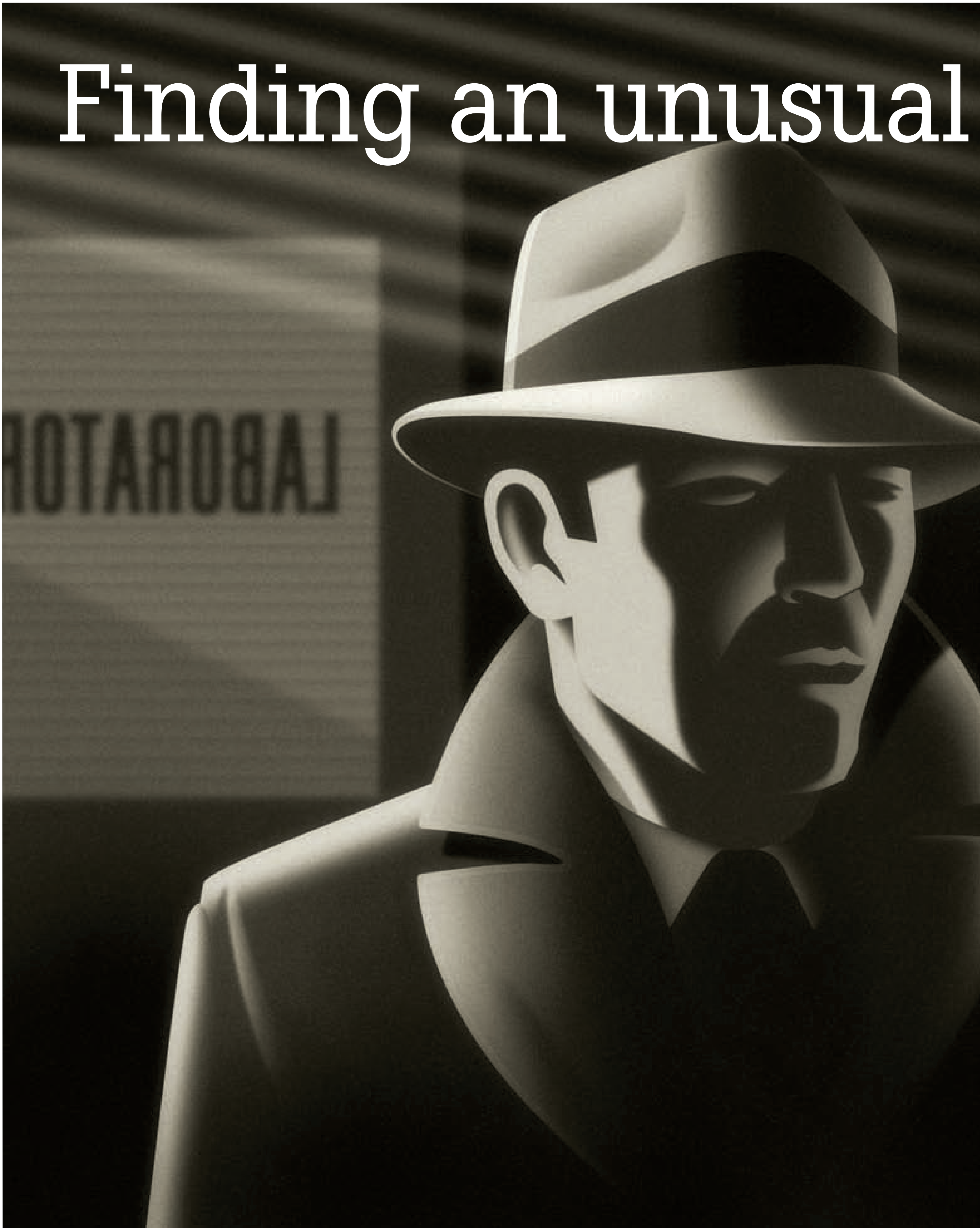
Finding an unusual



suspect

They may wear lab coats rather than trench coats, but, as *Michelle Brown* learns, BP's investigational analysis team at Pangbourne in the UK is setting new standards when it comes to detective work in the fuels and lubricants sector

Cracking cases in support of BP's global fuels and lubricants operations is a daily occurrence for investigational analysis team leader Tom Lynch and his colleagues. But their analytical skills were recently brought to bear on an unusual problem – the team was asked to track down a 'suspect' that was threatening to disrupt distribution operations across the entire UK fuels transportation network. The suspect was biodiesel.

