

# **PS From Here to Maturity: Estimating Thermal Maturity of Crude Oils\***

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## **Abstract**

Combining gas chromatography with tandem mass spectrometry to assess unresolved structural and stereoisomeric mixtures of steranes in crude oils began 35 years ago. C27-C29 20S/20R and diasterane/regular sterane ratios were often used to determine oil and source rock maturity and GC- MSMS techniques allowed for more precise measurements of these thermally sensitive biomarker ratios. Today, GC combined with triple quadrupole mass spectrometers not only allows for the better resolution of steranes and other biomarkers (e.g., carotenoids) found in oils, source rock bitumen and kerogen but also measures a wide variety of other, more volatile thermally dependent compounds such as alkyl naphthalenes/phenanthrenes and diamondoids. Simple ‘Dilute & Shoot’ injections of whole crude oils preclude evaporative loss, while the specificity of the tandem spectrometers allows for the discrimination of saturate and aromatic hydrocarbons, eliminating the need for liquid chromatographic separations. A combination of these thermally sensitive biomarker ratios can be subjected to principal component analysis, and the resulting first or primary factor often carries over 75% of the total variation in the dataset. The principal component calculated for each oil in each family can be converted to a ‘vitrinite reflectance equivalent’ (VRE) value in order to place each oil within the confines of the oil generation window (~0.6-1.2% Ro) and likely records the maturity of the corresponding source rock at the time the oil was expelled (primary migration). It is important to evaluate maturity in oils that are from the same source facies since some of these maturity ratios may also have a significant genetic or source component. At advanced oil maturity levels that yield volatile oils or condensates (~1.0-1.3% Ro), terpane and sterane biomarkers are thermally degraded and are often insufficient in abundance to be useful in predicting maturity levels. Also, these biomarker-derived maturity estimations reflect the maturity of the heavier-ends (C20+) of the oil; lighter components of the same oil may have been derived from more mature, biomarker-deficient fluids expelled from the same source rock at a later time, due to increasing geothermal heating during subsidence. Since many of the fluids produced from unconventional lateral completions are light oils or condensates with minimal biomarker concentrations, or may have high maturity lighter-end components in addition to typical biomarker distributions, we have developed an oil maturity calculation based on known differences in the thermal stability of alkyl-substituted benzenes, naphthalenes, and phenanthrenes. To derive VREQ values (vitrinite reflectance equivalent based on the triple quadrupole), a series of thirteen alkyl- substituted naphthalene and phenanthrene ratios are constructed such that they increase with increasing maturity, with the more thermally stable isomer in the numerator. The percentages of all thirteen are simply added together with the higher total values corresponding to higher maturity levels. To calibrate the scale, the upper end of fluid maturity is

fixed at 1.35% Ro and given to a number of clear condensates analyzed with the highest alkyl aromatic summations measured. Lower values are equated to oil standards of known or suspected maturities, as well as source rock extracts. Source rocks, with measured Ro values and Tmax determinations from pyrolysis, are crushed but not powdered, and the DCM extract (never taken to dryness to minimize evaporation) is injected on the GC-triple quadrupole after deuterated internal standards are added. Crude oils often have multiple maturity signals with the VRE from the heavier biomarkers recording the early, less mature products and the VREQ values the later, lighter, and more mature signal. This presentation will illustrate the 35+ year evolution of both Instrumental and Interpretive approaches to determine the thermal maturity of generated hydrocarbon fluids and their relationships to parent organic matter.

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