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Coal Sulfur Forms Determination Using Thermal Analysis Methods

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COAL SULFUR FORMS DETERMINATION USING THERMAL ANALYSIS METHODS

A Thesis
Presented to
the Faculty of the Department of Chemistry
Western Kentucky University
Bowling Green, Kentucky

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Bucheng Wang
December 1993

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COAL SULFUR FORMS DETERMINATION USING THERMAL ANALYSIS METHODS

Date Recommended November 22, 1993

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1/24/94
Graduate Studies **Date**

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Bucheng Wang

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COAL SULFUR FORMS DETERMINATION USING THERMAL ANALYSIS METHODS

Bucheng Wang October 30, 1993 67 Pages

Directed by: John T. Riley, Wei-Ping Pan and Lowell W. Shank

Department of Chemistry Western Kentucky University

By optimizing parameters including temperature, reaction time, reagent concentration and pressure, the optimum conditions for the mild oxydesulfurization of coals were determined to be 150°C-200°C and 10 atmospheres oxygen in aqueous slurries of coal reacted with 1 M NH_4OH for 1.5-2 hours. The total amount of sulfur removed from -60 mesh coals ranges from 51% to 78% with a mean of 64%, while the amount of inorganic sulfur removed from the coals ranged from 66% to 91% with a mean of 77%. The amount of organic sulfur removed from the samples ranged from 36% to 50% with a mean of 43%.

Thermal analysis of raw and cleaned coals was carried out. By using a heated gas line to connect the thermal gravimetric analysis to the Fourier transform infrared instrument (TG/FTIR), the main products from the combustion of raw and cleaned coals were found to be CO_2, H_2O, and SO_2. The IR spectral data for SO_2 were collected at 1375 cm^{-1} throughout the combustion process for raw and cleaned coals. The temperatures for aliphatic, pyritic and aromatic sulfur oxidation were determined

to be 320°C, 420°C, and 470°C, respectively. Based on the thermal analysis experiments, an instrumental analysis method for the determination of pyritic sulfur was designed. The amount of pyritic sulfur determined the TG/FTIR method compared favorably to data obtained using the ASTM D 2492 method.

X-ray absorption fine structure (XAFS) spectra of selected samples were obtained by Dr. Frank Huggins at the University of Kentucky. These spectra supported the results obtained in the oxydesulfurization and TG/FTIR experiments.

I. INTRODUCTION

The United States has large reserves of coal, but much of the readily available coal cannot be burned directly because its sulfur content is too high. During sulfur combustion, sulfur reacts with oxygen converting it to sulfur oxides which may cause corrosion in utility boilers, air pollution, and acid rain. Coal combustion contributes about 67% (on a sulfur tonnage basis) of man-made sulfur pollution and about 23% of all sulfur air pollution.[1]

As generally accepted, there are three forms of sulfur in coal which are characterized as sulfate, pyritic and organic forms. Figure 1 is a drawing of a representative chemical structure for coal proposed by Wiser.[2] Sulfate sulfur occurs mainly as $CaSO_4$ nH_2O or $FeSO_4$ nH_2O which is present in coal primarily as a result of oxidation of pyrite. Pyrite and marcasite are two crystalline forms of FeS_2 and are collectively referred to as pyrite.[3] The organic sulfur components can be classified as either aliphatic sulfur or thiophenic (aromatic) sulfur compounds. The thiophenic sulfur compounds are the most stable organosulfur compounds and are the most difficult to remove by chemical desulfurization processes.

Sulfur occurs in coal as inorganic sulfates, as pyrites, and in combination with the organic matter. Free sulfur as such does not occur in coal to any significant extent.[4] The amount of the sulfur-containing materials in coal varies considerably, especially for coals from different seams. This variation is not as great for coals from

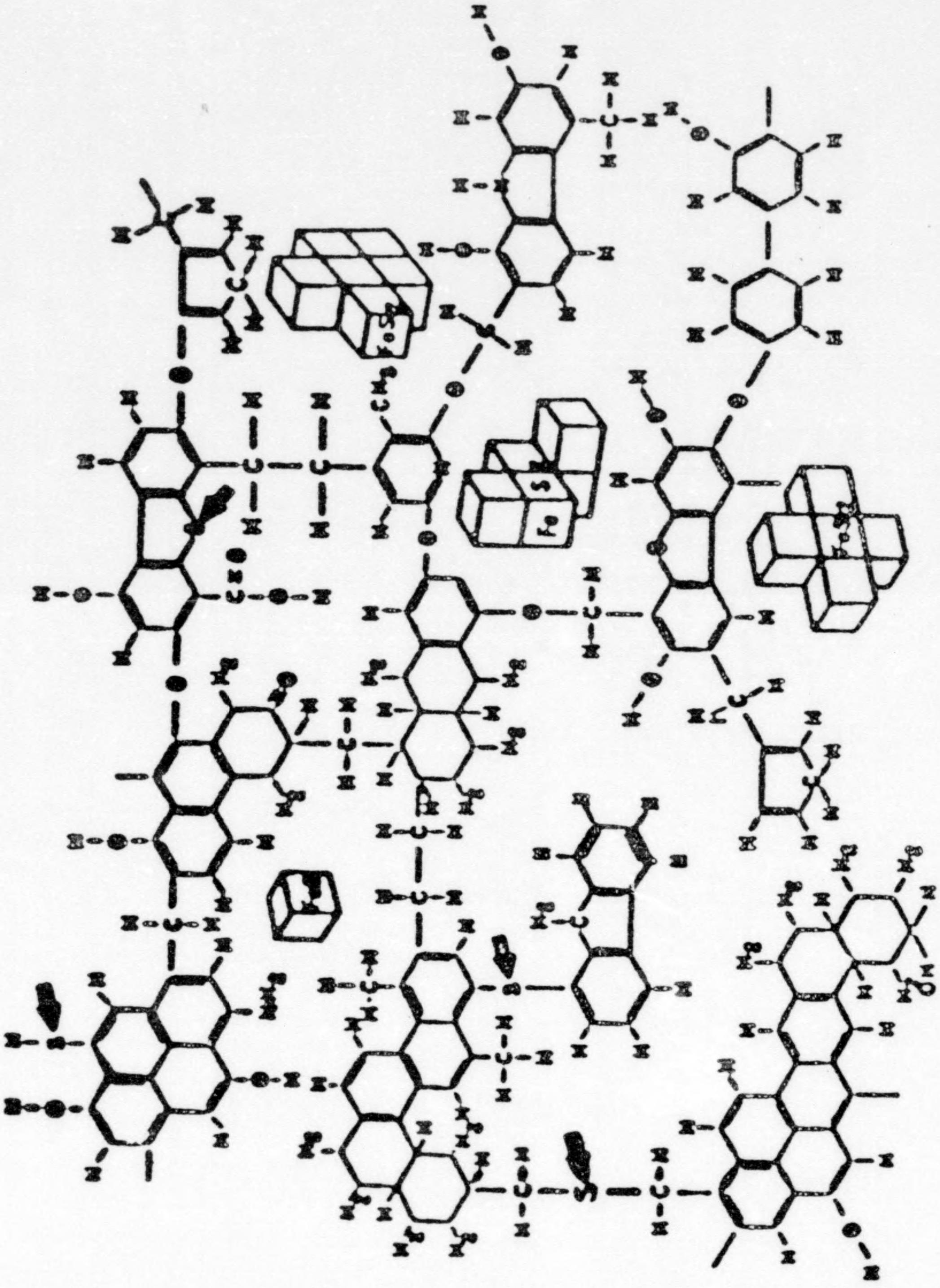


Figure 1. The proposed forms of sulfur in a coal matrix.[2]

a given field. On the average, coals from the Illinois Basin contain about equal amounts of organic and inorganic sulfur, although the relative amounts of these two sulfur forms may make up as much as 20-80% of the total sulfur in individual coals.[5] Organic sulfur and pyrites account for almost all the sulfur in coals. Sulfate sulfur is usually less than 0.1%, except for weathered coal containing an appreciable amount of pyrites. The pyritic sulfur varies considerably more than does the organic sulfur content and is of more interest because it is the form that can be most easily removed from coal by current preparation practices.[6]

Total sulfur data are necessary for the effective control of the emissions of oxides of sulfur whenever coal is used as a fuel. The emission of sulfur oxides may lead to the corrosion of equipment and slagging or fouling of boiler equipment, as well as contributing to atmospheric pollution and environmental damage. Sulfur data are therefore necessary for the evaluation of coals to be used for combustion purposes.[7]

The principal use of forms of sulfur data is in connection with the cleaning of coal. Within certain limits, pyritic sulfur can be removed from coal by gravity separation methods, whereas organic sulfur cannot. Pyritic sulfur content can therefore be used to predict how much sulfur can be removed from the coal and to evaluate cleaning processes. If the pyritic sulfur occurs in layers, it usually can be removed efficiently. If it occurs as fine crystals dispersed throughout the coal, its removal is very difficult.[8]

Other uses of forms of sulfur data are the inclusion of the pyritic sulfur value in the formula for the estimation of oxygen by difference and as a possible means of predicting the extent of weathering of coal. The sulfate concentration increases upon weathering, thus the sulfate sulfur value could be indicative the extent weathering of coal.[8]

The determination of the various sulfur forms in coal is among the most important analytical parameters used to characterize coal. The knowledge of the distribution of sulfate, pyritic, and organic sulfur forms in a coal is a measure of its quality and, furthermore, an indication of its potential quality that is attainable after beneficiation. The available methods for obtaining such information often can be difficult, tedious, expensive, not readily available, subject to many errors, and open to some criticism.[9]

ASTM Standard for Determination of Total Sulfur.

There are two ASTM methods for determining the total sulfur in coal and coke, with alternative procedures in each method.

ASTM method D 3177, "Total Sulfur in the Analysis Sample of Coal and Coke,"[10] has two alternative procedures referred to as the Eschka and the bomb washing methods.

ASTM method D 4239, "Sulfur in the Analysis Sample of Coal and Coke Using High-Temperature Tube Furnace Combustion Methods,"[11] has three alternative procedures. For the high-temperature combustion methods, a weighed sample is burned in a tube furnace at a minimum operating temperature of 1350°C in a stream of oxygen to ensure the complete oxidation of sulfur-containing components in the sample. Using these conditions, all sulfur-containing materials in the coal or coke are converted to sulfur dioxide in a reproducible way. The basic difference in the three procedures is the method of detection of the sulfur dioxide produced in the combustion of the coal or coke sample. Method A uses an acid-base titration for detection, the combustion gases are bubbled through a hydrogen peroxide solution in a gas absorption bulb. Sulfuric acid is produced by the reaction of sulfur dioxide with the hydrogen peroxide and is determined by titration with a standard base solution. Method B uses the iodimetric titration procedure, the combustion gases are bubbled through a diluent solution containing pyridine, methanol, and water. This solution is titrated with a titrant containing iodine in a pyridine, methanol, and water solution. Method C for measuring the sulfur dioxide in the combustion gases is by the absorption of infrared (IR) radiation. Moisture and particulate are first removed from the gas stream by traps filled with anhydrous magnesium perchlorate. The gas stream is then passed through an IR absorption cell tuned to a frequency of radiation absorbed by sulfur dioxide. The IR radiation absorbed during combustion of the sample is proportional to the sulfur dioxide in the combustion gases and therefore to the sulfur in the sample. The method is empirical, and the instrument should be calibrated before use.

ASTM Standard for the Determination of the Content of the Forms of Sulfur

The procedures for the determination of the forms of sulfur in coal are described in ASTM method D 2492.[12] Figures 2 and 3 show the procedure for forms of sulfur. In this method, the sulfate and pyrite sulfur are determined directly, and

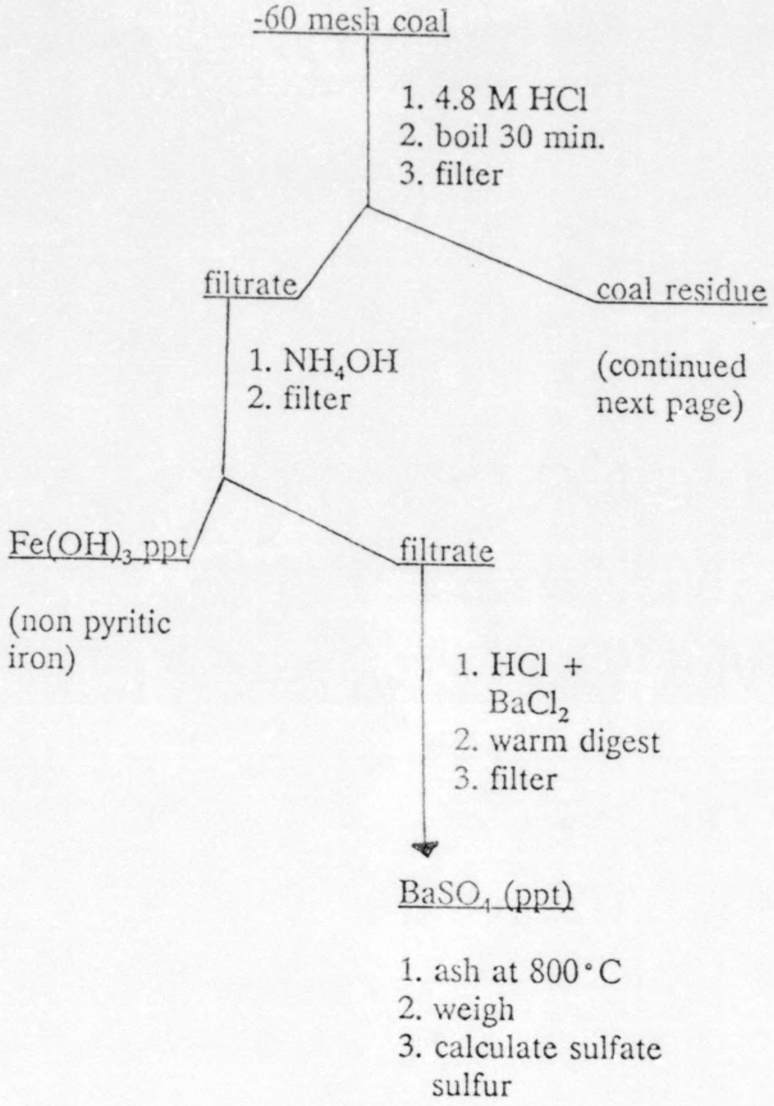
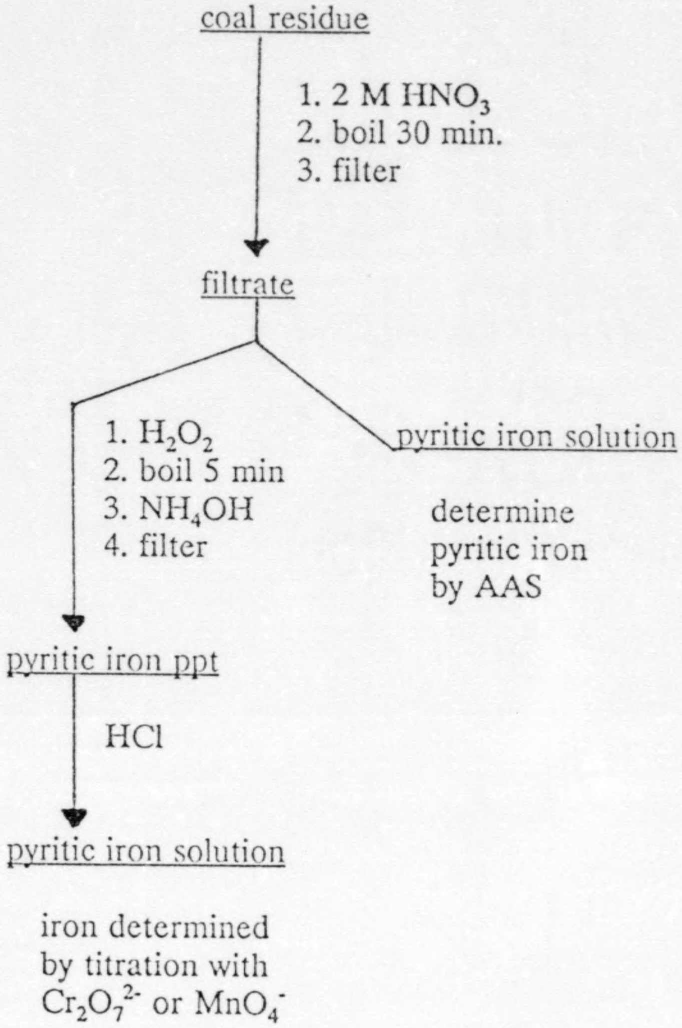


Figure 2. ASTM D 2492 Procedure for forms of sulfur in coal.



