

Preprint, to be presented at the 205th ACS National Meeting, Denver, Colorado, March 28-April 2, 1993.

**DETERMINATION OF SULFUR COMPOUNDS IN COAL BY
MASS SPECTROMETRY, CORRELATED WITH XANES AND XPS***

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*This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

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Keywords: Macerals, Sulfur, High Resolution Mass Spectrometry, XANES, XPS

INTRODUCTION

The objective of this study is to identify important organic sulfur-containing compounds in the Argonne Premium Coals and in selected, separated coal macerals. In-source, desorption/pyrolysis high resolution mass spectrometry is being used to characterize the volatile species of whole coals, macerals, and their extracts. To examine the possibility of secondary reactions and undesirable selectivity, the MS data is compared to data from direct techniques, XANES and XPS. The MS results correlate very well which supports the suggestion that the species seen are indigenous to the original sample. Therefore, specific structural assignments to the sulfur species can be made.

Quantitative speciation of organic sulfur in coals has been accomplished by both XANES^{1,2} and XPS² with what appears to be good reliability. Mass spectrometry approaches provide more detailed molecular information, but suffer from problems with sampling.³ In the past we have found it difficult to isolate aliphatic sulfur compounds by thermal desorption or pyrolysis due to their thermal transformation to aromatic species. However, recently we have found that with in-source pyrolysis the occurrence of secondary reactions is reduced significantly. Results from both a selected set of the Argonne Premium Coal Samples and a set of three macerals from the Lewiston-Stockton coal (APCS 7) will be discussed.

Table 1. Analysis of the APCS 7 Macerals.

	%C(maf)	H	Per 100 Carbons			fa
			N	S	O	
Whole Coal	85.5	76	1.6	.3	8.9	.76
Liptinite	81.7	110	1.0	.5	8.3	.56
Vitrinite	80.2	78	1.7	.3	11.5	.75
Inertinite	85.4	46	1.3	.7	7.5	.89

EXPERIMENTAL

The preparation of the macerals by a continuous flow density gradient technique has been discussed and analysis of these samples is presented in Table 1.⁴ The XANES and XPS methods have also been published.²

The desorption chemical ionization (DCI) and desorption electron impact (DEI) mass spectra were obtained on a three-sector high resolution, Kratos MS50 spectrometer operating at 10,000 resolving power. This lower resolution was used to enable a more rapid scanning rate (10 sec/decade). In the CI experiments iso-butane was the reagent gas. Samples are deposited on a small platinum coil that is inserted directly into the source body adjacent to the electron beam and heated electrically at 100°C/minute from 200° to 700°C.

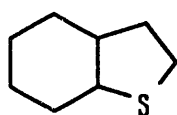
Table 2. Sulfur Distribution in a Selected Set of Argonne Premium Coal Samples.

Coal	%C	S/100C	XANES		XPS		HRMS	
			Al	Ar	Al	Ar	Al	Ar
Lignite	74.1	0.4	37	63	45	55	31-41	69-59
Upper Freeport	88.1	0.3	13	87	19	81	5-7	93-95
Pocahontas	91.8	0.2	13	87	0	100	3-4	96-97

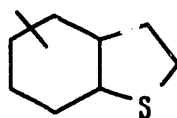
RESULTS AND DISCUSSION

Initially, a set of pyridine extracts was examined by DEIHRMS. Extracts have been found to be quite representative of the whole coal and they typically give higher yields of volatiles compared to the whole, unextracted coals. The results for a lignite and two high rank coals are shown in Table 2 along with the published XANES and XPS results.² Although the MS results are only semi-quantitative, they agree very well with the directly obtained data. The trend of decreasing aliphatic sulfur with increasing rank is evident. It can be concluded that the sulfur containing species seen in the mass spectrometer are likely to represent most of the coal.

