

A NOVEL APPLICATION OF ^{31}P NMR SPECTROSCOPY TO THE ANALYSIS
OF ORGANIC GROUPS CONTAINING -OH, -NH AND -SH FUNCTIONALITIES
IN COAL EXTRACTS AND CONDENSATES

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Abstract

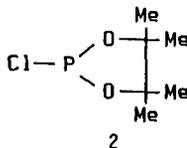
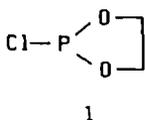
Over one hundred model organic compounds including phenols, aliphatic alcohols, aromatic acids, aliphatic acids, amines, and thiols have been derivatized with two members of a phospholane series of phosphorus-containing reagents, namely, $\text{ClPOCH}_2\text{CH}_2\text{O}$ and $\text{ClPOCMe}_2\text{CMe}_2\text{O}$. Measurement of proton-decoupled ^{31}P chemical shifts of these derivatives reveals that, in general, the resonances fall into well-separated regions for derivatized classes of these organic compounds. Both phosphorus reagents were also tested on pyridine extracts of Illinois No. 6 coal, revealing the presence of various phenols, carboxylic acids, and aliphatic alcohols. Similar derivatization of a low-temperature pyrolysis condensate from Illinois No. 6 coal showed no detectable concentrations of carboxylic acids, a relatively small amount of aliphatic alcohols, but considerable quantities of a variety of phenols. The current scope and limitations of this NMR technique and its applicability to the quantitation of -OH, -SH and -NH functionalities in organic solutions of coal-derived materials are discussed.

Introduction

Analysis of coal-derived materials, such as low-temperature pyrolysis condensates, is usually carried out by GC/MS methods. However, these techniques are relatively non-routine and time consuming. As an alternative as well as complementary approach, IR and NMR spectroscopic procedures have been developed in recent years. Although direct analysis of complex mixtures obtained in coal processing can sometimes be performed,¹ derivatization of certain classes of compounds with suitable reagents is advantageous in NMR spectroscopy if the reagent introduces an NMR-reactive label that gives a resonance signal specific for the component being analyzed.

Previous determinations of OH functionalities in coal-derived materials have been performed by silylation²⁻⁶ or acetylation^{6,7} followed by IR⁵, FT-IR^{2,7} and/or ^1H 2,3,6 , ^{29}Si 4 , and ^{13}C NMR^{2,6} measurements. In other studies, derivatization of various phenols with hexafluoroacetone allowed observation of ^{19}F NMR signals associated with the adducts.^{6,8,9} The ^{31}P nucleus is also suitable for NMR monitoring. The P(V) reagents diethylchlorophosphate and chloro(dimethyl)thiophosphinate have been used for the derivatization of variety of phenols; however, the resonances of the respective aromatic esters spanned regions of only about 1 ppm.¹⁰ In contrast, three P(III) organophosphorus reagents were examined previously in this laboratory, of which 2-chloro-1,3,2-dioxaphospholane appeared to be very promising in terms of widening the chemical shift range to achieve better peak separation.¹¹

In this report, we present preliminary results on the scope and limitations of 2-chloro-1,3,2-dioxaphospholane (**1**)¹² and its 4,4,5,5-tetramethyl analogue (**2**)¹³ as reagents for the derivatization and analysis by ^{31}P NMR spectroscopy of a variety of phenols, aliphatic alcohols, carboxylic acids,



amines, and thiols. In addition, the applicability of both reagents to the identification of components bearing -OH, -NH, and -SH functionalities in coal extracts and pyrolysis condensates is assessed. The condensates were obtained from a low-temperature preheating step intended to modify a chemical leaching process for desulfurization of coal.¹⁴

Experimental

An NMR tube (10 mm) was charged under N₂ with chloroform-d (2.0 mL), chlorophospholane (1, 0.20 mL or 2, 0.25 mL),² and triethylamine (0.31 mL). For qualitative measurements, the standard solutions were reacted at room temperature with model compounds (a drop of liquid or a few crystals of solid). ³¹P NMR spectra were recorded after successive additions of different model compounds until the reagent was almost exhausted. For application to coal-derived materials, approximately 100-200 mg of the coal extracts or pyrolysis condensates were added to the standard solutions, and ³¹P NMR spectra were recorded after 15 minutes.

