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FUNCTIONAL GROUP ANALYSIS IN COAL BY ^{31}P NMR SPECTROSCOPY

FOSSIL ENERGY QUARTERLY REPORT
October 1, 1988 - December 31, 1988

J. G. Verkade

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Iowa State University
Ames, Iowa 50011-3020

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ABSTRACT

Two reagents from a list of eleven were selected for the quantitative and qualitative ^{31}P nmr analysis of a substantial number of phenols in an Illinois No. 6 low-temperature pyrolysis condensate. In the course of our reagent evaluation, a promising lead for an improved reagent containing selenium was discovered. Preliminary results on the application of our ^{31}P nmr tagging technique to a solid carboxylic acid are discussed.

DEVELOPMENT OF INSTRUMENTAL TECHNIQUES FOR SURFACE ANALYSIS: FUNCTIONAL GROUP ANALYSIS IN COAL BY ^{31}P NMR SPECTROSCOPY

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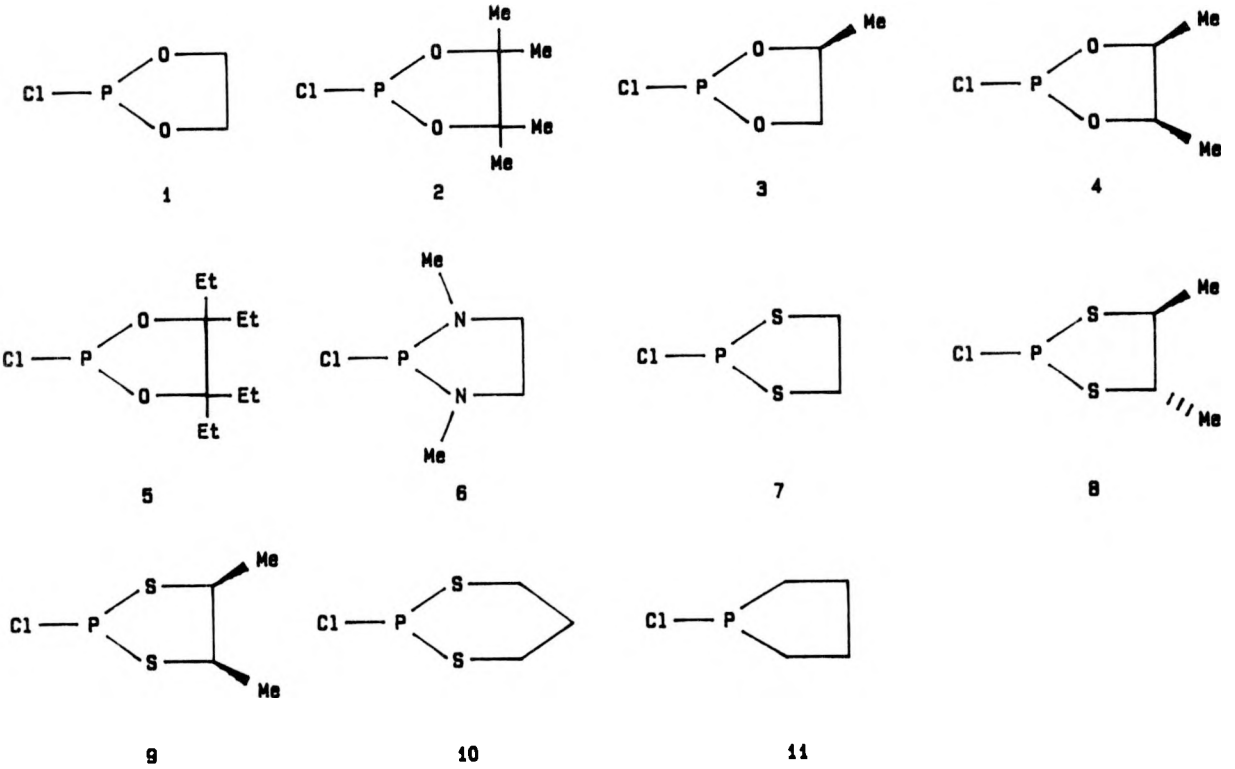
Ames Laboratory, Iowa State University

OBJECTIVE

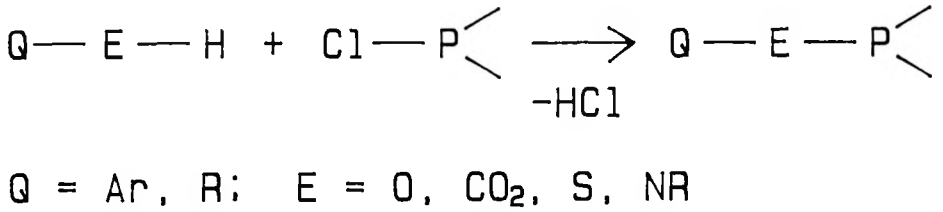
The primary aim of our research is to develop a convenient, sensitive, reliable and rapid technique for the qualitative and quantitative analysis of -COOH, -OH, -NH and -SH functionalities in coal, on coal surfaces, and in coal-derived materials such as condensates and extracts.

