

## Characterization of Coal-Derived Materials by Laser Desorption Mass Spectrometry\*

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Keywords: laser desorption mass spectrometry, coal, maceral

### ABSTRACT

Laser desorption time-of-flight mass spectrometry (LD/TOF MS) is used to characterize complex mixtures of large molecules derived from coals and separated coal macerals. Three groups of macerals, namely liptinite, vitrinite, and inertinite from Argonne Premium Coal Sample 7 were separated by a density gradient technique and subjected to small scale liquefaction. Samples of the maceral products were exposed to laser pulses from a XeCl-Excimer laser or the fourth harmonic output of a Nd:YAG laser. The general features of this method are the virtual absence of ion signal below  $m/z$  200, a distribution of masses from  $m/z$  200 to beyond  $m/z$  1000 and reduced mass fragmentation in contrast to EI and FAB, where much fragmentation is present below  $m/z$  200.

### INTRODUCTION

The chemically and physically heterogeneous nature of coals dictates that their structure and reactivity patterns be complicated. The determination of the structural building blocks in coals is of crucial importance in research on their reactivity. The problem is complicated by the fact that the molecular structure of the organic part of coal is not dependent on a single molecule, but on a complex mixture of molecules that vary according to the type of coal. A number of complementary approaches have been used to investigate the structure of coal. Mass spectrometry has played an increasing role in characterizing the organic part of coals and coal-related materials. The approaches have varied from pyrolysis MS (pyMS) to fast atom bombardment (FABMS) to desorption chemical ionization mass spectrometry (DCIMS). Each of these approaches has particular strengths. For example, pyMS has shown heteroatom containing molecules and field ionization MS (FIMS) has produced molecular weight distributions of volatile tars<sup>1,2</sup>.

Laser ablation techniques have been applied to coal characterization resulting in small molecules and in some cases fullerenes at high laser powers<sup>3-5</sup>. Our laser desorption (LDMS) study differs from previous laser ionization mass spectrometry studies. Our goal is to desorb ions characteristic of the molecular weight distribution present in the coal sample rather than to pyrolytically ablate material from the coal surface. The desorption laser is intentionally operated close to the ionization threshold to minimize any chance for fragmenting the desorbing material. In this paper the LD/TOF mass spectrometer is described and results on the molecular weight

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\*This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

distributions of coal derived materials are presented. These data are also compared to other mass spectral methods.

## EXPERIMENTAL

### Coals

A complete discussion of the characteristics of the coals used in this study has been reported. Vacuum pyrolysis tars of Upper Freeport mv bituminous coal (APCS 1) are used to compare with other ionization techniques<sup>6</sup>. A coal selected for a second study was a high-volatile West Virginia bituminous coal from the Lewiston-Stockton Seam (APCS 7)<sup>7</sup>. In this study, three groups of macerals, namely liptinite, vitrinite, and inertinite were separated by a density gradient technique and subjected to small-scale liquefaction in tetralin. The products of the liquefaction were separated into light gases and hexane-soluble (oils), toluene-soluble (asphaltenes), and tetrahydrofuran-soluble (preasphaltenes) fractions. The LD/TOF data for the toluene solubles is presented here.

### Lasers

The laser light source used for laser desorption is either a XeCl-excimer laser (308 nm, 10 ns pulse-width) or a Nd:YAG laser (266 nm, 200 ps pulse-width). The lasers are operated at a 1 to 100-Hz repetition rate at a constant fluence of approximately 10-100 mJ/cm<sup>2</sup>, close to the ionization threshold to minimize fragmentation on the surface or in the gas phase. Focusing is accomplished with a 300-mm spherical lens for the desorption laser. Positioning of the desorption laser on the 1.5 cm diameter sample is aided by a He-Ne laser collinear with the desorption laser and a closed-circuit video image of the sample surface.