The extracts and condensates were prepared from an Illinois No. 6 coal. For preparation of the extract, about 1 g of coal was refluxed for 2 hr. with dry pyridine under N₂. The condensate was obtained by pyrolyzing another sample of the same Illinois No. 6 coal at 455° for 45 min. in a protective atmosphere of N₂ and collecting the volatiles condensing in an air-cooled column packed with glass beads. For a 25-g charge of coal, the yield of condensate was about 1-2 g.

Results and Discussion

Regions associated with the ³¹P NMR resonances for representative model phenols, aliphatic alcohols, carboxylic acids, amines, and thiols derivatized with 1 and 2 are shown in Figures 1 and 2, respectively.

Derivatization of phenols with 1 at room temperature afforded the respective 2-aryloxy-1,3,2-dioxaphospholanes instantaneously. Most of these compounds gave ³¹P NMR resonances in a rather narrow region (128.5 to 129.1 ppm). Only derivatives of di-ortho substituted phenols showed signals at lower field (131.0 - 131.5 ppm), with a low-field limit of 136.42 ppm for 2,6-di-*t*-butyl-4-methylphenoxy-1,3,2-dioxaphospholane. With reagent 2, better separation of the ³¹P NMR signals of derivatized phenols (138.0 - 139.7 ppm) and di-ortho substituted phenols (142.9 - 143.7 ppm) was achieved. In these cases, the reaction was completed at room temperature in less than five minutes, except for 2,6-di-*t*-butyl-4-methylphenol which did not react at all, presumably because of its bulky nature.

Carboxylic acids rapidly reacted with 1 and 2 to give derivatives displaying ³¹P NMR signals between 127.4 and 129.5 ppm, and between 134.8 and 136.2 ppm, respectively. Although the sets of resonances for phenols and

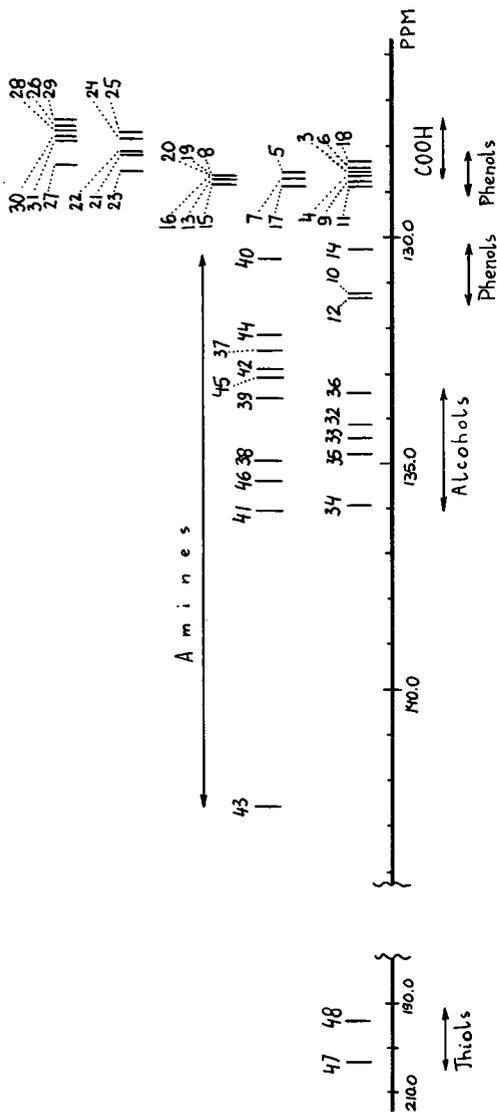


Figure 1. ^{31}P NMR chemical shifts (in ppm relative to 85% H_3PO_4) for selected model compounds derivatized with 2-chloro-1,3,2-dioxaphospholane (1) [secondary standard: $\delta(3\text{ip})$ 175.90 ppm].

PHENOLS: 3, phenol, 128.59; 4, o-cresol, 128.70; 5, m-cresol, 128.60; 6, p-cresol, 128.53; 7, 2,3-xyleneol, 128.74; 8, 2,4-xyleneol, 128.64; 9, 2,5-xyleneol, 128.81; 10, 2,6-xyleneol, 131.30; 11, 2,3,5-trimethylphenol, 128.90; 12, 2,4,6-trimethylphenol, 131.42; 13, 3,4,5-trimethylphenol, 128.72; 14, catechol, 130.30; 15, resorcinol, 128.83; 16, p-methoxyphenol, 128.62; 17, 2-methylresorcinol, 128.95; 18, p-methoxyphenol, 128.37; 19, α -naphthol, 128.63; 20, β -naphthol, 128.62.