Assume pyritic iron is equivalent to the pyritic sulfur.

$$S_{organic} = S_{total} - (S_{sulfate} + S_{pyritic})$$

(All values must be reported on the same basis.)

Figure 3. ASTM D 2492 Procedure for forms of sulfur in coal (continued).

the organic sulfur is taken as the difference between the total sulfur and the sum of the sulfate and pyritic sulfur.

Sulfate sulfur is determined by extracting the coal with dilute hydrochloric acid and determining the sulfur in the extract gravimetrically. Sulfates are soluble in hydrochloric acid, but pyritic and organic forms are not.

Pyrites are extracted quantitatively by heating the coal sample with dilute nitric acid. The extracted iron is determined by either titrimetric or atomic absorption techniques and the pyritic sulfur is calculated as a stoichiometric combination with the iron. Since dilute nitric acid will also dissolve the forms of iron and sulfur that are soluble in hydrochloric acid, pyritic iron is normally determined in the residue from the sulfate extraction; otherwise, it is necessary to determine quantitatively the HCl-soluble iron in order to specifically identify the pyritic iron by subtraction of the HCl-soluble iron from the total iron in the samples.

Organic sulfur is calculated by deducting the sum of the percentages of sulfate and pyritic sulfur from the total sulfur in the coal as determined by Test Methods D 4239 or D 3177.

Direct Determination of Total Organic Sulfur in Coal

A method for the direct determination of organic sulfur in coal was developed by Riley, Ruba and Lee.[13] The procedure for this method is shown in Figure 4. Samples of -60 mesh coal were extracted with boiling 2 M nitric acid, which removes essentially all mineral sulfur. After washing and drying, the extracted samples were analyzed for moisture, ash, and sulfur before reporting the sulfur values on a dry,

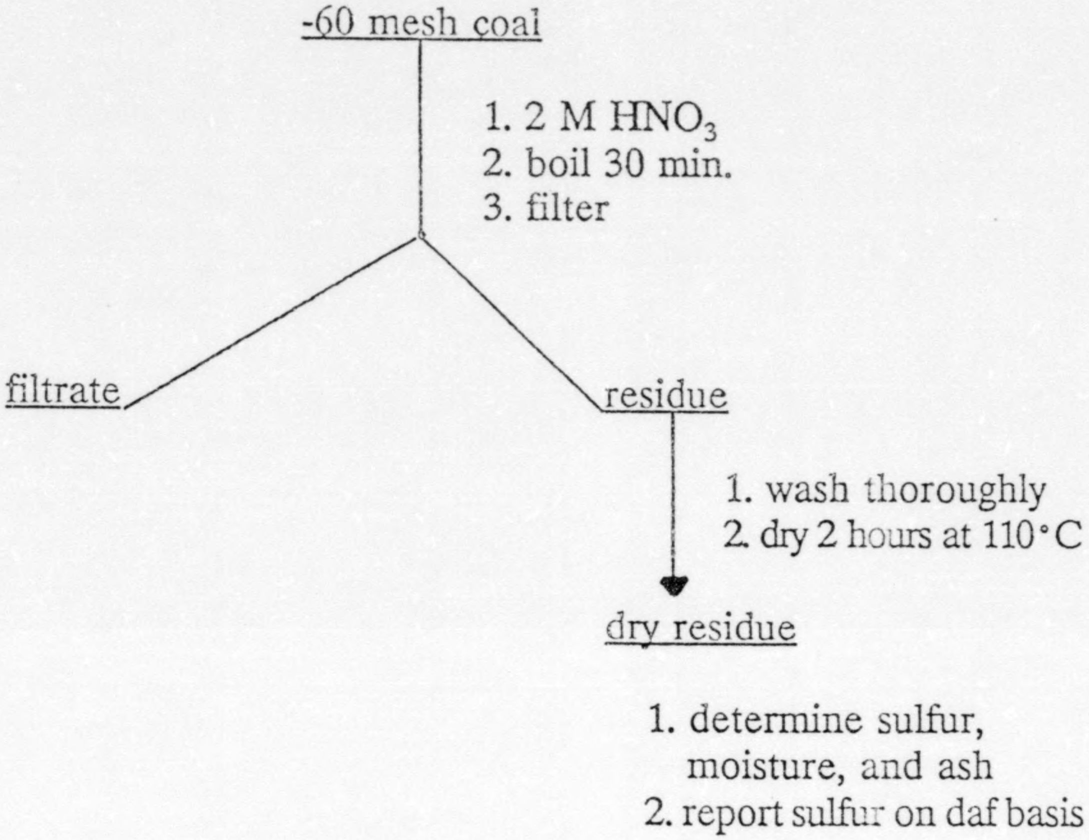


Figure 4. Direct determination of organic sulfur procedure.

ash-free (daf) basis. The organic sulfur values determined by the direct method were generally less than those obtained using ASTM Method D 2492. The precision for the new method was much better than that obtained with the ASTM method.

Reported Methods for Sulfur Forms Analysis

Many researchers have sought new and reliable methods for sulfur forms analysis via advanced physical methods. Among the most commonly used techniques are X-ray photoelectron spectroscopy (XPS) also known as electron spectroscopy for chemical analysis (ESCA), scanning electron microscopy (SEM), energy-dispersive X-ray microanalysis (XRMA), transmission electron microscopy (TEM), as well as X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopies.

J. K. Kuhn and coworkers studied a lithium aluminum hydride method for sulfur forms analysis. In this method, the sulfate sulfur and nonpyritic iron is removed with dilute HCl. Pyrite is extracted with $LiAlH_4$ in tetrahydrofuran. Organic sulfur is determined in the extracted residue. The determined organic sulfur values are 0.2-0.3% lower than the calculated ASTM organic sulfur values.[14]

X-ray photoelectron spectroscopy has been widely used for the examination of coal. However, this method can only distinguish between the di-, tetra-, and hexavalent forms of sulfur. Furthermore, the bulk concentration of sulfur determined by the ASTM method often differs significantly from that established by XPS.[15-17]

Hurley and White attempted to establish the organic and inorganic sulfur contents through XRMA. The shift in K emission for the different forms of sulfur, 1-2 eV, enables this analysis to be done. The results obtained by this method for pyritic, organic, and sulfatic sulfur were in fairly good agreement with the results that were realized with the ASTM procedures.[18]

Markuszewski and his associates described a method based upon SEM/XRMA that simultaneously monitors the signals of sulfur, iron, calcium, aluminum, and silicon.[19] This method can successfully avoid particles of pyrite, quartz, and calcium sulfate on the coal surface by a simple count rejection procedure. They investigated raw and chemically treated coals and, in many cases, obtained good agreement with the ASTM method.

Wert and his research associates developed a method to determine organic sulfur concentrations using TEM. They also reported that there was a very good linear correlation between the organic sulfur content of coal determined by the ASTM and TEM methods. The difference did not exceed 9%. The TEM method has also been successfully applied to the analysis of the organic sulfur content of macerals and for the study of their thermal decomposition.[20]

Among all the modern physical methods, XANES and EXAFS spectroscopy appear to hold promise for the evaluation of the sulfur functional group distribution. A least-squares method of analysis of the XANES region of the sulfur K-edge EXAFS spectrum of coal might provide a complete description of the gross forms of sulfur in coal. For example, the major organic functional groups, such as sulfide (thioether), thiophene, sulfoxide, and sulfone, and the two principal inorganic forms, pyritic and sulfate sulfur, can be identified. Although the XANES analysis lacks the sensitivity to provide information on specific organic compounds such as those detected by GC/MS in extracts and volatile fractions from coal, it is felt that information on the amount of organic sulfur in different functional groups is still valuable new information concerning sulfur in coal.[21]

The XANES transitions that were observed for the K-shell electrons of sulfur in the samples coincide with the transitions for the sulfur atoms in heterocyclic molecules such as dibenzothiophene and benzothiophene. Furthermore, the molecular spacing implied by the EXAFS portion of the spectrum, for example the 1.75 angstrom carbon-sulfur bond distance, are more compatible with the results expected for the heterocyclic compounds than for the aliphatic substances.[21]

George and Gorbaty[22] have investigated the XANES spectra of many pure sulfur compounds and have suggested that these spectra can provide fingerprints for several kinds of sulfur compounds including the sulfidic and thiophenic forms. They have extended the work in this area by showing that the amplitude of certain features in the third derivative are proportional to the relative amounts of sulfidic and thiophenic sulfur.

The standards and samples were prepared by grinding them to a very fine size and mixing them thoroughly with boric acid (H_3BO_3) and then cold pressing the resulting mixture into 3-5 mm thick pellets. Samples were examined by X-ray fluorescent experiments using a Stern-Herald type detector and scans were obtained for incident energies varying from 100 eV below to 300 to 600 eV above the sulfur K-edge energy (2472 eV).[23]

Characterization of Organic Sulfur in Coal by Programmed Temperature Oxidation.

A controlled-atmosphere, programmed-temperature, oxidation apparatus was constructed by R. B. LaCount and coworkers[24] at the Pittsburgh Energy and Technology Center. This apparatus was used to characterize the organic sulfur distribution in coals, partially desulfurized coals, and model compounds. At a programmed-temperature increase of 3°C/min, concentrations of sulfur dioxide, carbon dioxide, carbon monoxide, oxygen and water in the effluent gas were continuously measured until the runs were completed at 1000°C. Evolution patterns produced by the oxidation products characterize the coal and, upon integration, provide total C-H-S analyses consistent with classical coal analysis methods. The sulfur dioxide derived from coal pyrite evolves at a maximum at about 430°C, and that from the organic portion of coal produces principal evolution maxima at about 320°C (attributed to non-aromatic structure) and at about 480°C (for aromatic structure).

Forms of Organic Sulfur Determination by Mild Oxidative Desulfurization Process

The removal of organic sulfur from coal presents the most serious challenge in coal desulfurization. Most studies of the organic sulfur in coal have concentrated on compounds containing thiophenic sulfur groups. These compounds are the most stable and most difficult organosulfur materials to remove from coal.

Riley and coworkers[25] reported results on the removal of sulfur using mild oxidizing conditions. In this project, the optimum conditions for the mild oxydesulfurization of coals were designed. Parameters optimized included temperature, pressure, reaction time and reagent concentration, which included 150-200°C, 10 atmospheres oxygen and aqueous slurries of coal reacted with 1 M NH_4OH for 1.5-2 hours. The amount of organic sulfur compounds was quantified by using the mild oxydesulfurization processes. As much as 50% of organic sulfur in Illinois Basin coals can be removed by the mild oxydesulfurization process.

The oxidative desulfurization of seven Illinois Basin coals showed that the total amount of sulfur removed from -60 mesh (250 microns) coals ranged from 51% to 78% with a mean of 64%. The amount of inorganic sulfur (sulfatic, sulfidic,and pyritic) removed from the seven coals ranged from 66% to 91% with a mean of 77%. The amount of organic sulfur removed from the samples ranged from 36% to 50% with a mean of 43%. Aliphatic thiols, desulfides, and sulfides in coal were the most likely to be oxidized in these mild oxidative experiments.

The time-honored, tested, and accepted ASTM method[26] for sulfate and pyritic sulfur (Method D 2492) is still the standard against which ultimately all other methods are compared. These methods for sulfur forms are useful in coal analysis but are based on some assumptions and have limitations that can result in serious analytical errors. According to these ASTM procedures, the sulfur forms in coal are obtained by determining sulfate and pyritic sulfur in one sample and subtracting their sum from the total sulfur content, obtained on another sample, to get the organic sulfur by difference.

ASTM Method D 2492 for sulfur forms in coal poses many challenges. The initial step consists of extracting a sample of coal with boiling hydrochloric acid to dissolve all sulfate. The finish is the gravimetric determination of sulfate as barium sulfate. Although the gravimetric determination of sulfate is one of the most important analyses in chemistry,[27] it is tedious, time consuming, subject to error, and requires highly polished skills. In addition to the difficulties already mentioned, there are several other considerations in this step.

First of all, it is important that all of the non-pyritic iron forms are completely dissolved while none of the pyrite is solubilized. Samples of coal which have been treated chemically or subjected to high temperatures may have iron forms that are not readily soluble in dilute hydrochloric acid. Even air oxidation of pyrite in coal results in many different types of iron sulfates, some of that may not be readily acid soluble.[28] Also, coal that has been through a coal preparation plant may have incorporated significant amounts of magnetite from the heavy media circuit that may not dissolve rapidly enough in the 30 minutes allowed. Finally, there is some evidence that certain pyrites, especially after chemical or thermal treatment, may also dissolve to a small degree in hot dilute hydrochloric acid. All of these possibilities will have an effect on the next step, the determination of pyritic sulfur.

With such difficulties, it is not surprising that the ASTM reproducibility for a coal containing 2% pyritic sulfur is 0.04 for sulfate and 0.69 for pyritic sulfur. Although no reproducibility is given for organic sulfur, it must be at least as great as that for pyritic sulfur, since organic sulfur is calculated as the difference between total sulfur and the sum of sulfate and pyritic sulfur. The precision in measuring pyritic sulfur, total sulfur and sulfate sulfur would thus be applied to the organic sulfur.

The uncertainty in the organic sulfur value is not only due to mathematical propagation of errors but also to several other factors that can affect the determined value of organic sulfur in coal. One of these factors relates to the presence of elemental sulfur. Since elemental sulfur is not extracted by either of the acid treatments, it will not be included as sulfate or pyritic sulfur. Since it appears in the total sulfur determination, it will be added to the so-called organic sulfur. Sometimes, coals may contain a few tenths to a few hundredths ppm elemental sulfur, but occasionally some have been analyzed to contain 1000 to 2800 ppm.[29] Also, weathered coals can contain significant amounts of elemental sulfur.[30,31] Another source of error in the organic sulfur value can be due to the presence of sulfide minerals. Illinois Basin coals are especially prone to such errors because they contain considerable amounts of sphalerite, ZnS.[32]

This brief summary highlights some of the concerns and potential problems in the determination of sulfur forms, and especially organic sulfur, in coal. It is obvious that these concerns are even more serious for coals which have been chemically altered or treated at high temperatures. It poses a considerable problem in evaluating results from the chemical desulfurization of coal.

