

DIRECT IDENTIFICATION OF ORGANIC SULPHUR SPECIES IN
RASA COAL FROM S L-EDGE X-RAY ABSORPTION NEAR EDGE
SPECTRA

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DIRECT IDENTIFICATION OF ORGANIC SULPHUR SPECIES IN RASA COAL FROM
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ABSTRACT

High resolution (< 0.2 eV) sulphur L-edge X-ray absorption near edge structure (XANES) of several model organic and inorganic sulphur compounds, using monochromatized synchrotron radiation, have been recorded. The near edge features in the S L-edge spectra are much more sensitive to the sulphur chemical environments than those reported in previous studies using spectroscopic techniques such as XPS or S K-edge XANES. The S L-edge spectra of the model compounds have been used as a fingerprint to speciate the inorganic and, in particular, the organic forms of sulphur in Rasa coal. The results indicate that 70% of the organic sulphur in Rasa coal is thiophenic in origin and 30% is of aryl sulphide origin. No detectable quantities (> 1 wt%) of pyrite or oxidised form of sulphur was found in this coal.

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INTRODUCTION

Sulphur impurities in coal appear in different chemical forms such as mineral, inorganic and organic forms¹. While the mineral and the inorganic components are well characterized, the nature of organically-bound sulphur is not known in any detail. Most of the information available on sulphur is indirect and is based on the characterization of pyrolysis products², selective oxidation³⁻⁴, or chemical extracts⁵. Several organosulphur species have been identified in these products, but the species do not necessarily convey the exact nature of organic sulphur moieties in coal. Thus a method for direct characterization of organic sulphur in coal is very desirable.

In recent years, several non-destructive methods have been employed to characterize organically-bound sulphur directly. X-ray photoelectron spectroscopy (XPS) utilizing the S 2p signal⁶⁻⁸, and X-ray absorption spectroscopy using the S K-edge⁸⁻¹⁰, have been employed for identifying and quantifying sulphur in coal. Because of the overlapping of pyritic sulphur with the organic sulphur, the results have not been very reliable, unless the inorganic sulphur was removed prior to the analysis⁹. This is not always possible without affecting the nature of the organic sulphur⁶. Very recently, a curve fitting procedure has been applied to characterize organic sulphur in the presence of pyritic sulphur¹¹. We have recently demonstrated that the S L-edge X-ray absorption near edge structure (XANES) spectroscopy is capable of distinguishing pyritic sulphur from organically-bound sulphur¹².

Rasa coal from Yugoslavia, having a very high organic sulphur and very little inorganic sulphur, has been the focus of many recent studies^{5,10,11}. Direct speciation of organic sulphur in this coal has been attempted very recently^{10,11}. In this study we have used our S L-edge technique¹², with much improved resolution, compared with previous XPS or XANES methods, to identify the nature of the organosulphur species in Rasa coal.

EXPERIMENTAL

A well characterized sample of Rasa coal⁵ was obtained from C.T. Whit of the Pittsburgh Energy Technology Center, U.S. Department of Energy Pittsburgh, U.S.A. The mineral samples (marcasite, pyrite and galena) being mineralogically pure specimens, were polished before analysis to remove the surface contaminants. The model compounds were purchased from Aldrich Chemical Company in highest available purity and used without further treatment. The samples, all in solid form, were pressed lightly on a stainless steel sample holder using a copper conducting tape.

Sulphur L-edge X-ray absorption spectra were obtained at the Canadian Synchrotron Radiation Facility (CSRF)¹³ situated at the 1 GeV Aladdin storage ring, University of Wisconsin. The X-ray beam is monochromatized using a 1800/mm grating. This yields a photon resolution of better than 0.2 eV at the S L-edge. The photoabsorption spectra were recorded at 150-200 eV in the total electron yield mode using a microchannel plate. The energy scale was calibrated with reference to the lowest pre-edge peak in elemental sulphur at 162.7 eV. This value is not an absolute value, but is close to the binding energy of the S 2p level in elemental sulphur as measured by XPS¹⁴. A single scan, with good signal-to-noise ratio could be accomplished in \approx 2 minutes. However, in most cases at least three scans were digitally combined and the background was removed. The details of the technique will be described elsewhere¹⁵.

