6.2 Sulfur Forms in Coal

SULFUR FORMS IN COAL

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for the Period January 1, 1992, to June 30, 1992

by

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1.0 INTRODUCTION

The accurate and precise analysis of a solid material, such as coal, requires that the analytical method utilize energy, solvent, or reagent that can effectively permeate the matrix and contact the element of interest. Physicochemical barriers preventing such contact have proven formidable when sulfur analysis of solid coal by conventional technologies is attempted. Analysis of coal for sulfur by volatilization of sulfur moieties is limited by their volatilities and vapor transport through the matrix, and liquid extraction of those moieties is limited by conventional solubility and permeability. Chemical derivatization for ^{13}C nuclear magnetic resonance (NMR) spectroscopy is reagent-transport limited, ^{33}S NMR is limited by absorption bandwidth, and x-ray techniques are limited to surface analysis by the inability to penetrate the solid more than a few angstroms. Given these drawbacks, a technique that would allow solvent penetration into the entire sample and dissolution of the sulfur species, with the ability to obtain those species intact in a form that can be identified and quantified by conventional analytical methods, would advance sulfur science immeasurably.

A method that has potential for providing the desired improvement is supercritical fluid extraction (SFE). SFE as a separations method is superior to the other extraction methods, including Soxhlet extraction. Because of the relatively poor mass transfer in liquids, liquid solvent extractions are inherently slow. Compared to liquid solvents, supercritical fluids have several characteristics that make them attractive extraction solvents, as well as media for selective reactions. First, supercritical fluids have solvent strengths similar to those of liquid solvents but, in contrast to liquid solvents, they have lower viscosities (10^{-4} versus 10^{-3} N-sec/m^2) and higher solute diffusivities (10^{-4} versus 10^{-5} cm^2/sec), which greatly improve mass transfer and greatly reduce the time for quantitative extractions (and reactions) to be performed. Second, the polarity of a supercritical fluid changes with its density as described by several correlations (1-3), including the simple empirical correlation proposed by Giddings and others (4): $\delta = 1.25\ P_c^{1/2}(\rho/\rho_1)$ where δ is the Hildebrand solubility parameter, P_c is the critical pressure of the fluid, ρ is the density of the supercritical fluid, and ρ_1 is the density of the fluid in its liquid state. As shown by these correlations, the selectivity of a supercritical fluid for a target analyte can be optimized by simply controlling the extraction pressure (and to a lesser extent, the temperature). Supercritical fluids are also available that have widely varying polarities ranging from low-polarity fluids (e.g., ethane) to moderately polar fluids (e.g., CO_2) to polar fluids (e.g., water, although not to be construed to be as polar as liquid water), which, along with pressure and temperature control, give the analyst an extremely wide range of extraction solvent polarities to perform selective extractions. Third, in contrast to popular belief, analytical-scale (not process-scale) supercritical fluid extractions are experimentally simple and inexpensive to perform.

2.0 OBJECTIVES

The overall objective of this project is to develop methodology which will enable the rapid and accurate identification and quantitation of sulfur species in what is now referred to as the "organic" sulfur component of coal. To accomplish this, the following specific objectives must be met:

- To investigate and develop the use of SFE and pyrolysis/SFE (PYR/SFE) for the selective extraction of organic forms from coal
- To identify and quantitate the individual sulfur organics recovered using SFE procedures
- To investigate and develop the use of selective pyrolysis and/or chemical oxidation/reduction for the determination of organic sulfur forms in coal
- To evaluate and incorporate other promising sulfur speciation techniques

3.0 MATERIALS, EQUIPMENT, AND METHODS DESCRIPTIONS

3.1 Coal Characterization

Table 1 contains the proximate and total sulfur analyses of the test coals used in the sulfur analysis experiments this quarter. Well-characterized coals from the Illinois Basin coal sample program, (IBCSP) were supplied by the Illinois State Geological Survey. The proximate analyses of these coals, reported in Table 1, are those most recently obtained at the EERC. The sulfur analyses include results sent from the IBC sample program with the samples, results obtained from the Energy and Environmental Research Center (EERC) laboratory, and results obtained from an independent commercial laboratory, Minnesota Valley Testing Laboratory (MVTL). Table 2 contains the ASTM sulfur forms analyses results on the same coals. Although some of these values appeared in the previous quarterly report, they are included here again for the convenience of the interested reader. Most of the work in this semiannual period was carried out with IBC-101, some with IBC-102, and only selected tests with the remainder of the coals.

3.2 Experimental Apparatus and Materials

A description of the basic apparatus used in the SF extraction experiments is given in the July through September 1990 quarterly report (5). Figure 1 is a schematic of the SFE equipment currently in use, including the gas chromatography (GC) oven used to heat the cell during PYR/SFE experiments. Figure 2 shows a schematic of SFE equipment used in performing on-line analysis of SF extracts. Modifications to the previous apparatus include the use of commercial extraction cells purchased from Keystone™ and the replacement of the fused silica restrictor with the heated stainless steel restrictor. The latter had the constriction near the center of the tube rather than at the end, making the constriction easier to keep hot while still delivering the effluent into the collection solvent. The Keystone™ cells have been successfully used at temperatures of 450°C at 400 atm. (This does not imply endorsement of this company and should not be construed as a recommendation of these cells for SFE use. Identification is for information purposes only.) All other equipment used in this study was common laboratory equipment.

TABLE 1

Proximate and Sulfur Analyses of SFE Test Coals

Coal Samples (IBC):		101	102	106	107
Moisture		10.20	8.28	6.41	5.31
Volatile Matter		36.12	35.75	37.03	37.51
Fixed Carbon		44.69	50.90	48.82	46.01
Residue		9.01	5.08	7.72	11.19
Total Sulfur:	EERC	4.13	3.35	3.53	3.54
	IBCSP	4.36	3.30	3.77	3.72
	MVTL	4.44	3.27	3.68	3.59

EERC: Total sulfur values determined by the EERC.
IBCSP: Total sulfur values determined by the Illinois Basin coal sample program.
MVTL: Total sulfur values determined by MVTL Laboratories, Inc., Bismarck, ND.

TABLE 2

Sulfur Forms Analyses of Coal Samples Used in This Work

IBC	101	102	106	107
<u>Sulfatic Sulfur</u>				
a	0.05	0.06	0.01	0.26
b	0.67	1.17	0.73	0.37
c	0.07	0.16	0.11	0.29
<u>Pyritic Sulfur</u>				
a	1.22	2.26	1.86	0.48
b	0.53	0.61	0.72	0.42
c	1.09	1.66	1.50	0.51
<u>Organic Sulfur</u>				
a	3.08	0.98	1.90	2.98
b	3.24	1.48	2.24	2.80
c	1.09	1.58	2.29	2.76
<u>Total Sulfur</u>				
a	4.36	3.30	3.77	3.72
b	4.44	3.27	3.68	3.59
c	4.53	3.41	3.90	3.55
d	4.13	3.35	3.53	3.54

a. Data from IBCSP.
b. MVTL Laboratories, Inc., Bismarck, ND (12/9/91).
c. MVTL Laboratories, Inc., Bismarck, ND (9/21/90).
d. EERC.

