

Tandem Mass Spectrometry and the Structure of Coal Derivatives

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Introduction

The chemical nature of products derived from coal, whether resulting from liquefaction or some form of chemical degradation, is of particular interest 1) as a means of probing the chemical structure of coal, and 2) in order to optimize the products for potential uses, for example as a fuel or chemical feedstock. Studies of this nature can be enhanced by tandem mass spectrometry (MS/MS) which is particularly well-suited to the analysis of complex mixtures (1-4). Previous investigations have shown the applicability of MS/MS to the analysis of both polynuclear aromatic hydrocarbons (PNAs) and related compounds. Particular examples include hydrodenitrogenation products including tetrahydro nitrogen-containing PNAs (5), long chain alkyl PNAs in a boghead coal (6), and sulfur-containing PNAs in a coal liquid examined after chemical reduction (7). These analyses have made use of all three of the principal scanning modes (8) of MS/MS: daughter spectra for identification of specific constituents, parent spectra for characterization of components having a common substructure, and neutral loss spectra for characterization of constituents having a common functional group. A daughter spectrum is obtained by selecting the ion of interest in the first stage of mass analysis and passing it into the collision cell where it undergoes collision induced dissociation (CID). The resulting fragment ions are then mass analyzed with the second mass analyzer. To obtain a parent spectrum, the second mass analyzer is set to pass a selected fragment ion which results from CID and represents the substructure of interest. The first mass analyzer is scanned over the entire mass range of interest. Neutral loss spectra are obtained by scanning both mass analyzers simultaneously with a mass offset between the two analyzers corresponding to the mass of the selected functional group which is lost as a result of CID. Combining MS/MS with specific chemical degradation reactions as well as using differing modes of ionization, further enhances the utility of MS/MS as a means for addressing the complex nature of fuel materials. The focus of this paper is an attempt to tie a number of investigations, including characterization of products of specific chemical degradations, liquefaction processes and optimization of processing conditions, to a central theme; characterization of the chemical nature of coal.

EXPERIMENTAL

The MS/MS results were obtained using a Finnigan MAT triple quadrupole mass spectrometer (9,10). The samples were admitted into the mass spectrometer via the direct insertion probe. Isobutane chemical ionization was employed at a source pressure of 0.4 torr for a typical case. Argon was used as the collision gas and multiple collision conditions, 2 mtorr, were

chosen to increase the extent of fragmentation. The collision energy chosen was 20 eV.

The specific chemical degradation reactions which have been employed include: ruthenium tetroxide oxidation using ruthenium (III) trichloride in a mixture of water, acetonitrile and carbon tetrachloride at ambient temperature (11), calcium/mixed amine reduction (12), supercritical (steam) extraction (13) and potassium/crown ether reduction (14). In each instance the collaborators referenced provided the chemically degraded materials.

RESULTS AND DISCUSSION

Central to this work has been the identification of specific components not only to characterize them for their intrinsic importance but also to use this information to probe the nature of their possible precursors. Additionally, this work has focussed on the value of MS/MS as a method for comparing product distributions 1) as a means of improving processing conditions for obtaining the desired end product, and 2) to better understand the chemical nature of the original starting material, coal. With these objectives in mind, the differing types of specific chemical degradations as well as scan modes and ionization techniques amenable to MS/MS can be seen to represent an integrated approach to a well-defined problem.

A novel approach to the analysis of sulfur-containing PNAs used a calcium/mixed amine reduction of an SRC II middle heavy distillate (7). Using negative ion chemical ionization (NICI), a series of alkylbenzothiophenes were identified from their reduction products by obtaining a parent scan of m/z 122. The ion at m/z 122 corresponds to the thiotropylium radical anion which is a characteristic fragment of *o*-ethylthiophenol, the reduction product of benzothiophene. This methodology has been extended to an SRC II heavy distillate fraction as well as four coal samples with varying degrees of both total and organic sulfur content. Interestingly, the heavy distillates did not show the presence of alkylbenzothiophenes but rather displayed a series of alkyl dibenzothiophenes, again characterized using a parent scan of m/z 122. (The ion at m/z 122 is also a characteristic fragment ion of *o*-cyclohexylthiophenol, the reduction product of dibenzothiophene.) Furthermore, a number of higher molecular weight sulfur-containing PNAs have also been tentatively identified (using different parent scans) including a series of alkyl naphthothiophenes as well as alkyl benzonaphthothiophenes. The reduced coal sample with the highest organic sulfur content, PSOC 740, was found to have a large abundance of dibenzothiophene, as indicated by the presence of the reduction product at m/z 191 in the parent scan of m/z 122 (Figure 1). This brings up an interesting question with regard to the dibenzothiophene in the coal - is it part of the macromolecular network or interstitially trapped material. The amount of dibenzothiophene identified in the other three coal samples was negligible. All four coals had a significant amount of S_x present as determined by a NICI parent scan of m/z 64, which can correspond to S_2 . The amount of S_x found can be roughly correlated with the inorganic sulfur content of the four coal samples (see Table 1).