### Mass Spectrometer

The instrument used here is a time-of-flight mass spectrometer constructed in-house. The mass spectrometer is established by a sample surface (a stainless steel polished surface), an acceleration field, x- and y-deflection fields, and field-free region with an ion detector at the end (Figure 1).

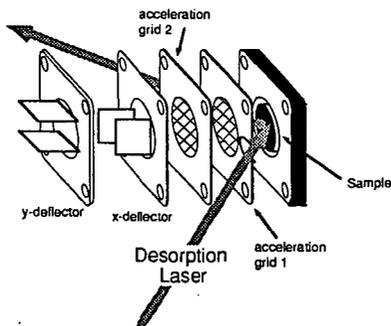


Figure 1. Schematic diagram of the ion-source region of the LD/TOF mass spectrometer.

This design is simpler than in conventional TOF instruments as the ionization source is already pulsed and therefore no pulsed acceleration voltage is needed. The resolution of the mass spectrometer is laser-pulse width limited with  $m/\Delta m$  of approximately 400 FWHM for the 308 nm-pulse and 1500 for the 266 nm-pulse. The mass spectrometer includes vertical and horizontal deflection plates for ion beam steering, a set of pulsed-deflection plates for eliminating high-intensity low-mass ions and an Einzel lens system. The overall flight path length is 120 cm with acceleration distances of 4 mm for each of the two acceleration regions. Ions are produced at threshold irradiances to minimize fragmentation of the desorbing molecules. The ions thus formed are accelerated to 10 keV and detected using a dual-channelplate detector with a modest post-acceleration potential. Ion currents are recorded in a LeCroy 8828 transient recorder with a maximum time resolution of 5 ns or by single-pulse counting in a LeCroy 4208 time-to-digital converter with a time resolution of 1 ns. Further processing of the data is accomplished in a PC-based software system. The typical operating vacuum is  $5 \times 10^{-9}$  Torr.

The samples are prepared in a nitrogen-purged isolation box by allowing solutions of the soluble coal material to evaporate as thin films on the stainless steel sample probe. Approximately  $50\mu\text{g}$  of sample is placed on the probe. Less than  $10^{-4}$  of the sample is consumed in a typical measurement. The remainder of the sample may be recovered intact following the measurement. LDMS spectra are produced by exposing the samples distributed as a thin layer on a stainless steel sample holder to the laser beam.

## RESULTS AND DISCUSSION

The LD/TOF mass spectrum obtained from an Upper Freeport mv bituminous coal tar is shown in Fig. 2.

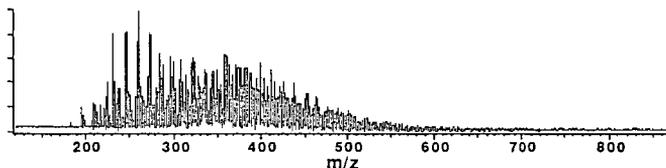


Figure 2. LD/TOF mass spectrum of Upper Freeport (APCS 1) vacuum pyrolysis tars.

The mass spectrum shows a virtual absence of ion signal below  $m/z$  200. This is in contrast to EI and FAB, where much fragmentation is present below  $m/z$  200. Several homologous ion series are present in the spectrum. A possible structure can be assigned to each of these series based on PyHRMS results from the same coal sample. The prominent series at  $m/z=230$  to 272 with a  $\Delta m$  of 14 is assigned to alkyl-pyrenes or fluoranthenes. Another major series contains two different species, alkylphenyl-naphthalenes and alkylhydroxy-pyrenes or fluoranthenes. In FAB MS the major cluster ions do not coincide with clusters seen in LD. The number average

molecular weight in the LD spectrum is 350. This compares favorably with DCI (325), while both FAB and FIMS show higher molecular weight distributions<sup>8</sup>. FAB and FIMS are known to be efficient in ionizing polar molecules and the higher molecular weight distributions may reflect a distribution skewed by minor amounts of higher molecular weight polar molecules.

