

**ORGANIC GEOCHEMICAL APPLICATIONS OF LASER MICROPYROLYSIS GAS  
CHROMATOGRAPHY–MASS SPECTROMETRY**

PAUL F. GREENWOOD<sup>a</sup>, SIMON C. GEORGE<sup>a</sup>, KHALED AL AROURI<sup>b</sup> AND PAT. G HATCHER<sup>c</sup>

- a. CSIRO Division of Petroleum Resources, PO Box 136, N. Ryde, NSW 1670, Australia.
- b. School of Earth Sciences, Macquarie University, N. Ryde, NSW, 2109, Australia
- c. Department of Chemistry, Ohio State University, Columbus, OH 43210. USA.

Lasers present a viable alternative to conventional pyrolysis techniques. When used in conjunction with a microscope they can provide selective pyrolysis with very high spatial resolution. This is particularly advantageous for the analysis of naturally occurring organic matter (OM) which is typically heterogeneous. Laser ablation/pyrolysis mass spectrometry is a popular method of analysis for a wide array of intractable materials. However, it is of only limited value for the analysis of complex OM due to the complexity of the spectral data obtained from such materials. A more thorough geochemical appraisal is obtained from GC-MS analysis. A laser micropyrolysis GC-MS apparatus<sup>1</sup> has been constructed in the CSIRO laboratories to selectively analyse individual entities within complex OM either *in situ* or following physical isolation. Several recent application studies of this technology will be described.

Several materials previously well characterised by other established pyrolysis and analytical methods have been studied to confirm the validity of the laser micropyrolysis GC-MS data. A homologous series of *n*-alkane/alkene doublets ranging from C<sub>6</sub> to greater than C<sub>30</sub> were the major products from a Sydney Basin torbanite. Such a high aliphatic content is consistent with previous analytical data obtained from this type I kerogen. Lesser concentrations of alkylated benzenes and naphthalenes were also detected in similar relative abundance to data from a solvent extractable fraction of the torbanite. Laser micropyrolysis studies of selected oil shales (Green River and Tasmanite) have shown that the tricyclic terpenoid, sterane and hopane biomarker content of these organic materials is measured accurately.

To demonstrate the separate analysis of distinct entities within a given sample, several microscopic entities within a synthetic soil have been separately analysed. The synthetic soil comprised humin, coal, lignin, humic acids and cuticle components and was additionally doped with <sup>13</sup>C labelled pyrene as part of a concurrent study concerned with the sequestration of PAH pollutants by sedimentary organic matter. The pyrolysis distributions detected from the coal and lignin moieties of the soil were consistent with molecular data determined from pure forms of these components by conventional analytical methods. The coal is characterised by alkylbenzenes, alkyl naphthalenes and *n*-alkane/alkenes in high abundance, whereas the lignin has a predominant alkyl-, hydroxy- and methoxy-phenyl dominated product distribution. The [<sup>13</sup>C]-pyrene doped compound was consistently detected as the major product throughout these analysis, suggesting that each of these compartments of sedimentary organic matter encounter significant PAH interaction.

The laser micropyrolysis GC-MS apparatus includes an elaborate gas inlet system designed to detect with high efficiency the small pyrolysate concentrations generated from the pyrolysis of very small amounts of sample. The high sensitivity of the method has been utilised in the analysis of several organic microfossils. Neoproterozoic acritarchs and *Tasmanites* are two very different types of microfossils and yield very different concentrations of pyrolysates. Very few pyrolysates were detected from the acritarchs, which are proposed to be a highly ordered and recalcitrant polyaromatic macromolecule, akin to the resting cyst wall biopolymer of dinoflagellate (a possible acritarch precursor). In contrast the *Tasmanites* produced a very high abundance of hydrocarbon pyrolysates. A distinctive distribution of tricyclic terpenoids included several novel C<sub>19</sub>-C<sub>21</sub> saturated and unsaturated tricyclic terpenoids. The corresponding 70eV mass spectra provide some significant structural information about these novel compounds. Further scrutiny of mass spectral data from full scan, selected ion and metastable reaction monitoring analysis showed that the tricyclic content of these fossils closely mirrors the tricyclic content of the parent Tasmanite oil shale, supporting previous suggestions of a direct *Tasmanites*/tricyclic terpenoid link. The tiny organic content of oil-bearing fluid inclusions (typically < 10 μm in diameter) presented an even harder test to the sensitivity of the laser micropyrolysis technique. Nevertheless, a limited amount of molecular data in the C<sub>6</sub> to C<sub>16</sub> (*n*-alkane) MW range could still be obtained from the analysis of such material.

1. Greenwood, P. F., George, S. C., Wilson, M. A. and Hall, K. J. (1996) *J. Anal. Appl. Pyrol.*, 38, 101-118 (1996).