

THE MOBILE PHASE IN COAL VIEWED FROM A MASS SPECTROMETRIC PERSPECTIVE

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INTRODUCTION

In recent years few topics have generated a more spirited discussion among coal scientists than the issue of the putative binary (mobile + network) phase nature of coals [1]. Initially based on NMR observations [2], the concept of a "mobile phase" in coal soon came to encompass a broad range of more or less readily extractable and/or distillable lower molecular weight (MW) components, variously referred to as "guest molecules" [3], "clathrates" [1,4] or simply, and perhaps most succinctly, "bitumen" [5].

None of these terms appears to be completely satisfactory. The concept of "mobility" in NMR spectroscopy is quite different from that in the field of separation science, where mobility generally requires a measurable degree of solubility and/or distillability in liquid or gaseous media, respectively. For example, polymethylene-like moieties, such as found in some coal components [6], are highly "mobile" in NMR terms [1], without necessarily being extractable by solvents or distillable by nondestructive heating.

The term "guest molecules", originally introduced to indicate specifically labeled marker molecules used in NMR studies of coal [7], is equally unsatisfactory for mobile phase components indigenous to the coal itself. Also, there appears to be insufficient evidence for the presence of sizeable quantities of true "clathrates" to rule out other possibilities, e.g., strong noncovalent bonding rather than physical entrapment.

Finally, completely equating the "mobile phase" with solvent (e.g. pyridine) extractable "bitumen" in coal ignores the potential presence of colloidal particulate matter in the pyridine extracts as well as possible solvent-induced scission of weak chemical bonds. Furthermore, the solvent-extractable fraction may well include macromolecular components, such as resinates.

Mass spectrometric observations have thus far played a rather limited role in the "mobile phase" discussions [1] but are starting to shed some light on the key question: is there conclusive evidence for the presence of a chemically and/or physically distinct "mobile phase", as opposed to a continuum of possible molecular sizes and structures?

In the context of the present discussion the term "mobile phase" will be used to describe those components which can be thermally extracted ("distilled", "desorbed") under vacuum at temperatures below the thermal degradation range of the coal. The residue, designated as the nonmobile ("network") phase, is

thermally degraded in the pyrolysis temperature range. Of course, the onset of pyrolysis may vary considerably, depending on heating rate, rank and coal type [8].

EXPERIMENTAL

Two samples of -100 mesh ANL-PCS (Argonne National Laboratory-Premium Coal Sample) coal, a Pittsburgh #8 seam (hvAb) and a Beulah Zap seam (lignite) sample, were analyzed by vacuum pyrolysis field ionization mass spectrometry (Py-FIMS) and Curie-point pyrolysis low voltage electron ionization mass spectrometry (Py-EIMS) in the time-resolved (TR) mode. In addition, a sample of fresh -60 mesh Hiawatha seam (hvBb) coal, obtained from an Emery County (Utah) mine was analyzed by TR Py-EIMS. Conventional characterization data on ANL-PCS coals can be found elsewhere [9].

For temperature-programmed pyrolysis in combination with TR-FIMS, about 100 ug samples were transferred into a quartz crucible and introduced into the high vacuum (10^{-3} Pa) of the ion source (200 C). The instrumental setup using a Finnigan MAT 731 double-focussing mass spectrometer, a combined EI/FI/FD/FAB ion source and a AMD Intectra direct introduction system has been previously described in detail [10]. The samples were heated linearly from 50 C to 750 C at a rate of 100 C/min. In general, 34 FI mass spectra were recorded in the m/z 50-900 mass range.

The Py-EIMS experiment was performed using an Extranuclear 5000-2 Curie-point Py-MS system. The coal sample was hand ground into a fine, uniform suspension in Spectrograde methanol (5 mg of sample per ml of methanol). A single 5 μ l drop of the suspensions was coated on the ferromagnetic filament (Curie-point temperature of 610 C) and air-dried under continuous rotation for approximately 1 min, resulting in 25 μ g of dry sample on the filament. The filament was inserted into a borosilicate glass reaction tube and introduced into the vacuum system of the mass spectrometer. Directly in front of the open, cross beam type electron ionization chamber the ferromagnetic wire was inductively heated for 0.4 s at a rate of approximately 1500 K/s to an equilibrium temperature of 610 C (as determined by the Curie-point temperature of the wire). The pyrolysis inlet was preheated at 200 C to reduce the condensation losses. Other MS conditions were as follows: electron impact energy 12 eV, mass range scanned 50-200 amu, number of scans 41, total scan time 15 s.

