

DIRECT DETERMINATION AND QUANTIFICATION OF SULFUR FORMS IN HEAVY PETROLEUM AND COALS. PART I: THE X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) APPROACH

S. R. Kelemen, G. N. George, and M. L. Gorbaty

Exxon Research and Engineering Company, Route 22 East, Annandale, NJ 08801

Abstract

We have used the results from model compound studies to deconvolute the sulfur 2p signal from coal and heavy petroleum samples in the terms of the amounts of alkyl sulfides (163.3 eV) and thiophenic-like (164.1 eV) forms. The determination of organic sulfur forms in Illinois #6 coal was accomplished by carefully monitoring the contributions due to iron sulfides and sulfates and application of the deconvolution procedure used with heavy petroleum samples. Our results show that thiophenic-like sulfur comprises the majority of organic sulfur species in fresh Illinois #6 and Rasa coal. Analysis of Rasa coal following air oxidation show that organic sulfidic forms are much more reactive toward oxidation than thiophenic-like species.

I. Introduction

The routine direct quantification of organic sulfur forms in solids and nonvolatile liquids has not yet been accomplished; however, progress has been made using X-ray Adsorption Near Edge Structure (XANES) (1-2). The capability is important for understanding the chemistry of sulfur in coal and heavy hydrocarbons. It has been long recognized that XPS could potentially impact this characterization area for coal (3-8). The characterization of sulfur on coal surfaces by XPS is complex due to the presence of pyrite and other inorganic sulfur species. Other complications are that both organic and inorganic sulfur forms are susceptible to ambient oxidation and that the surface composition may not be representative of the bulk. Despite this awareness there has been very little detailed attention paid to contribution of inorganic sulfur forms. An XPS study (7) of many different coals observed only trace iron signals. The authors associated the 164.2 eV sulfur 2p peak with organic sulfur and attributed it to the sum of thiophenes, sulfides and mercaptans. This study (7) also demonstrated a reasonable correspondence between surface and bulk organic sulfur levels. Our approach to avoid the problems posed by the presence of inorganic sulfur was to establish XPS methods for quantitative determination of sulfur forms using model compounds and petroleum based materials. The same methods were then applied to a coal with a low pyrite and high organic sulfur content for characterization of sulfur forms. Finally a coal with equivalent amounts of pyrite and organic sulfur was analyzed for organic sulfur species after accounting for the contribution of inorganic sulfur forms to the XPS sulfur 2p signal.

II. Experimental

Illinois #6 coal was obtained from the Argonne premium coal sample program. The Rasa coal sample was obtained courtesy of Dr. Curt White at the Pittsburgh Energy Technology Center PETC. Polyphenylene sulfide was obtained from Scientific Polymer Products Inc. and all other model compounds were obtained from the Aldrich Chemical Company, Inc. XPS spectra were obtained with a Vacuum Generators ESCALAB instrument using non-monochromatic $MgK\alpha$ or $AlK\alpha$ radiation.

The petroleum samples were deposited from solution onto a metallic sample block. The coal and powdered model compound samples were mounted to the metallic sample block by means of double sided nonconducting tape. An energy correction was made due to sample charging for coal based on the C(1S) peak position observed at 284.8 ± 0.1 (eV) for the thin films ($<10\text{\AA}$ thickness) of heavy petroleum samples and THF extracts from Illinois #6 samples. These samples are believed to be in electrical contact with the metallic sample block. The spectra were obtained at 0.9 eV resolution. Data acquisition and processing were by means of the VGS 2000 software package. Oxidation experiments were done in air with ~60% relative humidity.

III. Results and Discussion

An idealized XPS sulfur 2p signal is made up of $2p_{3/2}$ and $2p_{1/2}$ components having 2:1 relative intensity and separated in energy by about 1.2eV. We have measured the XPS sulfur 2p signal from a variety of model compounds to obtain the instrumental response for a single component species as well as determine the binding energy representative of different sulfur environments. Figure 1 shows the spectra from several model compounds. We have found that the sulfur 2p signal can be represented by components having an equally mixed Gaussian-Lorentzian line-shape and a FWHM of 1.4 eV. Figure 1 curves A, B and E are examples which have this idealized line-shape. There is a very small peak at several eV higher binding energy than the main 2p signal in curves A and B. This emission is primarily a result of $\pi \rightarrow \pi^*$ shake-up processes (9). We can identify departures from what would be expected for a pure component material. There is a slight broadening of the sulfur 2p signal in Curve C for 2-methyl-L-cysteine; however, the sample is only of 97% purity. The broadening of the higher binding energy peak from the partially oxidized FeS_2 sample, curve D, reflects the presence of oxidized sulfur in environments with slightly different apparent binding energy.

