Looking at Gas Chromatograms
with Paul Farrimond

Apologies for beginning this note with some history… When I worked on my Ph.D. project in the mid-1980s I witnessed the arrival of the first desk-top computers into our laboratory in Bristol. They were expensive and clunky, and we only had a few. At this time the gas chromatographs were still connected to pen chart recorders (younger readers may need to Google this!) that traced out the individual peaks. Peak integration was difficult; I measured peak heights with a ruler. The thing is though: you had to look carefully at the chromatograms to extract the information. You needed to identify the peaks, define the signal baseline, and then manually measure the peaks. In doing these things you also noticed anything unusual in the chromatogram – such as contamination, the effects of biodegradation, a weak signal, poor chromatography, or any other instrument problems. Recognising these features meant that you could make more reliable interpretations, with a good understanding of the quality (good or bad) of the data and the sample.

Over time, with the development of laboratory data systems, we have become accustomed to receiving data neatly packaged, the chromatograms labelled and typically accompanied by tabulated peak heights, areas, calculated concentrations and compound ratios. We can take these numeric data and show them on our favourite plots to estimate maturity, source characteristics, look for correlations, etc. – all without looking at the chromatograms! In a busy world it is easy to think you don't have enough time for this, but I argue that examination of the chromatograms should always be an essential step. When I must make interpretations of molecular geochemical data without the chromatograms (e.g. when using legacy numeric data dug out of old computer files) it feels like I have one hand tied behind my back.

This is equally true for mass chromatograms from GC-MS analysis as it is for gas chromatograms, but for the purpose of this Technical Note I intend to specifically consider Whole Oil Gas Chromatograms (WOGCs). So, what do I look for when I examine a WOGC?

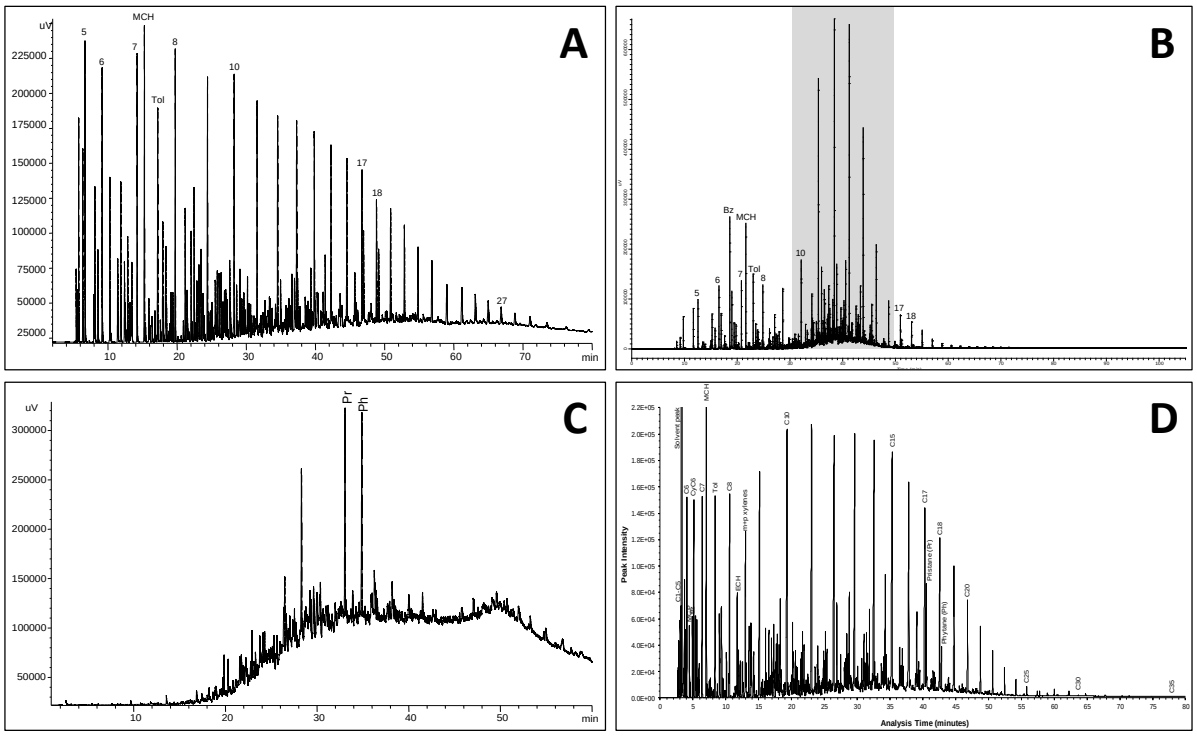

Figure 1: Four Whole Oil Gas Chromatograms of crude oils (North Sea, UK). (A) Shows a fairly typical oil, whilst the other chromatograms (B to D) show different features discussed in the text.

