

# LASER PYROLYSIS GAS CHROMATOGRAPHY/MASS SPECTROMETRY OF SINGLE SPHEROCARB PARTICLES IMPREGNATED WITH BITUMINOUS AND POLYMERIC SUBSTANCES

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## INTRODUCTION

A major bottleneck in the development of novel coal characterization methods, such as laser pyrolysis GC/MS, capable of analyzing individual coal particles, is the unavailability of suitable standard samples. Although carefully homogenized and characterized standard coals are now available through the Argonne National Laboratory Premium Coal Sample Program (ANL-PCSP) such "statistically homogeneous" coal powders are of limited value as reference materials for single particle analysis methods. Even if it would be feasible to prepare particles of closely similar chemical composition and size, e.g., by using highly concentrated coal maceral fractions and careful sieving, remaining variations in shape, density, porosity or thermal conductivity could still introduce an unacceptably high level of uncertainty for most optimization and calibration purposes.

In an attempt to find model coal char particles with well defined chemical [1,2] and physical properties, e.g., for the purpose of modeling char oxidation reactions, several authors have used Spherocharb® particles. Flagan et al [3] have even prepared spherical char particles spiked with mineral matter components in order to more closely mimic actual coal char particles. Although Spherocharb particles still show considerable variability with regard to size (rel. s.d. ~20% on a volume basis), other characteristics such as shape, density, porosity, thermal conductivity and chemical composition are assumed to be quite constant.

Unfortunately, Spherocharb particles are of little value for modeling coal devolatilization reactions due to their very low volatile matter yields. This prompted us to think of ways to increase volatile matter yields by introducing a variety of model compounds, ranging from low molecular weight, bitumen-like components to polymeric materials such as soluble lignins or resins. To the best of our knowledge this article represents the first reported use of bitumen and polymer impregnated Spherocharb particles for modeling devolatilization processes in individual coal particles.

## EXPERIMENTAL

Bitumen-like low MW compounds, consisting of a mixture of alkyl-naphthalenes prepared by open column LC subfractionization of a coal pyrolyzate, [4] with additional 1-3 ring alkylaromatics and hydroxyaromatics added in later were impregnated into a small batch of Spherocharb particles, in the 125-150  $\mu\text{m}$  dia. size range from a 8 mg/ml solution in methanol, followed by evaporation of the solvent at room temperature. The average amount of bitumen adsorbed by each particle was estimated to be approx. 70 ng. Soluble polymeric materials, such as steam-exploded cottonwood lignin and fossil resin derived from Utah (Blind Canyon seam)

coal were impregnated from 8 mg/ml solutions in 2:1 methanol/dichloromethane and toluene, respectively. Assuming complete absorption of the polymers into the Sphero carb particles the maximum average amount of polymer per particle was estimated at 70 ng. Experiments with actual coal particles in the 100-150  $\mu\text{m}$  size range, prepared by careful sieving, involved Illinois #6 coals from the ANL-PCSP program.

Laser pyrolysis gas chromatography/mass spectrometry (laser Py-GC/MS) experiments were performed with two different experimental configurations as shown in Figures 1a and 1b respectively. The first experimental set-up (Figure 1a) has been described before in more detail [5] and consists of an EDB (electrodynamical balance), a 50 W cw CO<sub>2</sub> laser and a Finnigan MAT ITMS system. The EDB type particle levitation cell was constructed in such a way as to provide line-of-sight access to the center of the cell for the two opposing CO<sub>2</sub> laser beams as well as for a stereo microscope and a two-color optical pyrometer. Typical cell operating parameters for levitating a 120  $\mu\text{m}$  dia. Sphero carb particle are: ring electrode 3000 V (60 Hz ac), upper end cap +100 V dc, lower end-cap -100 V dc. A second, novel experimental set-up (Figure 1b) uses copper electron microscopy grids with 45 x 45  $\mu\text{m}$  openings separated by 5  $\mu\text{m}$  thick bars (78% open, see Figure 2) to support individual coal particles in a downward directed flow of air or inert gas in the center of two CO<sub>2</sub> laser beams crossing at a 37° angle. Since the grids are mounted directly against the mouth of the sampling inlet, yields of volatile products are maximized. Furthermore, introducing, positioning, stabilizing and retrieving individual particles is greatly simplified compared to the set-up in Figure 1a, while conductive heat losses may be assumed to be minimal in view of the light construction of the grid.

