

# PROCEEDINGS

"Coal - Energy and the Environment"



**Ninth Annual International  
Pittsburgh  
Coal Conference**

**October 12-16, 1992**

*Hosted by:*

**The University of Pittsburgh  
School of Engineering  
Center for Energy Research**

ERL 92-038 (op+J)

01-0004717

# FINGERPRINTING SULFUR FORMS IN COAL AND COAL MACERALS USING SULFUR L-EDGE XANES: VALIDATION OF CLASSICAL METHODOLOGY

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## ABSTRACT

An organic sulfur rich Spanish lignite from the Mequinenza district and two fossilized latex samples collected from German brown coal of the Geiseltal Basin, have been examined by S L-edge X-ray absorption near edge (XANES) and X-ray photoelectron spectroscopies (XPS). Each sample was found to possess a unique mixture of thiophenic, alkyl, aryl and disulfide sulfur constituents. The S L-edge XANES and XPS S 2p spectra were highly complementary. XPS data also revealed the presence of minor pyrite and oxygenated sulfur (sulfones and/or sulfates). Validation of the scope, accuracy and precision of classical procedures (pyrolysis products, selective oxidation, chemical extracts) is now more feasible as high resolution L-edge XANES can be used to directly identify chemical forms of sulfur in coals.

## INTRODUCTION

More efficient and environmentally sound coal combustion for electrical power generation requires the removal of sulfur prior to or during combustion. Identifying sulfur forms in coals and residues is thus of special interest. Sulfur impurities in coal appear in organic and inorganic forms. The organic form is the integral part of coal and as such it has been difficult to characterize directly. In recent years, S K-edge absorption spectroscopy and X-ray photoelectron spectroscopy have been used to identify and quantify organic sulfur in coal [1]. We have recently shown that sulfur L-edge X-ray absorption near edge structure (XANES) is a powerful technique which can be used to identify different forms of sulfur in coal [2,3]. In this study we have extended our previous work to include an organic sulfur rich Spanish lignite mined in the Mequinenza region of the Ebro basin and two fossilized latex samples (Latex-1, Latex-2) collected from thick mats of hairlike cellular remains in Eocene brown coal deposits of the Geiseltal Basin, Halle, Germany. The latex is locally called "Affenhaar". The geological setting and chemical composition of the lignite [4] and fossilized latex [5] are reported elsewhere.

## EXPERIMENTAL

The model sulfur containing compounds used in this study were purchased from Aldrich Chemical company and used without further treatment. The lignite was examined as-received (-100 mesh) while both latex samples were crushed to -80 mesh prior to examination.

*X-RAY ABSORPTION NEAR-EDGE STRUCTURE SPECTROSCOPY (XANES).* Each sample was pressed lightly on a stainless steel sample holder using copper conducting tape for XANES analysis. Sulfur L-edge X-ray absorption spectra were obtained at the Canadian Synchrotron Radiation Facility (CSRF) situated at the Aladdin storage ring, University of Wisconsin [6]. The X-ray beam is monochromatized using a 1800/mm grating, yielding a photon resolution of better than 0.2 eV at the S L-edge. The details of the technique are described elsewhere [7,8].

*X-RAY PHOTOELECTRON SPECTROSCOPY (XPS).* X-ray photoelectron spectra were recorded with a modified Physical Electronics Industries PHI-548E X-ray photoelectron spectrometer using non-monochromatic Al K $\alpha$  X-ray radiation. The binding energy scale of the spectrometer was calibrated using gold foil (Au 4f $_{7/2}$  = 83.8 eV) and copper metal (energy separation of 857.8 eV between the Cu 2p $_{3/2}$  (932.8 eV) and Cu 3p (75.2 eV) photolines. The XPS spectra were referenced against the hydrocarbon C 1s peak arbitrarily chosen as 284.6 eV. An electron flood gun was used to minimize surface charging. The details of the technique are described elsewhere [9]. Spectra were curve fitted using an iterative non-linear least squares fitting routine [10]. Peak assignments are based on binding energy ( $E_b$ ) positions measured for pure sulfur containing compounds and/or taken from the NIST database [11].