Among the most important corrective efforts are experimental new methods for the direct determination of organic sulfur. Most of them involve very sophisticated and expensive instrumentation such as electron microscopy,[33] scanning electron microscopy with energy-dispersive X-ray analysis,[34,35] transmission electron microscopy,[36] and various X-ray methods.[37-39]

An ideal method for the determination forms of sulfur would be direct, simple, rapid, reliable, inexpensive, reproducible, widely applicable, and acceptable to all. Of course, such are the dreams of frustrated coal analysts. Still, there are many possibilities that need to be examined.

This project was designed to investigate a method for the determination of sulfur forms by using programmed temperature tube furnace combustion. Also the distribution of aliphatic and aromatic sulfur as components of the organic sulfur is to be measured.

The objectives of this project are as follows:

1. Develop a new method to determine the forms of sulfur in coal.
2. Determine the analysis conditions for sulfur forms in coal by TG/FTIR.
3. Apply the conditions to the LECO SC-432 Sulfur Analyzer for programmed temperature tube furnace combustion.
4. Quantify the aliphatic, pyritic, and aromatic sulfur in seven Illinois Basin coal samples.
5. Verify the results of sulfur forms analysis by using oxydesulfurized coals and XANES results.

II. EXPERIMENTAL

A. Materials

Seven bituminous coals from the Illinois Basin Coal Sample Program (IBCSP) were used in this study. The origins, types, and ranks of these coals are listed in Table 1. The -8 mesh coals were stored under nitrogen at 0°C. Samples of -60 mesh coals were used in all analysis and studies.

All reagents used in this research were of reagent grade. Calibration standards for the analysis of sulfur were National Institute for Standards and Technology (NIST) materials and LECO coal calibration standards. All water used was deionized by ion exchange columns. The samples and reagents were prepared by ASTM methods, by LECO instrumental requirements, or by the several procedures described in this chapter.

B. Instrumentation

A TA Thermal Analysis System model Du Pont 951 TG/DTA consisting of a horizonal balance and furnace was used for collecting the TG and DTG data. Figure 5 shows the instrumentation used in the TG/FTIR method.[40] A 15 mg coal sample was heated with programmed temperature in an air atmosphere and gradually oxidized. The gaseous products were removed by flowing air and the weight of the sample is recorded by the TG balance.

Table 1. Description of Coals Used in the Project

Coal No.	Seams	Type of sample
89020	Herrin, IL No.6	Preparation plant
89021	Colchester, IL No. 2	Preparation plant
89022	20% Herrin, IL No.6 and 80% Springfield, IL No. 5	Preparation plant
89023	Herrin, IL No. 6	Run-of-mine
89024	Springfield, IN No. V	Preparation plant
90003	Herrin, IL No. 6	Preparation plant
90008	Herrin, IL No. 6	Block of mine, same as APCSP[A] sample

[A] APCSP = Argonne Premium Coal Sample Program

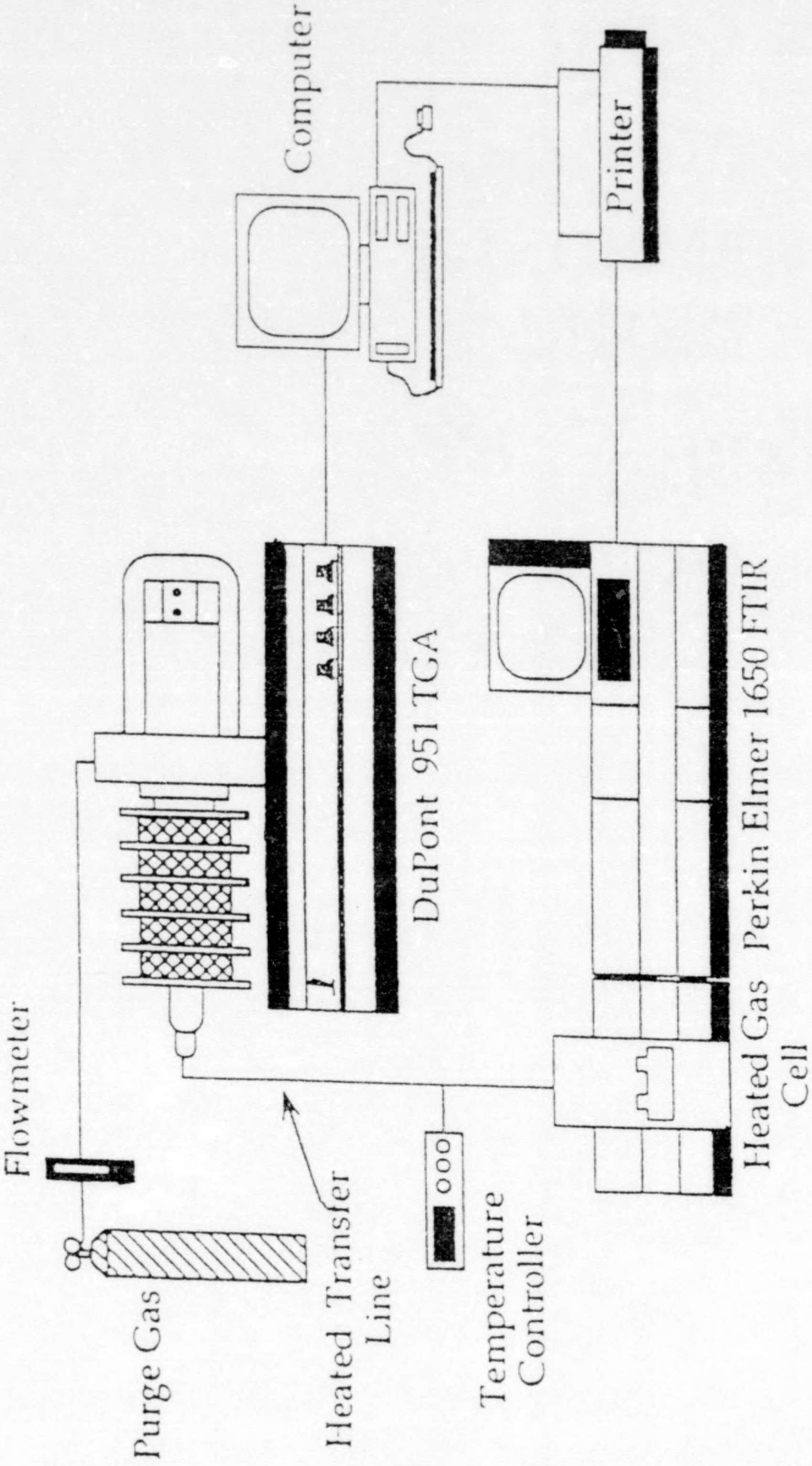


Figure 5. Schematic diagram of the TG/FTIR Data Collection Instrumentation.

A heated gas line connected the thermal analysis instrument and a Perkin Elmer model 1650 FTIR. A 10 cm heated sample cell with KBr window was used for all IR analysis of the gaseous products transferred from the TG. The detail of heated gas line and cell is shown in Figure 6.[41]

A LECO MAC-400 Proximate Analyzer was used to determine the moisture, ash, and volatile matter in coal (ASTM D 5142). In this instrument, measurements are obtained by monitoring the weight loss of each sample as it is heated in an atmospherically-controlled (nitrogen or oxygen) environment.

A LECO SC-432 Sulfur Analyzer was used for the determination of total sulfur in coals (ASTM D 4239). In the SC-432 coal samples were quickly burned in an oxygen atmosphere at 1350°C where sulfur is completely oxidized to SO_2. Moisture and dust are removed and then the sulfur dioxide gas is then measured by a solid state infrared detector.

An external furnace connected to the LECO SC-432 was used for the determination of forms of sulfur in coals. A coal sample of about 30 mg was slowly burned in air atmosphere at a given temperature where only certain sulfur compounds in coal can be oxidized to SO_2. The combustion gases from the heated coal were injected into the SC-432 where the sulfur-containing gases were oxidized to SO_2 and measured.

A LECO Plasmarray ICP-500 inductively coupled plasma spectrometer was used to analyze the concentration of iron in the pyrite extraction for sulfur forms determination. The ICP spectrometer uses a photodiode array detector which is capable of simultaneous as well as sequential multielement analysis with

Figure 6. Diagram of the heated gas cell for IR analysis

simultaneous background correction. The procedure for analysis follows ASTM D 2492. A 2-5 g sample of coal is extracted by dilute nitric acid (2 M) after the sample is treated with dilute hydrochloric acid. The extract is diluted to 250 mL in a volumetric flask, and the iron in the extract is determined using the ICP spectrometer.

An Autoclave Engineers Inc., Magnedrive II stirred autoclave was used as the chemical reactor for desulfurization. The stainless steel vessel is equipped with an electric heating jacket, a proportional temperature controller, and a baffle agitation system. With a 300 mL volume, it is capable of maintaining a maximum pressure of 5400 psig.

C. Experimental Procedures

Method for Deep-Cleaned Coal

1. Weigh at least 500 g of -60 mesh coal and mix it with 1.30 specific gravity $CaCl_2$ solution. Completely wet the coal by shaking and stirring.
2. The coal slurry is allowed to stand in the float/sink apparatus for about 24 hours until the $CaCl_2$ solution is clear between the layers of float and sink portions.
3. Collect the float portion and filter it using two layers of Whatman No. 1 filter paper. Wash the residue on the filter paper with DI water, then dried at 110°C in nitrogen atmosphere for 3 hours.

4. The float portion is milled in water using a stirred-ball slurry attritor mill for 2 minutes. The milled product is filtered and dried as described in part 3.
5. Mix 20 g of the milled coal with 150 mL of 1.30 specific gravity $CaCl_2$ solution. Then the slurry is centrifuged for 45 minutes at 1700 rpm. The final deep-cleaned coal is obtained after filtering and drying the coal using the same conditions described in part 3.

Procedure for Thermal Analysis

1. Weigh about 15 mg of -60 mesh coal sample on a TG weighing pan.
2. The sample is then gradually heated from room temperature to 800°C in air atmosphere at the heating rate of 10 °C per minute. The air flow rate is about 50 mL per minute.
3. The weight of sample is recorded by the TG balance every 10 seconds during the process.
4. The gaseous products from the decomposition of the sample are carried away by the air flow and go through the heated transfer line, which takes about 1 minute, into the gas cell of the FTIR.[42]
5. The IR spectra of the gaseous products, especially sulfur dioxide, are collected by scanning the gas cell every minute throughout the process.

Mild Oxidative Desulfurization Procedure

1. Weigh 5 g of coal sample and add to 100 mL 1.0 M NH_4OH solution in the autoclave reactor.

2. After sealing, the reactor is purged with oxygen gas until the pressure reaches 10 atm. Attach the heating jacket.
3. Start the agitation, heat the system to 200°C, and maintain the temperature for 2 hours.
4. After the reaction, the reacted coal is filtered, washed with water, and dried in an N_2 atmosphere at 110°C for 2 hours.
5. The desulfurized coal is then analyzed for total sulfur, organic sulfur, moisture, and ash.

Procedure for Direct Determination of Organic Sulfur

1. A sample of 2 to 5 grams of coal is mixed with 2 M HNO_3 (20 mL per gram of coal) thoroughly.
2. With constant stirring, the mixture is heated to boiling and boiled gently for 30 minutes.
3. The mixture is then filtered through Whatman No. 1 filter paper, the residue on filter paper is washed with 200-250 mL hot water.
4. The residue is dried in a nitrogen atmosphere at 110 °C for 2 hours.
5. Total sulfur, moisture, and the ash in the coal are measured, and the organic sulfur values are reported on a dry, ash-free (daf) basis.

Method of Instrumental Analysis of Forms of Sulfur

1. A sample of 30 mg of coal is loaded into a metal crucible inside a quartz tube and heated in an external furnace at a given temperature in an air atmosphere for 10 minutes.

2. The gaseous products are carried away by flowing air through the quartz tube into the LECO SC-432 Sulfur Analyzer.

3. The amount of sulfur dioxide in the gaseous products is determined by the solid state IR cell in the SC-432 Sulfur Analyzer.

III. RESULTS AND DISCUSSION

A. Mild Oxidative Desulfurization Experiments

Desulfurization of seven coals was studied using aqueous slurries of -60 mesh material in a stirred autoclave. Table 2 shows the total sulfur, inorganic sulfur (pyritic, sulfate sulfur) and organic sulfur content of the seven Illinois Basin coals. All sulfur values are reported on a dry, ash-free basis. Total sulfur values were determined by the ASTM D 4239 method. The organic sulfur values were obtained using direct determination method. Pyritic and sulfate sulfur are determined by the ASTM D 2492 method. For these coals, total sulfur ranged from 6.74 to 1.37%, pyritic sulfur ranged from 0.41 to 3.59%, sulfate sulfur ranged from 0.07 to 0.80%, and organic sulfur ranged from 0.60 to 3.03%.

Optimization of conditions for desulfurization were performed using samples of 89023 raw coal, which contains high inorganic and organic sulfur. Figure 7 shows the effect of changing the reaction temperature on the removal of total, inorganic, and organic sulfur from a -60 mesh sample of 89023 raw coal. Reaction conditions were 10 atm O_2, 4.2 M NH_4OH, and 2 hours reaction time. One can see from this graph that slightly more than 20% of the organic sulfur is removed from this coal at 50-100°C. Above 100°C an increasing amount of organic sulfur is removed until a temperature of 200°C is reached. Organic sulfur removal remains fairly constant at nearly 40% until 400°C is reached, at which point the percent removed begins to

Table 2. Total Sulfur, Inorganic Sulfur and Organic Sulfur Contents of Raw Coal[A]

Coal No.	Total Sulfur[B]	Inorganic Sulfur[C]		Organic Sulfur[D]
		Pyritic Sulfur	Sulfate Sulfur	
89020	4.83	1.47	0.07	3.03
89021	3.56	2.08	0.43	1.11
89022	2.43	1.08	0.09	1.33
89023	6.74	3.59	0.20	2.54
89024	4.04	1.79	0.13	1.91
90003	1.37	0.41	0.08	0.60
90008	5.31	1.94	0.80	1.94

[A] All sulfur values are reported on a dry, ash-free basis.
[B] Total sulfur values were determined by ASTM D 4239 method.
[C] Pyritic sulfur and sulfate sulfur were determined by ASTM D 2492 method.
[D] Organic sulfur values were determined by the direct determination method.