The cw CO<sub>2</sub> laser (Apollo 3050 OEM) is capable of electronic pulsed beam operation. The 8 mm dia. beam is split equally into 2 separate beams focussed at the center of the levitation cell or grid (beam waist ca. 400  $\mu\text{m}$ , typical power densities 4-10 MW/m<sup>2</sup>). A co-linear, parafocal HeNe laser beam permits positioning of the particle in the center of the CO<sub>2</sub> laser beam. Two IR detectors measure integrated pulse energy and time-resolved pulse energy, respectively.

Finally, a heated fused silica capillary GC column (2m x .18 mm DB5) equipped with a special air sampling inlet enables intermittent sampling of volatiles from the center of the levitation cell or grid into the ITMS vacuum system while providing a highly useful degree of GC separation. During a typical run the GC column is ballistically heated from 50 C to 200 C in approx. 2 minutes.

## RESULTS AND DISCUSSION

The novel laser pyrolysis GC/MS configuration shown in Figure 1b, in which coal and Sphero carb particles are supported on ultralight electron microscopy grids (Figure 2), promotes efficient collection of volatile pyrolysis products. As shown in Figure 3, this results in high quality Py-GC/MS profiles of single coal particles. Nevertheless, due to the inherent heterogeneity of individual coal particles with regard to physical and chemical characteristics, marked differences in absolute and relative yields of pyrolysis products are observed during successive analyses of actual coal particles, e.g. for the purpose of kinetic studies, as shown in Figure 4.

This prompted us to use Sphero carb particles spiked with known quantities of low MW bitumen-like substances (Figures 5 and 6) or soluble polymeric substances, such as lignin (Figure 7) and fossil resin (Figure 8). Laser desorption studies of bitumen-like substances, composed of alkynaphthalenes and other 1-3 ring alkylaromatics (Figures 5 and 6), are relevant in view of the well known presence of significant quantities of thermally extractable bitumen in many low or medium rank coals [6]. As illustrated in Figure 5, kinetic studies of bitumen release rates from Sphero carb particles as a function of laser pulse length do indeed show a markedly constant relative abundance of major bitumen components.

Since the bulk of the coal components undergoing devolatilization reactions consists of nonvolatile, macromolecular compounds which undergo bond scission reactions in addition to the thermal desorption behavior exhibited by low MW, bitumen-like compounds, it is desirable to work with polymeric materials when modeling coal devolatilization processes. Ideally, one would like to introduce high MW coal components, e.g., obtained by solvent extraction of suitable coals into the Sphero carb particles. Unfortunately, it tends to be quite difficult to remove effective solvents such as pyridine from these extracts, let alone from a strongly adsorbing Sphero carb matrix. These considerations led us to focus on soluble model polymers rather than on high MW vitrinite components. Because of its chemical resemblance to vitrinite components in peats and low rank coals, we chose a soluble lignin. Secondly, we selected a fossil coal resin, which appears to be the only high MW coal component readily soluble in common organic solvents.

Both the lignin and the resin are known to depolymerize readily under typical pyrolysis conditions, thus producing mixtures of characteristic building blocks. As expected from a hardwood lignin [7] the cottonwood lignin sample produces both guaiacylic (e.g.,  $m/z$  124, 138, 152) and syringylic (e.g.,  $m/z$  154) building blocks (see Figure 7). Similarly, the Blind Canyon seam resin, known to consist primarily of polymeric sesquiterpenoids [8], produces a characteristic series of sesquiterpenoid building blocks as shown in Figure 8, ranging from cadinenes ( $m/z$  204) through the partially aromatized calamenes ( $m/z$  202) to the fully aromatized cadalene ( $m/z$  198). It should be noted here that the resinite pyrolysis patterns shown in Figure 8 appear to be more simple than those obtained by conventional pyrolysis GC/MS techniques. Whether this is due to selective loss of less stable pyrolysis products in the Sphero carb particles or to differences in primary pyrolysis mechanisms at the much higher heating rates achieved by the  $CO_2$  laser ( $10^4$ - $10^5$  K/sec) needs to be investigated further.

