

THE DETERMINATION OF THE HYDROXYL AND CARBOXYLIC ACID CONTENT OF COAL MACERALS USING COMBINED CHEMICAL AND SPECTROSCOPIC TECHNIQUES

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ABSTRACT

Macerals were separated from two high volatile bituminous coals obtained from the Argonne Premium Coal Sample Program and one high volatile bituminous coal from the Pennsylvania State University Coal Sample Bank. A preliminary survey of the nature of these macerals using chemical and spectroscopic techniques are reported. Alkylation using ^{13}C enriched methyl iodide followed by solid ^{13}C NMR analysis were used to determine the concentrations of acidic OH and CH sites in these macerals. The relative quantities of various types of methyl ethers and methyl esters were also estimated from the NMR spectra.

INTRODUCTION

The combined use of alkylation using ^{13}C enriched reagents and solid ^{13}C NMR spectroscopy has been shown to be an effective procedure for the determination of the different types of acidic sites in coals (1-7). Alkylation using tetra-butylammonium hydroxide as base catalyst alkylates the acidic oxygen functional groups in coal such as phenols and carboxylic acids to produce ethers and esters (8). Certain acidic carbon sites in structures such as fluorene, indene, and benzanthrene can also be alkylated under these reaction conditions (3,5). The distinct chemical shift differences of methyls on carbon and oxygen allows the estimation of the relative degree of methylation on oxygen versus carbon. Furthermore, the O-methyl region of the ^{13}C spectra can be resolved into three distinct regions corresponding to the methyl carboxylates, unhindered aryl methyl esters and hindered aryl methyl ethers.

Macerals were separated from three high volatile bituminous coals by density gradient centrifugation (9). The concentration of the various types of hydroxyl and carboxylic acid groups in these macerals as estimated by ^{13}C enriched methylation and solid ^{13}C NMR spectroscopy are reported.

RESULTS AND DISCUSSION

Preliminary Survey. The coals used in this study were obtained from the Pennsylvania State University Coal Sample Bank and the Argonne Premium Coal Sample Program. These were the West Virginia Upper Kittanning seam hvA bituminous coal (PSOC-732), the Utah Blind Canyon seam hvB bituminous coal (APCS-6), and the West Virginia Lewiston-Stockton seam hvA bituminous coal (APCS-7). Maceral groups were separated from these coals using density gradient centrifugation (9). The elemental data for the coals and macerals, which can conveniently be discussed in terms of mole ratios, are shown in Table I. The

H/C values for the macerals follow the order: liptinite > vitrinite > inertinite for the West Virginia Upper Kittanning and the West Virginia Lewiston-Stockton macerals, and resinite > sporinite > vitrinite for the Utah Blind Canyon macerals. Nitrogen is more concentrated in the vitrinites than in the other macerals. The nitrogen content is substantially lower in the Utah Blind Canyon resinite than in the other macerals from this coal, and this finding is in accord with previous reports of other Utah resinites (10,11). The O/C values follow the order: vitrinite - inertinite > liptinite for all the macerals. It should be noted that the oxygen content was calculated by difference from the C, H, N microanalyses. The contributions from sulfur and mineral matter were not taken into consideration even though significant differences in the sulfur content of different maceral types in the same coal have been reported (12-14).

The solid ^{13}C -CP/MAS spectra of the macerals are shown in Figures 1-3. The NMR spectra are scaled to the intensity of the largest signal. The fraction of carbon aromaticity (f_a) in CP/MAS experiments are shown in Table II. Quantitative interpretations of CP/MAS experiments must be made with caution. Recent experiments suggest that f_a values determined by CP/MAS techniques may underestimate the aromatic carbon content of coals and macerals (15).

Hydroxyl and Carboxylic Acid Concentration. The macerals were alkylated with ^{13}C enriched methyl iodide (98% ^{13}C) using tetrabutylammonium hydroxide as the basic catalyst in tetrahydrofuran following Liotta's procedure (8). The degree of alkylation estimated from the elemental data as methyl groups that had been added to each 100 carbon atoms of the maceral group is shown in Table III.