INTRODUCTION

To achieve the above objective, we evaluated earlier this year, compounds **1-11** as reagents for tagging labile hydrogen functional



groups in coal liquids according to reaction (1). The 100% naturally abundant ^{31}P atom in these tags displays an nmr chemical shift that is



(1)

Q = Ar, R; E = O, CO_2, S, NR

sensitive not only to the type of functional group to which it is attached, but also to the organic substituent Q. From our extensive studies on model compounds, these chemical shift sensitivities appear to be greatest when the phosphorus atom is part of a five-membered phospholane ring rather than an open-chain or six-membered ring system. For reasons not yet clearly understood, this chemical shift sensitivity is particularly great when the five-membered ring system contains two oxygen heteroatoms adjacent to the phosphorus (**1-5**) or two sulfur atoms (**7-9**). Among these reagents, **2** and **7** are optimum in that **7** provides good separations of the chemical shift ranges for mixtures of alcohols and thiols. However, with this reagent, the chemical shift ranges for phenols and acids that may be present would overlap. On the other hand, **2** as a reagent exhibits excellent separation of the acid and phenol chemical shift ranges, and there is only partial overlap of the alcohol and phenol ranges. Thus, model compound mixtures containing alcohols, thiols, acids, and phenols can be qualitatively analyzed by using **2** and **7** in separate nmr analyses of a given mixture of this type. Moreover, since the ^{31}P

chemical shifts for a specific Q-E moiety in reaction 1 are different for the two reagents, an independent check on the indentities of Q and E exists. Using this newly developed technique, we have qualitatively analyzed an Illinois No. 6 low-temperature condensate. Some of the results of this phase of our studies have been published recently.[1,2]

The above experiments paved the way for accomplishing one of the two December 1988 milestones as set out in the September 1988 FWP document, namely, the quantitative analysis of coal condensates with reagents of choice. In the following section, the results of this effort are summarized, as well as our attempts to achieve the second December 1988 milestone, i.e., the determination of ^{31}P nmr chemical shifts of solid model compounds derivatized with our reagents of choice.

ACCOMPLISHMENTS

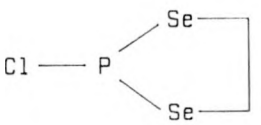
Before any quantitative analyses of a coal condensate were attempted, we deemed it necessary to identify qualitatively as many of the components as possible of such a mixture. While this had been accomplished earlier in the year for the chloroform-soluble fraction of an Illinois No. 6 low-temperature condensate with reagent **2**,[1] it was necessary to repeat this experiment with reagent **7**, which was one of the last reagents in the series to be synthesized and purified. The ^{31}P spectrum for this condensate with reagent **7** is shown in Figure 1. From our model compound studies it was possible to identify a substantial number of the phenols present in this highly complex mixture. Also present in the sample is water which gives a product with a chemical shift of 152.4 ppm. Thus, a side benefit of our

technique is the rapid and quantitative analysis of moisture in coal liquids. Interestingly, Figure 1 reveals that when the phenols derivatized with **7** bear substituents in both ortho positions, then the corresponding ^{31}P chemical shifts occur in a region separated from those phenols bearing only one or no such substituent.

For the quantitative analysis of a mixture by nmr means, it was first necessary to establish the experimental conditions for best absorption peak integration. Because of the relatively long T_1 relaxation times which we measured in a series of model compounds derivatized with **2** and **7** (5-10 sec.), the addition of a relaxation agent such as $Cr(acac)_3$ was required. This allowed reasonably short nmr pulses to be employed and good spectra were obtained with approximately 1M solutions under broad-band decoupling conditions.

Tables I and II list our data for the quantitative analysis of an Illinois No. 6 condensate using reagents **2** and **7**, respectively. It is clear that more work needs to be done in this area since there is considerable overlap of the peaks, leading to overestimates of some of the components. This is especially true in the case of **2**. The next step is to employ nmr peak deconvolution programs to obtain more realistic peak intensities. If such experiments are successful, analyses presently in the ±5% accuracy range should give rise to approximately ±1% accuracies.

