Application Note 30263

Molecular Characterisation of Petroleum

M. Ahmed,[1] S. Gong,[1] D. Fuentes,[1] S. Sestak,[1] F. Theobald,[2] and K. D'Silva[3];
[1]CSIRO Earth Science and Resource Engineering, North Ryde, Australia
[2]Environmental Consulting, Cologne, Germany
[3]Thermo Fisher Scientific, Bremen, Germany

Key Words
Analysis of aliphatic, aromatic and branched/cyclic hydrocarbon fractions, Thermo Scientific DFS High Resolution Mass Spectrometer

Introduction

Comprehensive molecular characterisation of petroleum is used to solve issues related to exploration and production of oil and gas. It can help identify processes that occurred in reservoirs and along migration pathways. It provides the ability to understand the key geological information encoded in the geochemistry of gas and liquid hydrocarbons and can help oil companies deduce the origin and maturity of petroleum hydrocarbons (natural gas, coal seam gas or oils). Geochemical fossils or biological markers, popularly called biomarkers, frequently convey genetic information about the types of organisms contributing to the organic matter of sediments. They are used for correlations (oil-oil and oil-source rock), for reconstitution of depositional environments, and also as indicators for diagenesis and catagenesis.[1]

CSIRO Organic Geochemistry Team is a world leading provider of research services to the petroleum industries and state and federal agencies.

Located in Sydney Australia, CSIRO Organic Geochemistry Team have conducted genetic characterisation of oils, fluid inclusion oils, natural gases and potential source rock extracts for various research projects on behalf of international energy companies including Chevron, PETRONAS, Woodside, Oil Search, Exxon-Mobil, Petrobras, Interoil, Origin Energy, Roc Oil, and BP Exploration & Production Inc.

CSIRO Organic Geochemistry Team currently use a Thermo Scientific™ DFS™ high resolution GC-MS for the molecular analyses of sedimentary organic matter, e.g., crude oils, fluid inclusion oils, condensates, potential source rock extracts, solid bitumen, pyrolyzates of ashpaltene/kerogen, etc. The DFS instrument provides a range of capabilities required for this application, including; high resolution, full scan, selected ion monitoring (also known as multiple ion detection, MID) and multiple reaction monitoring (MRM) with stable and predictable metastable product ion formation. All of these capabilities are combined by CSIRO for comprehensive analyses of petroleum hydrocarbons.

Thermo SCIENTIFIC

This application note presents a brief description of the methods and chromatographic conditions, using the DFS high resolution GC-MS for the analyses of:

- Aliphatic and aromatic hydrocarbon fractions of the North Sea Oil-1, a geochemical standard sample from the Norwegian Petroleum Directorate
- Branched /cyclic hydrocarbon fraction of a standard mixture of oils called AGSO STD obtained from Geoscience Australia (formerly, the Australian Geological Survey Organization)

Results of these analyses for the identification/ quantification of some selected hydrocarbon biomarkers are presented in the following section.

Methods

Gas Chromatographic Methods	
GC	Thermo Scientific Trace Ultra™ GC
Sampler	Thermo Scientific TriPlus XT™
Carrier gas	Helium
Carrier gas flow rate	Constant (1.5 mL/min)
Injector	Split/Splitless
Injection temperature	260°C
Injection volume	1 µL
Sample concentration	100 - 500 µg/mL in dichloromethane
GC column equivalent	TraceGOLD™ TG-1MS 60 m × 0.25 mm, 0.25 µm film P/N 26099-1540 and TraceGOLD TG-5MS 60 m × 0.25 mm, 0.25 µm film P/N 26098-1540
Temperature programs	A) 40 °C (2 min) @ 4 °C min^{-1} to 310 °C (40 min) B) 40 °C (2 min) @ 20 °C min^{-1} to 200 °C (0 min) 2 °C min^{-1} to 310 °C (40 min)

Mass Spectrometer Parameters	
MS	Thermo Scientific DFS
Electron energy	70 eV
Resolution	1000 at 5% peak height
Injection temperature	260 °C
Transfer line temperature	280 °C
Source temperature	280 °C

