DIRECT DETERMINATION AND QUANTIFICATION OF SULFUR FORMS IN HEAVY PETROLEUM AND COALS. PART II: THE SULFUR K EDGE X-RAY ABSORPTION SPECTROSCOPY APPROACH

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ABSTRACT

A Sulfur K Edge X-ray Absorption Spectroscopy method has been developed for the direct determination and quantification of the forms of organically bound sulfur in nonvolatile petroleum and coal samples. XANES spectra were taken of a number of model compounds, mixtures of model compounds, heavy petroleum and coal samples. A third derivative analysis of these spectra allowed approximate quantification of the sulfidic and thiophenic components of the model mixtures and of heavy petroleum and coal samples.

INTRODUCTION

Although many attempts have been made to determine the forms of organically bound sulfur in nonvolatile and solid hydrocarbonaceous materials, virtually all have involved in one way or another some chemical change to the structures, and leave open questions as to what is being measured (1). While less of an issue for petroleum based samples (2), chemical derivatizations of coal require good mass transport to be sure that the reaction is complete and all products are accounted for. Pyrolysis type experiments (3a) leave open the question as to whether sulfur forms are interconverting (3b). To remove these ambiguities, a direct measurement is required, which must be element specific, environment sensitive, and must be able to observe the entire sample. X-ray Absorption Spectroscopy (XAS) is one such method. In earlier work Hussain et al. (4), Spiro et al. (5), and later Huffman et al. (6,7) demonstrated the potential of sulfur X-ray absorption spectroscopy for the qualitative determination of sulfur forms in coals, however they made no attempt at quantification. This report investigates the applications of X-ray absorption near edge spectroscopy (XANES) for the purpose of speciating and quantifying the forms of organic sulfur in solids and nonvolatile liquids.

EXPERIMENTAL SECTION

The details of the XANES experimental setup and data analyses have been described previously (3b,8). All model compounds used in this study were obtained from Aldrich Chemical Company and were used without further purification. The asphaltene samples were prepared from their respective petroleum residua by precipitation from n-heptane following the procedure of Corbett (9). A sample of Rasa lignite was generously provided by Dr. Curt White. The sample of Illinois #6 coal was obtained from the Argonne Premium Coal Sample Bank.

RESULTS AND DISCSSION

XANES of Model Compounds

Table 1 lists the first inflection points of the sulfur K edge spectra for a series of model compounds whose structures are believed to be representative of the types of organically bound sulfur found in heavy petroleum and coals. Although the absolute value for the energy calibration contains some uncertainty, the relative accuracy of the energy scale proved to be reproducible to within less than 0.1 eV. The total span in energy is quite large, being some 12.4 eV between thiohemianthraquinone and potassium sulfate. As might be anticipated (10,11), the first inflections of compounds with more oxidized sulfur are notably higher in energy than for those with reduced sulfur. The sulfur XANES spectra of compounds with similar sulfur electronic environments were found to be similar. For example, dibenzothiophene and benzothiophene were found to give similar sulfur XANES spectra, whereas dibenzothiophene and thianthrene, whose sulfur atoms are in significantly different environments, exhibit dissimilar sulfur XANES.

Examination of Table 1 reveals that the edge of dibenzothiophene is displaced from that of benzyl sulfide, the first inflection energy being some 0.6 eV higher for the former compound. The XANES spectra of the compounds listed in Table 1 (3b,8) can readily be used as a fingerprint for the electronic nature of organically bound sulfur, and for distinguishing between the forms of sulfur in the pure compounds. From previous XANES data on dibenzothiophene and benzyl sulfide and physical mixtures of the two, it proved possible to identify each compound in the presence of the other (3b,8). Additionally by simply measuring the heights of the third derivative features at 2469.8 eV and 2470.8 eV relative to the base line in the model compound mixtures, a calibration was established which allowed an approximate estimate of the amounts of each component in hydrocarbon samples to be obtained.

