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# Single-Pulse Excitation $^{13}\text{C}$ NMR Measurements on the Argonne Premium Coal Samples

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In view of the results of this study and the well-documented inherent problems with cross-polarization (CP)  $^{13}\text{C}$  NMR concerning quantification for coals, it is now clear that the more time-consuming single-pulse excitation (SPE) or Bloch decay measurements are essential for obtaining aromaticities and other carbon skeletal parameters for coals. SPE  $^{13}\text{C}$  NMR has been carried out on the Argonne Premium Coal Samples at both a low and a high field strength (25 and 75 MHz, respectively), high-speed magic angle spinning (13 kHz) being used to suppress spinning sidebands at the higher field. Aromaticity values measured by SPE at low and high field were generally in excellent agreement and were consistently higher than those from CP, the greatest differences being found for the two low-rank coals in the Argonne suite. The use of tetrakis(trimethylsilyl)silane as an internal standard in the low-field measurements indicated that, in general, over 75% of the carbon in the coals is typically observed by SPE.

## Introduction

The combination of dipolar decoupling and magic angle spinning (MAS) with cross-polarization now enables  $^{13}\text{C}$  NMR spectra of carbonaceous materials to be obtained on a routine basis. Although  $^{13}\text{C}$  NMR has undoubtedly shown considerable potential for the characterization of coals, oil shales, and other humic materials,<sup>1,2</sup> there has been considerable doubt concerning the quantitative reliability of aromaticity and other skeletal parameter measurements using this technique.<sup>3,4</sup> Errors of only ca. 5% in aromaticity values will give significant distortions in structural models for coals. There is a consensus that significant errors can arise in CP/MAS  $^{13}\text{C}$  NMR due to the unfortunate spin dynamics of which typically result in only ca. 50% of the carbon being observed for bituminous coals. Although it is well established that the rate of magnetization transfer from abundant  $^1\text{H}$  to dilute  $^{13}\text{C}$  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  $^1\text{H}$  spins to relax too quickly in the rotating frame during CP, i.e., before polarization transfer to  $^{13}\text{C}$  spins has been achieved. In addition, carbons in the vicinity of paramagnetic centers are not observed due to a combination of shielding effects and rapid rotating frame relaxation. Thus, in general, there is often a clear discrimination against aromatic carbon. Additional prob-

lems 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. Nonetheless, commercially available probes can spin samples at the magic angle in excess of 12 kHz which is sufficient to reduce sideband intensities to respectable levels at field strengths corresponding to frequencies of up to 75 MHz.

In view of the well-documented inherent problems with CP  $^{13}\text{C}$  NMR concerning quantification for solid fuels,<sup>2,3</sup> it is now clear that the use of the more time-consuming Bloch decay or single-pulse excitation (SPE) technique is essential for obtaining accurate aromaticity values and other carbon skeletal parameters, particularly at low field strengths to avoid having to use extremely rapid MAS. Although, CP spin dynamics are likely to be adversely affected by structure-dependent modulation of the Hartmann-Hahn match at high MAS at speeds (above ca. 10 kHz), the same results should be obtained in principle by SPE at high and low field strengths. However, deviations in peak ratios of up to 10% have been found for individual carbons in the high field SPE spectra of model aromatic compounds obtained with high-speed MAS<sup>4</sup> although the overall aromaticities were close to the expected values. Provided that thermal relaxation is achieved between successive pulses, the only carbon not observed by SPE is that in the vicinity of paramagnetic species subjected to shielding effects. This paper compares the results obtained from SPE  $^{13}\text{C}$  NMR for the Argonne Premium Coal Samples in two independent studies carried out in our laboratories at frequencies of 25 and 75 MHz. Comparisons are made with CP data from both these and earlier studies<sup>5-7</sup> and with the SPE results recently

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reported by Muntean and Stock.<sup>8</sup> The generally close agreement obtained between our laboratories for the SPE-derived aromaticity values of the Argonne coals makes it is both extremely appropriate and timely to publish the findings in a joint paper.

### Experimental Section

Details on the Argonne Premium Coal Samples (APCS) including their elemental, proximate, and maceral analyses have been reported by Vorres<sup>9</sup> and their analyses are also in the User Handbook, together with a list of the numerous studies in which these samples have already been used.

