Spectrum

Oil spills leave tell-tale 'fingerprints'

Oil-soaked sediment collected beneath ailing mangroves on Botany Bay in September 1985 bears a molecular signature identical to that of a Bass Strait crude oil. This points to a spill from the tanker 'Arthur Phillip' 8 months previously as the likely source of the oil, and shows that it could not have come from another spill in September 1979, when the 'World Encouragement' lost 100 tonnes of Arabian crude.

The evidence comes from Mr Trevor Gilbert, an organic geochemist with the CSIRO Division of Exploration Geoscience. He used a sophisticated tool of trade — a computerised high-resolution gas chromatograph–mass spectrometer — to analyse oil and sediment samples he collected, as well as others gathered by the New South Wales State Pollution Control Commission.

Mr Gilbert tuned his instrument to look for the presence of what he calls 'molecular fossils'. These are stable hydrocarbon compounds (in this case, steranes and triterpanes) that retain their characteristic carbon skeleton even when they are set free into the environment and the forces of weathering and biological degradation act on them.

When fingerprinted in this way, the sample showed one triterpane compound (formula $C_{30}H_{52}$) that was absent from an Arabian crude oil sample. Furthermore, the chromatogram of the Arabian material had three tell-tale peaks, indicative of three particular steranes that the local product lacks (see the diagram).

The differences in the molecular fossil profiles relate to the different biological origins of the oils. Bass Strait oil owes its genesis to the ancient burial of terrestrial plant material — trees, ferns, mosses, and the like — whereas Middle East crudes result from the geological processing of marine organisms — largely phytoplankton and bacteria.

In fact, every one of the world's oil-fields will, because of a unique mix of precursors and geological history, have a characteristic profile of molecular fossils. Mr Gilbert and a former colleague, Dr Paul Philp, have characterised more than 100 Australian oils in this way. Their work helps exploration geologists gain clues about the geological history of productive (and non-productive) wells, and so gives them pointers as to where they should best concentrate future drilling.

As this relatively new field broadens, organic geochemists are piecing together a fuller picture of the origins of different oils. Gradually, more molecular fossils are being identified.

For example, *n*-alkanes indicate that algae or higher plants have been a source; isoprenoids derive from chlorophyll; and diterpenoids point to plant-resin origins.

Whereas the concept of identifying particular molecular fossils is easy to state, in practice it's not simple because these biological markers exist in trace quantities among a mixture of several hundred compounds.

Here is where the power of the new equipment shows itself to advantage. The gas chromatograph separates the mixture into its individual components and the mass spectrometer then analyses each component so it can be identified.