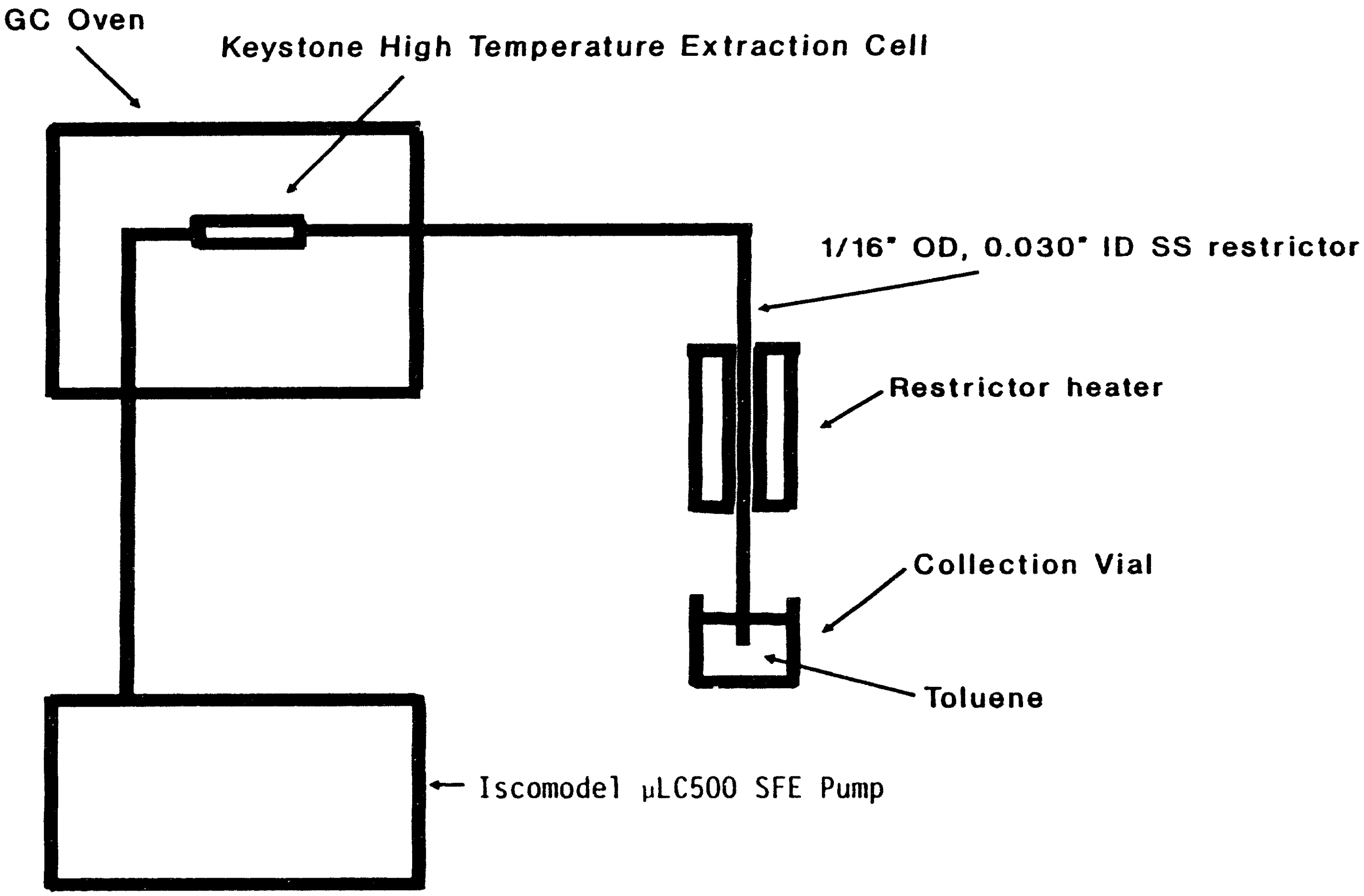

Figure 1. Schematic diagram of the SFE system outfitted for PYR/SFE.

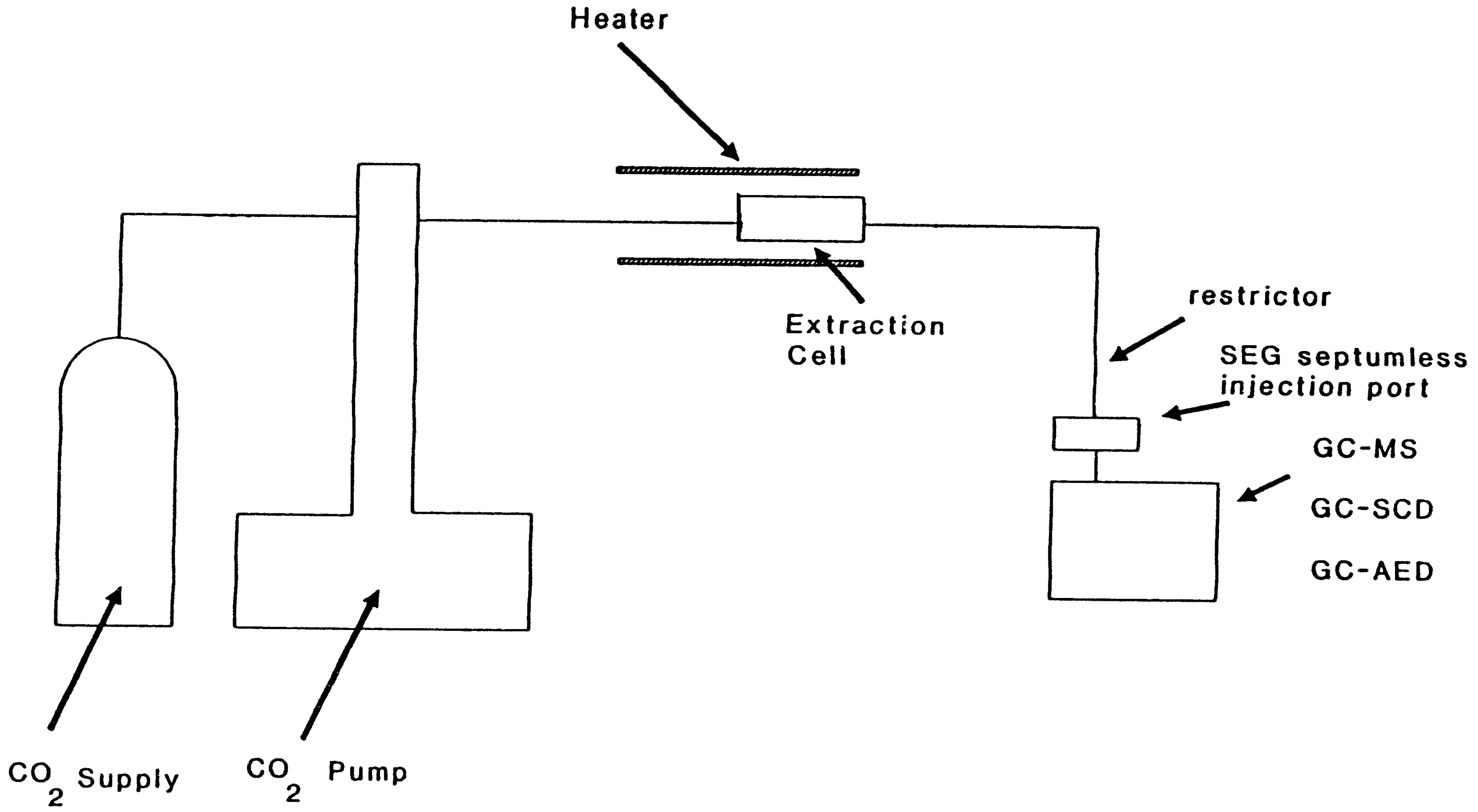

Figure 2. Schematic diagram of the SFE system outfitted for PYR/SFE/cryogenic trapping/GC/MS, atomic emission detection, and SCD.