RESULTS AND DISCUSSION

Is there a chemically and/or physically distinct "mobile phase" in coal as opposed to a continuum of molecular sizes and structures? The temperature-resolved total ion intensity (TII) profile of a Pittsburgh #8 coal in Figure 1 obtained by temperature programmed Py-FIMS shows the presence of a low temperature "hump" which appears to explain 25-30% of the total integrated FI signal intensity in the mass range m/z 50-900. Previously, Chakravarty et al. [11] reported a similar profile for Pittsburgh #8 coal obtained by Curie-point pyrolysis in combination with time-resolved low voltage EIMS and were able to demonstrate that the low temperature hump consisted primarily of homologous series of alkylsubstituted aromatic (e.g., benzenes, naphthalenes, phenanthrenes) and hydroaromatic (e.g., tetralins) compounds. These compounds were interpreted to represent the thermally extractable ("vacuum distillable") fraction of the well known "bitumen" component of most high volatile bituminous coals.

More recently, Yun et al. [12] confirmed the presence of this low temperature hump in vacuum thermogravimetry (TG)/MS studies of ANL PCS coals using low voltage EIMS. An important aspect of the latter study was that the mass spectra obtained for the thermally extractable components as well as for the main pyrolysis event were found to be virtually indistinguishable from those observed by Chakravarty et al. using Curie-point Py-EIMS, notwithstanding a 5 orders of magnitude lower heating rate (3.3×10^{-2} C/s vs. 1.5×10^3 C/s) and 3 orders of magnitude larger sample (50 mg vs. 25 μ g).

Furthermore, with proper preheating of the transfer zone between pyrolysis and ionization regions, the low voltage EI mass spectra of Pittsburgh #8 coal were shown to be highly similar to the corresponding FI mass spectra in the m/z 50-300 mass range when allowing for known differences in ion transmissivity between the different types of mass spectrometers used [13]. In other words, time-resolved TII profiles similar to those shown in Figure 1 as well as to the corresponding mass spectra in Figure 2a have been observed (up till m/z 300) by means of 3 separate Py-MS methods, together covering a broad range of different pyrolysis, ionization and mass spectrometric detection techniques.

The advantages of the FIMS data shown here are that little or no fragmentation of molecular ions occurs during the ionization process and that FI response factors for aromatic and hydroaromatic compounds tend to show relatively little variation [14]. In combination with the large mass range and nearly constant ion transmissivity of the magnetic sector instrument used, the FI ion profiles and FI spectra shown in Figures 1 and 2, respectively, are suited for making reliable semiquantitative estimates with regard to relative the yield and molecular weight distribution of coal tar fractions consisting primarily of aromatic and hydroaromatic or alicyclic compounds. Unfortunately, FI response factors for aliphatic compounds show a great deal more variation [15]. Consequently, for the purpose of this discussion no attempt will be made to quantitate the contributions or molecular weight distributions of aliphatic components in spite of their well recognized role in coal pyrolysis processes.

Comparison of the low temperature component ("mobile phase") and high temperature component ("bulk pyrolyzate") spectra in Figures 2b and 2c, respectively, reveals roughly similar average molecular weights ($M_n \sim 350$) but rather different MW distributions. Moreover, there are pronounced differences in relative FI signal intensities, especially in the mass range up to m/z 400.

Figure 3 shows the relationships between the temperatures and molecular weight distributions for 6 successive regions of the TII profile in Figure 1. Interestingly, regions a, b and c, primarily representing the low temperature components, show relatively narrow MW distributions around M_n values which markedly increase with temperature. This is consistent with the proposed interpretation of the low temperature "hump" as a vacuum desorption and distillation process rather than as a pyrolytic process. By contrast, regions d, e and f, representing the major TII maximum in Figure 1, exhibit much broader MW distributions characterized by a gradually decreasing average molecular weight of the pyrolyzate. This would seem to be consistent with the proposed interpretation of the major TII peak as the "bulk pyrolysis" event [11].

The transition between c and d is rather abrupt, suggesting that we may indeed be witnessing contributions from two more or less discrete populations of molecules with regard to molecular size distributions. However, in view of the extremely complex interplay between intramolecular and intermolecular, as well

as intraparticle and extraparticle, parameters in the experiments described here, the possible presence of a continuum of molecular sizes can certainly not be ruled out at this point.

