JEOL GCmate

Oil Fingerprinting: Biomarker Identification in Oil and Sediment Samples

Method 1: High-Resolution Selected Ion Monitoring (HRSIM)

Biological markers (*biomarkers*) are compounds such as terpanes, steranes, and steroids that are derived from organisms present in the original biomass from which organic-rich sediments and oils were formed. These compounds can be measured in both oils and source rock bitumens, and they can be used to establish a correlation between an oil sample and the original petroleum source rock.

Combined gas chromatography / mass spectrometry (GC/MS) can be used to analyze for biomarkers in oil samples. However, there are numerous interferences present that have the same integer mass as biomarkers, but different elemental compositions. Because these *isobaric* compounds have different exact masses than the biomarkers, the interferences can be separated by high-resolution mass spectrometry. Some examples of compounds that interfere with the detection of biomarkers are given in Table I.

Table I. Some of the many isobaric interferences present in oil

Compound class	***m/z***	***Compound class***	***m/z***
pentacyclic terpanes	191.1800	methyl phenanthrenes	191.0861
triaromatic steroids	231.1174	4-methyl steranes	231.2113
monoaromatic steroids	253.1956	*n*- and *i*- alkanes	253.2895

The *GCmate* benchtop high-resolution mass spectrometer is readily capable of separating these interferences at a resolving power of 3000. High-resolution selected ion monitoring (HRSIM) provides accurate, quantitative analysis of mass-to-charge rations that are specific for target compound classes. The advantage of using the HRSIM technique over low mass resolution SIM is that it is not necessary to separate the whole oils or bitumens into saturate and aromatic fractions prior to analysis. The HRSIM technique allows quick analysis of both saturated hydrocarbon terpanes and aromatic steroids without any sample preparation other than dilution of the whole sample with an appropriate solvent. This saves quite a bit of time when analyzing large numbers of samples for Petroleum Systems Resource Assessment studies. An example of HRSIM analysis of biomarkers in an oil sample from the Czech Republic is shown in Figure 1.

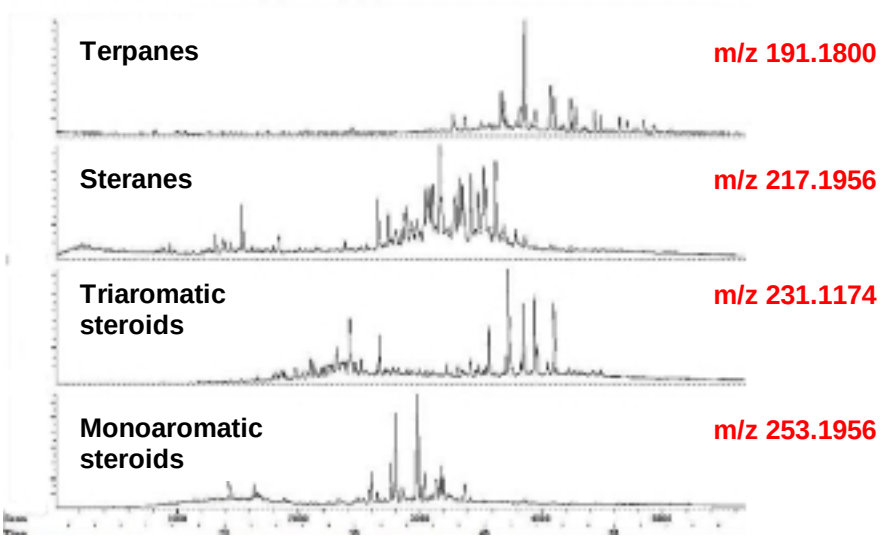

Figure 1. HRSIM analysis of biomarkers in oil from the Czech Republic.

Data and information courtesy of Dr. J. David King (U.S. Geological Survey, Denver, CO).