Bottled carbon dioxide containing 10% methanol was prepared by Scott Specialty Gas Company and was used directly from the bottle during SFE.

3.3 Methods

3.3.1 Supercritical Methanol-Modified CO_2 Extraction of Sulfur From Coal at Low Temperature

Extraction of elemental sulfur from coal has generally been more successful with methanol-modified SF CO_2 than with pure SF CO_2 at 110°C and 400 atm with 10% methanol/CO_2 (6). Eluted SF extracts were collected in ca. 2 mL of toluene for later analysis as previously described (5). Benzothiazole was added to each extract as an internal standard, and samples of each were transferred to septum vials. Analyses of these samples were obtained using a Hewlett-Packard 5890 GC with a Hewlett-Packard element-selective atomic emission detector (AED). Carbon and sulfur emissions were monitored simultaneously at 193 and 181 nm, respectively. Individual component IDs were obtained from a Hewlett-Packard 5985B GC/mass spectrometer (GC/MS).

3.3.2 Extraction With Supercritical Water

The apparatus shown in Figure 1 was used to extract IBC-101 with supercritical water at 450°C and 400 atm. The pump used was an Isco model μLC 500, and the water was HPLC-grade water from Fisher Scientific Company. The collection solvent was HPLC-grade water.

3.3.3 Acid Extraction of Sulfur From Coal

Inorganic sulfur extraction from coal with HNO_3 was carried out according to the Riley Method (7). Extraction of sulfatic sulfur was a hydrochloric acid extraction adapted from ASTM method D2492-90.

3.3.4 On-Line PYR/SFE

IBC-101 coal ground to pass 200 mesh was preextracted with 10% methanol/CO_2 at 110°C and 400 atm for 100 minutes to remove elemental sulfur. The extraction was continued for an additional 100 minutes with pure CO_2 at 110°C and 400 atm to remove traces of methanol and soluble organics. One milligram of this preextracted coal was extracted at 450°C with 400 atm CO_2 for 10 minutes while the extract was collected in a -50°C cryogenic trap and subsequently analyzed by GC/MS. The experiment was repeated using AED detection in place of MS.

4.0 ACCOMPLISHMENTS

The accomplishments for the 6-month period beginning January 1, 1992, and ending June 30, 1992, are reported by task. Therefore, Section 4.1 reports Task A, 4.2 reports Task B, and 4.3 reports Task C.

4.1 Task A. Selective Supercritical Fluid Extraction

The major objective of this study is to develop rapid, reliable, but relatively simple, methods for the direct determination of each of the forms of sulfur in coal. As a result of the current work, a procedure for the direct measurement of one of those forms, i.e., elemental sulfur, has been developed. Thus two of the forms of sulfur in coal can now be measured directly. The ASTM method (D2492-90) of analyzing coal for sulfatic sulfur already exists and is a satisfactory and reliable direct technique. The recently developed method for analyzing coal for elemental sulfur, besides being rapid, simple, and direct, produces little waste as a disposal concern. The technique has as its basis a nominal 30-minute supercritical 10% methanol/CO_2 extraction at 400 atm and 110°C temperature. This method and its development are described in an article which has been reviewed and accepted for publication in *Fuel*. The article, whose title occurs in Section 5.0 Presentations and Publications below, describes the method in detail.

4.2 Task B. Selective Chemical and Thermal Extractions

Sulfur removal from coal at low and elevated temperatures by extraction with supercritical CO_2 was described previously (5, 6). The suite of temperatures used included the range 40°-450°C for varying time periods. The current work included extraction with 10% methanol/CO_2 at 110° and 450°C.

4.2.1 PYR/SFE of Swelling Coal

Under pyrolysis conditions, IBC-101 softens and swells, resulting in reduced fluid-coal contact and the potential for SF-flow stoppage. To alleviate this problem, an accurately weighed amount of coal was mixed with washed sand and then extracted. The entire residue was analyzed for total sulfur after extraction. The percentage sulfur removal was then readily calculated:

$$1 - \frac{\text{Mass Sulfur in Residue After Extraction}}{\text{Mass Sulfur in Original Mass of Coal Sample}} \times 100 = \%\ \text{S Removal}$$

Figure 3 shows the calibration curve obtained from a plot of milligrams of total sulfur measured versus milligrams of IBC-101 mixed with an equal quantity of sand for absolute total sulfur determination.

4.2.2 Effect of Chemical Reactants on SFE of Sulfur

Methods of removal of sulfur tested included SFE of IBC-101 under mild pyrolysis conditions with and without the presence of chemical reagents. Dynamic extractions with supercritical CO_2 at 400 atm and 450°C in the absence of a chemical reactant was successful in removing nearly 50 wt% of the sulfur from the coal, while supercritical 10% methanol/CO_2 extraction under the same conditions was successful in removing nearly 60 wt% of the sulfur from the coal (Figure 4). SFE of IBC-101 containing 50 wt% added NaOH at the same conditions as above resulted in sulfur removals of slightly more than 50 wt% for each of the fluids. Dynamic SFE of 50 mg of IBC-101 spiked with 200 μL of 85% H_3PO_4 under the same conditions as the above resulted in >60 wt% sulfur reduction when extracted with 10% methanol/CO_2 and 85 wt% reduction of S when extracted with CO_2. H_3PO_4 solubility in SF 10% methanol/CO_2 was greater than in SF CO_2 as evidenced by the amount of H_3PO_4 in the extract. Therefore, the residence time of the acid in the reaction cell during a dynamic extraction was significantly shorter in the methanol/CO_2 extraction, allowing for shorter reaction time and accounting for reduced sulfur removal.