Methylation on carbon occurs to the extent of 10 to 25 percent of the total methyls added to the macerals of the West Virginia Upper Kittanning and Lewiston-Stockton coals. Methylation occurs on carbon to a lesser degree for the macerals of the Utah Blind Canyon coal, as expected for a less mature coal. The observation that less methyls were added on the whole coals rather than the individual macerals of the Utah Blind Canyon and West Virginia Lewiston-Stockton coals may be due to the larger particle size of the whole coals relative to the macerals. Thus, reagent accessibility may be a factor for these alkylations. However, the relative O- vs. C-methylation ratio for the whole coal is similar to that of the vitrinite, which suggests that the alkylatable oxygen and carbon sites are randomly dispersed.

The CP/MAS spectra of the Utah Blind Canyon macerals alkylated with ^{13}C enriched methyl iodide is shown in Figure 4. The O-methylation region of the ^{13}C NMR spectra appear in three distinct regions. The relative contributions of the three regions based on their relative intensities are summarized in Table IV. The most plausible structural elements in methylated coal that give rise to resonances centered at 50 ppm are the methyl carboxylates; centered at 55 ppm are the unhindered aryl ethers; and at 60 ppm are the hindered aryl ethers (16).

Methyl carboxylates represent a major proportion of the O-methylated products of the liptinites from all three coals while little or no methyl carboxylates are detected in the methylated vitrinites or inertinites. The higher concentration of carboxylic acid in liptinites relative to vitrinites have been noted by others using infrared spectroscopy (17-19), but the comparative estimates of the carboxylic acid concentration have not been previously reported for macerals.

The relative intensities of the two resonances centered at 55 ppm and 60 ppm that can be assigned to unhindered methyl ethers and hindered methyl ethers vary between the maceral types. The ratio of hindered methyl ethers to unhindered methyl ethers follow the order: liptinites > vitrinites > inertinites. This is consistent with the notion that this reflects the degree of alkyl substituents on the aromatic structures in these macerals.

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TABLE I. The Elemental Data of the Macerals Expressed as Molar Ratios.

Maceral Group	H/C	N/C	O/C ^a
<u>West Virginia Upper Kittanning (PSOC-732)</u>			
Whole Coal	0.67	0.015	0.11
Liptinite	0.88	0.012	0.05
Vitrinite	0.71	0.017	0.10
Inertinite	0.56	0.014	0.11
<u>Utah Blind Canyon (APCS-6)</u>			
Whole Coal	0.90	0.016	0.19
Resinite	1.41	0.005	0.05
Sporinite	1.07	0.013	0.13
Vitrinite	0.92	0.016	0.19
<u>West Virginia Lewiston-Stockton (APCS-7)</u>			
Whole Coal	0.75	0.016	0.12
Liptinite	0.97	0.012	0.10
Vitrinite	0.70	0.016	0.13
Inertinite	0.49	0.011	0.12

^aThe oxygen content was determined by difference from the C,H,N microanalyses.

TABLE II. Carbon Aromaticities Estimated by Cross-Polarization NMR.

Maceral Group	f ^a (CP)*
<u>West Virginia Upper Kittanning (PSOC-732)</u>	
Whole Coal	0.78
Liptinite	0.59
Vitrinite	0.79
Inertinite	0.87
<u>Utah Blind Canyon (APCS-6)</u>	
Whole Coal	0.60
Resinite	0.16
Sporinite	0.46
Vitrinite	0.63
<u>West Virginia Lewiston-Stockton (APCS-7)</u>	
Whole Coal	0.74
Liptinite	0.54
Vitrinite	0.76
Inertinite	0.87

*CP Experiments: 2 ms. mix time.

