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Chapter 18

Characterization of Organic Sulfur Compounds in Coals and Coal Macerals

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Abstract. Peroxyacetic acid oxidation has been used to investigate the type and distribution of organic sulfur species in samples of vitrinite, sporinite and inertinite, separated from the Herrin No.6 and an Indiana No.5 coal seam. It was established that organic sulfur species were selectively preserved during oxidation and their analysis led to some of the first sulfur-33 NMR spectra obtained for coal. The effects of maceral separation processes on model compounds were also studied. Results from our studies support the following conclusions: 1). Different macerals have different distributions and types of organic sulfur species. 2). Organic sulfur compounds in coal occur at the ends of macromolecular structures. 3). Maceral separation techniques do not affect organic sulfur species in coal. 4). Maceral separation is essential for the chemical characterization of coal. 5). GC-MS and sulfur-33 NMR data agree.

The combustion of sulfur-containing coals leads to the environmentally unacceptable problems associated with acid rain (1). Although current coal cleaning technologies can remove most of the inorganic sulfur from coal (2), no technology is presently in use for the effective removal of organic sulfur. The failure of organic desulfurization processes is due in part to a lack of information regarding the types of organic sulfur present in coal. The optimum approach therefore, would seem to be the initial characterization of the organic sulfur forms in coal followed by the design of appropriate desulfurization technologies.

There are methods for the direct determination of organic sulfur in coal (3, 4), but details regarding individual molecular structures are much harder to obtain. Much of the research designed to obtain this information has concentrated on the analysis of coal extracts (5, 6) and pyrolysis products (7, 8). Unfortunately the sulfur species from pyrolysis processes may be highly modified and usually account for only a very small percentage of the total sulfur in the coal. Extrapolating the data from these analyses to characterize the whole coal can be very misleading.

Other approaches have been used to characterize the organic sulfur in coal. Programmed temperature reduction (PTR) (9-14) as used by Attar is one such method as is programmed temperature oxidation (PTO) (15-17). Both methods rely on differences in reactivity of the different sulfur species. However, both procedures involve high temperatures and under such conditions transformation between sulfur species is possible. This reaction is highly probable if pyrite or elemental sulfur are present in the sample (18-20).

Further techniques for the determination of molecular structure of organic sulfur species in coal include Curie point pyrolysis (21) and X-ray absorption fine structure (XAFS) spectroscopy (22). In addition there are techniques which provide an overall view of the relationships between sulfur, metals and coal petrology. These include optical microscopy/electron probe microanalysis (10), X-ray photoelectron spectroscopy (XPS) (23) and scanning electron microscopy-energy dispersive X-ray analysis (SEM-EDAX) (l0). Although the above mentioned methods provide some information regarding organic sulfur species in coal, and some advances have been made, a routine, low-temperature, unambiguous method for organic sulfur characterization in coal is yet to be found.

In this study we have investigated selective oxidation as a potential organic sulfur characterization approach. In particular we have used the peroxyacetic acid oxidation procedure. Although this selective oxidant has received some attention in the study of lignin (24) and humic acid structures (25), its application to the study of coal has been limited to only a few instances (26, 27) with very little information about organic sulfur species being reported.

Peroxyacetic acid oxidation is similar to the peroxytrifluoroacetic acid (Deno) oxidation (28). These peroxide systems are reported to selectively oxidize the aromatic portions of molecules while leaving aliphatic portions intact (29). Peroxyacetic acid will oxidize aromatic units to phenolic units via hydroxylation. These phenolic moieties will oxidize rapidly to ortho and para quinones, the latter of which are unstable are undergo ring fission to form diene carboxylic acids (30).

The selective oxidation of aromatic portions of molecules was demonstrated using model compounds such as toluene, ethylbenzene, n-propylbenzene and iso-propylbenzene (28). The major oxidation products from these compounds were acetic, propionic, butyric and isobutyric acids respectively. In each case the carboxylic acid group marks the position that the aromatic unit used to occupy.

Although the selective oxidation of coal has been extensively studied (31-33), surprisingly little has been reported about sulfur species in the oxidation products. Even less is known about the distribution of organic sulfur species between different coal macerals despite the fact that this information is important for the development of any future desulfurization technology.

In view of these shortcomings we have combined the need to characterize organic forms of sulfur with the recent progress obtained in the separation of coal into its single maceral fractions (34). This affords an opportunity to compare the sulfur chemistries of individual macerals with that of their parent coals.

Experimental

Sample Preparation. Herrin No. 6 (Illinois No.6) and Indiana No. 5 (Illinois No. 5) coals obtained from the Illinois Geological Survey Sample Bank were used in this study. The whole coals were split into four fractions each of which was placed in a sealed, 5-gallon drum. The fourth fraction was ground to minus 200 mesh and then introduced into a nitrogen gas powered (100 psi) Sturtevant fluid energy mill. In this device the coal particle size is reduced to the micron level by impaction between coal particles themselves and with the impaction chamber walls. Proximate and elemental data for these micronized coals are reported in Table I.

Aliquots of the micronized coal were treated with HCl and HF to remove carbonate and silicate mineral matter, and aliquots of the micronized, acid treated coal were floated in a 1.67 specific gravity solution of CsCl to eliminate pyrite. Some of the floated samples were then separated by density gradient centrifugation (DGC) into sporinite, vitrinite and inertinite maceral fractions (34).

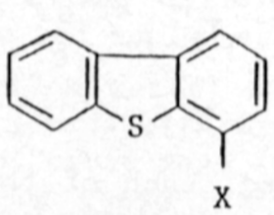
Table I. Proximate and Elemental Data

	Herrin No. 6	Indiana No. 5
Moisture	14.7	10.4
Volatile Matter	40.5	39.6
Fixed Carbon	49.5	51.4
H-T Ash	10.5	9.0
Carbon	69.20	71.73
Hydrogen	5.12	4.85
Nitrogen	1.28	1.71
Oxygen	9.49	8.93
Sulfate Sulfur	0.05	0.01
Pyritic Sulfur	1. 27	1.85
Organic Sulfur	3.00	1.91
Total Sulfur	4. 32	3.76
Total Chlorine	0.12	0.02

All percentages are reported on a moisture free basis except for moisture.

