

VeriFuel

Understanding Marine Fuel

INVESTIGATIVE ANALYSIS OF
MARINE FUEL OILS:
PROS & CONS



Move Forward with Confidence



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Introduction

Traditional fuel testing parameters are relatively well defined and well understood in the industry. Nevertheless, misconceptions are commonplace in the investigative analysis of marine fuels. Some fuel testing agencies claim to be able to predict potential operational problems that marine fuels may cause by using various (non-industry acknowledged) in-house methods. There are very few examples of investigative analysis performed in sufficient depth to provide an accurate and clear conclusion between components and operational problems. In some cases, these predictive analyses lead to unnecessary concern and the potential of financial losses for operators.

This paper will explore some of the more typically performed investigative analysis methods, their limitations and when/how to apply these methods in a way that provides useful information to the industry.

Marine Fuel Oils and Their Potential Operational Impact

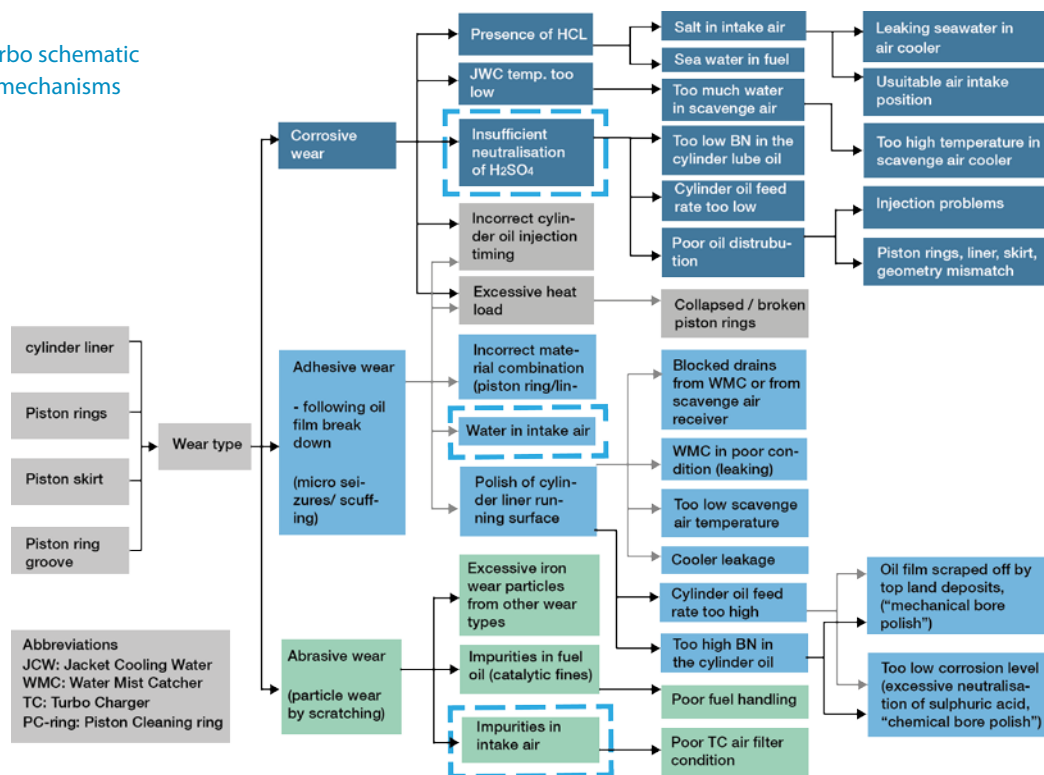
Despite a wealth of discussion regarding alternative marine fuel oils such as LNG and methanol, the preferred fuels are still the traditional petroleum products. Whereas distillates are relatively clean products, heavy fuel oils, by comparison, are usually a refinery by-product consisting of a wide range of blend components. The actual final composition of these fuels when delivered to a receiving vessel will depend on various factors, such as the crude source, the refinery, the refinery set up, the chosen blend components and the potential “contamination” from the supply chain.