Another chemical reduction scheme, involving potassium/crown ether in tetrahydrofuran, has been used in a similar type of investigation. The emphasis of this work has been to probe the chemical structure of coal because this reaction, carried out at room temperature and normal pressure, may reduce the extent of breakdown of the macromolecular structure. Detailed carbon and hydrogen NMR studies from the reduction products of an Illinois No. 6 coal have indicated an abundance of extended chain methylenes, partially hydrogenated PNAs and significant amounts of the hydroxy functionality. Figure 2 is a comparison of the daughter spectrum of m/z 131 an abundant ion in the spectrum of the reduced coal product,

with the daughter spectrum of protonated dihydronaphthalene. The dihydronaphthalene, the presence of which is inferred from the similarity of fragmentation with the authentic compound, and its alkyl homologs may result from a Birch-type reduction of the corresponding alkyl naphthalenes. A series of protonated alkyl phenols extending to C₇ was identified in the same sample using a parent scan of m/z 95 (Figure 3). The first two members of the series protonated phenol (m/z 95) and protonated methylphenol (m/z 109) do not undergo CID to m/z 95 and therefore are not present in the parent spectrum. However, the presence of these two components as well as the other protonated alkyl phenols, m/z 123, 137, 151, 165, 179, and 193, were confirmed using daughter spectra. The principal components identified by MS/MS therefore correlate with structures determined in the NMR studies. Considering the mild reaction conditions it is possible the identified components result from enhanced solubilization and not breakdown of the macromolecular structure.

In addition to the MS/MS analysis of reduction products, the ruthenium tetroxide oxidation products of an Illinois No. 2 coal have been examined (15). In this study the carboxylic acids resulting from oxidation have been identified using both positive ion chemical ionization (PICI) as well as NICI. The emphasis of this work lies not in the identification of given components *per se* but rather in correlating the components identified with possible precursor structures present in the unreacted coal. For example, aliphatic dicarboxylic acids are a major reaction product of ruthenium tetroxide oxidation. Since this reaction occurs via oxidation of an aromatic carbon, these dicarboxylic acids can be postulated as resulting from alkyl bridges, for example, oxidation of tetralin can result in a significant amount of adipic acid (Figure 4). Comparison of the daughter spectrum of protonated adipic acid with the daughter spectrum of m/z 147 from the oxidized coal sample confirms the presence of adipic acid. Table II lists the most abundant types of compounds which have been identified. The presence of aromatic di-, tri-, and tetra carboxylic acids, can be correlated with oxidation of fused-ringed systems. It should be noted that aromatic carboxylic acids are detected as the corresponding anhydrides as a result of dehydration occurring in the hot mass spectrometer ion source. The absence of malonic acid in the oxidation product does not indicate the absence of methylene linkages but rather arises because of the added reactivity of the enolizable protons which can promote further oxidation.

In addition to the identification of specific components, tandem mass spectrometry is valuable as a tool for comparing the character of different samples. An example involves the analysis of the liquefaction products of hand-sorted coal macerals (16), exinite and vitrinite, in order to assess possible chemical differences. Three different fractions of the tetralin-liquefied macerals were examined by MS/MS; maltenes, asphaltenes, and preasphaltenes. The mass and MS/MS spectra of the maltene and asphaltene fractions indicated that maceral-related differences were quite small. Parent scans, however, provided ample information with regard to the presence of alkylbenzenes and naphthalenes. Likewise, the preasphaltene samples also produced little in the way of maceral-related differences. While the compounds identified in the two preasphaltene samples were essentially the same, differences in the relative amounts between the two samples were observed. Twelve different series of alkylhydroxyaromatics, including phenols, pyridinols, dihydroxybenzenes, indenols, indanols, naphthols, di and tetrahydronaphthols, dihydroxynaphthalenes, acenaphthols, anthracenols, and naphthylphenols, were confirmed using both parent and daughter scans. The same series of compounds were present in each maceral sample but the exinite sample had roughly ten times the concentration of hydroxyaromatics as did the vitrinite.