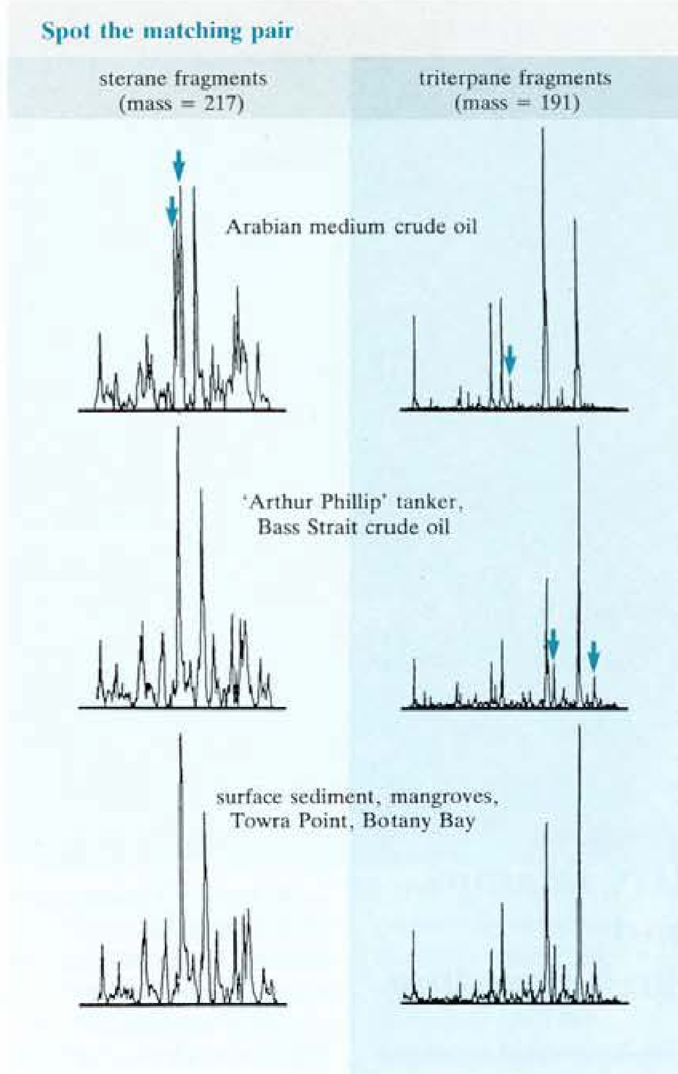
The CSIRO instrument (of commercial origin but one of only a few of its type in Australia) contains a high-resolution capillary column capable of separating components on the basis of their volatility. While, over some 80–90 minutes, the sample is progressively heated from 40°C to 300°C, helium gas carries the volatilised material from the end of the column directly into the mass spectrometer.

Here the molecules are bombarded by a stream of electrons, which both ionise them and split them into fragments. A magnetic field then performs the essential job of separating the ionised fragments according to their mass, a task that takes less than a fraction of a second.

A computer is an essential part of the data analysis, since recording a mass spectrum every second for 90 minutes results in some 5400 spectra. Later, the computer can sift through all the spectra looking at when certain fragments of defined mass were detected by the instrument.

For example, the ion with atomic mass 217 is characteristic of a sterane fragment, whereas triterpanes

Cleaning up Botany Bay after an oil spill.



Yes, the molecular 'fingerprints' of the bottom pair in each column are virtually the same (the arrows show tell-tale differences from top traces). This indicates that oil from the offending spill came from Bass Strait, not the Middle East.

are inclined to fragment into pieces of mass 191.

Thus, in the piece of detective work described in this story, Mr Gilbert got the computer to produce a plot of how the abundance of the sterane fragments (mass 217) changed in the course of the analysis, and similarly traced those of mass 191 (the triterpane fragments). Scientists call the signature of the fragments recorded like this a 'fragmentogram', and in this case it disclosed the presence of compounds that probably couldn't have been detected in any other way.

Another valuable function of the computer is to help identify unknown compounds. It can search through its built-in library of mass spectra — covering 39 000 known compounds — looking for a match.

As you may expect, not only does oil from each individual oil-field possess characteristic fragmentograms, but so too do the products from 'synthetic' oils. Mr Gilbert has analysed a specimen of Rundle shale oil and of an oil produced from Victorian brown coal by solvent refining. The fingerprints in these two cases differed dramatically. Even the effect of slightly different processing conditions readily showed up in his analyses.

Mr Gilbert has no doubt that he could trace any oil spill back to its source. Since tanker traffic in Botany Bay is expected to increase — it is proposed to allow super

Oil is the prime suspect in the death of these mangroves. Inset: the root zone contaminated with oil.

tankers to enter soon — that could prove valuable in deterring spillages.

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GC/MS profiling of molecular fossils — its use in the identification of environmental pollution by petroleum, coal and oil shale conversion. T.D. Gilbert. *Proceedings of the Ninth Australian Symposium on Analytical Chemistry, Sydney, April 1987.*

The detection and identification of biological markers by computerized gas chromatography–mass spectrometry. R.P. Philp and T.D. Gilbert. In 'Biological Markers in the Sedimentary Record', ed. R.B. Johns. (Elsevier: Amsterdam 1986.)