## RESULTS AND DISCUSSION

### XANES Analyses

The sulfur L-edge XANES peak positions obtained for various model compounds, the Mequinenza lignite and the two fossilized latex (Affenhaar) samples are listed in Table 1, while the L-edge XANES spectra for the lignite and latex samples are shown in Fig. 1 and Fig. 2 respectively. Pyrite's "peak a" can be resolved from all organosulfur compounds shown in Table 1. Speciation and quantitative determinations are performed by linearly combining spectra of model compounds. Combinations of these spectra are used to construct a synthetic spectrum that is then compared with the unknown. The spectral contribution made by each model compound is varied until a close fit between the synthetic spectrum and the actual spectrum is obtained. This procedure is illustrated in Fig. 1a-c. Thiophenic sulfur is the major constituent in each fit. However, the best fit is Fig. 1c where the spectrum was constructed from 40% 1,2-Benzodiphenylene sulfide, 20% poly(phenylene sulfide), 20% S-methyl-L-cysteine and 20% DL-cystine. Thus the sulfur in the Mequinenza lignite appears to be 40% thiophenic, 20% aryl sulfide, 20% aliphatic sulfide and 20% disulfide. Similarly, the S L-edge XANES spectra, Fig. 2, of Latex-1 appears to have 40% thiophenic, 40% aryl sulfide and 20% disulfide while

Latex-2 (Fig. 2) contains 50% thiophenic, 20% aryl sulfide and 30% disulfide sulfur. The synthetic and experimental XANES spectra compare well except in the 162-163 eV energy regions of Fig. 1c and Fig. 2 where two shoulders ( $S_1, S_2$ ) are seen. A small pyritic sulfur contribution is the most probable cause for these shoulders. The S L-edge spectrum of pyrite shows a peak located at 162.4 eV matching the position of  $S_1$ . The fitted XPS S 2p spectra, (Fig. 3a-b), discussed below support this assignment.

TABLE 1. Peak positions of sulfur L-edge XANES spectra for selected model compounds, Mequinenza lignite, Latex-1 and Latex-2.

Compound	S L-edge XANES Peak Energies, ( $\pm 0.05$ eV)		
	a	b	c
<u>1. Model compounds</u>			
a) 1,2-Benzodiphenylene sulfide	164.2	166.0	167.1
b) poly(phenylene sulfide)	163.9	165.4	166.7
c) Thianthrene	163.9	165.1	166.3
d) S-Methyl-L-cysteine	164.0	164.8	165.8
e) DL-Methionine	163.9	164.8	165.8
f) DL-cysteine	163.7	164.5	165.7
g) DL-cystine	163.0	164.5	165.7
h) Sulfur ( $S_8$ )	162.7	163.9	165.2
i) Pyrite ( $FeS_2$ )	162.4	163.6	---
<u>2. Coal Samples</u>			
a) Mequinenza Lignite	164.6	165.7	167.0
b) Latex-1	164.4	165.7	167.0
c) Latex-2	164.6	165.7	167.0

### XPS Analyses

The S 2p spectra of the three samples, shown in Fig. 3a-c, indicate that XPS is less sensitive to the sulfur chemical environment than S L-edge XANES. However, the S 2p spectra contain useful information. Semi-quantitative surface composition data indicates the Mequinenza lignite, Latex-1 and Latex-2 contain 4.9, 5.4 and 7.8 wt % sulfur respectively. The S 2p spectral data, represented by the small vertical error bars, indicate two energy regions of electron intensity. The largest, a broad asymmetric peak centered at -164 eV dominates and is indicative of sulfur sited as organosulfur compounds [11]. The S 2p peak for elemental sulfur also occurs at -164 eV however elemental sulfur was measured at only -1  $\mu$ g/g in the samples by bulk chemical analysis. The linewidth and slight asymmetry of the broad S 2p peak at 164 eV suggest the presence of at least two sulfur species. Since pyrite has been measured in the lignite sample at -0.6 wt % [4,12], this S 2p peak (Fig. 3a) likely has a small pyrite contribution centered at -162.6 eV. The region of lower intensity, centered at -169 eV is indicative of sulfur in sulfate and/or sulfone forms. The S 2p spectra for the lignite and Latex-1 samples, (Fig. 3a-b),