MS/MS can also be used as an aid to maximizing the information obtained from a chemical process. One such process on which this approach has been tested involved the supercritical steam extraction of sulfur from coal. Studies of this type are aimed at finding both economical and efficient means for reducing the sulfur content in coal prior to its being burned. Initial MS/MS studies used a parent scan of m/z 184 to identify the targeted species - alkyl dibenzothiophenes. However, no effect on the relative abundance of dibenzothiophene in the extracted residue was found when either the pressure or extraction time of the process was varied, in spite of large differences in total sulfur removed. Further studies in progress are aimed at extending the number of forms of sulfur being tested as well as including some additional process variables in the sampling scheme.

Tandem mass spectrometry is an efficient way of seeking differences in fuel samples. This can be illustrated by a case involving nine different samples obtained from the same coal, Illinois No. 6, using a variety of extraction and liquefaction conditions. This work is aimed at providing information on the guest-host model for coal structure. That is, are there conditions which can release a significant concentration of small molecules which are entrapped in the macromolecular network. The hexane-soluble extracts of these nine samples were analyzed by MS/MS. While the amount of hexane-soluble material extracted varied from sample to sample, the major alkyl series identified were essentially the same in all nine samples, being dominated by a series of alkyl acenaphthenes (Figure 5). The alkyl chain extends to C_9 as shown in the parent spectrum of m/z 155 from one of the tetralin-liquefied samples. The C_2 - C_9 alkylated acenaphthenes (m/z 183, 197, 211, 225) appear to be the most abundant. This is also consistent with the chemical ionization mass spectrum. These results imply that while progressively harsher extraction/liquefaction conditions can release more material, the chemical nature of that material, in terms of components as well as the alkyl nature, is very similar, at least within the narrow confines of this investigation.

Tandem mass spectrometry has been used to probe a number of questions involving the chemical nature of fuel-related materials. With the available scan modes - daughter, parent, and neutral loss - and ionization techniques it is possible to probe increasingly complex questions concerning the structure of coal. This allows the identification of specific components in coal-derived materials for coal structure characterization and liquefaction product analysis, in addition to comparative studies for process optimization, maceral-related comparisons and investigation of the guest/host coal structure model.

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Table I. Comparison of the amount of S_x determined from a parent spectrum of m/z 64 (S_2^-) with the inorganic sulfur content of the four coals studied.

Coal	Inorganic Sulfur	Counts of $S_x (\times 10^3)$
PSOC 685	1.3%	not detected
PSOC 1300	2.2%	2
PSOC 740	2.3%	7.5
PSOC 1143	3.9%	38

Table II. Dominant carboxylic acids identified in the ruthenium tetroxide oxidation of an Illinois No. 2 coal.

Dibasic Aliphatic Acids	$HOOC(CH_2)_xCOOH, x = 0, 2-8$
Dibasic Aromatic Acids	C_0-C_2
Tribasic Aromatic Acids	C_0-C_2
Tetrabasic Aromatic Acids	C_0-C_2

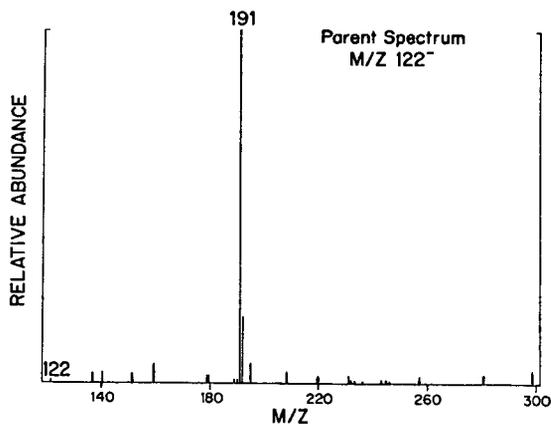


Figure 1. Parent spectrum of m/z 122 (negative ions) from the calcium/mixed amines reduction of a PSOC 740 coal sample, indicating the presence of the reduction product of dibenzothiophene (collision energy 20 eV; argon collision gas pressure 2.0 torr).

