LASER DESORPTION MASS SPECTROMETRY: 
TECHNICAL LIMITATIONS, FUNDAMENTALS, AND 
APPLICATION TO COAL*

Jerry E. Hunt and Randall E. Winans

Chemistry Division
Argonne National Laboratory
9700 So. Cass Avenue
Argonne, IL 60439

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Laser Desorption Mass Spectrometry: Technical Limitations, Fundamentals, and Application to Coal

Jerry E. Hunt and Randall E. Winans
Chemistry Division, Argonne National Laboratory, 9700 S. Cass Ave., Argonne, IL 60439, USA

The objective of this study is to assess the scope and limitations of laser desorption (LD) and matrix-assisted laser desorption (MALDI) as applied to coals. 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. MALDI is also being used for high molecular weight polymers. A good example, related to coal-type systems, is the report on lignin mass spectrometry by MALDI. 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 coals or coal extracts, MALDI is an attractive technique.

1. INTRODUCTION

We have previously reported laser desorption of coal extracts that show only low molecular weight ions (<1000 amu). 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 only low molecular weight ions (up to 2000 amu) are observed. In agreement with these reports, Hanley showed LD and MALDI data of pyridine extracts which produced a distribution of ions between 150 and 1500. In addition, field ionization mass spectrometry has found similar pattern in the low mass region. Recently, Herod et. al have interpreted their MALDI data in terms of high mass species being desorbed. We have presented alternate interpretations for these results.

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, polymer systems, and coal.

2. 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. 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 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 dendrimers were a gift from T. Miller at Bell Labs. The polyethylene sample were purchased from Petrolite. The polyethylene glycol samples were purchased from Aldrich.

3. RESULTS

3.1 Dendrimers

Hyperbranched chain polymers, such as “starburst” dendrimers, branch geometrically to form a densely packed macroscopic particle, which is a single molecule. We have characterized a dendrimer based on 1,3,5-trisubstituted benzene rings symmetrically attached to one another. A low molecular weight example (MW=1675), which consists of 22 benzene rings produces a single ion at m/z 1675. Such a structure might be considered a “zeroth-order” macro-molecule model for coal. A higher analog, the 46 benzene ring macromolecule produces a molecular ion at m/z 3502. No fragment ions are observed in the mass spectrum under optimal conditions. If a polymeric coal structure of linked aromatic structures exists in coal, one would expect to easily observe it in laser desorption. No such ions are present in laser desorption of coals or their extracts (see section 3.3).

3.2 Polymers

Direct laser desorption of polymers often produces only fragment ions and no molecular information. The MALDI technique was first applied to biopolymers, chiefly proteins. Sample preparation in MALDI is difficult, since the process depends on multiple parameters. One condition that is critical is that the analyte molecules must be completely surrounded by the matrix molecules. The matrix must crystallize around the analyte, therefore the analyte must not interfere with crystallization. However, the most important step is the choice of the matrix itself. It is not possible to find a matrix which works best for all analytes. The application of MALDI to polymers is in its infancy. In contrast to proteins, where protonation produces ions, alkaline ion cationization is the ionization mechanism most often displayed by polymers.

We have used HABA in the MALDI of polyglycols. The MALDI spectra of two different molecular weight distributions are shown in Figure 1.

The spectrum consists of a series of peaks which are due to ions of the type H(OCZ&),OHNa+. Here all ions are produced by cationization. The spectra are well resolved and show a repeat unit of 44 amu. The 3000MW polymer shows excellent
resolution (both sodium and potassium cationized polymer can be seen), while the 8000MW polymer shows a somewhat decreased resolution. A feature of MALDI in time-of-flight instruments is that at higher masses the resolving power decrease.

In the case of more nonpolar species, such as polyethylene, we have found that common matrices do not result in good 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.

3.3 Coals and coal extracts

Coals are a unique sample for LD and MALDI. They are chemically very complex, heterogeneous, and most likely polydisperse in mass. Figure 2 shows a positive ion 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 1000 amu.

![Figure 2. LD mass spectrum of the demineralized pyridine soluble fraction of APCS 1 (Upper Freeport).](image)

The major ion series seen are alkyl-pyrenes (-fluoranthenes), -chrysenes, -benzopyrenes, -phenlypyrenes (-pyreneobenzofurans), -carbazoles, and -benzoperylenes. Laser desorption favors the aromatic compounds. Laser desorption with 355 nm, 1064 nm and 266 nm show similar results. Matrix-assisted laser desorption/ionization using 2,5-hydroxybenzoic acid, HABA, nicotinic acid, sinapinic acid, 3-hydroxypicolinic acid, silver nitrate, silver acetate, and silver picolinate, 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.

We have been unable to generate ions higher in mass than those shown here. It is our belief that such high mass compounds are not present in these samples.

4. DISCUSSION

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. 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 proteins.
contained in the coal, either as contaminants or native. LDMS and MALDI are capable of producing intact, unfragmented molecular ions from biopolymers, macroscopic molecules based on aromatic building blocks, and polymers. MALDI provides 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, conditions must be found for successful ionization of model compounds. 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. 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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REFERENCES