# FINAL TECHNICAL REPORT

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Project Title: VHF EPR Determination of the Chemical Forms of Organic Sulfur in Coal

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## ABSTRACT

Very High Frequency Electron Paramagnetic Resonance (VHF EPR) spectroscopy has demonstrated the ability to observe organic sulfur in coal. We have constructed a unique VHF EPR instrument operating at the W-band (96 GHz), one of only four such instruments in the world, and the only one studying coal. We are employing this instrument, as well as collaborating with scientists at Cornell University, who have a 250 GHz spectrometer, to develop a clearer understanding of the relationships between the VHF EPR spectra we observe from Illinois coal and the organic sulfur species present in it.

Efforts in the first Quarter concentrated on three areas: recruitment of a postdoctoral fellow to join the coal research team, work on improving the W-band spectrometer, and studies of vitrinite, sporinite, and fusinite macerals at G-band (250 GHz). The first report showed that progress had been made in all areas, and discussed in detail the main features of the W-band instrument. Testing and comparison with the other four instruments in existence that can operate in this frequency range (90 - 250 GHz) showed it to have the highest sensitivity. Preliminary analysis of the 250 GHz data on macerals obtained by density gradient centrifugation from an Illinois #6 coal gives the first indication that at the very highest frequencies, there may be a separation of the heteroatom VHF EPR signals into a sulfur and an oxygen-containing component.

Work in the second Quarter was concerned with three main areas: (i) synthesis and analysis of model systems for thiophenic sulfur species in coal; (ii) VHF EPR of inertinites from an Illinois #6 coal, as well as evaluation of the sensitivity of the signals from this maceral to oxygen; (iii) VHF EPR of iodinated coal. The third Quarter continued the synthesis and analysis of model systems for thiophenic sulfur species in coal and the VHF EPR of inertinites from an Illinois #6 coal, particularly the effects of NO on this signal as described in the work plan. VHF EPR of coal subjected to PCE extraction and low-temperature pyrolysis, and preliminary interpretation of the spectra from these samples and implications for desulfurization effectiveness.

In the fourth Quarter, further studies using novel model heterocyclic aromatic radical compounds containing oxygen and sulfur showed that VHF EPR spectra could resolve differences not only between oxygen and sulfur, but also the extent of delocalization of the electrons within these compounds. These observations not only indicate that there is a possibility of identifying the heterocyclic aromatic molecules in coal, where most of the organic sulfur is located. In addition, theoretical considerations lead to a coherent model predicting that increased delocalization of heteroatom spin density over a larger molecular frame-work leads to reduced spin-orbit coupling.

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# EXECUTIVE SUMMARY

This program addresses the need for innovative approaches to characterize the organic sulfur in Illinois Basin coals. With support from the CRSC, the U. S. DOE, the Petroleum Research Fund (ACS) and the National Institutes of Health, we have developed a very high frequency electron paramagnetic resonance (EPR) spectrometer operating at the W-band of microwave frequencies (96 GHz), one of only three such instruments in the world, and the only one in the U.S.A. This instrument has shown unique sensitivity to heteroatoms in coal, and we believe the technique can be successfully applied for the **non-destructive, direct determination of organic sulfur in coal.** Preliminary data from Illinois coals and separated macerals indicate that **the method also may be able to distinguish aromatic from aliphatic sulfur, and may be useful in assessing the extent of conjugation in aromatic portions of the coal.** The only other currently existing method that has been used in an attempt to do this is EXAFS, NEXAFS, and XANES [3]. These high energy spectroscopic techniques, however invariably suffer from the fact that they are not truly non-destructive. By contrast, the low powers and relatively low energy radiation used in magnetic resonance techniques have virtually no effect on the physical structure or chemical composition of coal.

Our approach utilizes the naturally occurring unpaired electrons in coal as probes of their environment. Effects of neighboring atoms on the magnetic energy levels of the electron are reflected in changes in the EPR spectrum, and from this data, conclusions about the structure of the coal can be made. In the case of sulfur, the strongest interaction between the unpaired electron and S atoms usually is the spin-orbit (SO) coupling, which changes the value of the external magnetic field needed to cause the unpaired electron to resonate (absorb energy) in the presence of microwave radiation. The spectrometer records this sulfur-induced shift in the position of the EPR resonance, and it becomes a signature for the presence of organic sulfur. Because unpaired electrons are naturally occurring in all coal, and because few other species in coal give rise to EPR signals (and none in the region of the organic free electrons), the technique is non-destructive and very sensitive. While this spectrometer is being used for exploratory research with model systems, requiring the most precise spectroscopy and utmost care in sample handling, the experiments are quite time-consuming. However, when used routinely for specimen analysis and testing, this technique is relatively quick; a typical EPR spectrum of coal on the W-band instrument can take less than a minute to record.

There are a very few EPR spectrometers in existence which operate at high microwave frequencies. Some of these are discussed in a review by Belford et. al.[1]. Prior to this work, the rather simple resonance lineshapes at 9 and 35 GHz represented the state-of-the-art for the EPR of coal. Over the last three years a unique instrument has been built and developed. It now incorporates several important technical innovations that make it well-suited for the present research work. A detailed description of the instrument is included in the first quarter report and published elsewhere [2]. Few G- and W- band VHF EPR spectrometers have been constructed by individual groups for specialized purposes; moreover, they are not available to the general scientific public. Therefore, in coordination with the Illinois EPR Research Center (IERC) we have constructed and tested a general-purpose publicly accessible W-band (94GHz, 3mm waves) cw EPR Spectrometer at IERC. With it we have obtained spectra of various samples, including pure and mixed spin labels in aqueous and nonaqueous solutions, organic radicals in coal macerals [2-10], organometallic chelates (a polycrystalline and a very small single crystal sample), and several model compounds (typically free radicals of extracts from coal) under a variety of conditions.

In order to illustrate our method, consider Figure 1, which shows EPR spectra of an Illinois #6 whole coal taken at three different microwave frequencies: 9, 35, and 96 GHz. The rather simple resonance lineshapes at 9 and 35 GHz represent the state-of-the-art for the EPR of coal before the
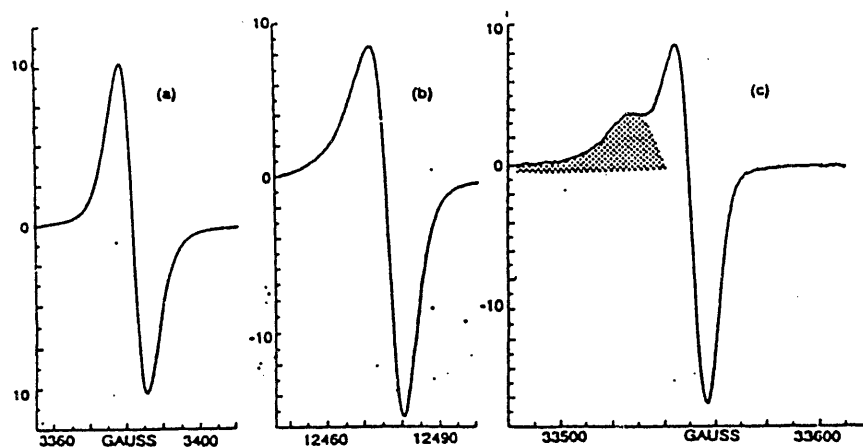


Figure 1. EPR spectra of a whole Illinois #6 coal taken at (a) 9 GHz, (b) 35 GHz, and (c) 96 GHz [2]. Highlighted portion of (c) is due to S (and perhaps O).

construction of our 96 GHz instrument. In these lower frequency spectra, sulfur atoms are shifting a portion of the EPR resonance, but the shift is too small to be resolved. The key to resolution of the effects of sulfur is higher field strengths (and higher frequencies). Thus, at 96 GHz, we see an EPR spectrum with two peaks. The resonance occurring at lower field strength, which is highlighted in Figure 1(c), is due to heteroatoms, and we have strong evidence that it is largely the result of organic sulfur. The goals of our current work have focused on developing a better understanding of the molecular forms of organic sulfur that are responsible for these spectra. To that end, a number of coals, inertinites, chars, and model thiophenic compounds have been studied using the W-band spectrometer under a variety of conditions.

In collaboration with Professor Jack Freed at Cornell University, VHF EPR study of coal on one of the highest frequency instruments in the world, the Cornell G-band (250 GHz) spectrometer was undertaken. This further 2.5-fold increase in $B_0$ produced even better resolution in the spectra, with only modest increases in spectral linewidth, as the spectra in Figure 1 illustrate. VHF EPR spectra at least one other higher frequency was necessary primarily to confirm field dependent parameters measured at W-band were not the result of multiple unresolved species. In addition to separated maceral samples, G-band spectra were observed from perylene cation radicals formed on a silica-alumina catalyst. This system has served us well as a model for the purely hydrocarbon aromatic component in coal, and was used in conjunction with dibenzothiophene (DBT+) to develop a simple, two-compound picture for analyzing W-band spectra from an Illinois #6.