Soxhlet extractions were performed on each of the coal and maceral samples. The micronized, acid treated and floated samples were extracted successively with hexane, toluene and finally THF. The maceral fractions were extracted with THF only. All extracts and extraction residues were isolated, weighed and the distribution of sulfur between them established. In addition, the extracts were examined using FTIR, proton and carbon-13 NMR spectroscopy, GLC-FID/ FPD and GC-MS.

Determination of the Effects of Separation Processes on Organic Sulfur Forms in Model Compounds. Three substituted dibenzothiophenes were subjected to the coal preparation and maceral separation processes. The model compounds used are shown below.



1. X = CH_2SH

2. X = SCH_3

3. X = $SC_6H_5CH_3$

Each compound was soaked for 1 hr in 38% (wt/v) HCl followed by soaking in 55% (wt/v) HF for 1 hr. Each was then rinsed exhaustively with water and dried under vacuum at room temperature. In a separate experiment each of the model compounds were exposed to a solution of cesium chloride. After sufficient exposure each compound was recovered and washed with copious quantities of distilled water. The percentage recovery, the melting point and spectroscopic data such as FTIR , proton and carbon-13 NMR were recorded.

Mild Oxidation of Coal and Macerals. Two grams of extracted coal was placed in a 3-necked 250mL r. b. flask. Fifty mL of glacial acetic acid was then added followed by 20 mL of 30% (wt/v) hydrogen peroxide. The flask was then heated under reflux and after 1 hr a further 40 mL of hydrogen peroxide was added dropwise so as to maintain the reaction. The reaction was allowed to reflux for a total of 24 h. Maceral oxidations were performed on a 0.5g scale. Other oxidations were performed using 5g of coal with, in some cases, only 40 mL of hydrogen peroxide. These experiments were conducted to generate samples for total sulfur analysis and to study the partial oxidation, dissolution and desulfurization of coal. Aliquots of the soluble oxidation products were retained for analysis including total sulfur, FTIR and NMR analysis. Another aliquot was methylated using the diazomethane method prior to GC-MS and GLC-FID/FPD analysis.

Instrumentation. Proton, carbon-13 and sulfur-33 nuclei were observed at 300, 75 and 23 MHz respectively, using a Varian VXR 300 MHz NMR spectrometer. Proton spectra were recorded using a pulse width of 12 μs and a pulse delay of 20 s. Typically 10 transients were obtained. Carbon-13 spectra were obtained using a pulse width of 4.3 μs and a pulse delay of 5 s. The number of transients recorded varied from 500 - 10,000 depending on sample concentration. Sulfur-33 spectra were obtained using a pulse width of 65 μs and a pulse delay of 5 ms. Typically between 400,000 and 500,000 transients were collected. Extracts were dissolved in either deuterated chloroform or deuterated THF and chemical shifts measured against internal TMS. Oxidation products were dissolved in acetone/deuterium oxide (9: 1) and chemical shifts measured against internal TMS for proton and carbon-13 spectra and external ammonium sulfate for sulfur-33 spectra. GC-MS analysis was performed on a Hewlett Packard 5970B MSD fitted with a 30m OV-1 column. Two temperature programs were used. Firstly the oven temperature was ramped from 100 - 300°C at 3°C/min and secondly a ramp from 100 - 300° C at 20° C/min was used. Injector and detector temperatures were maintained at 270°C and 300° C respectively. GLC-FID/FPD analysis was performed on a Varian 3400 gas chromatograph using the same chromatographic conditions as used in the GC-MS runs. FTIR spectroscopy was performed on a Nicolet instrument using the thin film on sodium chloride plates technique for liquids and the potassium bromide pellet technique for solids.

Results and Discussion

Treatment of Model Compounds. As anticipated, each of the sulfur-containing model compounds were recovered quantitatively after their exposure to the micronization, acid treatment and floatation processes used in coal and maceral preparation. In all cases the proton and carbon-13 NMR spectra, the FTIR spectra and the melting points of the recovered materials matched those of the starting materials, indicating that these sulfur species remain unchanged during the processing.

Solvent Extraction. The yields of extracts and extraction residues obtained by successive hexane, toluene and THF extraction of the floated coal samples, plus the percent of the total of the organic sulfur that each extract contained are shown in Table II.

Table II. Extraction yields and sulfur distributions

	Herrin No.6		Indiana No.5	
Extract Type	Yield Wt%	%Tot. O.S.	Yield Wt%	%Tot. O.S.
Hexane	0.5	2.0	0.6	6.6
Toluene	2.5	2.9	1.2	4.6
THF	7.1	4.2 1	4.9	14.2
Extract Residue	89.9	90.9	83.3	74.6

It is clear from Table II that most of the organic sulfur remains in the insoluble coal matrix and cannot be extracted. The Indiana No.5 coal has a higher quantity of extractable organic sulfur than the Herrin No.6.

Both the extractability and the organic sulfur distribution varies between the two coals. It is interesting that the hexane extracts from both coals and the toluene extract of the Indiana No 5 coal, contain a disproportionately high percentage of the total organic sulfur. Thus, there is organic sulfur enrichment in these extracts and a consequential depletion of the organic sulfur in the extraction residues. This would appear to be good criteria for a desulfurization process but the low extractabilities obtained with these solvents prevents this from being a viable process.

Characterization of Sulfur Compounds in Extracts. Each of the extracts and extraction residues were examined by FTIR spectroscopy. The hexane and toluene extracts gave spectra dominated by aliphatic features while the THF extracts had more aromatic and polar functional group characteristics. The extraction residues gave FTIR spectra dominated by aromatic and polar functional group characteristics with minor aliphatic features. All spectra contained peaks that could have arisen from organosulfur groups but the regions occupied by these peaks overlap with those occupied by other non-sulfur functional groups. Hence assignment of sulfur structures was not possible. This demonstrates the futility of trying to identify a minor constituent of a complex substance such as coal using nonselective techniques.

The same type of information was obtained from proton and carbon-13 NMR. Once again there are absorptions that may be due to carbon and hydrogen bonded to sulfur but contributions from other non-sulfur containing structures are highly likely and hence a firm assignment cannot be made.

It is obvious from the FTIR and NMR analyses of these extracts that in order to positively identify organosulfur structures we need an analytical technique that is sulfur selective. That is, a technique that responds to sulfur uniquely. One such technique, applicable to the problem in hand, is GLC-FID/FPD where the flame photometric detector is set in the sulfur selective mode.

