

COMPARISON OF SEVERAL CONTEMPORARY IONIZATION/MASS ANALYZER TECHNIQUES FOR LARGE COMPONENTS OF COMPLEX FOSSIL-DERIVED MATERIALS

Jerry E. Hunt and Randall E. Winans
Chemistry Division
Argonne National Laboratory
Argonne, IL 60439

Keywords: Argonne Premium Coals, mass spectrometry

INTRODUCTION

Coals and coal-derived samples provide a unique mixture for development and comparison of mass spectrometric techniques for high molecular weight analyses. The Argonne Premium Coal samples (APCS), a broad array of research grade standards collected, prepared, and stored under controlled conditions, are convenient for assessing classical and novel mass spectrometric techniques. Vacuum pyrolysis mass spectrometry of APCS 4 (Pittsburgh #8) has been reported.¹ Alkyl-substituted aromatic compounds and hydroxy- and dihydroxy-substituted aromatic compounds were observed. Newer techniques such as laser desorption (LD), as well as in-beam techniques, such as desorption chemical ionization (DCI) and desorption electron ionization (DEI) are better suited to the studies of mixture characterization as presented by fossil fuels.

We have previously reported laser desorption of coal extracts that show only low molecular weight ions (<1000 amu).^{2,3} The latter report compares LD with fast atom bombardment and DCI mass spectrometry. All three techniques produce similar data that differ only in minor details. Hanley reported LDMS of pyridine extracts produces a distribution of ions between 150 and 1500.⁴ Field ionization mass spectrometry shows similar patterns.⁵ Recently, others have interpreted their LD results in terms of high mass species (>12,000) being desorbed.^{6,7} The authors present data taken from single laser shots. We believe that the data presented can best be interpreted as electronic "noise" and that the observed signals are not related to the sample. In our hands, laser desorption mass spectrometry of coals and coal-derived materials does not show any reproducible ion intensity above 2000 u. Our results have been obtained on two different time-of-flight instruments, one constructed in-house and one a commercial instrument (Kratos Kompact MALDI III).

Laser desorption mass spectrometry has recently been used to identify high molecular weight proteins of mass in excess of 100,000 amu. Thus, if there are indeed large molecular species in coals or coal extracts, LDMS is an attractive technique. However, the conditions whereby large molecular ions can be desorbed intact are very specialized. The extension of LD to heavier molecules is made possible by embedding the sample in a chemical matrix (matrix-assisted laser desorption ionization, MALDI). Without this matrix, large mass species are not observed. Recently, Herod reported results using a time-of-flight mass spectrometer designed for MALDI analysis.⁸ He concluded that high mass species (up to 200,000 u) are observed in the mass spectrum. We have used our two TOF mass spectrometers for coal analysis by MALDI, have carefully analyzed our data and the instrumental conditions, and conclude that only low molecular weight ions (up to 1500 u) are observed. We interpret our results quite differently from Herod. First, results from both of our mass spectrometers are similar, i.e., ion intensities are in the mass range from about 200 to 1500. No ion peaks are observed at higher masses in either instrument. We did observe a problem with the detector in the Kratos instrument that may result in an over-interpretation of the data. The detector in the Kratos instrument is very sensitive to ion saturation, that is, high ion currents cause spurious peaks to be observed at times of flight which are uncorrelated in time and, thus, uncorrelated in mass. These may be incorrectly interpreted as "true" ion signals of high mass. If, indeed, large molecules do exist in coal, new matrices will need to be identified which are applicable to the types of compounds found in coal. We are currently investigating this area.

This study focuses on a number of complementary approaches that have been used to investigate fossil fuel-derived materials. LD, DCI, and DEHRMS are compared as methods of volatilizing high molecular weight species present in coal samples. Also, DEHRMS on a high resolution three-sector tandem mass spectrometer is compared to laser desorption with laser photoionization on a time-of-flight instrument for high mass mixture selectivity.

EXPERIMENTAL

The coals used in this study are the Argonne Premium Coal Samples 1 (Upper Freeport mvB) and 2 (Wyodak-Anderson subB). A complete discussion of the characteristics of the coals used in this study has been reported.⁹ Vacuum pyrolysis tars were prepared by heating coal in a vacuum at 400 °C and collected at room temperature. Pyridine extracts and KOH/glycol solubilization procedures have been reported.¹⁰ The EI and DCI mass spectra were recorded on a Kratos MS 50 triple analyzer. The reagent gas for the DCI studies was isobutane. The solids and extracts were heated in the source on a small platinum wire coil from 200 °C to 700 °C at 100 °C/min. with the source heated at 200 °C. The laser desorption and laser ionization mass spectra were recorded on a linear time-of-flight mass spectrometer constructed in-house and a Kratos Kompact MALDI III reflectron time-of-flight mass spectrometer. The fluence of the desorption laser is held constant at 10-100 mJ/cm² at a repetition rate of 20 Hz. For direct ion desorption the laser is operated close to the ionization threshold to minimize fragmentation of the desorbing material. The laser is operated at lower fluences for neutral ion desorption. The neutral molecules are then ionized by vacuum ultraviolet light. The 118 nm laser pulses are produced by third harmonic conversion of 355 nm light from a Nd:YAG laser in a high pressure Kr cell.

