

**LASER DESORPTION ION TRAP MASS SPECTROMETRY
OF THE MACROMOLECULAR COMPONENT OF COAL**

John A. Burroughs, Brian M. Cadre, and Luke Hanley
University of Illinois at Chicago
Department of Chemistry, m/c 111
Chicago, IL 60607-7061

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INTRODUCTION

The structure of coal has been proposed to be a macromolecular network in which smaller molecules are confined [1]. It follows that a portion of the organic sulfur and other heteroatoms present in coal are covalently bound to this network. This paper describes efforts to measure high molecular weight mass spectra representative of this macromolecular network and ultimately, determine the chemical structure of organic sulfur contained therein.

Indirect evidence for the existence of a two component coal structure has been provided by solvent swelling, nuclear magnetic resonance, and various other measurements [1,2]. Size exclusion chromatography (SEC) has been used to determine that the number average molecular weight (M_n) of polymers extracted from coal with pyridine and other solvents ranges from 1000 to above 10,000 amu [3-5]. However, SEC experiments on coal polymers are limited by the difficulty in calibrating the retention time of what are essentially unknown chemical compounds. Thus, M_n values obtained by SEC differ by ~20% from values obtained with vapor phase osmometry [4]. Furthermore, only the soluble portion of the coal sample is analyzed by these methods and SEC has not provided a detailed chemical description of these coal polymers. Mass spectrometry is a logical method for measuring M_n of coal polymers. Nevertheless, experiments which have utilized ion bombardment [6], pyrolysis [7,8], electric field gradients [9], or pulsed lasers [10-12] for desorption and ionization of coal polymers have only formed low molecular weight ions via thermal degradation and chemical transformation rather than intact, high molecular weight ions.

The experiments described here attempt to exploit recent advances in high molecular weight mass spectrometry to generate representative ions of coal polymers. Infrared and ultraviolet laser desorption methods are applied to pyridine solvent extracts of high sulfur coals, where any ions formed are detected by an ion trap mass spectrometer. Ion trap mass spectrometers can measure the mass to charge (m/z) ratio of ions over a wide mass range, can perform collision induced dissociation experiments for structural analysis of ions, and can be operated in a high resolution mode [13].

EXPERIMENTAL DETAILS

A schematic diagram of the experimental apparatus is shown in Figure 1. To obtain a mass spectrum up to ~650 m/z , ions formed by laser desorption from a coal sample are injected through holes in the end cap of the ion trap into its center [13]. The ions are contained

inside the trap by an initial radio frequency voltage applied to the ring electrode while the end cap electrodes are held at ground potential. After the ions have undergone many collisions with a helium buffer gas, the radio frequency amplitude is ramped linearly, causing ions of increasing m/z values to be ejected from the trap through holes in the end caps. The ions which exit the ion trap are detected by a conversion dynode/channeltron ion detector.

The mass range of the ion trap is extended via the application of an auxiliary frequency across the end cap electrodes concurrent with the rf amplitude ramp. Ions up to 10,000 m/z have been detected with this apparatus to date and future experiments should extend this towards the theoretical limit of ~40,000 m/z . Trapping of individual mass ions has also been accomplished, as a predecessor to collision induced dissociation experiments.

The ion trap mass spectrometer was constructed by mounting the electrodes from an commercially available ion trap detector (Finnigan MAT ITD 700) inside a diffusion pumped vacuum chamber with a base pressure of $\sim 2 \times 10^{-8}$ Torr. A 6 kV conversion dynode is located adjacent to the channeltron near the exit end cap electrode to allow for high mass detection. Roughly 10^{-3} Torr of helium buffer gas is introduced into the trap via a leak valve. Experimental timing sequences and data acquisition are controlled with an IBM compatible 80386 microcomputer interfaced to the commercial ion trap electronics via plug-in multifunction data acquisition boards (National Instruments models AT-MIO-16F-5 and PC-TIO-10). The end cap electrodes are connected to a function generator (Stanford Research Systems DS345) through a homemade buffer amplifier.

To perform infrared laser desorption experiments, pulses of 1064 nm radiation of ~7 ns duration from a Nd:YAG laser (Continuum Surelite) are focussed onto the sample probe resulting in power densities of 10^9 - 10^{10} W/cm². The power density is calculated by visual estimation of the laser spot diameter on the sample probe tip and by measuring the unfocussed laser power with a pyroelectric joulemeter (Molelectron). For ultraviolet laser desorption, fourth harmonic generation of the Nd:YAG fundamental wavelength gives 266 nm pulses in the 10^9 - 10^{10} W/cm² power density range.

Solvent extracts from coal are prepared by dissolving powdered coal in pyridine and allowing the samples to equilibrate for three days at room temperature, then filtering out the insoluble portion which remains. Experiments were performed using Pocahontas No. 3 and Illinois No. 6 coal from the Argonne Premium Coal Sample Program and Herrin No. 6 (IBC 101) coal from the Illinois Basin Coal Sample Program.