AROMATIC ACIDS: 21, benzoic, 128.24; 22, p-toluic, 128.19; 23, m-phthalic, 129.54; 24, 2,5-dihydroxybenzoic, 127.89; 25, 2,4,6-trimethoxybenzoic, 127.71. ALIPHATIC ACIDS: 26, oleic, 127.56; 27, mandelic, 128.47; 28, succinic, 127.63; 29, 3,3-dimethylglutaric, 127.47; 30, indole-3-acetic, 127.77; 31, trans-cinnamic, 127.93.

ALIPHATIC ALCOHOLS: 32, isoamyl, 134.10; 33, benzyl, 134.45; 34, menthol, 135.93; 35, benzhydrol, 134.70; 36, triphenylcarbinol, 133.41.

AMINES: 37, aniline, 132.55; 38, o-toluidine, 134.92; 39, anthranilic acid, 133.56; 40, diphenylamine, 130.46; 41, proline, 136.10; 42, 4-methylpiperidine, 137.80; 43, 2,6-dimethylpiperidine, 142.60; 44, 4-methylpiperazine, 137.17; 45, carbazole, 133.10; 46, indole-3-acetic acid, 135.37. THIOLS: 47, 1,3-propanedithiol, 203.12; 48, benzenedithiol, 194.28.

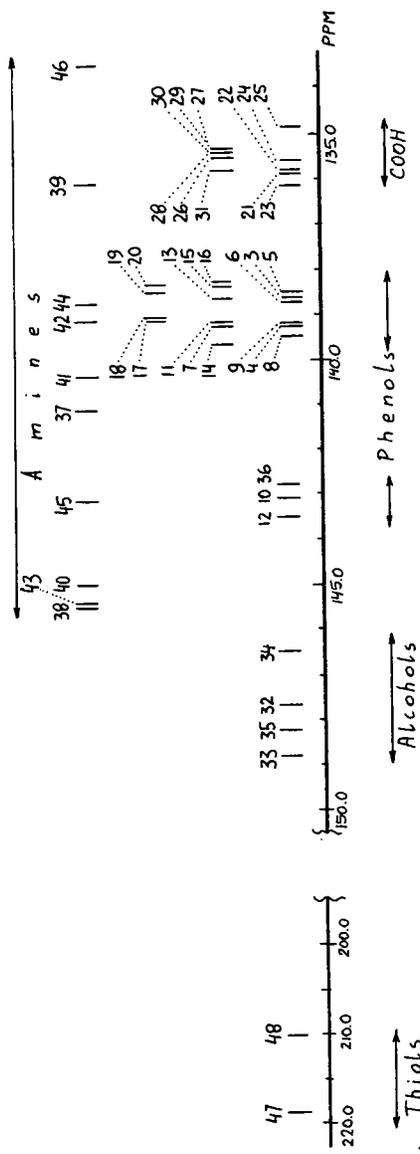


Figure 2. ^{31}P NMR chemical shifts (in ppm relative to 85% H_3PO_4) for selected model compounds derivatized with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (2) [secondary standard $\delta(31\text{P})$ 175.90 ppm].

PHENOLS: 3, phenol, 138.70; 4, o-cresol, 139.29; 5, m-cresol, 138.60, 6, p-cresol, 138.83; 7, 2,3-xyleneol, 139.29; 8, 2,4-xyleneol, 139.52; 9, 2,5-xyleneol, 139.21; 10, 2,6-xyleneol, 143.04; 11, 2,3,5-trimethylphenol, 139.21; 12, 2,4,6-trimethylphenol, 143.55; 13, 3,4,5-trimethylphenol, 138.68; 14, catechol, 139.71; 15, resorcinol, 138.44; 16, m-methoxyphenol, 138.33; 17, 2-methylresorcinol, 139.14; 18, p-methoxyphenol, 139.08; 19, α -naphthol, 138.54; 20, β -naphthol, 138.36.

AROMATIC ACIDS: 21, benzoic, 135.89; 22, p-toluic, 135.81; 23, m-phthalic, 136.17; 24, 2,5-dihydroxybenzoic, 135.62; 25, 2,4,6-trimethoxybenzoic, 134.91. **ALIPHATIC ACIDS:** 26, oleic, 135.51; 27, mandelic, 135.41; 28, succinic, 135.49; 29, 3,3-dimethylglutaric, 135.43; 30, indole-3-acetic, 135.48; 31, trans-cinnamic, 135.80; 32, isoamyl, 147.76; 33, benzyl, 148.80; 34, menthol, 146.53.