Comparison of G-band spectra from vitrinite and perylene (+) reveal a possible third component to the VHF EPR signals from coal, namely contributions from oxygen-containing aromatic compounds. This third component does not interfere with the lower field signal from aromatic sulfur, but does potentially answer the nagging question concerning the missing oxygen heteroatom effect in our earlier, two-compound picture. Thus, G-band experiments give preliminary evidence that VHF EPR spectra can report on sulfur *and* oxygen-containing aromatic compounds in coal, as well as on purely hydrocarbon aromatics. These experiments at 250 GHz will certainly help us to better interpret coal spectra more routinely obtained at 96 GHz, and they point to the opportunity which higher field techniques hold for the study of fossil fuels.

Because the information about the amount and chemical forms of organic sulfur in coal contained in VHF EPR spectra is new, it is very important that we develop correct interpretations of these data. For this reason, we continued this quarter to pursue the chemistry of synthetic thiophenic systems which mimic the properties of aromatic organic sulfur in coal. We discovered that an impurity in the dibenzothiophene sample obtained from Aldrich was responsible for small but observable secondary peaks in our spectra. The virtual elimination of these peaks with a very highly purified preparation of DBT+ now has convinced us that our method of preparation utilizing boric acid glass matrix isolation of the compounds followed by UV irradiation is producing only the cation radical species we desire, with no di-radical formation. We also have begun to develop synthetic methods for producing radical preparations of smaller sulfur compounds (thiophene, benzothiophene) which are more reactive and harder to form from parent compounds. The goal of Phase II work continues to be the elucidation of relationships between molecular structure and VHF EPR spectra that will allow us to make more accurate and insightful interpretations of the data from coal. Towards this end, a variety of compounds have been studied in this work. A representative sample of model compounds studied are shown in figure 2. All these compounds can be extracted from coal in large quantities, and in many cases are in fact commercially prepared from coal extracts.



**Benzo[*b*]naphtho[*2,1-d*]thiophene(BNT)**     **Dibenzothiophene(DBT)**

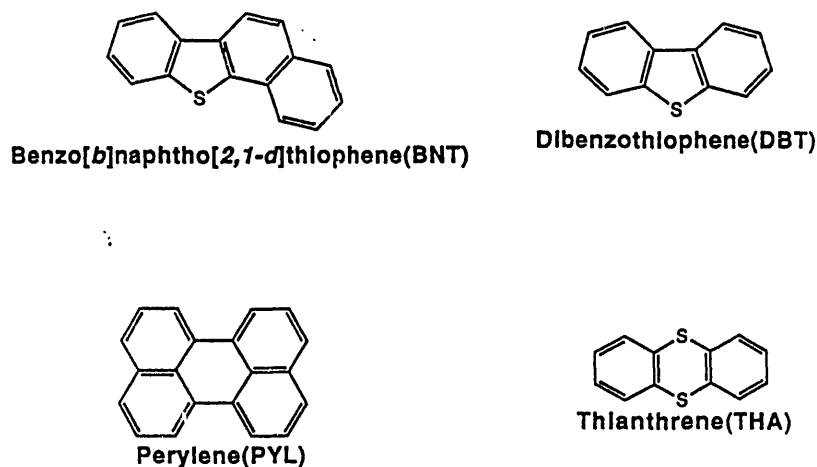**Perylene(PYL)**     **Thianthrene(THA)**

Figure 2. A representative group of the many samples which have been studied in this work. The oxygen heteroatom analogs of these compounds have also been studied.

In the second Quarter, two successful synthetic routes for the creation of radical systems that can serve as models for aromatic organic sulfur species in coal were developed. These preparative methods were used to synthesize the cation radicals of dibenzothiophene (DBT+), benzonaphthothiophene (BNT+), and dibenzofuran (DBF+), and we have examined them by VHF EPR. Figure 3 shows the spectra from DBT+ and BNT+. Differences in the g-anisotropy in these two compounds is believed to arise from differences in the nature of the spin-orbit (SO)
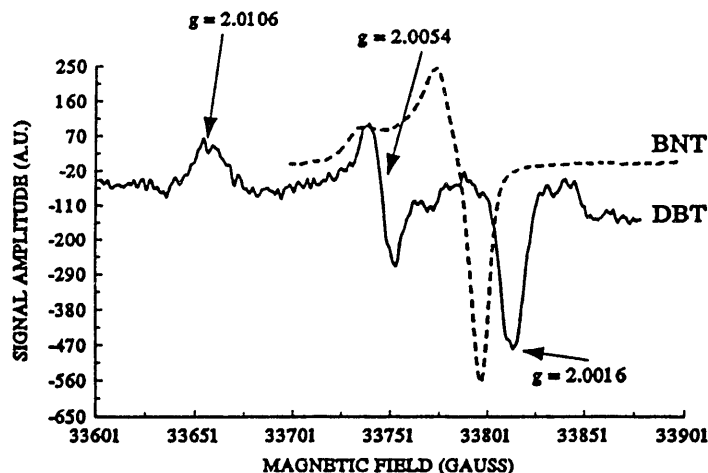


Figure 3. VHF EPR spectra of DBT+ (solid line) and BNT+ (dashed line) in boric acid glass.

coupling between the unpaired electron in the radical and sulfur, just as we believe occurs in high-sulfur coal. The analysis of such spectra, particularly from the standpoint of the dependence of SO coupling on the aromatic cluster size, is an important step in our work to understand the exact nature of the VHF EPR spectra from organic sulfur in coal.

A careful physical characterization of the effects of oxygen on the VHF EPR spectra of fusinite separated from an Illinois #6 coal was also developed in the second quarter. This phenomenon can be explained adequately by spin exchange theory. The spectra of inertinites, and especially fusinite, were very sensitive to the presence of gas-phase oxygen, and we showed data demonstrating that these effects are predictable, reproducible, and potentially useful as a means of assessing the extent of oxygenation of solid coal samples. In order to determine if these effects could be produced by other gases, we subjected fusinite samples to a variety of gas atmospheres, including strongly oxidizing ($F_2$) and non-reactive (He, $N_2$) gases. No major effects were noted from any of these treatments. Introduction of NO, another paramagnetic gas, did produce EPR linewidth increases, and we have calibrated this effect. The kinetics of formation of NO in an aqueous reaction were followed, and the results compare exactly with those predicted by chemical kinetic data. Finally, the EPR linewidth broadening produced by NO could be reversed by the introduction of $O_2$, indicating that the two reactive gases had combined to produce diamagnetic products ($O_2$ + NO → diamagnetic products). The implications of this discovery for the VHF EPR technique include making sure that all samples are well-evacuated prior to measurement.

In the third quarter, we began to apply our VHF EPR method to the determination of effects of desulfurization on Illinois coals. The first techniques for which we have "before and after" samples are perchloroethylene (PCE) extraction and low-temperature pyrolysis. Figures

4(a) and 4(b) show spectra from these systems. What is immediately apparent is that in the case of PCE extraction, very little change was produced in the EPR spectra, indicating that the extraction was not effective in removing the aromatic, organic sulfur to which our technique is sensitive. This conclusion was also reached by D. Buchanan and co-workers, from whom we obtained the sample [11]. A slight broadening of the low-field peak after PCE extraction may indicate a slight oxidation of the coal was produced by the treatment.
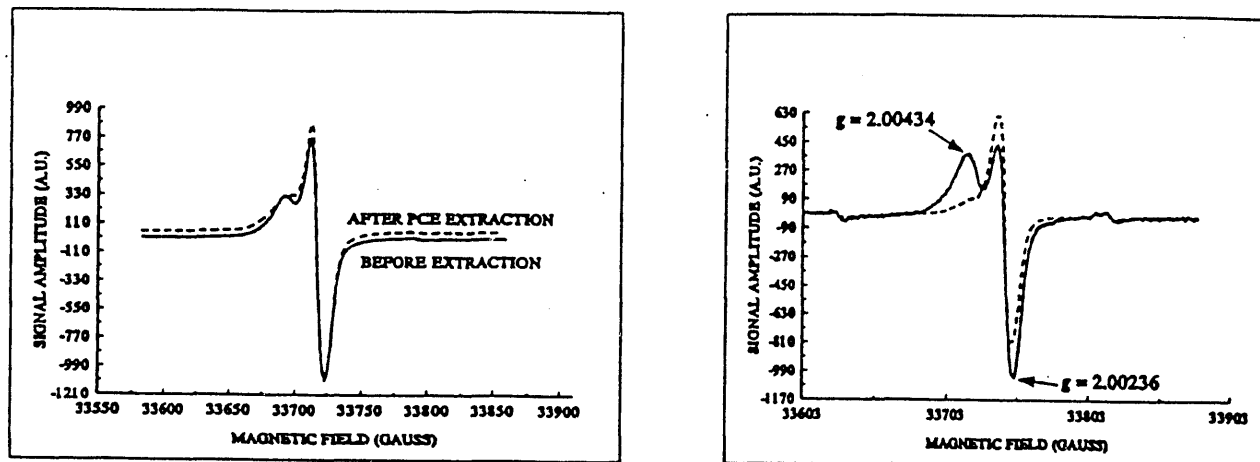


Figure 4. W-band VHF EPR spectra of a) PCE extraction, and b) low temperature pyrolysis of Illinois #6 coal (dashed lines), showing that PCE extraction is less effective than the char method for removal of sulfur. The solid lines are spectra of the coal prior to any treatment.