XANES of Petroleum Residua

On the left side of Figure 1 the sulfur K edge spectra for three different petroleum residua and the asphaltene samples prepared from them are shown. While the absorption spectra all appear to be similar, differences are revealed by examining the third derivatives of the spectra, which are shown on the right side of the figure. All the residua samples appear to contain sulfur bound in sulfidic and thiophenic forms, the amount of sulfidic sulfur increasing from sample 1 to sample 3. The asphaltene samples prepared from residua 2 and 3 also appear to contain both forms. Assuming that the composition of the sulfur forms in these samples is approximated by the simple two component mixture of dibenzothiophene and dibenzylsulfide models, an estimate of the relative molar quantities of sulfidic and thiophenic forms can be obtained as described above. These approximate values are listed in Table 2. In samples 1 and 3, it is clear that the predominant form of sulfur in the asphaltene fractions is thiophenic and the predominant form in the whole residuum is sulfidic. For sample 2, there appears to be no such discrimination.

In the latter case, the totals do not add to 100%. While thickness effects may play a role, a more probable explanation for this observation is that a range of slightly different sulfur types, of both sulfidic and thiophenic forms exist in this material, which causes a broadening of the features of the XANES spectrum and making quantification based on mixtures of two model compounds less

accurate. In agreement with this the structure of the third derivative spectra of both the resid sample 2 and the asphaltene derived from it do appear to be broadened relative to that of the spectra of sample 3 in Figure 1. Since the broadening takes place in the "sulfidic" region, both data sets were normalized to 100%, giving a rough approximation of the amounts of sulfidic and thiophenic sulfur, which are shown in parentheses in the table.

XANES of Coal

In Figure 2 are shown the XANES spectra and their third derivatives of the Rasa lignite and Illinois #6 coal samples, and Table 2 the approximate quantification of sulfur types. The former coal was chosen for this study because it has an unusually high amount of organically bound sulfur, and an unusually low level of pyritic sulfur (12). The latter was chosen because its relatively high pyritic sulfur content provides a means of defining to what extent pyritic sulfur interferes with data interpretation.

For Rasa lignite, this XANES analysis indicates that about 30% of the sulfur is sulfidic and 70% is thiophenic. These numbers are in agreement with those found by XPS (14). Partial confirmation of these values also comes from the work of Kavcic (13), who showed that about 75% of the sulfur in this lignite was not reactive toward methyl iodide; this lack of reactivity was attributed to the sulfur being bound in ring structures. Even recognizing the potential or inherent errors of the methyl iodide method such as degree of reaction, possible side reaction, etc., the extent of agreement of the direct and indirect techniques is good.

The XANES spectrum for the Argonne Premium Illinois #6 coal and its third derivative in Figure 2 clearly show that pyritic sulfur is a signficant component. As a first step to extract data on the organic sulfur content, the XANES spectrum of iron pyrite (determined separately and not shown in the figure) was mathematically subtracted from the XANES spectrum of the coal. The resulting spectrum and its third derivative are shown in Figure 2 below those of the whole coal, and from this third derivative approximate quantifications of 60% sulfidic and 40% thiophenic sulfur forms were determined (Table 2). It is interesting to note that these are in reverse order from what was found by XPS analysis on this same coal (14) and on another Illinois #6 sample by pyrolysis techniques (3a). The XANES approximations for this coal should be considered as tentative and subject to change due to possible errors in the subtraction method used. For example, if the pyrite actually present in the coal has different spectral characteristics than the pyrite sample examined by XANES, the sulfidic numbers could be higher than actual. Work is in progress to better define the interference effects of pyritic sulfur. It is interesting to note that if these data are shown to be valid, comparison with data obtained by pyrolysis would imply that sulfidic sulfur can interconvert to some extent to thiophenic sulfur on heating.

CONCLUSIONS

This work has demonstrated that organically bound sulfur forms can be distinguished and in some manner quantified directly in model compound mixtures, and in petroleum and coal. The use of the third derivative XANES spectra was the critical factor in allowing this analysis. The tentative quantitative

identifications of sulfur forms appear to be consistent with the chemical behavior of the petroleum and coal samples, although large amounts of pyritic sulfur may interfere with the accuracy. Further work is in progress to resolve the pyritic sulfur question and to extend these techniques to other nonvolatile and solid hydrocarbon materials.

