

QUANTITATIVE ^{13}C NMR MEASUREMENTS ON THE ARGONNE PREMIUM SAMPLES AND OTHER COALS

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ABSTRACT

In view of the well-documented inherent problems with cross-polarisation (CP) ^{13}C NMR concerning quantification for coals, the more time-consuming single pulse excitation (SPE) or Bloch decay technique has much to commend it. SPE ^{13}C NMR has been carried out on the Argonne Premium Samples and a selection of UK coals and maceral concentrates at a low field strength (25MHz) to avoid problems with spinning sidebands. In addition to aromaticity measurements, quaternary aromatic carbon concentrations have been determined by SPE dipolar dephasing. As anticipated, much greater proportions of the carbon were observed by SPE than by CP and the use of tetrakis(trimethylsilyl)silane as an internal standard has indicated that over 90% of the carbon in most of the coals is observed by SPE. Moreover, aromaticity values measured by SPE are consistently higher than those from CP. For anthracite, the concentration of bridgehead aromatic carbon measured by dipolar dephasing SPE is in close agreement with that from elemental analysis.

INTRODUCTION

The combination of dipolar decoupling and magic angle spinning (MAS) with cross-polarisation now enables ^{13}C NMR spectra of carbonaceous materials to be obtained on a routine basis. Although ^{13}C NMR has shown considerable potential for the characterisation of coals, oil shales and other humic materials [1,2], there has been considerable doubt concerning the quantitative reliability of aromaticity and other skeletal parameter measurements using this technique [3]. There is a consensus that significant errors can arise in CP/MAS ^{13}C NMR measurements of aromaticity and other skeletal parameters due to the unfortunate spin-dynamics of carbonaceous materials which typically result in only 50% of the carbon being observed for bituminous coals. Although it is well established that the rate of magnetisation transfer from abundant ^1H to dilute ^{13}C spins during CP is slower for quaternary aromatic carbons than for protonated carbons, the major problem for coals is undoubtedly the presence of paramagnetic species which cause ^1H spins to relax too quickly during CP, i.e. before polarisation transfer to ^{13}C spins has been achieved. In addition, carbons in the vicinity of paramagnetic centres are not observed due to a combination of shielding effects and rapid relaxation. Thus, in general, there is often a clear discrimination against aromatic carbon. Moreover, additional problems are posed by measurements at high field strengths where either much higher spinning speeds or special pulse sequences (e.g. TOSS) are needed to remove sidebands associated with aromatic peaks.

In view of the well-documented inherent problems with CP ^{13}C NMR concerning quantification for solid fuels [2,3], the use of the more time-consuming Bloch decay or single pulse excitation (SPE) technique has much to commend it, particularly at low field strengths to avoid problems with spinning sidebands. This paper covers the application of SPE ^{13}C NMR to the Argonne Premium Coal Samples, a number of UK coals and maceral concentrates, the results being compared with those reported here and by other workers from CP. In addition to aromaticity measurements, dipolar dephasing has been used with SPE to estimate the quaternary aromatic carbon concentration in an anthracite.

EXPERIMENTAL

All the Argonne Premium Coal Samples were analysed except Pocahontas. The 3 UK bituminous coals investigated were Linby, Gedling (both 83% dmmf C) and Point of Ayr (87% dmmf C),

together with an anthracite (Cynheidre). The maceral concentrates were obtained from a US Kentucky low volatile bituminous coal (88% dmmf C) by density gradient centrifugation.

Most of the measurements were carried out at 25MHz on a Bruker MSL100 spectrometer with MAS at 4.5 kHz to give virtually sideband free spectra. For CP, contact times were varied between 0.1 and 15 ms. A relaxation delay of 20s was used in SPE in view of the fact that the few published values of ^{13}C thermal relaxation times for coals are at least 5s [4-6]. No background signal was evident in the SPE spectra from the Kel-F rotor caps. Typically, between 3000 and 4000 scans were accumulated for both the CP and SPE spectra. Dipolar dephasing was carried out with both variable and fixed (50 μ s) dephasing periods. Some spectra were also obtained at high field (75 MHz) with rapid MAS (>10 kHz) using a Varian VXR300 spectrometer. Tetrakis(trimethyl)silane (TKS) was used as an internal standard to determine the proportions of carbon observed in the samples investigated. In experiments with TKS, the acquisition time was extended from 30 to 250 ms to avoid truncating the free induction decay.