In both the second and third Quarters, it was shown that the spectra of inertinites, and especially fusinite, were very sensitive to the presence of gas-phase oxygen, and we showed data demonstrating that these effects are predictable, reproducible, and potentially useful as a means of assessing the extent of oxygenation of solid coal samples. In order to determine if these effects could be produced by other gases, we subjected fusinite samples to a variety of gas atmospheres, including strongly oxidizing ($F_2$) and non-reactive (He, $N_2$) gases. No major effects were noted from any of these treatments. Introduction of NO, another paramagnetic gas, did produce EPR linewidth increases, and we have calibrated this effect. The kinetics of formation of NO in an aqueous reaction were followed, and the results compare exactly with those predicted by chemical kinetic data. Finally, the EPR linewidth broadening produced by NO could be reversed by the introduction of $O_2$, indicating that the two reactive gases had combined to produce diamagnetic products ($O_2$ + NO → diamagnetic products). The implications of this discovery for the VHF EPR technique include making sure that all samples are well-evacuated prior to measurement.

On the other hand, low-temperature (285C) pyrolysis under rigorous vacuum conditions produced a very great effect in the VHF EPR spectrum, almost eliminating the low-field peak at g = 2.00434 that we associate with organic sulfur. This desulfurization effect of low-temperature pyrolysis has been noted by Kruse and Shimp [12]. The entire area of pyrolytic effects on VHF EPR spectra is one that will require very careful study in order to produce correct spectral interpretations, but the data from our initial measurements gives clear evidence that our VHF EPR methods will allow us to monitor the removal of organic sulfur from coal.

In this fourth quarter, other novel model heterocyclic and non-heterocyclic aromatic

compounds containing oxygen and sulfur have been studied. g tensor are determined by advanced theoretical simulation and comparison. These values show direct correlation with the degree of aromatic character in the vicinity of the sulfur heteroatom. Such observations are possible only because the W-band spectra can more accurately resolve the g tensor anisotropies. More importantly, the results of the measurement of the g tensor anisotropy, determined by measuring the separation of spectral features of the W-band spectra show a clear dependence on the size of the ring system, and therefore the extent of delocalization of a radical electron in the conjugated pi orbital system (BNT > DBT > THA). These results are important both to the critical not only to the evaluation of the chemical nature of the sulfur in the organic matrix of coal, but also to the more general understanding the influence of heteroatom and pi orbital interactions on EPR spectra.

## OBJECTIVES

The goals of this program for the funding year 1990 - 1991 can be summarized in three key target areas. These will be referred to as Phase I, II, and III of the work.

Phase I. Develop a precise model for the analysis of the chemical forms of organic sulfur in Illinois coal by very high field EPR spectroscopy.
The W-band EPR spectrometer has been operational for over six months, allowing us to acquire some data on the relationships that exist between the VHF spectra and organic sulfur content. Clearly, we want to improve the precision of this method, and this will be the first priority of Phase I. It also is important to determine how the VHF EPR data relates to the chemical nature of the organic sulfur (e.g. aromatic? average size of conjugated system?). Such additional information would undoubtedly improve the overall analytical reliability of the approach, and might provide "bonus" information that could be used to better understand changes brought about in the organic sulfur by various desulfurization methods.

Phase II. Apply the analytical method to a variety of IBCSP coals and macerals separated from them, as well as to solvent-extracted coals and extracts, determine the chemical forms and content of organic sulfur, and compare these results to data from other analytical techniques whenever possible.
Clearly, the best test of this analytical procedure is to apply it to as many systems as possible. Our goal is to analyze a variety of coal samples from the Illinois Basin Coal Sample Program and from other sources by VHF EPR, in order to develop the data base necessary to evaluate the technique as a non-destructive analytical method for organic sulfur in coal. Whenever possible, we will look at macerals separated from a whole coal, in order to learn more about the distribution of organic sulfur in individual maceral components. Collaborating with Dr. Richard Harvey of the IGS, samples of coal components that have been mechanically separated under a microscope will be studies to further determine the distribution of chemical forms of sulfur, since the great sensitivity of our method allows us to look at less than a milligram of sample. We also will attempt to compare our results with those obtained by other methods, in order to understand better what different techniques actually measure when they report on the "organic sulfur content" in coal. In particular, we will compare our results with destructive chemical analysis data (proximate analysis) and, when possible, with XAFS. In the latter work, we will collaborate with Prof. G. P. Huffman and co-workers at the University of Kentucky, who has developed unique XAFS methods for sulfur in coal. We also will examine coals subjected to solvent extraction to learn more about the organic sulfur selectivity of these methods (i.e. what

types of sulfur are extracted), as well as the extracts themselves, which remain paramagnetic, but which may be chemically altered due to the extraction process. Finally, in collaboration with Mobil Research and Development Corporation, Princeton, NJ, we will examine several heavy petroleum samples with sulfur content ranging from 0.23% to 7.15%. Mobil has carefully examined these residues by a variety of chemical analytical methods, as well as by NMR, and they have made the entire suite of analytical data available to us. This set of samples will be another test for our VHF EPR method, and will add to our understanding of the relationships that exist between our spectra and the chemical forms of organic sulfur.

## Phase III. Measurement of Illinois Coals subjected to low-temperature pyrolysis.

In very preliminary experiments on the VHF EPR of an Illinois #6 coal subjected to mild pyrolysis, we have seen significant changes in the spectra with sample heating. These changes include variations in the low-field peak associated with organic sulfur. Since so many desulfurization techniques employ temperatures above ambient, we must learn more about the effects of mild heating on coal if we are to properly interpret our data on desulfurized coal samples.

## INTRODUCTION AND BACKGROUND

For the past five years, our laboratory has been working on a variety of non-destructive methods for the characterization of organic matter in coal. Our general approach is to use the naturally occurring unpaired electrons in coal as "spies" of their local environment; they report on the number, positions, and types of atoms with which they come in contact or close proximity, and we translate this information into models of coal structure. It has long been known that sulfur has one of the strongest and most characteristic interactions with unpaired electrons, and with funding from the U. S. Department of Energy, the Center for Research on Sulfur in Coal (IDENR), the Petroleum Research Fund (ACS), and the National Institutes of Health, as well as from an industrial sponsor, we have built a unique, Very High Frequency Electron Paramagnetic Resonance (VHF EPR) spectrometer operating at the W-band of microwave frequencies (ca. 96 GHz) to measure this interaction as a potential avenue to the direct, non-destructive analysis of organic sulfur in coal. This unique instrument is one of only three such devices in the world, and the only one currently operating in the U.S.A.

The fundamental motivation for building a spectrometer to perform the EPR experiment at a magnetic field of 3.4 T, instead of at the usual 0.34 T, is to improve spectral resolution and sensitivity of the technique to sulfur-containing compounds in order to analyze for sulfur in coal. The relationship between magnetic field strength and sensitivity to sulfur can be better understood by considering the energy of an unpaired electron in an external field, $\mathbf{B}$. If the atomic or molecular orbital of the electron is nondegenerate ($L = 0$), then the "spin only" energy is given by:

$$\mathcal{H}_{\alpha} = \beta_e \, \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S}, \qquad (i)$$

where $\mathcal{H}_{\alpha}$ is the spin Hamiltonian (electronic Zeeman interaction only), $\beta_e$ is the Bohr magneton, $\mathbf{B}$ is the external magnetic field, $\mathbf{g}$ is the g-tensor, and $\mathbf{S}$ is the electron spin operator. In this case, when the electron possesses only spin angular momentum, the g-tensor is isotropic and has the free electron value $g_e = 2.00232$.