When the European Union opted to legislate for the use of biofuels in road transportation fuels a few years ago, fuel suppliers knew that there would be technical challenges ahead in handling biodiesel and other biofuels, for example gasoline with a bioethanol component (*Frontiers*, December 2007). What was less obvious was the impact that the decision might have on the movement of aviation fuel.

'Aviation fuel does not contain biofuel,' explains Lynch. 'However, aviation fuels are transported in a network of distribution pipelines and vessels which at other times carry different products. The strict standards applied to the composition of aviation fuel do not allow cross-contamination with unapproved compounds, and therein lies the problem – when biodiesel came along, its particular characteristics made potential cross-contamination of aviation fuel in the transportation network much more of an issue than it had been before.'

Britain is served by a network of underground multi-product pipelines (MPPs) which › transport fuels from refineries located on the coast to local distribution terminals. Some of the MPPs are owned by individual oil companies, some by joint ventures, while others belong to the government. For example, BP is a partner in the 650-kilometre United Kingdom Oil Pipeline network, which is a joint venture that serves a range of customers, including the fuel distribution terminals for Heathrow, Gatwick and Birmingham airports. MPPs are also used extensively elsewhere around the world – in mainland Europe for instance, the Central European Pipeline System was originally set up by NATO and now serves airports in Paris and Frankfurt, among others.

30 million tonnes of fuel are moved through the UK's pipeline network each year

MPPs usually transport gasoline, diesel and aviation fuel, often referred to as jet fuel. According to the United Kingdom Petroleum Industry Association, 30 million tonnes of fuel are moved in this way around the UK every year, which is equivalent to about one million road tanker journeys. The products are shipped in separate batches or 'packages', with pipelines being controlled by computer systems linked to sensors and automated valves to optimise flow rates and limit any mixing of different product packages within the line.

Once jet fuel reaches a distribution depot through the pipeline, it is retested for quality before being sent on to airports by dedicated pipelines, trucks or railcars, into storage tanks at the airport.

The possibility of some cross-contamination in MPPs has always existed and there are well-established operational procedures for dealing with it, but adding biodiesel into the mix introduced a new factor, because the molecules in biodiesel behave differently.

The typical standard for biodiesel carried in MPPs is B5, which is a blend of five per cent biofuel with conventional diesel. The biofuel component is mainly composed of compounds called fatty acid methyl esters (FAME). Unlike the hydrocarbons commonly found in fuels derived from crude oil, FAME molecules contain oxygen and that makes them polar. This polarity means that FAME is far more likely to cling to the walls of a pipeline, only to be removed by the next product as it passes through.

'The supply chain has been built up over 100 years to deal with conventional fuels and we're

MAJOR UK COMMERCIAL FUELS PIPELINE SYSTEMS (SIMPLIFIED)

Aviation fuel is tested for quality more than any other fuel products

suddenly putting something quite different in there,' Lynch points out.

Testing times

Aircraft and engine manufacturers initially agreed that FAME content levels in jet fuel should not exceed five parts per million (ppm). But as the government's 2008 deadline for including biofuels in gasoline and diesel drew nearer, the need for an accurate test to ensure the level was not exceeded became more apparent. This led Air BP and BP's global fuels technology (GFT) group to approach Lynch and his team at the end of 2006, seeking a technique that would enable them to test for FAME contamination down to the specified low level.

'Aviation fuel is already tested significantly more than any other fuel product, but the tests at the time were not precise enough to detect this low level of FAME,' notes Air BP fuels advisor Kevin Bower. 'We needed a test that would give a contamination reading for five litres of FAME in one million litres of aviation fuel. Or to put it another way, it's like trying to find five pink balls – the FAME molecules – in a sack filled with a million red ones.'

BP's investigational analysis team had already been developing effective tests for FAME in lubricants, where excessive contamination can cause problems with wear and corrosion.

'We had successfully developed a test method for lubricants, although we were looking at a much higher level of 1000ppm not 5ppm,' says Lynch. 'Even so, we knew we had a technique that could pick out FAME from a complex background. We needed to develop it further.'

The resulting technique is based on a two-stage laboratory process that combines gas chromatography with mass spectrometry.

Gas chromatography separates volatile compounds according to a combination of their boiling points and chemical functionality. The sample to be tested is injected into a moving stream of inert gas and flows through a column that is coated with a polymeric stationary phase. The stationary phase has a chemical affinity with the compounds of interest in the sample. The temperature in the column is raised gradually, releasing the compounds sequentially in an order dependent upon their volatility and chemical affinity for the stationary phase.