ACKNOWLEDGEMENTS

X-ray absorption spectra were recorded at the Stanford Synchrotron Radiation Laboratory, which is funded by the Department of Energy, under contract DE-AC03-82ER-13000, Office of Basic Energy Sciences, Division of Chemical Sciences and the National Institutes of Health, Biotechnology Resource Program, Division of Research Resources. The writers wish to thank Dr. Curt White (PETC) for providing a sample of Rasa lignite, and Dr. K. Vorres (Argonne) for the sample of Illinois #6 coal.

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TABLE 1
Sulphur K edge First Inflection Energies (b)

Compound	First Inflection (a) (eV)
K2SO4	2478.5
anthraquinone 6-sulfonate(Na)	2477.6
tetramethylenesulfone	2475.6
diphenylsulfone	2474.8
dibenzothiophenesulfone	2474.7
dimethyl sulfoxide	2472.8
tetramethylenesulfoxide	2472.4
2-methylthiophene	2470.6
benzothiophene	2470.4
dibenzothiophene	2470.4
methionine	2470.3
thianthrene	2470.2
dioctylsulphide	2470.1
cystine	2470.1
tetramethylthiophene	2470.0
benzylphenylsulphide	2469.9
dibenzylsulphide	2469.8
2-naphthalenethiol	2469.8
cysteine	2469.2
diphenyldisulphide	2469.2
dibenzyldisulphide	2469.1
sulfur	2469.1
iron pyrite	2468.4
thiohemianthraquinone	2466.1

a. First inflection points were obtained from the position of the lowest energy maximum of the first derivative, and are considered accurate to better than 0.1eV.

b. Modified from Reference 8.

TABLE 2
Approximate Quantification of Organically Bound Sulfur Forms in Heavy Hydrocarbons

Sample	% Sulfidic (± 10)	%Thiophenic (± 10)
Petroleum		
Residuum 1	29	71
Asphaltene 1	0	100
Residuum 2	42(58)	30(42)
Asphaltene 2	43(54)	37(46)
Residuum 3	65	35
Asphaltene 3	50	50
Coal		
Rasa lignite	30	70
Illinois #6 (APSB)	60	40

Figure 1

S K-edge XANES and 3rd. Derivatives of Petroleums

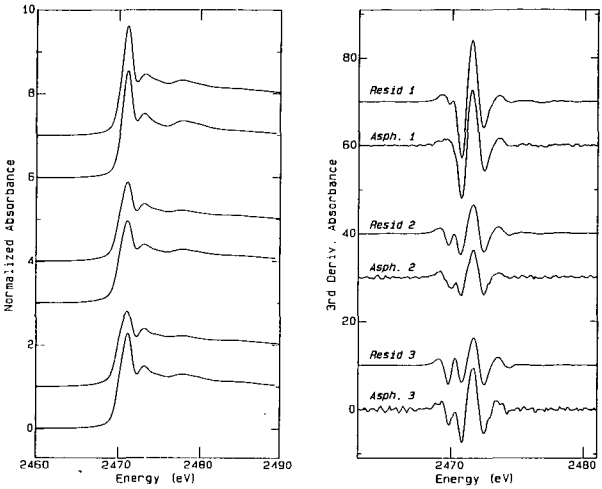
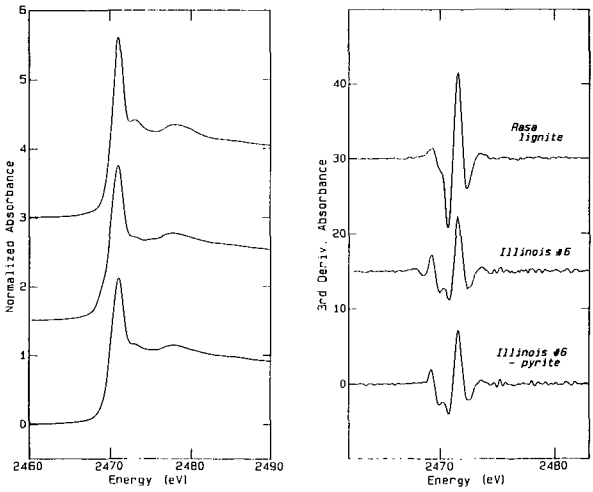


Figure 2

S K-edge XANES of Coals