As noted in the Introduction, there is a dramatic improvement in the separation of the ^{31}P nmr chemical shift ranges for the various functional groups from reagent **2** to reagent **7**. We also observed that substitution on the ring carbons of **7** (i.e., **8** and **9**) did not improve these separations. It appears that the main reason for the better performance of reagent **7** over **2** is the change of the heteroatom from oxygen to sulfur. This suggests that the increased polarizability of sulfur renders it more susceptible to small hybridizational variations induced by changes in the Q and E groups in reaction 1. This sensitivity of the sulfur to a remote chemical environment may be heightened by the electronic and steric restrictions imposed by the five-membered ring in **7**. The resultant electronic polarizations on sulfur are then registered as substantial chemical shift differences on the adjacent ^{31}P nucleus. This suggests that reagents **12** or possibly **13**, which contain the even more polarizable selenium atom, will constitute a further improvement in reagent properties. To our knowledge, neither of these compounds exist currently.



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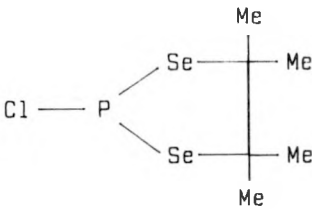

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Because of milestone commitments, we were deterred from pursuing this new avenue. We believe this to be a promising lead, however, because it would further our understanding of the origins of ^{31}P chemical shifts (a worthy goal in itself) and thus provide a more rational approach to selecting a reagent with the best chemical shift

resolution. Furthermore, the ^{77}Se isotope has a natural abundance of 7.5% and nuclear spin of 1/2. Thus, reagent **12** (or **13**, which may be easier to synthesize) would provide additional nmr information with which to characterize and identify Q and E in reaction 1. It should also be noted that if a reagent better than **2** and **7** can be found, only one reagent may be necessary for analyses of coal-derived liquids.

While we have preliminary data on our second milestone for December 1988, technical difficulties and time constraints have slowed our progress here. We reacted a carboxylic ion exchange resin with reagent **2** and recorded its solid state cross-polarized magic angle spinning ^{31}P nmr spectrum. Although we detected ^{31}P nmr peaks attributable to derivatized water (moisture in the resin) and excess reagent, the spectrum exhibited no peaks in the carboxylic acid region. It is possible that our first attempts at preparing samples of this type were faulty and/or the resin sample (which had been used in previous ion exchange experiments) was not properly regenerated. We will repeat this experiment with a variety of model solid substrates and also conclude the quantitative studies on coal condensates as soon as a replacement postdoctoral can be found for Dr. Lensink.

CONCLUSIONS

- Reagents **2** and **7** function well in the qualitative and quantitative analysis of labile-hydrogen functional groups in coal condensates.

- Reagent **12** and/or **13** may prove to be reagents with better peak-resolving powers. This would be advantageous not only for coal liquids but also for coal solids, for which solid state nmr peaks are typically broader than for solution absorptions.