RESULTS AND DISCUSSION

General Features and Model Compounds

The XANES region in the sulphur L-edge spectrum is rich in structure that is sensitive to electronic environment and local symmetry as well as the bond distances of the atom with its neighbours¹⁶⁻¹⁹. In this report we only deal with the peaks very near the edge of the S L-edge spectrum, these are the structures that can be effectively used to fingerprint sulphur in different chemical forms. In most fresh coal sulphur exists in reduced forms. The oxidized forms of sulphur are usually the product of weathering. This report only deals with unoxidized forms of sulphur.

species. We have shown previously that S L_{2,3}-edge XANES spectra cover a region extending from ≈ 162 to $180 \text{ eV}^{12,17}$. The pyritic and organically-bound sulphur features appear in the region of ≈ 162 - 168 eV , whereas the oxidized forms cover the region of 167 - 180 eV .

For example, Fig. 1 shows the sulphur L-edge spectra of elemental sulphur, DL-methionine and thioxanthen-9-one, and Table 1 lists the peak positions of near edge features for a series of model compounds. These compounds represent the type of organic and inorganic sulphur moieties believed to be present in coal. Also shown in Table 1, as a comparison, are the XPS and S K-edge peak positions. In contrast with XPS which gives a single broad peak for S 2p levels^{7,11}, L-edge spectra for each compound (Fig. 1) consist of three well resolved structures (a, b and c), with different relative intensities. Of the organic compounds studied, peak b had the highest relative intensity compared with a and c. Conversely for pyrite (see Fig. 3) and elemental sulphur, peak a had the highest intensity and peak c appeared as a shoulder in pyrite and marcasite spectra. Detailed analysis of the sulphur L-edge spectra is beyond the scope of this report and will be dealt with in a future paper. Nevertheless, it is apparent from Fig. 1 and Table 1 that the spectra have three important features. First, depending on the electronic environment of the sulphur atom, the position of the peaks shift considerably. Second, the relative intensity and position of peaks a, b and c changes considerably from one compound to another. Third, the linewidths of $\leq 0.8 \text{ eV}$ are considerably narrower than either XPS or S K-edge measurements. The good chemical sensitivity makes it possible to use these spectra as a fingerprint for organosulphur species in coal.

Before applying the S L-edge spectra recorded for model compounds to fingerprint the sulphur in Rasa coal, it is worthwhile to equate this data with the results of XPS and S K-edge studies for the same compounds. In all the compounds listed in Table 1 (except elemental sulphur), sulphur is formally in the reduced form, (S^{2-}), and energy positions in all three techniques decrease substantially from thioxanthen-9-one to galena. For example, comparing the shift between thiophenic sulphur and pyritic sulphur, the peaks shift by $\approx 2 \text{ eV}$ for all three techniques. However even in this case, the chemical sensitivity of the S L-edge technique is

much larger than that of the XPS^{6,7,11} or S K-edge⁹⁻¹¹ techniques because of the very different relative intensities of the peaks between organic and pyritic sulphur spectra (Fig. 1 and 3), and peak linewidths (≤ 0.8 eV) are much less than for XPS measurements (> 1 eV) or the S K-edge measurement (> 2 eV). Our photon widths are much narrower than those used for the XP or S K-edge measurement, and the S K-edge inherent linewidth is much larger than for the S L-edge linewidth. In addition, the L-edge spectra generally have more peaks than K-edge spectra due to different selection rules. As a result, sulphur in sulphidic form can be distinguished from sulphur in a thiophenic environment. The S L-edge spectrum of a 1:1 molar mixture of cystine and 1,2-benzodiphenylene sulphide (thiophenic form) is shown in Fig. 2. Also included in this figure (not to the same scale) are the spectra of each pure compound for identification. As evident from Fig. 2, the well-resolved S L-edge peak, labelled a, is assigned entirely to cystine while peak d belongs to the thiophenic form. The other two peaks, labelled b and c, arise due to contributions from both sulphur-containing phases and provide no additional fingerprinting information. Note, the clear distinction of these two organic sulphur compounds cannot be made with XPS or S K-edge techniques. Having achieved this capability, we are in a position to identify organic sulphur in coal.