Mass Spectrometer Data Acquisition Methods	
Full scan of analysis of aliphatic and aromatic hydrocarbons	*m/z* 50-550, scan rate 0.5 $sdec^{-1}$. GC program A.
Multiple ion detection (MID) analysis of aromatic hydrocarbon fraction, Method-A	*m/z* 128, 134, 142, 154, 156, 166, 168, 170, 178, 183. GC program A.
Multiple ion detection (MID) analysis of aromatic hydrocarbon fraction, Method-B	*m/z* 178, 180, 182, 183, 184.03, 184.12, 192, 197, 198.05, 198.14, 202, 206, 212, 216, 220, 234. GC program A.
Multiple ion detection (MID) analysis of aliphatic hydrocarbon or its branched chain and cyclic fraction	*m/z* 177, 183, 191, 205, 217,218, 231.11, 231.21,253, 259. GC program B.
Multiple Reaction Monitoring (MRM) analysis for hopanes	*m/z* 370>191, 384>191, 398>191, 412>191, 426>191, 440>191, 454>191, 468>191, 482>191. GC program B.
Multiple Reaction Monitoring (MRM) analysis for steranes	*m/z* 358>217, 372>217, 386>217, 400>217, 414>217, 414>231. GC program B.

Results

Crude oils and source rock extracts are complex mixtures of many classes of compounds including source and maturity related biomarkers such as *n*-alkanes, isoprenoids, terpanes, steranes and diasteranes. Some biomarkers are often present in very low concentrations requiring different modes of GC-MS analyses for their identification and/or quantification; full scan, multiple ion detection and multiple reaction monitoring (MRM).

Full scan analyses provide mass spectra for structural elucidation and chromatograms of all ions. Multiple ion detection (MID) methods acquire only selected ions, e.g., *m/z* 123, 191, 217, etc. and provide results of better sensitivity than full scan, providing information about trace components. This method can be used to determine the fingerprints for the selected compound types (e.g., bicyclic sesquiterpanes, hopanes, steranes and diasteranes). Multiple reaction monitoring analyses monitor a selected daughter ion (e.g., *m/z* 217) formed from molecular ions that decompose in the first field-free region of a double-focussing mass spectrometer. This method provides the necessary selectivity required to analyze these specific compounds in such a complex matrix; resulting in better sensitivity and signal-to-noise ratios.