TABLE III. Distribution of Added Methyl Groups as Estimated by Solid ¹³C NMR Spectra.

Maceral Group	Methyl Groups/100°C		
	Total	On Oxygen	On Carbon
<u>West Virginia Upper Kittanning (PSOC-732)</u>			
Whole Coal	4.8	3.8	1.0
Liptinite	6.0	5.0	1.0
Vitrinite	5.2	4.4	0.8
Inertinite	1.6	1.3	0.3
<u>Utah Blind Canyon (APCS-6)</u>			
Whole Coal	1.9	1.8	0.1
Resinite	0.9	0.9	<0.1
Sporinite	2.1	2.0	0.1
Vitrinite	3.1	2.8	0.3
<u>West Virginia Lewiston-Stockton (APCS-7)</u>			
Whole Coal	1.3	1.2	0.1
Liptinite	4.2	3.2	1.0
Vitrinite	3.1	2.8	0.3
Inertinite	2.5	2.0	0.5

TABLE IV. Relative Quantities of Methyl Ethers and Methyl Esters.

Maceral Group	60 ppm	55 ppm	50 ppm
<u>West Virginia Upper Kittanning (PSOC-732)</u>			
Whole Coal	1.1	2.7	0
Liptinite	1.2	2.4	1.4
Vitrinite	1.2	3.2	0
Inertinite	0.2	1.1	0
<u>Utah Blind Canyon (APCS-6)</u>			
Whole Coal	0.7	1.1	0
Resinite	0.3	0.2	0.4
Sporinite	0.9	0.9	0.2
Vitrinite	1.0	1.8	0
<u>West Virginia Lewiston-Stockton (APCS-7)</u>			
Whole Coal	0.4	0.8	0.1
Liptinite	1.5	1.2	0.5
Vitrinite	0.8	1.9	0.1
Inertinite	0.2	1.8	0

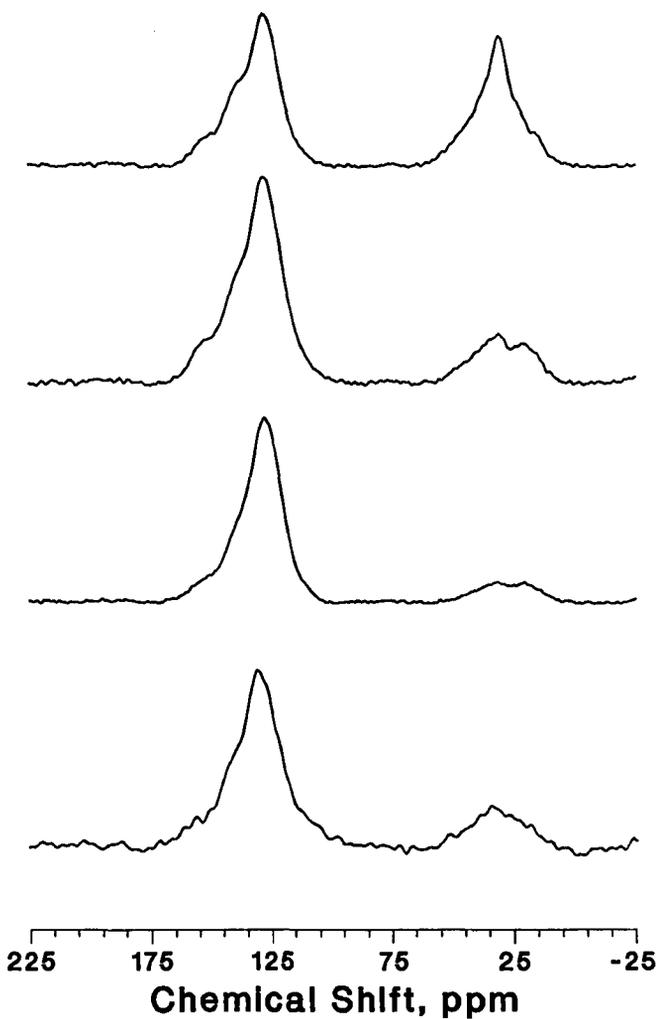


Figure 1. Solid ^{13}C CPMAS spectra of West Virginia Upper Kittanning Coal (PSOC 732). (A) Liptinite; (B) Vitrinite; (C) Inertinite; (D) Whole Coal.

