ABSTRACT

The overall goal of our work during the last five years has been the non-destructive elucidation of molecular structure in coal and coal-derived materials. Special emphasis has been placed on determining the concentration and molecular forms of organic sulfur in coal. Our approach has been to use the naturally occurring unpaired electrons in coal as reporters of their environment, making use of electron magnetic resonance (EMR) spectroscopy to develop a detailed picture of the types and arrangements of atoms "seen" by the electrons. During this period, we constructed the first 95 GHz (W-band) EMR spectrometer in the USA (and the second in the world). With this advanced spectrometer, we were the first to discover that the aromatic sulfur in coal produced a unique EMR signature. Extensive experimental and theoretical work on model aromatic sulfur compounds in the thiophene series (thiophene, benzothiophene, dibenzothiophene, etc.) has enabled us to develop a detailed understanding of the relationships between the molecular and electronic structure of these compounds and their EMR spectra. This new basic scientific knowledge in turn allowed us accurately to analyze the W-band EMR spectra from coal, desulfurized coal, and a variety of coal derived materials. We developed an automated computer program (based on spin quantum mechanics) which can analyze the EMR spectra and which reports the aromatic sulfur content of the coal as well as key spectral parameters. This analysis method has been tested on coal blends of know sulfur content as well as on a variety of coals from the IBCSP and elsewhere. The precision of the method is conservatively ± 0.1% of the aromatic sulfur in the sample. Identical samples measured both by EMR and XANES gave nearly identical results. The EMR technique has the twin advantages of simplicity and absolute concentration readout; an analysis takes less than five minutes to perform. Applications of the EMR technique include the determination of aromatic sulfur in coal, evaluation of the effectiveness of desulfurization technologies, and the evaluation of the effects of desulfurization on the rest of the molecular forms in coal.
EXECUTIVE SUMMARY

The United States has a quarter of the world's proven reserves in coal. These coal reserves account for 85 to 90% of the fossil energy resources of the United States. Full utilization of this energy resource has been hampered by the high levels of sulfur in many major U.S. deposits. Whether coal is used in the near term by the power generation industry as a combustible or as a feed stock for liquid fuels and chemicals in the next decades will depend on a better understanding of the structure and chemistry of sulfur contained in coal. This program addresses the need for better non-destructive analytical techniques to analyze organic sulfur in coal. In utilizing new instrumental methods, our laboratory has developed Very High Frequency Electron (VHF-EPR). The overall goal of our analytical work is to more precisely quantify and identify the chemical forms of sulfur present in coal.

VHF-EPR, is a magnetic resonance method that is capable of analyzing the organic sulfur in whole coal, separated macerals, treated and desulfurized coals, as well as in materials produced from coals (e.g. liquefaction and pyrolysis products). We have been developing the method for coal analysis over the past two years, with support from the ICCI and the U.S. Department of Energy (University Coal Research Program). Instrumentation we have built takes advantage of new developments in solid-state microwave and digital electronics, which have made the VHF-EPR approach possible to pursue at this time.

Our approach utilizes the naturally occurring unpaired electrons in coal as "observation posts" from which to analyze surrounding molecular structures. These unpaired electrons have always offered an attractive route to the non-destructive study of coal structure. In a typical Illinois #6 coal, for example, there are about $10^{19}$ unpaired spins/gram. Because coal is highly aromatic (in this Illinois #6, ca. 77% C, it is estimated that 65 - 70% of the carbon is aromatic, with an average aromatic cluster size of 20 - 25 carbon atoms [1]), unpaired electrons delocalize over many carbons. Thus, the unpaired electrons in an Illinois #6 interact directly with 1% of all the carbon, and 2% of the aromatic carbon in the coal. This good coverage of the atoms in coal, together with a reasonably uniform distribution of unpaired electrons throughout all maceral components and the exceptional sensitivity of electron paramagnetic resonance (EPR) spectroscopy ($10^3$ times the sensitivity of $^1$H NMR) makes the paramagnetic spins very attractive natural observation posts from which to non-destructively analyze coal molecular...
structure.

