

LASER MICROPYROLYSIS/GAS CHROMATOGRAPHY MASS SPECTROMETRY: A USEFUL TECHNIQUE FOR THE STUDY OF COAL MACERALS?

Paul F. Greenwood, Etuan Zhang, Patrick G. Hatcher, Frank Vastola and Alan Davis,
The Pennsylvania State University, University Park, PA 16802

INTRODUCTION

Structural information regarding the microscopic composition of heterocyclic, polymaceralic materials such as coal and kerogens has proved elusive. The primary reason for this is the limited number of techniques which can analytically probe involatile, thermally labile materials.

Pyrolysis (i.e., thermal degradation) of coal and other organic materials is one technique to show much promise.^{1,2} Conventional methods of coal pyrolysis include slow pyrolysis (heating rate between 25 °C/sec) and flash/fast pyrolysis (10,000 °C/sec). The pyrolysis of coal produces many gaseous fragments which can be analysed by mass spectrometry. The detected pyrolysates often reveal much structural information which can be related to the macroscopic composition of the parent coal.

The rapid heating from lasers has also been used to effectively induce coal pyrolysis.^{3,4} Laser pyrolysis offers the unique advantage of micro-selective *in situ* sampling. Since readily available optics can focus the laser output to very small areas, it is possible to analyse very small components within complex mixtures such as coal. Several independent groups, some using the commercially available LAMMA instrument,⁵ have demonstrated how individual components of coals and oil shales can be selectively irradiated with microscopic optics.⁶⁻¹⁶

Previous efforts to study individual maceral types involved the physical isolation of the selected macerals. This was performed either via hand-picked techniques¹⁷ or density-gradient centrifugation.¹⁸⁻²⁰ The severe and time consuming sample pre-treatment requirements associated with these techniques is not present with the *in situ* analysis of the micropyrolysis technique.

The majority of the coal micro-pyrolysis studies to date have been concerned only with the laser techniques which produce charged particles. Many more neutrals than ions are produced during any laser ablation process so the detection sensitivity of pyrolysis products will be significantly reduced when limiting the analysis to ionic species. Other studies, by one of us, have revealed that carbon clusters tend to dominate the charged population produced from the laser ablation of coals.²¹ This suggests analysis of directly produced ionic pyrolysates may not be an appropriate method to study the structural fragments from coal macerals.

In this paper we present a novel laser pyrolysis/GC-MS study using an instrument recently assembled in our laboratory. This apparatus includes a microscope to selectively pyrolyse individual coal macerals. The entire pyrolysate population, including neutrals, is subjected to the process of trapping (with a N₂ cold trap), separated by gas chromatography and analysed by electron impact mass spectrometry. In general, the product distribution from laser pyrolysis closely resembles that observed for flash pyrolysis. This exceptionally encouraging result suggests that laser micro-pyrolysis has

tremendous potential for the study of individual components not only within coals, but also other heterogeneous solids.

INSTRUMENTATION

The main components of the micropyrolysis apparatus used in this study include a laser, microscope, pyrolysis chamber and Kratos MS-80 GC-MS. A schematic illustration of the assembled system is shown in Figure 1.

Details of the laser (a pulsed ruby variety) and microscope can be found elsewhere.³ In brief, the visible output of the laser has a wavelength of 694.3 nm and a maximum energy of 0.1 Joule. The microscope is equipped for reflected light illumination and long working distance objectives to enable the sample chamber to be mounted directly on the microscope substage. The laser beam is focused by the 4x objective of the microscope onto the surface of a polished coal sample mounted in the pyrolysis chamber. Focussing the laser pulse to very small sizes ensures that the very high irradiances necessary for pyrolysis are reached. The microscope also allows close visual examination of the coal sample so that particular macerals can be selected.

The pyrolysis chamber, developed in this laboratory, was designed to meet the requirements of the pyrolysis/GC-MS experiment. The sample port was kept to a small size (ID 7 mm, depth 10 mm) to reduce the amount of dead volume. A silica glass window on the top allowed microscopic observation and laser penetration. The chamber was constructed of stainless steel and included a bore into which a thermocouple and heating element could be placed so as to heat the chamber (typically to 180 - 220 °C). Inlet and outlet carrier gas ports were also included. The pyrolysis chamber was connected to the column of the GC via (1/16") metal lined tubing (ID = 0.5 mm). A cold trap consisting simply of a loop of the column submerged in a liquid nitrogen bath is located in the oven of the GC. Heating ribbons were used to heat the transfer tubing as well as to pre-heat the helium carrier gas.

