

CHARACTERIZATION OF THE ARGONNE PREMIUM COAL SAMPLES BY FIELD IONIZATION MASS SPECTROMETRY

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INTRODUCTION

The technique of field ionization mass spectrometry (FIMS) has proven to be quite useful for analyzing complex mixtures, particularly fossil fuels. (1) The technique of field ionization (FI) consists of ionizing molecules by the application of an intense electric field and results in the formation of only the molecular ions for most organic compounds. (2) Thus, complications arising from fragmentation during ionization are minimized in this method. Another advantage of field ionization is that the relative field ionization efficiencies of various hydrocarbon types are within a factor of two of alkyl aromatics except for saturated acyclic hydrocarbons, which ionize about a third as efficiently. For many other ionization techniques such as field desorption or low-voltage electron impact, the relative ionization efficiencies can differ by as much as two orders of magnitude. Thus, even without any corrections for sensitivity, the FI mass spectra represent the true molecular weight profile fairly accurately.

In this paper we present the results obtained by pyrolyzing the eight coal samples from the Argonne Premium Coal Sample Program (APCSP) in the inlet of the mass spectrometer and analyzing the volatiles by FIMS. From these data we can deduce relative amounts of several structural types. We also identify salient rank-dependent trends. Some of these trends are known from other studies, (3-6) but FIMS provides an easy means for quantifying them and developing indices that could be used in modeling.

EXPERIMENTAL

The FIMS system used in this study has been described elsewhere. (7) It consists of an activated tantalum foil field ionizer interfaced with a 60° magnetic sector mass analyzer and a PDP 11/23 computer for data acquisition and processing. In a recent study of various configurations for mass spectrometric analysis of coals, Muezelaar and coworkers reported that a combination of direct insertion pyrolysis followed by FI and magnetic sector mass analysis provides the most detailed and accurate mass spectra. (4) We find this result gratifying because it basically vindicates our approach. Approximately 1-2 mg of the sample is introduced via a heatable direct insertion probe. Mass spectral data of the evolving tars are collected by repeatedly scanning the magnet over a preset range (50 to 1400 Da) while the sample is gradually heated at a fixed rate of 5°C/min from the ambient temperature to approximately 700°C. At the end of the run, the sample holder is retrieved and weighed to determine the fraction that was devolatilized during the analysis. For a given sample, many spectra are collected, each representing a certain range of temperature. The individual spectra are added and normalized to obtain a spectrum of the evolved tars. These spectra are also used to produce a thermal evolution profiles of the total tars or of selected mass peaks.

RESULTS AND DISCUSSION

Mass Spectral Profiles

The spectra for the total tars evolved during temperature-programmed pyrolysis for the Argonne coals are shown in Figures 1 and 2 in the order of increasing rank. Several features are immediately apparent and noteworthy. In general, the spectra appear to be composed of two groups of peaks: (a) there is a cluster of peaks consisting of various homologous series in the low molecular weight range (100-200 Da) and (b) a broad, roughly gaussian, distribution of peaks spanning the mass range of 150 to 1000 Da. The low molecular weight cluster is particularly dominant in the Beulah Zap lignite and the Wyodak subbituminous coal. With increasing rank, the prominence of this cluster decreases relative to the broad gaussian

envelope, whose mean appears to shift to higher masses with increasing rank. In the higher rank coals there is also a second cluster of homologous peaks in the 200 to 400 Da range riding on the broad profile. A few peaks in the 300 to 350 Da range that are substantially more intense than the general profile can be seen in the spectrum of the the Utah coal. These peaks are most likely due to biomarkers. The most intense among these is at 324 Da, which corresponds to a tetracyclic monoaromatic alkane (C₃₄H₃₆). There is also a peak at 320 Da, which would correspond to the diaromatic analogue. Interestingly, these peaks have also been observed in the terpenoid resins associated with other coals from Utah.(8)

Chemical Characterization

The most prominent peaks in the low molecular weight range are at m/z 84, 108, 110, 122, 124. These peaks correspond to homologous series of phenols and dihydric phenols. Although assigning structures on the basis of nominal masses only is generally risky, in this case there can be little doubt about the assignment because very few reasonable structures can be written for these masses. Besides, there is corroborating evidence for these structures from studies using high resolution mass spectrometry.(9) The ratio of monohydric to dihydric phenols generally increases with the rank. This trend is illustrated in Figure 3, which shows that the peak at m/z 108 (C₁-phenol) is only about 80% of that at m/z 110 (catechol) for the Beulah Zap lignite, but reaches about 5 times the peak due to catechol for the Upper Freeport and Pocahontas coals. In absolute terms, the intensity of the C₁-phenol peak has only declined by a factor of about 20, while that of the catechol peak has declined by a factor of about 100.

