

**DETERMINATION OF THE PRODUCTS FROM THE OXIDATION OF AQUEOUS  
HYDROGEN SULFIDE BY SULFUR K-EDGE XANES SPECTROSCOPY**

by

Appathurai Vairavamurthy, Bernard Manowitz, Yongseog Jeon\* and Weiqing Zhou

Applied Physical Sciences Division  
Department of Applied Science  
Brookhaven National Laboratory  
Upton, New York 11973

BNL--47363

DE93 010857

APR 07 1993  
OSTI

Submitted to an American Chemical Society Symposium Volume titled  
The Environmental Geochemistry of Sulfide Oxidation

January 1993

\*Present address: Department of Physics, Jeonju University, Hyojadong 3-ga 1200,  
Wansan-gu, Jeonju, Seoul, 560-759, Korea

By acceptance of this article, the publisher and/or recipient acknowledges the U.S.  
Government's right to retain a nonexclusive, royalty-free license in and to any copyright  
covering this paper

This research was performed under the auspices of the U.S. Department of Energy  
Division of Engineering and Geosciences of the Office of the Basic Energy Sciences under  
Contract No. DE-AC02-76CH00016 (KC-04)

**MASTER**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

## TABLE OF CONTENTS

ABSTRACT	3
1. INTRODUCTION	4
2. PRINCIPLES OF X-RAY ABSORPTION SPECTROSCOPY	6
2.1. Sulfur Speciation and Edge Shift	7
3. QUANTITATIVE ANALYSIS	8
3.1. The Approach	8
3.2. An Illustration of Self-Absorption Correction	10
3.3. Analysis of Standard Mixtures	11
4. ANALYSIS OF SULFIDE OXIDATION PRODUCTS	11
4.1. Experiment	11
4.1.1. Beamline Setup.	12
4.2. The Products of Sulfide Oxidation: Some Significant Results and Discussion	12
LITERATURE CITED	15

### DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

## ABSTRACT

The application of synchrotron radiation based XANES spectroscopy is described for the determination of the products formed from the oxidation of aqueous sulfide. This technique allows simultaneous characterization of all the different forms of sulfur both qualitatively and quantitatively. Thus, it is superior to other commonly used techniques, such as chromatography, which are usually targeted at specific compounds. Since the use of XANES-based technique is relatively new in geochemistry, we present here an overview of the principles of the technique as well as the approach used for quantitative analysis. We studied the sulfide oxidation under conditions of high sulfide to oxygen ratio using 0.1 M sulfide solutions and the catalytic effects of sea sand,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$ , were also examined. Significant results obtained from this study are presented to illustrate the value of the XANES technique for the determination of the products formed from the oxidation of sulfide at high concentrations.

## 1. INTRODUCTION

Recently there has been widespread interest in sulfur cycles from a biological, geochemical, biogeochemical, and environmental viewpoint. Sulfur transformations and speciation exhibit a great deal of complexity because sulfur exists in number of oxidation states between -2 and +6, and forms a large variety of organic and inorganic species. Extreme changes in sulfur speciation are prominent at the redox boundaries (oxic-anoxic interface) in marine systems including organic-rich sediments and anoxic basins such as the Black Sea and Cariaco Trench (1). In anoxic marine environments, hydrogen sulfide is the major reduced sulfur compound, and is formed as a result of bacterial reduction of sulfate associated with anaerobic oxidation of organic matter. The formation of hydrogen sulfide in hydrothermal systems probably occurs by a thermochemical reduction mechanism, although high-temperature bacterial reduction is also possible (2, 3). At the oxic-anoxic interface when water containing  $H_2S$  mixes with oxygenated water, the sulfide is oxidized by oxygen, resulting in the formation of several partially oxidized sulfur species, for example polysulfides, elemental sulfur, sulfite, thiosulfate, tetrathionates as well as sulfate (4-6). In natural waters, redox transformations of some metals and nonmetals are also frequently coupled to the oxidation of sulfide; however, dissolved oxygen is the principal oxidant (7).

Although hydrogen sulfide oxidation has been the subject of several past studies (8-14; reviews: 15-16), there are still many uncertainties regarding rates, mechanisms of oxidation, and the formation of the oxidation products. Serious drawbacks in these studies have been due to analytical limitations involved in the measurement of the different sulfur species. The methods widely used for the determination of various sulfur species are based on colorimetry or chromatography. In most sulfide oxidation studies, Urban's colorimetric method was used for thiosulfate (17), and sulfite was determined by the West and Gaeke colorimetric method (18); sulfate was estimated by difference. Colorimetric methods used for the determination of most inorganic sulfur species are, although selective, usually prone to interferences. For example, in the Urban's method for thiosulfate, sulfide causes a positive interference and must be removed by stripping with nitrogen at low pH. Recently, thiosulfate and sulfite were measured by a high performance liquid chromatographic (HPLC) method after precolumn

derivatization with 2,2'-dithiobis(5-nitropyridine) for reversed-phase separation and UV detection (19). Ion chromatography can also be used for the determination of sulfite and thiosulfate; however, it may not be suitable for analysis of ionic media such as seawater. While a choice is possible from either colorimetric or chromatographic methods for the determination of sulfite and thiosulfate, suitable methods are still lacking for other sulfur intermediates, for example, polysulfides. In both the colorimetric and chromatographic methods that are commonly used for the determination of various sulfur intermediates, there is a serious concern about alteration of sample composition in the lengthy sample preparation procedures or during the analysis.

Recently, synchrotron radiation based X-Ray Absorption Near-Edge Structure (XANES) Spectroscopy has emerged as an important tool for determining the speciation of sulfur in a variety of geochemical samples including coal, petroleum, and sedimentary rocks (20-23). In general, the XANES spectrum provides characteristic "fingerprint" information of a sulfur compound because of the sensitivity of the XANES to the electronic structure, oxidation state, and the geometry of the neighboring atoms (24). Consequently, the XANES spectroscopy has proved to be a valuable tool for qualitative characterization of sulfur-containing compounds based on spectral comparison with model compounds. The recent popularity of XANES spectroscopy for sulfur species determination is mainly due to the fact that accurate quantitative information of the different sulfur constituents can also be obtained with this technique. An important advantage of XANES is that it allows non-destructive analysis of samples either in the form of solid or liquid.

In this paper, we describe the use of XANES spectroscopy as an analytical technique for the determination of the products formed from the oxidation of aqueous sulfide. Since XANES is a relatively new technique in geochemistry, we also discuss the principles of x-ray absorption spectroscopy as well as the approach used to obtain quantitative information with XANES analysis. In this study, sulfide oxidation was examined with excess sulfide and limiting oxygen concentrations, conditions typically present in reducing marine sediments. At high concentrations, sulfide causes serious interference in the determination of the oxidation products with either chromatography or colorimetry (for example, in the determination of

sulfite and thiosulfate by the HPLC method involving DTNP derivatization), and may be a reason for the sparsity of studies under these conditions. We discuss here some significant results from sulfur XANES analysis which illustrate the value of this technique for the determination of the products formed from the oxidation of sulfide at high concentrations.

## 2. PRINCIPLES OF X-RAY ABSORPTION SPECTROSCOPY

An x-ray absorption spectrum is produced by the transition of a photoelectron from a core level to symmetry-available outer empty states and to the continuum (i.e., beyond the sphere of influence of the atom). The absorption spectrum is rather featureless until one observes an abrupt increase in the absorption coefficient, known as the "absorption edge", which occurs when the x-ray photon has sufficient energy to excite a core level electron in the atom. The fine structure usually appearing as peaks (the so called "white lines") at the high-energy side of each main absorption edge reflects the bound state transitions between the absorber core orbital and outer unoccupied atomic or molecular orbitals (e.g.  $1s \rightarrow 3p$ ). Continuum transitions contribute to subsequent oscillations in absorption (Figure 1) (25). Conventionally, the structured absorption occurring within ca. 50 eV of an element's absorption edge is referred to as the X-ray Absorption Near-Edge Structure (XANES). Thus, XANES includes both bound-state transitions and "continuum resonance" transitions. The region of the spectrum beyond this range is the Extended X-ray Absorption Fine-Structure (EXAFS), which consists typically of relatively broad and weak sinusoidal oscillations that diminish in intensity with increasing energy above the edge, but which may persist for as much as 1,000 eV above the edge (Figure 2). It is important to note here that the absorption spectra are usually measured as fluorescence excitation spectra with a fluorescence detector. This is possible because the fluorescent x-ray emission is proportional to the absorption coefficient for dilute samples.

The absorption fine structure due to continuum transitions is influenced mainly by the nature and geometry of the absorber's environment. When the absorbing atom is surrounded by other atoms, as in any condensed phase, the outgoing photoelectron can be backscattered by the surrounding atoms, where the backscattered waves can interfere either constructively or

destructively with the outgoing wave. Obviously, no backscattering will occur in the absence of near neighbors around the absorber (e.g., monoatomic gas). In the XANES region, the final state of the continuum transition is a low energy photoelectron. As a result of its long mean free path, the low energy photoelectron can undergo multiple scattering interactions. This makes XANES structure sensitive to the three-dimensional arrangement of atoms around the absorber, and potentially allows the use of XANES to determine geometry. However, despite recent progress on XANES theories, there is still much uncertainty in establishing a one-to-one correlation between "continuum resonances" and a specific geometric structure. Thus, continuum resonances are most often used as a fingerprint to compare a model compound and an unknown sample. In contrast, the spectral oscillations in the high energy EXAFS region can be well modeled by considering only the single scattering interactions of the excited photoelectron (26). In fact, the EXAFS oscillations provide useful data to determine the local radial distribution around the absorbing atom.

