

FOSSIL FUEL CHARACTERIZATION USING LASER DESORPTION MASS SPECTROMETRY: APPLICATIONS AND LIMITATIONS

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INTRODUCTION

High molecular weight compounds (>600 amu) in fossil fuels have been overlooked in the past principally because of inappropriate analytical techniques. Most of the techniques have accessed only the easily volatilizable fraction. Mass spectrometry characterization of any presumed heavy components has mostly depended on pyrolysis to break up the larger molecules prior to analysis, especially by pyrolysis gas chromatography mass spectrometry. The material that is outside of the volatilizable fractions has received little attention. However, laser desorption mass spectrometry (LDMS) and matrix-assisted laser desorption/ionization mass spectrometry (MALDI) are particularly applicable to those molecules which resist intact ionization by traditional gas-phase methods. The application and limitations of these techniques to model compounds and fossil-derived materials is discussed in this study.

LD and MALDI mass spectrometry are increasingly used to detect intact molecular species, such as proteins with masses from 1000 to 100,000 amu and beyond.¹ MALDI is also being used for a few high molecular weight polymers.² A good example, related to coal-type systems, is the report on lignin mass spectrometry by MALDI.³ Here the mass spectrum shows a wide molecular distribution of several hundred to larger than 16000, with the center of gravity of the distribution around 2600. The results are interpreted in terms of oligomeric lignin molecules. Thus, if there are indeed large molecular species in a polymeric content in fossil fuel extracts, MALDI is an attractive technique.

We have previously reported laser desorption of coal extracts that show only low molecular weight ions (<2000 amu).⁴⁻⁶ We compare LD with fast atom bombardment and desorption chemical ionization mass spectrometry, two other soft ionization techniques. All of these techniques produce similar data that differ only in minor details. 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 the bulk of coal material produces only low molecular weight ions (up to 2000 amu). In agreement with these reports, Hanley showed LD and MALDI data of pyridine extracts which produced a distribution of ions between 150 and 1500.⁷ In addition, field ionization mass spectrometry has found similar pattern in the low mass region.⁸ Recently, Herod et al.⁹⁻¹² have interpreted their LD and MALDI data in terms of high mass species being desorbed. We have presented alternate interpretations for these results.⁶

In our hands, LD or MALDI of coals and extracts do not show any reproducible ion intensity over mass 2000. The conditions whereby large molecular ions can be desorbed intact are very specialized. This paper will describe the scope and limitations of laser desorption and matrix-assisted laser desorption in time-of-flight mass spectrometers as applied to high molecular weight molecules, such as proteins and polymer systems.

EXPERIMENTAL

The coals used in this study are the Argonne Premium Coal Samples. The procedures for the pyridine extract of the Argonne Premium Coals have been reported previously.⁵ The laser desorption mass spectra and matrix-assisted laser desorption mass spectra were recorded on a linear time-of-flight mass spectrometer constructed at Argonne and a Kratos Kompact MALDI III linear/reflectron time-of-flight mass spectrometer. The spectra were produced by exposing the samples distributed as thin layer on a stainless steel sample holder to laser pulses from either a Nd:YAG or a

nitrogen laser. The laser is operated close to the ionization threshold to minimize possible fragmentation of the desorbing material and to optimize resolution.

The matrices used were dihydroxybenzoic acid, sinapinic acid, indoleacrylic acid and 2-(4-hydroxyphenylazo)-benzoic acid (HABA) purchased from Aldrich. The polyethylene sample were purchased from Petrolite. The polyethylene glycol was purchased from Aldrich.

RESULTS

Coals

Coals are a unique sample for LD and MALDI. They are chemically very complex, heterogeneous, and most likely polydisperse in mass. Figure 1 shows a positive ion LD mass spectrum of the pyridine extract of APCS 1 mv bituminous coal produced using 337 nm laser pulses, displaying a distribution of ions between roughly 200 and tailing to 2000 amu. The major ion series seen are alkyl-pyrenes (-fluoranthenes), -chrysenes, -benzopyrenes, -phenylpyrenes (-pyrenebenzofurans), -carbazoles, and -benzoperilynes. Laser desorption favors the aromatic compounds. Laser desorption with the Nd:YAG fundamental wavelength of 1064 nm, 532 nm (frequency doubled), and 266 nm (frequency quadrupled) show similar spectra.

The MALDI spectrum of the same sample from sinapinic acid is shown in figure 2. The matrix/laser combination is sinapinic acid with 337 nm laser light. At first glance the data indicate a continuum of high mass peaks, but the observed "signal" is actually a result of chemical noise from the matrix and ion saturation of the detector creating a false signal at the detector which is not correlated with the laser blast or sample. In an attempt to see higher mass ions, we have deflected the low mass ions using time-gated pulsed deflection, so that these intense ions do not impact the detector. The results show no high mass ions. Matrix-assisted laser desorption/ionization using 2,5-dihydroxybenzoic acid, HABA, nicotinic acid, sinapinic acid, 3-hydroxypicolinic acid, silver nitrate, silver acetate, silver picolinate and indole acrylic acid, have been attempted on the pyridine extracts of Argonne coals. No higher mass or other ions are observed in the MALDI experiments beyond those of the matrix and those seen in the neat coal extracts.

