

OIL FLOW ASSURANCE ISSUES: TETRAACIDS IN DEPOSITS AND CRUDE OILS

Calcium naphthenate deposition is a particular form of oil flow assurance issue. Unlike emulsion formation, which occurs when organic compounds with a single acid group form salts with metals (principally in produced water) calcium naphthenate dries on contact with the air to form hard deposits which can build up in topside equipment leading to costly production losses. Calcium naphthenate deposition usually occurs following introduction of injection water, but each incident may be different and a variety of oil parameters may be important. Reports of production equipment fouling due to the interaction of unknown acids and calcium ions pre-date the eventual discovery and identification of the high molecular weight naphthenic tetraacids named 'ARN' acids by Baugh and co-workers¹, which are now thought to be responsible. These tetraacids usually comprise around 20 - 40 wt% of the deposits once the entrained oil has been removed.

Chemically these tetraacids are isoprenoid compounds with about 80 carbon atoms arranged in an 'H'-shape with a carboxylic acid at the end of each arm and mainly six 5-membered (cyclopentyl) rings (Figure 1) but compounds with 81 and 82 carbon atoms and 4 to 8 cyclopentyl rings are also known^{2,3}. We use an abbreviated notation of $C_{n,R}$ to refer to the tetraacids such that n is the number of carbon atoms and R the number of rings. So $C_{80,6}$ would be a compound with 80 carbon atoms and 6 cyclopentyl rings, for instance. Since their discovery some 10 years ago, scientists have identified related compounds with 60, 62 and 64⁴, 60 - 77⁵, and 79 and 83⁶ carbon atoms, and compounds with between 0 - 8 cyclopentyl rings. Clearly the result is a large number of tetraacid compounds many or all of which can potentially form calcium naphthenate deposits.

It is not definitely known how the tetraacids are produced, but their structural resemblance to the tetraether membrane lipids of some microbes known as Archaea, suggest this is their source, perhaps after further modification of the Archaeal lipids by bacterial action in the oil reservoirs or in the source rocks³. Archaea with 'H'-shaped tetraether membrane lipids have been found in terrestrial and marine settings including hot springs and hydrothermal vents. Here the relative proportions of tetraethers with different ring-numbers (e.g. 0 - 6) might be related to some paleoenvironmental parameter(s) such as temperature, pressure, ionic strength and pH, but the relationship is not fully understood. Whilst tetraacids can become concentrated in deposits by complexation with calcium the concentration in the parent crude oils is usually relatively low. However even low concentrations can still be important at production volumes once the oil comes into contact with calcium: we have measured up to 38 ppm of total tetraacids in crude oil.

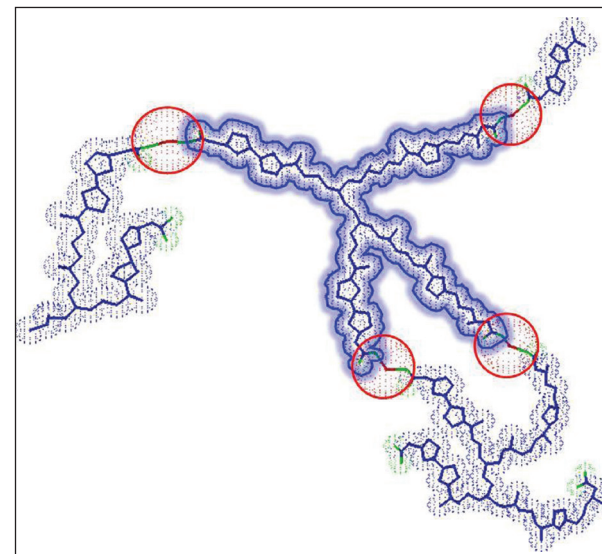


Figure 1. $C_{80,6}$ tetraacid molecule (outlined in blue) cross-linked via calcium ions (outlined in red) to other tetraacid carboxylate groups.