When the electron is in an orbital with angular momentum (L > 0), either by itself or via coupling to excited states, then the orbital angular momentum mixes with the spin angular momentum. Our Zeeman spin Hamiltonian now contains another term, reflecting this additional interaction:

$$\mathcal{H}_{ez} = \beta_e \, \mathbf{B} \cdot \mathbf{L} \;+\; g_e \beta_e \, \mathbf{B} \cdot \mathbf{S}, \text{ or}$$

$$= \beta_e \, \mathbf{B} \cdot (\mathbf{L} + g_e \, \mathbf{S}). \tag{ii}$$

In addition to modifying the electronic Zeeman energy, the orbital angular momentum of the unpaired electron (or the magnetic dipole moment induced by the orbital motion) also interacts directly with the unpaired electron, creating an additional energy term:

$$\mathcal{H}_{so} = \lambda \, \mathbf{L} \cdot \mathbf{S}, \tag{iii}$$

where $\lambda$ is the spin-orbit coupling constant, a term proportional to the nuclear charge of the atom (Z) and $1/r_3$, where r is the orbital radius. $\lambda$ may be positive or negative, reflecting the fact that the local orbital field may add to or subtract from the external static field.

The total spin energy for this system now is written:

$$\text{spin } \mathcal{H}_{ez} + \mathcal{H}_{so} = \beta_e \, \mathbf{B} \cdot (\mathbf{L} + g_e \, \mathbf{S}) \;+\; \lambda \, \mathbf{L} \cdot \mathbf{S}. \tag{iv}$$

The effect of orbital angular momentum is to alter the energy of the spin in an external magnetic field. We now must remember that in the EPR experiment, we measure the energy represented by spin, not by scanning frequency, but by scanning magnetic field. Field positions of resonance lines are related to energies by the simple resonance equation:

$$h\nu = g_{eff} \, \beta_e \, B_o, \tag{v}$$

where all symbols have their customary meaning, and geff is an "effective g-value" that characterizes the position of the line (analogous to the chemical shift parameter in NMR). If L = 0, then geff = $g_e$, as can be seen in Equ. (iv); if L > 0, then $g_{eff}$ will deviate from $g_e$ in a way determined by L and $\lambda$. In the coal system, spin-orbit coupling ( $\mathcal{H}_{so}$) is primarily responsible for this deviation, and this key fact allows us to observe the presence of organic sulfur compounds in the EPR spectra.

Since $g_{eff}$ differs from the free electron g-value, $g_e$ by an amount $\Delta g$, which is sensitive to the presence of sulfur, it is important to know what we can do experimentally to optimize our ability to measure this effect. It can be seen from equation (v) that, at a constant $\nu$, the change which sulfur makes in the magnetic field position of the EPR resonance line, B, is given by:

$$B_1 - B_2 = \Delta B = h\nu/\beta(1/g_1 - 1/g_2) = h\nu/\beta \{(1/g_e) - (1/g_e + \Delta g)\} \tag{vi}$$

Thus, the shift in field, $\Delta B$, of the resonance of our "spy" electrons due to sulfur, is dependent on $\Delta g$ and $\nu$. The sulfur "g-shift", $\Delta g$, is a feature of the coal sample; we cannot change this parameter without changing the chemistry of the sample itself. The experimental frequency, $\nu$, is ours to choose, however, and the higher the better, since the larger $\nu$ is, the larger $\Delta B$ will be, and the more sensitive our experiment will be to the presence of sulfur. It is for this reason that we have constructed a very high frequency EPR instrument, and with it we have observed the

$\Delta B$ due to sulfur, which is too small to be seen at lower spectrometer frequencies.

## EXPERIMENTAL PROCEDURES

A. Design and Building of the W-band VHF EPR spectrometer The rather simple resonance lineshapes at 9 and 35 GHz represent the state-of-the-art EPR of coal prior to the development and application of W-band spectrometry. This unique instrument has been built over the last three years, and now incorporates several important technical innovations that make it well-suited for the present research work. A detailed description of the instrument is included in this report.

B. Preparation of Ultra-Pure Thiophenes

The spectra of thiophene model compounds have shown secondary resonances that raised serious questions regarding the nature of products formed in our synthesis. Our most favored technique is to dissolve compounds in molten boric acid, after which the melt is allowed to cool into a glass. Samples then are UV irradiated for 15 minutes to produce matrix isolated radicals. The concern over minor products included the possibility that di-radical species were forming, a situation which could lead to erroneous spectral interpretations.

Ultra-pure boric acid was first melted to form a glass, and the blank material was UV irradiated to insure that no background signals were forming. After this, our focus turned to possible impurities in the starting thiophenic compounds purchased from Aldrich Chemical Co. We therefore obtained small quantities of recrystallized thiophenes, and repeated the preparation. Spectra at W-band from these preparations showed almost no secondary resonances.

In order to study the effects of electron delocalization on the magnitude of g-anisotropy in thiophenic systems, we need to synthesize stable radicals of materials with boiling points that are too low for the conventional boric acid preparation. Thiophene and benzothiophene cannot easily be incorporated into molten boric acid, so several new preparative routes are currently being investigated. One technique involves placing the desired starting material together with boric acid in a pressure pellet, which then is crimp sealed and heated to produce the matrix isolated thiophenes. Another technique is to dissolve the starting thiophene in rigorously dehydrated sulfuric acid. The solution then is frozen at liquid nitrogen temperatures and UV irradiated to produce radicals. In this second preparation, the sample must remain at 77K after irradiation in order to preserve the radicals. At present, neither of the techniques has produced samples of acceptable concentration for our work, although both have produced radicals. We are now optimizing both methods in order to allow the study of the homologous series of thiophenes from $C_4H_4S$ to $C_{16}H_{10}S$ and larger thiophenes.

C. VHF EPR spectra of Illinois #6 Coal and Vitrinite

The effects of NO on VHF spectra were also studied. Fusinite separated from inertinite lenses in Illinois #6 coal was acid washed and ground to < 100 mesh. Samples were placed in a vacuum system that allows the glass sample tube to reside in an X-band (9.5 GHz) EPR cavity, and samples then were evacuated for at least 24 hours, or until no further changes in the EPR linewidth were noted. Samples for use at W-band were similarly prepared under vacuum

conditions, but were sealed in quartz capillaries prior to insertion into the VHF EPR spectrometer. Varying pressures of NO then were admitted, and EPR spectra taken.

In order to ascertain whether the presence of water would effect the sensitivity of fusinite to NO, the decomposition of {Et$_2$N-N(N=O)-O}Na in water at pH 7.4 to form NO was studied. Fusinite previously acid washed and sieved was introduced in water containing phosphate buffer at pH 7.4. The secondary amine was dissolved in water containing pH 11 phosphate buffer, in which it will not react. Both solutions were vigorously deaerated with bubbling nitrogen through septum caps for at least 20 minutes. Then 0.2 ml of the secondary amine solution was injected into the vessel containing the fusinite at pH 7.4. The reaction vessel was placed on a microwave surface coil tuned for 1.1 GHz, and EPR spectra were taken every 10 seconds for 5 minutes, then at 10 minutes, 20 minutes, and 35 minutes. EPR peak-to-peak linewidths ($\Delta B_{PP}$) were determined by a program written in our laboratory. $\Delta B_{PP}$ vs time plots were compared to kinetic data for this reaction. Finally, when the reaction had gone to completion, additional pure oxygen was injected into the reaction vessel to test the reactivity of NO and its effect on fusinite linewidths.

## D. Effects of Desulfurization on VHF EPR Spectra

1. Perchloroethylene extracted Illinois #6 coal was obtained from Professor David Buchanan (Eastern Illinois University). His technique has been reported in a separate paper [11].

2. Low-temperature pyrolyzed coal was prepared by placing a sample of Illinois #6 in a 4mm quartz sample tube that subsequently was attached to a vacuum line and evacuated to P = 5 x 10$^{-6}$ Torr for 72 hours. The sample then was heated to 285C for 24 hours. Finally, the sample was transferred under vacuum to a quartz capillary tube and sealed for study at 96 GHz. Other samples were similarly prepared at temperatures of 50, 100, 150, and 200C.

## E. Preparation of thiophene model systems

Pure samples of dibenzothiophene (DBT) and benzonaphthothiophene (BNT) were purchased from Aldrich Chemical. Cation radicals of these materials, in addition to dibenzofuran (DBF), were prepared by two alternate routes. Each method was developed to produce stable populations of pure cation radicals in a powder or glassy matrix, thus duplicating the disordered state of chemical species in coal. It is essential that this disorder criterion be met for our model systems to provide accurate spectral information that directly relates to spectra from coal without theoretical intervention.

### Method 1. Preparation on Houdry catalyst.

In this approach, our method utilizes the oxidation catalyst Houdry M-26, a silica-alumina catalyst developed for petroleum cracking. This catalyst is first activated by calcining in air at 650C for 12 hours. Alternatively, the catalyst may be activated by heating to the same temperature in a vacuum. Following activation, the catalyst is transferred in a closed tube to a glove bag, where it is opened under an atmosphere of dry oxygen. In the glove bag, an amount of the desired thiophenic sulfur compound is added to the Houdry to make a powdered mixture that is 0.2% by weight in the thiophenic species.