RESULTS

Figure 1 shows a comparison mass spectrum of the vacuum pyrolysis tars from APCS 1. The lower panel is the direct laser desorption mass spectrum and the upper panel the DCI mass spectrum of the same sample. In each spectrum there are only a small number of low intensity peaks below $m/z=200$, indicating the overall soft ionization of each technique. The two methods show similar peaks, with some variation in intensity. Overall the LD spectrum shows fewer peaks up to a mass of about 275 as compared to a more dense region for the DCI data. In LD the more volatile species sublime and are not observed. Above this mass the spectra are quite similar. The peaks in the DCI data are generally +1 species as compared to the LD data, indicating the formation of $(M+H)^+$ ions. Several homologous series are observed in the LD and DCI data. Possible structures can be assigned to each of these series based on PyHRMS results from the same coal sample. The prominent series (especially in the LD data) at $m/z = 230, 244, 258, 272$ is assigned to alkyl-pyrenes or fluoranthenes. Another series contains two different species, alkylphenyl-naphthalenes and alkylhydroxy-pyrenes or fluoranthenes. Thus, there is good agreement in mass, if not intensity, for these two techniques.

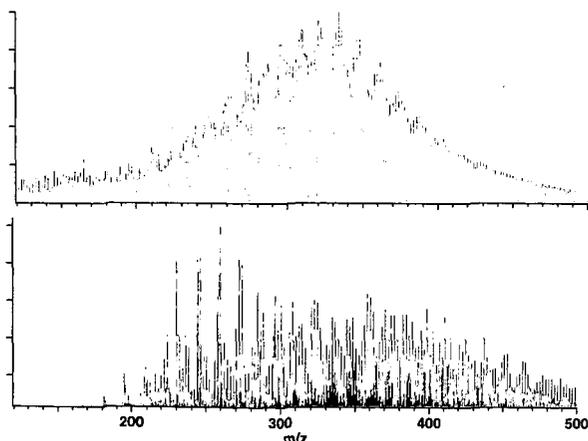


Figure 1. Comparison of LD (lower panel) and DCI (upper panel) methods for vacuum pyrolysis tars of APCS 1 (Upper Freeport mvB).

At higher masses there is also good agreement between the techniques. Several homologous series appear at these higher masses. A series at $m/z = 292, 306, 320, 334, 348, 362, 376$ is possibly alkylphenylpyrenes. Another series between 306 and 362, form an oxygen containing series with a suggested structure of methylbenzopyrenofuran.

The mass spectra of the demineralized pyridine extract of APCS 1 is shown in Figure 2. Spectrum A is the direct laser desorption mass spectrum of the pyridine extract and spectrum B the EI mass spectrum. Again the overall absence of ion intensity below 225 in the LD indicate soft ionization, i.e., the molecular fragmentation is minimum. Also, in laser desorption low molecular weight (volatile) molecules will be lost due to the high vacuum.

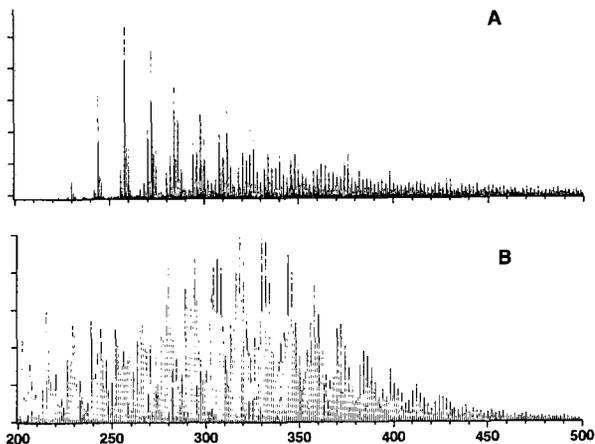


Figure 2. The pyridine extract of demineralized APCS 1. A, the LD and B, the EI mass spectrum.

Table 1. Major Ion Series in Laser Desorption of Pyridine Extract of APCS 1

Ion Series	Structural Type
230, 244, 258, 272, 286, 300, 314	alkyl pyrene or fluoranthene
242, 256, 270, 284, 298	alkyl chrysenes
252, 266, 280, 294, 308	alkyl benzopyrene or benzofluoroanthene
292, 306, 320, 334, 348, 362, 376	alkyl phenylpyrenes and pyrenobenzofuran
195, 209, 223, 237, 251	alkyl carbazoles
276, 290, 304, 318, 332	alkyl benzoperylene

In general the direct laser desorption mass spectra favor the aromatic compounds over the aliphatic, producing a simpler, cleaner mass spectrum, while the EI spectra show aliphatic as well as aromatic species.

