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Nota applicativa

Identification of Source Environment from the Analysis of Rock Oil Extracts Utilizing the High Selectivity of Triple Quadrupole GC-MS

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Abstract

It has long been known that a range of non-native, stable, saturated hydrocarbon biomarkers present in crude oil extracts could be used to identify the original facie from which the oil was formed. Routine analysis is completed using Gas Chromatography (GC) with Mass Spectrometric (MS) detection using a single quadrupole analyser. Selective Ion Recording (SIR) of the 217Da fragment ion is used to identify the steranes of interest. However, this type of analysis is prone to interferences from other families of compounds found in rock oil extracts including hopanes, methyl steranes, and bicadinanes. In this paper we will show, through the use of a Waters Micromass Quattro micro GC Triple Quadrupole Mass Spectrometer, that specificity can be improved through the use of GC-MS/MS to selectively identify branched steranes (and hence the rock oils facie) while eliminating interferences seen during SIR analysis.

Benefits

Specificity can be improved through the use of GC-MS/MS to selectively identify branched steranes while eliminating interferences seen during SIR analysis

Introduction

The use of biomarkers for the specific identification of the environment (ecosystem) from which oil is produced has become an important issue in recent years. Such biomarkers can be produced from organic compounds present in the original organic source material. Some of these compounds are converted through a number of complex chemical reactions during diagenesis. Diagenesis is a low temperature process prior to deep burial and thermal maturation. During this process the reduction of oxygen moities and unsaturated regions result in the production of non native, stable, saturated hydrocarbon biomarkers in crude oil. These biomarkers can be used to identify the original organic molecule and hence identify the source organism. This ultimately results in the identification of the environment (facies) from which the oil was produced.

Steranes are one such group of biomarkers. These have been identified as the resultant saturated skeletal backbones of sterols found to be present in a number of higher plants (terrigenous) and algae (sea and fresh water associated). Figure 1 shows the structural backbone and the respective side groups for C27- C30 steranes. The key shows the variation in carbon chain length which is used to determine the organism and hence environment from which the oil was produced.[1,2]