Aliquots of hexane, toluene and THF extracts were mixed together proportionately and the resulting combined extract separated by open-column liquid chromatography to give a saturate, an aromatic, a polar 1 and a polar 2 fraction. The saturate fractions from both coals did not contain any sulfur compounds detectable in our GC-FID/FPD system. However, the aromatic fractions from both coals contained a complex series of sulfur compounds. Subsequent GC-MS analysis of these fractions using the selected ion mode (SIM) identified these compounds as a series of benzothiophenes having one, two or three methyl group substituents and a series of dibenzothiophenes with one through four methyl group substituents. Dibenzothiophene itself was also detected but benzothiophene was not. Despite the inherent peculiarities of the FPD detector (non-linearity, compound dependance and quenching), comparison of the FPD traces with the composite SIM traces afforded a very good correlation, illustrating the fact that the composite SIM method did not miss major sulfur compounds.

GC analysis of underivatized polar fractions did not reveal any volatile sulfur compounds. However, once these fractions were methylated with diazomethane, a number of sulfur compounds were detected. (Presumably, the diazomethane methylated either carboxylic acid, phenolic, thiophenolic, sulfonic acid or even alcohol or thiol groups and thereby increased their parent molecules volatility). These additional sulfur compounds are currently under investigation in our laboratories and the results of these studies will be reported later.

Comparison of the extracts taken from the isolated macerals show them all to be very similar, not only to each other, but to the extracts taken from the unfractionated coal. This indicates that the composition of the extract does not vary with maceral type and suggests the extract is probably free to migrate throughout the coal matrix and disperse evenly among the various coal components.

Oxidation of Coal and Coal Macerals. Extraction residues were oxidized as outlined in the experimental section. Two oxidation procedures were adopted: - i). excess oxidant oxidation and ii). oxidant starved oxidation (partial oxidation).

i) Excess oxidant oxidation:- Under the conditions employed the extraction residues were oxidized to soluble products leaving very little residual matter. Typically the percentage of the coal dissolved was around 90-95% although some figures as high as 99% were recorded. The exceptions to this were the sporinite and inertinite macerals, both of which were more resistant to this oxidative dissolution, with only 50-60% dissolving. This no doubt reflects differences in the properties and chemical structures of these macerals. It is also important to note that the yields of oxidation products were higher for floated coal samples vs the micronized and the acid treated samples. This suggests that minerals influence the oxidation of the organic portion of the coal, perhaps catalyzing the production of carbon dioxide.

In the larger scale reaction (5g sample size) it was established that the soluble oxidation products had considerably enhanced sulfur contents when compared with the unoxidized samples. This is explained by the oxidation of carbon in the coals to carbon dioxide and the subsequent concentration of the organic sulfur that remained. It was also established that virtually all of the organic sulfur in the extracted and unoxidized samples could be accounted for by the organic sulfur found in the soluble oxidation products, indicating that very little was lost during the reaction and work-up procedures.

It was a concern to us that some of the organic sulfur may have been oxidized to sulfate. To check for this we tested the soluble oxidation products for sulfate using barium chloride solution. Both the micronized and the acid treated coal samples tested positive for sulfate. This is not surprising since each contains pyrite that would be oxidized to sulfate during the reaction. However, the floated coal samples and the macerals (which have very little residual pyrite (<0.1%) tested negative for sulfate indicating that 'over-oxidation' of organic sulfur to sulfate did not occur. This preservation and indeed concentration of the organic sulfur is due to the nature of the oxidant used. It is reported that under strong acidic conditions the peroxyacetic acid becomes protonated and then dissociates to form the hydroxyl cation (35). The hydroxyl cation is a strong electrophile and as such attacks centers of negative charge. For this reason structures bearing a high electron density, for example S, N, 0 and some aromatic units will be attacked faster than others. In the case of oxidation at sulfur, sulfoxides, sulfones and sulfonic acids would result. These oxidized sulfur forms are strong electron withdrawing groups and would deactivate their parent structures towards further electrophilic attack by the hydroxyl cation. This is our main reason for using peroxyacetic acid for the oxidation of the coal samples. The preservation and concentration of the organic sulfur compounds is essential for their eventual identification by chromatographic and spectroscopic techniques.

ii). Oxidant starved oxidation:- In order to study the early stages in the dissolution and desulfurization of coal using the peroxyacetic acid technique, a sample of the extraction residue from the Herrin No. 6 floated coal was oxidized using insufficient oxidant to dissolve the whole sample. After consumption of the oxidant the products were separated into a soluble fraction and an insoluble fraction by filtration. The insoluble fraction was then extracted with dilute aqueous sodium hydroxide to give a humic acid fraction and a final insoluble residue. The yields of each fraction and their sulfur contents are given in Table III.

As we can see from Table III, 86% of the sulfur contained in all of the oxidation products resides in the soluble oxidation products even though this product fraction only represents 52% by weight of the combined oxidation products. This indicates that organic sulfur compounds have been preferentially depolymerized from the coal matrix and that this oxidative procedure may be a possible desulfurization process.

Table III. Sulfur contents of the reaction products from the oxidant starved oxidation of Herrin No.6 floated coal

Product fraction	Yield	%Yield	Total S (Wt%)	% of Total S
Soluble products	2.72g	52.0	5.54	86
Humic acids	1.50g	28.7	0.63	6
Insoluble residue	1.00g	19.3	1. 33	8

To study the desulfurization of the coal as a function of its dissolution in more detail we devised another series of reactions where one gram portions of the extraction residue were reacted with the oxidant for periods of time ranging from 5 minutes to 24 hours. Each oxidation product was then filtered, the quantities of soluble and undissolved coal measured and the amount of sulfur remaining undissolved determined.

It was found that by dissolving only 4% of the coal extraction residue we can remove 25% of its organic sulfur. Similarly by dissolving 20% of the coal extraction residue we can remove 50% of its organic sulfur. It should be stressed that the coal used in this set of reactions had been floated and had no or very little pyrite and therefore the sulfur that was being dissolved must have been organic. The fact that preferential dissolution of sulfur compounds occurs in the early stages of oxidation suggests that a significant proportion of the organic sulfur is more reactive towards the oxidant than the bulk of the coal. This enhanced reactivity of some sulfur units over others may be due to the chemical nature of the sulfur functionalities concerned, for example, disulfides would oxidize and cleave easily under the conditions employed, or it may simply be due to a disproportionately high concentration of sulfur species on the surface of coal particles. These surface organosulfur units would naturally dissolve first because they are in immediate contact with the oxidant.

