persistent coal seams of the Latrobe Valley Coal measures represent very large peat swamps. Deposition must have

Figure 2.6: Classification of the coal measures into three groups based on two widespread geological events; i) the period of peneplanation and ii) the marine transgression.

Figure 2.7: Coal Regions of Eastern Australia.

Fig

Figure 2.8: Maps of the Latrobe valley showing a) the general location and b) the mine and drillhole locations.

occurred over an extensive period. It is thought that the Traralgon Group is of Eocene age while the Yallourn Group may be as young as mid-Miocene (27).

Paleobotanical studies have shown "that conifers formed the greater part of the plant material and, in particular, the wood, from which the brown coals were derived"(27). The conifers included Agathis, Araucaria, Dacrydium and Podocarpus. Plant remains of Casuarina and Northofagus have also been identified(27).

ii. Black Coals - Several of the fields mining black coal in Eastern Australia are shown in Figures 2.9 and 2.10.

a. New South Wales Region - The black coal is contained in the sediments of the Sydney basin which developed in the Permian era(29) and is described in detail in a recent New South Wales Geological Bulletin(30). The "Greta Depositional Episode"(30) initially involved marine and volcanic sedimentation. In the latter period of this deposition, a thick terrestrial sediment wedge (the Greta Coal Measures) emerged and penetrated south-westwards into the northern Sydney Basin(30) forming a "fluvio-deltaic" plain. A marine transgression followed and the widespread inundation of the low lying basin formed the "Upper Marine Series"(28) of sediments. The withdrawal of the sea at the close of the Permian marked the change from marine to fresh-water sedimentation. Large deltaic plains developed and the deposition of the "Upper Coal Measures" occurred. Two "distinct depositional sub-basins"(30) developed in the north and north-west. The resultant lower and upper coal measures are termed the Tomago and Newcastle Coal Measures, in the north, and the Wittingham and Wollombi Coal Measures, in the northwest. Both are split by the sediments of rapid marine transgressions and regressions. Estuarine and intertidal environments persisted in the southern Sydney Basin and the corresponding deposits are called the Illawarra Coal Measures.

Coal measure deposition was halted when the "Late Permian Illawarra-Newcastle Coal Measures were transgressed by estuarine conditions over wide areas"(30). The age of these Australian coal measures indicates that the vegetation from which it is derived would have been far more primitive than that of the Australasian Cretaceous and

Figure 2.9: Locations of mines from which New South Wales black coal samples were obtained.

Figure 2.10: Locations from which Queensland black coal samples were obtained.

Tertiary coals. The Permian time was a period of warming after the freezing temperatures of the late Carboniferous. The coastal peat swamps, that produced the Lower (Greta) Coal Measures, sustained shrubs, such as the pteridosperm (seed fern) Botrychiopsis, and some trees, such as Gangamopteris, which had aquatically adapted roots⁽³⁰⁾. By the late Permian, the fresh-water swamp forest communities were dominated by Glossopteris; a "woody gymnospermous tree with pteridospermous affinities"⁽⁵⁶⁾, (Upper Coal Measures). It was not until after these coal measures were inundated (Triassic) that conifers became abundant.

- b. The Queensland Region - The largest coal reserves in Queensland are located in the Bowen Basin sediments which developed in the Lower Permian as a series of troughs⁽³¹⁾. The oldest (but minor) coal measures were deposited in a number of separate areas prior to a basin-wide marine transgression. Coal measures formed only "near the margins, in deltas or during regressive and transgressive periods"⁽³¹⁾; eg the Collinsville Coal Measures. The Blair Athol coals are thought to be of about the same age but to have been deposited in an isolated basin adjacent to the Bowen Basin⁽³¹⁾. Another major marine transgression terminated this period of coal formation and the basin became wholly marine until regression once again initiated coal deposition. These sediments contain a great amount of volcanic material. The "depositional environment became wholly fluviatile and lacustrine with extensive coal swamps"⁽³¹⁾ upon completion of this regressive phase. The resultant coal measure formations contain some very thick units including the Baralaba Coal Measures (215 to 300 metres).

Coal swamp conditions were terminated abruptly in the Triassic period, probably due to "regional changes in both depositional and climatic conditions"⁽³¹⁾. It can be seen that these coal measures are of equivalent age and depositional environment to the black coals of New South Wales (Figure 2.11). Fossil plants including Glossopteris and Gangamopteris have been found in adjacent sediments⁽²⁸⁾. These deciduous Permian flora are now extinct taxa⁽⁵⁶⁾.

Million years		Stage		Coal Measures
220	Triassic	L		
230				
240	Permian	U	Tatarian	Baralaba, Newcastle, Illawarra, Tomago.
250			Kazanian	
			Ufimian	
260		L	Artinskian	Collinsville Great Greta
270			Sakmarian	
			Asselian	

Figure 2.11: Correlation of the black coal measures of Eastern Australia.

2.1.2 Chemical Origins

The precursor of coal, the peat, is not a simple chemical compound but consists of a myriad of complex organic structures derived from the different parts of plants and their decomposition products. Not all peats have the same combination of vegetable structures. Factors that influence the peat character include the relative proportions of higher to lower plants and the level of degradation (eg bacterial activity). It is only under special conditions, such as those that exist in peat swamps, that the fundamental biochemical cycles (Calvin, Krebs) are joined by the humification process.

2.1.2.1 Chemical components of plants

Plant components are not equally stable in the peat environment but most will contribute, in some form, to the chemical matrix of the coal.

i. Carbohydrates - The class of components called carbohydrates include simple sugars, starches and celluloses. Simple sugars, such as glucose, fructose and sucrose (Figure 2.12a), are constituents of many fruits and vegetables. Starches are the storage form of carbohydrates in plants. Cellulose is the main supporting structure of trees and plants being the main constituent of the cell wall⁽²⁾. For example, the strength of wood is derived principally from hydrogen-bonds between one cellulose chain and hydroxy groups of neighbouring chains. Wood consists of up to 60% cellulose⁽³²⁾, whereas algae contain very little of this complex sugar.

Other carbohydrate derivatives occurring in nature include pectin, which is a constituent of plant saps and fibres⁽²⁾ and alginic acid⁽³²⁾, which is a major component of some algae (Figure 2.12b). Also common are polymers of five membered ring sugars, such as arabinose and xylose, which form the pentosans or plant gums. Ribose and deoxyribose are constituents of the nucleic acids, RNA and DNA, the essential components of the cytoplasm and nuclei of cells (Figure 2.12c).

ii. Proteins and other nitrogen compounds - Proteins are polymers of a series of amino acids, which vary greatly in composition, but always contain the basic/acidic functionality which forms the peptide bond:

Figure 2.12: Common plant carbohydrates. a) Glucose (i), starch (ii), and cellulose (iii), b) pectin (i) and alginic acid (ii), c) xylose (i) and ribose (ii).

The majority of the R-functionalities are aliphatic compounds but some contain more complicated groups. Examples of larger amino acids are shown in Figure 2.13a. Insoluble proteins are readily degraded to the amino acids by enzymes which break the peptide bonds in the presence of water. Although the proteins are the least resistant plant "chemical" their monomer units, the amino acids, may contribute to the structure of coal. For example, phenyl alanine and tyrosine are irreversibly deaminated, by two naturally occurring enzymes to cinnamic acid and p-coumaric acid, respectively. These two acids are important precursors of lignin (see next section)(36).

Other naturally occurring nitrogen compounds include the porphyrin, chlorophyll (Figure 2.13b), which participates in photosynthesis and is therefore concentrated in algae and the leaves of higher plants.

Nucleic acids are also included in this group. These biopolymers are present in the cell nucleus, and consist of four monomer units called nucleotides (Figure 2.13c). Parts of these polymers, such as the nitrogen containing base units, may persist in the peats.

iii. Lignins and Lignans - "After cellulose, lignin is the second most abundant polymeric organic natural product."

H. Nimz, 1974(34)

Lignin formation is characteristic of vascular plants as it enables these plants to develop "large upright forms"(37). The stems of trees are mainly composed of xylem tissue which is characterised by "elongated cells with thickened walls, impregnated by lignin"(37).

It is thought that 22-34% of the total wood is lignin, although not all of the lignin may be extracted by chemical means(36) because of its resistant structure.

Lignin is a complex three dimensional polymer of phenyl propanoid ($C_6 - C_3$) units (Figure 2.14a). It has been known for some time that lignin varies with plant species(2,37). This trend is exemplified by the different precursor aromatic alcohols (Figure 2.14b) and related extractives from the woods(38). The 3-methoxy-4-hydroxy phenyl unit (guaiacyl), such as that in coniferyl alcohol, is abundant in softwood lignins (eg conifers). The 3,5-dimethoxy-4-hydroxy phenyl group (syringyl), such as that in sinapyl alcohol, is dominant in hardwoods (eg beeches) and grassland vegetation(38).

Figure 2.13: Proteins and other nitrogen-containing compounds. a) Amino acids lysine (i), histidine (ii), tyrosine (iii), b) chlorophyll A, c) portion of DNA molecule.

Figure 2.14: Lignin monomer units and lignans. a) Phenyl propanoid unit, b) cinnamic acid (i), p-coumaryl alcohol (ii), coniferyl alcohol (iii), sinapyl alcohol (iv), c) lignans, pinorezinol (i), dehydrodiconiferyl alcohol (ii), guaiacyl glycerol-coniferyl ether (iii).

In 1953 Freudenberg showed that certain common plant enzymes oxidised a mixture of the three p-hydroxy alcohols to yield a lignin-like polymer⁽³⁶⁾. He postulated that the monomer precursors must be polymerised in a random manner involving a free radical mechanism and complex interchain and side chain condensations⁽³⁷⁾.

The phenylpropanoid dimers observed by Freudenberg also occur naturally in woods and are termed "lignans"⁽³⁷⁾, or "dilignols"⁽³⁴⁾. Examples of guaiacyl type lignans (Figure 2.14c) indicate the types of condensations that must occur in lignin formation.

The proposals for the structures of spruce lignin ⁽³⁷⁾ and beech lignin ⁽³⁴⁾ incorporate a great variation in phenyl propane units and types of linkages, some or all of which may still exist in coals.

iv. Tannins - Tannins are high molecular weight polyphenols which can strongly bind proteins via the large number of phenolic hydroxyls, and thus "tan" leather. They are classified into two broad groups; the hydrolysable and the condensed (non-hydrolysable) tannins⁽³⁶⁾. Hydrolysable tannins usually contain a central core of a polyhydric alcohol such as glucose, esterified with gallic acid (gallotannins) or hexahydroxydiphenic acid (ellagitannins) (Figure 2.15a) The condensed tannins are mostly "flavolans" - polymers of flavan-3-ols (catechins) and/or flavan-3,4-diols (leuco-anthocyanidins) (Figure 2.15b)⁽³⁶⁾.

Tannins are associated with the higher plants with up to 17% concentrated in the bark and up to 6.5% in the leaves⁽³²⁾.

v. Fats and waxes - Fats and waxes belong to the family of water insoluble lipids. Seeds, spores and fruits are particularly rich in lipids⁽²⁾. Fats are esters of fatty acids and glycerol (Figure 2.16a)⁽³⁸⁾. The aliphatic tail of the fatty acid contains an even number (commonly 16 or 18) of carbons and is often unsaturated, particularly in vegetable oils (Figure 2.16b).

Waxes contain esters of longer (C_{24} to C_{36}) fatty acids with more complex alcohols either, of the sterol series or, primary aliphatic alcohols of even carbon number (C_{16} to C_{36})⁽³²⁾.

Fats generally act as food stores while waxes often fulfil protective functions (Figure 2.16c). For example, waxes form one of "the major

Figure 2.15: Tannin monomer units. a) Hydrolysable tannin precursors, gallic acid (i), hexahydroxydiphenic acid (ii), b) condensed tannin precursors, catechin (i), leuco-anthocyanidin (ii).

Figure 2.16: Fats and waxes. a) Formation of triglyceride (fat) from glycerol (i) and fatty acid (ii), b) examples of major fatty acids of leaves, palmitic acid (i), linoleic acid (ii), c) protective wax found in rye grass, d) structure of cutin.

constituents of the cuticle layer which covers the epidermal cells of the leaves, fruits and other tissues of higher plants"(40).

The highly resistant cutin is the other major constituent (50% to 90%) of the cuticle. Cutin is thought to be a "mixture of highly cross-linked hydroxy acids with a dominance of 16, 18 and 26 C-atoms"(2) (Figure 2.16d). Related compounds suberin (inside plant tissues and cell walls) and exine (from cell walls of spores) are also polymers of long chain acids.

vi. Resins and higher terpenes - Resins are one of the most highly resistant group of plant products(2) and are common in higher plants, particularly conifers. The main constituents of resins are the unsaturated resin acids (Figure 2.17a) which have a diterpenoid (C₂₀) structure and easily polymerise to "harden" the resin(41).

Triterpenoids, such as friedelin and betulin (Figure 2.17b) are abundant in higher plants(32). The hopane series of triterpenoids (Figure 2.17c) are dominant in bacteria and algae(32). Derivatives of these compounds, the "geohopanoids", are found in many fossil fuels(43).

The steroid derivatives of triterpenoids, such as sitosterol and stigmasterol (Figure 2.17d), are also abundant in the plant kingdom. The polyunsaturated tetraterpene (C₄₀) carotenoid pigments are common in higher plants where they are concentrated in the fruits and leaves, eg carotene (Figure 2.17e).

2.1.2.2 The inorganic content

There are thought to be three origins for the inorganic matter in coal:

- "a. inorganic matter from the original plants;
- b. inorganic-organic complexes and minerals which formed during the first stage of the coalification process or which were introduced by water or wind into the coal deposits as they were forming;
- c. minerals deposited during the second phase of the coalification process, after consolidation of the coal, by ascending or descending solutions in cracks, fissures or cavities, or by alteration of primarily deposited minerals."

M.-Th. MacKowsky(1)

Figure 2.17: Resins and higher terpenes. a) Diterpenes, abietic acid (i), sandaracopimaric acid (ii), b) triterpenoids, friedelin (i), betulin (ii), c) "hopane" structure, d) steroid derivatives, sitosterol (i), stigmasterol (ii), e) tetraterpene, β -carotene.

The minerals, either weathered or unaltered from original composition, are therefore only part of the inorganic content of coal. The types of minerals likely to be found in coals have been summarised by Black⁽²²⁾, and include quartz, feldspar, clays, hydroxides and sulphates, with the latter usually occurring as a result of weathering.

The other important form of inorganic constituents are the exchangeable cations (usually Na, K, Ca, Mg, Ba, Sr, Fe and Al) which can substitute for hydrogens of acidic groups⁽²²⁾ to form carboxylates.

2.1.2.3 Diagenesis

The beginnings of the formation of coal from peat occur in the period of "biochemical coalification" or "diagenesis"⁽¹⁾ which includes microbial and chemical changes as well as mechanical breakage and compaction⁽³²⁾.

At the surface of the peat (ie approximately 0.5m depth) aerobic bacteria and fungi decompose many of the less resistant biochemicals. Fungi tend to attack the lignin and cellulose of wood tissues. Cellulose is "more easily removed by hydrolysis, and thus preferentially lost relative to lignin"⁽³²⁾. Bacteria also attack the proteinaceous material as well as cellulose. The presence of "microbially derived compounds" such as lipid components, sugars and amino acids, is said to provide evidence for bacterial contribution to the peat⁽³²⁾. All these microbial processes are characterised by oxidation processes.

The lack of oxygen supply at increasing depth (and after initial burial by sediment) induces anaerobic bacterial activity. Eventually all suitable organic substrate is depleted and microbial activity ceases. This initial phase of diagenesis is characterised by the degradation of the less resistant biopolymers into aromatic, phenolic and carboxylic components.

The second stage of diagenesis occurs under reducing conditions and involves the polymerisation of these components with other resistant plant moieties, in a random fashion, to form the overall product of "peatification", the "humic" substances⁽³²⁾.

Diagenesis results in an increase in carbon content as the oxygen/hydrogen rich substances, such as cellulose and protein, are decomposed. An "enrichment of the relatively carbon-rich lignin"⁽¹⁾ and other stable plant compounds, such as the tannins and lipids, occurs. At

the same time, the increasing compaction of the peat causes the moisture content to decrease rapidly.

2.1.2.4 Coalification

After diagenesis, geochemical processes, ie the combination of pressure, temperature and time, take over the "coalification" or "carbonification" of the humic material "that survived the peat formation process"(32).

Geophysical influences, such as the pressure of the overburden, initially cause a rapid decrease in the porosity of the young coal. The continuing decrease in moisture content is partially dependent on the porosity, but it is also related to the "decomposition of hydrophyllic functional groups"(14), such as hydroxyl, carbonyl and methoxyl functionalities, in the early coalification stages.

The "last remnants of lignin and cellulose are transformed into humic materials"(14) during the lignite and subbituminous stages of coalification, and the carboxylic groups are eliminated.

The moisture content and porosity continue to fall, and the density increases, as coalification proceeds. Increasing coalification involves the loss of functional groups, particularly those containing heteroatoms (O, N, S). This is exemplified by the oxygen contents of coals at different stages of metamorphism (Figure 2.18b). The structure becomes increasingly condensed and polymerised and the amount of carbon in aromatic rings, or the aromaticity, increases. Both the loss of oxygen functionalities and the increasing aromatisation are exhibited in the series of diterpenes in Figure 2.18a. The compounds fichtelite and retene have been found in sedimentary rocks(42). Dehydroabietene is common in soils of Canadian pine forests and dehydroabietic acid has been found in buried wood (a seventeenth century coffin!)(42). All are "undoubtedly formed from the same starting material, abietic acid"(42), which, as mentioned earlier, is a major type of resin acid.

The amount of non-aromatic functionalities in the coal decreases in the latter stages of coalification, due partly to the increasing aromaticity, but also because of the removal of aliphatic and alicyclic groups by the process "catagenesis". This process results in an overall increase in methyl groups relative to other, chain aliphatic structures

Lignin	-27 %O
Peat	> 30 %O
Lignite	25-30 %O
Subbituminous	15-25 %O
Bituminous	3-15 %O
Anthracite	< 3 %O

b

c

Figure 2.18: Chemical processes involved in coalification. a) Increasing aromaticity, abietic acid (i), dehydroabietic acid (ii), retene (iii), dehydrobietenene (iv), fichtelite (v), b) oxygen loss, c) catagenesis.

(Figure 2.18c). Other reactions involved in the geochemical processes have also been studied^(42,46).

2.1.2.5 Summary

There have been many "mechanisms" of coalification postulated. The earlier examples have been reviewed by van Krevelen⁽²⁾. Davidson⁽⁴⁴⁾ discussed the current "models" which are said to represent the kinds of structures expected in the macromolecular skeleton of coal, ie the "average structures". The coal structure is so heterogeneous and alters so greatly with the degree of coalification, that it is unlikely that an "ideal" chemical structure will ever be discovered. However, the "representative partial structures" of Wender⁽⁴⁵⁾ do help to visualise the overall chemical changes that occur with increasing coalification (Figure 2.19). They demonstrate:

- i. increasing aromaticity, condensation and polymerisation;
- ii. decreasing functional groups, including aliphatic, alicyclic and oxygenated groups.

2.2 Classification of Coal

"Difficulties and ambiguities of classification are unavoidable for substances as varied and complex as the family of coals".

American Physical Society⁽⁴⁵⁾.

Labels are given to coals of increasing maturity. Coalification is said to proceed from peat, through the levels lignite, subbituminous, bituminous and anthracite. Certain properties have to be measured to classify a coal into one of these stages. There are two main systems for coal classification. The first is based on a large amount of chemical analyses. The second, called "petrography", studies the coal as a rock; ie on the microscopic level.

2.2.1 Chemical Analyses

Most of the chemical analyses of New Zealand coals are carried out by the Coal Research Association (CRA) of New Zealand. The standards of the International Standards Organisation (ISO) are usually followed but are supplemented by specific standards of the American Society for Testing and Materials (ASTM) and British and Australian standards⁽⁴⁷⁾. The analyses

a

b

c

d

e

Figure 2.19: Wender's representative partial structures for five coal ranks
a) lignite, b) subbituminous, c) high-volatile bituminous,
d) low-volatile bituminous, e) anthracite.

are divided into two general groups; "Proximate analysis" which is the set of analyses useful in deciding a coal's industrial applicability, and "Ultimate analysis" which is the set of elemental measurements⁽⁴⁸⁾.

2.2.1.1 Proximate Analysis

Proximate analysis includes the measurement of moisture, ash, volatile matter, fixed carbon (by difference) and certain other properties including heating characteristics.

i. Moisture content - There are several types of "moisture contents" that can be measured for coal which are dependent on the preparation of the sample and the determination procedures⁽⁴⁹⁾. The "moisture in the analysis sample" is determined by the weight loss of the "as-received" sample after drying in an oven at 105°C to 110°C swept by dry air. The measurement of the "air dried" moisture content involves the preconditioning of the sample to "equilibrium" in a controlled room at 20°C and 70% relative humidity. A "loss on air-drying" (LAD) moisture is also measured. This procedure is not applied to lignites as the equilibrium time is too long for practical purposes. The practice for lignites involves a rapid analysis on partially dried samples⁽⁴⁹⁾.

It is often necessary to know (or at least estimate) the bed moisture of the coal; ie the moisture content when the coal is in the ground. There are several methods for estimating this⁽⁴⁷⁾.

- a. Moisture determination on bed-moist samples obtained from the ground. This is not always possible. For example, many of the drilling techniques involve water, thus raising the moisture content. Alternatively, if the sample is taken from the coal face, it may be weathered and have a low moisture content.
- b. Determination of the "Moisture Holding Capacity" (MHC) which is assumed to be synonymous with bed moisture. However, it is only possible to measure MHC for coals that have not dried⁽⁴⁷⁾.
- c. Estimation of MHC from the air-dried moisture (ADM) using the equation:

$$\text{MHC} = 1.3 \text{ ADM}$$

This equation is thought to be valid for samples with less than 20% MHC⁽⁴⁹⁾.

ii. Ash Content - The ash content is measured by burning the sample to constant weight at a maximum temperature of 815°C. The ash content is not the same as the "mineral matter" (mm) content of the coal. The latter is required for determining "mineral matter free" (mmf) properties. For this purpose a mineral matter to ash factor of 1.04 for New Zealand subbituminous coal and lignites, and a factor of 1.08 for the bituminous coals, is applied to the ash (moist basis)⁽⁵⁰⁾.

iii. Volatile Matter - The volatile matter (VM) of a coal is the weight loss of a dry sample when it is heated in the absence of air, at a specified temperature, for a particular time period⁽⁴⁹⁾. This is a very variable property and is highly dependent on the methods of determination. A version of the appropriate ISO standard is used in New Zealand. The coal is heated at 900°C ($\pm 5^\circ\text{C}$) for seven minutes⁽⁴⁹⁾.

iv. Fixed Carbon - The fixed carbon (FC) content is the remainder when the moisture, ash and volatile matter are subtracted from the whole. The FC is meant to represent the non-volatile, combustible component of the coal. However, it "incorporates the errors, bias and scatter in the other three determinations"⁽⁴⁹⁾.

v. The Specific Energy - The specific energy (SE) of the coal is the heat produced when the sample is burned in air. It is measured in megajoules per kilogram (MJkg^{-1}) of sample. The gross results are subject to several corrections including an allowance for the "heat of dilution of the sulphuric and nitric acids formed during the combustion"⁽⁴⁹⁾; ie it is necessary to know or estimate the sulphur and nitrogen contents of the sample.

vi. Caking and Coking Properties - "New Zealand subbituminous coals and lignites do not possess caking and coking properties to any measurable extent"⁽⁴⁹⁾. However, many of the bituminous coals of the West Coast display these properties.

The crucible "swelling number" (SN) is the easiest characteristic to measure and involves heating the sample at approximately 800°C until volatile matter evolution has ceased. The size and shape of the resultant "coke button" is compared to a set of standard profiles and given a number in the series 1 to 9, in $\frac{1}{2}$ steps. Some West Coast coals exhibit a SN of 9+++ which represents complete filling of the crucible!

The measurement of the plastic properties of swelling coals is also of interest. A Geiseler plastometer gradually heats and "stirs" the coal at constant torque. The initial softening temperature, the maximum fluidity (in dial divisions per minute, ddm), the maximum fluidity temperature, the solidification temperature and the plastic range, are measured.

2.2.1.2 Ultimate Analysis

Ultimate analysis is defined as "the analysis of coal expressed in terms of carbon, hydrogen, nitrogen, sulphur and oxygen content"⁽⁴⁹⁾ and is usually quoted on a dry-ash-free (daf) basis. The methods used have been described by Gray⁽⁴⁹⁾. The results have to be corrected for moisture and for the composition of some minerals, such as carbonates and sulphates, included in the sample. The oxygen content is usually estimated by subtracting the percentage of carbon, hydrogen, nitrogen and sulphur, all on a dry mineral matter free (dmmf) basis from the total content. The results should be quoted as "oxygen, plus errors, by difference"⁽⁴⁹⁾, and includes any other elements such as phosphorus and chlorine, present in the coal structure.

2.2.1.3 Chemical "Rank"

There are many systems for classifying coals according to their apparent degree of coalification or "rank". Gray⁽⁴⁹⁾ has discussed the applicability of these systems to New Zealand coals. The ASTM standard (Table 2.2) is the "only national standard which provides a classification for coals over the range found in New Zealand"⁽⁴⁹⁾. The volatile matter (dmmf) is used to categorise the rank divisions for high rank coals, down to medium volatile bituminous coals with VM greater than 31%. The gross specific energy, on a moist mineral matter free (Mmmf) basis, is applied as the ranking criterion for the lower rank coals. The ASTM standard⁽⁵¹⁾ recommends the use of the "appropriate" Parr formulae which for specific energy calculated in MJkg⁻¹, are:

$$SE (Mmmf) = \frac{(SE_{(m)} - .116S) \times 100}{100 - (1.08 A + 0.55S)} \quad [2.1]$$

Approximate formula:

$$SE (Mmmf) = \frac{SE_{(m)} \times 100}{100 - (1.08 A + 0.1S)} \quad [2.2]$$

where $SE_{(m)}$ is the moist specific energy, and S and A are sulphur and ash contents, respectively. These formulae are based on two assumptions:

- a. the mineral to ash factor is 1.08 which is appropriate for

TABLE 2.2 : ASTM CLASSIFICATION SCHEME

Class/Group	Fixed Carbon (%) (Dmmf)	Volatile Matter (%) (Dmmf)	Heating Value (Mmmf) (MJ kg ⁻¹)
I. Anthracite			
1. Metaanthracite	>98	<2	
2. Anthracite	92-98	2-8	
3. Semianthracite	86-92	8-14	
I. Bituminous			
1. Low volatile	78-86	14-22	
2. Medium volatile	69-78 ^a	22-31	
3. High volatile A	<69	>31	>32.56
4. High volatile B			30.24-32.56
5. High volatile C			26.75-30.24
			24.42-26.75 ^b
II. Subbituminous			
1. Subbituminous A			24.42-26.75
2. Subbituminous B			22.10-24.42
3. Subbituminous C			19.31-22.10
V. Lignite			
1. Lignite A			14.65-19.31
2. Lignite B			<14.65

(a) All coals having >69% FC - independent of heating value

(b) Agglomerating

New Zealand's bituminous coals only;

- b. "the proportion of pyritic to total sulphur is 95.3% (numerator) and 95.5% (denominator)" which apparently is "completely wrong for most coals" and is the "main reason why all standard documents, apart from the ASTM, have abandoned Parr's formula long ago"⁽⁴⁹⁾.

The recommendations of many of the other standards for calculation of SE (Mmmf) involve corrections for carbon dioxide and the different types of sulphur (sulphate, organic, pyritic). For example, the British standard employs a correction for the heat of combustion of pyrite:

$$SE(Mmmf) = \frac{(SE_{(m)} - 0.126S_p) \times 100}{100 - mm} \quad [2.3]$$

where S_p is the pyritic sulphur content, and mm is the mineral matter which is derived from the ash using the mineral matter to ash ratio. Gray derived the relationships between pyritic and total sulphur, and thus the SE (Mmmf) by the British standard, for many of the New Zealand coal regions. Representative samples from New Zealand coal mines were then classified according to the specific energy (Mmmf) categories of the ASTM standard⁽⁴⁹⁾.

2.2.2 Petrographic Analysis

The different components of the coal, visible on the macroscopic scale (ie to the unaided eye) are called "lithotypes" or rock types⁽⁴⁸⁾. Lithotypes reflect the "paleoenvironmental position of the peat in the original peat swamp, and geochemical and biochemical conditions at the peat/water interface at that particular geographic and time point"⁽⁵²⁾. The Stopes-Heerlen system of nomenclature⁽⁴⁸⁾ for humic coals includes; i) "vitrain", which is the most common lithotype and is derived from wood or bark; ii) "clarain" and iii) "durain" which are of variable origin - the latter being the hardest coal component, and iv) "fusain" which is mineral charcoal believed to have the same origin as vitrain as it resembles wood charcoal. These lithotypes have been described in more detail by Stach⁽¹⁾.

Components of coal that were distinct on a microscopic scale were termed "macerals" by Marie Stopes in analogy to the minerals in rocks⁽⁴⁸⁾. It has since been found by paleobotanical analyses that correlations exist between certain macerals and particular plant types or tissues⁽¹⁾. The ICCP (International Committee for Coal Petrology) standard rules for petrographic microscopy studies classifies the macerals into three groups; "vitritinite", "exinite" and "inertinite".

In the peat, soft brown and dull hard brown coals (lignites), the humified material that is the precursor to (but shows little resemblance to) the vitrinite macerals, is defined as a separate "huminite" maceral group⁽¹⁾. Similarly, the "exinite" group observed in the lowest rank coals is called the "liptinite" group.

Each of the three main maceral divisions include a series of macerals (Table 2.3), grouped together because of either similar origin or similar type of preservation⁽¹⁾. For example, the process of "vitrinisation" transforms cell walls of wood into telinite (a vitrinite maceral) by humification and gelification. However, if the cell walls had firstly been charred by fire or mouldering, then the process of "fusinitisation" would produce fusinite or semifusinite (inertinite macerals)⁽¹⁾. The origins and properties of all macerals are documented in Stach's Textbook of Coal Petrology⁽¹⁾. - A summary of the origins of some of the main macerals in each group will follow.

2.2.2.1 Vitrinite Macerals

The vitrinites are the most abundant macerals and are the "coalification products of humic substances, which essentially originate from the lignin and cellulose of cell walls"⁽¹⁾. The well preserved humified plant matter, humotelinite, forms the vitrinite macerals; telinite, when the cell walls are distinct from cell infillings, or telocollinite, when the material is structureless. This latter maceral is then grouped with the other collinite macerals. Varying amounts of substances such as tannins, resins and waxes, cutins and pigments, that either impregnate the cell walls or are intimately mixed with the plant matter, are likely to be incorporated into these macerals.

Humic detrital matter is formed when the cellulose-rich parts of the plant, such as leaves and stems, are decomposed. "Finely divided gel particles" are formed between the detritus when strong decomposition occurs. The "intimate mixture" of this material is initially termed humodetrinite and eventually forms the vitrinite macerals, desmocollinite when gelification of detritus particles and dispersed gel produces a very dense homogeneous material, or vitrodetrinite when the detrital texture is still recognisable.

The other collinite macerals have the humocollinite submaceral as precursor and originate from colloidal gels. Gelocollinite is formed as a

TABLE 2.3 : SUMMARY OF COAL MACERALS

<p>a</p> <p align="center">Brown Coals → Hard Coals</p> <p align="center">←</p>			
Maceral Group		Maceral Group	
Huminite	Humotelinite Humocollinite Humodetrinite	Telinite Collinite Vitrodetrinite	Vitrinite
Liptinite	Fluorinite ^b Chlorophyllinite ^b Exsudatinite ^b Bituminite ^b	Sporinite Cutinite Resinite Suberinite Alginite ^b	Exinite
Inertinite		Liptodetrinite Fusinite Semi fusinite Sclerotinite Macrinite Inertodetrinite	Inertinite
		Micrinite	

- (a) Arrows show applicability of macerals to coal
- (b) Grouped together in the terminology of Black⁽⁵²⁾

result of the precipitation of "colloidal humic solutions" that have migrated into existing cavities⁽¹⁾. Corpocollinite is formed from cell excretions of either living or dead cells and, in particular, is likely to contain oxidation or condensation products of tannins.

2.2.2.2 The Exinite (Liptinite) Macerals

The exinites originate from the hydrogen-rich plant constituents including i) the resistant lipid material such as resin and waxes, cutin, fats and oils, and ii) the bacterial degradation products of the large biopolymers such as proteins and cellulose. The exinites contain a far greater amount of aliphatic components (eg n-alkanes) than the macerals of humic origin as a result of the chemical structures of the contributing compounds.

"Sporinite" originates from the outer cell walls (exines and perines) of spores and pollens⁽¹⁾, which consist of a highly cross-linked polymer of carotenoid structures (Figure 2.17e) called sporopollenin. The sporinite from Cretaceous and Tertiary coals is thought to mainly originate from pollen (eg of angiosperms) rather than spores⁽¹⁾.

Cutinite originates from the cuticle layers of, for example, the epiderms of leaves and thus consists mostly of cutin (Figure 2.16d). Cutinite is well preserved through humification and early coalification but appears to be altered strongly at the subbituminous/bituminous boundary⁽¹⁾.

Resinites are commonly formed from resins. They are often found in Tertiary coals because of the abundance of conifers, which "bleed" resin when wounded, in the Tertiary flora.

Suberinite is also found mainly in Tertiary coals and, in parallel to resinite, forms from the suberin of the cork cells in bark and on the surface of roots, stems and fruits. Earlier flora did not form cork.

The remaining exinite macerals are defined for brown coals only (liptinites) or are specific to a type of coal; eg alginite, which is found in oil shales and sapropelic coals only.

2.2.2.3 The Inertinite Macerals

As mentioned earlier, inertinite macerals originate from the same plant matter as the vitrinite macerals. However, the material had undergone "fusinitisation", caused by "charring, oxidation, mouldering" or "fungal attack, before deposition or on the peat surface"⁽¹⁾. The resultant macerals exhibit high carbon and low hydrogen contents and a high degree of aromatisation and condensation. The fusinitisation process effectively "pre-coalifies" the macerals so that they alter little during coalification.

Fusinite and semi-fusinite have the same origins but are distinguished by the degree of fusinitisation.

Sclerotinite is a term derived from "sclerotia", which are durable forms of fungal remains and it is from these that the sclerotinite of the Tertiary coals is formed.

Macrinite is derived from the same gel material from which gelocollinite forms, except that it has firstly been fusinitised.

Inertodetrinite is a mixture of redeposited (eg by wind) "debris of fusinite, semifusinite, sclerotinite and macrinite and of small plant remains which decomposed and fusinitised within the peat"⁽¹⁾.

Micrinite is a maceral only found in bituminous coals, which is thought to be related to exinite, but is of unclear origin.

2.2.2.4 "Rank" and Reflectance Measurements

In contrast to the other maceral groups, the chemical properties of vitrinite vary fairly uniformly with increasing coalification. The chemical changes include increasing aromaticity. The optical reflectance of vitrinite largely depends on the degree of aromatisation. It was therefore chosen as the petrographic ranking parameter.

The reflectance of light off the vitrinite surface is measured relative to a standard of known reflectance. Oil immersion objective lenses⁽⁴⁵⁾ are used to enhance the contrast of the macerals. The mean random reflectance values in oil, R_{mO} are usually measured for lower rank coals. At high ranks, vitrinites exhibit large anisotropies. Thus, the amount of light reflected is dependent on the orientation of the aromatic

lamallae in the vitrinite. The sample is rotated and the maximum and minimum reflectances, R_{Omax} and R_{Omin} respectively, are measured. The most comprehensive study of the reflectances of New Zealand coal mine samples was published by Professor Black in 1980⁽⁵²⁾, in which it is stated that reflectance measurements can only be used to quantify the rank of subbituminous and bituminous coals.

When coals are said to be of the same "rank" it is meant that they have achieved the same degree of "chemical coalification" or "thermal maturation"⁽⁵³⁾. However, substantial differences in physical and chemical properties can occur between coals of apparently equal rank. For example, samples taken from the same position in one seam (serial samples) can exhibit differing analyses⁽⁵⁴⁾. This difference is called "coal type" and is thought to be caused by variation in the deposition and composition of the peat⁽⁵³⁾. The vitrinite of the coal was chosen for rank assessment to "reduce the range of analytical variation"⁽⁵⁴⁾. However, it is still subject to type differences, such as varying volatile matter and moisture content, which must be taken into account.

2.2.3 Summary of "Rank" Classification Schemes

No one rank parameter is applicable over all rank stages (Table 2.4). Several parameters are introduced for most of the standard "chemical" classifications and it is necessary to perform a great many analyses on the coal before it can be categorised. The petrographic system does not cover the lower rank coals and there is some debate with respect to the influences of moisture content ("physical rank"⁽⁵⁵⁾) and "vitrinite type"⁽⁵³⁾ on reflectance measurements. Suggate has developed a classification system termed "R.P.S. Rank"^(4,55) which corrects the specific energy and volatile matter (ie chemical analyses) for the effects of coal type (ie petrographic concept), to obtain a "line of metamorphic development of 'average type' coal"⁽⁴⁾. The "isorank" lines constructed on the VM/SE graphs are given "RPS Rank" numbers, which have since been shown to effectively reflect the oxygen content of the coal⁽⁴⁹⁾.

In conclusion, it is obvious that the quantification of the "rank" of a coal is complicated by many factors. Many of the schemes developed overseas are not completely relevant for the levels of coalification observed in New Zealand coals which are concentrated at the "low-rank" end of the range.

TABLE 2.4 : APPLICABILITY OF RANKING PARAMETERS

"Scientific" Rank Stages	ASTM Classification	APPLICABILITY OF SOME PARAMETERS					
PEAT							
SOFT BROWN COAL	(Brown Coal)					moisture	
DULL HARD BROWN COAL	Lignite					bed	heating
BRIGHT	Subbituminous						value (Mmmf)
LOW- RANK BITUMINOUS HARD COAL	High volatile Bituminous Medium volatile						
HIGH- RANK	Low volatile Semianthracite						
ANTHRACITE	Anthracite Metaanthracite						

%H

volatile matter

%C

reflectance of vitrinite

%M

x-ray
diff.

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3.0 CARBON-13 SOLID STATE NMR3.1 Theory

The theory and use of the NMR technique in the study of liquids has been dealt with by many authors⁽¹⁻³⁾. It is not appropriate to cover this area once again. However, it is appropriate to outline the theory and methods of application of NMR to the solid state.

3.1.1 Nuclear Spin Interactions in Solids

In order to understand some of the problems associated with high-resolution NMR spectra of solids it is necessary to examine the important interactions that contribute to the terms of the nuclear spin Hamiltonian. A typical nuclear spin Hamiltonian ($\mathcal{H}$), is given by:

$$\mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{rf} + \mathcal{H}_Q + \mathcal{H}_D + \mathcal{H}_{CS} + \mathcal{H}_{other} \quad [3.1]$$

where $\mathcal{H}_Z$ and $\mathcal{H}_{rf}$ result from spin interactions with the "external" static and radio frequency (rf) fields, respectively. The remaining terms describe the "internal" interactions which depend upon the fundamental properties of the nucleus and its environment. Detailed discussions of spin interactions have been presented by many authors including Harris⁽³⁾, Abragam⁽⁴⁾, Mehring⁽⁵⁾, Wasylshen and Fyfe⁽⁶⁾. The following discussion is a brief summary of each term for a hypothetical two-spin system, with types of nuclei "I" and "S", both with spin $\frac{1}{2}$ ⁽⁶⁾.

- a. The Zeeman term, $\mathcal{H}_Z$, results from the interaction of the nuclear magnetic moment, μ_i of the nucleus i with the applied static field B_0 , and can be written as:

$$\mathcal{H}_Z = -\sum_i \bar{\mu}_i \cdot \bar{B}_0 = -\sum_i \gamma_i \hbar \bar{B}_0 \cdot \bar{I}_i \quad [3.2]$$

where $\bar{I}_i$ is a spin operator and γ_i is the magnetogyric ratio of nucleus i .

If the applied field lies in the z direction, then

$$\mathcal{H}_Z = -\gamma_I \hbar B_0 \bar{I}_z - \gamma_S \hbar B_0 \bar{S}_z \quad [3.3]$$

for the two spin system.

- b. The radio frequency term, $\mathcal{H}_{rf}$. The rf field, B_{rf} is applied perpendicularly to the static field direction:

$$B_{rf} = B_1 \cos \omega t \quad [3.4]$$

where B_1 is the amplitude and ω is the frequency. If B_{rf} is applied along the x-axis then

$$\mathcal{H}_{rf} = -\gamma_i \hbar \vec{B}_{rf} \cdot \vec{I}_x \quad [3.5]$$

The transition between two states, given by quantum numbers m_0 and m_1 , induced by the applied field has a frequency:

$$\nu_{0,i} = \frac{\gamma B_0}{2\pi} |m_i - m_0| \quad [3.6]$$

when considering the Zeeman interactions only.

- c. The quadrupolar term, $\mathcal{H}_Q$, only contributes to the Hamiltonian when the nucleus has a spin $I > \frac{1}{2}$.
- d. The dipole-dipole term, $\mathcal{H}_D$ is defined as:

$$\mathcal{H}_D = \mathcal{H}_{II} + \mathcal{H}_{SS} + \mathcal{H}_{IS} \quad [3.7]$$

where $\mathcal{H}_{II}$ and $\mathcal{H}_{SS}$ are the sums of homonuclear interactions and $\mathcal{H}_{IS}$ is the sum of heteronuclear interactions. For two isolated spins, I and S, it is given by:

$$\mathcal{H}_{IS} = \gamma_I \gamma_S \hbar^2 \vec{I} \cdot \hat{D} \cdot \vec{S} / r^3 \quad [3.8]$$

where r is the distance between the two spins and $\hat{D}$ is the dipolar coupling tensor. When converted to the spherical polar co-ordinates of Figure 3.1, $\mathcal{H}_{IS}$ is composed of six terms:

$$\mathcal{H}_{IS} = \gamma_I \gamma_S \hbar^2 (A + B + C + D + E + F) / r^3 \quad [3.9]$$

where

$$A = \vec{I}_z \cdot \vec{S}_z (1 - 3 \cos^2 \theta_{IS}) \quad [3.10]$$

A is the only term that commutes with the Zeeman operator. The other terms do not contribute to the Hamiltonian.

It can be shown that there are only two transitions allowed for the I-spin and two for the S-spin. For a single crystal, (ie for one orientation) the two levels are separated by:

Figure 3.1: Spherical polar co-ordinates for the two spins, I and S, separated by a distance r .

$$\gamma_I \gamma_S \hbar^2 (1 - 3 \cos^2 \theta_{IS}) / r^3 \quad [3.11]$$

All possible orientations must be averaged for a powder sample.

The homonuclear interaction terms are defined analogously to $\mathcal{H}_{IS}$ except that, for like spins, the B term must also be considered in the Hamiltonian. For a pair of like I-spins, I_1 and I_2 , the dipolar interaction terms are:

$$A = (1 - 3 \cos^2 \theta) \bar{I}_{1z} \cdot \bar{I}_{2z} \quad [3.12]$$

$$B = -\frac{1}{4} (1 - 3 \cos^2 \theta) (I_1^+ \cdot I_2^- + I_1^- \cdot I_2^+) \quad [3.13]$$

where $I_{\pm}$ are shift operators. The B term alters the nuclear spins by ± 1 and is referred to as the "flip-flop" or exchange term as it provides an efficient method for spin lattice relaxation.

The two allowed transitions for the homonuclear system are separated by:

$$\frac{3}{2} \gamma_I^2 \hbar^2 (1 - 3 \cos^2 \theta) / r^3 \quad [3.14]$$

In liquids, θ is modulated by the rapid isotropic reorientation of the molecules so that:

$$(1 - 3 \cos^2 \theta) = 0 \quad [3.15]$$

Thus, the dipolar term does not contribute to the liquid Hamiltonian.

- e. The chemical shielding term, $\mathcal{H}_{CS}$ arises from the effect of electrons on the field of the nucleus and is defined by;

$$\mathcal{H}_{CS} = \hbar \gamma \bar{I} \cdot \hat{\sigma} \cdot \bar{B} \quad [3.16]$$

where $\hat{\sigma}$ is the dimensionless chemical shielding tensor. The general chemical shielding tensor, in an axis system x, y, z is represented by:

$$\hat{\sigma} = \begin{bmatrix} \sigma_{xx} & \sigma_{xy} & \sigma_{xz} \\ \sigma_{yx} & \sigma_{yy} & \sigma_{yz} \\ \sigma_{zx} & \sigma_{zy} & \sigma_{zz} \end{bmatrix} \quad [3.17]$$

It is always possible to define a "principal axis" system in which all the off-diagonal terms are zero and $\hat{\sigma}$ can be described by three

principal values, σ_{11} , σ_{22} , σ_{33} and the three angles of orientation of the axis system.

In liquids, the principal values of the shielding tensor are averaged to the isotropic shielding constant σ_{iso} :

$$\sigma_{iso} = 1/3 (\sigma_{11} + \sigma_{22} + \sigma_{33}) \quad [3.18]$$

- f. Other interactions include the indirect electron-coupled spin-spin interaction given by:

$$\mathcal{H}_J = \hbar \bar{\mathbf{I}} \cdot \hat{\mathbf{J}}_{IS} \cdot \bar{\mathbf{S}} \quad [3.19]$$

where $\hat{\mathbf{J}}_{IS}$ is a tensor which is also isotropically averaged in liquids.

- g. Summary - The Hamiltonian describes simple splittings for a single pair of spins. For a real system, the full Hamiltonian is a sum of terms over all spins in the solid sample. This gives rise to a very broad line with no structure and hence little information. The effect of the major internal Hamiltonian terms $\mathcal{H}_D$, $\mathcal{H}_{CS}$ (and to a lesser extent $\mathcal{H}_J$) must be minimised in order to obtain a high-resolution spectrum of a solid.

3.2 High Resolution ^{13}C NMR Spectra of Solids

3.2.1 Experimental Techniques

Various techniques have been developed to observe dilute spins, S, in the presence of abundant spins I. "Dilute" is applied to a system where the homo-nuclear S-spin dipolar interactions ($\mathcal{H}_{SS}$) are quite small; eg 1kHz⁽⁶⁾. Carbon-13 satisfies this condition in most carbon containing solids as it has a natural abundance of 1.1%. In the present work the abundant spin I represents, ^1H .

3.2.1.1 High-Power Decoupling and Cross-Polarisation

The major source of line broadening in the ^{13}C NMR spectrum is the dipolar interaction between carbons and nearby protons (ie $\mathcal{H}_{IS}$).

This dipolar broadening is removed by applying a strong rf field to the I spins. This field induces a rapid change in the I-spin states relative to the I-S interaction; ie the I-spins are "decoupled" from the S-spins. The

rf field is applied in a sequence of pulses because of the heating effect of the large decoupling fields needed to remove the interactions.

The applied field can also be used to enhance the sensitivity of the dilute S-spin by the "cross-polarisation" (CP) technique. The CP experiment was introduced by Hartmann and Hahn in 1962⁽⁷⁾ and was first applied to ^{13}C NMR by Pines *et al*⁽⁸⁾, ten years later. Polarisation is transferred from the abundant I species which, in thermodynamic language, has a high heat capacity, to the S-system which has a low heat capacity (Figure 3.2).

The cross polarisation technique has another important advantage, in that it allows experimental recycle times to be governed by the rate at which the I-spin magnetisation recovers to equilibrium when the applied fields are turned off ($1/T_{1I}$) rather than the rate for S-spin magnetisation recovery ($1/T_{1S}$). T_{1C} can be of the order of tens of seconds for organic solids; ie much longer than T_{1H} which is usually less than one second. Thus, far more experiments can be accumulated in a given time using the CP technique.

3.2.1.2 Magic Angle Spinning

The remaining broadening of the solid NMR lines is due to the chemical shift anisotropy term, H_{CS} , in the Hamiltonian arising from the restricted molecular motion in the solid. The shielding experienced by the nucleus under static conditions, is defined by the three tensor components σ_{11} , σ_{22} , σ_{33} . The transformation of the tensor under rotation⁽⁵⁾ results in a spectrum referred to as a "powder pattern". Theoretical powder patterns for three general cases are shown in Figure 3.3. The convention $\sigma_{11} < \sigma_{22} < \sigma_{33}$ is used. The magic-angle-spinning (MAS) technique was proposed independently by Lowe⁽⁹⁾ and by Andrew *et al*⁽¹⁰⁾ to reduce the chemical shielding powder pattern to the isotropic value. This is performed by rotating the sample at an angle β relative to the external field, B_0 (Figure 3.4) such that:

$$(3\cos^2\beta - 1) = 0 \quad [3.20]$$

The magic angle, β , is therefore 54.7° ($54^\circ 44'$).

In high resolution decoupling and CP experiments, MAS eliminates the broadening due to dipolar interactions between S-spins and other dilute spins, including S-spin homonuclear interactions. These interactions are

Figure 3.2: Thermodynamic description of the transfer of polarisation between the two spin systems.

Figure 3.3: Schematic powder patterns for sites of
a) cubic symmetry, $\sigma_{11} = \sigma_{22} = \sigma_{33}$, b) axial symmetry, $\sigma_{11} = \sigma_{22} \neq \sigma_{33}$,
c) lower symmetry, $\sigma_{11} \neq \sigma_{22} \neq \sigma_{33}$.

Figure 3.4: Sample rotation at the magic angle, β , to the applied magnetic field.

usually small, except where the S-spin is coupled to a quadrupolar nucleus. MAS also reduces the magnitude of the coupling constant $\hat{J}$ which determines the $\mathcal{H}_J$ contribution to the Hamiltonian.

Therefore, under the line narrowing techniques of high power I-spin decoupling and MAS, and the sensitivity enhancing CP technique, a high-resolution solid NMR spectrum can be obtained with the S-spin resonances at characteristic Larmor frequencies.

For an S-spin nucleus i , the Larmor frequency (ν_i) is given by:

$$\nu_i = \gamma_S B_0 (1 - \sigma_i) / 2\pi \quad [3.21]$$

where σ_i is the shielding constant of nucleus i . The NMR spectra are usually reported in terms of a "chemical shift", δ_i , in parts per million (ppm) from the Larmor frequency of a reference standard (R) such as tetramethylsilane (TMS); ie

$$\delta_i = \frac{\nu_i - \nu_R}{\nu_R} \times 10^6 \approx (\sigma_R - \sigma_i) \times 10^6 \quad [3.22]$$

Thus, the position of the NMR signal on the chemical shift scale is dependent on the magnitude of the shielding that the nucleus experiences.

3.2.2 Spinning Side Bands

MAS is successful if the anisotropic component of the chemical shift is averaged leaving only the isotropic component. This occurs if the rate of spinning is comparable to the shielding anisotropy (in frequency units). However, this rotation rate cannot often be achieved in practice as it can be several kHz. Spinning at frequencies smaller than the shielding anisotropy results in a series of rotational echoes or "spinning side bands" (SSB) flanking the isotropic resonance line by multiples of the spinning frequency (Figure 3.5). These signals are the manifestation of the remaining anisotropic component. Therefore, the SSB properties are dependent on the chemical shift tensor of the particular functional group.

The symmetry of the carbon environment determines the relative magnitudes of the three tensor components. For example, the chemical shift tensor of benzene is defined by three inequivalent tensor directions⁽¹³⁾ where the σ_{33} element, perpendicular to the ring plane, is the most shielded direction. The least shielded, σ_{11} , is directed towards the proton (Figure 3.6). In aromatic systems, the σ_{33} tensor component is strongly influenced by the ring currents. This results in very large

Figure 3.5: NMR spectra of Webb bituminous coal obtained a) without MAS and b) with MAS. Spinning sideband signals are marked by (●).

a

b

c

Figure 3.6: Directions of the three principal values of the chemical shift tensors for three carbon functionalities. a) Unsubstituted aromatic carbon, b) carboxylic carbon, c) methylene carbon.

shielding differences between σ_{11} and σ_{33} and thus broad powder patterns, with widths ($\Delta\sigma = \sigma_{11} - \sigma_{33}$) of approximately 200 ppm⁽¹⁴⁾. The size of the σ_{22} component varies according to the site symmetry. For example, the site of the bridge carbons of condensed aromatic systems has more local symmetry than that of the carbon in benzene. Thus, the magnitude of the σ_{22} shielding component approaches that of the σ_{11} component; ie the powder pattern tends towards the example of the axially symmetric chemical shift tensor of Figure 3.3.

The carbon of the carboxylic functionality is more deshielded than the benzene carbon. Therefore, the isotropic resonance appears down-field of the aromatic resonances. The least shielded tensor component, σ_{11} is directioned along the C-C bond while the most shielded element, σ_{33} , is perpendicular to the O-C-O plane (Figure 3.6b). The difference between the σ_{11} and the σ_{33} elements is of the order of 130 ppm; ie not as large as that of the aromatic tensors. Therefore, the magnitude of the anisotropic component of the chemical shift is not correlated in a simple way to the size of the isotropic component.

Aliphatic carbon tensor values differ greatly from those of the aromatic and carboxylic carbon. The isotropic shifts occur at lower frequencies and the anisotropic component of the chemical shift is an order of magnitude weaker ($\Delta\sigma = 30\text{ppm}$). The axis system of a methylene group is shown in Figure 3.6c⁽¹⁵⁾. The most shielded element, σ_{33} occurs along the C-C chain direction while the least shielded component, σ_{11} , lies along the H-C-H plane.

It can be seen that the structure of the carbon fragment has a great influence on the chemical shielding. This is reflected in the powder pattern and also in the SSBs. The difference in shielding between the least and the most shielded tensor directions is reflected in the amount of signal intensity distributed in to the SSBs. For example, under the CP/MAS conditions of 50.3 MHz and 2.5 kHz, MAS frequency⁽¹⁶⁾, approximately 66% of the bridge carbon intensity is distributed in SSB signals whereas only 33% and 2% of the carboxylic and polymethylene chain carbon, respectively, is present in SSB signals (Figure 3.7).

The pattern of intensity distribution in the SSB signals also varies according to the carbon functionality as it reflects the relative magnitude of the σ_{22} tensor element. If the σ_{22} principal value is close to the

Figure 3.7: Typical SSB intensity patterns for three carbon functionalities a) aromatic bridge-head carbon, b) carboxylic carbon, c) methylene carbon.

isotropic chemical shift ($\bar{\sigma}$) then the SSB intensity pattern is symmetrical about the centre resonance (Figure 3.7b,c). However, as the σ_{22} component approaches either of the other elements; ie the tensor approaches axial symmetry, the relative intensity distribution in the SSB signals becomes very asymmetrical. The example given in Figure 3.7a shows that the first-order, high frequency SSB (I_{+1}) is greater than twice the size of the first-order, low frequency SSB (I_{-1}) which is a consequence of the similar magnitudes of the σ_{11} and σ_{22} principal values. If the magnitude of the σ_{22} tensor approaches the value of the most shielded σ_{33} tensor then this order is reversed ($I_{-1} > I_{+1}$). The simulated spectra in Figure 3.7 show that the SSB signals of aromatic and carboxylic carbon can be large while those of aliphatic carbon are insignificant. The occurrence of spinning side bands in the CP/MAS spectra of coals will be discussed in later chapters.

3.2.3 The CP/MAS Experiment

The experimental procedure and pulse sequence for the ^{13}C CP/MAS experiment are shown in Figures 3.8 and 3.9. The experiment is summarised below. The I and S spins represent the ^1H and the ^{13}C nuclei, respectively.

- a. The I spins are polarised, during the delay period D_1 , by the static field B_0 , aligned in the z-direction (Figure 3.9a).
- b. The rf field B_{1I} is applied for a brief time (P_1) along the y axis at the Larmor frequency of the I-spins so that the proton magnetisation is rotated into the xy plane. The pulse can be described as "90°y".
- c. The field is applied along the x axis (Figure 3.9b). The proton magnetisation is now "spin-locked" along B_{1I} as the applied field is stronger than the local dipolar fields. Any loss of the spin-locked magnetisation involves a flow of heat from the lattice to the I-spin system. This is assumed to follow first order kinetics governed by the time constant $T_{1\rho I}$ where "ρ" refers to the rotating reference frame and "1" implies a spin-lattice process.
- d. A second rf field B_{1S} , at the Larmor frequency of the S-spin, is applied along the x axis, under the Hartmann-Hahn condition:

$$\gamma_S B_{1S} = \gamma_I B_{1I} \quad [3.23]$$

Figure 3.8: Pulse sequence for the standard CP/MAS experiment on the XL200. Experimental settings are shown on the bottom line. These will be described in Chapter 4.

Figure 3.9: Summary of the experimental procedure. Relaxation times for the transfer of polarisation are shown using the thermodynamic model.
a) Polarisation of I spins, b) Spin-locking of I spins, c) Hartmann-Hahn match of applied rf fields.

The Zeeman levels in the rotating frame are matched and the dipolar interaction results in coupling between the I and S spins. Mutual spin flips tend to increase the S-spin magnetisation; ie a heat flow occurs from the S-spins to the I-spins with time constant, T_{IS} .

The two systems approach thermal equilibrium if both B_{IS} and B_{II} are applied (Figure 3.9c) for a "contact time", t , such that t is much greater than T_{IS} . For organic solids, the contact times for polarisation transfer from protons to carbon-13 are generally in the range 0.1 to 10 ms.

Although the S-spin magnetisation is spin-locked by B_{IS} , it is eventually degraded by a flow of heat from the lattice characterised by the time constant T_{IS}' . The prime indicates spin-locking of the I-spins.

- e. The field B_{IS} is turned off when the S-spin magnetisation has reached an acceptable level. The receiver channel is opened for the acquisition time, AT , to record the free-induction decay (FID). The field B_{II} is raised to decouple the I-spins.

The sequence can be repeated as soon as the I-spin magnetisation returns to equilibrium in B_0 . The recovery of the I-spin magnetisation during the waiting period, D_1 , is described by a single averaged time constant, T_{1I} as spin-diffusion in the I-spin system will generally average relaxation rates.

3.2.4 Relaxation Processes

3.2.4.1 Spin Dynamics

The high resolution obtained by the CP/MAS experiment allows the relaxation behaviour of the individual carbon functionalities to be followed. These relaxation processes can yield information about molecular motions and interactions. Three processes involved in the transfer of polarisation, which were described in the last section, need to be considered. The magnitude of the carbon signal, S , during the contact time, t , is given by:

$$dS/dt = (S_M/T_{IS})\exp(-t/T_{1I} \rho_I) - (S/T_{IS}) - (S/T_{1I} \rho_S) \quad [3.24]$$

where S_M is the maximum attainable carbon polarisation in the "absence of

dissipative relaxation processes"⁽¹¹⁾. The solution to this equation can be obtained by assuming the existence of simple first order time constants and that $S=0$ when $t=0$. The behaviour of the carbon signal S is governed by:*

$$S = -(S_M/T_{IS}) \frac{\exp(-t/T_1 \rho_I) \exp(-t(1/T_1 \rho_S + 1/T_{IS}))}{1/T_1 \rho_S + 1/T_{IS} - 1/T_1 \rho_I} \quad [3.25]$$

To obtain the relaxation constants from the curves of S versus contact time t , several simplifying assumptions are made:

- a. Spin-lattice relaxation of S (in the rotating frame, $T_1 \rho_S$, is ignored. That is,

$$T_1 \rho_S \gg T_{IS} \quad [3.26]$$

- b. It is assumed that

$$T_1 \rho_I \gg T_{IS} \quad [3.27]$$

so that these relaxation processes can be monitored separately.

Thus equation 3.25 reduces to two, first order, equations for the two contact time regions:

$$a) \quad t < T_{IS} \quad S = S_M (1 - \exp(-t/T_{IS})) \quad [3.28]$$

$$b) \quad t \gg T_{IS} \quad S = S_M \exp(-t/T_1 \rho_I) \quad [3.29]$$

The rate of loss of carbon polarisation to the lattice, governed by time constant $T_1 \rho_S$, is measured by inserting a delay between the completion of cross-polarisation to the lattice, (ie after the field B_{1S} is turned off) and the decoupling phase (ie the start of data acquisition). This procedure is represented in Figure 3.10. The carbon signal, S , can be followed as a function of time;

$$S = S_M \exp(-t/T_1 \rho_S) \quad [3.30]$$

The fourth relaxation process is important to the CP/MAS experiment. The magnitude of the delay between pulse sequences is dependent on the rate of I-Spin recovery ($1/T_{1I}$) to equilibrium after the applied rf field is removed. The delay required is set at three to five times the value of T_{1H} ⁽¹²⁾ to allow for the full restoration of proton magnetisation. The value of T_{1H} is obtained by an indirect method. The carbon-13 magnetisation is followed when variable delay times, t , are inserted between the pulse sequences (Figure 3.8). The carbon signal height is

* The 3-parameter fit was tested and discarded as the results were found to be highly dependent on the values of t chosen.

Figure 3.10: Pulse sequence for measurement of $T_{1\rho\text{C}}$. The extra delay, P3, is inserted.

governed by:

$$S = S_M (1 - \exp(-t/T_{1H})) \quad [3.31]$$

3.2.4.2 Measurement of the Relaxation Time Constants

Relaxation experiments were carried out for the simple organic compound, ammonium tartrate, to illustrate the methods for obtaining the four time constants. The spectrum of ammonium tartrate shows two centreband resonances at 180 ppm (carbonyl carbon) and 75 ppm (alcohol carbon) and associated SSB signals. The SSBs of the former signal are more prominent than those of the latter signal.

Selected spectra from the three relaxation experiments are shown in Figures 3.11 to 3.14. The signal heights are plotted on a logarithmic scale against the relevant time variable (Figures 3.15 to 3.17). The proton and carbon $T_{1\rho}$ values are calculated from the slopes ($1/T_{1\rho}$) of the best fit straight lines to the data (Figure 3.15a, 3.16). The proton slope is extrapolated back to the signal height intercept to gain an estimate of S_M (Figure 3.15a). The data from the initial portion of the cross-polarisation curve are converted to residuals ($S_M - S$) which are then plotted on a logarithmic scale (Figure 3.15b). The best-fit line to these residuals has the slope of $1/T_{CH}$. Care must be taken when choosing the data to be included in the estimate of T_{CH} . The points near the curve maximum are subject to both T_{CH} and $T_{1\rho H}$ influences and will bias the estimate of T_{CH} towards a longer time constant.

The proton T_1 is estimated according to equation 3.31. The residuals are calculated from the estimate of S_M , obtained from the flat area of the signal height curve (Figure 3.17a). Therefore, it is important to include data for long delay times so that the height of the fully relaxed signal can be measured. The slope of the residual logarithmic plot (Figure 3.17b) is then $1/T_{1H}$.

The relaxation time constants measured for ammonium tartrate are summarised in Table 3.1. The relaxation behaviour varies for the two carbon types, with similar T_{1H} and $T_{1\rho H}$ values, but different T_{CH} and $T_{1\rho C}$ constants. Variability has also been found in the relaxation parameters of carbon signals in the coal spectra. This will be studied in Chapter 7.

Figure 3.11: Relaxation experiment for the measurement of the T_{1H} values of ammonium tartrate. Spectra obtained with D1 values a) 0.03 s, b) 0.05 s, c) 0.08 s, d) 0.12 s, e) 0.2 s, f) 0.5 s.

Figure 3.12: Relaxation experiment for the measurement of T_{CH} . Spectra obtained with P_2 values of a) 0.1 ms, b) 0.2 ms, c) 0.5 ms.

Figure 3.13: Relaxation experiment for the measurement of $T_{1\rho H}$. Spectra obtained with P_2 values of a) 1.0 ms, b) 5.0 ms, c) 10.0 ms, d) 20.0 ms, e) 40.0 ms.

Figure 3.14: Relaxation experiment for the measurement of $T_1\rho_C$. Spectra obtained with P3 values of a) 0.01 ms, b) 0.1 ms, c) 0.3 ms, d) 0.75 ms, e) 1.2 ms, f) 2.0 ms.

Figure 3.15: Measurement of $T_1 \rho_H$ and T_{CH} values. a) Slope = $1/T_1 \rho_H$, determination of S_M values, b) residuals plotted, slope = $1/T_{CH}$. Data for signals at 180 ppm (open symbols) and 75 ppm (solid symbols).

b

Figure 3.16: Measurement of $T_1 \rho_C$ values. Slope = $1/T_1 \rho_C$.

Figure 3.17: Measurement of T_{1H} values. a) Determination of S_M values, b) plot of residuals, slope = $1/T_{1H}$.

TABLE 3.1 : RELAXATION CONSTANTS FOR AMMONIUM TARTRATE

T	C ₁ (180 ppm)	C ₂ (75 ppm)
T _{1H} (s)	0.113 (0.003) ^a	0.122 (0.002)
T _{1ρH} (ms)	18.4 (0.7)	19.3 (0.6)
T _{CH} (ms)	0.70	0.31
T _{1ρC} (ms)	1.19 (0.02)	0.227 (0.006)

(a) Standard deviation

NB T_{1H}, T_{1ρH}, T_{1ρC} values are dependent on the RF fields used.

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4.0 EXPERIMENTAL

4.1 Coal Samples

This study includes fifty-seven New Zealand coals, mostly "run-of-mine" (ROM), but supplemented by drillhole samples, particularly of higher rank coals. Ten samples from Australian coalfields were also studied to provide a comparison with overseas coals.

4.1.1 New Zealand Coals

The details of the samples are listed in Table 4.1. The data include a sample number and name which will be used to label each sample throughout this study, together with associated CRA sample codes, and location details including the coalfield.

The samples were obtained from two main sources. i) Dr R. B. Fieldes of Industrial Processing Division (IPD), DSIR donated lignite and subbituminous samples that had been the subject of a fast pyrolysis study⁽¹⁾. ii) CRA donated analyses residues; ie the remainder of samples after sufficient coal had been subjected to analysis. In addition, Professor Black of the Geology Department, Auckland University, donated a geological sample from the Fox river mouth area which has attained the rank of semianthracite.

Proximate analysis has been carried out on all of the residue samples from CRA and on many of the other samples. The CRA samples had all been air-dried prior to study by NMR. Therefore, their moisture content should remain fairly stable⁽²⁾. The remaining samples were analysed for their "as-received" moisture contents close to the time of NMR analysis.

Three subbituminous samples and five lignite samples do not have proximate analyses other than moisture and ash contents. The properties were approximated, where possible, by the average of five years of analyses for the same mines carried out by CRA in their sampling programme⁽³⁾. Representative bed moistures, and some other proximate data, for the lignites were obtained from the Liquid Fuels Trust Board (LFTB) lignite survey⁽⁴⁾.

The coal samples from IPD, and selected samples from CRA, have been subjected to ultimate analysis. Published ultimate analyses for the same mine were used to represent the other samples. The main sources for these

TABLE 4.1

NUMBER	SAMPLE	CRA CODE	DETAILS
	<u>Lignites</u>		
NZ 1	Hawkdun	24/645 d	CRA drillhole, composite sample
NZ 2	Idaburn	30/652 a	ROM, Idaburn o/c mine, Home Hills Field. October 1982
NZ 3	Roxburgh I	33/358 a (30/651)	ROM, Harliwich o/c mine. (MacPherson)
NZ 4	Roxburgh II	27/003 b	ROM, Harliwich o/c mine (MacPherson)
NZ 5	Roxburgh III	24/454 a etc	CRA drillhole 2086, composite of CRA 24/454, 463, 481, 494, 510
NZ 6	Mataura	33/361 a (30/654)	Face sample, NZ Paper Mills o/c mine
NZ 7	Ashers Waituna	33/657 a	Face sample, disused o/c mine (Ashers Siding)
NZ 8	Waimumu I	33/360 a (30/648)	ROM, Newvale o/c mine - May 1982
NZ 9	Waimumu II	30/655 a	ROM, Newvale o/c mine - October 1982
NZ 10	Waimumu III	30/645 a	Face sample, Goodwin o/c mine, Seam 5
NZ 11	Waimumu IV	30/646 a	Face sample, Goodwin o/c mine, Seam 6
	<u>Subbituminous Coals</u>		
NZ 12	Wangaloa	30/650 a (30/451)	ROM, Wangaloa o/c mine, Kaitangata Field - October 1982
NZ 13	Kai Pt	30/649 a (30/450)	ROM, Kai Point o/c mine, Kaitangata Field - October 1982
NZ 14	Braziers	30/653 a	ROM, Braziers o/c mine (Nightcaps), Ohai Field - October 1982
NZ 15	Kopuku	33/357 a	ROM Kopuku o/c mine, Maramarua Field, 1982
NZ 16	Kawhia	30/662 a	3m vertical channel sample, Pirongia (Okoko Road) o/c mine
NZ 17	Ohinewai	30/659 a (29/565)	CRA drillhold 9760, 1982 - Waikare Field
NZ 18	Garden Creek	33/342 b	ROM, Garden Creek o/c mine, Greymouth
NZ 19	Weavers	33/355 a (30/661)	ROM, Weavers o/c mine, 1981
NZ 20	Squires Creek	33/388 b	"Nut Grade", Squires Creek mine, Ohura

NUMBER	SAMPLE	CRA CODE	DETAILS
NZ 21	Mahons	33/754 b	Mahons o/c mine, Rotowaro
NZ 22	Maori Farm	33/750 b	Maori Farm State o/c mine, Rotowaro
NZ 23	Waipuna	33/752 b	Waipuna State o/c mine, Rotowaro
NZ 24	Mokau	30/663 a	Face sample, R. Farnsworth (Valley Collieries) mine
NZ 25	Ohura	33/387 b	"Peas", Ohura Collieries, Ohura
NZ 26	Huntly East	33/359 a (30/658)	Face sample from mine drive, Huntly East u/g mine, Huntly
NZ 27	Huntly West	30/657 a	3.5m vertical channel (full seam) from drive of No. 1 intake, Huntly West u/g mine, Huntly
NZ 28	Heaphys	33/479 b	"Peas", Heaphys's o/c mine, Buller
NZ 29	Terrace	30/342 b	ROM, Terrace u/g mine, Reefton
NZ 30	Ohai	33/356 a (30/656)	ROM, Wairakei, Morley and No. 16 o/c mines - October 1982, Ohai Field
<u>High Volatile Bituminous Coals</u>			
NZ 31	Mulken	30/341 b	ROM, Mulken (Burkes Creek) u/g mine, Reefton
NZ 32	Snowline	30/332 b	ROM, Snowline u/g mine, Greymouth
NZ 33	Alpine	30/353 b	ROM, Alpine u/g mine, Greymouth
NZ 34	Island Block	30/344 b	ROM, Island Block State o/c mine, Reefton
NZ 35	Strongman	30/329 b	ROM, Strongman State u/g mine, Greymouth
NZ 36	Kiwi	30/335 b	ROM, Kiwi u/g mine, Greymouth
NZ 37	Topline	30/346 b	ROM, Topline u/g mine, Reefton
NZ 38	Harrisons	30/331 b	ROM, Harrisons u/g mine, Greymouth
NZ 39	Moody Creek	33/786 b	ROM, Moody Creek mine, Greymouth
NZ 40	Echo	30/345 b	ROM, Echo u/g mine, Reefton
NZ 41	United	30/330 b	ROM, United u/g mine, Greymouth
NZ 42	Charming Creek	30/352 b	ROM, Charming Creek mine, Seddonville area, Buller
NZ 43	Escarpment	30/350 b	ROM, Escarpment State u/g mine, Denniston area Buller
NZ 44	Liverpool	30/773 b	ROM, Liverpool State u/g mine, Greymouth

NUMBER	SAMPLE	CRA CODE	DETAILS
NZ 45	Webb I	30/349 b	ROM, Webb State o/c mine, Stockton area, Buller
NZ 46	Webb II	31/033 b	Baynes Block, "Buller Drilling Program", drilling hole 1214, composite
NZ 47	Webb III	31/035 b	Same program as number 46, but u/g 2 composite
NZ 48	Webb IV	33/197 b	Mix of ROM from Webb/Stockton mines, Buller - October 1983
NZ 49	Stockton I	33/205 b	ROM, Stockton No. 2 mine, Stockton area, Buller - October 1983
NZ 50	Stockton II	32/776 b	"Stockton No. 2 and Rockies Drilling Program"
NZ 51	Sullivan	30/351 b	ROM, Sullivan State u/g mine, Denniston area, Buller
NZ 52	Sullivan North I	33/343 b	Sullivan North, G-Panel, Buller
NZ 53	Sullivan North II	33/344 b	H-Panel, Buller
<u>Medium Volatile Bituminous Coals</u>			
NZ 54	Webb V	31/032 b	Same program as number 46, but o/c 1 composite
NZ 55	Rockies II	32/778 b	Rockies sample from same drilling program as number 50, but drill hole 1255, composite
NZ 56	Rockies I	34/875 b	Same as number 55, but drillhole 1265 composite
<u>Semi-Anthracite</u>			
NZ 57	Fox River	33/060 c	Geological specimen from outcrop, Buller

ROM = run of mine
u/g = underground
o/c = opencast

- (a) Samples donated by Dr R. B. Fieldes (Industrial Processing Division, DSIR)
- (b) Samples donated by Coal Research Association (Inc)
- (c) Samples donated by Professor P. M. Black, Geology Department, University of Auckland
- (d) Sample donated by Dr D. E. Rogers, DSIR

include R. P. Suggate's work on the properties of New Zealand coals⁽⁵⁾ and a recent study by V. Gray on New Zealand coal quality⁽⁶⁾. The ultimate analyses are also tabulated in Appendix 1.

The ASTM rank determinations of the samples were made following the approximate Parr formula (Equation 2.2) using the mineral matter to ash factors of Gray⁽²⁾. The specific energy, ash and sulphur contents were converted firstly to a dry basis then recalculated to a bed moist basis. The bed moistures were represented by the MHC of higher rank coals and by the as-received moistures of the lower rank subbituminous coals. The lignite bed moistures were assumed to be the quantities reported by the LFTB⁽⁴⁾. The specific energies, on a Mmmf basis, are given in Table 4.2 with the corresponding ASTM rank classification. The rank classification for the same mine, calculated by Gray using the British standard for the Mmmf specific energy, are also tabulated for comparison.

It can be seen that there is general agreement on the classifications. Differences that occur at the borderlines of some groups can be accounted for by sample variation. The only major difference is apparent in the lignites. Gray classifies all (except Idaburn) as being of lignite A rank. In this study, only three of the Waimumu samples are assigned to the lignite A category which is consistent with the LFTB results⁽⁴⁾. This discrepancy may be caused by the different methods employed for deriving bed moistures. Gray used the "as-sampled" moistures which, if they are represented by the results of the CRA five year analyses⁽³⁾, are less than the LFTB bed moistures, particularly for the Central Otago lignites.

4.1.2 Australian Coals

The suite of Australian coal samples includes two brown coals from the Latrobe Valley and eight black coals from Queensland and New South Wales. The majority of the samples were donated by Dr D. G. McGavin of Chemistry Division, DSIR. The samples are described in Table 4.3.