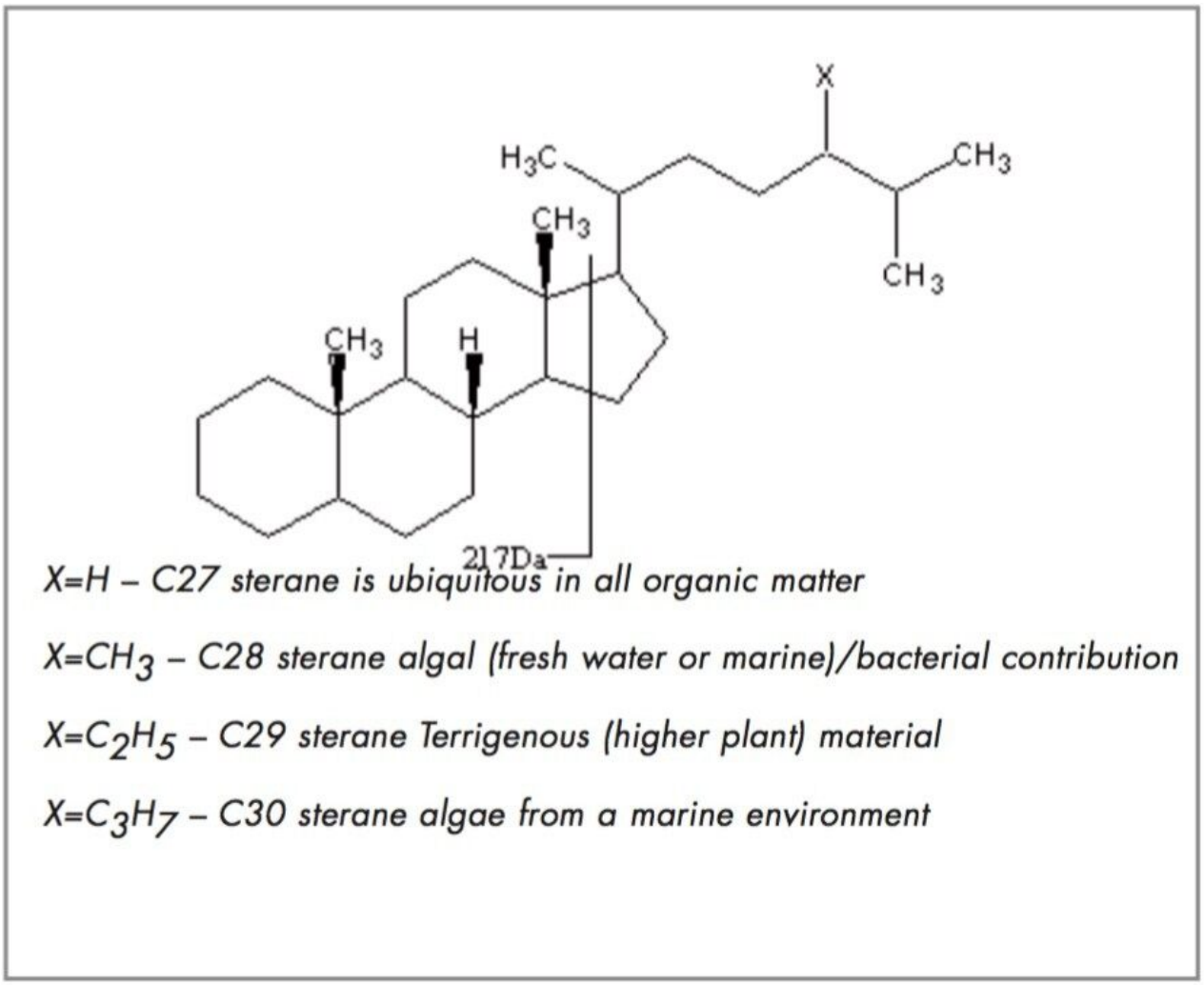

Figure 1. The sterane structure, relevant side chain length, the associated organism and hence environment from which the compound was produced.

These trace components from crude oil source rock extracts can be difficult to specifically identify due to the complexity of the extract. The current method used for sterane analysis is GC-MS (single quadrupole instrument) using Selective Ion Recording (SIR) of a known fragment (217 Da) from the sterane molecule. However, it is known that a number of compounds, e.g. bicadinanes from tree resins, hopanes and methyl steranes, can co-elute with many of the steranes, and produce a fragment ion of 217 Da. These compounds can be at much higher concentrations than the steranes of interest swamping the signal and making the unambiguous identification of these biomarkers difficult.

Experimental

Two South East Asia samples were prepared for analysis from significantly different facies, these were a marine ecosystem and a terrigenous (higher land plant) ecosystem. The source rock was solvent extracted and the resulting residue was fractionated by polarity to produce a non-polar hexane fraction. The samples were analysed on an Agilent 6890 GC attached to a Waters Micromass Quattro micro GC Triple Quadrupole Mass Spectrometer operated in EI+ mode (Figures 2 & 3).

Figure 2. Waters Micromass Quattro micro GC MS System.