### 2.1. Sulfur Speciation and Edge Shift

In the XANES spectrum, the fine structure corresponding to bound-state transitions (i.e., the absorption maxima in the edge region) is rich in information about the electronic structure, charge density, and the bonding environment of the absorbing atom. This is mainly because the orbitals involved in the bound-state transitions are essentially the regions of interatomic orbital overlap. For sulfur, the edge correlates with the  $1s \rightarrow 3p$  transition which occurs as an intense well resolved transition corresponding to the "white-line" maximum of the XANES spectrum. Several recent studies clearly show that both the energy and the intensity of the sulfur  $1s \rightarrow 3p$  transition are sensitive to the oxidation state of sulfur (22,23,27). This is reflected by the fact that the "white-line" maximum changes by ca. 10 eV between elemental sulfur and sulfate with formal oxidation states of 0 and +6 respectively. It is shown in Figure 3 that each of the XANES spectra of the variety of sulfur forms is richly endowed with characteristic features, including the edge energy, which allow ready qualitative recognition among various oxidation states and structures.

XANES spectroscopy provides an experimental technique of inferring the charge density (and hence the oxidation state) of an atom in a molecule (24,28). The evidence in the x-ray spectrum for a change in atomic charge density is the shift in the position of an x-ray absorption edge towards either the positive or the negative side relative to that in the pure element (note: the edge shift is also referred to as the chemical shift). Kunzl (29) was one of the first workers who suggested a linear relationship between edge shift and valency based on a critical study regarding the shift of the K-absorption discontinuities of the oxides of several elements. For sulfur, previous studies (22,27) have shown a nearly linear correlation between edge energy and (formal) oxidation state, especially with inorganic sulfur species (Figure 4). Thus, XANES spectroscopy can be a useful technique for determining sulfur oxidation states using Kunzl's law. In fact, in a recent study (30), this correlation was the basis for assigning new oxidation states for the two different sulfur atoms in thiosulfate (-1 and +5 for the terminal and inner sulfur atoms respectively).

### 3. QUANTITATIVE ANALYSIS

#### 3.1. The Approach

The use of XANES for quantitative characterization of the different forms of sulfur present in a sample is a relatively new development. Several methods were attempted by a number of workers for the quantification purpose and are briefly discussed below. In one approach, a differential treatment of the XANES was used to distinguish and quantify different forms of sulfur in petroleum asphaltenes. In this method, the heights of certain features in the third derivative of XANES were considered proportional to the relative amounts of the different organic sulfur forms in the sample (21). In a second method, developed and applied by Huffman and co-workers (23,31) for the analysis of sulfur forms in coal, a least-squares fitting of the XANES spectrum with a series of artificial functions representing the spectral features of the different sulfur forms ( for example pyrite, sulfide, thiophene, sulfoxide, sulfone, sulfate) is used for quantitative characterization. An arctangent function is typically used to model the step-function-feature in the spectrum corresponding to 1s excitations into continuum states. The s->p transition peaks (in the sample spectra) are fitted by peak functions (which are 50%

Lorentzian and 50% Gaussian) specific to different forms of sulfur and converted to weight percentage of sulfur by using calibration constants derived from standard compound mixtures. A third method for quantitative analysis is that developed by Waldo and co-workers at the University of Michigan (22) which is currently used by us for sulfur analysis. Essentially, it involves a non-linear least-squares fitting procedure which uses linear combinations of normalized spectra of model compounds to obtain quantitative information of the different forms of sulfur.

The fact that the XANES spectra are usually measured as fluorescence excitation spectra presents a problem in quantitative analysis for concentrated samples. As pointed out in Section 2, a linear correlation between fluorescence signal and central atom absorption is only true for dilute samples and for thin film samples. In the case of concentrated (or thick) samples, the fluorescence signal is considerably distorted (reduced amplitude especially) due to self-absorption or the thickness effect. Self-absorption is especially important for elements of low atomic number, such as sulfur, because x-ray absorptions are typically quite large at the low energy range (2-4 keV). Ideally, self-absorption effect can be avoided by diluting the sample; however, this can be difficult or impossible for insoluble samples and will also degrade the signal-to-noise ratio. The numerical method developed by Waldo and Penner-Hahn allows the fluorescence excitation spectra to be corrected for the self-absorption effect prior to least-squares deconvolution of the spectrum (22,32).

There are four main steps in the method by Waldo et al. (22): (1) background absorption correction (the correction is determined first by low-order polynomial fitting in the pre-edge region and then extrapolated it to the post-edge region followed by subtracting the background curve from the entire spectrum); (2) normalization of the spectrum in the post-edge region to fit a tabulated x-ray absorption cross section (McMaster table) (33); (3) correction for attenuation of the fluorescence signal due to the self-absorption effect; and (4) fitting the normalized spectrum with linear combinations of absorption spectra of model compounds using a non-linear least-squared procedure. The use of experimentally-obtained spectra of model compounds for fitting has a unique advantage over the other methods when a model compound has several major peaks, for example, thiosulfate. Furthermore, even if the edge

energies overlap and do not provide adequate species-specific information, other spectral features (for example, the multiple scattering resonance peaks at higher energies) can be of use for distinguishing among the different sulfur forms because the entire spectrum is used for fitting. The fitting range is usually selected so that it covers the white-line maxima for all of the model compounds. In fitting, as given in equation 1, the adjustable parameters for each model spectrum are an optional energy offset ( $\Delta E$ ) and a scaling factor ( $c_i$ ) which is constrained to  $\sum_i c_i = 1$ .

$$\mu_{\text{sample}}(E) = \sum_i c_i \mu_{\text{model}}(E + \Delta E_i) \quad (1)$$

Under ideal operational conditions, no energy offset is required; however, in practice, there is some uncertainty which is usually less than 0.5 eV. The scaling factor directly reflects the quantitative amount of each sulfur form.

In the XANES technique, the basis for quantification, which is reflected in the scaling factor described above, is a linear correlation between step height in the spectrum and the mass of sulfur in the corresponding sample. We verified this relationship between step height and sulfur mass using sodium sulfate solutions in different concentrations. The  $\text{Na}_2\text{SO}_4$  solutions were each mixed with an exact amount of NaCl for normalization of the sulfur absorption coefficient against that of chlorine which was assigned a value of unity in each spectrum. Thus, the step heights in Figure 5 represent values normalized against chlorine x-ray absorption peak (2833.4 eV). Needless to say, the data shown in Figure 5 clearly reaffirm the linear relationship between step height and the concentration of sulfur. It is important to note that step height is invariant of the self-absorption effect which affects the shape of peaks in the edge region in fluorescence excitation spectra.

### 3.2. An Illustration of Self-Absorption Correction

Figure 6 shows the sulfur K-edge fluorescence excitation spectra of two different  $\text{Na}_2\text{SO}_4$  solutions of 0.025 M and 0.1 M concentrations prepared in deionized water. The peak height of the more concentrated solution (0.1 M) is lower than that of the less concentrated solution (0.025 M) after pre-edge subtraction and post-edge normalization to the same step height (McMaster x-ray absorption cross section value) which is consistent with the self-

absorption effect. After applying the self-absorption correction (using the numerical expression for fluorescence intensity as a function of sample elemental composition, weight percentage or concentration, and sample thickness), the corrected spectrum of the 0.1 M solution matches well with that of the 0.025 M solution (see the top two curves in Figure 6). This excellent agreement strongly supports the view that self-absorption correction is an essential step in the analysis of x-ray fluorescence spectra distorted by the concentration effect.

### **3.3. Analysis of Standard Mixtures**

We examined the validity of the XANES method for quantitative analysis using test mixtures prepared in deionized water with sulfite, thiosulfate, and sulfate. The approach involved preparing standards of accurately known composition, collecting the spectra (at beamline X19A) and analyzing the data (computer fitting). The XANES spectrum of a solution containing  $\text{Na}_2\text{S}_2\text{O}_3$  (50 mM),  $\text{Na}_2\text{SO}_3$  (50 mM), and  $\text{Na}_2\text{SO}_4$  (50 mM) after spectral deconvolution is shown in Figure 7 which indicates excellent agreement of the sum of basis model spectra with the experimental spectrum. Both the scaling and the energy-offset parameters were varied in a non-linear least-squares fit. The results with different test solutions are summarized Table 1. It is clear from these data that XANES analysis combined with the spectral deconvolution method provides a reliable method for quantifying major forms of sulfur in samples.

## **4. ANALYSIS OF SULFIDE OXIDATION PRODUCTS**

### **4.1. Experiment**

Time-series experiments were conducted using a 0.1 M NaHS solution in deionized water and in 0.7 M sodium chloride solution at 25°C and pH 8.0. Catalytic effects of sea sand,  $\text{Fe}^{2+}$ , and  $\text{Ni}^{2+}$  on the rate of oxidation were also examined. Sulfide and its oxidation products were both detected and quantified using XANES spectroscopy performed at the National Synchrotron Light Source (NSLS) X-19A beamline. For x-ray analysis, the samples (the different oxidation time-series of sulfide solutions) were prepared by packaging in thin Mylar film bags. Sulfur standards were also analyzed in the same way. Deionized water was

produced with a Milli-Q water purification system (Millipore, Bedford, MA). Sodium sulfide and other sulfur standards were obtained from Aldrich Chemical (Milwaukee, WI). Sea sand was obtained from Fluka Chemical (Ronkonkoma, NY) and prewashed with 1 M HCl and deionized water prior to use.