Proximate analyses have been carried out on some of the samples. Proximate and ultimate data for the Latrobe Valley coals were obtained from published reports⁽⁷⁻⁹⁾, including the reports of the State Electricity Commission (SEC) of Victoria. The majority of the analysis data for the black coals are from the Joint and Queensland Coal Boards' (JQCB) reports on Australian black coals, first published in 1976 but later revised in 1979⁽¹⁰⁾. Where analyses for duplicate samples have been quoted in the SEC

TABLE 4.2

COAL	BM		MM(m)	S (m)	SE/MJkg ⁻¹			Rank	
					(daf)	(m)	(Mmf)	ASTM	"Gray"(2)
NZ 1	47.9	a	7.9	0.5	26.78	11.92	12.95	Lig B	-
NZ 2	51.8		4.6	0.3	26.59	11.65	12.22	Lig B	Lig B
NZ 3)			5.4	0.4	28.03	12.67	13.40	Lig B	Lig A
)									
NZ 4)-	49.6		5.2	0.4	29.12	13.22	13.95	Lig B	Lig A
)									
NZ 5)			4.7)	(0.4)	(27.69)	(12.71)	(13.34)	Lig B	Lig A
NZ 6	46.4		3.9	0.3	25.39	12.67	13.19	Lig B	Lig A
NZ 7	54.9		2.9	0.4	(26.07)	(11.05)	(11.38)	Lig B	-
NZ 8)			2.9	0.3	25.82	14.18	14.61	Lig B	Lig A
)									
NZ 9)	42.3		4.0	0.4	(26.65) ^b	(14.34)	(14.94)	Lig A	Lig A
NZ10)			4.1	0.3	(27.06) ^b	(14.56)	(15.19)	Lig A	Lig A
)									
NZ11)	42.3		3.6	0.7	(27.06) ^b	(14.67)	(15.23)	Lig A	Lig A
NZ 12	24.6	1 ^a	3.4	3.4	29.30	21.13	21.95	Sub C	Sub C
NZ 13	29.7	1	2.0	3.2	28.99	19.83	20.30	Sub C	Sub C
NZ 14	24.9	1	9.2	0.2	28.19	18.69	20.59	Sub C	Sub C
NZ 15	22.8	1	5.0	0.2	27.77	20.11	21.17	Sub C	Sub C
NZ 16	26.3	1	4.9	2.9	(28.68) ^b	(19.79)	(20.87)	Sub C	Sub C
NZ 17	21.1	1	3.3	0.2	29.39	22.25	23.01	Sub B	-
NZ 18	18.4	2	2.4	4.5	28.89	22.91	23.58	Sub B	Sub B
NZ 19	15.8	2	4.7	0.3	28.60	22.79	23.92	Sub B	Sub B
NZ 20	19.2	1	7.0	0.9	29.13	21.59	23.24	Sub B	Sub B
NZ 21	18.3	2	3.7	0.2	29.83	23.30	24.20	Sub B	Sub B
NZ 22	19.5	2	3.2	0.2	29.85	23.10	23.87	Sub B	Sub B
NZ 23	17.5	2	6.6	0.2	29.73	22.65	24.26	Sub B	Sub B
NZ 24	14.9	2	9.1	3.2	(29.62) ^b	(22.60)	(24.95)	Sub A	Sub B
NZ 25	17.3	2	2.0	1.8	30.19	21.50	24.48	Sub A	Sub B
NZ 26	15.8	2	1.9	0.2	29.54	24.34	24.82	Sub A	Sub A
NZ 27	15.3	2	3.2	0.2	(29.88) ^b	(24.41)	(25.22)	Sub A	Sub B
NZ 28	19.2	2	3.8	1.8	30.93	23.85	24.84	Sub A	Sub B
NZ 29	15.9	2	2.1	1.2	30.73	25.23	25.80	Sub A	Sub A
NZ 30	11.5	2	9.4	0.2	30.05	23.89	26.37	Sub A	Sub A

COAL	BM		MM(m)	S (m)	SE/MJkg ⁻¹			Rank	
					(daf)	(m)	(Mmmf)	ASTM	"Gray"(2)
NZ 31	11.5	2	2.5	1.2	30.93	26.66	27.38	hv Cb	hv Cb
NZ 32	9.6	2	4.2	0.3	33.08	28.61	29.87	hv Cb	hv Cb
NZ 33	9.3	2	4.2	0.5	33.08	28.71	29.98	hv Cb	hv Bb
NZ 34	4.3	2	3.7	1.3	32.86	30.33	31.54	hv Bb	hv Bb
NZ 35	6.9	2	6.3	0.4	33.39	29.15	31.12	hv Bb	hv Bb
NZ 36	6.6	2	3.8	0.3	33.59	30.20	31.40	hv Bb	hv Bb

NZ 37	2.8	2	7.0	1.7	33.18	30.09	32.41	hv Bb	hv Ab
NZ 38	6.9	2	3.6	0.3	33.72	30.28	31.42	hv Bb	hv Bb
NZ 39	4.7	2	5.7	0.3	34.75	31.28	33.18	hv Ab	hv Bb
NZ 40	3.2	2	3.8	0.5	33.47	31.23	32.63	hv Ab	-
NZ 41	4.5	2	4.6	0.3	34.49	31.45	32.98	hv Ab	hv Ab
NZ 42	3.1	2	1.4	5.2	33.79	32.30	32.93	hv Ab	hv Ab
NZ 43	3.7	2	3.6	0.5	33.92	31.55	32.75	hv Ab	hv Ab
NZ 44	1.4	2	5.9	0.4	36.17	33.67	35.80	hv Ab	hv Ab
NZ 45	1.1	2	1.8	2.4	35.07	34.09	34.80	hv Ab	hv Ab
NZ 46	1.0	2	15.2	1.2	35.84	30.43	35.94	hv Ab	hv Ab
NZ 47	1.5	2	1.3	2.7	35.46	34.50	35.05	hv Ab	hv Ab
NZ 48	1.6	2	1.1	1.4	36.06	35.12	35.56	hv Ab	hv Ab
NZ 49	2.3	2	1.3	0.5	36.00	34.74	35.22	hv Ab	hv Ab
NZ 50	1.5	2	3.0	3.3	35.92	34.38	35.56	hv Ab	hv Ab
NZ 51	2.0	2	6.0	1.6	35.00	32.34	34.46	hv Ab	hv Ab
NZ 52	0.8	2	1.7	4.1	36.14	35.27	36.03	hv Ab	hv Ab
NZ 53	1.0	2	0.9	1.6	36.14	35.75	36.13	hv Ab	hv Ab
NZ 54	2.1	2	0.2	1.2	35.22	34.41	34.52	mhb	-
NZ 55	1.4	2	4.0	1.6	36.15	34.31	35.80	mhb	-
NZ 56	1.2	2	1.5	1.8	36.24	35.30	35.90	mhb	-
NZ 57	2.1	2	2.6	0.6	36.41	35.65	36.62	sa	-

(a) Bed Moistures from LFTB report

(b) See Appendix 1

(c) Method for estimating bed moisture (see text)

TABLE 4.3

NUMBER	SAMPLE	CRA CODE	DETAILS
A 1	Morwell	- a	Morwell mine, Latrobe Valley. Drum 289, 100 tonne bulk sample, 1979, SEC, Victoria
A 2	Loy Yang	- b	Loy Yang Field, Latrobe Valley Bore LY1277, 67-68 metres
A 3	Great Northern	- b	ROM Great Northern seam, Newvale Colliery, Newcastle Field, Sydney Basin, NSW
A 4	Wallarrah	- b	ROM, Wallarah seam, Wallarah Colliery, Newcastle Field, Sydney Basin, NSW
A 5	Liddell	33/062 b	ROM, Liddell seam, Foybrook o/c Colliery, Singleton-Muswellbrook Field, Sydney Basin, NSW
A 6	Tangorin	- b	ROM, Tangorin seam, Great Greta Colliery, S-M Field, Sydney Basin, NSW
A 7	Bulli	33/061 b	ROM, Bulli seam, Appin Colliery, Southern Field, Sydney Basin
A 8	Wongawilli	- b	Wongawilli seam, Huntly Colliery, Southern Field, Sydney Basin, NSW
A 9	Blair Athol	- b	Big seam, Blair Athol Field, Central Queensland
A 10	Yarrabee	33/063 b	Yarrabee seam, (Baralaba) Bowen Basin, Queensland

(a) Donated by Dr D. E. Rogers

(b) Donated by Dr D. G. McGavin

- Both of Chemistry Division, DSIR

TABLE 4.4

COAL	BM	MM(m)	S(m)	SE/MJ kg ⁻¹			RANK	
				(daf)	(m)	(Mmmf)	ASTM	JQCB ^a
A 1	58.4	1.6 ^b	0.1	27.04	10.84	11.02	lig B	-
A 2	60.0	0.2	0.1	27.62	10.99	11.01	lig B	-
A 3	3.2 ^c	14.2 ^d	0.3	34.29	29.01	33.82	hvAb	hvAb
A 4	3.4	11.5	0.3	33.70	29.18	32.96	hvAb	hvAb
A 5	2.8	10.0	0.5	34.62	31.05	34.52	hvAb	hvAb
A 6	1.7	12.2	5.6	35.01	31.19	35.83	hvAb	hvAb
A 7	1.6	11.2	0.4	35.58	32.31	36.40	mzb	hv-lvb
A 8	1.4	15.2	0.5	36.08	30.56	36.02	mzb	hv-mzb
A 9	7.9	-	0.3	-	-	-	(hvAb) ^e	-
A 10	5.7	7.8	0.5	34.52	30.76	33.38	sa	sa

(a) Reference 4.10

(b) MM/Ash factor of 1.04 assumed

(c) Assumed BM = 1.13 AD

(d) Mineral matter analyses (Reference 4.10)

(e) Assumed from high value of FC

and JQCB reports, the averages of the data have been transposed to this study. The proximate and ultimate analyses are tabulated in Appendix 2.

4.2 Instrumental Procedures

4.2.1 Sample Preparation

The sample capacity of the solid state NMR apparatus is less than 0.5g. The average coal particle size must therefore be small in order to reduce the risk of studying a non-representative sample. The samples obtained from CRA were already prepared to a particle size of less than 200μ . Other samples were crushed, using an agate pestal and mortar, and seived to the same size.

Approximately 0.3g of sample was packed into a Kel-F (polytetrafluoroethylene) rotor, which has a 1cm diameter (Figure 4.1). A machine-precision press with a cylindrical plunger was used to compress the sample under a weight of approximately 500kg⁽¹¹⁾. The small particle size facilitates uniform packing of the coal but occasionally samples lacked the cohesion necessary to withstand the high frequency spinning. A layer of boric acid was compacted on top of the coal to ensure that the sample did not break apart. This provided a smooth, hard surface that rarely cracked during spinning.

4.2.2 The NMR Operating Procedures

The rotors were spun on an air cushion, using air pressures up to 0.4 MPa, in the standard CP/MAS probe of a Varian XL-200 NMR spectrometer. The standard spinning frequency of 2.5 ± 0.1 kHz was chosen for reasons including the fact that this was the maximum spinning speed that could be routinely achieved with the available air pressures. The advantage of this choice will be discussed in the next chapter.

Tuning of the NMR instrumentation (calibration of the Hartmann-Hahn match and the pulse width PW) was performed following standard equipment tests using hexamethylbenzene (HMB). These tests were carried out before each NMR session to ensure that the spin-locking field was maintained at a consistent strength. Relaxation experiments must be carried out under identical spectrometer conditions for the results to be comparable. For example, "a change in the spin-locking field strength or a change in the temperature can alter $T_1\rho_H$ "⁽¹²⁾. Chemical shifts were scaled according to the external tetramethylsilane (TMS) standard. The methyl signal (17.4 ppm) of HMB was used as a secondary reference⁽¹³⁾.

Figure 4.1: Shape and position of rotor within stator with respect to the applied rf field.

The two CP/MAS pulse sequences of Figures 3.8 and 3.10 involve several operating settings which must be optimised, namely:

- i. P1 = the proton "90°y" pulse
- ii. P2 = spin-lock/contact time
- iii. D1 = delay/recycle time
- iv. AT = decouple/acquisition time
- v. P3 = second delay

P1 is set to the same value as the pulse width (PW). The values of P2, P3 and D1 were chosen following the results of extensive relaxation experiments (see Chapter 7). The optimum contact time must satisfy the condition:

$$T_{CH} < P2 < T_{1\rho H} \quad [4.1]$$

and was chosen to be 1ms. This value is identical to that used in studies on American^(14,15) and British⁽¹⁶⁾ coals. For example, Dudley and Fyfe⁽¹⁷⁾ fitted theoretical expressions to the magnetisation curves and found only small deviations between the optimised parameters and the results for a 1ms contact time.

The acquisition time must be greater than 20% of the following delay. The majority of spectra were obtained with 15ms of data acquisition followed by a delay of 0.15s (lignites and subbituminous), 0.2 to 0.9s (bituminous coals) or 0.4s (semianthracite) which were found to be adequate for the recovery of proton magnetisation.

The P3 term was set to zero except when the spin-locking pulse sequence (Figure 3.10) was used to measure $T_{1\rho C}$.

The transmitter was placed near to the centre of the coal spectrum (ie 100 ppm) and free induction decays were zero filled to at least 4K before Fourier transformation. The spectral width (SW) was set at 40 kHz. This provided ample baseline on both sides of the signal envelope to allow for phase adjustment of the spectrum.

The number of CP sequences averaged (ie the number of transients NT) varied according to the detail required and the magnitude of the line broadening functions applied to the spectrum. Standard spectra (NT > 5000) were broadened by the application of a sensitivity enhancement function consisting of the product of an exponential decay curve (time constant SE, of 20ms) and a Gaussian apodisation function (time constant AF, of 10ms).

Other combinations of broadening functions ($SE=AF=2$ to $10ms$) were used in relaxation experiments so that signal heights could be measured after the accumulation of 500 to 2000 transients.

Resolution-enhanced (RE) spectra were produced by a Lorentzian-to-Gaussian transformation⁽¹⁸⁾ involving an exponentially increasing function (time constant RE of $1ms$) and a Gaussian curve (AF of $2ms$). These time constants were chosen after trial-and-error testing⁽¹¹⁾.

4.2.3 Computation of Relaxation Parameters

The graphical methods for measurement of relaxation parameters were described in the previous chapter. To perform least squares measurements to the logarithmic data for each sample would be very time-consuming⁽¹¹⁾. In practice, an appropriate exponential curve is fitted to the raw data (t_i, h_i) where t_i is the i^{th} recovery interval and h_i is the signal height corresponding to t_i . The program FTFIT, developed by Dr R. Palmer⁽¹⁹⁾, is used for this purpose. FTFIT "performs the direct (non-linear) least-squares analysis of spin-relaxation measurements"⁽¹⁹⁾, to obtain an estimate of the relaxation times. Three types of curves can be fitted to the experimental data. The saturation-recovery Fourier transform (SRFT) curve, given by equation 3.31, is fitted to the signal height data of T_{1H} relaxation experiments. The Freeman-Hill modification of inversion-recovery (FH-IRFT) curve, represented by equations 3.29 and 3.30, is used to fit the data for $T_{1\rho C}$ and $T_{1\rho H}$ estimation. In the latter case, the choice of appropriate experimental signal heights is most important. Figure 4.2 shows the results of a variable contact time (P2) experiment for a lignite. If points at the maximum that are still influenced by cross-polarisation are included in the curve fitting, the slope would be depressed resulting in an apparently long time constant. Contact time intervals greater than, and including, $1ms$ were used consistently for the $T_{1\rho H}$ estimation.

The cross-polarisation time constant T_{CH} was the only parameter estimated by the manual least squares fit methods described in the previous chapter.

Figure 4.2: Data for the measurement of $T_{1\rho H}$ values for the aromatic (open symbols) and aliphatic (solid symbols) carbon of Mataura lignite.

4.2.4 Measurement of the Apparent Aromaticity

The aromaticity, f_a , is defined as⁽¹¹⁾:

$$f_a = (\text{C in aromatic rings})/(\text{Total C}) \quad [4.1]$$

An estimation of f_a can be obtained from the standard coal spectra by defining a boundary between the aromatic and aliphatic bands. The area on either side is integrated by the "cut-and-weigh" method. Figure 4.3 shows the spectrum of a subbituminous coal divided in this way. A vertical line is positioned at 65 ppm, which is coincident with the minimum between the two signal envelopes. This simple approach includes several systematic errors which will be discussed in Chapter 10. Therefore, the ratio is redefined as the "apparent aromaticity, f_a' ";

$$f_a' = (\text{signal area} > 65 \text{ ppm})/\text{Total Signal Area} \quad [4.2]$$

4.3 Summary

The experimental procedures and parameters described in this chapter are those that will be used throughout the NMR study. Many other instrumental and chemical methods were also employed for particular purposes but, for ease of reference, the experimental details are included in the relevant sections.

Figure 4.3: Standard CP/MAS ^{13}C spectrum of Squires Creek subbituminous coal showing the division at 65 ppm into aliphatic and aromatic signal areas.

4. REFERENCES

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5.0 SIGNALS IN THE COAL SPECTRA

5.1 The Coal Spectrum

Standard ^{13}C CP/MAS NMR spectra of four coals of increasing ASTM rank are shown in Figure 5.1. The spectra can be divided into five regions with boundaries defined by the minima between distinct spectral envelopes. The main centreband signals are contained in divisions B and D. The B-division contains signals assigned to sp^3 -hybridised carbon. The D-division contains the signals assigned to sp^2 -hybridised carbon, including aromatic carbon.

The remaining bands of signals are dominated by the SSBs of the sp^2 -hybridised carbon. Division E is dominated by the high-frequency (high ppm) SSB signals. Divisions C and A contain the first- and third-order low-frequency (low ppm) SSBs, respectively.

The divisions illustrate the major advantage in choosing the routine spinning frequency to be 2.5 ± 0.1 kHz. This frequency produces an SSB spacing of 50 ± 2 ppm on the chemical shift scale. The strongest signals of the aliphatic and aromatic bands are approximately 100 ppm apart. Therefore, the first order low-frequency SSB signal is observed in the centre of the gap between the centreband envelopes. However, the second order low-frequency SSB is obscured by the aliphatic band in division B. It will be demonstrated in Chapter 9 that the hidden signal represents approximately 9% of the intensity assigned to aromatic carbon in the spectrum of a high rank coal (Fox River).

The rate of sample spinning in the ideal situation would be such that the first order low-frequency SSB is positioned in division A. However, the required rotation rate would be greater than 6.5 kHz, which is impossible with current equipment. Spinning frequencies between 6.5 and 2.5 kHz (if routinely attainable) would place the large first order SSB in division B. Thus, a spinning frequency higher than 2.5 kHz would cause a greater overlap of aromatic and aliphatic signal intensity.

The choice of the 2.5 kHz spinning frequency is practical, not only from a technical point of view, but also in order to maximise the simplicity of the spectrum.

Figure 5.1: Standard CP/MAS ^{13}C NMR spectra of coals divided into five chemical shift regions (see text). a) Fox River (sa), b) Escarpment (hvAb), c) Kopuku (sub) and d) Ashers Waituna (lig).

5.2 Assignment of Observed Signals

There are many overlapping signals in the NMR spectrum of coal. The signals are not always clearly resolved which hinders the identification of their positions on the chemical shift scale. The spectra are resolution enhanced (RE) to improve the separation of the signals. This process does not conserve relative signal areas and therefore cannot be used for quantitative NMR. The signal-to-noise ratio (S/N) is lowered but the resultant improvement in signal detail is evident when Figure 5.2 is compared with Figure 5.1. The signals observed in the RE spectra have been assigned according to the large quantity of ^{13}C chemical shift data (eg 1-5) tabulated in the literature.

5.2.1 Signals of Aliphatic Carbon

The signals between 0 and 50 ppm are assigned to aliphatic carbon functionalities. The chemical components of plants, summarised in Chapter 2, contain many types of aliphatic structures, including straight- or branched-chains and cyclic structures. In addition, aliphatic structures may be present in the coal as groups attached to unsaturated carbon (aromatic rings, alkene derivatives) and heteroatom-substituted carbon. Carbon-13 chemical shifts of model compounds for these types of aliphatic structures are listed in Tables 5.1 and 5.2(1,2). These simple structures will not be present as distinct entities in the coal matrix but they do show clearly the trends in signals of aliphatic carbon discussed by Snape *et al* (3) and Ward and Burnham (4).

The main signals observed in the division B can be assigned to certain carbon functionalities. The peak that occurs between 14 and 16 ppm is consistent with the terminal methyl groups of aliphatic chains. The series of alkyl substituted benzenes (Table 5.2) shows that the chemical shift of the methyl carbon remains relatively constant at a position γ - or further from the aromatic ring (3). The signal centred between 20 and 24 ppm includes contributions from α -methylene carbons of aliphatic chains. Signals of methyl groups of branched structures, and those substituted onto ring systems, would also occur in this chemical shift region.

The main structures contributing to the signals between 27 and 34 ppm are the interior methylene carbons of alkyl chains and cyclohexane rings. The signals observed between 35 and 42 ppm are consistent with carbon in

Figure 5.2: Resolution-enhanced spectra of the coals (samples as for Figure 5.1) showing improvement in signal detail.

TABLE 5.1 : CHEMICAL SHIFTS OF ALIPHATIC CARBON (i)

STRUCTURE	1	2	3	4	5
13.9	22.9	32.0	-	-
14.1	23.0	32.4	29.9	30.3
14.1	20.7	27.8	41.8	22.5
11.3	29.3	36.7	18.6
15.9	32.9	38.1	27.2
27.8
34.1	23.8
38.0	38.0	29.9	23.7	14.5

TABLE 5.2 : CHEMICAL SHIFTS OF ALIPHATIC CARBON (ii)

STRUCTURE	1	2	3	4	5
21.3
29.3	16.8
38.5	25.2	14.0
36.0	34.0	22.9	14.1
36.6	32.1	31.5	23.1	14.3
38.9	24.2
47.5	31.7
30.3	24.1
37.7
29.2
35.7	24.1	14.9
25.5	23.1
38.2	30.6	23.5	14.5	28.6
34.5	25.2	32.6	23.7	14.8
33.1	26.1	32.3	23.1	14.5
34.0	29.7	23.0	14.3	

methylene groups adjacent to ring systems or heteroatom-substituted carbons. Signals from the methine carbon of branched aliphatic chains are also found in this chemical shift region.

Few of the simple structures shown in the tables exhibit signals in the 46 to 50 ppm chemical shift region. Snape *et al*⁽³⁾ predicted that the methine and quaternary carbon of highly branched derivatives (particularly those in the vicinity of an aromatic ring) would exhibit signals in this zone.

5.2.2 Signals of Other sp^3 -Hybridised Carbon

Signals of sp^3 -hybridised carbon bonded to oxygen, nitrogen and sulphur may also contribute to the coal spectrum. Examples, and a summary, of aliphatic C-X chemical shifts are given in Table 5.3. Most of the signals of oxygen and nitrogen substituted carbon will occur in division C. Therefore, the signals will be obscured by aromatic SSB signals, unless the former are particularly intense. For example, the spectrum of Ashers Waituna lignite (Figure 5.2d) exhibits two signals in this chemical shift region (56 ppm, 74 ppm) that cannot be assigned to SSB signals. It is likely that these signals originate from aliphatic alcohols and ethers, as oxygen is far more abundant than nitrogen in low rank coals.

The signals of S-substituted sp^3 -hybridised carbon are generally observed at chemical shifts similar to those of alkane-carbon. The organic sulphur content of coals is small. Therefore, any signals of carbon bonded to sulphur will not be significant in comparison with the hydrocarbon signals.

5.2.3 Signals of Aromatic Carbon

The signals in division D are mainly assigned to aromatic carbon bonded to hydrogen, carbon and oxygen. The signals of aromatic carbon bonded to hydrogen generally occur at chemical shifts less than 130 ppm (Table 5.4). The signals of aromatic carbon bonded to an alkyl group are found at frequencies higher than 135 ppm. The signals of ring junction carbons in polycyclic aromatic systems occur at chemical shifts intermediate between the signals of benzene and alkyl substituted aromatic carbon.

The effect of heteroatom substituents on the chemical shifts of

TABLE 5.3 : C - X CHEMICAL SHIFTS

Table 5.3a - Examples

STRUCTURE		STRUCTURE
62.2		44.5
67.5		57.1
72.6		26.5
73.2		57.0 (1)
54.0		26.0 (2)

Table 5.3b - Summary

X =	C	S	N	O
CH ₃ -X	5-30	10-20	12-42	38-50
-CH ₂ -X	22-45	17-33	43-58	42-70
>CH-X	32-60	55-65	55-68	65-78
-X	28-52	52-72	60-75	73-85

TABLE 5.4 : CHEMICAL SHIFTS OF AROMATIC CARBON

STRUCTURE	1	2	3	4
128.7
133.9	128.3	126.1
132.4	130.3	125.7	132.8
137.2	129.6	126.0
137.3	128.0	128.0
134.9	130.8
137.8	129.3	128.5	125.6
144.1	128.1	128.5	125.9
148.7	126.6	128.6	126.1
149.2	125.4	128.4	125.9

aromatic carbon is demonstrated by the examples given in Table 5.5. The signals of O-substituted aromatic carbon are found at the highest chemical shifts. The signals of aromatic carbon adjacent to the O- and N-substituted carbon are shifted to positions lower than 120 ppm. The chemical shifts of S-substituted aromatic carbon are similar to those of the R-substituted aromatic carbon (Table 5.4). Once again, the signals of N- and S-substituted aromatic carbon are unlikely to be observed because of the overlap with the positions of signals of other aromatic carbon and also because of the low abundance of N and S in coal.

The strong signal observed at approximately 154 ppm is consistent with the chemical shifts of O-substituted aromatic carbon. The signals between 140 ppm and 150 ppm can be assigned to either R- or O-substituted carbon. Signals at chemical shifts below 130 ppm can be assigned to H-substituted aromatic carbon. The signals that are observed below 120 ppm are assigned to aromatic C-H groups in highly substituted ring systems.

5.2.4 Signals of Other sp^2 -Hybridised Carbon

Structures not considered in the previous section include sp^2 -hybridised carbon in alkenes and in unsaturated heteroatom derivatives. The chemical shifts of alkene-carbon (Table 5.6) are similar to those of aromatic carbon. The carbons in carbonyl functionalities give signals in division E; ie will overlap with the high-frequency SSB signals of the aromatic bands. The chemical shifts of the analogous sulphur and nitrogen functionalities (Table 5.6b) are intermediate between the chemical shifts of alkene and carbonyl derivatives. The signals of carbon in unsaturated heterocycles are found at similar chemical shifts to the signals of substituted aromatic carbon.

It is unlikely that the signals of non-aromatic sp^2 -hybridised carbon could be detected in the coal spectrum as they would be obscured by the wide range of signals assigned to aromatic carbon. The carbonyl signals are the exception to this generalisation. A large amount of intensity in division E, which could not be assigned to SSB signals alone, would indicate the presence of significant quantities of carbonyl functionalities in the coal. For example, the lignite spectrum (Figure 5.2d) exhibits an SSB signal, at approximately 180 ppm which is large in comparison with the main aromatic signal (128 ppm). In contrast, the corresponding SSB signal in the subbituminous spectrum (Figure 5.2c) is smaller than the main

TABLE 5.5 : -X CHEMICAL SHIFTS

X	C-1	Ortho	Meta	Para
-OH	155.6	116.1	130.5	120.8
-OMe	159.9	114.1	129.5	No S
-NH ₂	147.9	116.3	130.0	119.2
-N(CH ₃) ₂	151.3	113.1	129.7	117.2
-SH	130.7	129.2	128.8	125.4
-SCH ₃	138.9	126.9	129.1	125.1

TABLE 5.6 : CHEMICAL SHIFTS OF OTHER sp^2 HYBRIDISED CARBON

Table 5.6a - Examples

STRUCTURE	1	2	$CH_3(CH_2)_5-\overset{\overset{O}{\parallel}}{C}-R_1$
113.5	137.8	$R_1 = OCH_3$	173.4
130.4		$= OH$	180.2
127.2	123.2	$= H$	201.8
127.2		$= CH_3$	206.8
135.8	112.3	$= C_6H_{11}$	208.5

Table 5.6b - Summary

STRUCTURE	C	S	N	O
$\begin{matrix} R_1 \\ \diagdown \\ C = X(R)_n \\ \diagup \\ R_2 \end{matrix}$	100-	190-	145-	$R_1 = C$ 200-225
	150	200	160	$= H$ 185-205
				$= OH$ 170-185
				$= OR$ 165-175
132	126	119	143
-	-	151	-

"n" represents the appropriate substitution pattern for the particular nucleus

aromatic signal. This trend suggests that a substantial carboxylic acid signal is present under the SSB signal in the lignite spectrum.

5.2.5 Summary

The signals observed in the coal spectra have been assigned to general carbon functionalities following the chemical shift trends of simple organic compounds. There are many chemical shift regions where signals could have several assignments. These ambiguities may be solved by studying the plant components that must have been present in the original peat and, therefore, may make a recognisable contribution to the coal spectrum.

5.3 Origin of Signals

The roles of lignin and cellulose in the formation of coal have been the subject of debate⁽⁶⁾. Both lignin and cellulose may contribute to the spectra of Australasian coals, particularly as these coals are thought to have predominantly terrestrial origins (see Chapter 2). An extracted lignin and a cellulose sample were studied by CP/MAS NMR.

5.3.1 The Spectrum of Kauri Lignin

A Klason lignin was isolated from Kauri wood following the procedures described in Tappi Standard Method, T-13m-54. A sample of Wiley-milled (40 mesh) wood was initially extracted for 6 hours with an ethanol/benzene mixture, to remove resins, fats and waxes. This treatment was followed by digestion in water at 373K for 3 hours. The cellulose was removed by acid-extraction in 72% sulphuric acid for 2 hours at 291-293K. The acid was then diluted to 3% and refluxed for 4 hours. The lignin residue was washed and air-dried at 378K.

The RE spectrum of the Klason lignin is shown in Figure 5.3. Kauri is an example of a softwood and would therefore be expected to contain large amounts of guaiacyl-type lignin units (Chapter 2). The strong signal at 56 ppm is assigned to the aryl-methoxyl carbon⁽⁷⁻⁹⁾. The signals of the propyl side-chain are found on either side of the methoxyl signal. Oxygen-substituted side-chain carbons exhibit signals between 60 ppm and 90 ppm, which overlap with SSB signals. The broad band of signals at chemical shifts less than 50 ppm is assigned to unsubstituted side-chain carbon.

Figure 5.3: R.E. Spectrum of Klason lignin from Kauri wood. Structure is of a guaiacyl-type lignin unit.

The signal at 134 ppm is assigned to the C-1 ring carbon which is linked to the side chain. The signals of unsubstituted ring carbon appear between 100 ppm and 130 ppm. The SSBS of these signals are observed at chemical shifts greater than 150 ppm.

The strong signal at 148 ppm is assigned to the C-3 carbon of the guaiacyl lignin unit which is not significantly affected by etherification at C-4(10, 11). The signals of the C-4 carbon would be found at 153 ppm and 146 ppm, in β -O-4 etherified and non-etherified units, respectively. The non-etherified C-4 signal is not visible as a distinct peak but probably contributes to the strength of the signal at 148 ppm. There is no signal at 153 ppm. The absence of etherified guaiacyl units is consistent with the results of Leary *et al*(11) who found that a large proportion of β -O-4 linkages in lignin are hydrolysed by the acid treatment.

The Klason lignin represents the "portion of the total lignin which is highly polymerised in the original wood and which remains polymerised"(11) upon acid treatment. It has been shown that the Klason method also removes a significant amount of lignin-like material, probably in the form of lignans and lignin oligomers(11). The discrepancy between the "Klason" lignin content and the whole-wood lignin content is large for some gymnosperms(11). Therefore, the spectrum of the Klason lignin may not represent the lignin as it occurs in the wood. However, the spectrum in Figure 5.3 does provide evidence for the lignin origin of the signals at 56 ppm and 148 ppm in the spectra of lignites.

5.3.2 The Spectrum of Cellulose

The cellulose sample was obtained by Wiley-milling Whatman No. 1 filter papers. The RE spectrum of cellulose is shown in Figure 5.4. The assignments of the signals have been discussed in detail(7,12,13). The doublet observed at approximately 74 ppm is assigned to the resonances of the C-2, C-3 and C-5 carbons. The signal at 105 ppm is assigned to the C-1 (anomeric) carbon of cellulose. The remaining signals are the sharp and broad component resonances of the C-4 (84 ppm, 89 ppm) and C-6 (66 ppm, shoulder at 63 ppm) carbon signals. The signal at 105 ppm can also be separated into two peaks (106 ppm, 105 ppm) with stronger resolution enhancement.

The sharp signals are assigned to the resonances of "cellulose monomers" in the "more highly ordered environment"(13). This variation in

Figure 5.4: R.E. Spectrum of cellulose and numbering of carbons in the monomer unit.

structural order is thought to reflect either the degree of crystallinity⁽¹³⁾ (ie crystalline versus amorphous), or the morphology⁽¹²⁾ (ie interior versus exterior) of the cellulose.

The spectrum of cellulose indicates that the signal observed at 74 ppm in the lignite spectrum originates from cellulose remaining in the coal. A sharp signal at 105 ppm, which is observed in conjunction with the peak at 74 ppm in many lignite spectra, may also be assigned to the presence of cellulose.

5.3.3 The Spectra of Plant Fractions

Lignin and cellulose are not the only components contained in higher plants. The whole wood, bark and leaves of native flora were studied. Four gymnosperms and two angiosperms were selected from the modern examples of the plant families listed in Table 2.1.

The wood samples were sawn from planks of dry timber. The flax "wood" was obtained from the dried stalk of a dead flower head. The bark and leaf samples were partially air-dried and ground prior to the NMR study. The species chosen were the gymnosperms:

1. Agathis australis (Kauri)
2. Podocarpus totara (Totara)
3. Podocarpus dacrydiodes (Kahikatea)
4. Podocarpus trichomanoides (Celery Pine)

and the angiosperms:

5. Northofagus truncata (Hard Beech)
6. Phormium tenax (NZ Flax).

The common names will be used in descriptions of the spectra.

5.3.3.1 Spectra of Wood Samples

The RE spectra of the wood samples are shown in Figure 5.5. The cellulose signals at 74 ppm and 105 ppm dominate the spectra and obscure signals from, for example, the propyl side-chains of lignin. Therefore, the region between 60 ppm and 100 ppm has not been plotted. The signals at 22 ppm and 174 ppm can be assigned to the methyl and carbonyl carbons, respectively, of the acetate groups of hemicellulose⁽⁷⁾.

The signals of lignin structures are evident in the spectra. The signal of methoxyl carbon at 56 ppm is strong in all of the spectra. The

Figure 5.5: R.E. spectra of whole wood samples. Cellulose region (60 to 110 ppm) omitted for clarity. a) NZ flax, b) Hard Beech, c) Celery Pine, d) Kahikatea, e) Totara and f) Kauri.

aromatic C-H and C-l linkage signals are present between 110 ppm and 135 ppm. The most interesting signals are those assigned to oxygen-substituted aromatic carbon. The expected chemical shifts for lignin units⁽¹⁰⁾ are summarised in Table 5.7. The terminology of Newman *et al*⁽¹⁰⁾ has been adopted for describing the three monomer types. The four softwood spectra exhibit a broad asymmetric signal centred at 148 ppm. This signal is assigned to the C-3 resonance and non-etherified C-4 resonance of the G-unit; ie the same origin as the equivalent signal in the Klason lignin spectrum. The shoulder on the high-frequency side of this signal indicates the presence of substantial amounts of β -0-4 linkages in the whole wood.

The sharp signal at 153 ppm in the hardwood spectra is assigned to the C-3 and C-5 carbons of etherified S-units. The small signal on the low-frequency side of the peak at 153 ppm is assigned to the C-3 and C-5 carbons of non-etherified S-units. The signal of the C-4 carbon, in both types of S-unit, is evident as a shoulder on the high-frequency side of the C-l signal at 134 ppm. The trend for softwoods to contain predominantly etherified S-units can also be seen in the results of Newman *et al*⁽¹⁰⁾ and Leary *et al*⁽¹¹⁾.

5.3.3.2 Spectra of Bark Samples

The spectra of the bark samples (Figure 5.6) are very similar to the wood spectra with exceptions in two chemical shift regions. The aliphatic carbon content of the bark is higher than that of the wood. A distinct signal at 30 ppm is evident in all of the spectra. Conifers contain quantities of resin acids in the canals of the bark⁽¹⁴⁾ which would contribute signals in this chemical shift region. Bark also contains suberin which is involved in the wound healing process^(15,16). Suberin is a polymer containing a mixture of lignin-like monomer units linked to long-chain lipid material. The solid state NMR spectrum of potato skin⁽¹⁸⁾ exhibited a band centred at 32 ppm, which was assigned to the methylene groups in the chains. The signal at 174 ppm may be assigned to the carboxylic esters of suberin, although this signal, and the peak at 22 ppm, can also be attributed to hemicellulose.

The lignin-like units of suberin were found to be predominantly G-type⁽¹⁸⁾. The signal at 56 ppm can be assigned to the aryl methoxyl carbons. The broad band observed at approximately 150 ppm in the spectrum

TABLE 5.7 : CHEMICAL SHIFTS OF O-SUBSTITUTED CARBON

p-hydroxyphenyl
(H)

guaiacyl
(G)

syringyl
(S)

	H C-4	G C-3 C-4		S C-3,C-5 C-4	
R = OH	158	148	146	148	138
R = O-	163	148	153	153	137

Figure 5.6: R.E. spectra of bark samples. a) Hard Beech, b) Celery Pine, c) Kahikatea, d) Totara and e) Kauri.

of potato skin is similar to the signal in the spectrum of Kahikatea bark. However, this relatively featureless band is not assigned to high quantities of suberin. The bark sample was obtained from a young Kahikatea tree. Some woody material was unavoidably included in the sample. The "bark" that was collected contained very little tannin (ie was very pale in colour). Therefore, the Kahikatea spectrum does not exhibit the pair of strong signals at 144 ppm and 154 ppm.

The ^{13}C NMR spectra of tannins (proanthocyanidins) in solution have been analysed in detail(19-21). The proanthocyanidins are polymers of flavanols such as catechin (Figure 5.7). The meta-substituted phenols of the A-ring would contribute to the signal at 154 ppm in the bark spectra. The signal at 144 ppm is assigned to the ortho-substituted phenols of the B-ring. (This latter unit will be called a "diphenol" structure.) Two signals at 145 ppm and 155 ppm occasionally observed in the spectra of Klason lignins(10,11) were also assigned to tannins.

5.3.3.3 Spectra of Leaves

The RE spectra of the leaves are shown in Figure 5.8. The spectrum of the Flax "leaf" is substantially different from the other leaf spectra. The spectrum contains the signals of cellulose and hemicellulose carbon but no evidence is observed for other contributing structures. The flax spectrum is very similar to the NMR spectra of whole grass material(22). The two grass species studied by Himmelsbach *et al*(22) contained between 50% and 70% carbohydrate, but only 2% to 4% lignin.

The other five spectra of leaves are similar to the bark spectra, in that, the signals assigned to the tannin structures are strong. The ratio of the signal heights at 154 ppm and 144 ppm also varies greatly between spectra. The major difference between the bark and leaf spectra is observed in the envelope of aliphatic signals. The chemical shift dispersion in this region of the leaf spectra is significantly wider than in the bark spectra. The signal at 30 ppm is the dominant resonance.

Leaves contain substantial quantities of lipids (Chapter 2). The aliphatic signals can be assigned to the carbon of:

- i. The long-chains contained in the wax coatings of leaves(23)
- ii. Cutin (Figure 2.16d)
- iii. The cyclic structures of resin acids which are contained in the resin canals of leaves(14)
- iv. The phytol side-chain of chlorophyll(24) present in the leaves.

Figure 5.7: Structure of catechin. Chemical shifts for oxygen-substituted aromatic carbons.

Figure 5.8: R.E. spectra of leaf samples. a) NZ flax, b) Hard Beech, c) Celery Pine, d) Kahikatea, e) Totara and f) Kauri.

The spectrum of the Celery Pine leaves is of particular interest. The shape and size of the aliphatic envelope is very similar to the corresponding band in the lignite spectra (Figure 5.2d). For this reason, the cellulose was extracted from the leaves of the five higher plants so that the other signals could be studied in more detail. The two-part acid-treatment, used in the lignin extraction⁽¹⁷⁾, was applied to the leaves. The benzene/ethanol treatment was not repeated as it is the signals of the components removed by this treatment that are of interest.

The spectra of the extracted leaves are shown in Figure 5.9. Signals of residual cellulose are evident presumably because the lipid material provides a measure of protection from acid-hydrolysis. The envelopes of aliphatic signals are now intense in all of the spectra. The main peak is observed at approximately 31 ppm. This signal is flanked by shoulder signals in a pattern identical to that observed in the lignite spectra. The aliphatic band in the spectrum of Beech leaves is significantly narrower than the corresponding signal in the softwood spectra. This observation suggests that the lipid content of the leaves of hardwood species contains a higher proportion of straight-chain than branched- or cyclic-aliphatic material.

5.3.4 Resin Spectra

Conifers are well known for their production of resins. Kauri resin is the most common local example. Significant amounts of fossilised resin have been found in New Zealand^(14,25) and Australasian coal deposits^(26,27). A sample of fresh resin and a hand picked resinite fragment from Waimumu lignite (Oligocene/Miocene) were studied by NMR. The RE spectra are shown in Figure 5.10.

The modern^(14,27,28) and ancient^(14,25,28-30) resins (or ambers) of many countries have been studied. The types of structures present in the resin are variable and appear to be dependent on the plant of origin. For example, the resin of Agathis robusta (dundathu pine/South Queensland Kauri) contains large amounts of abietic and communic type resin acids but none of the agathic type^(14,27). In contrast, the New Zealand Kauri resin was found to contain approximately 35% of agathic type resin acids⁽¹⁴⁾.

The assignments of the resin signals can be made following the chemical shifts of three of the four basic types of resin acids (Table 5.8). The strong signal at 39 ppm originates mainly from methylene

Figure 5.9: R.E. spectra of extracted leaf samples. a) Hard Beech, b) Celery Pine, c) Kahikatea, d) Totara and e) Kauri.

Figure 5.10: R.E. spectra of a) Resinite from Waimumu lignite and b) fresh Kauri resin. Structure of agathic acid showing numbering system.

TABLE 5.8 : CHEMICAL SHIFTS OF RESIN ACIDS

CARBON	DIMETHYL ^a AGATHATE	ABIETIC ^b ACID	SANDARACOPIMARIC ^c ACID
1	39.0	38.3	38.4
2	19.8	18.1	18.3
3	38.0	37.2	37.1
4	44.2	46.3	47.2
5	56.1	44.9	48.7
6	26.1	25.6	24.9
7	38.5	120.5	35.5
8	147.4	135.5	136.2
9	55.2	51.0	50.7
10	40.1	34.5	37.8
11	21.5	22.5	18.8
12	39.6	27.5	34.6
13	160.5	145.1	37.4
14	114.7	122.5	129.3
15	166.9	34.8	149.0
16	19.0	20.9	110.5
17	106.2	21.4	26.2
18	28.6	185.4	185.3
19	177.3	16.7	16.8
20	12.4	14.0	15.3

a. Reference 31)

b. Reference 32)- See Figure 5.10

c. Reference 33)

carbon. The resonances on the low-frequency side of the main signal are assigned to the remaining methylene and methyl carbons. The signals between 40 ppm and 60 ppm are assigned to methine and quarternary aliphatic carbon. The small remaining signals are assigned to the exocyclic olefinic carbons and the resonances at 178 ppm and 185 ppm are attributed to carboxylic acid groups.

The aliphatic envelope is not significantly altered by fossilisation. The main difference between the spectra of fresh and ancient resins is the number and intensities of olefinic resonances. The lower frequency carboxylic acid signal is absent from the resinite spectrum. These differences are similar to those observed by Wilson *et al*⁽²⁹⁾ between the spectra of agathic acid and a brown coal resin. Both changes are consistent with the loss of the carboxylic acid group at C-14 in a polymerisation reaction of the diterpenoid structure^(29,34). It is thought that this polymerisation may be a photochemically induced reaction of agathic acid and a conjugated diene such as that present in *trans*-communic acid. This polymerisation would produce a structure with diterpene units attached to a side-chain backbone. A similar scheme was proposed for the Dipterocarp resins of Indonesia⁽³⁰⁾.

The most interesting feature of the agathic acid polymer model is that cyclisation at the C-8 and C-14 carbons has not occurred, despite the fact that the condensation is sterically favoured⁽²⁹⁾. This implies that the diagenetic conditions of approximately 30 million years ago were "extremely mild"⁽²⁹⁾.

5.3.5 Peat Spectrum

The formation of peat is the intermediate phase between plant components and lignite. Peat accumulation continues in low-lying areas and the RE spectrum of a "Kauri peat" is shown in Figure 5.11. The sample is a composite from six locations in the Kaimaumu swamp (Northland) and has a composition of 16.0% M, 3.6% A, 63.1% C(daf), 5.0% H(daf), 30.3% O(daf), 0.6% N(daf), 1.0% S(daf)⁽³⁵⁾.

Many of the features observed in the spectra of plant components are also recognisable in the peat spectrum. The cellulose signals between 63 ppm and 105 ppm are strong but are greatly reduced in intensity in comparison with the wood, bark and whole leaf spectra. The presence of softwood lignin structures is indicated by the broad asymmetric resonance

Figure 5.11: R.E. spectrum of a Kauri peat from the Kaimaumau swamp, Northland.

centred at 147 ppm, and the aryl-methoxyl signal at 56 ppm. The aliphatic envelope resembles that observed in the extracted Kauri leaf spectrum. The signals at 39 ppm and 45 ppm are stronger in the peat spectrum which may reflect a Kauri resin contribution to the peat. The pair of tannin signals at 144 ppm and 154 ppm are not evident in the spectrum but may be obscured by the broad lignin band in this chemical shift region.

5.3.6 Discussion

The spectra of four lignites, two from Central Otago and two from Southland, are shown in Figure 5.12. The similarities between the lignite and the peat spectra are evident; the main difference being the size of the cellulose contribution to the spectra. However, the amount of cellulose remaining in the lignites is also variable.

The fate of the cellulose content of the vascular plants in the peat swamps has been a subject of many studies. The loss of cellulose during early diagenesis^(37,38,39), and consequent enrichment of lignin, is often given as evidence for the non-involvement of cellulose in the coalification process⁽⁴⁰⁾. The cellulose may not be completely removed from the young coal and may contribute, in an altered form, to the coalifying material⁽³⁷⁾. For example, a study of the degradation of cellulose by hydrogen sulphide⁽⁴¹⁾ showed that thiophenes were formed. The pyrolysis of cellulose at 773K produced highly aromatic material which had an NMR spectrum very similar to that of high rank coals⁽⁴²⁾. However, such temperatures are not generally reached in the coalification process. Artificial coalification experiments suggest that thermal alteration of cellulose alone does not result in a coal-like product⁽⁴³⁾. It is likely that the cellulose contribution to the coal structure is minor due to the acidic nature of the deposition environment⁽⁴⁴⁾.

In previous studies^(45,46), the aliphatic content of humic acids was said to have been derived from algal or bacterial lipids, in parallel with the origin of marine humic acids. However, it is more likely that the hydrocarbon constituents of the leaf resins and waxes of higher plants are the source of the aliphatic structures found in coals of terrestrial origin. These lipids protect the leaf against dessication and possibly fungal attack⁽¹⁴⁾. The compounds survive the mild conditions present in peat swamps (low levels of oxidation and microbial activity) and, like the lignin, are probably concentrated during diagenesis.

Figure 5.12: R.E. spectra of lignites a) Ashers Waituna, b) Mataura, c) Roxburgh (III) and d) Hawkdun.

The origin of the oxygenated aromatic carbon signals is also evident in the series of plant, peat and lignite spectra. The chemical shift region between 140 ppm and 160 ppm in the Kauri peat spectrum is very similar to that observed in the wood and some of the lignite spectra. Many of the lignite spectra contain a stronger signal at 154 ppm than the shoulder observed in the peat spectrum. There are several possible reasons for this strong signal. The lignites may be derived from both softwood and hardwood lignins which give signals at 153 ppm when β -0-4 linkages are present. Evidence for a mixed plant origin is given by the pollen assemblages of the lignites (section 2.1.1.3).

The increase in the signal at 154 ppm occurs at the same time as a reduction in the signals at 148 ppm and 56 ppm. This trend was also noted by Russell and Barron⁽⁴⁷⁾ in studies of increasing gelification of soft brown coal woods. In combination with the hydrolysis of β -0-4 linkages, the demethoxylation of guaiacyl and syringyl units would produce p-hydroxy benzene rings⁽⁴⁸⁾. This structure would contribute a signal at approximately 155 ppm.

The reduction in the dominant signal at 148 ppm would expose the signals at 155 ppm and 144 ppm of tannin structures present in the coal. It is interesting to note that the loss of the methyl group (demethanation) from the lignin structures would result in a diphenol structure⁽⁴⁸⁾, which would also contribute a signal at 144 ppm. There is no signal evident at 144 ppm in the spectra of lignites, but two strong signals at 154 ppm and 144 ppm are found in the spectra of subbituminous coals (Figure 5.13). The presence of these signals, and the absence of signals attributable to methoxyl groups (56 ppm, 148 ppm), suggests that the coalification of lignites involves considerable degradation of lignin structures, in combination with a concentration of tannin structures.

The signals observed in the coal spectra have been assigned to carbon functionalities following the chemical shift data of model compounds and plant components. (Additional discussion of these signal assignments can be found in References 49 to 52). A summary of the signal assignments is given in Table 5.9. The plant origins of some signals are shown in Figure 5.14.

Figure 5.13: R.E. spectra of subbituminous coals. a) Braziers, b) Kai Point, c) Kawhia and d) Mokau

TABLE 5.9 : SIGNAL ASSIGNMENTS

Ar = Aromatic Ring
R = Alkyl group

CARBON TYPE	POSITION (ppm)	ASSIGNMENTS
Aliphatic	15	$R-\text{CH}_2-\text{CH}_3$
	22	$R-\text{CH}_2-\text{CH}_3$, $\text{Ar}-\text{CH}_3$
	30	$-(\text{CH}_2)_n$
	39	$-\text{CH}-$, $\text{Ar}-\text{CH}_2-$
	48	$-\text{C}-$, $\text{AR}-\text{CH}-$
O-substituted aliphatic	56	$\text{Ar}-\text{OCH}_3$
	64 to 105	Alcohol, ether (eg cellulose)
Aromatic	100 to 120	C-H adjacent to C=O
	120 to 130	C-H adjacent to C-H or C-R
	130 to 140	R or Ar substitution
O-substituted aromatic	144	Adjacent -OH, -OH substitution
	148	Adjacent -OH, -OCH ₃ substitution
	154	Isolated -OH substitution
Other	170 to 180	Carboxylic acids and salts

Figure 5.14: Summary of plant origins of signals observed in the NMR spectra of lower rank coals.

5.4 Changes in Signals with Coalification

5.4.1 Chemical Shifts

A selection of spectra of lignite and subbituminous coals were presented in the last section. Spectra of four bituminous coals of increasing rank are shown in Figure 5.15. The spectrum of the semi-anthracite was shown in Figure 5.2. The changes in the signals indicate that major structural alteration occurs as coalification progresses. A summary of the chemical shifts observed in the RE spectra of New Zealand coals is given in Table 5.10⁽⁴⁹⁾. Several trends are evident.

The range of chemical shifts observed in lignite spectra is large. There are many overlapping bands which are not resolved but contribute to the breadth of the bands (and to the standard deviations of the mean chemical shifts). The dispersion of chemical shifts reflects the high oxygen content of the lignites. Not only are there many types of oxygenated functionalities, both aliphatic and aromatic, but also many types of "adjacent" carbon structures. This factor is particularly evident in the distribution of low frequency aromatic signals assigned to C-H groups adjacent to oxygen. The lack of signals between 135 ppm and 145 ppm, attributable to alkyl substituted aromatic carbon, suggests that few condensation reactions have taken place in the formation of lignites.

The carboxylic carbon content of the lignites is thought to be high because of the broad band centred at 177 ppm. This resonance contains a significant contribution from the first order aromatic SSB but the signal is too intense for this alone. Support for the presence of a discrete signal of carboxylic carbon was gained from the spectrum of a humic acid from Waimumu lignite. The sample was obtained with a MAS frequency greater than 3kHz⁽¹⁸⁾. A large signal was observed at 177 ppm, which could not be assigned to an SSB signal.

The progression in rank from lignite to subbituminous is marked by several changes in the observed signals. The signals directly attributable to cellulose and lignin units are insignificant in the spectra of subbituminous coals. The loss of oxygenated functionalities is reflected in a narrowing of the range of low frequency aromatic chemical shifts. Very few of the spectra of subbituminous coals exhibit aromatic centreband signals at chemical shifts below 110 ppm. The chemical shift region between 135 ppm and 145 ppm contains significant intensity indicating an

Figure 5.15: R.E. spectra of four bituminous coals. a) Rockies (I), b) Liverpool, c) United and d) Kiwi.

TABLE 5.10 : AVERAGE CHEMICAL SHIFTS

Data for signals observed in the RE spectra of many coals (A) or only in spectra of coals of specific ASTM ranks (B). Standard deviations given in brackets.

Mean Chemical Shift (ppm)

A	B
15.4 (0.7)	
21.6 (0.8)	
30.8 (0.9)	
39.4 (1.7)	
48.5 (1.9)	
	56.3 (0.4)
	64.3 (1.6)
	74.3 (0.8)
	82.7 (1.2)
	88.6 (0.6)
	105.3 (0.4)
	107.3 (1.2) lig + few sub.
112.0 (1.9)	
117.4 (1.9)	
127.6 (0.9) ^a	125.0 (1.5)
	130.0 (1.2)
138.0 (1.0) ^a	
	143.6 (1.4) sub, hvbC, hvbB
	147.7 (0.8) lig.
153.8 (0.9)	
	177.4 (1.1) lig.

a - sub and higher ranks

increased content of alkyl substituted aromatic carbon. The main signals of oxygen substituted aromatic carbon occur at 154 ppm and 144 ppm.

The transition from subbituminous to low rank bituminous coal is not marked by any obvious changes in the spectra. However, there are significant changes in signal positions through the spectra of high volatile bituminous coals. The aromatic envelope is continually "line-narrowing"⁽⁵³⁾ with low frequency signals appearing as small shoulders only. The signal at 144 ppm weakens and disappears in the spectra of high volatile bituminous B coals. This signal loss occurs in conjunction with the appearance of a distinct signal at 138 ppm. The signal at 154 ppm, assigned to phenolic carbon, persists through to the spectrum of the semianthracite.

5.4.2 Signal Intensities

Significant changes occurred in positions of the signals with increasing coal rank. However, it is the relative intensities of the resonances that undergo the most dramatic alteration with coalification.

The decrease in the range of chemical shifts observed for signals of aromatic carbon occurs in conjunction with a marked increase in the intensity of the main aromatic band (128 ppm). This signal is of equal intensity to many of the other aromatic signals in the lignite spectra, but is the dominant signal in the spectra of high volatile bituminous A coals. The size of the first order, high frequency SSB in the spectra of high rank coals increases relative to the centreband. This trend is caused by an increasing content of poly-cyclic aromatic systems in high rank coals. The ring junction carbons of such systems would contribute intensity to the main aromatic band but the associated SSB will be larger because the chemical shift tensor of these carbons is highly anisotropic. Thus, the changes in the signals of aromatic carbon reflect the increase in condensation and aromaticity with increasing coalification which was predicted in Chapter 2.

In contrast, the aliphatic signals gradually lessen in intensity relative to the aromatic envelope. The rate of intensity loss becomes rapid between the spectra of low and high rank bituminous coals (Figure 5.15). The decrease in the intensity of the polymethylene signal (30 ppm) is far greater than that observed for the other signals of aliphatic carbon. These changes in the aliphatic structures epitomise the

process of "catagenesis" described in Chapter 2. The average length of the aliphatic chain is reduced as thermal cracking releases low-molecular weight hydrocarbons. Variable spinning rate experiments showed that small aliphatic signals persist in the spectrum of the semianthracite but they are partly obscured by the second-order low frequency SSB of the main aromatic band.

The loss of oxygen functionalities from the coal structure, the third of the coalification processes, is evident in two phases. The first phase was described in the last section and involves a decrease in the range of oxygenated-carbon signals through the lignite and subbituminous spectra. Only the signal of the most stable form of oxygen functionality, the phenol signal at 154 ppm, is observed in the spectra of coals of high volatile bituminous A rank. The second phase involves the continual decrease in intensity of this signal until it is of negligible size in the semianthracite spectrum.

5.4.3 Signal Height Ratios

The changes in the signal intensities can be qualitatively assessed by selecting specific ratios of signal heights measured from the RE spectra. This approach has been demonstrated to be useful for following structural alterations induced by the coalification of New Zealand coals⁽⁵²⁾ and in comparing the structure of Australian brown coals with New Zealand lignites and subbituminous coals⁽⁵¹⁾. The success of these techniques is evident and the results will not be recycled here.

However, the signal height data (Appendix 3) has not been used to compare the higher rank Australian coals with the New Zealand coals. The two parameters described by Davenport and Newman⁽⁵²⁾ are plotted against carbon content in Figures 5.16 and 5.17. The ratio of aliphatic signal heights is "related to the average length of the alkyl sidechains in the polymeric coal structure"⁽⁵²⁾. The decrease in the aliphatic signal height ratio at higher ranks is reflecting the process of catagenesis⁽⁵²⁾.

The scatter in the data, particularly for the low rank coals, has been attributed to the influence of source variations. For example, the Central Otago lignites (eg Figure 5.12c,d) exhibit an average ratio of 1.7 (standard deviation, SD = 0.3) which is significantly higher than the corresponding value of 1.2 (SD = 0.2) for the Southland lignites (eg Figure 5.12a,b). Petrographic studies^(54,55) have shown that the

Figure 5.16: The ratio of heights of aliphatic carbon signals plotted against the carbon content. Numbers in brackets refer to relevant chemical shift. Carbon content is on a dry ash free basis. Symbols refer to lignites (●), subbituminous (■), high volatile B, C bituminous (▼), high volatile A bituminous (▲), medium volatile bituminous and higher ranks (◆). Unless otherwise stated, these symbols and the daf carbon content will be used throughout the study. Australian coals (open symbols).

Figure 5.17: The ratio of the heights of the phenol and main aromatic signals, against carbon content. Australian coals (open symbols).

Central Otago lignites were deposited in a limnic (fresh water) environment and are highly degraded. The Southland lignites were deposited in a paralic (marine) environment and contain more undegraded plant tissues and woody material. The high degree of degradation in the Central Otago lignites is reflected in high quantities of exinite macerals which are traditionally associated with aliphatic structures (see Chapter 2). The aliphatic signal height ratios indicate that the exinite macerals must contain high quantities of long chain aliphatic structures rather than branched or cyclic structures.

The ratio of the phenol signal height to the main aromatic signal (Figure 5.17) decreases steadily with increasing carbon content ($R = 0.946$). This parameter is reflecting the loss of oxygen from the aromatic portion of the coal as coalification proceeds.

The data for the Australian coals (open symbols) appear to follow the same trends as the New Zealand coals. The Australian brown coals exhibit very low values for the aliphatic ratios which lead to a prediction of lower alkene yields from pyrolysis of brown coals in comparison with New Zealand lignites⁽⁵¹⁾. The phenol ratio indicates that the oxygen substitution of the aromatic rings in the brown coals is similar to that observed in lignites and subbituminous coals⁽⁵¹⁾.

The data plotted in both Figures indicate that two distinct groups of high volatile A bituminous coals exist in New Zealand. Five of the samples resemble the lower rank bituminous coals while the remaining ten samples exhibit spectra that are similar in character to those of medium volatile bituminous coals. No New Zealand coal sample has been identified that shows intermediate properties⁽⁵⁶⁾. It can be seen that the data, particularly the phenol ratios, of the Australian high volatile A bituminous coals are located directly between the two New Zealand coal groups. Thus, the incorporation of the Australian samples with the New Zealand coal suite will result in an interesting comparison of coals that span a large range of coalification levels.

5.5 Summary

The initial aim of the study - to assign, and identify the structural origins of, the signals observed in the NMR spectra of coals - has been completed. The survey of model compound chemical shifts and the spectra of individual plant components has produced a large amount of information about the structure of the coal spectrum. Evidence has been found for the influence of the depositional environment on the structure of coals. The changes in the signal height ratios with increasing rank have provided an easily attainable, qualitative handle on the degree of coalification of the sample.

The following chapters investigate properties of coal that may affect the NMR response, in preparation for quantitative NMR analysis.

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6.0 ELECTRON PARAMAGNETIC RESONANCE

6.1 Introduction

The presence of paramagnetic species in the coal sample may affect the NMR spectrum. The NMR "visibility" and the relaxation behaviour of carbon-13 nuclei may be altered when they are in the vicinity of an unpaired electron. This may influence the quantitative reliability of the NMR response. Therefore, it is necessary to study the nature of the paramagnetic content of coals.

The electron paramagnetic resonance (EPR) technique provides the ideal method for investigating unpaired spins. Since the discovery of EPR absorption in carbonaceous materials by Uebersfeld (1) and Ingram (2), numerous workers have reported EPR data for coals. These studies indicated that "stable free radicals or other species containing unpaired electrons are present in all coals"(3). Systematic EPR studies have been published for a large variety of coals and petrographic components from many countries. Only Yokono *et al* (4-6) have examined the EPR and NMR spectra of the same coals and attempted to correlate the results. Their measurements were performed on samples prepared under vacuum conditions. Therefore, the results may not be strictly comparable to this study, in which the NMR spectra are obtained in air.

6.2 EPR Theory

The basis of EPR is similar to that of NMR, in that it is dependent on the absorption of electromagnetic radiation by a species in a magnetic field. However, in the case of EPR, the absorbing species is an unpaired electron. There are several treatises which provide a detailed explanation of the theoretical and experimental aspects of EPR(7-9). There follows a brief introduction to the parameters that can be extracted from the EPR spectra of coals. The subscript "e" is used to distinguish EPR parameters from the equivalent NMR parameters.

The difference in energy between the parallel and the anti-parallel spin states in the magnetic field is given by:

$$\Delta E = g \beta_e B \quad [6.1]$$

where g is the splitting factor, β_e is the electron Bohr magneton and B is the magnetic flux density. The g -factor for a free electron is 2.0023.

The frequency of the transition between the two electron spin-states, ν_e , is therefore defined as:

$$\nu_e = g \beta_e B/h \quad [6.2]$$

where h is Planck's constant. For example, for X-band operation ($\nu_e = 9.5$ GHz) a g -factor = 2 corresponds to a magnetic flux density $B = 0.35$ T.

Any alteration in the environment of the unpaired electron results in broadening of the resonance band to a finite width which is measured by the line width at half-height, $\Delta H_{\frac{1}{2}}$. Dipole-dipole interactions in the spin system contribute to the line broadening. The spin-spin relaxation time, T_{2e} , characterises these interactions and is given by⁽⁸⁾:

$$T_{2e} = 1/\gamma \Delta H_{\frac{1}{2}} \quad [6.3]$$

$$\text{where } \gamma = g \beta_e/h \quad [6.4]$$

for a Lorentzian line shape.

The interaction between the spins and the surrounding structure is characterised by the spin-lattice relaxation time, T_{1e} , given by:

$$T_{1e} = 1/(2 T_{2e} \gamma^2 B_{\max}^2) \quad [6.5]$$

where $B_{\max}$ is the magnetic flux density at which complete saturation occurs (ie the maximum signal height is observed).

The saturation behaviour depends on the mode of line-broadening; ie whether homogeneous or inhomogeneous broadening is dominant. Homogeneous line broadening is the result of transitions between two spin levels that are not sharply defined. An inhomogeneously broadened line consists of a distribution of several component resonant lines which have merged to form one envelope. The many sources of these broadening modes are outlined by Poole⁽⁷⁾. Typical saturation curves for both cases are shown in Figure 6.1.

6.3 Experimental

6.3.1 Samples

Seventeen coals, selected from both the New Zealand and Australian sample suites, were chosen for study by EPR. The suite included five lignites, four subbituminous coals, five high volatile and one medium volatile bituminous coals, and two semi-anthracites. Approximately 0.25g of sample was packed into a standard 3mm quartz EPR tube to a level of approximately 5cm, giving an average sample weight per unit length (W/L) of

The frequency of the transition between the two electron spin-states, ν_e , is therefore defined as:

$$\nu_e = g \beta_e B/h \quad [6.2]$$

where h is Planck's constant. For example, for X-band operation ($\nu_e = 9.5$ GHz) a g -factor = 2 corresponds to a magnetic flux density $B = 0.35$ T.

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$$T_{1e} = 1/(2 T_{2e} \gamma^2 B_{\max}^2) \quad [6.5]$$

where $B_{\max}$ is the magnetic flux density at which complete saturation occurs (ie the maximum signal height is observed).

The saturation behaviour depends on the mode of line-broadening; ie whether homogeneous or inhomogeneous broadening is dominant. Homogeneous line broadening is the result of transitions between two spin levels that are not sharply defined. An inhomogeneously broadened line consists of a distribution of several component resonant lines which have merged to form one envelope. The many sources of these broadening modes are outlined by Poole⁽⁷⁾. Typical saturation curves for both cases are shown in Figure 6.1.

6.3 Experimental

6.3.1 Samples

Seventeen coals, selected from both the New Zealand and Australian sample suites, were chosen for study by EPR. The suite included five lignites, four subbituminous coals, five high volatile and one medium volatile bituminous coals, and two semi-anthracites. Approximately 0.25g of sample was packed into a standard 3mm quartz EPR tube to a level of approximately 5cm, giving an average sample weight per unit length (W/L) of

Figure 6.1: Typical saturation curves for homogeneous and inhomogeneous broadening of the EPR signal. P represents the power.

0.05gcm⁻¹. The W/L was measured for each sample to reduce errors associated with uneven packing densities. The spectra of the empty tubes showed no background resonances.

6.3.2 The Instrument

EPR spectra were obtained on a Varian V4502 X-band spectrometer at 9.5 GHz. In general microwave power levels of 0.01W were used. Measurements were carried out at room temperature (~293 K) and atmospheric pressure. The Varian "strong pitch" standard (0.1% pitch in KCl) was used as the reference sample for all measurements. Spectra were recorded as the first derivative of the absorption resonance. An example of an EPR signal (strong pitch sample) is given in Figure 6.2, to illustrate the measurement of line-shape and line-position parameters.

6.3.3 Measurement of the g-factor and line-width

The g-factor is calculated from the point on the magnetic flux density scale, the resonant frequency, V_e (in Hz), using the resonance equation (6.2), ie:

$$g = (7.14 \times 10^{-3}) \times V_e/B \quad [6.6]$$

The "peak-to-peak" line width, ΔH_{pp} , is also measured from the first derivative curve. It is related to the line width at half-height by (7):

$$\Delta H_{pp} = \Delta H_{\frac{1}{2}}/3^{\frac{1}{2}} \quad [6.7]$$

Both the g-factor and ΔH_{pp} were calibrated against the strong pitch parameters, $g=2.0028$ and $\Delta H_{pp} = 0.17 \text{ mT}^{(10)}$.

The lineshapes of the derivative curves were determined for several of the coals following the procedure outlined by Alger⁽⁸⁾. The signal heights are measured relative to the maximum height. Distances from the centre of the resonance are measured at points where the signal has decayed to a certain intensity (eg 60% of the maximum signal). These distances are expressed in terms of "a" where:

$$a = \Delta H_{pp}/2 \quad [6.8]$$

and are then compared with the theoretical positions for Gaussian and Lorentzian line-shapes (Figure 6.3). The comparison for the line shape of a bituminous coal is shown below:

Figure 6.2: Parameters associated with the first derivative representation of the absorption resonance.

Figure 6.3: Theoretical traces for Gaussian (×) and Lorentzian (•) line-shapes with identical I_{pp} values.

Signal Height	Position (Lorentzian)	Position (Gaussian)	Position (Experimental)
100% of maximum	a	a	a
80% of maximum	1.65a	1.5a	1.6a
60% of maximum	2.10a	1.8a	2.0a
40% of maximum	2.75a	2.1a	2.5a
20% of maximum	3.80a	2.5a	3.2a
10% of maximum	5.0 a	2.8a	3.8a

It was found that the EPR signals of coal samples have line shape parameters intermediate between Gaussian and Lorentzian but with a tendency to be closer to the Lorentzian line shape. This is consistent with the results for other coals(11, 12). The near-Gaussian lines observed by Retcofsky *et al*⁽¹³⁾ for lower rank coals was not noted in this study.

6.3.4 Measurement of the "Q-Factor"

The EPR signal intensity at resonance is proportional to the amount of power (P) absorbed by the sample; ie is dependent on the average microwave flux density of the sample⁽⁷⁾:

$$B = k (Q P)^{\frac{1}{2}} \quad [6.9]$$

where k is a constant calculated from the cavity dimensions, and Q is the "quality factor" of the cavity. The Q-factor can be divided into two terms (14):

$$1/Q = 1/Q_0 + 1/Q_s \quad [6.10]$$

where Q_0 is the quality factor of the cavity and Q_s reflects the microwave loss caused by the sample. Q_s is due entirely to the rf susceptibility, χ'' , and the filling factor, η , of the sample⁽¹⁴⁾:

$$1/Q_s = 4\pi\eta\chi'' \quad [6.11]$$

where

$$\eta = V_s/V_c \quad [6.12]$$

ie the ratio of the sample volume to the volume of the cavity.

Since the volume, V_s , is kept fairly constant, it follows that the EPR sensitivity is effectively proportional to the rf susceptibility of the sample, ie the detuning capability of the sample. Therefore, it is necessary to have a knowledge of the relative sample Q factors before the signal intensities can be compared.

For frequencies, ω , close to the resonance frequency, ω_0 , the loaded Q is determined by:

$$Q = \omega_0 / \Delta\omega \quad [6.13]$$

The change in the cavity Q at resonance can be estimated from the oscilloscope trace of the cavity mode by assuming that the maximum of the klystron mode corresponds to the total reflected power⁽¹⁴⁾. Thus, the half-width of the cavity mode represents the change in the cavity Q measured on, and off resonance (Figure 6.4). A cavity wavemeter was used to measure the microwave frequency.

The loaded Q -factor for the strong pitch standard, Q_{sp} , was estimated to be 5500 (with a standard deviation of 110) from repeated measurements. The Q_s values for the coal samples were standardised against Q_{sp} .

6.3.5 Measurement of Spin Counts

The spin count, N_g (spins g^{-1}) of the sample is estimated from the area of the signal with respect to the signal area of the standard. The relative loaded Q -factors, and amplifier gain (AG) of the sample and the standard, must be known. Since the spin-count of the standard pitch is in the units of spins cm^{-1} , it is also necessary to know the W/L (ie $g\ cm^{-1}$) in order to convert the observed intensity into the required N_g units of spins g^{-1} .

There are several methods for estimating the intensity (A) of the absorption band. The most common method is:

$$A = I_{pp} * \Delta H_{pp}^2 \quad [6.14]$$

where I_{pp} is the peak-to-peak signal height (Figure 6.2). However, this approximation does not take the line-shape into account. Whether the resonance is of Lorentzian, Gaussian or some other shape, can alter the amount of intensity in the "wings" of the absorption band. In addition, the peak-to-peak amplitude is severely affected by cavity loading⁽¹⁴⁾ and would therefore result in a biased estimate of the signal area.

Kwan and Yen⁽¹¹⁾ have published a detailed study of the line-shapes of the EPR signals of coal and have derived methods for estimating the signal area which are independent of the line-shape. However, double integration of the first derivative is the most reliable and reproducible method for obtaining the resonance intensity⁽¹⁴⁾.

The spectra were digitised (by hand) at 0.1 mT intervals into signal heights from the baseline (Figure 6.2). The signal area was computed using

Figure 6.4: Representation of the cavity mode showing the measurement of the width at half-height, $\Delta\omega$.

the program "DBINT" which was developed for this purpose by Dr R. Palmer of Chemistry Division. Repeated measurements on strong pitch indicated that the standard deviation in the area estimates was approximately 6%.

The spin count is then estimated by:

$$N_g = \frac{A_s}{A_{sp}} \times \frac{Q_{sp}}{Q_s} \times \frac{AG_{sp}}{AG_s} \times \frac{3 \times 10^{15}}{(W/L)} \quad [6.15]$$

Varian⁽¹⁰⁾ estimated the accuracy of the spin count of the strong pitch sample (3×10^{15} spins cm^{-1}) to be $\pm 25\%$, which may have introduced a large systematic error into the spin count determination. The relative spin count determinations were estimated to have an uncertainty of between 15 and 20%; ie if the coal sample measurements were assumed to entail the same variation as that observed for the strong pitch sample. This was tested by repeating the EPR measurements for two samples under the same conditions (ie samples not repacked) after a delay of four weeks. This delay represents the time span over which the EPR measurements were collected. The spin count of one sample increased by 17%, while that of the other decreased by 14%. Therefore, the maximum uncertainty of 20% appeared to be appropriate.

6.3.6 Saturation Experiments

In order to determine the spin-lattice relaxation constant, T_{1e} , it is necessary to know the magnetic flux density, B_{max} at which the maximum signal is observed (Equation 6.5). This was obtained from the saturation behaviour of the coal, following the steps described by Alger⁽⁸⁾:

1. "Determine that the line shape is Lorentzian". As mentioned previously, the line shapes of the coal spectra were not always pure Lorentzian but, for the purposes of obtaining an estimate of the relaxation parameters, it was assumed that the line shapes were close to Lorentzian.
2. "Measure T_2 ". Values of T_{2e} were obtained using equation 6.3; ie

$$T_{2e} = 1/(1.52 \times 10^8 \times \Delta H_{pp}) \quad [6.16]$$
3. "Find the value of (B_{max}) which gives the largest attainable signal". This is obtained by plotting the change in signal height as the power is increased. Curves similar to the homogeneous saturation behaviour shown in Figure 6.1, were obtained.

The magnetic flux density is proportional to the square root of the power (Equation 6.9). The maximum power available was 0.2W. In some

cases, the signal height maximum was observed at magnetic flux densities close to this upper power limit. Therefore the type of broadening present could not always be ascertained. $B_{\max}$ is then calculated from the power incident on the cavity, the cavity dimensions⁽¹⁰⁾ and the Q-factor:

$$B_{\max} = 1.41 \times 10^{-6} (Q_S P_{\max})^{\frac{1}{2}} \quad [6.17]$$

4. " T_1 is calculated from" equation 6.5; ie

$$T_{1e} = 1/(6.2 \times 10^{22} \times T_{2e} \times B_{\max}^2) \quad [6.18]$$

6.4 EPR Spectra of Coals

The EPR spectra of coals exhibit several resonances. The main signal is a single, nearly symmetrical, broad band near $g=2$, which is assigned to free radicals. Other resonances occur which are several orders of magnitude smaller than the main signal. These signals have been assigned to the resonances of paramagnetic metal ions.

6.4.1 Metal Ion Signals

The EPR spectra of four coals of different rank are shown in Figure 6.5. The spectrum of the Waimumu lignite is very similar to the EPR spectra of Victorian brown coals described by Dack *et al*⁽¹⁵⁾.

The group of signals in the $g=2$ region are thought to be the components of the six line Mn(II) multiplet, as manganese has a nuclear spin, $I = 5/2$ ⁽¹⁶⁾. Similar signals were observed in the EPR spectra of, for example, a natural clay with a high Mn(II) content⁽¹⁷⁾, and a Cretaceous petrified wood⁽¹⁸⁾.

The remaining signals can be attributed to various forms of iron. The signal at $g = 4.2$ is assigned to high spin d^5 iron (III) in many structural sites⁽¹⁵⁾. The spectra that contain this signal also show an additional weak absorption at $g=9$ which has been predicted by quantum mechanical equations⁽¹⁸⁾ for Fe^{3+} with orthorhombic symmetry.

The broad signal under the free radical signal at $g=2$, in the spectra of the higher rank coals, is consistent with iron (III) occupying a different site from that in the low rank coals⁽¹⁵⁾. The intensities of the signals do not correlate with the quantities of metal in the coal samples. For example, the iron and manganese contents determined by X-ray fluorescence (XRF) analysis for the four samples (Figure 6.5) were:

Figure 6.5: EPR spectra of coals showing signals of metal ions. a) Waimumu (I) (lig), b) Kopuku (sub), c) Topline (hvBb) d) Fox River (sa). ($AG = 2.5 \times 10^4$)

	<u>Fe (ppm)</u>	<u>Mn (ppm)</u>
Waimumu Newvale	5170	160
Kopuku	3300	10
Topline	5620	10
Fox River	4740	52

The iron content of the Kopuku subbituminous coal is less than that of the lignite yet the intensity of the $g=4.2$ signal, in the spectrum of the former coal, is more than double that of the lignite signal. The two higher rank coals also contain large amounts of iron but the $g=4.2$ signal is insignificant or absent.

The manganese signals were only observed in the spectra of lignites, even though the manganese content of the Fox River semi-anthracite is only 25% less than that of one of the Roxburgh samples (68 ppm). Retcofsky *et al*⁽¹⁶⁾ observed the Mn(II) multiplet in the spectrum of a high volatile bituminous A coal.

The lack of proportionality between the signals and iron contents has been observed in EPR studies of brown coals⁽¹⁵⁾ and natural clays⁽¹⁷⁾. Dack *et al*⁽¹⁵⁾ proposed that the presence of a large and variable proportion of iron (II) (which is not detectable by EPR) causes the variation in the iron (III) signal intensities.

An unusual signal was occasionally observed in the region of $g = 2.6$ in the coal spectra. The appearance of the signal was not confined to any samples in particular and was erratic; ie the signal disappeared when the sample was repacked. Examples of EPR spectra with and without this signal are shown in Figure 6.6 for the Huntly East subbituminous coal. A recent publication on the application of the ferromagnetic resonance (FMR) technique to coal⁽¹⁹⁾ contains coal spectra which exhibit a prominent signal at $g = 2.6$. This signal occurred only in one of three spectra of randomly selected samples and was assigned to the presence of magnetite.

The spectra in which this signal appeared did not necessarily correspond to samples with high iron contents (eg Huntly East coal contains 2110 ppm of iron) which is consistent with the observation of Malhotra and Graham⁽¹⁹⁾ that "only one or two grains of a ferromagnetic material can drastically alter the observed spectrum".

The sample of Liddell bituminous coal which was included in the EPR study was known to contain large amounts of magnetite (see Chapter 8). The

minous coal a) without and
)

Figure 6.6: EPR spectra of Huntly East subbituminous coal
(b) with the signal at $g = 2.5$ ($AG = 2.5 \times 10^4$)

spectrum of this coal showed an extremely broad signal centred at $g = 4.2$, which was greater than the signals observed for other coals by at least two orders of magnitude (Figure 6.7). A sample of Liddell coal was acid-washed (AW) with HCl following the example of Malhotra and Graham⁽¹⁹⁾ (experimental details are given in Chapter 8). However, this treatment only reduced the signal intensity and shifted the signal to $g = 4.8$. A second sample of Liddell coal was oven-dried (OD) at 383 K for 16 hours. This treatment produced an identical change in the EPR spectrum as the AW procedure (Figure 6.7b,c). This is in contrast to the results of Dack *et al*⁽¹⁵⁾ who observed a 420% increase in the $g = 4.3$ signal intensity for a sample dried at 323K for 24 hours.

Broad signals were also observed in the spectra of three other coals. The three equivalent spectra to the Liddell example are shown in Figure 6.8 for the Ohai subbituminous coal. In this case the broad signal is centred at $g = 2.4$ and the $g = 4.3$ signal is observed as a very small resonance. Oven drying did not alter the spectrum significantly. The AW treatment reduces the broad signal slightly and shifts the resonance to $g = 2.3$.

The spectra of the Strongman bituminous coal are shown in Figure 6.9. The spectrum of the raw coal shows a broad resonance at $g = 2.7$. This signal is considerably narrower than the signals observed in the previous examples. Both AW and OD treatments remove this signal and the resultant spectra resemble those of the higher rank coals in Figure 6.5. The spectrum of the OD coal differs from that of the AW sample in the size of the $g = 4.3$ signal and the broad resonance under the $g = 2$ signal. This may be due to the oxidation⁽¹⁵⁾ of iron (II) to the form of iron (III) producing the resonance at $g = 2$. Alternatively, loss of water of hydration may cause a change in the site symmetry of the iron (III). This could also alter the position of the signal.

The spectra of the raw and treated Yarrabee samples are shown in Figure 6.10. The broad signal in the spectrum of the raw coal is centred at $g = 2.1$. Both treatments reduce the intensity of the signal, with the AW procedure being the most effective in this regard. OD results in the signal shifting to $g = 3.0$.

The spectra presented in Figures 6.7 to 6.10 show very broad signals which do not have constant g -factors - nor do they alter in the same manner after various sample pre-treatments. The origins of these signals remains

Figure 6.7: EPR spectra of Liddell hvA bituminous coal a) raw coal ($AG = 1.25 \times 10^2$), b) oven-dried coal ($AG = 5.0 \times 10^2$), c) acid-washed coal ($AG = 5.0 \times 10^2$)

Figure 6.8: EPR spectra of Ohai subbituminous coal a) raw coal ($AG = 1.25 \times 10^3$), b) OD coal ($AG = 1.25 \times 10^3$), c) AW coal ($AG = 1.0 \times 10^3$)

Figure 6.9: EPR spectra of Strongman hvB bituminous coal. a) raw coal ($AG = 2.5 \times 10^3$), b) OD coal ($AG = 2.5 \times 10^4$), c) AW coal ($AG = 2.5 \times 10^4$)

Figure 6.10: EPR spectra of Yarrabee semianthracite. a) raw coal ($AG = 2.5 \times 10^3$), b) OD coal ($AG = 1.25 \times 10^4$), c) AW coal ($AG = 2.5 \times 10^4$)

an enigma. The signals assigned to metal ions in the spectra of the eight remaining coals were similar to the spectra of equivalent coal rank shown in Figure 6.5.

6.4.2 The Free Radical Signal

The origin of the main signal at $g = 2.0$ has previously been a topic of considerable debate⁽¹⁶⁾. It is now widely accepted that the signal arises from the presence of large concentrations of organic free radicals in the coal, which are "stabilised in the aromatic skeletons"⁽¹²⁾.

The properties of the organic free radical signal have been studied for coals or coal lithotypes from, for example, USA^(13,16,20,24), Japan⁽²¹⁾, Canada⁽²²⁾, Russia⁽²³⁾, Pakistan and Yugoslavia⁽²⁵⁾, Europe^(25,26) and Australia⁽¹⁵⁾. The purpose of the following discussion is to test the EPR trends found for overseas coals on Australasian coals. The EPR parameters should indicate whether any unusual electronic properties exist that might be reflected in the NMR spectra. Values of the three standard EPR parameters for the seventeen coals are given in Table 6.1.