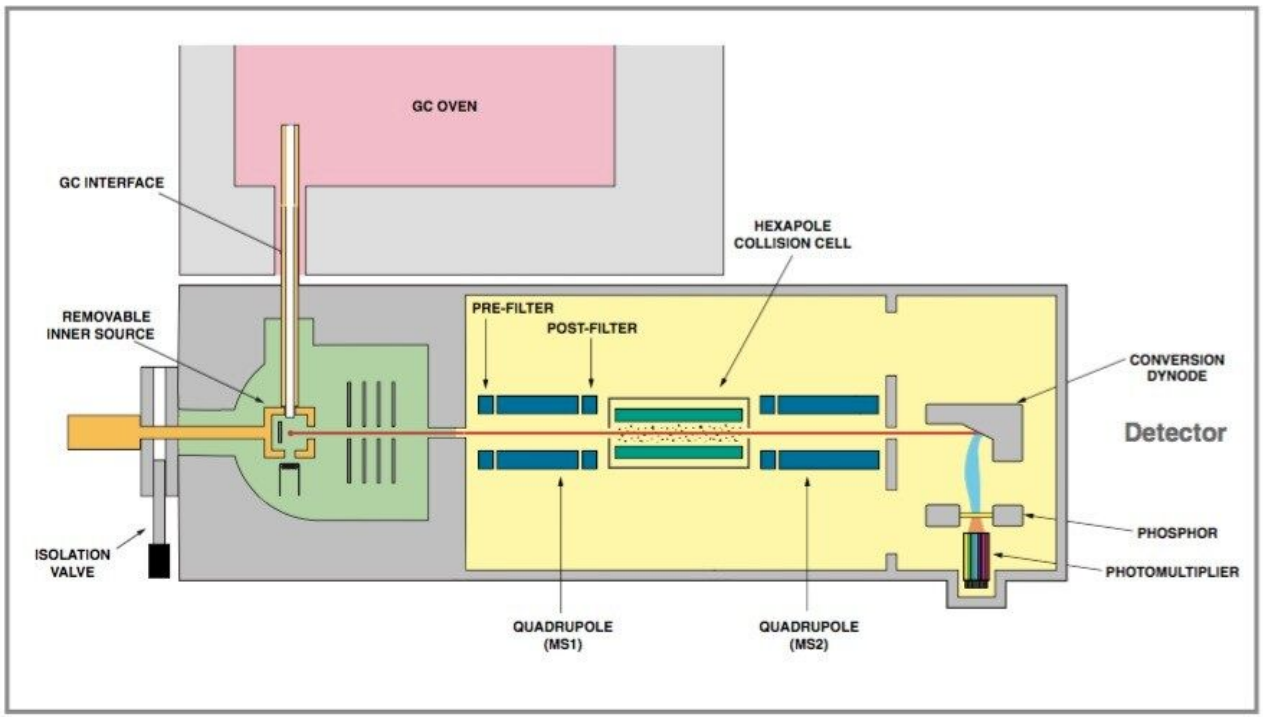

Figure 3. Waters Micromass Quattro micro GC schematic.

The samples were injected splitless (1 uL injection). Helium was used as carrier gas with a constant flow rate of 1.0 mL/min. The injector temperature used was 250 °C. The GC capillary column employed was a J&W Scientific DB-5MS column, 30 m x 0.25 mm i.d. x 0.25 um film thickness. The temperature of the transfer line was held at 280 °C during the chromatographic run. The temperature ramp rate employed was 120 °C (1 min hold) to 300 °C (8 minutes hold) at 15 °C/min, producing a total run time of 38 minutes.

Selective Ion Recording (SIR)

The ion source was operated at 200 °C with an electron energy of 70 eV and a trap current of 150 mA. The corresponding selected ions for each compound, the analogous fragment formula and their associated dwell times can be seen in Table 1.

Compounds	SIR fragment	Fragment formula	Dwell Time (secs)
Steranes/ Bicadinanes/ Hopanes/ Methyl steranes	217 217 217	$C_{16}H_{31}$ $C_{16}H_{31}$ $C_{16}H_{31}$	0.1 0.1 0.1
Bicadinanes/ Hopanes	119 119	$C_{14}H_{23}$ $C_{14}H_{23}$	0.1 0.1
Bicadinanes	369	$C_{30}H_{54}$	0.1

Table 1. Compound type, their associated SIR fragment mass, fragment formula and dwell time.

Multiple Reaction Monitoring (MRM)

The ion source was operated at 200 °C with an electron energy of 70 eV and a trap current of 150 mA. The collision gas for the MRM transitions was argon with the gas pressure in the collision cell being held at $5e^{-3}$ mbar. The following ion transitions, molecular formula, their associated dwell time, and collision energy can all be seen in Table 2.

Compounds	MRM Formula	Molecular formula	Fragment formula	Dwell Time (secs)	Collision energy
C27 Sterane	372.4 >217.2	$C_{27}H_{48}$	$C_{16}H_{31}$	0.1	10
C28 Sterane	386.4>217.2	$C_{28}H_{50}$	$C_{16}H_{31}$	0.1	10
C29 Sterane	400.4 >217.2	$C_{29}H_{52}$	$C_{16}H_{31}$	0.1	10
C30 Sterane	414.4>217.2	$C_{30}H_{54}$	$C_{16}H_{31}$	0.1	10
Bicadananes	412>369	$C_{30}H_{52}$	$C_{27}H_{45}$	0.1	10

Table 2. Compound type, their associated MRM transitions, molecular formula, fragment formula, dwell time, and collision energy.

Results and Discussion

Figures 4 and 5 show the SIR analyses of oils formed in a marine and terrigenous environment respectively showing the selected ions described in Table 1. The 85 Da channel shows the oil sample containing a high concentration of alkane compounds while the 369 Da and 191 Da channels show the presence of a number of bicadinane and hopane components. The bicadinanes are significantly more concentrated inthe terrigenous sample (Figure 5, 369 Da ion) due to the fact that the compounds originate from a resin exuded from higher plants.[3] The 217 Da channel shows the presence of not only C27-C30 steranes but also any bicadinane, hopanes and methyl sterane interferences.