For the FAME in jet fuel analysis a highly polar wax stationary phase was employed, which gave enhanced retention of the polar FAME molecules and allowed them to be selectively separated from the jet fuel hydrocarbons with similar boiling points.

Having separated the FAME molecules, ›

mass spectrometry was then applied, breaking up the molecules to form a collection of charged particles, or ions. As these passed through an electromagnetic field, they were detected and characterised according to their mass-to-charge ratio.

BP's FAME test, referred to as GC-MS, combined both tests to get a much finer degree of substance identification than either one on its own. However, even this was not enough to achieve the 5ppm FAME requirement, so Lynch's team refined the test even further using a technique called selective ion monitoring (SIM). This means that the MS unit ignores the majority of charged molecular fragments and looks only for certain ions that are characteristic of the specific molecules of interest.

The added complication in the case of biodiesel detection is that it can include a whole range of FAME compounds, which vary depending on factors such as where the fuel was produced and whether the original 'bio' source was rapeseed, sunflower, palm or soybean oil. 'We looked at the composition of a range of different biodiesels and came up with six FAME compounds that together comprise more than 95 per cent of the vast majority of biodiesel formulations,' says Lynch. 'They vary in their amounts relative to one another, but if you add them together they will account for more than 95 per cent of the total.'

For each of these six FAME compounds, the team then identified the 'unusual suspects' – characteristic ions that the GC-MS technique could home in on using SIM. 'We're looking for ions that are only found in FAME, so we get a great sensitivity enhancement,' adds Lynch.

BP's GC-MS technique incorporating SIM can give a result within an hour

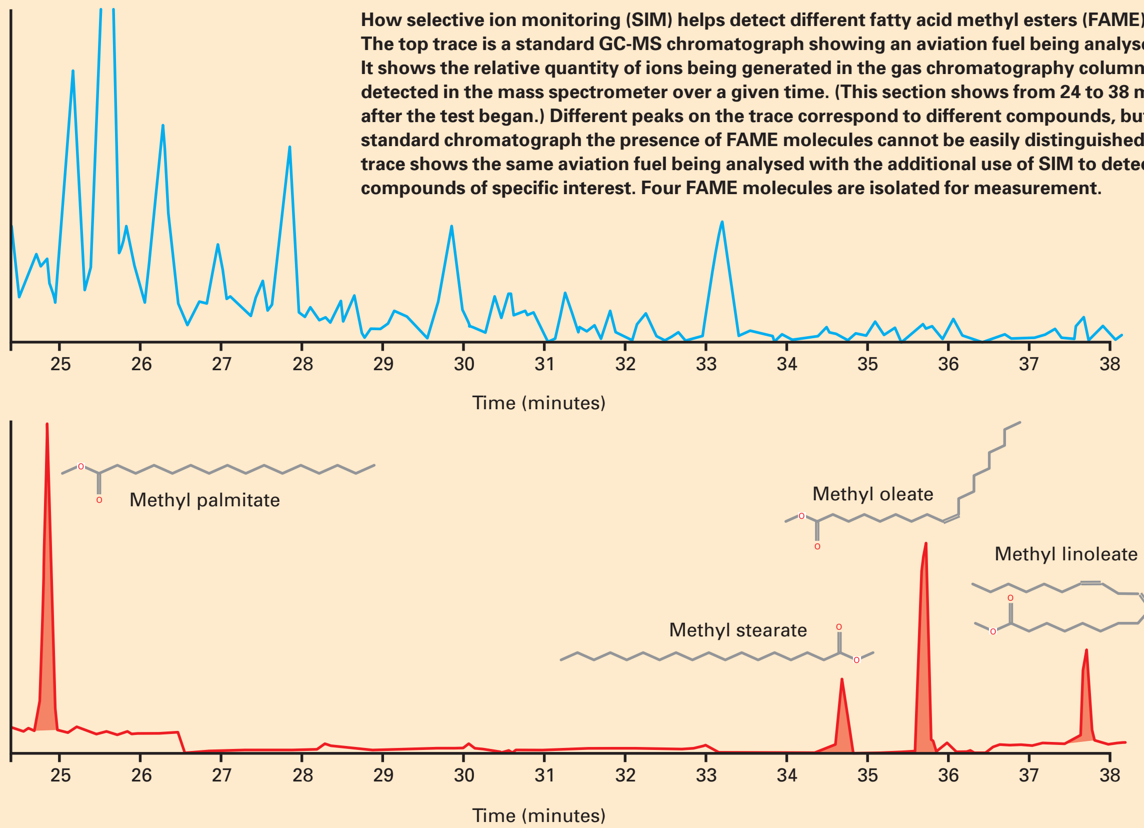
According to GFT fuel technologist Gary Crosby, the secret behind the BP technique's success lies in getting the complex calibration procedures right when the system is set up. 'You need to develop separate calibration curves for each different FAME species over your expected range of concentrations,' he explains. 'You have to plot them all and then amalgamate them, then carry out a multi-regression analysis.'

