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

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April 1991

SUBMITTED TO THE JOURNAL FUEL

ENERGY RESEARCH LABORATORIES DIVISION REPORT ERL 91-21 (J) Crown Copyrights Reserved

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

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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 signal 6-8, 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 analysis. This is not always possible without affecting the nature of the organic sulphur. Very recently, a curve fitting procedure has been applied to characterize organic sulphur in the presence of pyritic sulphur. 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 sulphur.

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

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A well characterized sample of Rasa coal⁵ was obtained from C.T. Whit of the Pittsburg 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 lighting a stainless steel sample holder using a copper conducting tape.

Sulphur L-edge X-ray absorption spectra were obtained at the Canadia Synchrotron Radiation Facility (CSRF) 13 situated at the 1 GeV Aladd. storage ring, University of Wisconsin. The X-ray beam is monochromatized using a 1800/mm grating. This yields a photon resolution of better the 0.2 eV at the S L-edge. The photoabsorption spectra were recorded at 15 200 eV in the total electron yield mode using a microchannel plate. The energy scale was calibrated with reference to the lowest pre-edge peak elemental sulphur at 162.7 eV. This value is not an absolute value, be close to the binding energy of the S 2p level in elemental sulphine measured by XPS 14 . A single scan, with good signal-to-noise ratio coube accomplished in \approx 2 minutes. However, in most cases at least threscans were digitally combined and the background was removed. The detail of the technique will be described elsewhere 15 .

RESULTS AND DISCUSSION

General Features and Model Compounds

The XANES region in the sulphur L-edge spectrum is rich in structue that is sensitive to electronic environment and local symmetry as well the bond distances of the atom with its neighbours 16-19. In this report 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 fingerprisulphur in different chemical forms. In most fresh coal sulphur exists reduced forms. The oxidized forms of sulphur are usually the product 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 \approx 162 to 180 eV^{12,17}. The pyritic and organically-bound sulphur features appear in the region of \approx 162-168 eV, whereas the oxidized forms cover the region of 167-180 eV.

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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. 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 1,11, 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 ≤ 0.8 eV are considerably narrower than either XPS or S K-edge measurements. The good chemical sensitivity makes it possible to use these spectra as arepsilonfingerprint 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. It all the compounds listed in Table 1 (except elemental sulphur), sulphur i 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 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 $XPS^{\delta,7,11}$ or S K-edge⁹⁻¹¹ techniques because o the very different relative intensities of the peaks between organic an pyritic sulphur spectra (Fig. 1 and 3), and peak linewidths (≤ 0.8 eV) ar 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 muc larger than for the S L-edge linewidth. In addition, the L-edge spectr generally have more peaks than K-edge spectra due to different selectic 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 mola mixture of cystine and 1,2-benzodiphenylene sulphide (thiophenic form) i shown in Fig. 2. Also included in this figure (not to the same scale) ar the spectra of each pure compound for identification. As evident from Fig. 2, the well-resolved S L-edge peak, labelled a, is assigned entire! to cystine while peak d belongs to the thiophenic form. The other tw peaks, labelled b and c, arise due to contributions from both sulphi 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

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Rasa coal has been known for many years and the recent convention chemical analysis shows that it contains mostly organic sulphur (10.4 and a small amount of inorganic sulphur (0.3%). In order to investiga this non-destructively, and show directly that Rasa coal does conta almost entirely organic sulphur, a sample of Rasa coal was fortified wi pyrite. Figure 3 shows the S L-edge spectra of the Rasa coal along wi pyrite and a mixture of Rasa coal and pyrite. Figure 3 clearly shows th this is indeed the case. Peaks a and b correspond to pyrite whereas c, and e belong to Rasa coal. This is the first time that organic sulph has been distinguished directly and unambiguously from pyrite spectroscopic methods. As Fig. 3 indicates, there are no detectably 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. 3 Besides other recently made an extensive study on Rasa coal. 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. include large families of These thiophenic, a few anthracenic and some sulphidic species. The molecular formula assignment is based on mass measurements and confirmation is available. Gorbaty and co-workers 8,10,11 used XPS and S Kedge 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 spectrall, 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 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 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 direct $^{10-11}$ and indirect 20,21 findings. Gorbaty and coworkers10 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 coworkers 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 el. 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 present2,5. 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.