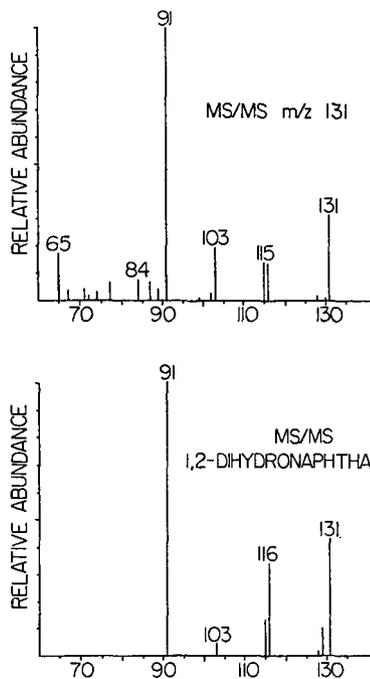


Figure 2. Comparison of the daughter spectrum of protonated dihydronaphthalene with the daughter spectrum of m/z 131 from the potassium/crown ether reduction of an Illinois No. 6 coal (collision energy 20 eV; argon collision gas pressure 2.0 torr).

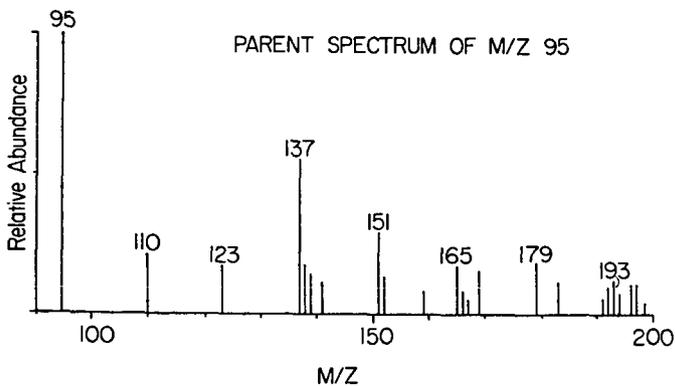


Figure 3. Parent spectrum of m/z 95, for the presence of alkyl phenols, from the potassium/crown ether reduction of an Illinois No. 6 coal (collision energy 20 eV; argon collision gas pressure 2.0 torr).

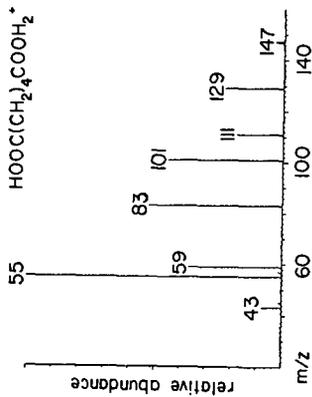
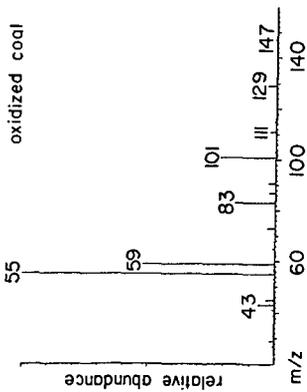


Figure 4. Comparison of the daughter spectrum of protonated adipic acid with the daughter spectra of m/z 147 from the ruthenium tetroxide oxidation of an Illinois No. 2 coal (collision energy 20 eV) argon collision as pressure 2.0 mtorr).

Parents of 155*

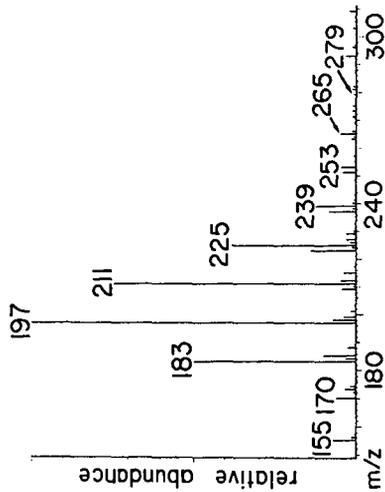


Figure 5. Parent spectrum of m/z 155, for the presence of alkylacetophenones, from the tetralin-liquefied Illinois No. 6 coal hexane soluble fraction (collision energy 20 eV) argon collision gas pressure 2.0 mtorr).