The complexity of the crude oil matrix makes the detection and quantification of tetraacids in crude oil a considerable analytical challenge and even if they are detected, deposit formation and flow compromise does not always follow. However, measurement of tetraacids in crude oil allows production engineers to plan mitigation strategies at an early stage which is usually cheaper than remedial measures. We have developed a sequential solid phase extraction (SPE) and derivatisation method that removes matrix interferences and allows detection with liquid chromatography coupled with electrospray ionisation-mass spectrometry (LC/ESI-MS)⁶. The SPE sequence involves removing basic compounds before isolating an acid fraction, which is then esterified (-CH₃ group replaces each of the four acidic protons) and further refined by separation based on hydrophobicity and hydrogen deficiency. Using liquid chromatography this refined fraction is then separated based on carbon number and number of cyclopentyl rings (i.e. providing $C_{n,R}$ distributions) and the concentration measured based on mass spectral response. In this way we can not only obtain the total tetraacid content but also the distribution of individual tetraacids. Typically we use two 1 gram samples of crude oil and add 1 ppm of an authentic $C_{80,8}$ tetraacid as an internal standard to one of them before the SPE process. The $C_{80,8}$ isolated from an oilfield deposit, is used because it is quite rare and its purity was checked using high temperature gas chromatography and ESI/MS. To the other sample of crude oil we do nothing, except conduct the analysis. In this way we can check whether the oil contained any natural $C_{80,8}$ tetraacid and, if so, we can compensate for this in our calculations. We have published our method⁶ but the results shown there were obtained using an ion trap mass spectrometer which had a limit of quantification (LOQ) of around 0.1 ppm per individual tetraacid and a limit of detection (LOD) around 0.03 ppm per individual tetraacid. We have now replaced this instrument with a high resolution Q Exactive™ Focus Orbitrap mass spectrometer and significantly lowered our LOQ to around 0.98 ppb and LOD to around 0.10 ppb for individual tetraacids. This improved sensitivity means we should now be able to analyse tetraacids in a single drop of oil rather than in one gram!

We have designed the above analytical method to be specific enough for the rigorous identification and measurement of derivatised tetraacids but still to be broad enough to allow us to detect other related unknown compounds of similar molecular weight and structure. Using these methods in some oils we observe that the known tetraacids are present with a high molecular weight 'hump' of unknown acids and these may also be important in calcium naphthenate deposit formation and should be the subject of further research.

Why would the distribution of tetraacids be of interest? If it is accepted that tetraacids are derived from tetraether archaeal membrane lipids then, as observed in the terrestrial and marine environments, the ring-number distribution of tetraacids may also reflect palaeoenvironmental conditions at the time of biosynthesis. Whilst we observe different ring-number distributions of tetraacids in oils and oilfield deposits across the world from sources ranging from Miocene to Upper Jurassic in age, there is much that we do not know. For example, we do not know whether the source microorganisms were living at the time the organic matter was deposited, whether they survived on the buried organic matter throughout oil generation, or whether they survive in the crude oil or interstitial water. Also, it is not known whether the ring-number distribution of tetraacids is related to the thermal history of the crude oil. We have found tetraacids present in some 80% of oils tested so far with distributions typically dominated by C_{80} compounds with 6-rings, but some oils contained different distributions and were dominated by 4-ring, 5-ring, 7-ring or 8-rings or C_{81} compounds. We think that if we can understand