Characterization of organic sulphur in Rasa coal

Rasa coal has been known for many years and the recent conventional chemical analysis⁵ shows that it contains mostly organic sulphur (10.4%) and a small amount of inorganic sulphur (0.3%). In order to investigate this non-destructively, and show directly that Rasa coal does contain almost entirely organic sulphur, a sample of Rasa coal was fortified with pyrite. Figure 3 shows the S L-edge spectra of the Rasa coal along with pyrite and a mixture of Rasa coal and pyrite. Figure 3 clearly shows that this is indeed the case. Peaks a and b correspond to pyrite whereas c, d, and e belong to Rasa coal. This is the first time that organic sulphur has been distinguished directly and unambiguously from pyrite by spectroscopic methods. As Fig. 3 indicates, there are no detectable quantities (> 1 wt%) of pyrite in this coal.

Characterization of the organic nature of sulphur in Rasa coal can now be attempted using this information. Several indirect studies have been reported in the literature regarding the nature of organic sulphur in Rasa coal. Kavcic²⁰ and Ignasiak et al.²¹ have shown by chemical methods that about 75% of sulphur in this coal is thiophenic. White et al.⁵ recently made an extensive study on Rasa coal. Besides other investigations, they have used low-voltage, high-resolution mass spectrometry to identify the organic species in the chemically-extracted products from Rasa coal. From the mass spectra a great number of compounds have been identified. These include large families of thiophenic, a few anthracenic and some sulphidic species. The molecular formula assignment is based on mass measurements and no direct confirmation is available⁵. Gorbaty and co-workers^{8,10,11} used XPS and S K-edge XANES spectroscopy to characterize and quantify organic sulphur in Rasa and other coal samples. They found from XPS that 70% of sulphur in Rasa coal is thiophenic, 26% is sulphidic, and 4% is pyritic. As explained above these two techniques have their limitations and because of the lack of required resolution, are not able to visually resolve different forms of sulphur compounds. In the case of XPS, extensive curve reconstructions are required to identify different components contributing to observed spectra¹¹, and for S K-edge a third-derivative analysis of the spectra is needed to distinguish different compounds¹⁰.

The chemical sensitivity of S L-edge spectroscopy is shown in Fig. 4 and 5 where spectra of Rasa coal are given along with those of cystine and 1,2-benzodiphenylene sulphide (thiophenic sulphur), respectively. It is obvious from Fig. 4 that, based on the chemical shift and different relative intensity of peaks a, b and c, the chemical forms of sulphur in Rasa coal substantially differ from those of cystine. On the other hand, the thiophenic spectrum in Figure 5, as far as the peak positions are concerned, is very similar to that of Rasa coal. The energy positions of peaks a, b and c in Rasa coal are 164.4, 165.7 and 166.9 eV, respectively whereas those of the thiophenic form are 164.4, 166.0 and 167.1 eV, respectively. As expected, this indicates that either the thiophenic form (forms) in the coal has a different substitutional arrangement or we are dealing with a mixture. The former possibility was investigated by

digitally combining the spectra of the model compounds with the thiophenic form. Table 1 shows that polyphenylene sulphide has the appropriate energy to be used in this respect. Figure 6 shows the spectrum of Rasa coal along with the combined spectra of 70% thiophenic and 30% polyphenylene sulphide. As shown, the combined spectrum closely resembles that of Rasa coal. No other combinations, whether with polyphenylene sulphide or other model compounds, could reproduce the Rasa coal spectrum. As far as the thiophenic portion is concerned, our results are in agreement with direct¹⁰⁻¹¹ and indirect^{20,21} findings. Gorbaty and co-workers¹⁰ found that 70% of the organic sulphur in Rasa coal is thiophenic and 30% is sulphidic (alkyl sulphide). Figure 7 shows the spectrum of Rasa coal and combined spectrum of 70% thiophenic and 30% alkyl sulphide. The alkyl sulphide, DL-methionine, used in the construction of this spectrum is very similar to S-methyl-L-cystine used by Gorbaty and co-workers^{10,11}. As indicated in the figure, the combined spectrum is not as similar to the Rasa coal spectrum as that in Fig. 6. This suggests that the presence of alkyl sulphide in Rasa coal is doubtful. White et al.⁵ using mass spectrometry did not detect any alkyl sulphide, while several phenyl sulphides were observed. This supports the results presented in this work. However, it is possible that several other thiophenic sulphur compounds having different substitutions were present^{2,5}. This would result in slightly different spectral shapes. More work is being pursued using other varieties of model compounds to better define the nature of organic sulphur not only in Rasa coal but in several other coal samples from different localities.