The Nature of the MALDI Event

In order to assess the characteristics of the MALDI mass spectrum, we present a protein mass spectrum. The inset in the figure 2 shows the MALDI of a protein in the sinapinic acid matrix. Here the molecular ion is easily observed above the background without detector saturation. A feature of MALDI in time-of-flight instruments is that at higher masses the resolving power decrease. The peak width for each of the two protein ions using this matrix is about 4000 mass units at the baseline. An important aspect of MALDI is the low resolution, especially at higher masses. In the case of two single proteins the mass resolution is $\sim 150 \text{ m}/\Delta\text{m}$ full width at half maximum. This means that a distribution of molecules, for example from 10000 to 200000 amu, would appear only as a broad unresolved hump in the mass spectrum. In fact, MALDI for polymers above 10,000 amu the resolution for a linear time-of-flight mass spectrometer is insufficient to identify individual oligomers. Sharp peaks are not be observed. The amount of available charge in the MALDI event to span such a large mass region is also questionable.

The MALDI mass spectrum (HABA matrix) of polyethylene glycol 3000 is shown in figure 3. The distribution of oligomers is clearly observed. In the case of more nonpolar species, such as polyethylene, we have found that common organic matrices do not result in mass spectra. Silver nitrate or other silver salt must be added to polyethylene to produce mass spectra of silver cationized oligomers. We have easily observed polyethylene up to 2500MW with this method.

CONCLUSIONS

LDMS and MALDI time-of-flight instruments are easy to operate, fast, and are suitable for quantitative measurement of molecular weight distributions of certain coal components. LD, in particular, is better suited to mixture analysis than MALDI.

Although matrix-assisted laser desorption time-of-flight analysis has been touted as a universal molecular weight distribution tool, it is hardly that. The successful application of the MALDI is greatly dependent on the chemical structure of the system under investigation. Different chemical structures may require significantly different sample preparation. The sample preparation step is perhaps the most important component of a MALDI experiment. First, nonpolar compounds (e.g., polyethylenes) have not been successfully analyzed by any organic matrix-assisted technique that the authors are aware. Second, ion intensities from mixtures of compounds rarely show true abundances. Third, in mixed systems the lowest concentration species may not be observed at all because of the high background noise levels that are a feature of matrix-assisted laser desorption. The fact that spectra are easy to obtain should not overshadow the fact that sample preparation is the critical factor in successful analyses. Furthermore, the conditions useful for one system may not be useful for others. The conditions and matrices presently used for coal in MALDI are most appropriate for proteins. Thus, there is a strong possibility that any observed high mass ions may be from contaminant proteins contained in the coal.

However, the fact remains that LDMS and MALDI are capable of producing intact, unfragmented molecular ions from biopolymers, macroscopic molecules based on aromatic building blocks, and polymers. MALDI can provide values for the molecular weight as well as shows the entire distributions of polymer species. The question arises, if there were high mass material in coals and extracts, would they be detected by this technique. First, optimal matrices must be found. There is good reason to believe that good miscibility of matrix and the coal in the condensed form is the prerequisite for a good matrix, as has been found to be true for protein desorption. Matrices working well for polar biopolymers will not be optimal for coals. Most of the protein matrices actively exclude ionic components, which are needed for cationization. Second, if the mass distribution is extremely polydisperse it may be difficult to detect the high mass material above background as the contribution at any mass may be low even if the contribution to the total mass over a wide range is high. Finally, the mass spectrum is sensitive to the number average molecular weight; a low value, however, does not preclude the presence of high molecular weight species.

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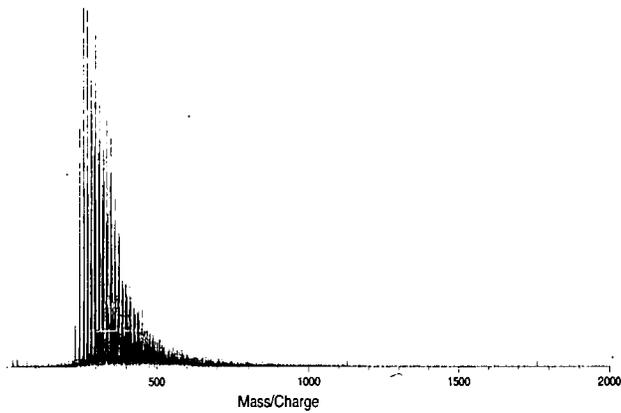


Figure 1. LD mass spectrum of the demineralized pyridine soluble fraction of APCS 1 (Upper Freeport).

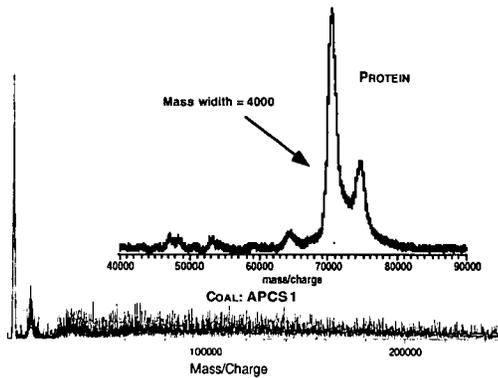


Figure 2. MALDI linear mass spectrum of APCS 1 (Upper Freeport) using sinapinic acid as matrix showing the effect of detector saturation. The inset is the MALDI of two proteins, synapsin IA, IB, in sinapinic acid.

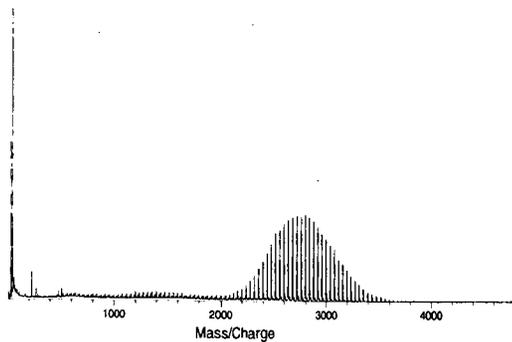


Figure 3. MALDI reflectron spectrum of polyethylene glycol showing intact cationized molecular ion formation.