The FIMS data are typically organized in a table with fourteen columns. This arrangement places intensities of ions of a given homologous series in the same column. Thus the intensities of benzene, toluene, C₂-benzenes and so on, all fall in the same column one below the other. An abrupt change in intensity of ions belonging to the same column (apparent degree of unsaturation or \bar{z}) is often an indication of the start of another homologous series. For example, acyclic alkanes and alkyl-naphthalenes share the same nominal masses (i.e., have the same \bar{z} value), and it would not be possible to determine their relative amounts using low resolution FIMS data. However, an examination of the intensities for the homologous series corresponding to acyclic alkanes and alkyl-naphthalene (58, 72, 86, 100, 114, 128, 142, and so on) shows an abrupt increase (about 3 fold) in going from 114 to 128 reflecting the fact that most of the intensity is due to naphthalenes. In general the peak at m/z 156 (C₂-naphthalenes) is the most prominent in that series. Therefore, we have used that peak as a representative of the hydrocarbon (non-oxygenated) structure and compared its intensity with that at m/z 108 (C₁-phenol). Figure 4 shows that the ratio of the intensity at 108 (C₁-phenol) to that at 156 (C₂-naphthalene) decreases with coal rank (primarily due to a decrease in the intensity of m/z 108). The Pittsburgh coal is somewhat at variance with the trend, due to a jump in the cresol evolution.

A examination of the column corresponding to $\bar{z} = -8$, (pentacyclic alkanes or tetralins) often shows a jump in ion intensities at m/z 202, and indicates the start of the pyrene (or fluoranthene) homologous series. This discontinuity is apparent in the high rank coals but not in the low rank coals, and is consistent with increasing importance of polycyclic aromatic structures in the higher rank coals. The Pocahontas and Upper Freeport coals best illustrate the growth of multi-ring systems. Figures 5 shows the intensities of the ions in that column ($\bar{z} = -8$) for the Pocahontas coal. As expected, the intensity of this series begins increasing at m/z 202, due to the prominence of pyrene (and fluoranthene), and reaches a maximum at m/z 244, representing C₃-pyrenes. Less obvious in origin is the periodicity in the intensity of the $\bar{z} = -8$ series. The maxima in this series are nine nominal CH₂ units apart. However, it makes little sense that alkylpyrenes would show maxima at C₃, C₁₂, C₂₁, etc. Much more likely is that the 126 Da difference arises from successive naphthylation of the pyrene nucleus rather than from addition nine methylenes.

Inspection of the spectra for Pocahontas and Upper Freeport coals also reveals the growth of PCAH structures through peri- and cata-condensation. In other words, for a given intense peak there is often another intense peak 50 Da higher, which corresponds to peri-condensation as in the naphthalene to phenanthrene transformation. Often there is an intense peak at 24 Da higher, which corresponds to cata-condensation, for example phenanthrene to pyrene transformation. Two successive peri-condensations followed by a cata-condensation result in a net addition of 224 Da. Interestingly, because 224 is an integral multiple of 14 (16 times), this peak has the same \bar{z} value, and can obscure the naphthylation sequence discussed above. The progressive growth of PCAH structures is not apparent in the lower rank coals, although the start of phenanthrene and pyrene series is clearly indicated even in the Illinois No. 6 coal.

Rather than manually inspect and uncover the prominent repeat units (Δ), we attempted to determine them through Fast Fourier Transform (FFT) procedures. However, chemically significant Δ 's, such as 14, 50, and 126 do not persist for sufficient number of cycles to be easily identified, before they are blurred by other variations. For example, varying degrees of hydrogenation and oxygenation coupled with simple homologation with methylenes cause 2-mass unit shifts, and thus obscure the importance of a given Δ by making $\Delta \pm 2$ also important. Consequently, we have not been able to uncover anything meaningful from FFT analysis.

Liquefaction of low rank coals is known to be more difficult than that of medium and higher rank coals, and requires better liquefaction solvents to achieve reasonable conversion to liquids. One possible reason for this required solvent quality is that the low rank coals are deficient in indigenous "donors" and therefore need them in the solvent. However, if we examine the ratio of the peaks at m/z 132 and 128 (representing tetralin and naphthalene respectively), we find that the ratio actually decreases with increasing rank. Thus, the lack of indigenous donors is not an appropriate explanation for the difficulty of liquefying low rank coals, and the propensity for the structures in low rank coals to undergo crosslinking reactions (and/or the crosslinked nature of the starting structures themselves) is a more likely explanation.