The problem which had prevented the use of EPR as a successful method of structural analysis for coal was one of spectral resolution. Information about molecular structure and atomic environment was hidden within the EPR spectral lineshape of typical data obtained at 9.5 GHz and 0.34 T. (X-band EPR), and in most cases it could not be deconvoluted. This lack of spectral resolution was especially maddening in the case of heteroatom (N, O, S) analysis, where indications of the effects of atomic spin-orbit coupling between the unpaired electrons and heteroatoms were seen even in X-band spectra [2], and which higher magnetic field strength experiments were predicted to resolve. In 1990, our laboratory pioneered in the development of a novel 95 GHz, 3.4 T. (W-band) VHF-EPR instrument†, and demonstrated that this prediction was correct by examining several coals, as well as a vitrinite, sporinite, and inertinite maceral separated from an Illinois #6 coal by density gradient centrifugation [3,4]. Work during the past year has extended this VHF-EPR technique to desulfurized coals. All coals containing sulfur exhibit an EMR spectrum which has a characteristic or signature lineshape indicative of the sulfur content.

Chemical and EMR evidence strongly suggests that the complex lineshapes seen in the VHF EPR spectra of a coal like Illinois #6 (and fusinite and sporinite macerals separated from it) are the result of contributions from several molecular populations, some of which contain sulfur. In order to better understand the basic physical interactions responsible for the observed spectra, we continue to pursue a program designed to relate coal spectra and coal structure. This work has made use of model compounds that mimic the organic sulfur in coal, including a series of thiophenes and furans. Extensive quantum mechanical molecular orbital calculations also have been carried out to better understand the spectral/structural relations in some of the model systems. This work provides the solid scientific basis for interpreting VHF-EPR spectra of coal, and it opens the possibility of using spectral data to characterize the molecular forms of organic sulfur in coal. The data obtained by computer simulation of VHF-EPR spectra contains much more information on sulfur than just the amount present, and work reported in this Quarterly Report focusses on important new developments in this area of the project tasks. Developments which clarify the detailed scientific relationships that exist between VHF-EPR spectra and molecular

[†]This is the only spectrometer of its kind in the United States, and one of only two in the world.
structure of heteroatomic (S and O) aromatic compounds lead directly to the application of this technique to the speciation of sulfur compounds in coal.

In order to analyze experimental spectra in a quantitative fashion, we have completed a general-purpose computer technique, based on the simplex multi-variable optimization strategy, to simulate experimental data in order to obtain spectral parameters (g-values, linewidths, and composition coefficients) which can be correlated to chemical structure. This program is based on an understanding of the relationships between molecular structure and VHF-EPR spectra that developed out of our basic scientific study of model compounds. Overall theoretical modeling is based on the very successful QPOW algorithm for powder EPR spectral simulation developed by Belford and co-workers [5].

We have now tested this analytical approach in several ways. First, at the suggestion of Dr. Ken Ho (ICCI), we prepared blends of two coals which had organic sulfur contents of 0.5% and 2.5% (dmf) respectively. VHF-EPR analyses of the blends yielded sulfur contents that agreed precisely with the calculated content. The technique then was applied to a range of coal samples from many different geologic regions, covering an organic sulfur content range from less than 0.2% to greater than 10%. Again, VHF-EPR successfully analyzed these coals. Finally, we have examined two suites of coal samples provided to us by Dr. Steven Palmer, Southern Illinois University-Carbondale. These included IBCSP coals, as well as coals subjected to several chemical cleaning technologies. The first set of 10 samples were air-oxidized, while the second set of 12 samples were carefully kept under nitrogen after collection. Identical sets of samples were sent to Professor Gerry Huffman at the University of Kentucky for analysis by XANES. While there were considerable variations between VHF-EPR and XANES results for the oxidized samples, the results from the unoxidized samples were nearly identical for the two methods. Huffman has suggested that air oxidation may bias XANES results; a similar effect is not detected with VHF-EPR.