4.1.1. Beamline Setup. In the X-19A beamline at NSLS, the x-ray beam emitted from the storage ring is collimated by an adjustable vertical slit (1 mm) and is diffracted by a double crystal monochromator [Si(111)], which passes a narrow energy band. The overall energy resolution was estimated to be 0.5 eV at 2.5 keV photon energy. The monochromator was detuned by ca. 80% to minimize higher order-harmonics in the x-ray beam. The incident beam intensity ( $I_0$ ) was monitored by ion chamber which absorbs a few percent of the beam to ionize a gas such as helium. The data were collected as fluorescence excitation spectra using a Lytle fluorescence detector (34) placed at 90 degrees to the x-ray beam. A typical beamline setup is shown in Figure 8. Samples were run in a helium atmosphere to minimize the attenuation of the x-ray beam by air. The spectra were recorded in such a way that the scanning procedure yields sufficient pre-edge and post-edge data for precise background determination needed for analysis. The x-ray energy was calibrated using XANES spectra of elemental sulfur measured in between sample runs, assigning 2472.7 eV to the "white-line" maximum of elemental sulfur spectrum. The uncertainty of the energy calibration, determined by comparing the spectra of model compounds obtained at different times, was better than  $\pm 0.15$  eV.

#### 4.2. The Products of Sulfide Oxidation: Some Significant Results and Discussion

Figure 9 shows the XANES spectra of 0.1 M sulfide in deionized water after different periods of exposure to air. We obtained excellent fitting of these spectra using sulfide, sulfite, thiosulfate and sulfate as the bases. The XANES spectra of the various sulfur standards used for fitting are shown in Figure 10. Thiosulfate was detected as the predominant product of sulfide oxidation with sulfite and sulfate amounting to < 10 % of the product sulfur. In a 0.7 M NaCl medium and in those deionized water series containing added  $\text{Fe}^{2+}$  and sea sand, the pattern of product formation was similar to that of pure deionized water medium but the rate of

oxidation was accelerated (Table 2). In previous studies, which have been conducted mostly under pseudo-first order conditions with a low initial ratio of sulfide to oxygen, sulfate was found as the major product; sulfite and thiosulfate contributed as minor products (5,10). Our results suggest that thiosulfate is the favored product at high sulfide concentrations with a high ratio of sulfide to oxygen. These results are in agreement with a previous study which describes thiosulfate as the major product of sulfide oxidation in strongly reducing marine sediments containing millimolar levels of sulfide (35). Furthermore, these results support the suggestion that the ratio of sulfide to molecular oxygen is an important factor, in addition to other factors (e.g. pH), in controlling the type and extent of formation of different sulfur species (10).

A striking feature in the  $\text{Ni}^{2+}$  series is the presence of a peak at 2476.1 eV in the spectra of the initial oxidation period. After about 100 hours of air oxidation, this peak completely disappeared in both deionized water and 0.7 M NaCl solution media (Figure 11). Our fitting results indicate significant formation of polysulfides in the  $\text{Ni}^{2+}$  series which contrasts with the other series (Figure 12 A and B). Although we obtained excellent fitting of the spectra for the period after ca. 100 hours of air exposure with sulfide, polysulfide, thiosulfate, and sulfate (Figure 12 B), the same standards could not be used to fit the spectra of the initial oxidation period mainly due to the peak at 2476.1. Based on the linear correlation between oxidation state and peak energy discussed in Section 2.1, the position of this peak corresponds to an oxidation state of +2. However, there is no inorganic sulfur compound with a +2 oxidation state of sulfur, although in organic sulfoxides sulfur is present with a relative charge density of +2 (Figure 4). The unknown peak cannot be due to an organic sulfoxide because no organic compound was added to the system. Previous studies postulate that oxidation proceeds probably through the formation of an intermediate  $\text{HSO}_2^-$  having a +2 oxidation state sulfur (12), but so far there has been no experimental evidence for its formation. The peak at 2476.1 eV probably indicates the formation of the  $\text{HSO}_2^-$  intermediate. For quantitative analysis of the spectrum, we used an organic sulfoxide (benzyl sulfoxide) as a surrogate to fit the unknown peak and such a fitting is shown in Figure 12 A.  $\text{Ni}^{2+}$  accelerates oxidation rate dramatically probably by enhancing the rate of the  $\text{HSO}_2^-$  formation. Our results suggest that catalysis by

transition elements such as  $\text{Ni}^{2+}$  is probably important for the formation of polysulfides in marine sediments.

The results discussed above clearly indicate the potential of XANES spectroscopy for the determination of the different sulfur species formed from the oxidation of aqueous sulfide. In this technique, quantitative measurements of the different sulfide oxidation products, including polysulfides, are not affected by the presence of high concentrations of sulfide (as high as 0.1 M) because of the lack of sulfide interference. Popular techniques such as chromatography would not have detected the presence of the +2 oxidation state species because they are usually targeted at specific compounds. The ability to obtain both qualitative and quantitative information of all the sulfur forms present in a sample provides a unique advantage of using XANES spectroscopy over other techniques, including chromatography. Furthermore, since this technique involves no cumbersome sample preparation, the problems of artifacts formation and the alteration of sample composition usually associated with lengthy sample preparatory procedures are greatly minimized.

### **Acknowledgments**

This research was performed under the auspices of the U.S. Department of Energy Division of Engineering and Geosciences of the Office of the Basic Energy Sciences under Contract No. DE-AC02-76CH00016 (KC-04).

## LITERATURE CITED

1. Millero, F. J. *Deep-Sea Research*, 1991, 38, Suppl. 2, pp S1139-S1150.
2. Orr, W. L. *AAPG Bull*, 1974, 58, pp 263-276.
3. Jorgensen, B. B.; Isaksen, M. F.; Jannasch, H. W. *Science* 1992, 258, pp 1756-1757.
4. Cline, J.D.; Richards, F.A. *Environ. Sci. Technol.* 1969, 3, pp 838-843.
5. Luther, G. W. III; Church, T. M.; Giblin, A. E.; Howarth, R. W. In *Organic Marine Geochemistry*; Editor, Sohn, M. L.; ACS Symposium Series 305; American Chemical Society: Washington, DC, 1986; pp 340-357
6. Vazquez, F; Zhang J. -Z.; Millero, F. J. *Geophys. Res. Lett.* 1989, 6, pp 1363-1366.
7. Jacobs, L.; Emerson, S. *Earth Planet. Sci. Lett.* 1982, 60, pp 237-252.
8. Avrahami, M.; Golding, R.M. *J. Chem. Soc. (A)* 1968, pp 647-651.
9. Chen, K.Y.; Morris, J.C. *Environ. Sci. Technol.* 1972, 6, pp 529-537.
10. O'Brien, D.J.; Birkner, F.G. *Environ. Sci. Technol.* 1977, 11, pp 1114-1120.
11. Hoffman, M.R. *Environ. Sci. Technol.* 1977, 11, pp 61-66.
12. Hoffman, M.R.; Lim, B.C. *Environ. Sci. Technol.* 1979, 13, pp 1406-1414.
13. Weres, O.; Tsao, L.; Chhatre, R. M. *Corrosion-NACE* 1985, 41, pp 307-316.
14. Millero, F.J.; Hubinger, S.; Fernandez, M.; Garnett, S. *Environ. Sci. Technol.* 1987, 21, pp 439-443.
15. Millero, F.J. *Mar. Chem.* 1986, 18, pp 121-147.
16. Morse, J.W.; Millero, F. J.; Cornwell, J. C.; Rickard, D. *Earth Sci. Rev.* 1987, 24, pp 1-42.
17. Urban, P.J. *Z. Anal. Chem.* 1961, 179, pp 415-26.
18. West, P.W.; Gaeke, G.C. *Anal. Chem.* 1956, 28, pp 1816-1819.
19. Vairavamurthy, A.; Mopper, K. *Environ. Sci. Technol.* 1990, 24, pp 333-336.
20. Spiro, C. E.; Wong, J.; Lytle, F; Greegor, R. B.; Maylotte, D.; Lampson, S. *Science* 1984, 226, pp 48-50.
21. George, G. N.; Gorbaty, M. L. *J. Am. Chem. Soc.* 1989, 111, p 3182.

22. Waldo, G.S.; Carlson, R. M. K.; Moldowan, J. M.; Peters, K. E.; Penner-Hahn, J. *E. Geochim. Cosmochim. Acta* 1991, 55, pp 801-814.
23. Huffman, G. P.; Mitra, S.; Huggins, F. E.; Shah, N.; Vaidya, S.; Lu, F. *Energy & Fuels* 1991, 5, pp 574-581.
24. Bart, J. C. J. In *Advances in Catalysis*; Editor, Eley, D. D.; Pines, Herman; Weisz, P. B.; Academic Press: Orlando, Florida, 1986, Vol. 34; pp 203-296.
25. Parratt, L. G. *Rev. Mod. Phys.* 1959, 31, pp 616-645.
26. Bart, J. C. J.; Vlaic, G. In *Advances in Catalysis*; Editor, Eley, D. D.; Pines, H.; Weisz, P. B.; Academic Press: Orlando, Florida, 1987, Vol. 35; pp 1- 138.
27. Frank, P.; Hedman, B.; Carlson, R. M. K.; Tyson, T. A.; Roe, A. L.; Hodgson, K. O. *Biochemistry* 1987, 26, pp 4975-4976.
28. Wong, J.; Lytle, F. W.; Messmer, R. P.; Maylotte, D.H. *Physical Review B* 1984, 30, pp 5596-5607.
29. Kunzl, V. *Collect. Czech. Commun.* 1932, 4, pp 213-224.
30. Vairavamurthy, A; Manowitz, B; Luther, G. W. III; Jeon, Y. J. *Geochim. Cosmochim. Acta*, 1993, in press.
31. Huffman, G. P.; Huggins, F. E.; Francis, H. E.; Mitra, S.; Shah, N. In *Processing and Utilization of High Sulfur Coals III*, Editors, Markuszewski, R.; Wheelock, T. D., Elsevier: Amsterdam, 1990, pp 21-32.
32. Waldo, G. S. Ph.D. Thesis, University of Michigan, 1991.
33. McMaster, W. H.; Kerr Del Grande, N.; Mallett, J. H.; Hubbell, J. H. In *Compilation of X-ray Cross Sections*, National Technical Information Service: Springfield, VA, 1969.
34. Stern, E.A.; Heald, S.M. *Rev. Sci. Instrum.* 1979, 50, pp 1579-1582.
35. Jorgensen, B.B. *Science* 1990, 249, pp 152-154.
36. Gordon, B. M.; Jones, K. W. In *Biological Trace Element Research*, American Chemical Society Symposium Series No. 445, Editors, Subramanian, K. S.; Iyengar, G. V.; Okamoto, K. A., American Chemical Society, Washington, DC, 1991, Chapter 23, pp 290-305.