ACKNOWLEDGEMENTS

The authors are indebted to C.M. White, PETC, USDOE, Pittsburgh for generously providing the Rasa coal and to R. Prokopuk, ERL, CANMET, Ottawa for his assistance in procuring the Rasa coal and several other coals currently being studied. This study was financially supported by CANMET, Energy, Mines and Resources Canada contract #23440-9-9283/01 through the Federal Panel on Energy Research and Development, the National Research Council of Canada, and the Natural Sciences and Engineering Research Council of Canada. The authors are grateful to the staff of the Synchrotron Radiation Centre, University of Wisconsin for their technical support.

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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 (Sg)	162.7	163.9	165.2	163.7	2469.1
Marcasite (FeS ₂)	162.5	163.6	bs		_
Pyrite (FeS ₁)	162.4	163.6	bs	162.4 ⁵	2468.4
Galena (PbS)	160.8	162.0	163.8	160.5 ⁵	_

Present work, + 0.1 eV From Ref. 11, except for pyrite and galena From Ref. 10

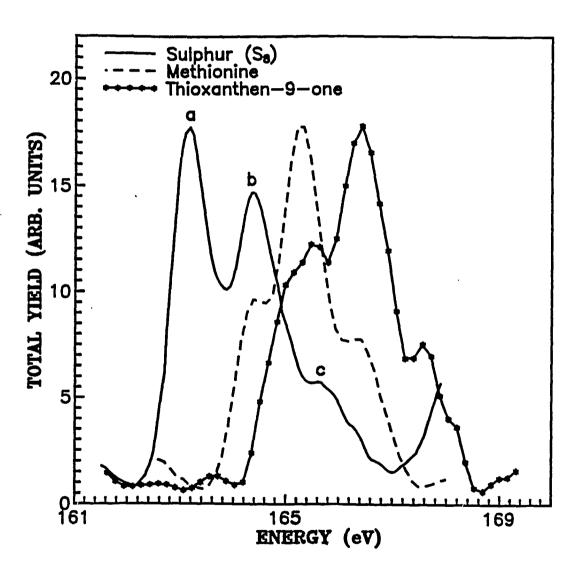
Value is for dibenzothiophene From Ref. 14

bs: Broad shoulder

CAPTIONS

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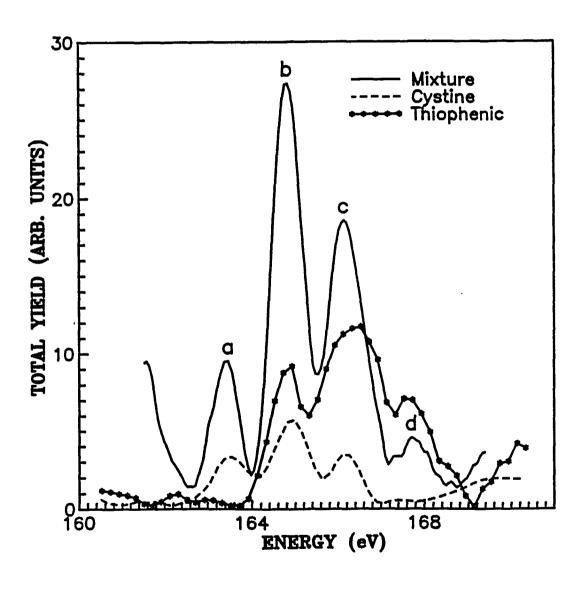
- Figure 1. Sulphur L-edge X-ray absorption spectra of elemental sulphur, DL-methionine and thioxanthen-9-one.
- Figure 2. Sulphur L-edge X-ray absorption spectrum of 1:1 molar mixture of cystine and 1,2-benzodiphenylene sulphide (thiophenic) as compared with the spectra of pure components. The spectra 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%).



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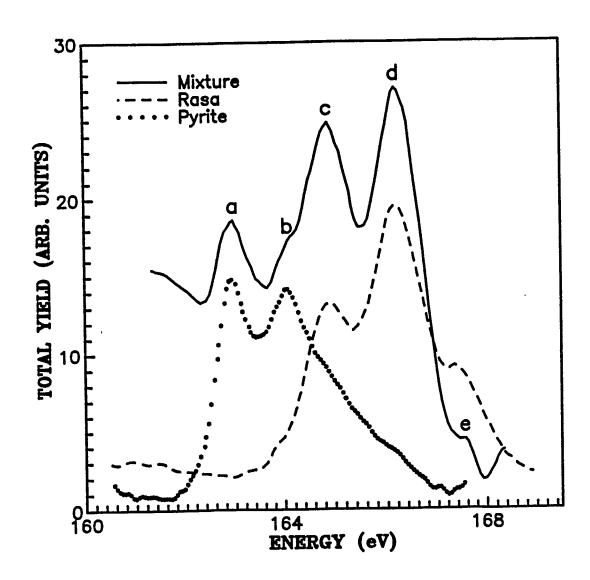