The LD mass spectra of the toluene-soluble (asphaltenes) macerals are shown in Fig. 3.

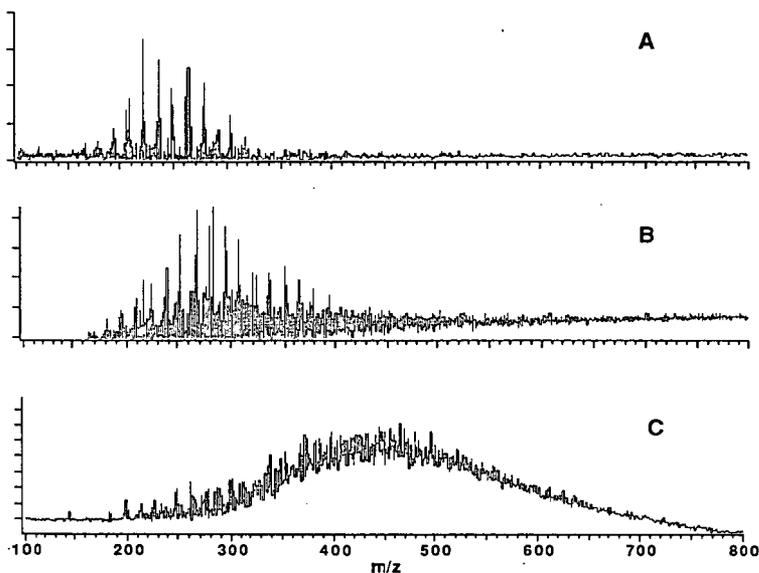


Figure 3. The LD/TOF mass spectra of toluene soluble (asphaltenes) macerals. A, liptinites; B, vitrinites; C, inertinites.

The three different maceral groups were placed in well-defined areas on a single sample probe for the mass measurement. The 200-ps 266-nm laser beam was then translated to each spot to ensure identical irradiance and desorption conditions. The first striking feature is that the LD/TOF data is consistent with carbon aromaticity and hydrogen content data. The most significant differences among the macerals are known to be their hydrogen content and carbon aromaticity<sup>7</sup>. The hydrogen content and the hydrogen/carbon ratio decrease in the order liptinite>vitrinite>inertinite, while the aromaticity shows the opposite trend. The inertinite, which is the least reactive maceral, is often thought to contain 'char-like material. It contains large multinuclear aromatic clusters. There is a clear trend of increasing average molecular weight of the ions with increasing carbon content (rank). This suggests that for a given irradiance LD/TOF is a good indicator of coal rank.

The LD/TOF MS of the liptinite (Fig. 3A) shows a single ion series separated by 14 amu extending from  $m/z$  180 to 350. This alkyl type separation suggests a strong aliphatic methyl group content. This is supported by IR measurements. The number average molecular weight for the liptinite is 239. The vitrinite (3B) and the inertinite (3C) show increasing average molecular weights of 281 and 453. Note that the inertinite, which is thought to contain large multinuclear aromatic clusters, shows the broadest and least well-resolved spectrum. This implies a relatively low aliphatic content for the inertinite.

## CONCLUSIONS

The mechanism at work in laser desorption of ions from surfaces is a subject of much speculation and conjecture. In spite of the complexity of the ionization mechanism, the fact remains that mass spectra of a large number of volatile organic compounds can be generated by laser desorption at threshold powers and that fragmentation of the parent molecule is minimal at best. Higher laser fluences may alter the ionization process to result in destructive fragmentation, in structurally significant fragmentation, or even ion-molecule reactions. Our goal here is to produce ions from the surface of coal-related samples with minimal fragmentation. For the coal products examined here, the LD/TOF mass spectra show no low  $m/z$  fragment ions and show molecular weight distributions that increase with rank. Although these are only preliminary experiments, the LD/TOF mass spectrometry approach to coal characterization looks promising with many variables in laser desorption conditions remaining to be explored.

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