ALIPHATIC ALCOHOLS: 35, benzhydrol, 148.24; 36, triphenylcarbinol, 142.82. **AMINES:** 37, aniline, 141.19; 38, o-toluidine, 145.56; 39, anthranilic acid, 136.14; 40, diphenylamine, 145.00; 41, proline, 140.41; 42, 4-methylpiperidine, 139.15; 43, 2,6-dimethylpiperidine, 145.48; 44, 4-methylpiperazine, 138.75; 45, carbazole, 143.14; 46, indole-3-acetic acid, 133.46. **THIOLS:** 47, 1,3-propanedithiol, 217.85; 48, benzenethiol, 210.31 ppm.

carboxylic acid derivatized with 1 were partially superimposed, good separation of these regions was observed when 2 was used as the derivatizing reagent.

Aliphatic hydroxy functionalities can also be analyzed by ^{31}P NMR spectroscopy after derivatization with the reagents 1 and 2. Alkoxyphosphites derived from 1 presented ^{31}P NMR signals between 133.4 and 136.0 ppm, while those obtained from 2 revealed absorptions from 146.4 to 148.8 ppm, with exception of derivatives of tertiary alcohols (triphenylcarbinol and t-butanol) which resonated far upfield (both at 142.8 ppm). In both cases the regions of absorptions for derivatized aliphatic alcohols are well separated from those of phenols and carboxylic acids.

^{31}P NMR resonances of amines derivatized with reagents 1 and 2 are widely spread, overlapping regions represented by aliphatic alcohols, phenols and carboxylic acids. On the other hand, ^{31}P NMR signals of compounds having the P-N bond are significantly broader than those from other derivatives, thus making their assignment to amines easy.

The few thiols examined showed that the ^{31}P NMR signals for their reaction products with 1 and 2 (190 to 210 ppm and 210 to 220 ppm, respectively) are downfield from the regions observed for phenols and aliphatic alcohols. Thus, the technique shows good promise for identification of SH-bearing groups.

Derivatization of a low-temperature pyrolysis condensate from Illinois No. 6 coal with 1 and 2 revealed the almost exclusive presence of a variety of phenols (Figures 3 and 4, respectively). In addition, residual quantities of aliphatic hydroxyl groups were detected at 135 - 135.5 ppm and 147 - 148 ppm, respectively. No carboxylic acids were found, however. An identification of phenols was carried out by the addition of selected authentic compounds to the derivatized condensate containing an excess of 2. This procedure allowed us to tentatively assign most of the prominent signals to specific substituted phenols (Figure 4). The presence of such a variety of phenolic compounds is consistent with the well-documented role that phenols play during low-temperature pyrolysis of coal.^{15,16}

A pyridine extract of Illinois No. 6 coal was derivatized with both reagents to give deep-brown opaque solutions. Examination of these solutions by ^{31}P NMR spectroscopy showed broad absorptions (Figures 5 and 6), which revealed the presence of mostly phenols (at 138-140 ppm), together with a small amount of di-ortho substituted phenols (at about 143 ppm). In addition, significant amounts of carboxylic acids were found in the extract at 135-136 ppm. Identification of particular phenolic and/or acidic components was precluded by the breadth of signals. Furthermore, the extract derivatized with 1 displayed apparently significant amounts of aliphatic OH functionalities (at about 135 ppm), while the extract derivatized with 2 showed only a relatively small quantity of this functionality. This contradictory result is currently under further investigation.

Conclusions

Reagents of the type 1 and 2 provide improved ^{31}P chemical shift dispersion for compounds derived from carboxylic acids, phenols, alcohols, amines, and thiols. Therefore, they offer considerable promise for the