6.4.2.1 The g-factor

"The g-factor is a parameter which is particularly sensitive to the chemical environment of the unpaired electron in a radical"⁽²⁴⁾. A plot of the g-factor against the carbon content is given in Figure 6.11. The deviation from the value of the free-electron is greatest for the lignite g-factors, which indicates that the unpaired electrons are "localised or partially localised on atoms having strong spin-orbit interactions"⁽¹⁶⁾. For example, the g-factors of the lignites (2.0037 to 2.0039) fall into the range expected for phenoxy⁽¹⁴⁾ and methoxy benzenes (2.0035 to 2.0040)⁽²⁴⁾. G-factors for nitrogen and sulphur containing radicals are of the order 2.0031 and 2.0080-2.0081, respectively⁽²⁴⁾.

As coalification progresses (ie heteroatoms are lost) the g-factors decrease to the magnitude typical of hydrocarbon free radicals (2.0025 to 2.0028)⁽²⁴⁾. The decrease in g-factor for coals between 67% and 91% carbon has been observed in many of the studies in the literature. The unusual g-factor behaviour at the coalification extremes was not observed as the range of coal ranks studied is not as large as that covered in the work of Retcofsky et al⁽¹⁶⁾.

TABLE 6.1

Coal	No.*	%C (daf)	% H (daf)	% O (daf)	g-factor	ΔH_{pp} (mJ)	$N_g \times 10^{-18}$ (spin g ⁻¹)
Mataura	6	68.6	4.0	26.0	2.0037	0.43	0.35
Waimumu	8	68.4	4.7	25.6	2.0039	0.40	0.18
Roxburgh I	3	69.9	5.8	22.7	2.0037	0.53	0.57
Roxburgh II	4	(67.1)	(5.6)	(26.3)	2.0038	0.50	0.15
RoxburghIII	5	(67.1)	(5.6)	(26.3)	2.0038	0.45	0.47
Kopuku	15	72.8	4.8	21.2	2.0037	0.58	1.5
Weavers	19	73.7	5.0	20.0	2.0037	0.65	2.7
Huntly East	26	75.1	4.8	18.6	2.0036	0.65	4.1
Ohai	30	75.2	5.3	18.3	2.0038	0.63	4.4
Strongman	35	(80.0)	(5.5)	(12.7)	2.0034	0.63	4.7
Topline	37	-	-	-	2.0035	0.73	4.9
Charming Creek	42	(79.2)	(5.5)	(7.7)	2.0037	0.68	4.0
Webb	45	84.0	5.4	6.9	2.0033	0.65	4.9
Liddell	A5	(82.0)	(5.5)	(10.0)	2.0028	0.53	5.0
Bulli	A7	(87.1)	(4.8)	(6.1)	2.0030	0.35	12
Yarrabee	A10	(87.8)	(3.4)	(6.5)	2.0032	0.32	14
Fox River	57	90.6	4.0	3.7	2.0028	0.45	18

* Coal number from Tables 4.1 and 4.2

Figure 6.11: The g-factors of the free-radical signal plotted against a) the carbon content and b) the atomic fraction of oxygen. RL stands for "Retcofsky's line" from Reference 17. Open symbols represent samples for which actual elemental analyses are not known (see Chapter 4).

The plot of g-factor against the atomic fraction of oxygen (Figure 6.11b) shows that the correlation observed by Retcofsky *et al*⁽¹⁶⁾ (RL) is also relevant for Australasian coals.

6.4.2.2 The line-width ΔH_{pp}

The behaviour of the peak-to-peak linewidth with increasing coal rank is shown in Figure 6.12a. The broad maximum observed in the ΔH_{pp} of the low-rank bituminous coals is similar to that found by Retcofsky *et al*⁽²⁰⁾ for vitrains. However, the linewidths of the signals of coals between 72% and 87% carbon, measured in air by Petrakis and Grandy⁽²⁴⁾, exhibit a completely opposing trend. Toyoda *et al*⁽²¹⁾ did not observe an initial increase in linewidth, but noticed a sudden decrease in ΔH_{pp} for Japanese vitrains with carbon contents greater than 88%.

The trend shown in Figure 6.12a can be rationalised as being caused by the increasing influence of "spin-spin interactions between the free radical electrons and protons in the coal"⁽¹³⁾, which are not resolved as hyperfine structure. The narrow linewidths exhibited by the semi-anthracites reflect the low hydrogen contents. Figure 6.12b shows that there is a relationship between the hydrogen content of the coal and the line-width. It should be noted that Khulbe *et al*⁽²²⁾ found that larger line-widths were obtained for Canadian coals with low hydrogen contents and suggested that other atomic species, such as oxygen, may also influence the line-widths.

The g-factors and line-widths of Australasian coals exhibit properties which are generally consistent with the results of overseas work and the overall chemical processes involved in coalification.

6.4.2.3 The spin-count - N_g

The non-linear increase in spin-count with carbon content, found by other workers^(13,21,24,26) was also observed for Australasian coals (Figure 6.13). The strong exponential relationship between these two parameters observed for vitrains^(20,21), was not found for Australasian coals (Figure 6.14). Although a straight line can be drawn to the data ($R = 0.925$) the points could also be justified as fitting into two linear areas or a curve.

The magnitude of the spin counts observed for Australasian coals was often smaller than those obtained for overseas coals of a similar carbon

Figure 6.12: The peak-to-peak width of the free-radical signal plotted against a) the carbon content and b) the hydrogen content on a moist-ash-free basis.

Figure 6.13: Plot of the spin counts against carbon content. Error bars represent the + 20% uncertainty in the spin count estimations. Symbols as for Figure 5.16.

Figure 6.14: Data from Figure 6.13 replotted on a logarithmic scale.

content. This is particularly evident in the spin-counts of lignites. For example, the sample of Beulah-Zap lignite (%C = 67.81) studied by Retcofsky *et al*⁽¹³⁾ exhibited a spin-count of 56×10^{17} spins g^{-1} . However, the New Zealand lignites (67% - 70% C) show spin-counts in the range 1×10^{17} to 6×10^{17} spins g^{-1} ; ie an order of magnitude less. This discrepancy may be due to the different origins of the coal, but it is more likely that variations in experimental conditions influence the final N_g values.

It has been noted by some workers^(22,26,27) (but not all⁽²⁴⁾) that N_g increases when measurements are performed under vacuum. It is thought that the oxygen diradical forms a complex with the organic free radical⁽²⁷⁾ causing an apparent decrease in the spin-count.

Dack *et al*⁽²⁷⁾ have carried out a comprehensive study of the free-radical involvement in the drying and oxidation of brown coal. They found that drying the coal prior to vacuum sealing also produces an increase in the spin-count. Drying of the samples at 373K to 423K is a common pretreatment for EPR studies^(13,21,24). The effect of drying was tested on a New Zealand lignite. A sample of Mataura lignite was dried at 383K for 20 hours. The N_g -value increased from 3.5×10^{17} spins g^{-1} to 2.2×10^{18} spins g^{-1} for the dried sample; ie by approximately the order of magnitude discrepancy between the results of this study and the published spin-counts for lignites. This increase can not be due to the removal of the water content alone as the ratio of the Q_g -factors compensates for the change in the dielectric loss due to water.

Dack *et al*⁽²⁷⁾ rationalised the formation of free-radicals upon heating by, for example, decarboxylation of carboxylic acids, which are abundant in low rank coals:

Dack *et al*⁽²⁷⁾ also studied the influence of air exposure on the free radical content. They found that, after an initial increase, the spin-

count decreased significantly over long periods of exposure. It should be emphasised that the Victorian brown coal samples had been obtained under nitrogen from unexposed bulk samples; ie had not been equilibrated in air prior to EPR study. The New Zealand coal samples were not "fresh" and had presumably stabilised in air prior to study, as both the EPR spin-counts (section 6.3.5) and the NMR relaxation parameters (following chapter) were found to be relatively stable over time. (The EPR measurements were performed immediately prior to, and interspersed with the NMR relaxation experiments, to minimise the effects of sample alteration.)

One of the consequences of the low spin-counts is an apparently high number of carbon atoms for each unpaired spin (Table 6.2). For example, Retcofsky *et al*⁽¹³⁾ found one spin per 23,000 carbon atoms, for a peat sample, and one spin per 2,000-3,000 carbon atoms for bituminous coals. Dack *et al*⁽²⁸⁾ measured an average of one free-radical site per 7,000 carbon atoms for the brown coals.

An extension can be made to this estimation by including the apparent aromaticity, f_a' , measured by NMR. The number of aromatic rings associated with each free radical can be calculated (Table 6.2). The ratio exhibits a broad exponential relationship with carbon content (Figure 6.15). This trend is consistent with the heteroatom free radical concept for lower rank coals as a large amount of the oxygen at this rank is in the form of methoxyl and hydroxyl groups, substituted onto aromatic rings. The unpaired electron is only partially localised onto the heteroatom and is therefore associated with an aromatic ring.

6.4.2.4 Relaxation Constants

i. Saturation Behaviour

The saturation behaviour of the free radical signal is typified by the spectra of the Huntly East subbituminous coal, shown in Figure 6.16. The variable saturation behaviour observed for brown⁽¹²⁾ and bituminous^(28,29) coals (under vacuum), assigned to the presence of more than one type of free radical, was not observed in this study.

The variation in signal height with increasing power levels is shown in Figure 6.17 for the Huntly East coal and also for the Liddell bituminous coal. The latter curve exhibits the problem mentioned

TABLE 6.2

Coal	$N_g \times 10^{-18}$ (spin g ⁻¹)	1 spin/X carbon atoms*	f_a'	1 spin/X aromatic rings*
Mataura	0.35	98,000	0.63	10,000
Waimumu	0.18	190,000	0.65	21,000
Roxburgh I	0.57	62,000	0.52	5,300
Roxburgh II	0.15	220,000	0.58	22,000
Roxburgh III	0.47	72,00	0.54	6,400
Kopuku	1.5	24,000	0.61	2,500
Weavers	2.7	14,000	0.66	9,000
Huntly East	4.1	9,200	0.66	1,000
Ohai	4.4	8,600	0.69	990
Strongman	4.7	8,500	0.67	950
Topline	4.9	-	0.66	-
Charming Creek	4.0	9,900	0.68	1,100
Webb	4.9	8,600	0.69	990
Liddell	5.0	8,200	0.68	930
Bulli	12	3,600	0.77	470
Yarrabee	14	3,100	0.86	450
Fox River	18	2,500	0.83	350

* To two significant figures

Figure 6.15: The number of aromatic rings per free radical plotted against carbon content.

Figure 6.16: Free radical signals for the Huntly East coal obtained at different power levels (a) 5 mW, b) 100 mW, c) 180 mW (AG = 50)

Figure 6.17: Saturation curves for the free radical signal of the Huntly East (●) and Liddell coals (■).

earlier; ie that the maximum power level available did not saturate the free-radical signal. No evidence of saturation behaviour was observed in the spectra of the Fox River semianthracite or two of the Australian coals; Bulli (mnb) and Yarrabee (sa). Smidt and Van Krevelen⁽²⁶⁾ also observed that "no saturation, and hence no T_1 , could be measured" for anthracites. This is thought to be caused by the increased electrical conductivity associated with high rank coals. The lack of saturation behaviour for three coals of rank lower than anthracite may be due to the presence of oxygen. Published saturation studies were performed on samples under vacuum^(21,28,30) or in a nitrogen atmosphere^(12,29).

ii. The T-values

The estimated relaxation constants are given in Table 6.3, and plotted against carbon content in Figure 6.18. The curve observed for spin-spin relaxation constant T_{2e} resembles that of Figure 6.12a because T_{2e} is obtained directly from the line-widths.

The magnitudes of the T_{2e} values are similar to those measured, using the same method, for Japanese vitrains⁽²¹⁾ and Polish coals⁽³¹⁾. It has been stated that "these estimates of coal spin-spin relaxation times T_2 are purely operational measures of overall line-width and do not allow for unresolved superpositions of narrow lines"⁽²⁹⁾. Spin-echo decay experiments⁽²⁹⁾ have shown that the free-radical resonance of coal is comprised of unresolved hyperfine multiplets with $T_{2e} = 1.3 \times 10^{-6}$ s (90-110K); ie two orders of magnitude larger than the standard values. Simulation of the power saturation curves of oil shales⁽³¹⁾ has also resulted in longer T_{2e} values than previously measured.

If the T_{2e} values estimated from the line-widths are "erroneously short"⁽³¹⁾, then the values of T_{1e} will be systematically large. However, for comparative purposes, the T_{1e} values are of interest.

Figure 6.18(b) shows that the T_{1e} values increase with increasing rank. Once again, the T_{1e} values are of similar magnitude to those of the Japanese vitrains⁽²¹⁾ and the Polish coals⁽³⁰⁾ (although the values of the latter decreased with increasing carbon content). As

Figure 6.18: Electronic relaxation constants plotted against carbon content. a) Spin-spin relaxation constants and b) spin-lattice relaxation constants.

TABLE 6.3

Coal	ΔH_{pp} (mT)	$B_{max} \times 10^6$ (T)	$T_{2e} \times 10^8$ (s)	$T_{1e} \times 10^6$ (s)
Mataura	0.43	24	1.4	2.0
Waimumu	0.40	27	1.8	1.2
Roxburgh I	0.53	15	1.3	5.5
Roxburgh II	0.50	32	1.3	1.2
RoxburghIII	0.45	25	1.5	1.7
Kopuku	0.58	17	1.2	4.7
Weavers	0.65	16	1.1	6.0
Huntly East	0.65	18	1.0	5.0
Ohai	0.63	25	1.0	2.6
Strongman	0.63	14	1.1	7.5
Topline	0.73	12	0.9	12.5
Charming Creek	0.68	10	1.0	16.1
Webb	0.65	12	1.0	11.2
Liddell	0.53	(> 41)	1.3	(<0.7)
Bulli	0.35	-	1.9	-
Yarrabee	0.32	-	2.1	-
Fox River	0.45	-	1.5	-

predicted, the T_{1e} values are shorter than those estimated from T_{2e} values obtained by other methods. For example, Das *et al*⁽²⁹⁾ measured $T_{1e} = 225 \times 10^{-6}s$ for a Pittsburgh bituminous coal and Yokono *et al*⁽⁵⁾ found a T_{1e} of $61 \times 10^{-6}s$ for Yubarishinko coal (86%C).

The maximum in T_{1e} found by several workers, for coals of approximately 86%(21) to 90%(26) carbon, was not observed in this study. Saturation behaviour was only observed for coals containing < 85%C.

The scatter observed in Figure 6.18(b) may be due to the fact that the equations used to calculate the T_{1e} values are based on the assumption that the line-shape of the signal is Lorentzian. Therefore, the error in T_{1e} will vary according to the degree of deviation from the Lorentzian line-shape.

It has also been stated that "mineral constituents may reduce spin-lattice relaxation time independently of rank"⁽³²⁾. The Ohai, Strongman and Liddell coals were all found to have high contents of ferromagnetic material (Chapter 8), and all three exhibit low T_{1e} values, in comparison with other coals of the same rank.

Van Krevelen⁽³³⁾ proposed that the T_{1e} values were controlled by the accessibility of oxygen to the structure; ie the unpaired electron interacts with the orbitals of the atomic oxygen. Thus, the porosity of the coal would influence the T_{1e} values. Coal porosity reaches a minimum in the bituminous rank⁽³²⁾ and therefore corresponds to the T_{1e} maximum.

It has been reported that the electron spin-lattice relaxation times (T_{1e}) correlate with the proton spin-lattice relaxation times (T_{1H})⁽⁴⁾. In the following chapter, the characteristics of T_{1H} values of Australasian coals will be studied.

6.5 Summary

The EPR characteristics of Australasian coals measured in this study are not always in complete agreement with those published for other coals. Austen *et al*⁽³⁴⁾ suggested three possible explanations for the genesis and nature of free-radicals in coal:

1. Stable free radicals were formed during diagenesis of the organic sediment (probably by enzymatic action accompanied by aerial oxidation) and these have persisted;
2. Radicals were formed in pyrolytic reactions during metamorphosis as a result of homolytic splitting of certain functional groups; and
3. Radicals were produced by radiolysis.

Retcofsky *et al*⁽¹³⁾ have discussed the evidence behind each possibility. The second hypothesis is consistent with the increase in N_g with coal rank. In the metamorphic process few of the coals have been subjected to temperatures above 200°C (Chapter 10). The pyrolytic reactions must therefore have occurred under relatively mild conditions. This is consistent with i) the production of oxy-radicals in low rank coals and hence explains the higher g-values observed; ii) the progressive loss of oxygen and aliphatic functionalities to form stable aromatic-free radicals.

It is unlikely that the differences in free radical characteristics are due to differing coal origins as, although variations in actual structures may exist, the type of low temperature reactions involved in free-radical formation are likely to be the same.

It is considered more probable that the differences in experimental conditions (ie the exposure to air and no pre-drying) are responsible for the low spin counts, and lack of saturation behaviour in high rank coals. It must be emphasised that the EPR measurements were designed to be performed under identical conditions to those that exist during NMR measurements. In this way, the results of both magnetic resonance techniques should be directly comparable.

6. REFERENCES

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7.0 RELAXATION BEHAVIOUR

The origins and measurement of the relaxation parameters were discussed in Chapters 3 and 4 respectively. It is necessary to know the magnitude of the relaxation time constants, and whether these parameters alter with the degree of coalification, before quantitative NMR can be contemplated.

7.1 Proton T_1

The proton spin-lattice relaxation times, T_{1H} , were measured for the aromatic and aliphatic bands in the spectra of many low rank coals and all of the high rank coals. The T_{1H} values and standard deviations are tabulated in Appendix 4.1. The relaxation constants are plotted against the carbon content in Figure 7.1.

The aliphatic protons (solid symbols) have longer T_{1H} values than the aromatic protons (open symbols). (The average difference is 0.015s with a standard deviation of 0.017s.) This trend is contrary to the relaxation behaviour observed in most organic solids in which spin diffusion causes all of the protons to have the same T_{1H} value⁽¹⁾. Sullivan and Maciel⁽²⁾ also observed a longer T_{1H} for aliphatic protons than aromatic protons and rationalised this behaviour as evidence for a lack of "intimate spin contact" between separate aliphatic-rich and aromatic-rich domains.

The T_{1H} values are very low for the low rank Australasian coals, increase dramatically as the rank increases to high volatile bituminous and then decrease again for medium volatile bituminous and higher rank coals. This trend is consistent with the T_{1H} behaviour observed by Yokono and Sanada⁽³⁾ for Japanese coals, and also with the findings of Hirata and Akiyama⁽⁴⁾ that T_{1H} increases with the rank of coals with less than 80% carbon.

The magnitudes of the T_{1H} values for high volatile bituminous coals are more random than the smooth curves indicated by other workers^(3,4). Therefore, the rate of proton relaxation cannot be determined solely by rank. Several mechanisms must be involved, to varying degrees, in the transfer of polarisation from the spin to the lattice. The diffusion of excess proton polarisation through the sample is thought to occur by spin "flip-flops", until a suitable mechanism initiates rapid spin-lattice

Figure 7.1: Spin-lattice relaxation constants plotted against carbon content. Symbols as for Figure 5.16. Open and solid symbols represent T_{1H} values for aromatic and aliphatic protons, respectively.

relaxation. In general, any mechanism which gives rise to a fluctuating magnetic field at the nucleus is a potential relaxation mechanism. The most likely mechanisms that would create a fluctuating magnetic field are:

- i. motions of nuclear dipole moments on neighbouring molecules; eg rotating methyl groups or water molecules, or oscillating polymer chains etc,
- ii. interaction with paramagnetic species in the vicinity of the protons; eg free radicals, molecular oxygen or metal ions.

7.1.1 The Effect of Free Radicals

EPR has shown that large concentrations of free-radicals are present in the coal. The conclusion that free radicals are stabilised in the aromatic ring system would therefore explain the faster relaxation of aromatic protons. However, it is unlikely that the concentration of free-radicals is the determining factor for the magnitude of T_{1H} as it was found that the spin content of the Australasian coals studied increases uniformly (Figure 6.13) with increasing carbon content. Gerstein *et al*⁽⁵⁾ noted that spin-lattice relaxation times increased with increasing free-radical concentration which can be seen in Figure 7.2 at high spin concentrations.

Yokono and Sanada⁽³⁾ have indicated that the proton T_1 values correlated with the electron T_1 values for "various ranks of coal". T_{1e} values have been shown to alter in a similar manner as T_{1H} with increasing rank^(6,7). The data plotted in Figure 7.3 shows that the electron spin-lattice time may be a factor in determining proton relaxation. It is unfortunate that T_{1e} values could not be measured for the higher rank coals. It is impossible to assess whether a reduction in T_{1e} is responsible for the faster proton T_1 's of these ranks. Sullivan and Maciel⁽²⁾ have shown, by variable temperature experiments, that electron relaxation processes can not be the sole source of spin-lattice relaxation. T_{1e} should be relatively independent of temperature but T_{1H} was found to increase as the temperature was lowered.

Figure 7.2: T_{1H} values plotted against the spin counts on a logarithmic scale, for coals studied by EPR.

Figure 7.3: T_{1H} values plotted against the electronic T_1 values.

7.1.2 The Effect of Paramagnetic Ions

Free radicals are not the only form of unpaired spin present in coals. A significant proportion of the inorganic content of coals is in the form of metal ions (such as the paramagnetic Fe^{3+}) organically bound to exchangeable proton sites⁽⁸⁾. The effect of the addition of paramagnetic iron to "heterogeneous environmental matrices" (eg wood pulp and protein) has been studied by Pfeffer *et al*⁽⁹⁾. They found that the T_{1H} values of the hydrophilic components in particular, dropped dramatically when approximately 2% Fe^{3+} was added to the sample. Sullivan and Maciel⁽³⁾ noted a decrease in the T_{1H} of polystyrene doped with chromium III. Several workers^(10,11) using CP/MAS NMR to study large organic compounds, have exploited this phenomena by adding small amount of paramagnetic species to reduce the proton T_1 's and therefore the time scale of the experiment.

Reduction of proton T_1 's by paramagnetic iron is more likely to be a factor for the lower rank coals which contain high organic-oxygen and mineral matter contents. The difference between the aromatic and aliphatic T_{1H} values could be explained if the exchangeable sites are mainly oxygen functionalities substituted on aromatic rings which are isolated from the aliphatic protons.

The influence of the paramagnetic ions (either organically bound or in the mineral phase) on the spin lattice relaxation can be studied by reducing the inorganic content. The same seventeen coals that were studied by EPR (Chapter 6) were extracted with HCl. The iron contents were determined before (by XRF) and after (by AA) acid washing (the experimental details are given in Chapter 8). The spin counts were remeasured to assess whether changes in spin-lattice relaxation are produced by altered free-radical contents.

The results of this study are given in Appendix 4.2 and are summarised in Table 7.1. Acid-washing does not cause a consistent change in either the spin-counts or the T_{1H} values. In most cases the changes in T_{1H} are not greater than the sum of the standard deviations of the relaxation constants. The spin-lattice relaxation times are not dependent on the total iron content (Figure 7.4a). The percentage T_{1H} changes do not correlate with the amount of iron removed (Figure 7.4b).

The variable effect of acid-washing on the free-radical content of coal is also evident in the literature. For example, Dack *et al*⁽¹²⁾ found

TABLE 7.1

Coal	%Fe removed	$\Delta N_g \times 10^{-18}$ spins g^{-1}	ΔT_{1H} (s)		SD + SD (AW) ^a	
			Al	Ar	Al	Ar
Mataura	61	+0.02	-0.003	-0.002	0.008	0.009
Waimumu	63	+0.34	0.005	0.007	0.010	0.005
Roxburgh I	64	+0.10	0.017	0.008	0.006	0.004
Roxburgh II	-	+0.14	0.017	0.008		
Roxburgh III	44	-0.01	0.021	0.008	0.006	0.003
Kopuku	45	-0.6	-0.001	0.003	0.007	0.006
Weavers	43	-1.4	0.001	0.004	0.008	0.006
Huntly East	43	-2.4	-0.010	0.000	0.009	0.005
Ohai	64	-0.4	0.004	0.004	0.006	0.005
Strongman	68	+1.7	0.028	0.018	0.014	0.009
Topline	13	+1.0	0.013	0.004	0.025	0.013
Charming Creek	43	+0.5	0.026	0.021	0.025	0.028
Webb	33	+0.4	0.011	-0.010	0.031	0.038
Liddell	83	+0.3	0.007	0.004	0.016	0.011
Bulli	88	+2.0	0.006	0.008	0.031	0.016
Yarrabee	58	-2.0	-0.035	-0.029	0.029	0.010
Fox River	72	-5.0	-0.034	-0.028	0.021	0.014

Δ = Change in parameter with acid-washing (before - after)

a = Sum of standard deviations of T_{1H} and $T_{1H}(AW)$

Figure 7.4: a) T_{1H} values plotted against the iron content of the coals.
 b) The change in the T_{1H} values after acid-washing plotted against the relative amount of iron removed by the treatment.

that the organic free-radical signal of Victorian brown coal was reduced in intensity, but Wachowska *et al* (13) noted that the "removal of mineral components results in a marked increase in the number of free radicals in brown coal".

A large proportion of the iron content is removed by acid-washing. Some of this iron may not have contributed to the spin-lattice relaxation; eg iron in a separate mineral phase. However, the fact that no significant change occurs in the relaxation rates, suggests that paramagnetic iron in coal plays no more than a minor role in determining the T_{1H} values. (In the following chapter, the influence of the paramagnetic content on other aspects of quantitative NMR will be assessed.)

7.1.3 The Effect of Moisture

The fast proton relaxation in low rank coals may be due to their intrinsically high water contents. Molecular motion of water molecules within the pore structure of the coals could, under certain conditions, provide a relaxation "sink" for proton polarisation. The effect of the moisture content on the T_{1H} value can be quantified by drying and D_2O exchange studies. Three experiments were designed to test the influence of water on T_{1H} . (Results are given in Appendix 4.3.)

i. Air drying at RT

Experimental - A large chunk of Mataura lignite, that had been stored under water since it was collected from the mine (R. H. Newman, 1983), was crushed to 200 μ and exposed to air at room temperature (RT) for six months. At the time of crushing, and at monthly intervals, 1.5g samples were removed, the moisture content of 1g measured and the T_{1H} values determined.

Results - The moisture contents and T_{1H} values are plotted against time in Figure 7.5. The moisture content appears to stabilise after an initial drop. The oscillation may reflect changes in the atmospheric moisture.

The T_{1H} values are very short and have a standard deviation of approximately 20%. This high value reflects the fact that the relaxation time is faster than the shortest delay time that can be inserted between pulse sequences (0.025s). The variation of the T_{1H} values with the

Figure 7.5: The influence of air-drying Mataura lignite at room temperature for six months on a) the moisture content and b) the T_{1H} values. The dotted line in a) represents the average value for the final six values. The error bars in b) represent the standard deviations in the T_{1H} values.

Figure 7.6: Plot of the moisture contents and T_{1H} values from Figure 7.5. The vertical scale was split to separate the T_{1H} values for the aromatic and aliphatic protons.

moisture content is shown in Figure 7.6. There appears to be a slight decrease in the T_{1H} values with increasing moisture content. However, the overall changes are too small to be significant; ie less than the standard deviations of the relaxation constants.

ii. Oven drying

Experimental - Samples of Waimumu Newvale lignite (NZ 8) were dried in air at 383 K for varying lengths of time. The moisture contents were determined and the T_{1H} values measured. The sample with 0% moisture was then left to re-equilibrate at RT for 26 hours.

Results - The changes in T_{1H} values are shown in Figure 7.7. The loss of approximately two-thirds of the moisture (20% of coal weight) does not alter the relaxation rate. However, the removal of the remaining water content, particularly the last 5% (of coal weight), dramatically increases both the aliphatic and the aromatic T_{1H} values. The ratio of the T_{1H} values, at 0% and 29.7% water contents, is 2.9 for both aliphatic and aromatic protons; ie a three-fold increase.

The "dry" sample, that was exposed to air for 26 hours, absorbed only 0.5% moisture. The T_{1H} values had reduced slightly and are plotted in Figure 7.7 as square symbols.

iii. Exchange with D₂O

Experimental - A sample of the same Waimumu lignite was soaked in D₂O for 48 hours. The D₂O was changed twice during this period. The suspension was rapidly filtered and the exchanged coal was stored in an evacuated dessicator over P₂O₅. The D₂O content was estimated by weight loss on drying and the T_{1H} values were determined. The exchanged sample was then re-moistened with distilled water and the moisture content and T_{1H} values measured again.

Results - The exchanged sample contained 8.7% D₂O and exhibited T_{1H} values of 0.061 (SD = 0.005) and 0.020 (SD = 0.001) for the aliphatic and aromatic protons, respectively. The re-moistened sample contained 25% moisture and the measured T_{1H} values were 0.030 (SD = 0.004) and 0.012 (SD = 0.002) for the aliphatic and aromatic protons, respectively. These values are of the magnitude expected for the high moisture content although the presence of remaining D₂O may be lengthening the time constants slightly.

Figure 7.7: The effect of oven-drying on the T_{1H} values of Waimumu (I) lignite.

iv. Discussion

The results of these three brief experiments show that the moisture content of the low rank coals plays a significant part in the proton spin-lattice relaxation. The first two experiments indicate that not all of the water is involved. The important water content appears to be that which is most strongly linked with the coal structure.

The fact that both the aliphatic and aromatic proton T_1 's exhibit a three-fold increase upon drying negates the suggestion that water molecules, that are preferentially associated with the oxygenated-aromatic functionalities, are initiating the faster aromatic proton relaxation rates (unless there are remaining water molecules which are so closely linked with the aromatic functionalities that they are not removed by drying at 383K for 48 hours).

The short relaxation times of low rank coals appear to be caused by a small portion of their high moisture content. Therefore, an attempt was made to increase the moisture content of a high volatile A bituminous coal. A sample of Sullivan North coal (NZ 52) was soaked in distilled water for 26 hours. However, it was found that the high rank coal would not absorb moisture, ie would not "wet". The coal contained 0.7% moisture prior to moistening, but only 1.1% moisture after soaking.

The T_1 's for aliphatic and aromatic protons were:

%M	T_{1H} (s)	
	aliphatic	aromatic
0.7	0.327 (0.015)	0.348 (0.012)
1.1	0.345 (0.012)	0.352 (0.010)

Moistening of high rank coals, with long T_{1H} values, will not increase the relaxation rates.

The relaxation rates of the dried and D_2O exchanged lignite are still relatively fast, at approximately 0.06s. Therefore, other factors must be contributing to the relaxation mechanism.

7.1.4 The Influence of Coal Structure

Many models have been developed to represent the structure of coal⁽¹⁴⁾. The representative partial structures of Wender (Figure 2.19) demonstrate the type of structures that contribute to the polymer lattice of coals of different ranks. An appreciation of the macrostructure of the coals can be gained from these subunits. Hirsch⁽¹⁵⁾ developed a schematic picture of the packing of aromatic and aliphatic material in coal. An adaptation of his concept is shown in Figure 7.8.

Coals of lower ranks have an "open structure"^(15,16) within which the aromatic lamellae are randomly oriented and connected by many cross-links (Figure 7.8a). At higher ranks the number of linkages decreases as the aliphatic and heteroatom contents diminish and the aromaticity increases. The degree of alignment of the lamellae has also increased. "The pores gradually disappear, and the packing of the local parallel groups is essentially liquid type"⁽¹⁵⁾ (Figure 7.8b). The coal has an "anthracite" structure at very high ranks, which is tending towards being graphitic in nature. There are virtually no cross-links and the aromatic units are highly layered. Polyaromatic structures are common (Figure 7.8c).

The concept of a liquid-like structure for the bituminous coals is supported by the behaviour of many physical properties which exhibit maxima or minima at this rank. Minima occur in the magnitude of the coal density^(17,18,19), pore volume⁽²⁰⁾, porosity^(19,21) and surface area^(19,20). Maxima are found in coal reactivity properties such as plasticity^(21,22) and grindability^(17,20). Miyazawa *et al*⁽²³⁾ have correlated proton spin-lattice relaxation times of coals with the optical texture of the corresponding cokes.

The swelling number (SN) is the only physical property that has been measured for all of the bituminous coals. The plot in Figure 7.9 shows that there is a broad correlation between the proton T_1 and the SN. The SN provides only a preliminary measure of relative coking characteristics⁽²⁴⁾. Gieseler fluidity tests have been performed on four high swelling bituminous coals (NZ46 to 49). The data plotted in Figure 7.10 indicate that the two order of magnitude change in plasticity (as measured by the maximum fluidity) does not influence the T_{1H} value.

The main difference between the plasticity tests and the SN measurement is the rate of heating. Fluidity tests involve heating the

Figure 7.8: An adaptation of the Hirsch⁽¹⁵⁾ model of the physical structure of coals of increasing ranks. a) "Open structure", b) "liquid structure", c) "anthracite structure".

Figure 7.9: Plot of the T_{1H} values against the swelling number (SN). Lignites, subbituminous and very high rank coals have SN = 0. Therefore, the average T_{1H} values for these ranks were plotted.

Figure 7.10: T_{1H} values for four high volatile A bituminous coals that exhibit variable maximum fluidities.

coal slowly at a constant rate and are thought to be a measurement of the micellar and lamellar mobility⁽²⁵⁾. The measurement of the SN, however, involves the very rapid heating of the coal and depends on the "rate of degasification"⁽²²⁾. The SN is highest when the volatile matter can not escape quickly but swells the coal to form a large coke button.

The fact that the magnitude of T_{1H} exhibits a broad correlation with the SN, but not the fluidity, is significant. The mobility of the sub-units in the coal (ie fluidity) must be partly determined by the number of cross-links and how easily these linkages are broken. If spin diffusion is being inhibited by the small number of cross-links, then it would be expected that T_{1H} would exhibit a partial dependence on fluidity. The SN, on the other hand, is probably an inverse indication of the porosity of the coal; ie a low porosity would inhibit the release of volatile matter.

A low porosity would also limit the accessibility of oxygen to the coal structure. Molecular oxygen can initiate spin-lattice relaxation as it is a di-radical. The influence of oxygen could not be directly assessed in this study. However, it has been found that spin-lattice relaxation times increase when the sample is evacuated^(3,9).

The porosity of American coals has been studied by Gan *et al*⁽¹⁹⁾. Three types of pore volumes were defined; macropores (300-29600 Å), transitional pores (12-300 Å) and micropores (4-12 Å). The porosity of lower rank coals was primarily due to the presence of macropores. In the bituminous range, the transitional pores and micropores determine the porosity. T_{1H} values would be expected to increase with increasing microporosity as the micropores would inhibit the access of oxygen to the structure.

The macroporosity of the low rank coals may explain the fast relaxation even after intensive drying. Not only would the structure be easily accessible to oxygen, but the large pores would also provide space for the movement of flexible units, eg allow rotation of methyl groups and motion in alkyl chains⁽¹⁾.

Microporosity is dominant in higher rank coals. It would be expected therefore that these coals would have very long relaxation rates. This is not observed. The number of cross-links decreases as coalification proceeds, and the poly-aromatic units become increasingly rigid. The decreased mobility would also be expected to lengthen relaxation rates.

However, the concentration of free-radicals in these coals has greatly increased, which enhances the likelihood of spin diffusion occurring to a proton in the vicinity of a free radical.

7.1.5 Summary of T_{1H} Behaviour

It is evident from the previous discussion that "spin-lattice relaxation ... is sensitive to chemical and physical properties of coal"(26).

The fact that the aromatic protons exhibit consistently faster spin-lattice relaxation than the aliphatic protons (despite various treatments) is in agreement with the conclusions of Sullivan and Maciel(2); ie that this difference is a result of intrinsic aromatic-rich and aliphatic-rich regions within the coal structure. For example, derivatives of the original plant fragments, such as the aromatic lignin and tannin structures, and the aliphatic lipid material, may persist during coalification as distinct entities. The semi-isolation of these macroscopic particles would cause the breakdown of spin-diffusion.

The contributing influences, which determine the magnitudes of the T_{1H} values for particular coal ranks, can be distinguished.

The spin-lattice relaxation is fast for low rank coals because of the high degree of functional group mobility allowed by the "open structure". The short proton T_1 's are enhanced by the presence of strongly held water molecules within the coal structure and the presence of molecular oxygen in the macropores.

The functional group mobility and the moisture content have decreased in the bituminous rank of coals. The proton T_1 's appear to be strongly influenced by the porosity of the "liquid structure". A low porosity results in a low accessibility of molecular oxygen to the structure. The increase in T_{1H} values may also be associated with changes in the types of functional groups present; ie changes in the modes of molecular motion. Therefore, spin-lattice relaxation can be an order of magnitude slower than that observed in low rank coals.

The rate of spin-lattice relaxation increases in higher rank bituminous coals and semianthracites despite the rigid structure(27) and low porosity. The short proton T_1 's are assumed to be due to the presence of large concentrations of free-radicals and efficient spin diffusion.

7.2 Other Relaxation Time Constants

The remaining time constants, the cross-polarisation time, T_{CH} and the proton and carbon spin-lattice relaxation constants in the rotating frame, $T_{1\rho H}$ and $T_{1\rho C}$, were measured for nineteen samples that span the rank range of the Australasian coals. The time constant data are tabulated in Appendix 4.4.

7.2.1 T_{CH}

The cross-polarisation rates were fast (<0.4 ms), in general. It was not possible to measure T_{CH} values accurately for all of the signals present in the coal spectra.

The T_{CH} values of the main aliphatic and aromatic signals are plotted against carbon content in Figure 7.11. The T_{CH} values of the aromatic signals are consistently larger than those measured for the aliphatic signals. This difference is greater for the low rank coals than for the high rank coals; ie the cross-polarisation rate of the aromatic carbons increases with increasing coal rank. The T_{CH} values of the aliphatic carbons also decrease with increasing rank but the change is not as marked as that of the aromatic carbons. Longer T_{CH} values for aromatic carbons than for aliphatic carbons have been observed for coals^(3,28-31), model compounds⁽³²⁾ and wood⁽³³⁾.

The rate of cross-polarisation is determined by a number of factors⁽³²⁾. The T_{CH} values are principally dependent on the sixth power of the 1H to ^{13}C internuclear distances^(32, 34). For example, "cross-polarisation in $-CH_2$ should be twice as effective as in $-CH$, all other factors being equal"⁽³²⁾. Motion within the lattice also influences T_{CH} values. The cross-polarisation rates are longer for more mobile carbons as "molecular motion attenuates the $^{13}C-^1H$ and $^1H-^1H$ dipolar interactions"⁽³²⁾. T_{CH} values also increase with faster spinning rates⁽³²⁾ (particularly rates greater than 3kHz). However, the T_{CH} values are directly comparable in this study, as the samples were rotated at approximately the same rate (2.5kHz).

The faster cross-polarisation rates of the aliphatic carbon reflects the higher degree of protonation. The decrease in T_{CH} values with increasing carbon content is probably the result of the increasing rigidity of the coal lattice at higher ranks. The decrease in the T_{CH} values of

Figure 7.11: T_{CH} values for aromatic (open) and aliphatic (solid) carbons plotted against carbon content.

aromatic carbons can be partly attributed to the increasing concentration of aromatic carbons bonded to hydrogen (see Chapter 10); ie the degree of oxygen substitution of the aromatic rings is decreasing rapidly. The fact that the magnitudes of the two T_{CH} values are similar for high rank coals is the result of the increasing influence of the aromatic SSB signal on the aliphatic band.

7.2.2 $T_{1\rho H}$

The $T_{1\rho H}$ values for the main aliphatic and aromatic signals are plotted against carbon content in Figure 7.12. $T_{1\rho H}$ values were also measured for the methoxyl signal in the five lignite spectra (56 ppm), and the methyl signal (15 ppm) and aromatic C-O signal (lignites-148 ppm, other coals 154 ppm) in spectra of fifteen coals. All of the $T_{1\rho H}$ values fall into a narrow range of values (1.6 to 4.0 ms) and were relatively constant with increasing rank. A trend was observed in the magnitudes of the relaxation rates for particular carbon types and is summarised below:

<u>Carbon Type</u>	<u>Signal (ppm)</u>	<u>$T_{1\rho H}$ (ms)</u>	<u>SD (ms)</u>
-CH ₃	15	2.2	0.3
-CH ₂	30	2.4	0.3
-OCH ₃	56	2.7	0.3
Aromatic C-H	128	2.9	0.4
Aromatic C-O	154(148)	3.2	0.4

The longer relaxation rates observed for aromatic protons than for aliphatic protons has been noted by some^(30,32,35) but not all^(3,29) workers. The efficiency of spin-diffusion in the rotating frame must also be hindered by the presence of aromatic-rich and aliphatic-rich domains as "the ideal solid should have a uniform $T_{1\rho H}$ throughout"⁽³²⁾. The relative magnitudes of the relaxation rates of the aliphatic functional groups are consistent with the sensitivity of $T_{1\rho H}$ to molecular motion⁽³²⁾.

The $T_{1\rho H}$ values for coals published in the literature exhibit a large range of magnitudes. Measurements performed on instruments operating at ¹³C fields of 15.1 MHz^(28,35) resulted in $T_{1\rho H}$ values in the range 3.8 to 5.6 ms. Results from experiments performed at ¹³C fields of 22.6 MHz gave varied ranges of $T_{1\rho H}$ values; from 0.15 to 4.0 ms⁽³⁴⁾ to 1.9 to 5.5 ms⁽³⁰⁾. These relaxation experiments were performed on a variety of coals of different rank. However, it is more likely that this great diversity in $T_{1\rho H}$ values is a result of the variation in spin-locking field strengths used by the different workers⁽³²⁾.

$T_{1\rho H}$ values have been found to be inversely dependent on the paramagnetic ion content; eg iron⁽⁸⁾ and copper⁽³⁶⁾. Therefore, $T_{1\rho H}$

Figure 7.12: $T_{1\rho H}$ values for the polymethylene signal at 30 ppm (solid) and the main aromatic signal at 128 ppm (open) plotted against carbon content.

values were also measured for the seventeen acid-washed samples. The results are summarised in Table 7.2. Acid-washing does not consistently affect the magnitudes of $T_{1\rho H}$ for all coal ranks. However, the relaxation rates of the protons in lignites do show a consistent increase. The $T_{1\rho H}$ values for both types of aromatic carbon increase on average by 0.8 ms (SD = 0.4ms). The $T_{1\rho H}$ value for the methylene signal increases by 0.4 ms (SD = 0.1 ms). The methyl and methoxyl $T_{1\rho H}$ values are not consistently altered but show an average increase of 0.5 ms (SD = 0.6 ms). If the paramagnetic iron is associated with the large fraction of oxygen substituted aromatic functionalities present in the lignite, then the acid-washing treatment would be expected to preferentially lengthen the aromatic relaxation rate. The observed changes represent an approximately 25% decrease in the relaxation rates of aromatic protons in comparison with an average 19% decrease in aliphatic proton relaxation rates. However, this difference is not significant when the measurement error (~5%) is taken into account.

The data in Table 7.2 shows that the increase in $T_{1\rho H}$ values is not substantial and is not uniform for all coal ranks. Acid-washing is not an effective sample pre-treatment in this regard.

7.2.3 $T_{1\rho C}$

The magnetisation decay in spin-locking experiments was found to be non-exponential (Figure 7.13). Therefore, the reported $T_{1\rho C}$ values are average time constants which are weighted towards the initial part of the slope^(1,37). The causes of $T_{1\rho C}$ behaviour have been studied in detail by Schaefer *et al*⁽³⁸⁾. The relaxation rates are not averaged as there is little spin-spin contribution to $T_{1\rho C}$ (ie spin-diffusion). The "observed $T_{1\rho}$ is a sum of relaxation rates, producing a non linear appearance to a standard semilog plot"⁽³⁹⁾. It is thought that the initial slope represents a $T_{1\rho C}$ dominated by spin-lattice processes while the final slope reflects a $T_{1\rho C}$ determined by spin-spin processes⁽³⁹⁾. However, the relative $T_{1\rho C}$ data can be compared as long as similar parts of the relaxation curves are studied⁽³⁹⁾.

The absence of spin-diffusion also results in different magnitudes of $T_{1\rho C}$ values for different carbon types. The relaxation times were consistently found to be in the order:

TABLE 7.2

Coal	%Fe removed	$\Delta T_{1\rho H}$ (ms)			Ar C-H	Ar C-0
		-CH ₃	-CH ₂ -	-OCH ₃		
Mataura	61	0.8	0.4	1.2	1.2	1.6
Waimumu	63	-0.5	0.3	-0.2	0.1	0.5
Roxburgh I	64	1.0	0.4	0.8	1.0	0.8
Roxburgh II	-	0.7	0.5	-0.3	0.9	0.4
Roxburgh III	44	0.2	0.5	0.9	1.0	0.7
Kopuku	45	0.2	0.5	-	0.4	0.7
Weavers	43	-0.3	-0.1	-	-0.1	0.2
Huntly East	43	0.7	0.1	-	0.5	0.1
Ohai	64	0.6	-0.5	-	-0.9	-1.0
Strongman	68	0.1	-0.2	-	-0.3	-0.7
Topline	13	-0.1	-0.8	-	-0.4	-0.4
Charming Creek	43	0.0	0.0	-	-0.2	0.0
Webb	33	-0.9	-0.2	-	-1.0	-1.0
Liddell	83	-	-0.7	-	-0.8	-
Bulli	88	-	0.5	-	0.2	-
Yarrabee	58	-	1.2	-	0.4	-
Fox River	72	-	0.4	-	0.4	-

Δ = Change upon acid-washing (after -before)

Figure 7.13: Plot showing non-exponential decay of signal intensity. Signals as for 7.12.

which is consistent with $T_{1\rho C}$ behaviour observed by other workers(28,35,40). The trend in $T_{1\rho C}$ values follows the pattern expected⁽¹⁾ for relaxation arising from "the effect of molecular motion within the lattice on internuclear dipolar interactions"(38).

The $T_{1\rho C}$ values for the main aliphatic and aromatic signals are plotted against carbon content in Figure 7.14. The tendency of the $T_{1\rho C}$ values to merge towards a common value at higher carbon contents reflects the influence of the aromatic SSB on the aliphatic envelope. Wilson *et al*⁽⁴⁰⁾ noted that the aromatic signal of a Loy Yang brown coal decayed more slowly than that of a Liddell bituminous coal. However, they also observed a similar behaviour for the aliphatic signals which is contrary to the trend shown in Figure 7.14.

7.3 Summary

The results of this relaxation study serve two purposes:

- i. They provide an insight into the important properties of coal that are controlling this facet of their NMR behaviour.
- ii. They indicate the magnitude of the instrumental settings necessary for quantitative NMR of coals.

The best signal-to-noise ratio (S/N) is obtained using a delay of approximately $1.2 T_{1H}$ between pulse sequences⁽²⁾. However, it is necessary to leave a delay of five times the longest measured T_{1H} value, to obtain signals that are representative of the relative amounts of carbon in the sample⁽²⁾. The relatively small proton T_1 values, measured for the low rank coals, means that a short delay (eg 0.15 s) can be used. The proton T_1 must be measured for individual samples for coals of rank higher than subbituminous, and the delay set accordingly.

The requirement that T_{CH} be significantly smaller than both $T_{1\rho H}$ and $T_{1\rho C}$ was found to hold for coals of all ranks. A standard contact time of 1 ms was chosen as appropriate, in that it fulfils the condition:

$$T_{CH} < \text{contact time} \ll T_{1\rho H}, T_{1\rho C}$$

ie, to allow for maximum cross-polarisation of all carbons before significant deterioration of the intensity occurs via $T_{1\rho H}$ and $T_{1\rho C}$ processes. The selection of a 1 ms contact period has been made by many workers studying coal by CP/MAS NMR(41-44).

Figure 7.14: Plot of the $T_{1\rho C}$ values against carbon content.

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8.0 NMR VISIBILITY

8.1 Introduction

"The fundamental pre-requisite for quantitative applications ... demands that the measurement of C_t does in fact reflect the unit intensity response from all carbons in coal"(1).

The possibility that the NMR technique is not "seeing" all of the carbon has been subject to great debate⁽¹⁻⁴⁾. Attempts to evaluate the "NMR visibility" have resulted in estimates ranging from 36%(2) to 100%(3) response. It is also not clear whether the signal obscured from NMR represents the broad range of carbon functionalities or whether one particular type of carbon is invisible to the technique.

It was observed that the signal-to-noise ratios (S/N) of the spectra of Australasian coals were not proportional to the amount of carbon in the sample. Evidence was also found for detuning of the coil by the coal sample. This detuning effect has also been observed by other workers^(2,4). The characteristics of coal that are detrimental to the NMR response must be evaluated. It has been suggested that the magnetic properties (eg the paramagnetic content⁽⁴⁾) of the samples are the cause of variable response. An "NMR visibility" study was therefore designed with the following aims:

- i. To quantify the magnetic properties of the samples by a magnetic susceptibility study.
- ii. To quantify the response of the carbon content by the use of a signal amplitude standard.
- iii. To assess possible pre-treatments that might improve the NMR response of the carbon content of coal.

8.2 Experimental

8.2.1 Magnetic Susceptibility

The magnetic susceptibility is defined as the ratio of the intensity of magnetisation, I , to the magnetic field strength, H ⁽⁵⁾. The mass susceptibility, χ , is defined as:

$$\chi = I/dH \quad [8.1]$$

where d is the density. The magnetic susceptibility data will be reported here in terms of the cgs-emu (Gaussian) conventions^(6,7) for ease of comparison with published magnetic susceptibility studies.

Diamagnetic substances have a slightly negative magnetic susceptibility ($\chi_d \sim -10^{-6} \text{ emu g}^{-1}$) which is independent of temperature (T)

and field strength (H). Paramagnetic substances exhibit a positive susceptibility ($X_p \sim 10^{-6}$ to 10^{-3} emu g⁻¹) which is proportional to T^{-1} but is also independent of H. The susceptibility of ferromagnetic substances is dependent on T^{-1} and H^{-1} .

The magnetic susceptibility can be divided into three contributions by the Honda-Owen equation⁽⁸⁾:

$$X = X_p + X_d + (\sigma / H) \quad [8.2]$$

where σ is the ferromagnetic saturation magnetisation. In practice, the sum of the diamagnetic and paramagnetic susceptibilities, X_0 , is obtained from:

$$X = X_0 + (\sigma / H) \quad [8.3]$$

ie, X_0 is the intercept of the plot of observed susceptibility against the inverse of the field strength (Figure 8.1). The magnitude of the ferromagnetic content is estimated from the slope of the plot.

8.2.1.1 Measurement of X and σ

Magnetic susceptibilities of the coal samples were measured on a Faraday balance. A microbalance was used to measure the apparent increase in weight due to the applied magnetic field. The interaction of the applied magnetic field with the mechanism of the microbalance caused the weight readings to show a small linear dependence on the field strength. All weight readings were corrected for this systematic error.

The susceptibility is obtained from the weight readings (W) using the expression:

$$KX = \frac{\Delta W}{W} = \frac{\text{apparent change in mass with magnetic field}}{\text{mass of substance}} \quad [8.4]$$

K is the constant for the apparatus which was determined by studying standards of known susceptibility. The main compound used as a standard was Hg[Co(CNS)₄] which has a susceptibility of 16.44×10^{-6} emu g⁻¹. Three other standards were also studied to check the calibration of the instrument; Ni(en)₃ S₂O₃ ($X = 0.109 \times 10^{-8}$ emu g⁻¹), Analar Al ($X = 16.5 \times 10^{-6}$ emu g⁻¹) and, D-glucose ($X = -0.563 \times 10^{-6}$ emu g⁻¹)⁽⁹⁾.

Repeated magnetic susceptibility measurements on small samples (<100mg) of one coal often produced variable X_0 and σ -values ($\pm 50\%$). This result suggested that the magnetic material was not uniformly distributed throughout the samples. The X_0 values of the acid-washed coals varied by a smaller amount ($\pm 15\%$).

Figure 8.1: Dependence of the magnetic susceptibility on the magnetic field strength.

8.2.2 Chemical Treatments

8.2.2.1 Treatment with Acid

Concentrated HCl was used for the acid-washing treatment following the recommendations of Schaefer⁽¹⁰⁾. The acid treatment was performed on 1g of coal. Where larger or smaller samples were acid-washed, the following quantities were scaled appropriately.

1g of coal was soaked in 10ml of 6M HCl at room temperature (RT) for five days. The acid-treated coal was washed with distilled water and air-dried (room temperature) over silica gel for several days. The acid-wash solution was diluted to three strengths for atomic absorption (AA) analysis.

Acid-washing experiments were also performed for various lengths of time. In this case, eleven samples (0.5g) of the same coal were soaked in 5ml of acid. The coal samples were removed from the solution after various time periods had elapsed.

8.2.2.2 Iron Exchange

The iron-exchange procedure used in this study is that developed for coal by Schaefer⁽¹⁰⁾. 1g of acid-washed coal was soaked in 20ml of freshly prepared 0.05M ferrous sulphate solution for two days. The iron-exchanged coal was washed and dried in the same manner as the acid-washed coals.

8.2.3 Determination of Iron Contents

The iron contents of the coals were determined by X-ray fluorescence XRF (Soil Bureau, DSIR) when large amounts of sample were available. Iron contents of very small samples (eg ashes) were determined by Spark Emission Spectroscopy, SES (Chemistry Division, DSIR). The iron contents of the acid-wash solutions were determined by Atomic Absorption Spectroscopy (Analytical Facility, VUW).

8.2.4 Other Techniques

8.2.4.1 Infra-Red

The coal samples were oven-dried prior to infra-red (IR) study, to reduce the interference of moisture. Disks were prepared from 198 mg of KBr and 2mg of coal sample which had been thoroughly mixed in a miniature ball mill for two minutes.

Spectra were recorded on a Digilab Qualimatic FTIR instrument (courtesy of Bio-Rad Laboratories Pty Limited, Australia).

8.2.4.2 Moessbauer

Spectra of selected samples were recorded on Moessbauer instruments at Spectroscopy Section (DSIR), Chemistry Department (VUW) and Soil Bureau (DSIR).

8.3 Magnetic Susceptibility Study

"Most measurements of magnetic susceptibility of coals have been directed toward an understanding of their aromatic ring hydrocarbon structure through the diamagnetism"⁽¹¹⁾.

The first study of the magnetic properties of coal was reported by Wooster and Wooster⁽¹²⁾. It was observed that acid-treated coal was diamagnetic at RT, but that the magnitude of this diamagnetism was variable between samples. Honda and Ouchi⁽⁵⁾ also studied the diamagnetic susceptibility of acid-washed coals. Recent magnetic studies have concentrated on untreated coals (ie including "impurities") with a view to improving magnetic desulphurisation methods for the industrial use of coal^(8,11,14). Alexander et al⁽⁸⁾ found that most samples did not show a ferromagnetic component but that σ was large for particular samples.

8.3.1 Results

The dependence of the observed magnetic susceptibility on the field strength is shown in Figure 8.2, for three coals with varying ferromagnetic contents. The straight lines indicate that the ferromagnetic material is completely saturated by the applied field⁽¹⁴⁾. The slopes, σ , and intercepts, X_0 , were obtained for all of the selected coals and are given in Table 8.1.

Figure 8.2: Examples of the variable dependence of coal magnetic susceptibility on field strength. a) Roxburgh (II), b) Strongman, c) Ohai.

TABLE 8.1

Coal	No.	% C (daf)	Fe (ppm)	Magnetic Properties (emu g^{-1})	
				$\chi_o \times 10^6$	$\sigma \times 10^4$
Roxburgh I	NZ 3	69.9	4170	0.153	0.06
Roxburgh II	NZ 4	(67.1)	—	0.340	0.70
Roxburgh III	NZ 5	(67.1)	6300	0.625	0.41
Mataura	NZ 6	68.6	7130	1.037	0.73
Ashers Waituna	NZ 7	66.7	—	1.611	0.00
Waimumu I	NZ 8	68.4	5170	0.295	0.00
Waimumu II	NZ 9	68.9	—	0.439	0.00
Waimumu III	NZ 10	68.8	—	0.871	0.00
Waimumu IV	NZ 11	69.4	—	0.596	0.00
Kopuku	NZ 15	72.8	3300	0.028	0.52
Weavers	NZ 19	73.7	2570	-0.140	0.55
Huntly East	NZ 26	75.1	2110	-0.436	0.00
Ohai	NZ 30	75.2	9410	0.916	6.81
Mulken	NZ 31	(74.4)	—	-0.313	0.83
Island Block	NZ 34	74.7	—	0.323	0.68
Strongman	NZ 35	(80.0)	4410	0.212	1.18
Topline	NZ 37	—	5620	-0.328	0.83
Charming Creek	NZ 42	(79.2)	150	-0.511	0.56
Webb	NZ 45	84.0	2110	-0.561	1.10
Liddell	A 5	(82.0)	2760	0.420	70.74
Bulli	A 7	(87.1)	3630	0.126	2.53
Yarrabee	A 10	(87.8)	3450	0.242	0.69
Fox River	NZ 57	90.6	4740	-0.249	0.25

8.3.2 Discussion

The magnitudes of the magnetic parameters fall well within the range of values observed by Alexander *et al*⁽⁸⁾ for American coals. They measured a maximum magnetic susceptibility of $\chi_o = 10.6 \times 10^{-6} \text{ emu g}^{-1}$ for one sample and a maximum saturation of $\sigma = 312.1 \times 10^{-4} \text{ emu g}^{-1}$ for another coal. It is interesting to note that a ferromagnetic component is more common in the Australasian coals studied here than the American coals.

The magnetic parameters exhibit great variability with rank. For example, the magnetic susceptibility shows only a minor correlation ($R = -0.521$) with the carbon content (Figure 8.3). Alexander *et al*⁽⁸⁾ and Honda⁽¹⁵⁾ found that the paramagnetic susceptibility correlated inversely with the carbon content. The slight correlation shown in Figure 8.3 may therefore be caused by the paramagnetic component of χ_o .

The most negative susceptibility value ($\chi_o = -0.56 \times 10^{-6} \text{ emu g}^{-1}$) was observed for the Webb bituminous coal. This value is similar to the diamagnetic susceptibility of coal⁽⁷⁾ which arises from "free-radicals, unpaired electrons and broken bonds"⁽⁸⁾. High paramagnetic susceptibility values have been assigned to the presence of the mineral matter in coals⁽⁸⁾. However, no correlation was observed between the magnetic susceptibility data and the ash content of either the Australasian coals (Figure 8.4) or the American coals⁽⁸⁾. The data plotted in Figure 8.5 suggest that the magnitude of χ_o is partly dependent on the iron content, but the correlation is not good ($R = 0.752$).

The ferromagnetic saturation values exhibit no significant correlation with carbon content (Figure 8.6), ash content (Figure 8.7) or total iron content (Figure 8.8). There is a slight tendency for susceptibilities of higher rank coals to contain a ferromagnetic component. It can be seen that two samples exhibit anomalously high σ values. Alexander *et al*⁽⁸⁾ have studied similar "abnormal" samples and assigned the unusually high magnetisation constants to the presence of distinct ferromagnetic particles; eg fragments of magnetite.

In conclusion, the Australasian coals contain varying amounts of paramagnetic and ferromagnetic material; but the magnetic character of the coal is unpredictable.

Figure 8.3: Plot of the sum of the diamagnetic and paramagnetic susceptibilities against the carbon content. Symbols as for Figure 5.16.

Figure 8.4: Plot of the sum of susceptibilities against the ash content on a dry basis.

Figure 8.5: Plot of the sum of susceptibilities against the iron content of the coals.

Figure 8.6: Plot of the ferromagnetic saturation value against the carbon content.

Figure 8.7: Plot of the ferromagnetic saturation values against the ash content.

Figure 8.8: Plot of the ferromagnetic saturation values against the iron content.

8.4 Signal Amplitude Standard

The use of an internal signal amplitude standard to characterise the NMR visibility of coal has been attempted previously by Wenner, Pines and Whitehurst⁽³⁾. This method has the advantage that the signal intensities can be directly compared without reference to the total intensity. Any comparison of the absolute intensities of separate coal and model compound spectra relies on the assumption that the spectrometer conditions (eg probe tuning) do not alter.

8.4.1 The Selection of a Standard

A useful reference standard would have the following characteristics:

- i. The compound should be able to be easily mixed with the coal (eg be a powder of similar mesh size);
- ii. It should have a short proton T_1 so that a reasonable number of transients (eg $NT = 1000$) can be acquired in a short period;
- iii. It should have a relatively simple NMR spectrum containing signals that are easily distinguished from the signals of the coal spectrum;
- iv. It should have a high NMR "visibility".

Five materials were selected as being possible standards:

- i. ammonium tartrate (AT), "ANALAR" grade
- ii. syringic acid (SA)
- iii. Dopa (3-hydroxy-tyrosine)
- iv. Cellulose
- v. Klason lignin (Kauri)

The first three compounds are crystalline and readily blend with powdered coal. Finely ground Klason lignin is also suitable for mixing. Cellulose will not easily combine with coal, as it has a light "fluffy" texture.

The spectra of these five materials are shown above the spectrum of a lignite in Figure 8.9. The aromatic region of lignin spectrum is similar in features to that in the coal spectrum. The strong signals in the lignin spectrum (57 ppm, 148 ppm) overlap with signals in the coal spectrum. Therefore, the relative changes in signal strength, that will occur when the coal and lignin standard are mixed, cannot be readily assessed. The cellulose spectrum contains a strong signal at 74 ppm which lies between

Figure 8.9: Spectra of six model compounds in comparison with the spectrum of a lignite. Dotted lines define the chemical shift regions - 60 to 90 ppm, 165 to 195 ppm. a) AT, b) SA, c) Dopa, d) cellulose, e) Klason lignin, f) Waimumu (I) lignite.

the aromatic and aliphatic envelopes of the coal spectrum. The Dopa and SA spectra exhibit several strong peaks, but these tend to overlap with signals in the coal spectra. The Dopa and SA spectra are also complicated by the presence of many SSB signals. The spectrum of AT is the least complex with only two strong signals (75 ppm, 180 ppm) and very weak SSBs. Both signals are in convenient positions for monitoring the relative signal changes.

The proton relaxation constants are given in Table 8.2. A contact time of 1000 μ s was ample for cross-polarisation in all cases. The carbon contents of the lignin sample were estimated from the composition of conifer lignins published by Freudenberg and Neish⁽¹⁶⁾ ($C_9 H_{7.95} O_{2.40} (OCH_3)_{0.92}$) and by Haw *et al*⁽¹⁷⁾ ($C_9 H_{8.83} O_{2.37} (OCH_3)_{0.96}$).

It can be seen that AT exhibits the most suitable relaxation behaviour, ie the shortest T_{1H} and longest $T_{1\rho H}$.

The NMR visibility of SA, Dopa, cellulose and lignin were measured relative to AT. The visibility was determined in the following manner. The spectra of the compounds were divided into three areas which were defined so that the middle area (B) overlapped with a strong signal in the AT spectrum. Two conventions for dividing the spectrum were defined according to the diagram in Figure 8.10. The ratio of the middle area (B) to the total area ($T = A+B+C$) was estimated from the spectra of 0.3g of sample. The B/T value was then compared with the same ratio obtain from the spectrum of a 0.3g mixture composed of 50% compound and 50% AT.

The convention employed for dividing the spectra was dependent on the overlap of the signals with those of AT. The spectra in Figure 8.9 show that the AT signal at 75 ppm coincides with regions containing very little signal intensity in the spectra of SA and Dopa. Conversely, this AT signal overlaps with the very strong cellulose signal and with a band of considerable intensity in the lignin spectrum. The AT signal at 180 ppm coincides with an SSB in the lignin spectrum and with a very small second order SSB in the cellulose spectrum (not visible in Figure 8.9). Thus, convention (i) was used to divide the spectra of SA and Dopa, while convention (ii) was employed for division of the lignin and cellulose spectra.

TABLE 8.2 : RELAXATION CONSTANTS FOR MODEL COMPOUNDS

	% C	% M	ppm ^a	T _{1H} (s)	T _{1ρH} (ms)
AT	26.1	-	75 180	0.122 (0.002) ^b 0.113 (0.003)	19.3 (0.6) 18.4 (0.7)
SA	54.5	-	59	1.28 (0.02)	13.4 (0.6)
Dopa	54.8	-	144	1.03 (0.04)	11.8 (0.2)
Cellulose	44.5	7.8	74	1.12 (0.08)	4.2 (0.7)
Lignin	69.2 ^c 64.8 ^d	23.9	56 148	0.38 (0.03)	4.8 (0.3) 7.7 (0.6)

(a) Position of signal for which T measured

(b) Standard deviation

(c) Lignin composition - Freudenberg⁽¹⁷⁾

(d) Lignin composition - Maciel⁽¹⁸⁾

TABLE 8.3 : VISIBILITY DATA FOR MODEL COMPOUNDS

	a	I _i	F _{mix}	K ^C	K ^T	V
AT	i ii	0.374 0.276	- -	- -	- -	- -
SA	i	0.053	0.188	1.408	2.089	67.4
Dopa	i	0.140	0.245	1.410	2.100	67.1
Cellulose	ii	0.018	0.148	1.185	1.706	69.5
Lignin	ii	0.086	0.179	1.207	1.954 ^b	61.8

(a) Convention used (Figure 8.10)

(b) Using average of lignin compositions

Figure 8.10: Definition of conventions for dividing spectra of mixtures of AT (reference) and sample of interest.

The fraction, F , defined as

$$F = B/T \quad [8.5]$$

was determined for all of the spectra. The ratio of the observed carbon in the sample relative to observed carbon for AT is given by:

$$K^E = (F_{AT} - F_{MIX}) / (F_{MIX} - F_i) \quad [8.6]$$

where F_{AT} and F_i are the fraction for AT and the second sample, respectively, and F_{MIX} is the fraction observed for the 50:50 mixture.

The K -values are then corrected for loss of signal area due to $T_{1\rho H}$ effects. The $T_{1\rho H}$ values listed in Table 8.2 were used to calculate the lost signal area relative to AT. Where more than one $T_{1\rho H}$ value was measured, the weighted average was used in the estimation. The corrected K -values are labelled K^C .

The theoretical ratio, K^T , defined as:

$$K^T = \% C_i / \% C_{AT} \quad [8.7]$$

was calculated from the carbon contents listed in Table 8.2. The moisture (Table 8.2) contents of the cellulose and lignin samples were taken into account when estimating $\%C_i$. The NMR visibility " V ", expressed as a percentage relative to AT, is given by:

$$V = (K^C / K^T) * 100 \quad [8.8]$$

The results of these visibility estimations are given in Table 8.3. The V -values show that the NMR visibility of AT appears to be considerably greater than that of the other possible standards. The results of a detailed study into the NMR response of many organic compounds⁽¹⁸⁾ showed that there are other model compounds (eg ammonium oxalate, ammonium carbonate) that exhibit significantly higher NMR visibilities than AT. However, AT is readily available in analytical purity and was found to be the most suitable reference material of the five compounds studied. AT was therefore selected as the signal amplitude standard for the coal visibility study.

8.4.2 Coal Visibility

The NMR visibilities of all lignites and selected higher rank coals were studied in comparison with AT as an external and internal standard.

8.4.2.1 External Standard

The spectrum of 0.3g of oven-dried coal was compared with the spectrum of 0.3g of AT obtained under identical spectrometer conditions. A visibility value V^* was defined as the ratio of the total signal area measured for the coal relative to the signal area of the AT spectrum. The "*" indicates the use of an external standard. The signal areas were corrected for the relative carbon contents. The V^* -values were not corrected for $T_1\rho_H$ effects as the relaxation constants of the signal areas were not determined. Therefore, the V^* -values will be slightly lower than the actual visibilities. However, a comparison of the relative V^* -values is valid as the $T_1\rho_H$ values do not vary greatly with increasing rank (Chapter 7). The coal samples were oven-dried prior to weighing and the carbon contents were corrected for the ash content of the coals.

The V^* -values are listed in Table 8.4 and are plotted against the carbon content in Figure 8.11. The NMR visibilities are very low in comparison with AT. There is a tendency towards lower visibility at higher rank, although the wide range of V^* -values obtained for the lignites (15% to 32%) obscures this trend.

The V^* -values are plotted against the two magnetic susceptibility parameters in Figures 8.12 and 8.13. The variable visibility is not related to variations in either the paramagnetic (χ_o) or the ferromagnetic (σ) susceptibility values. However, the data shown in Figure 8.13 indicate that a high ferromagnetic content in the coal may cause a low NMR visibility.

8.4.2.2 Internal Standard

The measurement of visibility data using AT as an internal standard was described in section 8.4.1. The data for the coals were obtained using convention (i) of Figure 8.10 for the division of spectra and are listed in Table 8.5. These V -values were also not corrected for $T_1\rho_H$ effects.

The V -values are plotted against the carbon contents in Figure 8.14. The V -values show the tendency to decrease for higher ranks. The V -values

TABLE 8.4 : VISIBILITY DATA FOR COALS - EXTERNAL STANDARD

COAL	% A (d)	% C (d)	W*	V* (%)
Hawkdun	14.6	58.1	0.0789 ^a	21.0
Idaburn	10.2	61.2	0.0938	22.3
Roxburgh I	10.3	62.7	0.1367	31.8
Roxburgh II	9.9	60.5	0.1301	31.3
Roxburgh III	8.9	61.1	0.1139	27.2
Mataura	7.0	63.8	0.0874	20.0
Ashers Waituna	6.1	62.6	0.0670	15.6
Waimumu I	4.6	65.3	0.1244	27.8
Waimumu II	6.7	64.3	0.0869	19.7
Waimumu III	4.8	65.5	0.0863	19.2
Waimumu IV	6.0	65.2	0.0868	19.4
Kopuku	6.0	68.4	0.1477	31.5
Weavers	5.4	69.7	0.1151	24.1
Huntly East	2.1	73.5	0.1027	20.4
Ohai	10.9	67.0	0.0863	18.8
Strongman	6.3	75.0	0.0948	18.4
Topline	6.7	-	0.0828	-
Charming Creek	1.3	78.2	0.1012	18.9
Webb	1.7	82.6	0.1003	17.7
Liddell	7.7	75.7	0.0880	14.5
Bulli	7.7	80.4	0.0589	9.1
Yarrabee	5.5	83.0	0.0959	14.4
Fox River	3.0	87.9	0.1074	15.2
AT		26.1	0.1791	100.0

(a) Signal area - arbitrary units.

Figure 8.11: Plot of the coal visibility, derived using an external standard, against carbon content.

Figure 8.12: Plot of the visibility data, derived using an external standard, against the sum of the diamagnetic and paramagnetic susceptibilities.

Figure 8.13: Plot of the visibility data, derived using an external standard, against the ferromagnetic saturation parameter.

TABLE 8.5 : VISIBILITY DATA FOR COALS - INTERNAL STANDARD

COAL	Visibility Parameters					DF
	F_i	F_{mix}	K	K^T	V	
Hawkdun	0.076	0.238	0.580	2.23	26.1	0.826
Idaburn	0.117	0.247	0.643	2.35	27.0	0.811
Roxburgh I	0.102	0.249	0.565	2.40	23.5	0.776
Roxburgh II	0.102	0.258	0.474	2.32	20.5	0.885
Roxburgh III	0.119	0.239	0.775	2.34	33.1	0.782
Mataura	0.102	0.268	0.386	2.45	15.8	0.820
Ashers Waituna	0.123	0.295	0.215	2.40	9.0	0.798
Waimumu I	0.125	0.274	0.389	2.50	15.6	0.830
Waimumu II	0.132	0.271	0.439	2.46	17.8	0.845
Waimumu III	0.102	0.266	0.402	2.51	16.0	0.860
Waimumu IV	0.114	0.262	0.473	2.50	18.9	0.858
Kopuku	0.085	0.247	0.525	2.62	20.0	0.847
Weavers	0.090	0.241	0.603	2.67	22.6	0.906
Huntly East	0.097	0.239	0.655	2.82	23.3	0.847
Ohai	0.113	0.224	0.973	2.57	37.9	0.668
Strongman	0.096	0.252	0.513	2.87	17.9	0.784
Topline	0.097	0.270	0.358	-	-	0.874
Charming Creek	0.111	0.260	0.483	3.00	16.1	0.870
Webb	0.101	0.269	0.375	3.16	11.8	0.895
Liddell	0.111	0.196	1.6	2.90	55.2	0.401
Bulli	0.103	0.263	0.431	3.08	15.2	0.761
Yarrabee	0.133	0.259	0.579	3.18	16.7	0.884
Fox River	0.126	0.261	0.523	3.37	15.6	0.858

Figure 8.14: Plot of the coal visibility data, derived using an internal standard, against the carbon content. a) Southland lignites, b) Central Otago lignites.

obtained for the lignites vary from 9% to 38%, ie a wider range than that observed in the V^* -values. The large differences in visibilities observed for the lignites is of particular interest. The Central Otago lignites exhibit consistently higher V -values (average $V = 28.0\%$, $SD = 3.4\%$) than those of the Southland lignites (average $V = 15.5\%$, $SD = 3.1\%$).

The V -values are, in general, not significantly different from the V^* -values. The average difference between the two values was -2% with a standard deviation of 6% . It can be seen that there are two major exceptions to this generalisation. The V -values measured for the Ohai and Liddell samples are very high in comparison with the data obtained for the other coals.

A clue to the origin of this deviation can be gained from the data shown in Figures 8.15 and 8.16. The V -values show no correlation with the X_O values. However, the high ferromagnetic content of the Liddell and Ohai coals appears to be responsible for the high visibility values. This trend is in contrast to that observed in Figure 8.13 and is the reverse of the expected influence of a high magnetic content. The fact that the visibility data obtained with and without an internal standard are not similar provides direct evidence for a detuning effect.

8.4.2.3 Evidence for Detuning

The probe detuning effect of the coal sample can be seen in the spectra plotted in Figure 8.17. The Weavers-AT spectrum (Figure 8.17b) is typical of those obtained for most of the coals. The fact that the AT signals in Figures 8.17d,f are reduced in conjunction with the coal signals is consistent with probe detuning.

The examples given in Figure 8.17 also show that the AT signals are not equally affected by the detuning. The signal at 75 ppm is stronger than the signal at 180 ppm in the AT and Weavers-AT spectra. However, the reverse is true for the spectra of Liddell-AT and Ohai-AT mixtures. The uneven loss of intensity probably reflects significant differences in $T_1\rho_H$ values for the two samples, ie as a result of the probe detuning.

It was stated in the introduction to this section that the use of an internal standard should avoid the influence of probe detuning. This would be true if the detuning affected the signal area of the standard in a uniform manner. The uneven loss of AT signal area is reflected in a low

Figure 8.15: Plot of the visibility data, derived using an internal standard, against the sum of susceptibilities.

Figure 8.16: Plot of the visibility data, derived using an internal standard, against the ferromagnetic saturation parameter.

Figure 8.17: Evidence for probe detuning. Spectra of: a) 100% Weavers coal, b) 50:50 Weavers : AT mixture, c) 100% Ohai coal, d) 50:50 Ohai : AT mixture, c) 100% Liddell coal, f) 50:50 Lidell : AT mixture, g) 100% AT plotted at 50% of total intensity.

measurement for the area "B" (Figure 8.10) from the mixture spectrum. Therefore, F_{mix} is also smaller than expected and the corresponding K-value is large. Thus, the method for the measurement of V-values overcompensates for detuning when the effect is very strong. This trend can be seen in the Ohai and Liddell data listed in Table 8.4.

The sensitivity of the signal area labelled "B" to probe detuning provides a handle on the magnitude of the detuning. The theoretical AT contribution to the "B" signal area of the mixture spectrum (B_{mix}) is half the observed "B" area of the pure AT spectrum (B_{AT}) obtained at identical spectrometer gain; ie $B_{AT}/2$. The observed AT contribution to B_{mix} was estimated by subtracting half of the observed "B" area of the pure coal spectrum (B_i) from B_{mix} ; ie $B_{mix} - (B_i/2)$. This latter estimate includes the assumption that the coal detuning effect on the coal spectrum is not significantly altered by a reduction in the quantity of coal present.

A detuning factor, DF, was defined as the ratio of the observed and expected AT contribution to the B_{mix} signal area; ie

$$DF = (B_{mix} - (B_i/2)) / (B_{AT}/2) \quad [8.9]$$

Thus, a DF value of 1 would indicate that no detuning effect was evident. A DF value approaching 0 would suggest that extreme detuning was observed.

The DF values are listed in Table 8.5 and are plotted against the ferromagnetic saturation parameter in Figure 8.18. It can be seen that a high ferromagnetic component in the coal causes substantial probe detuning. There appears to be a small detuning effect observed in the spectra of all coals ie DF is always less than 1. This may be due to the fact that B_i , and hence $B_i/2$, is a small number which would introduce error into the estimation. However, it may be that all coal contains an intrinsic component that has a detrimental influence on probe tuning.

8.4.3 Discussion

Two main observations have arisen from the study of coal visibility by the use of an internal standard:

- i. The NMR response of coal is significantly altered when the sample contains a substantial ferromagnetic content. The fact that the detuning effect does not uniformly alter the AT signals indicates that the coal spectra may not be representative of the distribution of carbon functionalities in such samples.
- ii. The NMR response of the lignites is particularly variable. This

visibility appears to be related to the locality from which the lignite was mined; ie Southland lignites exhibit a significantly lower NMR response than the Central Otago lignites. Therefore, there must be an inherent difference in the coals from the two areas that is causing the visibility trend; eg differences in the nature of the inorganic content.

The remaining part of this study was directed towards improving the NMR response of the coals affected by these two factors. Alexander *et al*⁽⁸⁾ found that the ferromagnetic particles could be removed from the "anomalous" samples with a hand magnet (ie a crude version of magnetic separation). Malhotra and Graham⁽¹⁹⁾ observed that the signal assigned to magnetite in the fmr (ferromagnetic resonance) spectrum disappeared when the sample was treated with HCl. Acid-washing is also a standard method for removing the paramagnetic content of coal. For example, Honda and Ouchi⁽⁵⁾ acid-washed the coal samples in order to study the diamagnetic susceptibility of the organic matter.

Magnetic separation and acid-washing were therefore assessed as possible pre-treatments for NMR studies of coal.

8.5 Magnetic Separation

8.5.1 Experimental

The apparatus erected for separating the strongly magnetic material from the coal is shown in Figure 8.19. The electromagnet of the magnetic susceptibility instrument was used as it provides a strong magnetic field strength and can be conveniently "switched-off". A glass tube (7mm diameter, 35cm length), with a receptacle at one end, was clamped at an angle such that the sample would flow through the centre of the magnetic field.

Approximately 1g (measured) was placed in the receptacle and the magnet was turned on. The tube was gently tapped to cause a small but steady flow of sample down the tube. The non-magnetic material was collected at the bottom of the tube. The field was turned off and the magnetic portion of the coal was collected in a separate container.

Figure 8.19: Schematic diagram of the magnetic separation apparatus.

Error may be introduced by:

- i. non-magnetic material adhering to the glass tube,
- ii. magnetic material being forced out of the field by the flow of non-magnetic material.

Four coals that span the range of coal rank, and also exhibit a ferromagnetic component, were chosen for magnetic separation. The separated fractions of samples of Mataura, Ohai, Strongman and Liddell coal were weighed, the magnetic susceptibilities measured, and the NMR responses assessed.