FTIR and NMR Analysis of Oxidation Products. As expected, the FTIR spectra of the soluble oxidation products are dominated by the strong absorptions due to the hydroxyl and carbonyl groups of carboxylic acids. There are absorptions in the spectra which occur in the regions expected for sulfones (1350-1310 and 1160-1120 cm^{-1}) and sulfonic acids (1420-1330 and 1200-1145 cm^{-1}), but these are probably due to non-sulfur containing functional groups , especially carbon-oxygen bonds which are presumably present in much higher concentrations.

In addition each soluble oxidation product was examined by proton and carbon-13 NMR. Each spectrum can be split up into three regions: an aliphatic region, an aromatic region and a carbonyl region . If we compare the NMR spectra for a THF extract before and after oxidation, we can see that the oxidized sample is much less aromatic than before oxidation. This would suggest that the peroxyacetic acid oxidation is similar to that of the peroxytrifluoroacetic acid or "Deno" oxidation (28,29) in which preferential preservation of aliphatic units is observed.

As with the NMR spectra taken of the unoxidized extracts, there are resonances that can be assigned to organic sulfur compounds. However, these resonances are probably due to the more abundant non-sulfur containing species which absorb in the same regions. Thus it is very difficult to characterize organosulfur compounds using proton and carbon-13 NMR alone. This is why the sulfur selective technique sulfur-33 NMR has such great potential for the characterization of organosulfur groups in coal.

Sulfur-33 NMR. Although sulfur-33 NMR spectroscopy is non-destructive, low temperature, sulfur selective and examines the sulfur atoms directly, there are a number of problems that make routine sulfur-33 NMR of coal very difficult. To begin with the active isotope, sulfur-33, has a low natural abundance (only 0.75%). This coupled with its relatively low sensitivity makes the NMR signals hard to detect. In addition, the sulfur-33 nucleus has a quadrupole moment. This leads to considerable line broadening especially when there is an unsymmetrical electric field gradient surrounding the nucleus. Other problems that are encountered result from the low concentration of sulfur in the coal and from coals inherent insolubility. Fortunately some of these problems can be overcome. For instance, certain oxidation techniques can render coal soluble and at the same time convert its sulfur species to various sulfones and sulfonic acids which have relatively symmetrical electric field gradients about the sulfur atom. Also, since quadrupolar nuclei relax very fast , many of the problems associated with low sensitivity can be overcome in theory, by simply using rapid pulse repetition rates and long accumulation times. However, sulfur NMR still has a long way to come before it can be routinely applied to structural determinations.

Many of the oxidation products analyzed by sulfur-33 NMR gave poor signal to noise ratios and little information was obtained. However the oxidation products derived from the floated Herrin No.6 coal did produce organic sulfur signals at -6.8 ppm relative to external aqueous ammonium sulfate (See Figure 1). Since this coal sample had been extracted with THF and floated prior to oxidation, the sulfur signal observed could not be due to sulfate derived from oxidized pyrite nor could it be from oxidized organosulfur compounds present in the extractable component of this coal. This peak must therefore come from organosulfur groups attached to the THF insoluble matrix of coal that is solubilized upon oxidation. The peak at -6.8 ppm can be attributed to dialkyl sulfones, aryl sulfones, aryl alkyl sulfones, dibenzothiophene sulfones and sulfonic acids. We believe this peak is due to sulfonic acids since these have been detected as prominent sulfur compounds in the oxidation products by GLC-FID/FPD and GC-MS analysis (See next section). Although this peak can be attributed to a number of structures it must be pointed out that sulfur NMR is in its infancy and that this spectrum represents a significant advancement in sulfur NMR of coal products. The potential of sulfur NMR in the analysis of sulfur in coals and other fossil fuels was realized by Retcofsky (36, 37). His pioneering work on model compounds led to some of the first sulfur NMR spectra of organic sulfur species. Subsequently the sulfur NMR spectra of many organic compounds, predominantly sulfones, have been obtained (38-40). More recently some sulfur NMR spectra of fuel related products have been published (41, 42). It should be pointed out that the spectrum presented in Figure 1 is derived from a coal product that contains 90% of the total organic sulfur in the original coal. (The remaining 10% of the organic sulfur was removed by solvent extraction prior to oxidation). The lines or bars associated with each sulfur compound in Figure 1 represent the chemical shift range over which those sulfur nuclei are reported to resonate (38-40). The broken lines represent chemical shift ranges that are at present uncertain because in the authors opinion insufficient numbers of model compounds of that type have been studied.

GLC-FID/FPD and GC-MS Analysis of Oxidation Products. To obtain information regarding the molecular structure of the organic sulfur compounds present in samples, each of the soluble oxidation products were methylated using the diazomethane method and then analyzed, initially by both dual FID/FPD gas chromatography, and by GC-MS. Representative FID and FPD traces obtained from the Herrin No.6 samples are shown in Figures 2 and 3 respectively, while those for the Indiana No.5 samples are shown in Figures 4 and 5 respectively.

It is clear from these FID traces that significant differences exist between all of the samples analyzed. Not only do the different macerals from the same coal exhibit differences, but so do similar macerals from different coals. Thus, not all vitrinites are the same, not all sporinites are the same and not all inertinites are the same. This is especially clear when we compare the two inertinite FID traces. The Indiana No.5 inertinite contains significant amounts of both low and high retention time products which are absent in the Herrin No.6 inertinite. Although the absence of the lower boiling constituents may be due to their evaporation in the work-up procedures, we believe this not to be the case since an identical work-up procedure was used for all samples.

Although many of the oxidation products are common to all of the samples analyzed, their distribution varies considerably from sample to sample. In addition, there are some oxidation products that appear exclusively in the FID traces of some samples. For instance, there are compounds in sporinite and inertinite samples which do not appear in the FID trace obtained for their parent floated coal. The absence of these compounds in the FID traces of the floated coals is explained by the presence of the more abundant maceral vitrinite, the oxidation products of which either swamp or dilute those from the lesser macerals, making their detection very difficult. Here we see how maceral separation is important for the characterization, not only of the individual macerals themselves, but of the whole coal. Observation of sulfur constituents that are unique to minor macerals components may be difficult to detect during the analysis of a whole coal, but are easily observed during analysis of individual macerals.