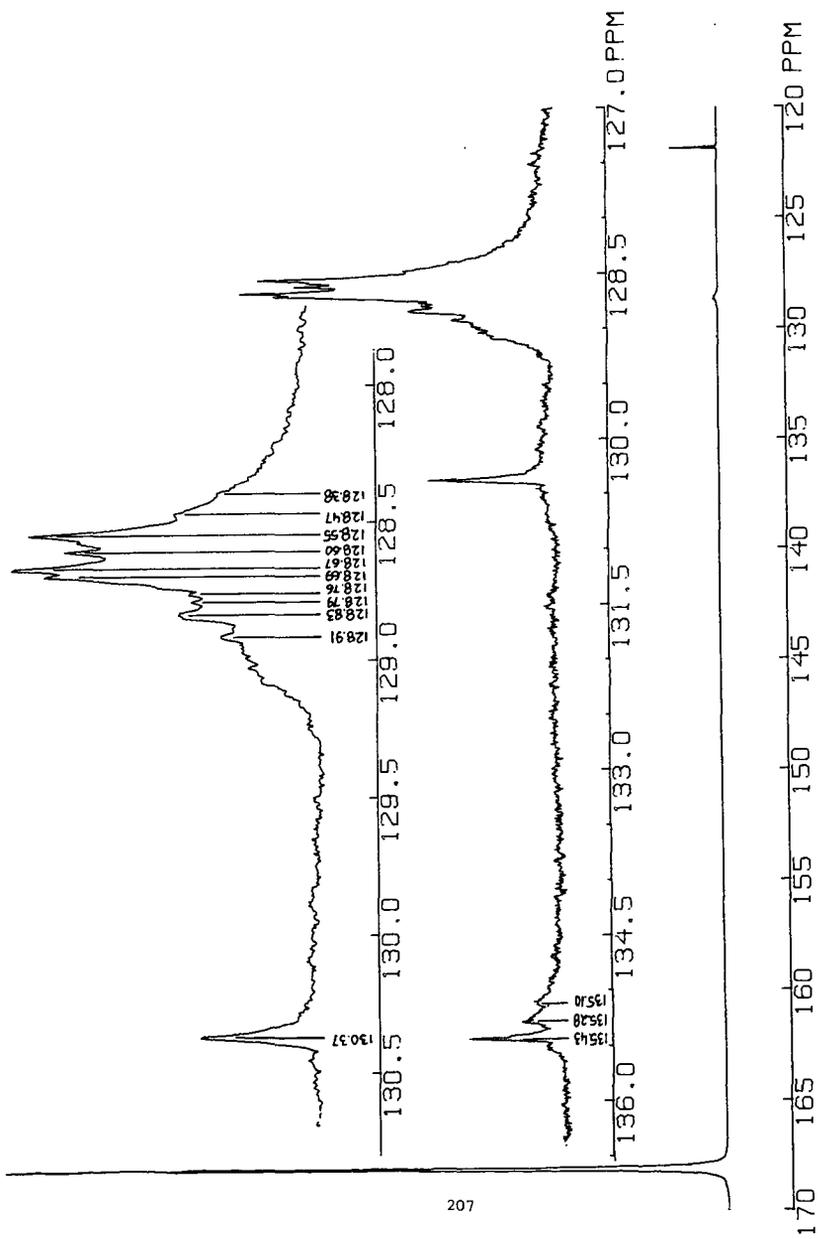


Figure 3. ^{31}P NMR spectrum of low-temperature pyrolysis condensate of Illinois No. 6 coal derivatized with **1**.