8.5.2 Results

The amount of magnetic material separated and the magnetic susceptibilities of the non-magnetic coal are given in Table 8.6. The technique separated a significant portion of the Liddell coal only. The magnetic susceptibilities of all four coals have reduced in size, but the most dramatic change occurs in the magnetic properties of the Liddell coal. The magnetic susceptibility of the coal is negative after separation, but there remains a ferromagnetic contribution.

The effect of magnetic separation on the NMR spectra are shown in Figures 8.20 and 8.21. The spectra in Figure 8.20 indicate that magnetic separation does not increase the NMR response for the Mataura, Ohai and Strongman coals. The signal areas were altered by less than 2%, which is of the same order of magnitude as the error involved in determining the area by the cut-and-weight method. The spectra in Figure 8.21, however, show that removing 3.1% of the Liddell coal results in a significant increase in the NMR visibility; ie the signal area increased by 38%.

The apparent aromaticity of the Liddell spectrum did not alter significantly after magnetic separation, which indicates that the uneven detuning effect observed for AT is not evident in the coal spectra.

The magnetically separated Liddell sample was mixed with AT to quantify the change in the NMR response. The spectra in Figure 8.22 show that, in comparison with Figure 8.17, the detuning effect has reduced significantly but that the AT signals are not as strong as those observed in other coal-AT mixture spectra (cf. Weavers spectra in Figure 8.17). The DF value has increased from 0.40 for the total coal, to 0.67 for the non-magnetic fraction.

TABLE 8.6 : MAGNETIC SEPARATION STUDY

COAL	Magnetic Fraction (% of Coal)	Magnetic Properties (emu g ⁻¹)			
		$\chi_o \times 10^6$	non-magnetic	$\sigma \times 10^4$	non-magnetic
Mataura	<0.2	1.04	0.58	0.73	0.16
Ohai	0.3	0.92	0.62	6.81	3.85
Strongman	0.3	0.21	0.20	1.18	1.00
Liddell	3.1	0.42	-0.15	70.74	4.27

Figure 8.20: Results of magnetic separation. a) c) e) Spectra of raw Mataura, Ohai and Strongman coals, respectively. b) d) f) Spectra of non-magnetic fraction of the same three coals, respectively.

Figure 8.21: The effect of magnetic separation on the spectrum of Liddell coal. a) Raw coal, b) non-magnetic fraction.

Figure 8.22: Visibility study of the effect of magnetic separation of Liddell coal. a) 100% non-magnetic fraction, b) 50:50 non-magnetic fraction : AT, c) 100% AT plotted at 50% total intensity.

Magnetic separation substantially increases the NMR visibility of the Liddell coal, but there remains a residual detuning influence which is of the order observed for the Ohai coal.

8.5.3 The Magnetic Fraction

Approximately 50g of Liddell coal was magnetically separated and the magnetic fraction (~ 1.6g) was analysed by Moessbauer spectroscopy.

The Moessbauer spectrum of the magnetic fraction (Figure 8.23a) exhibits the double set of six lines that is characteristic of magnetite⁽²⁰⁾. The average isomer shifts were 0.27 (SD = 0.06) mms^{-1} and 0.65 (SD = 0.04) mms^{-1} . Published values include isomer shifts of 0.30 and 0.63 mms^{-1} ⁽²¹⁾ and isomer shift ranges of 0.27-0.36 mms^{-1} and 0.61-0.67 mms^{-1} ⁽²²⁾, respectively. The remaining intensity is similar to the signals observed in the spectrum (Figure 8.23b) of the Ohai coal (not separated). The bands can be tentatively attributed to other iron-bearing minerals⁽²⁰⁻²²⁾ including pyrite (FeS_2) and iron sulphates etc, which have similar isomer shifts and quadrupole splittings. The strong pyrite signals, often found in the Moessbauer spectra of coals from other countries⁽²⁰⁻²²⁾, were not observed in the spectra of the few New Zealand coals studied in this work.

No attempt was made to fit the Moessbauer spectrum of the Ohai coal because of the low signal intensity. It should be noted that, of the Australasian coals studied, the Ohai coal contained the highest quantity of iron. The spectra obtained for other New Zealand coals exhibited very poor S/N ratios. Therefore, the Moessbauer study was not extended. The Ohai spectrum is included for comparative purposes only.

The origin of the large quantity of magnetite in the Liddell coal is not known. However, the bulk sample had been "washed" in Australia. Magnetite is often used, in conjunction with a magnetic stirrer, in the washing process⁽²³⁾. Some magnetite may have remained and been ground with the coal prior to this study. Magnetite should also be removed by acid-washing.

Figure 8.23: Mössbauer spectra. a) Magnetic fraction of Liddell coal, b) Ohai coal.

8.6 Acid-washing Treatment

8.6.1 Introduction

"Whereas univalent cations are readily removed under room temperature conditions, the complete removal of divalent cations is only rapidly achieved by boiling or using increased acid concentration"(10).

Variations of the acid-washing treatment have been used for the removal of both the organically bound cations and the mineral matter. The EPR studies of Dack *et al*⁽²⁴⁾ and Malhotra and Graham⁽¹⁹⁾ included treatment of the coal samples with 5M HCl, and 1M HCl at 373K, respectively. Brooks and Sternhill⁽²⁵⁾ refluxed samples in 5M HCl, to remove organically bound cations prior to an IR study of the oxygen-containing functional groups of coal. Honda and Ouchi⁽⁵⁾ used boiling 6M HCl to remove the paramagnetic content of coal. Lefelhocz *et al*⁽²⁶⁾ extracted iron present as carbonates, oxides, sulphates, etc, with 25% HCl prior to a Moessbauer study of coal. Demineralisation of coal by treatment with HCl and HF is a standard method for removing the mineral content of coal⁽²⁷⁾. However, Wachowska *et al*⁽²⁸⁾ warned that this dual acid treatment leads to changes in the "coal polymeric structure". The treatment employed in this study (6M HCl at RT) avoids the use of boiling acids and therefore may not completely demineralise the coal.

8.6.2 Results

8.6.2.1 Acid-washing and Magnetic Properties

The magnetic susceptibilities of the acid-washed coals ($X_O(AW)$) are diamagnetic (Table 8.7). These $X_O(AW)$ values do not necessarily represent the diamagnetic content of the coal as there may be a residual paramagnetism which is temperature dependent^(5,8). This remaining paramagnetic content has been assigned to the free radical content of the coal⁽⁵⁾. However, the spin-counts increase with rank while the $X_O(AW)$ values tend to decrease with increasing carbon content (Figure 8.24a).

The susceptibilities of the high rank coals (ie $X_O(AW) < -0.5 \times 10^{-6}$ emu g⁻¹) are similar in magnitude to those obtained by Honda and Ouchi⁽⁵⁾ for strongly leached coals. The magnetic susceptibilities of the acid-washed lignites are the least diamagnetic, ie $X_O(AW) = -0.37$ (SD = 0.08) $\times 10^{-6}$ emu g⁻¹. The lignite values can be further divided into an average susceptibility for the Southland lignites ($X_O(AW) = -0.41 \times 10^{-6}$ emu g⁻¹, SD = 0.05 $\times 10^{-6}$ emu g⁻¹) which is more diamagnetic than the average value for the Central Otago lignites ($X_O(AW) = -0.28 \times 10^{-6}$ emu g⁻¹, SD = 0.05 $\times 10^{-6}$ emu g⁻¹).

TABLE 8.7 : MAGNETIC SUSCEPTIBILITIES OF ACID-WASHED COALS

COAL	Fe (ppm)		Magnetic Properties (emu g^{-1})		
	wash	remainder	$\chi_{\text{O(AW)}} \times 10^6$	$\sigma(\text{AW}) \times 10^4$	$\Delta\chi_{\text{O}} \times 10^6$
Roxburgh I	3500	670	-0.295	0	-0.448
Roxburgh II	4050	-	-0.218	0	-0.558
Roxburgh III	2800	3530	-0.329	0	-0.954
Mataura	4000	3130	-0.484	0	-1.521
Ashers Waituna	6110	-	-0.350	0	-1.961
Waimumu I	3250	1920	-0.401	0	-0.696
Waimumu II	2880	-	-0.465	0	-0.904
Waimumu III	5530	-	-0.379	0	-1.250
Waimumu IV	3590	-	-0.407	0	-1.003
Kopuku	1500	1800	-0.447	0	-0.475
Weavers	1100	1470	-0.433	0	-0.293
Huntly East	900	1210	-0.436	0	-0.249
Ohai	6000	3410	-0.177	0	-1.093
Strongman	3000	1410	-0.476	0	-0.688
Topline	750	4870	-0.471	0	-0.143
Charming Creek	650	850	-0.592	0	-0.081
Webb	700	1410	-0.562	0	-0.001
Liddell	2300	460	-0.469	0	-0.889
Bulli	3200	430	-0.546	0	-0.682
Yarrabee	2000	1450	-0.583	0	-0.750
Fox River	3400	1340	-0.508	0	-0.334

Figure 8.24: Magnetic susceptibility of acid-washed coals plotted against a) carbon content and b) the iron remaining in the coal after acid-treatment.

The apparently anomalous $\chi_o(AW)$ value (circled in Figure 8.24a) was measured for the Ohai subbituminous coal. The raw Ohai coal contains the largest quantity of iron (9410 ppm) and a significant proportion of this was removed by the mild acid treatment. However, the quantity of acid used may have been less than that required to reduce the magnetic susceptibility to the degree of diamagnetism exhibited by other subbituminous coals.

The unusual $\chi_o(AW)$ value of the treated Ohai coal, and the low diamagnetism of the lignites, might be expected to be determined by the iron remaining in the acid-washed coals. However, the $\chi_o(AW)$ values show virtually no dependence ($R = 0.373$) on the residual iron content (Figure 8.24b).

This lack of a significant correlation suggests that the remaining iron content is present in a different spin state which is less paramagnetic; ie acid-washing removes the strongly paramagnetic iron. The χ_o values of the raw coals and the change in magnetic susceptibility with acid-washing ($\Delta \chi_o$) both exhibit a dependence on the amount of iron removed (Figures 8.25 and 8.26) with correlation coefficients $R = 0.835$ and $R = 0.811$, respectively.

The data listed in Table 8.7 shows that acid-washing completely removes the ferromagnetic component from all of the coals, including the Liddell coal. The complete removal of the σ component is consistent with the observation of Malhotra and Graham⁽¹⁹⁾ that the ferromagnetic material (eg magnetite) is not "deeply embedded in the organic coal material".

8.6.2.2 Calibration with AT

The visibilities of the acid-washed coals were estimated by mixing the coal with AT. The results are listed in Table 8.8. The ash contents were not determined for these samples. The lower limit of K^T was estimated by assuming that none of the ash content is removed by acid-washing (ie K^T is identical to that of the raw coals). The upper limit of K^T was calculated by assuming that acid-washing removes all of the ash content. The upper and lower limits for the V-value were calculated from the two K^T values. (Note that the lower V-value corresponds to the removal of all of the ash.) The average of the two V-values, is plotted against the carbon content in Figure 8.27. There are two significant differences between the visibility data shown in Figure 8.27 and the corresponding plot of the raw coal visibility data (Figure 8.14).

Figure 8.25: The magnetic susceptibility of the raw coals plotted against the amount of iron removed by the acid treatment.

Figure 8.26: The change in the magnetic susceptibility of the coals upon acid-washing plotted against the amount of iron removed.

TABLE 8.8 : VISIBILITY DATA FOR ACID-WASHED COALS

COAL	K	K^T		V	$\bar{V}$
		low ^a	high ^b	low ^b	high ^a
Idaburn	0.70	2.35	2.61	26.8	29.8
Roxburgh I	0.89	2.40	2.68	33.2	37.1
Roxburgh II	0.70	2.32	2.57	27.2	30.2
Roxburgh III	0.82	2.34	2.57	31.9	35.0
Mataura	1.15	2.45	2.63	43.7	46.9
Ashers Waituna	0.79	2.40	2.56	30.9	32.9
Waimumu I	1.36	2.50	2.62	51.9	54.4
Waimumu II	0.89	2.46	2.64	33.7	36.2
Waimumu III	0.90	2.51	2.64	34.1	35.9
Waimumu IV	0.87	2.50	2.66	32.7	34.8
Kopuku	0.75	2.62	2.79	26.9	28.6
Weavers	0.98	2.67	2.82	34.8	36.7
Huntly East	0.82	2.82	2.88	28.5	29.1
Ohai	0.75	2.57	2.88	26.0	29.2
Strongman	0.62	2.87	3.07	20.2	21.6
Topline	0.44	-	-	-	-
Charming Creek	0.44	3.00	3.04	14.5	14.7
Webb	0.35	3.16	3.22	10.9	11.1
Liddell	0.53	2.90	3.14	16.9	18.3
Bulli	0.41	3.08	3.30	12.4	13.3
Yarrabee	0.52	3.18	3.40	15.3	16.4
Fox River	0.52	3.37	3.50	14.9	15.4

(a) Assuming that no ash is removed

(b) Assuming that all ash is removed

- i. The Ohai and Liddell coals exhibit V-values that are consistent with the visibilities of other acid-washed coals of similar rank.
- ii. The visibilities of the lignites, and to a lesser extent the subbituminous coals, are increased by acid-washing, while those of the high rank coals are essentially the same.

The visibilities of the Southland lignites show the most significant change. The average increase in the V-value with acid washing is 23.5% (SD = 7.8%) for the Southland lignites, but only 5.4% (SD = 4.7%) for the Central Otago lignites. (This trend will be analysed in detail in the next section.)

The removal of the ferromagnetic component (σ) upon acid-washing suggests that no significant probe detuning should be observed. The DF values were all less than 1 and, with the exception of the Liddell sample (DF(AW) = 0.889), the small amount of detuning observed for the raw coals was not significantly changed by acid-washing (average change = -0.01, SD = 0.08).

Acid-washing removes the ferromagnetic material from coal. It is more successful, in this regard, than magnetic separation. However, the small detuning effect noted for the raw coals cannot be caused by ferromagnetic matter.

8.6.3 Acid-washing and Lignites

8.6.3.1 Introduction

What is acid washing changing in the lignites that it can cause an increase in the NMR visibility by up to a factor of 2? Possible answers were sought through three different spectroscopic techniques.

i. Infra-red

The FTIR spectra of a Southland (Mataura) lignite and a Central Otago (Roxburgh II) lignite, and their acid-washed derivatives, are shown in Figure 8.28. The main features of the spectra are similar to those observed by Brooks *et al*⁽²⁹⁾ and Grigor and Howe⁽³⁰⁾.

Aliphatic C-H absorptions occur at 2950 and 2570 cm^{-1} (stretching vibrations) and at approximately 1450 cm^{-1} (in-plane deformations). Bands assigned to $-\text{CH}_2-$ and $-\text{CH}_3$ rocking modes appear between 900 and 700 cm^{-1} .

Figure 8.28: FTIR spectra of the Mataura and Roxburgh (II) lignites before (a,c) and after (b,d) acid-washing, respectively.

The strong band at 1612 cm^{-1} is assigned to aromatic ring stretching modes⁽³²⁾. Aromatic C-H out-of-plane bending modes give signals in the 900 to 700 cm^{-1} region; ie overlapping and forming composite signals⁽³¹⁾ with the aliphatic rocking modes.

The broad band between 3600 and 3330 cm^{-1} is assigned to hydroxyl stretching⁽³³⁾ and is probably dominated by water absorptions⁽³¹⁾. The broad unresolved band from 1500 to 900 cm^{-1} includes absorptions from C-O stretching and hydroxyl in-plane deformation vibrations⁽²⁹⁾. The signal at 1710 cm^{-1} is characteristic of carboxyl groups substituted onto either aromatic or aliphatic structures⁽²⁵⁾.

The mineral region (1300 to 1000 cm^{-1}) contains bands assigned to, for example, the Si-O and Al-O stretching vibrations of clays etc present in the lignites⁽³⁰⁾.

Acid-washing results in changes in the bands between 2000 and 1000 cm^{-1} (Figure 8.29) which are consistent with the conversion of carboxylate ions to carboxylic acid groups^(25,34).

- a. The band at 1710 cm^{-1} , assigned to a carboxylic acid mode, increases in intensity.
- b. The main aromatic band (1612 cm^{-1}) becomes more sharply defined in the spectra of acid-washed coals due to the weakening of the carboxylate absorption near 1565 cm^{-1} .
- c. The bands between 1280 and 1150 cm^{-1} increase in intensity due to the loss of carboxylate ion absorption between 1460 and 1300 cm^{-1} , and the gain in the intensity of C-O stretching and -OH deformation vibration absorptions between 1280 and 1150 cm^{-1} .

The changes in the IR spectra indicate that acid-washing removes organically bound ions that were present in the coal as carboxylate salts.

ii. EPR

The gradual alteration in the fine structure of the EPR spectrum caused by acid-washing can be seen in Figure 8.30. The multiplet assigned to Mn(II) disappears rapidly, ie was almost completely removed after one hour of acid-washing (Figure 8.30b). No Mn(II) signals were observed in the spectra of acid-washed lignites.

The Fe(III) signal at $g = 4.2$ was substantially reduced in intensity after one hour, but a further five days of treatment failed to remove the

Figure 8.29: Expansion of the 2000 - 1000 cm^{-1} region of the FTIR spectra. Samples as for Figure 8.28.

Figure 8.30: The effect of the length of acid-washing time on the metal ion signals of the EPR spectrum of Mataura lignite. a) 0 hours, b) 1 hour, c) 5.5 hours, d) 120 hours.

signal from the Mataura spectrum. A small Fe(III) signal was observed in the spectra of all of the acid-washed coals, up to the high volatile bituminous rank. The Fe(III) signal in the spectrum of the Roxburgh (III) sample, for example, is reduced by approximately 50% by acid-washing (Figure 8.31). The presence of a small but persistent Fe(III) signal after acid-washing is in contrast to the results of Dack *et al*⁽²⁴⁾ who observed that all of the signals assigned to metal ions were removed by acid-washing.

iii. NMR Signals

The possibility exists that the low NMR visibility is confined to particular signals within the coal spectrum; ie acid-washing may be increasing the response of certain types of carbon functionality.

The spectra of the four samples of Mataura lignite that had been acid-washed for varying lengths of time are shown in Figure 8.32. The fa' values do not vary greatly ($fa' = 0.63 \pm 0.01$), indicating that acid-washing does not preferentially alter the intensity of the aromatic or the aliphatic envelopes. A visual analysis of the spectra shows that no individual signal is significantly altered (ie by more than the S/N ratio) relative to the rest of the spectrum.

It should be noted that it is unlikely that the conversion of carboxylate groups to carboxylic acids will be observed in the NMR spectra as the relevant signals (~ 180 ppm) are obscured by the first order high-frequency SSB of the aromatic band. The average carbon-13 chemical shifts of carboxylic acid (176 ppm, SD = 5 ppm) and carboxylate (178 ppm, SD = 6 ppm) groups in model compounds⁽³⁵⁾ indicate that any alteration in the signal position would be very small.

Cellulose is hydrolysed by concentrated acid (eg Klason lignin extraction, Chapter 5). It would therefore be expected that cellulose fragments remaining in the lignites would be destroyed by acid-washing. The spectrum of the Waimumu (I) lignite (Figure 8.33a) exhibits strong cellulose signals at 105 ppm (C-1) and 74 ppm (C-2, C-3, C-5). The second spectrum (Figure 8.33b) shows that oven-drying has no effect on the NMR visibility. The third spectrum, of acid-washed Waimumu (I), shows the large increase in signal area. Acid-washing slightly reduces the signal intensity of the cellulose signals relative to the other bands but this small change might also be caused by sample heterogeneity.

Figure 8.31: The effect of acid-washing on the EPR spectrum of the Roxburgh (III) lignite. a) Raw lignite, b) acid-washed lignite.

Figure 8.32: The effect of the length of acid-washing time on the NMR spectrum of Mataura lignite. a) 0 hours, b) 1 hour, c) 5.5 hours, d) 120 hours.

Figure 8.33: The effect of oven-drying and acid-washing on the cellulose signals (•) observed in the spectrum of Waimumu (I) lignite. a) Raw lignite, b) oven-dried lignite, c) acid-washed lignite, d) difference spectrum (c-a).

8.6.3.2 Visibility and Iron Content

In order to quantify the change in lignite response with acid-washing, the ash contents were determined for the raw and acid-washed samples that were used for the NMR visibility experiments. The iron contents of these ashes were measured by SES. The iron contents are not identical to those measured by XRF and AA, presumably because the SES measurements were carried out on very small samples (0.3 to 50mg).

The ash and iron contents of the coals before and after acid-washing, listed in Table 8.9, show a striking difference between the Southland lignites and the Central Otago lignites. The ash contents of the Southland lignites are reduced by an average 94% (SD = 2%), while those of the Central Otago lignites are only reduced by an average 51% (SD = 6%). This trend is reflected in the iron contents of the two lignite areas which are reduced by an average 97% (SD = 2%) and 60% (SD = 11%), respectively.

The visibilities with respect to AT are also given in Table 8.9. The ratio of the raw coal response to the acid-washed coal response is given by $V(\text{raw})/V(\text{acid-washed})$. These ratios were low for large increases in NMR response. As the Southland lignites show the greatest improvement in visibility, and the largest loss of iron, it might be expected that the ratios would decrease with increasing iron content. However, high amounts of iron in the raw coal are not directly responsible for low ratio values (Figure 8.34). The data plotted in Figure 8.34 indicate that the response characteristics of the two lignite areas vary significantly. Therefore, the visibility data of the two groups of lignites were assessed separately.

The V-values for the untreated and acid-washed coals are plotted against iron content in Figure 8.35. The visibilities of the Central Otago samples (Figure 8.35a) exhibit a weak dependence on the iron content ($R = 0.507$) which suggests that the iron content is only a small factor in determining the NMR response of these coals. The equivalent plot for the Southland lignites (Figure 8.35b) has a completely different form. The iron content appears to be a significant influence on the magnitude of the NMR response, ie the V-values increase sharply when the iron content is reduced to below 0.1% (of coal weight).

In order to investigate the apparent correlation of NMR visibility with the origin of the lignites, two lignites were chosen for further study; the Mataura lignite from Southland and the Roxburgh (I) lignite from Central Otago.

TABLE 8.9 : VISIBILITY DATA FOR LIGNITES

COAL	%A (d)	%Fe (d)	K	K ^T	V
Hawkdun ^a	13.8	0.90 $\pm$ 0.14	0.58	2.23	26.1
Idaburn ^b c	8.4	0.71 $\pm$ 0.09	0.63	2.35	27.0
	3.9	0.23 $\pm$ 0.04	0.70	2.51	
Roxburgh I	9.8	0.39 $\pm$ 0.10	0.57	2.40	23.5
	5.7	0.11 $\pm$ 0.06	0.89	2.42	36.8
Roxburgh II	8.2	0.57 $\pm$ 0.06	0.47	2.32	20.5
	4.3	0.28 $\pm$ 0.04	0.70	2.46	28.5
Roxburgh III	8.8	0.53 $\pm$ 0.08	0.78	2.34	33.1
	5.1	0.28 $\pm$ 0.05	0.82	2.44	33.6
Mataura	6.5	0.75 $\pm$ 0.06	0.39	2.45	15.8
	0.3	0.015 $\pm$ 0.006	1.15	2.62	43.9
Ashers Waituna	5.2	1.17 $\pm$ 0.13	0.22	2.40	9.0
	0.1	0.023 $\pm$ 0.002	0.79	2.55	31.0
Waimumu I	3.2	0.30 $\pm$ 0.04	0.39	2.50	15.6
	0.2	0.007 $\pm$ 0.003	1.36	2.62	54.8
Waimumu II	6.3	0.54 $\pm$ 0.06	0.44	2.46	17.8
	0.4	0.020 $\pm$ 0.006	0.89	2.63	33.8
Waimumu III	5.8	0.58 $\pm$ 0.04	0.40	2.51	16.0
	0.3	0.032 $\pm$ 0.004	0.90	2.63	34.2
Waimumu IV	5.4	0.97 $\pm$ 0.06	0.47	2.50	18.9
	0.4	0.042 $\pm$ 0.006	0.87	2.65	32.8

(a) Hawkdun sample not acid-washed

(b) First row contains data for raw coal

(c) Second row contains data for acid-washed coal.

Figure 8.34: Plot of the ratio of the visibilities (internal standard) of the raw and acid-washed lignites against the iron content of the dry coal. Central Otago lignites (open symbols), Southland lignites (solid symbols).

Figure 8.35: Visibilities (internal standard) of the raw (solid symbols) and acid-washed (open symbols) lignites plotted against the iron content of the dry coal. a) Central Otago lignites, b) Southland lignites.

8.6.3.3 Study of Two Lignites

Larger samples (~ 10g) of each lignite were acid-washed for this study.

i. NMR Visibility

The differences between the NMR responses of the Mataura and Roxburgh (I) lignites can be seen in the spectra in Figure 8.36. The relaxation parameters were determined for the signal areas of the aliphatic and aromatic envelopes (Table 8.10). The only significant change is the increase in the $T_1\rho_H$ values of the Mataura lignite which is consistent with the observations of the effect of paramagnetic ions on $T_1\rho_H$. This trend is not evident in the $T_1\rho_H$ values of the Roxburgh lignite. However, the increase in the Mataura $T_1\rho_H$ values can not be solely responsible for the large increase in visibility.

The NMR visibility was calibrated with AT. Lignite (not dried) and AT were mixed in proportions ranging from 10% to 90% AT, in 10% steps. An example of the F_{mix} curves that were obtained are shown in Figure 8.37. The following equation was fitted to the curves to obtain the response factor K:

$$F_{mix} = \frac{(F_{AT} \times \%AT) + (F_C \times K(1-\%AT))}{\%AT + K(1-\%AT)} \quad [8.10]$$

where F_C is the F-value for the pure coal.

The $T_1\rho_H$ values (Table 8.10) and the fa' values (Figure 8.36) were used to calculate the loss of aliphatic and aromatic signal area and therefore the K^C values. The average $T_1\rho_H$ value for AT ($T_1\rho_H = 18.9ms$) was used for the correction.

The K^T values were calculated from the carbon content of the lignites, corrected for the ash and moisture contents, and are listed in Table 8.11 with the V-values. The $T_1\rho_H$ correction increases the NMR visibilities to approximately 50% of the AT response. The large increase in the visibility of the Mataura lignite must be related to the almost total removal of the ash and iron contents of the coal.

Figure 8.36: The effect of acid-washing on the NMR spectra of the two lignites. a) Raw and b) acid-washed Mataura lignite, c) raw and d) acid-washed Roxburgh (III) lignite.

TABLE 8.10 : RELAXATION CONSTANTS OF SIGNAL AREAS

COAL	T_{1H} (s)		$T_{1\rho H}$ (ms)		T_{CH} (ms)		$T_{1\rho C}$ (ms)	
	Al	Ar	Al	Ar	Al	Ar	Al	Ar
Mataura	0.033	0.021	2.09	2.61	0.13	0.36	0.98	3.53
	0.006 ^a	0.002	0.15	0.18	-	-	0.15	0.26
Mataura (AW)	0.034	0.018	2.45	3.36	0.28	0.50	1.11	3.77
	0.005	0.001	0.15	0.09			0.12	0.22
Roxburgh	0.044	0.017	2.11	2.82	0.16	0.50	0.89	4.10
	0.007	0.002	0.15	0.18			0.14	0.40
Roxburgh (AW)	0.048	0.013	1.94	2.62	0.20	0.56	0.77	3.50
	0.007	0.003	0.09	0.13			0.11	0.42

(a) Standard deviations

TABLE 8.11 : VISIBILITY DATA FOR TWO LIGNITES

COAL	%C (daf)	%M	%A (m)	%Fe (m)	%S (m)	K ^C	K ^T	V
Mataura	68.61	11.9	5.1	0.62 ±0.04	0.5	0.908	2.183	41.6
Mataura (AW)	68.61	10.1	0.5	0.049 ±0.005	-	1.520	2.351	64.7
Roxburgh	69.94	11.9	8.6	0.30 ±0.07	0.7	1.132	2.131	53.1
Roxburgh (AW)	69.94	12.3	5.9	0.26 ±0.06	-	1.161	2.193	52.9

Figure 8.37: Curves of the F_{mix} values obtained for mixtures of Mataura lignite and AT in various proportions. Raw lignite (open symbols), acid-washed lignite (solid symbols)

ii. The Ash Content

The fact that the ash contents of Southland coals are substantially reduced by acid-washing, while those of the Central Otago lignites are only slightly altered, suggests that the inorganic matter in the coals from the two areas are very different. Black^(36,37) has studied the inorganic content of the two groups of lignites.

The major constituents of the clay mineral assemblages were found to be⁽³⁶⁾ :

Kaolinite $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$

Illite $(\text{K}, \text{H}_3\text{O})(\text{Fe}, \text{Mg}, \text{Al})_2[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{OH})_2 \cdot \text{H}_2\text{O}$

Chlorite $(\text{Fe}, \text{Mg}, \text{Al})_6[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{OH})_8$

Smectite $(\text{Ca}, \text{Na})_{0.33}(\text{Fe}, \text{Mg}, \text{Al})_2[(\text{Si}, \text{Al})_4\text{O}_{10}](\text{OH})_2 \cdot n\text{H}_2\text{O}$

and an illite-smectite interlayer mineral.

The mineral content of the Central Otago lignites is dominated by kaolinite, with small amounts of illite, smectite and the interlayer mineral. The Southland lignites contain a complex mixture of illite, smectite, chlorite, kaolinite and interlayer minerals. The ash of the Central Otago lignite is very pale in colour (Figure 8.38b), which reflects the high kaolinite content (ie high Al and Si content). The ash of the Southland lignite has an ochre colouring (Figure 8.38a), which is presumably caused by the more diverse mixture of mineral components.

The clay minerals are not removed by acid treatment⁽³⁸⁾. For example, the colour of the ash of the acid-washed Roxburgh lignite (Figure 8.38d) is similar to the ash of the untreated coal. A large proportion of the inorganic content of the Central Otago lignites is probably in the form of clay minerals. The iron content of the untreated Central Otago coal is less than that of the Southland lignite, which possibly reflects the fact that kaolinite does not contain iron. A strong linear correlation has been observed⁽³⁷⁾ between the Fe and Mg content of the Central Otago lignite ashes. This was assigned to the Fe and Mg being substituted into similar crystallographic sites in the illite and smectite clays.

Pyrite (FeS_2) is not removed by acid treatment, but studies on the sulphur content of New Zealand coals^(27,39) have shown that the pyrite content is very small. For example, only 5% (SD = 10%) of the sulphur content (<2% of dry coal) of Southland and Central Otago lignites is in a

Figure 8.38: Photograph of the high-temperature ashes of the a) raw and c) acid-washed Mataura lignite, b) raw and d) acid-washed Roxburgh (III) lignite.

pyritic form. Therefore, the iron content of the Central Otago lignites cannot be present as pyrite.

The quantity and colour of the acid-washed Mataura lignite (Figure 8.38c) is very different from the original ash which suggests that the majority of the inorganic content (particularly the iron content) is not present in the lignites as clay minerals. The fact that there is little correlation between the high Fe levels and other inorganic constituents, of the Southland lignite ashes⁽³⁷⁾ supports this suggestion.

Moessbauer studies have shown that acid-washing removes carbonates (eg siderite, FeCO_3) and sulphates, such as szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) and rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$)^(38,40). However, the sulphur content of the Mataura lignite is small (Table 8.9) and would have to be completely in the sulphate form to account for the removal of most of the iron as iron sulphates. It has been shown⁽²⁸⁾ that less than 10% of the sulphur content is in the sulphate form.

iii. Magnetic Separation

A magnetic separation of the two lignites should indicate whether the Mataura lignite does in fact have a low mineral content (ie assuming that the minerals are not held within the coal structure). Unfortunately, there was an insufficient supply of the Mataura and Roxburgh (I) samples to allow for the large quantity needed to obtain a reasonable separation. The bulk sample of Mataura lignite therefore came from a different source; that used for the drying experiment described in Chapter 7.

A second composite of plies from drill hole 2086 was used as the bulk sample of Roxburgh lignite (ie similar to Roxburgh (III) sample, Chapter 4). Both samples were crushed to $<200 \mu$. The fraction of the coal that was found to be $<53 \mu$ was removed as this size is the lower limit needed for adequate "flow" in the apparatus. The "-53" split was analysed separately and found to have the same moisture, ash and iron contents as the bulk material. A Frantz Isodynamic Separator (Industrial Processing Division, DSIR) was used with the following settings; 15° forward slope, 20° side slope and 1.5 amps operating current. The moisture, ash and iron contents of the fractions were determined and are listed in Table 8.12.

The amount of material separated from the Roxburgh lignite was an order of magnitude greater than that separated from Mataura lignite, which

TABLE 8.12 : MAGNETIC SEPARATION OF LIGNITES

COAL	% of Bulk	%M	%A (m)	%Fe (m)	T _{LH}	
					Al	Ar
Mataura Bulk		38.2	3.7	0.28	0.017	0.010
Non-Magnetic Magnetic	99.0	35.6	3.3	+0.04	0.003	0.003
				-0.33	0.023	0.011
	1.0	22.4	7.7	+0.03	0.004	0.002
				-2.3 ± 0.2	-	-
Roxburgh		11.4	9.5	0.52	0.029	0.015
Non-Magnetic Magnetic	89.9	11.4	7.8	+0.10	0.003	0.003
				-0.43	0.028	0.013
	10.1	12.1	13.7	+0.08	0.002	0.003
				-0.89 +0.14	-	-

TABLE 8.13 : ACID-WASHING vs TIME

TIME (min)	%M	%A (m)	%Fe (wash) ± 10%	Mag. Props (emu g ⁻¹)		W*
				X _O x 10 ⁶	σ x 10 ⁴	
0	11.9	5.1	0	1.037	0.7	0.263 ^a
1			0.077			0.270
2			0.094			0.279
6			0.113			0.297
10			0.127			0.297
15	13.9	1.0	0.139	0.021	0	0.287
20			0.147			0.291
30			0.153			0.316
45			0.191			0.326
60			0.202			0.389
120	14.0	0.5	0.257	-0.250	0	0.405
330			0.302			0.432
7200			0.487			0.495

(a) Arbitrary units

confirms that there is a substantially smaller mineral content in the latter lignite. Both magnetic fractions have larger ash and iron contents than the bulk material. The high iron content of the Mataura magnetic fraction corresponds to the fact that the small quantity of mineral matter in the Southland lignites contains chlorite, which "when it occurs as a clay is usually iron-rich"(37).

The spectra of the lignites and the non-magnetic fractions are shown in Figure 8.39. The relatively flat difference spectra indicate that this thorough magnetic separation does not increase the visibility of the lignites. The iron in the mineral matter of the Mataura lignite is not causing the low NMR response. If the crucial iron content is not in the mineral matter then it must be present predominantly as organically bound cations.

iv. Length of acid-washing time

If the increase in the visibility of the Mataura lignite is dependent on the removal of organically bound iron, then the improvement in the NMR response should be able to be followed as the iron is successively removed, ie by varying the period of exposure to the acid.

Approximately 1g samples of the standard Mataura lignite were acid-washed for times between 1 minute and 5.5 hours. The iron content of the washes was measured by AA and the NMR signal area W^* , corresponding to 0.3g of sample, was determined. The moisture and ash contents, and the magnetic susceptibilities, were also measured for several samples. The data are listed in Table 8.13. The iron content was initially reduced very rapidly by acid-washing, but the rate of Fe loss decreases with longer washing periods (Figure 8.40a). The magnetic susceptibility becomes paramagnetic after 30 minutes of soaking (Figure 8.40b). None of the acid-washed samples exhibited a ferromagnetic component.

The increase in signal area exhibits a good correlation ($R = 0.952$) with the amount of iron removed from the samples (Figure 8.41), despite the fact that the W^* figures are uncorrected for variation in moisture and ash contents.

Figure 8.39: Results of a magnetic separation of the minerals from the lignites. NMR spectra of the Matura lignite before (b) and after (c) separation and the difference spectrum ($a = c - b$). Equivalent spectra of the Roxburgh (III) lignite before (e) and after (f) separation and the difference spectrum ($d = f - e$).

Figure 8.40: The effect of acid-washing time on a) the iron content of the Mataura lignite and b) the magnetic susceptibility of the lignite.

Figure 8.41: Plot of the uncorrected signal area of the Mataura lignite spectrum against the amount of iron removed as a percent of the total sample.

v. Replacement of the Iron

The EPR spectra of the untreated, the acid-washed and the iron-exchanged lignite samples are shown in Figure 8.42. The iron exchanges back into the same co-ordination site that produces the Fe(III) signal ($g = 4.2$) in the spectra of both lignites. In the case of the Roxburgh sample, there are more of these iron-substituted sites than in the untreated lignite.

The major difference between the spectra of the Roxburgh (I) and the Mataura iron-exchanged samples is the presence of a large signal at $g = 2$ in the latter spectrum. Dack *et al*⁽²⁴⁾ also observed this new, broad signal and assigned the signal to organically bound iron "involved in polynuclear hydroxy- or carboxylato-bridged forms".

The analyses and NMR data for the iron-exchanged samples are listed in Table 8.13. The iron exchanged Mataura sample contains twice the amount of iron that was present in the original lignite. Presumably acid-washing removes other organically bound cations (eg Na^+ , Ca^{++} etc) which results in a greater quantity of acidic proton sites available for re-exchange with iron. The iron-exchanged Roxburgh sample contains slightly more iron than is found in the untreated lignite.

The spectra of the original and treated samples are shown in Figures 8.43(a to f).. The reduction in the signal area of the spectrum of the iron-exchanged Mataura lignite is far greater than that observed for the corresponding Roxburgh sample. The signal areas, W^* (corrected for the moisture and ash contents) are listed in Table 8.14. It is significant that the signal area of the Roxburgh spectrum is reduced slightly after iron-exchange. This decrease suggests that some of the iron is exchanging into the organic matrix, in co-ordination sites that were not significantly occupied by iron in the original lignite, and are thus affecting the NMR response.

Figure 8.42: The effect of iron-exchange on the EPR spectra of the two lignites. a) Raw, b) acid-washed and c) iron-exchanged Mataire lignite. d) Raw, e) acid-washed and f) iron-exchanged Roxburgh (III) lignite.

Figure 8.43: The effect of iron-exchange on the NMR spectra of the two lignites. (a-c) Mataura lignite, (d-f) Roxburgh (III). Spectra order as for Figure 8.42.

TABLE 8.14 : IRON EXCHANGE STUDY

COAL	%M	%A (m)	%Fe (m)	W*	T _{1H} ^b	
					Al	Ar
Mataura	11.9	5.1	0.62	0.1693	0.033	0.021
			<u>+0.04</u>		0.006	0.002
Mataura (AW)	10.1	0.5	0.049	0.2794	0.034	0.018
			<u>+0.005</u>		0.005	0.001
Mataura (Fe) ^a	11.0	2.2	1.32	0.1415	0.019	0.016
			<u>+0.11</u>		0.002	0.002
Roxburgh	11.9	8.6	0.30	0.2581	0.044	0.017
			0.07		0.007	0.002
Roxburgh (AW)	12.3	5.9	0.26	0.2900	0.048	0.013
			<u>+0.06</u>		0.007	0.003
Roxburgh (Fe)	3.9	4.8	0.38	0.2160	0.036	0.013
			0.05		0.005	0.004

(a) (Fe) = iron exchanged sample

(b) By signal area

vi. Discussion

The difference in NMR visibility between the Central Otago and the Southland lignites can be explained by the presence of iron in different phases in the coal. The Central Otago lignites contain substantially higher quantities of clay minerals than are present in the Southland lignites. Iron is substituted into the co-ordination sites of specific types of mineral (illite, smectite) and, as most of the iron in the Central Otago lignites is inaccessible to acid, it appears that a significant proportion of this iron is in the mineral phase.

The clay minerals (particularly chlorite) of the Southland lignites are also high in iron. However, this forms only a minor proportion of the iron content of these lignites as more than 90% of the iron is removed by acid-treatment. The results of the experiments described in this section suggest that it is the large content of organically bound iron that hinders the NMR response of the Southland lignites. The observed reduction in the response of the iron-exchanged Roxburgh lignite also provides evidence for the detrimental role of organically bound iron in determining the NMR visibility. Probe detuning and the selective loss of signals due to unfavourable relaxation, have been eliminated as causes of the intensity reduction.

8.7 Summary

The NMR visibility of coal is low relative to certain model compounds. However, the NMR response of pure organic compounds is also variable⁽¹⁸⁾. Thus, the visibility problem is not confined to coal. Newman^(18,42) has studied the NMR "visibility" of many organic compounds. He has attributed the variable response to the magnitude of the proton spin-spin relaxation time, T_{2H} ⁽⁴²⁾. The T_{2H} values measured for organic solids are generally in the range 10-20 μ s^(18,41), which is of the same order of magnitude as the 90° preparation pulse employed in CP/MAS NMR. Newman⁽¹⁸⁾ estimated T_{2H} values of 13 μ s and 18 μ s for protons in aliphatic and aromatic structures, respectively, of a Roxburgh lignite. These values are similar to those measured by Gerstein *et al*⁽⁴¹⁾. The low NMR visibilities of coals can therefore be explained by the occurrence of significant spin-spin relaxation during the 90°-pulse. The fact that lower rank coals contain a component with a longer T_{2H} value ($\sim 100 \mu$ s)⁽⁴¹⁾ may explain the trend for higher visibilities in these coals in comparison with the response of higher rank coals.

The low response of coal has been partially correlated with the magnetic content. In particular, the amount of carbon in low rank coals that is "seen" by NMR can be increased by pretreatment of the sample with acid. This improvement in visibility was assigned to the removal of organically bound iron. This iron must shorten the T_{2H} values in a parallel manner to the iron effect on $T_{1\rho H}$ values. The remaining invisibility is caused by the inherent T_{2H} values of the heterogeneous structure of coal.

Despite the fact that not all of the carbon is NMR visible, the signals that are observed appear to be representative of the range of carbon functionalities found in coal. This result reflects the fact that the T_{2H} values for proton functionalities are similar^(18,41). Therefore, the way is clear for the quantitative interpretation of the NMR spectra of coals.

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9.0 THE SPINNING SIDE BAND PROBLEM

9.1 Introduction

"For amorphous materials we do not expect major gains, if any, in fractional resolution at a higher static field"⁽¹⁾. This statement was published in 1981 when it was considered that the "present-day" carbon-13 spectra obtained at 15.1 MHz (1.4 T spectrometers) exhibited the "highest possible resolution"⁽¹⁾. The notion that the use of superconducting NMR technology "choked"⁽²⁾ the spectra with SSBs hindered the application of high field NMR to complex materials. The "obvious solution" was to perform the experiment at lower operating frequencies, that is, if the laboratory had the "luxury of operating their magnets at low field"⁽³⁾. It was soon realised that the increased sensitivity and resolution (chemical shift dispersion) achievable with the high fields provided great potential for studying the structure of materials such as "soils, lignins and coals"⁽³⁾. Attention was focused on the development of methods for reducing or eliminating the contribution of SSBs to the spectrum.

9.2 Correction for SSBs

9.2.1 The Qualitative Methods

The earliest techniques for SSB reduction utilised the fact that the position of the SSBs in the spectrum depended on the spinning rate^(3,4). These methods are useful for qualitative studies only because the SSB intensity is discarded⁽⁴⁾.

The synchronisation of data acquisition with sample rotation was proposed by Maricq and Waugh⁽⁵⁾. Barron and Wilson⁽⁶⁾ introduced the block multiplication (BM) of spectra obtained at different spinning frequencies. BM was demonstrated in the NMR study of a brown coal xylite and a silt loam. The reduction in SSB intensity enabled the unequivocal assignment of the centreband signals, ie "signals which cannot arise from spinning side bands"⁽⁴⁾. BM appears to have been useful in that particular application but Dixon *et al*⁽³⁾ found that it did not significantly reduce the SSBs in the spectrum of a lignin.

Both BM and the synchronisation method require a section of the spectrum to be free of centrebands so that the shifts in the SSB positions can be monitored. The spectra of Australasian coals do not generally contain such "windows"⁽³⁾.

9.2.2 The "Dixon" Pulse Sequences

Dixon *et al*^(2,3) developed two pulse sequences that result in sideband suppression but also retain the quantitative information contained in the spectrum. The Phase-Alternated Spining Sideband (PASS) sequence employs a series of 180° re-focusing pulses which produce echo spectra (Figure 9.1). The time intervals between the Π -pulses determine the phase of the echo spectra. The appropriate linear combination of the echo spectra results in the cancellation of SSB signals and the generation of the PASS isotropic spectrum. Dixon *et al*⁽³⁾ demonstrated that PASS successfully added the SSB intensity to the centrebands of a lignin spectrum. PASS was used to remove first order SSBs from the spectra of vitrinite concentrates but was found to be "not uniformly successful"⁽⁷⁾. A modified version of PASS has been shown to produce an SSB-free spectrum of a bituminous coal⁽¹⁰⁾.

The main problems associated with the use of PASS are the low resultant S/N ratio and the need for operator intervention in the phase adjustments⁽⁸⁾. Dixon *et al*⁽²⁾ developed a simplified version of the pulse-train termed TOSS (Total Suppression of Sidebands). TOSS eliminates the need for the addition of several spectra by aligning the Π -pulses with the spinning rate. The delays between Π -pulses are specifically chosen to cause the automatic cancellation of SSB signals.

TOSS-generated spectra of model compounds usually exhibit small residual SSB signals^(2,4,9). Dixon *et al*⁽⁸⁾ compared the TOSS spectra and standard 50 MHz spectra of an "aromatic coal" obtained with spinning frequencies between 1.5 and 3.0 kHz. Some "minor lineshape distortions" were attributed to residual SSBs. TOSS was observed to be most successful for the highest spinning rate although 20% of the aromatic-carbon intensity was "missing" from the TOSS isotropic peak.

The TOSS sequence is included in the Varian XL200 software. The TOSS-generated spectra of three New Zealand coals of varying rank are shown below the corresponding CP/MAS spectra in Figures 9.2 to 9.4. The TOSS spectrum of the Fox River semianthracite is relatively free of SSBs although an out-of-phase component persists. The success of TOSS is reduced as the rank of the coal decreases. The phasing difficulties that are evident in the TOSS spectra were also observed by Painter *et al*⁽⁷⁾ in PASS-generated spectra.

Figure 9.1: Dixon pulse sequence for the suppression of SSB signals.

Figure 9.2: The standard CP/MAS (a) and TOSS (b) spectra of Ohai subbituminous coal. Both spectra were acquired under identical spectrometer conditions (NT = 20000) and are plotted on the same vertical scale.

Figure 9.3: The standard CP/MAS (a) and TOSS (b) spectra of Webb (I) hvA bituminous coal (NT = 5000).

Figure 9.4: The standard CP/MAS (a) and TOSS (b) spectra of Fox River semianthracite (NT = 5000)

The "Dixon pulse-sequences" are quantitatively accurate when the T_2 values are large in comparison with the time delay for the four refocusing pulses. The delay is approximately equal to the period of two rotor revolutions⁽²⁾; ie 0.8 ms for a 2.5 kHz spinning frequency. It is also assumed that the T_2 values are uniform for all carbons⁽⁴⁾.

The T_2 values were measured for the aromatic and aliphatic bands of the Webb spectrum. It is necessary to know the T_{1C} value of the signals, rather than the T_{1H} value, as cross-polarisation is not used in the determination of T_{2C} . The experimental delay must be three to five times the magnitude of T_{1C} . T_{1C} was determined by the inversion-recovery method⁽¹¹⁾. The T_{1C} -values for the aliphatic and aromatic bands were found to be 0.9 ms (SD = 0.1) and 2.7 ms (SD = 0.6), respectively. The observation that the spin-lattice relaxation of the aliphatic carbon is faster than that of the aromatic carbon is consistent with the results of Sullivan and Maciel⁽¹¹⁾.

The T_{2C} values were measured using the Carr-Purcell-Meiboom-Gill T_2 sequence (CPMG2) and were estimated to be 1.7 ms (SD = 0.2) and 0.6 ms (SD = 0.3) for the aliphatic and aromatic bands respectively*. The T_2 values are of the same order of magnitude as the time scale of the TOSS experiment and are not uniform throughout the coal spectrum. Therefore, the TOSS pulse sequence cannot be used for quantitative NMR of coals.

9.2.3 CROMASS

The computer program CROMASS (Computer Recognition of Magic Angle Spinning Sidebands) was originally designed to replace the identification of SSB signals "by visual comparison of spectra run at different spinner frequencies"⁽¹²⁾. The program assigns the centrebands to be the signals that are "persistent" through all of the spectra. The first-order SSBs are located by their change in magnitude, as well as position, when the spinning frequency is altered. The SSB intensity is transferred to the centreband by a series of iterations. The CROMASS-generated spectrum of a procyanidin polymer (ie a tannin) showed no obvious residual SSBs⁽¹²⁾.

The program has been translated from BASIC into PASCAL computer language (Appendix 7.1) in order to test CROMASS on the spectra of coals. Spectra were obtained at four different spinning rates for each of the

* T_{2C} should be less than T_{1C} . These values are given as estimates of the order of magnitude of the relaxation constants only due to the low S/N ratio observed. The SD values are for the fit to the data and do not reflect the errors in the curve obtained.

Ohai, Webb and Fox River coals (Figures 9.5 to 9.7). The spectra were digitised into 200 signal heights between -100 ppm and +300 ppm; ie a resolution of 2 ppm. Two iterations were used as further iterations resulted in only minor changes in relative signal areas.

The three CROMASS-generated spectra are shown in Figure 9.8. CROMASS does reduce the SSBs but they are not completely removed from the coal spectra. The incorporation of a search for second and higher-order SSBs may improve CROMASS although the overlap of SSBs and centrebands in the spectra of lower rank coals would probably be too complex for CROMASS to function adequately.

9.2.4 Prediction by the Method of Herzfeld and Berger

The discussion in Section 3.2.2 outlined the influence of the carbon environment on the chemical shift tensor and, therefore, on the distribution of intensity in SSB signals. The procedures developed by Herzfeld and Berger (HB) were originally designed for the extraction of shielding anisotropies from the SSB intensities⁽¹³⁾. However, the logic of the HB method can be used in reverse. The magnitudes of the SSB intensities can be calculated from the three principal values (δ_{11} , δ_{22} , δ_{33}) of the chemical shift tensor and the HB contour plots.

An estimate of the principal values of the aromatic envelope can be obtained from the spectrum of Fox River semianthracite which exhibits a clearly-resolved SSB pattern (Figure 9.7). The ratios of the SSB to centreband intensities ($I \pm n/I_0$) were measured from a spectrum obtained with a spinning rate of 2.36 kHz. The ratios are plotted on the HB contour maps of theoretical intensity ratios (Figure 9.9). The values of ρ and μ are measured from the intersection of the contours. The μ and ρ parameters are functions of the principal values (σ_{11} , σ_{22} , σ_{33}) of the chemical shielding tensor:

$$\mu = (\sigma_{11} - \sigma_{33}) / \nu \quad [9.1]$$

$$\rho = (\sigma_{11} - \sigma_{33} - 2\sigma_{22}) / (\sigma_{11} - \sigma_{33}) \quad [9.2]$$

where ν is the spinning frequency (in ppm). The σ -values are converted to the principal values of the chemical shift tensor using the chemical shift of the centreband $\bar{\delta}$, ie

$$\delta_{xx} = \bar{\delta} + \sigma_{xx} \quad [9.3]$$

Figure 9.5: Standard CP/MAS spectra of Ohai coal obtained at four spinning frequencies. a) 2.0 kHz, b) 2.35 kHz, c) 2.8 kHz, d) 3.0 kHz.

Figure 9.6: Standard CP/MAS spectra of Webb (I) coal obtained at four spinning frequencies. a) 1.95 kHz, b) 2.2 kHz, c) 2.5 kHz, d) 2.8 kHz.

Figure 9.7: Standard CP/MAS spectra of Fox River coal obtained at four spinning frequencies. a) 2.1 kHz, b) 2.5 kHz, c) 2.7 kHz, d) 2.85 kHz

Figure 9.8: Results of the application of the program CROMASS to the spectra of a) Ohai, b) Webb (I) and c) Fox River coals.

Figure 9.9: Example of the contour-map method of Herzfeld and Berger using the SSB intensity ratios of the aromatic band in the spectrum of Fox River semianthracite.

The principal values of the chemical shift tensor of the aromatic envelope were found to be:

$$\delta_{11} = 254 \text{ ppm}, \delta_{22} = 98 \text{ ppm}, \delta_{33} = 28 \text{ ppm}^{(14)}.$$

The expected SSB distribution at 2.5 kHz MAS frequency is calculated from these tensor values:

	I_{-3}	I_{-2}	I_{-1}	I_0	I_{+1}	I_{+2}	I_{+3}
% Intensity	1	5	29	36	17	9	2

The Fox River tensor values are not "true" tensor values as a range of structures, with differing chemical shift tensors, contribute to the aromatic envelope. The Fox River chemical shift tensor will not be appropriate for the prediction of SSB intensity in the spectra of low rank coals as the types of aromatic carbon present in a semianthracite are not identical to those present in a lignite or subbituminous coal.

The SSB intensities for individual signals in the coal spectrum can be estimated from the chemical shift tensors of model compounds that contain the relevant carbon functionality. For example, the SSB intensity distribution of the "diphenol" signal at 144 ppm should be similar to that exhibited by the signal assigned to the phenolic carbons of Dopa (Figure 9.10). Six spectra of Dopa were obtained at spinning rates between 2.0 and 2.8 kHz. The ρ and μ values were estimated from the signal area ratios of the centreband and SSBs in each spectrum. The average principal values were calculated to be:

$$\delta_{11} = 231 \text{ (SD = 2) ppm}, \delta_{22} = 132 \text{ (SD = 5) ppm}, \delta_{33} = 70 \text{ (SD = 3) ppm}.$$

The expected SSB intensity distribution at a spinning rate of 2.5 kHz will be:

	I_{-3}	I_{-2}	I_{-1}	I_0	I_{+1}	I_{+2}	I_{+3}
% Intensity	0	3	19	58	15	4	1

The HB method was also applied to the phenol signal (156 ppm) in three Tyrosine spectra run at spinning rates between 2.1 and 2.6 kHz (Figure 9.11). The average principal values were:

$$\delta_{11} = 263 \text{ (SD = 5) ppm}, \delta_{22} = 148 \text{ (SD = 5) ppm}, \delta_{33} = 58 \text{ (SD = 4) ppm}$$

which result in an SSB intensity distribution of:

Figure 9.10: Spectrum of Dopa showing the "diphenol" signal at 144 ppm and associated SSB signals (*).

Figure 9.11: Spectrum of Tyrosine showing the phenol signal at 156 ppm and associated SSB signals (*).

	I ₋₃	I ₋₂	I ₋₁	I ₀	I ₊₁	I ₊₂	I ₊₃
% Intensity	1	6	19	46	22	5	1

Despite the fact that both signals are assigned to hydroxy-substituted aromatic carbon, the principal values of the chemical shift tensor are different. It should be possible to predict, and therefore compensate for, the SSB intensity distribution based on the signal assignments of the coal spectrum.

9.3 DOFIC

The use of model compound, chemical shift anisotropy data to calculate the SSB intensity patterns observed in coal was introduced on a small scale by Burgar⁽¹⁵⁾. The program DOFIC (Determination of Functionalities in Coal) is based on the same principles but includes a far greater variety of carbon functionalities and results in the full simulation of the NMR spectrum. The background and development of DOFIC is described at length in a Chemistry Division report⁽¹⁶⁾ (Appendix 8.5) and will not be repeated in this text.

The model compound database used by DOFIC was based on the large amount of published chemical shift tensor data^(17,18). This data was supplemented by the chemical shift tensor data of the tyrosine compounds and a substantial number of lignin model compounds⁽¹⁹⁾. There are, however, many types of carbon functionality that may be present in the coal but are not represented in the model compound database. The scope of DOFIC could be expanded by a comprehensive chemical shift tensor survey of model compounds.

The essence of the DOFIC method for spectrum simulation is shown in Figure 9.12. The appropriate SSB intensity patterns are selected from the database and fitted to the coal spectrum. The complete DOFIC simulations of the spectra of the Fox River, Webb, Ohai and Mataura coals are shown in Figure 9.13 to 9.16. The intensity distributions observed in the coal spectra are adequately simulated from the SSB patterns in the present database. The difference spectrum should reflect the S/N ratio of the experimental spectrum. Minor deviations from this ideal occur when the

BRAZIERS

Figure 9.12: Diagram showing the method of spectrum simulation used in DOFIC. Experimental spectrum of Braziers subbituminous coal shown as a dashed line. Contributing SSB intensity patterns for the main aromatic (128 ppm) and aliphatic (30 ppm) bands shown as solid lines.

Figure 9.13: Simulation using DOFIC of the spectrum of Fox River semi-anthracite. Experimental (dashed line), simulated (solid line) and difference (dotted line) shown.

Figure 9.14: Simulation using DOFIC of the spectrum of Webb (I) coal. Lines as for Figure 9.13.

Figure 9.15: Simulation using DOFIC of the spectrum of Ohai subbituminous coal. Lines as for Figure 9.13.

MATAURA

Figure 9.16: Simulation using DOFIC of the spectrum of Mataura lignite. Lines as for Figure 9.13.

observed line-widths differ from the representative line-widths (see Appendix 8.5).

9.4 Summary

In 1983 it was stated that the use of the HB method for the compensation of SSB signals was "not yet practical for materials as complex as coals"⁽⁷⁾. The success of DOFIC indicates that the automatic analysis of intensity distributed into SSBs, based on model compound data, is a viable technique for overcoming the "otherwise troublesome spinning sidebands"⁽¹⁵⁾.

DOFIC was designed for carbon-13 NMR at 50.3 MHz and a MAS frequency of 2.5 $\pm$ 0.1 kHz, but this is not a limiting factor. The SSB intensity patterns of the model compounds can be re-calculated for other combinations of operating frequencies using the HB method.

The deconvolution of the spectrum performed by DOFIC results in a quantitative functional group analysis of the coal. An example of the typical DOFIC output is shown in Figure 16 of Appendix 8.5. DOFIC was applied to the spectra of 57 New Zealand coals and 10 Australian coals. The results will be discussed in the next chapter.

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10.0 CHARACTERISATION OF AUSTRALASIAN COALS

10.1 Introduction

It has been established that, although not all of the carbon is visible to NMR, the signals that are observed in the NMR spectrum appear to be representative of the range of carbon functionalities present in the coal. Therefore, the signal area will provide the quantitative information necessary to characterise the Australasian coals.

10.2 Apparent Aromaticity

The advent of solid state NMR allowed the direct measurement of the aromaticity of coal. The aromaticity, f_a , is the most basic signal area measurement and has become the "most common type of information provided by ^{13}C CP/MAS NMR"(1).

The aromaticity of coal is theoretically defined as the fraction of the total carbon that is contained in aromatic rings. However, the NMR aromaticity does not necessarily represent this ratio. There are several errors that are inherent in the measurement of f_a by integration of the signals. For this reason, the parameter measured by dividing the spectrum at 65ppm is called the "apparent aromaticity", f_a' (2,3).

10.2.1 Errors in f_a' measurements

The systematic errors in the f_a' determination have been discussed previously(1) and will only be summarised here.

The labelling of the signal area $> 65\text{ppm}$ as being "aromatic" is an over-simplification as the signals of other sp^2 -hybridised carbon are also found in this chemical shift range. The presence of olefinic and carbonyl resonances is ignored which will result in erroneously high f_a' values for coals that contain significant amounts of these carbon types. Several workers (3,4) have corrected the f_a' values for the carbonyl contribution by excluding signal intensity at chemical shifts $> 165\text{ppm}$. This correction cannot be applied to the f_a' values of these Australasian coals because of the overlap of a large SSB with the chemical shift region of the carbonyl resonances.

The boundary was specifically placed at 65ppm in order to include the first-order, low-frequency SSB in the "aromatic" fraction. However, the

signals of oxygen substituted sp^3 -hybridised carbon are located in the chemical shift region between 65ppm and 105ppm. Therefore, the f_a' values of coals containing aliphatic ethers and alcohols will also be overestimated. The choice of a boundary at a higher frequency value would result in a larger error because of the incorporation of the SSB signal in the "aliphatic" fraction. The second and third order low-frequency SSB signals of the aromatic bands are unavoidably included in the "aliphatic" fraction. This problem is also evident in published aromaticity estimations(2,3,5-10).

The chemical shift tensor determined for the aromatic band of the Fox River spectrum (Section 9.2.4) can be used to predict the error in f_a' . It was estimated that 9% and 2% of the aromatic carbon intensity is contained in the second- and third-order low-frequency SSBs, respectively. Thus, 11% of the aromatic signal intensity is included in the "aliphatic" fraction. This figure could be used to correct the f_a' values. However, this assumes that the chemical shift tensor values of the semianthracite are the same as those of a lignite which is not necessarily true.

Miknis et al⁽³⁾ attempted to correct the f_a' values for the contributions of SSB intensity to the aliphatic fraction. They also renormalised the signal area to exclude the carboxylic resonances. The corrected aromatic and aliphatic carbon percentages were found to be "essentially equivalent" to the uncorrected values; ie the errors in each fraction were balanced.

10.2.2 f_a' and Relaxation Behaviour

The lignite relaxation behaviour, studied in Chapter 8, can also be used to assess the influence of relaxation on the f_a' values because the change in aromatic and aliphatic signal areas was measured.

The f_a' values are plotted against the delay time and the contact time in Figure 10.1. The f_a' values decrease as the recycle delay is increased (Figure 10.1a) which reflects the faster spin-lattice relaxation rate of the aromatic protons. The f_a' values of the Roxburgh lignite exhibit a greater decrease than the values of the Mataura lignite. This trend is the result of the different magnitudes of the aliphatic proton relaxation rates. The ratios of the aliphatic to aromatic T_{1H} values are 2.6 and 1.6 for the Roxburgh and Mataura lignites, respectively. Therefore, the f_a'

Figure 10.1: Dependence of the apparent aromaticity values on the a) delay time, b) contact time. f'_a values are for Matura (solid symbols) and Roxburgh (III) (open symbols) lignites.

values of the Mataura lignite are closer to the "true" f_a' values at shorter D_1 values. The f_a' values stabilise at 0.54 (± 0.03) and 0.62 (± 0.02) for the Roxburgh and Mataura lignites, respectively. (The errors involved in these f_a' determinations are greater than those of the standard f_a' values due to the measurement of very small signal areas.) Wilson *et al*⁽¹¹⁾ reported f_a' values that were independent of recycle times greater than 0.3s.

The f_a' values increase with increasing contact time (Figure 10.1b). The initial steep rise reflects the fact that, for both lignites, the cross-polarisation rate of the aliphatic carbon is three times faster than that of the aromatic protons. This trend has been observed by several workers^(3,6,11,12). The rate of increase slows as the $T_{1\rho_H}$ effects influence the f_a' values. The overall increase in f_a' values at contact times greater than 1.0ms reflects the slightly faster decay of the aliphatic intensity. The plateau in f_a' , noted by other workers^(11,12) was not observed. The very low total signal intensity observed at long contact times produces the considerable amount of scatter in the corresponding f_a' values.

10.2.3 f_a' and Coalification

Van Krevelen described coalification as "a process in which the degree of condensation and aromaticity of the starting material increase continuously"⁽¹³⁾. The changes in the f_a' values of thirty-one coals, that span the range of rank found in New Zealand have been discussed in detail⁽¹⁾. That particular suite of coals has now been expanded to include 57 New Zealand and 10 Australian coals. The plot of the remeasured f_a' values (Table 10.1) against the carbon content (Figure 10.2) shows the large amount of scatter that was previously observed by Newman *et al*⁽¹⁾, particularly at low carbon contents.

A correlation between the fixed carbon content and the aromatic carbon content has been noted by several groups^(1,3,14). The aromatic carbon content is defined as;

$$\% \text{aromatic C} = f_a' \times \%C(\text{daf}) \quad [10.1]$$

The corresponding plot for the Australasian coals is shown in Figure 10.3. The significance of this correlation ($R = 0.97$) has been the subject of some discussion⁽¹⁴⁻¹⁷⁾. The trend is said to indicate that the non-volatile fraction of the coal is almost entirely aromatic and also, that

TABLE 10.1 : "APPARENT AROMATICITIES"

COAL	%C (daf)	%FC (daf)	f _a ' (+/-0.02)	COAL	%C (daf)	%FC (daf)	f _a ' (+/-0.02)
Hawkdun	68.0	42.8	0.62	Island Block	79.7	57.3	0.67
Idaburn	68.2	45.6	0.63	Strongman	80.0 ^a	57.0	0.67
Roxburgh I	69.9	38.1	0.52	Kiwi	80.9	60.7	0.68
Roxburgh II	67.1 ^a	39.4	0.58	Topline	-	57.6	0.66
Roxburgh III	67.1 ^a	38.6 ^a	0.54	Harrison	80.2 ^a	57.1	0.69
Mataura	68.6	46.0	0.63	Moody Creek	81.3 ^a	54.9	0.66
Ashers Waituna	66.7	42.8 ^a	0.66	Echo	80.6	57.3	0.67
Waimumu I	68.4	44.0	0.65	United	81.7	56.7	0.64
Waimumu II	68.9	44.2 ^a	0.64	Charming Creek	79.2 ^a	55.4	0.68
Waimumu III	68.8	44.9 ^a	0.61	Escarpment	82.3	60.3	0.64
Waimumu IV	69.4	44.9 ^a	0.62	Liverpool	85.5	61.4	0.69
Wangaloa	72.6	50.9	0.66	Webb I	84.0	63.6	0.69
Kai Point	70.7	49.7	0.67	Webb II	86.4	62.5	0.71
Braziers	72.2	54.7	0.69	Webb III	84.3	61.4	0.73
Kopuku	72.8	52.3	0.61	Webb IV	84.5 ^a	65.4	0.70
Kawhia	69.3	47.0 ^a	0.64	Stockton I	86.8 ^a	67.8	0.74
Ohinewai	72.4	53.2	0.66	Stockton II	85.3	64.7	0.72
Garden Creek	-	49.4	0.62	Sullivan	84.6	66.1	0.71
Weavers	73.7	54.6	0.66	Sullivan N I	86.4	68.1	0.72
Squires Creek	-	56.2	0.71	Sullivan N II	87.6	68.6	0.75
Mahons	-	53.9	0.68	Webb V	86.3	72.6	0.74
Maori Farm	75.6 ^a	54.0	0.66	Rockies II	86.2 ^a	70.7	0.74
Waipuna	74.9 ^a	54.6	0.70	Rockies I	88.3	74.2	0.77
Mokau	73.8	49.6 ^a	0.60	Fox River	90.6	89.8	0.83
Ohura	-	49.4	0.64	Morwell	70.4 ^a	50.7	0.67
Huntly East	75.1	55.4	0.66	Loy Yang	69.6 ^a	50.3 ^a	0.68
Huntly West	74.0	52.5 ^a	0.63	Great N. Seam	82.9 ^a	64.7 ^a	0.72
Heaphys	73.7 ^a	54.2	0.64	Wallerah	82.1 ^a	65.4 ^a	0.71
Terrace	76.1 ^a	55.3	0.67	Liddell	82.0 ^a	60.2	0.68
Ohai	75.2	61.4	0.69	Tongarin	79.2 ^a	53.9 ^a	0.59
Mulken	74.4 ^a	55.5	0.66	Bulli	87.1 ^a	76.4	0.77
Snowline	79.5	57.0	0.69	Wongawilli	87.1 ^a	69.9 ^a	0.77
Alpine	-	55.5	0.67	Blair Athol	81.6 ^a	66.8 ^a	0.74
				Yarrabee	87.8 ^a	88.1	0.86

(a) Estimate only. See Appendices 1 and 2.

Figure 10.2: Plot of f_a' values against carbon content. Data for lignites ($\bullet$), subbituminous ($\blacksquare$), hvB,C bituminous ($\blacktriangledown$), hvA bituminous ($\blacktriangle$), medium volatile bituminous and higher ($\blacklozenge$) ranks. Open symbols represent data for Australian samples.

Figure 10.3: Plot of the % aromatic carbon derived from the f_a' values against the fixed carbon content. Symbols as for Figure 10.2.

the volatile fraction is predominantly aliphatic. The positive value of the intercept suggests that approximately 7% of the coal is in the form of volatile aromatic material which is consistent with the loss of small aromatic products upon strong heating⁽¹⁵⁾. However, Solomon⁽¹⁷⁾ noted that this conclusion could be fortuitous. He suggested that aromatic carbon is trapped in the thick bed used in the measurement of volatile matter. Thus, the correlation is the result of the method of determination rather than the structure of the coal.

The measurement of f_a' provides a rough estimate of the degree of coalification. However, the discussion of trends in, and influences on, f_a' will not be extended further in this section as the analysis of the coal spectrum by DOFIC will provide an estimate of the aromaticity which is not subject to most of the systematic errors inherent in f_a' determination.

10.3 Area Increments

The signal area of the coal spectra can be divided into area increments for quantitative study. Such a method was employed by Newman and Davenport⁽¹⁸⁾ to investigate correlations between certain chemical shift regions of lignite spectra and the yields of products from fluidised-bed pyrolysis. A PASCAL program (Appendix 7.2) was written to automate this procedure and to produce "yield-correlation spectra"⁽¹⁸⁾.

The approach has proved useful for providing an indication of the quantitative properties of coals but suffers from, for example, the problem of SSB overlap with centrebands which may disguise the presence of strong correlations. The wider application of the correlation program will not be discussed as, once again, the DOFIC procedure is free of such problems and should provide more reliable quantitative results.

10.4 Characterisation of Coals by the DOFIC Procedure

The results of the DOFIC analysis of the spectra of the Australasian coals are tabulated in Appendix 6. The coals are assigned to four approximate groups during the DOFIC procedure. These groups, or "ranks", are loosely correlated with the ASTM ranks in the following way;

DOFIC "Rank"	ASTM Rank
Low	Lignites
Medium-low	Subbituminous
Medium-high	High volatile bituminous B,C and some A
High	High volatile bituminous A to semianthracite.

These DOFIC "ranks" will be used in the discussion of data generated by the program.

10.4.1 The Aromaticity f_a

The aromaticity value calculated by DOFIC is the most accurate estimate of the "true" aromaticity that can be provided by solid state NMR. Hence there is no "''" attached to the abbreviation. One systematic error remains in the estimation of f_a . The contribution of signals of olefinic carbon to f_a cannot be estimated. These signals are hidden beneath the main aromatic band and their SSB intensity distribution is very similar to the SSB pattern of aromatic carbon⁽¹⁹⁾. It is assumed that the contribution of olefinic intensity to the aromatic envelope is small, in order to assess the aromaticity of the carbon.

The f_a -values are plotted against the carbon content in Figure 10.4. This plot is drawn on the same scale as the corresponding f_a' diagram (Figure 10.2). Two points are evident when the graphs are compared;

- i. The scatter in the f_a values is very similar to that observed in the f_a' -values.
- ii. The range of f_a -values (0.46 to 0.94) is considerably larger than that observed for the f_a' -values (0.52 to 0.83).

The differences in the range of values can be analysed further. The f_a -values of the low rank coals tend to be lower than the f_a' -values, while the reverse is true for the higher rank coals. This trend is summarised in Table 10.2 and arises from the systematic errors in f_a' . The low rank coals contain large amounts of carboxylic carbon and oxygen-substituted aliphatic carbon. The signal intensity of both of these carbon types is included in f_a' but is excluded from f_a . The discrepancy between the two aromaticity values of the high rank coals is caused by the exclusion of the intensity of the second and third order low-frequency SSBs from the f_a' -value but incorporation of this intensity in the f_a -value.

Figure 10.4: Plot of the corrected aromaticity derived using the DOFIC method of analysis. Symbols represent the four "DOFIC ranks", "low" (●), "medium-low" (■), "medium-high" (▲), "high" (◆). Open symbols represent Australian samples.

TABLE 10.2 : AVERAGE AROMATICITY VALUES

	Nos. ^a	Average f_a'	Range	Average f_a	Range
Low	11	0.61 (0.04) ^b	0.52 -0.66	0.55 (0.06)	0.46 -0.66
Medium-high	15	0.67 (0.02)	0.64 -0.74	0.74 (0.03)	0.71 -0.82
Medium-low	21	0.66 (0.03)	0.61 -0.71	0.67 (0.03)	0.61 -0.74
High	20	0.73 (0.05)	0.59 -0.83	0.82 (0.06)	0.67 -0.94

(a) Nos. = Number of coals for which data averaged

(b) SD = Standard deviation

The wider range of aromaticity values obtained using DOFIC can also be seen in Figure 10.5, in comparison with Figure 10.3. The range of aromatic carbon contents has increased, particularly at higher ranks. It is interesting to note that the intercept of the best-fit line is now negative (-9.5%) and can be taken to indicate that some aliphatic carbon is included in the fixed carbon content.

Studies have shown that the aromaticity values, of low rank coals in particular, are sensitive to the depositional conditions^(7,20). The maceral contents of coals often reflect the original environment of the coal. For example, the high exinite contents of the Central Otago lignites are the result of degradation in a freshwater environment^(22,23). Petrographic data were taken from Professor Black's studies of New Zealand coals⁽²⁴⁾. Representative maceral data for the Australian coals were obtained from the same sources as the analytical data^(25,26). In general, Australian coals tend to have low exinite contents. The New Zealand coals with high exinite contents include Roxburgh (lig), Mokau (sub) and United (hvAb). The effect of the exinite (liptinite) content on the aromaticity values is shown in Figure 10.6. It is evident that coals containing high quantities of exinite exhibit lower f_a -values than the average observed for coals of the same carbon content. This trend is consistent with the generally low aromaticity of the exinite macerals^(13,27,28).

It must be emphasised that the petrographic data are for samples from the same localities and not for the actual samples studied by NMR. A perfect correlation cannot be expected. For example, the maceral analysis reported for Tangorin coal⁽²⁵⁾ suggests that the exinite content of this Australian coal is not unusual (8%). However, the spectrum obtained for the Tangorin sample exhibits a very intense aliphatic envelope for a coal of high volatile A bituminous rank ($f_a = 0.67$).

The aromaticities for several of the high rank Australian coals are high in comparison with the f_a -values of New Zealand coals with equivalent carbon contents (Figure 10.4). The maceral analyses of coals from the same areas⁽²⁵⁾ indicate that the inertinite contents of these samples may be very high (up to 65%!). These high inertinite contents have been attributed to the nature of the coal forming flora⁽²⁹⁾. Permian flora were susceptible to "dessication and oxidation" during the peat-forming process because of inherently low contents of protective resins and waxes. Semi-fusinite, which has characteristics intermediate between vitrinite and

Figure 10.5: Plot of % aromatic carbon derived from the f_a values against the fixed carbon content. Symbols as for Figure 10.4.

Figure 10.6: f_a values of coals for which petrographic analyses were available. Symbols represent: exinite (mmf) $\geq 15\%$ (●), $15\% > \text{exinite} > 10\%$ (◐), inertinite/vitrinite ratio > 0.4 (○).

fusinite^(24,30), is the dominant inertinite maceral in the Permian Australian coals⁽²⁵⁾. NMR studies have shown that high aromaticities are exhibited by vitrinite and inertinite macerals in general^(27,28), and by fusinite⁽¹⁵⁾ in particular. Therefore, it is not surprising to observe relatively high aromaticities in coals with high inertinite contents (Figure 10.6). An "anomalously high f_a value" has also been observed for an inertinite rich low rank coal⁽³¹⁾. None of the New Zealand coals studied were reported to have inertinite contents greater than 9%⁽²⁴⁾.

The aromaticities of separated macerals have been shown to correlate with the atomic H/C ratio⁽³¹⁾. This correlation would also be expected to hold for coals as aromatic systems contain less hydrogen than aliphatic structures⁽¹⁾. Several workers have observed some degree of correlation between the aromaticity and the H/C ratio^(1,4,6,8,16,32). The plot for the Australasian coals is shown in Figure 10.7. The shape of the graph suggests an explanation for the fact that a "smooth correlation"⁽⁸⁾ through to "considerable scatter"⁽¹⁾ have been observed previously.

For high rank coals ($f_a > 0.75$) a correlation ($R = 0.960$) is observed between the aromaticity and the H/C ratio. This trend is similar to the smooth correlation of Maciel *et al*⁽⁸⁾ and suggests that both parameters vary uniformly at high levels of coalification. However, for coals of lower aromaticity, the f_a -values show no correlation with the H/C ratio. Several factors could contribute to the scatter.

i. Low rank coals contain large amounts of carbon functionalities, other than aromatic structures, that have lower H/C ratios than aliphatic structures. High quantities of aliphatic alcohols and ethers, and carboxylic groups would lower both the H/C ratio and the aromaticity.

ii. The degree of oxygen-substitution of the aromatic rings is very high in lower rank coals. This fact would result in low H/C ratios but would not affect the aromaticity of the coal. The f_a -values would not be expected to correlate with the oxygen contents as it is only the oxygen bonded to the aromatic rings that would affect the aromaticity. The f_a -values show a slight correlation with oxygen content (Figure 10.8) but no better a relationship than that exhibited with the carbon content. In other words, the oxygen contents of these and other⁽¹⁶⁾ coals are only reflecting the degree of coalification not the aromatic structure.

The two points suggest that the aromaticities and H/C ratios are highly influenced by the structures that contribute to the low rank coals.

Figure 10.7: Plot of f_a against the atomic H/C ratio. Line is the best fit for data with $f_a \geq 0.75$. Symbols as for Figure 10.4.

Figure 10.8: Plot of f_a against the oxygen content. Symbols as for Figure 10.4.

Thus, coals of similar origin, and therefore with similar contributing structures, would exhibit H/C ratios and f_a -values that were determined by the effects of coalification only. The aromaticities of a "sedimentologically homogeneous series"⁽¹⁶⁾ of samples increased progressively with the H/C ratio but even these values exhibited considerable scatter. The trends in f_a -values indicate that the aromaticity is not a simple function of "rank" but is determined by a complex combination of source and coalification factors.

10.4.2 The Carbon Functionalities

The results of the DOFIC analysis of the spectrum includes a list of the intensities of each signal and therefore, the amount of carbon present in each type of functionality. The qualitative changes in the coal spectra that have been observed with increasing rank can now be studied on a quantitative basis.

10.4.2.1 The Signals of Non-aromatic Carbon

The intensity of the main aliphatic signal can be seen to decrease in the spectra of the coals of increasing rank shown in Chapter 5. This decrease is also observed when the quantitative measurement of the intensity in the polymethylene signal is plotted against the carbon content (Figure 10.9). The scatter observed in the values for low rank coals has a similar origin to the diversity shown in the f_a -values. Greater than 20% of the carbon content of Roxburgh lignites is present in polymethylene chains. Similarly, the figure of 16% measured for the Mokau sample is significantly higher than the values observed for other subbituminous coals.