**Low Field.** The 25-MHz measurements were carried out at Strathclyde on a Bruker MSL100 spectrometer with MAS at 4.5–5.0 kHz to give spectra in which the sideband intensities are only ca. 3% of the central aromatic bands. Prior to analysis, the coals were vacuum dried and the Upper Freeport and Pocahontas samples were partially demineralized by washing with dilute hydrochloric acid. It was possible to pack ca. 250 mg of sample into the zirconia rotors. For CP, contact times were varied between 0.1 and 10 ms and the <sup>1</sup>H decoupling and spin-lock field was ca. 60 kHz. <sup>13</sup>C thermal relaxation times (*T*<sub>1</sub>s) of the Illinois No. 6 and the partially demineralized Pocahontas samples were determined using the CP pulse sequence devised by Torchia.<sup>10</sup>

Relaxation delays of between 20 and 100 s were used for the SPE measurements. No background signal was evident in the SPE spectra from the Kel-F rotor caps and, for SPE, the 90° <sup>13</sup>C pulse width was 4.5 μs. Typically, between 2000 and 4000 scans were accumulated for both the CP and SPE spectra. All the FIDs were processed using a line broadening factor of either 50 or 100 Hz. Tetrakis(trimethylsilyl)silane (TKS) was used as an internal standard to determine the proportions of carbon observed in the coals principally by SPE. In experiments with TKS, the acquisition time was extended from 30 to 250 ms to avoid truncating the free induction decay. The measurement of aromatic and aliphatic peak areas manually was found to be generally more precise than using the integrals generated by the spectrometer software.

**High Field.** For the high-field measurements at Pacific Northwest Laboratory, the coals were opened under nitrogen, dried under vacuum, and loaded into sample rotors in a nitrogen glovebag. The 75-MHz spectra were obtained with a MAS speed of 13 kHz using a Varian VXR300 instrument equipped with a Doty Scientific Inc. high speed CP/MAS probe. The rotors were 5-mm silicon nitride cylinders with vespel end caps and were packed with between 69 and 83 mg of coal. Most CP spectra were obtained with a 21-kHz proton field corresponding to the spinning modulation maximum at 13 kHz below the nonspinning match at 34 kHz and with a recycle time of 5 s which was extended to 20 s for Pocahontas coal. Further details on the CP measurements have been reported elsewhere.<sup>11</sup>

For both the low- and high-field experiments, the intensities of the aromatic and aliphatic bands in the spectra from the variable contact time experiments were fitted to an expression of the form

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

where *T*<sub>CH</sub> is the time constant for CP and *T*<sub>1ρ</sub> is the <sup>1</sup>H rotating frame relaxation time.

Typically between 400 and 1800 scans were accumulated for the SPE spectra with a relaxation delay of 200 s, a 90° <sup>13</sup>C pulse

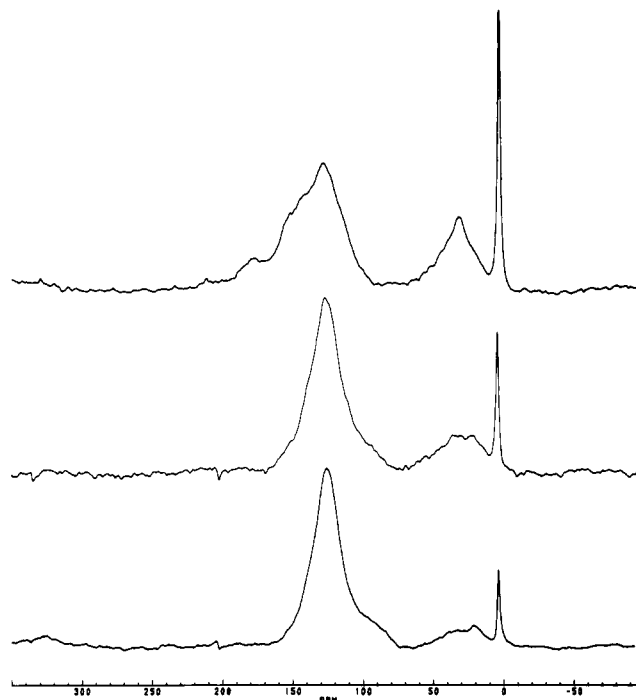


Figure 1. 25-MHz SPE spectra of (top to bottom) (a) Wyodak, (b) Upper Freeport, and (c) Pocahontas coals.