**Table 1. XANES analysis of different test mixtures containing aqueous solutions of sodium sulfite, sodium thiosulfate and sodium sulfate. The values represent ratios of concentrations in g. atom sulfur units. Initial concentrations are given in molar units within parentheses.**

	<b>Sulfite</b>	<b>Thiosulfate</b>	<b>Sulfate</b>
<b>Test mixture</b>	<b>0.33 (50 mM)</b>	<b>0.67 (50 mM)</b>	<b>-</b>
<b>XANES analysis</b>	<b>0.33</b>	<b>0.67</b>	<b>-</b>
<b>Test mixture</b>	<b>-</b>	<b>0.67 (50 mM)</b>	<b>0.33 (50 mM)</b>
<b>XANES analysis</b>	<b>-</b>	<b>0.71</b>	<b>0.29</b>
<b>Test mixture</b>	<b>0.25 (50 mM)</b>	<b>0.50 (50 mM)</b>	<b>0.25 (50 mM)</b>
<b>XANES analysis</b>	<b>0.22</b>	<b>0.52</b>	<b>0.26</b>

Table 2. Percentage of products formed from the oxidation of aqueous sulfide containing different co-substances

Medium	Co-substance	[H <sub>2</sub> S] (mM)	[O <sub>2</sub> ] (mM)	t <sub>1/2</sub> (hour)	Product ratio after 48 hours				
					SO <sub>3</sub> <sup>2-</sup>	S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	S <sub>n</sub> <sup>2-</sup>	Other (+2 sp.)
water	none	100	0.255	385	9	83	8	n.d.	n.d.
water	sea sand	100	0.255	257	4	92	4	n.d.	n.d.
water	100 μM FeSO <sub>4</sub>	100	0.255	210	3	92	5	n.d.	n.d.
water	100 μM NiCl <sub>2</sub>	100	0.255	40	n.d.	67	1	20	12
0.7 M NaCl	none	100	0.232	289	10	90	n.d.	n.d.	n.d.
0.7 M NaCl	100 μM NiCl <sub>2</sub>	100	0.232	35	n.d.	58	2	24	16

## Figure Captions

- Figure 1. Absorption spectrum for gaseous argon resolved into transitions to allowed bound states and to the continuum. (source: reference 25).
- Figure 2. High intensity x-ray absorption fine structure spectrum of elemental sulfur showing phenomenological energy ranges.
- Figure 3. Normalized XANES spectra of various sulfur compounds showing characteristic features including edge energies.
- Figure 4. Plot of white-line peak energy (eV) versus sulfur oxidation state for some sulfur compounds fitted with a linear least-squares line.
- Figure 5. Correlation between x-ray absorption step height and the concentration of sulfur using  $\text{Na}_2\text{SO}_4$  solutions prepared in deionized water.
- Figure 6. The sulfur K-edge fluorescence excitation spectra of two different  $\text{Na}_2\text{SO}_4$  solutions (0.025 M and 0.1 M in deionized water) with and without self-absorption correction.
- Figure 7. Non-linear least-squares fit of the XANES spectrum of an aqueous solution containing sulfite, thiosulfate and sulfate with spectra of model compounds.
- Figure 8. Schematic diagram of a typical x-ray absorption beamline setup. The storage ring to sample distance at NSLS X-19A is 20 m. (source: reference 36).
- Figure 9. Sulfur K-edge XANES spectra of 0.1 M sulfide in water after different periods of exposure to air. Conditions:  $t = 25 \pm 1^\circ\text{C}$ ;  $\text{pH} = 8$ ;  $[\text{O}_2]_0 = 255 \mu\text{M}$ .
- Figure 10. XANES spectra of the various sulfur standards used for fitting. Benzyl sulfoxide was used in the solid form; all other standards were prepared as 10 - 50 mM liquids.

**Figure 11.** Sulfur K-edge XANES spectra of 0.1 M sulfide with added NiCl<sub>2</sub> (100 μM) after different periods of exposure to air: (A) deionized water; (B) 0.7 M NaCl solution. Conditions:  $t = 25 \pm 1^\circ\text{C}$ ; pH = 8; [O<sub>2</sub>]<sub>0</sub> = 255 μM in water and 232 μM in 0.7 M NaCl solution.

**Figure 12.** Non-linear least-squares fit of the XANES spectrum of aqueous sulfide (0.1 M in deionized water) with added NiCl<sub>2</sub> (100 μM) after different periods of air oxidation: (A) 63 hours, (B) 172 hours. Benzyl sulfoxide was used as a surrogate to quantify the unknown sulfide oxidation intermediate with peak at 2476.1 eV.