The two Australian brown coals contain the lowest amounts (<7%) of polymethylene carbon measured for all of the lignites and all, but one, of the subbituminous coals. This observation is consistent with the results of a study of signal height ratios in low rank coal spectra⁽²¹⁾. Representative maceral data⁽²⁶⁾ for the Morwell and Loy Yang samples show that the liptinite contents are not unusually low, at 6.4% and 7.4%, respectively. The low polymethylene carbon contents could be explained if the liptinite content of the brown coals was derived mainly from cyclic or branched aliphatic structures. Australian brown coals are known to contain large amounts of "resin drops and amber fragments"⁽⁷⁾. The NMR spectra of

Figure 10.9: Plot of the intensity contained in the polymethylene signal against carbon content. Numbers in brackets represent the chemical shift of the signal. Symbols as for Figure 10.4.

brown coal resin⁽³³⁾ and resinite from lignite (Chapter 5) contain a broad range of aliphatic signals.

Variations in the aliphatic signals observed for different exinite macerals are documented. Comparison of alginite and sporinite spectra⁽¹⁵⁾ indicates that the type of exinite maceral present may be more important than the overall quantity of this maceral group. It would therefore be expected that, for coals with a common exinite source, the polymethylene signal would decrease uniformly with rank. Dereppe *et al*⁽⁴⁾ observed a "gradual decrease" in this resonance relative to the other aliphatic signals in their spectra of a series of samples ranging from lignites to bituminous rank.

The intensities of the "other" aliphatic carbon signals, at chemical shifts <50ppm, are shown in Figure 10.10. This sum includes the intensity for all aliphatic carbon in branched or terminating structures. The decrease at higher ranks occurs in parallel with the trend in the polymethylene signal and reflects the overall loss of aliphatic structures with increasing coalification.

The initial increase in this value could be due to several processes. The polymethylene chains may be splitting to produce more branched structures. However, the amount of carbon in the polymethylene chains does not alter significantly between the lignite and subbituminous ranks. The values for the Central Otago lignites are the exception to this generalisation but the low values observed in Figure 10.10 are not confined to these lignites. The average sums of intensities for the Central Otago and Southland lignites are 15.1% (SD = 3.2%) and 14.9% (SD = 1.0%), respectively. Therefore, it is only the amount of carbon in the polymethylene chains that distinguishes the aliphatic content of the Central Otago lignites from the Southland lignites.

The remaining processes that might cause the initial increase observed in Figure 10.10 involve the oxygen-substituted aliphatic carbon. Deoxygenation of these aliphatic functionalities may result in the formation of structures that would contribute to the resonances in question. Alternatively, the complete loss of cellulose material from the coal would result in the concentration of the more resistant aliphatic structures, such as resins, which contribute intensity to these "other" aliphatic resonances.

Figure 10.10: Plot of intensity contained in signals of "other" hydrogen substituted aliphatic carbon.

The signal intensities plotted in Figure 10.11 quantify the changes observed in Chapter 5 for the signals of oxygen-substituted carbon at 56ppm, 74 ppm and 177 ppm. A large amount of scatter is evident in these signal intensities. This scatter is reflected in the total cellulose content calculated by DOFIC for the low rank coals. The total content of cellulose-like structures in the lignites varied between 4% and 16% which is a wide range for coals of apparently similar rank. This variation can be attributed to localised differences in the depositional environment. For example, differences in the cellulose and lignin content of brown coal woods has been assigned to variations in "edaphic conditions"⁽²⁰⁾; ie are a function of acidity and oxidising conditions of the peat swamp.

The clear distinction between the intensity data for the lignites and subbituminous coals is consistent with the trends observed in signal heights at 56ppm and 74ppm⁽¹⁹⁾. The data for the Australian brown coals are intermediate between those measured for the two ranks of New Zealand coals - a characteristic that was predicted by the study of signal height ratios⁽²¹⁾.

The amount of intensity observed in the signal assigned to carboxylic acids and salts gradually decreases with increasing rank. This trend indicates that the carbonyl functionalities are more resistant to coalification processes than the methoxyl and cellulose groups. The DOFIC results for the spectrum of the Kauri Peat (63.1 %C daf) support this pattern of relative stability. The amounts of intensity in the signals at 56 ppm and 74 ppm were 7.2% and 6.6%, respectively, which are considerably larger than the respective lignite values. (The total cellulose content of the peat was 21.1%.) The intensity in the signal at 177 ppm was 3.8% which is similar in magnitude to the carboxylic acid and salt content of lignites. Dereppe *et al*⁽⁴⁾ also observed that the signals assigned to aliphatic carbons linked to oxygen decreased rapidly in the peat stage while intensity assigned to carbonyl groups was found in coals containing up to 80% C (maf).

Figure 10.11: Plot of intensities contained in the signals assigned to non-aromatic, oxygen-substituted carbon. a) Cellulose signal, b) methoxyl signal, c) signal of carboxylic acids and salts.

10.4.2.2 The Signals of Aromatic Carbon

The signals assigned to aromatic carbon can be divided into three types - carbon bonded to hydrogen, to alkyl groups or other aromatic rings and to oxygen.

The total intensity measured in the signals of aromatic C-H is shown in Figure 10.12. An overall increase in the aromatic C-H content was observed with increasing rank which is consistent with the overall increase in aromaticity. However, the scatter in this data is very large. The fact that the low rank coals contain the lowest quantity of aromatic C-H groups reflects the high degree of oxygen-substitution of the aromatic rings.

It might be expected that, at very high ranks, the amount of aromatic carbon bonded to hydrogen would decrease as the size of the polycyclic aromatic structures increased. Any decrease is masked by the scatter in the data. However, the data for the Fox River and Yarrabee semi-anthracites are low (48.6% and 52.6%, respectively) in comparison with the data for other high rank coals. The formation of extensive polycyclic aromatic structures must occur at ranks higher than semianthracite.

The amounts of aromatic carbon bonded to either alkyl groups or adjacent aromatic rings are shown in Figure 10.13. The values for the lower coal ranks indicate that very little of the aromatic rings are substituted by aliphatic or aromatic carbon. The intensity data rise, in a non-linear manner, with increasing carbon content; ie the rate of structural condensation is greater at higher coal ranks.

A similar pattern emerged in the quantities of aromatic carbon that are substituted by oxygen functionalities (Figure 10.14). The intensity data for the lignite and subbituminous coals are very similar. The rate of loss of these oxygenated functionalities increases greatly at higher ranks.

The relative amounts of the different aromatic carbon functionalities are summarised in Figure 10.15 as a function of the total aromatic carbon. The major change in the carbon content of lower rank coals occurs in the non-aromatic fraction of the coal; ie the loss of carbon in cellulose, methoxyl and carboxylic functionalities. However, at higher coal ranks the loss of aliphatic carbon occurs in parallel with a dramatic change in the composition of the aromatic carbon.

Figure 10.12: Plot of intensity contained in signals of hydrogen substituted aromatic carbon.

Figure 10.13: Plot of intensity contained in signals of aromatic carbon substituted by an alkyl group or another aromatic ring.

Figure 10.14: Plot of intensity contained in signals of oxygen substituted aromatic carbon.

Figure 10.15: Summary of the proportions of aromatic carbon relative to the total fraction of aromatic carbon (f_a).

The carbon types are not the only form of functionality that can be investigated by NMR. The signal intensities also provide information about the range of hydrogen and oxygen functionalities present in the coal.

10.4.3 The Hydrogen Functionalities

The amount of hydrogen in the coal can be estimated from the carbon distribution⁽¹⁹⁾. Hydrogen is associated with three main functionalities in the coal. The major fraction of the hydrogen is contained in aliphatic structures (Figure 10.16a). Significant amounts of hydrogen are also found in the aromatic structures (Figure 10.16b), and bonded to oxygen in phenols (Figure 10.16c). The remaining hydrogen ("other") is associated with aliphatic ethers and alcohols, and carboxylic acids (Table 10.3).

There is considerable scatter in the quantities of aliphatic hydrogen. This variation can be attributed to the influence of the source material (eg as reflected by the exinite content) on the proportion of aliphatic material in the coal.

The increase in the amount of hydrogen bonded to aromatic carbon reflects the overall increase in this carbon functionality (Figure 10.12). However, the rise is very steady in comparison with the scatter observed in the corresponding data for aromatic carbon.

The amount of hydrogen present in phenols decreases with rank reflecting the overall loss of oxygenated aromatic functionalities. The low values for the lignites can be attributed to the presence of methoxyl substituted aromatic carbon. (This will be discussed in the next section.)

The proportions of the different types of hydrogen functionality are plotted cumulatively in Figure 10.17.

The hydrogen functionalities can be described by the ratio of aromatic to aliphatic hydrogen, H_{Ar}/H_{Al} (Figure 10.18). The ratios reflect the rapid decrease in the aliphatic hydrogen content at high ranks. The scatter can be attributed to the source influences in parallel to the variation in f_a results. Coals with high exinite contents exhibit low hydrogen ratios while the reverse is true for coals with high inertinite contents.

The distribution of hydrogen in vitrinite concentrates has been studied by FTIR techniques^(34,35). The intensities of certain bands,

Figure 10.16: Quantities of hydrogen functionalities in the coals estimated from the distribution of carbon functionalities. a) Hydrogen bonded to aliphatic carbon (not oxygen-substituted), b) hydrogen bonded to aromatic carbon and c) hydrogen bonded to oxygen in phenol groups.

TABLE 10.3 : HYDROGEN FUNCTIONALITIES

COAL	H _{Al}	H _{Ar}	H _{ph}	H ^T	COAL	H _{Al}	H _{Ar}	H _{ph}	H ^T
Hawkdun	3.8	2.0	0.6	7.4	Island Block	3.9	3.1	0.7	7.7
Idaburn	3.7	2.0	0.6	7.5	Strongman	3.8	3.0	0.6	7.5
Roxburgh I	4.9	1.7	0.5	8.1	Kiwi	3.5	3.4	0.6	7.5
Roxburgh II	4.7	2.1	0.6	8.1	Topline	3.8	3.0	0.8	
Roxburgh III	4.3	1.7	0.4	7.7	Harrison	3.2	3.2	0.7	7.1
Mataura	3.5	2.2	0.7	7.5	Moody Creek	3.8	3.1	0.6	7.4
Ashers Waituna	2.3	2.3	0.7	6.6	Echo	3.6	3.3	0.7	7.6
Waimumu I	2.7	1.9	0.6	6.9	United	3.8	3.3	0.6	7.7
Waimumu II	2.6	2.1	0.6	6.6	Charming Creek	4.3	3.5	0.5	8.3
Waimumu III	3.0	2.2	0.7	7.1	Escarpment	3.4	3.3	0.6	7.3
Waimumu IV	3.2	1.8	0.6	6.9	Liverpool	3.5	3.8	0.4	7.7
Wangaloa	3.5	2.5	0.9	7.2	Webb I	3.3	4.0	0.4	7.7
Kai Point	3.1	2.6	1.1	7.2	Webb II	3.2	3.8	0.4	7.4
Braziers	2.7	2.7	1.0	6.8	Webb III	3.1	3.2	0.5	6.8
Kopuku	4.0	2.6	0.9	7.6	Webb IV	3.0	3.8	0.4	7.2
Kawhia	3.3	2.2	0.9	6.9	Stockton I	2.6	3.4	0.4	6.4
Ohinewai	3.2	2.4	0.8	6.8	Stockton II	2.8	3.9	0.4	7.1
Garden Creek	3.7	2.5	1.0	7.5	Sullivan	2.8	3.9	0.4	7.1
Weavers	3.3	2.5	0.8	6.9	Sullivan N I	2.7	4.1	0.2	7.1
Squires Creek	2.6	2.7	1.0	6.6	Sullivan N II	2.5	3.9	0.3	6.7
Mahons	3.5	2.9	0.8	7.3	Webb V	2.5	4.2	0.4	7.1
Maori Farm	3.8	2.5	0.7	7.1	Rockies II	2.9	3.3	0.4	6.6
Waipuna	2.6	2.5	0.8	6.5	Rockies I	2.6	4.5	0.2	7.3
Mokau	5.0	2.7	0.8	8.5	Fox River	1.0	3.8	0.0	4.8
Ohura	3.3	2.6	0.9	7.2	Morwell	2.4	2.6	0.9	6.6
Huntly East	3.2	2.6	0.8	7.0	Loy Yang	2.6	2.7	1.0	6.5
Huntly West	3.7	2.7	0.7	7.5	Great N. Seam	2.7	3.1	0.5	6.3
Heaphys	3.3	2.8	0.9	7.2	Wallarrah	2.5	3.7	0.5	6.7
Terrace	3.3	2.8	0.8	7.2	Liddell	3.3	3.4	0.6	7.3
Ohai	3.0	2.9	0.9	7.0	Tongarin	4.5	2.8	0.4	7.7
Mulken	3.5	3.1	0.8	7.4	Bulli	2.1	2.9	0.2	5.2
Snowline	3.1	3.3	0.7	7.1	Wongawilli	2.0	3.8	0.4	6.2
Alpine	3.0	3.1	0.8	6.9	Blair Athol	2.3	3.8	0.7	6.8
					Yarrabee	1.2	4.0	0.0	5.2

Figure 10.17: Summary of the proportions of hydrogen functionalities relative to the total hydrogen content estimated from the NMR results.

Figure 10.18: Ratio of the quantities of aromatic and aliphatic hydrogen plotted against carbon content.

assigned to aliphatic C-H, aromatic C-H and hydroxyl modes, were calibrated using the hydrogen content from elemental analysis. The FTIR aliphatic hydrogen includes hydrogen bonded to carbon in aliphatic ether and alcohol groups. This hydrogen is included in the "other" NMR hydrogen. Similarly, the hydrogen of aliphatic alcohols is included in the FTIR hydroxyl hydrogen but in the "other" NMR hydrogen. The phenol hydrogen calculated from NMR results is therefore not directly comparable to the FTIR parameter.

The trends in hydrogen functionalities obtained from FTIR and NMR were, in general, similar; ie the aliphatic and phenol hydrogen proportions decrease at high carbon contents while the aromatic hydrogen content increases at higher ranks. However, the NMR results indicate that a much larger proportion of the hydrogen is associated with aromatic rings than is obtained from FTIR results or from proton NMR of coal extracts⁽³⁶⁾. The aliphatic hydrogen contents measured from FTIR⁽³⁵⁾ ranged from 2% to 4% which are consistent with the NMR estimates (Figure 10.16a). The contents of hydroxyl hydrogen were less than 0.5% for vitrinites of greater than 82% carbon content. However, the FTIR derived quantity of aromatic hydrogen reached a maximum of 2.5% which is considerably less than the corresponding NMR maximum of approximately 4% for equivalent carbon contents.

The opportunity to directly compare the hydrogen functionalities estimated by FTIR and NMR is provided in the literature. PSMC vitrinite concentrates have been characterised by both methods^(35,37). The NMR data include the aromaticity and the fraction of non-protonated aromatic carbon, R_{np} . The aromatic hydrogen contents were calculated directly from the NMR data; ie

$$H_{Ar} = (1/12) \times \%C \times f_a (1-R_{np}) \quad [10.2]$$

The aliphatic hydrogen contents were estimated by assuming an aliphatic H/C ratio of 2⁽¹⁹⁾; ie

$$H_{Al} = (2/12) \times \%C \times (1-f_a) \quad [10.3]$$

The remaining hydrogen content was contained in hydroxyl and carboxylic functionalities and could not be estimated from the reported data.

A "good correlation" has been claimed⁽³⁷⁾ between the aromatic hydrogen contents derived from the NMR and FTIR results for nineteen vitrinite samples. However, the two datasets did not exhibit a 1:1

correspondence. In fact the H_{Ar} values estimated from the NMR data were, on average, 1.0% (SD = 0.2%) higher than the corresponding FTIR values. Similarly, the NMR derived H_{Al} values were, on average, 0.6% (SD = 0.4%) higher than the FTIR values. The overall difference between the NMR and FTIR values of the sum ($H_{Ar} + H_{Al}$) was 1.6% (SD = 0.4%). This value is similar to the discrepancy observed between the hydrogen contents of New Zealand coals as estimated by Ultimate and DOFIC analyses⁽¹⁹⁾.

It is not surprising that the FTIR values for total hydrogen content were similar to those from Ultimate analysis as the latter was used to calibrate the former. The ratio H_{Ar}/H_{Al} should therefore provide a better comparison of the NMR and FTIR data. The H_{Ar}/H_{Al} values calculated from the NMR data of the vitrinites range between 0.34 and 1.24. These values are higher than the FTIR derived ratios by an average 0.22 (SD = 0.10). Thus, the NMR results indicate that the FTIR methods are underestimating the aromatic C-H content of coal samples. The correlation observed between the FTIR data and proton NMR measurements of coal extracts⁽³⁵⁾ suggests that the extraction techniques did not remove all of the aromatic material from the coal.

Further evidence for the discrepancy between NMR and FTIR data was recently provided by studies of a selection of New Zealand coals⁽³⁸⁾. An H_{Ar}/H_{Al} value of 2.4 was obtained by FTIR for the Fox River semi-anthracite. NMR analysis resulted in a considerably higher value of 3.8 for a sample from the same source. The FTIR ratio of 0.34 (± 0.08) for a Sullivan West bituminous coal is lower than the average value of 1.54 (± 0.02) obtained for two samples of Sullivan North coal. The observation that the FTIR spectra of lignites contain no detectable aromatic bands (ie $H_{Ar}/H_{Al} < 0.1$) is in contrast to the NMR derived H_{Ar}/H_{Al} ratios for eleven lignites which lie between 0.29 and 0.66.

The viability of the methodologies used to obtain the FTIR data has been a subject of considerable debate^(17,35,38), particularly the use of model compound extinction coefficients. If the suggestion that "the best approach will be to closely compare FTIR and ^{13}C NMR spectra of identical coal samples"⁽³⁸⁾ is followed, then some of the controversy may be resolved.

10.4.4 The Oxygen Functionalities

The oxygen functionalities present in the coal can be estimated from the quantities of carbon directly bonded to oxygen⁽¹⁹⁾. The oxygen functionality data were divided into four types; phenolic (ph), carboxylic (C=O), methoxyl (OCH₃) and cellulosic (cell) oxygen. The changes in the four values with increasing carbon content are shown in Figure 10.19. The trends in the non-phenolic functionalities (Figures 10.19a-c) generally mirror the behaviour observed for the corresponding carbon functionalities (Figure 10.11). Significant amounts of these oxygen types are only observed in the low rank coals. Small amounts of carboxylic oxygen may be present in higher rank coals⁽⁴⁾ but this quantity is difficult to evaluate⁽¹⁹⁾.

The phenolic oxygen present shows a steady decrease at higher ranks (Figure 10.19d), a trend also observed by Snyder *et al*⁽³⁹⁾. The low rank coals contain low quantities of this oxygen type which is consistent with the trends observed in the amount of aromatic carbon bonded to oxygen. This decrease in values for low rank coals is, however, accentuated by the fact that the oxygen present in aryl-methoxyl groups has been separated from the oxygen contained in phenols.

The possible explanations for this initial increase in phenolic oxygen content are essentially the same as those discussed in Chapter 5 to explain the increase in the signal at 154ppm. The loss of easily degraded structures, such as cellulose fragments, between the lignite and subbituminous ranks would result in an overall concentration of the more resistant phenol structures. At the same time, the decomposition of methoxyl groups (and other ether linkages) would produce either isolated phenolic structures (demethoxylation) or "diphenol" structures (demethanation)⁽⁴⁰⁾.

Abdel Baset *et al*⁽⁴¹⁾ studied the phenol content, of coals with greater than 74% carbon, by chemical methods. The relationship that they observed between the phenol and carbon contents is plotted for comparison in Figure 10.19d. The line falls well below the values obtained from analysis of the NMR spectra. The wet chemical methods may be underestimating the phenol content of coals. Alternatively, coals from America may contain lower quantities of phenol functionalities than the Australasian coals.

Figure 10.19: Quantities of oxygen functionalities in the coals estimated from the distribution of oxygenated-carbon functionalities. a) Oxygen present as carboxylic acids and salts, b) oxygen in cellulose or cellulose-like structures, c) oxygen in methoxyl groups, d) phenolic oxygen.

TABLE 10.4 : OXYGEN FUNCTIONALITIES

COAL	ph	C=O	-OCH ₃	O ^T	COAL	O ^{Ta}
Hawkdun	10.2	7.5	1.7	23.7	Mulken	13.7
Idaburn	9.1	6.7	2.3	23.7	Snowline	11.3
Roxburgh I	7.9	9.1	2.0	22.4	Alpine	12.3
Roxburgh II	9.8	8.4	1.9	22.1	Island Block	10.8
Roxburgh III	6.2	9.3	2.3	23.8	Strongman	10.4
Mataura	10.3	5.3	2.4	22.1	Kiwi	10.4
Ashers Waituna	11.3	5.7	2.7	24.1	Topline	12.1
Waimumu I	9.0	8.9	2.9	28.8	Harrison	10.7
Waimumu II	9.2	11.9	2.5	27.9	Moody Creek	9.3
Waimumu III	10.4	5.8	3.3	23.4	Echo	10.5
Waimumu IV	9.5	9.4	2.7	26.8	United	9.9
Wangaloa	12.5	3.6	0.7	18.2	Charming Creek	8.0
Kai Point	17.0	0.0	0.7	19.2	Escarpment	10.3
Braziers	15.5	5.3	0.4	22.6	Liverpool	5.7
Kopuku	14.7	7.0	0.0	21.7	Webb I	7.2
Kawhia	14.3	7.0	0.5	24.0	Webb II	5.7
Ohinewai	12.7	8.2	0.5	22.8	Webb III	8.1
Garden Creek	15.6	3.1	0.7	20.6	Webb IV	6.9
Weavers	11.9	7.9	0.7	21.5	Stockton I	7.1
Squires Creek	16.4	7.3	0.5	25.0	Stockton II	6.8
Mahons	13.5	6.2	0.1	19.8	Sullivan	6.6
Maori Farm	12.0	8.5	0.0	20.5	Sullivan N I	4.0
Waipuna	13.8	4.3	0.7	21.3	Sullivan N II	5.3
Mokau	12.4	2.8	0.0	15.2	Webb V	5.6
Ohura	15.7	4.3	0.4	21.9	Rockies II	6.4
Huntly East	13.3	5.8	0.4	20.5	Rockies I	3.8
Huntly West	11.3	5.5	0.5	18.5	Fox River	0.6
Heaphys	14.0	4.0	0.6	18.6	Great N. Seam	8.5
Terrace	13.5	3.8	0.4	18.3	Wallarrah	8.1
Ohai	15.0	1.4	0.4	17.2	Liddell	9.2
Morwell	15.1	6.7	1.0	25.2	Tongarin	6.1
Loy Yang	16.8	7.2	0.7	24.7	Bulli	3.0
					Wongawilli	6.0
					Blair Athol	11.6
					Yarrabee	0.0

(a) O^T = phenolic oxygen

Yoshida *et al*^(42,43) have combined CP/MAS NMR and chemical methods to estimate the oxygen functionalities present in an Australian brown coal. The distribution of oxygen in aliphatic (5.6%) and carboxylic (8.1%) functionalities is similar to that estimated in this study. However, the phenol content measured by the acetylation method (10.2%) is significantly lower than the average of 16% (SD = 1%) estimated from the NMR spectra of two Australian brown coals.

Brooks and Sternhill⁽⁴⁴⁾ also studied the oxygen in "reactive" groups in brown coals. Their results for a Morwell sample included an estimate of 9.0% phenolic oxygen. It is interesting that the sum of this value and the "unreactive" oxygen (6.4%) is similar to the phenol content (15.1%) derived from the NMR intensities. The unreactive oxygen is usually assigned to ethers^(44,45). However, the chemical methods would underestimate the phenol content if some phenol groups were inaccessible to the reagents. Chemical analyses of the oxygen functionalities present in the samples used in this study would provide an interesting test of the DOFIC method of analysis.

The relative amounts of oxygen functionalities are plotted on a cumulative scale in Figure 10.20. The total oxygen contents estimated from the NMR results show a good correlation with carbon contents ($R = -0.957$). The values are also in good agreement with the oxygen contents measured by Ultimate analysis⁽¹⁹⁾.

The rapid loss of non-phenolic oxygen functionalities is evident at low carbon contents. A similar trend is evident in a diagram published in a recent review on the nature of coking coals⁽⁴⁶⁾. The methods used for determining the published data were not stated. The main difference between the published diagram and Figure 10.20 is the incorporation of carbonyl oxygen functionalities in the former. The NMR results indicated that insignificant quantities of carbonyl carbon, other than that in carboxylic groups, were present; ie the intensity in the appropriate chemical shift region (190-220 ppm) can be entirely accounted for by SSB signals⁽¹⁹⁾.

The cumulative representation of the data against the carbon content does not adequately reflect the individual trends in oxygen functionalities. The data are replotted in Figure 10.21 as relative fractions of the total oxygen content. This diagram provides a clear

Figure 10.20: Summary of the proportions of oxygen functionalities relative to the total oxygen content estimated from the NMR results.

Figure 10.21: Oxygen functionality data replotted to show the relative changes in the types of functionalitites present as coalification proceeds.

representation of the pattern of oxygen functionality loss. Low rank coals contain the largest variety of oxygen groups. The range of functionalities decreases rapidly with increasing coalification, as measured by the total oxygen content. The phenol groups increasingly dominate the oxygen content until, at high ranks, all of the oxygen is present in phenol functionalities. Solid state NMR results indicate that essentially no oxygenated carbon functionalities, and therefore no oxygen functionalities, remain in the semianthracite rank of coal.

10.4.5 Combinations of Signal Intensities

Various combinations of signal intensities were tested for suitability as indicators of certain coal characteristics.

10.4.5.1 Prediction of Lignite Pyrolysis Yields

Signal area increments have been correlated with the yields of products from a flash pyrolysis study of lignites⁽¹⁸⁾. Signal intensities were also tested for correlations.

A strong polymethylene signal is associated with high yields of ethane ($R = 0.94$) as indicated in Figure 10.22. The intensity of this signal also correlated, to a lesser extent, with the ethylene yield ($R = 0.87$). These correlations are consistent with the results of other NMR studies^(18,47); ie that gaseous alkanes and alkenes are produced by "fragmentation of polymethylene chains"⁽¹⁸⁾. The correlation between the signal and the sum of the ethane and ethylene yields was $R = 0.92$. The degree of correlation decreased as the other aliphatic gaseous components (eg propane, methane etc) were included in the test. This trend indicates that the other gaseous products are not produced directly from the polymethylene chains but are derived from either cyclic or branched aliphatic structures or are the products of secondary reactions. The lack of correlations between the CO and CO₂ yields, and any of the intensities of oxygenated carbon signals, suggests that these gases may also be the product of secondary reactions. Alternatively, several of the oxygenated carbon functionalities may only partially decompose to CO and CO₂. A direct correlation between intensity and yield would not therefore be expected.

Tars are generally thought to originate from the aliphatic content of the coals. For example, tar yields have been correlated with atomic H/C ratios⁽⁴⁸⁾ and inversely correlated with the aromaticity⁽⁴⁹⁾. The

Figure 10.22: Plot of the yields of ethane gas from pyrolysis of lignites against the intensity contained in the polymethylene signal.

equivalent plots for the seven lignites are shown in Figure 10.23. Degrees of correlation are evident ($R = 0.83$ and $R = -0.85$, respectively). The tar yields have also been correlated with the fraction of methylene hydrogen⁽⁴⁹⁾. However, the lignite tar yields are not dependent on the polymethylene chain content (Figure 10.24a) but do show a correlation with the quantities of carbon in terminal chain positions (Figure 10.24b); ie the sum of intensities at 22 ppm and 15 ppm ($R = 0.90$). These results are consistent with the earlier findings⁽¹⁸⁾. The correlation is rationalised in terms of the tar originating from branched aliphatic structures rather than straight chain structures.

The quantity of tar produced by a coal is generally the most important factor in terms of utilisation processes⁽⁵⁰⁾. However, the origin of the resultant char is also of interest. The natural progression from the correlation between tars and gaseous products, and the aliphatic carbon content, is that the chars are the product of the aromatic carbon content. The lignite char yields showed a degree of dependence ($R = 0.87$) on the aromaticity (Figure 10.25a).

A better correlation ($R = 0.91$) was observed between the yields of char and the sum of intensity in signals assigned to unsubstituted aromatic carbon (Figure 10.25b). This trend suggests that highly substituted aromatic rings may be partially degraded in the pyrolysis process. The oxygen-containing products may decompose further to yield CO and CO₂ which would be included in the gaseous products.

This brief correlation of pyrolysis yields and the functional group analysis results indicate the potential for studying coal processes with high resolution NMR⁽⁵¹⁾.

10.4.5.2 The Polymethylene Chains

The amount of carbon present in polymethylene chains decreases with increasing rank (Figure 10.9) but not in a uniform manner. The ratio of this signal intensity to the total aliphatic carbon (excluding oxygen-substituted carbon) also decreases with increasing carbon content (Figure 10.26). It is interesting to note that the shape of the plot is very similar to that obtained with signal height ratios (Figure 5.16). However, this parameter gives a quantitative assessment of the changes in aliphatic carbon character with increasing degree of coalification; ie there is no interference from SSB signals.

Figure 10.23: Plot of the tar yields from the lignites against a) the atomic H/C ratio and b) the aromaticity.

Figure 10.24: Plot of the tar yields against a) the intensity in the polymethylene signal and b) the intensity contained in the signals assigned to "terminating" carbons.

Figure 10.25: Plot of the char yields from lignite pyrolysis against a) the f_a values and b) the intensity contained in signals assigned to unsubstituted aromatic carbon.

Figure 10.26: Plot of the ratio of intensities in aliphatic carbon signals against carbon content. The numbers in brackets refer to the chemical shifts of the relevant signals. Data for a) Central Otago lignites, b) Waimumu lignites.

The scatter observed in the lignite signal height ratios is also evident in the ratios of intensities. The Central Otago lignites exhibit an average ratio of 0.60 (SD = 0.06) while the average for the Southland lignites is 0.44 (SD = 0.04). It is interesting to note that the ratios of the four samples from the Waimumu coalfield are very similar.

The clustering of ratios for lignites from similar areas suggests that, at this rank, the quantity of carbon in the polymethylene chains is a function of the source. The average chain length can be estimated from the intensity data. The model compound data studied in Chapter 5 indicated that, for chains longer than three carbon atoms, all but three of the carbons will contribute to the resonance at 30 ppm; ie the approximate chemical shift pattern is:

The signal at 15 ppm is assigned entirely to terminal methyl groups. The chain length can therefore be estimated from;

$$\text{Chain length} = 3 + [\%C(30) / \%C(15)] \quad [10.14]$$

where the number in brackets is the relevant chemical shift.

The average chain lengths estimated for the Central Otago and Southland lignites are 9.9 (SD = 2.3) and 6.9 (SD = 0.7) carbon atoms, respectively. These values are not true chain lengths because the presence of cyclic aliphatic structures has not been taken into account. However, this simple calculation confirms that there is a fundamental difference between the aliphatic carbon character of the lignites from the two areas.

A source influence was also observed for the magnitude of the aromaticity values. A plot of the ratio of aliphatic carbon intensities against the aromaticity (Figure 10.27) indicates a close relationship between the two parameters. A low aromaticity value is not necessarily the result of a high content of all types of aliphatic carbon; ie including branched and oxygen-substituted carbon, but does indicate a high polymethylene chain content.

The data plotted in Figure 10.27 gives an excellent summary of the major changes in the aliphatic carbon content with the increasing degree of

Figure 10.27: Plot of the ratio of aliphatic carbon signal intensities against the f_a values. Range of values observed for i) lignites, ii) hvA bituminous coals.

coalification as estimated by the aromaticity. The first major variation occurs in the aliphatic character of the lignites and is the result of source differences in the original depositional environment. Very little change is apparent in aliphatic content of the subbituminous and low rank high volatile bituminous coals.

The second major period of alteration occurs during the high volatile A bituminous rank. The amount of carbon present in polymethylene chains, relative to the amount of other aliphatic carbon, reduces substantially throughout this coalification stage. The very low ratios observed for semianthracites indicates the remaining aliphatic carbon is present in very short or branched chains which are probably substituted onto aromatic rings. In other words, the process of catagenesis, or the thermal cracking of aliphatic chains (Figure 2.18c), can be followed in quantitative terms by NMR. Thus, the stage of oil generation that a coal, or sample of coalified material, has reached can be determined very rapidly. This fact indicates that NMR analysis could fill an important role in the petroleum exploration field.

10.4.5.3 Oxygen Substitution of Aromatic Rings

The amount of carbon that is present as oxygen-substituted aromatic functionalities decreased with increasing carbon content (Figure 10.14) for coals of subbituminous rank and higher. The ratio of this quantity to the total amount of aromatic carbon (A_rC-O) provides an indication of the degree of oxygen-substitution of the aromatic rings. The ratio shows a steady decrease as the degree of coalification increases (Figure 10.28). In contrast to the aliphatic carbon character, the major change in the quantity of oxygenated aromatic carbon occurs through the subbituminous and low rank bituminous rank. This trend is reflecting the loss of the signal at 144 ppm assigned to hydroxyl substitution on adjacent aromatic carbons.

The second major alteration in the fraction of O-substituted aromatic carbon is observed through the high volatile A bituminous range. This decrease corresponds to the loss of the signal at 154 ppm assigned to the isolated phenol functionality.

The order of the degradation of these oxygenated aromatic functionalities is consistent with the results of a thermal decomposition study of New Zealand coals⁽⁵¹⁾. The signal of the less stable functionalities (144 ppm) was absent from the spectra of coals heated to

Figure 10.28: Plot of the amount (%) of aromatic carbon that is oxygen substituted against carbon content. Range of values observed for i) subbituminous and hvB,C bituminous coals, ii) hvA bituminous coals.

temperatures higher than 400°C. However, the signal at 154 ppm persisted in the spectra of chars produced at 600°C.

These results suggest that the thermal decomposition studies may be simulating the coalification reactions. Several workers have shown that artificial coalification can be induced solely by heating lignin and clay⁽⁵²⁾ or brown coal⁽⁵³⁾ under controlled conditions. One hour of heating at 290°C is equivalent to eleven years of pyrolysis at 200°C⁽⁵⁴⁾. Therefore, the maximum temperature to which the coalifying material had been exposed may be important in determining the resultant quantity of oxygenated functionalities.

Suggate⁽⁵⁵⁾ has derived methods for estimating the formation temperatures and the depths of burial of the sample. The data are obtained from the moisture content and specific energy of the sample, on an "average type" basis. The correction for type variations is performed by comparing the specific energy and bed moisture⁽⁵⁷⁾ with the volatile matter (on a dmm.S.free basis). "Isometamorphic lines" are extrapolated to a curve of the "metamorphic development of average-type coal". This procedure obviously involves many assumptions⁽⁵⁶⁾ and a large amount of extrapolation error. However, the resultant data (Table 10.5) should provide insight into this particular coalification process.

The relative content of oxygenated aromatic content ($A_{\text{rC-O}}$) is plotted against the estimated maximum temperature (T) in Figure 10.29. A broad relationship is observed which indicates that the highest temperature attained during coalification influences the degree of oxygen substitution of the aromatic rings. The broad band may reflect the scatter in the original data points used to construct the contour plots⁽⁵⁵⁾. However, the depth of burial (D) may also be influencing the data. Lyons *et al*⁽⁵⁸⁾ found that the depth of burial ("load pressure") had "no perceptible effect on coalification up to an including a rank of semianthracite".

The effect of the depth of burial on the degree of oxygen substitution of aromatic rings is shown in Figure 10.30. The data are clustered into regions. This is not surprising since coals from deposits in close proximity are likely to have been buried to approximately the same depth. For example, the data for the subbituminous coals listed in Table 10.5 have been divided into North and South Island origins. The South Island subbituminous coals were buried to an average depth of 1100m (SD = 60m)

TABLE 10.5

COAL	%M ^a	SE ^b (dmmSf)	%VM (dmmSf)	SE ^b (Av. Type)	T (°C)	D (m)	ArC-O
Idaburn	43.5	6529	54.3	6230	43	930	0.23
Roxburgh	32.0	6907	57.6	6350	51	1350	0.22 ^c
Mataura	43.5	6415	51.0	6240	43	930	0.23
Waimumu Newvale	38.2	6437	55.4	6110	44	1100	0.25 ^c
Waimumu Goodwin	38.9	6621	54.9	6720	46	1080	0.25 ^c
Wangaloa	27.4	7381	47.0	7200	65	1010	0.19
Kai Point	29.9	7297	52.2	6970	62	1070	0.24
Heaphys	23.1	7312	42.4	7300	67.5	1100	0.21
Terrace	20.0	7446	44.8	7350	70	1200	0.20
Ohai	20.2	7430	43.4	7410	70	1120	0.20
Kopuku	25.1	7008	48.8	6810	63	1380	0.25
Kawhia	25.1	7158	50.4	6920	64	1320	0.25
Weavers	20.8	7093	45.5	7040	67	1450	0.19
Squires Creek	20.7	7112	45.1	7080	68	1400	0.26
Maori Farm	22.7	7132	46.3	7080	67	1340	0.19
Waipuna	19.0	7041	45.7	6970	68	1650	0.21
Mokau	21.1	7393	47.5	7200	68	1280	0.20
Ohura	19.5	7155	46.4	7090	69	1500	0.25
Huntly East	21.1	7255	45.9	7170	67	1340	0.20
Huntly West	21.9	7202	47.0	7030	68	1420	0.18
Mulken	16.3	7511	43.5	7440	75	1410	0.18
Snowline	14.6	7970	43.3	7870	77	1100	0.14
Alpine	13.4	7997	43.9	7870	79	1200	0.15
Island Block	9.1	7576	42.7	7530	90	2280	0.14
Stongman	13.8	8093	44.1	7920	78	1190	0.13
Kiwi	10.4	8155	44.1	7980	83	133	0.13
Topline	8.2	8142	41.8	8090	94	1500	0.15
Harrison	12.2	8095	43.4	7930	81	1250	0.13
Moody Creek	9.7	8246	44.1	8060	84	1300	0.12
Echo	8.7	8052	41.1	8020	86	1520	0.13
United	9.9	8284	42.3	8170	83	1160	0.13
Charming Creek	5.3	843	41.3	8330	111	1700	0.10
Liverpool	6.2	8694	38.6	8560	99	1200	0.06
Webb	6.1	8469	34.9	8490	100	1320	0.07 ^c
Sullivan	4.0	8727	31.1	8735	113	1470	0.05 ^c
Loy Yang ^d	60.0	6619	49.5	6470	42	500	0.26
Morwell	58.4	6500	48.9	6360	41	550	0.25

(a) "As sampled at the mine" - Reference (39)

(b) kcal/kg

(c) Average of values for several samples

(d) No bed moisture data for other Australian samples

Figure 10.29: Plot of the amount (%) of aromatic carbon that is oxygenated, against the estimated maximum temperature attained during coalification of the samples.

Figure 10.30: Plot of the amount of aromatic carbon that is oxygenated against the estimated depth of burial. Data for a) South Island subbituminous coals, b) North Island subbituminous coals, c) Reefton bituminous coals, d) Greymouth bituminous coals and e) Buller bituminous coals.

which is significantly less than the average value of 1400m (SD = 110m) for the North Island subbituminous coals.

The scatter in the data (Figure 10.30) indicates that the burial depth does not exert a strong influence on this NMR measure of the degree of coalification. However, the influence of pressure (the depth of burial) can be observed by separating the coal data into groups defined by certain depth divisions. The arbitrary divisions chosen were 1000m and 1400m. Twenty-one coals were estimated to have been buried to depths between these two values. The $A_{\text{r}}\text{C-O}$ values were replotted against T for these coals (Figure 10.31a). The linear-least-squares fit gives the relationship;

$$A_{\text{r}}\text{C-O} = 0.433 - 0.0036 T \quad [10.5]$$

with a coefficient $R = -0.921$. The equivalent plot (Figure 10.31b) of the data for the twelve coals buried at depths greater than 1400m exhibits the relationship;

$$A_{\text{r}}\text{C-O} = 0.423 - 0.0031 T \quad [10.6]$$

with $R = -0.892$.

The two equations give the same $A_{\text{r}}\text{C-O}$ value (0.361) for an ambient temperature of 20°C. However, the slope of the line for the coals buried at shallower depths is greater than that for the increased depths. Thus, the degree of oxygen substitution of aromatic rings, for coals that have been exposed to the same maximum temperature, is inversely dependent on the pressure resultant from the depth of burial. In other words, the NMR results are consistent with the concept that the overburden pressure acts as a retardant in the coalification process^(55,59).

It is interesting to assess the D and T data estimated for the Australian brown coals. The two samples appear to have been exposed to maximum temperatures of similar magnitude to those estimated for the New Zealand lignites. However, the brown coals were buried to significantly shallower depths, approximately 500-550m, in comparison with an average depth of 1080m (SD = 150m) for the New Zealand lignites. Thus, the rate of coalification of the brown coals should have been less inhibited by overburden pressure relative to the rate for New Zealand lignites. This would provide an explanation for the consistent observation that the structural properties of Australian brown coals are intermediate between those measured for NZ lignites and subbituminous coals⁽²¹⁾.

Figure 10.31: Data from Figure 10.29 replotted according to the estimated depth of burial. a) $1000 \text{ m} \leq D < 1400 \text{ m}$, b) $D \geq 1400 \text{ m}$.

10.5 Summary

The simulation of the CP/MAS NMR spectra using DOFIC has resulted in the comprehensive characterisation of the carbon, hydrogen and oxygen functionalities present in Australasian coals. One of the most interesting results is that the data for the ten Australian coals are consistent within the trends observed in the properties of the fifty-seven New Zealand coals. This fact suggests that, while the source material and depositional environments differed substantially, the processes that coalified the humic matter must be essentially very similar. Differences are observed in parameters which are sensitive to source variations (f_a , polymethylene chain parameter). The high inertinite content of some Australian bituminous coals is reflected in these NMR parameters.

The fact that Australasian coals are similar in structure, however, does not imply that coals from the northern and southern hemisphere are also alike⁽⁶⁰⁾. The analysis methods used for Australasian coals could easily be applied to samples from other countries to solve this controversy.

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11. CONCLUSION

The qualitative survey of the signal origins and the thorough relaxation and "visibility" studies have paved the way for the quantitative application of solid state CP/MAS NMR to coal. The development of the program DOFIC to automatically simulate the signals observed in the NMR spectra of coal is seen as a valid new approach to the investigation of the heterogeneous structure of coal. An excellent elemental mass balance is achieved between the results generated by DOFIC and the Ultimate analyses of coals, that range in rank from lignite to semianthracite. This fact provides encouraging evidence for the reliability of CP/MAS NMR as a quantitative technique.

In conclusion, the results of this research show that NMR is an extremely versatile technique for studying not only the chemical alterations induced by coalification, but also the influence of the diversity of source and depositional environment on the coal structure. Thus, this study supports the statements made by Dr G. H. Taylor, in the closing address of the 1985 International Conference on Coal Science, that solid state NMR is set to become one of the most important analytical techniques for bridging Dr R. C. Neavel's concept of a "real-life gap" between industrial problems and coal science.

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13. APPENDICES

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 - 8.1 R. H. Newman, S. J. Davenport and R. H. Meinhold, "An Assessment of Carbon-13 Solid State NMR Spectroscopy for Characterisation of New Zealand coals", Report CD2346, Chemistry Division DSIR NZ (1984)
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APPENDIX 1 : ANALYSES OF NEW ZEALAND COALS

No. NZ	PROXIMATE								ULTIMATE (daf)				
	%M AD AR		%A(d)	%FC (daf)	%VM (daf)	SE (daf)	SN	S	C	H	O	N	S
1	-	28.0	14.6	42.8	57.2	26.78	0	1.0	68.0 ^a	4.8	26.0	0.7	0.5
2	18.9	38.9	10.2	45.6	54.4	26.59	0	0.5	68.2	4.5	26.0	0.6	0.7
3	-	22.0	10.3	38.1	61.9	28.03	0	0.7	69.9 ^a	5.8	22.7	0.8	0.8
4	18.3	33.6	9.9	39.4	60.6	29.12	0	0.7	67.1 ^a	5.6	26.3	0.6	0.4
5	-	49.6 ^a	8.9 ^a	38.6 ^a	61.4 ^a	27.69 ^a	0	0.8 ^a					
6	-	15.4	7.0	46.0	54.0	25.39	0	0.6	68.6	4.0	26.0	0.8	0.6
7	-	17.7	6.1	42.8 ^a	57.3 ^a	26.07 ^a	0	0.9	66.7	4.4	27.2	0.8	1.0
8	-	31.9	4.6	44.0	56.0	25.82	0	0.7	68.4	4.5	25.6	0.6	0.6
9	-	43.2	6.7	44.2 ^b	55.8 ^b	26.65 ^b	0	0.7	68.9	4.1	25.6	0.8	0.7
10		32.3	4.8						68.8	4.4	25.3	0.8	0.6
11	18.4 ^c	41.6	6.0	44.9 ^c	55.1 ^c	27.06 ^c	0	1.2 ^c	69.4	4.6	23.8	0.8	1.3
12	18.9	24.6	4.3	50.9	49.1	29.30	0	4.5	72.6	5.0	16.7	0.8	5.0
13	18.4	29.7	2.7	49.7	50.3	28.99	0	4.6	70.7	4.8	19.4	0.6	4.5
14	18.6	24.9	11.7	54.7	45.3	28.79	0	0.8	72.2	4.6	21.7	1.2	0.4
15	14.3	17.9	6.0	52.3	47.7	27.77	0	0.2	72.8	4.8	21.2	1.0	0.2
16	18.2	26.3	6.4	47.0 ^b	53.0 ^b	28.68 ^b	0	4.0	69.3	4.6	21.0	0.8	4.3
17	16.6	21.1	4.1	53.2	46.8	29.39	0	0.2	72.4	4.9	21.6	0.9	0.2
18	16.3	29.4	2.9	49.4	50.6	28.89	0	5.5					
19	13.9	15.2	5.4	54.6	45.4	28.60	0	0.3	73.7	5.0	20.0	0.3	1.1
20	18.5	19.2	8.3	56.2	43.8	29.13	0	1.2					
21	16.2	18.0	4.4	53.9	46.1	29.83	0	0.3					
22	17.3	20.9	3.9	54.0	41.0	29.85	0	0.2	75.6 ^d	5.4	17.4	1.2	0.3
23	15.5	17.9	7.7	54.6	45.4	29.73	0	0.3	74.9 ^d	4.8	18.8	1.2	0.4
24	13.2	16.7	10.3	49.6 ^b	50.4 ^b	29.62 ^b	0	3.8	73.8	5.8	15.2	1.0	4.2
25	15.3	15.6	13.9	49.4	50.6	30.19	0	2.1					
26	14.0	15.6	2.1	55.4	44.6	29.54	0	0.2	75.1	4.8	18.6	1.2	0.2
27	13.5	16.1	3.6	52.5 ^b	47.5 ^b	29.88 ^b		0.2	74.0	5.2	19.4	1.2	0.2
28	17.0	20.3	4.6	54.2	45.8	30.93		2.3	73.7 ^e	5.2	17.9	1.5	1.7
29	14.1	20.1	2.3	55.3	44.7	30.73		1.5	76.1 ^e	5.2	16.1	1.1	1.5
30	10.2	8.3	10.9	61.4	38.6	30.05		0.2	75.2	5.3	18.3	1.0	0.2
31	10.2	20.8	2.6	55.5	44.5	30.93	1	1.4	74.4 ^e	5.4	16.5	1.1	2.6
32	8.5	15.8	4.3	57.0	43.0	33.08	1	0.4	79.5	5.5	13.4	1.2	0.4
33	8.2	13.8	4.2	55.5	44.5	33.08	1	0.5					
34	3.8	11.9	3.5	57.3	42.7	32.86	2	1.4	79.7	5.5	12.3	1.2	1.4
35	6.1	15.7	6.3	57.0	43.0	33.39	1	0.4	80.0 ^e	5.5	12.7	1.4	0.4
36	5.8	11.3	3.8	60.7	39.3	33.59	2	0.3	80.9	5.7	11.9	1.3	0.3
37	2.5	8.5	6.7	57.6	42.4	33.18	4	1.8					
38	6.1	11.9	3.5	57.1	42.9	33.72	2	0.3	80.2 ^e	5.9	12.4	1.1	0.4
39	4.2	9.1	5.5	54.9	45.1	37.75	4	0.3	81.3 ^e	5.8	11.3	1.3	0.3
40	2.8	10.6	3.6	57.3	42.7	33.47	2	0.5	80.6	5.5	11.9	1.3	0.5

APPENDIX 1 : ANALYSES OF NEW ZEALAND COALS
(Continued)

No. NZ	PROXIMATE								ULTIMATE (daf)				
	%M		%A(d)	%FC (daf)	%VM (daf)	SE (daf)	SN	S	C	H	O	N	S
	AD	AR											
41	4.0	9.1	4.5	56.7	43.3	34.49	3	0.3	81.7	5.9	10.9	1.2	0.3
42	2.7	5.5	1.3	55.4	44.6	33.79	7½	5.4	79.2 ^e	5.5	7.7	1.0	6.6
43	3.3	8.0	3.4	60.3	39.7	33.92	1	0.5	82.3	5.6	10.2	1.3	0.5
44	1.2	6.4	5.6	61.4	38.6	36.17	9	0.4	85.5	6.0	6.3	1.8	0.4
45	1.0	10.2	1.7	63.6	36.4	35.07	9	2.5	84.0	5.4	6.9	1.2	2.5
46	0.9	-	14.2	62.5	37.5	35.84	9	1.2	86.4	5.9	5.0	1.3	1.5
47	1.3	-	1.2	61.4	38.6	35.46	9+	2.8	84.3	5.6	6.5	1.2	2.5
48	1.4	7.2	1.0	65.4	34.6	36.06	9	1.4	84.5 ^e	5.5	6.4	1.2	2.4
49	2.0	9.8	1.2	67.8	32.2	36.00	9	0.5	86.8 ^f	5.3	5.4	1.8	1.2
50	1.3	-	2.8	64.7	35.3	35.92	9+	3.3	85.3	5.5	4.6	1.2	3.4
51	1.8	4.6	5.7	66.1	33.9	35.00	7½	1.64	84.6	5.5	6.7	1.4	1.7
52	0.7	-	1.6	68.1	31.9	36.14	9++	4.2	86.4	5.4	2.6	1.4	4.2
53	0.8	-	0.8	68.6	31.4	36.41	9+	1.6	87.6	5.5	3.7	1.6	1.6
54	1.9	-	0.2	72.6	27.4	35.22	2	1.2	86.3	5.0	6.5	1.1	1.2
55	1.2	-	3.7	70.7	29.3	36.15	9	1.6	86.2 ^f	5.1	5.2	1.1	2.4
56	1.1	-	1.4	74.2	25.8	36.24	8½	1.8	88.3	5.1	3.6	1.2	1.8
57	2.1	1.2	3.0	89.8	10.2	36.41	0	0.6	90.6	4.0	3.7	1.1	0.7

(a) Reference 4.4

(b) Reference 4.3

(c) Composite analysed as 30/455

(d) V. R. Gray and T. A. Daly NZJSc. 24, 179 (1981)

(e) Reference 4.5

(f) Reference 4.6

APPENDIX 2 : ANALYSES OF AUSTRALIAN COALS

No.	PROXIMATE								ULTIMATE (daf)				
	%M AD	AR	%A(d)	%FC (daf)	%VM (daf)	SE (daf)	SN	S	C	H	O	N	S
1	10.8 ^a	58.4 ^b	3.6 ^a	50.7 ^a	49.3 ^a	27.04 ^b	0	0.3 ^a	70.4 ^a	4.9	23.9	0.5	0.3
2	-	60.0 ^b	0.6 ^b	50.3 ^b	49.7 ^b	27.62 ^b	0	0.3 ^b	69.6 ^b	4.9	24.6	0.6	0.3
3	2.8 ^c		12.6 ^c	64.7 ^c	35.3 ^c	34.29 ^c	1 ^c		82.9 ^c	5.2	9.9	1.6	0.4
4	3.0 ^c		10.3 ^c	65.4 ^c	34.6 ^c	33.7 ^c	1 ^c		82.1 ^c	4.9	10.1	1.6	0.3
5		3.2	7.7	60.2	39.8	34.62	4½	0.6					
	2.5 ^c		9.0 ^c	58.3 ^c	41.7 ^c	34.47 ^c	7 ^c		82.0 ^c	5.5	10.0	2.0	0.5
6	1.5 ^c		9.3 ^c	46.1	53.9 ^c	35.01 ^c	6 ^c		79.2 ^c	5.8	8.4	1.2	5.7
7		1.4	7.7	76.4	23.6	35.58	2½	0.4					
	1.4 ^c		9.8 ^c	73.0 ^c	27.0 ^c	35.39 ^c	5 ^c		87.1 ^c	4.8	6.1	1.6	0.4
8	1.2 ^c		14.1 ^c	69.9 ^c	30.1 ^c	36.08 ^c	8 ^c		87.1 ^c	5.3	5.3	1.8	0.5
9	7.0 ^d		6.3 ^d	66.8 ^d	33.2			0.3 ^d	81.6 ^d	4.7	11.5	1.9	0.3
10		4.2	5.3	88.1	11.9	34.52	0	0.5					
	5.0 ^c		6.8 ^c	88.2 ^c	11.8 ^c	34.03 ^c	0 ^c		87.8 ^c	3.4	6.5	1.8	0.5

(a) Reference 4.9

(b) Reference 4.8

(c) Reference 4.10

(d) Reference 10.47

APPENDIX 3 : SIGNAL HEIGHTS FROM RE SPECTRA

COAL NUMBER	CHEMICAL SHIFT (ppm)						Low ranks only			
	15	22	30	128	144	154	56	74	148	177
1	36.5	54	159.5	45	-	39.5	41.5	35.5	40	38.5
2	26.5	47	160.5	45	-	39.5	37.5	37	34	30
3	51.5	64.5	166.5	55	-	42	58.5	48	52.5	52.5
4	53.5	64.5	159	42	-	30.5	33.5	28	35.5	35
5	37	47.5	158	28	-	25	43	39.5	31.5	26.5
6	49.5	66	157.5	63.5	-	51	64	55.5	64.5	47.5
7	73	94	163.5	106	-	116	122.5	88	117	86.5
8	73.5	90	160.5	70.5	-	73	126	122	100.5	75
9	44	66	160	73	-	69	88	53.5	78	69
10	45	75	160	66	-	61.5	86	48.5	70	55
11	52	67	162	56.5	-	47.5	74	59	64	55
12	51.5	57.5	162.5	68	45.5	46	27	33	-	-
13	65	79.5	160.5	106.5	79.5	72.5	36	49	-	-
14	74	102	160	117	99	69.5	39	54.5	-	-
15	65.5	88.5	159	69.5	40	60	19	25.5	-	-
16	84	107.5	160	88.5	70	77	45	52	-	-
17	56	84.5	161	78	55	63.5	34.5	34.5	-	-
18	60	72.5	159.5	78	74.5	52	31	36	-	-
19	55	79.5	160	78.5	45.5	57.5	29	33	-	-
20	63	72	160	52	31.5	34.5	8	20	-	-
21	62.5	95	160	112	91.5	90	45	42	-	-
22	87	110	161	90.5	60	67.5	27.5	41.5	-	-
23	69	91	161	79	44.5	67	24	25	-	-
24	81.5	99	165	115.5	86	87.5	55	60.5	-	-
25	62	83	160.5	78.5	65	60.5	29	34	-	-
26	56	86.5	160.5	81	51.5	63.5	31.5	38.5	-	-
27	52.5	73.5	163	62	39	44.5	23.5	29	-	-
28	60	81.5	161	85.5	52	67	34	31	-	-
29	66.5	72.5	160	82	43.5	66	27.5	34	-	-
30	98.5	131.5	199	158	108	90	41	60.5	-	-
31	60	75	160	79.5	45	54	-	-	-	-
32	52	82.5	160	112	(56) ^a	57	-	-	-	-
33	80	106.5	159.5	124.5	(68)	67.5	-	-	-	-
34	62.5	85.5	159.5	88	(46.5)	56.5	-	-	-	-
35	57	77.5	160	92.5	(49)	52.5	-	-	-	-
36	73.5	103.5	160	121	(61.5)	59	-	-	-	-
37	90	106.5	160	107	(48.5)	71	-	-	-	-
38	68.5	98	162	124.5	(69.5)	70.5	-	-	-	-
39	-	-	161	94	(42)	42	-	-	-	-
40	62.5	88	159.5	104	(43)	62.5	-	-	-	-
41	50	73.5	159.5	92	(36)	41	-	-	-	-
42	88	113	158	120.5	(38)	55.5	-	-	-	-
43	82.5	105	161	124	-	59.5	-	-	-	-
44	87	128	179	162.5	-	38	-	-	-	-
45	79	113	129	162	-	51	-	-	-	-
46	76	119	124.5	160.5	-	37.5	-	-	-	-
47	81	121	134.5	161	-	53.5	-	-	-	-
48	68	106	118.5	162.5	-	48	-	-	-	-
49	60	96	104	161	-	41	-	-	-	-
50	82.5	112	110	163	-	45	-	-	-	-
51	60.5	106	112.5	161	-	40	-	-	-	-
52	66	101.5	88.5	160.5	-	27.5	-	-	-	-
53	60	105	84	160.5	-	32	-	-	-	-
54	63	100.5	82	162	-	38	-	-	-	-
55	65	111	92.5	162	-	32.5	-	-	-	-
56	60	103	64	160	-	32.5	-	-	-	-
57	-	29	11	125	-	-	-	-	-	-
A1	73	91.5	159	108	84	94	64	60	-	82.5
A2	75	97	159	113.5	88	103	51	47	-	87
A3	72	95	133	162	-	53	-	-	-	-
A4	50	103	116	164	-	60	-	-	-	-
A5	51	82	159	108.5	-	42	-	-	-	-
A6	54	68	160	82	-	29	-	-	-	-
A7	68.5	82	65.5	159	-	20.5	-	-	-	-
A8	61	87	78	161	-	33	-	-	-	-
A9	60	94	139	163	-	59	-	-	-	-
A10	b ₋	-	-	160	-	0	-	-	-	-

(a) Brackets indicate that the signal was not resolved

(b) Variable spinning speed experiments were not successful in removing SSB

APPENDIX 4.1

COAL	No.	T_{1H} (s)			
		Aliphatic		Aromatic	
Morwell	A 1	0.014	0.002 ^a	0.012	0.001
Loy Yang	A 2	0.029	0.004	0.020	0.001
Roxburgh I	NZ3	0.038	0.003	0.016	0.002
Roxburgh II	NZ4	0.031	0.003	0.011	0.001
Roxburgh III	NZ5	0.034	0.003	0.015	0.002
Mataura	NZ6	0.042	0.005	0.029	0.005
Ashers Waituna	NZ7	0.015	0.002	0.009	0.003
Waimumu I	NZ8	0.036	0.005	0.017	0.003
Waimumu II	NZ9	0.019	0.002	0.012	0.003
Waimumu III	NZ10	0.014	0.002	0.009	0.003
Waimumu IV	NZ11	0.019	0.002	0.009	0.003
Kopuku	NZ15	0.027	0.004	0.016	0.003
Weavers	NZ19	0.027	0.004	0.014	0.003
Huntly East	NZ26	0.038	0.005	0.022	0.003
Ohai	NZ30	0.031	0.002	0.023	0.002
Mulken	NZ31	0.063	0.005	0.050	0.006
Snowline	NZ32	0.079	0.004	0.060	0.003
Alpine	NZ33	0.056	0.003	0.045	0.002
Island Block	NZ34	0.160	0.006	0.170	0.010
Strongman	NZ35	0.108	0.007	0.102	0.004
Kiwi	NZ36	0.106	0.005	0.088	0.004
Topline	NZ37	0.201	0.010	0.170	0.006
Harrison	NZ38	0.097	0.005	0.078	0.003
Moody Creek	NZ39	0.113	0.005	0.099	0.004
Echo	NZ40	0.100	0.005	0.072	0.003
United	NZ41	0.099	0.006	0.076	0.005
Charming Creek	NZ42	0.318	0.010	0.316	0.013
Escarpment	NZ43	0.148	0.005	0.106	0.005
Liverpool	NZ44	0.189	0.017	0.168	0.013
Webb I	NZ45	0.292	0.015	0.309	0.013
Webb II	NZ46	0.299	0.021	0.267	0.012
Webb III	NZ47	0.322	0.019	0.270	0.013
Webb IV	NZ48	0.293	0.009	0.259	0.010
Stockton I	NZ49	0.294	0.017	0.226	0.007
Stockton II	NZ50	0.299	0.019	0.276	0.015
Sullivan	NZ51	0.157	0.009	0.153	0.007
Sullivan North I	NZ52	0.348	0.012	0.327	0.013
Sullivan North II	NZ53	0.327	0.015	0.337	0.020
Webb V	NZ54	0.144	0.011	0.135	0.016
Rockies II	NZ55	0.235	0.022	0.242	0.022
Rockies I	NZ56	0.188	0.017	0.201	0.013
Fox River	NZ57	0.141	0.008	0.121	0.003
Great North Seam	A 3	0.095	0.005	0.082	0.005
Wallarrah	A 4	0.098	0.008	0.082	0.004
Liddell	A 5	0.105	0.008	0.094	0.005
Tongarin	A 6	0.363	0.015	0.289	0.011
Bulli	A 7	0.125	0.017	0.121	0.005
Wongawilli	A 8	0.163	0.017	0.142	0.012
Blair Athol	A 9	0.054	0.006	0.053	0.005
Yarrabee	A 10	0.130	0.014	0.120	0.007

(a) Standard deviation

APPENDIX 4.2

ACID-WASHED COAL	No.	Fe Coal	(ppm) Wash	Ng x Coal	10 ⁻¹⁸ AW Coal	T ₁ ^ρ H (s)		-CH ₃	-CH ₂ -	T ₁ ^ρ H -O CH ₃	Arc-H (ms)		Arc-O-
						Aliphatic	Aromatic				Arc-H		
Mataura	NZ 6	7130	4370	0.35	0.37	0.039	0.027	2.9	2.7	3.7	4.2		5.3
Waimumu I	NZ 8	5170	3250	0.18	0.52	0.003	0.004	2.5	2.8	2.9	3.3		3.9
Roxburgh I	NZ 3	4170	2650	0.57	0.67	0.041	0.024	2.8	2.6	3.6	3.9		4.0
Roxburgh II	NZ 4	-	1970	0.15	0.29	0.005	0.025	2.5	2.8	3.0	3.4		4.2
Roxburgh III	NZ 5	6330	2800	0.47	0.46	0.003	0.001	2.4	2.7	3.7	3.5		4.0
Kopuku	NZ15	3300	1500	1.5	0.9	0.003	0.019	2.3	2.4	-	3.3		3.4
Weavers	NZ19	2570	1100	2.7	1.3	0.026	0.003	2.2	2.2	-	3.1		3.2
Huntly East	NZ26	2110	900	4.1	1.7	0.028	0.003	2.7	2.4	-	3.1		3.1
Ohai	NZ30	9410	6000	4.4	4.0	0.004	0.022	1.8	1.9	-	2.6		2.5
Strongman	NZ35	4410	3000	4.7	6.4	0.035	0.027	2.4	2.2	-	2.8		2.9
Topline	NZ37	5620	750	4.9	5.9	0.004	0.120	2.2	2.0	-	2.6		3.1
Charming Creek	NZ42	1500	650	4.0	4.5	0.007	0.005	2.2	2.3	-	2.5		2.8
Webb	NZ45	2110	700	4.9	5.3	0.227	0.191	1.7	2.4	-	2.0		3.0
Liddell	A 5	2760	2300	5.0	5.3	0.015	0.025	1.8	1.9	-	2.7		2.8
Bull	A 7	3630	3200	12	14	0.016	0.098	-	3.1	-	3.1		-
Yarrabee	A 10	3450	2000	14	12	0.008	0.129	-	3.7	-	3.0		-
Fox River	NZ57	4740	3400	18	13	0.014	0.011	-	3.3	-	2.6		-
						0.096	0.092						
						0.015	0.003						
						0.106	0.092						
						0.013	0.006						

APPENDIX 4.3

a)

Time (months)	%M	T _{1H} (s)			
		Aliphatic	(SD)	Aromatic	(SD)
0	37.6	0.016	(0.002)	0.013	(0.001)
1	32.3	0.023	(0.005)	0.011	(0.002)
2	29.3	0.024	(0.003)	0.010	(0.005)
3	32.0	0.018	(0.003)	0.008	(0.004)
4	33.4	0.024	(0.004)	0.010	(0.004)
5	32.4	0.030	(0.006)	0.018	(0.003)
6	29.8	0.020	(0.004)	0.014	(0.003)

b)

%M	T _{1H} (s)			
	Aliphatic	(SD)	Aromatic	(SD)
0	0.064	(0.004)	0.026	(0.002)
0.5	0.058	(0.005)	0.025	(0.003)
0.7	0.051	(0.004)	0.023	(0.003)
1.9	0.037	(0.003)	0.018	(0.001)
2.2	0.036	(0.004)	0.018	(0.002)
4.3	0.028	(0.003)	0.016	(0.002)
6.9	0.026	(0.003)	0.010	(0.002)
9.6	0.022	(0.003)	0.011	(0.002)
14.4	0.025	(0.003)	0.012	(0.002)
20.8	0.021	(0.003)	0.009	(0.002)
29.7	0.022	(0.003)	0.009	(0.002)

APPENDIX 4.4

COAL	No.	T_{CH} (ms)		-CH ₃	-CH ₂ -	$T_1 \rho_H$ (ms)		AFC-O	T_{CH} (ms)		$T_1 \rho_C$ (ms)		AFC-O-
		-CH ₂ -	AFC-H			-OCH ₃	AFC-H		-CH ₃	-CH ₂ -	-OCH ₃	AFC-H	
Mataura	NZ 6	0.05	0.13	2.1	2.3	2.5	3.0	3.7	0.9	0.7	1.4	3.9	5.6
Waimumu I	NZ 8	0.08	0.33	3.0	2.5	3.1	3.2	3.4	1.8	0.9	3.1	4.4	6.9
Roxburgh I	NZ 3	0.09	0.35	1.8	2.2	2.8	2.9	3.2	1.1	0.7	3.4	4.9	5.1
Roxburgh II	NZ 4	0.11	0.20	1.8	2.3	3.3	3.5	3.8	1.2	0.8	1.8	4.0	5.7
Roxburgh III	NZ 5	0.12	0.29	2.2	2.2	2.8	2.5	3.3	1.2	0.7	2.5	3.8	6.7
Kopuku	NZ15	0.11	0.15	2.1	1.9	-	2.9	2.7	1.4	0.8	-	4.0	5.8
Weavers	NZ19	0.07	0.20	2.5	2.3	-	3.2	3.0	1.4	0.8	-	3.7	5.5
Huntly East	NZ26	0.07	0.23	2.0	2.3	-	2.6	3.0	1.6	0.8	-	3.9	5.7
Ohai	NZ30	0.03	0.07	2.4	2.4	-	3.5	3.5	1.5	1.1	-	4.1	4.2
Mulken	NZ31	0.08	0.24	2.1	2.0	-	2.2	2.7	2.4	1.1	-	4.2	5.3
Island Block	NZ34	0.07	0.16	1.6	2.3	-	2.4	2.5	2.5	1.3	-	4.2	5.3
Strongman	NZ35	0.03	0.08	2.3	2.4	-	3.1	3.6	1.6	1.2	-	3.5	4.6
Topline	NZ37	0.03	0.06	2.3	2.8	-	3.0	3.5	1.7	0.8	-	3.1	4.0
Charming Creek	NZ42	0.09	0.20	2.3	2.3	-	2.7	2.8	1.6	0.7	-	2.9	4.5
Webb	NZ45	0.03	0.12	2.6	2.6	-	3.0	4.0	1.6	0.7	-	2.9	4.0
Liddell	A 5	0.04	0.14	-	2.6	-	3.5	-	1.9	1.5	-	2.9	2.4
Bull	A 7	0.03	0.10	-	2.6	-	2.9	-	-	2.0	-	3.1	-
Yarabee	A 10	0.08	0.08	-	2.9	-	2.6	-	-	2.5	-	2.6	-
Fox River	NZ57	0.06	0.09	-	2.8	-	2.2	0	0	2.9	-	2.2	-

APPENDIX 5a : VISIBILITY DATA FOR RAW COALS

COAL	PURE COAL			COAL : AT MIXTURES		
	A	B	C	A	B	C
NZ 1 ^a	0.0375	0.0060	0.0054	0.0594	0.0275	0.0288
NZ 2	0.0473	0.0109	0.0356	0.0652	0.0295	0.0248
NZ 3	0.0611	0.0140	0.0616	0.0614	0.0300	0.0289
NZ 4	0.0564	0.0133	0.0604	0.0704	0.0320	0.0214
NZ 5	0.0484	0.0136	0.0519	0.0657	0.0300	0.0298
NZ 6	0.0443	0.0089	0.0342	0.0590	0.0289	0.0197
NZ 7	0.0382	0.0083	0.0205	0.0514	0.0278	0.0151
NZ 8	0.0726	0.0156	0.0362	0.0631	0.0324	0.0288
NZ 9	0.0470	0.0115	0.0284	0.0664	0.0308	0.0165
NZ 10	0.0468	0.0088	0.0307	0.0616	0.0299	0.0211
NZ 11	0.0452	0.0099	0.0317	0.0637	0.0304	0.0220
NZ 15	0.0809	0.0126	0.0542	0.0689	0.0314	0.0266
NZ 19	0.0601	0.0103	0.0447	0.0763	0.0320	0.0246
NZ 26	0.0514	0.0100	0.0413	0.0718	0.0301	0.0
NZ 30	0.0449	0.0098	0.0316	0.0643	0.0247	0.0213
NZ 35	0.0492	0.0091	0.0365	0.0634	0.0278	0.0189
NZ 37	0.0440	0.0080	0.0308	0.0609	0.0299	0.0199
NZ 42	0.0488	0.0112	0.0412	0.0656	0.0314	0.0240
NZ 45	0.0512	0.0101	0.0390	0.0649	0.0316	0.0210
A 5 ^b	0.0494	0.0098	0.0288	0.0339	0.0168	0.0104
	0.0583	0.0131	0.0447	0.0618	0.0264	0.0174
A 7	0.0330	0.0061	0.0198	0.0586	0.0256	0.0132
A 10	0.0611	0.0128	0.0220	0.0753	0.0326	0.0181
A 57	0.0677	0.0135	0.0262	0.0757	0.0322	0.0185
AT ^a	0.0953	0.0593	0.0245			
	0.0605	0.0526	0.0056			

(a) Spectra obtained at higher spinning frequency.