The XPS sulfur 2p binding energy provides a sensitive measure of the electronic character of sulfur within a molecule. (10-12) The binding energies of oxidized organic sulfur forms are fairly well established (8-14) i.e. sulfoxides \sim (166 eV), sulfones \sim (168 eV) and sulfonic acid/sulfate \sim (169 eV). Figure 1 curve E is the sulfur 2p spectrum from dibenzothiophene sulfone which shows a binding energy 168.2 ± 0.1 eV. This agrees favorably with the values reported for sulfone in different polymeric materials (9). The details of the surface oxidation of FeS_2 are complex and will be discussed in greater detail later. The sulfur 2p spectrum of partially oxidized FeS_2 is shown in Figure 1 curve D. The lower binding energy peak occurs at 162.5 eV and is consistent with previously reported values for pyritic sulfur (15-19) which range from 162.3 eV to 163.0 eV. The higher binding energy peak occurs at 168.6 eV and is associated with sulfate. Sulfate was observed as a surface product following air oxidation of pyrite with binding energies of 168.5 eV (19) and 169.1 eV (16). These values are close to those anticipated for ferrous and ferric sulfate (12). Indeed we find the binding energy of ferrous sulfate at 168.9 eV. Brion (16) found 169.4 eV and 169.5 eV for ferric and ferrous sulfate respectively. Values as high as 171.0 eV and 172.2 eV have been published (4, 6) for ferric and ferrous sulfate respectively; however, no attempt was made to account for sample charging in these studies. The binding energy for polyphenylene sulfide in Curve B is 163.7 ± 0.1 eV which quantitatively agrees with a previous finding (9). The 164.1 eV binding energy for sulfur in a thiophenic-like environment (Tilorone Analogue) also agrees with that found for thiophene (12). We find a 163.3 eV binding energy for an alkyl sulfide containing

molecule S-methyl-L-cysteine.

We have measured the XPS sulfur 2p signal from several heavy petroleum samples. The XPS sulfur 2p signal for a single species, based on the instrumental response of pure model compounds, was used in a deconvolution procedure. It was possible in all cases to deconvolute the spectrum from petroleum asphaltene samples into two signals with binding energies of 164.1 eV and 163.3 eV (23). This observation was interpreted in light of available model compound results. The 163.3 eV component is representative of mostly sulfidic forms while the 164.1 eV corresponds to thiophenic-like environments.

We have analyzed the XPS sulfur 2p signal from fresh Rasa lignite coal. The spectrum is shown in Figure 2. It is an unusual coal, having very high levels of organic sulfur (11.68 wt%) and very little inorganic sulfur. The sulfur to carbon atom ratio as determined by XPS was in excellent agreement with that determined by elemental analysis. As we found with petroleum asphaltene, it was possible to deconvolute the main sulfur 2p peak into 164.1 and 163.3 eV components. The 164.1 eV peak makes up 70% of the signal and is assigned to organic sulfur species in thiophenic-like environments. Air oxidation for 5 days at 125°C changes the sulfur 2p spectrum as shown in Figure 3. The presence of oxidized sulfur forms is apparent at high binding energies and these forms make up about 24% of the total sulfur on the surface of Rasa coal. Upon oxidation, the amount of thiophenic-like components remains nearly constant, but the sulfidic components drop dramatically. The distribution of sulfur forms remains about the same following subsequent oxidation in air at 125°C up to 60 days. These results show that the thiophenic-like sulfur components in Rasa lignite are much less reactive toward oxidation relative to sulfidic forms.

Accounting for possible inorganic sulfur forms is essential for an accurate determination of organic sulfur surface species in pyrite containing coals. Figure 4 Curve A shows the iron 2p spectrum from Illinois #6 coal. The Illinois #6 sample was obtained from the Argonne premium sample program in a sealed ampule. The sample was prepared in an N₂ dry box, placed in a sample transfer device, evacuated and then inserted into the VG fast entry air lock for XPS sample analysis. The procedure nearly eliminated exposure to laboratory air. About half of the bulk sulfur in this coal is present as pyrite. The XPS iron spectrum contains a number of peaks that will be identified on the basis of 2p_{3/2} and 2p_{1/2} components from at least two distinct chemical forms. We can identify a sharp iron 2p_{3/2} peak at 708.5 eV and another very broad 2p_{3/2} peak at 713.5 eV. The energies were determined after correction for sample charging based on the C(1S) coal peak. Notice that the corresponding sulfur 2p spectrum, shown in Figure 5 Curve A, does not possess an easily discernible sulfate peak. The sulfur 2p signal appears over the energy loss envelope from the silicon 2s line. The maximum of this broad energy loss envelope occurs near 178 eV.