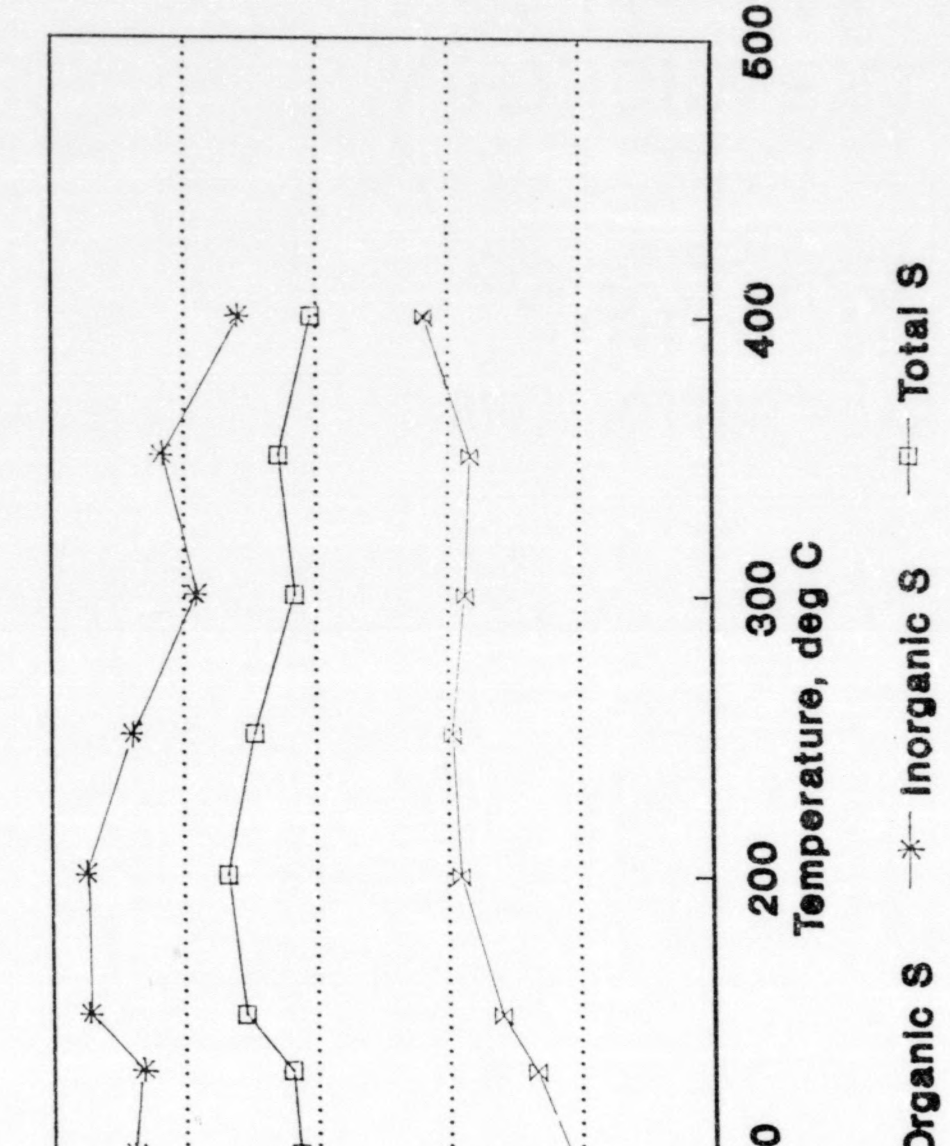


Figure 7. Effect of temperature on sulfur removal from 89023 coal.

increase again. One can speculate that the various stages, or plateaus, of sulfur removal that occur as the temperature is increased represent the types and amounts of chemically labile organic sulfur species present in this coal. Since aliphatic thiols, disulfides, and sulfides are the most likely organic sulfur species to be oxidized and removed from the coal under these conditions, it is quite possible these are the species being removed.

Under the reaction conditions of 10 atm O_2, 4.2 M NH_4OH and 200°C, the effect of reaction time on removal of sulfur from 89023 Coal was studied as is illustrated in Figure 8. The removal of inorganic sulfur reached a steady rate after 90 minutes, while the removal of organic sulfur continued to increase slightly through 150 minutes. The optimum reaction time chosen for the process was 2 hours (120 minutes).

The effect of ammonia concentration on the removal of total sulfur and organic sulfur from coal is illustrated in Figures 9 and 10. Reaction conditions for this experiment are 5% coal in aqueous ammonia under 10 atm O_2 at 200°C for 2 hours in a stirred autoclave. The total sulfur content of the coals ranged from 1.37% to 6.74% (dry, ash-free basis). As illustrated by Figure 9, the percentage of sulfur removed from the coal is only slightly dependent on the sulfur contents of the coals. Also, the presence of ammonia enhances the desulfurization process. Although there were variations in the ammonia needed for some of the coals, sulfur reduction in the coals is dependent on the ammonia concentration. The result is also confirmed by Figure 10, which illustrates the effect of ammonia concentration on the removal of organic sulfur from coal. The average percent reductions of total sulfur

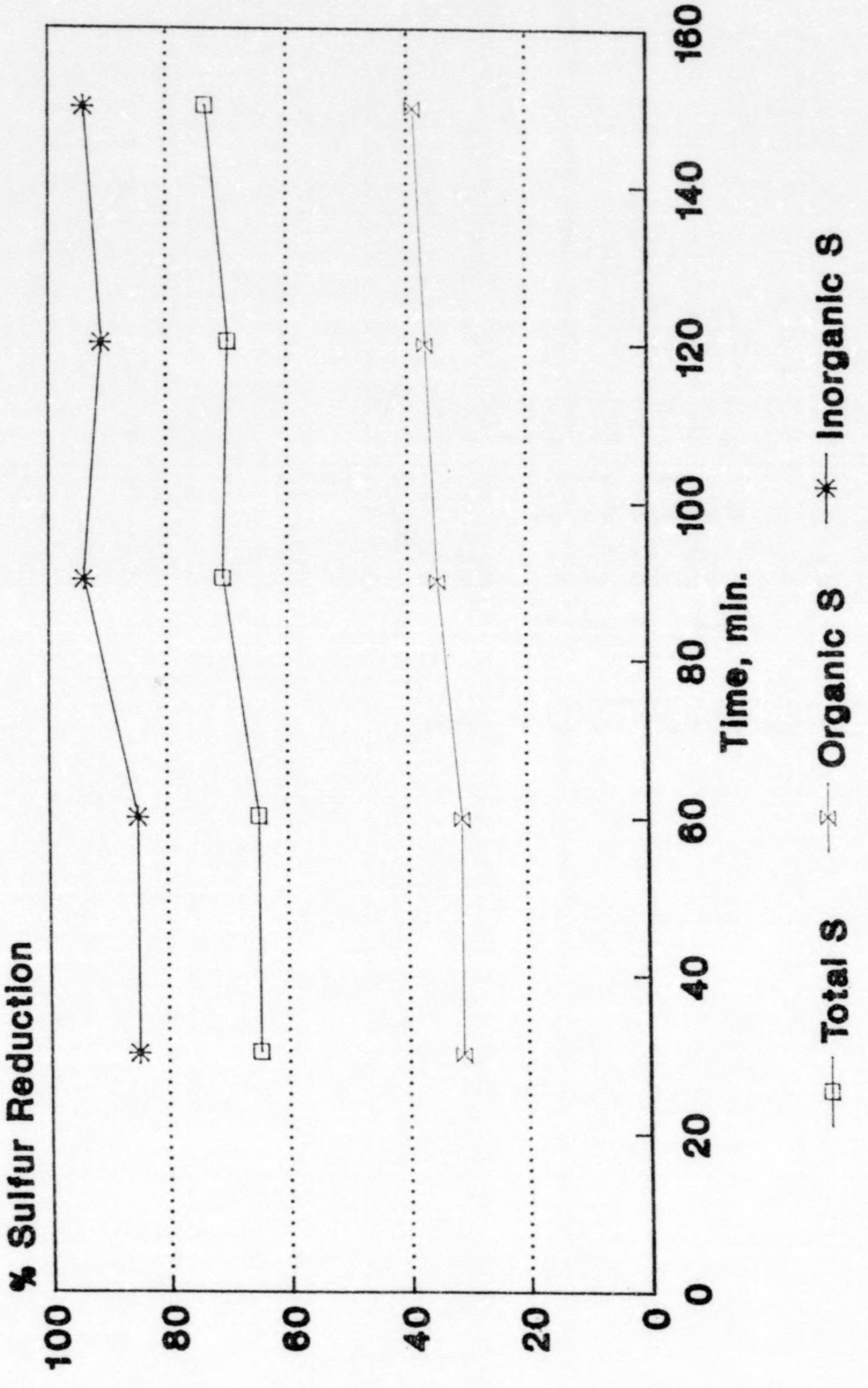


Figure 8. Effect of time on sulfur removal from 89023 coal.

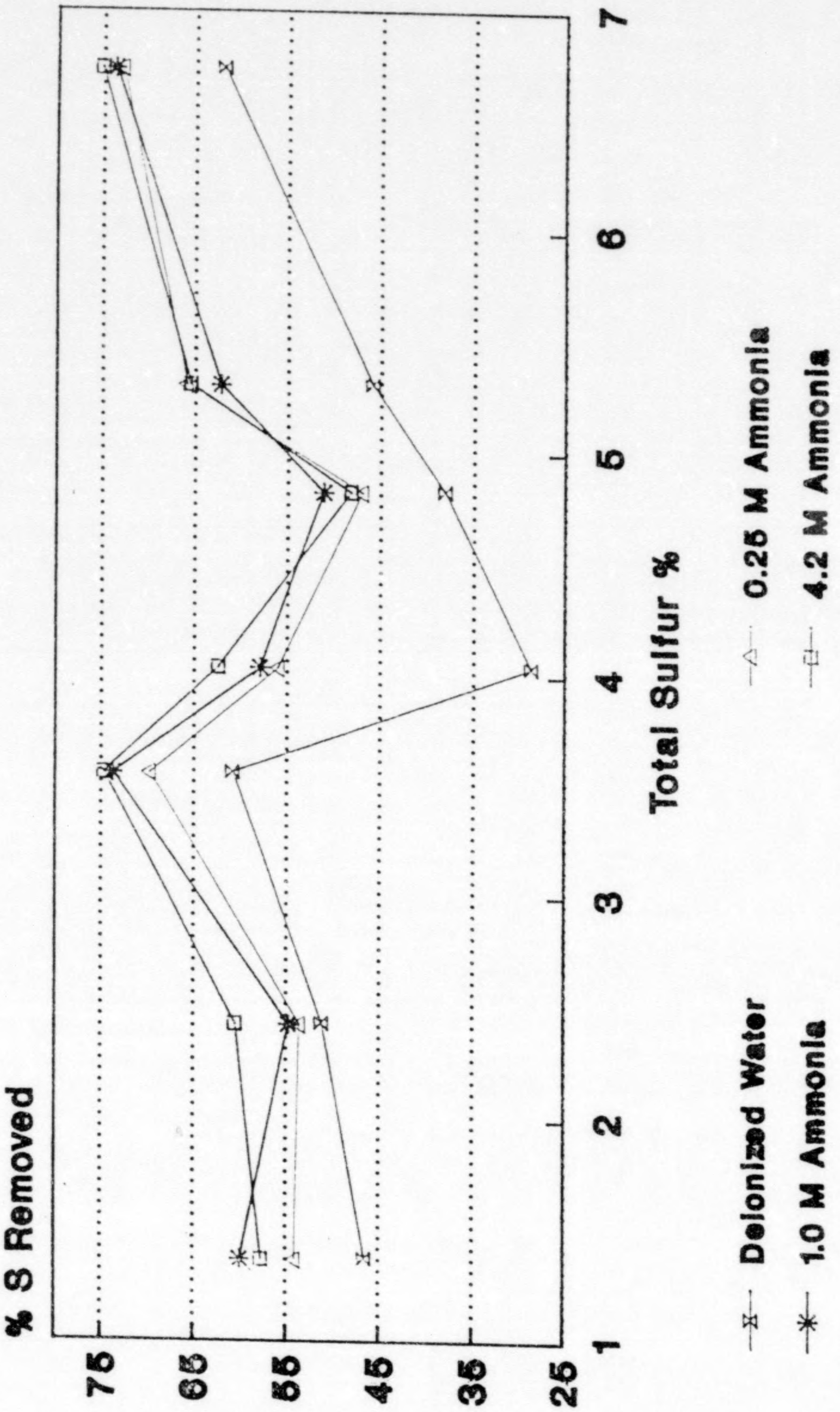


Figure 9. Effect of ammonia concentration on removal of total sulfur from coals.

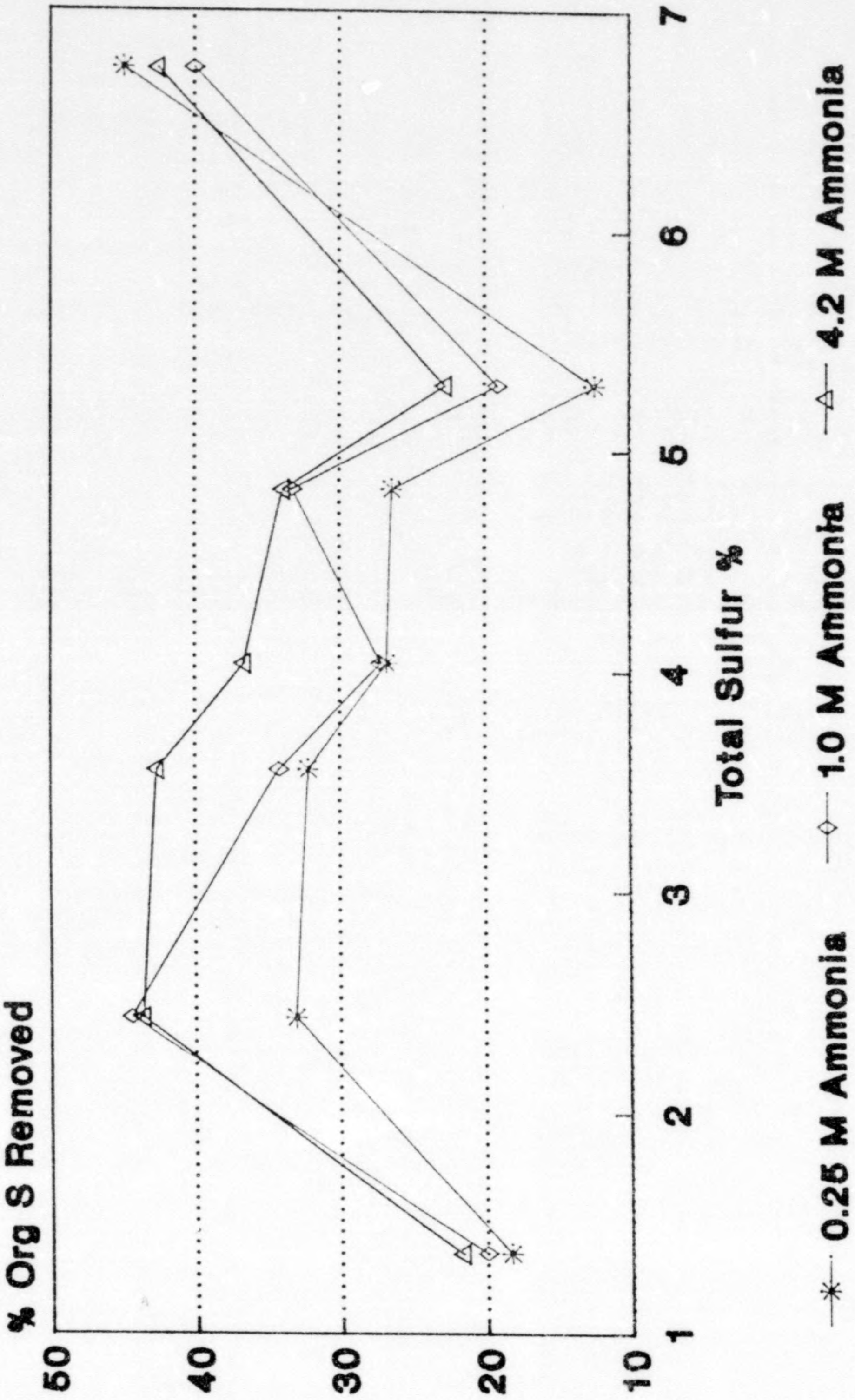


Figure 10. Effect of ammonia concentration on removal of organic sulfur from coals.

for the seven coals were 47.8% with deionized water, 51.1% with 0.25 M NH_4OH, 61.9% with 1.0 M NH_4OH, and 63.5% with 4.2 M NH_4OH. The average reductions of organic sulfur were 27.7% in 0.25 M NH_4OH, 31.2% in 1.0 M NH_4OH, and 34.8% in 4.2 M NH_4OH. Based on these data we chose the optimum ammonia concentration for these desulfurizations as 1.0 M.