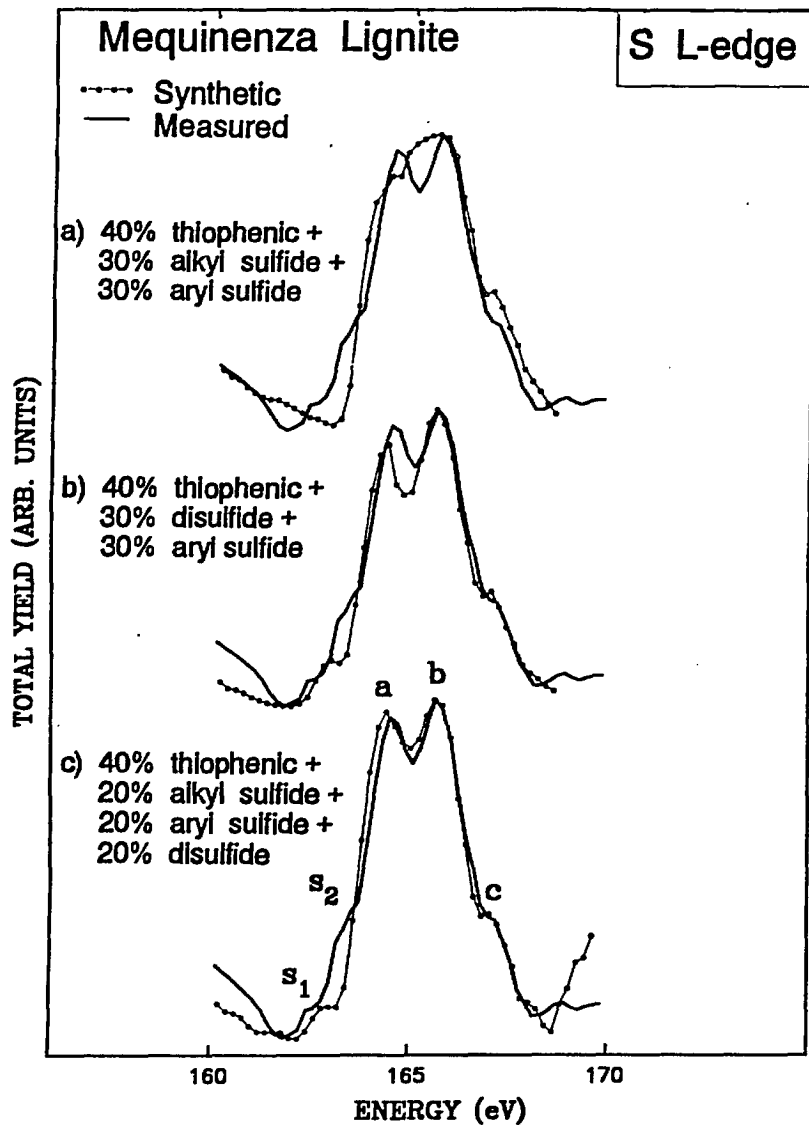


Figure 1. Sulfur L-edge XANES measured spectrum of Mequinenza lignite and its synthesized spectra.