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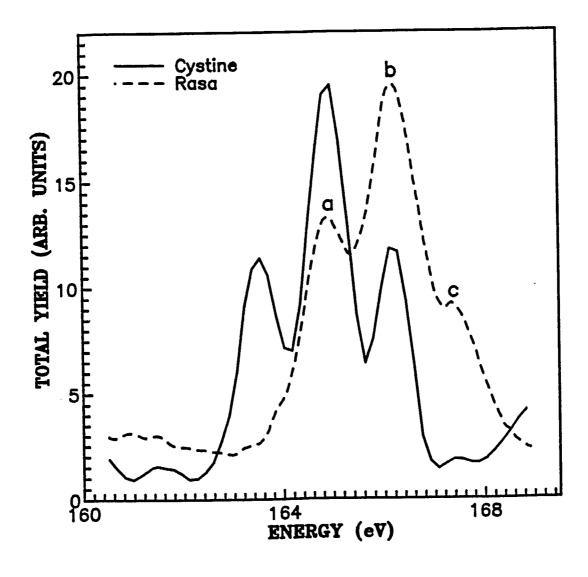
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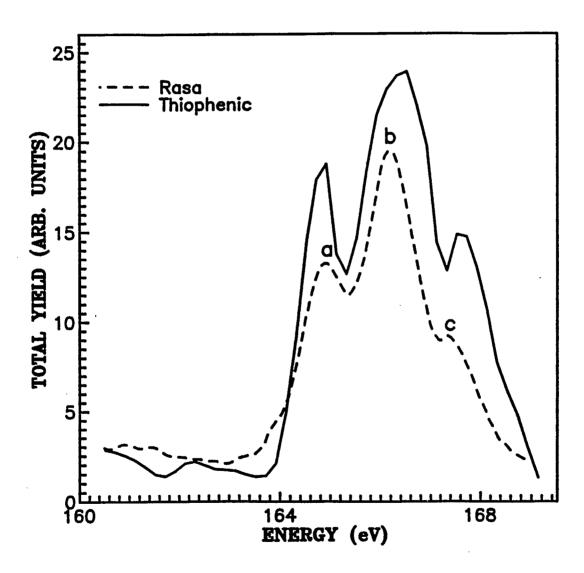
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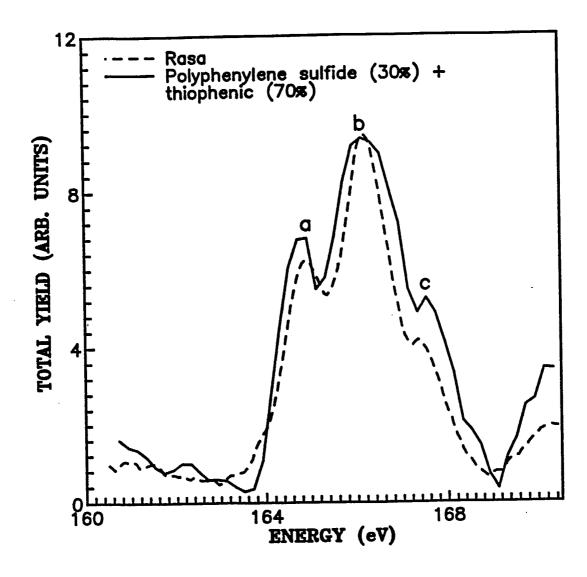
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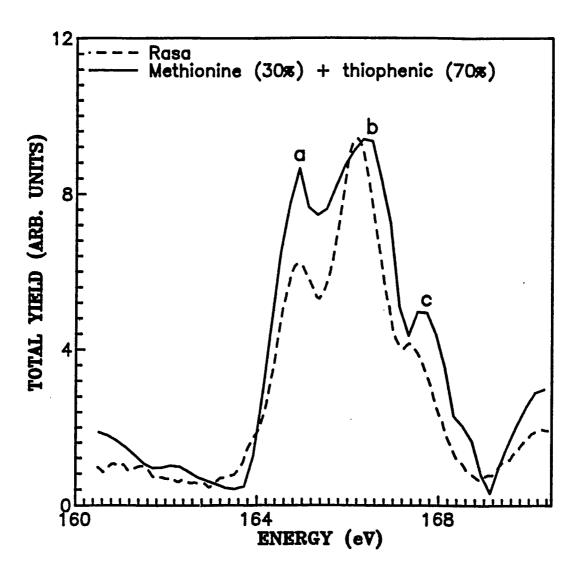


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