Although the experiments with polymer impregnated Sphero carb particles are still in a relatively early stage, the selected ion chromatograms in Figures 7 and 8 demonstrate that it is indeed possible to introduce readily detectable amounts of such polymers. Unknown at present, however, are the answers to the following fundamental questions:

- (1) what is the maximum weight % of polymeric materials that can be introduced;
- (2) how can the amount of polymeric material adsorbed into each Sphero carb be conveniently controlled and measured;
- (3) to what extent does the Sphero carb matrix influence the devolatilization mechanisms and kinetics; and
- (4) are polymer impregnated Sphero carb particles well enough defined to achieve the desired reduction in interparticle heterogeneity during devolatilization experiments?

The primary objective of several experiments currently underway in our laboratory is to find answers to the above questions.

## CONCLUSIONS

The feasibility of producing bitumen and polymer impregnated Sphero carb particles for coal devolatilization modeling experiments has been established. Bitumen-impregnated Sphero carb particles show a markedly decreased level of interparticle heterogeneity compared to actual coal particles. Sphero carb particles impregnated with (soluble) polymeric materials produce readily detectable volatile products thought to represent characteristic building blocks produced by bond scission reactions. Although the "volatile matter enhanced" Sphero carb particle approach appears to offer promise for modeling coal devolatilization reactions, several fundamental questions regarding the quantitative and qualitative behavior of such systems remain to be answered before this approach can be recommended as a general tool for devolatilization studies in individual coal particles.

## ACKNOWLEDGEMENTS

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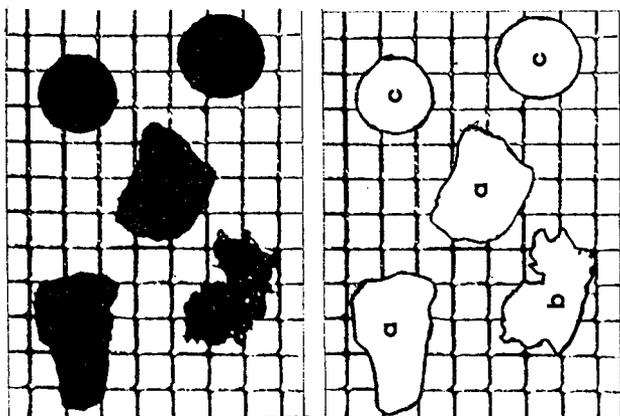


Figure 2. Microscopic view of coal and char particles on 400 mesh copper electron microscope grid; (a) fresh particles of Illinois #6 coal, (b) char particle, (c) Spherocharb particles. (a) and (c) were added later. Note degree of size and shape variation present.

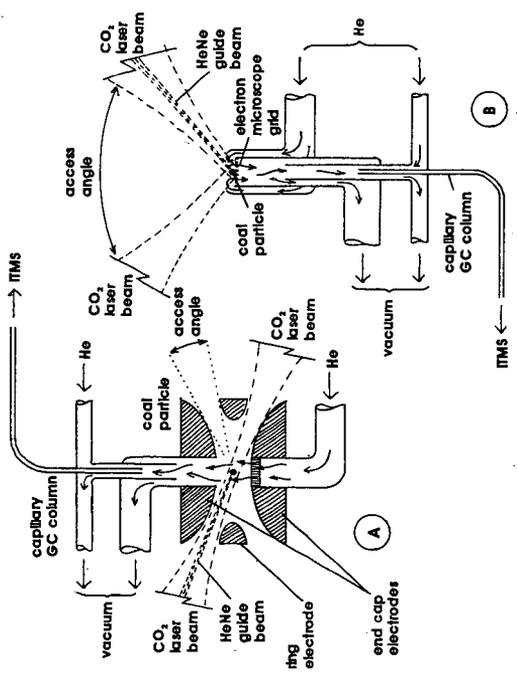


Figure 1. Laser Py-GC/MS configurations used: (a) electrodynamic balance (EDB) with opposing laser beams; (b) electron microscope grid with crossed laser beams. Note special sample inlet and capillary GC transfer line connection to ion trap mass spectrometer (ITMS).