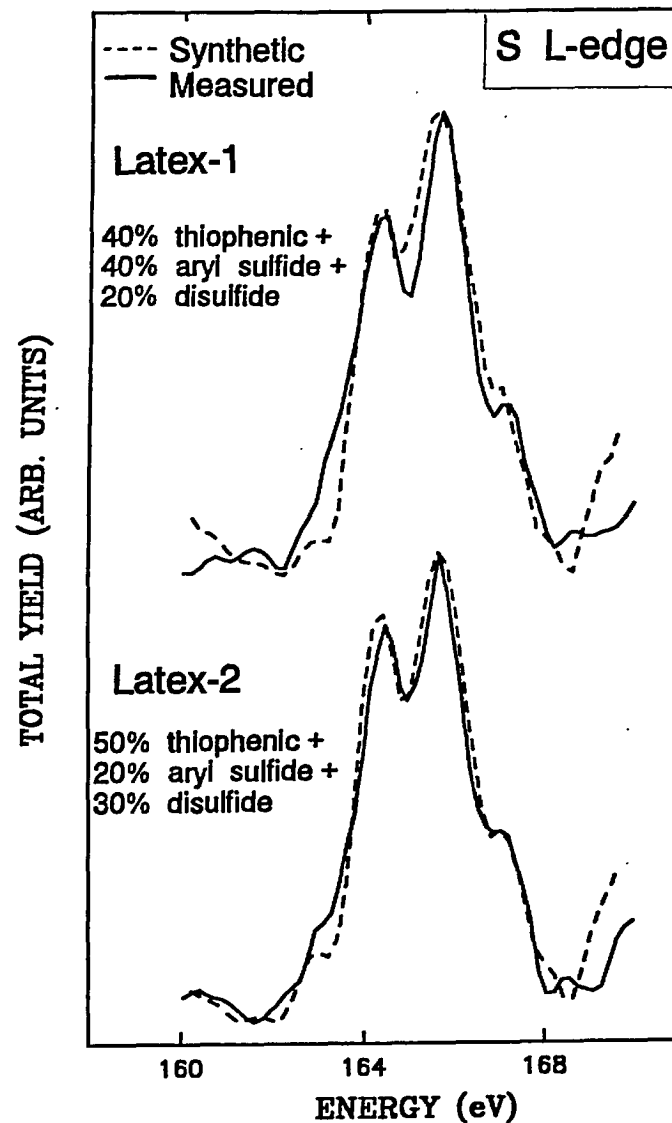


Figure 2. Sulfur L-edge XANES spectra of fossilized latex-1, latex-2 and their synthesized spectra.