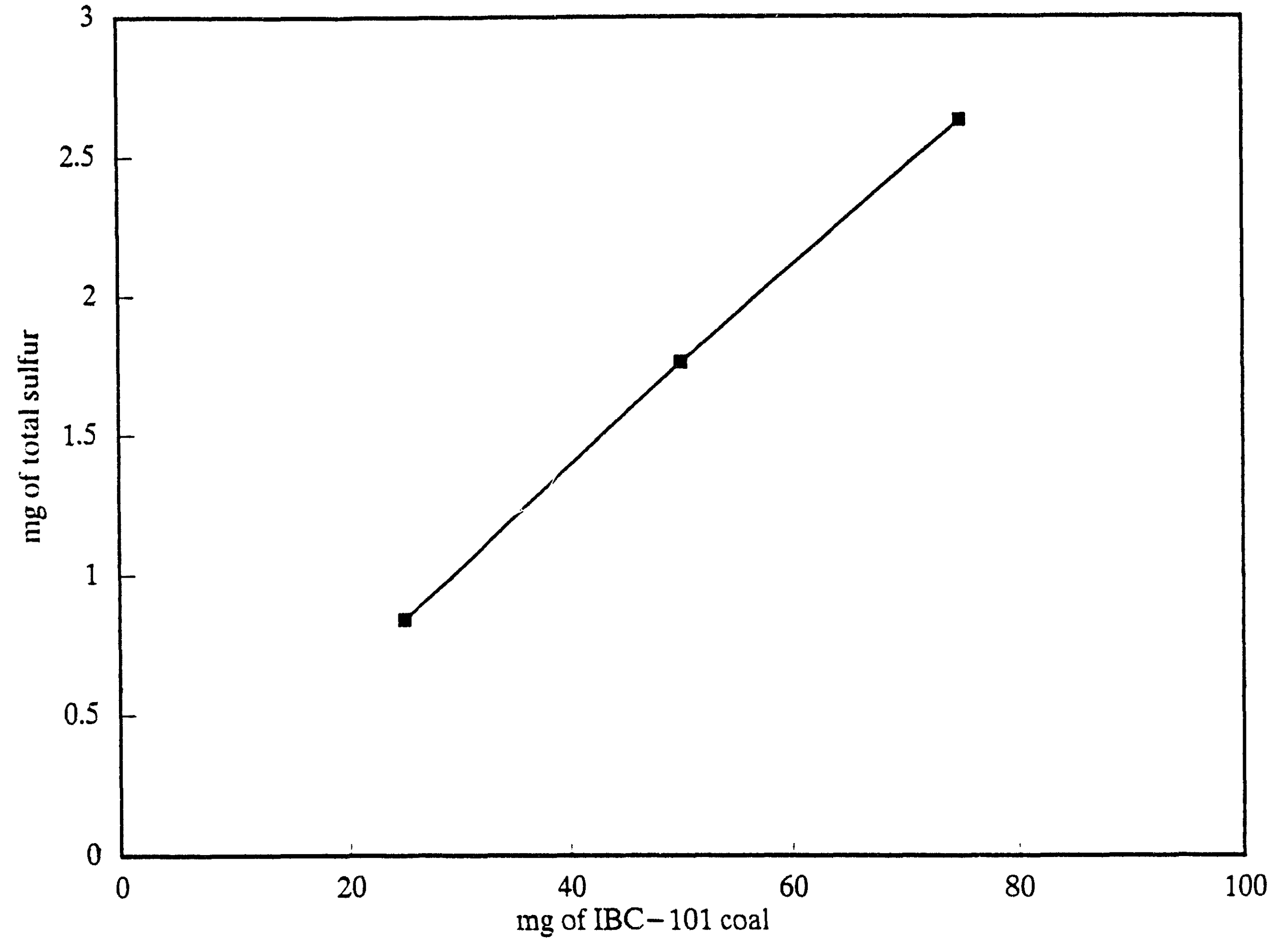

Figure 3. A sulfur standard calibration curve for LECO determination of total sulfur in 100% of a coal/sand-extracted mixture.

Extraction of coal with supercritical water has several attractive aspects. Included in the list of attractive features are the environmental acceptability of water, the polar nature (although not nearly the polarity of the liquid) of water as a SF with respect to other commonly used fluids, the variety of modifiers available for use with water, the specific heat capacity of SF water, and the cost of the water. At the test conditions of the initial supercritical water extraction of IBC-101, >50% by weight of the sulfur, as measured on an absolute scale as shown in Figure 4, was extracted. Additional extractions and extraction strategies with SF water are planned.

4.2.3 High-Temperature On-Line Extraction

Initial results utilizing on-line PYR/SFE/cryogenic trapping/GC with the MS as a detector to analyze elemental sulfur-free IBC-101 are shown in Figure 5. This technique reduces loss of sulfur compounds normally encountered in the solvent-trapping procedure which allows the more volatile of the major gas-chromatographable species to be identified. The total ion chromatogram shows all gas-chromatographable components detected by the MS rather than only the desired sulfur compounds. Figure 6 shows the AED chromatograms of carbon-containing species (top) and sulfur-containing species (bottom). Correlation of peaks in the bottom chromatogram with those of the top show which

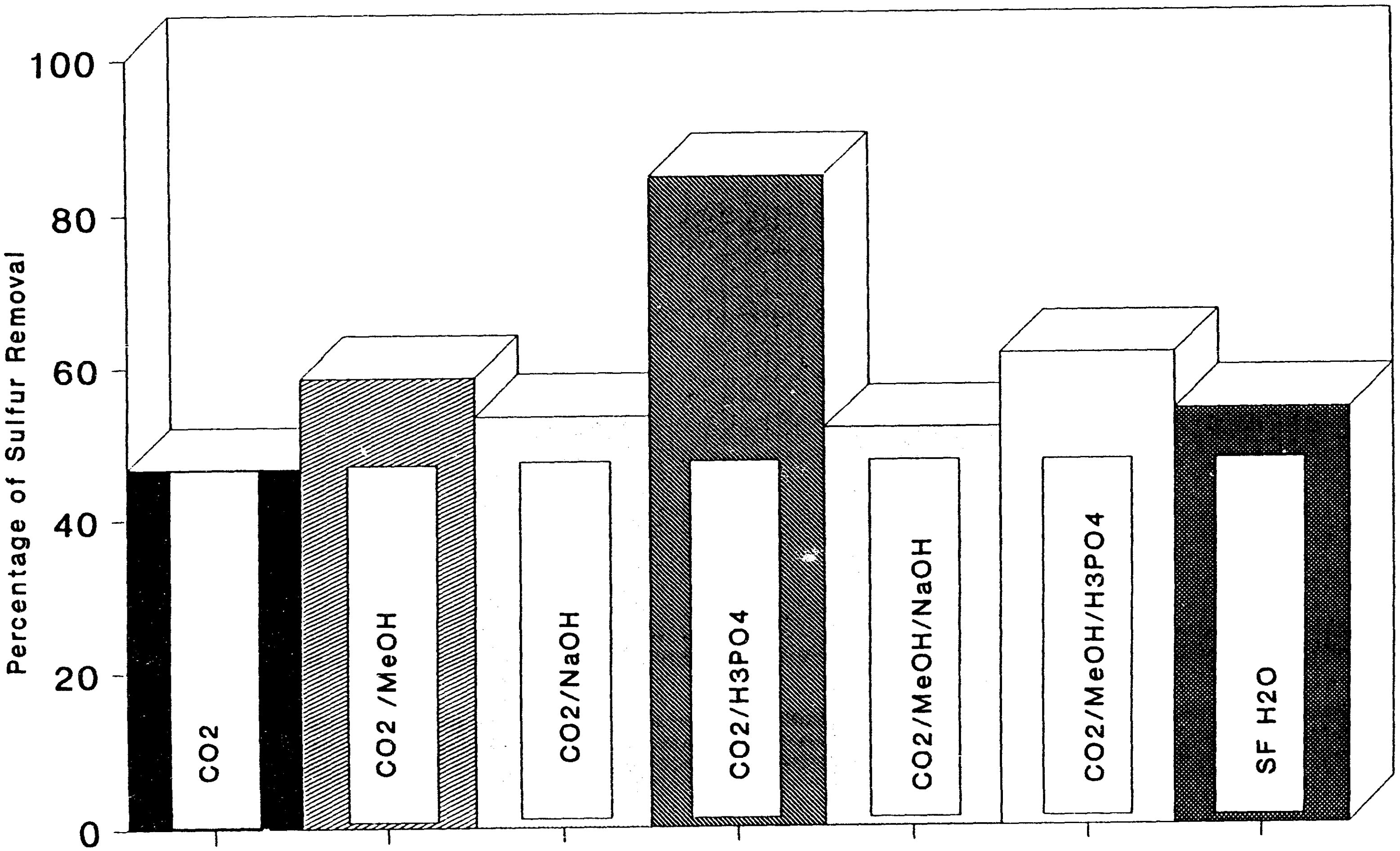

Figure 4. Sulfur removal from IBC-101 at 450°C and 400 atm by CO_2 and 10% methanol/CO_2 with/without reagents.