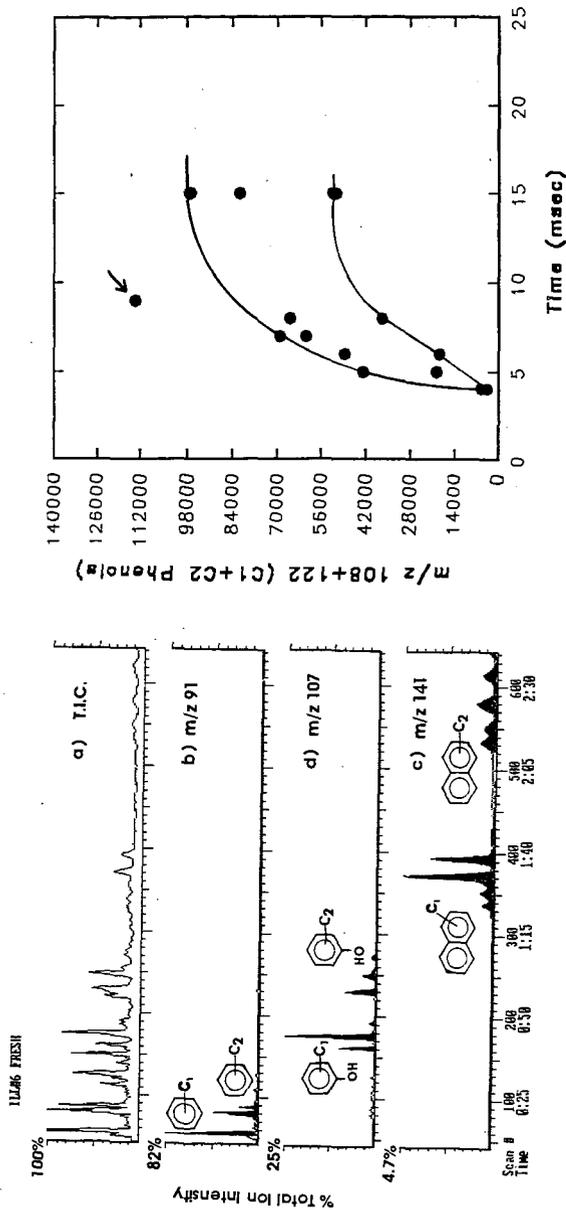


Figure 3. Laser Py-GC/MS profiles of single Illinois #6 coal particle obtained with system configuration shown in Figure 1b. Note good signal-to-noise ratio and useful degree of chromatographic separation. Highly similar patterns can be obtained with the system configuration shown in Figure 1a as well as by conventional Curie-point Py-GC/MS.

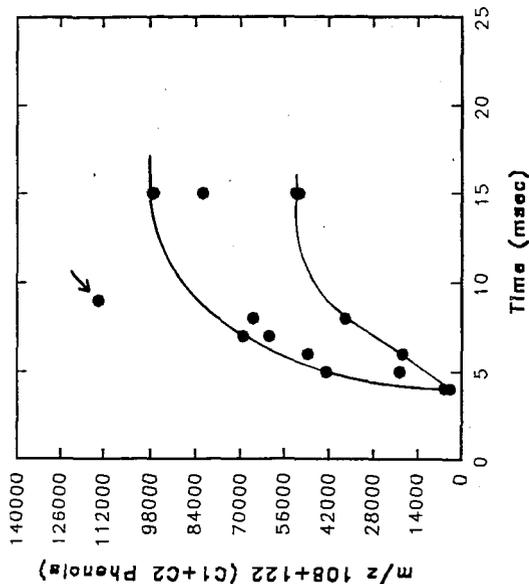


Figure 4. Relationship between laser pulse time and yield of specific pyrolysis products (C<sub>1</sub> and C<sub>2</sub> alkylphenols) during 14 consecutive laser Py-GC/MS runs on individual Illinois #6 coal particles. Note large variations in yield. Curves fitted to maximum and minimum values only. Arrow indicates outlier with anomalous GC/MS pattern. Experimental conditions as in Figure 1b.