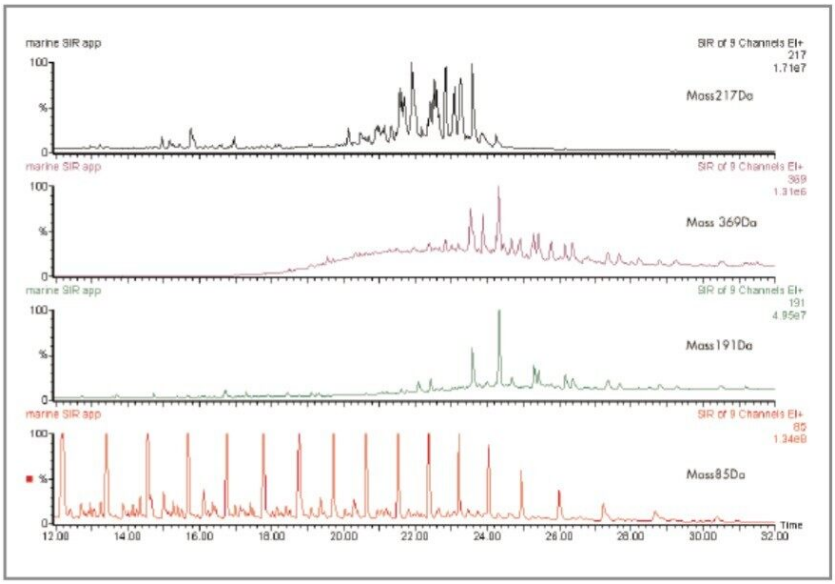

Figure 4. SIR analyses of an oil formed in a marine environment.

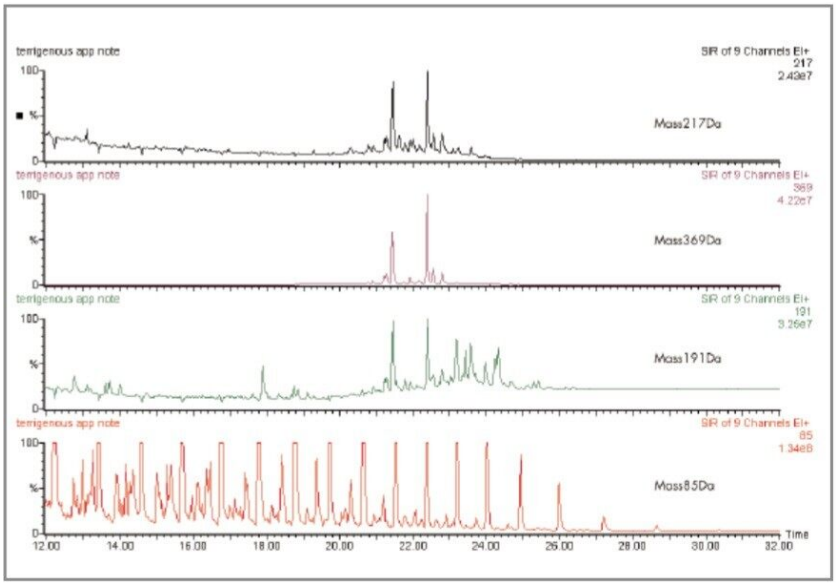

Figure 5. The SIR of an oil formed in a terrigenous environment.

Figures 6 and 7 show the MRM analysis of the marine and terrigenous oils with the five MRM transitions described in Table 2. The presence of the four steranes (their associated isomers) are confirmed from the relevant transitions displayed. The presence of C28 steranes in figure 6 indicates an algal contribution and with the significant quantities of C30 steranes this confirms the marine environment. The presence of C29 steranes in this sample also identifies the presence of some plant life. However, the low levels of the

bicadinanes confirm the environment to be non terrigenous. Figure 7 shows a higher quantity of C29 steranes compared to the C28 sterane (possibly from freshwater algae or bacteria) and indicates a terrigenous rather than a marine environment. The lack of any C30 steranes and the presence of a significant quantity of bicadinane material further confirm this.