The same conclusions can be made by looking at the FPD traces. Once again we see that there are considerable differences between all of the samples analyzed. It is clear that a significant portion of the total peak area in the FPD chromatograms is attributable to only nine major sulfur-bearing components. The sulfur chemistry of these samples therefore , as revealed by peroxyacetic acid oxidation, appears to be much less complex than extract and pyrolysis data may lead us to believe. The nine significant sulfur species have been detected in a variety of oxidation products derived from these samples. This includes the oxidation products derived from the partial oxidation of these samples. In no instances were any additional sulfur compounds detected. In other experiments oxidation products were separated by liquid chromatography into GC volatile and GC involatile fractions. The involatile fractions were then re-oxidized and the resulting volatile products analyzed for additional sulfur compounds. None were found. The FPD traces that were obtained were very similar to those obtained for the original volatile oxidation products, indicating that the material initially too involatile to pass through the GC column was simply an undegraded version of that which could.

Once again, we see sulfur compounds present in some macerals but not in others, and indeed sulfur compounds in macerals which appear to be absent in the floated (unfractionated) coal. For instance, sulfur compounds III and IV contribute significantly to the FPD traces of oxidized Herrin No.6 floated and vitrinite samples and the Indiana No.5 sporinite sample, but are very weak or apparently absent in the remaining samples. Also sulfur compound number VII appears in the Herrin No.6 inertinite sample but no other. We attribute the fact that certain sulfur compounds appear in the sporinite and inertinite chromatograms but not in the chromatograms of their parent floated coals to the presence of a large excess of vitrinite in the floated coal samples.

Without retention time data for authentic standards, all that GLC-FID/FPD analysis can tel1 us is the number and distribution of the sulfur compounds in the various samples. It cannot tel1 us what the individual sulfur compounds are. To obtain this information we turn to GC-MS analysis.

Employing exactly the same chromatographic conditions as for GLC-FID/FPD, each sample was analyzed using GC-MS instrumentation. Using the retention time information obtained from the dual FID/FPD gas chromatography, most of the sulfur compounds could be located on the GC-MS TIC and their mass spectra were obtained. Based on the molecular weight and fragmentation pattern information that was forthcoming, structural assignments for sulfur compounds I through IX were made where possible. These are shown in Table IV. The assignment of structure to compounds I, II and IV was verified using authentic compounds. No authentic compounds VIII and IX were available and consequently their structural assignment must be considered tentative. The presence of the M+2 peak from the sulfur-34 isotope in the mass spectra helped to confirm the fact that sulfur was present in these molecules.

Table IV. Sulfur compounds identified in oxidation products by GC-MS and GLC-FID/FPD analysis.

Sulfur compound	Identification
I	Methylsulfonic acid
II	Ethylsulfonic acid
III	Unknown
IV	Benzenesulfonic acid
V	Unknown
VI	Unknown
VII	Unknown
VIII	Carboxytrimethylbenzene sulfonic acid (T)
IX	Carboxytrimethyldibenzothiophene-1,l-dioxide (T)

T - tentative assignment

Sulfur compounds I, II and IV, methylsulfonic acid, ethylsulfonic acid and benzenesulfonic acid could have been derived from a number of precursors in the parent coal samples. Firstly, mercaptans and thiols will form sulfonic acids when oxidized with peroxides. However, the presence of methylmercaptan, ethylmercaptan and benzenethiol in an exhaustively extracted coal sample is highly unlikely and we believe that the sulfonic acids did not arise from these compounds. In addition, there is a possibility that these sulfonic acids may have come from pendant or terminal thioether groups.

A more feasible route for the formation of these sulfonic acids would be via the oxidation of disulfides. Under peroxide oxidation the disulfide bond is ruptured giving rise to two sulfonic acid groups. Thus the presence of methyldisulfide, ethyldisulfide and benzenedisulfide units in these coals is suggested. The presence of disulfides may explain the desulfurization results given earlier where 25% of the organic sulfur can be removed by dissolving only 4% of the coal.

Sulfur compound VIII, a carboxytrimethylbenzene sulfonic acid, could have come from an aryl disulfide, a thiol or could be derived from the further oxidation of compound IX, a carboxytrimethyldibenzothiophene-1,1-dioxide. This latter possibility is indicated by the lower concentration of compound IX relative to compound VIII in the oxidation products of coals containing mineral matter. Once again, the catalytic effect of the mineral component of coal is indicated.

Another significant point to note about these sulfur compounds is that they all, with the exception of compound VIII, only have one acidic group (whether it be carboxylic or sulfonic). Since the acid group marks the position at which the molecule was bonded into the coal structure, we can conclude that these compounds were only bonded into the coal matrix by one bond, and hence the sulfur compounds must occur as terminal or pendant groups on macromolecular structures. If a sulfur compound was in the middle of a chain or an aromatic cluster for instance, then they would exhibit two, three or more acidic groups depending on their degree of bonding to the chain or cluster. Many of the oxidation products exhibit these features but none of them contain sulfur. These other compounds include short chain dicarboxylic acids and a number of di-, tri- , tetra- and pentacarboxylic acids of benzene. Methyl and hydroxyl derivatives of these benzene carboxylic acids have also been identified. Several of the sulfur compounds remain to be identified. When this is accomplished, we will be able to investigate the terminal sulfur group theory in more detail.

Conclusions

The results of this study support the following conclusions:

1. Coal preparation processes such as micronization, acid treatment, floatation and maceral separation do not affect a series of representative sulfur-containing model compounds. We believe this conclusion can be extrapolated to include those sulfur structures present in coal.

2. Different macerals have different distributions and types of organosulfur compounds. The sulfur chemistry varies not only between macerals from the same coal, but between similar macerals from different coals.

3. Only through maceral separation can some of the sulfur compounds be detected. Maceral separation is therefore to be considered essential not only for the characterization of individual macerals but the characterization of whole coals as well.

4. There are only a limited number of major sulfur structures present in the oxidation products of the extraction residue of coal. These are dominated by sulfonic acids.

5. The majority of the sulfur compounds detected to date are bonded to the coal matrix by only one bond. We believe these sulfur compounds are terminal or pendant groups on macromolecular coal structures.

6. Sulfur NMR spectra have been obtained that represent the organic sulfur derived from the extraction residue of coal. This NMR data agrees very well with the GC-MS data.

