

Chemical reaction

Geoff Jones of Lintec looks at the growing problem of chemicals being detected in marine bunker fuels



It has been well documented that the current high level of demand for the higher quality and lower emissions fuels for land-based industries has resulted in only fuels of inferior quality being made available for marine applications. In addition, the need to blend cutter stocks of variable quality with poor quality residuals has given rise to many instances of chemicals being detected in marine bunker fuels.

Following a number of cases where chemicals were detected in bunker fuels, the need for 'forensic' methods of analysis, which previously were perhaps considered only as part of an investigative process – after the event, so to speak – has been brought to the forefront for both shipowners and fuel testing agencies.

Before the marine industry takes the quantum leap of specifying limits and methods of analysis, a common sense review of these 'forensic' methods is needed in order to understand what is feasible and what is not.

There has been a call for the testing industry to work together towards harmonisation for these high-value methods of analysis. This in itself will not ensure that that ship operators have the opportunity to burn substantially better quality fuel in the future.

This will only be achieved by an in-depth research programme involving ship operators, engine manufacturers and testing agencies.

The correlation between concentrations of defined chemicals against operational problems needs to be clearly established.

To review the types of chemicals found in bunkers, and the most appropriate methods of analysis, we need to look at recent history.

Over the last 10 years, there have been several instances of chemicals being detected in bunker fuels. The 'red' list includes organic acids (which will be further discussed later), paint stripper, polystyrene, trichloroethylene, styrene monomer and, more recently, fatty acids and phenols.

Firstly, we need to consider the process for validation of any test method, whether physical or forensic.

The **International Organization**

for Standardization's *ISO 8217:2005* specifies the analytical methods to be used when testing.

Section 5.1 of this standard specifies that the fuel shall be homogeneous blends of hydrocarbons derived from petroleum refining and should not include any added substance of chemical waste which:

- a) jeopardises the safety of ships or adversely affects the performance of the machinery; or
- b) is harmful to personnel; or
- c) contributes to overall air pollution.

The methods specified in ISO 8217 have a long history of evolution and refinement.

In the days when the author was a 'boy chemist' these physical methods were purely manual in their operation; but over the ensuing years, as technology advanced, these methods were updated to allow the use of automated equipment.

In most instances automated equipment improved the precision of the methods and this served to reduce the expertise needed by the chemist to perform accurate analysis.

For the automated methods to be accepted by bodies such as **Institute of Petroleum** (now the **Energy Institute**) and the **American Society for Testing & Materials (ASTM)**, an in-depth inter-laboratory programme was carried out, with very specific objectives.

On satisfactory completion of this programme, and once the equipment was seen to have test precision at least as good as the manual equipment, the methods were updated to include the new equipment.

In essence, these were the methods adopted by ISO for inclusion into ISO 8217 and, of course, other ISO standards.

The process to validate a test method includes:

- (i) a draft of the method
- (ii) a pilot of the programme
- (iii) an inter-laboratory programme
- (iv) evaluation of results and exclusion of outliers.

ISO 4259:2006 - Determination and application of precision data in relation to methods of test recommends that for any inter-laboratory programme there need to be at least five participating laboratories,

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preferably more.

The whole process outlined above takes considerable time and, more importantly, defines the method of test, conditions of operation, acceptable equipment, reporting criteria and test precision.

There are many instances where test methods are specific for certain petroleum products and a good example of this is the method used for determination of Acid Number – previously called Total Acid Number (TAN) – in bunker fuels.

The test method commonly used is *ISO 6619:1988*.

The precision of this method is specific for lubricating oils rather than other petroleum products and, as would be expected, the precision achievable for tests on used lubricating oils is significantly worse than that for new oils.

The method does not have any precision for Strong Acid Number (SAN) and therefore we would urge a degree of caution in assessing whether very low SAN values can be considered to be indicative of corrosive activity for the fuel under test.

There is no doubt that SAN is, however, an indicator of the presence of corrosive mineral acids in bunker fuels, and this is one area where more work is needed to correlate low SAN values with damage to fuel injection equipment.

It is well documented that many crude oils contain relatively high levels of naturally occurring naphthenic acids. Consequently a high Acid Number – greater than 3.0 mg KOH/g – may not be an indicator of chemical contamination.

A high value may simply be a consequence of the crude source used to process the bunkers.

Lintec employs Fourier Transform Infra Red (FT IR) to differentiate between naphthenic and other organic acids that may cause corrosive activity.

This is often used as a precursor to analysis by Gas Chromatography Mass Spectrometry (GC MS).

GC MS techniques

GC MS has been a favoured analytical technique within the testing industry for some time.

A Gas Chromatograph, containing a highly specific separation column, is linked

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to a mass spectrometer detector to identify target chemicals in petroleum products.

The effectiveness of this technique depends on factors such as selection of the correct chromatography column, expertise of the analyst and selection of the correct sample preparation medium.

Heavy bunker fuels naturally contain many chemicals, ranging from relatively low carbon number compounds to very high carbon number – and hence high molecular weight compounds.

It is the high molecular weight compounds that are critical factors for the so-called ‘direct injection’ GC MS technique.

Specific sample preparation is needed prior to injection into the GC MS, otherwise the chemicals for identification will be masked by many others present in the bunker fuel.

Techniques such as solid phase extraction (SPE) and derivatisation are often required, to ensure that the target chemicals are more amenable to detection by GC MS.

Fatty acids can be determined by means of this technique, as well as other acidic compounds not found naturally in bunker fuels.

The above technique is ideally suited as an investigative procedure required to ascertain the possible cause of damage to a marine engine. It is labour intensive and requires high level analytical skills.

Another GC MS technique used within the testing industry is ‘head space’ GC MS. This is ideal for the determination of Volatile Organic Compounds (VOCs), as it can be automated to reduce the time needed by the laboratory analyst, and can be performed prior to the fuel being burnt rather than afterwards, as is the case for the

direct injection technique.

Head space is a very convenient technique for volatile chemicals such as styrenes, many chlorinated hydrocarbons such as methylene chloride, chloroform and carbon tetrachloride, as well as many others, including alcohols.

Dichloropentadiene (DCPD) may also be determined using this technique.

Although not applicable for detection of high molecular weight chemicals, Lintec feels that head space offers the most appropriate and cost effective means of protecting ship operator’s interests.

Since it has started using head space analysis, Lintec has been involved in many instances where the fuel has needed to be debunkered based on chemical screening analysis and prior to the fuel being used.

Indeed over the past few months, Lintec has found many cases where styrene was present in bunker fuels at greater than 100 parts per million (ppm), with the highest value found being over 600 ppm.

Analysing our figures shows that over 6% of fuels tested for chemical screening during September 2008 were found to have elevated styrene levels of over 100 ppm.

Styrene at these concentrations may cause serious blockage of filters.

There are many ports throughout the world where bunkers have been found to contain styrene; the problem fuels are not isolated to one geographical region.

During October, Lintec also found several cases where a chlorinated hydrocarbon (dichloroethane) was present in bunker fuels at over 100 parts per million.

It is open to debate whether chemicals of non-petroleum refining origin have been actually present in fuels for many years. There is no doubt that improvements in analytical capability have meant that it is easier to look for and find these waste chemicals.

The more we look for chemicals, the more we will find.

The real test now is to link the types of chemicals to actual machinery damage and in time develop and refine a limit for chemicals for inclusion in a bunker fuel specification.

To achieve this, in-depth input from all sectors of the marine industry will be needed.