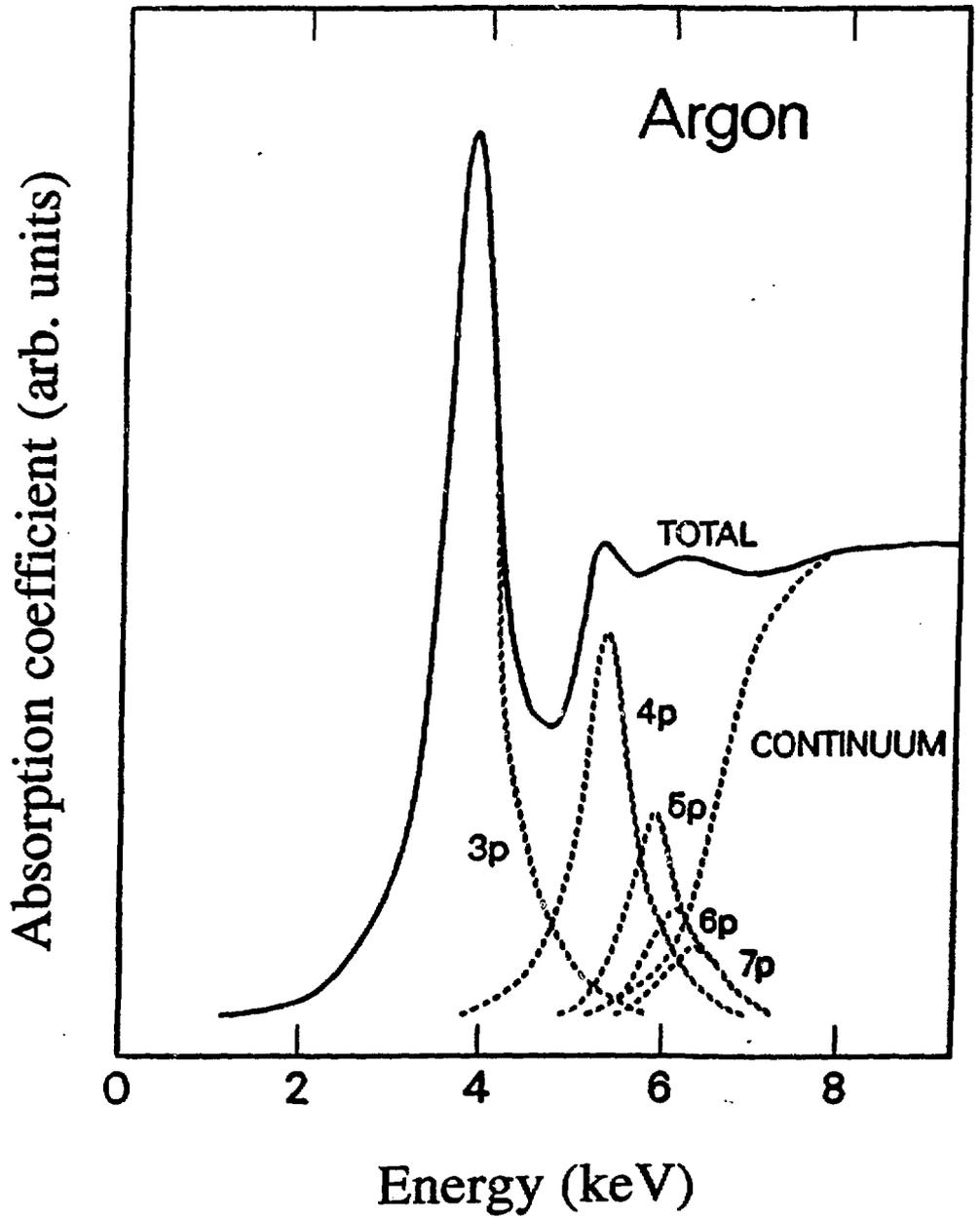


Figure 1

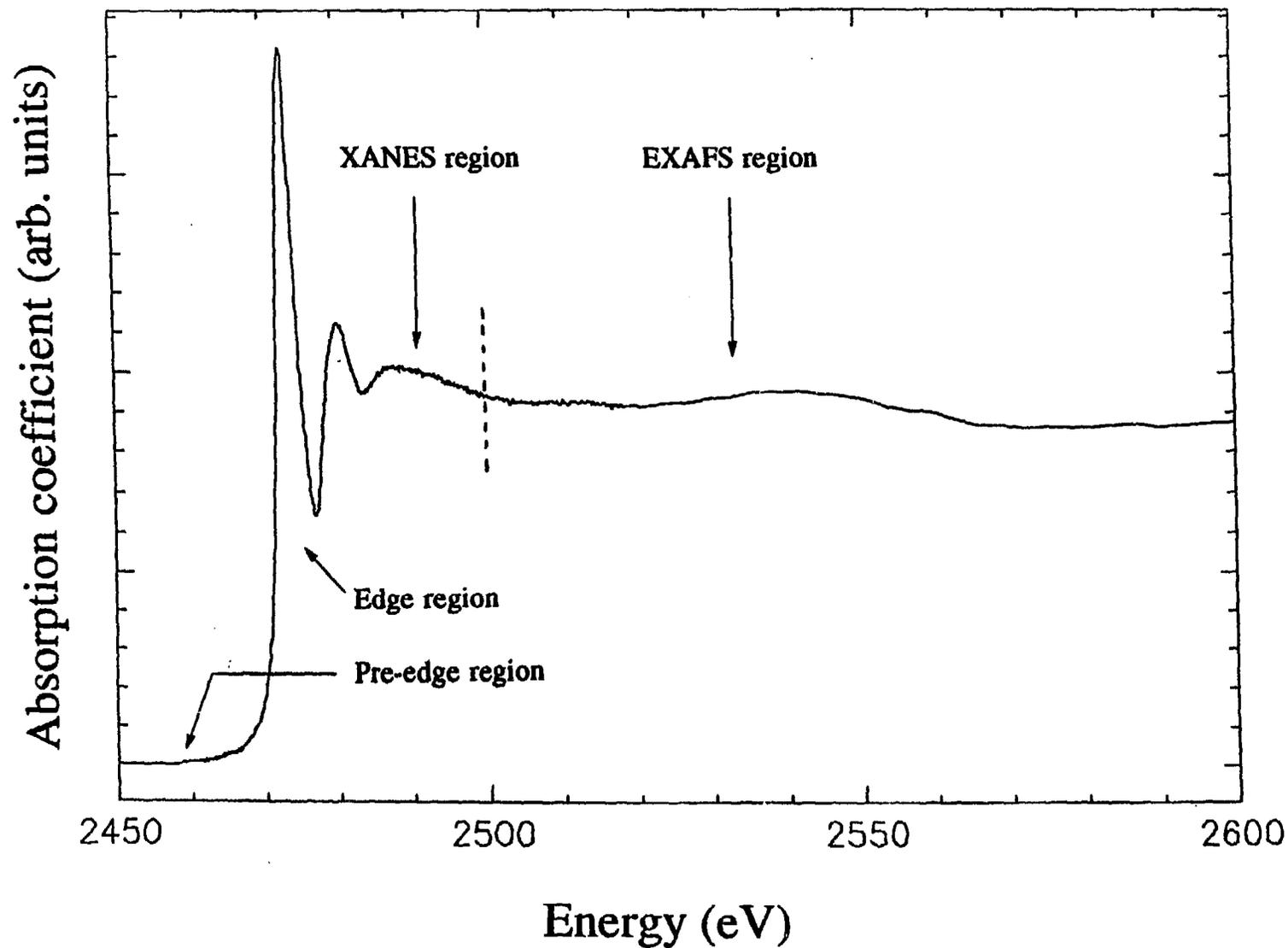


Figure 2

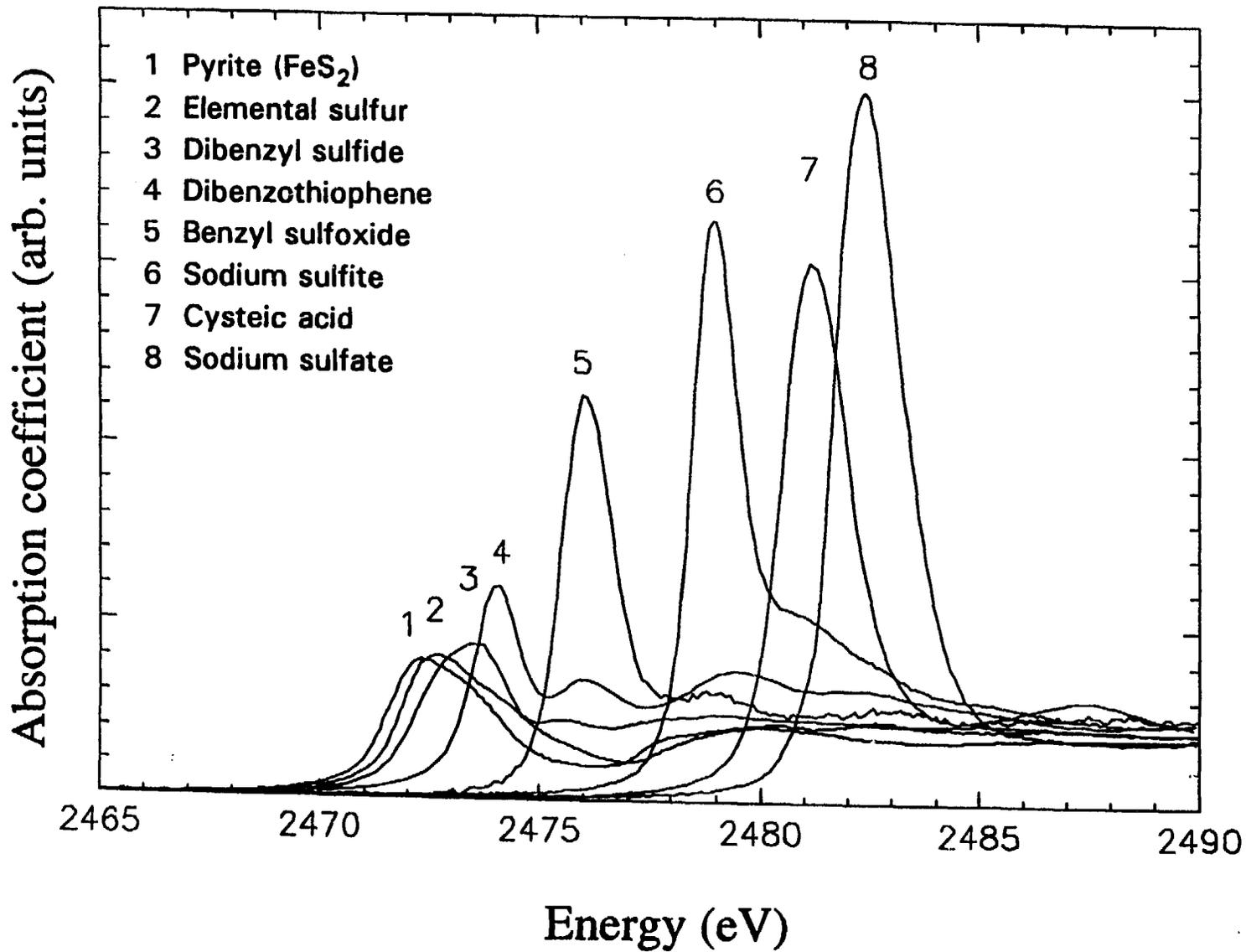


Figure 3

