

Is UV laser ablation a suitable tool for geochemical analysis of organic rich source materials?

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The use of ultra-violet (UV) lasers at 213 nm wavelength (quintupled Nd:YAG) has opened up new possibilities for micro-probing of materials. It is possible to equate laser output wavelength to energy in Electron Volts (eV):

- **1064 nm = 1.2 eV (IR), 213 nm = 5.8 eV (UV)**

This is significant because most chemical bonds have bond energies of ~2-4 eV. Hence, UV laser radiation is often very effectively absorbed by organic material resulting in “soft” cleavage of structural units by complex photochemical pathways [1]. The versatility of a UV laser allows drilling deeply into transparent quartz or writing letters onto a human hair with no scorching [2].

Although the literature contains several articles on UV laser ablation of polymer materials [3] 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-GCMS).

In this paper, we demonstrate the use of a 213 nm UV laser beam for ablating organic rich rocks to liberate and analyse hydrocarbon signatures. A solvent-extracted kerogen consisting mainly of higher plant material (Cretaceous, ca. 70 Ma) was used for these experiments. Initially, laser ablation work was performed off-line in a static helium cell followed by solvent extraction of the laser cell. The extract was then analysed using an Agilent 5973 GCMS system. Separate analysis of the same samples using a more traditional flash pyrolysis approach was performed with a CDS pyroprobe (model 2000) for comparative purposes. Preliminary GCMS data are shown in Figure 1. The UV LA mass chromatogram faithfully represents the high molecular weight (MW) distribution of the predominant higher plant inputs to the kerogen, and also preserves the odd over even predominance, typically only detected from immature plant material extracts. While the flash pyrolysis data also show this odd-over-even predominance, this feature is less pronounced than in the LA-GCMS approach.

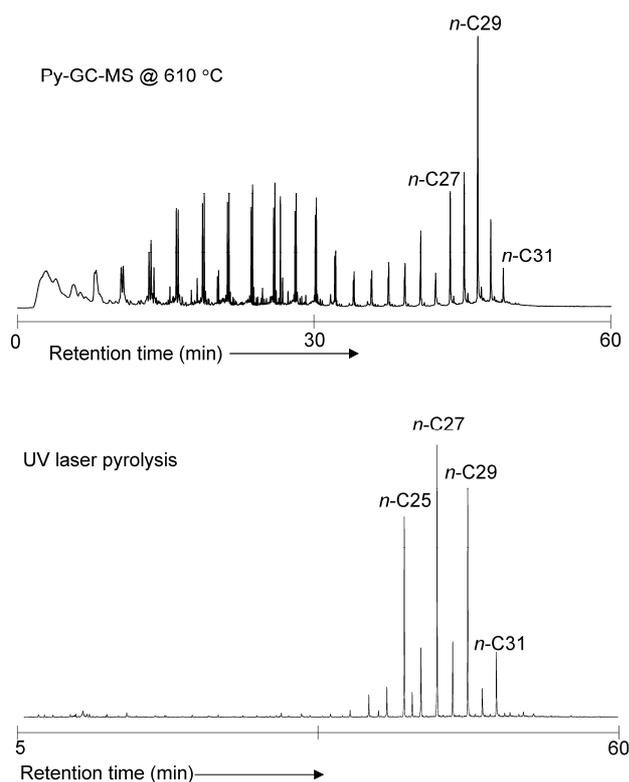


Figure 1: m/z 57 chromatograms for a solvent extracted kerogen isolate of higher plant material from the late Cretaceous Period, ~70 Ma (KT Boundary, Brownie Butte, Montana). The top chromatogram shows the m/z trace for the sample analysed by conventional Pyroprobe pyrolysis at 610°C. The bottom m/z trace is for the same sample analysed by LA at 213 nm.

Another difference is the significant concentration of lower MW hydrocarbons (HCs) in the flash pyrolysis analysis formed by thermal degradation of the high MW biopolymers of the fossil wood, as evident from the occurrence of alkene/alkane doublets. The kerogen was solvent extracted prior to analysis, hence prior to pyrolysis should only contain minimal amounts of low MW HCs. In contrast the LA mass chromatogram shows almost no low MW HCs and no pyrolysis-induced alkenes. We attribute this to clean photochemical cleavage rather than thermal break-down of the woody biopolymers. Lack of heating associated with the LA analyses is supported by several laser ablation pits showing no thermal alteration halos.

This preliminary study suggests that UV laser ablation is a suitable tool for analysing macromolecular structures of source rock macerals. This technique appears to better preserve structural units of the macromolecules compared to conventional and IR laser pyrolysis.

References

- [1] Zhigilei, L.V., Kodali, P.B.S. and Garrison, B.J., 1997. On the threshold behaviour in laser ablation of organic solids, *Chem. Phys. Lett.*, Vol. 276, pp. 269-273.
- [2] Srinivasan, R., 2005. Ablation of Polymers and Biological Tissue by UV Lasers", *Science*, Vol. 234, No. 4776, pp. 559-565.
- [3] Meruva N.K., Metz, L.A., Goode, S.R. and Morgan, S.L., 2004. UV Laser fast gas chromatography time of flight mass spectrometry for rapid characterisation of synthetic polymers: instrument development, *J. Anal. App. Pyroly.*, Vol. 71, pp. 313-325.