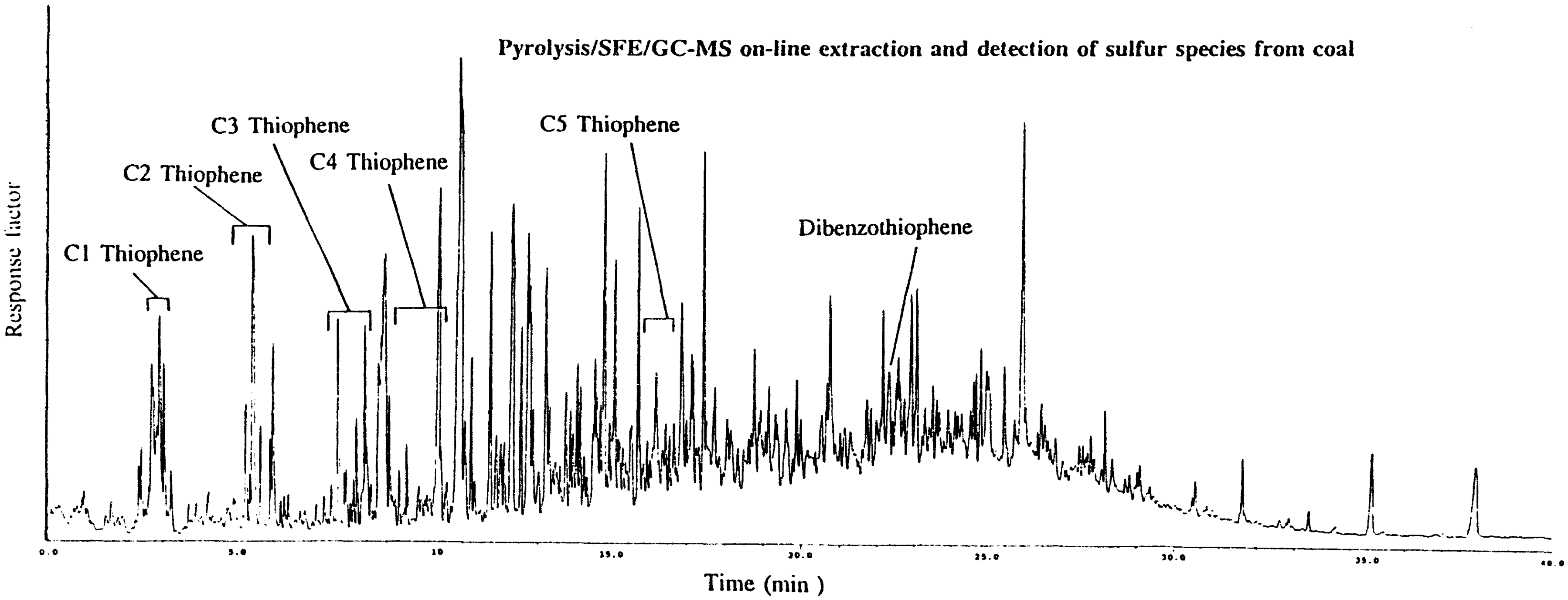

Figure 5. Chromatogram of extract from PYR/SFE/GC/MS.

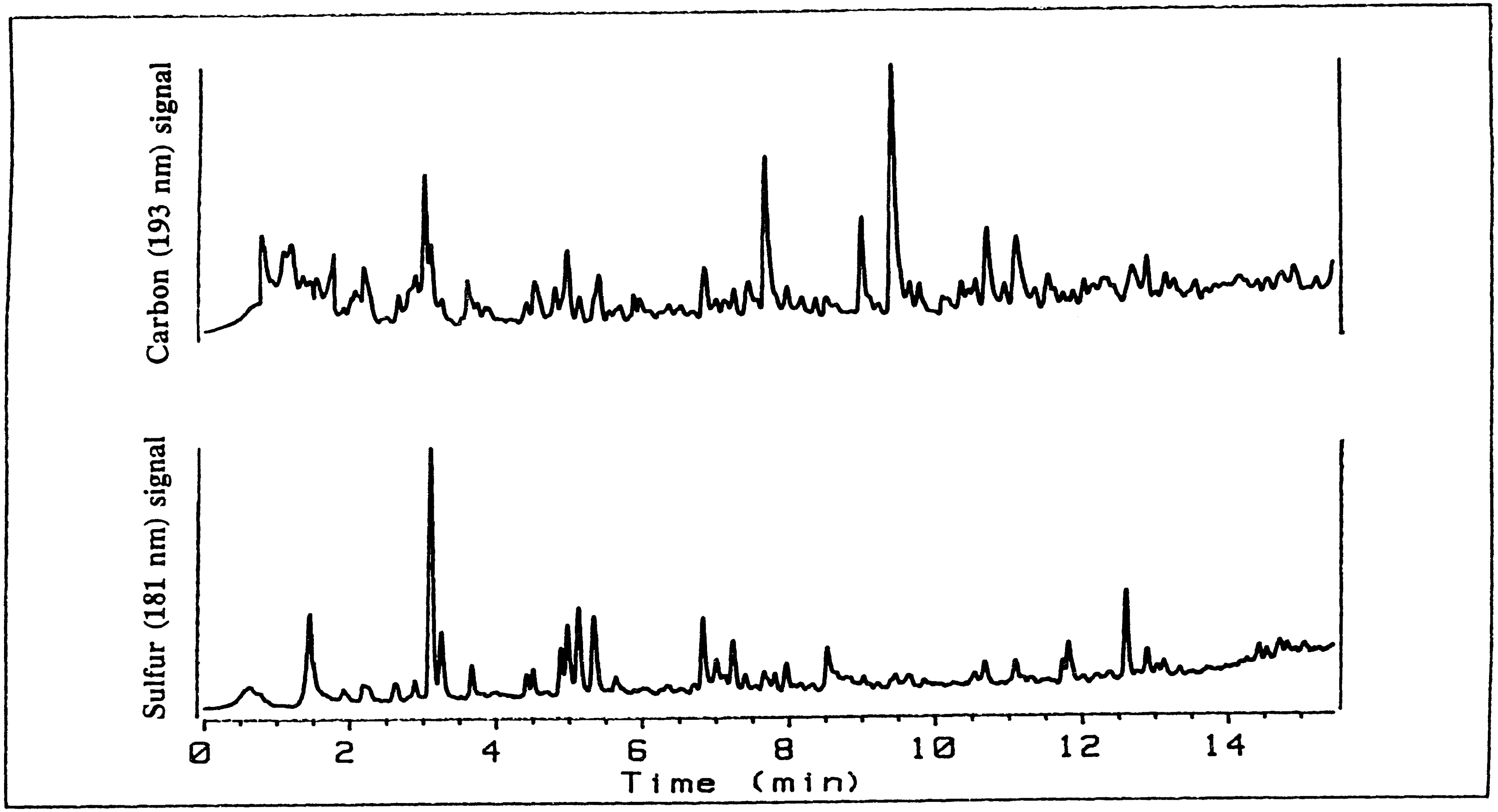

Figure 6. A typical GC-AED chromatogram of an SFE coal extract (IBC-101) showing the carbon (193 nm) and sulfur (181 nm) channels displayed.

components are true organosulfur compounds. The AED information enables the sorting of peaks in the total ion chromatogram of the MS, allowing identification of individual sulfur compounds in the extract.