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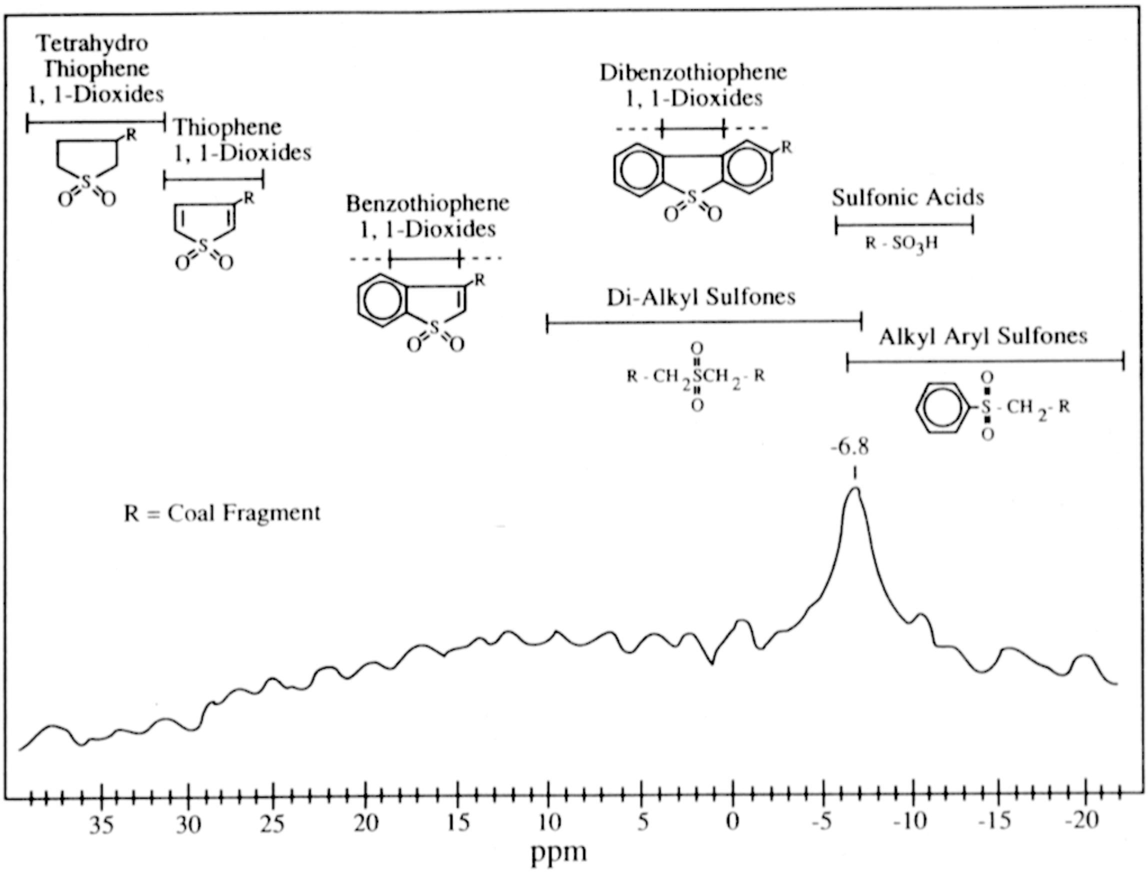

Figure 1. Sulfur-33 NMR spectra of oxidized extraction residue from floated Herrin No.6 coal.

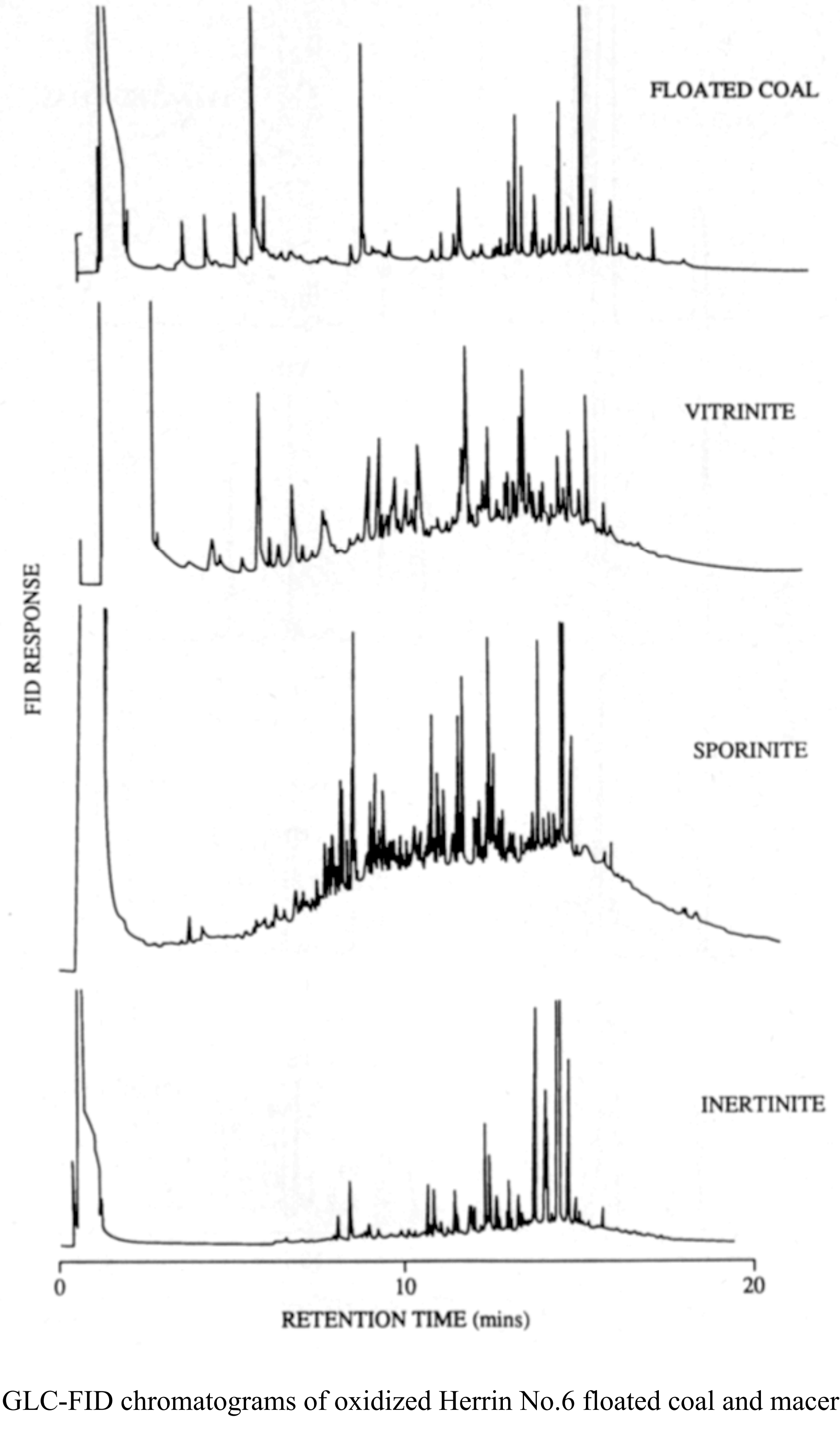

Figure 2. GLC-FID chromatograms of oxidized Herrin No.6 floated coal and maceral samples.