RESULTS AND DISCUSSION

Figure 1 shows the 25 MHz SPE spectra of N.Dakota lignite, Pittsburgh No.8 coal and Cynheidre anthracite and indicates that the signal to noise levels are high (50 Hz line broadening routinely used). Moreover, the intensities of the sidebands are below 5% of the central aromatic peaks with MAS at 5 kHz. The 25 MHz SPE and CP spectra of one of the bituminous coals (Gedling) are shown in Figure 1 and it is evident that significantly more aromatic carbon is observed by SPE. Table 1 compares the aromaticity values derived by SPE and CP for the coals investigated and the same trend is found in most cases. Indeed, differences in the measured aromaticity values by the two methods range from 3 to 10 mole%. For CP, the differences are small between the values obtained with a contact time of 1 ms and those obtained by fitting the intensities of the aromatic and aliphatic bands from multiple contact experiments to the form.

$$I_0 = I_t \exp(-t/T_{CH}) \cdot \exp(-t/T_{1\rho})$$

where T_{CH} is the time constant for CP and $T_{1\rho}$ is the ^1H rotating frame relaxation time.

For the Argonne samples, the CP-determined aromaticities are generally in reasonable agreement (± 2 mole %) with those reported by Botto and Axelson [5] and Pugmire et al [7]. However, at relatively long contact times (>4 ms), the values obtained were typically 2-3% higher than those from using a contact time of 1ms and multiple contacts (Table 1). Illinois No.6, Pittsburgh No.8, Lewiston-Stockton, Linby, Gedling and Point of Ayr coals all have H/C ratios between 0.76 and 0.78 despite their carbon contents varying between 80 and 87%. Interestingly, their 25 MHz SPE-determined aromaticities fall in the relatively narrow range of 0.77-0.81. Indeed, one of the authors has argued previously that such aromaticities are more consistent with the H/C ratios than the considerably lower CP-determined values of 0.72 ± 0.04 (Table 1). Of the coals investigated, the lowest proportion of the carbon was observed by SPE for Upper Freeport coal (80%, Table 1) and, with the exception of the anthracite, this was the only coal for which CP and SPE gave the same aromaticity value within the experimental error of about $\pm 1\%$. From the H/C ratio of 0.67 for this coal and the SPE-determined aromaticities discussed above, a value close to 0.85 would have been anticipated. Indeed, if it is assumed that the 20% of the carbon not observed is aromatic, then the measured value of 0.81 increases to 0.84. Although aromaticities derived from the high-field SPE spectra (Figure 3 shows the 75 MHz spectrum for Linby coal) were less precise due to a combination of the greater sideband intensities, the high-field sidebands overlapping with the aliphatic bands and some background signal being obtained from the Kel-F rotor caps, reasonable agreement was obtained with values from the low-field spectra (Table 1).

Figure 4 shows the SPE spectra for the liptinite, vitrinite and inertinite concentrates and, as anticipated, aromaticity increases in going from liptinite to vitrinite to inertinite. However, as for the whole coals, the respective aromaticity values of 0.60, 0.80 and 0.89 are considerably higher than those determined by CP and over 85% of the carbon was observed.

The concentration of quaternary aromatic carbon was estimated by dipolar dephasing using both CP and SPE for the anthracite. Figures 5 and 6 present the decays of the aromatic carbon intensities with increasing dephasing time for CP (10 ms contact time) and SPE, respectively; it was expedient to obtain

more data points for CP because of the superior signal to noise ratios obtained with the much shorter recycle times. Figure 5, in particular, indicates the modulation of the decaying aromatic peak by the MAS. However, in both plots, the expected two component decay is observed. As anticipated with a relatively short contact time (1 ms), the value obtained of about 50 mole % quaternary aromatic carbon was considerably lower than that of 0.67 from the H/C ratio and the SPE-determined aromaticity. Considerably higher values of 67 and 69 mole % C were obtained from Figures 5 and 6 for long contact time CP and SPE, respectively. Moreover, these values are in close agreement with the estimate discussed above from elemental analysis. It should be pointed out that the anthracite investigated here has a slightly higher atomic H/C ratio than that investigated by Gerstein and co-workers [8] and this is consistent with the value obtained with a contact time of 1 ms (50%) being lower than that of about 65% reported in Gerstein's study with a similar contact period. The dipolar dephasing SPE experiment is being extended to the other coals and also being used to estimate methyl concentrations.