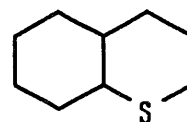
There are some interesting trends in the aliphatic sulfur species seen in the lignite coal. Molecules containing eight and nine carbons tend to dominate. This is especially true at a hydrogen deficiency (rings + double bonds = HD) of two. Possible structures could be:



I

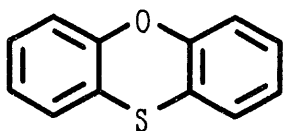


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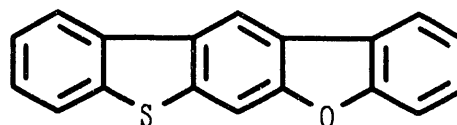


III

Thiolanes (I and II) have been observed in sediments.⁵ In addition, partially reduced thiophenes such as dihydrobenzothiophenes are also quite abundant.



IV



V

In the higher rank coals polycyclic thiophenes and sulfur-oxygen species (for example IV or V) dominate. There is evidence that phenoxathiim (IV) occurs in high sulfur bituminous coals.⁶ The distribution for the Pocahontas IV bituminous coal is shown in Figure 1.

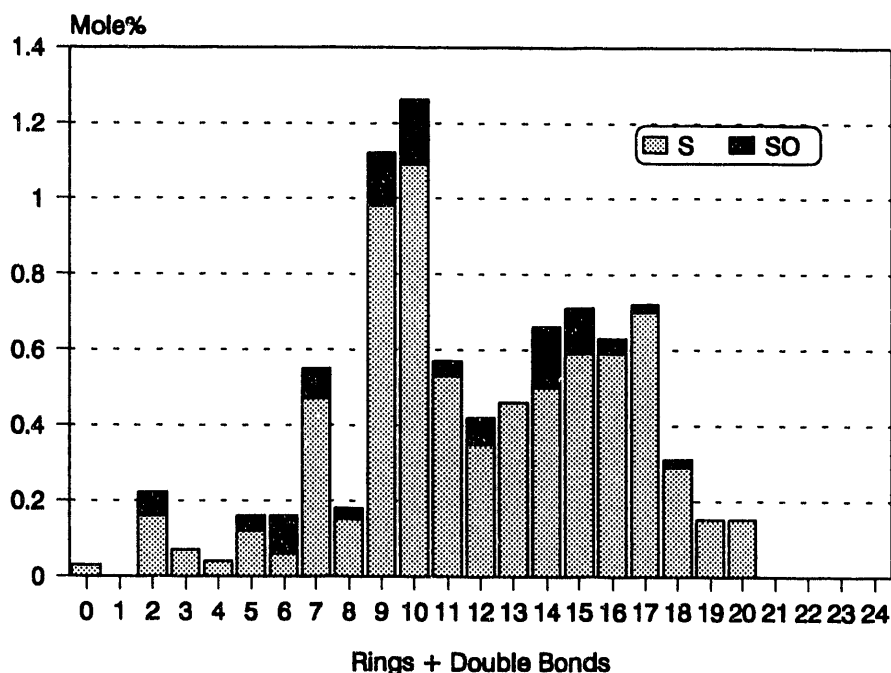


Figure 1. Distribution of organic sulfur containing species as a function of hydrogen deficiency.

XANES and the first XPS results for a set of separated macerals are shown in Table 3. Huffman and co-workers have examined a different set of macerals by XANES.⁴ They found, as is shown in this study, that sporinites typically contain much more aliphatic sulfur compared to either vitrinite or inertinite. The amounts are very similar to those found in lignite coals (Table 2). Since these sporinite macerals have been subjected to more rigorous coalification conditions than the lignite, the sulfur compounds such as those seen in lignite (i.e., thiolanes) would be aromatized. Initial examination of the MS data shows a lack of these compounds. The sulfur compounds are possibly incorporated into extended straight-chain aliphatic networks, which has been observed with alginites.³ As expected the inertinites contain more aromatic thiophenes similar to those seen in the high rank coals. Analysis of this data is continuing.

Table 3. Sulfur Distribution in Lewiston-Stockton Coal and Separated Macerals.

	<u>XPS</u>		<u>XANES</u>		<u>HRMS</u>	
	Al	Ar	Al	Ar	Al	Ar
Whole Coal	14	86	20	80		
Liptinite	35	65	50	50		
Vitrinite	8	92	0	100	Pending	
Inertinite	9	91	0	100		

CONCLUSIONS

Results on the distribution of sulfur compounds determined by in-source pyrolysis HRMS correlates very well with organic sulfur data from XANES and XPS.

ACKNOWLEDGMENT

This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

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