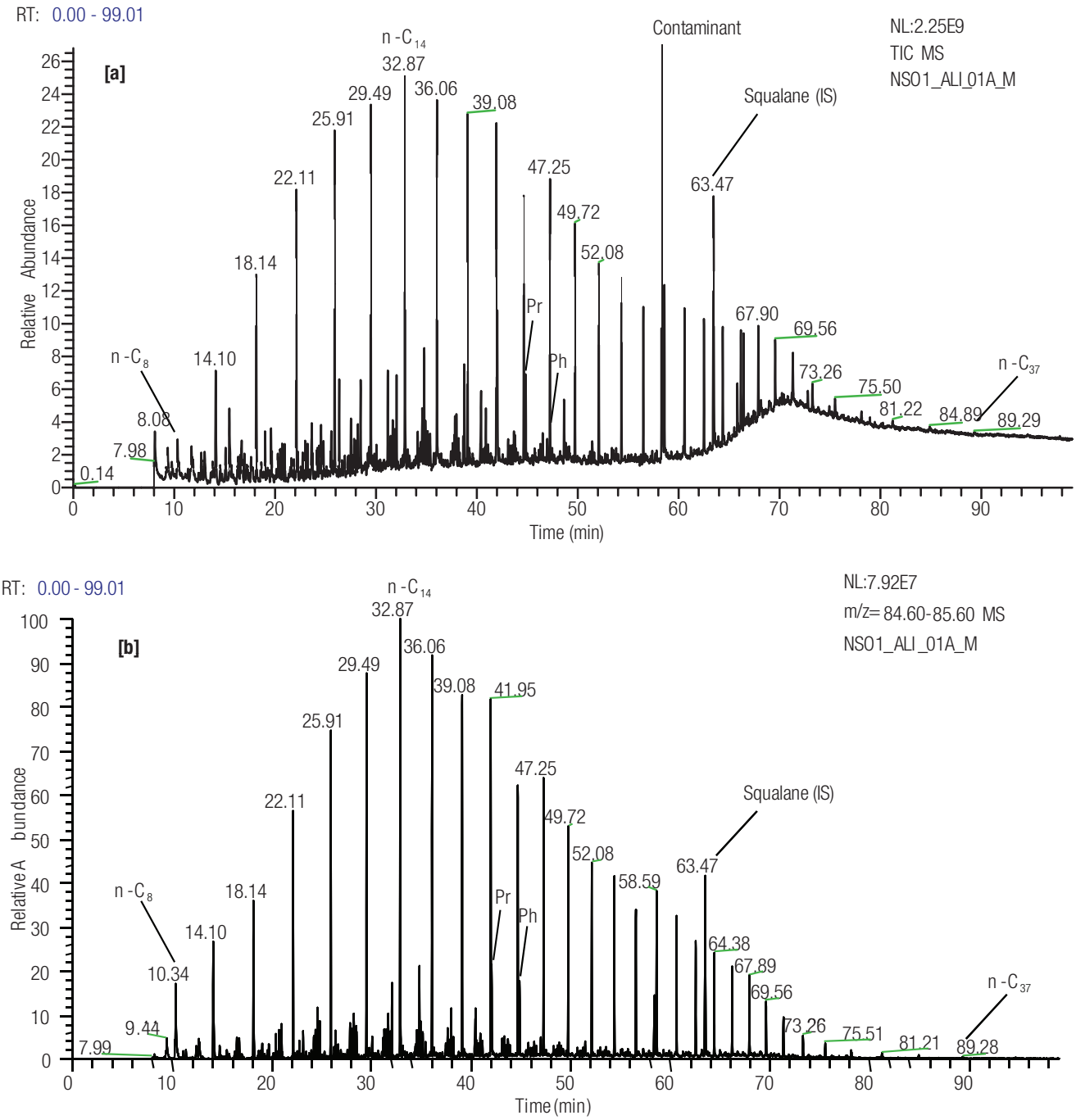

Figure 1. Full scan (a) Total ion chromatogram and (b) *m/z* 85 extracted ion chromatogram of the aliphatic hydrocarbon fraction showing the distributions of *n*-alkanes and isoprenoids. Pr = Pristane, Ph = Phytane.