The effect of changing the oxygen partial pressure on the desulfurization of the 89023 coal is illustrated in Figure 11. The experimental conditions were 5% coal slurry heated to 200°C, 4.2 M NH_4OH and 2 hours reaction time. From Figure 11, one can see that the sulfur removal is directly proportional to the oxygen partial pressure. Inorganic sulfur removal improves more than that of organic sulfur with increasing oxygen partial pressure. At about seven atmospheres pressure the effect of oxygen pressure on the removal of organic sulfur appeared to peak, at which point about 40% of the organic sulfur was removed.

After studying the optimization of conditions for desulfurization using samples of raw coal (89023), the optimum conditions obtained for 5% aqueous slurries of -60 mesh coal were reacted for 2 hours under 10 atm O_2 at 200°C, using 1.0 M NH_4OH. The data in Table 3 show the total sulfur, inorganic sulfur and organic sulfur in the coals that were reacted using the optimum desulfurization conditions. The total sulfur for desulfurized coals ranged from 0.50 to 2.36%, inorganic sulfur ranged from 0.14 to 0.94%, and organic sulfur ranged from 0.36 to 1.83%.

Based on the data in Tables 2 and 3, the percentage sulfur reduction in these Illinois Basin coals were calculated and are summarized in Table 4. The total amount of sulfur removed from -60 mesh coals ranged from 51% to 78% under the

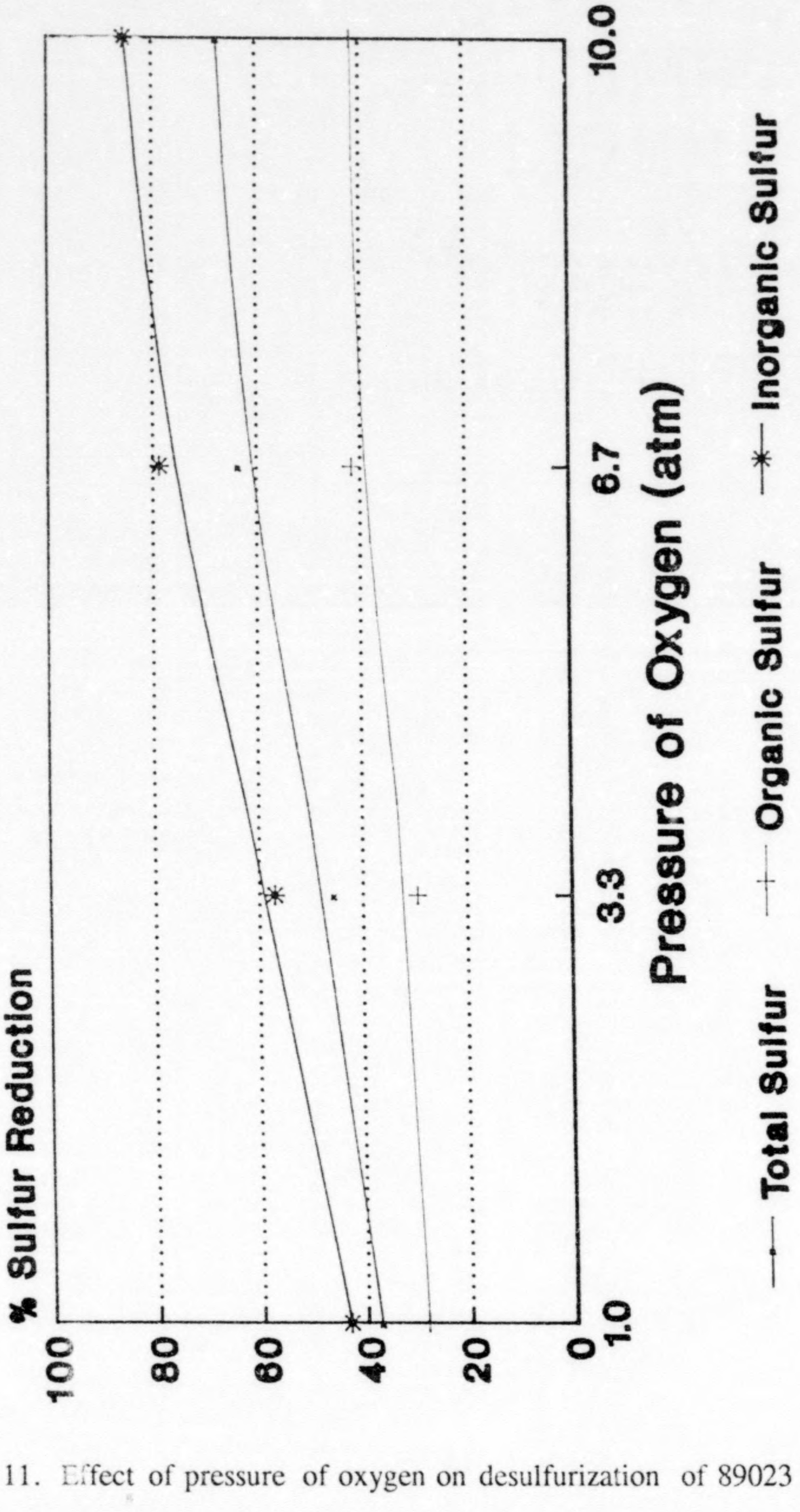


Figure 11. Effect of pressure of oxygen on desulfurization of 89023 coal.

Table 3. Total Sulfur, Inorganic Sulfur and Oganic Sulfur Contents of Reacted Coals

Coal No.	Total Sulfur[B]	Inorganic Sulfur[C]	Organic Sulfur[D]
89020	2.36	0.53	1.83
89021	0.78	0.23	0.55
89022	0.90	0.21	0.69
89023	1.94	0.61	1.33
89024	1.62	0.45	1.17
90003	0.50	0.14	0.36
90008	2.18	0.94	1.24

[A] All sulfur values are reported on a dry, ash-free basis.

[B] Total sulfur values were determined by ASTM D 4239 method.

[C] Inorganic sulfur values were calculated by subtracting organic sulfur from total sulfur values.

[D] Organic sulfur values were determined by the direct determination method.

Table 4. Reduction of Sulfur in Illinois Basin Coals Using Mild Oxydesulfurization Conditions[A]

Coal No.	%Total Sulfur Removed	%Inorganic Sulfur Removed	%Organic Sulfur Removed
89020	51.1	65.6	39.6
89021	78.1	90.8	50.4
89022	63.0	82.0	48.1
89023	71.2	84.0	47.6
89024	59.9	76.6	38.7
90003	63.5	71.4	40.0
90008	58.9	65.7	36.1
Mean	63.7	76.6	42.9

[A] All calculations were based on the data in Tables 2 and 3.

oxidative desulfurization conditions. Most of the inorganic sulfur (ranging from 66% to 91%), which is sulfatic, sulfidic, and pyritic sulfur, is removed from these coals. It is speculated that the organic sulfur removed, which ranges from 36% to 50% for the seven coals treated with ammonia, represents the chemically liable aliphatic thiols, disulfides and sulfides present in the raw coals. Desulfurization experiments with dibenzothiophene mixed with 89021 raw coal reacted for 2 hours under 10 atm O_2 in solutions of NH_4OH showed no reduction in the amount of dibenzothiophene sulfur in the mixture. The result is a strong indication that the thiophenic sulfur in coal is not removed in the oxidative desulfurization process used in this project.

B. Thermal Analysis Experiments

The purpose of the thermal analysis experiments was to determine the temperatures at which different sulfur forms will react in an air atmosphere. By connecting the TG system with a heated gas line to the FTIR instrument, IR spectral data could be collected throughout the thermal analysis process. A relationship between the sulfur concentration and temperature can be established by integrating the peak area of sulfur dioxide absorption. The IR spectral method is very fast and accurate.

The first step in this research project was to determine the optimum sample weight. The initial sample size chosen was 50 mg for the coal and the coal sample was placed as flat as possible in the combustion tube. However 50 mg of clean coal samples caused ignition at about 350°C, which could be observed by large increases in sample temperature. This problem was solved by reducing the sample size to 15 mg, which still allow enough gas to evolve during the process.

The second step was to try both air and pure oxygen as reaction atmospheres. In an oxygen atmosphere the coal sample was more likely to ignite (oxidation was more active), which made it harder to control the sample temperature. This situation was avoided when air was used as the reaction atmosphere by spreading the coal sample thoroughly in order to prevent accumulation of the reaction heat.

Two raw coals (89024 and 90008) and their cleaned coals were used in the thermal analysis studies. The definition of cleaned coal is the coal that is cleaned following the procedure previously described for the deep-cleaned coal method.

Table 2 summarizes the total sulfur and forms of sulfur values for seven raw coals, as determined by ASTM D 4239 and D 2492. The data in Table 2 shows the total sulfur of 89024 and 90008 raw coals as 4.04% and 5.31%, respectively. Forms of sulfur were determined by ASTM method D 2492. For 89024 raw coal the pyritic sulfur is 1.79%, sulfate sulfur is 0.13% and organic sulfur is 1.91%. The forms of sulfur number determined for 90008 raw coal as 1.94% for pyritic sulfur, 0.80% for sulfate sulfur and 1.94% for organic sulfur. Upon calculating the ratio of pyritic sulfur to total sulfur, 44.3 was obtained for 89024 raw coal and 36.5 for 90008 raw coal.

Figures 12 and 13 show the TG heating curve for combustion of a sample of 89024 raw and cleaned coals from room temperature to 800°C at the heating rate of 10°C/minute. The TG heating curve reveals that 89024 raw and cleaned coals lose weight gradually at 40°C to 300°C, which is caused by the loss of moisture and

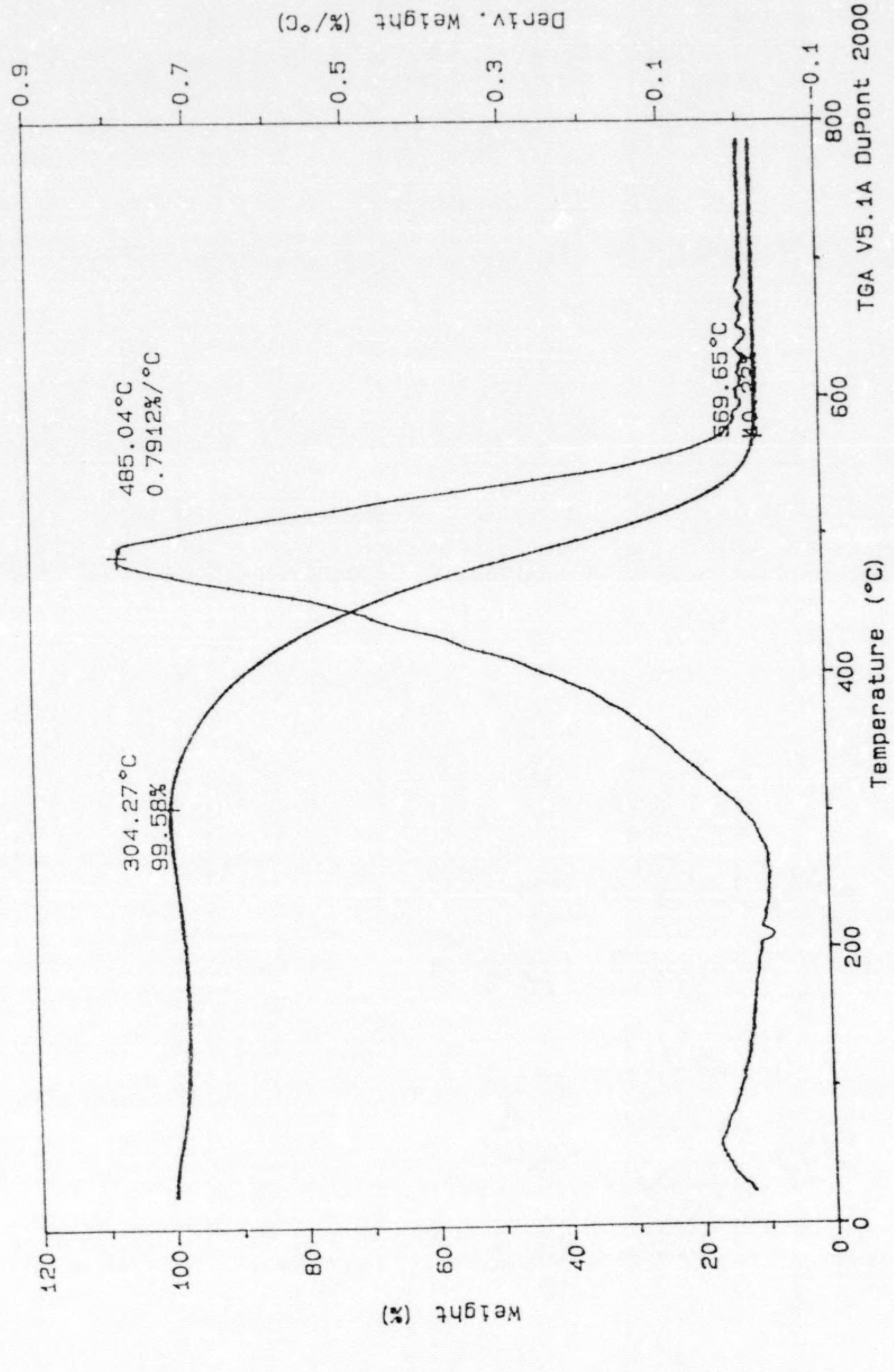


Figure 12. TG heating curve of 89024 raw coal in air.