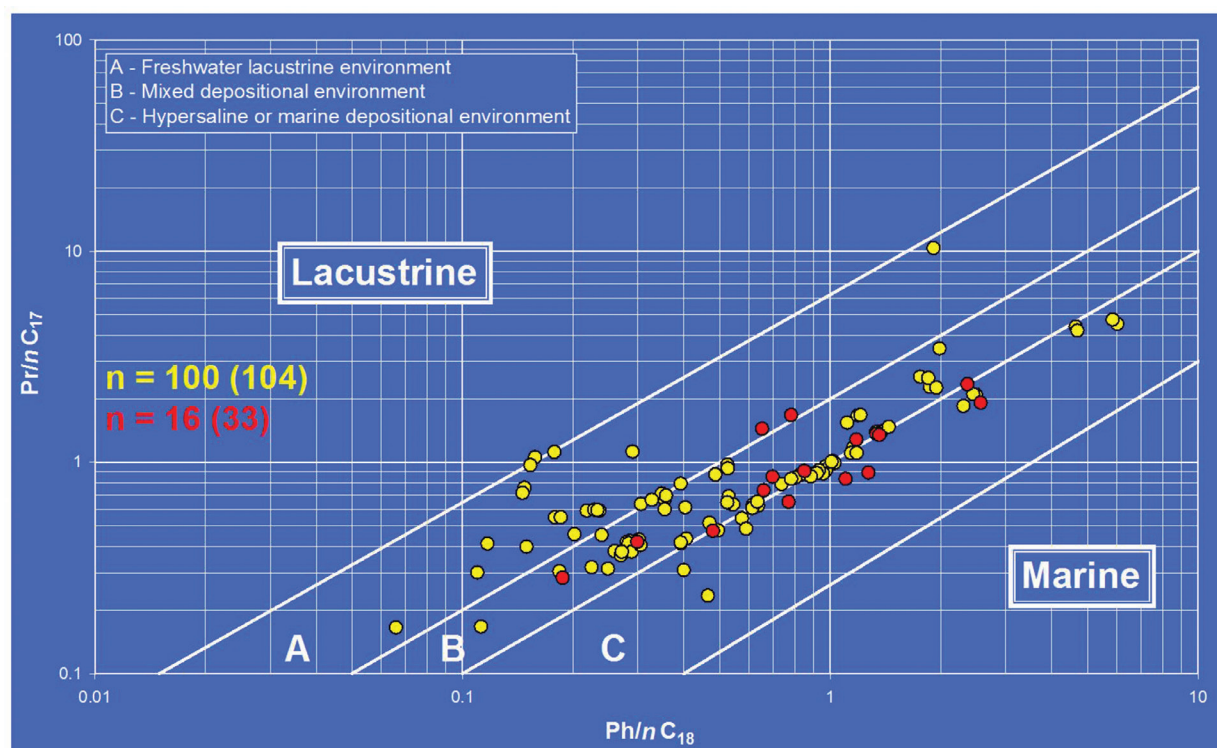


Figure 2. Cross-plot of phytane/nC18 and pristane/nC17 ratios for assessment of paleoenvironmental depositional setting (Connan and Cassia 1980 *Geochim. Cosmochim. Acta* 44, 1–23). Red circles are tetraacid-containing oils, yellow circles are oils not tested for tetraacids, n = number of data points, figures in brackets are number of samples tested.

what these different distributions mean then we can make deductions about some important petroleum parameters, for example, whether it is related to thermal maturity or source organism/environment.

It is not only tetraacids that are of interest. The use of high resolution mass spectrometry also allows us to identify the elemental composition of unknowns that are often encountered when analysing the tetraacid content of crude oils, with more certainty. For example, we have recently identified compounds that appear to be diacid diols (two carboxylic acid groups and two hydroxyl groups). This is really interesting because it provides a putative link in the oil between precursor molecules and the tetraacids that are thought to arise from biodegradation. In a similar vein we have recently submitted an article for publication with Heinrichs' group in Bremen that identifies the series of products that may reasonably be expected to be present due to the sequential biodegradation of glycerol dialkyl glycerol tetraethers in marine and hot spring sediments, seep carbonate and a marine theaumarchaeon. So now the parts of the puzzle are starting to come together and it is likely that the near future will be an exciting time in this research area.

Calcium naphthenates are generally considered to comprise calcium salts of tetraacids and in general we have found that this is the most abundant metal (>2 wt%) in deposits we have analysed to date. Sodium (0.4 – 2.0 wt%) and sulphur (0.2 – 1.1 wt %) are also relatively abundant in our experience whilst iron and magnesium co-deposits have also been reported⁷. We have observed high iron and sulphur in at least one deposit and high phosphorus in another. The latter was linked to a calcium naphthenate deposit formed in the presence of a phosphate-containing oil field chemical.

We measured the concentration of 23 elements (Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, S, Si, Sn, Ti, V and Zn) in 34 oils in which we had detected tetraacids and in 103 oils which we have yet to examine for tetraacids, using inductively coupled plasma-optical emission spectroscopy (ICP-OES) against a multi-element crude oil standard. Most of the elemental concentrations (Ag, Al, B, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Mo, P, Pb, Sn, Ti, and Zn) in the tetraacid oils were comparable to those of the untested oils. Of the other elements, all the tetraacid oils contained low calcium and silica, whilst sodium (~140 ppm) and vanadium (~27 ppm) was higher in some tetraacids oils