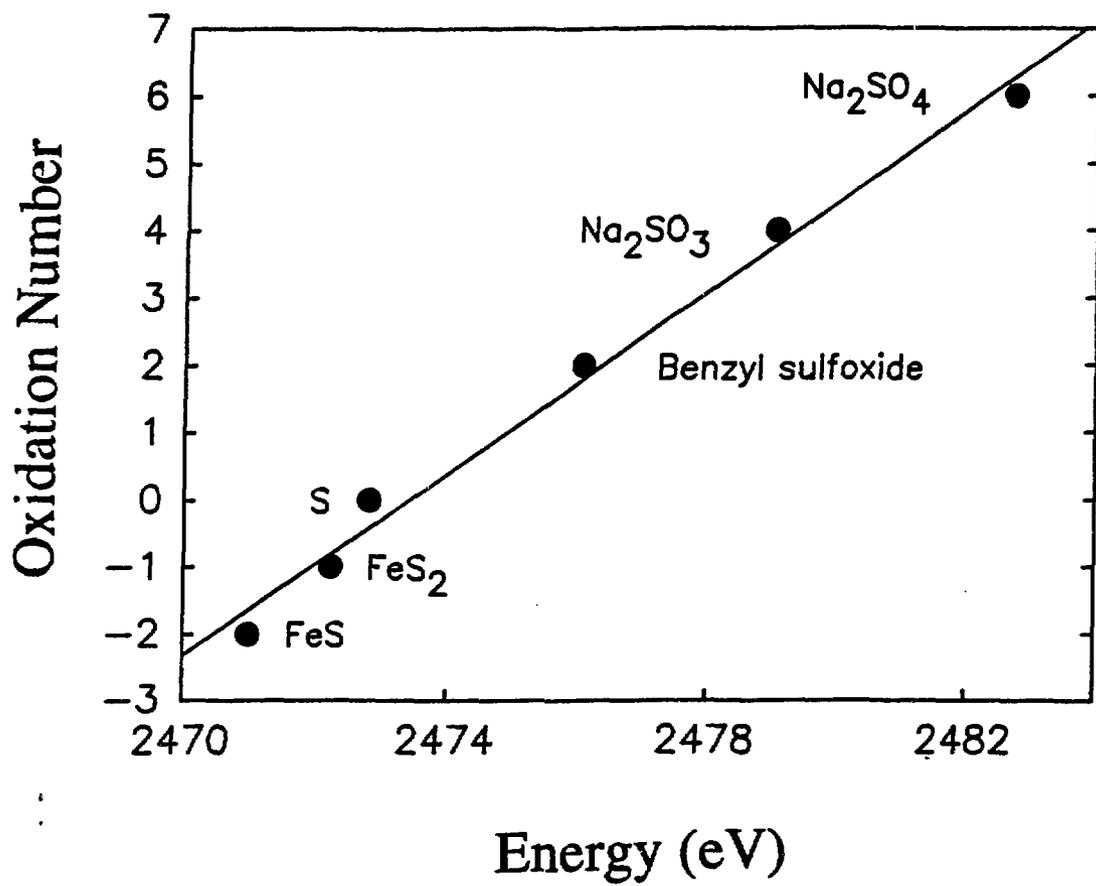


Figure 4

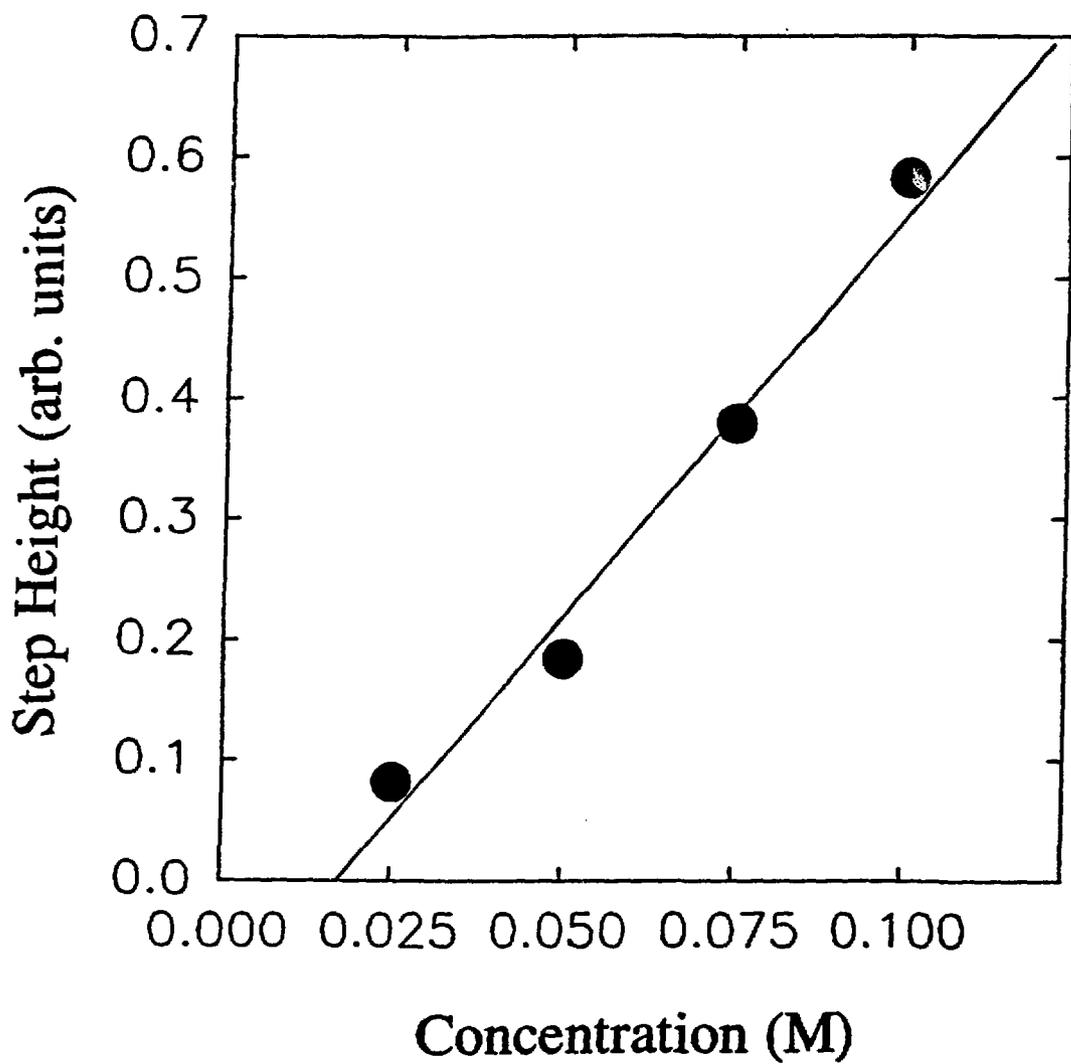


Figure 5

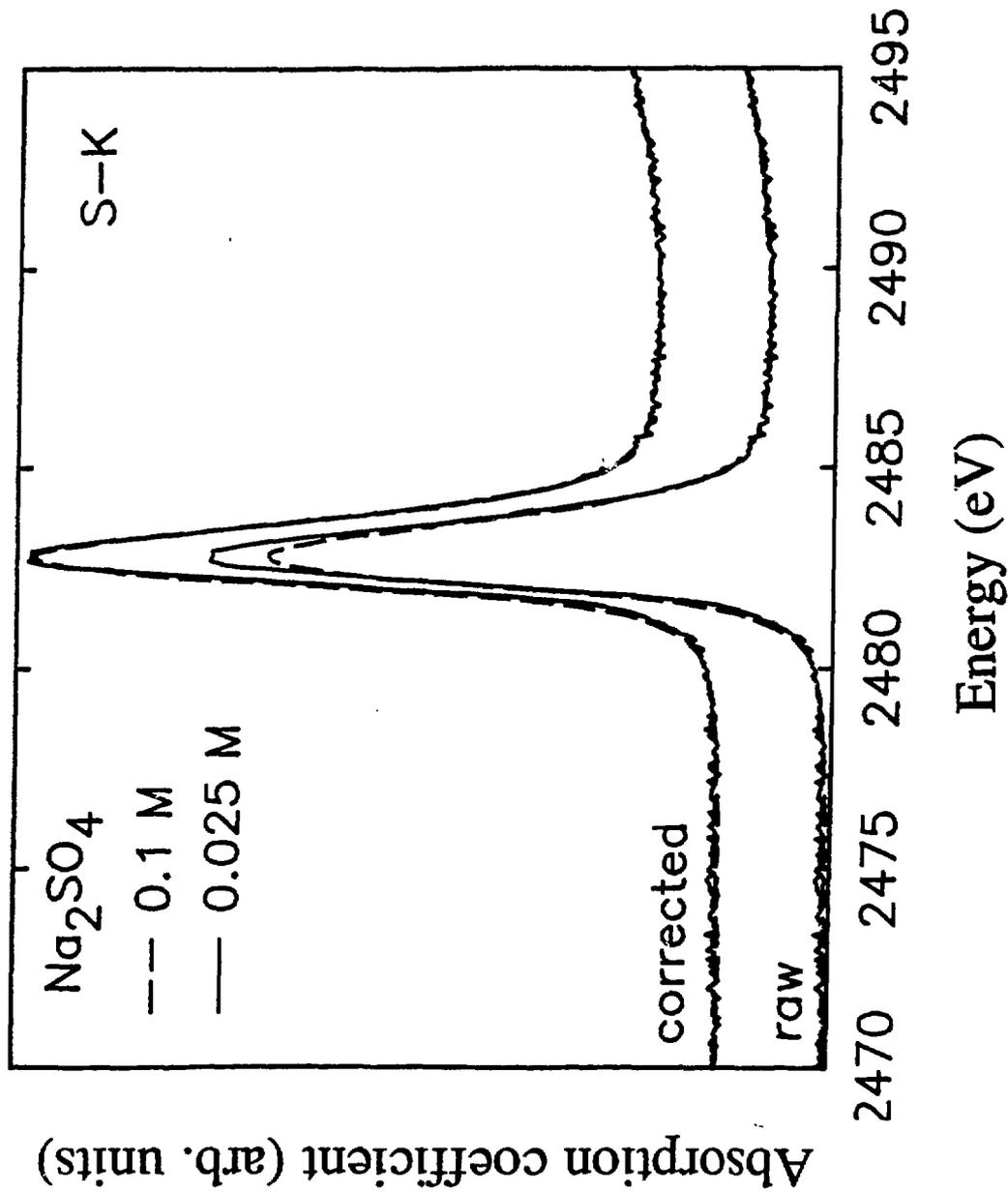


Figure 6