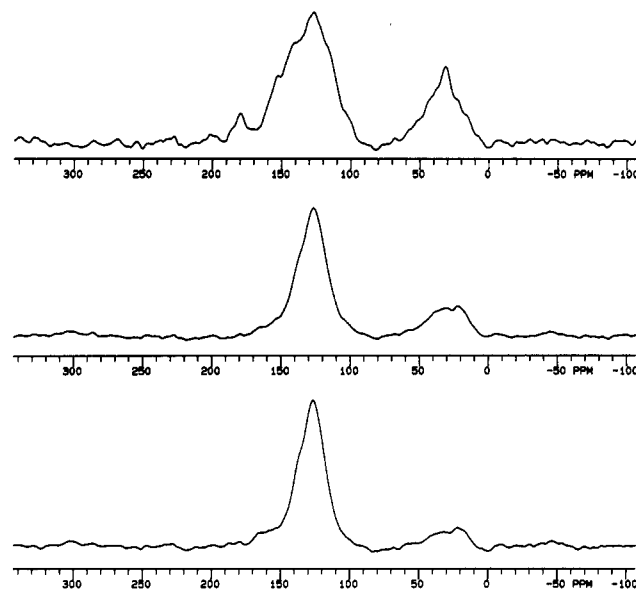


Figure 2. 75-MHz SPE spectra of (a, top) Wyodak, (b, middle) Upper Freeport, and (c, bottom) Pocahontas coals.

of 4.5 μs, and a dipolar decoupling field of 74 kHz. The relaxation delay of 200 s was a conservative choice based on the results for model compounds<sup>4</sup> where it was found that the <sup>13</sup>C *T*<sub>1</sub> for the isolated bridgehead aromatic compound in acenaphthene was 105 s. It was necessary to correct the SPE spectra for the background signal from the rotor caps and/or probe components (ca. 20% of the total signal) by careful subtraction of this component from the FID.

### Results and Discussion

**Spectra.** Figures 1 and 2 show the 25- and 75-MHz SPE spectra, respectively, of the Wyodak, Upper Freeport, and Pocahontas samples. The signal to noise levels are higher in the 25-MHz spectra (50-Hz line broadening used in Figure 1) due to a combination of the larger sample size (250 vs 69–83 mg) and, in most cases, more scans being

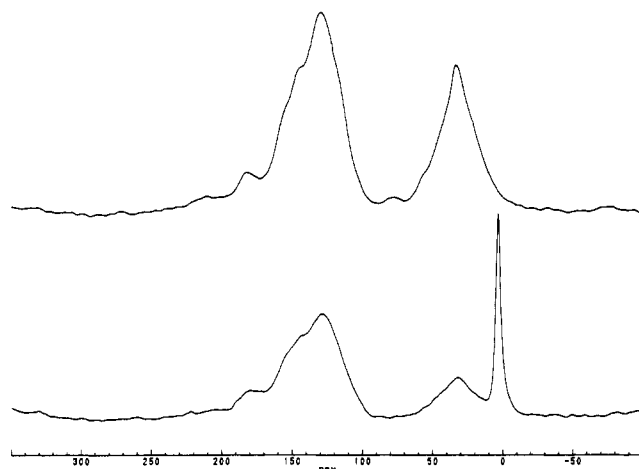
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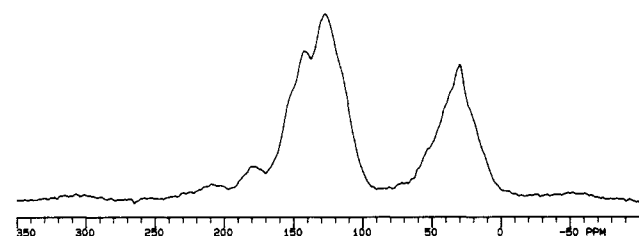
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**Figure 3.** Comparison of 25-MHz spectra of North Dakota lignite obtained by (a, upper) CP with a contact time of 1 ms and (b, lower) SPE.