The powder then is placed in a 1mm O.D. quartz tube that has been sealed to a ground

glass joint suitable for attachment to a high vacuum system. A stopcock at the top of the apparatus is closed, and the device removed from the glove bag and placed on a vacuum line, where it is opened and evacuated to $P < 10^{-5}$ Torr for several hours. Then the sample stopcock is closed and the sample slowly is heated to the melting point. Sublimation of the thiophenic compound results in an even adsorption throughout the Houdry catalyst, where electron transfer produces a cation radical species (DBT+, BNT+, or DBF+). The small quartz capillary holding the sample then is flame sealed, and is ready for examination in the W-band EPR spectrometer.

### Method 2. Preparation in Boric Acid Glass by UV Irradiation

Powdered boric acid and the desired thiophenic compound are mixed together in a 1:100 ratio by weight. The powder then is heated slowly to the melting point of boric acid (ca. 125C). The glass is allowed to cool, broken into small fragments, and loaded into a quartz sample tube. The tube is placed in a Ray-O-Net irradiation unit and subjected to UV irradiation and 3260 nm for 30 minutes. After this, the sample is removed, sealed with high-purity mass spectrograph grease, and taken to the W-band spectrometer for analysis.

## F. Vacuum preparation.

All coal samples were carefully evacuated to a pressure less than $10^{-5}$ Torr for at least 24 hours prior to being sealed in quartz glass tubes.

## G. Spectroscopy

All spectroscopy at W-band (ca. 96 GHz) is done on the instrument constructed in our laboratory and described elsewhere [2]. 250 GHz EPR spectra of coal and maceral samples were obtained through the courtesy of Professor Jack Freed and colleagues at Cornell University. L-, S-, X-, and Q-band EPR spectra were obtained on instruments located in the Illinois EPR Research Center.

## RESULTS AND DISCUSSION

### A. W-band VHF EPR Spectrometer

Figure 1 in the Executive Summary section illustrated the increase in resolution obtained when VHF EPR experiments on Illinois #6 samples are performed at 250 GHz. The shaded portion of each spectrum corresponds to the contribution from sulfur-containing radicals. It is very clear that in the higher field data, not only does the organic sulfur signal move farther downfield, the main peak at higher field also begins to display a partially resolved central feature. In order to better understand how this additional splitting correlates to coal molecular structure, we measured the VHF EPR spectrum of perylene (+) radicals at 250 GHz. Figure 5 shows the perylene (+) spectrum superimposed on that from the vitrinite.

The downfield movement of the spectral feature related to organic sulfur is expected as we go from 95 GHz to 250 GHz, since this effect is due to spin-orbit coupling of NO in water generated by the decomposition of a secondary amine. Again, the signal linewidth grows as more and more NO is produced, and the rate of growth is exactly proportional to the kinetics of formation, indicating that it is really NO that is responsible for the linewidth increase. Finally, Figure 6 shows the EPR linewidth of the fusinite at the completion of the NO producing reaction, as well as after the injection of 2 ml of pure $O_2$ (STP) into the reaction chamber. The linewidth decrease following oxygen injection indicates that $O_2$ and NO have reacted to form diamagnetic products which do not broaden the EPR signal. Thus, this sensitivity of the fusinite linewidth to the presence of NO is an effect which is very sensitive, useful in aqueous environments, and which preserves the reactivity of NO to $O_2$.
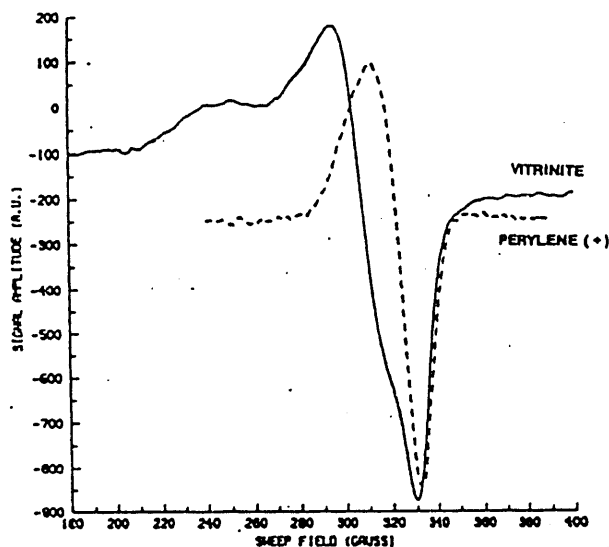


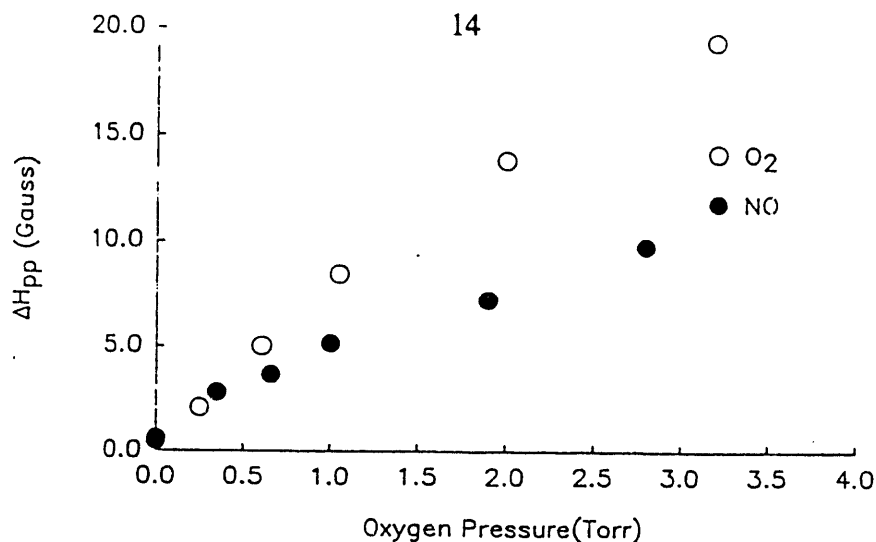Figure 5. 250 GHz VHF EPR coal spectra of a vitrinite and perylene (+) radical.

Figure 6. Fusinite EPR linewidth $\Delta B_{PP}$ vs pressure of NO and $O_2$.

## B. Effects of Desulfurization on VHF EPR Spectra of Illinois #6

Figure 4 shows spectra of an Illinois #6 before and after desulfurization using two different methods. In Figure 4.a), the coal was subjected to extraction with perchloroethylene (PCE) at 120C for 3.5 hours. As can be seen by inspection, very little changed in the VHF EPR spectra as a result of this treatment, suggesting that little organic sulfur (of the aromatic variety to which our method is believed to be sensitive) was removed, in agreement with D. H. Buchanan and co-workers, from whom the samples were obtained [11]. The slight broadening of the low-field feature in this spectrum may be due to modest oxidation of the coal during extraction, although this was done under a nitrogen atmosphere to suppress oxidative effects.

Figure 4.b) shows spectra of the Illinois #6 before and after low temperature (285C) pyrolysis for two hours under vacuum conditions (P = 5 x $10^{-6}$ Torr). The greatly reduced low-field peak (g = 2.00434) in the pyrolyzed coal suggests that this treatment significantly altered and removed aromatic organic sulfur, as has been reported by Kruse and Shimp [12]. We currently are employing VHF EPR to study the effects of low-temperature pyrolysis on coal structure, and have observed complex spectral changes which need to be understood before a complete interpretation of these effects can be made. Samples of an Illinois #6, and vitrinite separated from this coal, have been subjected to the heating/evacuation procedure at ultimate temperatures of 50, 100, 150, 200, and 285C. Significant reduction of the low-field peak begins at 200C, although other changes in the VHF EPR spectra occur at even the lowest temperature (ca. 100C.). Samples also have been powdered with KBr to dilute the coal and prevent inter-particle interactions from confusing the chemical changes brought about by pyrolysis. We believe that a more extensive study of the effects of pyrolysis on the structure and composition of high-sulfur coals will be extremely productive in discovering details of the mechanisms of desulfurization.

## C. Model Thiophenic Systems

One key theoretical question in the interpretation of VHF EPR spectra of high-sulfur coal is the role that aromatic ring size plays in modulating the magnitude of sulfur spin-orbit coupling contributions to the anisotropic Zeeman interaction. If we recall that in the previous section, the influence of sulfur on VHF EPR spectra was thought to be primarily through this spin-orbit (SO)

interaction, then the key form of this interaction was presented in equations (ii) and (iii).