Since residual fuels can contain virtually any components found in a refinery in different concentrations, it is an almost impossible task to standardise marine fuel oil composition. No one can say for sure which combination and concentration of chemical components will be encountered in a given fuel, at a given port, at a given time.

Although mechanical challenges on-board vessels are fairly routine, it is fortunate that only on rare occasions do marine fuel oils cause serious operational problems to ships. Typically, fuel related issues will manifest themselves as one of the following: filter blocking, excessive separator sludging, fuel pump sticking/seizures or wear in the combustion chamber.

- Filter blocking and sludging situations can be caused by the fuel being unstable or due to compatibility issues. Compatibility issues can occur when two fuels are mixed in the fuel system during change over from one fuel to the other
- Another reason for filter blocking is wax depositing on filters at too low temperatures caused by inadequate fuel cold flow properties
- Although it is not always the fuel causing the problems as illustrated in the MAN B&W schematic (figure 1), high wear in the combustion chamber is often associated with the presence of the highly abrasive catalytic fines which have not been efficiently removed in the fuel treatment system on-board.

Figure 1:
MAN Diesel & Turbo schematic
on engine wear mechanisms



One less common cause of operational issues is the presence of harmful chemical contaminants. Chemical contaminants are more difficult to identify and prove with absolute certainty. First of all, the sequence of events has to be investigated thoroughly.

- Which fuel(s) were in use at the time?
- What happened?
- When did it occur?

Only after excluding the more common causes of operational difficulties should the investigative work of looking at the chemical composition of the fuel begin.

Investigative Analysis Methods

Typically, sophisticated methods such as Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography Mass Spectrometry (GCMS) are used to get an in-depth view of the marine fuel composition. It must be emphasised that not all components

can be detected by FTIR or GCMS and analysis of the same fuel may give different results depending on the set-up and the library of chemical spectra used (as explained later in this paper).

Marine fuels consist of a wide range of different hydrocarbons. Therefore, in the preparation stage, before starting the characterisation, the chemist must separate the hydrocarbons in order to facilitate the identification of the individual molecules.

There are many different ways to pre-treat the sample before starting the identification, e.g. filtration, vacuum distillation, solid phase extraction, acid extraction or esterification. Determining which pre-treatment to apply depends on the chosen investigative method as well as which components the chemist expects to find in the fuel. Some of these pre-treatment methods also carry the risk of certain compounds decomposing, meaning that the components found may not be representative of the components initially present in the fuel.

FTIR

FTIR can be used to characterize organic components such as alcohols, ketones, polymers and acids. Not all components (e.g. acids) can be fully identified by FTIR but require further analysis, such as GCMS. Polymers can, however, typically be identified by the use of FTIR.

Identification is achieved by comparing the resulting spectra to a library containing spectra of known components.

