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Potential of short wavelength laser ablation of organic materials

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Although the literature contains several articles on UV laser ablation of synthetic polymers \cite{Meruva2004} and human tissue for surgical applications, to our knowledge there is no published record on organic geochemical applications for UV laser pyrolysis–gas chromatography–mass spectrometry (LA-GC-MS). In this study we have demonstrated the use of a 213 nm UV laser beam for ablating kerogens and organic rich rocks to liberate and analyse hydrocarbon signatures and compared the results against IR laser pyrolysis and traditional Py-GC-MS.

It is possible to equate laser wavelength to electron volts where 1064 nm (IR) = 1.2 eV and 213 nm (UV) = 5.8 eV. Most chemical bonds have an energy between 2-4 eV and C-C bonds are \textasciitilde3.6 eV. Organic materials can absorb radiation from a UV laser and chemical bonds can be cleaved cleanly by complex photochemical pathways by a single photon \cite{Zhigilei1997}. Ablation occurs with almost no heating of the sample and hence the term laser ablation instead of pyrolysis. Visible or IR lasers have insufficient energy to break bonds with a single photon this results in the heating of sample by the absorption of energy into the vibrational modes of the molecule which can then result in pyrolysis.

A solvent-extracted kerogen consisting mainly of higher plant material (Brownie Butte, Montanna, \textasciitilde70 Ma) was used for initial experiments. A number of other samples have also been analysed. Laser ablation work was performed off-line in a static helium cell followed by solvent extraction of the laser cell. Separate analysis of the same samples using a more traditional flash pyrolysis approach was performed with a CDS pyroprobe and IR laser pyrolysis \cite{Greenwood1998} for comparative purposes.

As can be seen in Fig 1 UV laser ablation is able to liberate relatively high molecular weight fragments with no alkenes or other pyrolysis artefacts detected. SEM images of ablation pits indicate there is no obvious thermal alteration of the sample. The results of the pyrolysis techniques (on-line and IR laser pyrolysis) are similar and display a number of artefacts related to the pyrolysis process. Laser ablation of a number of samples has also shown that the distributions of biomarkers are comparable with the solvent extracts. Product yields although not quantified appear to be much higher than traditional pyrolysis techniques.

Based on published work on UV laser ablation of synthetic polymers \cite{Meruva2004}, geological samples behave in a similar manner with little or no thermal heating.

![Fig. 1. TIC of UV laser ablation, on-line pyrolysis and IR laser pyrolysis of a kerogen (Brownie Butte, Montanna, \textasciitilde70 Ma).](image)

References

\cite{Meruva2004}
\cite{Zhigilei1997}
\cite{Greenwood1998}