After nearly two years of testing, we believe the VHF-EPR method is now demonstrated to be a robust, quick, and quite simple method for the analysis of aromatic sulfur in coal. Tests show that the method has a precision of better than ± 0.1%. These still are several key scientific questions regarding the method which should be addressed, but the method is on-line and ready as a useful analytical method for coal and coal-related materials.


OBJECTIVES

This project was comprised of two parallel Task Areas of work for the 12 months grant period, with the following specific goals and objectives:

Task Area 1 - Refine and calibrate VHF-EPR as an analytical method for organic sulfur in coal.

(a) Develop mixtures of IBCSP coals and separated macerals with known organic sulfur concentrations in the range from 0.1% to 5%. Analyze these mixtures by VHF-EPR and calibrate the precision of the method, including error limits, utilizing multiple aliquots for statistical purposes.

(b) Make careful measurements in the presence of known quantities of pyritic sulfur, in order to determine if small, hitherto undetected, effects may be present which could influence analytical results on organic sulfur.

(c) Make VHF-EPR and XANES measurements on duplicate calibrated samples, in collaboration with Prof. G. Huffman, University of Kentucky, in order to establish a clear relationship between the two non-destructive, bulk coal analytical techniques.

(d) Refine the computer analysis of VHF-EPR coal samples by exploring more comprehensive models involving multiple species and symmetries lower than axial. Determine the consequences of model choices on analytical precision.

(e) Make use of even higher frequency VHF-EPR instruments to guide the development of models (Task 1 (d)), through collaboration with Prof. Jack Freed, Cornell University, who has built a 250 GHz spectrometer (the highest continuous field EPR instrument in the world), and who is happy to study this problem with us.

Task Area 2 - Work with model systems to elucidate relationships between coal structure and coal spectra that lead to sulfur speciation by VHF-EPR.

(a) Develop an aromatic organic sulfur model system to explore the effects of electron spin exchange on VHF-EPR spectra. This work will lead to a better understanding of the observed dependence of spectra on coal rank, and
will utilize static magnetic susceptibility measurements with a SQUID magnetometer as well as VHF-EPR measurements. It also could provide an important key for utilizing coal spectral parameters for sulfur speciation.

(b) Study mixed heteroatomic aromatic species (S,O and S,N) as well as sulfur and oxygen heterocycles to better evaluate the possible contributions of such structures to the VHF-EPR spectra from coal. Recent work analyzing coals and separated macerals by HRMS, XANES, and XPS has suggested that mixed heteroatomic forms may be quite abundant in some coals [1].

(c) Extend and refine MOPAC and ab initio calculations of the electronic properties of model systems in order to further clarify the relationships between chemical structure and VHF-EPR spectra.

(d) Apply theoretical models to analyze VHF-EPR spectra from selected coal and separated maceral samples that have been studied with other methods (e.g. HRMS, XANES), in order to begin the utilization of spectral data for sulfur speciation.

INTRODUCTION AND BACKGROUND

The goal of this work is the development of VHF-EPR into an analytical technique for the nondestructive determination of the amount and structure of organic sulfur in both native and desulfurized coal. VHF-EPR spectra taken using the unique W-band instrument we have designed and built for this purpose show special sensitivity to heteroatoms in coal. The technique thus can be applied to the problem of non-destructive detection, study, and determination of organic oxygen and sulfur aromatic species in coal. W-band spectra show a great sensitivity to the presence of small amounts of organic sulfur. Data from Illinois coals and separated macerals indicate that it is possible to distinguish aromatic from aliphatic sulfur in a coal. XANES/EXAFS also can provide information on bulk sulfur in a non-destructive fashion, but no single technique should be relied upon completely without other methods for corroboration. Extensive research on the g-matrix values measured from model compounds, together with detailed theoretical studies of the relationships between molecular and electronic structure and VHF-EPR spectroscopic parameters, have allowed us to develop an approach which allows us to computer simulate the spectra and determine
composition. Good computational simulations of Illinois #6 coal W-band spectra, coupled with detailed comparisons of EPR and other analytical data, give us confidence that this method is accurate and robust. Several supporting projects continue to aid in the development of W-band EPR instrumentation, methodology, and interpretation. A regular routine protocol for handling and preparing coal samples has been developed which should be used to give consistent results. VHF-EPR seems to have especially great potential for the routine commercial analysis of aromatic heteroatoms with greater accuracy than can be achieved using some modification of existing methods.