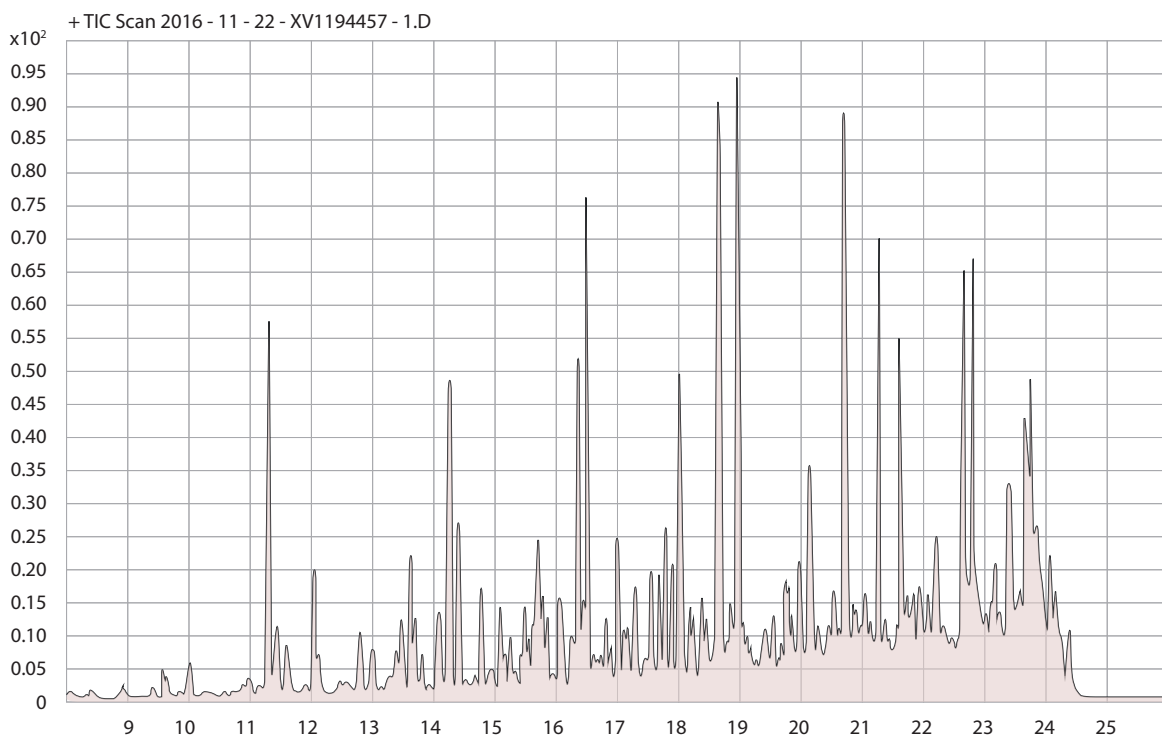
GCMS

The GCMS analysis generates a detailed spectrum (figure 2) showing all of the detected components. Components are then identified by comparing them to a library of known spectra. The concentration of each component is known by its signal strength.

Since these steps are time-consuming (often taking up to a week to process), some labs apply fast screening methods such as Headspace GC-MS (HS GCMS), that can provide results within a few hours. It goes without saying that when a complicated analysis is reduced to just a couple of hours it is less accurate and less conclusive than the full analysis. As HS GCMS compromises on time and accuracy, it will, therefore, detect only the more volatile components that can be separated from the fuel in a relatively short period of time.

Determining which components will be picked up by HS GCMS depends on the temperature and time permitted for the test setup. Laboratories offering HS GCMS apply their own in-house combination of temperature and time and as such, the results are likely to differ between one testing facility to another.

Figure 2:
Example of GCMS spectrum



The Real Challenge

Running a representative fuel sample through investigative analyses such as GCMS is only the start. The real challenge lies in interpreting the results and understanding the link, if any, to the vessel's problems. The composition of marine fuel oil is dependent on multiple factors. There is no compiled list of components or concentrations expected to be found by the analysis of marine fuels.

The Chemical Abstract Service (CAS) register contains more than 100 million substances. No library will contain all components and finding one could be viewed as like finding a needle in a haystack.

- What was not found?
- Is the found component harmful?
- Are they harmful?
- What about the components not found?

GCMS will always find a number of components in various concentrations; however, fuel testing companies will only report what they consider "unusual components". The problem here is manifold:

- No testing facility runs full investigative analysis routinely on marine fuel oils. As such, no reference database exists and no one knows which components are commonly found in harmless fuels nor at which concentration
- No one has performed an in-depth study of individual components and their combinations, in varying concentrations and the operational impact on engines as well as fuel systems

Many fuel testing companies base their conclusions on their own experiences that

are heavily biased towards fuels causing problems when on-board issues have been reported. Unfortunately, since reference data is not available, an objective evaluation of the found component becomes difficult. As such, testing facilities are left with questions such as:

- Is this component only found in fuels that cause problems?
- Or is it present in non-problematic fuels too?
- At which concentration does this component cause problems?
- What is the condition of the engine the fuel is being used on?