Careful studies on the surface oxidation of pyrite have shown that initial air oxidation products are an iron deficient sulfide, iron oxides and/or ferric sulfate (19). The binding energy of the metal-deficient sulfide is believed to be similar to unaltered pyrite (19), -707 eV (15-19). Iron oxides and ferric sulfate occur at -711 eV. We have measured a binding energy of 711.0 eV for ferrous sulfate. Sulfate was observed (19) by XPS as a later oxidation product of pyrite exposed to air. No evidence was found for the presence of elemental sulfur up to 14 day air exposure (19); however, elemental sulfur is an observed component in weathered coal samples (26).

The iron 2p_{3/2} binding energies from Illinois #6 coal cannot be chemically interpreted in a straight-forward way because the value falls outside of known limits. To conform to accepted values, the inorganic components would have to experience enhanced sample charging of about 1.0eV to 3.0eV relative to the main organic carbonaceous components. The possibility of enhanced sample charging for inorganic components in coal has been noted before (24,25). If we assume nonuniform sample charging, then the 708.2 eV peak is assigned to iron pyrite or the metal deficient sulfide shifted by ~+1.2eV and the broad peak at ~713.5 eV to iron oxides and/or sulfates shifted by ~+2.5eV. It would follow that the ~722 eV feature is due to the 2p_{1/2} peak from pyrite and the broad 727eV peak due to 2p_{1/2} from iron oxides and/or sulfates. These results show that the substantial portion of the observable iron from a fresh sample surface of Illinois #6 coal is non-pyritic in nature and in poor electrical contact with the organic matrix.

When the XPS sulfur 2p signal from iron pyrite is shifted by 1.2eV toward higher binding energy, it will directly overlap the region for unoxidized organic sulfur species. The total amount of iron present, as determined by the combined area of the 2p_{3/2} peaks from all iron species relative to the total amount of carbon, is only about a third of the amount determined by bulk analysis (Fe/C = 0.0071). Lower than expected iron XPS signals have been noted before (7). Two possible explanations are that the pyrite particles are encapsulated by organic material or that they have a particle size distribution significantly greater than the carbonaceous matter. The pyritic 2p_{3/2} peak is only 20% of the total 2p_{3/2} iron signal. We would, therefore, expect a pyritic XPS sulfur 2p signal that corresponds to a relative intensity of (S/C=0.001) or about 7% of the total sulfur 2p signal. The apparent binding energy of pyritic sulfur would be 163.7 eV due to enhanced sample charging. The pyritic XPS 2p_{3/2} signal decreases substantially upon exposure to air. Figure 4 curve B shows the decline in the iron 2p_{3/2} signal and Figure 5 curve B shows the appearance of a very small sulfate peak near 171.5 eV after a two day exposure to air at 22°C and ~60% relative humidity. Pyritic sulfur is initially present in very small quantities at surfaces of fresh Argonne premium Illinois #6 samples and the amount declines further upon exposure to air.

It was possible to deconvolute the XPS organic sulfur 2p signal from Illinois #6 coal using the same methods as used with Rasa coal and heavy petroleum samples after consideration of the pyritic sulfur contributions as just described and background subtraction of the silicon 2s signal. Figure 6 shows the results. The 164.1 eV peak contributes 64% and the 163.3 eV peak 29% to the total signal. These peaks are interpreted to arise from thiophenic-like and alkyl sulfide environments respectively. These results show that organic sulfur species dominate the XPS sulfur 2p spectrum of fresh Illinois #6 coal and that about 2/3 of the surface organic sulfur exists in thiophenic-like environments.

IV. Conclusions

It is possible to deconvolute the organic XPS sulfur 2p spectrum of coal and heavy petroleum samples into 163.3 eV and 164.1 eV components. These peaks have been interpreted in terms of alkyl sulfides and thiophenic-like sulfur species respectively. Thiophenic-like sulfur represents the majority organic species in Rasa and Illinois #6 coal. Air oxidation of Rasa coal results in the loss of organic sulfides and the production of oxidized species. Detailed analysis of the iron and sulfur XPS sulfur 2p signals shows that inorganic

sulfur species represent a very small fraction of the total sulfur present on surfaces of fresh Argonne Premium Illinois #6 coal.