CONCLUSIONS

The results clearly demonstrate that, for most coals, aromaticity and other skeletal parameters measured by SPE ^{13}C NMR are quantitatively reliable with typically over 90% of the carbon being observed. The SPE-determined aromaticities of high volatile bituminous coals having H/C ratios of about 0.78 are close to 0.8 and these values are consistently higher than those in the range 0.68-0.75 measured by CP. The development of larger rotors for MAS [6] will help make SPE measurements an even more attractive proposition for quantitative ^{13}C NMR analysis of solid fuels.

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Table 1. Aromaticity values derived from the 25 MHz spectra of the coals

Sample	% dmmf C	Aromaticity values				% of carbon observed by SPE
		CP-1ms	CP-7ms	CP-fit	SPE	
N.Dakota lignite	73	0.66	0.69	0.65 (0.65)	0.76	94
Wyodak sub-bit.	75	0.62	0.65	0.63 (0.63)	0.75	100
Illinois No.6	80	0.70	0.73	0.70 (0.72)	0.78 [0.76]	92
Pittsburgh No.8	83	0.72	0.73	0.72 (0.72)	0.77	89
Blind Canyon	81	0.62	0.62	0.63 (0.63)	0.65	96
Linby	83	0.68	0.72	0.68 (0.68)	0.81 [0.79]	100
Gedling	83	0.68	0.74	0.67 (0.67)	0.78	95
Lewis.-Stockton	84	0.69	n.d.	n.d.	0.79	100
Point of Ayr	87	0.71	0.75	0.71	0.79	92
Upper Freeport	88	0.75	0.79	0.77 (0.80)	0.81	83
Cynheidre anthracite	95	0.96	0.98	0.96 (0.98)	0.99	94

CP-fit = from multiple contact experiments, () = values from fitting aromatic carbon band to two components for T_{CH} and T_{IP} which gave much better fits.

[] = values from 75 MHz spectra. n.d. = not determined.