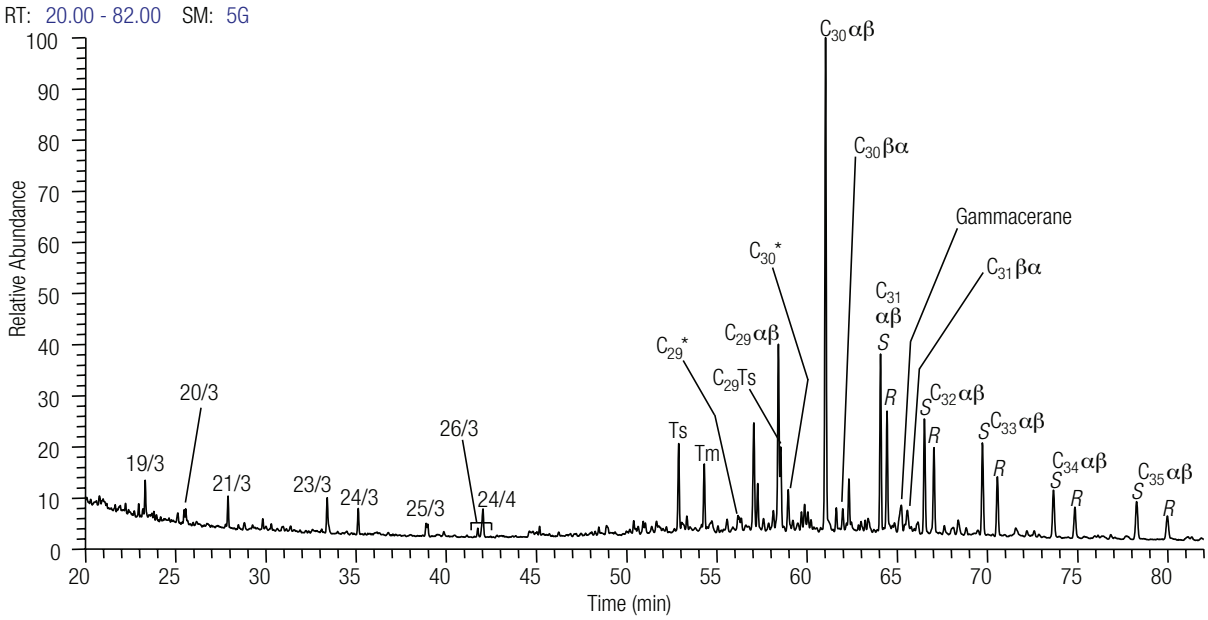

Figure 2. MID mass chromatogram *m/z* 191 of the aliphatic hydrocarbon fraction showing the distribution of terpanes. Peak assignments define stereochemistry at C-22 (*S* and *R*); αβ and βα denote 17α(H), 21β(H) -hopane and 17β(H), 21α(H)-moretane, respectively. 19/3 – 26/3 = C_{19} – C_{26} tricyclic terpanes, 24/4 = C_{24} tetracyclic terpane, Ts = C_{27} 18α(H), 22,29,30-trisnorneohopane, Tm = C_{27} 17α(H), 22,29,30-trisnorhopane.