The magnitude of $\mathcal{H}_{so} = \lambda\, L \cdot S$ depends on all three terms, $\lambda$, $L$, and $S$. Consider the two thiophenic compounds shown in Figure 2. The compound on the left, dibenzothiophene (DBT+) is a cation radical formed by the techniques discussed above. Its single unpaired electron is delocalized over a carbon frame containing 12 carbon atoms as well as the sulfur. On the right is a structure for benzonaphthothiophene (BNT+), which also is a cation radical, with one unpaired electron delocalized over 16 carbon atoms. Now the magnitude of the SO interaction depends on the average unpaired electron density found at the sulfur atom in both these compounds. Supposing that the hybridization of the sulfur atom is roughly the same in both species, we would predict that DBT would show a stronger SO interaction than BNT. This prediction should be testable by examining the VHF EPR spectra of the two radicals.

Not only unpaired spin density and hybridization, but also the type of element plays a role in determining the magnitude of SO interactions. Figure 7 shows the W-band spectra of dibenzofuran (DBF), the oxygen analogue of DBT. Here, the SO coupling constant $\lambda$ for oxygen is about 40% that of sulfur, and the overall interaction, a combination of $\lambda$, unpaired electron density, and atomic orbital hybridization, is very much less than that. While our primary focus always is on organic sulfur in coal, we cannot neglect to consider the effects of other heteroatoms like oxygen on the VHF EPR spectra of coal, and so we are working with DBF+ in order to more correctly account for the role of oxygen compounds in our spectra.
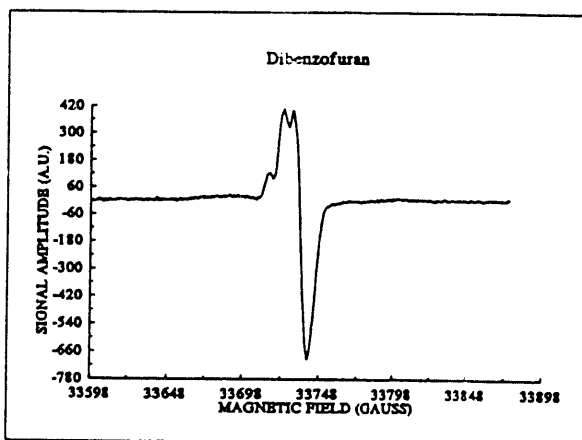


Figure 7. W-band VHF EPR spectra of the DBF+ radical.

A comparison of the VHF EPR spectrum of DBF+ with that of BNT+ or DBT+ clearly demonstrates that the combination of effects makes this spectrum much less anisotropic than those of the sulfur-containing species. Next steps in this phase of the work will be to make careful comparisons of the spectra of thiophenic compounds prepared by both synthetic routes, in order to determine whether there is a chemical difference between species formed from the same starting compound by the different procedures. It will be advisable to perform ENDOR spectroscopy on some of these preparations in order to verify their molecular structure. We are pleased of our synthetic achievements, but want to be careful in characterizing these never before studied radicals.

While a study of model compounds represents a very important component of our overall program, a word needs to be said about its connection to the analysis of coal and maceral spectra. Figure 8 is a VHF EPR spectrum of Argonne Premium Coal Sample #301, the Illinois #6. This spectrum should be compared to the three previous spectra from model compounds.
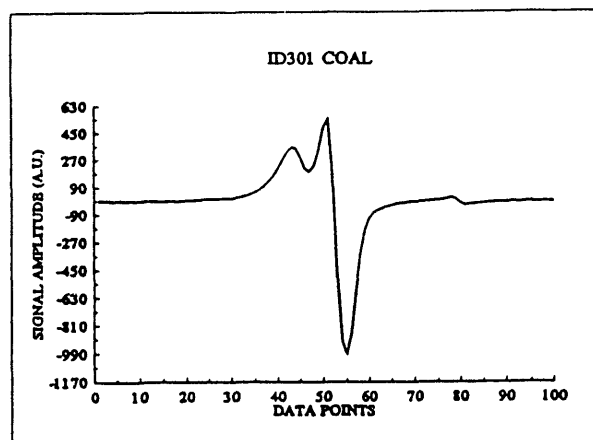
'Figure 8. VHF EPR spectrum of APCS #301 (Illinois #6).

What becomes evident immediately is that if our hypothesis concerning the origin of the anisotropic spectra in the VHF EPR of coal is correct, the average aromatic organic sulfur species in the Illinois #6 must have an extent of conjugation that is slightly larger than that in BNT. Further, while there are many aromatic oxygen species in this coal, the VHF EPR spectrum at 96 GHz probably cannot resolve them, due to the very small extent of g-anisotropy, as suggested by the DBF+ spectrum, which could be an upper limit on the g-anisotropy in aromatic oxygen compounds, and which is not comparable to the spectrum from the Illinois #6. Higher frequency spectroscopy at 250 GHz may be able to resolve both sulfur and oxygen in coal, however, and we are currently working on that experiment in collaboration with Professor Jack Freed and colleagues at Cornell University.

Theoretical simulations, by which our theories are tested against experimental data, are being performed utilizing software developed by Professor Belford and his students. This aspect of the work has assumed a much greater importance since our successful development of synthetic methods of producing model compounds for study, and we hope to report on our progress here in the next Quarterly Report.

## D. VHF EPR of Separated Inertinites

In the course of studying separated macerals, as planned in Phase II of our project, we have carefully characterized the unique the oxygen-sensitive EPR spectral response of fusinite, an inertinite maceral from Illinois #6 coals. The spectrum of fusinite is characterized by a spin-exchange narrowed lineshape that broadens from 500 mG to over 4 Gauss when the oxygen partial pressure over the material is changed from zero to 200 Torr.

Our preliminary model for the effect of oxygen on the EPR lineshape has been built around the idea that, in the limit of fast exchange,

$$>> |g_i - g_j|\beta B_o,$$

where "fast enough" is parameterized in terms of the range of g-values over which one wants to average. If the inequality is obeyed, then the EPR lineshape will be exchange narrowed. As we increase the magnetic field strength at which our EPR experiment is performed, the inequality should be less and less well-obeyed, since $B_o$ will increase, while the exchange energy remains constant. Finally, we should see the linewidth increase with increasing $B_o$ as the exchange narrowing condition fails to be met.

VHF EPR is ideal for evaluating this effect, and we have performed EPR experiments on fusinite separated from an Illinois #6 coal at microwave frequencies from 1 GHz to 250 GHz. Figure 9 shows the variation in linewidth as a function of observation frequency, revealing that
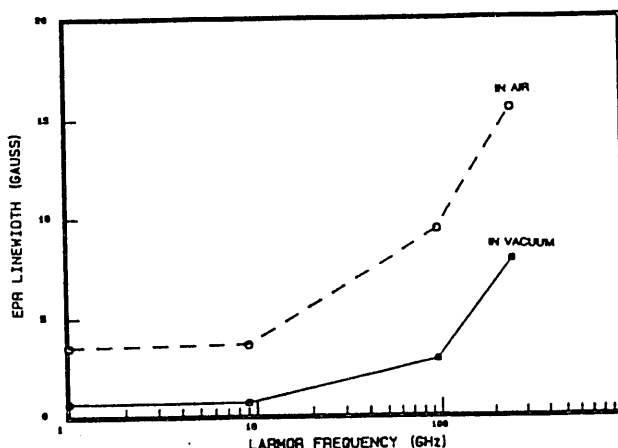


Figure 9. EPR linewidth in fusinite as a function of microwave frequency.

above 9 GHz, the strong exchange inequality progressively fails to hold. The importance of understanding this oxygen effect on fusinite cannot be overemphasized — the effect can be used to provide an in situ measurement of oxygen pressure. Our work on this class of macerals continues, and we hope to finish the physical characterization of the effect in the next six months.

E. VHF EPR of Iodinated Coal

Professor Harry Marsh, University of Newcastle upon Tyne in England, has developed techniques for studying coal structure that employ iodine as a reagent to produce radicals by means of electron charge transfer from aromatics to the electrophilic $I_2$. In collaboration with Professor March and Herb Retcofsky of the U. S. DOE (PETC), we have examined some of these iodinated coals by VHF EPR. Figure 10. illustrates one of these samples both before and after treatment with iodine. The sample is a Gedling coal, which is very weakly coking.
The anisotropic EPR signal, which is not observable at conventional (9.5 GHz) frequencies, is very reminiscent of samples with g-anisotropy due to SO coupling. Considerable variation is noted in going from a good coking coal to this weakly coking sample, suggesting that iodination may be diagnostic of structural differences in the coal that account for its coking properties. We feel this system may provide important insights into the mechanism of SO coupling by giving us another system (iodine) for comparison to sulfur, and we plan to investigate the effects of these chemical treatments on sulfur-containing compounds and coals.
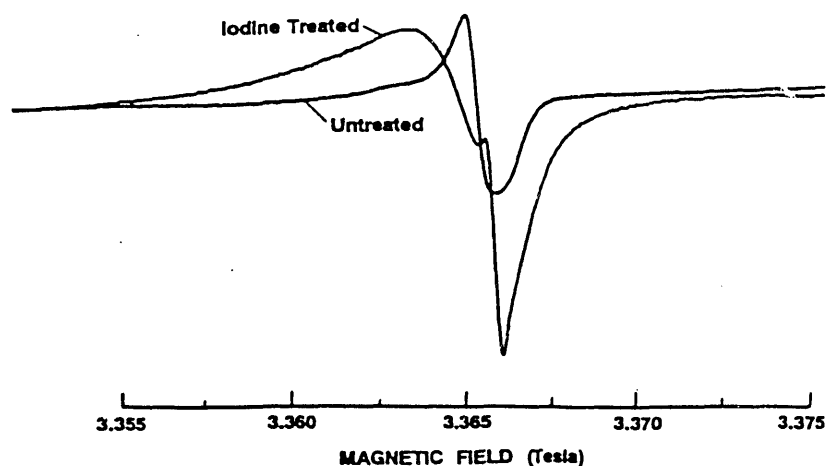
Figure 10. VHF EPR of a Gedling (English) coal, both before and after treatment with iodine.