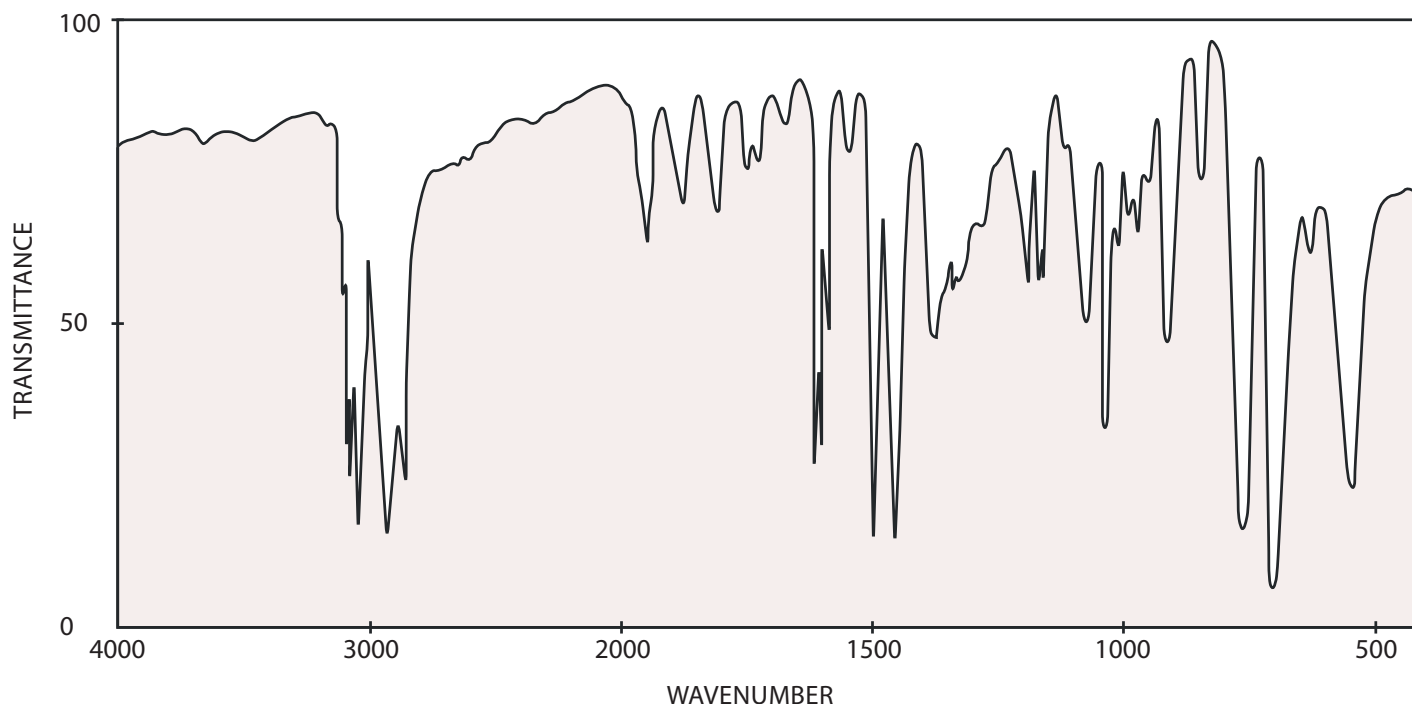
Example: Styrene

A classic example of how misleading a component can be is styrene. Styrene is a volatile component which is picked up by HS GCMS. Styrene has the ability to polymerise forming polystyrene. Polystyrene (figure 3) is known to cause filter blocking. As such, some fuel testing agencies recommend that fuels containing styrene are not to be used, but is this advice helpful to an operator?

Studies show that styrene does not polymerise in marine fuels, likely as the fuel itself acts as an inhibitor on styrene polymerisation.