(b) Magnetically separated sample

APPENDIX 5b : VISIBILITY DATA FOR ACID-WASHED COALS

COAL	PURE COAL			COAL : AT MIXTURES		
	A	B	C	A	B	C
NZ 2	0.0872	0.0159	0.0513	0.0704	0.0299	0.0255
NZ 3	0.0903	0.0187	0.0733	0.0814	0.0339	0.0363
NZ 4	0.0784	0.0174	0.0859	0.0754	0.0333	0.0331
NZ 5	0.0762	0.0177	0.0700	0.0763	0.0334	0.0348
NZ 6	0.1097	0.0228	0.0728	0.0886	0.0328	0.0320
NZ 7	0.1075	0.0178	0.0479	0.0856	0.0341	0.0279
NZ 8	0.1122	0.0234	0.0588	0.0955	0.0329	0.0281
NZ 9	0.1143	0.0217	0.0561	0.0816	0.0333	0.0302
NZ 10	0.0949	0.0177	0.0573	0.0859	0.0334	0.0301
NZ 11	0.0960	0.0189	0.0580	0.0796	0.0331	0.0323
NZ 15	0.0653	0.0135	0.0533	0.0551	0.0325	0.0314
NZ 19	0.1249	0.0221	0.0974	0.0782	0.0317	0.0290
NZ 26	0.0752	0.0128	0.0620	0.0781	0.0307	0.0302
NZ 30	0.0818	0.0157	0.0510	0.0746	0.0298	0.0222
NZ 35	0.0547	0.0092	0.0408	0.0738	0.0302	0.0224
NZ 37	0.0437	0.0080	0.0395	0.0650	0.0301	0.0218
NZ 42	0.0445	0.0079	0.0394	0.0669	0.0315	0.0241
NZ 45	0.0580	0.0086	0.0330	0.0674	0.0323	0.0208
A 5	0.0621	0.0109	0.0422	0.0710	0.0318	0.0243
A 7	0.0447	0.0087	0.0217	0.0684	0.0307	0.0151
A 10	0.0643	0.0133	0.0196	0.0771	0.0339	0.0169
A 57	0.0432	0.0082	0.0181	0.0590	0.0264	0.0164

APPENDIX 6.1 : "LOW" RANK

DOFIC PARAMETERS	NZ COAL NUMBER										
	1	2	3	4	5	6	7	8	9	10	11
RMSD	2.865	3.977	1.790	2.418	2.507	2.626	3.441	2.722	2.393	2.312	2.397
%C 15	3.2	2.2	4.2	5.6	2.8	4.4	2.8	2.9	2.4	2.8	3.1
22	4.8	4.1	6.4	6.9	6.2	4.2	3.9	4.4	4.4	5.1	5.8
30	20.3	22.9	25.0	20.0	23.1	14.1	7.5	11.5	11.6	11.7	13.8
39	4.0	0	3.6	3.6	1.5	4.0	3.6	3.9	3.5	4.1	3.6
48	2.2	3.5	3.2	3.1	4.4	3.0	3.7	3.4	3.0	3.5	3.9
56	1.9	2.5	2.2	2.0	2.5	2.5	2.9	3.4	2.9	3.4	3.0
64	1.9	1.7	1.1	0.5	2.0	1.2	2.0	2.9	2.0	1.1	1.5
74	1.9	2.9	2.1	1.3	3.4	2.2	2.0	4.8	1.9	1.8	2.7
84	0.2	1.1	1.2	0.4	2.0	0.8	1.5	1.5	2.2	1.3	1.6
89	1.2	0.9	0	0.2	0.9	0.7	0.7	1.3	0.4	0.6	1.3
105	0.5	1.0	0.3	0.3	0.3	0.6	0	1.0	0	0.9	0.8
107	0	0	1.9	0	7.7	2.1	6.9	7.5	10.1	0	0
112	10.4	7.1	6.2	9.9	3.0	9.6	5.4	0	1.7	12.6	12.6
117	4.0	7.6	4.9	2.9	4.3	4.5	7.0	11.9	8.2	3.0	1.4
125	9.7	2.8	6.8	10.6	6.6	11.2	8.8	2.2	9.5	10.4	10.8
130	12.4	18.7	10.3	12.1	8.8	12.2	13.4	14.0	9.5	13.2	8.4
138	6.2	4.9	4.9	3.5	6.1	6.2	9.5	4.2	6.6	6.7	6.8
144	3.9	2.2	2.7	3.7	1.4	3.1	1.7	2.9	3.6	3.2	3.5
148	3.0	3.8	3.4	3.6	4.1	5.0	5.8	6.0	4.5	5.1	5.0
154	6.1	6.3	4.6	5.3	3.7	5.4	7.5	5.0	5.3	6.3	5.2
177	4.1	3.6	4.9	4.5	5.1	2.8	3.1	5.2	6.8	3.1	5.3
f _a	0.56	0.53	0.46	0.52	0.46	0.59	0.66	0.54	0.59	0.61	0.54
ARC-O	0.23	0.23	0.23	0.24	0.20	0.23	0.23	0.26	0.23	0.24	0.26
% Cellulose	8.8	11.8	7.2	4.3	12.8	8.5	9.3	16.4	9.2	8.6	11.3
O/C	0.344	0.344	0.323	0.316	0.348	0.314	0.347	0.448	0.425	0.336	0.404
H/C	0.108	0.109	0.117	0.115	0.112	0.106	0.095	0.107	0.100	0.102	0.104
%C	68.9	68.8	69.5	69.8	68.5	70.4	69.3	64.3	65.5	69.5	66.3
%H	7.4	7.5	8.1	8.1	7.7	7.5	6.6	6.9	6.6	7.1	6.9
%O	23.7	23.7	22.4	22.1	23.8	22.1	24.1	28.8	27.9	23.4	26.8

APPENDIX 6.2 : "MEDIUM-LOW" RANK

DOFIC PARAMETERS	NZ COAL NUMBER																		
	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
RMSD	2.410	2.351	2.439	3.106	2.463	2.180	2.206	1.808	2.056	4.602	4.716	2.141	2.551	2.272	1.896	2.098	2.338	2.972	3.350
%C 15	4.0	3.8	3.9	5.6	4.6	3.6	4.9	4.0	3.2	5.6	6.0	2.2	6.7	3.7	3.7	4.2	3.9	4.6	4.3
22	3.8	4.3	4.7	6.7	5.3	5.0	5.0	5.0	4.1	5.8	6.0	4.3	6.8	4.5	5.3	5.2	5.2	4.3	4.6
30	11.4	8.4	7.4	11.7	8.3	10.0	10.9	9.8	7.3	9.7	11.5	6.8	16.0	9.7	9.6	12.6	9.7	10.0	7.3
39	7.5	6.4	5.0	6.4	7.6	7.0	7.7	6.3	6.9	4.1	4.2	6.4	6.5	8.3	6.2	6.5	6.6	5.4	5.1
48	3.2	3.8	2.9	2.2	3.9	3.2	3.0	3.0	2.6	1.5	0.8	4.7	2.0	3.8	3.0	3.1	2.9	3.1	2.6
56	0.7	0.7	0.5	0	0.6	0.5	0.7	0.7	0.5	0.1	0	0.8	0	0.4	0.4	0.5	0.6	0.4	0.4
64	0.7	1.2	0.8	-	1.2	0.6	0.7	0.4	0.4	-	-	1.3	-	1.1	0.4	0.6	-	0.5	0.4
74	0.5	0.2	0.5	0	0.7	0.6	0.3	0.4	0.1	0	0	0.5	0	0.00	0.4	0	0	0.0	0
84	0.6	0.1	0.2	-	0.7	0.5	0.1	0.1	0.8	-	-	1.0	-	0.9	0	0.8	-	0.4	0
89	0.1	0.2	0.4	-	0.4	0.4	0.2	0.5	0.0	-	-	0.7	-	0	0.6	0.3	-	0	0.1
107	1.7	0.7	0.2	0.2	3.1	0	1.1	7.3	0	5.6	0	1.9	0	0	1.6	6.7	0	2.3	0
112	6.4	5.5	9.3	11.5	8.3	13.8	4.0	0	16.3	8.6	9.9	10.9	7.0	11.1	8.4	4.9	10.7	6.8	7.3
117	8.2	9.8	6.2	3.8	3.7	3.0	9.9	10.9	0.3	0.7	2.9	4.3	7.3	3.4	7.3	7.3	5.7	8.9	5.4
128	25.4	28.7	31.0	29.4	24.4	24.5	27.1	24.4	30.9	33.4	28.5	26.2	28.3	29.2	26.7	24.9	28.8	27.3	43.1
138	11.4	8.9	7.3	3.0	7.5	9.4	6.5	10.5	4.6	4.4	8.1	11.4	5.8	4.8	9.5	8.1	9.7	10.5	12.2
144	4.9	7.9	9.0	5.6	6.6	5.0	8.9	4.4	8.2	7.8	6.8	5.7	4.8	7.9	5.1	4.4	4.5	3.5	6.9
154	7.8	9.5	7.9	10.1	9.5	8.6	7.5	8.1	9.8	9.5	10.9	8.6	7.5	8.8	8.7	7.1	9.7	10.1	8.6
177	1.8	0	2.8	3.7	3.8	4.4	1.7	4.2	4.0	3.2	4.4	2.2	1.4	2.3	3.0	2.8	2.0	1.9	0.7
f _a	0.66	0.71	0.71	0.64	0.63	0.64	0.65	0.66	0.70	0.70	0.67	0.69	0.61	0.65	0.67	0.63	0.69	0.69	0.74
ArC-O	0.19	0.24	0.23	0.25	0.25	0.21	0.25	0.19	0.26	0.20	0.19	0.21	0.20	0.25	0.20	0.18	0.21	0.20	0.20
frac C-O	1.000	1.000	0.954	1.000	0.918	1.000	1.000	1.000	1.000	0.553	0.221	1.000	1.000	0.986	1.000	1.000	1.000	1.000	0.903
O/C	0.244	0.260	0.321	0.308	0.346	0.324	0.287	0.300	0.365	0.272	0.283	0.296	0.200	0.310	0.283	0.250	0.250	0.246	0.228
H/C	0.097	0.097	0.096	0.108	0.099	0.097	0.104	0.096	0.097	0.101	0.098	0.900	0.112	0.101	0.097	0.101	0.097	0.096	0.093
%C	74.6	73.6	70.6	70.7	69.1	70.4	71.9	71.6	68.4	72.9	72.4	72.2	76.3	70.9	72.5	74.0	74.2	74.5	75.8
%H	7.2	7.2	6.8	7.6	6.9	6.8	7.5	6.9	6.6	7.3	7.1	6.5	8.5	7.2	7.0	7.5	7.2	7.2	7.0
%O	18.2	19.2	22.6	21.7	24.0	22.8	20.6	21.5	25.0	19.8	20.5	21.3	15.2	21.9	20.5	18.5	18.6	18.3	17.2

APPENDIX 6.4 : "HIGH" RANK

DOFIC PARAMETERS	44	45	46	47	48	49	50	51	52	53	54	55	56	57
	NZ COAL NUMBER													
RMSD	2.610	3.978	3.002	2.565	2.379	2.188	2.689	2.215	2.335	2.553	2.329	3.001	4.100	2.862
%C 15	4.2	4.5	4.1	4.0	3.8	3.0	3.6	2.9	3.4	2.7	3.3	3.4	4.2	1.0
22	5.2	5.0	5.8	5.0	5.0	4.5	4.5	5.0	5.0	4.8	4.9	5.1	5.1	1.7
30	6.6	4.6	4.5	4.4	3.9	3.4	3.6	3.9	2.7	2.9	2.6	3.0	2.0	0.6
39	6.8	6.6	5.6	6.1	6.7	5.7	6.6	6.2	5.5	5.1	4.7	4.4	4.2	2.3
48	1.7	0.8	2.2	1.9	1.7	2.6	1.4	2.2	1.0	1.1	1.2	2.1	0	0.6
112	0	0	0	0	0	0	0	0	0	0	2.9	0	0	0.4
117	11.2	10.3	5.5	7.6	10.2	5.9	8.1	5.8	6.9	7.3	4.9	7.9	10.3	2.9
128	43.1	46.9	47.2	43.6	49.8	53.8	46.4	51.2	55.0	5.0	56.4	54.1	58.0	77.1
138	16.3	14.9	20.1	20.2	12.8	15.1	19.8	17.0	17.1	16.6	14.3	14.5	12.9	13.0
154	4.9	6.3	5.0	7.1	6.1	6.1	5.9	5.8	3.4	4.5	4.8	5.6	3.2	0.4
F _a	0.76	0.78	0.78	0.79	0.79	0.81	0.80	0.80	0.82	0.83	0.83	0.82	0.85	0.94
Arc-O	0.06	0.08	0.06	0.09	0.08	0.08	0.07	0.07	0.04	0.05	0.06	0.07	0.04	0.00
frac C-H	0.951	1.000	1.000	0.867	0.847	0.756	0.988	0.947	0.904	0.826	0.890	0.776	0.851	0.587
O/C	0.065	0.084	0.066	0.095	0.081	0.082	0.079	0.077	0.045	0.061	0.064	0.074	0.043	0.006
H/C	0.088	0.091	0.085	0.079	0.084	0.074	0.083	0.082	0.080	0.076	0.081	0.076	0.082	0.051
%C	86.6	85.1	86.9	85.1	85.9	86.5	86.1	86.3	88.9	88.0	87.3	87.0	88.9	94.6
%H	7.7	7.7	7.4	6.8	7.2	6.4	7.1	7.1	7.1	6.7	7.1	6.6	7.3	4.8
%O	5.7	7.2	5.7	8.1	6.9	7.1	6.8	6.6	4.0	5.3	5.6	6.4	3.8	0.6

APPENDIX 6.3 : "MEDIUM-HIGH" RANK

DOFIC PARAMETERS	NZ COAL NUMBER												
	31	32	33	34	35	36	37	38	39	40	41	42	43
RMSD	3.167	2.099	2.555	3.161	3.602	3.838	5.759	3.437	2.503	2.691	1.950	3.748	3.766
%C 15	4.0	3.1	3.3	4.4	4.1	4.4	6.1	3.9	3.5	4.0	3.8	6.5	3.8
22	4.7	4.2	4.4	5.6	5.3	5.0	6.1	4.9	4.9	5.5	5.0	6.4	4.9
30	8.6	7.4	6.6	7.7	7.8	7.3	8.1	6.3	8.9	7.4	9.3	7.9	5.9
39	7.8	7.1	6.9	9.6	9.3	6.1	5.8	6.3	7.6	8.0	8.3	7.1	8.3
48	3.0	2.4	2.3	1.5	2.8	1.8	0.2	3.1	2.4	2.2	2.0	0	3.0
112	11.7	4.5	5.0	5.6	4.6	3.2	0.5	6.8	4.4	4.1	3.3	6.9	5.0
117	3.7	8.0	8.0	8.6	9.3	10.1	7.4	5.5	6.6	11.0	7.8	6.3	8.1
128	32.0	36.0	33.7	32.1	31.2	36.6	35.0	36.1	35.4	33.7	36.6	37.2	35.6
138	7.8	12.3	13.2	10.7	12.3	12.9	15.8	12.1	14.8	11.8	11.4	13.8	13.1
144	7.1	6.3	7.4	5.8	5.9	4.6	3.5	6.8	4.3	4.0	5.0	1.1	4.1
154	9.7	8.7	9.2	8.4	7.4	7.9	11.3	8.4	7.3	8.3	7.6	6.8	8.1
f _a	0.72	0.76	0.77	0.71	0.71	0.75	0.74	0.76	0.73	0.73	0.72	0.72	0.74
ArC-O	0.18	0.14	0.15	0.14	0.13	0.13	0.15	0.13	0.12	0.13	0.13	0.10	0.13
frac C-O	0.470	0.263	0.303	0.271	0.364	0.342	0.0	0.203	0.264	0.341	0.294	0.360	0.315
O/C	0.173	0.139	0.153	0.132	0.127	0.127	0.151	0.130	0.112	0.129	0.121	0.096	0.125
H/C	0.094	0.087	0.086	0.094	0.091	0.091	0.094	0.087	0.089	0.093	0.093	0.100	0.088
%C	78.9	81.6	80.8	81.5	82.1	82.1	80.3	82.2	83.3	81.9	82.4	83.7	82.4
%H	7.4	7.1	6.9	7.7	7.5	7.5	7.6	7.1	7.4	7.6	7.7	8.3	7.3
%O	13.7	11.3	12.3	10.8	10.4	10.4	12.1	10.7	9.3	10.5	9.9	8.0	10.3

APPENDIX 6.5 : AUSTRALIAN COALS

DOFIC PARAMETERS	AUSTRALIAN COAL NUMBER									
	1	2	3	4	5	6	7	8	9	10
RMSD	1.238	2.829	3.093	3.434	2.748	2.544	4.613	3.485	3.059	3.779
Rank	ML	ML	H	H	MH	H	H	H	MH	H
%C 15	2.7	3.3	3.4	2.1	4.6	4.4	4.2	2.5	2.0	2.4
22	3.8	3.9	3.5	3.7	4.8	5.6	3.7	3.6	3.4	2.3
30	6.5	6.9	4.4	4.1	6.0	10.5	1.7	2.0	4.7	0
39	7.0	6.4	6.7	7.2	6.5	10.5	1.5	4.1	5.7	0
48	4.2	3.4	1.2	1.7	1.2	2.9	1.5	2.4	1.8	1.0
56	1.1	0.8	-	-	-	-	-	-	-	-
64	1.1	-	-	-	-	-	-	-	-	-
74	0.9	0	-	-	-	-	-	-	-	-
84	0.9	-	-	-	-	-	-	-	-	-
89	0.6	-	-	-	-	-	-	-	-	-
107	4.0	4.0	-	-	-	-	-	-	-	-
112	10.7	8.4	0	4.0	0	0	0	3.6	2.5	1.2
117	4.5	6.7	11.0	7.3	8.1	6.6	5.2	4.7	7.8	6.2
128	27.1	28.7	44.2	43.3	41.4	33.6	64.2	53.0	46.4	87.0
138	4.6	4.3	18.2	19.4	13.5	21.3	15.6	19.0	7.7	0
144	7.5	8.1	-	-	6.6	-	-	-	9.7	-
154	9.2	11.2	7.5	7.1	7.3	5.4	2.5	5.1	8.3	0
177	3.7	3.9	-	-	-	-	-	-	-	-
f _a	0.68	0.71	0.81	0.81	0.77	0.67	0.87	0.85	0.82	0.94
Arc-O	0.25	0.26	0.09	0.09	0.11	0.08	0.03	0.06	0.13	0
frac CO	1.000	0.883	-	-	0.154	-	-	-	0.243	-
frac CH	-	-	0.737	0.953	-	1.000	0.506	0.844	-	0.519
O/C	0.370	0.358	0.100	0.095	0.111	0.071	0.033	0.068	0.143	0
H/C	0.096	0.095	0.074	0.079	0.088	0.090	0.056	0.071	0.083	0.055
%C	68.2	68.8	85.2	85.2	83.5	86.2	91.8	87.8	81.6	94.8
%H	6.6	6.5	6.3	6.7	7.3	7.7	5.2	6.2	6.8	5.2
%O	25.2	24.7	8.5	8.1	9.2	6.1	3.0	6.0	11.6	0

```

PROGRAM CROMASS (cromass,spectra);

CONST  numspins = 4;
       numpts   = 200;

TYPE
    datvec = ARRAY[1..numpts] of REAL;
    datarray = ARRAY[1..numpts,1..numspins] of REAL;

VAR
    cromass,spectra:TEXT;
    A,B:datarray;
    E,P,Q:datvec;
    W:ARRAY[1..10] of REAL;
    T:INTEGER;

{*****}

PROCEDURE title;

VAR
    title:CHAR;
    I:INTEGER;

BEGIN
    I:=0;
    WHILE NOT EOLN (cromass) DO
    BEGIN
        READ(cromass,title);
        WRITE(spectra,title);
        I:=I+1;
    END;
    READLN(cromass);
    WRITELN(spectra,' ');
END; { of title }

{*****}

PROCEDURE printdata (VAR J:INTEGER);

VAR
    I,K:INTEGER;

BEGIN
    WRITELN(spectra,'No of Rows Read ',J);
    FOR I:=1 TO numpts DO BEGIN
        FOR K:=1 TO numspins DO BEGIN
            WRITE(spectra,' ',A[I,K]:4:1);
        END;
        WRITELN(spectra,' ');
    END;
END; { of printflag }

{*****}

PROCEDURE bascorrect(VAR PFC:INTEGER);

{Parabolic baseline corrections in AB specify corrections
for I=200,100,0 respectively}

VAR
    I,K:INTEGER;
    S,V,Y,Z:REAL;
    U:ARRAY[1..numspins] of INTEGER;
    AB:ARRAY[1..3,1..numspins] of REAL;

BEGIN
    FOR I:=1 TO 3 DO BEGIN
        FOR K:= 1 TO numspins DO BEGIN
            READ(cromass,AB[I,K]);
        END;
    END;
    FOR K:=1 TO numspins DO BEGIN
        S:= (AB[1,K]-2*AB[2,K]+AB[3,K])/20000;
        Y:= (-AB[1,K]+4*AB[2,K]-3*AB[3,K])/200;
        Z:= AB[3,K];
        FOR I:=1 TO numpts DO BEGIN
            V:=S*I*I+Y*I+Z;
            A[I,K]:= A[I,K] - V;
        END;
    END;
END;

```

```

IF PFC>0 THEN BEGIN
WRITELN(spectra,'Data Corrected For Parabolic Baseline');
FOR I:=1 TO numpts DO BEGIN
  U[1]:= ROUND(A[I,1]);
  U[2]:= ROUND(A[I,2]);
  U[3]:= ROUND(A[I,3]);
  U[4]:= ROUND(A[I,4]);
  WRITELN(spectra,I,U[1],U[2],U[3],U[4]);
END;
END;
END; { of basecorrect }

{*****}

PROCEDURE getdata;

VAR
  I,J,K,L,PF,BC,PFC:INTEGER;
  S:REAL;

BEGIN {reading data array}
  J:=0;
  FOR I:=1 TO numpts DO BEGIN
    FOR K:=1 TO numspins DO BEGIN
      READ(cromass,A[I,K]);
    END;
    J:=J+1;
  END;
  READ(cromass,PF);
  IF PF > 0 THEN printdata(J);
  {reading spinner frequencies}
  S:=0;
  WRITELN(spectra,'spinner frequencies');
  FOR L:=1 TO numspins DO BEGIN
    READ(cromass,W[L]);
    WRITE(spectra,' ',W[L]:4:1);
    S:=S+W[L];
  END;
  S:=S/4;

  FOR L:=1 TO numspins DO BEGIN
    W[L+ numspins]:= (W[L] - W[1])/(S - W[1]);
  END;
  WRITELN(spectra,' ');
  {reading nos. of iterations}
  READ(cromass,T);
  WRITELN(spectra,'No of iterations ',T);
  {Iterations = 0 for a single pass}
  READ(cromass,BC,PFC);
  IF BC > 0 THEN basecorrect(PFC);
END;{ of getdata }

{*****}

PROCEDURE persistents ;

VAR
  I,K:INTEGER;
  M:REAL;

BEGIN
  WRITELN(spectra,'Persistent Signals ');
  FOR I:=1 TO numpts DO BEGIN
    M:= 1000;
    FOR K:=1 TO numspins DO BEGIN
      IF A[I,K] < M THEN M:=A[I,K];
    END;
    P[I]:=M;
    E[I]:=M;
    {WRITELN(spectra,P[I]:4:1);}
  END;
END;{ of persistents }

{*****}

PROCEDURE residuals;

VAR I,K:INTEGER;

BEGIN
  FOR I:=1 TO numpts DO BEGIN
    FOR K:=1 TO numspins DO BEGIN
      B[I,K]:= A[I,K] - P[I];
    END;
  END;
END;

```

```

FOR I:=1 TO numpts DO BEGIN
  Q[I]:=1;
  IF P[I] = 1 THEN Q[I] := P[I];
END;
{Signals in Q are mostly centrebands, Q[I] could upset Z calculation}
END; { of residuals }

{*****}

PROCEDURE tidyoutput(VAR R,F,G,H:datvec);
VAR
  I:INTEGER;
  S,Y,Z:REAL;
  U:ARRAY[1..5] of INTEGER;
BEGIN
  Y:=0;
  Z:=0;
  FOR I:=1 TO 5 DO BEGIN
    Y:=Y+ R[I];
    Z:=Z + R[201-I];
  END;
  S:= (Z-Y)/1000;
  Y:=Y/5;
  FOR I:=1 TO numpts DO BEGIN
    R[I]:=R[I]-I*S-Y;
  END;
  WRITE(spectra,'          I          P          R');
  Writeln(spectra,'          F          G          H ');
  FOR I:= 1 TO numpts DO BEGIN
    U[1]:= ROUND(P[I]);
    U[2]:= ROUND(R[I]);
    U[3]:= ROUND(F[I]);
    U[4]:= ROUND(G[I]);
    U[5]:= ROUND(H[I]);
    Writeln(spectra,I,U[1],U[2],U[3],U[4],U[5]);
  END;
END; { of tidyoutput }

{*****}

PROCEDURE ssbcoinc(VAR F,G,H:datvec);
{Arrive here if job not done,search for ssb coincidences + remove
them from P}
VAR
  I,K,N:INTEGER;
  C,D,M,S:REAL;
BEGIN
  FOR I:=1 TO numpts DO BEGIN
    IF P[I]=0 THEN BEGIN
      M:=1000;
      FOR K:=1 TO numspins DO BEGIN
        N:= ROUND(W[K]);
        C:=0;
        D:=0;
        IF (I+N)(<= numpts THEN C:=H[I+N];
        IF (I-N)(>=1 THEN D:=G[I-N];
        S:=F[I]*W[K+4]+C+D;
        IF S<=M THEN M:=S;
      END;
      IF M=1 THEN BEGIN
        P[I]:=E[I]-M;
        IF P[I]<=0 THEN P[I]:=0;
      END;
    END;
  END;
  FOR I:=1 TO numpts DO BEGIN
    FOR K:=1 TO numspins DO BEGIN
      B[I,K]:=A[I,K] - P[I];
    END;
    Q[I]:=F[I]+G[I]+H[I];

    IF Q[I]<=1 THEN Q[I]:=1;
  END;
END;{ of ssbcoinc}
{Arrays B+Q are now ready for another loop}

{*****}

```

```

PROCEDURE testiters(VAR R,F,G,H: datvec);
BEGIN
  T:= T - 1 ;
  IF T <= -0.5 THEN tidyoutput(R,F,G,H)
  ELSE ssbcoinc(F,G,H);
END; { of testiters }

{*****}

PROCEDURE iteration;

{ Array F = centre-band additions, array G = low frequency ssb's,
  array H = high frequency ssb's. Residuals distributed according
  to the magnitude of the elements in Q}

VAR
  I,K,N: INTEGER;
  R,F,G,H: datvec;
  C,D,Z,M,S: REAL;

BEGIN
  REPEAT BEGIN
    FOR I:=1 TO numpts DO BEGIN
      F[I]:= 0;
      G[I]:= 0;
      H[I]:= 0;
    END;
    FOR I:= 1 TO numpts DO BEGIN
      FOR K:= 1 TO numspins DO BEGIN
        N:= ROUND(W[K]);
        C:=1;
        D:=1;
        IF (I+N)<=numpts THEN C:=Q[I+N];
        IF (I-N)>=1 THEN D:=Q[I-N];
        Z:= B[I,K]/(Q[I]+C+D);
        F[I]:=F[I]+(Z*Q[I]);
        C:=Z*C;
        D:=Z*D;
        IF (I+N)<= numpts THEN BEGIN
          IF C>P[I+N] THEN F[I]:=F[I] + C;
          IF C<P[I+N] THEN G[I+N]:=G[I+N] + C;
        END;
        IF (I-N)>=1 THEN BEGIN
          IF D>P[I-N] THEN F[I]:=F[I] + D;
          IF D<P[I-N] THEN H[I-N]:=H[I-N] + D;
        END;
      END;
    END;
    {F,G,H, averaged over 4 spectra}
    FOR I:= 1 TO numpts DO BEGIN
      F[I]:=F[I]/4;
      G[I]:=G[I]/4;
      H[I]:=H[I]/4;
      R[I]:=P[I]+F[I]+G[I]+H[I];
    END;
  testiters(R,F,G,H);

  END;
  UNTIL T< -0.5;
END; { of iteration }

{*****}

BEGIN {main program so far }

RESET(cromass);
REWRITE(spectra);

title;
getdata; { calls printdata and basecorrect }
persistents;
residuals;
iteration; { calls testiters which calls tidyoutput or ssbcoinc }

END.

{*****}

```

```

PROGRAM CORRELATE (pyrolprod,pyrollig,pyrolysis,pyrolplot);
{ Program to correlate the coal spectra with the flash pyrolysis results}

CONST
    maxlig = 15;

TYPE
    dataset = ARRAY[1..maxlig,1..maxlig] OF REAL;
    ppmvec = ARRAY[0..400] OF REAL;
    datarray = ARRAY[0..400,1..maxlig] OF REAL;
    ratioarray = ARRAY[1..maxlig,0..400] OF REAL;
    totalarray = ARRAY[1..maxlig] OF REAL;
    titlearray = ARRAY[1..maxlig] OF VARYING[30] OF CHAR;
    codename = ARRAY[1..maxlig] OF VARYING[8] OF CHAR;

VAR
    numlig,numprod,numchannel,Sp,Wp:INTEGER;
    pyrolprod,pyrollig,pyrolysis,pyrolplot:TEXT;
    Max:REAL;
    ppm:ppmvec;
    R,H:ratioarray;
    lig:datarray;
    yield:dataset;
    ligname,nameprod:titlearray;
    totallig,maxprod:totalarray;
    ref:codename;

{*****}

PROCEDURE readdata;

VAR
    I,J,K:INTEGER;

BEGIN
    READLN(pyrollig,numlig);
    READLN(pyrolprod,numprod);
    READLN(pyrollig,Sp,Wp,numchannel);
    FOR K:=1 TO numlig DO
        READLN(pyrollig,ligname[K]);
    FOR K:=1 TO numlig DO
        READ(pyrollig,ref[K]);
    READLN(pyrollig);
    FOR J:=0 TO numchannel DO BEGIN
        READ(pyrollig,ppm[J]);
        FOR K:=1 TO numlig DO
            READ(pyrollig,lig[J,K]);
        READLN(pyrollig);
    END;
    FOR I:= 1 TO numprod DO BEGIN
        READLN(pyrolprod,nameprod[I]);
        FOR K:=1 TO numlig DO
            READ(pyrolprod,yield[I,K]);
        READLN(pyrolprod);
    END;
END; { of readdata }

{*****}

PROCEDURE productfit;

VAR
    I,J,K:INTEGER;
    AvX,AvY:ppmvec;
    A,B,C,D:ratioarray;
    sig:datarray;
    prod:dataset;

BEGIN
    FOR K:=1 TO numlig DO BEGIN
        totallig[K]:=0;
        FOR J:=0 TO numchannel DO
            totallig[K]:= totallig[K] + lig[J,K];
        END;
    FOR K:= 1 TO numlig DO BEGIN
        FOR J:=0 TO numchannel DO
            lig[J,K]:= (10000 * lig[J,K])/totallig[K];
        END;
    END;

```

```

FOR J:= 0 TO numchannel DO BEGIN
  AvX[J]:=0;
  FOR K:=1 TO numlig DO
    AvX[J]:=AvX[J]+ lig[J,K];
  AvX[J]:=(AvX[J]/numlig);
END;
FOR I:= 1 TO numprod DO BEGIN
  AvY[I]:=0;
  FOR K:=1 TO numlig DO
    AvY[I]:=AvY[I]+ yield[I,K];
  AvY[I]:=(AvY[I]/numlig);
END;
FOR J:= 0 TO numchannel DO BEGIN
  FOR K:=1 TO numlig DO
    sig[J,K]:=lig[J,K] - AvX[J];
  END;
FOR I:= 1 TO numprod DO BEGIN
  FOR K:=1 TO numlig DO
    prod[I,K]:=yield[I,K] - AvY[I];
  END;
Max:=0;
FOR I:=1 TO numprod DO BEGIN
  Maxprod[I]:=0;
  FOR J:= 0 TO numchannel DO BEGIN
    A[I,J]:=0;B[I,J]:=0;C[I,J]:=0;
    D[I,J]:=0;R[I,J]:=0;H[I,J]:=0;
    FOR K:=1 TO numlig DO BEGIN
      A[I,J]:=A[I,J] + (sig[J,K]*prod[I,K]);
      B[I,J]:=B[I,J] + (sqr(sig[J,K]));
      C[I,J]:=C[I,J] + (sqr(prod[I,K]));
    END;
    D[I,J]:=sqrt(C[I,J]*B[I,J]);
    R[I,J]:=A[I,J]/D[I,J];
    H[I,J]:=R[I,J]/(1-R[I,J]);
    IF H[I,J] > Maxprod[I] THEN
      Maxprod[I]:=H[I,J];
    IF Maxprod[I] > Max THEN
      Max := Maxprod[I];
    END;
  END;
END; { of productfit }

{*****}

PROCEDURE plotratio;

VAR
  I,J,K: INTEGER;

BEGIN
  FOR I:=1 TO numprod DO BEGIN
    WRITELN(pyrolplot,Sp,Wp);
    WRITELN(pyrolplot,nameprod[I]);
    WRITELN(pyrolplot,numchannel);
    FOR J:=0 TO TRUNC((numchannel/10)-1) DO BEGIN
      FOR K:= 0 TO 9 DO
        WRITE(pyrolplot,H[I,J*10+K]:5:1,' ');
      WRITELN(pyrolplot);
    END;
    WRITELN(pyrolplot,H[I,numchannel]:5:1);
    WRITELN(pyrolplot,Max:5:1);
    WRITELN(pyrolplot);
  END;
  FOR K:=1 TO numlig DO
    WRITELN(pyrolysis,ligname[K]);
  WRITE(pyrolysis,'ppm ');
  FOR K:=1 TO numlig DO
    WRITE(pyrolysis,ref[K], ' ');
  WRITELN(pyrolysis);
  FOR J:=0 TO numchannel DO BEGIN
    WRITE(pyrolysis,ppm[J]:3:0,' ');
    FOR K:=1 TO numlig DO
      WRITE(pyrolysis,lig[J,K]:4:1,' ');
    WRITELN(pyrolysis);
  END;
  WRITELN(pyrolysis);
  FOR I:=1 TO numprod DO
    WRITE(pyrolysis,nameprod[I], ' ');
  WRITELN(pyrolysis);
  WRITE(pyrolysis,'ppm ');
  FOR I:=1 TO numprod DO
    WRITE(pyrolysis,' R/1-R ');
  WRITELN(pyrolysis);

```



```

FOR J:=0 TO numchannel DO BEGIN
  WRITE(pyrolysis,ppm[J]:3:0,' ');
  FOR I:=1 TO numprod DO
    WRITE(pyrolysis,H[I,J]:5:1,' ');
  Writeln(pyrolysis);
END;
Writeln(pyrolysis,' Maximum R/1-R for each product fit');
FOR I:= 1 TO numprod DO
  WRITE(pyrolysis,Maxprod[I]:4:1,' ');
Writeln(pyrolysis);
Writeln(pyrolysis,' Maximum R/1-R obtained: ',Max:4:1);
END; { of plotratio }

{*****}

BEGIN { main program }

  RESET(pyrollig);
  RESET(pyrolprod);
  REWRITE(pyrolysis);
  REWRITE(pyrolplot);
  readdata;
  productfit;
  plotratio;
  CLOSE(pyrolysis);
  CLOSE(pyrolplot);
END.

{*****}

```

AN ASSESSMENT OF CARBON-13 SOLID-STATE N.M.R.
SPECTROSCOPY FOR CHARACTERISATION OF
NEW ZEALAND COALS

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ABSTRACT

Solid samples of New Zealand coals were characterised by cross-polarisation nuclear magnetic resonance with magic-angle spinning in a superconducting magnet. Aromaticity measurements required only 10 minutes of instrument time for lignites and subbituminous coals, but up to an hour of instrument time for higher-ranking coals because of the less favourable proton spin relaxation times. Aromaticity values ranged from 0.49 (for an Otago lignite) to 0.83 (for a semianthracite), but this parameter was found to be a poor measure of rank. Aromaticity values alone could not be used to distinguish bituminous from subbituminous coals, or even bituminous coals from Southland lignites. Signals assigned to phenolic carbon showed a strong correlation with rank; these signals dominated the aromatic region of some lignite spectra, were prominent in the spectra of subbituminous coals, weak in the spectra of bituminous coals and absent from a spectrum of semianthracite. Precise chemical shift measurements for phenols in a sample of coalified wood identified the source as softwood lignin. The most detailed spectra were obtained for lignites. Carbon-13 NMR can be used to estimate the methoxyl content and cellulose content of lignites, besides providing qualitative comparisons of other structural features.

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1 INTRODUCTION

The first high-resolution ^{13}C NMR spectrum of solid coal was reported by VanderHart and Retcofsky¹ in 1976. Since then, solid-state NMR has been used to characterise coals and oil shales from a wide variety of sources². The improved sensitivity of the cross-polarisation (CP) NMR technique is now well established². The introduction of "magic-angle" spinning (MAS) techniques led to reduced linewidths and hence better separation of signals from aromatic and aliphatic carbon³. The earlier ^{13}C CP/MAS NMR studies of coal made use of electromagnet NMR spectrometers^{3,4}. More recent studies show the improved sensitivity that can be obtained from a superconducting NMR spectrometer⁵⁻⁹.

The ^{13}C CP/MAS NMR technique is new and there is thus far no accepted set of standard experimental conditions for obtaining spectra of coal. Published spectra have been obtained with a wide variety of magnetic fields, spinner frequencies and radio-frequency power levels. It is therefore difficult to compare published spectra of coals from different sources, in order to test for systematic trends such as the effects of increasing rank. The published spectra have been mainly of coals from the USA, and the conclusions are therefore not necessarily valid for coals from other parts of the world; e.g. Retcofsky¹⁰ found that the ^{13}C CP/MAS NMR spectra of 3 Chinese coals did not fit generalisations based on coals from the USA.

We have chosen a collection of New Zealand coals to span the ASTM rank classification from lignite to semi-anthracite, with a bias towards the lower ranks because of the economic importance of these coals. All spectra were run on the Varian XL-200 superconducting NMR spectrometer at Chemistry Division, using experimental conditions based on a study of nuclear spin relaxation in coals of various ranks¹¹. In assessing the use of the ^{13}C CP/MAS NMR technique, we set out to answer two questions;

- (i) do the spectra show details which may be useful in characterising New Zealand coals?
- (ii) can satisfactory spectra be obtained within a reasonable

amount of instrument time?

2 EXPERIMENTAL

All samples were crushed to $<200\text{ }\mu\text{m}$. About 0.3 g of each sample was packed in a 10 mm diameter rotor made of Kel-F, and a layer of powdered boric acid was spread over the top to a depth of 1 mm. The composite sample was then compressed by a cylindrical plunger held down by a weight of approximately 500 kg. A cross-section of a filled rotor is shown in Fig.1. The layer of boric acid provided a smooth, hard surface which seldom cracked during sample spinning. Samples run without a boric-acid cap sometimes lacked the cohesion required to withstand high-speed spinning. Rotors were spun at $2.5 \pm 0.2\text{ kHz}$ on a cushion of air, using air pressures up to 0.4 MPa. The standard Varian XL-200 spectrometer air hosing was replaced with PVC hosing capable of accepting this pressure.

The Varian XL-200 NMR spectrometer operates at a ^{13}C NMR frequency of 50.3 MHz. Proton spins were decoupled with a radiofrequency field strength of 1.0 mT (i.e. $\gamma\text{B}_2/2\pi = 40\text{ kHz}$). This was reduced to 0.5 mT during cross-polarisation, in order to establish the Hartmann-Hahn condition. A contact time of 1 ms was chosen as a compromise between the requirement of full cross-polarisation:

contact time $\gg$ cross-polarisation time constant,

and the need to maintain adequate proton spin magnetisation in the rotating frame:

contact time $< T_{1\rho}(\text{H})$.

Spin relaxation studies¹¹ of New Zealand coals have shown cross-polarisation time constants in the range 0.02-0.6 ms, and values of $T_{1\rho}(\text{H})$ in the range 2-4 ms. The choice of a contact time of 1 ms is consistent with the observation of Sullivan and Maciel¹² that for the majority of United States coals studied, no marked changes in relative signal areas were observed for contact times greater than 1 ms. Hays¹³ and Packer *et al.*¹⁴ have reported similar conclusions for British coals. Dudley and Fyfe¹⁵ have

fitted magnetisation curves to a theoretical expression, and found small deviations between the best-fit parameters and the results for a 1 ms contact time; e.g. for a lignite, the apparent percentage of aromatic carbon was $70 \pm 3\%$ for the curve-fitting experiment, but 75% for a single measurement with a contact time of 1 ms. We have avoided full curve-fitting experiments, because of the instrument time involved. We accept the possibility of a bias in relative signal areas resulting from the fact that the 1 ms contact time is neither much longer than the cross-polarisation time constant, nor much shorter than $T_{1\rho}(H)$.

Each 15 ms of data acquisition was followed by a delay of 0.1 s (lignites and subbituminous coals), 0.2-0.9 s (bituminous coals), or 0.4 s (semianthracite). Measurements of the proton spin-lattice relaxation time constant showed that these delays were adequate for recovery of the proton magnetisation¹¹. Delays less than 0.9 s were used for bituminous coals only when relaxation experiments showed that these were acceptable. Proton magnetisation recovery is slowest for coals in this rank; a similar observation has been reported by Yokono and Sanada¹⁶.

Transients from 5000 cross-polarisation sequences were averaged, except for experiments intended for resolution enhancement - in which case up to 7×10^4 transients were averaged. A spectral width of 40 kHz was used, in order to provide adequate baseline on either side of the spectrum during adjustment of the phase controls. The transmitter was placed close to the centre of the coal spectrum ($\delta \sim 100$) and quadrature detection was used. Free induction decays were zero filled to at least 4K before Fourier transformation. Resolution-enhanced spectra were produced by Lorentzian-to-Gaussian transformation¹⁷, involving an exponentially increasing function (time constant 1 ms) and a Gaussian apodisation function (time constant 2ms). All other spectra were broadened by application of a sensitivity enhancement function, consisting of the product of an exponential decay curve (time constant 20 ms) and a Gaussian curve (time constant 10 ms). These combinations of time constants were chosen after trial-and-error testing.

Chemical shifts were adjusted to a scale based on external tetramethylsilane, with hexamethylbenzene used as a secondary reference. A literature value of $\delta(\text{methyl}) = 17.4$ was used for this purpose¹⁸.

Sample details are shown in Table 1, and sample locations are shown in Fig.2.

3 SIGNAL ASSIGNMENTS

3.1 Resolution Enhancement

Figs 3-6 show resolution-enhanced spectra of samples selected to illustrate particular spectral details. The resolution-enhancement process does not conserve relative signal areas, so it cannot be used for quantitative NMR; but the improved separation of overlapping signals can assist assignments.

Resolution enhancement has been used in other published ^{13}C CP/MAS NMR studies of coal^{5,10}, but the results have shown less detail than can be seen in Figs 3-6. This detail could be a characteristic of the selected samples, rather than the particular resolution enhancement technique used by us. Hatcher *et al.* have shown that the amount of resolvable detail can vary from one sample to another, even when no resolution enhancement is used²⁰.

3.2 Spinning sidebands

The signal assignments are complicated by the presence of "spinning sidebands", marked "SSB" in Figs 3-6. These extra signals are produced by modulation of the magnetic shielding of ^{13}C nuclei during sample rotation.

Spinning sidebands can be recognised by the regular spacing at intervals of the spinning frequency, on either side of the centreband. In this case, the spinning frequency corresponds to a spacing of 50 ppm on the chemical shift scale. The spinning frequency of 2.5 kHz was chosen as the maximum that could be maintained on a routine basis. Slower spinning speeds would have resulted in more crowded spectra.

The effects of spinning sidebands are most noticeable for ^{13}C in aromatic structures, since the ^{13}C nuclei are more shielded by about 100-200 ppm (parts per million) when the magnetic field is perpendicular to the plane of the ring, compared with orientations in which the magnetic field is parallel to the ring²¹. Chemical shift anisotropies are smaller by about an order of magnitude for tetrahedrally-bonded carbon, e.g. in methyl, methoxyl or alcoholic functional groups²¹. Spinning sidebands from such groups are too small to be seen in the coal spectra shown here.

3.3 Coalified wood

Fig.3 shows the ^{13}C NMR spectrum of a sample taken from a coalified log. This log was one of many embedded in the face of the Newvale opencast lignite mine at Waimumu. Hatcher et al. have published spectra of coalified logs alongside spectra of lignin, pointing out the similarities²⁰. The signals of Fig.3 can be assigned by comparison with Nimz's assignments for lignin²²; $\delta = 113$ (CH groups at aromatic ring positions adjacent to oxygen), $\delta = 130$ (other aromatic carbon, whether substituted or not). The chemical-shift compilation of Snape et al.²³ shows that a signal close to $\delta = 153$ would be expected for phenolic C-O groups in structures containing only one oxygen per benzene ring. No significant signal appears at this position in Fig.3, and this observation is consistent with the low abundance of such substitution patterns in lignin. Substitution by a second oxygen at an adjacent ring position moves the phenolic C-O signal several ppm to low δ ; e.g. the 3-methoxy-4-hydroxyphenyl group (abundant in softwood lignins) provides signals at $\delta = 148.5$ (C-3), $\delta = 147$ (C-4)²². Etherification at C-4 moves this signal to $\delta = 150.4$, without significant effect on the C-3 signal²². Carbon substitution at C-5 or C-6 can move the C-O signals to a few ppm either side of the chemical shifts for the basic building units of the polymer. The signal at $\delta = 147$ is consistent with structures based on the 3-methoxy-4-hydroxyphenyl group.

Hardwood lignins contain a preponderance of structures based on 3,5-dimethoxy-4-hydroxyphenyl groups. The C-3 and C-5 signals

appear at $\delta = 148.5$, while the C-4 signal is shifted to $\delta = 136$ ppm by the presence of oxygen at both adjacent ring positions²². Etherification of C-4 moves the C-3 and C-5 signals to $\delta = 154.5$, and the C-4 signal to $\delta = 138.5$. Fig.3 shows no signals in the regions $\delta = 149-155$ or $\delta = 136-139$, and it is therefore not consistent with a hardwood lignin structure.

Signals at $\delta = 63, 74$ and 106 are assigned to cellulose. Similar signals have been reported for ^{13}C CP/MAS NMR spectra of coalified wood from Poland²⁰, Germany²⁰ and Australia²⁴. Hatcher *et al.* have shown that the strengths of cellulose signals were consistent with the results of wet chemical analysis for cellulose²⁰.

Signals in the region $\delta = 10-41$ are assigned to resin acids, following the assignment of Hatcher *et al.*²⁰.

3.4 Lignite

Fig.4 shows the spectrum of a sample of homogeneous dark lignite taken from the vicinity of the coalified log discussed above. The dominant feature is a signal at $\delta = 32$, assigned to methylene groups. This is close to the value of $\delta = 35$ reported²⁵ for the polymethylene chains in crystalline $n\text{-C}_{20}\text{H}_{42}$. A signal at $\delta = 15.5$ is assigned to methyl groups on saturated hydrocarbon structures.

Signals in the aromatic region are similar to those observed for the coalified log, except for a signal at $\delta = 154$. This is not consistent with a lignin-like structure. The chemical shift is close to that expected for C-3 and C-5 of etherified hardwood lignin units, but this possibility can be eliminated because of the lack of a corresponding C-4 signal at $\delta = 139$. The signal at $\delta = 154$ could be explained by phenols with only one oxygen per ring²³, or by structures with two oxygens per ring if these are in positions meta to each other. In the latter case, the second oxygen has little effect on the chemical shift of the first phenolic functional group. Tannins provide one example of naturally-occurring phenolics with three oxygen atoms placed at mutually meta positions around a ring. The

A-ring C-O signals form a band centred on $\delta \sim 155$ ²⁶. The amino acid tyrosine provides an example of a naturally-occurring phenolic compound with only one oxygen per benzene ring, contributing a signal at $\delta = 157$ in the ^{13}C NMR spectrum²⁷.

The signal at $\delta = 153$ can be seen in the spectrum of Morton Mains lignite also (Fig.5). Again, it is of similar intensity to the signal at $\delta = 147$. This sample was selected as an example of a lignite so rich in phenolic structures that the signals at $\delta = 147$ -153 dominate the aromatic region, while the corresponding methoxyl signal at $\delta = 56$ is the tallest peak in the spectrum.

The observation of a difference in phenolic structures between the woody and non-woody components of South Island lignite is consistent with published ^{13}C CP/MAS NMR spectra of Australian (Yallourn) brown coal. Yoshida *et al.*²⁸ were unable to resolve a shoulder at $\delta \sim 158$ from the main phenolic peak at $\delta = 150$; but Wilson *et al.*²⁴ selected the xylite (i.e. woody) component from this coal, and published a spectrum which shows no sign of the shoulder. Neither of these two groups of authors used resolution enhancement, which we found necessary for separation of the two phenolic signals in the spectrum of the Morton Mains lignite.

3.5 Subbituminous coal

Fig.6 shows a spectrum of a subbituminous coal. Signals at $\delta = 110$ -120 are assigned to CH groups adjacent to phenolic groups (as for lignites). As coalification proceeds, these signals are lost along with the phenolic signals in the region $\delta = 145$ -155. The result is an apparent sharpening of the aromatic signal at $\delta = 129$.

The phenolic signal at $\delta = 155$ is close to the position of the corresponding lignite signal, but the signal at $\delta = 147$ has been replaced by a weaker signal at $\delta = 144$. This is shifted a little too far to low δ for lignin-like structures, and there is no evidence of a lignin-derived methoxyl signal at $\delta = 56$. The signal at $\delta = 144$ could be the result of alkyl substitution

of aromatic rings; Snape et al. have pointed out that the spectra of alkyl benzene model compounds include signals in the range $\delta = 142-149$, corresponding to substituted aromatic carbon²³. The presence of phenolic groups, as in lignin or lower-rank coals, results in a shift of several ppm to low δ ²². The assignment of the signal at $\delta = 144$ to alkyl substitution positions would therefore be reasonable only in coals with a low abundance of phenolic functional groups.

4 GENERAL TRENDS

4.1 Routine spectra

A limit of 5000 transients was arbitrarily chosen for routine characterisation of coal by ¹³C CP/MAS NMR. A collection of 31 such spectra appears in the appendix to this report. The limited number of transients is adequate for a display of general trends, but is generally insufficient for resolution enhancement. Any improvements in resolution can only be achieved at the expense of signal-to-noise ratio.

The standard total of 5000 transients meant that each of the spectra of lignites and subbituminous coals required only 10 minutes of data accumulation. The rapid sample-changing capability of the Varian XL-200 obviates any need to remove the probe from the magnet in between experiments. It is therefore possible to produce routine spectra of low-rank coals at a rate of several samples per hour.

Bituminous coals required longer pulse delays for recovery of the proton magnetisation (see Section 2), so each spectrum required up to 75 minutes of data accumulation before 5000 transients could be completed. The sole example of a semi-anthracite required 35 minutes of data averaging.

4.2 Lignites (A1-A13)

The most obvious difference between the various lignite spectra is the variable contribution from the methylene signal. This is a minor contribution in the case of the Morton Mains lignite (Spectrum A1). The signal is the tallest in the spectra of

Ashers Waituna, Mataura and Waimumu lignites (Spectra A2-A7) and it dominates the spectra of all of the Otago lignite samples (Spectra A8-A13).

Pugmire et al.²⁹ have pointed out that maceral composition must be considered when interpreting ¹³C NMR spectra of coal. These authors have isolated maceral groups from two high-volatile bituminous coals²⁹, and maceral-rich concentrates from six other coals³⁰. They found that the methylene signal dominated spectra of alginite; it was the tallest peak in spectra of sporinite, but only a minor peak in spectra of vitrinites and inertinites. Roxburgh lignites have a particularly large sporinite component (16-17%) compared with other New Zealand lignites³¹, but even this level of sporinite is not sufficient to explain the observation that the saturated hydrocarbon signals account for almost half of the signal area in the spectra of Roxburgh lignites (Spectra A8-A11). Furthermore, Zilm et al.³⁰ have pointed out that the saturated-hydrocarbon signal in the sporinite spectrum consists of a broad band of component signals, rather than a discrete polymethylene signal. Zilm et al.³⁰ found a sharp polymethylene signal in the spectrum of alginite, but this maceral is not found in normal humic coals³¹. Even if the entire exinite/liptinite group of macerals is considered, the range of abundances in New Zealand lignites³² (4-20%) is too small to explain the saturated hydrocarbon content. It therefore appears that the saturated hydrocarbon structures must be distributed among other macerals, i.e. those in the vitrinite/huminite and inertinite groups.

The lignite spectra also differ in the relative importance of the phenolic signal amongst the aromatic band. The phenolic hydroxyl content tends to decrease as coalification proceeds³³. ¹³C NMR could provide a particularly useful method for studying such trends, since it is faster than the acetylation procedure (employing ¹⁴C-labelled acetic anhydride) originally used to establish the correlation between phenolic hydroxyls and rank³⁴. There is also some doubt about the accessibility of acetylation reagents to reactive sites, since exposure of coals to the vapours of polar solvents can swell the microporous structure,

thus exposing more phenolic hydroxyl groups for determination³⁵. The NMR results (Spectra A1-A11) suggest the following order of increasing coalification; Morton Mains << Ashers Waituna < Mataura ~ Waimumu ~ Hawkdun < Home Hills ~ Roxburgh.

Spectra A4 and A5 provide an opportunity to compare samples from different seams in the same mine; in this case, seams 5 and 6 of the Goodwin mine. No significant differences can be seen.

Spectra A6 and A7 correspond to run-of-mine samples, both taken from the same (Newvale) mine, but on different dates. In this case, a small difference can be seen; the earlier sample (Spectrum A6) contains a trace of cellulose, contributing signals at $\delta = 75$ and 106.

4.3 Subbituminous coals (A14-A24)

The subbituminous coals show variations in the contribution from polymethylene carbon, although the range of variation is not as wide as for the lignites. The Mokau sample (Spectrum A14) shows a particularly strong, sharp polymethylene signal at $\delta = 30$, superimposed on a broader band of saturated hydrocarbon signals. The Ohai sample (Spectrum A21), at the other extreme, shows a relatively broad band of saturated hydrocarbon signals.

There are differences in the contribution from phenolic carbon also; e.g. the phenolic signal at $\delta \sim 153$ is slightly more prominent in the Huntly East and Kopuku spectra, compared with spectra of the other three Waikato samples (Huntly West, Weavers and Ohinewai). The phenolic signal is weak in the spectra of South Island subbituminous coals (Spectra A21-A24) compared with North Island subbituminous coals (Spectra A14-A20).

4.4 High-volatile bituminous coals (A25-A30)

The most obvious variation within this group is the sharpening of the aromatic signal as the phenolic signals disappear. A sequence of increasing coalification, based on the relative heights of signals at $\delta = 130$ and 153, is; Topline ~ Mulken < Island Block ~ Strongman < Charming Creek << Webb. This trend

does not follow values for the specific energy of each coal, i.e. 33.2, 30.9, 32.9, 33.4, 33.8 and 35.1 kJ/kg (daf) for the six samples in the order given above. The trend in phenolic carbon does not follow the values for percent volatile matter either. These values were found to be 42.4, 44.5, 42.7, 43.0, 44.6 and 36.4% volatile matter (daf). The NMR results therefore provide a measure of coalification which is independent of the two parameters (specific energy, percent volatile matter) chosen by the ASTM as indicators of "rank".

The polymethylene signal is particularly weak in the spectrum of Webb coal (Spectrum A30). Spectra run with variable spinning frequencies have confirmed that the peak labelled "methylene + SSB" consists of a polymethylene signal of similar intensity to the methyl signal at $\delta = 21$ plus a minor contribution from a second-order spinning sideband.

4.5 Semianthracite (A31)

Spectrum A31 shows the phenolic signal entirely absent in the case of a semianthracite. Small methylene and methyl peaks persist, but the spectrum is dominated by the aromatic centre-band and spinning sidebands out to third order.

5 AROMATICITY

5.1 Measurement of aromaticity

Coalification has been described as "a process in which the degree of condensation and aromaticity of the starting material increase continuously"³⁵. Historically, the most common type of information provided by ¹³C CP/MAS NMR has been the aromaticity, f_a , defined as²;

$$f_a = (\text{C in aromatic rings})/(\text{total C}) \quad [1]$$

We follow Miknis et al.³⁶ in using the symbol f'_a for our estimates of aromaticity, since the apparent values of f_a measured directly by integration of NMR spectra must inevitably include systematic errors, as a result of overlapping signals and spinning sidebands.

The simplest approach is to draw a vertical line in the spectrum at the position of the minimum between the "aromatic" and "aliphatic" resonance regions, and to count intensity to the left of that boundary as aromatic and to the right as aliphatic. Miknis *et al.*³⁶ chose $\delta = 85$ as the boundary; we prefer $\delta = 65$, so as to include the first-order spinning sideband in with the other aromatic signals. This simple approach fails to account for the possible contribution from olefinic carbon, indistinguishable from aromatic carbon in the ^{13}C NMR spectrum. It is also difficult to resolve carbonyl, carboxylic and quinone signals from the high- δ side of the aromatic band, particularly if (as in the present case) this region contains spinning sidebands from the aromatic signal. The so-called "aliphatic" region also includes alicyclic structures, and methoxyl groups on aromatic rings. The parameter f'_a is therefore more correctly described as:

$$f'_a \sim (\text{sp}^2\text{-hybridised carbon})/(\text{total carbon}).$$

The presence of spinning sidebands adds to the problems of measuring f'_a . Spinning sidebands can be reduced to negligible levels if the sample is spun sufficiently fast. Miknis *et al.*³⁶ recommend a spinning frequency of 2.5 kHz for a magnetic field of 1.4 T, and proportionately higher speeds for higher fields. This would mean a minimum spinning frequency of 8.4 kHz for the Varian XL-200 spectrometer, a frequency which is not yet attainable for commercial equipment. Sideband-free NMR spectra of coal can be constructed by use of the appropriate pulse sequences, such as PASS^{7,37}; but these sequences are dependent on minimal spin relaxation over periods of a millisecond or so, while refocussing pulses are applied. We have found that the relative area of the methylene signal (in particular) tends to diminish after a spin-refocussing pulse sequence, so we have avoided the use of PASS in aromaticity determinations.

Furimsky *et al.*^{38,39} and Cyr *et al.*⁴⁰ used spinning speeds of 3.4-3.5 kHz and a magnetic field of 4.2 T in their studies of Canadian coals. This combination reduced the spinning sideband intensities below the levels seen in our Spectra A1-A31, but it had the unfortunate effect of placing the first-order low- δ

sideband in the region assigned to "aliphatic" carbon. We suggest that if attainable spinning frequencies are not sufficient to place the first-order sideband on the low- δ (or negative- δ) side of the spectrum, then the spinner should be deliberately slowed down to place the first-order sideband at a position clearly resolved from the sp^3 -hybridised carbon band, on the high- δ (left-hand side) of that band. Our reasoning is as follows; Herzfeld and Berger⁴¹ have shown how spinning-sideband intensities can be calculated from the principal values of a chemical-shift tensor. The logic can be inverted to obtain a chemical-shift tensor from ratios of sideband intensities. We have taken the spectrum of semianthracite (Spectrum 31) as an example of a clearly-resolved sideband pattern. The relative intensities of the first-order sidebands and the high- δ second-order sideband provide principal values of $\delta_{11} = 254$, $\delta_{22} = 98$ and $\delta_{33} = 28$ for the effective chemical shift tensor; this is not a true tensor, because the spectrum contains contributions from a range of chemical structures with different tensors. The effective tensor values allow us to estimate the intensity of sidebands which were not extracted from the signal area of the saturated-hydrocarbon signal. In the case of the semi-anthracite, the low- δ second and third-order sidebands account for 11% of the aromatic signal, so the corrected aromaticity is $f_a' = 0.92$. If the sample was spun at 3kHz, the low- δ first-order sideband would merge with the saturated-hydrocarbon signal, and the systematic error would be even higher; about 23% of the aromatic signal would be ignored in the simplified method of estimating f_a' . This systematic error diminishes as higher spinner frequencies are used (Fig.9), but the systematic error does not drop back down to 11% until a spinning frequency of 5 kHz is reached.

Some authors have attempted to correct estimates of f_a' for spinning sideband intensities. We have chosen to ignore these corrections until a reliable procedure is established. The chemical shift "tensor" values for semianthracite are not necessarily appropriate for the lower-rank coals, so (for consistency) all values of f_a' in Table 2 are uncorrected.

5.2 Trends in aromaticity values

The mean aromaticity for New Zealand bituminous coals was found to be $f_a' = 0.65$, indistinguishable from the mean value of $f_a' = 0.66$ for New Zealand subbituminous coals - or even the mean value of $f_a' = 0.63$ for Southland lignites. Furimsky et al.³⁹ have pointed out that CP/MAS NMR results are affected only by the organic portion of the coal, while the ASTM ranking is based on heating value of the moist mineral-matter free coal. Two coals may be structurally similar when compared on a dry basis, even if they have different heating values when moist. Aromaticity is therefore more directly related to coal structure than to rank.

Several authors have tried to correlate aromaticity with the extent of coalification, as evidenced (e.g.) by plots of aromaticity against weight-% carbon content^{1,10,36,42-44}. Early plots did show some correlation for United States coals^{1,36,44}, but Retcofsky found discrepancies when aromaticity values for three Chinese coals were plotted on the same graph¹⁰. More recent CP/MAS NMR studies of coals from Canada³⁹, Australia⁴² and Indonesia⁴³ have produced correlations which differ significantly from the best-fit curve for United States coals. The four best-fit curves are shown in Fig.8. The straight line shown for Canadian coals was obtained by linear least-squares analysis of data published in Ref.39; the remaining curves were taken directly from Refs. 36, 42 and 43. Our data for New Zealand coals show a considerable scatter, straddling all of the published best-fit curves (Fig.8).

Since aromatic structures tend to have less hydrogen than saturated-hydrocarbon structures, one might expect the aromaticity to drop as the H/C ratio rises. Again the New Zealand coals show a considerable scatter around a weak correlation (Fig.9). Similar weak correlations between aromaticity and H/C have been reported for coals from Canada³⁹, Australia⁴² and Indonesia⁴³.

Furimsky et al. have demonstrated a correlation between aromaticity and the weight-% oxygen content of Canadian coals³⁹.

Our results show a considerable scatter about the published best-fit curve (Fig.10).

Painter et al. have suggested multiplication of the weight-% carbon content by the aromaticity, to obtain the weight-% aromatic carbon content of a sample of coal⁶. They found a good correlation between this parameter and the fixed-carbon content for a collection of United States coals and concentrated maceral fractions. We have likewise found a good correlation for New Zealand coals (Fig.11). Linear least-squares analysis yields:

$$(\% \text{ aromatic carbon, d.a.f.}) = 8.9 + 0.745 (\% \text{ fixed carbon, d.a.f.}), \quad [2]$$

with $R = 0.969$ for 22 coals. While this correlation is far more convincing than correlations against weight-% carbon or weight-% oxygen, it does not make aromaticity measurements redundant. Aromaticities predicted from Eq.[2] sometimes differ significantly from the experimental values; e.g. Eq.[2] predicts $f'_a = 0.73$ for Ohai coal, compared with an experimental value of 0.65. The difference is several times larger than the experimental uncertainty.

6 CONCLUSION

We have shown that it is possible to measure coal aromaticities at a rate of several samples per hour for subbituminous coals and lignites, with a slower sample throughput for coals of higher rank. We have also shown that such measurements of aromaticity do not simply duplicate results that could be obtained by coal petrography or ultimate analysis.

Routine ¹³C CP/MAS NMR spectra of coal also show details of chemical functionality beyond a simple division into aromatic and nonaromatic carbon, although we have not attempted to estimate the content of the various functional groups on a quantitative basis. In some cases (e.g. methoxyl groups and cellulose) this is already feasible, provided a suitable baseline is assumed. In other cases (e.g. phenolic carbon), the intensity of the centreband would have to be corrected for

intensity spread into sidebands. Estimation of the carboxylic content may not provide reliable results, unless higher spinning frequencies can be attained, because the carboxylic signal coincides with a spinning sideband of the aromatic band. The possibility of using the cellulose content (in lignites) and the phenolic content (in all ranks) as parameters related to the degree of coalification could provide some incentive for development of procedures for more detailed functional group analysis.

Resolution-enhancement experiments have shown that New Zealand coals can yield more fine detail than can be seen in published ^{13}C CP/MAS NMR spectra of coals from sources overseas. This could lead to paleobotanical uses of NMR - e.g. the distinction between hardwood and softwood sources for woody matter, based on precise chemical shift measurements in the phenolic region.

The use of NMR seems most promising in characterisation of lignites, since these samples show the most spectral detail and since samples from different sources can have very different chemical structures, even if they are of similar rank according to the ASTM classification scheme.

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TABLE 1. Details of samples used to generate the ^{13}C CP/MAS NMR spectra collected in the Appendix of this report. CRA code numbers refer to analyses by Coal Research Association of New Zealand (Inc); ROM = run of mine, O/C = opencast, U/G = underground. Rank classifications were based on ASTM criteria⁴⁶.

Number	Location	CRA codes	Sample details
LIGNITES			
1	Morton Mains	24/688	CRA drillhole.
2	Ashers Siding	30/647	Face sample, disused O/C mine (formerly Ashers Waituna).
3	Mataura	30/654	Face sample, NZ Paper Mills O/C mine.
4	Waimumu	30/645	Face sample, Goodwin O/C mine, Seam 5.
5	Waimumu	30/646	As for 4, but Seam 6.
6	Waimumu	30/648	ROM, Newvale O/C mine, May 1982.
7	Waimumu	30/655	ROM, Newvale O/C mine, Oct 1982.
8	Roxburgh	27/003	ROM, Harliwich (MacPherson's) O/C mine.
9	Roxburgh	30/651	ROM, Harliwich O/C mine.
10	Roxburgh		Face sample, outcrop formerly mined as Crossan's Pit.
11	Roxburgh	24/454 etc	CRA drillhole 2086. Composite of CRA 24/454, 463, 481, 494, 510.
12	Home Hills	30/453	ROM, Idaburn O/C mine, formerly known as Bate's Pit. Oct 1982.

TABLE 1 (Cont'd)

Number	Location	CRA codes	Sample details
13	Hawkdun	24/635	CRA drillhole, composite sample. SUBBITUMINOUS COALS
14	Mokau	30/663	Face sample, R. Farnsworth (Valley Collieries) mine, Mahoenui, 1981.
15	Kawhia	30/662	3m vertical channel sample, Pirongia (Okoko Rd) O/C mine.
16	Huntly East	30/658	Face sample from mine drive, Huntly East U/G mine.
17	Huntly West	30/657	3.5m vertical channel (full seam) from drive of No.1 intake, Huntly West U/G mine.
18	Weavers	30/661	ROM, Weavers O/C mine, Huntly, 1981.
19	Ohinewai	29/565	CRA drillhole 9706, 1982.
20	Kopuku	30/660	ROM, Kopuku O/C mine, Maramarua, 1982.
21	Ohai	30/458	ROM, Wairakei, Morley and No.16 O/C mines, Oct 1982.
22	Braziers	30/457	ROM, Braziers O/C mine (formerly known as Night-caps), Oct 1982.
23	Kai Point	30/450	ROM, Kai Point O/C mine, Kaitangata, Oct 1982.
24	Wangaloa	30/451	ROM, Wangaloa O/C mine, Kaitangata, Oct 1982.

TABLE 1 (Cont'd)

Number	Location	CRA codes	Sample details
BITUMINOUS COALS			
25	Mulken	30/341	ROM, Mulken (Burkes Creek) U/G mine, Reefton.
26	Island Block	30/344	ROM, Island Block U/G & O/C mine, Garvey Creek, Reefton.
27	Topline	30/346	ROM, Topline U/G mine, Reefton.
28	Strongman	30/329	ROM, Strongman U/G mine, Greymouth.
29	Charming Creek	30/352	ROM, Charming Creek mine, Seddonville, Buller.
30	Webb	30/359	ROM, Webb O/C mine, Stockton, Buller.
SEMIANTHRACITE			
31	Fox River	33/066	Geological specimen from outcrop.

TABLE 2. Data for the 31 coal samples listed in Table 1.
Values in brackets refer to representative values
for other samples from the same locality, taken from
Ref.47 (Samples 4 and 7), Ref.32 (other lignites),
Ref.31 (Sample 30), Ref.48 (other samples).

Number	Locality	% C (d.a.f.)	% H (d.a.f.)	% O (d.a.f.)	Fixed carbon (d.a.f.)	f _a ' (by NMR)
1	Morton Mains	(62.9)	(4.7)	(28.5)	(42.1)	0.64
2	Ashers Waituna	66.7	4.4	(27.9)	(42.8)	0.63
3	Mataura	68.6	4.0	26.0	46.0	0.62
4	Waimumu	68.8	4.4	25.3	(43.8)	0.62
5	Waimumu	69.4	4.6	23.8	(43.8)	0.61
6	Waimumu	68.4	4.7	25.8	44.0	0.64
7	Waimumu	68.9	4.1	25.6	(44.2)	0.65
8	Roxburgh	-	-	-	38.6	0.52
9	Roxburgh	69.9	5.8	22.7	38.7	0.52
10	Roxburgh	-	-	-	-	0.49
11	Roxburgh	(65.7)	(5.5)	(25.7)	(38.6)	0.55
12	Home Hills	68.2	4.5	26.0	(44.4)	0.64
13	Hawkdun	(66.5)	(4.7)	(25.5)	(41.6)	0.53
14	Mokau	73.8	5.8	15.2	-	0.62
15	Kawhia	69.3	4.6	21.0	-	0.68
16	Huntly East	75.1	4.8	18.6	55.4	0.65
17	Huntly West	74.0	5.2	19.4	52.5	0.65
18	Weavers	73.7	5.0	20.0	54.6	0.65
19	Ohinewai	72.4	4.9	21.6	-	0.68
20	Kopuku	72.8	4.8	21.2	52.3	0.65
21	Ohai	75.2	5.3	18.3	61.4	0.65
22	Braziers	72.2	4.6	21.7	-	0.73
23	Kai Point	70.7	4.8	19.4	(50.1)	0.67
24	Wangaloa	72.6	5.0	16.7	(49.9)	0.66
25	Mulken	(73.5)	(5.3)	(14.7)	55.5	0.64
26	Island Block	-	-	-	57.3	0.65
27	Topline	-	-	-	57.6	0.66
28	Strongman	(80.8)	(5.8)	(11.0)	57.0	0.67
29	Charming Creek	(79.2)	(5.5)	(7.7)	55.4	0.64
30	Webb	(85.4)	(5.0)	(5.7)	63.6	0.66
31	Fox River	(92.5)	(3.9)	(3.9)	89.8	0.83

9 FIGURE CAPTIONS

- Fig. 1 Cross-section of the rotor/stator assembly used for magic-angle spinning on the Varian XL-200 NMR spectrometer. Details of the compressed-air supply lines and air jets have been omitted for clarity.
- Fig. 2 Locations of sources for all samples.
- Fig. 3 Resolution enhanced NMR spectrum of a fragment of coalified log taken from the Newvale opencast lignite mine at Waimumu; sample collected by R H Newman, August 1982.
- Fig. 4 Resolution-enhanced NMR spectrum of lignite taken from the vicinity of the coalified log used for Fig.3. This lignite showed no obvious woody texture. Sample collected by R H Newman, August 1982.
- Fig. 5 Resolution-enhanced NMR spectrum of lignite from Morton Mains; see entry (1) of Table 1.
- Fig. 6 Resolution-enhanced NMR spectrum of subbituminous coal from Huntly West; see entry (17) of Table 1.
- Fig. 7 Systematic errors in estimating the total signal intensity for aromatic carbon, resulting from spinning sidebands which cannot be resolved from saturated-hydrocarbon signals. Lower curve; the first-order sideband can be resolved for spinning frequencies up to 2.5 kHz. Upper curve; the first-order sideband merges with the saturated-hydrocarbon signal at higher spinning frequencies.
- Fig. 8 Aromaticity of New Zealand coals, plotted against the carbon content (dry ash free basis). Best-fit lines are shown for data published for coals from United States (solid line), Australia (dots only), Indonesia (dashes only) and Canada (dots and dashes).

- Fig. 9 Aromaticity of New Zealand coals, plotted against the atomic hydrogen/carbon ratio (dry ash free basis).
- Fig.10 Aromaticity of New Zealand coals, plotted against the oxygen content (dry ash free basis).
- Fig.11 Aromatic carbon content of New Zealand coals, obtained by multiplying aromaticity by the results of ultimate analysis, plotted against fixed carbon (dry ash free basis). The broken line shows results for United States coals⁶.

Figure 1 : Rotor and Stator

Fig. 2 : Sample locations

Figure 3 : Coalified log

Figure 4 : Waimumu lignite

Figure 5 : Morton Mains lignite

Figure 6 : Huntly West coal

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

10 APPENDIX

Routine ^{13}C CP/MAS NMR spectra for the 31 New Zealand coals listed in Table 1. Spectra have been collated in the following order; Southland lignites, Otago lignites, North Island subbituminous coals, South Island subbituminous coals, bituminous coals, semianthracite. All spectra were obtained with the same experimental conditions, except that delay between pulses was adjusted to allow recovery of the proton spin magnetisation.

Southland lignite
MORTON MAINS

A1

Southland lignite
ASHERS WAITUNA

A 2

Southland lignite
MATAURA

A 3

Southland lignite
WAIMUMU / GOODWIN

A 4

Southland lignite

WAIMUMU / GOODWIN

A 5

Southland lignite

WAIMUMU / NEWVALE

A 6

Southland lignite

WAIMUMU / NEWVALE

A 7

Otago lignite
ROXBURGH / HARLIWICH

A 8

Otago lignite

ROXBURGH / HARLIWICH

A 9

Otago lignite

ROXBURGH / CROSSAN'S PIT

A 10

Otago lignite

ROXBURGH / DRILLHOLE 2086

A 11

Otago lignite

HOME HILLS / IDABURN

A 12

Otago lignite
HAWKDUN

A 13

North Island sub-bituminous

MOKAU

A 14

North Island sub-bituminous

KAWHIA

A 15

North Island sub-bituminous

HUNTLY EAST

A 16

North Island sub-bituminous

A17

HUNTLY WEST

North Island sub-bituminous

WEAVERS

A 18

North Island sub-bituminous

OHINEWAI / DRILLHOLE 9706

A 19

North Island sub-bituminous

KOPUKU

A 20

South Island sub-bituminous

A 21

OHAI

South Island sub-

BRAZIER

bituminous

A 22

South Island sub-bituminous

A 23

KAI POINT

South Island sub-bituminous

A 24

WANGALOA

High-volatile bituminous

MULKEN

A25

High-volatile bituminous

ISLAND BLOCK

A 26

High-volatile bituminous

TOPLINE

A 27

High volatile bituminous

STRONGMAN

A 28

High-volatile bituminous

CHARMING CREEK

A 29

High-volatile bituminous

WEBB

A 30

Semi-anthracite

FOX RIVER

A 31

Comparison of Australasian Tertiary coals based on
resolution-enhanced solid-state ^{13}C nmr spectra

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ABSTRACT

Carbon-13 solid-state nuclear magnetic resonance spectroscopy was used to characterise 32 low-rank coals from New Zealand and Australia. A combination of high magnetic field (4.7 T) and resolution enhancement was used to extract spectral details beyond those seen in published spectra of coals of similar rank. Signal heights were used to characterise organic functional group distributions. The spectra showed close similarities between Australian brown coals and low-rank New Zealand subbituminous coals, particularly those mined in the North Island. The spectra of New Zealand lignites all showed stronger signals from cellulose, methoxyl groups and phenols. Almost all of the New Zealand coals showed a relatively strong signal from polymethylene chains, compared with the Australian brown coals. This led to a prediction of higher alkene yields from pyrolysis of the New Zealand coals. Variations in phenolic substitution patterns were attributed to variations in the relative proportions of tannins and lignins in the depositional environments.

Solid-state ^{13}C nuclear magnetic resonance spectroscopy has been used to characterise the organic content of a number of low-rank coals from Australia¹⁻⁷ and New Zealand⁸. A variety of types of spectrometer have been used, with magnetic fields ranging from 1.4 T to 7.0 T. As a result of the diversity of field strengths, the published spectra do not provide a useful basis for comparison of Australian brown coals with New Zealand coals of similar geological age. We have found that a combination of a superconducting spectrometer and digital resolution enhancement can reveal more spectral detail than that seen in published spectra of Australian brown coals. We have therefore run a collection of samples on the same spectrometer, for direct comparison. The collection consisted of 19 New Zealand subbituminous coals, 11 New Zealand lignites and 2 Australian brown coals.

All of the coals were sampled from Tertiary deposits. Paleobotanical studies have shown similarities in the vegetation which contributed to coals deposited throughout Australasia during this geological period. Lumps of resin from trees of the genus Agathis (kauri) are common in Australian brown coals⁹ and New Zealand lignites¹⁰, and fragments of similar resins have been found in subbituminous coals from both the North Island and South Island of New Zealand¹¹. Other plant remains found in both Australian¹² and New Zealand¹³ Tertiary coals include foliage and pollens from conifers of the genera Dacrydium (c.f. modern rimu), Phyllocladus (c.f. modern celery pine) and Podocarpus (c.f.

modern totara). Remains of hardwoods of the genus Nothofagus (beech) have also been found in both the Australian brown coals¹² and New Zealand lignites¹³. The plant communities which formed the Australasian Tertiary coals were different from those which formed other coal deposits elsewhere in the world during the same period of time; e.g. the conifers which contributed to the German brown coals were mostly Taxodium (swamp cypress) and Sequoia trees¹⁴.

The term "brown coal" is commonly used in Australia to describe deposits which would be classified as lignite B in the ASTM scheme¹⁵. Published analyses for samples of Australian brown coals from the Morwell mine show carbon contents in the range 66 to 71% on a dry ash-free basis¹⁶. These values are similar to typical values for New Zealand lignites⁸ (67 to 71%), but less than typical values for New Zealand subbituminous coals⁸ (73 to 78%). We have retained the term "brown coal" to distinguish the Australian deposits from New Zealand lignite deposits, since we have found distinct differences in the nmr spectra despite similarities in ASTM ranks and carbon contents.

EXPERIMENTAL

Samples

Most of the coals were run-of-mine samples which had been collected and prepared for routine analysis. Four of the coals were sampled from drillholes. Each sample was ranked according to the ASTM classification scheme¹⁵. The lignites

and brown coals were partly dried before proximate analysis, so specific energies were converted to a moist basis with published bed moistures for other samples of lignites¹⁷ or brown coals¹⁶ taken from the same localities. In the following list of sources, the lignites are labelled "A" or "B" and the subbituminous coals "A", "B" or "C" according to the ASTM classification scheme¹⁵.

Central Otago lignites; Hawkdun/drillhole (B), Home Hills/Idaburn mine (B), Roxburgh/Harliwich mine (2 samples, B), Roxburgh/drillhole (B).

Southland lignites; Mataura mine (B), Ashers-Waituna/Ashers Siding mine (B), Waimumu/Newvale mine (2 samples, A and B), Waimumu/Goodwin mine (2 samples, A).

South Island subbituminous coals; Kaitangata/Wangaloa mine (C), Kaitangata/Kai Point mine (C), Braziers mine (C), Garden Creek mine (B) Terrace mine (A), Heaphys mine (A), Ohai/mine composite (A).

North Island subbituminous coals; Maramarua/Kopuku mine (C), Kawhia/Pirongia mine (C), Ohinewai/drillhole (C), Mokau/Valley Collieries mine (B), Ohura/Squires Creek mine (B), Rotowaro/Mahons mine (B), Rotowaro/Maori Farm mine (B), Huntly/Weavers mine (B), Rotowaro/Waipuna mine (A), Huntly East mine (A), Huntly West mine (A), Ohura/Collieries mine (A).

Australian brown coals; Morwell mine and Loy Yang/drillhole, both sites in the Latrobe Valley, Victoria. The Morwell sample was taken from Drum 289 of the 1979 100 tonne bulk sample, prepared by the State Electricity Commission of Victoria for research purposes. The Loy Yang sample was taken from a depth of 67-68 metres down bore LY1277, in a band described as medium-light lithotype¹⁶.

Ultimate analyses for most of the New Zealand samples have been published in Reference 8. Literature data for the Morwell sample are¹⁸; 70.4% C, 4.9% H, 0.5% N, 0.3% S, 23.9% O (wt% mineral-matter free). Data are not available for the Loy Yang sample, but literature data for coal from the same lithotype band of Bore LY1277 are¹⁶; 69.6% C, 4.9% H, 0.6% N, 0.3% S and 24.6% O.

All of the samples were crushed to <200 μm .

Nuclear magnetic resonance

About 0.3 g of powder was packed in a rotor made of Kel-F, and a layer of boric acid was spread over the top to a depth of about 1 mm. The composite sample was then compressed by a cylindrical plunger, and the layer of boric acid provided a smooth, hard surface which seldom cracked during sample spinning. Rotors were spun at 2.5 ± 0.2 kHz in the standard CP/MAS probe of a Varian XL-200 nmr spectrometer. All of the nmr spectra were run at 50.3 MHz. A cross-polarisation contact time of 1 ms was followed by 15 ms of data

acquisition and a recovery delay of 150 ms before the next contact time. Cross-polarisation rates and proton spin-lattice relaxation rates were measured for selected samples. The results showed that the contact time was adequate for cross-polarisation, and that the recovery delay was adequate for restoration of the proton magnetisation. Between 5×10^3 and 4×10^4 transients were accumulated.

Resolution-enhanced spectra were produced by Lorentzian-to-Gaussian transformation¹⁹, involving an exponentially-increasing function (time constant 1 ms) and a Gaussian apodisation function (time constant 2 ms). The time constants were chosen after trial-and-error testing⁸. The data tables were zero-filled to 8K before Fourier transformation. Chemical shifts were adjusted to a scale based on tetramethylsilane.

Aromaticity values were estimated by plotting spectra without resolution enhancement, drawing a vertical line at $\delta = 65$, and defining;

$$f'_a = (\text{signal area for } \delta < 65) / (\text{total area}).$$

The prime on the symbol f'_a is used to indicate that this parameter is an apparent aromaticity, not corrected for spinning sideband signal areas, or for contributions from carboxylic acids, carbonyl groups and cellulose. The boundary was chosen to coincide with a dip in the spectral

envelope, between the aliphatic band and a first-order spinning sideband from the aromatic band (Fig. 1). As much as 11% of the aromatic signal could be contained in spinning sidebands obscured by the aliphatic band⁸, but this should not affect the reliability of the parameter f'_a as a test for relative differences in aromaticity.

RESULTS AND DISCUSSION

Aromaticities

Fig. 1 shows the ^{13}C CP/MAS nmr spectrum of the Ashers-Waituna lignite, plotted without resolution enhancement. Broken lines differentiate the signal areas used in calculating the aromaticity. The results of such aromaticity measurements are shown in Table 1. Most of the values of f'_a were scattered around a mean value of 0.65, but the values for Central Otago lignites were consistently lower than this. Petrographic analyses have shown that Central Otago lignites tend to have higher exinite contents than Southland lignites²⁰. Exinite macerals show strong aliphatic signals in ^{13}C nmr spectra, compared with vitrinite or inertinite macerals²⁰. The nmr results are therefore consistent with the petrographic data.

Verheyen et al. have shown² that aromaticity differs between lithotypes in the case of the Australian brown coals. They found values of $f_a = 0.56$ for a pale lithotype and $f_a = 0.65$ for a dark lithotype from bore LY1276 of the Loy Yang field. The dark lithotype included charcoal

(fusinite), which is one of the inertinite macerals known to have a particularly high aromaticity²¹. Inertinite macerals account for no more than a few percent by weight of the New Zealand lignites²⁰, so variations in the inertinite content are too small to be responsible for the observed variations in lignite aromaticity.

Aromaticities of $f_a = 0.53$ and 0.59 have been reported for samples from the Loy Yang field^{4,6}, and a value of $f_a = 0.57$ has been reported for a sample from Yallourn³, which is adjacent to Morwell. When these values are combined with data for the 5 Loy Yang lithotypes², the mean is $f_a = 0.57$ with a standard deviation of 0.04 . The scatter is so close to experimental uncertainty that the published values show no clear evidence for variations in aromaticity around the Latrobe Valley. The mean is significantly different from our mean value of f'_a (Table 1), but this can be explained by a difference in the definitions of f_a and f'_a . We were not able to separate the carboxylic or carbonyl signals from spinning sidebands, so these signals were included in our definition of f'_a . Spinning sidebands are normally less prominent in spectra run on electromagnet spectrometers, so the published values of f_a were easily corrected for carboxylic and carbonyl signals. Signal intensities tabulated in References 2 and 3 show that these signals account for about a tenth of the total signal area, and were therefore strong enough to explain the difference between published values of f_a and our values of f'_a .

Resolution enhancement

A comparison of Figs. 1 and 2a shows the improvement gained from resolution enhancement by Lorentzian-to-Gaussian transformation. Resolution enhancement has already been used to improve the spectra of coals from the United States^{22,23}. Those spectra do not show as much detail as can be seen in Figs. 2-4. Two factors could contribute towards this difference. Firstly, the Australasian coals are of comparatively low rank. Miknis et al.²⁴ have suggested that as the carbon content of coal increases, the heteroatom content decreases, providing less opportunity for a wide range in chemical shift dispersion and therefore an apparent lack of fine structure in the aromatic region of the higher rank coals. Secondly, we have used a superconducting spectrometer. The improved signal dispersion gained by using a higher field strength can be seen by comparing spectra of Yallourn brown coal run at³ 1.4 T and⁷ 7 T, or by comparing spectra of xylite fractions from Yallourn brown coal run at⁵ 2.1 T and¹ 7 T.

Signal assignments

Signals were assigned as in earlier work on Australasian coals¹⁻⁸ and model compounds^{25,26}. Chemical shifts given here are averages for signals observed in the spectra shown in Figs. 2-4.

$\delta=15,31$; methyl and methylene groups in alkyl chains.

$\delta=22$; methylene groups bonded directly to methyl groups in alkyl chains.

Methyl groups on aromatic rings would also contribute to this signal²⁵.

$\delta=56$; methoxyl groups in lignin-like aromatic structures²⁶.

$\delta=76$; carbohydrate structures, e.g. cellulose. A spinning sideband from the aromatic signal contributed to this region in all spectra, so the presence of a signal at $\delta=76$ in Figs. 2-6 can not be taken alone as evidence for cellulose. The presence of a real signal was confirmed for some of the lignites, by running spectra at different spinning frequencies.

$\delta=105-115$; carbon in aromatic rings, with oxygen-substitution on the adjacent carbon atom.

$\delta=129$; other carbon in aromatic rings, except for carbon atoms directly bonded to oxygen.

$\delta=145$ and 155 ; aromatic carbon bonded to oxygen in phenols, methoxylated phenols and phenolic ethers. The signal at $\delta=155$ was assigned to structures with isolated phenolic groups, as suggested by Snape et al.²⁵, while the signal at $\delta=145$ was assigned to structures with oxygen substitution on adjacent carbon atoms, i.e. diphenolic structures as found in lignin²⁶ and coalified wood⁸. Snape et al.²⁵ have suggested that phenolic ether signals contribute to the region $\delta=158-165$, but the work of Nimz²⁶ has shown that signals can also be found in the region $\delta=147-155$ for lignin-like diphenolic structures. Assignments in this region are discussed in more detail below.

$\delta=178$; carboxylic acids plus a spinning sideband of the aromatic signal at $\delta=129$. Experiments with faster spinning frequencies demonstrated the presence of a real signal under the spinning sideband, but the frequencies required for this work were too high for routine use.