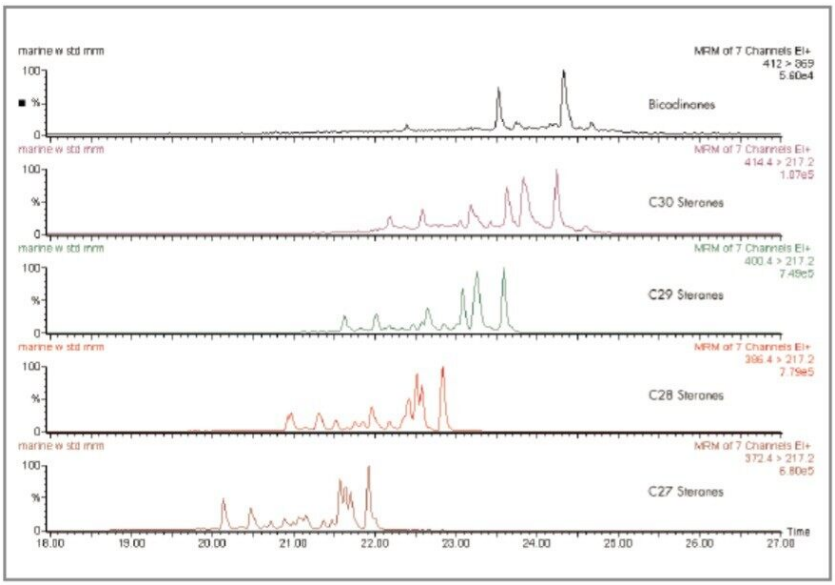

Figure 6. MRM analysis of marine oils.

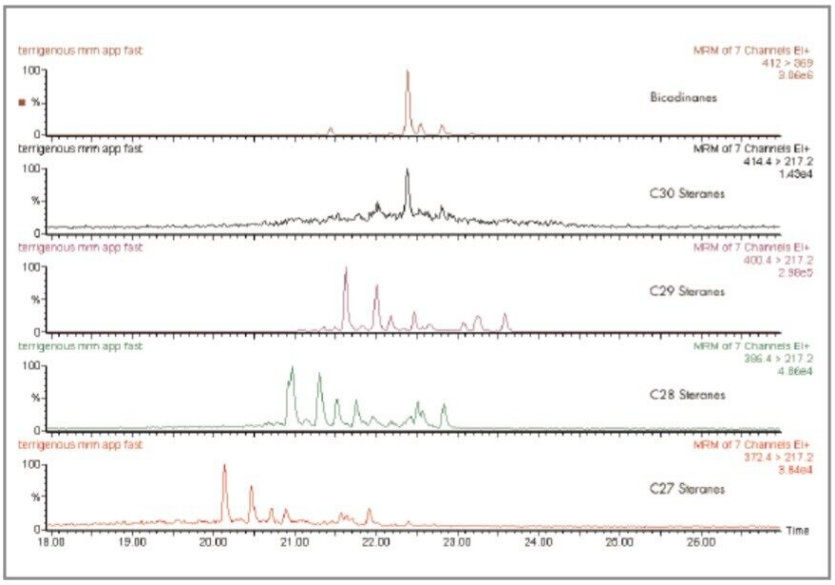

Figure 7. MRM analysis of terrigenous oils.

Conclusion

Through the use of the Waters Micromass Quattro micro GC Triple Quadrupole Mass Spectrometer we have been able to specifically identify C27-C30 steranes and use the information to accurately identify the facie of the rock oil under investigation. Comparison with the SIR analyses clearly identifies the difficulties encountered when undertaking such an investigation on a single quadrupole instrument and that for rapid unambiguous routine analysis a triple quadrupole mass analyzer is required. The bicadinane interferences seen in the SIR experiments are clearly identified and shown to cause no interference when the same samples are analysed by MRM.

References

1. Interpreting Molecular Fossils in Petroleum and Ancient Sediments. Kenneth. E. Peters and J. Michael Moldovan 1993. Prentice-Hall Inc, New Jersey. ISBN 0-13-086752-7.
2. Biomarkers for Geologists – A practical Guide to the Application of Steranes and Triterpanes in Petroleum Geology. AAPG Methods in Applications Series No 9. Douglas. W. Waples and Tsutomu Machchara. 1991 The American Association of Petroleum Geologists. ISBN 0-89181-659-3.
3. Peter Abohlin and Awang Awang Sapawi, Private Communication.

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