EXPERIMENTAL PROCEDURES

A. Coal Sample Preparation

Significant progress has been made in the development of a standard protocol for coal sample preparation. Following the same protocol for all the samples allows the direct comparison of results from various types of coals. The development of a standard method also allows the calibration of the precision of the techniques and calculation of error limits. The techniques developed must allow for the sensitivity of coal samples to oxygen.

Since the EPR lineshape changes when samples are exposed to oxygen, preparation of coal samples for EPR analysis is done in a nitrogen atmosphere glove bag. All the necessary items needed for coal sample preparation, including the coal samples are exposed to nitrogen environment for two to three days. The oxygen concentration inside the bag is monitored continuously by keeping an oxygen sensitive electrode in the glove bag. The oxygen meter used is manufactured by "Yellow Springs Instrument Company" Yellow Springs, Ohio. The electrode utilizes a membrane with a KCl solution on the inside. The membrane must be kept wet so the electrode is stored in a beaker of distilled water. This meter gives oxygen concentration directly in ppm. EPR sample tubes are prepared at the oxygen level ~4-6 ppm. The EPR sample tubes (.7 mm O.D. quartz tube) are sealed at one end before being placed inside the glovebag. After the tubes are filled, a high quality vacuum grease is applied on the open end and tubes were carefully transferred in small labeled plastic vials. The vials are removed from the glovebag only when EPR
spectroscopy is done.

B. W- Band EPR Spectroscopy

The key to our work plan is the W-band spectrometer. 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 may be found in previous reports. All spectroscopy at W-band (ca. 96 GHz) is done on the instrument constructed in our laboratory. Routine spectra were taken under nitrogen gas flow to avoid any possible oxygen sensitive changes. Lower power (15 db) is used to avoid saturation effects. Different modulation amplitudes were tried and finally a best compromise was achieved between the S/N ratio and the resolution of the spectrum. Data is acquired by a computer, which also controls the magnetic field sweep of the experiment.

C. Model Compounds

A 1000:1 mole ratio mixture of powdered boric acid (Alrich) and dibenzothiophene (DBT) or dibenzofuran (DBF) (Alrich) is heated to the melting point of boric acid (190°C). The molten mass is vortexed to maximize the dispersion of DBT or DBF in the molten solution and then allowed to cool to a glass. The glass is crushed into fine powder and loaded into a quartz sample tube. The tube is placed in a Ray-O-Net irradiation unit and subjected to UV irradiation at 254 nm for 20 to 30 minutes. The sample tube is then removed from the UV light and sealed for analysis. Degassing before and after the irradiation shows no effect on the EPR spectra. This method is a convenient way to produce matrix-isolated ionic radicals at room temperature. Their disordered state closely approximates the environment of similar compounds found in coal.

We have used four microwave frequencies, S-band (2-4 GHz), X-band (9.5 GHz), Q-band (35 GHz), and W-band (95 GHz) to study the radicals produced by this method. CW saturation behavior of organic radicals have been obtained. Modulation amplitude profiles of the sample are routinely probed to achieve the best compromise between the S/N and resolution of possible hyperfine structure. Wide magnetic field scans have been performed for the sample at X-band to make sure all signals are accounted for. Low temperature experiments at the liquid nitrogen (77 K) were also performed for the sample at 9.5 GHz,
no discernible difference in EPR parameters (g and linewidth) is observed, suggest the radical is part of the rigid structure at room temperature. Care has also been taken to avoid distortion of the signal by RC filters.

X-band and Q-band spectra are obtained from Varian E-line EPR spectrometer outfitted with a tracking Varian NMR gaussmeter and a HP frequency divider with a Fluke frequency counter. W-band EPR is performed using the spectrometer system built in our laboratory. All g-value measurements are based on direct field and frequency measurements. A statistical treatment of the g-matrix measured from seven independently prepared samples of DBT in BAG shows that experimental errors are very small (max. standard deviation, \( \sigma_{n-1}=11\times10^{-5} \)). S-band ESEEM is done on a locally-built Electron Spin Echo (ESE) spectrometer.