More informative, perhaps, are the marked differences in relative FI signal intensities between the mass spectra shown in Figures 2b and 2c. In agreement with the previously mentioned results reported by Chakravarty et al. [11] and Yun et al. [12], the mass spectrum of the low temperature component (Figure 2b) appears to be dominated by homologous series of aromatic and hydroaromatic compounds. Chemical identification of many of the compounds up to MW 350 has been accomplished by high resolution GC/MS [16,17], although precise identification of the many possible isomeric structures involved will have to await the availability of suitable reference compounds.

The spectrum of the bulk pyrolysis event in Figure 2c appears to be dominated by hydroxy aromatic compounds, e.g., alkylsubstituted phenols and naphthols. Positive identification of these compounds is much less straightforward, although a surprisingly high degree of correspondence can be found with Py-GC/MS data on Pittsburgh #8 coal [18]. Moreover, Chakravarty et al. have demonstrated that the main pyrolysis event can be deconvoluted into at least three overlapping events involving vitrinitic moieties in addition to alginite/cutinite-like and sporinite-like components [11].

In Curie-point Py-MS studies of maceral concentrates [19], vitrinitic moieties were shown to be the main source of the hydroxy aromatic components. Consequently, the hydroxy aromatic signals observed in Figure 2c appear to be primarily derived from vitrinite-like components by means of pyrolytic processes. Presumably, therefore, the "nonmobile phase", rather than the "mobile phase", is the main source of the phenols observed in TG/MS and Py-MS studies of Pittsburgh #8 coal. Further support for this conjecture comes from the observation that phenolic products are also observed in Py-MS analysis of pyridine extracts of Pittsburgh #8 coal known to contain colloidal matter whereas the corresponding tetrahydrofuran extracts, free of colloidal material, produced no phenols [18].

In low rank coals, such as lignites, vitrinitic components have been shown to produce abundant (alkyl) dihydroxy benzene and methoxy hydroxy benzene compounds of a structural type which can be traced back to fossil lignin moieties [20]. In agreement with these earlier studies, the high temperature component spectrum of a Beulah Zap lignite (Figure 4c) exhibits dominant (alkyl) dihydroxy benzene signals at m/z 110, 124, and 138. The low abundance of FI signals above m/z 200 can be attributed to the more highly crosslinked nature of the macromolecular network phase in lignites.

As shown in Figure 4b, the low temperature fraction of Beulah Zap lignite reveals a completely different type of mass spectrum. From previous studies on soil organic matter by Hempfling et al. [21], the FIMS signals in Figure 4b are known to represent various plant-derived compounds such as n-fatty acids or monomeric esters (m/z 368, 396, 424, 452, 480) and aromatic diesters (m/z 544). Apparently, we are dealing with thermally extractable "biomarker" compounds which have not yet been linked into the macromolecular network phase of the lignite.

The above observations point to the importance of rank and depositional environment in defining the molecular characteristics of the "mobile phase" as

well as the "network phase" of coals. To complicate matters further, post-depositional factors, such as "weathering" during storage or transportation, also strongly effect the composition of both phases, as reported by Jakab et al. [22]. Figures 5 and 6 illustrate the effects of mild oxidation of a Hiawatha hvb coal for 100 hours at 100 C under controlled laboratory conditions, as measured by time-resolved Curie-point Py-MS. Both the low temperature hump as well as the bulk pyrolysis event are markedly reduced. Moreover, the composition and nature of the low temperature components have undergone a dramatic change (Figure 5b). The alkyl substituted naphthalenes and tetralins dominating the spectrum of fresh coal (Figure 5a) are nearly completely gone. Instead, we now find low MW, oxygen-containing mass signals apparently representing aliphatic carboxylic and carbonylic functionalities, e.g., liberated by low temperature pyrolysis of weak oxygen bonds [22]. These observations would seem to indicate that it is pointless to study "mobile phase"/"network phase" phenomena in coal samples of uncertain weathering status.

CONCLUSIONS

Temperature-programmed vacuum pyrolysis in combination with time-resolved soft ionization mass spectrometry allows principally to distinguish between two devolatilization steps of coal which are related to the "mobile" and "non-mobile" phase, respectively. The mass spectrometric detection of almost exclusively molecular ions of the thermally extracted or degraded coal products enables to study the change of molecular weight distribution as a function of devolatilization temperature. Moreover, major coal components can be identified which are released at distinct temperature intervals.