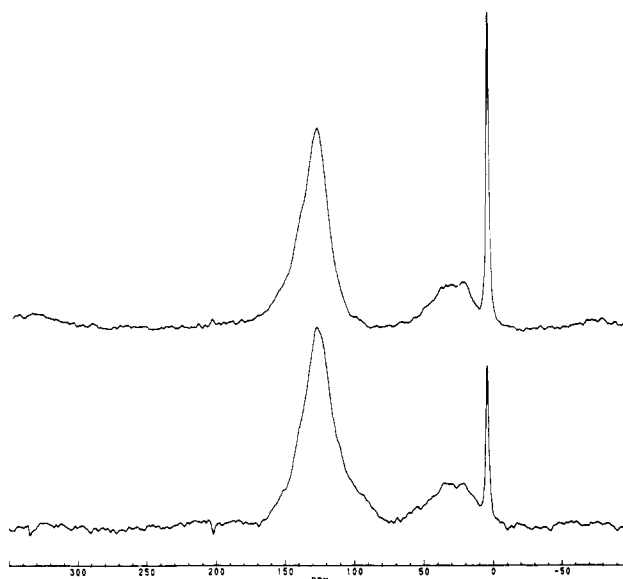


**Figure 4.** 75-MHz spectrum of North Dakota lignite obtained by CP with a contact time of 0.7 ms.

accumulated. However, as indicated above, the intensities of the sidebands are well below 5% of the central aromatic peaks. The 25-MHz SPE and CP spectra of the North Dakota lignite are compared in Figure 3 and a 75-MHz CP spectrum is shown in Figure 4. The 25-MHz SPE spectra of Upper Freeport coal before and after partial demineralization with HCl are compared in Figure 5.

**Cross Polarization.** Table I compares the aromaticity values derived by multiple contact time CP experiments at 25 and 75 MHz in this study and by Pugmire and co-workers<sup>7</sup> and Muntean and Stock<sup>8</sup> at low field in previous studies. The values are in close agreement with the exception of the high-field values for Pittsburgh No. 8.

A number of attempts have been made to measure the fraction of carbon in coals by CP<sup>3,6,12</sup> as it was recognized at an early stage from the shortest  $^1\text{H}$   $T_{1\rho}$  component for most coals which is only a fraction of a millisecond<sup>13</sup> that not all the carbon is going to be sampled by CP. Internal standards offer the most rigorous approach for carbon counting as spectrometer variations between different samples are obviated. In this study, at low field, TKS was chosen principally for the SPE measurements (see following) rather than CP, although it has the inherent advantage of giving a single resonance which does not significantly overlap the aliphatic carbon. However, for CP, TKS has limitations in that it has a long  $T_{CH}$  (ca. 4 ms at 25 MHz with the  $B_1$  field strength corresponding to 60 KHz used here) and, thus, the intensity at different contact times has to be fitted to the same expression (1) as used for the coals. Further, a long acquisition time is required (ca. 250 ms) to ensure that the FID is not truncated and the Hartmann-Hahn match condition is



**Figure 5.** Comparison of SPE spectra of Upper Freeport coal obtained (a, upper) before and (b, lower) after partial demineralization with HCl.

**Table I.** Aromaticity Values Derived from CP Spectra of the Argonne Coals<sup>a</sup>

sample	% dmmf C	aromaticity (total sp <sup>2</sup> carbon)			
		75 MHz	25 MHz		
			this study	ref 7	ref 8
North Dakota lignite	73	0.67	0.67	0.66	0.70
Wyodak subbit.	75	0.54	0.63	0.63	0.65
Illinois No. 6	80	0.73	0.72	0.72	0.72
Pittsburgh No. 8	83	0.79	0.72	0.72	0.74
Blind Canyon	81	0.67	0.63	0.65	0.67
Lewis-Stockton	84	0.77	0.71	0.75	0.75
Upper Freeport	88	0.78	0.80	0.81	0.82
Pocahontas	91	0.86	0.86	0.86	0.86

<sup>a</sup> At low field, values from fitting aromatic carbon band to two components for  $T_{CH}$  and  $T_{1\rho}$  which gave much better fits.