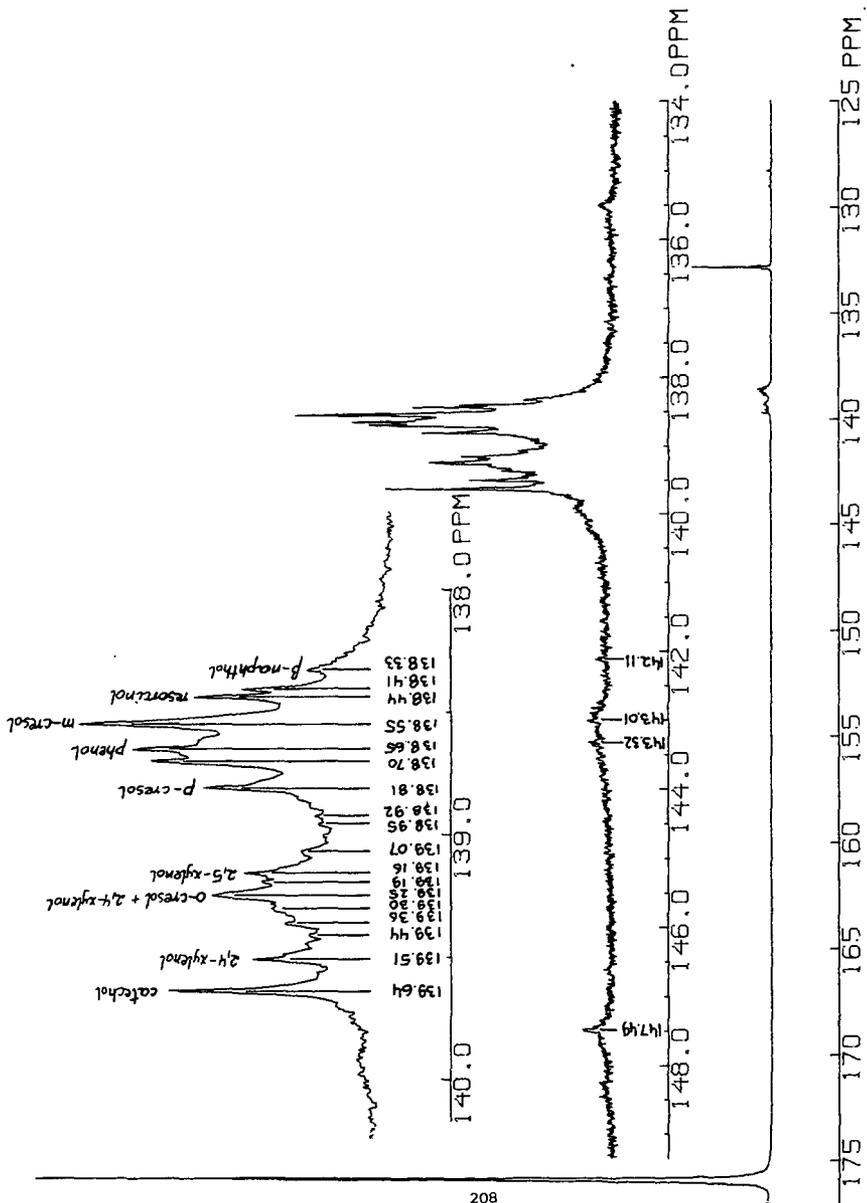


Figure 4. 31P NMR spectrum of low-temperature pyrolysis condensate of Illinois No. 6 coal derivatized with 2.

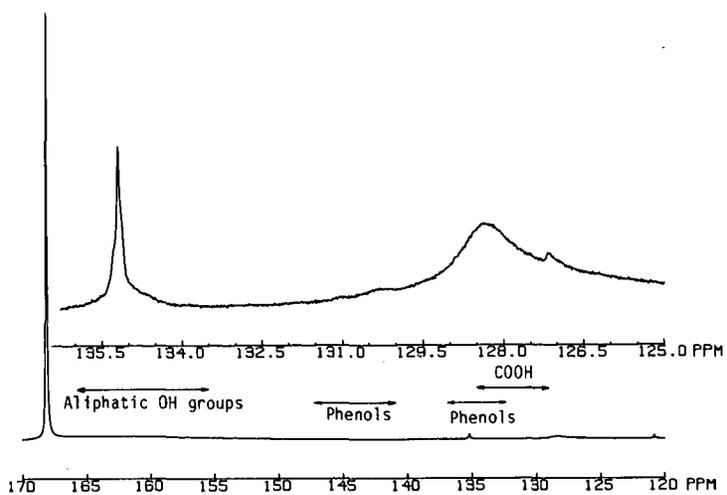


Figure 5. ^{31}P NMR spectrum of a pyridine extract of Illinois No. 6 coal derivatized with 1.

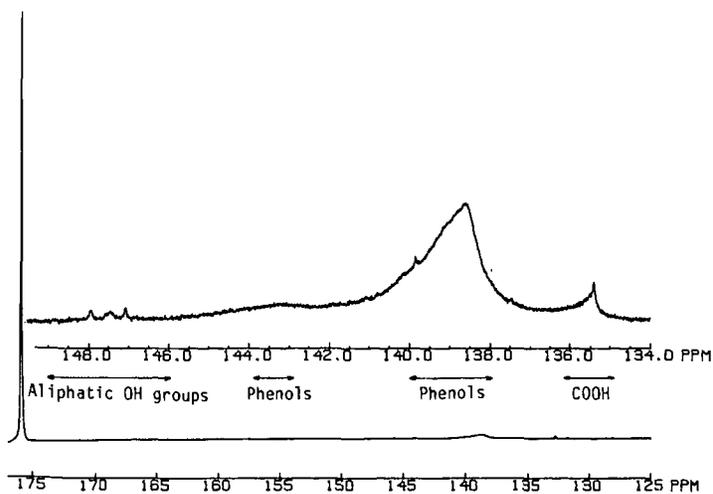


Figure 6. ^{31}P NMR spectrum of a pyridine extract of Illinois No. 6 coal derivatized with 2.

identification (and possibly quantification) of coal-derived organic moieties bonded to -OH, -NH, and -SH functionalities. Such a capability will be extremely useful in characterizing coal extracts, pyrolysis condensates, and liquefaction products.

Acknowledgements

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