The good news is that once the system is properly set up, carrying out the test is relatively straightforward. 'You put the sample in and

Alex Ttofi, a specialist in gas chromatography and mass spectrometry in BP's investigational analysis team, loads samples of aviation fuel into the GC-MS system in Pangbourne

SELECTIVE ION MONITORING: IDENTIFYING THE SUSPECTS

How selective ion monitoring (SIM) helps detect different fatty acid methyl esters (FAME): The top trace is a standard GC-MS chromatograph showing an aviation fuel being analysed by BP. It shows the relative quantity of ions being generated in the gas chromatography column and detected in the mass spectrometer over a given time. (This section shows from 24 to 38 minutes after the test began.) Different peaks on the trace correspond to different compounds, but in this standard chromatograph the presence of FAME molecules cannot be easily distinguished. The lower trace shows the same aviation fuel being analysed with the additional use of SIM to detect only compounds of specific interest. Four FAME molecules are isolated for measurement.



have a result within the hour, which is important because we often need a fast response,' says Lynch.

Gold standard

The organisation in the UK charged with finding an industry-wide solution for FAME detection is the Energy Institute (EI). In early 2008, it brought all interested parties together to assess possible detection methods and drew up a shortlist of candidate techniques that then underwent a short ruggedness trial – one aspect of the trial was to check on how straightforward it was for any good laboratory to apply a particular test and deliver reliable results. Following the trial, BP's technique was deemed the one most able to go ahead quickly and was provisionally adopted as a standard method by the end of the year. The only other method to receive a provisional recommendation relies on two-dimensional gas chromatography but this calls for expensive, non-standard equipment that is not available in many commercial laboratories. GC-MS, in contrast, is very widespread.

A comprehensive 'round robin' assessment of the BP test is now being made across the industry to convert its provisional status into a formal industry standard. Yet the technique has already been included in the UK Ministry of Defence's aviation fuel specification – Defence Standard 91-91 – and is being used in labs around the world, including Australia, Singapore and France.

'Developing a standard method usually takes three or four years, with each company protecting its own preferred solution. But because there was an urgent need for a solution we were fast-tracked in less than a year,' says Lynch.

Despite the considerable development effort involved in designing the FAME test, BP decided not to restrict its use through licensing or other intellectual property devices. 'It was a deliberate decision to be a good neighbour within the industry,' says Crosby. 'Any decent laboratory will have the necessary kit to carry out the test and the calibration protocols were developed so that any qualified lab technician can do it.'

The level of BP's contribution has also been recognised by the EI, which praised the 'hard work and outstanding performance' of Lynch and his fellow investigators.

Since being accepted, BP's GC-MS method has helped the industry to manage several potential FAME contamination incidents.

'This test method is very important,' says Bower. 'The industry has established a number of protocols to manage the distribution of biodiesel, but incidents can still occur because we're talking about such low levels of contamination. Pipeline operators, be they private, national or military owners, have to examine their whole system for potential problems. Everything has to be first class.'

In fact, the current 5ppm limit is so stringent that the EI is now running a research programme to provide evidence that might enable the aviation industry to relax the FAME contamination limit to 100ppm. 'At its heart this is a specification and product quality issue, not a safety or product performance issue,' stresses Crosby. 'The aviation industry is understandably very conservative and there are huge safety margins built into everything they do.'

> BP's test method looks set to be the accepted standard for judging other FAME tests

If the 100ppm level can be agreed then other analysis methods might soon be developed. But however the situation evolves in the future, the BP method looks set to be the 'gold standard' reference test by which all other potential FAME tests are judged. The biodiesel 'suspect' has not only been successfully tracked down by BP's investigational analysts, but also brought to book. ■