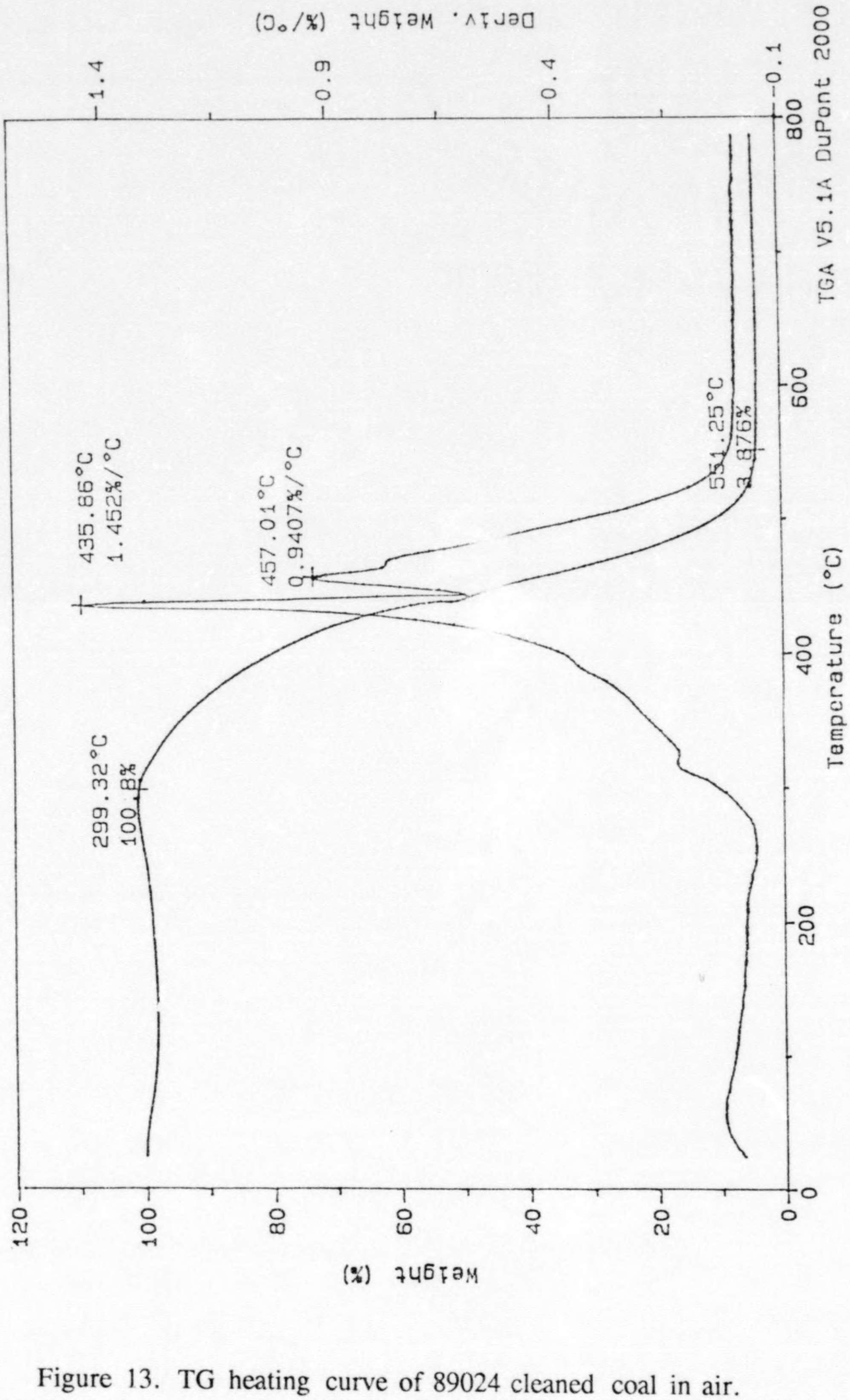


Figure 13. TG heating curve of 89024 cleaned coal in air.

volatile matter. The temperature at which the 89024 raw and cleaned coals began to combust is 304°C and 299°C. Exothermic reactions occur between 304°C and 570°C, which results in a 90% weight loss for 89024 raw coal. For 89024 cleaned coal, it loses weight very rapidly from 299°C to 551°C, where oxidation occurs. The temperature (T_{max}) at which the 89024 raw coal has a maximum weight loss rate is 485°C. There are two T_{max} temperatures for 89024 cleaned coal, at 436°C and 457°C, where the cleaned coal sample reaches its maximum weight loss rate. The weight of its 89024 raw and cleaned coal samples remain constant after 600°C since only the mineral oxides and sulfates remain.

The TG heating curves shown in Figures 14 and 15 reveal that, in air, 90008 raw and cleaned coals begin to decompose at 316°C and 295°C, respectively. Rapid combustion occurs between 300°C and 550°C and result in the loss of most of the sample mass. A small weight loss is recorded after 550°C.

The TG heating curve for the 89024 and 90008 cleaned coals show that they lose less weight in the 170 to 300°C region than the raw coals by absorbing oxygen. Figure 16 is a TG heating curve for the 90008 raw coal after treatment with $CaCl_2$ solution which was used in the coal clean process. It shows that the coal treated with $CaCl_2$ does not gain weight in the 170°C to 300°C region, indicating the metal ions remaining in the coal is not the reason for chemsorption of oxygen molecules. During the coal cleaning process, the coal is ground to smaller particle sizes (<10 microns), which means it has a larger surface area than the raw coal, and may cause more oxygen molecules to chemisorb on its surface. Another reason for the cleaned coal to loss less weight may be because the pore size and pore volume had been

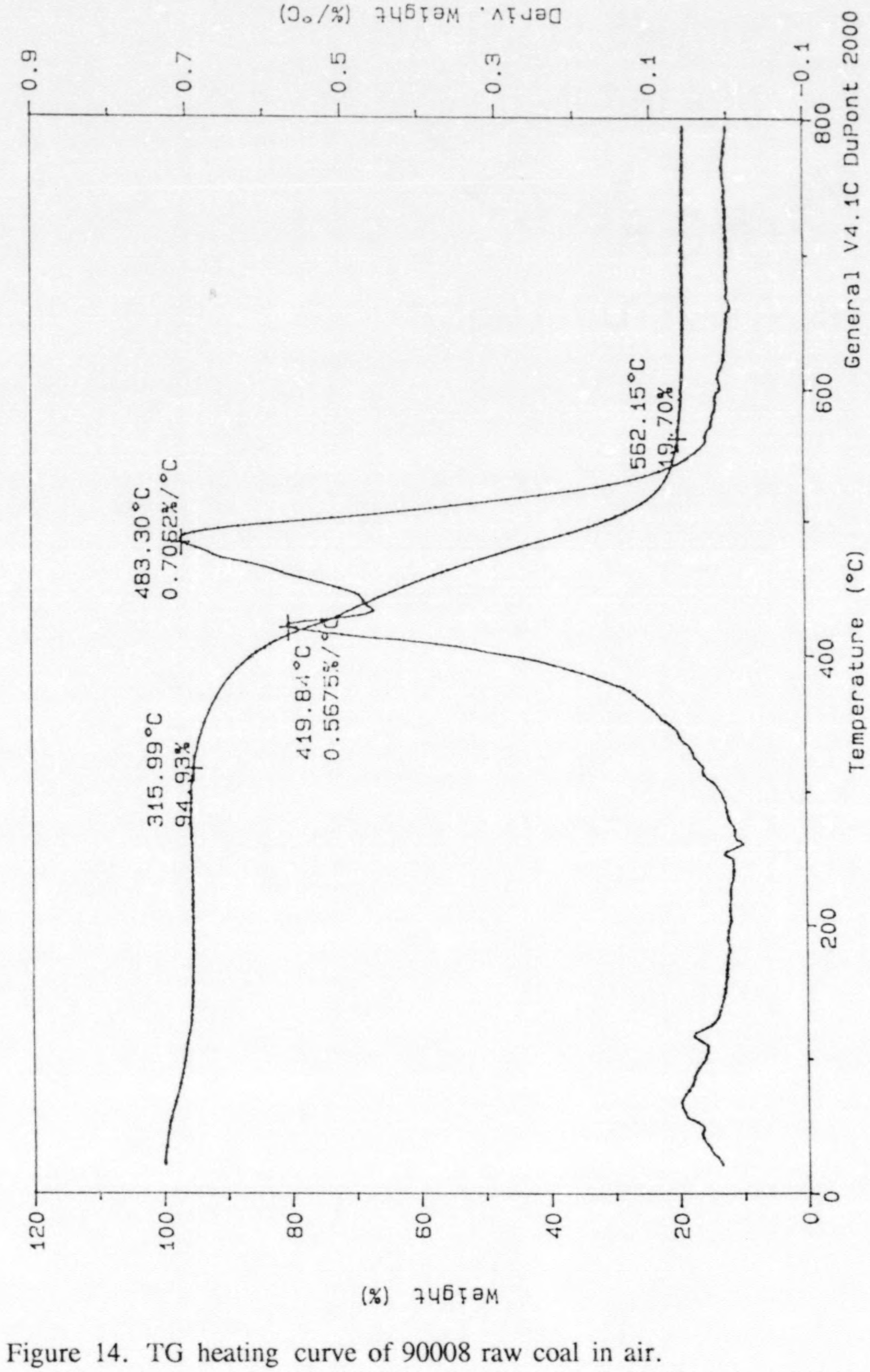


Figure 14. TG heating curve of 90008 raw coal in air.

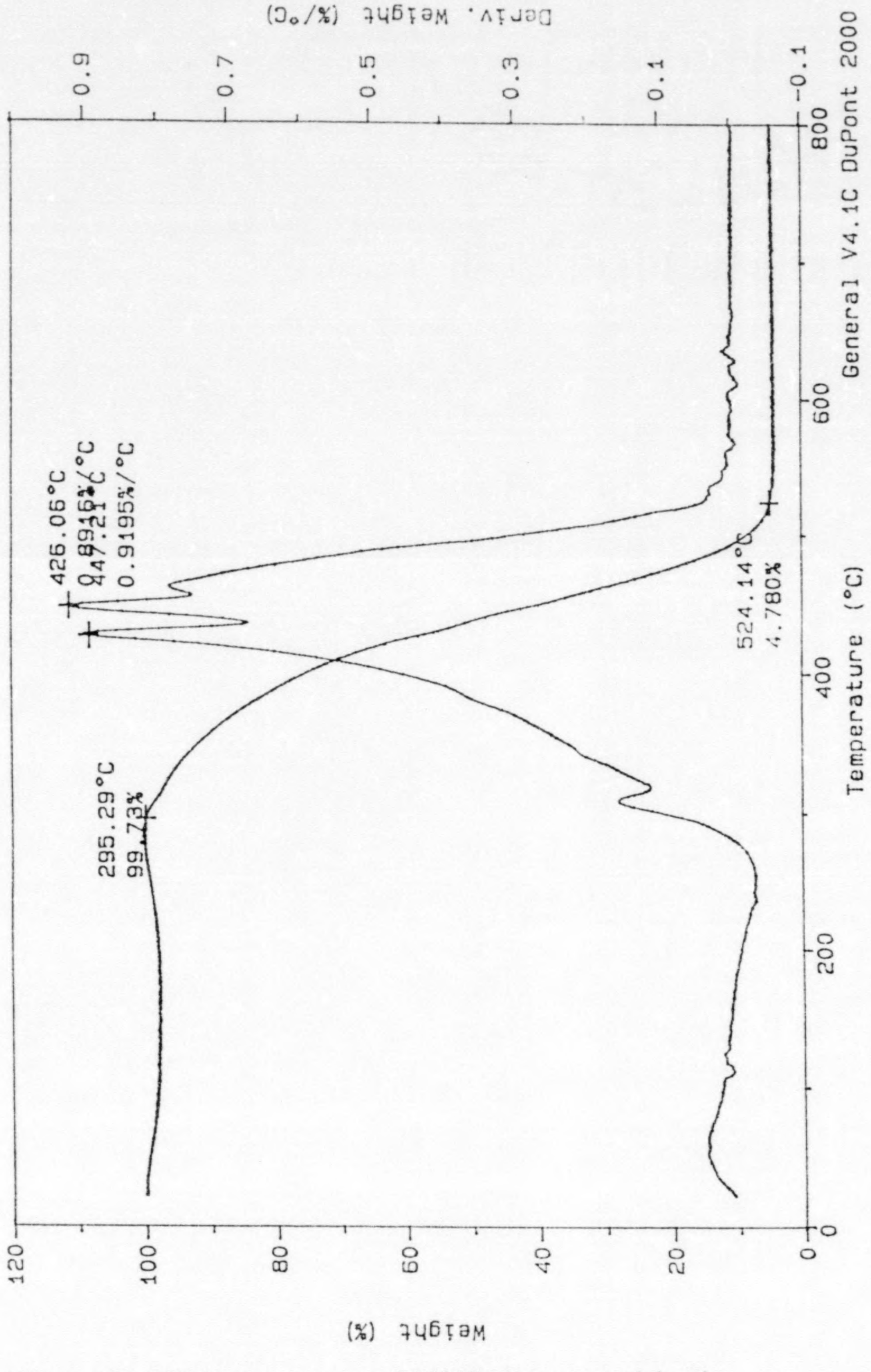


Figure 15. TG heating curve of 90008 cleaned coal in air.

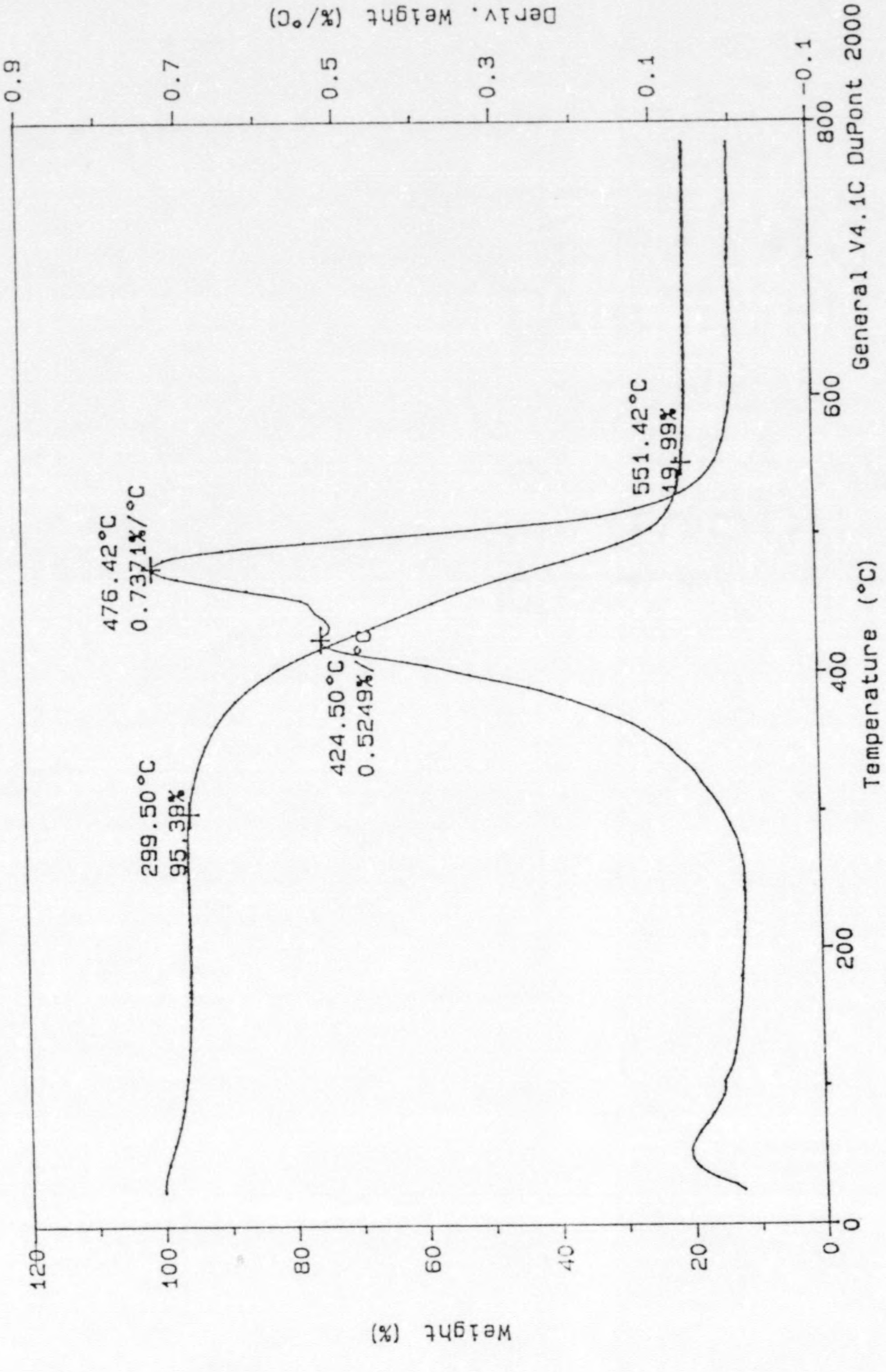


Figure 16. TG heating curve of 90008 coal treated with $CaCl_2$.

changed during the cleaning process, causing the absorption of oxygen on the cleaned coal surface.