The Kratos MS-80 interfaces a Carlo-Erba GC with a scanning magnetic sector mass spectrometer. The GC is fitted with a fused-silica capillary column (30m x 0.25 mm ID) with stationary phase consisting of 50% phenylmethyl polysiloxane (J&W, DB-17). The column was temperature programmed from 40 to 280 °C at 4 °C/min. Mass spectra were obtained under EI conditions at 70 eV, a scan rate of 1500 m/z s⁻¹ and an m/z 40 to 500 mass range. The individual peaks were identified by comparison of mass spectra to published spectra.

EXPERIMENTAL

Two coal samples were selected for analysis from the Penn. State Coal Sample Bank. These comprised a subbituminous humic coal (PSOC-1532) with a maximum vitrinite reflectance of 0.33% and a high volatile C bituminous cannel coal (PSOC-1109) with a vitrinite reflectance value of 0.44%. These particular coals were selected to examine the ability of this technique to differentiate the different types of macerals.

Sample pretreatment included: cutting the sample to small block sizes which could be accommodated by the sample port of the pyrolysis chamber; polishing by hand with grinding and polishing wheels according to conventional methods; and heating for considerable time (i.e., > 24 hrs) in an inert atmosphere (i.e., He) to remove absorbed volatiles.

The procedure for the pyrolysis experiments of this study is briefly as follows. Pyrolysis is induced by the focussed laser output. The microscope used to focus the laser

also allows particular coal surface sites to be selectively irradiated. The pyrolysed craters from the laser beam can be varied by altering the degree of focussing to between 10 to 250 μm in diameter. These craters can be 5 to 10 μm in depth. The actual depth is also dependent upon the size of the irradiated area as well as the energy setting of the laser. Throughout pyrolysis the volatile products are swept by He gas through the heated transfer line to the column and trapped in the liquid N_2 bath. The transfer efficiency of the volatiles being dependent on the temperature of the transfer line. This relationship between transfer efficiency and temperature is also observed to be mass discriminate with higher molecular weight species being filtered out by lower temperatures. Once the volatiles from a number of laser pulses (typically 10 - 20) have been collected, the oven of the GC is heated (at 4 $^\circ\text{C}/\text{min}$ from 40 $^\circ\text{C}$ to 280 $^\circ\text{C}$) effectively releasing and separating them according to size as they pass through the column.

The separated samples are continually analysed by electron impact mass spectrometry as they emerge from the column.

RESULTS

Laser parameters such as duration of irradiation, wavelength, power density, and size of the irradiated area have been identified from the previous laser pyrolysis studies of coal³. Optimum spectral conditions are also investigated for the present experiments. A sufficient number of volatiles were produced from 20 laser shots at different surface sites. It was necessary to investigate fresh surfaces with each pulse so that char produced from a previous pulse is not subsequently analysed. The coal samples were successfully pyrolysed with tightly focussed (i.e., high energy) pulses. Different products were obtained by varying the laser power either through defocusing the microscope or using a neutral density filter control.

The volume of volatiles produced by the laser proved insufficient in itself to facilitate continual signal detection by the Kratos MS-80 mass spectrometer. Because of this it was necessary to extend the mass range to m/z 40 - 600 so that CO_2 (i.e., $m/z = 44$) contributes to the background ion signal. The signal from CO_2 is much larger than the signal from the pyrolysis volatiles which often remain hidden in the baseline (i.e., CO_2 signal) of the total ion chromatogram (TIC). A large signal present in all laser pyrolysis TIC's at a retention time of ~ 3 - 4 minutes can also be assigned to CO_2 . This result is consistent with many of the earlier studies in which CO_2 was observed to be the most dominant pyrolysis product. Other low abundant pyrolysis products may only be successfully revealed by individual and summed ion chromatograms.

Summed ion chromatograms for the subbituminous coal and high volatile C bituminous cannel coal are shown in Figures 2 and 3, respectively. Ions of mass 108, 122 and 136 are summed in the case of the subbituminous coal to reveal the pyrolysis production of alkyl phenols. The 108 ion identifies cresol (i.e. C_1 -phenol), the 122 ion C_2 -phenol and the 136 ion C_3 -phenol. Such products, previously observed from flash pyrolysis,²² are thought to dominate the vitrinite component of these coals. The resolution of ortho-Cresol isomer from the para and meta isomers was also observed from flash pyrolysis. The detection of these known pyrolysis products highlights the suitability of the laser as a pyrolysis source. Other species identified from the laser pyrolysis TIC include C_n -benzenes ($n \leq 2$), phenol, indene and naphthalene. Although low molecular weight alkyl - aromatics such as these are typically produced from coal pyrolysis some of these products may arise from simple evaporation from the coal surface at the high temperatures (180 - 220) of the pyrolysis chamber. Studies are presently under way to determine which species do arise from simple evaporation.