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Contamination: Oils can be contaminated, most often by either oil-based drilling mud (Fig.1B) or from organic additives in water-based mud (e.g. a series of glycol peaks or others, not shown). The shaded area in Fig.1B represents the interval of the WOGC that is dominated by input from an oil-based mud (OBM), overprinting the peaks in that region that occur naturally in the oil. Depending on the OBM used in the well this can overprint important peaks that are routinely used in geochemical interpretation, such as pristane, phytane and the associated *n*-alkanes. In the example shown (Fig.1B) the contamination may not include much pristane, but caution would still be needed in interpreting the pristane/phytane ratio in case it has been increased slightly by the OBM contamination.

With glycols and other organic additives to water-based muds, the effects may not be too problematic, so long as the peaks do not overlap or co-elute with any peaks of interest in the oil.

Instrument problems: Data showing evidence of instrument problems such as poor peak shape and resolution (separation between peaks) should not leave the laboratory but be re-analysed after the fault has been rectified, and so will not be considered here. There are various websites available online with information about gas chromatography troubleshooting.

An originally weak signal should also be resolved within the laboratory by the re-running of the sample at a higher concentration (partial evaporation of the solvent). Weak signals are more usually a problem of biomarker data in GC-MS analysis, particularly in gas condensates and high maturity oils; this is outside the scope of this Technical Note (but may be discussed in a future one).

Alteration of oil: Recognising what alteration processes an oil may have undergone in the subsurface is important not only in it its own right but also because these processes can modify an oil composition to overprint other characteristics that are normally used to interpret the source and its maturity.

The effects of biodegradation are obvious from the WOGC when the process has been extensive, resulting in the removal of most or all of the *n*-alkane peaks and the formation or amplification of a pre-existing unresolved complex mixture (UCM) – the "hump" above the baseline signal (Fig.1C). However, when biodegradation is less severe, or when dealing with mixed oils, its recognition requires more care, and may not be apparent from the interpretation of purely numeric data without examination of the WOGC. This is one situation where misleading interpretations can be made!

Evaporative fractionation can result in the partial (or extensive) loss of the more volatile compounds in an oil, changing its bulk and molecular composition – particularly of the gasolines. The WOGC in Fig.1D shows an oil with a relatively minor loss of some of the light-end (volatile) hydrocarbons, most notably the *n*-alkanes. It can be difficult to distinguish evaporative loss from slight biodegradation, but of course it is critical to recognise the alteration effects in the first place, in order to allow more detailed examination and interpretation (beyond the scope of this note).

Oil character: I also look at a WOGC to get an impression of the overall oil character, by which I mean the broad nature of its source rock (marine vs. terrestrial) and its general maturity level. The WOGCs in Fig.2A, 2B & 2C are of three oils of very different characteristics. The marine oil is Fig.2A is a fairly typical North Sea oil sourced by the Kimmeridge Clay Formation, a marine shale. By contrast, the WOGC shown in Fig.2B is of a lacustrine-sourced oil with a highly waxy character (the long-chain *n*-alkanes being derived from specific lacustrine algae in this case, rather than land plants). The gas condensate shown in Fig.2C is highly characteristic in its dominance of the gasoline-range hydrocarbons and very low relative abundance of larger compounds including pristane and phytane. The biomarker compounds in this fluid are likely to be very weak in the GC-MS analysis of this fluid,

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unless an aliquot is "topped" (deliberate removal of volatiles in the laboratory) to increase their concentration.