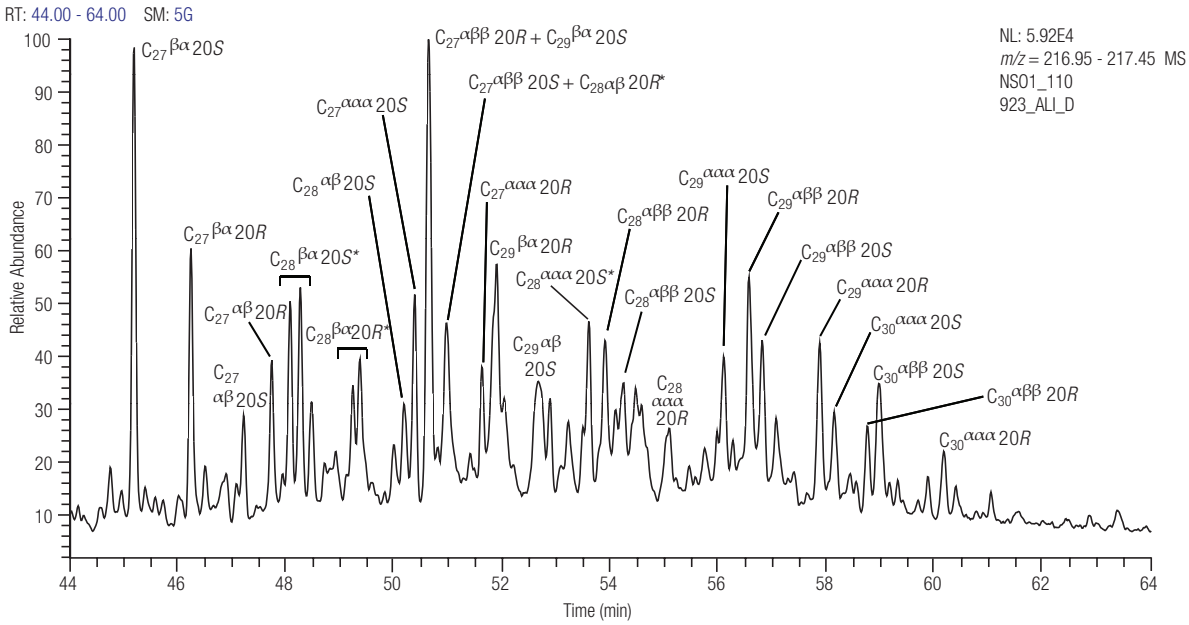

Figure 3. MID mass chromatogram *m/z* 217 of the aliphatic hydrocarbon fraction showing C_{27}–C_{29} steranes and diasteranes. Peak assignments define stereochemistry at C-20 (*S* and *R*); βα, αβ, ααα and αββ denote 13β(H),17α(H)-diasteranes, 13α(H),17β(H)-diasteranes, 5α(H),14α(H),17α(H)-steranes and 5α(H),14β(H),17β(H)-steranes, respectively. * = isomeric peaks (24*S* and 24*R*).