considerably more sharper than for the coals. Taking these factors into consideration, the error for carbon counting in CP is considerably greater than in SPE (cf. estimated errors ca.  $\pm 10\%$  with  $\pm 5\%$ ). However, despite these limitations, it was estimated that only 60% of the carbon was observed for Pocahontas coal and this value is similar to that reported by Muntean and Stock<sup>8</sup> and close to the range of values of 40–55% reported for whole coals and vitrinites by Botto et al.<sup>6</sup>

Our estimates and those by others are further substantiated by comparing the overall peak intensities in CP and SPE spectra. Although this procedure obviously suffers from day to day variations in spectrometer response, it has been found consistently that the maximum CP intensities at close to 1 ms contact time are only ca. 2–3 times those from SPE for the same number of scans. This factor increases typically by ca. 10–15% by taking,  $M_0$ , the equilibrium rather than the maximum intensity in expression 1, but, if all the carbon is observed by both techniques and the CP Hartmann-Hahn match condition has been maintained, the CP intensities should be close to 4 times more than those from CP.

**Single-Pulse Excitation.** Table II compares the aromaticity values obtained at 25 and 75 MHz in this study and those at 25 MHz recently reported by Muntean and Stock<sup>8</sup> are included for comparison. Remarkably good agreement has been achieved between low and high field

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**Table II. Aromaticity Values Derived from SPE Spectra of the Argonne Coals**

sample	% dmmf C	aromaticity (all sp <sup>2</sup> carbon)			% of C obsd at 25 MHz <sup>d</sup>
		75 MHz	25 MHz		
			this study	ref 8 <sup>a</sup>	
North Dakota lignite	73	0.77	0.76	0.74	95
Wyodak subbit.	75	0.76	0.75	0.66	95
Illinois No. 6	80	0.72	0.75	0.72	85
			0.75 <sup>b,c</sup>		100 <sup>b</sup>
Pittsburgh No. 8	83	0.75	0.75	0.75	90
Blind Canyon	81	0.67	0.67	0.68	75
Lewis-Stockton	84	0.77	0.78	0.71	75
Upper Freeport	88	0.80	0.81	0.83	75
			0.84 <sup>c</sup>		90 <sup>c</sup>
Pocahontas	91	0.89	0.90	0.89	90

<sup>a</sup> Initial samples. <sup>b</sup> = 100 s delay. <sup>c</sup> After demineralization. <sup>d</sup> This study;  $\pm 5\%$ .

bearing in mind that the results were obtained independently in our laboratories. Illinois No. 6 is the only sample where the difference in aromaticity of 0.03 lies outside the experimental errors for the low- and high-field measurements (ca. 1–2 mol % carbon). Further, the use of TKS as an internal standard in the low-field measurements has indicated that over 75% of the carbon (estimated measurement error of  $\pm 5\%$ ) has been observed for all the coals. Table II indicates that the SPE values are invariably higher than the CP values particularly for the two low-rank coals but also to a lesser extent for Illinois No. 6, Pittsburgh No. 8, Lewis-Stockton and Pocahontas coals (Table II, neglecting the high-field value for Illinois No. 6 coal). However, the latter differences are less than those found for other bituminous coals, notably those from the UK reported elsewhere<sup>16</sup> where the SPE-determined values were up to 10 mol % higher than the corresponding CP values. As reported by Muntean and Stock,<sup>8</sup> the fact that the aromatic carbon bands are broader in the SPE spectra than the corresponding CP spectra (Figures 3–5) indicates qualitatively that more carbon is observed, particularly that close to paramagnetic centers which is missed by CP due to short <sup>1</sup>H T<sub>1ρ</sub>s.<sup>13</sup> Indeed, paramagnetic centers may be partially responsible for the large differences between SPE and CP-determined values for North Dakota lignite and Wyodak subbituminous coal as it is known that these low-rank coals contain relatively large amounts of paramagnetic iron in intimate contact with the organic matter.<sup>17</sup>

Much greater care was taken to avoid exposure to air in the high-field measurements, but the generally good agreement with the low-field results suggests that the influence of paramagnetic oxygen on SPE measurements is limited. The likely effects are a reduction of <sup>13</sup>C T<sub>1ρ</sub>s and possibly less carbon being observed. However, there may have been an effect at low field for the Pocahontas sample as the resolution was poor compared to the high-field spectrum until the coal had been treated with HCl which obviously removes inorganic paramagnetics.

