TECHNICAL REPORT
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Project Title: Mass Spectral Study of Organic Sulfur in the Polymeric Matrix of Coal
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Principle Investigator: Luke Hanley, Assistant Professor
Department of Chemistry, m/c 111
University of Illinois at Chicago
Chicago, IL 60680-4348
phone: (312) 996-0945
Bitnet: u46654@uicvm

Other Investigator: John Burroughs
Graduate Research Assistant
Department of Chemistry
University of Illinois at Chicago

Project Monitor: Ken Ho, CRSC

ABSTRACT

These experiments will examine the chemical environment of organic sulfur in the polymeric matrix of Illinois coal by novel mass spectrometric techniques: High molecular weight ions from the polymeric coal matrix will be formed by laser desorption and photoionization of powdered coal samples. These ions will be subsequently injected into an ion trap mass spectrometer for single and multiple mass analysis for the identification of sulfur containing moieties in the polymeric matrix. Furthermore, comparison of the mass spectra of various separated macerals with that of whole coal will be made to determine whether chemical modification occurs during the separation process.

The experimental apparatus for this project has been constructed during this past quarter. The ion trap has been mounted in the vacuum chamber and the entire system has been pumped down to a base pressure of 2×10^{-7} Torr. Work has begun on the development of mass spectrometry capability inside the ion trap.

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EXECUTIVE SUMMARY

Organically bound sulfur in coal, part of which resides in the polymeric matrix [Palmer], is perhaps the most significant impediment to the economical utilization of Illinois coal. It follows that the elucidation of the chemical environment of organic sulfur in the polymeric matrix would assist the development of chemical, microbial, and enzymatic treatments for sulfur removal from Illinois coal [PETC, CRSC]. This project will apply novel mass spectrometric methods for the analysis of organic sulfur in this polymeric matrix.

It has been found that the analysis of organic sulfur in separated macerals of coal is much simpler than analysis of whole coal [Palmer]. Macerals are separated by the density gradient centrifugation process, which is assumed to not alter the overall polymeric and chemical structure from that in whole coal. While it has been shown that model compounds are unaffected by the density gradient centrifugation process, it is entirely possible that these compounds are not accurate representations of the complex and unexpected chemical processes which might occur in whole coal. To support the present emphasis on maceral separation [CRSC], this project will demonstrate an independent method of verifying the absence of chemical modification during the separation of macerals.

This project will utilize a combination of recently developed methods in high molecular weight mass spectrometry [Burlingame, Grant] to study the chemical environment of organic sulfur in the polymeric matrix of whole and separated macerals of Illinois coal: A pulsed Nd:YAG laser will desorb polymeric fragments from coal samples for subsequent laser photoionization. The high molecular weight ions thus formed will be injected into an ion trap mass spectrometer where single and multiple mass spectrometry experiments will be performed.

The experiments to be examined by this project are divided into three sections: Development of techniques for obtaining high molecular weight spectra from coal, comparison of the polymeric mass spectra from whole Herrin No. 6 coal with that of its separated macerals, and determination of the chemical environment of organic sulfur in the polymeric matrix of these samples.

The milestone scheduled for completion in the first quarter is the assembly of the vacuum chamber. This task has been completed: The ion trap has been mounted in the vacuum chamber and the entire system has been pumped down to a base pressure of 2×10^{-7} Torr. Work has begun on the second quarter milestone, the development of mass spectrometry experiments in the ion trap.

OBJECTIVES

These experiments will examine the chemical environment of organic sulfur in the polymeric matrix of Illinois coal by laser desorption of high molecular weight fragments into an ion trap mass spectrometer. Furthermore, the validity of the maceral separation method for the analysis of coal will be tested by comparing the mass spectra of different separated macerals to determine whether the separation process also chemically alters the coal.

The milestones scheduled to be completed this year are as follows:

Task 1: Assembly of the vacuum system was to have been completed during this (the first) quarter.

Task 2: Development of single and tandem mass spectrometry capability inside the ion trap is scheduled for completion in the second quarter.

Task 3: Testing of laser desorption on trial species is scheduled for completion in the third quarter.

Task 4: Injection of ions into the ion trap and development of photoionization is scheduled for completion in the fourth quarter.