$\delta=195-205$; carbonyl groups plus spinning sidebands from phenolic signals. The sidebands appeared to dominate this region, since variable spinning frequencies failed to provide any clear evidence for a real signal.

Signal heights

Signal heights depend on a number of experimental conditions (e.g. the strength of the magnetic field, spinning frequency, decoupler power) as well as data processing parameters (e.g. time constants for resolution enhancement and the number of data points transformed), so it is important that any discussion of relative signal heights should be based on spectra obtained under the same conditions, as in the case of the data presented here.

A height measured from a single peak is not a useful parameter, because it is subject to an arbitrary scaling factor based on spectrometer amplification settings. All signal heights reported in this work have been expressed relative to the height of another peak measured from the same plot. The peak at $\delta=129$ was chosen for this purpose. One reason for this particular choice was the fact that this peak (considered along with the associated spinning

sidebands) was the most intense signal in almost all of the spectra. Other reasons are given below, in subsections dealing with each signal-height ratio.

Heights of aliphatic signals at $\delta=22$ and $\delta=40$ tended to correlate with the height of the principal aliphatic signal at $\delta=31$, but this can be explained (at least in part) by signal overlap. Aromatic signals at $\delta=105-115$ likewise tended to correlated with the aromatic signal at $\delta=129$. Signal heights measured at $\delta=178$ showed only small variations relative to the signal at $\delta=129$, so these ratios were not used for characterisation of the coals. Signals at $\delta=195-205$ were ignored, because of the large spinning-sideband component. Signal heights for all other prominent peaks are shown in Figs. 5-7.

Alkyl moieties

Fig. 5 shows signal-height ratios for the methylene and methyl signals relative to the principal aromatic signal. This plot shows that the Central Otago lignites could be distinguished from the other samples, because the aliphatic signals were particularly strong compared with aromatic signals. The same conclusion was reached (above) through aromaticity measurements, but Fig. 5 shows that peak heights are more sensitive to the structural differences which distinguish organic matter in the Central Otago lignites from organic matter in the other samples.

The clustering of data points in Fig. 5 suggests that aliphatic structures in the Southland lignites are similar to those in subbituminous coals. The Australian brown coals showed relatively weak signals in the aliphatic region, but the data points fall within the cluster of points for subbituminous coals.

Typical ranges of atomic H/C ratios are⁸ 0.79-1.00 for Central Otago lignites and 0.70-0.90 for Southland lignites. The tendency towards higher H/C ratios is consistent with the relatively strong signals from hydrogen-rich structures (e.g. methylene and methyl groups) in the spectra of Central Otago lignites. The nmr signal heights provide a clearer distinction between the two types of lignite.

Calkin et al.²⁷ have shown that the strength of the methylene signal in ^{13}C CP/MAS nmr spectra can be used to predict the yields of alkenes obtained by flash pyrolysis. That work was based on signal areas. We tested the possibility of using signal-height ratios for the same purpose. Yields of ethylene have been reported for New Zealand lignites pyrolysed at 500°C ²⁸. Of the samples used in that work, 3 Central Otago lignites and 4 Southland lignites were taken from the same bulk samples used here for ^{13}C CP/MAS nmr spectra. Data for these 7 lignites are shown in Table 2. Ethylene yields were strongest for the lignites with the strongest methylene signal, as determined

by signal-area increments (correlation coefficient 0.95) or by signal-height ratios measured from resolution-enhanced spectra (correlation coefficient 0.94). Signal-height ratios can be measured more rapidly, and would therefore be more useful in screening of lignites for potential pyrolysis feedstock.

The Australian brown coals gave such weak methylene signals that alkene yields are expected to be lower than those obtained from New Zealand lignites or subbituminous coals. No results are available yet, to test this conclusion.

Cellulose and methoxyl moieties

Fig. 6 shows signal heights for functional groups that contribute strong signals in the spectra of modern woods. Signal heights were measured relative to the height of the principal aromatic signal, because the aromatic rings of lignin tend to persist through the early stages of coalification while the other components of wood (e.g. cellulose) are degraded²⁹.

Clustering of data points shows a clear distinction between the lignites and the subbituminous coals. The Australian brown coals resembled the latter in that the cellulose and methoxyl moieties appear to have been chemically degraded. Russell and Barron³⁰ have used CP/MAS nmr to compare samples of coalified wood from the Yallourn and Morwell mines. They found that the cellulose and methoxyl contents

varied from one specimen to another. The highest cellulose and methoxyl contents were similar to those found in a single specimen of coalified wood from a New Zealand lignite mine⁸. Variations were attributed to localised differences in the oxidation/reduction potential or acidity of the depositional environment³⁰. Differences between the two clusters of points in Fig. 6 could likewise reflect differences in depositional environments rather than differences in the extent of coalification.

Aromatic moieties

Fig. 7 shows signal heights for oxygen-substituted aromatic carbon. The signal heights were measured relative to the height of the principal aromatic signal, to provide parameters related to the degree of oxygen substitution of aromatic rings. Signals at $\delta=147$ and 155 were particularly strong in the spectra of the lignites. This observation is consistent with the overall loss of oxygen during coalification, and the loss of phenolic -OH groups in particular³¹. Data points for the Australian brown coals fell close to the area of overlap between lignites and subbituminous coals. This observation does not reflect the total oxygen contents of the different coals. Typical atomic O/C ratios are 0.24-0.29 for New Zealand lignites⁸ and 0.15-0.23 for New Zealand subbituminous coals⁸. Atomic O/C ratios for the Australian brown coals were 0.25 (Morwell) and 0.27 (Loy Yang). Although the O/C ratios for brown coals fall within the range for lignites, the nmr spectra

suggest that the two types of coal differ in the distribution of oxygen in different functional groups. Evidence for differences in phenolic contents is not confined to the signals at $\delta=147-155$. The signals in the region $\delta=105-120$ show that the lignites have a relatively high content of aromatic carbon at sites adjacent to oxygen substitution sites, providing indirect evidence for phenolic structures. This difference can be seen by comparing the spectra in Fig. 2 with those in Fig. 4.

The ratio of signal heights in the region of $\delta=144-155$ showed a wide variation, particularly in the case of the subbituminous coals; e.g. Fig. 3 shows a particularly strong signal at $\delta=144$ in the spectrum of Braziers coal, but a particularly strong signal at $\delta=155$ in the spectrum of Kopuku coal. This variation could reflect differences in organic source material; e.g. differences in the relative contributions from leaves, bark and wood. Leaves and bark contain tannins, e.g. the proanthocyanidin structure illustrated in Fig. 8a. The A-ring of each monomer unit is substituted by oxygen on alternate carbon atoms, so the C-O groups contribute a ^{13}C nmr signal in the region characteristic of isolated phenolic functional groups, i.e. a band centred on $^{32}\delta=155$. The B-ring is substituted by oxygen on adjacent carbon atoms, so it contributes a ^{13}C nmr signal in the region characteristic of diphenolic structures, i.e. at $^{32}\delta=145$. These two signals are illustrated in Fig. 9, which shows a resolution-enhanced

spectrum of fresh leaves from Dacrydium cupressinum (rimu).

Lignins, on the other hand, contain very few aromatic structures with isolated phenolic groups²⁶. The 3-methoxy-4-hydroxyphenyl group (Fig. 8b) is particularly abundant in softwood lignins, contributing ¹³C nmr signals at²⁶ $\delta=147$ and 148 . The C-4 signal moves to $\delta=150$ when the free phenolic group is etherified, and further small shifts upfield or downfield can result from carbon substitution at C-5 or C-6. Fig. 10 shows a signal at $\delta=148$ in the spectrum of rimu wood, assigned to the lignin content. The chemical shift of this signal is consistent with the signal observed at $\delta=147$ in the spectra of lignites (Fig. 2).

The signal assigned to isolated phenolic groups was found at approximately the same chemical shift ($\delta=155\pm 1$) in all spectra, but the signal assigned to diphenolic structures was found at $\delta=147$ in spectra of lignites, $\delta=145$ in spectra of brown coals and $\delta=144$ in spectra of subbituminous coals. This variation in chemical shift provides supporting evidence for our assignment of the signal to methoxylated lignin-like structures in lignites and similar non-methoxylated structures in other coals, since methoxylation of a phenolic -OH group results in a shift of +3 ppm for the directly-bonded carbon atom³³.

The North Island and South Island subbituminous coals could not be distinguished by signal heights measured at

$\delta=144$, but the two sets of spectra tended to differ in heights measured at $\delta=155$. Mean signal heights measured at the latter chemical shift were $h(\text{isolated phenolic}) = 0.81$ and 0.70 for North Island and South Island subbituminous coals, respectively, with standard deviations of 0.08 and 0.07 . The mean signal height for the Australian brown coals was $h(\text{isolated phenolic}) = 0.89$, which was outside the range observed for South Island subbituminous coals. The three points closest to symbols for the Australian brown coals in Fig. 7 correspond to North Island subbituminous coals of relatively low rank; namely Kawhia and Ohinewai (both subbituminous C) and Squires Creek (subbituminous B). The spectrum of the Squires Creek sample was barely distinguishable from that of the Australian brown coals, even in the band assigned to polymethylene chains.

The resolution of two distinct signals in the phenolic region has demonstrated the improvement of current methods over those used to obtain published spectra of Australian brown coals¹⁻⁷. None of the published spectra show two distinct signals in this region. Two spectra of Loy Yang coal show only a shoulder on the side of the aromatic band^{4,5}, while spectra of Yallourn coal³ and lithotypes from Loy Yang² show a single peak in the phenolic region. A high-field nmr spectrum of Yallourn brown coal⁷ shows a shoulder on the side of the phenolic signal, but resolution-enhancement techniques were not used. A high-field nmr

spectrum of Yallourn coalified wood¹ shows only a single phenolic signal at $\delta=147$, and the simplicity of this spectrum can be explained by the absence of other macerals. Published spectra of lignites sampled elsewhere around the world show only a shoulder or a single peak partly resolved from the aromatic band^{23,34-37}.

CONCLUSION

Our results suggest that there are close similarities between the organic chemical structures found in Australian brown coal and low-rank New Zealand subbituminous coals. The deposits do however differ in moisture contents. Typical moisture contents are 56-62% for brown coals from the Morwell mine¹⁶, and 15-26% for subbituminous coals from New Zealand mines³⁸. This difference is a major reason for the difference in ASTM rank. The ASTM classification scheme is based on the specific energy of moist coal, so a higher moisture content lowers the apparent rank even if the organic structures are the same in both cases. The ¹³C nmr spectrum is not affected by the presence of moisture, except for an overall reduction in signal intensity due to the lower weight-percentage of carbon.

Even if ultimate analyses show similarities between coal samples, nmr can detect differences. In the present work, nmr signals showed that brown coals and lignites differed in the distribution of oxygen between various types of

functional groups, even though the total oxygen contents were similar. Characterisation by nmr therefore gathers "similar" coals into categories in a manner which differs from traditional ranking schemes. A classification scheme based on nmr could be useful in some aspects of coal utilisation, eg coal pyrolysis.

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TABLE 1. Aromaticity values determined by ^{13}C nmr.

Coal	Number of samples	Mean f'_a	Standard deviation
Central Otago lignites	5	0.58	0.05
Southland lignites	6	0.64	0.01
South Island subbituminous	7	0.66	0.04
North Island subbituminous	12	0.65	0.03
Australian brown coals	2	0.66	0.04

TABLE 2. Yields of ethylene obtained by fluidised-bed
pyrolysis of lignites at 500°C.

Coal	A(31) ^a	$\frac{h(31)^b}{h(129)}$	ethylene yield ^c
Central Otago lignites;			
Roxburgh/Harliwich	2.04	5.7	0.26
Roxburgh/drillhole	1.78	5.8	0.23
Home Hills/Idaburn	1.51	4.2	0.18
Southland lignites;			
Waimumu/Newvale	1.07	2.4	0.17
Waimumu/Goodwin	1.09	2.8	0.17
Waimumu/Goodwin	1.22	2.5	0.16
Ashers Waituna	0.78	1.5	0.14

^a area increment between $\delta=30.5$ and $\delta=31.5$, expressed as percent of the total area of the spectrum.

^b height of the methylene ^{13}C nmr signal, relative to the height of the principal aromatic signal at $\delta=129$.

^c percent by weight of d.a.f. coal, from Reference 28.

FIGURE CAPTIONS

- FIGURE 1 ^{13}C nmr spectrum of Ashers-Waituna lignite, without resolution enhancement. A broken line outlines the areas used in aromaticity determinations.
- FIGURE 2 Resolution-enhanced ^{13}C nmr spectra of New Zealand lignites from (a) Ashers-Waituna (Southland), (b) Hawkdun (Central Otago).
- FIGURE 3 Resolution-enhanced ^{13}C nmr spectra of New Zealand subbituminous coals from (a) Braziers (South Island), (b) Kopuku (North Island).
- FIGURE 4 Resolution-enhanced ^{13}C nmr spectra of Australian brown coals from (a) Morwell, (b) Loy Yang.
- FIGURE 5 Signal heights for the methyl signal at $\delta=15$ and the methylene signal at $\delta=31$, for Southland Central Otago lignites (O), Southland lignites (●), North Island subbituminous coals (□), South Island subbituminous coals (■) and Australian brown coals (Δ).
- FIGURE 6 Signal heights for the cellulose signal at $\delta=74$ and the methoxyl signal at $\delta=56$; symbols as for Fig. 5.
- FIGURE 7 Signal heights for carbon in isolated phenolic groups ($\delta=155$) and in diphenolic structures ($\delta=144-147$); symbols as for Fig. 5.

FIGURE 8 Structures for typical monomer units in
(a) proanthocyanidin polymers (tannins),
(b) softwood lignins.

FIGURE 9 Resolution-enhanced ^{13}C nmr spectrum of leaves
from Dacrydium cupressinum.

FIGURE 10 Resolution-enhanced ^{13}C nmr spectrum of wood
from Dacrydium cupressinum.

FIG. 1

Fig. 2

FIG. 3

FIG. 4

Fig. 5

FIG. 6

Fig. 7

FIG. 8

FIG. 9

FIG. 10

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ABSTRACT

A combination of Lorentzian-to-Gaussian digital resolution enhancement plus the improved chemical-shift dispersion of a superconducting spectrometer has resulted in separation of spectral details not previously reported in CP/MAS NMR studies of coal. Signal assignments were based on simulation of spinning sideband intensity patterns. The spectra provided evidence for major chemical alteration during coalification through the ASTM rank of h.v. bituminous A.

KEYWORDS

N.M.R. (Spectra); organic matter; characterisation; functional groups; phenols.

INTRODUCTION

Carbon-13 nuclear magnetic resonance (NMR) spectra of solid coal have often shown no more than two broad bands, one in the aliphatic region (about 0-90 ppm) and one in the aromatic/olefinic region (about 90-170 ppm). Digital resolution-enhancement techniques have been used with some success (Hagaman and Woody, 1982; Sullivan and Maciel, 1982). High-field magnets have also been used to resolve overlapping signals. The success of high-field NMR can be demonstrated by comparing spectra of brown coal run in magnetic fields of 1.4 T (Yoshida and others, 1982) and 7 T (Ohtsuka and others, 1984). We have combined resolution enhancement and high-field NMR to resolve spectral details not previously reported in NMR studies of coal.

EXPERIMENTAL

The 57 New Zealand coals were a mixture of run-of mine samples and drill-hole composites, with one geological specimen of semi-anthracite. All samples were classified by specific energy and volatile matter according to the ASTM ranking scheme. The coals were crushed to <200 μm , and about 0.3 g of each was packed in a Kel-F rotor and spun at 2.5 ± 0.1 kHz in the magic-angle spinning (MAS) probe of a Varian XL-200 spectrometer operating at 50.3 MHz for cross-polarisation (CP) NMR. Each 1 ms contact time was followed by 15 ms of data acquisition and a recovery delay of 0.15-1 s, varied according to the proton spin-lattice relaxation time. Between 5000 and 360000 transients were accumulated. Lorentzian-to-Gaussian transformations were used for resolution enhancement (Ferrige and Lindon, 1978). This involved multiplication of the data table by an exponentially-increasing function (time constant 1 ms) and a Gaussian function (time constant 2 ms) before Fourier transformation.

RESULTS AND DISCUSSION

Fig 1a shows a typical spectrum for a subbituminous coal. Most of the signals were assigned from data published for model compounds (Snape, Ladner and Bartle, 1979) as follows: 15 ppm, methyl groups on alkyl chains; 22 ppm, methyl groups on aromatic rings and methylene groups bonded to methyl groups in alkyl chains; 30 ppm, methylene groups in alkyl chains; 129 ppm, aromatic carbon; 154 ppm, aromatic carbon bonded to oxygen in phenols and phenolic ethers. A signal at 144 ppm could be assigned to aromatic carbon bonded to alkyl groups (Snape, Ladner and Bartle, 1979) or to aromatic structures with oxygen substitution at two adjacent ring sites (Newman, Davenport and Meinhold, 1984). Spinning sidebands (SSB's) appear at intervals of 50 ppm on either side of the principal aromatic signals. The first-order SSB's of the principal aromatic signal are marked "*" in each spectrum.

Strong SSB signals can be a useful feature of carbon-13 CP/MAS NMR spectra,

because differences in aromatic substitution result in different patterns of SSB intensities. Burgar (1984) has used SSB intensities to estimate relative contributions from various aromatic functional groups in coal. We have now used a similar procedure to resolve the ambiguity in the assignment of the signal at 144 ppm. Simulated spectra (Figs 1b and 1c) were generated from published values of typical chemical shift tensors, following Burgar's procedure. The peaks were broadened by convolution with a Gaussian function. Patterns of SSB intensities were also determined for two additional model compounds, dihydroconiferyl alcohol (Fig. 2a) and 4-isopropyl phenol. These provided SSB patterns for oxygen substitution at two adjacent sites and for alkyl-substituted carbon. Figs. 1b and 1c show spectra simulated for assignment of the 144 ppm signal to each of the alternative structures. Fig. 1c shows a poor fit, because the SSB intensities for alkyl-substituted aromatic carbon are stronger than those observed. The signal was therefore assigned primarily to aromatic structures with oxygen substitution at two adjacent sites. Such structures contribute signals at about 144 ppm in the NMR spectra of plant phenolics, e.g. tannins (Czochanska and others, 1979).

A weak signal at 144 ppm was resolved in the spectra of a few coals ranked as high-volatile bituminous B and C, but no more than a weak shoulder was observed in spectra of coals of higher rank, e.g. Fig. 2b. A signal was observed at or near 154 ppm in all spectra. The signal at 144 ppm was the first of the pair to disappear from spectra of chars formed by pyrolysis at progressively higher temperatures (McGavin and others, 1985). Aromatic structures with oxygen substitution at two adjacent sites appear to be less stable than structures with oxygen substitution at a single site or alternate sites, when these structures are subjected to coalification or pyrolysis.

The signal at 154 ppm tended to weaken with increasing coal rank (Fig. 3a). Coals of ASTM rank high-volatile bituminous A showed the widest spread of data points for any single ASTM rank. Substantial loss of the more stable form of phenolic oxygen therefore seems to be a characteristic of coalification through this rank.

Fig. 1. Resolution-enhanced carbon-13 CP/MAS NMR spectra of subbituminous coal from Braziers mine; (a) experimental; (b) and (c) simulated with assignment of the 144 ppm signal to oxygen-substituted and alkyl-substituted aromatic carbon (respectively).

Fig. 2. Carbon-13 CP/MAS NMR spectra of; (a) dihydroconiferyl alcohol (no resolution enhancement); (b) high-volatile bituminous A coal from Liverpool mine (with resolution enhancement).

Fig. 3. Signal-height ratios measured from resolution-enhanced spectra of lignites (circles), subbituminous coals (squares), high-volatile bituminous coals (triangles), medium-volatile bituminous coals (diamonds) and a semi-anthracite (hexagon). Solid symbols represent high-volatile bituminous A coal. Numbers in brackets are chemical shifts of NMR peaks.

Peaks clearly resolved in this study included signals at 56 ppm (methoxyl groups) and 74 ppm (cellulose). These were observed in spectra of all 11 lignites, but never in any other spectra. A SSB at 180 ppm may have obscured signals from carboxylic acids, but calculated SSB intensities were sufficient to account for observed intensities for ranks above subbituminous. Our studies suggest that the loss of these functional groups accounts for much of the oxygen loss in the early stages of coalification of New Zealand coals.

The effects of catagenesis are illustrated in Fig. 3b. The signal-height ratio is related to the average length of alkyl sidechains in the polymeric coal structure. The signal at 30 ppm becomes weaker as polymethylene chains are broken during catagenesis. The scatter of data points for lignites is attributed to differences in depositional environments. Alkyl chains were longer for the 5 Central Otago lignites than for the 6 Southland lignites. Apart from the lignites, the widest spread of data points was found in the ASTM rank high-volatile bituminous A. This observation is consistent with the fact that coals of high-volatile bituminous A rank are commonly associated with zones of oil generation, i.e. active catagenesis.

Aromaticity values for New Zealand coals tend to increase with ASTM rank, but are not useful as a measure of rank. A study of New Zealand coals has shown that high volatile bituminous coals could not be distinguished from subbituminous coals or even Southland lignites on a basis of aromaticity values alone (Newman, Davenport and Meinhold, 1984). Our studies of resolution-enhanced spectra have indicated that parameters based on signal heights (e.g. as in Fig. 3) are more useful than parameters based on signal areas (e.g. aromaticity values) for elucidation of the chemical processes involved in coalification (Teichmuller, 1982).

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PREDICTION OF LIGNITE PYROLYSIS YIELDS BASED ON CARBON-13 NUCLEAR
MAGNETIC RESONANCE SPECTROSCOPY

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ABSTRACT

Carbon-13 NMR spectroscopy was used to characterise 7 New Zealand lignites, in an attempt to explain differences in yields of products from fluidised-bed pyrolysis. Each NMR spectrum was divided into chemical-shift increments of 1 part per million. Variations in the area in each increment were then compared with variations in the published yields of each pyrolysis product. The correlation coefficient R was calculated for each increment, and the function $R/(1-R)$ was plotted against the chemical shift to generate a "yield-correlation spectrum".

This new approach to the search for correlations has confirmed two published predictions; namely, high yields of gaseous hydrocarbons and chars were associated with relatively strong NMR signals assigned to polymethylene chains and aromatic rings (respectively). It has also produced a new correlation linking high yields of tar to NMR signals assigned to alicyclic or branched aliphatic structures.

INTRODUCTION

Pyrolysis of coal yields char, tar and gases in various proportions, depending on the pyrolysis conditions and the origin of the coal. A number of reserach groups have sought to identify the particular coal properties which determine pyrolysis yields. Correlations have been based eg on elemental analyses (Tyler, 1980), maceral analysis (Fieldes et al., 1983; Tyler, 1980), and on carbon-13 NMR spectroscopy (Furimsky et al., 1984; Calkin et al., 1984).

We have assessed a new approach to the search for correlations between the abundance of chemical functional groups in coal and the yields of corresponding pyrolysis products. We have used carbon-13 NMR to characterise the samples of coal, but rather than test pre-conceived ideas about the importance of a few specific functional groups we have divided each NMR spectrum into narrow chemical-shift increments and tested each increment for a correlation with pyrolysis yields. We call the result a "yield-correlation spectrum" for the specified product. Tall peaks mark any chemical shifts for which relatively strong NMR signals are associated with relatively high yields of that particular product.

This statistical approach is complementary to the approach described by McGavin et al. earlier in the conference. McGavin et al. sought correlations between NMR spectra and product yields for a single lignite pyrolysed at several temperatures, but we have used data for several lignites pyrolysed at a single temperature.

Our work is based on published data for pyrolysis yields from 7 New Zealand lignites (Fieldes et al., 1983).

EXPERIMENTAL

Samples

Sources of the 7 lignites are listed in the Table. Each sample was taken from the bulk supply used by Fieldes et al., (1983).

TABLE

Sources of the lignites.

Sample Code	Source	Coal Field	CRA Code
AS	Ashers Siding	Ashers Waituna	30/647
NV	Newvale mine	Waimumu	30/648
G5	Goodwin mine	Waimumu	30/645
G6	Goodwin mine	Waimumu	30/646
IB	Idaburn mine	Home Hills	30/652
RD	Drillhole 2086	Roxburgh	-
RH	Harliwich mine	Roxburgh	30/651

Pyrolysis

We selected from the results of Fieldes et al. only data for rapid pyrolysis in a fluidised bed of sand at 500°C.

Carbon-13 NMR

Samples were spun at 2.5 kHz in the magic-angle spinning probe of a Varian XL-200 spectrometer, for NMR at 50.3 MHz. Each cross-polarisation contact time of 1 ms was followed by 15 ms of data acquisition and a recovery delay of 0.15 s. Between 5000 and 40000 transients were averaged in each experiment. Preliminary NMR spectra of these lignites have been published by Newman et al. (1984), as spectra A2, A4, A5, A6, A9, A11 and A12.

Computer program

Yield-correlation spectra were generated by a PASCAL program. The m spectra were divided into n increments, and incremental areas were normalised so that:

$$\sum_{i=1}^{i=n} a_{ik} = 1 \quad k=1 \text{ to } m \quad [1]$$

where a_{ik} is the area of the i 'th increment in the k 'th spectrum. A correlation coefficient R_i was then computed for the m data pairs available for that value of i ; ie (a_{ik}, y_k) , where y_k is the yield of one particular product for the k 'th coal. Values of R_i approaching unity were not clearly distinguishable when R_i was plotted against i . Improved discrimination was achieved by plotting values of F_i against

i, where:

$$F_i = R_i / (1 - R_i). \quad [2]$$

In this case, $m=7$ and $n=400$ for chemical shift increments of 1 ppm, from $\delta=-100$ to $\delta=+300$.

RESULTS

Chars

Fig. 1 shows that high char yields are associated with strong NMR signals in the region $\delta=100-160$, assigned to aromatic carbon. This is consistent with reports of strong correlations between the "aromaticity" of coal and the percent fixed carbon (Furimsky *et al.*, 1983).

Gases

Fig. 2 shows that NMR signals at $\delta=27, 29$ and 31 are associated with relatively high yields of ethane. Similar (but weaker) correlations were found for ethylene, with peaks at $\delta=24$ ($R=0.977$) and $\delta=34$ ($R=0.973$). Propane and propylene were not determined separately for all lignites, but the yield-correlation spectrum for the total showed a peak at $\delta=30$ ($R=0.85$). These results are consistent with production of gaseous alkanes and alkenes by fragmentation of polymethylene chains.

Calkin *et al.* (1984) found a similar correlation ($R=0.94$) between the NMR signal at $\delta=31$ and the yield of ethylene. Those authors also found weaker correlations with nearby signals, eg $R=0.86$ for the signal at $\delta=44$. These weaker correlations may be explained by overlap between the signals at $\delta=31$ and $\delta=44$, resulting from the use of a low-field spectrometer in the work of Calkin *et al.* (1984).

Yield-correlation spectra for methane, CO, CO₂ and O₂ showed no significant peaks in the range $\delta=0$ to 200 .

Tars

Fig. 3 shows that high tar yields are associated with NMR signals in the range $\delta=13$ to $\delta=47$; but there is a dip in the region $\delta\sim 30$. This suggests variations in the abundance of polymethylene chains have no significant effect on tar yields. The range of chemical shifts contributing to Fig. 3 is characteristic of alicyclic or branched aliphatic structures.

Kauri resin (Fig. 4) is an example of an alicyclic plant product, incorporated in lignite as "resinite". Alicyclic and aliphatic structures could also be associated with pollen and spores, incorporated in lignite as "sporinite". Resinite and sporinite are included as liptinite in maceral analysis. Our results are therefore consistent with the correlation between liptinite content and tar yield, as reported by Fieldes *et al.* (1983).

Tyler *et al.* (1980) found a correlation between elemental H/C ratios and tar yields, but Furimsky *et al.* (1984) found no such correlation for low-rank coals. Our results help to resolve this contradiction. Both polymethylene chains and alicyclic structures have high H/C ratios. Tar yields would therefore be correlated with H/C, provided the polymethylene content is negligible or constant.

Prediction of yields

Our results suggest that tar and char yields could be predicted from parameters T and C describing composites of area increments,

$$T = \sum_i a_i \quad i = 14-20, 34-47 \quad [3]$$

$$C = \sum_i a_i \quad i = 111-140 \quad [4]$$

The best-fit relationships are:

$$Y = 252T - 18.2 \quad [5]$$

for tar, with $R=0.94$ (Fig. 5a), and:

$$Y = 360C + 1.0 \quad [6]$$

for char, with $R=0.93$ (Fig. 5b). The yield Y is expressed as percent of daf coal.

The parameters T and C can be measured directly from NMR spectra, by cutting strips of paper as shown in Fig. 6 and comparing each weight with the weight of paper enclosed by the total spectrum. Good signal-to-noise ratios can be achieved with between 15 and 60 minutes of data accumulation, so carbon-13 NMR shows promise as a fast screening procedure for selection of potential pyrolysis feedstock.

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FIGURE 1. Yield-correlation spectrum for char. The tallest peak corresponds to $R=0.956$ for $\delta=113$.

FIGURE 2. Yield-correlation spectrum for ethane, plotted for a reduced vertical scale. The tallest peak corresponds to $R=0.995$ at $\delta=31$.

FIGURE 3. Yield-correlation spectrum for tar. The tallest peak corresponds to $R=0.934$ for $\delta=14$.

FIGURE 4. Carbon-13 NMR spectrum of fresh, solid kauri resin.

FIGURE 5. Prediction of tar and char yields from the parameters T and C.

FIGURE 6. Carbon-13 NMR spectrum of lignite sample RH, showing signal areas assigned to the parameters C and T.

DETERMINATION OF FUNCTIONALITIES IN COAL BY COMPUTER
SIMULATION OF CARBON-13 CP/MAS N.M.R. SPECTRA

by

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ABSTRACT

The program DOFIC (Determination of Functionalities in Coal) has been developed to simulate the carbon-13 CP/MAS NMR spectra of coal. A series of databases enables DOFIC to reproduce the range of isotropic and spinning side band (SSB) signals typical of coal spectra obtained at a carbon-13 NMR frequency of 50.3 MHz and 2.5 kHz MAS frequency. The SSB database was generated from chemical-shift anisotropies collated for a large number of model compounds. Trends observed in the spectra of 54 New Zealand coals form the basis of empirical chemical-shift and line-shape databases. DOFIC was tested on the spectra of these 54 coals, ranging in A.S.T.M. rank from lignite to semi-anthracite. The results compare favourably with the results of elemental analyses.

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1 INTRODUCTION

Qualitative descriptions of the CP/MAS spectra of coals are now common 1-5. However, very few workers have attempted quantitative analysis further than the standard measurement of "aromaticity", f_a . Several groups have estimated additional carbon fractions, either by extrapolating data obtained in relaxation experiments², or by arbitrarily assigning boundaries with vertical lines^{3,4}. Both methods involve substantial uncertainties.

Two new approaches to quantitative analysis have recently appeared in the literature. Both methods aim at a more reliable analysis by attempting to simulate the coal spectra. Ohtsuka *et. al.*⁵ simulated the spectrum for one possible structural model of Yallourn coal and attempted to compare this spectrum with the experimental spectrum. However, they dismissed the likelihood of spinning side band (SSB) contributions and did not account for all of the signal intensity in the experimental spectrum.

Burgar⁶ has developed a method which utilises the large SSB signals obtained at 75 MHz carbon-13 NMR frequency and 3 kHz MAS frequency. He used model-compound chemical-shift anisotropy data of Wemmer, Pines and Whitehurst⁷ to calculate the expected SSB intensity patterns for three types of aromatic carbon, following the graphical method of Herzfeld and Berger⁸. Together with aliphatic and alkoxyl carbon, the three aromatic carbon SSB patterns were fitted to the observed spectrum of an Australian bituminous coal.

This report describes the development of a similar but far more comprehensive method for the full characterisation of coal. The program DOFIC (Determination of Functionalities in Coal) simulates the isotropic and SSB intensities observed in the carbon-13 CP/MAS NMR spectra of coals. This version of DOFIC is written specifically for carbon-13 NMR at 50.3 MHz and a MAS frequency of 2.5 ± 0.1 kHz, but could be modified to suit other combinations of operating frequencies.

In order to optimise essential fitting parameters, such as signal positions and line shapes, DOFIC was tested on the spectra of coals that span the range of ASTM ranks found in New Zealand. The test functional group analyses, obtained for the 54 New Zealand coals, are summarised and discussed.

2 OVERVIEW OF PROGRAM STRUCTURE

The program DOFIC is structured in four phases.

- i) Peak-height ratios are tested to provide an initial estimate of the "rank" of the coal, based on empirical correlations.
- ii) The initial estimate of "rank" is used as a basis for selection of appropriate fitting parameters from the three databases. The databases contain;
 - a) the SSB intensity patterns for particular carbon functionalities,
 - b) The chemical shifts and assignments of signals,
 - c) the lineshape and line width parameters.

The use of empirical databases, containing the fitting parameters, is more appropriate to the "routine analysis" aim than the time-consuming, trial-and-error parameter fitting of each spectrum.
- iii) A set of simultaneous equations is then constructed to relate experimental signal heights to predicted contributions from the overlap of centreband and SSB signals at selected chemical shifts. Decisions are based on trends in signals observed previously in the CP/MAS studies of coal 1,9-11. Where it is known that several signals occur at a similar chemical shift, the contribution of each resonance to the band is estimated.
- iv) The intensities of the carbon signals, obtained from the solution of the simultaneous equations, are converted into functional group data for the coal. Structural characteristics are estimated from combinations of functional group abundances. An elemental analysis (C,H,O) is calculated by summation of H and O atoms attached to each type of functional group.

This report is intended to trace and discuss the development of DOFIC, and also to describe how DOFIC can be used as an analytical technique for coal.

3 SIGNAL ASSIGNMENTS

The principal features of the spectra and their assignments have been discussed in detail in an earlier report¹. The SSB signals dominate the spectra in the regions 65 to 105 ppm and above 165 ppm, i.e. 50 ppm either side of the aromatic centrebands.

Signals assigned to oxygen-substituted carbon were stronger than the SSB signals in the spectra of some of the lignites. The assignments in Table 1 were based on the considerable amount of carbon-13 chemical shift data in the literature¹²⁻¹⁵, as well as the results of model-compound studies performed in this laboratory^{11,16,17}.

The signals that occur between 0 and 50 ppm have been assigned according to the aliphatic structures that are likely to be present in coal. The five signals in this region are assigned (in Table 1) to:

- i) polymethylene chains^{13,15} e.g. from plant lipids.
- ii) branched aliphatic chains^{18,19} e.g. the phytane sidechain of chlorophyll.
- iii) cycloalkane units e.g. the bicyclic and tricyclic terpenoid structures of the resin acids²⁰⁻²³.
- iv) aliphatic structures substituted onto aromatic rings^{13,15}.

The signals between 65 and 105 ppm are consistent with those observed in the spectrum of cellulose²⁴. Signals originating from unsaturated carbon, other than aromatic carbon, may be present but would be obscured by the main aromatic signals. All signals have been assigned to carbon bonded to hydrogen or oxygen. Other elements such as nitrogen and sulphur may be included in the carbon matrix as heterocyclic or alicyclic functionalities. Table 2 shows the distribution of signals expected from such structures, in comparison with the appropriate carbon and oxygen substituted functionalities. It can be seen

that the sulphur and nitrogen derivatives of aliphatic functionalities give chemical shifts intermediate between values for the corresponding carbon- and oxygen-substituted carbon. The alicyclic and heterocyclic derivatives, however, exhibit a different pattern. The signals from sulphur-substituted carbon occur in the same chemical-shift region as hydrogen- and carbon-substituted carbon. The corresponding nitrogen derivatives give chemical shifts in similar positions to those of oxygen-substituted carbon. It is, however, unlikely that signals from sulphur- and nitrogen-substituted carbon will contribute significantly to the coal spectrum because of the small abundance of sulphur and nitrogen relative to carbon, hydrogen and oxygen.

4 INITIAL ESTIMATE OF "RANK"

The majority of the signals, listed in Table 1, are present in the spectra of low rank coals. However, the range of signals observed in the spectrum decreases as the coal rank increases. For example, the spectrum of a semi-anthracite coal contains only a third of the signals listed in Table 1. DOFIC will not succeed if it is used in an attempt to include contributions from a number of signals that are absent because this leads to the formation of a singular matrix which cannot be inverted to solve the set of simultaneous equations. In the future, a more sophisticated method may be developed to allow for matrix singularities. At present, however, DOFIC has been designed for an initial test of the likelihood of signals being absent. To achieve this, DOFIC requires only an estimate of the coal rank and a list of signals likely to be present in the spectra of coal in each rank. The ASTM ranking scheme was found to be unsatisfactory for this purpose, since the boundaries between ASTM ranks do not necessarily correspond to distinct changes in NMR spectra. A ranking scheme was therefore devised so that coals could be divided into 4 "ranks" based on NMR signals, as follows.

It is known that¹⁰ the signal height at 154 ppm, measured relative to the main aromatic signal height at 128 ppm, provides a good estimate of oxygen loss and therefore the degree of coalification. The study described in Ref. 10 was based on resolution-enhanced spectra. Since DOFIC is intended for use on spectra plotted without resolution-enhancement, the potential use of this ratio was reassessed. Figure 1 shows that the ratio, termed "phenol" in DOFIC, would be particularly useful in an initial separation of the "high rank" coals.

It was noticed that a distinct peak at 144 ppm occurred in the spectra of low-rank coals, but not in spectra of coals ranked as high-volatile bituminous or higher. A second ratio of signal heights at 144 ppm and 128 ppm, termed "diphenol", is therefore used in conjunction with the "phenol" ratio to define a

"medium-high rank" of coal. Figure 2 shows the variation of "diphenol" with the "phenol" ratio. This combination of ratios fails to separate only one subbituminous coal from the "medium-high rank". The exceptional sample, from the Mokau coalfield, showed a relatively strong aliphatic signal at 30 ppm compared with other coals placed in the "medium-high rank". A further parameter, termed "ali" was therefore used to distinguish "medium-high rank" coals from lower ranks. The parameter "ali" is defined as the ratio of signal heights at 30 ppm and 128 ppm. Coals were excluded from the "medium-high rank" unless "ali" < 2.0 . The "high rank" coals deviate from the "diphenol"/"phenol" behaviour, observed for the lower rank coals in Figure 2, in that there is no band at 144 ppm and the signal height at 144 ppm is actually measured on the side of the increasingly strong aromatic C-C band at 138 ppm. The diphenol ratio of the lower rank coals shows far more scatter due to the existence of a discrete signal of variable strength at 144 ppm. The parameter "diphenol" can not be used to separate the lowest rank coals as the signal height at 144 ppm is measured on the flank of a strong peak at 148 ppm observed in the lignite spectra.

A fourth signal-height ratio, termed "methoxyl" is employed to separate the "low rank" coals from the "medium-low rank" coals. It is known⁹ that the methoxyl content (associated with lignin-like units) is relatively high in lignites, and these coals are readily distinguished from more coalified samples by the ratio of signal heights at 56 ppm and 128 ppm (Figure 3).

Thus, four "ranks" can be generally distinguished on the basis of four signal height ratios. These "ranks" are loosely correlated with ASTM ranks, as follows:

"Rank" for DOFICASTM Rank

Low	(11)	Lignites
Medium-low	(16)	Subbituminous
Medium-high	(13)	High-Volatile B,C, and some A Bituminous
High	(14)	Some High-Volatile A Bituminous and higher ranks

The numbers in brackets represent the number of samples in each "rank", of the total of 54 samples studied.

5 DATABASES FOR DOFIC

5.1 Spinning Sideband Intensities

When the NMR spectrum of a powder is obtained without magic angle spinning, a broad "powder pattern" is observed. This is the sum of resonance bands for all the possible orientations of the molecules. The shape of the powder pattern is described in terms of three principal shift components, δ_{11} , δ_{22} , δ_{33} of the chemical shift tensor.

The isotropic chemical shift $\bar{\delta}$, is given by;

$$\bar{\delta} = (1/3)(\delta_{11} + \delta_{22} + \delta_{33}) \quad [1]$$

If the sample is spun at frequencies less than the frequency range of the static chemical shift powder pattern ($\Delta\delta = \delta_{11} - \delta_{33}$) then the result is a centreband and a set of spinning side bands spaced at multiples of the spinning frequency, on either side of the centreband. The theory of chemical shift anisotropy and shielding tensors has been reviewed in detail by several authors 7,25,26.

In attempts at quantitative analysis, three main problems arise from the presence of SSB signals in the coal spectra. Firstly, the signal intensity is shared between the centreband and the SSB signals. For example, at 2.5 kHz MAS frequency and 50.3 MHz carbon-13 frequency, two-thirds of the intensity assigned to condensed aromatic carbon is contained in SSB signals spaced at multiples of 50 ppm ($2.5 \times 10^3 / 50.3 \times 10^6$) from the centreband. Secondly, the intensity ratios of the SSBs are not constant for all carbon atoms, but depend on the chemical shift tensor for the particular carbon functionality. Thirdly, the likelihood of overlapping of sidebands and centrebands is high, when ever more than one type of carbon functionality is present. This is particularly the case with such a heterogenous substance as coal, where many of the centrebands, as well as sidebands, overlap.

Any attempt at quantitative analysis of the functional groups in coal from the CP/MAS spectra must include an assessment of this

distribution of sideband intensity.

Since the amount of intensity in the SSBs is determined by the chemical shielding anisotropy of a particular carbon functionality, it is necessary to determine typical chemical shift tensors for the wide range of carbon types observed in the coal spectra. The methods available for determining chemical shift tensors have been reviewed by Veeman¹⁸. Many carbon-13 chemical shift parameters have been published^{7,18,19}. In addition, principal values of the chemical shift tensors of a number of substituted benzenes have been measured in this laboratory^{14,16}. SSB intensities were determined from the principal values of the chemical shift tensors by employing the method of Herzfeld and Berger⁸ in reverse. That is, the SSB to centreband intensity ratios ($I_{\pm n}/I_0$) are recovered from the published contour plots, for functions of the three principal values of the chemical shift tensor.

Table 3 contains the averages and standard deviations of the SSB intensities, for carbon in each particular functional group. It should be noted that Table 3 contains the summary of all the model compound data available at present. The database is limited and does not necessarily represent the range of structures present in the coal, i.e. the average chemical shifts listed in Table 3 may not correspond directly to the chemical shifts of signals observed in the coal spectrum.

It can be seen that the variation (as indicated by the standard deviation) in SSB intensities is generally small for a given functionality. Aliphatic structures show very small anisotropies but alkoxy carbons exhibit significant anisotropies when bonded to aromatic rings. Aromatic ring carbons have large shielding anisotropies, and adjacent substituents also have an effect on the size of the SSB signals. For example, the SSB intensity patterns change substantially for aromatic carbon bonded to hydrogen at sites with no, one or two adjacent substituents (Table 3). Carbon atoms in aromatic condensed-ring structures have the largest anisotropies and therefore the greatest amount

of intensity in SSB signals. The reasons for these trends in shielding anisotropies are discussed by Veeman²⁵ and Wemmer, Pines and Whitehurst⁷.

The SSB intensity patterns for the carbon functionalities, contained in Table 3, are utilised by the program DOFIC to simulate the SSB patterns observed in the coal spectra. The form of the SSB database is shown in Appendix 1.

5.2 The Chemical Shift Database

Resolution enhancement procedures^{1,9} were employed to separate overlapping bands, in order to determine typical positions of the signals observed in the coal spectra the standard deviations, listed with the chemical shifts in Table 4, are, in general, not large when signals from many spectra are averaged. The "standard" set of signals is defined as the set of signals observed as distinct peaks or as shoulders in the majority of the spectra of all coal ranks.

The tallest aliphatic signal occurs at slightly higher chemical shifts in lignite spectra than in the spectra of other ranks (Table 4). DOFIC therefore searches the region between 26 and 34 ppm for the main aliphatic signal in the spectra of "low-rank" coals. The alcohol and ether signals between 60 and 105 ppm, assigned to cellulose-like fragments²⁴, are only separated as distinct peaks in the lignite spectra. The signal at 105 ppm was observed in association with a strong signal at 74 ppm, i.e. when complete cellulose structures have persisted into the lignite rank. The cellulose signals probably contribute to the spectra of some sub-bituminous coals, since the intensity in this region can be stronger than that expected for SSBs alone. Similarly, the band at 177 ppm is strong in the lignite spectra because of a signal assigned to carboxylic salts and acid groups overlapping with the aromatic SSBs. Support for the presence of such a band was gained from a spectrum of a humic acid separated from a Waimumu lignite, which was spun faster than 3 kHz¹⁷. A strong signal at 177 ppm could not be assigned to a SSB of other

observed signals. In higher rank coal spectra, this region is dominated by SSBs although some carboxylic groups are likely to be present in subbituminous coals. Signals from carbonyl carbon in aldehyde or ketone functionalities would be expected in the chemical shift region of 200 ppm. However, no such peaks were found in the spectrum of the humic acid, and the observed intensity in this region of the lignite spectra could be entirely accounted for by SSBs of the signals assigned to oxygen-substituted aromatic carbon. Other workers^{3,27} have also not observed evidence for the existence of these signals in the carbon-13 NMR spectra of coals.

The signal at 144 ppm labelled "diphenolic" is intense in the spectra of subbituminous coals and occurs occasionally in the spectra of low rank bituminous coals. Since this signal is thought to originate from tannin-like structure^{28,29}, it probably contributes in lignite spectra also, but is overshadowed by the band centred at 148 ppm assigned to the methoxylated aromatic functionalities common in lignin-like structures^{1,30}.

The spectra of lignites exhibit a far greater range of aromatic C-H functionalities due to the large aromatic oxygen content and lack of condensed-ring structures. The range of aromatic chemical shifts narrows as the rank of the coal increases⁴. Signals from aliphatic structures and phenolic groups are much weaker for high ranks. The phenolic signal is not distinct in the spectrum of the semi-anthracite.

The chemical shift database includes an assignment for each band (following Table 1) and an indication of the numbers of hydrogens ("NosH") and oxygens ("NosO") associated with the particular functional group. For example, the methyl signal at 15 ppm has a "NosH" of 3 and a "NosO" of 0, while the isolated phenol group associated with the signal at 154 ppm has both a "NosH" and a "NosO" of 1. Some alteration of these values occurs in DOFIC when there can be more than one assignment of a signal, but this will be dealt with later.

5.3 Line-Shape and Line-Width Database

The two line shapes most commonly observed in NMR are the Gaussian and the Lorentzian, defined respectively as³¹:

$$F(\nu - \nu_0) = (\ln 2 / \pi L)^{1/2} \exp[-(\nu - \nu_0)^2 \ln 2 / L^2] \quad [2]$$

$$F(\nu - \nu_0) = (L / \pi) [(\nu - \nu_0)^2 + L^2]^{-1} \quad [1]$$

where $F(\nu - \nu_0)$ is the amplitude at the position $(\nu - \nu_0)$ from the centre of the resonance (ν_0) , and L is the half line-width at half-height of the resonance. The Lorentzian line-shape is narrower at the top and has far more intensity in the wings of the band than the Gaussian line-shape.

The program DOFIC can be used to simulate either Lorentzian or Gaussian line-shapes, or a mixture of both, where the amount of each is set by "fracgauss", i.e. the fraction of Gaussian character. Line-widths at half-height and typical values of "fracgauss" were determined by extensive trial-and-error fitting of the 54 coal spectra. The linewidths observed in the coal spectra are not "natural" linewidths, i.e. it cannot be assumed that the linewidths are similar to those observed in model compound spectra. The linewidths also reflect the heterogeneity of structures present in the coal, in that, a range of chemical shifts is observed for a particular carbon type.

Each simulated spectrum was optimised for the best fit to the lowest points between each of the assigned bands. The best fit was chosen to minimise the parameter "MinRMS" where

$$\text{"MinRMS"} = \left[\sum_{i=1}^x (e_i - c_i)^2 \right]^{1/2/x} \quad [4]$$

where e_i and c_i are the experimental and calculated signal heights, respectively, at each point i , and x is the number of positions fitted, i.e. x is one less than the number of centreband signals included in the simulation. Where bands

appeared as shoulders only, the position half-way between signals was chosen for the test. The trial-and-error testing method employed for fitting these parameters is exemplified in Figures 4 and 5, for two of the line-shape parameters, the "fracgauss" and the line-widths of the main aromatic signals. Minima for the "low rank" line-shapes are shallow and wide, reflecting crowding of signals observed in the spectra of these coals. The aromatic signal is more clearly resolved in spectra of "high rank" coals so the fitting minima were more sharply defined.

The optimised "fracgauss" and aromatic line-widths are plotted against the "phenol" ratio in Figures 6 and 7. The spectra of coals at the top end of the "high rank" group exhibit:

- i) a significant narrowing in the line-width of the aromatic signals, a trend consistent with the decreasing variation in carbon functionalities as coalification advances towards the anthracite structure⁴, and
- ii) an increased Gaussian contribution which may be caused by the increasing condensation and aromaticity, and decreasing aliphatic content (i.e. a more rigid system³¹).

The amount of scatter shown in Figures 6 and 7 and the other line-width plots (not shown) is large. Therefore, line-width and line-shape parameters were not expressed as smooth functions of "rank", e.g. through the parameter "phenol". An alternative method, involving the averages of experimental values for each of the four "ranks", is summarised in Table 5. Although the standard deviations of the data sets are large, these trends were incorporated into DOFIC as the line-shape and line-width database. Sudden jumps in line-shape parameters at the "rank" boundaries, inherent in this approach, were found to be reflected by only minor changes in results for functional group analyses. This was tested by lowering or raising the "rank" boundary criteria, i.e. by overriding the normal DOFIC assignment of "rank". For example, the experimental spectrum of a Kawhia

subbituminous coal was simulated for line-shape and line-width parameters appropriate to a "medium-low" and a "low rank" coal. The carbon intensities obtained from the two simulations were:

chemical shifts	%C ("medium-low")	%C ("low")
15 to 50	29.7	30.2
50 to 100	3.6	3.6
100 to 140	47.0	48.8
140 to 180	19.9	17.6
	<hr/> 100.2	<hr/> 100.2

The largest differences between the two simulations occur in the chemical shift region greater than 100 ppm. However, these changes are not solely due to the alteration of the line-width and line shape parameters. The more important factor to be considered when overriding the "rank" boundary condition is the inclusion of two extra signals at 125 ppm and 148 ppm in the fitting of the "low rank" coals. (This will be dealt with in the next section).

6 INTERPRETATION OF SPECTRA

6.1 Inclusion or Exclusion of Signals

The set of signals to be fitted to the experimental spectrum are chosen in accordance with the trends in observed signals listed in Table 4. The ten "standard" signals are assigned to the "high rank" spectrum and the appropriate "extra" bands are added to the lower ranks. The band at 144 ppm is added to the spectra of "medium high rank" coals and below. The aliphatic alcohol/ether signals, the carboxylic signal and the extra aromatic C-H signals are added to the "medium low" and the "low" rank coal spectra. In the "low rank" spectra, the signal at 128 ppm is shifted to 130 ppm and the signals at 125 ppm and 148 ppm are added to the set of signals. If the signal assigned to the main cellulose band at 74 ppm is strong ($>1.2\%$), the cellulose C1 ether band at 105 ppm is also added.

The sequence of signal assignment is summarised in the flow diagram of Figure 8.

6.2 Contribution to Mixed Signals

There are four regions in the spectra that have ambiguous assignments. One of these is the peak at 144 ppm, primarily assigned to aromatic structures with hydroxy-substitution at adjacent ring sites (Figure 9a). This peak may also contain a contribution from carbon-substituted aromatic structures. The C-1 environment of dihydroconiferyl alcohol (Figure 9b) is used as the example of this structure. Similarly, the main aromatic signal at 128 ppm is assigned to aromatic C-H groups (Figure 9c), but in the "high-rank" coal spectra, a contribution from ring junctions in polycyclic structures is suspected because of the observed increase in the size of the aromatic SSBs relative to the centreband, i.e. the effect of the increased anisotropy of the chemical shift tensors of ring junction carbons.

The other two regions of ambiguity are confined to the lower rank classifications and involve the overlap of SSBs with centreband

signals. Signals in the region 60 to 100 ppm (assigned to the cellulose-fragment signals), and a broad signal at 177 ppm (assigned to carboxylic acids and salts), are partially ("low rank") or entirely ("medium-low rank") obscured by the first order low- and high-frequency aromatic SSB signals, respectively.

The first two regions are dealt with as follows.

The expected sizes of the first high-frequency SSB signals (h_1, h_2) are calculated from the height of the centreband and the known SSB intensity pattern for each of the contributing structures (labelled "1" and "2"). Contributions from other signals are included in this calculation if they occur at the same chemical shift. The second structure is assigned to be that involving carbon substitution. The chemical shift tensor of the second structure is the more highly anisotropic, i.e. $h_2 > h_1$. The fraction of the two types of carbon, C_1 and C_2 , contributing to the signal are then calculated from the observed signal height, h_e , at the chemical shift of the first high-frequency SSB;

$$\text{Fraction of } C_1 \text{ ("fracC1")} = (h_2 - h_e) / (h_2 - h_1) \quad [5]$$

$$\text{Fraction of } C_2 \text{ ("fracC2")} = 1 - \text{"fracC1"} \quad [6]$$

When $h_e < h_1$, it is assumed that only the first type of carbon functionality is responsible for the signal and conversely, if $h_e > h_2$, it is assumed that only the type-2 carbon is present. However, if $h_e > h_2$ a warning is printed in the output. A low spinning frequency may be the cause of the high h_e . Therefore, if the MAS frequency is less than 2.4 kHz (48 ppm) a statement to this effect is also printed in the output.

A slightly different procedure is used to decide whether genuine centreband signals contribute to the two SSB regions (60 to 100 ppm and greater than 160 ppm). The expected SSB intensity in the region is calculated from the observed aromatic centreband intensity. If there is more intensity than can be accounted for by the expected SSB intensity then, respectively, the four cellulose signals (64 to 89 ppm) and the carboxylic signal (177

ppm) are included in the data set to be fitted. (Refer to the previous section with regards to the fifth cellulose signal at 105 ppm).

A problem arises when the signals of ring junction aromatic carbon (128 ppm) and carboxylic acid carbon (177 ppm) occur in the spectrum. Since both contribute intensity in the region of the first-order high-frequency aromatic SSB (178 ± 2 ppm), neither contribution can be calculated from this SSB alone. The relative contributions could be found by including, in the estimation, the observed height of another aromatic SSB such as the next largest, first-order, high-frequency SSB. However, these smaller SSB signals are not as sensitive as the main SSB signal to the different types of carbon functionality contributing to the resonance. This problem is likely to occur at the border between the "medium-high" and "medium-low" rank coals and has not been completely resolved. The approach taken was to include the carboxylic acid signal (if needed) in the fitting of the "medium-low rank" coal spectra but not in the "medium-high rank" coal spectra. This may lead to an over-estimation of the oxygen contents of the "medium-low rank" coals and, conversely, an underestimation of the oxygen contents of the medium-high rank" coals.

6.3 Compensation for SSB Signals

Deconvolution of the experimental spectrum is performed by solving a set of simultaneous equations. These equations describe the effect of other signals, or their SSBs, on the signal height at the chemical shift of each centreband. A matrix of intensity coefficients is constructed. An external routine (FOLAAF) inverts the matrix and the intensities of each signal are then calculated from the heights of all the contributing signals.

6.4 Quality of the Fit

The quality of the simulation is given by the root-mean-square-deviation ("RMSD") which defined as follows:

$$\text{"RMSD"} = \left[\sum_{i=1}^n (e_i - c_i)^2 / n \right]^{1/2} \quad [7]$$

where e_i and c_i are the experimental and the calculated spectra, respectively and n is the number of points across the spectrum. The "RMSD" is not dimensionless and has the units in which the signal heights are measured, e.g. in mm. Therefore, the RMSD is a measure of the "quality of fit" to that particular spectrum. It is partly dependent on the plotting scale chosen for the experimental spectrum, but the tallest peak is normally plotted at a signal height of 150 to 180 mm so an "RMSD" of between 1 and 3 mm would correspond to typical noise levels. An "RMSD" value larger than this would indicate either (i) a bad fit to the experimental data, or (ii) an experimental spectrum with a particularly low signal-to-noise ratio.

7 OUTPUT PARAMETERS

7.1 Functional Groups

The calculated intensities are converted to percentage of total carbon assuming that the sum of the intensities represents all of the carbon in the sample. The functional-group-analysis output consists of the chemical shift, the % carbon observed, the line-width used and the assignment of the band.

7.2 Elemental Composition

The carbon intensity distribution is converted to the elemental composition, on a dry ash, nitrogen, and sulphur free (daNSf) basis, according to the assigned values of "NosH" and "NosO" (Appendix 1). The "NosH" for the aliphatic signals were estimated from the types of contributing structure given in Table 1. For example, the carbons in the resin acids that give a signal at approximately 39 ppm 20-23, have an average "NosH" of 1.4. The remaining chain and branched aliphatic structures contain either methylene ("NosH"=2) or methine ("NosH"=1) carbons that give signals in this chemical shift region. Therefore, the average "NosH" of 1.5 was assigned to the signal at 39 ppm.

Where there are dual assignments to a band, the "NosH" and "NosO" are corrected according to the calculated contributions to the mixed signals (which are also quoted in the output). For example, the "NosH" of 1 for the aromatic C-H signal at 128 ppm is corrected for the carbon-substituted aromatic carbon content by:

$$\text{"NosH" (128 ppm)} = 1 \times \text{"fracCH"} \quad [8]$$

where "fracCH" is the relevant "fracCl" of equation 5.

The "NosH" for the 148 ppm signal is corrected for the methoxyl content.

Once the "NosH" and "NosO" have been corrected, the elemental analysis is calculated from the % carbon (%Ci) of each signal.

The hydrogen-to-carbon and the oxygen-to-carbon ratios are calculated by:

$$O/C = \sum_{i=1}^z (16/12) \times (\%C_i \times "NosH"_i / 100) \quad [9]$$

$$H/C = \sum_{i=1}^z (1/12) \times (\%C_i \times "NosH"_i / 100) \quad [10]$$

The total of the hydrogen, oxygen and carbon contents are summed;

$$Total(O, H, C) = 100 + (1/12) \sum_{i=1}^z (\%C_i) ("NosO_i" + 16 \times "NosH"_i) \quad [11]$$

and the percentages are calculated from this;

$$\%C = 104 / Total(O, H, C) \quad [12]$$

$$\%H = 104 / 12 \times \left[\sum_{i=1}^z (\%C_i \times "NosH"_i) \right] / Total(O, H, C) \quad [13]$$

$$\%O = 104 \times 16 / 12 \times \left[\sum_{i=1}^z (\%C_i \times "NosO_i") \right] / Total(O, H, C) \quad [14]$$

where z is the number of signals to be fitted to the spectrum.

7.3 Other Parameters

In addition to the functional group analyses, several other parameters are defined, under the two general headings, "Aromatic Carbon Character" and "Aliphatic Carbon Character".

7.3.1 "Aromatic Carbon Character"

These parameters include a value for the aromaticity, f_a , defined

as the sum of the intensity in aromatic signals (106 to 160 ppm) as a fraction of the total intensity. This is a true aromaticity, in contrast to the apparent aromaticity, f_a , defined in an earlier report¹. The value of f_a produced by DOFIC takes into account the intensity in all the SSB signals and excludes the carboxylic carbon intensity.

The second parameter is the fraction of aromatic carbon bonded to oxygen and includes contributions associated with the signals between 144 ppm and 154 ppm. The former signal intensity is corrected for the aromatic C-C content.

7.3.2 "Aliphatic Carbon Character"

This parameter is normally found in the output for "low rank" coals. If there is significant intensity ($>1.2\%$) assigned to the main cellulose signal at 74 ppm the amount of intensity in all signals assigned to cellulose-like structures is totalled. The carbon, hydrogen and oxygen content of the coal contained in these structures is calculated in the same manner as the overall elemental analysis, and given in the output as the "Estimated content of cellulose or cellulose-like structures in the coal".

8 TEST RESULTS

The reliability of the DOFIC results were tested against the conventional analyses of the 54 New Zealand coals. The spectra of the coals were obtained using the standard spectrometer operating parameters described in Reference 1. It must be stressed that DOFIC was not tested as a potential replacement for ultimate analysis. The program is intended to provide detailed information about functional groups, but no independent analytical results are available to test performance in this area. The tests were therefore confined to elemental analysis.

The carbon, hydrogen and oxygen contents calculated by DOFIC are plotted versus the corresponding quantities determined by chemical analysis, in Figures 10 to 12. The carbon and oxygen contents correlate well, with standard deviations of 1.7% and 1.8% respectively. The good correlation between values for the oxygen contents is particularly interesting, considering that the oxygen contents determined by ultimate analysis are by "difference", i.e. the remainder once the carbon, hydrogen, nitrogen and sulphur contents have been determined, and are therefore considered less reliable than values for elements determined directly.

The DOFIC hydrogen contents do not correspond to those determined by ultimate analysis. The DOFIC results are consistently higher. The average discrepancy is 1.9% with a standard deviation of 0.5%.

The chemically-determined hydrogen contents cover a very small percentage range, and are not reconcilable with the signals observed in the NMR spectra. For example, one Roxburgh sample has a carbon content of 71%, determined by ultimate analysis, and therefore an aliphatic carbon content of 38% ($f_a=0.46$) by weight. Since the average aliphatic structure corresponds to each carbon being bonded to 2 hydrogens³² (i.e. average of methyl, methylene and methine structures), the aliphatic hydrogen content must be approximately 6.3% by weight. This does not include the aromatic

C-H and OH groups. Therefore, the hydrogen content of 5.9%, derived by chemical analysis is not consistent with an aromaticity value of $f_a=0.46$.

It is important to check the internal consistency of the DOFIC results for New Zealand coals with NMR data published by other workers. For example, Yoshida *et. al.*³³ have estimated the carbon and oxygen distribution from the CP/MAS NMR spectrum of Yallourn brown coal. Using their assignments, the NMR elemental analysis was calculated to be 59.7%C, 5.3%H and 35.0% O(daNSf). Both the hydrogen and oxygen contents are significantly larger than the chemically determined values; 3.9%H and 29.5%O. A similar estimate can be made from the NMR data Ohtsuka *et. al.* for another sample of Yallourn coal. The NMR results give 68.0%C, 7.9%H and 24.1%O in comparison with the ultimate analysis of 66.7%C, 5.3%H and 28.0%O.

Dereppe *et. al.*³ and Wilson *et. al.*² have also divided the NMR spectra of Indonesian, Australian, British and American coals into protonated - and nonprotonated-carbon distributions. The hydrogen contents can be estimated by assuming an average hydrogen-to-carbon mole ratio of 2 for the aliphatic protons and (in the case of the Indonesian coals) assuming that the aliphatic carbon adjacent to oxygen is bonded to one hydrogen. The hydrogen associated with phenolic and carboxylic oxygen is not included in the NMR estimate. The NMR hydrogen contents are plotted against the chemically determined hydrogen contents (daONSf) in Figure 13. Once again, the NMR results are higher than the ultimate analyses. The results shown in Figure 13 are based on somewhat arbitrary assumptions regarding H/C ratios for contributing functional groups, but these assumptions seem likely to underestimate hydrogen contents rather than overestimate them.

The results of several research groups therefore point to a consistent discrepancy between NMR results and ultimate analyses. Further work will be required to decide which is the more reliable technique for determination of hydrogen contents.

9 INSTRUCTIONS FOR USE OF DOFIC

The listing of the source code of program DOFIC is contained in Appendix 2. It will not be described in detail as the listing contains sufficient comment statements for DOFIC to be understood and altered, if necessary. The following sections describe how to use DOFIC in either the "black-box" mode or with more control of the program.

9.1 The "Black-Box" Approach

The instructions for using DOFIC as a "black-box" will be illustrated using the NMR spectrum of a subbituminous coal from the Braziers mine.

9.1.1 The NMR spectrum

The care taken in the running and layout of the NMR spectrum is particularly important to the success of DOFIC. These steps should be followed:

- a) A high signal-to-noise ratio is desirable in order that the signal intensities observed are representative of the carbon functionalities in the sample,
- b) The spectrum must be obtained with the sample spinning in the narrow frequency range of 2.5 ± 0.1 kHz. This is necessary because the model compound SSB intensity patterns have been calculated specifically for this spinning speed, and they alter considerably for different rotation rates, particularly for lower MAS speeds.
- c) The spectrum must be carefully phased. The spectrum should therefore be plotted with sufficient chemical shift width to enable the drawing of an adequate baseline, e.g. from -200 ppm to +400 ppm.
- d) The spectrum should be plotted on gridded paper from a start-of-plot ("SP") of -100 ppm with a width-of-plot ("WP") of 400 ppm (figure 13).

The spectrum is now ready for digitisation. An arbitrary baseline is drawn below the spectrum (e.g. on the next dark gridline) and the signal heights are measured from this line by ruler, with a spacing of 1 ppm. Thus, the spectrum is digitised into 401 points (i.e. - 100 ppm to +300 ppm). The correction for the arbitrary baseline must be estimated, as follows. The true baseline (based on the wide plot) is drawn onto the digitised spectrum and the difference between the true baseline and the arbitrary baseline, is taken at 3 points; namely the first (-100 ppm) and last (+ 300 ppm) positions and the midpoint (100 ppm), as shown in Figure 13. DOFIC includes a parabolic baseline correction based on this data.

Finally, if the exact spinning frequency is not known, it must be ascertained from the experimental spectrum. The difference between the main aromatic signal at 128 ppm and the first order SSB signals is estimated in parts per million and then converted into a frequency by multiplying by 50.3, e.g. a 50 ppm spacing is equivalent to a MAS frequency of 2515 Hz (see Figure 13).

The running of DOFIC is controlled by a command procedure (Appendix 3) which is initiated by entering the word "DOFIC". The first inquiry that will appear on the screen is "Edit the Database File ?(Y/N)" to which a negative answer is required for the "black-box" approach. The second question, "Input Title File Name (.Dat)" asks for a name for the experimental data file (e.g. "Braziers") and assigns this file name to be the current input file. The following question will then be "Edit Braziers.Dat ? (Y/N)" to which a "Y" answer results in the creation of the new input file. Standard editing commands are then used to enter the experimental data is given in Figure 14. The data is entered in the following sequence;

- i) The first line contains the "SP" and the "WP", in ppm i.e. -100 400.
- ii) The second line contains the name of the coal sample (not exceeding 50 characters), e.g. "Braziers".

- iii) The third line contains a sample reference number such as the Coal Research Association analysis number, e.g. for the Braziers sample this is 30/653. If the sample does not have a code number, a "-" should be entered.
- iv) The fourth line contains the spinning frequency in Hz and the number of data points (excluding the first) called "numchannel", i.e. 2515 400.
- v) The experimental spectrum is then entered as 40 rows of ten numbers, e.g. the first line contains the first to tenth data points i.e. heights at -100 to -91 ppm.
- vi) The 401th data point (i.e. the height at +300 ppm) is entered after row 40.
- vii) The last line contains the baseline correction in the following order; the correction at +300 ppm, at the midpoint (100 ppm) then at -100 ppm, e.g. in this example, 4 4.5 4.5.

Following the saving of the file (i.e. using the exit command) DOFIC is started and the message "Running the Simulation Now" appears on the screen.

9.3.1 The Output

When the simulation is complete the inquiry "Inspect Output File ? (Y/N)" appears on the screen. A positive response enables the operator to read the output data, i.e. the functional group and elemental analyses etc. The format of the Braziers output is shown in Figure 15. To leave the file the "quit" command should be used. The next inquiry is "Print Output File ?(Y/N)" which allows for a hard copy of the output file to be obtained.

The following three questions relate to the plotting of the base-corrected experimental spectrum, the simulated spectrum and the difference spectrum (i.e. difference between the experimental and simulated spectra). The program that processes the spectra

was written in this laboratory (by Dr. K.R. Morgan) to read and convert the data into the appropriate graphics commands for the Chemistry Division plotter. This program would have to be replaced by another suitable routine if any different plotting system is to be used. The form of the three spectra is shown in Figure 16 for the Braziers coal spectrum.

9.2 More Advanced Uses

DOFIC was primarily designed to function using the standard parameters described in the last section. However, some provision was included in DOFIC for alteration of these working parameters to allow for more advanced manipulation of the program.

Options available are:

- i) The parameters defining the spectrum, "SP", "WP" and "numchannel" can be changed. It is advisable that a plot width no smaller than 400 ppm, be used in order to span an adequate range of signals, including the SSBs. A larger digitisation interval, such as 2 ppm (i.e. "numchannel" = 200) may be used.
- ii) The input file may contain more than one set of experimental data e.g. all the lignite spectra may be entered into one file called "lignite.dat". Since only the top set of data is read by DOFIC, a positive response to the "Edit Lignite.Dat? (Y/N)" inquiry enables the operator to rotate the datasets.
- iii) A positive response to the "Edit the Database File ? (Y/N)" question allows the reader to read or partially alter the database (Appendix 1).

The first line of the database consists of the number of "standard" and "extra" signals, i.e. "numbands" and "extrabands" respectively. It should be remembered that some of the "extrabands" might not necessarily be fitted. The line ends with a number "printflag" that, if larger than 0, indicates that the

total matrix of standard and extra signal position and lineshape data is to be printed in the output file. This matrix, which is ("numbands" + "extrabands") * 5 in size, consists of the four columns containing the standard and the extra signal positions, the initial line-widths, the associated "NosH" and "NosO", followed by the assignment, in brief, of the signal, again not exceeding 50 characters.

The positions of all of the extra signals and many of the standard signals (15 ppm, 22 ppm, 39 ppm, 128 ppm, 154 ppm) cannot be altered unless the program itself is also changed to incorporate the new chemical shifts at all the relevant program steps. Since many of the linewidths are also altered in DOFIC in accordance with the rank trends, changing an initial line-width in column 2 will not always be effective. Most of the "NosH" and "NosO" may be altered although DOFIC calculates several of these (for 128 ppm, 144 ppm and 148 ppm) independently, so once more, some changes confined to the database will not alter the results. All of the signal assignments can be changed through editing the database.

The final matrix in the database contains the relevant SSB intensity data of Table 3. The SSB intensity patterns may also be changed. This capability is fundamental to the continued use of DOFIC as a routine analysis tool, in that it allows for the incorporation of new chemical shift anisotropy data as it appears in the literature.

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TABLE 1

SIGNAL ASSIGNMENTS

A = branched chain, cycloalkane or aromatic ring.

Chemical Shift (± 1 ppm)	Assignment	Structure
15	Methyl Groups	$-\text{CH}_2\text{CH}_2\text{CH}_3$
22	-Methylene, Methyl	$-\text{CH}_2\text{CH}_2\text{CH}_3$ $\text{A}-\text{CH}_3$
30	Cyclic and poly-methylene	$\{\text{CH}_2\}_n$
39	Methylene, Methine	$\text{A}-\text{CH}_2-$ $-\text{CH}-$
48	Methine, Quarternary carbon	$\text{A}-\text{CH}-$ $-\text{C}-$
56	Methoxyl	$\text{A}-\text{OCH}_3$
64	)	C_6
74	)	$\text{C}_2, \text{C}_3, \text{C}_5$
84, 89	) Alcohol and Ether	cellulose carbon
105	)	C_1
107	Aromatic C-H adjacent to C-O and C-R	
112	Aromatic C-H adjacent to C-OR	
117	Aromatic C-H adjacent to C-OH	
125	Aromatic C-H adjacent to C-R	
130	Aromatic C-H adjacent to C-H	
128	i) Aromatic C-H adjacent to C-H or C-R	
	ii) Ring junctions in polycyclic groups	
138	Carbon substitution sites	
144	i) Rings with adjacent hydroxyls	
	ii) Carbon substitution sites	
148	Adjacent ring C-OH and C-OR	
154	Phenolic carbon	
177	Carboxylic acids and salts	$-\text{CO}_2\text{H}$ $-\text{CO}_2^-$

TABLE 2 C-X CHEMICAL SHIFTS

Data from References 12 and 15. "n" represents the appropriate substitution for the particular nucleus. Chemical shifts in ppm.

X =	C	S	N	O
-XH _n	137	131	147	155
-X(CH ₃) _n	149	139	151	160
XH _n	132	126	119	143
XH	-	-	151	-
CH ₃ -XH _n	5-30	10-20	12-42	38-50
-CH ₂ -XH _n	22-45	17-33	43-58	42-70
-CH-XH _n	32-60	55-65	55-68	65-78
-C-XH _n	28-52	52-72	60-75	73-85
R ₁
C=X(R) _n	100-150	190-200	145-160	200-225
R ₂				

TABLE 3. SSB INTENSITY PATTERNS OF MODEL COMPOUNDS

Averaged signal positions (σ), %intensity in SSB ($I \pm n$) and standard deviations below. Number in brackets indicates the number of compounds for which data averaged. A standard deviation <0.5 is quoted as "0".

Carbon Type			σ	I_{+3}	I_{+2}	I_{+1}	I_0	I_{-1}	I_{-2}	I_{-3}
Aromatic Carbon
R_1	R_2	R_3								
H	H	H	128	1	6	26	39	19	8	1
		(8)	4	0	1	2	4	1	1	0
H	H	C	127	1	5	25	43	18	7	1
		(14)	3	0	1	2	5	1	1	1
H	H	H or C	128	1	5	25	41	19	8	1
		(22)	3		1	2	5	1	1	
H	H	OH	117	0	4	20	53	16	5	1
		(7)	2		1	1	2	1	1	
H	H	OR	112	0	4	22	51	16	6	1
		(11)	4		0	1	3	0	1	
H	O-	C-	107	0	3	22	52	15	6	1
		(8)	4		1	2	4	1	1	
C-	H	H	136	1	5	27	41	17	9	1
		(17)	5		1	3	3	2	1	
CO ₂ H	H	H	121	1	4	23	48	17	7	1
		(3)	1			1	0	1		
OR	H	H	158	0	4	19	56	17	5	0
		(4)	4			2	3	1		
OH	H	H	154	0	5	18	51	20	5	1
		(4)	3		1		5	2	1	
OH	OH	H	144	0	3	19	58	15	4	1
		(1)								
OH	OR	H	149	0	3	18	61	15	4	0
		(4)	4		1	1	2	1		
OH	OR	OR	139	0	2	16	66	13	4	0
		(3)	3		1	2	4	1	1	

TABLE 3 (Cont'd) "Ar" = aromatic

Carbon Type			σ	I+3	I+2	I+1	I ₀	I-1	I-2	I-3
OR	OH	H	148	0	2	16	65	13	4	0
		(7)	1			1	2	1		
OR	OR	H	153	0	3	17	62	14	4	0
		(4)	2		1	1	2	1	0	
ring junction			131	1	5	33	34	14	12	2
		(4)	3	0	1	1	2	1	1	0
Aliphatic										
-CH ₂ -			34	0	0	1	98	1	0	0
		(2)	2			0.5	0.5	0.5		
R-CH ₃			14	0	0	1	98	1	0	0
		(3)	3				0.5			
Ar-CH ₃			19	0	0	1.5	97	1.5	0	0
		(5)	1				1			
R-CH ₂ -CH ₃			23	0	0	1	98	1	0	0
		(3)	3				0.5			
Ar-OCH ₃			54	0	0	6	88	5	0	0
		(3)	2				1			
Ar-OCH ₂ -R			69	0	0	3	93	3	1	0
		(2)	0				0			
CH-OH			64	0	0	2.5	95	2	0.5	0
		(2)	2				1			
-C=C-			127	1	6	20	43	23	6	1
		(5)	2	0	0	1	2	0	1	0
Carbonyl										
-CO ₂ H			176	0	3	14	66	14	3	0
		(15)	5		1	2	5	2	1	
-CO ₂ ⁻			178	0	2	13	71	13	2	0
		(7)	6		1	3	6	2	1	
-CO ₂ H or CO ₂ ⁻			176	0	3	14	67	14	2	0
		(25)	5		1	2	5	2	1	
-CO ₂ R			169	0	5	12	61	19	2	0
		(5)	8		0.5	1	2	1	0.5	

TABLE 4 AVERAGED CHEMICAL SHIFTS

Averages of the chemical shifts of signals observed in the spectra of 54 NZ coals. The standard deviation, the number of spectra in which signal is distinct and the general "rank" of coal in which the signal observed as a distinct signal or as a shoulder, are also given.

mean chemical shift (ppm)	standard deviation	number	"rank"
15.4	0.7	32	all
21.6	0.8	46	"
30.4	0.5	43	"medium-low" and above
32.2	0.8	11	"low"
39.4	1.7	28	most
48.5	1.9	25	"
56.3	0.4	11	"low"
64.3	1.6	10	"
74.3	0.8	14	"low" and "medium-low"
82.7	1.2	12	"
88.6	0.6	4	"low"
105.3	0.4	8	"
107.3	1.2	10	"low" and "medium-low"
112.0	1.9	24	most
117.4	1.9	14	"
125.0	1.5	8	"low"
130.0	1.2	8	"
127.6	0.9	43	"medium-low" and above
138.0	1.0	22	most
143.6	1.4	21	"medium-high" and below
147.7	0.8	11	"low"
153.8	0.9	53	all
177.4	1.1	11	"low"

TABLE 5 OPTIMISED LINE-WIDTH AND LINE-SHAPE PARAMETERS

Line-width data in ppm for peaks specified by the chemical shift.

Lineshape parameters given in the final row. "n.d." = not determined.

Standard deviations given in brackets. SD of line-widths <0.5 are quoted as "0".

Chemical shift	"Rank"			
	"low"	"medium -low"	"medium -high"	"high"
15 - 33	5 (1)	4.5(0.5)	4(0)	4(0)
39, 48	5.5 (2)	6.5(0.5)	8(2)	8(1.5)
56	3 (1)	n.d.	-	-
74	4 (1)	n.d.	-	-
64, 84, 89	5 (1)	n.d.	-	-
105	2.5 (1.5)	-	-	-
106 to 140	7 (1.5)	8.5(2.5)	8.5(2.5)	8.5(1)
144, 154	4 (1)	5 (0.5)	5.5 (0)	5.5(1)
148	4 (1)	-	-	-
177	8 (2)	n.d.	-	-
"fracgauss"	0.3 (0.1)	0.5(0.2)	0.5(0.2)	0.5(0.1)

12 FIGURE CAPTIONS

- Fig. 1 Plot of the ratio of signal heights at 154 ppm and 128 ppm versus % Fixed Carbon showing the boundary assigned to the "high rank".
- Fig. 2 Plot of the signal heights at 144 ppm and 154 ppm as ratios relative to the signal height at 128 ppm, showing the boundaries assigned to the "medium-high rank".
- Fig. 3 Plot of the signal heights at 56 ppm and 154 ppm both relative to the signal height at 128 ppm, showing the boundary between the "medium-low" and "low rank".
- Fig. 4 Plot of the "MinRMS" parameter versus "fracgauss" for a Waimumu Newvale lignite (●) and a Rockies m.v. bituminous coal (◆), showing the "trial-and-error" method of optimising line-shape parameters.
- Fig. 5 Plot of "MinRMS" versus the half line-width at half-height, L, for the aromatic signals between 106 and 140 ppm, for a Waimumu Goodwin lignite (●) and a Stockton No. 2 h.v. bituminous A coal (▲).
- Fig. 6 Optimised "fracgauss" versus "phenol", where the symbols represent the rank groups "low" (●), "medium-low" (■), "medium-high" (▲), "high" (◆)
- 7 Optimised aromatic line-widths versus "phenol".
- Fig. 8 Flow diagram for the program DOFIC showing the initial estimates of rank (8a) and the decisions made on the inclusion of signals(8b). "I" =include the following signal-chemical shift given in brackets; "H" - observed signal height; "S" = shift main aromatic signal; "M" = calculate mixed contribution.
- Fig. 9 Compounds that exhibit the types of structures that contribute to the mixed signals at 144 ppm (a,b) and 128 ppm (c,d).