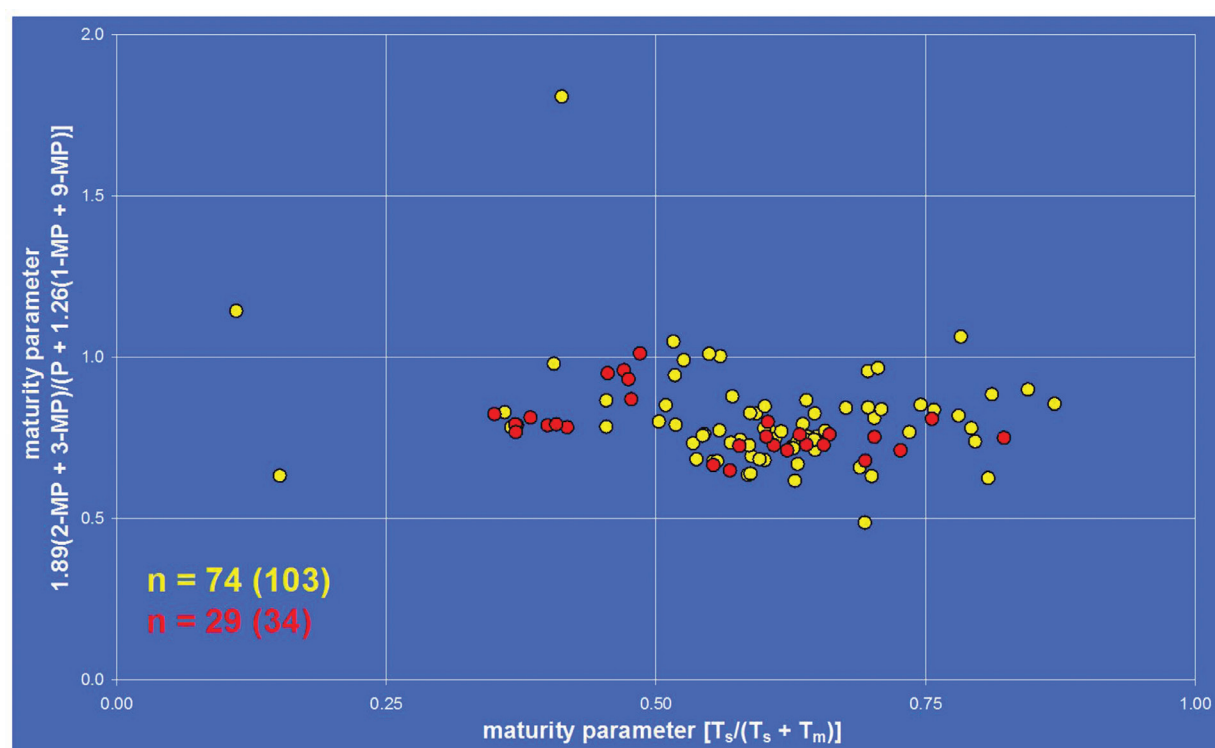


Figure 3. Cross-plot of maturity parameters C27 homohopane $[T_s/(T_s + T_m)]$ (Seifert and Moldowan 1978 *Geochim. Cosmochim. Acta* 42, 77-95) and methyl phenanthrene index (Cassani et al. 1988 *Org. Geochem.* 13, 73-80). Red circles are tetraacid-containing oils, yellow circles are oils not tested for tetraacids, n = number of data points, figures in brackets are number of samples tested.

but <LOD in others. We noted that all the tetraacid-containing oils contained nickel (~3 – 26 ppm) and sulphur (~50 – 420 ppm), but that the nickel and sulphur concentrations were not correlated with each other. Nickel is most commonly thought to be associated with porphyrins, as is vanadium, but we did not observe a similar correlation with vanadium. We now intend to test for the presence of tetraacids in some of the previously untested oils which were high in nickel and sulphur to see whether these elements can be used diagnostically.

It has previously been reported that tetraacids occur in immature biodegraded oils, so we thought we would test whether

tetraacid-containing oils could be differentiated based on their biomarker ratios or other petroleum parameters⁸ indicative of source organisms, biodegradation level, depositional environment or oil maturity. We tested from 6 – 33 crude oils found to contain tetraacids and 104 oils that had not been tested for tetraacids. Our hypothesis was that if the results from tetraacid oils were closely grouped but separated from the bulk of the other data, or grouped with some of the other data, then this might prove useful in future studies. However, we found that no patterns could be discerned at all. For example, half of the tetraacid oils contained the depositional biomarkers (it is presumed the others had been biodegraded) but these plotted over the mixed depositional region of the untested oils (Figure 2). Similarly, whilst just under half of the tetraacid oils appeared to be immature, the range of maturity was similar to that of the untested oils (Figure 3). Even if some of the oils not tested for tetraacids contained tetraacids, the spread of our data suggests that this approach is not useful in predicting the presence of tetraacids in oil.

All of this work was undertaken at Plymouth University and represents a collaboration with colleagues including Prof Steve Rowland, Dr Anita Young (most of the biomarker work and ICP-OES), Dr Andrew Fisher (ICP-OES) and Dr Paul McCormack (high resolution LC/ESI-MS). Wax analysis was carried out courtesy of Kernow Analytical Technology Ltd., Cornwall, UK, and some of the initial work reported here was carried out under a Joint Industry Project sponsored through Oil Plus Ltd., Newbury, UK, by BG Group, BP, Chevron, Nalco and Total.

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