In the second year, laser desorption will be combined with photoionization and the technique will be refined for coal samples to obtain high molecular weight mass spectra representative of the polymeric matrix. Finally, a mass spectral comparison of whole Herrin No. 6 coal with its separated macerals will be performed followed by an analysis of organic sulfur in both types of samples via collision induced dissociation experiments.

INTRODUCTION AND BACKGROUND

Organically bound sulfur in coal, part of which resides in the polymeric matrix [Palmer], is perhaps the most significant impediment to the economical utilization of Illinois coal. It follows that the elucidation of the chemical environment of organic sulfur in the polymeric matrix would assist the development of chemical, microbial, and enzymatic treatments for sulfur removal from Illinois coal [ETC, CRSC]. This project applies new mass spectrometric methods to the analysis of organic sulfur in the polymeric matrix of coal.

It has been found that the analysis of organic sulfur in separated macerals of coal is much simpler than analysis of whole coal [Palmer]. Macerals are separated by the density gradient centrifugation process, which is assumed to not alter the overall polymeric and chemical structure from that in whole coal. While it has been shown that model compounds are unaffected by the density gradient centrifugation process, it is entirely possible that these compounds are not accurate representations of the complex and unexpected chemical processes which might occur in whole coal. Given the present emphasis on maceral separation [CRSC], these experiments will provide an independent method of verifying the absence of chemical modification during the separation of macerals.

EXPERIMENTAL PROCEDURES

This project utilizes a combination of recently developed methods in high molecular weight mass spectrometry [Burlingame, Grant] to study the chemical environment of organic sulfur in the polymeric matrix of whole and separated macerals of Illinois coal: A pulsed Nd:YAG laser will desorb polymeric fragments from coal samples for subsequent ionization by a single photon excitation with vacuum ultraviolet radiation or multiphoton excitation with ultraviolet radiation. The high molecular weight ions thus formed will be injected into an ion trap mass spectrometer where mass spectrometry experiments will be performed. Ions will be structurally analyzed in a tandem mass spectrometry (MS^2) experiment, where ions of a single mass are isolated, fragmented by collision induced dissociation with noble gas atoms, and the resultant daughter ions are mass analyzed. The ion trap mass spectrometer is uniquely suited to structural analysis of high molecular weight ions because it can perform many sequential mass selection/fragmentation (MS^n) experiments [Cooks].

These experiments will obtain high molecular weight mass spectra representative of the polymeric matrix of coal. Chemical identification of mass spectral peaks, rather than "fingerprint" comparisons of complex spectra, will be emphasized in all of the experiments. Collision induced dissociation will be used to identify the chemical structure of the polymeric matrix for Herrin No. 6 coal from the Illinois Basin Coal Sample Program. In particular, determination of the chemical environment of organic sulfur bound in the polymeric matrix will be emphasized. Analyses will be performed on both whole Herrin No. 6 coal and its separated coal macerals, providing an independent test of the maceral separation approach. This information will be useful in the design of chemical methods for the removal of organic sulfur from Illinois Coal.

RESULTS AND DISCUSSION

The milestone scheduled for completion in the first quarter is the assembly of the vacuum chamber. This task has been completed: The ion trap has been mounted in the vacuum chamber and the entire system has been pumped down to a base pressure of 2×10^{-7} Torr. The ion trap has been assembled in a preliminary configuration whereby ions are formed inside the trap via electron bombardment. Helium for the ion trap passes through a liquid nitrogen cooled zeolite trap, through a leak valve, and into the ion trap itself.

At present, the entire device is being interfaced with an IBM-AT/386 clone computer via several data acquisition boards. Software control of the ion detector voltage, radio frequency potential on the ion trap, the electron impact filament, and electron gate lens have all been accomplished via the data acquisition board. Once the signal output of the ion detector can be read into the data acquisition board, crude mass spectra of residual gases inside the vacuum chamber should be obtainable.

During this quarter, most of the equipment for the experiment has been ordered, including the Nd:YAG laser, the laser power meter, the delay gate generator and various optical components. The excimer laser to be used for photoionization has been received and is operating.

CONCLUSIONS AND RECOMMENDATIONS

- 1) The project is proceeding on schedule and as expected, there are no experimental results to report at present.
- 2) Work has begun on the second quarter milestone, the development of single and tandem mass spectrometry experiments in the ion trap.

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