References

1. George, G.N. and Gorbaty, M.L. J. Am. Chem. Soc. (1989), in press.
2. Huffman, G.P., Higgins, F.E., Mitra, E., Shah, N., Pugmire, R.J., Davis, B., Lytle, F.W., and Greeger, R.B. Energy and Fuels 3 (1989) 200.
3. Schultz, H.D. and Proctor, W.G. Applied, Spectroscopy 27 (1973) 347.
4. Frost, D.C., Leeder, W.R. and Tapping, R.L., Fuel 53 (1974) 206.
5. Frost, D.C., Leeder, W.R., Tapping, R.L. and Wallbank, B., Fuel 56 (1977) 277.
6. Samarendra, N., Dutta, N. and Frost, D.C., Fuel 62 (1983) 840.
7. Perry, D. L. and Grint, A. Fuel 62 (1983) 1029.
8. Jones, R.R., McCourt, C.B. and Swift, P. Proc. Int. Conf. Coal Sci. Dusseldorf (1981) 657.
9. Gardella, J.A., Jr., Ferguson, S.A., and Chin, R.L., Applied Spectroscopy 40 (1986) 224.
10. Siegbahn, K., Phil. Trans. R. Soc. London. A 268 (1970) 33.
11. Gassman, P.G., Callstrom, M.R., Martin, J.C. and Rongione, J.C., J. Am. Chem. Soc. 110 (1988) 8724.
12. Wagner, C.D., Rigg, W.M., Davis, L.E., Moulder, J.F. and Muhlenberg, G.E., Handbook of X-ray Photoelectron Spectroscopy (Perkin-Elmer Corporation, Eden Prairie, MN, 1979).
13. Clark, D.T., and Munro, H.S., Polymer Degradation and Stability 8 (1984) 213.
14. Thomas, H.R., Ph.D. Thesis, University of Durham, U.K. (1977).
15. Van der Heide, H., Hemmel, R., VanBruggen, C.F., and Haas, C. J. Solid State Chem. 33 (1980) 17.
16. Brion, D. Appl. Surf. Sci 5 (1980) 133.
17. Ennaoui, A., Frechter, S., Jaegermann, W. and Tributsch, H., J. Electrochem. Soc. 133 (1986) 97.
18. Jaegermann, W. and Tributsch, H., J. Appl. Electrochem. 13 (1983) 743.
19. Buckley, A.N., and Woods, R., App. Surf. Sci. 27 (1987) 437.
20. Clark, D.T. and Wilson, R., Fuel 62 (1983) 1034.

21. Clark, D.T., Wilson, R., and Quirke, J.M.E., Chem. Geol. 39 (1983) 215.
22. Clark, D.T., and Wilson, R., Org. Geochem. 6 (1984) 455.
23. Kelemen, S.R., George, G.N., Gorbaty, M.L., Fuel Process Technol. in press.
24. Kelemen, S.R., and Freund, H. ACS Fuel Div. preprints 33 (1988) 706.
25. Weitzsacker, C.L., Schmidt, J.J. and Gardella, J.A., Jr., ACS Fuel Div. preprints 34 (1989) 545.
26. Duran, J.E., Mahasay, S.R. and Stock, L.M., Fuel 65 (1986) 1167.

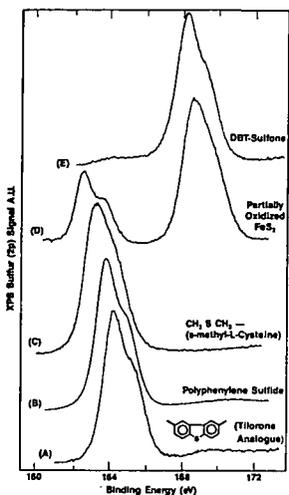


Figure 1

XPS sulfur 2p spectra from model compounds.

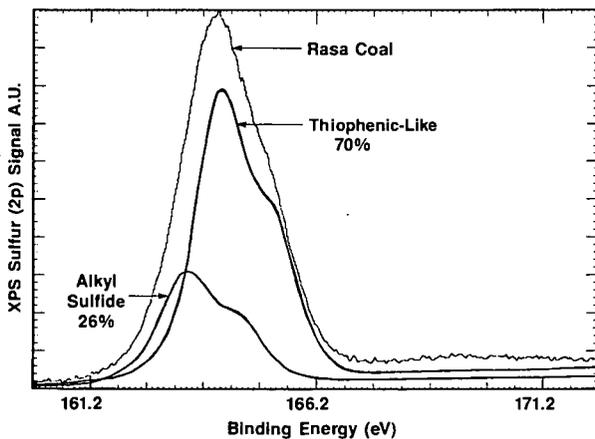


Figure 2

XPS sulfur 2p spectrum from fresh Rasa coal and deconvolution into 163.3eV and 164.1 eV components.

