Laser Ablation GC-MS: New Instrument Interface for *In Situ* Analysis of Volatile Organic Compounds

Matt Horton, Ben Rougeau, and Dr. Robyn Hannigan
Graduate Program in Environmental Sciences
Arkansas State University, State University, AR. 72467.

Abstract

Studies of organic matter in solid samples include the analysis of bitumen, kerogen, organic carbon, various hydrocarbons, and fatty acids. Our research focused on developing an in situ analytical method for the detection and characterization of organic matter in black shales. Black shale is a limited source for oily hydrocarbons generated from the processes of diagenesis and catagenesis. Current methods of analysis of organic matter and various hydrocarbons derived from black shale involve a series of organic extractions. These methods include extraction of total organic matter (TOM) and extractable organic matter (EOM) followed by further extractions which are necessary to isolate saturated hydrocarbons, normal, branched, and cyclic alkanes, other hydrocarbons (n-alkanes, steranes, and hopanes), and fatty acids.

New instrument interfaces provide the means for analysis of many compounds and elements in a variety of new and existing applications. Therefore, as an alternative to the existing standard operating procedures for organic analysis, a new sample cell and laser ablation-gas chromatograph (LA-GC) instrument interface was designed to deliver ideal sample volumes and transfer efficiencies necessary for analysis by GC-MS. We determined that by changing ablation parameters such as energy, pulse repetition rate, and bursts (4.5 mJ, 10 Hz, 10 shots), our system effectively and efficiently desorped organic compounds and introduced these volatilized compounds into the GC. We also investigated in-injector pyrolysis as an alternative to the pyrolysis cell typically interfaced to a GC-MS. Both in-injector pyrolysis and the LA-GC interface were efficient sample introduction methods allowing for characterization of organic matter in solid samples while by-passing traditional extraction procedures.

Introduction

➢Black shale is a dark, thinly laminated shale, rich in organic matter (5 - 10% or more carbon content) and can be classified as a limited source for oily hydrocarbons generated from the processes of diagenesis and catagenesis.

➢Studies concerning the organic diagenesis of black shale and other oil bearing rocks include the analysis of bitumen, kerogen, organic carbon, various hydrocarbons, and fatty acids (Ahmed et al., 2004).

➢Current methods of analysis of organic matter and various hydrocarbons derived from bitumen held in black shale involve a series of organic extraction methods. These methods include extraction of total organic matter (TOM) and extractable organic matter (EOM) followed by further extractions which are necessary to isolate saturated hydrocarbons, normal, branched, and cyclic alkanes, other hydrocarbons (n-alkanes, steranes, and hopanes), and fatty acids (Taguchi et al., 1986).

➢In this study the organic material in black shale is desorbed-pyrolyzed and locally extracted with the laser ablation system before being separated by the GC and detected by the MS detector. In this manner, the effectiveness of LA-GC-MS for sampling, separation, and identification is explored and compared to typical extraction analysis performed with GC-MS.

➢Using LA-GC (Laser Ablation-Gas Chromatography) with a Mass Spectrometry Detector (MS)) to directly sample the black shale matrix may dramatically save analysis time by eliminating the need for tedious extraction steps and may prove to be a good technique for characterization of volatile organic materials stored in black shale source rocks.

➢GC has been used for many decades in successful separations of a wide range of compounds derived from many types of samples (Rubinson and Rubinson, 2000) and mass spectrometry detectors are excellent for analysis of organic compounds because they are compound specific and can provide unambiguous identification of the constituents in a sample.

➢In this study, the laser energy is altered by varying the laser spot size, pulse frequency, number of pulses, and energy level to determine optimum operating conditions for desorption and characterization of organic matter in bitumen stored in black shale.

➢GC temperature programming is also incorporated and injector temperatures are explored to optimize preservation of the products of laser desorption-pyrolysis.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. Anna Cruse, Oklahoma State University for providing samples and the Environmental Sciences Students, ASU for assistance. Joe Brady, CETAC Technologies for technical support.

Instrumentation and Interface (LA-GC-MS)

Laser ablation system - CETAC LSX-500

- Wavelength 266 nm
- Energy range 1.5 - 9 mJ (5 – 100%)
- Spot sizes 10 - 200 µm
- The 266 nm is a sufficient wavelength for thorough ablation of most colored and colorless solid materials (Jackson, 2001).

Perkin Elmer Clarus 500 GC-MS

- Temperature programmable – oven, injector, and detector, carrier gas flow rate, timed events
- MS Mass Range 35 – 600 Da
- EI Source 70eV
- Selected Ion Mode
- NIST Reference Library
- GC capillary column 30 meter, 0.25mm inner diameter, 0.1 mf DB-5
- A 5 cm3, low volume sample cell was designed and constructed for this study to achieve appropriate sample introduction into the GC.