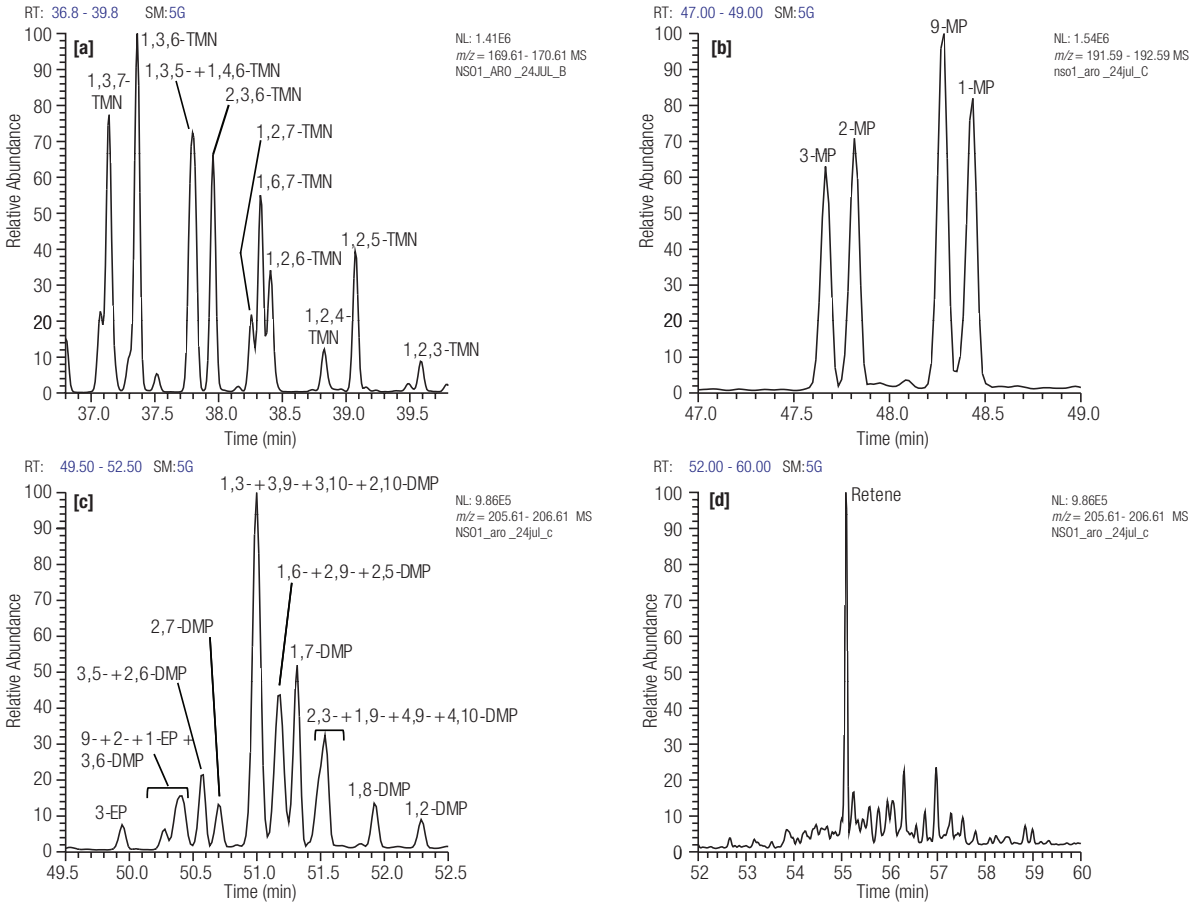

Figure 4. (a) *m/z* 170.11, (b) *m/z* 192.09, (c) *m/z* 206.11 and (d) *m/z* 234.14 mass chromatograms of the aromatic hydrocarbon fraction showing the distributions of C_3-alkylnaphthalenes, methylphenanthrenes, C_2-alkylphenanthrenes and retene, respectively. TMN = Trimethylnaphthalene, MP= Methylphenanthrene, EP = Ethylphenanthrene, DMP = Dimethylphenanthrene.

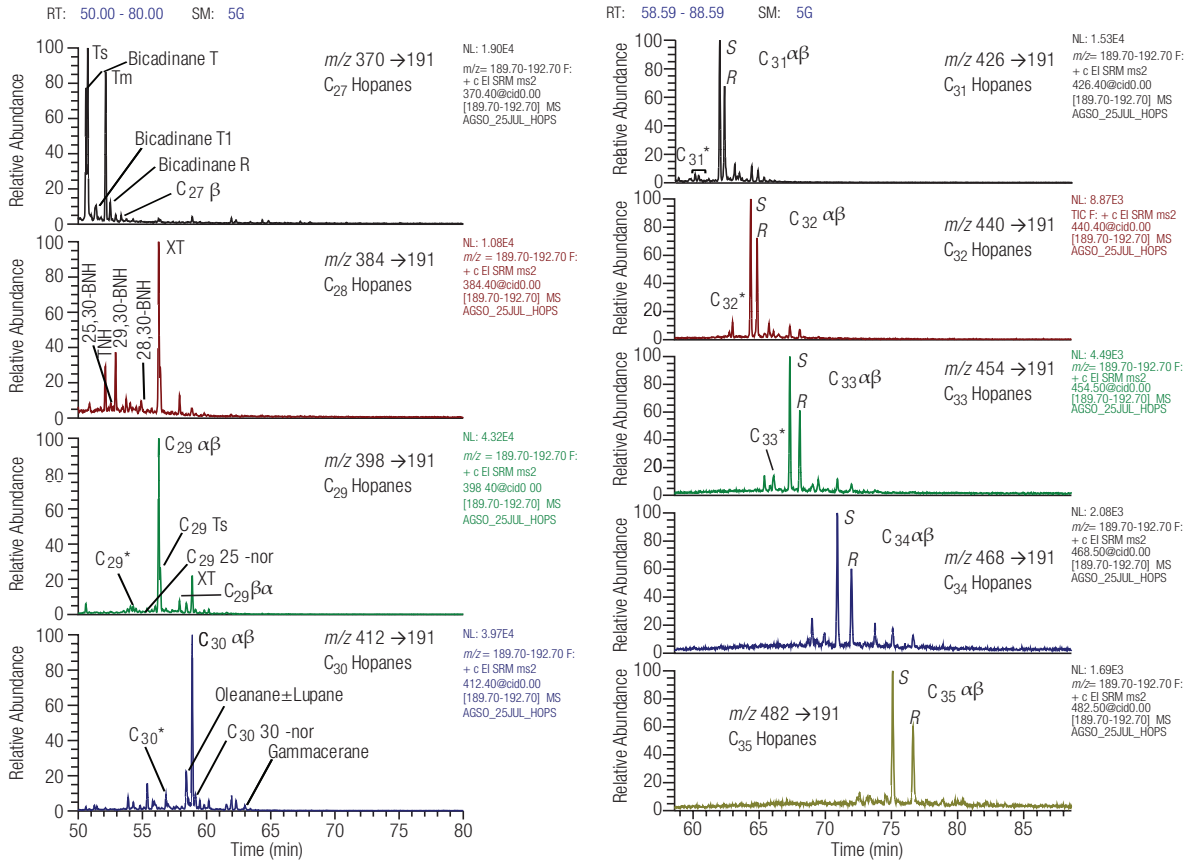

Figure 5. MRM chromatograms showing *m/z* M⁺>191 metastable transitions of C_{27}, C_{28}, C_{29}, C_{30}, C_{31}, C_{32}, C_{33}, C_{34} and C_{35} hopanes. XT = cross talk, BNH = Bisnorhopane, TNH = 17 α(H), 18 α(H), 21 β(H)-trisnorhopane.