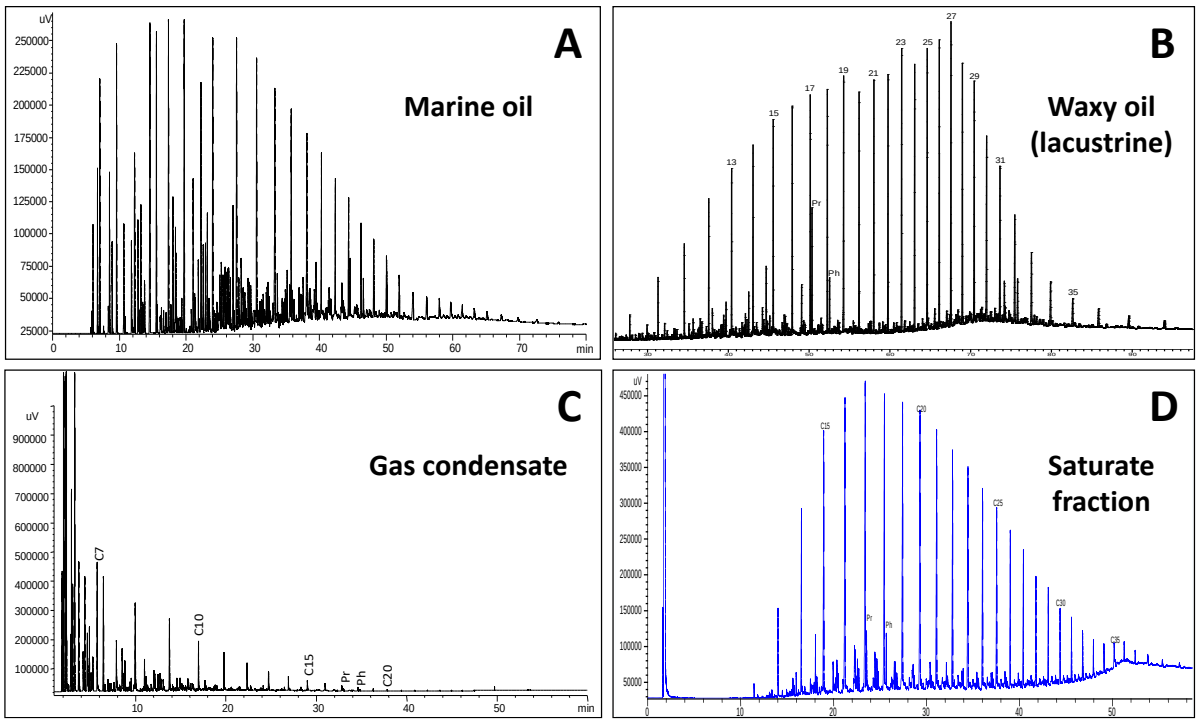

Figure 2: (A) to (C) Three Whole Oil Gas Chromatograms of crude oils with very different origins and characteristics. (D) Shows a saturated hydrocarbon fraction of an oil (discussed in the text).

Finally, in Fig.2D I show a saturated hydrocarbon fraction of a marine oil alongside the WOGCs in order to emphasize that such fractions will always have lost most or all of their more volatile components due to the evaporation of solvent in the laboratory during the fractionation process es prior to analysis by gas chromatography. Consequently, the gasoline-range hydrocarbons will have been lost or extensively depleted and modified; WOGCs must be used for these compounds.

The chromatogram of this saturate fraction (Fig.2D) also shows another characteristic seen in many GC traces – the rising baseline towards the right-hand side. This represents an increased background (baseline) signal due to increasing "bleed" of the phase from the capillary column used in the GC analysis. It is not always so obvious, depending on the intensity of the peaks in the chromatogram; with a weaker signal the baseline will be higher. This rise in the baseline due to column bleed should not be confused with the UCM due to biodegradation (Fig.1C), although the WOGCs of biodegraded oils typically have low-intensity peaks and consequently a raised baseline due to column bleed is usually present and should be allowed for when identifying the UCM in the chromatogram (Fig.3).

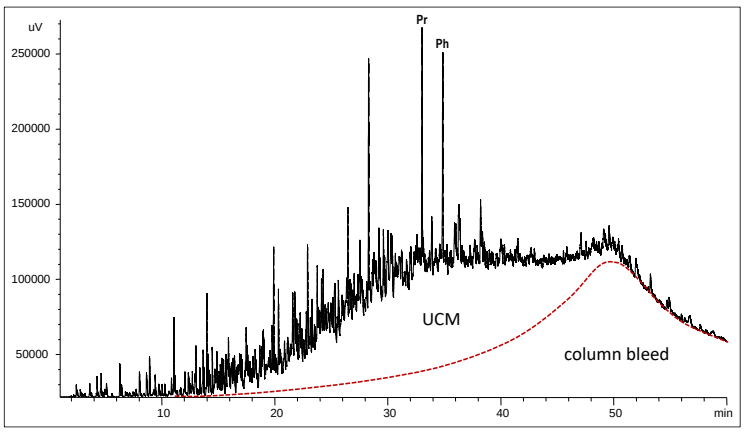

Figure 3: A WOGC of a severely biodegraded North Sea oil with the presence of a large unresolved complex mixture (UCM); the approximate position of the rising baseline due to column bleed has been estimated by the red line.

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Concluding remark: Please don't ignore your chromatograms – they can help your interpretations enormously by avoiding potential pitfalls, recognising something you would otherwise miss, and giving you greater confidence in your work.

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