Additional IBC-101 bituminous coal was then extracted with supercritical 10% methanol/CO_2 at 400 atm to remove elemental sulfur. Several fractions of the elemental-sulfur-free IBC-101 were then extracted using the on-line method recently developed. Figure 7 shows a total ion chromatogram of extract collected by cryogenic trapping during pyrolysis at 450°C. Selected ion-current chromatograms on the same figure show the C_1-C_5 thiophenes which make up a large portion of the volatile species.

Several additional sulfur compounds along with benzene, phenol, toluene, indan, indene, and other polynuclear aromatics are identified on Figure 8. Again the thiophenes are identified, but ethylene sulfide, benzo[*b*]thiophene, dibenzothiophene, and thianthrene are also prominent peaks in this chromatogram.

To gain additional information on the distribution of sulfur forms in coal, an extraction scheme was devised which enables the individual quantitative determination of elemental, sulfatic, other inorganic and true organic sulfur. It consists of SFE of elemental sulfur, HCl extraction of sulfatic sulfur from raw and elemental-sulfur-free coal, HNO_3 extraction of total inorganic sulfur from raw and elemental-sulfur-free coal, and true organic sulfur of residue on elemental-sulfur-free, acid-extracted coal. The scheme is shown in Figure 9 and will be evaluated in future work.

4.3 Task C. Other More Conventional Methods of Analysis

4.3.1 Sample Preparation for Stable Sulfur Isotope Experiments and Background Information Related to This Work

The results of sulfur forms analysis shown in Table 2 indicate that sulfatic sulfur increases on prolonged (>6 months) exposure to air. The pathway followed by the sulfur seems to be by way of pyritic sulfur oxidation, as also indicated by Table 2. A method of investigating the pathway has been designed using a coal (IBC-107) that has a natural sulfur probe, i.e., unusually high levels of stable ^{34}S isotope, and is described below. The high $^{34}S/^{32}S$ in the original coal and in the residue from acid-extracted IBC-107 makes them excellent candidates for testing the potential for organic and pyritic sulfur conversion to elemental sulfur.

Coal IBC-107 was selected for stable sulfur isotope analysis because of the large isotopic difference of ~22 $^{\circ}/_{\circ\circ}$, between pyritic and organic sulfur (8). Because of this large isotopic difference, sulfur isotopic determination on the elemental sulfur obtained selectively by SFE may be applied to resolve the source of elemental sulfur in coal. A schematic description of the extraction scheme used in this study is depicted in Figure 10. Initially, two portions of ~4.5-g IBC-107 (-200 mesh size) coal were extracted with SF 10% methanol in CO_2 in a 10-mL Keystone extraction cell fitted with a stainless steel restrictor for 2 hours. An additional 15-min extraction was performed during which no elemental sulfur was extracted as determined by GC-AED. The large coal sample sizes extracted were necessary in order to obtain a sufficient quantity (~4 mg) of elemental sulfur for isotopic determination. About half of the SF-extracted coal was extracted with nitric acid (7) to

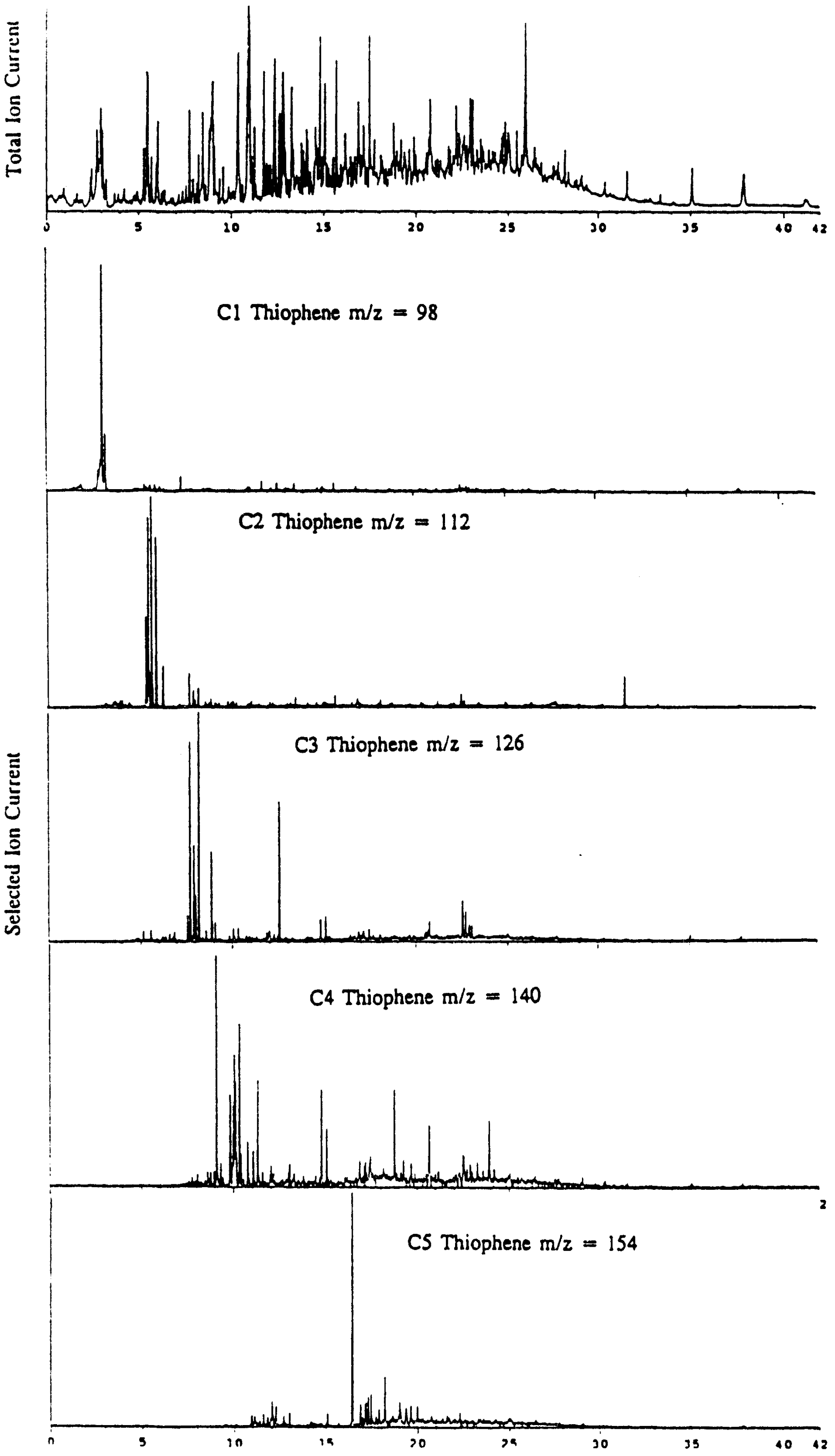

Figure 7. Total ion and selected ion chromatograms of extract from PYR/SFE/GC/MS of IBC-101.