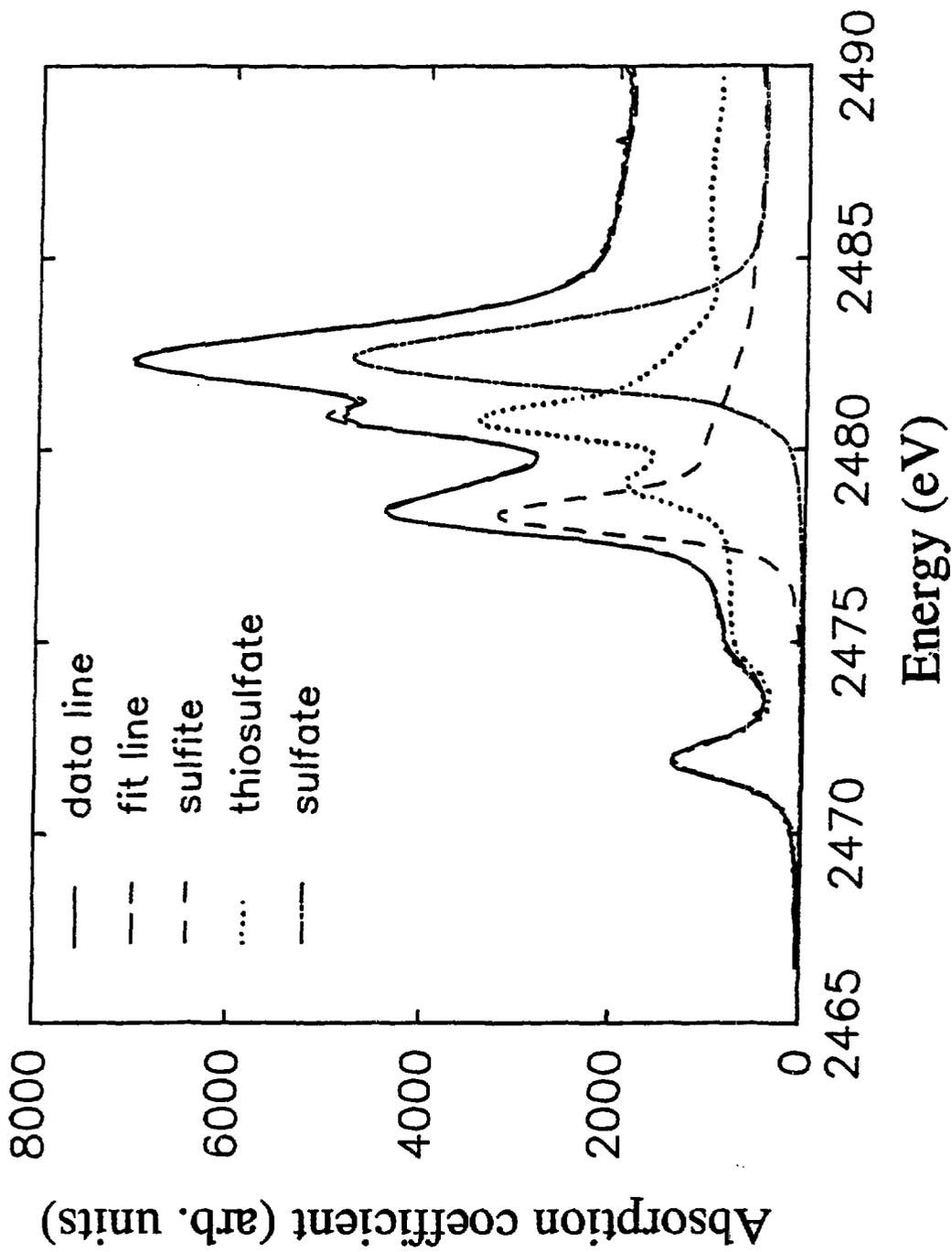


Figure 7

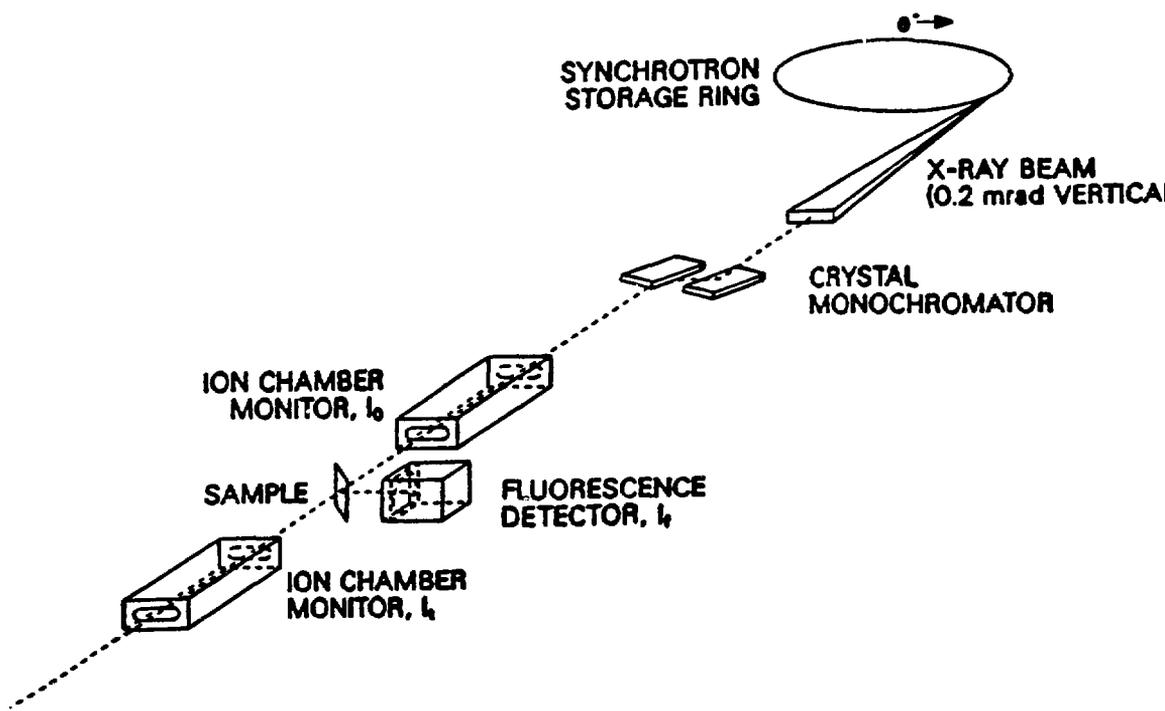


Figure 8

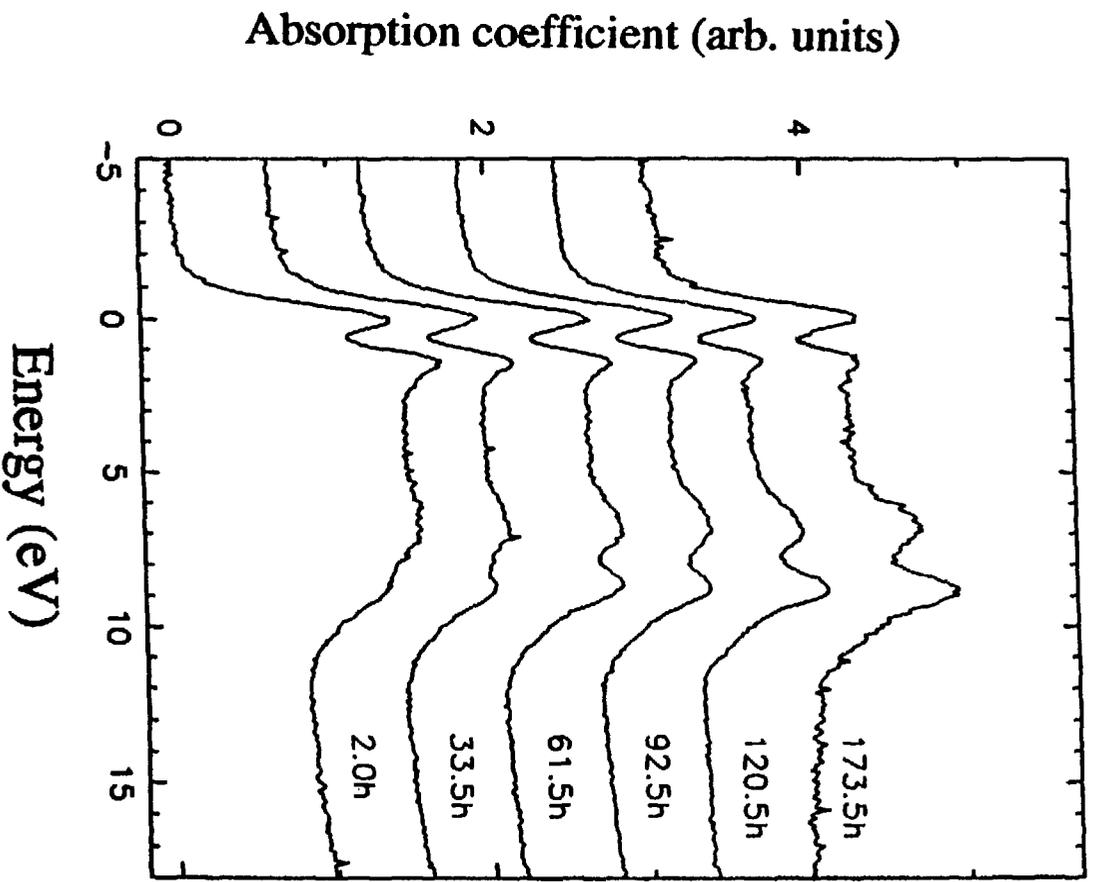


Figure 9

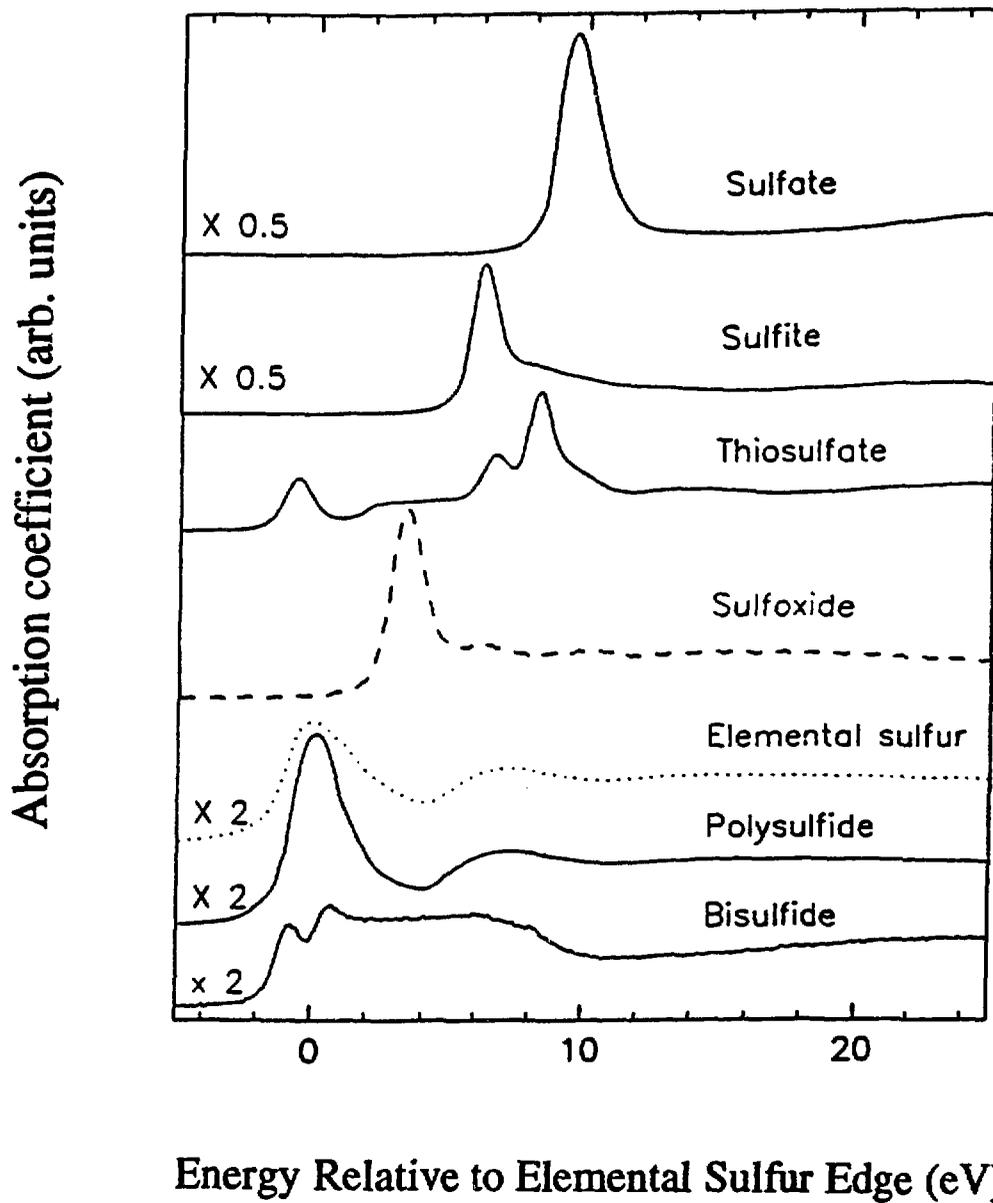