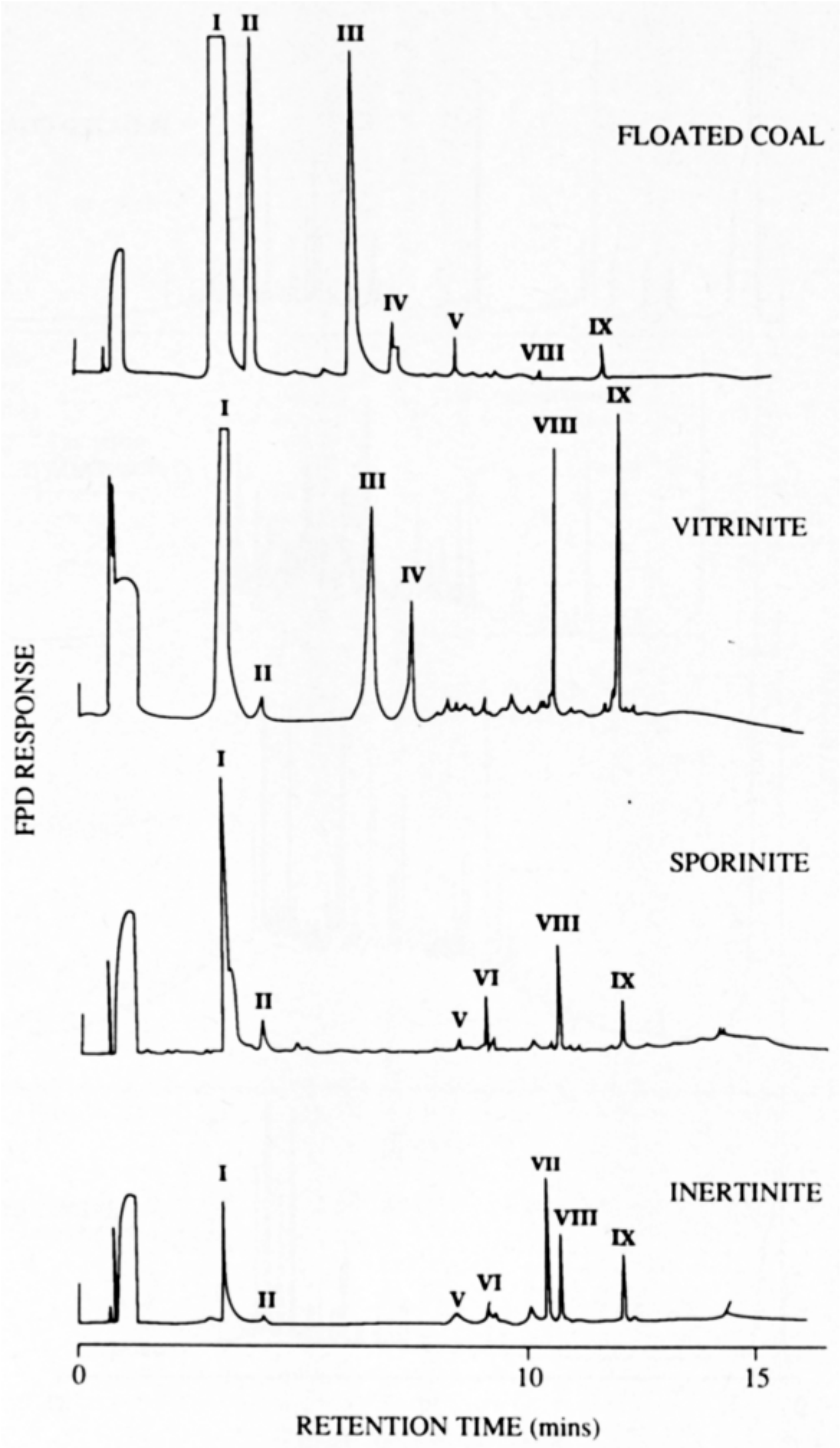

Figure 3. GLC-FPD chromatograms of oxidized Herrin No.6 floated coal and maceral samples.