In this fourth quarter, a number of other novel model heterocyclic and non-heterocyclic aromatic compounds have been studied in depth. The measurement of the g tensor shift and anisotropy of these compounds, possible only in the VHF EPR W band spectra, both show a direct correlation to the delocalization of electron density (radical, and heteroatom) over conjugated ring systems. Spectra of three of these compounds (see figure 2) are shown in figure 11. The W-band spectra show that the resolution of the g tensor anisotropies is enhanced to the point where they can begin to be measured with little effort. More over the results of the measurement of the g tensor anisotropy, determined by measuring the separation of spectral features of the W-band spectra show a clear dependence on the size of the ring system, and therefore the extent of delocalization of a radical electron in the conjugated pi orbital system (BNT > DBT > THA).

Figure 11 shows X- and W-band spectra of the two compounds. As is immediately apparent, DBT has a much more anisotropic spectrum than BNT, which is what our simple model predicted. In fact, the actual change in g-values with the size of the aromatic cluster is not well understood, and we are actively studying the theory of spectra in such compounds to develop a detailed description of the effect. With the development of this theory, it should be possible to analyze VHF EPR spectra and obtain good information on the size distribution of aromatic clusters containing sulfur in coal.

Figure 11 This figure shows the X-band (right hand side) and W-band (left hand side) spectra of BNT+, DBT+, and THA+. The extent of the conjugated pi system, and therfore electron delocalization, decreases in the order BNT > DBT > THA.

The dependence of the principle g values, g shift, g average, and variously defined g anisotropies are shown in table 1. The extent of the conjugated pi system, and therefore electron delocalization, decreases in the order BNT > DBT > THA. This is paralleled by an increase in all individual tensor values, the average g tensor value, the g shift, and variously defined g tensor anisotropies.

Table 1. g tensor values and anisotropies from best fits experimental and simulated of X- and W-band spectra.

| R | Principal g Values | | | g average | g shift | g anisotropy | |
|---|---|---|---|---|---|---|---|
| | $g_x$ | $g_y$ | $g_z$ | $<g>$ | $(<g>-g_e) \times 10^4$ | $|g_x-g_y| \times 10^4$ | $|(g_x+g_y)/2-g_z| \times 10^4$ |
| BNT | 2.0064 | 2.0035 | 2.0022 | 2.0041 | 18 | 29 | 27 |
| DBT | 2.0111 | 2.0061 | 2.0023 | 2.0065 | 42 | 50 | 64 |
| THA | 2.0138 | 2.0084 | 2.0023 | 2.0082 | 59 | 54 | 88 |
| PYL | 2.0027[a] | 2.0027[a] | 2.0024[a] | 2.0026 | 3 | 0[b] | 3[b] |

a) estimated error ±0.0001

b) measured from experimental spectra

## CONCLUSIONS AND RECOMMENDATIONS

The development of chemical procedures to synthesize reliable models of thiophenic species in coal has been a year-long effort, which we now believe will provide extremely useful information needed to interpret the VHF EPR spectra from coal. With the elimination of secondary resonance peaks in the spectra of radical thiophene systems, we have the necessary information to proceed with confidence in this experimental and theoretical phase of the work. During the next quarter, we will attempt to optimize the synthesis of low molecular-weight models.

The sensitivity of fusinite spectra to NO suggests that we need to be cautious in our preparative methods, particularly when employing reactive conditions like elevated temperatures, to prevent the broadening of spectral features. Vacuum pumping is absolutely necessary for all this work in order to prevent the build-up of NO, and to eliminate $O_2$, which also causes broadening, as we reported in the Second Quarterly Report. Of course, the sensitivity of fusinite spectra to NO, even in aqueous environments, also can be a very great bonus if the goal is analysis for NO, and there is significant interest among analytical chemists to develop fusinite as an EPR reagent for non-invasive measurements of nitric oxide and oxygen concentrations. We will cooperate with these scientists to provide potentially new markets for the use of this maceral.

The sensitivity of VHF EPR to the effects of PCE extraction and low-temperature pyrolysis of Illinois coal clearly shows that our method can be very useful in determining the effectiveness of desulfurization techniques. In the last quarter, we will attempt to locate "before and after" coal samples that have been subjected to microbial cleaning, in order to evaluate what forms of organic sulfur this procedure attacks. We also will continue to work on the low-temperature pyrolysis study, in order to gain a clearer understanding of the effects of modest temperatures on the sulfur composition and structure of Illinois coals.

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11) David Buchanan

12) Kruse & Shimp

# PROJECT MANAGEMENT REPORT -- FINAL REPORT
## September 1, 1990 through August 31, 1991

Project Title:  VHF EPR Determination of the Chemical Forms of Organic Sulfur in Coal
Principal Investigator: R. B. Clarkson, UIUC
Co-Principal Investigator: R. L. Belford, UIUC
Project Monitor: Dr. Ken Ho, CRSC

## COMMENTS

During the last quarter, the arrival of a new, highly qualified postdoctoral associate, Dr. Frank Auteri, and the purchase of the final components of our W-band instrument improvement project spurred a special burst of activity which leave us well-positioned for progress during the next grant year.
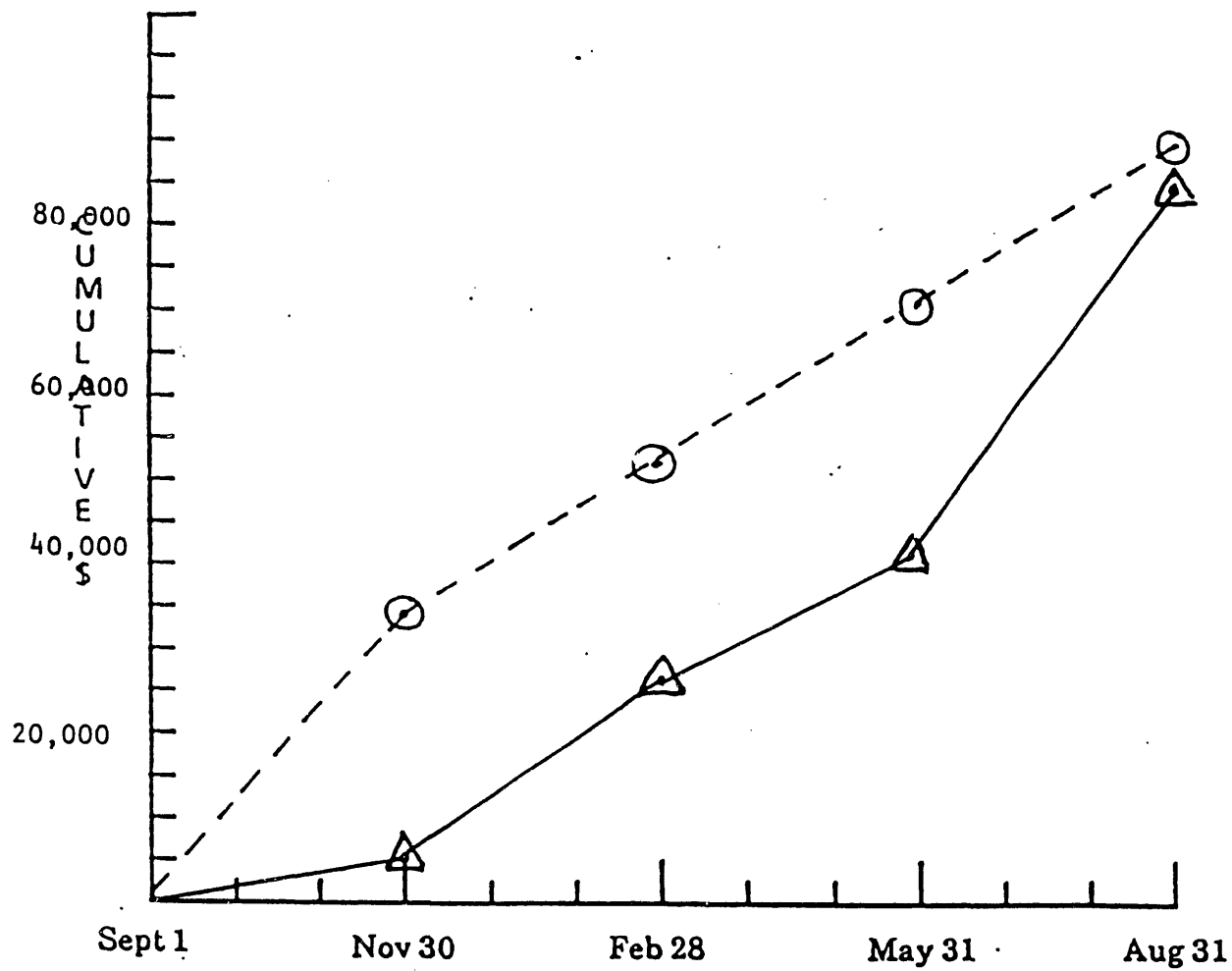
## EXPENDITURES - EXHIBIT B