When limiting our analysis and discussion of mobile phase components to the thermally extractable fraction, we may conclude that the yields and compositions of these products (estimated to constitute 5-15% of dmmf coal weight) are strongly dependent on rank, coal type and weathering status. In coals of hvb and higher rank the nature of the thermally extractable bitumen fraction is consistent with that of a natural pyrolyzate formed by catagenetic processes during the "oil formation window" stage of maturation with subsequent loss of the more reactive oxygen containing moieties. Not surprisingly, in low rank coals various types of relatively little altered "biomarkers" molecules appear to be important constituents.

Furthermore, artificial "weathering" of coal under carefully controlled conditions in the laboratory, reveals a rapid loss of thermally extractable mobile phase components (possibly by "grafting" to the network phase [23]) accompanied by a decrease in total pyrolysis yields. This points out that in future discussions of "mobile phase" phenomena only results obtained on coals of known weathering status, e.g., ANL-PCS coals, should be used.

With regard to the central question whether there exists a chemically and/or physically distinct "mobile phase" in coals, mass spectrometric data on ANL-PCS coals (only 2 of 8 are presented here) strongly support the presence of a thermally extractable, bitumen-like fraction which is chemically distinct from the remaining coal components.

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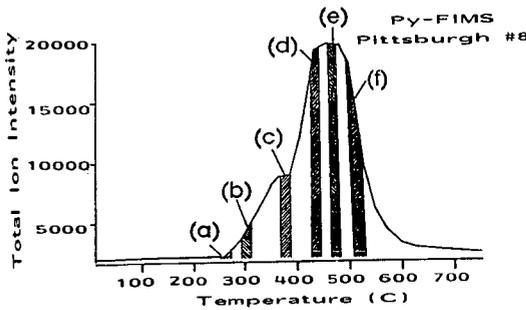
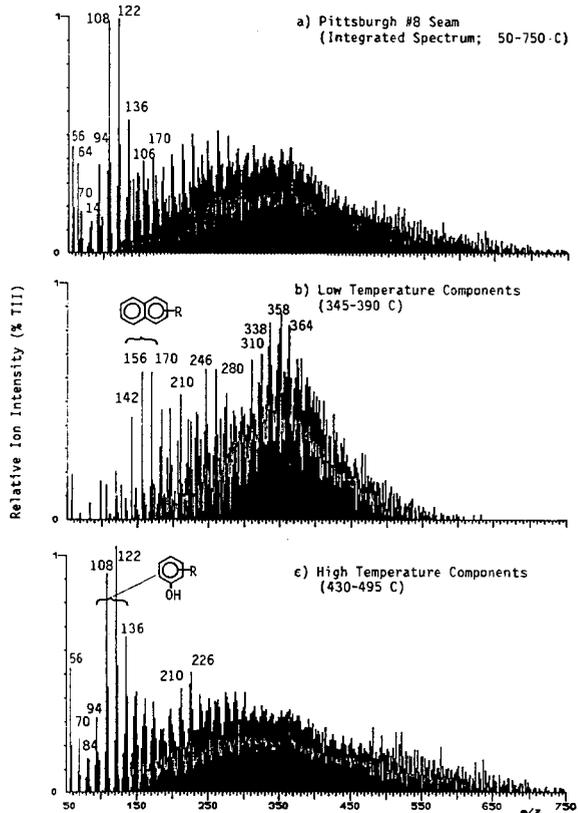


Figure 1. Thermogram of a Pittsburgh #8 coal sample showing a distinct low temperature release of mobile phase components. Crosshatched intervals a-f correspond to molecular weight profiles of FI ions in Figs. 3a-f, respectively.

Figure 2. Comparison of Pittsburgh #8 (hvb) coal Py-FI mass spectra recorded over different temperature intervals. Note marked differences between low temperature components in (b), thought to represent primarily vacuum distillable "mobile phase" constituents, and high temperature components in (c), thought to represent mainly pyrolysis products derived from the macromolecular "network phase".



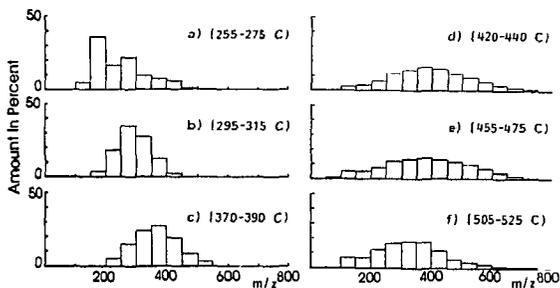


Figure 3. Molecular weight distributions of pyrolyzates in six successive temperature intervals during Py-FIMS analysis of Pittsburgh #8 coal. Each interval corresponds to a cross-hatched region in Figure 1. The FI signal intensities were added in arbitrarily chosen mass classes of 50 daltons.