Thermal Evolution Behavior

As mentioned above, FIMS data are collected over the temperature range as many individual spectra. From these spectra, we can construct the evolution profiles of either total tars or of selected ions. In order to compare the absolute amounts of these ions from different coals it is necessary to correct for the total weight of tars evolved. However, the total weight loss obtained at the end of FIMS analysis also includes light gases, such as CO, CO₂, water, and methane, which are generally excluded from FIMS analysis primarily for two reasons. First, they do not field ionize efficiently, and second, scanning the magnet down to these low mass range requires an inordinately longer time that could compromise the data of the bulk of the materials. These gases are more readily analyzed by TG-FTIR, and in that regard FIMS complements this technique. For inter-sample comparisons we corrected the normalized FIMS intensities for the tar yields reported by Solomon and coworkers for pyrolysis of these coals at a comparably slow heating rate. We examined the thermal evolution profile of several compound types. The principal finding is that while the amounts of these compound types changed substantially with rank, the evolution profile of most compound types, except phenolics, showed only a slight shift to higher temperatures with increasing rank. This result is consistent with the essence of the FG-DVC model of Solomon and coworkers.⁽⁶⁾

Table 1

Coal	Weight Loss During FIMS (%)	Number Average Molecular Weight	Weight Average Molecular Weight
Beulah Zap	42	239	370
Wyodak	39	274	404
Illinois No. 6	42	402	441
Utah Blind Canyon	45	444	568
Lewiston-Stockton	31	436	521
Pittsburgh	39	379	459
Upper Freeport	27	422	496
Pocahontas	16	455	501

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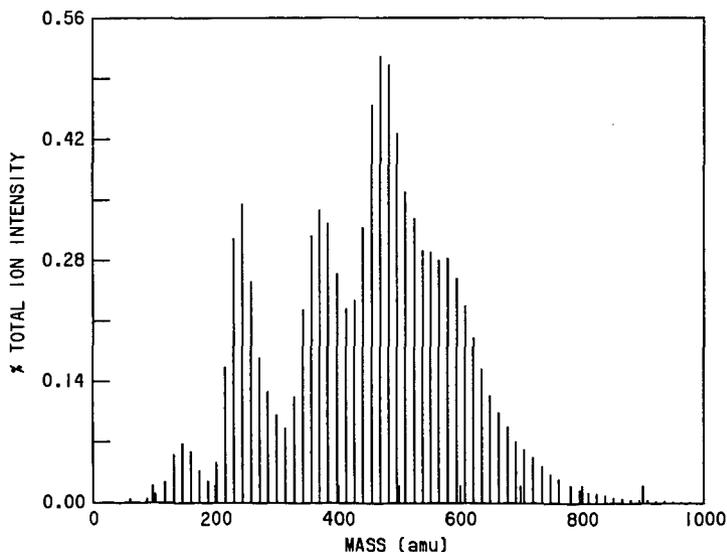
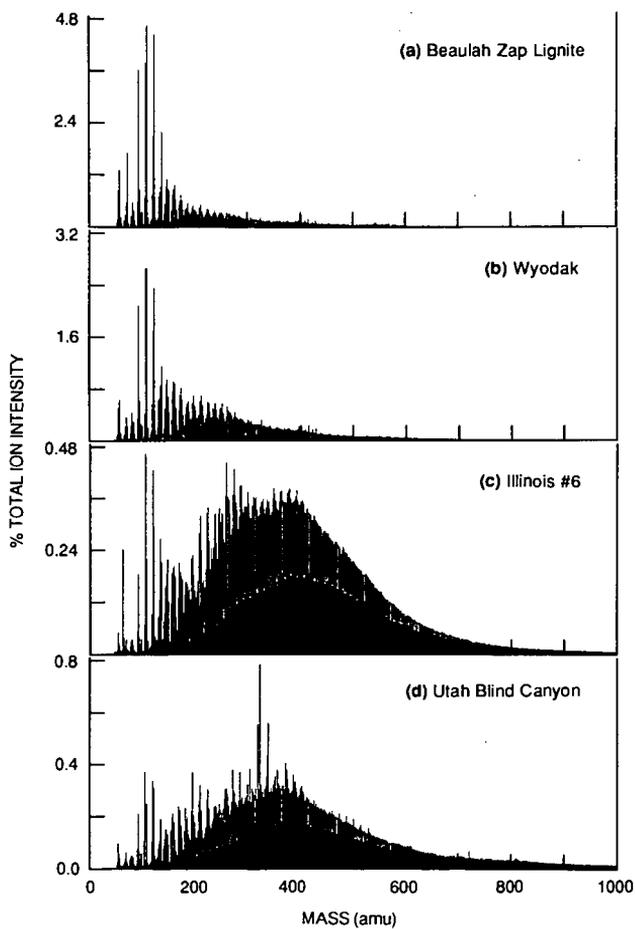
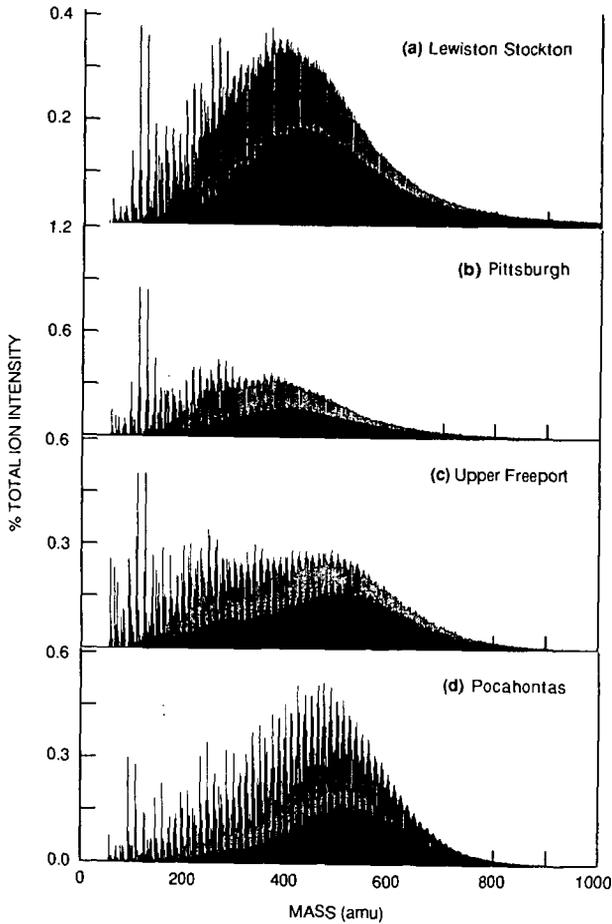