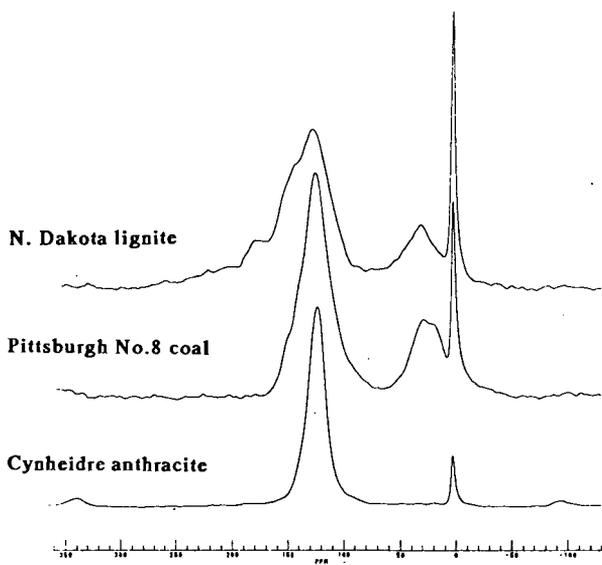


FIGURE 1 25 MHz SPE ¹³C NMR SPECTRA OF SOME OF THE COALS

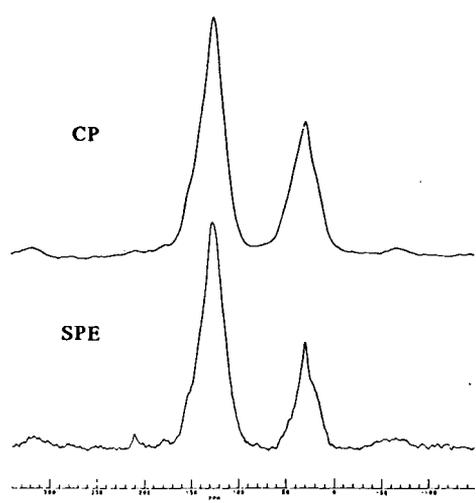


FIGURE 2 25 MHz CP AND SPE ¹³C NMR SPECTRA OF GEDLING COAL

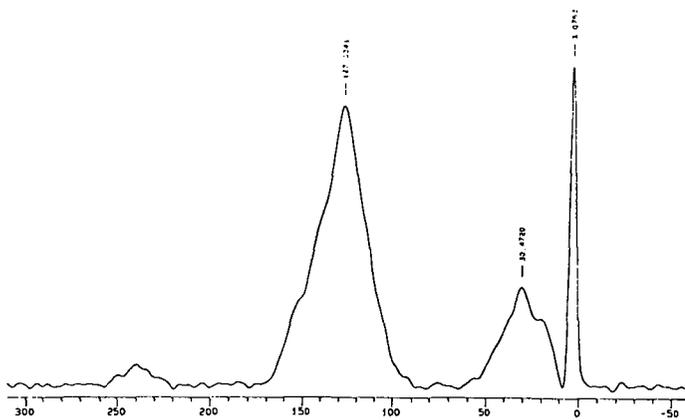


FIGURE 3 75MHz SPE SPECTRUM OF ILLINOIS No. 6 COAL

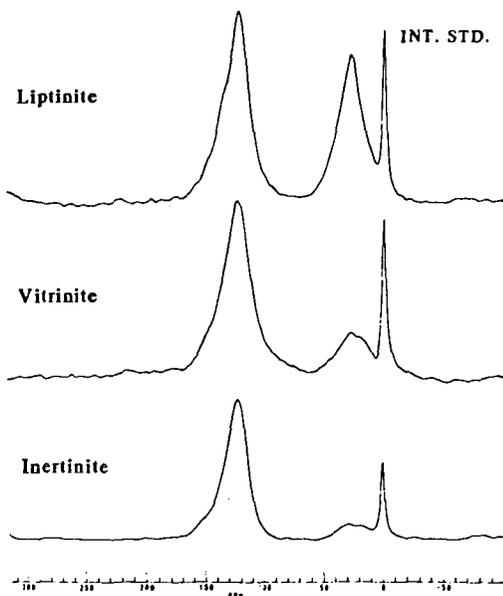


FIGURE 4 25 MHz SPE SPECTRA OF MACERAL CONCENTRATES

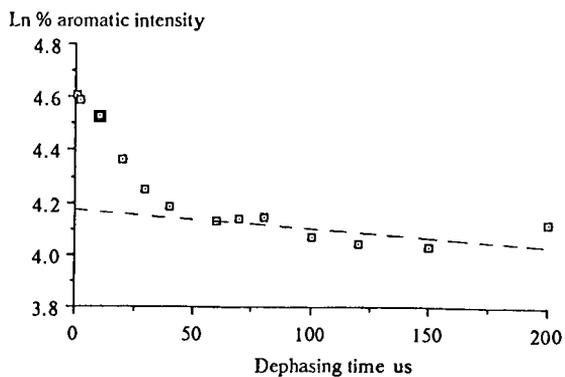


FIGURE 5 AROMATIC CARBON INTENSITIES FROM CP DIPOLAR DEPHASING EXPERIMENT ON THE ANTHRACITE

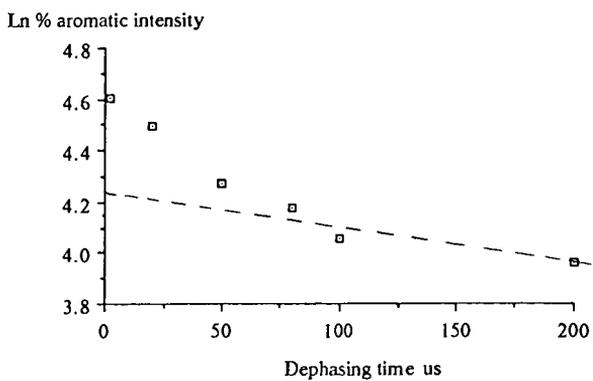


FIGURE 6 AROMATIC CARBON INTENSITIES FROM SPE DIPOLAR DEPHASING EXPERIMENT ON THE ANTHRACITE