Interface components

- 3 meter, 0.53 mm inner diameter fused silica transfer column with no stationary phase
- 5 cm^3 sample cell (see picture below)
- GC injector
- The fused silica transfer line is connected to the sample cell using a 1/8" to 1/16" steel converter.
- The other end of the transfer column is inserted 2 inches through the septum in the injector nut.
- Glass wool is placed into the injector liner to prevent particulate matter from entering the GC column.

Figure 1. LSX-500, GC-MS, and fused silica transfer line (red arrow).

Figure 2. Specialized low volume (5 cm^3) sample cell specific for LA-GC studies.

Figure 3. Placement of fused silica transfer capillary through injector nut and septum and into injector liner.

Figure 4. Powdered black shale (A), extracted bitumen (B), pelletizer (C), black shale pellets (D)

Sample Preparation

Black shale pellets are made using a steel nut with a 1/8" threaded inner diameter. The black shale powder is placed in the nut and flat bottom screws are tightened around the powder to compress it into a pellet. This pellet is placed into the sample cell. Extracted bitumen is prepared for laser sampling by placing a small amount onto a slide. The slide is placed into the sample chamber. Bitumen samples for direct injection GC-MS analysis were prepared by dissolving 3 mg into 20 mL of hexane to create a solution of 150 ppm.

LA-GC-MS Method Parameters

Laser Energy	**50 % (4.5 mJ)**	
Pulse Frequency	**10 Hz**	
Pulse Number	**10 shots**	
Spot size	**200 µm**	
Oven Program	**Initial Temperature**	**40ºC hold 1 min**
	Hold Time 1	**1 minute**
	Oven Ramp	**5ºC/minute**
	Final Temperature	**280ºC**
	Hold Time	**2 - 11 minutes**
Injector Program	**Temperature**	**250ºC**
	Flow Rate 1	**External 2 mL/min flow (Removed after 1 minute)**
	Flow Rate 2	**1 mL/min (Applied at 1 minute)**
	Split	**20:1 (Applied at 1.01 minute)**

Results

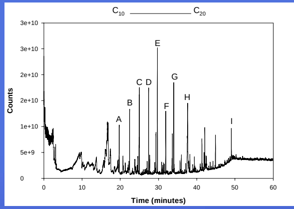

Figure 5. LA-GC-MS chromatogram of organics in black shale obtained by direct laser desorption.

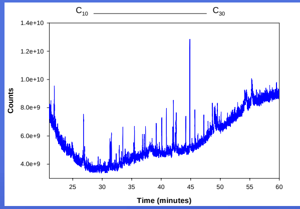

Figure 6. GC-MS chromatogram of extracted bitumen obtained by direct injection.

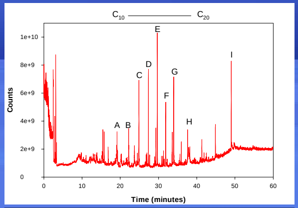

Figure 7. LA-GC-MS chromatogram of extracted bitumen obtained by direct laser desorption.

Compound		Retention Time (minutes) – Black Shale	Retention Time (minutes) - Bitumen
A	Undecanal (C_{11})	19.72	19.15
B	Dodecanal (C_{12})	22.43	22.18
C	Tridecanal (C_{13})	24.99	24.88
D	Tetradecanal (C_{14})	27.41	27.36
E	Tetradecanal (C_{14})	29.71	29.69
F	Hexadecanal (C_{16})	31.90	31.89
G	Tetradecanal (C_{14})	33.98	33.97
H	1-Eicosanol (C_{20})	37.61	37.60
I	Squalene (C_{30})	49.04	49.02

➢LA-GC-MS chromatograms using direct laser sampling of black shale pellets and bitumen reveal an assortment of alcohol, aldehyde, ketone, alkane, and alkene peaks with carbon content ranging from C_{10} to C_{20}.

➢GC-MS analysis of bitumen by direct injection produces poorer resolution of compounds. Nearly all compounds were identified as alkanes and alkenes.

➢Many of the same compounds and retention times with laser sampling of black shale and bitumen (Figure 8).

➢Signal to Noise ratios greatly enhanced using the laser sampling technique. S/N = 150, 180, and 66.5 for tallest peak in figures 5, 7, and 6 respectively.

Conclusion

➢LA-GC-MS interface effectively and efficiently desorped organic compounds and introduced these volatilized compounds into the GC.

➢Small volume sample cell appropriate for sample transfer into GC.

➢When combined with laser desorption, injector temperature of 250ºC is adequate for in-injector pyrolysis as an alternative to the pyrolysis cell typically interfaced to a GC-MS.

➢Laser desorption is an efficient sample introduction method allowing for characterization of organic matter in solid samples while by-passing traditional extraction procedures.