A computer-assisted analysis using an EPR powder spectrum simulation program (Nilges, 1979) and the spectral parameter optimization routine based on the SIMPLEX algorithm are performed to: 1) confirm the direct measurements of principal g values, 2) extract possible hyperfine interaction, and 3) accurately assess the linewidths and lineshapes. The calculation of principal values of the g matrix is based on Stone's theory (ref Stone) with certain modifications. The SCF-MO wave function and orbital energies are obtained from the semi-empirical method PM3 in MOPAC (ref QCPE 455) All calculations employ an IBM R6000 workstation.

D. Computer Simulations

Computer software to automatically analyze the VHF-EPR spectra has been written in FORTRAN, utilizing a simplex convergence technique to guide parameter optimization. The program reports the area under the spectral region associated with sulfur-containing radicals, as well as the area under the spectral region assigned to purely hydrocarbon radicals. It also reports the three principal g-values for each spectral region, as well as the apparent linewidths. Line shape may be either Gaussian, Lorentzian, or Voigt.

Results and Discussion

The anisotropic g matrix is one of the most important and fundamental EPR parameters. It is generally viewed as characteristic of the electronic structure of the molecule that contains one or more unpaired electrons. But for most
organic radicals, the elements of the g matrices are very close to the free-electron value \( g_0 = 2.00232 \). Experimentally resolving such small differences was difficult using conventional 9.5 GHz EPR, and this greatly limited the usefulness of g matrix as a structure indicator. The development of very high frequency EPR (VHF-EPR) has overcome this problem. From the simple resonance condition one can see easily that the difference in resonance fields for two slightly different g factors is proportional to the product of the microwave frequency and the difference between the two g factors.

\[
B \quad B_1 \quad B_2 \quad \frac{2}{g_2g_1} \begin{pmatrix} 1 \\ -\frac{1}{g_2} \end{pmatrix} \quad (2\gamma)(-\frac{g_1}{g_2})
\]

Therefore the g resolution will be enhanced by a factor of 10 on going from X-band (9.5 GHz) to W-band (95 GHz) providing the line does not broaden substantially with microwave frequency.

At a sufficiently high field, the electronic Zeeman interaction will dominate the electron-nuclear hyperfine interaction, and both the electron and nuclear spins will be quantized along the external field. Under favorable conditions, the anisotropic hyperfine coupling matrix, A, can be resolved or partially resolved along the canonical directions of g matrix, yielding additional valuable information about molecular structure and other properties related to the ground electronic state of a molecule. Indeed, we have observed the anisotropic A matrix in the continuous wave VHF-EPR spectra of a series of thiophenic radicals. In addition, an auxiliary experiment using a low frequency pulsed spectrometer at S-band (2-4 GHz) also reveals the anisotropic hyperfine interactions between the electron spin and the ring protons.

The multifrequency approach has resulted in a unified set of magnetic parameters (g and A matrices), from which it is possible to identify and characterize the radical species in terms of properties related to its molecular orbital structure. The total spin energy Hamiltonian for an electron with spin S is written:

\[
H_{\text{spin}} = H_N + H_e = B \cdot (L \cdot g \cdot S) + L \cdot S
\]
The shift due to organic heteroatoms (O and S) results from a change in resonance energies caused by anisotropy in $g_e$ and the spin-orbit constant $\delta$, coupling the spin and orbital angular momenta ($L$). The larger the field shift $\Delta B$, the more sensitive our experiment will be to the presence of sulfur. It is for this reason that we observed the shift due to sulfur at higher spectrometer frequencies. Since XANES results from Illinois coals shows that thiophenic sulfur is the aromatic form in which the majority of organic sulfur is found in these coals, the connection between molecular and electronic structure found in the series of model thiophenes can be used as a basis for the analysis of VHF-EPR spectra from coal.