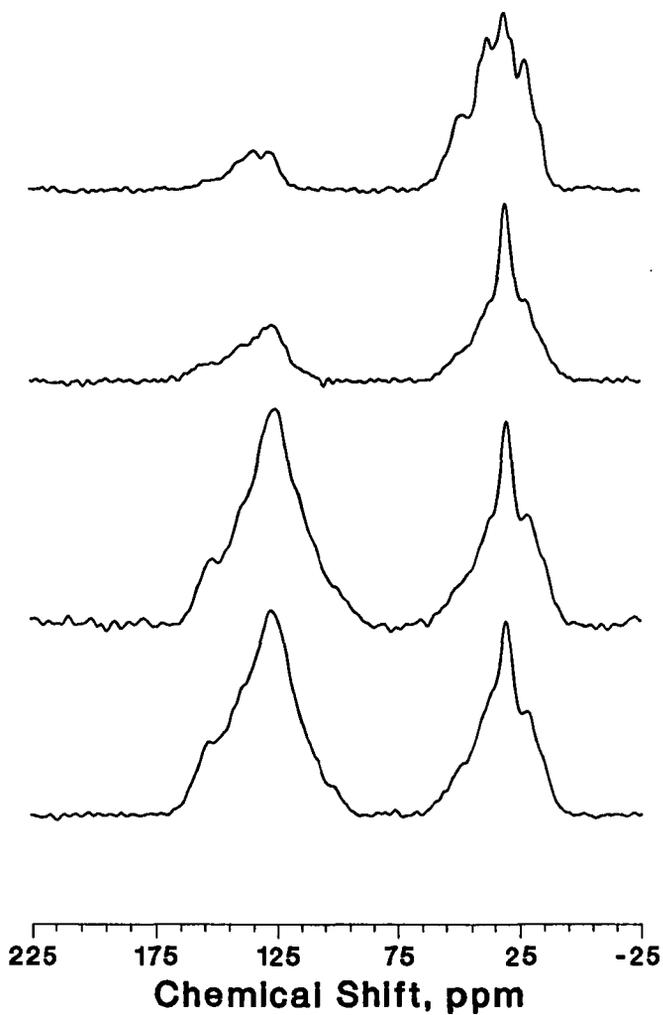


Figure 2. Solid ^{13}C CPMAS spectra of Utah Blind Canyon Coal (APCS #6).
(A) Resinite; (B) Sporinite; (C) Vitrinite; (D) Whole Coal.