RESULTS AND DISCUSSION

Laser desorption MS using infrared radiation has been used for the analysis of various nonvolatile organic molecules, biomolecules, and synthetic polymers [14]. The technique usually involves irradiating the sample at power densities from 10^7 - 10^{10} W/cm². In many cases the sample is doped with an inorganic salt to assist the formation of cation-attached molecular ions. Here, infrared laser

desorption was used to generate spectra from a series of poly(ethyleneglycol) standards of known molecular weight (American Polymer Standards) doped with KCl. Cation-attached molecular ions up to $\sim 10,000$ m/z were successfully formed and detected using this method.

Laser desorption experiments utilizing infrared radiation to desorb and ionize either disburbed solid coal or solvent extracts of same have been unsuccessful in generating any meaningful information regarding the macromolecular structure of coal. The only observable peaks above ~ 300 m/z in these spectra were due to the presence of carbon cluster ions, as verified by comparison with similar clusters formed in laser desorption of graphite samples. Attempts to dope the coal samples with KCl, NaCl, and CsCl to enhance the formation of cation attached ions have all failed to produce intact molecular ions. It is concluded that regardless of the sample preparation method, infrared laser desorption of coal and coal extracts is not a useful method for generating the desired high molecular weight ions, in agreement with previous experiments along these lines [10-12].

Ultraviolet matrix assisted laser desorption/ionization (UVMALDI) has recently emerged as a useful tool for forming intact molecular ions up to $300,000$ m/z of various biopolymers including proteins and carbohydrates as well as synthetic polymers [15-17]. The technique requires that the analyte molecule, usually exhibiting only moderate optical absorption at the desorption wavelength, be sparsely dispersed in a strongly absorbing matrix [15]. Much lower power densities (i.e. 10^6 - 10^7 W/cm²) are used in a typical UVMALDI experiment than with infrared laser desorption [18], but the former method is capable of desorbing intact far larger and more labile species than the latter. Although time-of-flight mass spectrometers are most often employed in such experiments, ion traps have been used to detect ions formed by UVMALDI [19-21].

The matrix which was used for both test compounds and for coal extract samples is 2,5-dihydroxybenzoic acid (DHB). For the first test sample, gramicidin S was dissolved in a water/ethanol solution in a 1000:1 molar mixture of matrix/analyte. A second test sample of bovine insulin was similarly prepared in a 5000:5000:1 DHB/d-fructose/bovine insulin mixture. Intact molecular ion peaks from gramicidin S (1140 m/z) and bovine insulin (5733 m/z) have been formed and detected with UVMALDI and the spectra for the later is shown in Figure 2; The intact molecular ion and the ionized chain B portion of the molecule are present, but no other fragments are observed.

Unfortunately, attempts to generate intact macromolecular ions from the pyridine soluble portion of various coals using the UVMALDI technique have not yet been successful. Detection of sample molecules using UVMALDI requires that the analyte molecule be capable of forming a stable ion in the gas phase, presumably by accepting or donating a proton or other cation. The various proposed structures of coal all contain numerous ionizable groups such as S or N-containing heterocyclic rings, hydroxides, or sulfides [22]. Therefore, it should be possible to produce intact molecular ions from coal using UVMALDI.

It is postulated that the failure of UVMALDI to generate intact ions from coal polymers derives from improper sample preparation. Preparing a proper sample of a new compound for UVMALDI is at present

a trial and error process in which matrix type, matrix-to-analyte ratio, and concentration of cation donating dopants are all varied [15,23]. Furthermore, while some samples produce positive ions, others generate only negative ions. To date, only positive ions have been sought in these experiments. New sample preparations and negative ion formation are presently under exploration. Therefore, a final conclusion cannot yet be drawn regarding the applicability of laser desorption ion trap mass spectrometry to the study of polymers from coal.

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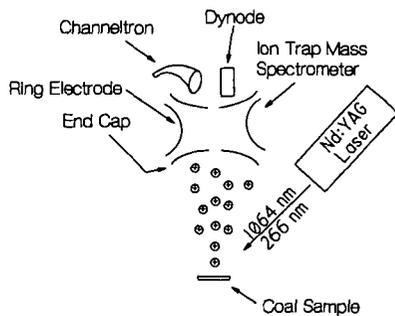


Figure 1: Schematic diagram of the laser desorption ion trap mass spectrometer.

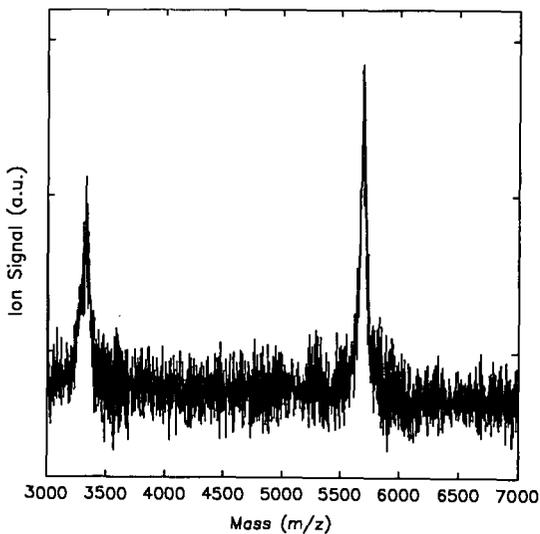


Figure 2: UVMALDI spectrum of a trial compound, bovine insulin, demonstrating the feasibility of the method for labile high molecular weight compounds such as coal polymers.