Figure 5. Intensities of ions belonging to the $z = -8$ series for the Pocahontas coal.



CA-2302-2

Figure 1. FI-Mass spectra of the four lower rank coals from the Argonne Premium Coal Sample Program.



CA-2302-3

Figure 2. FI-Mass spectra of the four higher rank coals from the Argonne Premium Coal Sample Program.

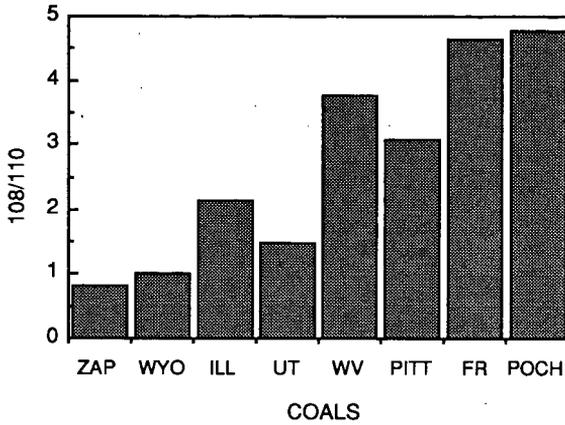


Figure 3. Variation of the relative amounts of representative monohydric and dihydric phenols with coal rank.

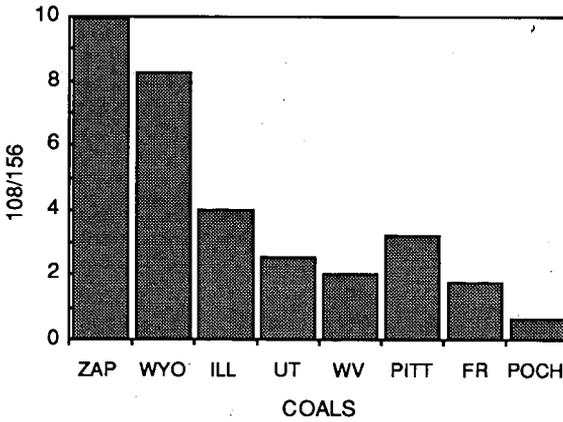


Figure 4. Variation of the relative amounts of representative phenols and hydrocarbons with coal rank.