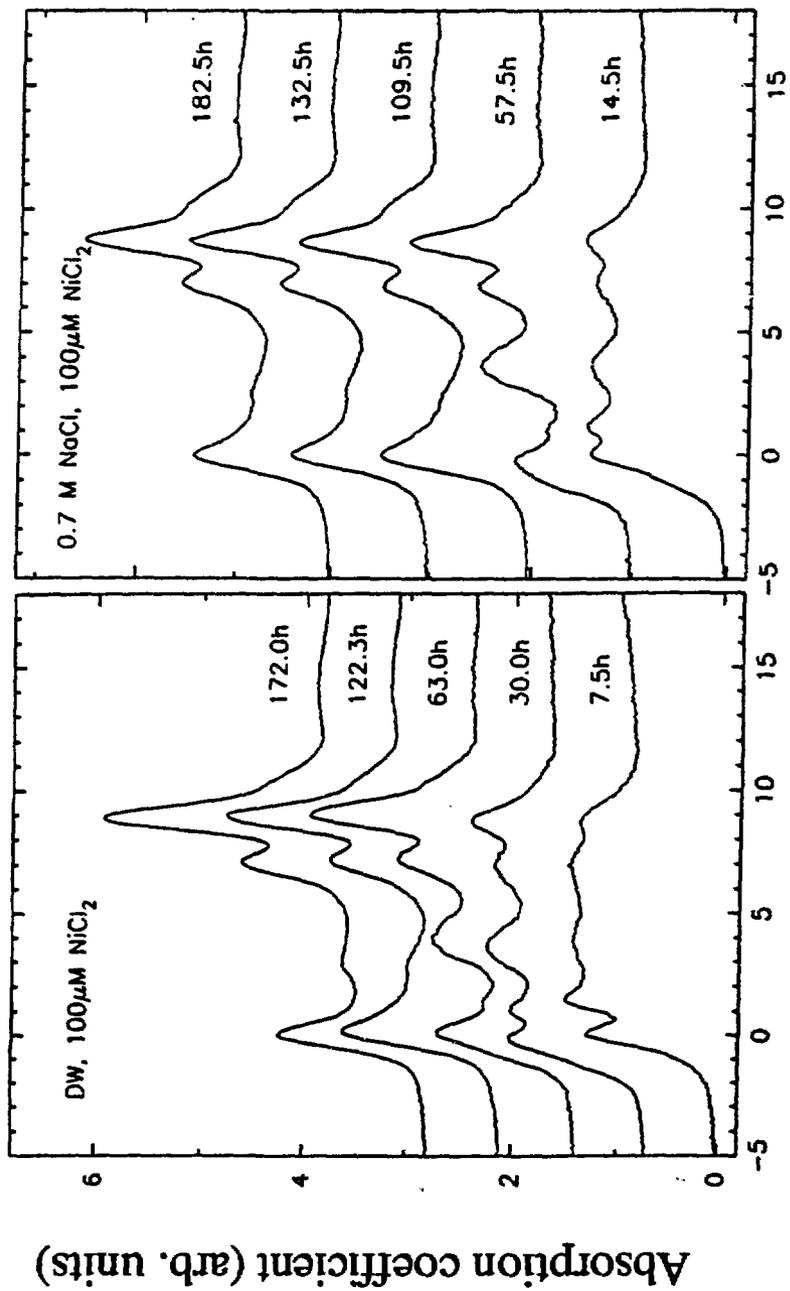


Figure 10



Energy Relative to Edge (eV)

Figure 11

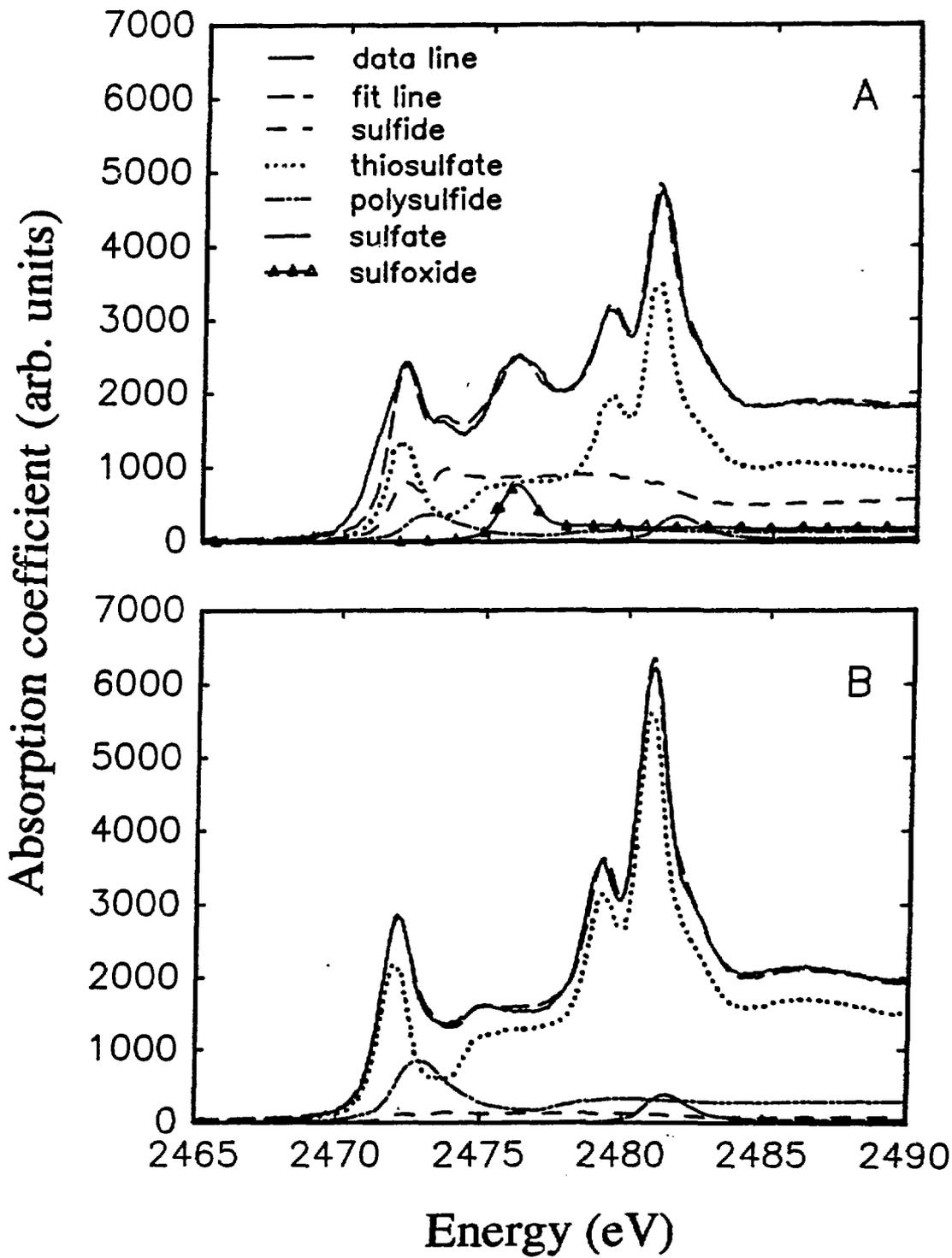


Figure 12