All ions from 46 - 600 contribute to the summed chromatogram associated with the high volatile coal (i.e., Fig. 3) This trace effectively reflects the CO₂ subtracted TIC. Low molecular weight products such as alkyl benzenes, toluene, indene and naphthalene are again observed. In addition, a prominent homologous series of dominant n-alkanes which range to above n-C₂₉ are observed. This distribution of n-aliphatic hydrocarbons is typical of immature, lignite-rich terrestrial organic matter.²³ The biomarker 17β(H)-22,29,30-trisnorhopane is also detected at a retention time of ~ 70 minutes. The production and detection of this species is particularly encouraging since pentacyclic triterpenoids with the hopane type skeleton are a widely utilized group of biomarkers found in organic geochemical materials.²⁴ The detection of these large molecular weight products indicates the successful transfer, trapping and column separation of high molecular weight species by this technique. It is likely that these alkanes and biomarkers are released from the coal not as pyrolysis fragments but as trapped molecules released during laser heating.

Interpretation of the different mass spectra does suggest that there exists a fundamental difference between the chemical and structural compositions of the two coals.

CONCLUSIONS

The initial results presented in this paper demonstrate that coal macerals can be successfully investigated by laser micropyrolysis. The energy from the focussed laser beam was sufficient to induce coal pyrolysis and the microscope offers the added advantage of irradiating specific areas of the coal surface. Heating the pyrolysis chamber and transfer line prevents condensation of the laser emitted volatiles which are successfully flushed into the column of the GC by the pre-heated He carrier gas.

Products typical of coal pyrolysis were detected from the two samples. The different results for the respective samples reflects the contrasting maceral components of the coals and the ability of this technique to differentiate these differences is established. The investigation of individual components within a whole range of heterogeneous geochemical materials should now be possible with this technique.

REFERENCES

1. T. I. Elington, S. R. Larter and J. J. Boon, *J. Anal. Appl. Pyrolysis*, 20, 20 (1991).
2. B. Horsfield, *Geochimica. et. cosmochimica. acta*, 53, 891 (1989).
3. a) F. J. Vastola and L. J. McGahon, *Fuel*, 66, 886 (1987).
b) F. J. Vastola and A. J. Parone, *Am. Chem. Soc. Div. Fuel Chem., Prepr.*, 10, 53 (1966).
c) F. J. Vastola, A. J. Parone, P. H. Given and R. R. Dutcher, "Spectrometry of Fuels", Plenum Press, N. Y., (1970), p29.6.
4. a) S. A. Stout and K. Hall, *J. Anal. Appl. Pyrolysis*, 21, 195 (1991).
b) S. A. Stout and R. Lui, *Org. Geochem.*, In Press (1992).
5. D. M. Hercules, R. J. Day, K. Balasanmugam, T. A. Dang and C. P. Li, *Anal. Chem.*, 54, 280A (1982).
6. J. J. Morelli, D. M. Hercules, P. C. Lyons, C. A. Palmer and J. D. Fletcher, *Mikrochim. Acta [Wien]*, 111, 105 (1988)

7. A. F. Gaines and F. M. Page, *Fuel*, 62, 1041 (1983).
8. P. K. Dutta and Y. Talmi, *Fuel*, 61, 1241 (1982).
9. F. S. Karn, R. A. Friedal and A. G. Sharkey, *Carbon*, 5, 25 (1967).
10. F. S. Karn, A. G. Sharkey, A. F. Logar and R. A. Friedal, *US Bur. Mines Rep. Invest.* 7328, 32 (1970).
11. W. H. Joy, W. R. Ladner, and E. Pritchard, *Fuel*, 19, 26 (1968).
12. J. P. Biscar, *J. Chromatogr.*, 56, 348 (1971).
13. R. L. Hanson, N. E. Vanderborgh and D. G. Brookins, *Anal. Chem.*, 47, 335, (1975).
14. R. L. Hanson, D. G. Brookins and N. E. Vanderborgh, *Anal. Chem.*, 48, 2210, (1976).
15. R. L. Hanson, N. E. Vanderborgh and D. G. Brookins, *Anal. Chem.*, 49, 390, (1977).
16. N. E. Vanderborgh, W. J. Verzino, M. A. Fletcher and B. A. Nichols, *J. Anal. Appl. Pyrolysis*, 4, 21 (1982).
17. D. R. Dyrkacz, C. A. A. Bloomquist and L. Rusic, *Fuel*, 63, 1367 (1984).
18. N. Bostick and B. Alpern, *J. Microscopy*, 109, 41 (1971).
19. P. Robert in "Organic Metamorphism and Geothermal History: Microscopic Study Organic Matter and Thermal Evolution of sedimentary basins", D. Reidel Publishing Comp., Boston, 1988, p311
20. M. Nip, J. W. deLeeuw, and J. C. Crelling, *Energy and Fuels*, 6, 125 (1991).
21. P. F. Greenwood, M. G. Strachan, G. D. Willett and M. A. Wilson, *Org. Mass Spectrom.*, (1991).
22. P. G. Hatcher, H. E. Lerch, III, R. K. Kotra and V. T. Vincent, *Fuel*, 67, 1069 (1988).
23. S. R. Larter in "Analytical Pyrolysis, Techniques and Applications", Ed. K. J. Voorhees, Butterworths, Boston, 1984, pp 212 - 275.
24. G. Ourisson, P. Albrecht and M. Rohmer, *Sci. American*, 251, 44 (1984).