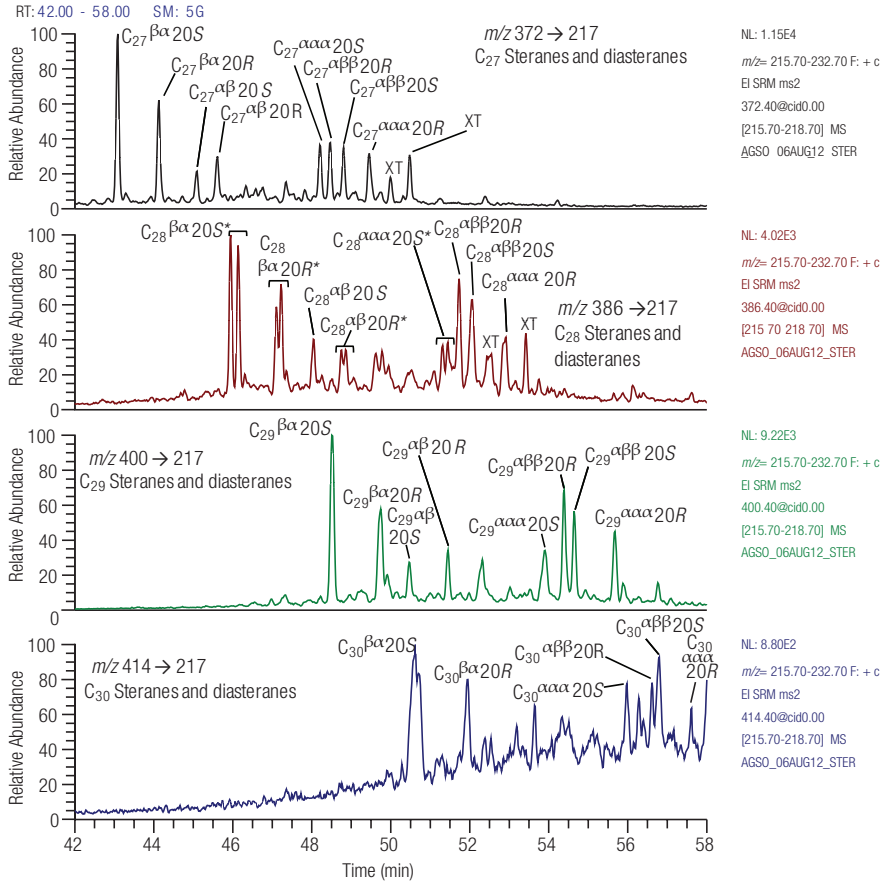

Figure 6. MRM chromatograms showing *m/z* M⁺>217 metastable transitions of C_{27}, C_{28}, C_{29} and C_{30} steranes and diasternaes. Peak assignments define stereochemistry at C-20 (*S* and *R*); βα, αβ, ααα and ααβ denote 13β(H),17α(H)-diasteranes, 13α(H),17β(H)-diasteranes, 5α(H),14α(H),17α(H)-steranes and 5α(H),14β(H),17β(H)-steranes, respectively. XT = cross talks, * = isomeric peaks (24*S* and 24*R*).

Conclusions

The capabilities of the Thermo Scientific DFS high resolution mass spectrometer have enabled the continuation and development of oil biomarker research at CSIRO Organic Geochemistry Laboratories.