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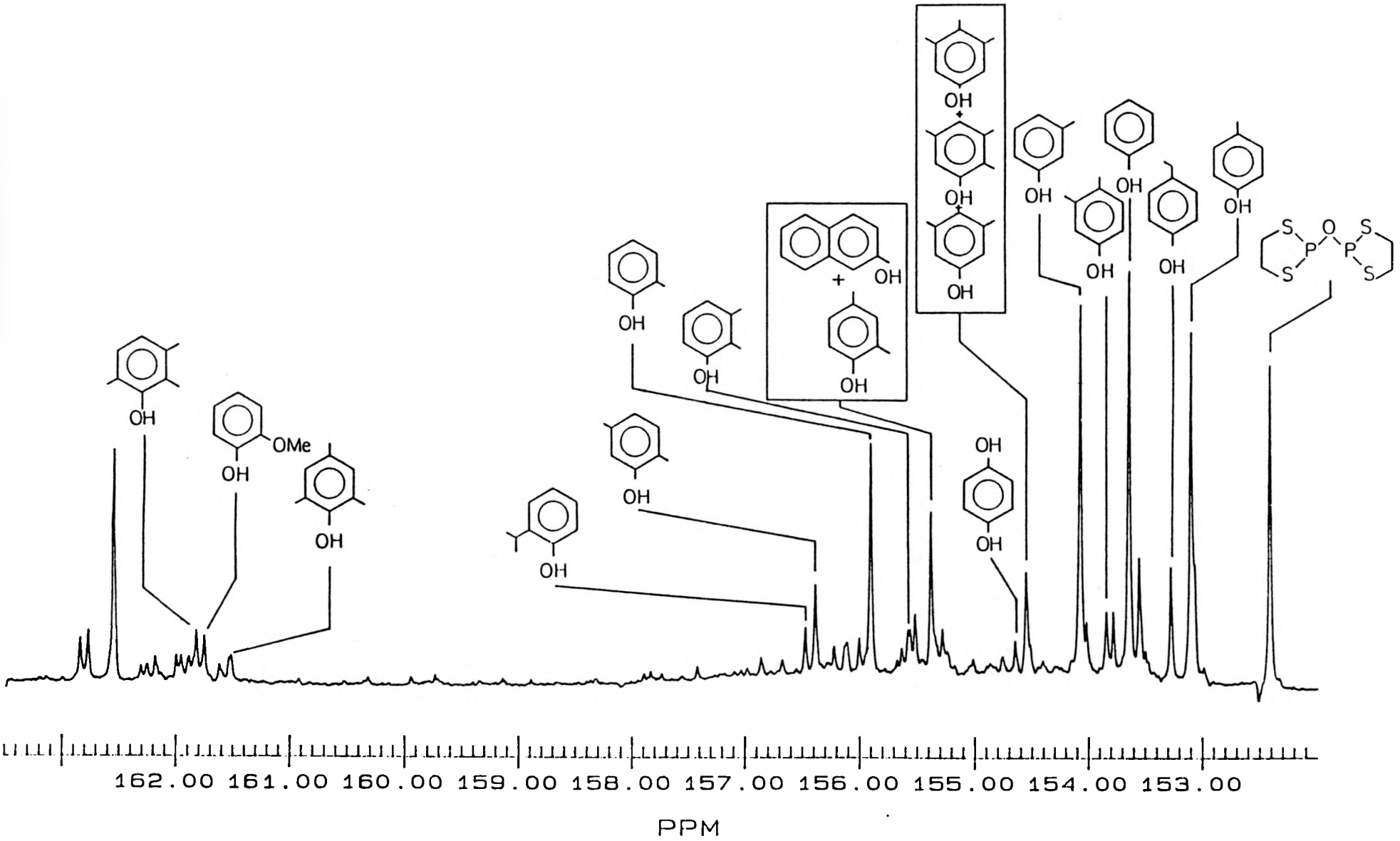

Figure 1. ^{31}P nmr spectrum of Illinois No. 6 coal low-temperature pyrolysis condensate derivatized with **7**.

Table I. Quantitative Analysis of an Illinois No. 6 Coal Low-Temperature Pyrolysis Condensate Derivatized with Reagent **2**.[a]

Compound	mmol	mg	Weight % in Sample
2,4,6-trimethylphenol	1.84	0.25	0.18
2,6-dimethylphenol	4.47	0.55	0.39
catechol	9.45	1.04	0.75
2,4-xylenol	24.68	3.02	2.16
o-cresol + 2,3-xylenol	68.13	7.37[b]	5.28
p-cresol	38.71	4.19	3.00
phenol	72.68	6.84	4.91
m-cresol	55.19	5.97	4.28
3,5-xylenol	21.56	2.63	1.89
l-menthol (standard)	90.23	14.1	standard

[a] 5 mol % $Cr(acac)_3$, number of runs = 10000, relaxation delay = 0.5 sec.

[b] Calculated as o-cresol.

Table II. Quantitative Analysis of an Illinois No. 6 Coal Low-Temperature Pyrolysis Condensate Derivatized with Reagent 7.[a]

Compound	mmol	mg	Weight % in Sample
p-cresol	0.0383	4.1	1.5
p-ethylphenol	0.0124	1.5	0.5
phenol	0.0537	5.0	1.8
m-cresol	0.0427	4.8	1.7
3,5-dimethylphenol 2,3,5-trimethylphenol 3,4,5-trimethylphenol	0.0178	2.4[b]	0.9
2-naphthol 2,4-dimethylphenol	0.0564	8.1[c]	2.9
o-cresol	0.0240	2.6	0.9
o-isopropylphenol	0.0207	2.8	1.0
2,3,6-trimethylphenol	0.0114	1.6	0.6

[a] Internal standard = $P(OAr)_3$ (Ar = 2,6 dimethylphenyl), 5 mol % $Cr(acac)_3$, number of scans = 1000, relaxation delay 3 sec., broad band decoupling.

[b] Calculated as dimethyl phenol.

[c] Calculated as 2-naphthol.

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