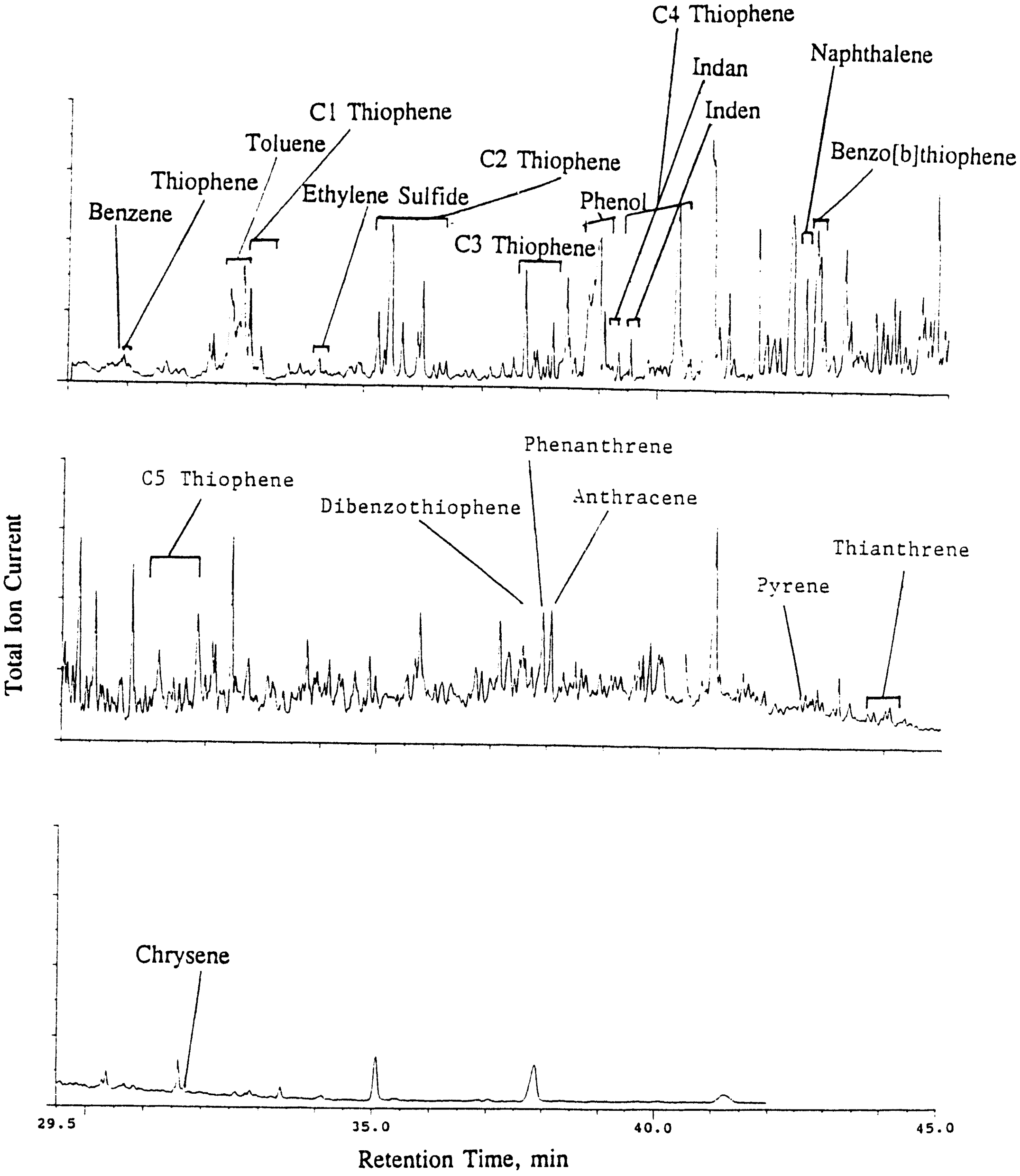

Figure 8. Total ion chromatogram (shown in three parts) of extract from PYR/SFE/GC/MS of IBC-101 with several major peaks identified.

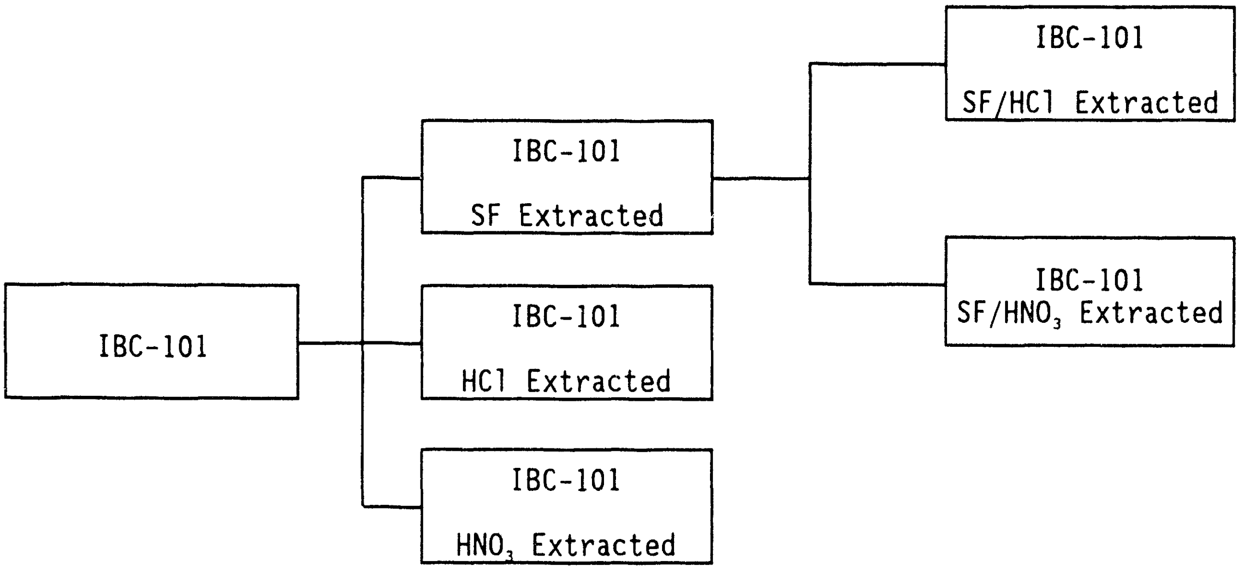

Figure 9. Flow diagram of the differential extraction of sulfur forms from coal.

collect the pyritic and sulfatic sulfur from the coal. Another portion of the SF-extracted coal was extracted by the Canfield technique (9) to obtain the pyritic sulfur in coal. Stable sulfur isotope determinations were performed on the seven coal extracts and residues by an experienced research group headed by Professor Simon Bottrell in Leeds, UK, using an established procedure with stable sulfur isotope MS. In addition, total sulfur determination on all the five solid residues were carried out. Data from the stable isotope determinations coupled with the total sulfur values of the five solid residues and original coal samples provided information regarding sulfur forms transformation mechanisms in the coal matrix, which should lead back to the original source of elemental sulfur in coal. Table 3 shows the data obtained from the stable sulfur isotope analyses.