Table 5 summarizes the results of the TG analyses of 89024 and 90008 raw and cleaned coal samples. From Table 5, one can see that the samples began to decompose in the 300°C to 320°C range, and the reactions end between 520°C and 570°C. The temperature corresponding to the maximum weight loss rate is between 420°C and 490°C. There is only a broad peak for the DTG curve of 89024 raw coal, which corresponds to one T_{max}. It is believed there are two T_{max} values and the peaks overlap on the DTG curve.

Figure 17 shows representative FTIR spectra for the combustion of coal at 400°C. The main degradation products are CO_2 and H_2O. The sulfur dioxide, indicated by the cursor in the Figure 17, absorbs IR radiation at 1375 cm^{-1}. The gradual evolution of SO_2 as a function of temperature from 89024 and 90008 raw and cleaned coals is shown in Figures 18 and 19 as absorbance vs. temperature at 1375 cm^{-1}. There are three peaks in Figures 18 and 19 for the sulfur dioxide evolved. The first small peak, which occurs at about 320°C, is from aliphatic sulfur that is easily degraded at low temperatures. The second sharp peak comes from pyritic sulfur. This assignment is confirmed by the reduced peak areas of 89024 and 90008 cleaned coals. Most of the pyritic sulfur is removed by the deep-cleaning process. The broad peak near the high temperature region (470°C) is due to aromatic sulfur which is hardly decomposed. These observations are summarized in Table 6 as T_{max} values for coal combustion.

Table 5. Summary TGA Data for 89024 and 90008 Coals

Coal	Temperature(°C) Decomposition Begins	Temperature(°C) Decomposition Ends	T_{max1}(°C)	T_{max2}(°C)
89024-Raw	304	570		485
89024-Cleaned	299	551	436	457
90008-Raw	316	562	420	483
90008-Cleaned	295	524	426	447

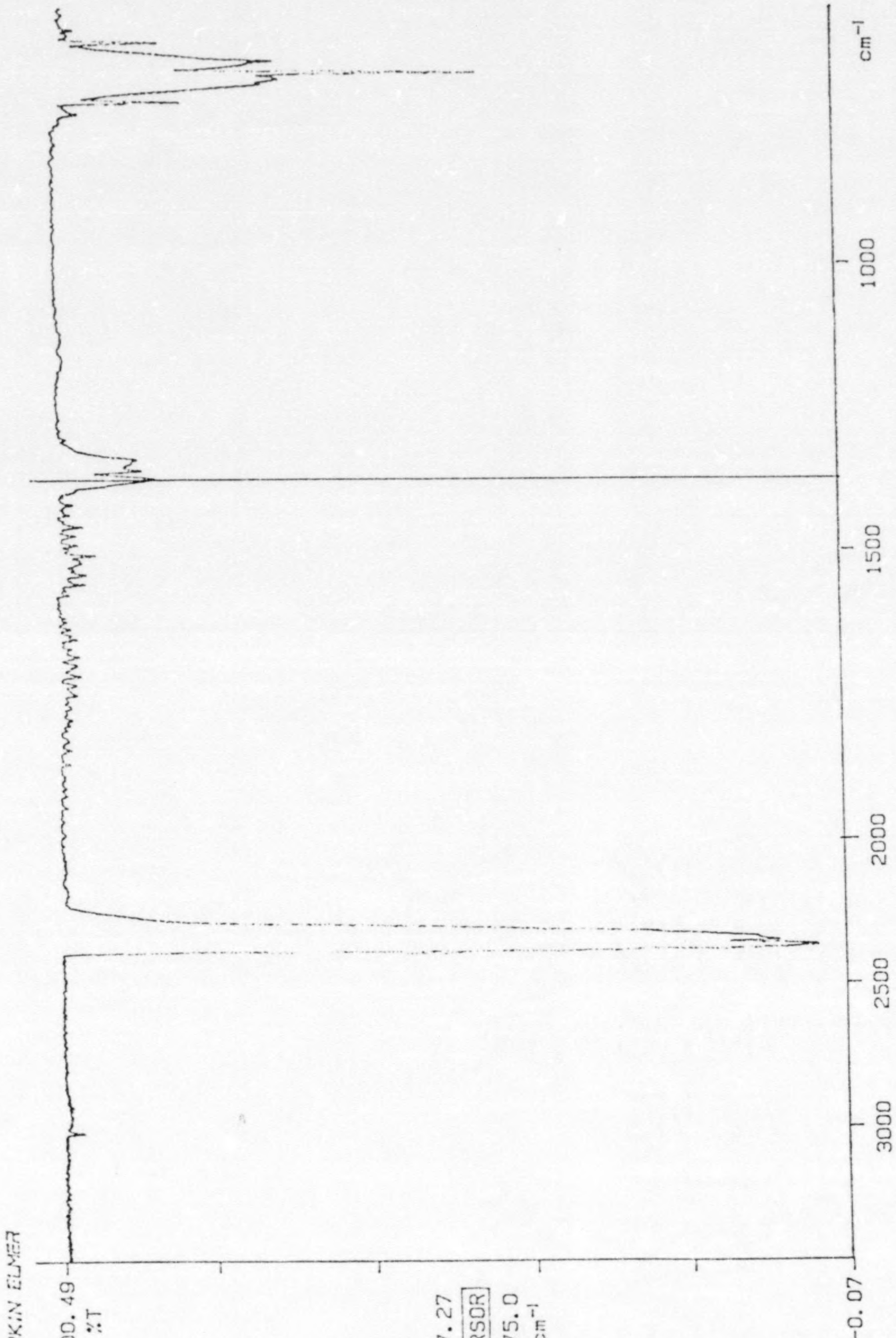


Figure 17. A typical FTIR spectrum of evolved gas from coal in air.

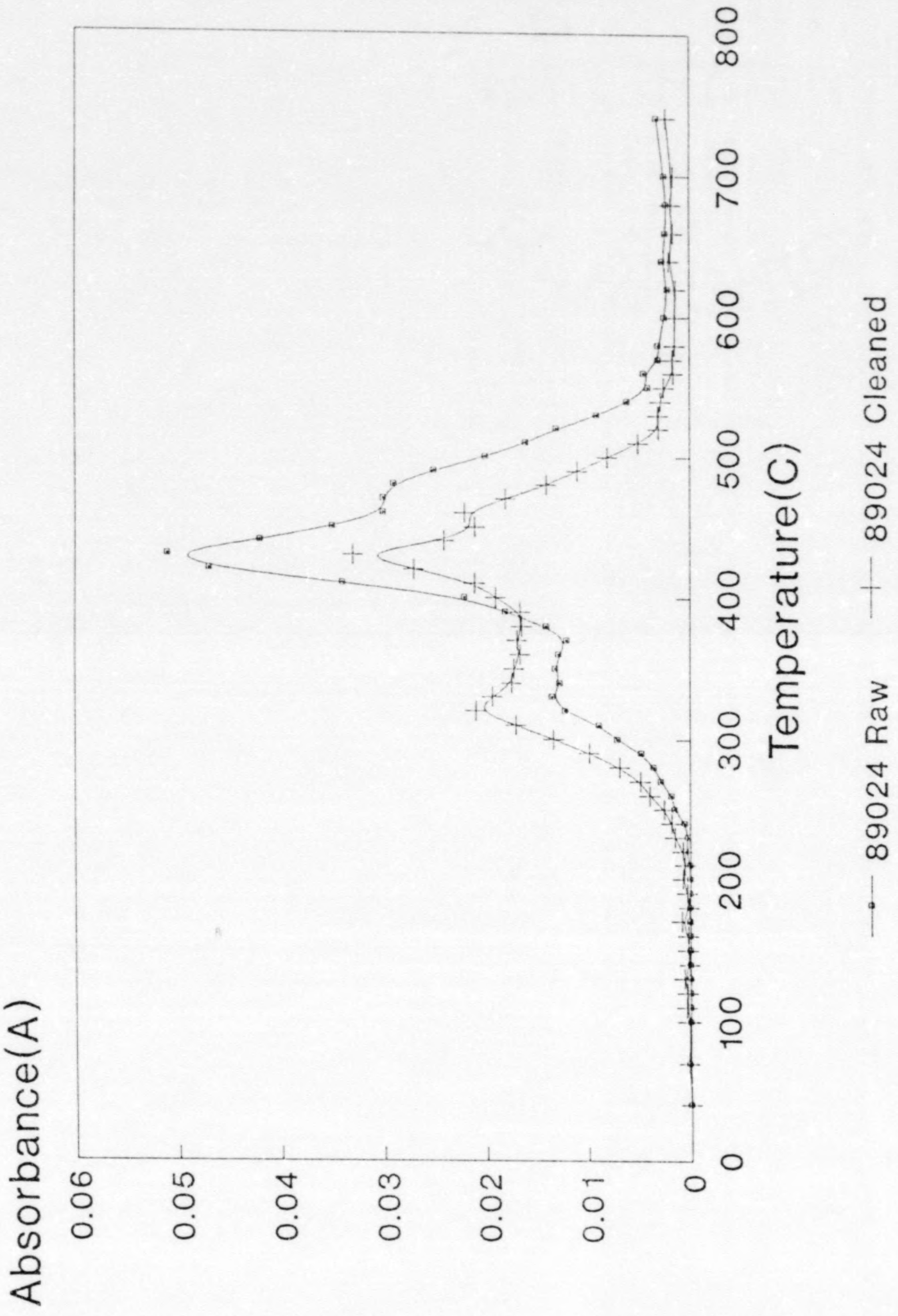


Figure 18. A composite plot of SO_2 absorbance vs. temperature from the combustion of 89024 raw and cleaned coals in air.

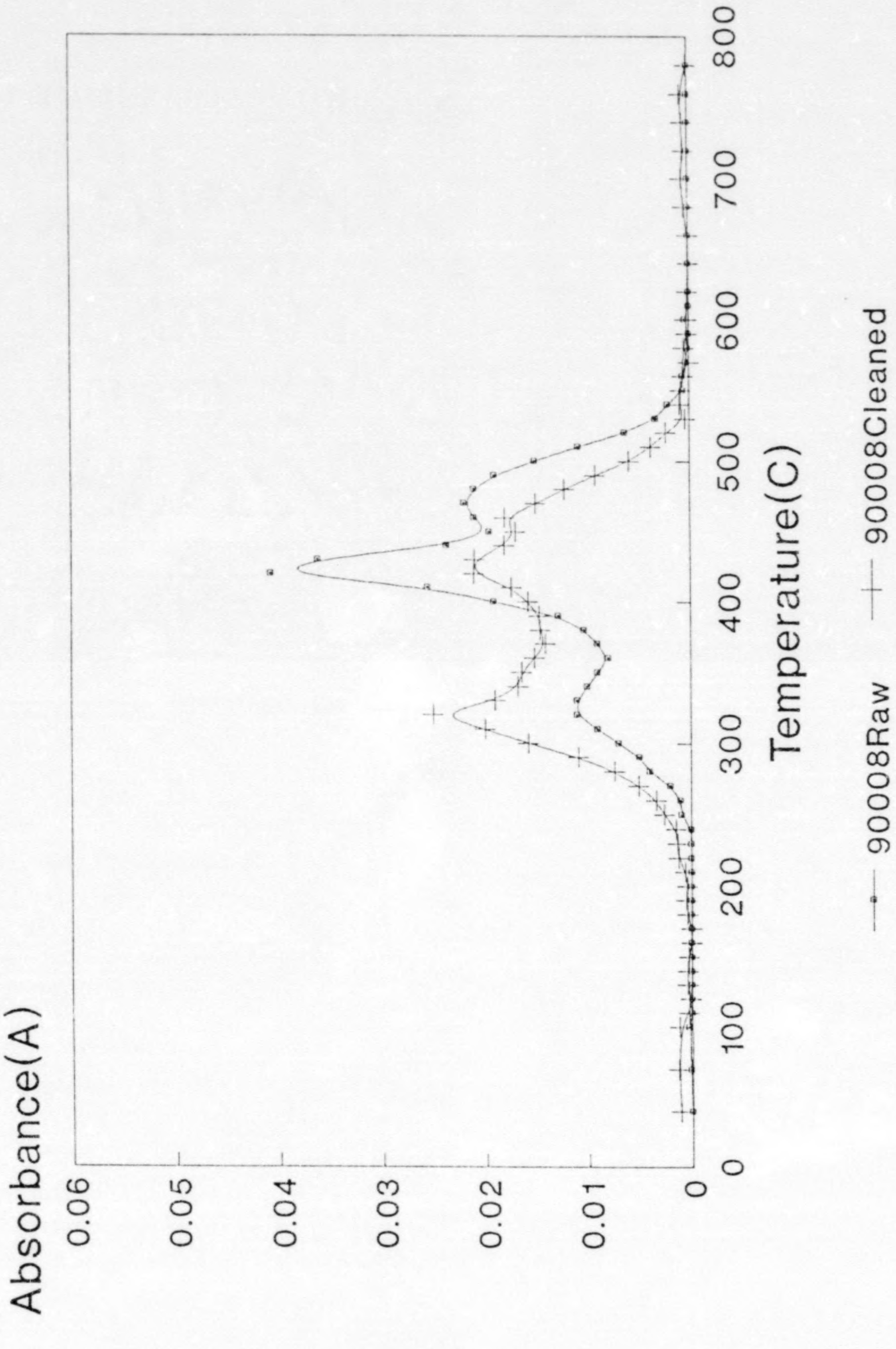


Figure 19. A composite plot of SO_2 absorbance vs. temperature from the combustion of 90008 raw and cleaned coals in air.