CONCLUSIONS

We have shown that the near edge region of S L-edge X-ray absorption spectra is very sensitive to the electronic environment and local symmetry of the sulphur atom. As a result, the fine features in this region can be effectively used to fingerprint sulphur impurities in coal. For the first time, it has been possible to distinguish unequivocally the pyritic sulphur from organic sulphur. In that respect other X-ray methods such as XPS and S K-edge as well as optical methods have failed to achieve this

capability. Using several model organic compounds it has been possible to identify organic sulphur species in Rasa coal. It was found that organic sulphur in this coal is $\approx 70\%$ in the thiophenic form and $\approx 30\%$ in the form of phenyl sulphide. Further work is under way to identify the exact nature of the thiophenic form.

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Table 1. Peak positions of sulphur L-edge as compared with the XPS and the K-edge data.

Compound	L-edge ¹			XPS ²	K-edge ³
	a	b	c		
Organic Sulphur					
Thioxanthen-9-one	165.0	165.9	167.1	164.1	-
1,2-Benzodiphenylene sulphide	164.2	166.0	167.1	164.0	2470.4 ⁴
Thianthrene	163.9	165.1	166.3	-	2470.2
poly(phenylene sulphide)	163.9	165.4	166.7	163.7	2470.4
DL-Methionine	163.9	164.8	165.8	163.1	2470.3
DL-cysteine	163.7	164.5	165.7	162.7	2469.2
DL-cystine	163.0	164.5	165.7	163.2	2470.1
Inorganic Sulphur					
Sulphur (S ₈)	162.7	163.9	165.2	163.7	2469.1
Marcasite (FeS ₂)	162.5	163.6	bs	-	-
Pyrite (FeS ₂)	162.4	163.6	bs	162.4 ⁵	2468.4
Galena (PbS)	160.8	162.0	163.8	160.5 ⁵	-

¹Present work, + 0.1 eV

²From Ref. 11, except for pyrite and galena

³From Ref. 10

⁴Value is for dibenzothiophene

⁵From Ref. 14

bs: Broad shoulder

CAPTIONS

Figure 1. Sulphur L-edge X-ray absorption spectra of elemental sulphur, DL-methionine and thioxanthen-9-one.

Figure 2. Sulphur L-edge X-ray absorption spectrum of 1:1 molar mixture of cystine and 1,2-benzodiphenylene sulphide (thiophenic) as compared with the spectra of pure components. The spectra are scaled for ease of comparison.

Figure 3. Sulphur L-edge X-ray absorption spectrum of a mixture of Rasa coal and pyrite as compared with the spectra of pure components. The spectra are scaled for ease of comparison.

Figure 4. Sulphur L-edge X-ray absorption spectrum of Rasa coal compared with the spectrum of cystine.

Figure 5. Sulphur L-edge X-ray absorption spectrum of Rasa coal compared with the spectrum of 1,2-benzodiphenylene sulphide (thiophenic).

Figure 6. Sulphur L-edge X-ray absorption spectrum of Rasa coal compared with digitally combined spectra of poly phenylene sulphide (30%) and 1,2-benzodiphenylene sulphide (70%)

Figure 7. Sulphur L-edge X-ray absorption spectrum of Rasa coal compared with digitally combined spectra of 1,2-benzodiphenylene sulphide (70%) and DL-methionine (30%).