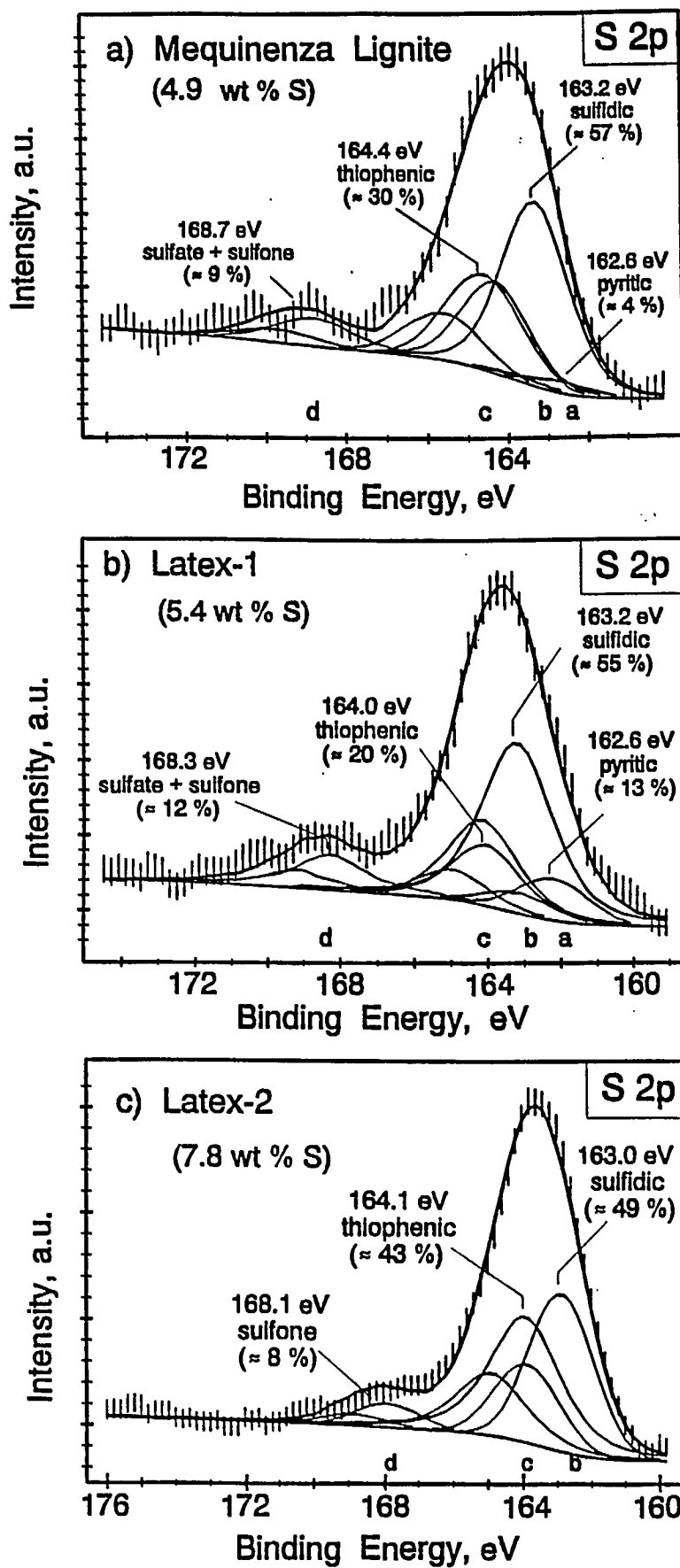


Figure 3. Curve fitted XPS S 2p spectra of: a) Mequinenza lignite, b) fossilized latex-1 and c) fossilized latex-2.

have been curve-fitted using four sets of S 2p<sub>1/2</sub> and S 2p<sub>3/2</sub> transitions (a-d) separated by 1.1 eV due to spin-orbit splitting with the 2p<sub>1/2</sub> peak at higher energy. The solid curve drawn through the raw data (error bars) is the computed area summation of the 4 doublets shown. Two S 2p<sub>3/2</sub> peak positions are constrained in both spectra; peak "a", is fixed at 162.6 eV (pyritic sulfur) and peak "c" is constrained at 164.2 ± 0.2 eV (thiophenic sulfur). Thiophenic sulfur has been identified by our L-edge XANES as well as by indirect chemical methods [13] and K-edge XANES [1,14,15]. The intensities of the four S 2p<sub>3/2</sub> peaks were not constrained nor were the binding energy positions of the remaining two peaks.

The XPS results indicate the Mequinenza lignite contains -57% organosulfides, 30% thiophenic, 9% sulfate/sulfone and 4% pyritic sulfur while Latex-1 consists of -55% organosulfides, 20% thiophenic, 12% sulfate/sulfone and 13% pyritic sulfur. The S 2p spectrum recorded for Latex-2, shown in Fig.3c, was curve fitted as above but without a doublet assigned to pyrite. The synthetic and recorded XANES spectrum of Latex-2, Fig. 2, compares very well indicating pyrite is below detection limits. Latex-2 contains -49% organosulfides, 43% thiophenic and 8% sulfate/sulfone.

A recent study using controlled atmosphere programmed temperature oxidation (CAPTO) and low voltage high resolution mass spectrometry (LVHRMS) to characterize Mequinenza lignite and extracts respectively, indicate thiophenic sulfur is the predominant form of organic sulfur [4]. This is in excellent agreement with our L-edge XANES and XPS results. Very good qualitative agreement between the CAPTO, XANES and XPS results is encouraging although CAPTO cannot distinguish between aryl and thiophenic sulfur nor between non-aromatic sulfur (disulfides and aliphatic sulfides). Likewise, XPS does not distinguish between alkyl sulfides, aryl sulfides and disulfides but reports their sum. The L-edge XANES technique is thus contributing substantially to the development of reliable analytical techniques for the speciation and quantitative determination of organic and inorganic sulfur forms in fossil fuels.

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