The other significant difference between the low- and high-field measurements was that a much longer recycle time of 200 s was used at high field. The value of 20 s for the low-field measurements was chosen initially on the few published <sup>13</sup>C T<sub>1ρ</sub>s of coals<sup>5,14,15</sup> close to 5 s. In this

study, it was found that the aromatic carbon <sup>13</sup>C T<sub>1ρ</sub> for the Pocahontas sample was 6 s while particularly the aliphatic carbon values for Illinois No. 6 coal were somewhat longer (a two-component fit being found for the aliphatic carbon with ca. 50% having a value of 10 s and the remainder a value of 2 s). Indeed, increasing the relaxation delay increased the amount of carbon observed at low field to well over 90% for Illinois No. 6 coal but, like partial demineralization with HCl, this had little effect on the measured aromaticity (Table II). The HCl treatment also narrowed the aromatic carbon band for Illinois No. 6 coal.

There are significant discrepancies between our SPE results and those reported by Muntean and Stock<sup>8</sup> for the Wyodak and Lewis-Stockton samples (Table II). Since nearly all the carbon was observed at low-field for untreated Wyodak coal, we believe that their value of 0.66 (cf. 0.75–0.76) is grossly underestimated. Further, as all the carbon is observed without any pretreatment, it is difficult to reconcile our values with those of Muntean and Stock<sup>8</sup> who claim that significantly more carbon is observed after samarium iodide treatment to reduce the concentration of organic free radicals. On the basis of the anticipated correlation between aromaticity and H/C ratio, it can be argued that the aromaticity for Lewis-Stockton should occur closer to 0.8 rather than 0.7 (cf. 0.77–0.78 with 0.71 reported by Muntean and Stock, Table II). As no spectra were published in their recent article, the quality of the respective spectra cannot be compared objectively. However, the signal to noise ratios in our SPE spectra (Figure 1–5) are significantly better than those for the dipolar dephased SPE spectra of Pocahontas coal published in the second article by Muntean and Stock.<sup>8</sup>

If only 10% of the carbon is not observed and this happens to be all aromatic, then the aromaticity can only be underestimated by 0.02. Thus, we have considerable confidence that, in general, the SPE-determined aromaticity values are accurate. Further, although the Illinois No. 6, Pittsburgh No. 8, and Lewis-Stockton samples have differing carbon contents, their H/C ratios are between 0.75 and 0.78 and their SPE-determined aromaticities lie coincidentally in the narrow range of 0.75–0.78 (Table II, neglecting the high-field value for Illinois No. 6).

From the H/C ratios and the aromaticity values in the range 0.75–0.78 obtained for the three high-volatile bituminous APCS, it was anticipated that the aromaticity of Upper Freeport coal should be over 0.80. Indeed, if it is assumed that the carbon not observed by SPE at low field with a recycle time of 25 s is all aromatic, then a value of approximately 0.85 is deduced. At low field, increasing the recycle delay to 100 s to take account of the aromatic <sup>13</sup>C T<sub>1ρ</sub>s possibly being longer than ca. 5 s found here for Pocahontas coal and elsewhere<sup>5,14,15</sup> for other samples, raised the observed aromaticity within experimental error to only 0.82. However, partially demineralizing the sample with HCl had a more profound effect broadening the aromatic band (Figure 5) and increasing the measured aromaticity to 0.84 (Table II). Thus, paramagnetic iron species rather than organic radicals are thought to be chiefly responsible for the relatively low carbon count on the initial coal sample bearing in mind the Upper Freeport has the second highest nonpyritic iron content of the APCS. In view of the fact that HCl treatment proved to be beneficial for the Upper Freeport and Pocahontas samples, this is probably a worthwhile preliminary to use on a routine basis both to improve

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spectral resolution and observe more of the carbon due to removal of inorganic paramagnetics.

While acceptable signal to noise ratios have been achieved for SPE with high-speed MAS at 75 MHz, this approach cannot be considered convenient for routinely obtaining coal spectra due to the somewhat disappointing operational lifetimes of the soft stator material in the probe used. Moreover, the use of large volume probes<sup>15</sup> will

further increase the attractiveness of low-field measurements.

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