A conservative estimate states that 40% of marine fuel oils supplied in some major ports contain styrene. In order to better understand the impact of styrene, the following incidents were analysed:

- An investigation of vessels that, unknowingly, have bunkered fuels containing styrene, reveals that none experienced any issues consuming fuel



- A small number of vessels have reported filter blocking and styrene was detected in the fuel by GCMS analysis. However, investigative work performed on filter deposits showed neither a presence of styrene nor polystyrene
- In the rare occasions of polystyrene (not styrene) being present in the fuels, filters block. Analysis have shown that these filter deposits contain polystyrene

Figure 4: Polystyrene

Often when a fuel contains styrene, DCPD and / or indene are also found. A Dow product data sheet lists 'DCPD' and 'indene' as part of their European Fuel Oil Blend component for bunker fuels. Although not supported by experience, some fuel testing companies report these components as unusual and potentially harmful.

In one specific case, a GCMS screening had shown the presence of styrene. The vessel did not experience any problems consuming this fuel but a local port authority found that the fuel was to be categorised as chemical waste based on the analysis report. The vessel was detained and the operator



was requested to debunker the fuel as a chemical waste. (Later the courts ruled that the local authorities had misinterpreted the legislation).

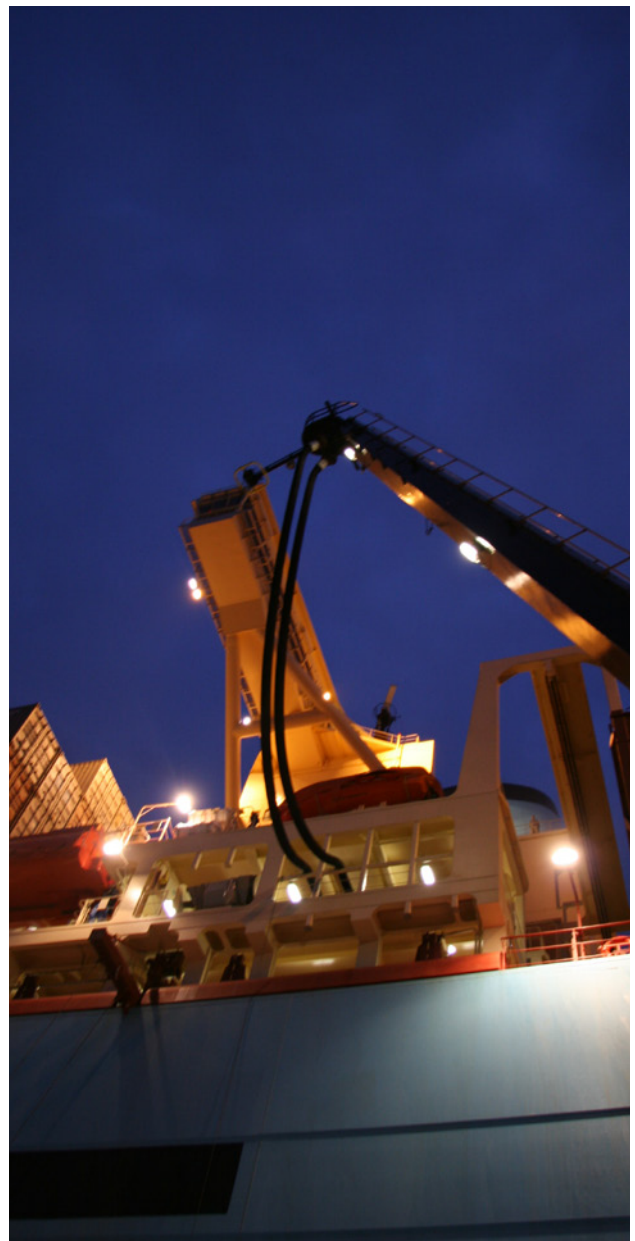
There are numerous examples of operators putting their suppliers on notice – or even requests that the operators debunker the fuel – based on the presence of various components detected through GCMS screening methods. Typically, suppliers would reject such cases, partly as the screening methods do not quantify the concentrations of found components, partly as there is insufficient evidence of found components being harmful. The operator risks losing face, creating unnecessary vessel delay and may even incur financial penalties for refusal to use a fuel that can be consumed without problems.