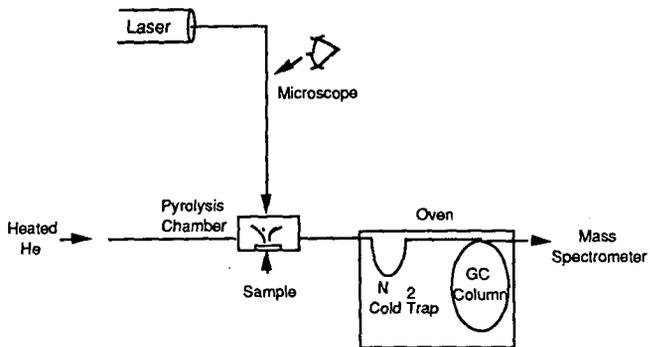


Figure 1 Assembly of Apparatus Used in the Micropyrolysis Experiment.

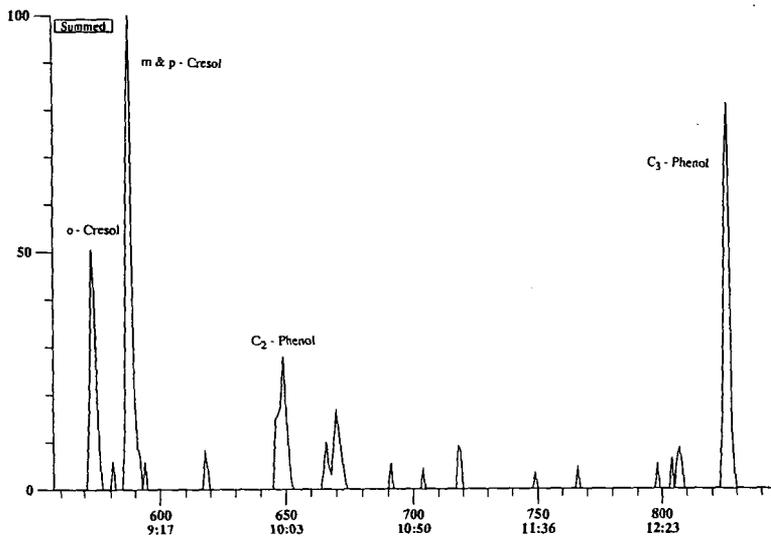


Figure 2 Summed chromatogram of the m/z 108, 122, 136 ions from the laser pyrolysis of a subbituminous coal.

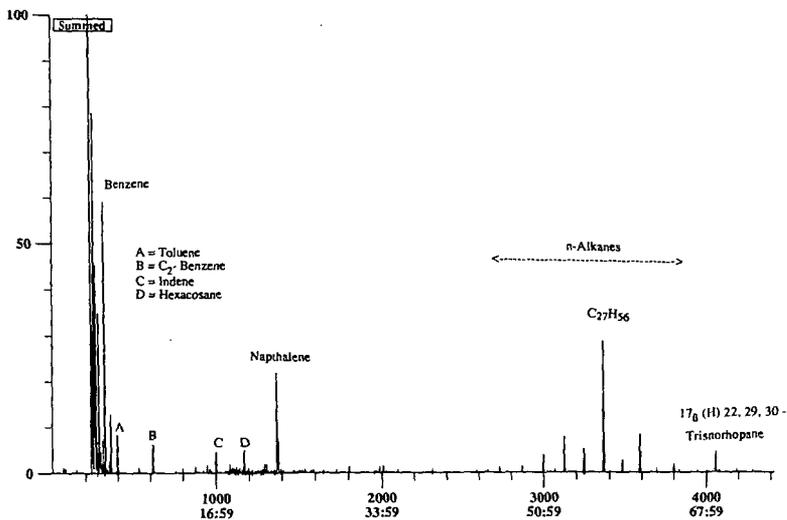


Figure 3 Summed chromatogram of all m/z 46 - 600 ions from the laser pyrolysis of a high volatile C bituminous canal coal.