As an example of the information obtained from model compounds, let us consider results from one molecule in the thiophene series. The second derivative representation of the EPR spectra of dibenzothiophene radical ions in boric acid glass (DBT/BAG) are shown in Fig. 1, where we see also the importance of choosing instrumental settings - in this case modulation amplitude - carefully to avoid suppressing information. The spectra at

![Figure 1. The modulation amplitude profile of DBT/BAG at W-band.](image)

higher frequencies (Q-and W-band) show greatly enhanced $g$ spectral resolution for the powder sample. All canonical points are revealed from the spectrum. They are so well separated in the W-band spectrum that all three principal values of the $g$ matrix can be read directly from the simplified, almost ideal spectrum of a rhombic $g$ matrix. In
contrast, the X-band spectrum only shows a signal with anisotropic hyperfine interactions intertwined with g anisotropy. The g matrix is not resolved at all and the hyperfine interaction is not well resolved either. This has resulted in a very complicated spectrum that is difficult to analyze. However, one should note that there are hyperfine interactions resolved in the W-band spectrum along the high field direction. A five-line pattern of 1:4:6:4:1 intensity proportions, suggests that there is one set of four, or two sets of two very similar, chemically equivalent I=1/2 nuclei.

We also obtained an S-band ESEEM (Electron Spin Echo Envelope Modulation) spectrum of DBT/BAG. The analysis of the ESEEM spectrum of DBT yields following possible anisotropic hyperfine coupling constants tabulated in the Table 1. Note that there are two sets of two chemically equivalent protons; but the two protons of a chemically equivalent set are magnetically inequivalent. Assuming that one of the principal axes in which the A matrix is diagonal is along the CH bond, then a simple geometrical model shows that they have different Euler angles $\varphi$, where the definition of Euler angles conforms with the convention of Rose (Rose, 1957). With the hyperfine matrices obtained from the S-band ESEEM peaks, simulation of the W-band EPR spectrum of DBT has been attempted, and the reconstructed EPR spectrum is in good agreement with the experimental spectrum.

Table 1. Hyperfine Coupling Constants for DBT as Measured by ESEEM, and Initial Assignments of ESEEM Peaks*

<table>
<thead>
<tr>
<th>INTENSITY (A.U.)</th>
<th>$\Box_n$ (MHz)</th>
<th>$A = 2(\Box_0 \pm \Box_n)$ (MHz)</th>
<th>Tentative Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.6</td>
<td>0.62</td>
<td>13.0, 10.2</td>
<td>$^{10}$B matrix peak</td>
</tr>
<tr>
<td>5.2</td>
<td>0.74</td>
<td>14.3, 9.0</td>
<td>$A_x(a,a',b,b')$</td>
</tr>
<tr>
<td>2.0</td>
<td>1.3</td>
<td>14.9, 8.4</td>
<td>$A_x(b,b')$</td>
</tr>
<tr>
<td>1.5</td>
<td>1.6</td>
<td>16.6, 6.7</td>
<td>$A_y(b,b')$</td>
</tr>
<tr>
<td>1.9</td>
<td>2.5</td>
<td>18.2, 5.2</td>
<td>$A_y(a,a')$</td>
</tr>
<tr>
<td>1.1</td>
<td>3.3</td>
<td></td>
<td>$A_x(a,a')$</td>
</tr>
</tbody>
</table>

*Note: $\Box_0 = 5.8$ MHz for the matrix protons. Each hyperfine tensor deduced from the $\Box_n$ has two possible solutions (and
both solutions are possible), the bold numbers represent our initial guesses and from which the tentative assignment is made.

With the help of the SIMPLEX optimization routine, EPR parameters can be optimized to give a best fit for the W-band spectrum of DBT. At the high frequency, the goodness of fit between the simulation and experimental spectra is very sensitive to the variation of the g matrix, so the g matrix is best obtained from the high-frequency fitting. With the same g matrix, an X-band EPR spectrum can be also reconstructed and optimized to yield a better A matrix. This set of parameters optimized for X-band is then in turn used for another round of optimization for W-band. After the iteration process converges, a single set of the spin Hamiltonian parameters used in the reconstruction of the best fit spectra at all three frequencies is found (Table 2). The best-fit simulations are shown in Figure 2.