In one case, a charterer was returning a vessel to the owner. The fuel analysis report from the last bunkering stated that the fuel would be harmful to the operation based on non-industry standard tests performed by the testing facility. Other fuels with similar composition from the same supplier, same port and same time period, did not cause any operational problems. Still, the owner insisted that the fuel was debunkered before accepting the vessel and the charterer had no other option than to bear all the costs.

Another challenge is the wide range of in-house methods applied by various fuel analysis companies. The various testing facilities may not detect the same components or the same concentrations. Within the past five years a standardised method has been made available to the industry – the ASTM D7845 – which

quantifies about 30 components. The method is continuously being developed in order to include more chemical species. With an industry acknowledged method in place, the foundation is laid to better understand marine fuel composition and its potential impact to on operations.

Although sophisticated analysis methods have their limitations and serve poorly as a safeguard towards harmful fuels, they can be very useful when evaluation and investigative work is thoroughly performed.



Example: Polymethacrylates, Houston Area, 2010-2011

Some years back a series of fuels supplied in the Houston area contained polymethacrylates. The fuels complied with ISO8217:2012, table 2 limits, but caused severe fuel pump sticking. The polymethacrylates were not detected by GCMS and therefore, other advanced techniques involving FTIR had to be applied.

In-depth investigative work revealed that polymethacrylates were only present in fuels supplied from specific barges. The barges occasionally carried other bunker fuels with similar properties but without the presence of polymethacrylates. None of these fuels caused fuel pump sticking.

It became apparent that the barges in question carried cargos containing polymethacrylates between the bunker fuels deliveries. As barges are typically not cleaned before loading different products, the remaining cargo contaminated the fuels. All fuels containing polymethacrylates caused problems.

No screening methods could have detected this component. It was only by intensive evaluation and testing of several problematic as well as usable fuels from the same location, period, suppliers and barges, a clear conclusion could be made. Polymethacrylate was the cause.

FTIR and GCMS have their limitations. Not all components are detected in the spectrum and no individual spectra library contains all hydrocarbons.

As such, it may be that some components are not identified despite being present. The polymethacrylates case was the first time, this type of component was detected in a marine fuel oil and only the work of

skilled chemists made it possible to make the identification.

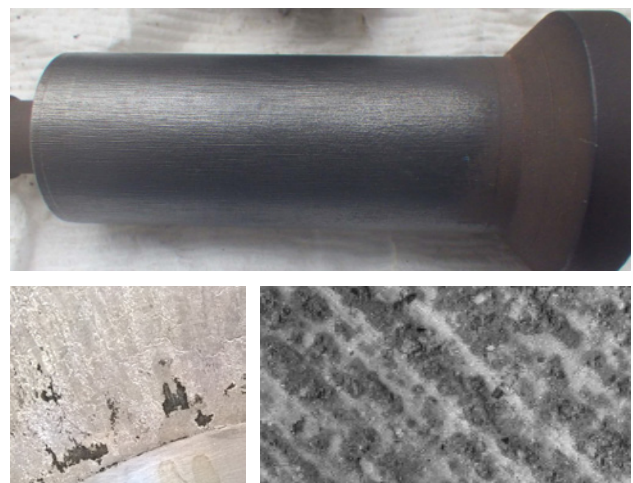
In other situations, nothing will be detected on either FTIR or GCMS and chemists must develop alternative ways to investigate the behaviour of certain fuels. Methods that simulate the conditions on-board vessels are achievable but also complex due to the temperatures, pressures and mechanical conditions that fuels are exposed to on ships.