Figure 4. As Figure 2 but representing Beulah Zap seam lignite. Note biomarker pattern of vacuum distillable low temperature component in (b). Further note marked difference with Pittsburgh #8 in Figure 2.

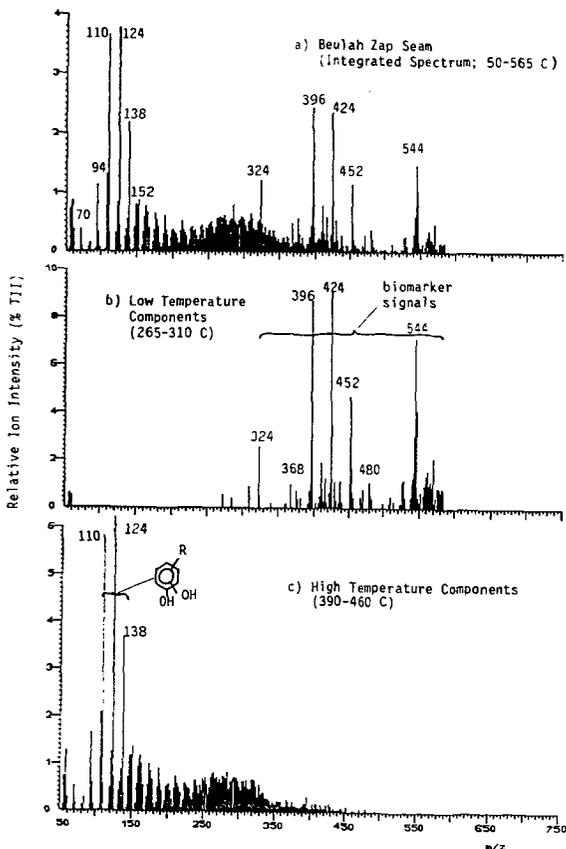


Figure 5. Time-resolved TII profiles of a Hiawatha seam (hvBb) coal obtained by Curie-point pyrolysis in combination with low voltage EIMS. Note effect of artificial "weathering" compare with Figure 6.

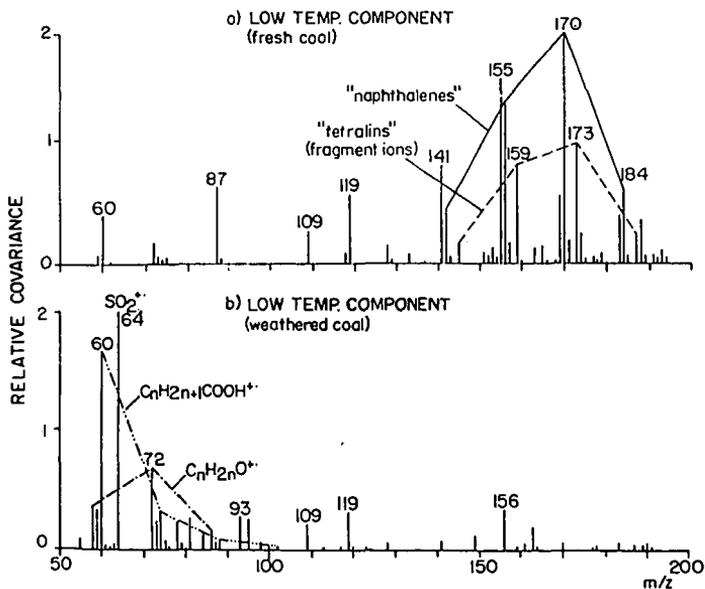
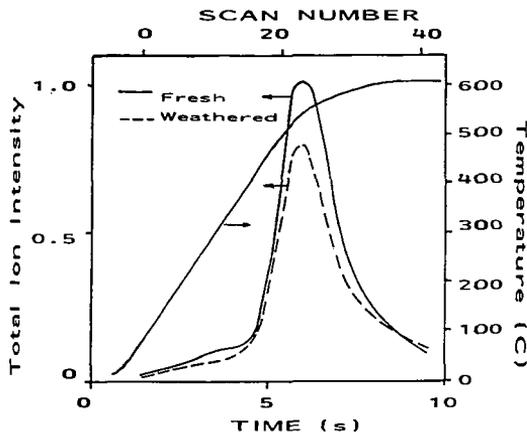


Figure 6. Comparison between low temperature component spectra obtained by low voltage EIMS. Note pronounced effect of mild artificial "weathering". Compare with Fig. 5.