- Fig. 10 The carbon contents determined by DOFIC and by ultimate analysis. Open symbols indicate representative ultimate analysis for a sample from the same locality (see Appendix 4).
- Fig. 11 Same as for Figure 10 but for the oxygen contents.
- Fig. 12 Same as for Figure 10 but for the hydrogen contents.
- Fig. 13 Plot of NMR and chemically determined hydrogen contents (daONSf). Data from Ref. 2(●), Ref. 3(▲), Ref. 5 (◆) and Ref. 32 (■). Data corrected and transposed from Fig. 12 ringed in solid line.
- Fig. 14 The experimental spectrum of Braziers subbituminous coal, showing the relationships between signal heights, provisional baseline and the baseline correction terms.
- Fig. 15 The input file for the experimental data for the Braziers coal, showing the required format.
- Fig. 16 The output file for the Braziers coal, showing the layout of the typical DOFIC functional group analysis.
- Fig. 17 Typical graphical output of DOFIC for the Braziers coal, showing the basecorrected experimental spectrum (expt), the simulated spectrum (sim), and the difference spectrum (diff).

Figure 1

Figure 2

Figure 3.

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8a

Figure 8b.

Figure 9.

Figure 10

Figure 12

Figure 13

Figure 14

-100 400
 Braziers
 30/653
 2515 400
 4.5 4.5 4.5 4.5 4.5 4.5 4.5 4.5 4.5 4.5
 5 4.5 4.5 4.5 4.5 4.5 4.5 4.5 4.5 5
 5 4.5 4.5 4.5 4.5 4.5 4.5 4.5 4.5 4.5
 4.5 4.5 4.5 5 5 5 5 5 5 4.5
 4.5 5 5 5 4.5 4.5 4.5 5 5.5
 5 5 5 5 5.5 6 6.5 6.5 6
 6 7 7 7.5 7.5 8 8.5 9 9.5 9
 9 9 9.5 9.5 10 10.5 11 11 11.5 12
 12 11.5 11.5 11 11 11 11 11 11 11
 12 12 12.5 12.5 13 13 13.5 14 15 16 17
 18 18.5 20 21 23 25 28 32 35 38
 42 47 51 55 58.5 61 63 67 70 74
 77 79.5 81 83 85 87 90 96 101 104
 106 102 96 89 82 75 71 68 65 62
 60 57 55 53 50 48.5 47 45.5 44 42
 41 39.5 39 38.5 38 37.5 36 35 33 33.5
 33.5 33.5 33 34 34.5 34.5 35 37 38 39
 41 42.5 44 45.5 46 47 48 48.5 48 47.5
 47 45 43 41.5 40 37.5 37 36 36 36
 35.5 36.5 36.5 36.5 36.5 35.5 35 35.5 36 37
 39 41.5 43 44 45 46 46.5 48 49 50.5
 52.5 54.5 56 58 60 61.5 63 65 67 69
 72 75 78 81 84 86 87 87.5 87.5 87
 85 82 79 75 72 69 67 66 66.5 68
 70 73 74.5 75 74.5 71.5 67 63 61 59
 58.5 59 59 58.5 58 56 53 49 46 43
 41.5 40 38.5 37.5 37 37 37 38.5 39.5 41
 43 46 49 53 56 59 61 62 63.5 63.5
 61.5 60 57 54 50 47 44 41 39.5 38
 37.5 37 37 36.5 35.5 34 32 31.5 29 28
 27.5 27.5 27 26 26 26 24.5 23 22 21
 19 18 17 15 14 13.5 13 12.5 12 12
 12 12.5 13 13.5 14.5 14.5 14.5 14.5 15.5 16.5
 16.5 16.5 15.5 14.5 14 13 13 12 11 11
 10.5 10.5 10 10 10 10 9 9 9.5 9
 9 9 8.5 9 9.5 8.5 8 8 7.5 7.5
 7 7 6.5 6 5.5 5.5 5.5 5.5 5 4.5
 4.5 4.5 4 4.5 5 5 4.5 4.5 5 5
 5 5 5.5 5 4.5 4 4.5 4 4.5 4
 4 4.5 4.5 4.5 3.5 4 4.5 4 4 4
 4
 4 4.5 4.5

Figure.15

COAL : Braziers
Reference No. : 30/653

Estimate of Rank : MEDIUM LOW

RMSD For The Spectrum (mm) = 2.439

Fraction of gaussian contribution to bands : 0.5

Functional Group Analysis

ppm	%C	Line Width	Carbon Functionality
15.0	3.9	4.5	terminal-methyl
22.0	4.7	4.5	methylene(adj.CH3)/methyl-ar.
30.0	7.4	4.5	polymethylene-chain
39.0	5.0	6.5	methine/methylene-ar.
48.0	2.9	6.5	quarternaryC/methine-ar.
56.0	0.5	3.0	methoxyl-ar.
64.0	0.8	5.0	alcohol (cellulose-C6)
74.0	0.5	4.0	alcohol (cellulose-C2,C3,C5)
84.0	0.2	5.0	ether (cryst.cellulose-C4)
89.0	0.4	5.0	ether (amorph.cellulose-C4)
107.0	0.2	8.5	arom. C-H between C-O+C-R
112.0	9.3	8.5	arom. C-H ortho to C-OR(H)
117.0	6.2	8.5	arom. C-H ortho to C-OH
128.0	31.0	8.5	aromatic C-H ortho to C-H/C-C
138.0	7.3	8.5	aromatic C-C
144.0	9.0	5.0	diphenol
154.0	7.9	5.0	phenol
177.0	2.8	8.0	carboxylic acids + salts

Aromatic Carbon Character

- 1 Aromaticity, fa : 0.71
- 2 Fraction of Aromatic C bonded to O : 0.23

Contributions to band at 144 ppm
: fraction C-O = 0.954 fraction C-C = 0.046

Elemental Analysis

O/C Ratio (%wt) : 0.321
H/C Ratio (%wt) : 0.096

% Carbon : 70.6
% Hydrogen : 6.8
% Oxygen : 22.6
N.B. dry-ash-free, do not account for %N or %S.

BRAZIERS

Figure 17

13 APPENDICES

- 13.1 The Database File
- 13.2 DOFIC Source Code
- 13.3 DOFIC Command Procedure
- 13.4 Details of the NZ Coal Samples

10 11 0

{ numbands, numextrabands, printflag }

Chemical Shift and Line Databases

ppm	L	"NosH"	"NosO"	Assignment
15.0	4	3	0	terminal-methyl
22.0	4	2.5	0	methylene(adj.CH3)/methyl-ar.
30.0	4	2	0	polymethylene-chain
39.0	8	1.5	0	methine/methylene-ar.
48.0	8	0.5	0	quarternaryC/methine-ar.
112.0	8.5	1	0	arom. C-H ortho to C-OR(H)
117.0	8.5	1	0	arom. C-H ortho to C-OH
128.0	8.5	1	0	aromatic C-H ortho to C-H/C-C
138.0	8.5	0	0	aromatic C-C
154.0	5	1	1	phenol
56.0	3	3	0	methoxyl-ar.
64.0	5	3	1	alcohol (cellulose-C6)
74.0	4	1.67	0.83	alcohol (cellulose-C2,C3,C5)
84.0	5	1	0.5	ether (cryst.cellulose-C4)
89.0	5	1	0.5	ether (amorph.cellulose-C4)
105.0	2.5	1	1	ether (cellulose-C1)
107.0	8.5	1	0	arom. C-H between C-O+C-R
125.0	7	1	0	arom. C-H ortho to C-R
144.0	5	1	1	diphenol
148.0	4	1	1	adjacent phenol/C-OR
177.0	8	0.5	2	carboxylic acids + salts

SSB Intensity Pattern Database

0 0 1 98 1 0 0	{ 15 ppm }
0 0 1 98 1 0 0	{ 22 }
0 0 1 98 1 0 0	{ 30 }
0 0 1 98 1 0 0	{ 39 }
0 0 1 98 1 0 0	{ 48 }
0 4 22 51 16 6 1	{ 112 }
0 4 21 53 16 5 1	{ 117 }
1 5 25 41 19 8 1	{ 128, C-H }
1 6 27 41 17 9 1	{ 138 }
0 5 18 51 20 5 1	{ 154 }
0 0 6 89 5 0 0	{ 56 }
0 0 2.5 95 2 0.5 0	{ 64 }
0 0 8 90 2 0 0	{ 74 }
0 0 3 93 3 1 0	{ 84 }
0 0 3 93 3 1 0	{ 89 }
0 0 7 93 0 0 0	{ 105 }
0 4 22 52 15 6 1	{ 107 }
1 5 25 41 19 8 1	{ 125 }
0 3 19 58 15 4 1	{ 144, C-O }
0 2 17 64 13 4 0	{ 148 }
0 3 14 67 14 2 0	{ 177 }
1 5 33 34 14 12 2	{ 128, C-C }
1 5 31 36 15 10 2	{ 144, C-C }

```
PROGRAM DOFIC (exptspec,coalcomp,compspec,plotspec,diffspec,database);
```

```
{ Program DOFIC ,Determination Of Functionalities In Coal,simulates  
the C13 NMR spectrum of and provides a comprehensive functional  
group analysis coals of all ranks. }
```

```
CONST
```

```
maxbands = 30;  
numssb = 7; {numssb = number of ssb (6) + centreband(1)}  
Pi = 3.1415926;  
Ln2 = 0.6931471706;
```

```
TYPE
```

```
datvec = ARRAY[0..400] OF DOUBLE;  
datarray = ARRAY[1..maxbands,1..numssb] OF DOUBLE;  
intarray = ARRAY[1..maxbands] OF DOUBLE;  
titlearray = ARRAY[1..maxbands] OF VARYING[50] OF CHAR;  
titlevec = VARYING[50] OF CHAR;  
intvec = ARRAY[1..numssb] OF DOUBLE;  
coefarray = ARRAY[1..maxbands,1..maxbands] OF DOUBLE;  
wkarray = ARRAY[1..maxbands] OF DOUBLE;
```

```
VAR
```

```
numbands,extrabands,numchannel,sp,wp,w:INTEGER;  
max,fracgauss:DOUBLE;  
exptspec,plotspec,coalcomp,compspec,diffspec,database:TEXT;  
allarray,allextra,issbextra,issb:datarray;  
issbCC,issbCD,issbC,issbCH:intvec;  
e:datvec;  
bandtitles,extratitles:titlearray;
```

```
{*****}
```

```
{ External procedure used to calculate the inverse of the matrix  
of intensity coefficients }
```

```
[asynchronous, unbound] procedure F01AAF (  
%ref a: array [10..u0: integer; 11..u1: integer] of double;  
ia: integer;  
n: integer;  
%ref unit: array [12..u2: integer; 13..u3: integer] of double;  
iunit: integer;  
%ref wkspe: array [14..u4: integer] of double;  
var ifail: integer); external;
```

```
{*****}
```

```
PROCEDURE title;
```

```
{ Reads and writes the title, reference number and plot scales }
```

```
VAR
```

```
title,ref:titlevec;
```

```
BEGIN
```

```
READLN(exptspec,sp,wp); { sp = start of plot in ppm}  
WRITELN(plotspec,sp,wp); { wp = width of plot in ppm}  
WRITELN(diffspec,sp,wp);  
WRITELN(compspec,sp,wp);  
WRITE(coalcomp,'COAL : ');  
READLN(exptspec,title);  
WRITELN(compspec,title);  
WRITELN(coalcomp,title);  
WRITELN(plotspec,title);  
WRITELN(diffspec,title);
```

```
READLN(exptspec,ref);  
WRITELN(coalcomp,'Reference No. : ',ref);  
WRITELN(coalcomp);
```

```
END; { of title }
```

```
{*****}
```

```
PROCEDURE bascorrect;
```

```
{parabolic baseline correction : in b specify corrections for  
1 = numchannel,numchannel/2,0 respectively. }
```

```

VAR
  i,j:INTEGER;
  s,y,z,v:REAL;
  b:ARRAY[1..3] OF REAL;

BEGIN
  FOR i:=1 TO 3 DO
    READ(exptspec,b[i]);
    READLN(exptspec);

    s:=(b[i]-2*b[2]+b[3])/(numchannel*100);
    y:=(-b[i]+4*b[2]-3*b[3])/numchannel;
    z:=b[3];
    FOR i:=0 TO numchannel DO BEGIN
      v:=s*i+y*i+z;
      e[i]:=e[i]-v;
    END;

    { Writes out the basecorrected experimental spectrum,e. }

    FOR i:=0 TO TRUNC((numchannel/10)-1) DO BEGIN
      FOR j:= 0 TO 9 DO
        WRITE(compspec,e[i*10+j]:4:1,' ');
      WRITELN(compspec);
    END;
    WRITELN(compspec,e[numchannel]:4:1);
  END; {of basecorrect}

  {*****}

  PROCEDURE readdatabase;

  VAR
    x,i,j,printflag:INTEGER;

  BEGIN
    RESET(database);

    { numbands: the nos. of bands in the basis set;
      extrabands: the nos of other bands needed for lower rank coals;
      printflag: indicates if whole dataset of bands to be printed out.}

    READLN(database,numbands,extrabands,printflag);

    { The "all" arrays contain: the band position in ppm;
      : the linewidth;
      : the number of hydrogens associated with
        that type of carbon;
      : the number of oxygens " " " " " ";
      : the observed intensity at that ppm.}

    FOR i:=1 TO numbands DO BEGIN
      FOR j:=1 TO 4 DO
        READ(database,allarray[i,j]);
      READLN(database,bandtitles[i]);
      x:=ROUND((allarray[i,1]-sp)/(wp/numchannel));
      allarray[i,5]:=e[x];
    END;

    FOR i:=1 TO extrabands DO BEGIN
      FOR j:=1 TO 4 DO
        READ(database,allextra[i,j]);
      READLN(database,extratitles[i]);
      x:=ROUND((allextra[i,1]-sp)/(wp/numchannel));
      allextra[i,5]:=e[x];
    END;

    IF printflag = 1 THEN BEGIN
      WRITELN(coalcomp,' Database Set of Bands');
      WRITE(coalcomp,' ppm linewidth ');
      WRITELN(coalcomp,' Carbon functionality');
      FOR i:=1 TO numbands DO BEGIN
        WRITE(coalcomp,' ,allarray[i,1]:4:1,' ,allarray[i,2]:3:1);
        WRITELN(coalcomp,' ,bandtitles[i]);
      END;
      WRITELN(coalcomp,' Auxilliary Set of Bands');
      WRITE(coalcomp,' ppm linewidth ');
      WRITELN(coalcomp,' Carbon functionality');
      FOR i:=1 TO extrabands DO BEGIN
        WRITE(coalcomp,' ,allextra[i,1]:4:1,' ,allextra[i,2]:3:2);
        WRITELN(coalcomp,' ,extratitles[i]);
      END;
    END;

    { issb_ = arrays of intensities of the ssb's from model compounds-
      there are two assignments for the 120 and 144ppm peak,
      which appear after the issb arrays respectively. }

```

```

FOR i:= 1 TO numbands DO BEGIN
  FOR j:= 1 TO numssb DO
    READ(database,issb[i,j]);
  READLN(database);
END;
FOR i:= 1 TO numbands DO BEGIN
  IF allarray[i,1]=128 THEN BEGIN
    FOR j:= 1 TO numssb DO
      issbCH[j]:=issb[i,j];
    END;
  END;
END;

FOR i:= 1 TO extrabands DO BEGIN
  FOR j:= 1 TO numssb DO
    READ(database,issbextra[i,j]);
  READLN(database);
  IF allexta[i,1]=144 THEN BEGIN
    FOR j:= 1 TO numssb DO
      issbCO[j]:=issbextra[i,j];
    END;
  END;
END;

FOR j:= 1 TO numssb DO
  READ(database,issbC[j]);
READLN(database);
FOR j:= 1 TO numssb DO
  READ(database,issbCC[j]);
END; { of readdatabase}

{*****}

FUNCTION gauss(x,mean,linewidth,totintensity:DOUBLE):DOUBLE;

VAR
  factor:DOUBLE;

BEGIN
  factor:= SQR((x-mean)/linewidth)*Ln2;
  gauss:=totintensity*SQR(Ln2/Pi)*EXP(-factor)/linewidth;

END; { of the function gauss}

{*****}

FUNCTION lorentz(x,mean,linewidth,totintensity:DOUBLE):DOUBLE;

VAR
  factor:DOUBLE;

BEGIN
  factor:= 1/(SQR(linewidth) + SQR(x-mean));
  lorentz:=totintensity*(linewidth/Pi)*factor;

END; { of the function gauss}

{*****}

PROCEDURE totalspect(int:intarray;intssb:datarray;VAR c:datvec);
{Calculates total spectrum from the contributing bands and side-bands.}

VAR
  i,j,k,cstart,cend:INTEGER;
  linewidth,mean,devs,ppm,intensity,totintensity:DOUBLE;
  channel:datvec;

BEGIN
  FOR i:=0 TO numchannel DO
    channel[i]:=0;

  FOR i:= 1 TO numbands DO BEGIN
    linewidth:=allarray[i,2];
    devs:=15*linewidth;
    intensity:=int[i];
    FOR j:=1 TO numssb DO BEGIN
      mean:=allarray[i,1]-((j-4)*w); { position of the sideband }
      totintensity:=intensity*intssb[i,j]; { the intensity in the ssb }
      cstart:=ROUND((mean-devs-sp)*numchannel/wp); { start of band }
      cend:= ROUND((mean+devs-sp)* numchannel/wp); { end of band }
      IF (cstart(=numchannel) AND (cend)=0) THEN BEGIN
        IF cstart<0 THEN cstart:=0;
        IF cend>numchannel THEN cend:=numchannel;
        FOR k:= cstart TO cend DO BEGIN
          ppm:=k/numchannel*wp + sp;

```

```

        channel[k]:=channel[k]
        +fracgauss*gauss(ppm,mean,linewidth,totintensity)
        +(1-fracgauss)*lorentz(ppm,mean,linewidth,totintensity);
    END;
END;
END;
END;

FOR i:=0 TO numchannel DO
    c[i]:=channel[i];      { c is the final computed spectrum }
END; { of trialspect }

{*****}

PROCEDURE printspectrum( c:datvec);

{ Calculates the rms for the total spectrum;
  Prints out the simulated spectrum ready for plotting.
  ( d is the difference spectrum, i.e. computed - experimental) }

VAR
    i,j,x1,x2,x:INTEGER;
    rms,ppm:DOUBLE;
    d:datvec;

BEGIN
    rms:=0;
    FOR i:=0 TO numchannel DO BEGIN
        d[i]:=e[i]-c[i];
        rms:=rms + SQR(d[i]);
    END;
    rms:=SQRT(rms/(numchannel+1));
    WRITELN(coalcomp);
    WRITELN(coalcomp,'RMSD For The Spectrum (mm) = ',rms:5:3);
    WRITELN(coalcomp);

    FOR i:=0 TO TRUNC((numchannel/10)-1) DO BEGIN
        FOR j:= 0 TO 9 DO BEGIN
            WRITE(plotspec,c[i*10+j]:4:1,' ');
            WRITE(diffspec,d[i*10+j]:4:1,' ');
        END;
        WRITELN(plotspec);
        WRITELN(diffspec);
    END;
    WRITELN(plotspec,c[numchannel]:4:1);
    WRITELN(diffspec,d[numchannel]:4:1);
    WRITELN(plotspec,max:4:1);
    WRITELN(diffspec,max:4:1);
END; { of printspectrum }

{*****}

PROCEDURE coefficients(l:INTEGER;ppm:DOUBLE;
    VAR coef:coefarray;intssb:datarray);

{ Calculates overlap at one position(ppm) of the relevant centre or
  sidebands; i.e. the individual members of the intensity coefficient
  array,"coef". }

VAR
    i,j:INTEGER;
    linewidth,mean,devs,intensity,bstart,bend:DOUBLE;

BEGIN
    FOR i:= 1 TO numbands DO BEGIN
        coef[i,1]:=0;
        linewidth:=allarray[i,2];
        devs:= 15*linewidth;
        FOR j:=1 TO numssb DO BEGIN
            IF intssb[i,j]>0 THEN BEGIN
                mean:=allarray[i,1]-((j-4)*w);
                bstart:=(mean-devs);
                bend:= (mean+devs);
                IF (bstart=(wp+sp))AND (bend)=sp THEN BEGIN
                    IF bstart(sp THEN bstart:=sp;
                    IF bend(wp+sp) THEN bend:=(wp+sp);
                    IF (ppm>bstart) AND (ppm<bend) THEN BEGIN
                        intensity:=intssb[i,j];
                        coef[i,j]:=coef[i,1]
                            +(fracgauss*gauss(ppm,mean,linewidth,intensity))
                            +(1-fracgauss)*lorentz(ppm,mean,linewidth,intensity);
                    END;
                END;
            END;
        END;
    END;
END; { of coefficients }

```

```

*****}

PROCEDURE intensities(zero:INTEGER;VAR int:intarray;
                     VAR intssb:datarray);

{ Calculates the intensity of a centre-band from the observed intensity
  in the experimental spectrum and the contributions from overlapping
  sidebands. }

VAR
  i,j,l,k,IFAIL,notband:INTEGER;
  ppm:DOUBLE;
  coef,invcoef:coefarray;
  wkspce:wkarray;

BEGIN
  REPEAT BEGIN
    FOR l:=1 TO numbands DO BEGIN
      ppm:=allarray[l,1];
      coefficients(l,ppm,coef,intssb);
    END;
    { Inversion of coefficient array by external procedure }

    F01AAF(coef,maxbands,numbands,invcoef,maxbands,wkspce,IFAIL);

    { Calculation of individual intensities from observed intensities }

    FOR l:=1 TO numbands DO BEGIN
      int[l]:=0;
      FOR i:= 1 TO numbands DO
        int[l]:= int[l] + (invcoef[l,i]*allarray[i,5]);
      IF int[l]<0 THEN int[l]:=0;
    END;

    { If a final fit then remove any zero-intensity centreband from
      the database }

    IF zero > 0 THEN BEGIN
      notband:=0;
      FOR i:= 1 TO numbands DO BEGIN
        IF int[i]=0 THEN BEGIN
          notband:= notband+1;
          FOR j:= i TO (numbands-notband) DO BEGIN
            FOR k:=1 TO 5 DO
              allarray[j,k]:=allarray[j+notband,k];
            int[j]:=int[j+notband];
            bandtitles[j]:= bandtitles[j+notband];
            FOR k:=1 TO numssb DO
              intssb[j,k]:=intssb[j+notband,k];
          END;
        END;
      END;
      numbands:=numbands-notband;
    END;
  UNTIL notband=0;
END; { of intensities }

{*****}

PROCEDURE coalfunctgroup( mix128,mix144:INTEGER;alc_int:DOUBLE;
                          int:intarray;fracCH,fracCO:DOUBLE);

{ Calculates the %Carbon, %Hydrogen, %Oxygen in each band and then
  several other properties such as the aromaticity, aromatic oxygen
  content e.t.c. }

VAR
  i,j:INTEGER;
  total,OMe,OC,OCtot,HC,Hctot,OHC,per_H:DOUBLE;
  per_C,per_O,arom,fa,Aroxygen,cell,Hcell,Ocell,fracCC,fracC:DOUBLE;
  p_int,t:intarray;

BEGIN
  fracC:=1-fracCH;
  fracCC:=1-fracCO;

  { Add up all Intensity and convert to percentages }

  FOR i:=1 TO numbands DO
    t[i]:=allarray[i,1];
  total:=0;
  FOR i:=1 TO numbands DO
    total:= total + int[i];
  FOR i:= 1 TO numbands DO
    p_int[i]:=(int[i]/total)*100;

```



```

WRITELN(coalcomp,' Fraction of gaussian contribution to bands : ',
                                                fracgauss:2:1);
WRITELN(coalcomp);
WRITELN(coalcomp,' Functional Group Analysis');
WRITELN(coalcomp);
WRITE(coalcomp,' ppm      %C      Line Width      ');
WRITELN(coalcomp,' Carbon Functionality      ');
FOR i:= 1 TO numbands DO BEGIN
    WRITE(coalcomp,' ',t[i]:4:1,' ',p_int[i]:4:1,' ');
    WRITE(coalcomp,allarray[i,2]:3:1,bandtitles[i]);
    WRITELN(coalcomp);
END;

{ The aromaticity calculation }

WRITELN(coalcomp);
WRITELN(coalcomp,' Aromatic Carbon Character' );
arom:=0;
FOR i:=1 TO numbands DO BEGIN
    IF (t[i]>105) AND (t[i]<160) THEN
        arom:=arom + p_int[i];
END;
fa:= (arom/100);
WRITELN(coalcomp);
WRITELN(coalcomp,'1 Aromaticity, fa : ',fa:3:2);

{ Calculation of aromatic oxygen content }

Aroxygen:=0;
FOR i:=1 TO numbands DO BEGIN
    IF t[i]=144 THEN Aroxygen:=Aroxygen+(fracCO*p_int[i]);
    IF (t[i]=148) OR (t[i]=154) THEN
        Aroxygen:= Aroxygen+p_int[i];
END;
Aroxygen:=Aroxygen/(arom);
WRITE(coalcomp,'2 Fraction of Aromatic C bonded to O : ');
WRITELN(coalcomp,Aroxygen:3:2);
WRITELN(coalcomp);

{ Calculate the carbon,hydrogen and oxygen ratios then
percentage content }

Otot:=0;Htot:=0;OC:=0;HC:=0;OHC:=0;per_C:=0;per_H:=0;per_O:=0;
FOR i:= 1 TO numbands DO BEGIN
    IF t[i]= 56 THEN OMe:=p_int[i];
    IF t[i]= 148 THEN allarray[i,3]:=(p_int[i]-OMe)/p_int[i];
    IF t[i]= 144 THEN BEGIN
        allarray[i,3]:=fracCO*allarray[i,3];
        allarray[i,4]:=fracCO*allarray[i,4];
    END;
    IF t[i]= 128 THEN allarray[i,3]:=fracCH*allarray[i,3];
    Otot:=Otot + (16*p_int[i]*allarray[i,4]);
    Htot:=Htot + (p_int[i]*allarray[i,3]);
END;
OC:=Otot/((12*100)); { oxygen to carbon ratio }
HC:=Htot/((12*100)); { hydrogen to carbon ratio }
OHC:=(12*100)+Htot+Otot; { total carbon,hydrogen and oxygen }
per_C:=((12*100)/OHC)*100; { percentage carbon e.t.c. }
per_H:=(Htot/OHC)*100;
per_O:=(Otot/OHC)*100;

{ Estimation cellulose or degraded cellulose type structures
in the coal,if coal is of low NMR rank .}

IF alc_int > 1.2 THEN BEGIN
    WRITELN(coalcomp,' Aliphatic Carbon Character');
    cell:=0; Hcell:=0; Ocell:=0;
    FOR i:=1 TO numbands DO BEGIN
        IF (t[i]<60) AND (t[i]<106) THEN BEGIN
            cell:=cell+p_int[i];
            Hcell:=Hcell+(allarray[i,3]*p_int[i]);
            Ocell:=Ocell+(16*allarray[i,4]*p_int[i]);
        END;
    END;
    cell:=100*((12*cell)+Hcell+Ocell)/OHC;
    WRITELN(coalcomp,'1 Estimated content of cellulose or ');
    WRITE(coalcomp,' cellulose-like structures in the coal : ');
    WRITELN(coalcomp,cell:3:1,'%');
END;

{ If "bandmix" performed then print out contributions to mixed bands }

WRITELN(coalcomp);
IF mix128 = 1 THEN BEGIN
    WRITELN(coalcomp,'Contributions to band at 128 ppm');

```

```

WRITELN(coalcomp,' fraction C-H = ',fracCH:4:3,' ',
        'fraction C-C = ',fracC:4:3);
END;
IF mix144 = 1 THEN BEGIN
  WRITELN(coalcomp,'Contributions to band at 144 ppm');
  WRITELN(coalcomp,' fraction C-O = ',fracCO:4:3,' ',
        'fraction C-C = ',fracCC:4:3);
END;
WRITELN(coalcomp);
WRITELN(coalcomp,' Elemental Analysis');
WRITELN(coalcomp);
WRITELN(coalcomp,'O/C Ratio (%wt) : ',OC:4:3);
WRITELN(coalcomp,'H/C Ratio (%wt) : ',HC:4:3);
WRITELN(coalcomp);
WRITELN(coalcomp,' % Carbon : ',per_C:3:1);
WRITELN(coalcomp,' % Hydrogen : ',per_H:3:1);
WRITELN(coalcomp,' % Oxygen : ',per_O:3:1);
WRITELN(coalcomp,'N.B. dry-ash-free, do not account for %N or %S.');
```

END; { of coalfunctgroup}

```

PROCEDURE mixspectrum(ppm:DOUBLE;VAR intssb:dataarray;
                     issbC1,issbC2:intvec);
{ Mixes the ssb intensities for the two assignments in intssb }

VAR
  i,j:INTEGER;

BEGIN
  FOR i:= 1 TO numbands DO BEGIN
    IF allarray[i,1]=ppm THEN BEGIN
      FOR j:= 1 TO numssb DO BEGIN
        intssb[i,j]:=(fracC1*issbC1[j])+(1-fracC1)*issbC2[j];
      END;
    END;
  END;
END; { of mixspectrum}
```

```

PROCEDURE bandmix(ppm:DOUBLE;VAR fracC1:DOUBLE;VAR int:intarray;
                  VAR intssb:dataarray; issbC1,issbC2:intvec);
{ Calculates the relative contributions of the two assignments from
  the intensity in the first downfield ssb. This does not always work
  if the spectrum is noisy or the sample has not been spun fast enough}

VAR
  i,x:INTEGER;
  r1,r2,expt,band:DOUBLE;
  coefssb:coefarray;

BEGIN
  band:=ppm+w; { position of first downfield ssb }
  x:=ROUND((band-sp)/(wp/numchannel));
  expt:=e[x];

  { Calculates expected intensity for the first assignment }

  coefficients(1,band,coefssb,intssb);
  r1:=0;r2:=0;
  FOR i:=1 TO numbands DO
    r1:=r1 + (coefssb[i,1]*int[i]);
  mixspectrum(ppm,0,intssb,issbC1,issbC2);
  intensities(0,int,intssb);

  { Calculates expected intensity for the second assignment and works
    out contribution of each from observed intensity }

  coefficients(2,band,coefssb,intssb);
  FOR i:=1 TO numbands DO
    r2:=r2 + (coefssb[i,2]*int[i]);
  IF (r1(expt) AND (r2>expt) THEN
    fracC1:=(r2 - expt)/(r2 - r1);

  { Not able to calculate contributions }

  IF r2<=expt THEN BEGIN
    WRITE(coalcomp,'Warning: not able to calculate contributions ');
    WRITELN(coalcomp,'to band at ',ppm:4:1);
    WRITE(coalcomp,' as there is too much intensity on ');
    WRITELN(coalcomp,'the sideband at ',band:4:1);
    IF w < 48.0 THEN
      WRITE(coalcomp,'Cause: This coal sample has been spun at ');
      WRITELN(coalcomp,'less than 2.4 kHz');
```

```

    fracC1:=0;
END;
IF r1)=expt THEN fracC1:=1;

mixspectrum(ppm,fracC1,intssb,issbC1,issbC2);
intensities(1,int,intssb);
END; { of bandmix }

{*****}

PROCEDURE interleave (ppm:DOUBLE;VAR intssb:datarray);
{ Interleaves the data from the auxilliary database into the main database }
VAR
    i,j,k:INTEGER;
BEGIN
    FOR i:=1 TO numbands DO BEGIN
        IF (ppm > allarray[i,1]) THEN BEGIN
            IF (ppm < allarray[i+1,1]) OR (i=numbands) THEN BEGIN
                IF (ppm < allarray[i+1,1]) THEN BEGIN
                    FOR j:= (numbands+1) DOWNTO (i+2) DO BEGIN
                        FOR k:=1 TO 5 DO
                            allarray[j,k]:=allarray[j-1,k];
                        bandtitles[j]:=bandtitles[j-1];
                        FOR k:=1 TO numssb DO
                            intssb[j,k]:=intssb[j-1,k];
                        END;
                    END;
                FOR j:=1 TO extrabands DO BEGIN
                    IF allextra[j,1]= ppm THEN BEGIN
                        FOR k:=1 TO 5 DO
                            allarray[i+1,k]:=allextra[j,k];
                        bandtitles[i+1]:=extratitles[j];
                        FOR k:=1 TO numssb DO
                            intssb[i+1,k]:=issbextra[j,k];
                        END;
                    END;
                    numbands:=numbands+1;
                END;
            END;
        END;
    END; { of interleave }

{*****}

PROCEDURE initialspectrum;
{ Estimates the approximate rank of the coal
  :firstly by the signal height ratio of phenol to the main
  :aromatic band;
  :further for lower rank coals by the ratio of
  :methoxyl " " " " "
  Adds bands where considered appropriate including secondary
  alcohol/ether bands for lower rank coals.
  Calculates contributions to 128 ppm and 144 ppm bands if necessary. }
VAR
    j,i,k,x,x1,x2,mix128,mix144:INTEGER;
    methoxyl,fracCO,fracCH,expt,alc,total,ali,
    phenol,diphenol,r,ppm,obs,alc_int:DOUBLE;
    int:intarray;
    intssb:datarray;
    c,d:datvec;
    coefssb:coefarray;
BEGIN
    FOR i:= 1 TO numbands DO BEGIN
        FOR j:= 1 TO numssb DO
            intssb[i,j]:=issb[i,j];
        END;
    { Calculate the phenol ratio }

    x1:=ROUND((128-sp)/(wp/numchannel));
    x2:=ROUND((154-sp)/(wp/numchannel));
    phenol:=e[x2]/e[x1];

    {Separates the "High rank" coals (approx.=high rank h.v. A.bituminous
    coals and above from) the other coals. If very high rank the aromatic
    linewidth is reduced due to narrowing of the range of chemical shifts}

    mix128:=0;fracgauss:=0.5;alc_int:=0;
    IF phenol <= 0.4 THEN BEGIN
        WRITELN(coalcomp);
        WRITELN(coalcomp,' Estimate of Rank : HIGH ');
    
```

```

FOR i:=1 TO numbands DO BEGIN
  IF allarray[i,1]=154 THEN
    allarray[i,2]:=5.5;
END;
IF phenol < 0.15 THEN BEGIN
  fracgauss:=0.55;
  FOR i:=1 TO numbands DO BEGIN
    IF (allarray[i,1]>100) AND (allarray[i,1]<140) THEN
      allarray[i,2]:=7.5
    END;
  END;
  intensities(1,int,intssb);
  mix128:=1;
  bandmix(128,fracCH,int,intssb,issbCH,issbC);
END

ELSE BEGIN
  x2:=ROUND((144-sp)/(wp/numchannel));
  diphenol:=e[x2]/e[x1];
  x2:=ROUND((30-sp)/(wp/numchannel));
  ali:=e[x2]/e[x1];

  { Separates the "Medium High Rank" coals from the others on the basis
  of phenol and diphenol ratio.}

  IF (ali<2.0) AND (phenol<0.7) AND (diphenol<0.7) THEN BEGIN
    WRITELN(coalcomp,' Estimate of Rank : MEDIUM HIGH ');
    interleave(144,intssb);
    FOR i:=1 TO numbands DO BEGIN
      IF (allarray[i,1]=144) OR (allarray[i,1]=154) THEN
        allarray[i,2]:=5.5;
    END;
  END

  { Further separates the low rank coals on the basis of the estimated
  methoxyl content.Changes linewidths where necessary.}

  ELSE BEGIN
    interleave(56,intssb);
    interleave(107,intssb);
    interleave(144,intssb);
    coefficients(1,177,coefssb,intssb);
    r:=0;
    FOR i:=1 TO numbands DO
      r:=r+(coefssb[i,1]*int[i]);
    x:=ROUND((177-sp)/(wp/numchannel));
    IF (r < e[x]) THEN
      interleave(177,intssb);
      x2:=0;
      x2:=ROUND((56-sp)/(wp/numchannel));
      methoxyl:=e[x2]/e[x1];

    { High methoxyl ratio = "Low Rank" so firstly the central position
    of the methylene peak is found ;then more variation in aromatic
    oxygen assignments is introduced.( The linewidths of the original
    bands are narrowed as more bands are added-result of optimisation
    procedure). }

    IF methoxyl > 0.7 THEN BEGIN
      WRITELN(coalcomp,' Estimate of Rank : LOW ');
      fracgauss:=0.3;
      FOR i:=1 TO numbands DO BEGIN
        IF allarray[i,1]=30 THEN BEGIN
          FOR j:=26 TO 34 DO BEGIN
            x:=ROUND((j-sp)/(wp/numchannel));
            IF allarray[i,5] < e[x] THEN BEGIN
              allarray[i,1]:=j;
              allarray[i,5]:=e[x];
            END;
          END;
        END;
        FOR j:=1 to i DO
          allarray[j,2]:=5;
        END;
      END;

      FOR i:=1 TO numbands DO BEGIN
        IF allarray[i,1]=128 THEN BEGIN
          allarray[i,1]:=130;
          x:=ROUND((130-sp)/(wp/numchannel));
          allarray[i,5]:=e[x];
        END;
        IF (allarray[i,1]>105) AND (allarray[i,1]<140) THEN
          allarray[i,2]:=7.0;
        IF (allarray[i,1]>35) AND (allarray[i,1]<50) THEN
          allarray[i,2]:=5.5;
        IF (allarray[i,1]=144) OR (allarray[i,1]=154) THEN
          allarray[i,2]:=4.0;
      END;
    END;
  END;

```

```

END;
interleave(125,intssb);
interleave(148,intssb);
END

{ Medium low rank fitted-if needed an acidic band at
177 ppm is introduced}

ELSE BEGIN
  WRITELN('coalcomp,' Estimate of Rank : MEDIUM LOW ');
  FOR i:=1 TO numbands DO BEGIN
    IF allarray[i,1]<35 THEN
      allarray[i,2]:=4.5;
    IF (allarray[i,1]>35) AND (allarray[i,1]<50) THEN
      allarray[i,2]:=6.5;
    IF allarray[i,1]=56 THEN
      allarray[i,4]:=1;
  END;
END;

{ Calculates if a band at 74ppm is needed. If so, then this and
other secondary alcohol/ether (e.g. from degraded cellulose)
bands are added to the database. If this content is high (alc_int)
then the coal probably contains intact cellulose structures and
a band assigned to the C1 ether linkages of cellulose, is also
added to the database. }

intensities(1,int,intssb);
coefficients(1,74,coefssb,intssb);
r:=0;
FOR i:=1 TO numbands DO
  r:=r+coefssb[i,1]*int[i];
FOR i:=1 TO extrabands DO BEGIN
  IF allextra[i,1]=74 THEN BEGIN
    alc:= allextra[i,5];
    IF alc > r THEN BEGIN
      FOR j:=(i-1) TO (i+2) DO BEGIN
        ppm:=0;
        ppm:=allextra[j,1];
        interleave(ppm,intssb);
      END;
      intensities(1,int,intssb);
      total:=0;
      FOR j:= 1 TO numbands DO
        total:= total + int[j];
      FOR j:=1 TO numbands DO BEGIN
        IF allarray[j,1]=74 THEN BEGIN
          alc_int:= (int[j]/total) * 100;
          IF alc_int >=1.2 THEN BEGIN
            interleave(105,intssb);
            intensities(1,int,intssb);
          END;
        END;
      END;
    END;
  END;
END;
END;
END;
END;
END;
END;

{ If the 144 band is now present in the database then its two possible
assignments are mixed. }

mix144:=0;

IF methoxyl<0.7 THEN BEGIN
  FOR i:=1 TO numbands DO BEGIN
    IF allarray[i,1]=144 THEN BEGIN
      bandmix(144,fracCO,int,intssb,issbCO,issbCC);
      mix144:=1;
    END;
  END;
END;
IF mix144=0 THEN fracCO:=1;

{ The full database for the coal sample is set up and the total
spectrum is now simulated. }

totalspect(int,intssb,c);
printspectrum(c);
coalfuncgroup(mix128,mix144,alc_int,int,fracCH,fracCO);
END; { of initialspectrum }

(*****)

```

```

PROCEDURE readdata;

{ Reads the experimental data and searches for the highest point in the
  base-corrected experimental spectrum. All spectra are then plotted
  to this scale.}

VAR
  i,j:INTEGER;
  ww:DOUBLE;

BEGIN
  READLN(exptspec,ww,numchannel); { spin rate in Hz}
  ww:=ww/50.3; { spin rate in ppm }
  w:=ROUND(ww);
  WRITELN(compspec,numchannel);
  WRITELN(plotspec,numchannel);
  WRITELN(difspec,numchannel);
  FOR i:=0 TO TRUNC((numchannel/10)-1) DO BEGIN
    FOR j:= 0 TO 9 DO
      READ(exptspec,e[i*10+j]);
      READLN(exptspec);
    END;
    READLN(exptspec,e[numchannel]);
    basecorrect;
    max:=1;
    FOR i:= 0 TO numchannel DO BEGIN
      IF e[i] > max THEN
        max:= e[i];
    END;
    WRITELN(compspec,max:4:1);
    readdatabase;
    initialspectrum;
  END; { of readdata }

  {*****}

  BEGIN { main program }

  { exptspec - data input including digitised experimental spectrum;
    plotspec - final computed spectrum;
    difspec - difference spectrum;
    compspec - basecorrected experimental spectrum;
    coalcomp - calculated intensity data and functional group analysis.}

  OPEN(plotspec);
  OPEN(difspec);
  OPEN(compspec);
  OPEN(coalcomp);

  RESET(exptspec);
  REWRITE(plotspec);
  REWRITE(difspec);
  REWRITE(compspec);
  REWRITE(coalcomp);

  title;
  readdata; {calls readdatabase,initialspectrum,difspec}

  CLOSE(compspec);
  CLOSE(coalcomp);
  CLOSE(plotspec);
  CLOSE(difspec);
  END.

  {*****}

```

```

$ ! DOFIC.COM
$ ! DOFIC input is 'P1'.DAT
$ RUN_AGAIN:
$ INQUIRE ANS " EDIT THE DATABASE FILE ? (Y/N)"
$ IF F$EXTRACT(0,1,ANS) .EQS. "N" THEN GOTO NODAT_EDT
$ ASSIGN/USER_MODE SYS$COMMAND SYS$INPUT
$ EDT [SRGCRHN.SSB]DATABASE.DAT
$ NODAT_EDT:
$ IF F$LENGTH(P1) .EQ. 0 THEN
$ INQUIRE P1 "INPUT TITLE FILE NAME (.DAT)"
$ IF F$LENGTH(P1) .EQ. 0 THEN GOTO ERROR
$ WRITE SYS$OUTPUT "INPUT DATA FILE : 'P1'.DAT"
$ INQUIRE ANS " EDIT 'P1'.DAT ? (Y/N)"
$ IF F$EXTRACT(0,1,ANS) .EQS. "N" THEN GOTO NO_EDT
$ ASSIGN/USER_MODE SYS$COMMAND SYS$INPUT
$ EDT 'P1'.DAT
$ NO_EDT:
$ SETP79 LA100
$ ASSIGN/USER [SRGCRHN.SSB]DATABASE.DAT DATABASE
$ ASSIGN/USER [SRGCRHN]'P1'.DAT EXPTSPEC
$ WRITE SYS$OUTPUT "OUTPUT DATA IS IN COALCOMP.DAT"
$ WRITE SYS$OUTPUT " RUNNING THE SIMULATION NOW"
$ RUN [SRGCRHN.SSB]dofic
$ INQUIRE ANS "INSPECT OUTPUT FILE ? (Y/N)"
$ IF F$EXTRACT(0,1,ANS) .EQS. "N" THEN GOTO PRINT
$ ASSIGN/USER_MODE SYS$COMMAND SYS$INPUT
$ EDT COALCOMP.DAT
$ PRINT:
$ INQUIRE ANS "PRINT OUTPUT FILE ? (Y/N)"
$ IF F$EXTRACT(0,1,ANS) .EQS. "N" THEN GOTO SKIP1
$ PCD [SRGCRHN]COALCOMP.DAT
$ SKIP1:
$ INQUIRE ANS "PLOT BASE-CORRECTED EXPT. SPECTRUM ? (Y/N)"
$ IF F$EXTRACT(0,1,ANS) .EQS. "N" THEN GOTO SKIP2
$ ASSIGN/USER [SRGCRHN]COMPSPEC.DAT CHANNEL
$ ASSIGN/USER [SRGCRHN]PLOTSPEC.CRT CRT
$ RUN [SRGCRHN.SSB]CHANPLOT
$ PCD [SRGCRHN]PLOTSPEC.CRT
$ SKIP2:
$ INQUIRE ANS "PLOT SPECTRUM ? (Y/N)"
$ IF F$EXTRACT(0,1,ANS) .EQS. "N" THEN GOTO SKIP3
$ ASSIGN/USER [SRGCRHN]PLOTSPEC.DAT CHANNEL
$ ASSIGN/USER [SRGCRHN]PLOTSPEC.CRT CRT
$ RUN [SRGCRHN.SSB]CHANPLOT
$ PCD [SRGCRHN]PLOTSPEC.CRT
$ SKIP3:
$ INQUIRE ANS "PLOT DIFFERENCE SPECTRUM ? (Y/N)"
$ IF F$EXTRACT(0,1,ANS) .EQS. "N" THEN GOTO SKIP4
$ ASSIGN/USER [SRGCRHN]DIFFSPEC.DAT CHANNEL
$ ASSIGN/USER [SRGCRHN]DIFFSPEC.CRT CRT
$ RUN [SRGCRHN.SSB]CHANPLOT
$ PCD [SRGCRHN]DIFFSPEC.CRT
$ GOTO SKIP4
$ ERROR:
$ WRITE SYS$OUTPUT " ERROR...NO INPUT FILE NAME SPECIFIED"
$ SKIP4:
$ INQUIRE ANS " ANOTHER SIMULATION ? (Y/N)"
$ IF F$EXTRACT(0,1,ANS) .EQS. "Y" THEN GOTO RUN_AGAIN
$ WRITE SYS$OUTPUT " SIMULATION COMPLETE"
$ EXIT

```


13.4 SAMPLE DETAILS

Location given is of the mine or drilling program from which sample originated.

Analysis data in brackets refer to representative values for other samples from the same locality. See Reference 1 for details. Elemental analysis is daNSf.

Location	CRA code	Ultimate Analysis			DOFIC Analysis		
		%C	%H	%O	%C	%H	%O
LIGNITES							
Mataura	33/361	69.6	4.1	26.3	70.4	7.5	22.1
Waimumu Newvale	33/360	69.2	4.7	26.1	64.3	6.9	28.8
Waimumu Newvale	30/655	69.9	4.1	26.0	65.5	6.6	27.9
Waimumu Goodwin	30/645	69.8	4.5	25.7	69.5	7.1	23.4
Waimumu Goodwin	30/646	70.9	4.7	24.3	66.3	6.9	26.8
Ashers Waituna	30/647	67.9	4.5	27.7	69.3	6.6	24.1
Roxburgh Harliw.	33/358	71.0	5.9	23.1	69.5	8.1	22.4
Roxburgh Harliw.	27/003	(67.8)	(5.6)	(26.6)	69.8	8.1	22.1
Roxburgh DH 2086	-	(67.8)	(5.6)	(26.6)	68.5	7.7	23.8
Idaburn	30/652	69.1	4.6	26.3	68.8	7.5	23.7
Hawkdun	24/635	(68.8)	(4.9)	(26.3)	68.9	7.4	23.7
SUBBITUMINOUS							
Kopuku	33/357	73.7	4.9	21.4	70.7	7.6	21.7
Weavers	33/355	74.7	5.0	20.3	71.6	6.9	21.5
Kawhia	30/662	73.0	4.8	22.1	69.1	6.9	24.0
Kai Point	30/649	74.5	5.1	20.4	73.6	7.2	19.2
Wangaloa	30/650	77.0	5.3	17.7	74.6	7.2	18.2
Braziers	30/653	73.3	4.7	22.0	70.6	6.8	22.6
Ohinewai	30/659	73.2	5.0	21.8	70.4	6.8	22.8
Squires Creek	33/388	-	-	-	68.4	6.6	25.0
Garden Creek	33/342	-	-	-	71.9	7.5	20.6
Ohura	33/387	-	-	-	70.9	7.2	21.9
Heaphys	33/479	(76.1)	(5.4)	(18.5)	74.2	7.2	18.6
Mokau	30/663	77.8	6.1	16.0	76.3	8.5	15.2
Huntly West	30/657	75.0	5.3	19.7	74.0	7.5	18.5

13.4 SAMPLE DETAILS (Cont'd)

Location	CRA code	Ultimate Analysis			DOFIC Analysis		
		%C	%H	%O	%C	%H	%O
Huntly East	33/359	76.2	4.9	18.9	72.5	7.0	20.5
Terrace	30/342	(78.1)	(5.3)	(16.5)	74.5	7.2	18.3
Ohai	33/356	76.1	5.1	18.5	75.8	7.0	17.2
BITUMINOUS							
Mulken	30/341	(78.6)	(5.7)	(15.7)	78.9	7.4	13.7
Alpine	30/353	-	-	-	80.8	6.9	12.3
Snowline	30/332	80.8	5.6	13.7	81.6	7.1	11.3
Harrisons	30/331	(81.4)	(6.0)	(12.6)	82.2	7.1	10.7
Kiwi	30/335	82.2	5.8	12.1	82.1	7.5	10.4
Topline	30/346	-	-	-	80.3	7.6	12.1
Island Block	30/344	81.8	5.6	12.6	81.5	7.7	10.8
Strongman	30/329	(82.2)	(6.0)	(11.8)	82.1	7.5	10.4
Moody Creek	33/786	(82.6)	(5.9)	(11.4)	83.3	7.4	9.3
Charming Creek	30/352	(85.7)	(6.0)	(8.3)	83.7	8.3	8.0
Echo	30/345	82.2	5.7	12.2	81.9	7.6	10.5
United	30/330	83.0	6.0	11.1	82.4	7.7	9.9
Escarpment	30/350	83.9	5.7	10.4	82.4	7.3	10.3
Webb	30/349	87.2	5.6	7.2	85.1	7.7	7.2
Webb/Baynes Blk.	31/033	88.8	6.1	5.1	86.9	7.4	5.7
Webb/Baynes Blk.	31/035	87.5	5.8	6.7	85.1	6.8	8.1
Liverpool	30/773	87.4	6.1	6.5	86.6	7.7	5.7
Webb/Stockton	33/197	(87.7)	(5.7)	(6.6)	85.9	7.2	6.9
Stockton No. 2	33/205	(89.5)	(5.5)	(5.6)	86.5	6.4	7.1
Stockton No. 2 DH	32/776	89.4	5.8	4.8	86.1	7.1	6.8
Sullivan	30/351	87.4	5.7	6.9	86.3	7.1	6.6
Sullivan North	33/343	91.6	5.7	2.7	88.9	7.1	4.0
Sullivan North	33/344	90.5	5.7	3.8	88.0	6.7	5.3

SAMPLE DETAILS (Cont'd)

Location	CRA code	Ultimate Analysis			DOFIC Analysis		
		%C	%H	%O	%C	%H	%O
Webb	31/032	88.3	5.1	6.6	87.3	7.1	5.6
Rockies DH	32/778	(89.3)	(5.3)	(5.4)	87.0	6.6	6.4
Rockies DH	34/875	91.0	5.3	3.7	88.9	7.3	3.8
SEMI-ANTHRACITE							
Fox River	33/060	92.2	4.1	3.7	94.6	4.8	0.6

Characterisation of New Zealand
Coals by Carbon-13 Solid-State

N.M.R. Spectroscopy

by

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Approved:

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This note is an outline of a paper presented to the 1984 Annual Conference of the Geological Society of New Zealand, held at Victoria University of Wellington, 10-14 November 1984.

Why might geologists not have heard of nuclear magnetic resonance before?

Firstly, there is only one NMR spectrometer in New Zealand that is capable of handling solid samples. This is the Varian 200 MHz instrument at Chemistry Division (1).

Secondly, advances in NMR instrumentation have been so rapid that useful applications in geology have only recently begun to emerge.

Fig. 1 shows that the sensitivity of commercial NMR spectrometers has improved by two orders of magnitude over the past ten years. Increased sensitivity means a faster sample throughput and more economic use of expensive equipment. Analysis by NMR could become cheaper than conventional methods in certain areas of solid-state chemistry.

Fig. 2 shows the basis of the NMR technique. A nucleus with a magnetic moment is placed in a strong magnetic field. Carbon-12 does not have a magnetic moment, but carbon-13 is suitable. Carbon-13 is a stable isotope, distributed reasonably evenly throughout nature in about 1.1% natural abundance. There are two possible spin states: parallel or antiparallel relative to the applied field. The energy gap corresponds to quanta in the radiofrequency region. As the frequency is tuned through resonance, transitions are induced and energy is absorbed. The exact frequency of the resonance depends on the bonding patterns around the carbon atom, since electronic orbitals can partially shield the nucleus from the effect of the applied field, thus NMR can be used to distinguish carbon atoms in different types of chemical structures within a lump of coal.

Fig. 3 shows an example of a carbon-13 NMR spectrum. The sample came from the Ohai field. About 0.5 g was used. The experiment required about 10 hours of instrument time. Computer processing was used to improve the resolution of spectral details - otherwise, the experiment could have been completed in a few minutes. The frequency scale at the bottom is expressed in parts per million deviation from a reference signal at 50.30 MHz; i.e. a range of 200 ppm corresponds to a scan from 50.30 to 50.31 MHz. The area under each peak is roughly proportional to the amount of carbon in the corresponding chemical environment.

The spectrum has been labelled according to possible source material.

Fig. 4 lists a variety of different sources of coal organic matter. Some of these are so easily degraded that they disappear during the early stages of diagenesis: e.g. cellulose is the major component of wood, but it is only a minor component of lignite (2).

Fig. 5 shows spectra of two lignites resulting from different mixtures of source materials. The signal at 56 ppm is assigned to methoxyl groups in lignin-like structures (1). Lignin is associated with woody material, so the strength of the signal points to a woody origin for the Ashers Waitura lignite. In contrast, the Roxburgh lignite contains a high proportion of alkyl chains - perhaps of microbial or algal origin. Petrographic analyses have confirmed this conclusion by demonstrating a larger exinite content in the case of the Roxburgh lignite.

Fig. 6 illustrates one of the coalification processes which can be studied by NMR - i.e. the increase in aromaticity (3).

Fig. 7 illustrates loss of the oxygen content. This can be estimated through the strength of NMR signals assigned to carbon atoms directly bonded to oxygen (e.g. 145-155 ppm).

Fig. 8 illustrates catagenesis, which results in separation of crude oil from the coal deposit. The extent of catagenesis can be estimated from the strength of NMR signals assigned to residual alkyl chains in the coal (at 15-50 ppm).

Fig. 9 shows how NMR spectra differ for coals over a range of ranks. The Mataura lignite contains a high proportion of alkyl chains (at 30 ppm) and signals at 148 and 152 ppm indicate a high degree of oxygen-substitution on aromatic rings - as expected for lignin-like structures from woody material. By comparison, the semi-anthracite contains a high proportion of aromatic rings, with little evidence for oxygen substitution (i.e. a weak signal at 150 ppm).

Fig. 10 shows quantitative data for a collection of NZ coals. "Aromaticity" is defined as the area of signals assigned to carbon in aromatic rings, expressed as a fraction of the total NMR spectral area. Aromaticity tends to increase with rank (as defined by the ASTM classification scheme (4), but this NMR parameter is obviously unreliable as a rank indicator. This confirms NMR studies carried out overseas on coals from USA (5), Canada (6), Australia (7), Indonesia (8), and China (9). Variations in aromaticity values probably reflect variations in source material rather than rank, in the lower ranks at least.

Fig. 11 shows a new approach which we have assessed for ranking coals by NMR. The signal-height ratio plotted along the horizontal axis is a measure of the average length of alkyl chains, and can therefore be used to estimate the extent of catagenesis. The signal height ratio plotted along the vertical axis is a measure of oxygen-substitution of aromatic rings, and can therefore be used to estimate the extent of oxygen loss. The symbols represent lignite (circles), subbituminous coal (squares) high-volatile bituminous coals (triangles) and higher ranks (diamonds). The data points fall into a wedge, showing a wide spread for lower ranks. This spread is attributed to differences in source material. Such differences seem to become less important as the less stable chemical structures are destroyed.

Fig. 12 shows how source materials can affect the spread of data points. Petrographic data were taken from Professor Black's 1980 Reconnaissance Survey of NZ Coals. Solid squares represent coals with exinite/vitrinite ratios (mmf basis) ≥ 0.25 , while half-shaded squares represent coals with ratios ≥ 0.15 . The petrographic data refer to samples from the same areas, rather than the identical samples used for NMR, so a perfect correlation cannot be expected; but in general, the high exinite coals appear on the right-hand side of the wedge. The exinite macerals include lipids and waxes, with relatively long alkyl chains, so the NMR data are consistent with petrographic analyses.

We have defined a parameter called "NMR rank" which is (in effect) the distance from the lowest corner of the wedge, measured on a plot such as this. The "NMR rank" is therefore a measure of the combined effects of catagenesis and oxygen loss on coal chemical structures.

Fig. 13 shows a plot of the "NMR rank" against the ASTM rank. The two ranking scales are correlated, but "NMR rank" is particularly sensitive to coalification through the high-volatile A bituminous rank. This appears to be a particularly active stage of chemical alteration, as far as New Zealand coals are concerned. "NMR rank" may be useful in subdividing the high-volatile A bituminous category. The plot shows that 5 of these coals resembled high-volatile B bituminous coals, while 10 resembled medium-volatile bituminous coals. We have not yet identified any NZ mine supplying coal with intermediate properties.

Fig. 14 shows spectra of 4 bituminous coals, demonstrating the major chemical changes that occur at this stage of coalification. The observations are not surprising since:

(a) Coals of ranks high-volatile C to medium-volatile bituminous are commonly associated with zones of oil generation, i.e. active catagenesis (11).

(b) Teichmuller introduced the concept of a "first coalification jump" to explain sudden changes in other parameters as coal matures through the high-volatile A bituminous mark (11).

Finally, why should we use NMR parameters as rank indicators, when so many other methods of analysis are available?

Firstly, NMR analysis requires small samples (less than 1g) so that it can be used for ranking small fragments of organic matter found in sedimentary rocks.

Secondly, mineral contents up to 80% or 90% can be tolerated, although sample throughput drops dramatically - being proportional to the square of the organic content.

Thirdly, the NMR ranking procedure does not require the geologist to locate a fragment of one particular coal maceral. The results presented today suggest that the effects of differing source material and of coalification can be separated by taking suitable combinations of signal heights.

Carbon-13 NMR could therefore be useful in studies of the geology of sedimentary rocks, even if these do not contain commercial coal deposits.

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DEVELOPMENT OF NMR SPECTROMETERS

FIGURE 1

A nuclear magnetic resonance experiment

FIGURE 2

Origin of NMR Signals

FIGURE 3

SOURCE MATERIAL FOR COAL

protein
chlorophyll
oils
carbohydrates
lignins
epidermis
seed coats
pigments
cuticles
spores and pollen
waxes
resins

INCREASING
CHEMICAL
STABILITY

FIGURE 4

Lignite

Otago

Roxburgh/
Harliwich

Southland

Ashers
Waituna

FIGURE 5

INCREASING AROMATICITY

FIGURE 6

OXYGEN LOSS

lignin (from wood, grass) 27% O
 ↓
 lignite 25-30% O
 ↓
 subbituminous coal 15-25% O
 ↓
 bituminous coal <15% O

FIGURE 7

CATAGENESIS

FIGURE 8

FIGURE 9

FIGURE 10

FIGURE 11

FIGURE 12

FIGURE 13

BITUMINOUS

high volatile A

medium volatile

FIGURE 14

Spinning Sidebands in Carbon-13

CP/MAS NMR

by

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THIS TECHNICAL NOTE MUST BE CITED ONLY AS "UNPUBLISHED RESULTS"

INTRODUCTION

Magic-angle spinning (MAS) improves resolution in carbon-13 nuclear magnetic resonance spectra of solids, but leaves "spinning sideband" signals. These result from the orientational dependence of chemical shifts; e.g. in the case of benzene, the carbon-13 nuclei are more shielded when the magnetic field is oriented normal to the ring than when the magnetic field is oriented parallel to the plane of the ring. Spinning the sample modulates the resonance frequency around an averaged value, generating sideband frequencies at intervals of the MAS frequency.

Running spectra at a higher magnetic field improves the chemical-shift dispersion, but the MAS frequency must be increased in proportion to the field strength if sideband signals are to be kept suppressed. This introduces technical difficulties. A different approach has been taken by the NMR group at Chemistry Division. A standard MAS frequency of 2.5 kHz has been chosen for all routine carbon-13 NMR spectra run at 50.3 MHz on a Varian XL-200 spectrometer. A reason for the choice of this precise MAS frequency is explained in the Discussion section of this note. It is close to the operational limits of the spectrometer, but it is still too low to suppress sideband signals. Correction factors are therefore applied to any measurements of signal areas. The magnitudes of the corrections are based on literature reports of principal values for chemical-shift tensors (1-25) and a graphical method for calculating MAS sideband intensities from the principal values (26).

This note summarises the derivation of the set of correction factors currently in use. It is intended for distribution to users of Chemistry Division's solid-state NMR service. The authors hope it will provide some assistance in any estimation of the relative proportions of various functional groups, based on signal-area measurements.

This note can be cited as "unpublished work", or it could be used as a guide to source literature on relevant model compounds. The scope of this note has been confined to a selection of the organic functional groups most likely to be encountered in solid organic matter, e.g. in wood, soil or coal. A recent review (25) of carbon-13 chemical-shift tensors includes data for a number of functional groups excluded from this note.

The results summarised here should not be used for interpretation of spectra run on other instruments, unless the ratio (NMR frequency)/(MAS frequency) is close to 20000.

RESULTS

The calculated intensity distributions are shown in Tables 1-3. Sideband intensities are labelled $I(n)$, where the centreband corresponds to $n=0$ and positive values of n are used for sidebands on the high-frequency (low-field) side of the centreband. All intensities were normalised to a total of

100%; but high-order sidebands have been omitted from Tables 1-3, so totals across most rows add up to less than 100%.

In some cases, solid-state spectra show distinct signals for carbon atoms that would be regarded as equivalent in solution NMR. E.g. the -OH groups of quinol are constrained so that the H atom is closer to one or other of the adjacent ring carbons (5). In such cases, spinning-sideband patterns were calculated for each carbon atom and were considered as independent sets of data when the results were averaged.

In some cases, crystal packing results in small chemical shift differences between molecules in distinct crystal sites. In these cases, spinning-sideband patterns were calculated for each site, but sets of results for corresponding carbon atoms in each molecule were averaged before the results were combined with those for other molecular structures; otherwise, the final results would have been biased towards crystal structures studied by high-field NMR. E.g. carbon-13 CP/MAS NMR of quinol at 75.5 MHz has resulted in resolution of signals from 3 distinct molecules per unit cell (5); but most studies described in References 1-25 were based on low-field NMR, and it is unlikely that such detail could have been resolved.

Aromatic carbon

Sources of all data for substituted benzenes are shown in Table 4. The "Compound Number" refers to Fig. 1. The final 3 columns of Table 4 show that spinning-sideband intensities were calculated for 6 O-substituted carbon atoms, 11 C-substituted carbon atoms, and 24 C-H groups. Spinning-sideband intensities were also calculated for ring-junction sites in 4 polycyclic aromatic structures (Compounds 16-19 of Fig. 1). Chemical-shift data for these were all taken from Ref. 1.

Data for penta- and hexa-substituted benzenes were excluded from these calculations, because such sterically-crowded structures are unlikely to be of interest in the interpretation of NMR spectra of natural substances. Toluene was also excluded, because the results (14) did not distinguish between non-equivalent CH groups.

Data sets for C-substituted aromatic carbon included 5 for substitution by sp^2 -hybridised carbon, and 6 for substitution by sp^3 -hybridised carbon. When these were separated, any differences in the intensity patterns were smaller than the standard deviations.

Data sets for C-H groups included 9 for sites with O-substitution at the adjacent ring site. When these were separated from the other 15 data sets, they showed a significant difference in centreband intensities; i.e. the 2 mean values differed by more than the sum of the standard deviations. The proximity of O-substitution resulted in more signal intensity being concentrated in the centreband (Table 1).

A similar effect was observed for O-substituted carbon. In this case, the chemical shifts available for O-substitution at 2 adjacent sites were limited to data sets for 2 carbon atoms in Compound 12(3). Experimental centreband intensities have been published (27) for 4 more structures, Compounds 23-26 of Fig. 1. These results are summarised in Table 5, along with results calculated for Compound 12. The mean of 8 values of $I(0)$ is 63%, with a standard deviation of 3%. It is consistent with the entry in Table 1. The additional evidence therefore confirms the effect of O-substitution at an adjacent ring site.

Carboxylic groups

Table 2 summarises spinning-sideband intensities calculated for data from the sources listed in Table 6. Mean values were calculated for 4 amino acids (Compounds 32-35), 6 other compounds with free acid groups (Compounds 27-31 plus part of Compound 39), and 2 carboxylate anions (Compounds 38 and 39). The values of $I(0)$ varied over a range 61-73%, which is not much wider than the standard deviations listed in Table 2. All 14 sets of results were therefore averaged, as shown at the bottom of Table 2.

Ref. (25) provides chemical shifts for several more compounds containing carboxylic functional groups. Data for oxalic-acid derivatives were not included in Table 2, because these compounds contribute NMR signals outside the range normally associated with other carboxylic functional groups. Data for several other structures were excluded, because the reports do not distinguish between protonated acid groups and ionised groups when both are present.

Miscellaneous functional groups

Table 3 summarises data based on chemical shifts gathered from the sources listed in Table 7. All of these functional groups contain carbon atoms with 4 bonds arranged in approximately tetrahedral geometry. This symmetry results in low chemical-shift anisotropies, and therefore weak spinning sidebands.

DISCUSSION

Experimental uncertainties

Carbon-13 NMR chemical shifts for solid p-xylene (Compound 21) have been published in two different reports (1, 23). This provides an unusual opportunity to assess the reproducibility of such measurements. Ref. (1) reports a difference of 199 ppm between extreme principal values of the chemical-shift tensor for methyl-substituted ring sites. Ref. (23) reports a difference of 227 ppm. Calculations based on the two references lead to $I(0)$ =43% and 35%, respectively.

This is probably an extreme example of unreliable results. The standard deviations shown in Tables 1-3 are too small for such experimental uncertainties to be common. Ref. (23) appears to be based on a more thorough study of p-xylene, so we have

followed the example of Veeman (25) in selecting data from Ref. (23).

Applications

Carbon-13 NMR spectra of solids sometimes show clearly-resolved centreband signals at a chemical shift that is characteristic of a specific type of functional group. In such cases, it is possible to determine the total signal area associated with this type of functional group by measuring the area of the centreband signal and multiplying by a correction factor $100/I(0)$ to allow for sideband signals. Hemmingson and Newman (27) used this approach to estimate the lignin content of wood. In this case a signal at $\delta \sim 150$ was assigned to O-substituted aromatic carbon, in sites with O-substitution at just one adjacent site. The mean value of $I(0)$ for model compounds (Table 5) is 63%, so the correction factor is $100/63 = 1.6$. Two of the 10 carbon atoms in a typical softwood lignin monomer unit contribute to this NMR signal; so the carbon in lignin, expressed as a fraction of total carbon in the wood, can be estimated by measuring the area of the signal at $\delta \sim 150$ and multiplying it by $1.6(10/2) = 8$. Further adjustments are necessary to convert the result from a carbon-only basis to a weight basis.

In general, the interpretation of carbon-13 NMR spectra of solids can be assisted by dividing the spectra into four regions, each approximately 50 ppm wide.

(i) Aliphatic and alicyclic structures lacking O-substitution contribute signals that are usually confined to the region $\delta = 10-60$. Such structures can include lipids, resin acids, or sidechains on proteins.

(ii) Carbohydrates and related structures, e.g. C_3 chains in lignin, contribute NMR signals that are usually confined to the region $\delta = 60-110$.

(iii) Aromatic rings, e.g. in lignin or tannin, contribute signals that are usually confined to the region $\delta = 110-160$.

(iv) Carbonyl groups in carboxylic acids, salts and esters, in amides and in ketones contribute signals which are usually confined to the region $\delta = 160-210$.

The regular 50 ppm spacing of those boundaries is fortunate, because it makes it possible to select a MAS frequency which places the spinning sidebands from each region precisely inside the adjacent regions, with no overlap across boundaries. The appropriate MAS frequency is 2.5 kHz for NMR at 50 MHz, since this corresponds to an interval of 50 ppm between sidebands.

An example

To illustrate this approach, suppose that the carbon-13 NMR spectrum of a solid humic acid is divided into four regions, as above. Suppose that the signal area in each region is expressed as a percentage of the total area, and assigned a symbol as follows:

<u>Symbol</u>	<u>Chemical shift range</u>
A	$\delta > 210$
B	$210 > \delta > 160$
C	$160 > \delta > 110$
D	$110 > \delta > 60$
E	$60 > \delta > 10$
F	$\delta < 10$

Suppose that the true fraction of carbon associated with each region is assigned a lower-case symbol, a-f, with a=0 and f=0 because no centreband signals are expected to appear outside the range $210 > \delta > 10$. Tables 1-3 can be used to express the values of A-F in terms of the values of b-e, as follows:

Suppose that the final row of Table 2 is taken as representative for functional groups associated with b. The $n=+1$ and $n=+2$ sidebands would then contribute an area component of $17b$ to the observed area A. The centreband would contribute an area component of $67b$ to B, the $n=-1$ sideband would contribute an area component of $15b$ to area C, and the $n=-2$ sideband would contribute an area component of $2b$ to area D.

Suppose that relative signal strengths at about $\delta=150$ and $\delta=130$ are consistent with O-substitution at an average of about 2 sites per ring, and suppose that the first row of Table 1 is taken as representative of spinning sideband intensities for these sites. Rows labelled "H" and "C" show almost identical intensity distributions for unsubstituted or C-substituted ring sites; suppose mean values of entries in these two rows are used for all aromatic carbon other than O-substituted ring sites. These approximations lead to a generalised pattern of intensities for aromatic carbon, calculated by adding together one third of each entry for rows labelled "O", "H" and "C" in table 1:

Sideband $n =$	+2	+1	0	-1	-2
Intensity (%) =	4	23	49	17	6

The area components are then $4c$ in A, $23c$ in B, $49c$ in C, $17c$ in D and $6c$ in E.

Suppose that the final row of Table 3 is used for carbohydrate-like structures. The area components are then $4d$ in C, $91d$ in D and $4d$ in E.

Suppose that the row labelled $-\text{CH}_2-$ in Table 3 is used for the chemical structures associated with the region $60 > \delta > 10$. The area components are then $2e$ in D, $96e$ in E and $2e$ in F.

Adding together the area components results in six simultaneous equations:

$$\begin{aligned} 17b + 4c &= A \\ 67b + 23c &= B \\ 15b + 49c + 4d &= C \\ 2b + 17c + 91d + 2e &= D \\ 6c + 4d + 96e &= E \\ 2e &= F \end{aligned}$$

Regions A and F contain no centrebands, but are likely to include a significant area component from overlap of the broad wings of signals in the neighbouring areas. It therefore seems wise to combine the first two and last two of the above equations, leaving only four:

$$\begin{aligned} 84b + 27c &= A + B \\ 15b + 49c + 4d &= C \\ 2b + 17c + 91d + 2e &= D \\ 6c + 4d + 98e &= E + F \end{aligned}$$

These equations can now be solved for values of b-e.

Fig. 1 shows a spectrum of humic acid from Pomare soil, divided into area regions A-F. In this case, the relative areas are $A = 7$, $B = 13$, $C = 15$, $D = 18$, $E = 38$ and $F = 9$. The solutions are $b = 0.16$, $c = 0.24$, $d = 0.14$ and $e = 0.45$, i.e. the distribution of carbon is:

Carbon in carbonyl groups, e.g. acids and amides:	16%
Carbon in aromatic rings:	25%
Carbon in carbohydrate-like structures:	14%
Carbon in polymethylene, methyl and methoxyl groups:	45%
	<hr/>
	100%
	<hr/>

These results are based on somewhat arbitrary assumptions, but the procedure could be useful for comparisons within a series of samples. Particular weak points are:

- (i) arbitrary divisions between areas associated with overlapping peaks.
- (ii) Spinning sideband intensities based on a small collection of available examples.

Further development could include simulation of spectra based on trial combinations of broadened Gaussian component peaks. The simulations would include spinning sideband signals with intensities based on the data shown in Tables 1-3. Such an approach has been used for interpretation of carbon-13 NMR spectra of solid coal (28).

CONCLUSION

Patterns of spinning-sideband intensities appear to be determined almost entirely by the arrangement of atoms directly bonded to the carbon-13 nucleus. Any more distant structural changes are generally so small that they are of similar magnitude to experimental uncertainties. An exception is the effect of O-substitution at an adjacent ring site in a benzene ring. This effect is transmitted through two bonds.

The localisation of contributing effects makes it easy to predict patterns of spinning-sideband intensities for a given type of functional group in poorly-characterised organic structure. These generalised predictions can be used to set up simultaneous equations which express relationships between the distribution of carbon in various functional groups and the distribution of signal intensity in various chemical-shift ranges across the NMR spectrum.

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Substituent	I(+2)	I(+1)	I(0)	I(-1)	I(-2)
O	3 (1)	17 (2)	60 (3)	16 (2)	4 (1)
O(a)	2 (0)	17 (1)	64 (2)	13 (0)	5 (1)
O(b)	4 (1)	18 (2)	58 (2)	17 (1)	4 (1)
H	5 (1)	25 (3)	45 (7)	17 (2)	7 (2)
H(a)	3 (1)	23 (1)	51 (2)	16 (1)	6 (1)
H(b)	5 (1)	26 (2)	41 (6)	18 (1)	8 (2)
C	5 (1)	27 (2)	40 (4)	17 (2)	9 (1)
C(c)	5 (1)	26 (1)	42 (4)	17 (1)	8 (1)
C(d)	5 (1)	28 (3)	38 (3)	17 (2)	9 (1)
ring junctions	5 (1)	33 (1)	34 (3)	14 (1)	12 (1)

TABLE 1. Averaged spinning-sideband intensity distributions for aromatic carbon. Numbers in brackets are standard deviations.

Footnotes:

- (a) With O-substitution at an adjacent site.
- (b) No O-substitution at either adjacent site.
- (c) sp^2 -hybridised carbon.
- (d) sp^3 -hybridised carbon.

Structure	I(+2)	I(+1)	I(0)	I(-1)	I(-2)
amino acids	2 (1)	12 (4)	73 (8)	12 (3)	2 (1)
other acids	3 (1)	14 (2)	65 (5)	15 (2)	3 (1)
methyl esters	5 (1)	14 (1)	61 (4)	19 (1)	2 (0)
salts	2 (0)	14 (0)	68 (0)	14 (0)	3 (1)
all above	3 (1)	14 (2)	67 (6)	15 (3)	2 (1)

TABLE 2. Averaged spinning-sideband intensity distributions for carboxylic acids, esters and ammonium salts. Numbers in brackets are standard deviations.

Functional group	I(+2)	I(+1)	I(0)	I(-1)	I(-2)
-CH ₃ ^(a)	0 (0)	1 (1)	98 (1)	1 (1)	0 (0)
-CH ₃ ^(b)	0 (0)	1 (0)	98 (0)	1 (0)	0 (0)
-CH ₂ -	0 (0)	2 (1)	96 (2)	2 (1)	0 (0)
-OCH ₃	0 (0)	6 (1)	88 (1)	5 (0)	1 (1)
-OCH ₂ -	0 (0)	4 (2)	91 (5)	4 (2)	0 (0)

TABLE 3. Averaged spinning-sideband intensity distributions for miscellaneous functional groups. Numbers in brackets are standard deviations.

Footnotes:

- (a) on aromatic rings,
(b) on non-aromatic structures.

Compound number	Reference number	Substituent types		
		O	C	H
1	5	1	0	2
2	4	1	0	2
3	4	1	0	2
4	1	0	1	1
5	1	0	1	1
6	1	0	1	1
7	1	1	0	2
8	1	0	1	2
9	2	0	1	5
10	1	0	1	0
11	1	0	1	0
12	3	2	1	3
13	1	0	0	1
21	23	0	1	1
22	18	0	2	1

TABLE 4. Sources of data for substituted benzene structures. The last 3 columns show the number of chemical shift tensors for which principal values have been published, categorised according to the substituent.

Compound number	Substituent	I (0)
12	methoxyl	65
12	"	62
23	"	68
24	"	64
25	"	62
26	"	66
25	hydroxyl	57
26	"	63

TABLE 5. Centreband intensities for 0-substituted carbon in structures with 0-substitution at an adjacent ring site.

Compound number	Reference number	Functional group	Name
27	14	A	acetic acid
28	19	A	malonic acid
29	20	A	dihydromuconic acid
30	16	A	benzoic acid
31	19	A	pyromellitic acid
32	9	A	glycine
33	8	A	alanine
34	7	A	threonine
35	6	A	serine
36	14	E	methyl acetate
37	20	E	polymethylmethacrylate
38	11	S	ammonium tartrate
39	10	S,A	ammonium hydrogen malonate

TABLE 6. Sources of data for carboxylic acids (A), esters (E) and salts (S).

Compound number	Reference	Functional group
7	1	-CH ₃ (aromatic)
20	14	" "
21	23	" "
22	18	" "
33	8	-CH ₃ (non-aromatic)
34	7	" "
40	22	" "
40	22	-CH ₂ -
28	19	" "
29	20	" "
41	24	" "
7	1	-OCH ₃
12	3	" "
15	1	" "
14	15	-OCH ₂ -
42	14	" "
43	14	" "

TABLE 7. Sources of data for miscellaneous functional groups. Compound 40= n-eicosane, Compound 41=polyethylene, Compound 42=ethanol, Compound 43=diethyl ether.

FIGURE 1a

FIGURE 1b

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FIGURE 1c

FIGURE 2 Carbon-13 CP/MAS NMR spectrum of humic acid from Pomare soil: 1 ms contact time, 15 ms data acquisition, 100 ms pulse delay, 2×10^4 transients accumulated.