Example: The East Russia Fuels, 2015

In 2015, a series of harmful fuels were supplied in the Slavyanka area. The fuels met all limits of ISO8217:2012, Table 2. However, these fuels were heavily corrosive. Filters, separator disks and fuel pumps were impacted but none of the general investigative methods applied (such as GCMS and FTIR) indicated anything out of the ordinary.

A dedicated testing method intended for testing these specific fuels was developed by Bureau Veritas' Inspectorate laboratory in Antwerp. The findings indicated that the fuels behaved differently from the regular heavy fuel oils with regards to their potential corrosiveness.

Figure 5:
Consequence of operating on certain East Russia fuels, 2015



Concluding Remarks

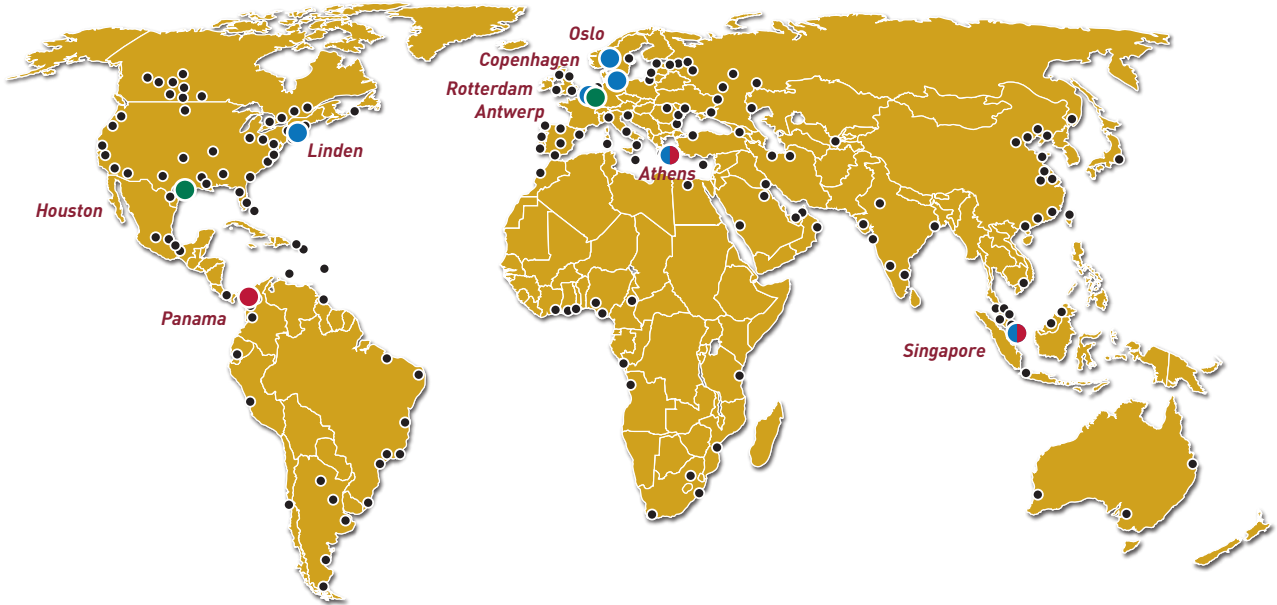
Whereas FTIR and GCMS are sophisticated tools that can provide detailed information about the fuel composition, the challenge lies in evaluating the results. There is no reference list to compare to. No list that indicates harmful components with concentrations and combinations that are proven to be harmful for engine use. Moreover, analysis has only been performed on a select few components to understand their true impact.

Screening tools often serve to concern and alarm the industry instead of assisting it.

There is too little unsupported evidence to link identified components to the cause of operational problems. Having said that, sophisticated methods can be very useful especially in endemic cases. When an identical component is found in measurable concentrations in fuels that have caused similar problems to numerous ships, and where the same component is not found in fuels having caused no problems, can the industry have a clear indicator of a harmful, cause-and-effect component. This is considered a time-consuming and expensive procedure that not all testing agencies are willing to commit to.

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