![Figure 2. Fit of simulated to experimental W-band spectra of DBT in BAG.](image)

It is interesting to compare the multifrequency EPR spectra of DBT with its oxygen analogue DBF (Fig. 3) from both a chemical and spectroscopic point of view. Although they are thought be similar structurally, the EPR spectra of these two species are drastically different at each of the corresponding
frequencies. Unlike the DBT cation radical, the DBF ionic radical shows little g anisotropy but large hyperfine anisotropy. Therefore, the EPR spectra of these two at the corresponding frequencies are very different. We suggest that the profound differences may prove to be the key to being sure that we are looking at sulfur-cainting species in coal rather than oxygen-containing ones, but this point needs considerable exploration. The best fit spin Hamiltonian parameters are listed in the Table 3.
Table 2. The Spin Hamiltonian Parameters of DBT/BAG

<table>
<thead>
<tr>
<th></th>
<th>xx</th>
<th>yy</th>
<th>zz</th>
<th>□</th>
<th>□</th>
<th>□</th>
</tr>
</thead>
<tbody>
<tr>
<td>g tensor</td>
<td>2.01135</td>
<td>2.00630</td>
<td>2.00237</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A tensor of a, a' (MHz)</td>
<td>19.16</td>
<td>3.84</td>
<td>11.88</td>
<td>±21</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A tensor of b, b' (MHz)</td>
<td>7.87</td>
<td>14.38</td>
<td>10.41</td>
<td>±141</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>linewidths (MHz) @ W-Band</td>
<td>11.94</td>
<td>5.16</td>
<td>3.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>linewidths (MHz) @ Q-band</td>
<td>6.63</td>
<td>4.10</td>
<td>3.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>linewidths (MHz) @ X-Band</td>
<td>3.30</td>
<td>3.08</td>
<td>3.20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 3. W-band spectrum of BNT, dibenzofuran, with simulation, for comparison with DBT, Figure 2.
Table 3. The Spin Hamiltonian Parameters of DBF/BAG

<table>
<thead>
<tr>
<th></th>
<th>xx</th>
<th>yy</th>
<th>zz</th>
<th>$\pm$</th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>g tensor</td>
<td>2.0031</td>
<td>2.00210</td>
<td>2.00259</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A tensor of a, a' (MHz)</td>
<td>29.55</td>
<td>6.00</td>
<td>10.00</td>
<td>$\pm16$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>A tensor of b, b' (MHz)</td>
<td>9.44</td>
<td>3.57</td>
<td>3.54</td>
<td>$\pm74$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>linewidths (MHz) @ W-Band</td>
<td>2.59</td>
<td>2.28</td>
<td>2.74</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>linewidths (MHz) @ Q-band</td>
<td>1.29</td>
<td>6.02</td>
<td>3.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>linewidths (MHz) @ X-Band</td>
<td>1.50</td>
<td>1.50</td>
<td>1.50</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

If we use $\Delta g = g_1 - g_2$ to measure the g anisotropy and $\Delta A = A_{\text{max}} - A_{\text{min}}$ to measure the hyperfine anisotropy then we can examine the relations between the g and A anisotropy. For DBF at W-band, the g anisotropy is on the same order of magnitude as that of g matrix. In this case, the interplay between the g and hyperfine anisotropy is most strong, resulting in a complicated spectrum. From a spectroscopic point of view, this is similar to the case of DBT at X-band. Therefore, we predict that the spectrum of DBT at a much lower frequency, say at 0.5 GHz, will be similar to that of DBF at X-band. This frequency should be closer to the lower limit of the frequency range of the multifrequency analysis than the X-band frequency that we used experimentally. The anisotropic A matrix would be determined more accurately if the 0.5 GHz frequency data were available. On the other hand, the spectrum of DBF at a much higher frequency, e.g. 1000 GHz, will probably behave similarly to that of DBT at W-band, which means that the g matrix of the DBF would be measured with less uncertainty if 1000 GHz data were available. It is one of the goals of our laboratory to develop this multifrequency capability in order to achieve better results in the characterization of molecular structure in coal and other disordered materials.