### Projected and Estimated Actual Expenditures by Quarter

| Quarter* | Types of Cost | Direct Labor | Materials and Supplies | Travel | Major Equipment | Other Direct Costs | Indirect Costs | Total |
|---|---|---|---|---|---|---|---|---|
| Sept. 1, 1990 to Nov. 30, 1990 | Projected | $11,515 | $1500 | 0 | $15,590 | $1550 | 3717 | $33,872 |
| | Estimated Actual | 634 | 100u | 0 | 2,305 | 200 | 408 | 4,542 |
| Sept. 1, 1990 to Feb. 28, 1991 | Projected | 23,030 | 3000 | 500 | 15,590 | 3100 | 7435 | 52,655 |
| | Estimated Actual | 15,461 | 2684 | 0 | 4519 | 1200 | 2156 | 26,020 |
| Sept. 1, 1990 to May 31, 1991 | Projected | 34,545 | 4500 | 500 | 15,590 | 4650 | 11,525 | 71,310 |
| | Estimated Actual | 25,230 | 3700 | 0 | 8000 | 2000 | 2317 | 41,247 |
| Sept. 1, 1990 to Aug. 31, 1991 | Projected | 46,060 | 6000 | 500 | 15,590 | 6200 | 14,870 | 89,220 |
| | Estimated Actual | 45,000 | 6000 | 500 | 15,000 | 4000 | 14,100 | 84,600 |

* Cumulative by quarter

# COSTS BY QUARTER - EXHIBIT C

VHF EPR DETERMINATION OF THE CHEMICAL FORMS OF ORGANIC SULFUR
IN COAL



Months and Quarters

0  = Projected Expenditures    --------------------

Δ  = Actual Expenditures       _____

Total CRSC Award $___89,220___

## 5.2. Communication.

The group working on this coal program meets once a week for a research seminar/discussion. Contributions from all members are required for each Quarterly Report.

## 5.3. Safety.

No unusually hazardous procedures are anticipated in this work. Prof. Belford reports to the Safety Committee of the School of Chemical Sciences, and that group monitors laboratory safety in the program.

## 5.4. Collaborative Arrangements.

No formal collaborative arrangements are planned for this work. Informal cooperation between the VHF EPR group and other groups interested in coal characterization have developed over the last few years, and we anticipate continued fruitful interactions with Dr. Richard Harvey, IGS, and Professors Crelling and Hippo, SIU/Carbondale. We currently have a formal collaborative agreement with the SIU/Carbondale group under our present CRSC grant that mandates bimonthly meetings of the principal investigators, and this has been an extremely useful practice which we will continue informally in this project.

## 5.5. Schedule.

Section 3.1. of this proposal outlined the major tasks to be accomplished in the work. The schedule of milestones will thus consist of the following tasks:
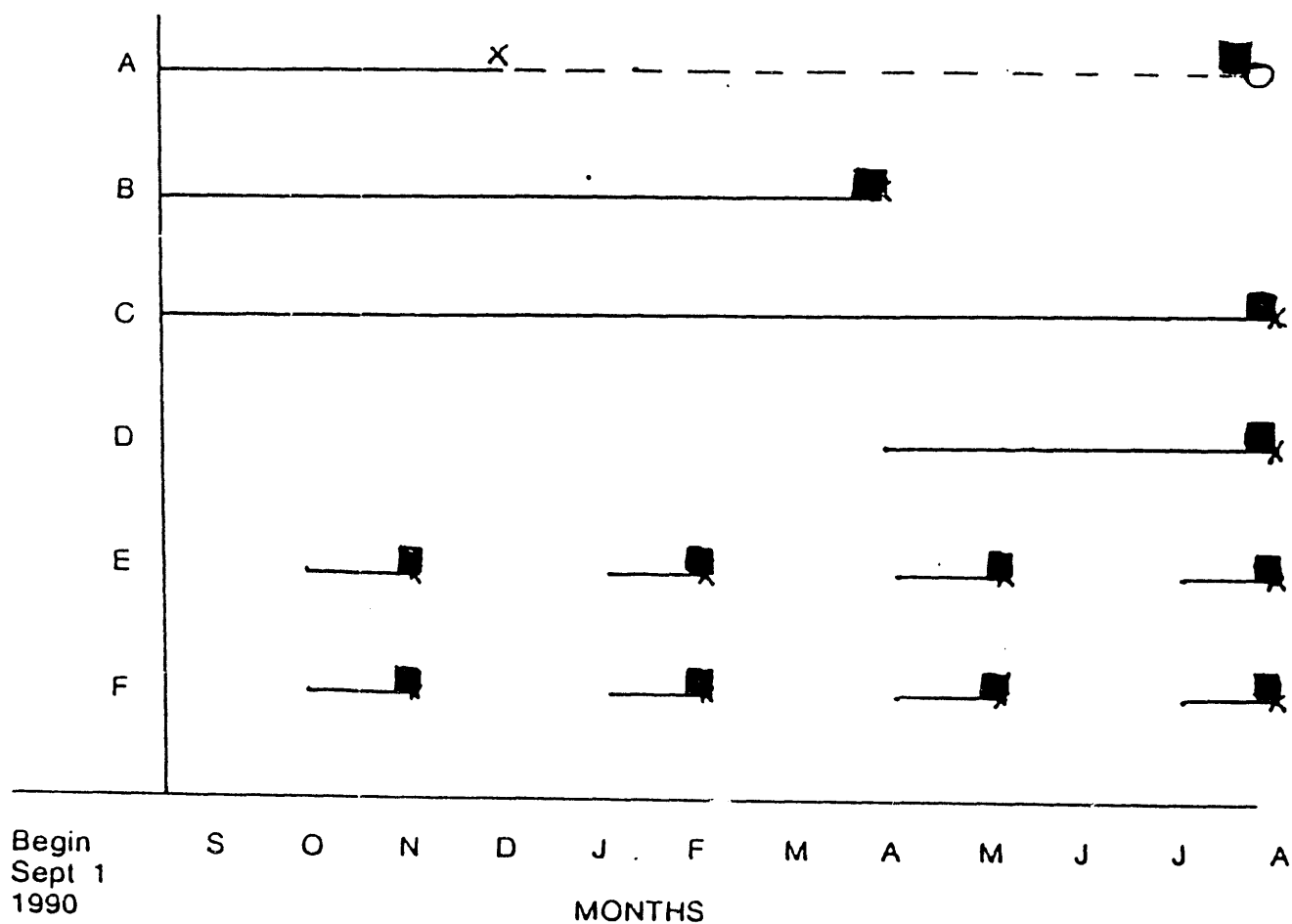
| Milestone | Description |
| --- | --- |
| A | Equipment ordered and received |
| B | Phase I research task completed |
| C | Phase II research task completed |
| D | Phase III research task completed |
| E | Technical Reports prepared and submitted |
| F | Project Management Reports prepared and submitted |

## 5.6. Financial Plan

Management Perspective. The major costs of this project are personnel salaries and the purchase of components to improve the performance of the W-band EPR spectrometer for the specific tasks required in the work. Allocation of project costs by tasks therefore is largely a matter of time spent on each part of the work. We estimate that Phase I will require 30% of the effort, Phase II 50%, and Phase III 20%. Therefore, estimated costs for the three main areas of work will be in the ratio 3:5:2, with equipment and supplies distributed in a similar pattern.

At this time, no additional proposals in support of this work. are pending or contemplated.

# SCHEDULE OF PROJECT MILESTONES



| | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Begin<br>Sept 1<br>1990 | S | O | N | D | J | F | M | A | M | J | J | A |

MONTHS

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# END

DATE
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01/31/92