Since direct laser desorption favors aromatic species at the expense of aliphatic species a method to enhance LD was employed. First, at low fluence, neutral molecules are desorbed, then a second laser pulse of 10.5-eV is used to ionize the neutrals. Since multiple photons can be absorbed increased ionization efficiency is expected for aliphatic species. A comparison of DEIHRMS and LD of neutral with photoionization is shown in Figure 3. The sample in this case is the hexane extract of the KOH/glycol reaction of APCS 2 (Wyodak-Anderson). The overall similarity of the spectra is compelling. The peak from $m/z = 368$ to 508 are assigned as acid with the base structure $H(CH_2)_nCO_2H$, $n = 23-33$. An important difference in the spectra is the appearance of high mass ions in the LD/LI spectra. Coupled with time of flight mass spectrometry, the spectra exhibit parent ion abundance which conventional 70 eV electron impact lack. The peaks near $m/z = 800$ do not appear in the DCI MS spectra. These peaks may be assigned as very long chain fatty acids on the order of C_{30} .

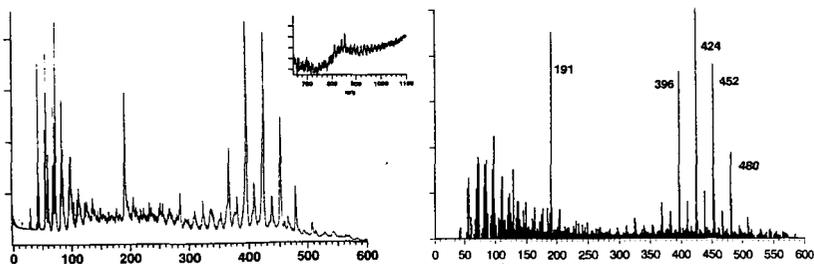


Figure 3. The laser desorption/laser ionization mass spectrum (left) and DEIHMS (right) of the hexane extract of KOH/glycol reaction of APCS 2.

CONCLUSION

The mass spectra show different molecular weight distributions, but similar ion series. In general LD, DCI, and EI give progressively lower distributions. Furthermore, the ions present in the LD and DCI spectra are directly comparable, while LD and EI produce different ion distributions. Information on neutrals is available from LD-photoionization. The appearance of an ion series in the $m/z = 700-1000$ range demonstrates an advantage of 10.5-eV ionization and TOF analysis. Mass spectral data from both LDMS, DCIMS, and EIHRMS are being analyzed for all eight Argonne Premium Coal samples.

ACKNOWLEDGMENT

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.

REFERENCES

1. Yun, Yongseung; Meuzelaar, Henk L.C.; Simmleit, N.; Schulten, H.-R. *Energy Fuels* **1991**, *5*, 22-29.
2. Hunt, J.E.; Lykke, K.R.; Winans, R.E. *Preprints, Am. Chem. Soc., Div. Fuel Chem.* **1991**, *36*, 1325-1328.
3. Winans, R.E.; McBeth, R.L.; Hunt, J.E.; Melnikov, P.E. *Proc., 1991 International Conference on Coal Science*; University of Newcastle upon Tyne, UK, September 16-20, 1991, pp. 44-47.
4. Burroughs, J.A.; Cadre, B.M.; Hanley, L. *Proc., 41st American Society of Mass Spectrometry*; San Francisco, CA, May 30-June 4, 1993, p. 441.
5. Herod, A.A.; Stokes, B.J.; Schulten, H.-R. *Fuel* **1993**, *72*, 31-43.
6. John, P.; Johnson, C.A.F.; Parker, J.E.; Smith, G.P.; Herod, A.A.; Gaines, A.F.; Li, C.-Z.; Kandiyoti, R. *Rap. Commun. Mass Spectrom.* **1991**, *5*, 364-367.
7. Herod, A.A.; Kandiyoti, R.; Parker, J.E.; Johnson, C.A.F.; John, P.; Smith, G.P.; Li, C.-Z. *J. Chem. Soc., Chem. Commun.* **1993**, 767-769.
8. Herod, A.A.; Parker, J.E.; Johnson, C.A.F.; John, P.; Smith, G.P.; Li, C.-Z.; Kandiyoti, R. *Proc., 7th International Conference on Coal Science*; Banff, Alberta, Canada, September 12-17, 1993, pp. 1282-1285.
9. Vorres, K.S. *Energy Fuels* **1990**, *4*, 420-425.
10. Winans, R.E.; McBeth, R.L.; Hunt, J.E. *Preprints, Am. Chem. Soc., Div. Fuel Chem.* **1993**, *38*, 561-564.