Method 2: Selected Reaction Monitoring (SRM)

Another method for identifying biomarkers makes use of the selected reaction monitoring (SRM) technique. SRM uses tandem mass spectrometry (MS/MS) techniques to monitor specific fragmentation reactions. For example, one can monitor the fragmentation of specific sterane precursor masses to produce the common fragment ion at m/z 217. This allows one to identify homologous series of steranes such as C_{26}-C_{29} steranes. Similar reactions exist for hopanes, mono- and tri-aromatic steroids, etc. The information that one extracts from, for example, sterane and hopane distributions provides information related to the thermal maturity, source and type of organic matter in sediments, oil-source correlation etc., and helps in the reconstruction of depositional environments.

If the collision gas option is installed, the *GCmate* can perform linked-scan MS/MS experiments, including selected reaction monitoring. Although there are some limitations on precursor selectivity, linked scans can provide reproducible, informative, high-energy collision-induced dissociation MS/MS data. An example of the SRM experiment for monitoring steranes is shown below for a sample of Cretaceous calcareous shale (USA). Figure 2 shows low-resolution mass chromatograms for selected precursors and the common fragment at m/z 217, while Figure 3 shows the improved signal-to-noise and selectivity resulting from the selected reaction monitoring experiment.

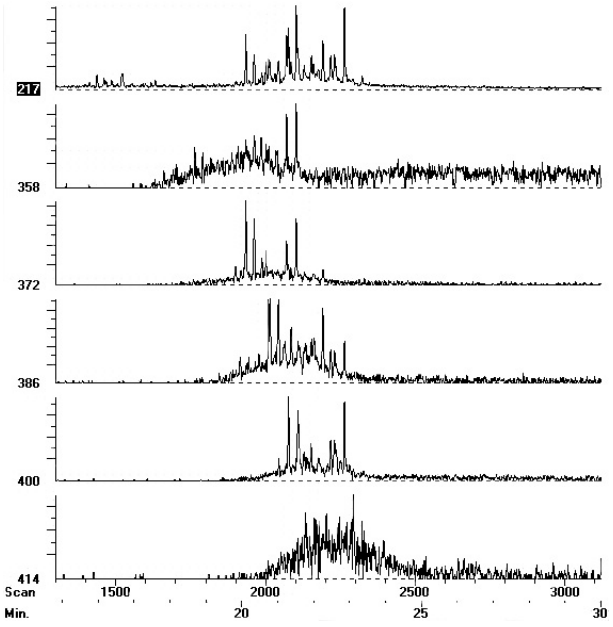

Figure 2. Mass chromatograms for selected sterane mass-to-charge ratios

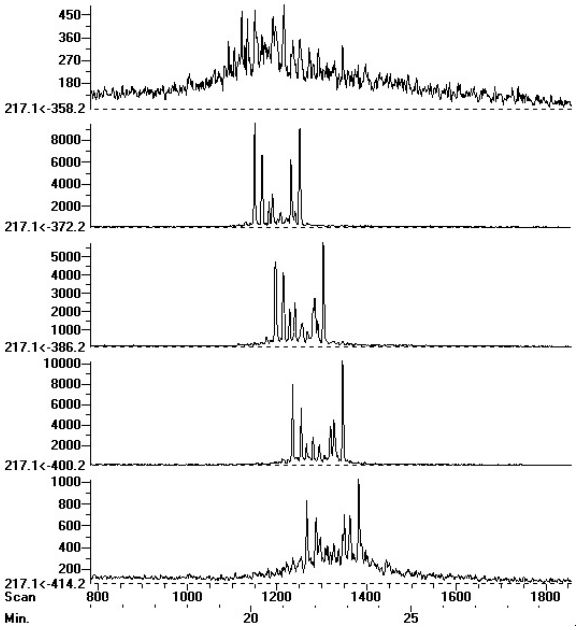

Figure 3. Selected reaction monitoring for homologous steranes

Sample and information courtesy of Dirk-Jan H. Simons and Dr. Fabien Kenig, (Organic Geochemistry Laboratory, University of Illinois at Chicago)

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