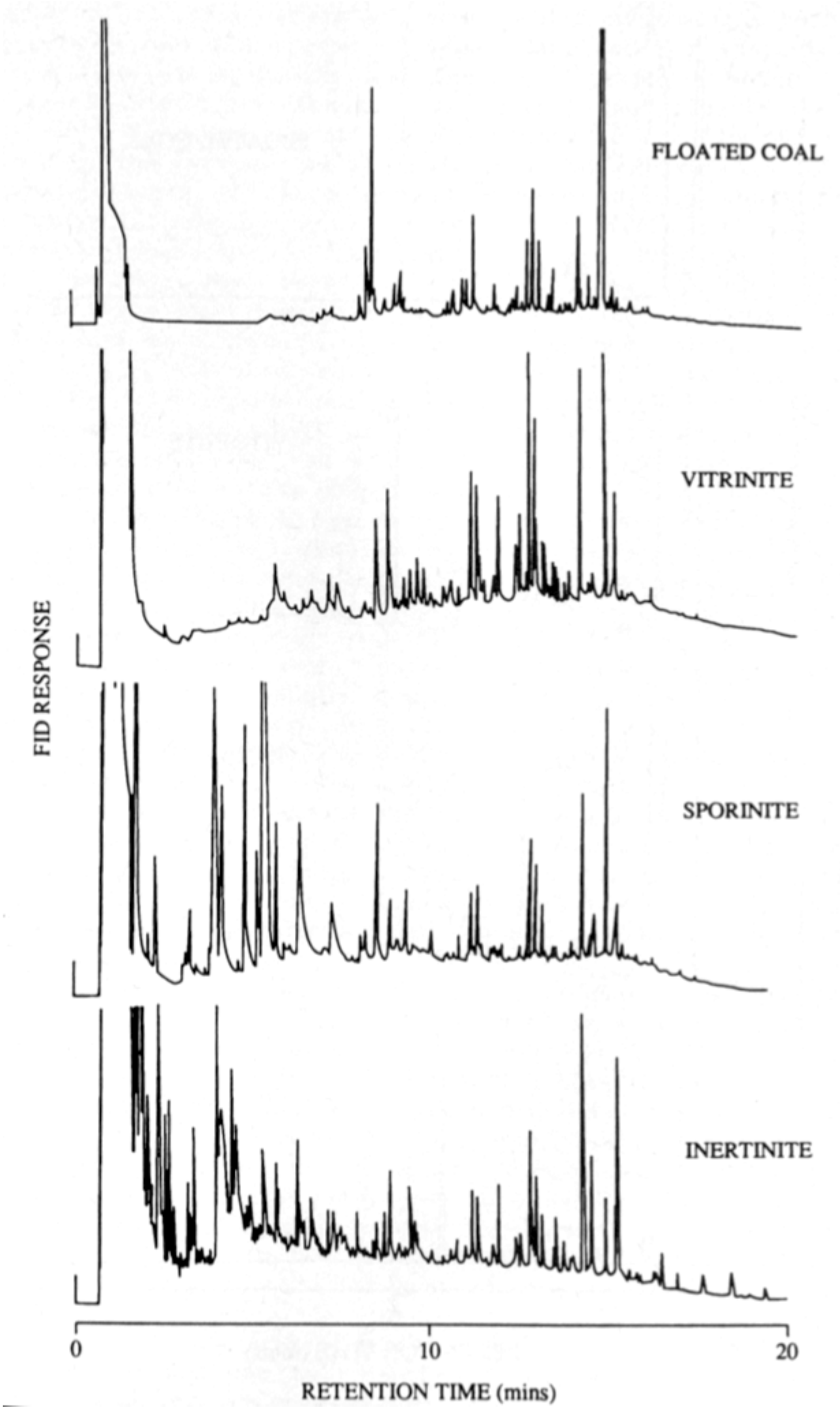

Figure 4. GLC-FID chromatograms of oxidized Indiana No.5 floated coal and maceral samples.

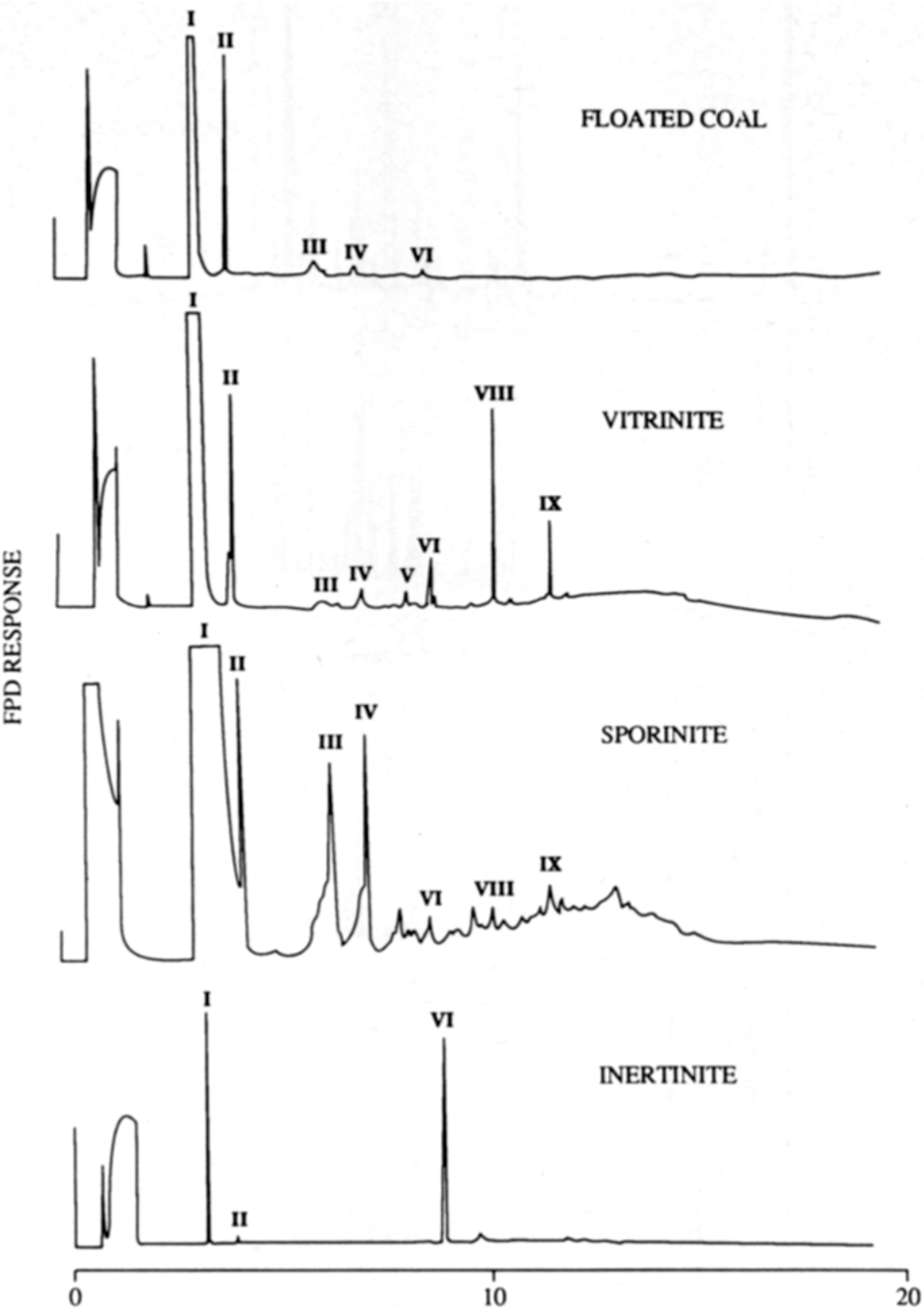

Figure 5. GLC-FPD chromatograms of oxidized Indiana No.5 floated coal and maceral samples.