APPLICATION OF LOW IONISATION ENERGY GCGC/TOF-MS TO BETTER DETECT BIOMARKERS IN CRUDE OIL AND SOURCE ROCK EXTRACTS

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Introduction

Biomarkers are a fundamental component in petroleum system studies. Characterisation of biomarkers is typically achieved using conventional GC/MS and GC/MSxMS techniques with an electron impact ion source. However, the ionisation energy of 70eV results in a high degree of non-characteristic fragmentation and sometimes loss of the molecular ion. This could hamper compound identification, specifically of (unknown) branched alkanes such as botryococcane (Maxwell et al., 1968; Moldowan and Seifert, 1980) or highly branched isoprenoids (Yon et al., 1980), when present in relatively low concentrations.

A solution to reduce (but still keep) fragmentation and better preserve the molecular ion is to significantly lower the ionisation energy to around 12-16 eV (low eV mass spectrometry). The disadvantage of using this on conventional instruments is that the electron beam becomes unstable, resulting in a considerable overall reduction or even complete loss of the signal. ALMSCO (now MARKES) has introduced a newly designed ion source that solves this problem by making use of an 'ion gun' to focus the electron beam.

Results

This presentation demonstrates the combination of the MARKES low-eV time-of-flight mass spectrometer with the enhanced chromatographic separation of a comprehensive 2-dimensional GC setup for the analysis of a set of oils and algal rich source rock samples. The low-eV mass spectra show much less fragmentation and in most cases exhibited enhancement of molecular ions. Importantly it was recognised that the ion source temperature was a critical control within this system. It should be high enough to allow good performance of the GCxGC system, but not too high to prevent losing the advantages of low-eV MS. Therefore, the ion source temperature might be adjusted depending on the component of interest.
The low-eV mass spectra were generally easier to interpret, although in some cases they do differ from conventional 70eV spectra, e.g. steranes may be characterised by an m/z 218 ion rather than an m/z 217 ion. In addition, enhanced preservation of ions fragmented around branching points (tertiary carbons) allows for precise computational mass filtering of compounds of interest. This latter application allowed a swift and clear identification of markers such as highly branched isoprenoids, but also facilitated the recognition of extended and contracted members of homologue series, e.g. for ring-A methylated drimanes. A larger set of samples is currently being analysed to test reproducibility and to determine if automated filtering helps to more rapidly analyse larger datasets for branched alkane content.

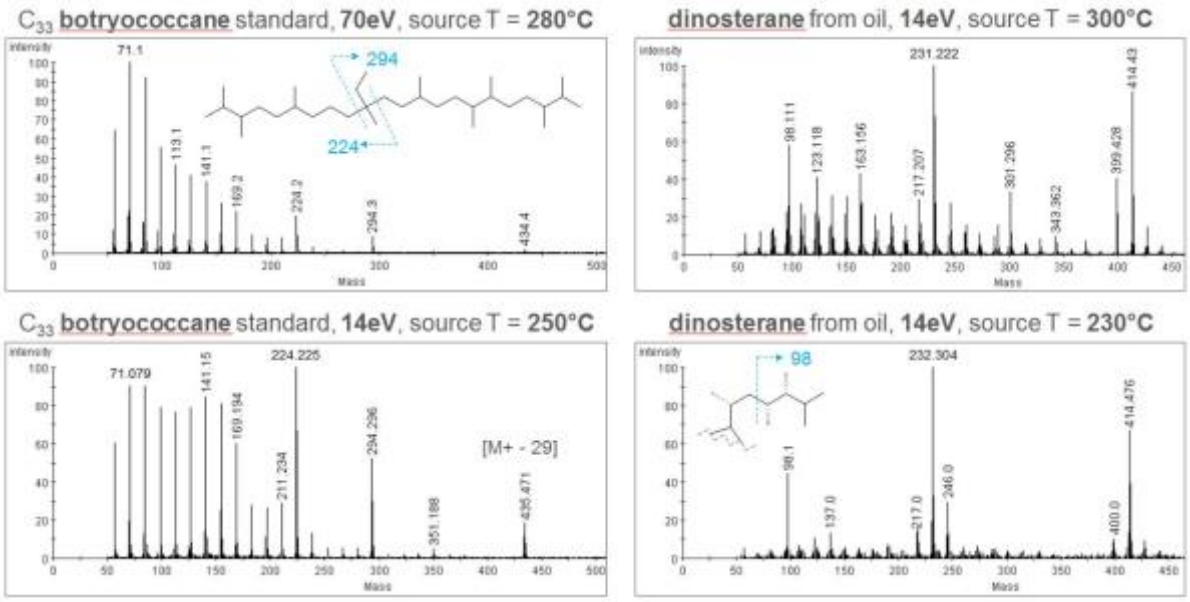

Figure 1 *Examples of mass spectra showing the difference between normal and low-eV ionisation and the effect of source temperature.*

References

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