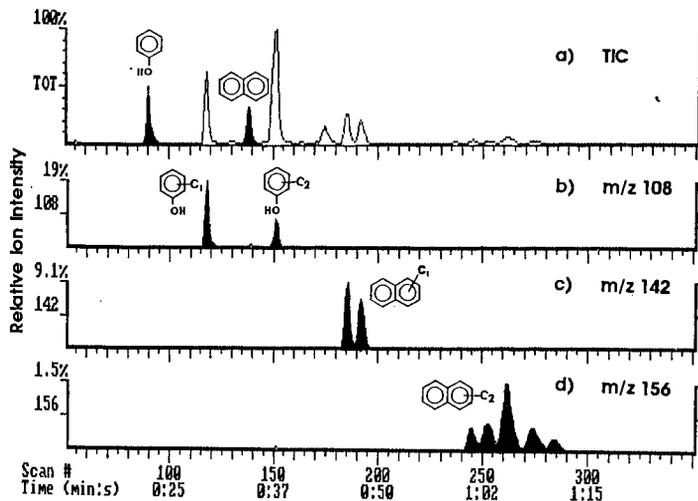


Figure 5. Laser desorption GC/MS profiles of a single Spherocharb particle impregnated with a mixture of bitumen-like compounds. Note separation of various alkylaromatic isomers. Experimental configuration as in Figure 1a.

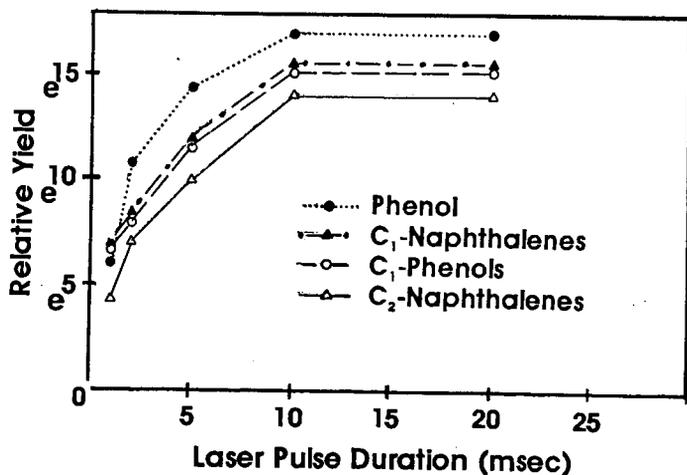


Figure 6. Relationship between laser pulse time and desorption yields of some of the model compounds shown in Figure 5. Each dot represents the average of 2 different laser desorption GC/MS analyses. Note closely similar relative abundances at all pulse durations, except for phenol.

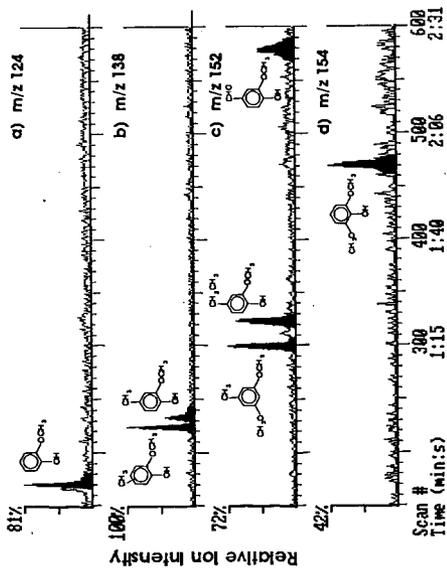


Figure 7. Selected ion chromatograms obtained by Laser Py-GC/MS analysis of a single, lignin impregnated Spherocarb particle. Note presence of characteristic hardwood lignin building blocks. Experimental conditions as in Figure 1b.

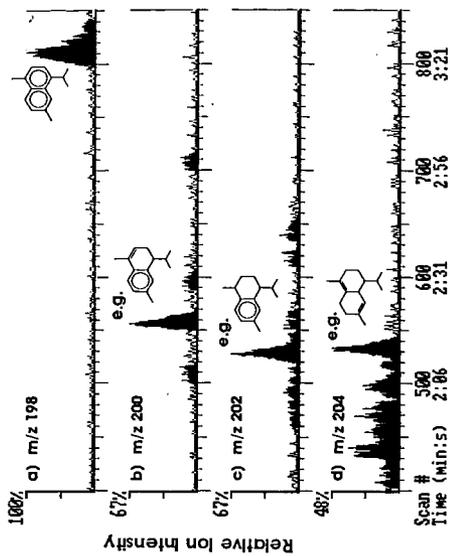


Figure 8. As Figure 5 but using a single, fossil resin impregnated Spherocarb particle. Note characteristic sesquiterpenoid building blocks. It should be noted here that a minor portion of the signals at m/z 198 (cadalene) and 202 (calamenes) represents low MW (monomeric) rather than polymeric components. Experimental conditions as in Figure 1b.