The results generated using the DFS instruments allow CSIRO to elucidate and quantify the molecular distributions of the aliphatic and aromatic hydrocarbon biomarkers, such as, n-alkanes, regular isoprenoids, steranes and diasteranes, tri- and tetracyclic terpanes, hopanes, alkylnapthalenes, alkylphenanthrenes, retene, etc. (Figs 1 – 6). These results provide useful tools for the assessment of:

- Secondary alteration processes
  - biodegradation, evaporative fractionation, water washing
- Source or origin of organic matter
  - higher plants, algae, prokayriotic, eukaryotic
- Thermal maturity
  - immature, mature, over mature
- Palaeo-environmental condition
  - marine, deltaic, lacustrine, terrigeneous
- Lithology
  - clay rich, carbonates
- Geological age
- Oil-oil and/or oil-source correlations

Applications of such results in petroleum exploration geochemistry are described in numerous papers[2–5] and also in CSIRO publications.[6–9]

Acknowledgements

We would like to thank the team at CSIRO Sydney for the analysis of all samples and preparation of this application note.

References

1. Tissot, B.P., Welte, D.H., 1984. Petroleum formation and occurrence, pp. 699. Springer, Berlin.
2. Seifert, W.K., Moldowan, J.M., Jones, R.W., 1979. Applications of biological marker chemistry to petroleum exploration, 2, pp. 425-438. Heyden, London.
3. Mackenzie, A.S., 1984. Applications of biological markers in petroleum geochemistry. In: J.M. Brooks, D.H. Welte (Eds.), Advances in Petroleum Geochemistry 1 (Ed. by J.M. Brooks, D.H. Welte), pp. 115-212. Academic Press, London.
4. Peters, K.E., Walters, C., Moldowan, J.M., 2005. The Biomarker Guide, pp. 1155 pp. Cambridge University Press, Cambridge.
5. Alexander, R., Larcher, A.V., Kagi, R.I., Price, P.L., 1988. The use of plant derived biomarkers for correlation of oils with source rocks in the Cooper/Eromanga Basin System, Australia. APEA Journal, 28(1), 310-324.
6. George, S.C., Volk, H., Dutkiewicz, A., Ridley, J., Buick, R., 2008. Preservation of hydrocarbons and biomarkers in oil trapped inside fluid inclusions for >2 billion years. Geochimica et Cosmochimica Acta, 72, 844-870.
7. Gong, S., George, S.C., Volk, H., Liu, K., Peng, P., 2007. Petroleum charge history in the Lunnan Low Uplift, Tarim Basin, China - Evidence from oil-bearing fluid inclusions. Organic Geochemistry, 38, 1341-1355.
8. Volk, H., Kempton, R.H., Ahmed, M., Gong, S., George, S.C., Boreham, C.J., 2009. Tracking petroleum systems in the Perth Basin by integrating microscopic, molecular and isotopic information on petroleum fluid inclusions. Journal of Geochemical Exploration, 101, 109.
9. Ahmed, M., Volk, H., Allan, T., Holland, D., 2012. Origin of oils in the Eastern Papuan Basin, Papua New Guinea. Organic Geochemistry, 53, 137-152.

Thermo Fisher Scientific Bremen, GmbH is ISO 9001:2008 Certified

Africa-Other +27 11 570 1840
Australia +61 3 9757 4300
Austria +43 1 333 50 34 0
Belgium +32 53 73 42 41
Canada +1 800 530 8447
China +86 10 8419 3588
Denmark +45 70 23 62 60
Europe-Other +43 1 333 50 34 0
Finland/Norway/Sweden +46 8 556 468 00
France +33 1 60 92 48 00
Germany +49 6103 408 1014
India +91 22 6742 9434
Italy +39 02 950 591
Japan +81 45 453 9100
Latin America +1 561 688 8700
Middle East +43 1 333 50 34 0
Netherlands +31 76 579 55 55
New Zealand +64 9 980 6700
Russia/CIS +43 1 333 50 34 0
South Africa +27 11 570 1840
Spain +34 914 845 965
Switzerland +41 61 716 77 00
UK +44 1442 233555
USA +1 800 532 4752

AN30263_E 03/13S

Thermo SCIENTIFIC
Part of Thermo Fisher Scientific