B. Tests of the Method on Coals
Several experiments have been performed to test the accuracy of the VHF-EPR method for aromatic sulfur analysis in coal. The first of these tests was suggested by Dr. Ken Ho, ICCI project monitor, and consisted of making blends of two coals of known sulfur composition. VHF-EPR analyses of these blends then could be checked against the known sulfur content. Accordingly, a vitrinite (organic sulfur 2.9% dmf) and a sporinite (organic sulfur 4.25%) were blended, and the sulfur content of these blends measured by VHF-EPR was compared to the known composition. Figure 4 shows the results of this test. The VHF-EPR results agree with the known values to better than ± 0.1%.

Figure 4. VHF-EPR sulfur analysis test on vitrinite/sporinite blends.

The second type of test which was performed to evaluate the method was the direct analysis of organic sulfur content in a variety of coals of widely differing character, spanning the range of sulfur content from less than 0.5% to more than 11%. These coals were selected because each had been carefully analyzed for organic sulfur content by other chemical and physical methods. Figure 5 shows the excellent correlation between VHF-EPR analyses and the published organic sulfur content of these coals.
Figure 5. Correlation between VHF-EPR and other analyses for organic sulfur in a series of coals.

The third type of test which we performed to validate the VHF-EPR method was a direct comparison of results from the method and those obtained by XANES on identical samples. XANES is the other non-destructive analytical method for sulfur in coal. Sets of samples prepared by Dr. Steve Palmer, Southern Illinois University-Carbondale, were sent to Prof. G. Huffman, University of Kentucky, for analysis by XANES, as well as to us for analysis by VHF-EPR. Figure 6 shows the comparison of the two methods on four IBCSP coals. Nearly perfect agreement is seen in IBC 101, 102, and 106, while a considerable disagreement is seen in values for IBC 109. Figure 7 shows a similar comparison between VHF-EPR and IBCSP published values for organic sulfur in these coals.

Figure 6. Comparison of VHF-EPR and XANES analyses on four IBCSP coals.
Figure 7. Comparison of VHF-EPR analytical results and IBCSP values for organic sulfur in four coals. A comparison of Figures 6 and 7 show that the VHF-EPR determination of aromatic sulfur is at variance with both XANES and proximate analytical data in the case of IBC 109, and that a much better correlation exists for the XANES data than for the proximate analytical data. The reasons for disagreement in the case of IBC 109 are currently being investigated.

CONCLUSIONS AND RECOMMENDATIONS

This research and development project has demonstrated a new analytical method for determining the aromatic sulfur content of coals and coal-related materials. It is based on VHF-EPR technology, and is non-destructive, quick, and precise. The method requires only a few tenths of a milligram of sample. The precision of this measurement seems less sensitive to sample oxidation than does XANES, although a much more detailed comparison of the two methods clearly is in order. VHF-EPR analysis for aromatic sulfur seems a good choice for routine coal characterization. It also should be very useful in the evaluation of various desulfurization technologies, and as a monitor of the extent of desulfurization.

Several scientific questions remain for future work. These include: (a) the effects of spin exchange in modifying observed g-values in coals; (b) the effects of oxygen and sample oxidation; and (c) the advantages of working at magnetic fields higher than 3.4 T. Additional instrument development and some fundamental research on items (a) - (c) could extend the technique into the analysis of heteroatomic oxygen as well as sulfur.

REFERENCES

HAZARDOUS WASTE MANAGEMENT REPORT
September 1, 1993 through August 31, 1994

Project Title: VHF EPR QUANTITATION AND SPECIATION OF ORGANIC SULFUR IN COAL

DOE Grant Number: DE-FC22-92PC92521 (year 2)
ICCI Project Number: 93-1/6.1A-2P
Principal Investigator: R. B. Clarkson, UIUC
Co-Principal Investigator: R. L. Belford, UIUC
Project Manager: Ken K. Ho, ICCI

COMMENTS

There were no hazardous waste generate by this project.