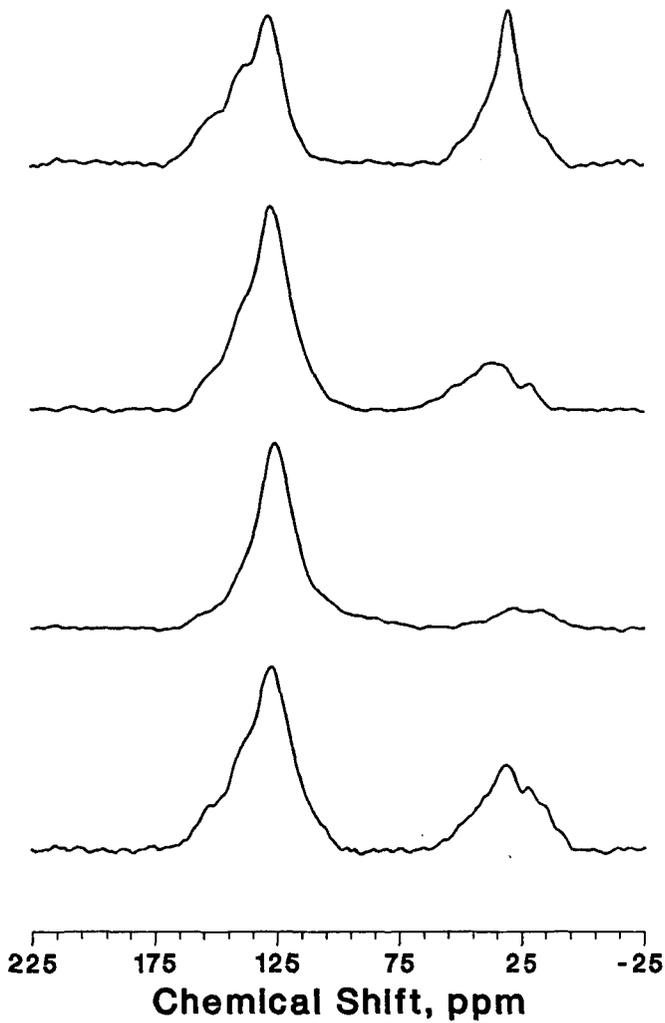


Figure 3. Solid ^{13}C CPMAS spectra of West Virginia Lewiston-Stockton Coal (APCS #7). (A) Liptinite; (B) Vitrinite; (C) Inertinite; (D) Whole Coal.

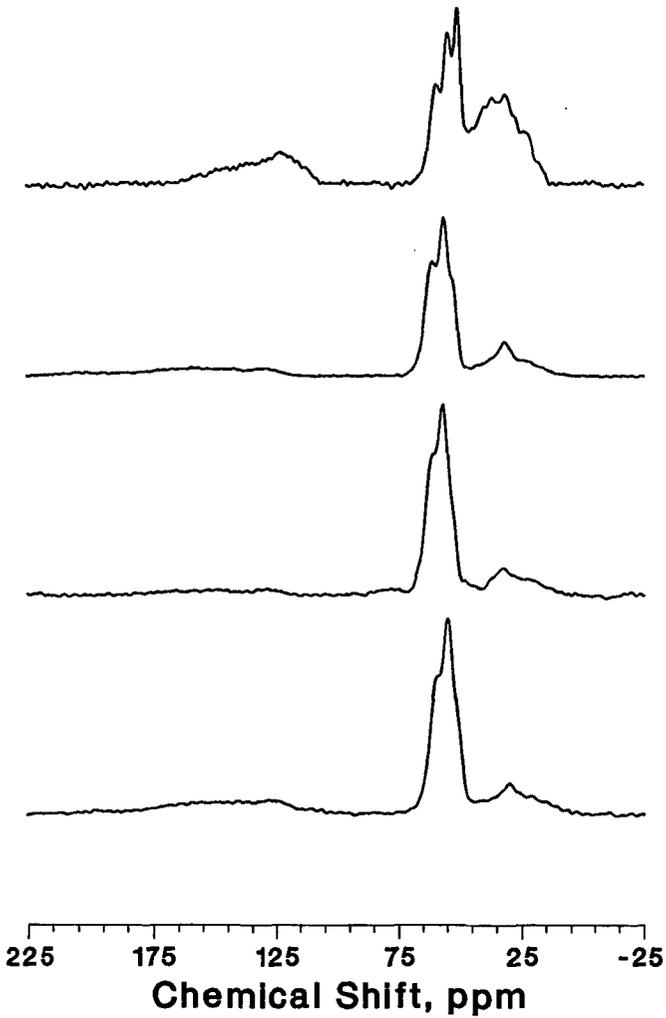


Figure 4. Solid ^{13}C CPMAS spectra of Utah Blind Canyon Coal (APCS #6) methylated with ^{13}C enriched methyl iodide. (A) Resinite; (B) Sporinite; (C) Vitrinite; (D) Whole Coal.