Table 6. Sulfur Dioxide Evolution T_{max} Summary for Coal Combustion

Coal	T_{max}(°C)	T_{max}(°C)	T_{max}(°C)
89024-Raw	330	430	470
89024-Cleaned	320	430	460
90008-Raw	320	420	470
90008-Cleaned	320	420	460

Figure 20 confirms that the SO_2 from aliphatic sulfur evolves around 320°C, while the SO_2 from pyritic sulfur evolves at 420°C. Figure 20 shows the absorbance of SO_2 vs. temperature for the combustion of coals. There are five kinds of coals represented in this Figure: 90008 raw coal; 90008 reacted coal obtained from the mild oxydesulfurization process; 90008 cleaned coal that is from the deep-cleaning method; 90008 (320°C) and 90008 (420°C) coals are the 90008 raw coal preheated in an oven at 320°C and 420°C for 30 minutes. The figure indicates that the mechanism of the combustion reaction is different for each differently treated coal. The 90008 raw coal and reacted coal undergoes three combustion reactions, one is at 320°C and the others are at 420°C and 470°C. The peak area around 420°C is reduced for the 90008 cleaned coal because most of the pyritic sulfur is removed by the deep-clean process. The 90008 reacted coal and 90008 preheated at 320°C coal undergoes two reaction. For the 90008 reacted coal, there is a small peak at 320°C and a sharp peak at 470°C. It occurs because the mild oxydesulfurization process removed most of the aliphatic and pyritic sulfur from the coal. For 90008 coal preheated at 320°C, two peaks around 420°C and 470°C were observed, which means the aliphatic sulfur was removed by heating the coal at 320°C. There is only one decomposition reaction that occurs for the 90008 coal that had been preheated at 420°C. The reaction occurs at 470°C, which indicates that all the aliphatic and pyritic sulfur were removed by heating at 420°C, leaving only aromatic sulfur in this preheated coal.

Using thermal analysis methods, we attempted the measurement of pyritic sulfur by an instrumental method. We assumed that one could analyze the sulfur

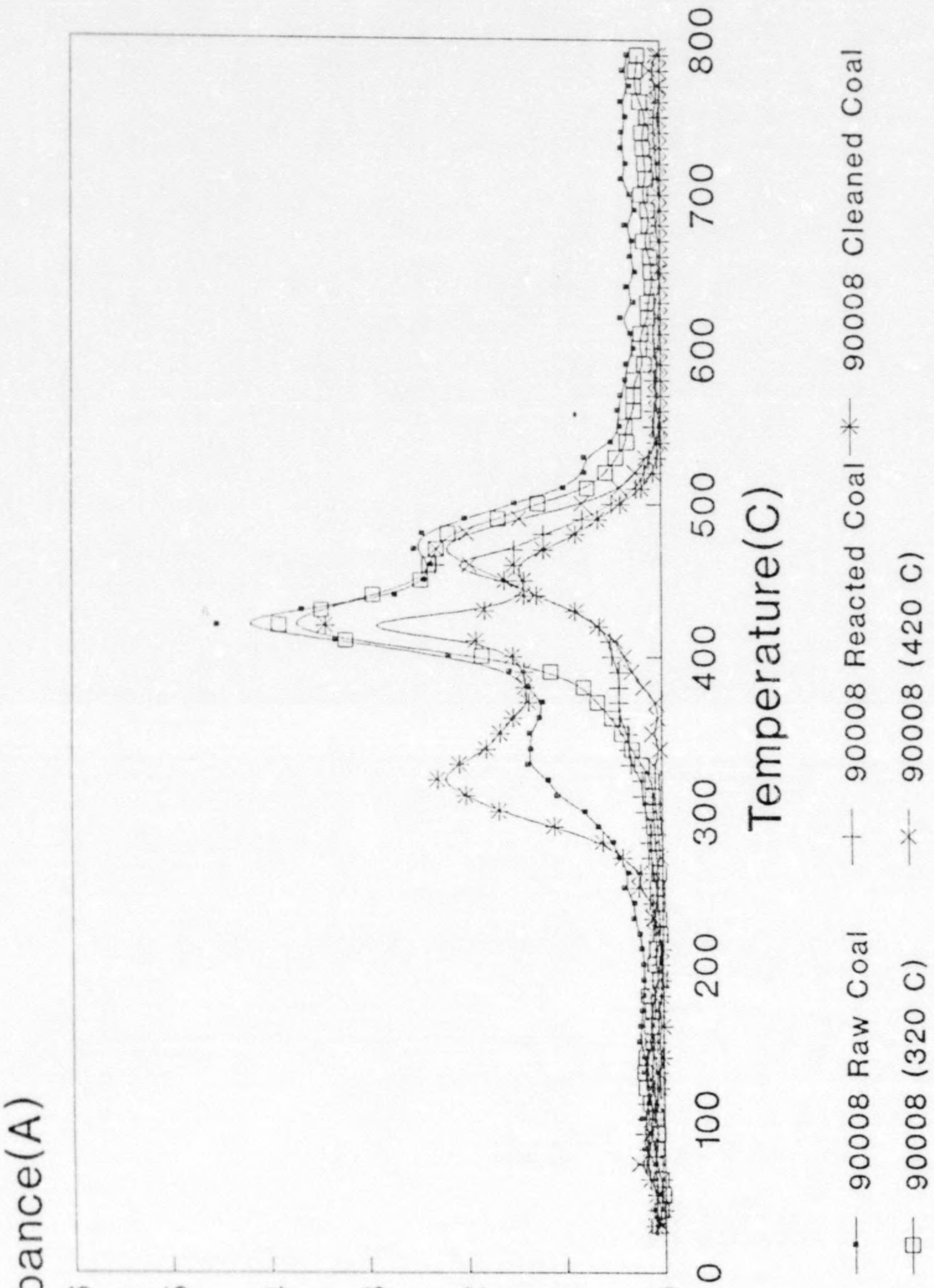


Figure 20. A composite plot of SO_2 absorbance vs. temperature from the combustion of 90008 raw, cleaned, reacted and preheated coals in air.

content of coal by heating it at 320°C and 420°C using the LECO SC-432. The pyritic sulfur would be equal to the difference in sulfur content of coal after heating at 420°C and 320°C.

C. Instrumental Analysis for Forms of Sulfur

Based on thermal analysis experiments, we designed the experimental conditions for instrumental analysis for forms of sulfur in coal. We loaded 30 mg of -60 mesh (250 microns) coal in a metal crucible and heated it in air in an external furnace at 320°C, or 420°C, for 10 minutes. The gaseous products were carried by flowing air through a quartz tube into the LECO SC-432 Sulfur Analyzer. The sulfur released by heating the coal sample at 320°C or 420°C was determined by the solid state IR cell in the sulfur analyzer. The aliphatic sulfur is determined as the sulfur released by heating the coal at 320°C. The pyritic sulfur is determined as the difference between sulfur released at 420°C and sulfur released at 320°C.

Table 7 summarizes the dry, ash-free sulfur releases for the aliphatic and pyritic sulfur in the raw coals. The aliphatic sulfur ranges from 0.10 to 0.82% for the seven Illinois Basin coals. The pyritic sulfur varies from 0.45 to 2.17% for these coals.

Table 8 gives the aliphatic sulfur and pyritic sulfur for reacted coals. Almost all the aliphatic sulfur was removed using the mild oxydesulfurization conditions. The pyritic sulfur could be obtained only from the 89020 and 90008 coals; the other coals ignited at 420°C. Perhaps it was due to the residual ammonium ion from the reagent used in the mild oxydesulfurization process. This cation may increase the

Table 7. Aliphatic and Pyritic Sulfur Values of Raw Coals[A,B]

Coal	S(320°C) (Aliphatic)	S(420°C)	S(420°C)-S(320°C) (Pyritic)
89020	0.82	2.64	1.82
89021	0.79	1.99	1.20
89022	0.13	0.98	0.85
89023	0.31	2.48	2.17
89024	0.24	1.91	1.67
90003	0.10	0.55	0.45
90008	0.21	2.25	2.04

[A] All sulfur values are reported on a dry, ash-free basis.

[B] The sulfur losses st 320°C and 420°C were determined using the LECO SC-432 Sulfur Analyzer.

Table 8. Aliphatic and Pyritic Sulfur Values of Reacted Coals[A,B]

Coal	S(320°C) (Aliphatic)	S(420°C)	S(420°C)-S(320°C) (Pyritic)
89020	0.02	1.02	1.00
89021	0	NA	NA
89022	0	NA	NA
89023	0.07	NA	NA
89024	0.02	NA	NA
90003	0	NA	NA
90008	0.06	NA	NA

[A] All sulfur values are reported on a dry, ash-free basis.

[B] The sulfur losses st 320°C and 420°C were determined using the LECO SC-432 Sulfur Analyzer.

oxidative reaction rate as a catalyst and cause ignition of the coal. The same problem was observed in the thermal analysis of cleaned coal. Because of the sensitivity of the TG and FTIR methods, the problem was partially solved by reducing the sample size from 30 mg to 15 mg and gradually increasing the temperature at 10°C/min. However the total solution to this problem is not possible for this instrumental analysis method. All the cleaned coals ignited at 320°C. This problem needs to be solved in the future.

The comparison of the aliphatic sulfur removal and organic sulfur reduction for raw coals is shown in Table 9. All sulfur values are reported on a dry, ash-free basis. The ratio of aliphatic sulfur to organic sulfur ranges from 10% to 71% with a mean of 23%. Most of the values for the ratio of aliphatic sulfur to organic sulfur are less than those of organic sulfur reduction that are given in Table 4 (with a mean of 43%). There is poor agreement between the two methods of removing aliphatic sulfur species from the coals, indicating the heating at 320°C may not remove all the aliphatic sulfur. Most of the aliphatic sulfur species are removed under the conditions used for the oxydesulfurization experiments.

Table 10 gives the comparison of the pyritic sulfur values obtained using the ASTM D 2492 method and the instrumental analysis method for the raw coals. All sulfur values are reported on a dry, ash-free basis. The percent relative error for instrumental pyritic sulfur varies from -42% to 24% with a mean of -10%. For some of the coals the values for the pyritic sulfur are close enough for the normal determination of pyritic sulfur. The negative numbers for the relative error are

Table 9. Comparison of Aliphatic Sulfur/Total Organic Sulfur Ratios and Percent Organic Sulfur Removal by Mild Oxydesulfrization Process[A]

Coal	S(320°C)[B] (Aliphatic)	S_{org} [C]	Ratio(%) S(320°C)/S_{org}	%Organic[D] Sulfur Removal
89020	0.82	3.03	27.1	39.6
89021	0.79	1.11	71.1	50.4
89022	0.13	1.33	10.0	48.1
89023	0.31	2.54	12.2	47.6
89024	0.24	1.91	12.6	38.7
90003	0.10	0.60	16.7	40.0
90008	0.21	1.94	10.8	36.1

[A] All sulfur are reported on a dry, ash-free basis.

[B] Aliphatic sulfur values were determined by Instrumental Analysis method.

[C] Organic sulfur values were determined by Direct Determination method.

[D] Percent organic sulfur removalvalues are based on data in Table 4.

Table 10. Comparison of Pyritic Sulfur Values Determined By ASTM D 2492 Method and Instrumental Analysis Method[A]

Coal	S_{pyr} [B] (ASTM D 2492)	S_{pyr} [C] (Instrumental)	Relative Error(%)
89020	1.47	1.82	23.8
89021	2.08	1.20	-42.3
89022	1.08	0.85	-21.3
89023	3.59	2.70	-39.6
89024	1.79	1.67	-6.7
90003	0.41	0.45	9.8
90008	1.94	2.04	5.2
Mean			-10.2

[A] All sulfur values are reported on a dry, ash-free basis.
[B] S_{pyr} (ASTM D 2492) values are from Table 2.
[C] S_{pyr} (Instrumental) values are from Table 7.

probably due to the incomplete combustion of the coal and the overlap of the pyritic sulfur with the aromatic sulfur content.

D. X-ray absorption fine structure (XAFS) experiments

The sulfur X-ray absorption fine structure (XAFS) spectra were subdivided into X-ray absorption near-edge (XANES) and extended X-ray absorption fine structure (EXAFS) regions in the usual manner and then the sulfur XANES spectra were analyzed using the least-squares fitting procedure. In one or more of the spectra, peaks could be attributed to sulfur in the form of pyritic, organic sulfide, thiophenic sulfur, sulfide, sulfone and sulfate. The area under the different peaks were converted to weight percentage of sulfur.

Dr. Frank Huggins at the University of Kentucky obtained the XAFS spectra for three of our coal samples: 90008-raw coal, its reacted coal from the mild oxydesulfurization process, and its treated coal by preheating in air at 320°C. The results show that the reacted coal appears to contain very little pyritic sulfur, which was been removed during the mild oxydesulfurization process. In the sample heated to 320°C, the pyritic sulfur appears to be largely retained, but a significant fraction of the organic sulfidic sulfur has gone from the sample which matches the results shown in Figure 20. Dr. Huggins also reported that the ratio of pyritic sulfur to total sulfur for 90008-raw coal is 41% which shows agreement to the result (38%) we obtained by the Instrumental Analysis Method.

IV. FURTHER WORK

The instrumental analysis method for forms of sulfur can be improved as follows:

1. Because of the ignition of reacted coal and cleaned coal, the method needs to be improved, especially in controlling the atmosphere. Using a lower oxygen atmosphere instead of an air atmosphere should help solve the ignition problems.

2. The LECO SC-432 can only analyze for sulfur over a 10-minute period. Thus, it is possible all the coal was not completely combusted. If we can preheat the coal in an oven at 320°C and 420°C for enough time, and then obtain the total sulfur at 1350°C for raw coal, preheated coal at 320°C and preheated coal at 420°C. The amount of aliphatic sulfur in the coal would then be the difference between the total sulfur of raw coal and preheated coal at 320°C. The pyritic sulfur value can be calculated as the difference between the sulfur content of the coal preheated at 420°C and that of the coal preheated at 320°C.

V. CONCLUSIONS

1. The optimum conditions for the mild oxydesulfurization of coals are defined as 150°C-200°C, 10 atmospheres oxygen, and aqueous slurries of coal reacted with 1 M NH_4OH for 1.5-2 hours.

2. The total amount of sulfur removed from -60 mesh coals using the optimum oxydesulfurization conditions ranges from 51% to 78% with a mean of 64%, the amount of inorganic sulfur removed from the coals ranges from 66% to 91% with a mean of 77%. The amount of organic sulfur removed from the samples ranged from 36% to 50% with a mean of 43%.

3. The thermal analysis of raw and cleaned coals has been carried out. Using a heated gas line to connect the TG to the FTIR spectrometer instrument, the main products for raw and cleaned coals combustion were found to be CO_2, H_2O, and SO_2. The IR spectral data of SO_2 were collected at 1375 cm^{-1} throughout the combustion of raw and cleaned coals.

4. The temperatures for aliphatic, pyritic and aromatic sulfur oxidation were determined as 320°C, 420°C, and 470°C, respectively.

5. Based on thermal analysis experiments, an instrumental analysis method for the determination of pyritic sulfur was designed. The amount of pyritic sulfur was quantified using the instrumental method, and compared with the data obtained from the ASTM D 2492 method.

6. The X-ray Absorption Fine Structure (XAFS) spectra confirmed the results of the instrumental pyritic sulfur determination of an Illinois 90008 coal.

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