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. 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 μJ, 10 Hz, 10 shots), our system effectively and efficiently desorbed 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 bypassing traditional extraction procedures.

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
- Pulse Frequency: 10 Hz
- Pulse Number: 10 shots
- MS Mass Range: 35 – 600 Da
- EI Source: 70 eV
- Oven Program:
  - Initial Temperature: 40°C hold 1 min
  - Oven Ramp: 5°C/minute
  - Final Temperature: 280°C
  - Hold Time: 2 - 11 minutes
- Oven Program Table:
  - Flow Rate: 1
    - External 2 mL/min flow
  - Injector Program Temperature: 250°C
  - Injector Line (red arrow)
  - Detector: FID
  - Injector: Septum

LA-GC-MS Method Parameters

- Laser Energy: 50 μJ (4.5 μJ)
- Pulse Frequency: 10 Hz
- Pulse Number: 10 shots
- Spot size: 200 μm
- Oven Program:
  - Initial Temperature: 40°C hold 1 min
  - Hold Time: 1 minute
  - Oven Ramp: 5°C/minute
  - Final Temperature: 280°C
  - Hold Time: 2 - 11 minutes
- Injector Program:
  - Temperature: 280°C
  - Flow Rate 1: 2 mL/min flow
  - Flow Rate 2: 1 mL/min
  - Split: 20:1

Results

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

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 C10 to C20. 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 illustrate the benefits of the LA-GC-MS method over direct injection GC-MS analysis were prepared by dissolving 3 mg into 20 mL of hexane to create a solution of 150 ppm.

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.

Conclusion

LA-GC-MS interface effectively and efficiently desorbed 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 250°C 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 bypassing traditional extraction procedures.