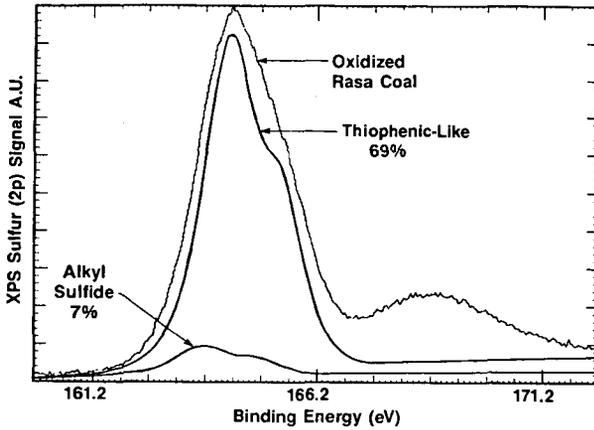


Figure 3 XPS sulfur 2p spectrum from Rasa coal oxidized for 5 days at 125°C and deconvolution into 163.3 eV and 164.1 eV components.

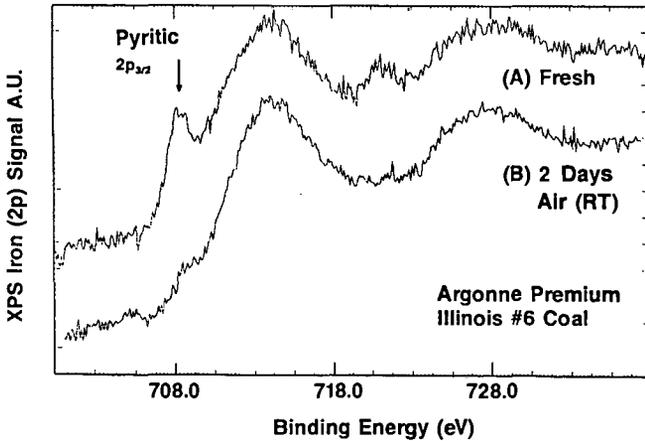


Figure 4 XPS iron 2p spectra from Argonne Premium Illinois #6 coal: a) Fresh; b) after air exposure at 22°C for 2 days

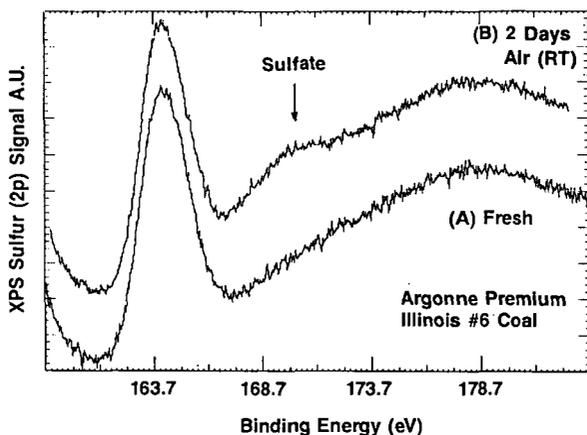


Figure 5 XPS sulfur 2p spectra from Argonne Premium Illinois #6 coal; a) Fresh; b) after air exposure at 22°C for 2 days.

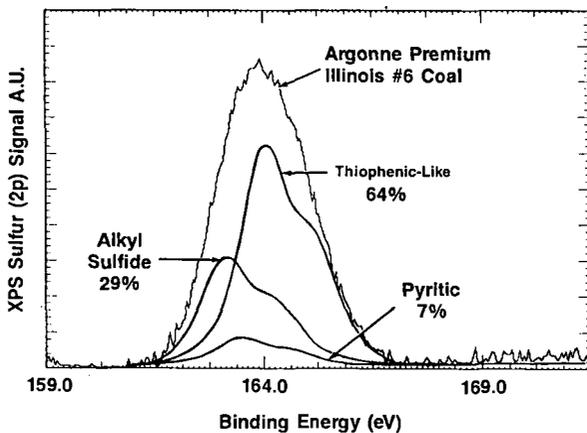


Figure 6 XPS sulfur 2p spectrum from fresh Illinois #6 coal and deconvolution into different components.