The analytical values for organic sulfur in the residues following Riley and Canfield extractions were identical within the precision of the isotope measurement. The analyses of the inorganic sulfur fraction collected during each of the extractions are not the same, but the difference is easily explained. Whereas the Canfield method liberates sulfur as H_2S exclusively from metallic sulfides, the Riley method oxidizes metallic sulfides to sulfates which cannot be separated from inherent sulfate. The Canfield method, then, gives what is expected to be a more accurate estimate of pyritic sulfur by measuring the isotope ratio in the liberated H_2S, while the inorganic sulfur in the Riley extract is determined from the total sulfate. In samples with low sulfate, the latter measurement fairly represents the pyritic sulfur, whereas in samples with high sulfate levels, the sulfur in the Riley extract is interpreted as inorganic, but not exclusively pyritic, sulfur.

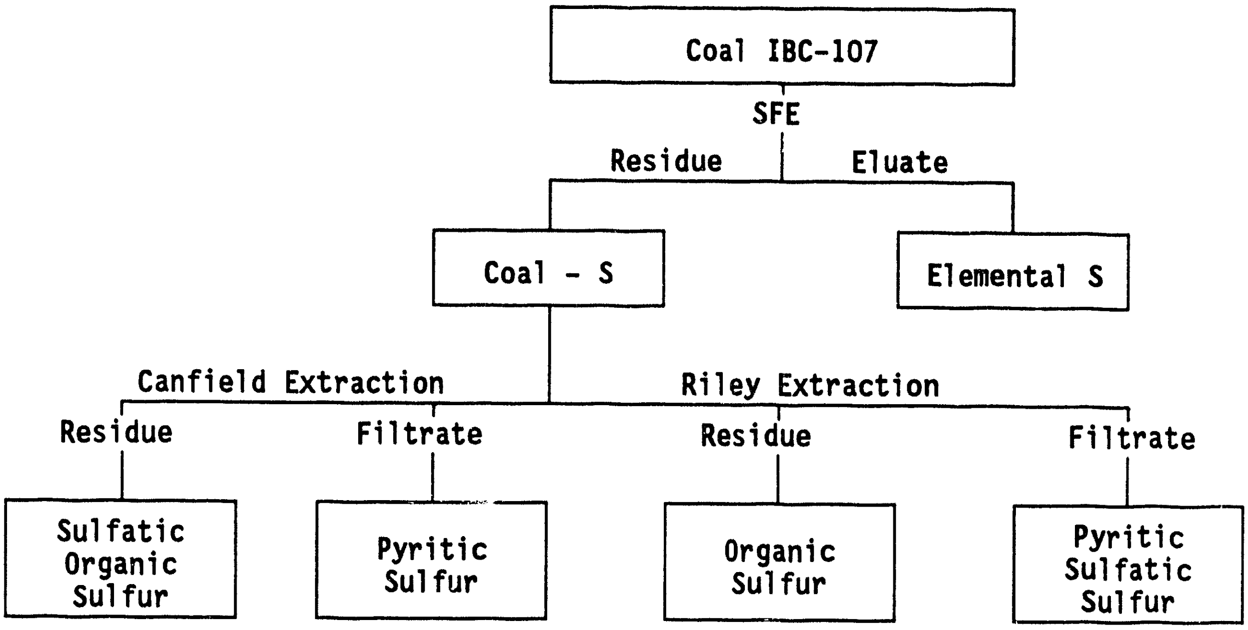

Figure 10. Flow diagram of sample preparation for stable sulfur isotope analysis.

TABLE 3

Sulfur Isotopic Composition of Fractions Obtained From IBC-107

Sample	Preparation	$\delta^{34}S_{CDT}$	Error (%)
PL-1	Parr bomb oxidation of total coal	+6.5	±0.2
PL-2	Parr bomb oxidation of S_8 in SF extract collected in toluene	+13.4	±0.2
PL-3x	Pyrite sulfur extracted from PL-3 by acidic chromous chloride (Canfield method)	+26.4	±0.4
PL-3r	Organic S (residue from Canfield extraction) by Parr bomb oxidation	+1.6	±0.2
PL-4	Inorganic S in Riley* extract of PL-3	+12.1	±0.2
PL-5	Organic S (residue from Riley extraction) by Parr bomb oxidation	+1.5	±0.2

* Boiling 2 N HNO_3 for 30 minutes.

Table 3 shows that the Riley acid extraction and the Canfield extraction separate the coal sulfur into fractions having nearly identical organic $^{34}S/^{32}S$ isotope ratios. The organic, pyritic, and total sulfur ratios compare favorably with those of other researchers (10). Interpretation of the data shown in Table 3 suggests that the elemental sulfur (PL-2) is related to the inorganic sulfur, but is inconclusive as to whether the relationship is exclusive; i.e., the argument can also be made that both inorganic and organic sulfur contribute to the formation of elemental sulfur.

To expand on the above findings, two additional coals, IBC-102 and IBC-106, were prepared for sulfur stable isotope analysis. The preparation included SFE to collect the elemental sulfur from the coal and Riley extraction to remove inorganic sulfur from the SF-extracted residue. The Canfield extraction is carried out on the SF-extracted residue at the Stable Isotope Laboratory. These samples, along with raw coal, were sent to the Stable Isotope Analysis group in Leeds, UK, for analysis at no charge to the EERC.

5.0 PRESENTATIONS AND PUBLICATIONS

1. Louie, P.K.K.; Timpe, R.C.; Hawthorne, S.B.; Miller, D.J. "Determination of Elemental Sulfur in Coal by Supercritical Fluid Extraction (SFE) and Gas Chromatography with Atomic Emission Detection (GC/AED)," *Fuel* **1992**, in press.

2. Louie, P.K.K.; Timpe, R.C.; Hawthorne, S.B.; Miller, D.J. "Determination of Elemental and Organic Sulfur in Coal Using Supercritical Fluid Extraction (SFE) and Pyrolysis/SFE," Presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, New Orleans, LA, March 9-12, 1992.

3. Louie, P.K.K.; Timpe, R.C.; Hawthorne, S.B.; Miller, D.J. "Application of SFE/AED for Sulfur Species Analysis in Coal," Presented at the Second HP AED User Group Meeting, New Orleans, LA, March 9-12, 1992.

6.0 FUTURE WORK

- Perform additional SF water extractions of sulfur from coal.
- Determine effect of additional chemical reactants on SFE of sulfur from coal.
- Determine effect of pretreatment of coal on SFE of sulfur from coal.
- Prepare the final report.

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10. Hackley, K.C.; Buchanan, D.H.; Coombs, K.; Chavan, C.; Kruse, C.W. "Solvent Extraction of Elemental Sulfur from Coal and a Determination of its Source Using Stable Sulfur Isotopes," *Fuel Processing Technology*, **1990**, *24*, 431-436.