MARINE FUEL CONTAMINATION

GCMS ANALYSIS SERVICES

PROTECTION AGAINST ENGINE DAMAGE
CHEMICAL CONTAMINATION IN MARINE FUELS

In the 1990s, Veritas Petroleum Services (VPS) was the very first marine fuel testing company to find corrosive compounds in diesel oils supplied in Rotterdam. Over the years, the type and frequency of fuel contamination encountered and detected has increased with such contaminants causing accelerated wear of fuel pumps, fuel valves and other damages to ship machinery being more varied and frequent. In the most severe cases, the affected ships lost propulsion due to contaminated fuel, resulting in the vessels being towed back to port.

ACCORDING TO ISO8217 & MARPOL ANNEX VI:

“Marine fuel should not include any added substance or chemical waste which jeopardizes the safety of the ship; or adversely affects the performance of machinery; is harmful to personnel; or contributes overall to additional air pollution.”

The presence of such material would contravene Regulation 18 of Annex VI and Section 5 of ISO8217. Later revisions of ISO8217 expand Section 5, by stating, “Fuels shall be free from any material which renders fuel unacceptable for use in marine applications.” The standard also includes further clauses to cover the presence of fatty acid methyl esters (FAME) and deleterious materials.
HOW DOES CHEMICAL CONTAMINATION OF MARINE FUELS ARISE?

Refiners and their processes will make every attempt to minimise the presence of any unnecessary chemicals or compounds within marine fuels, however varying crude sources and production processes can still on occasion, give rise to potential elevated concentrations of waste materials. The blending of fuels using blend or cutter stock materials of unregulated quality is also a potential cause of unusual substances entering the fuel supply chain. This is also true of bio-material, which is now more widely used within other transportation modes.

Blending is carried out in order to meet commercial, operational and environmental limits for specific parameters such as density, viscosity and sulphur. Such blending components may adversely affect other quality parameters, through the introduction of harmful substances into the blending products. Blending can also alter the internal chemistry of a fuel, for instance if paraffinic-based blend materials are employed, which can potentially destabilise a fuel, causing asphaltene precipitation and possible sludge formation.

GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GCMS)

The widening variety and complexity of modern-day marine fuels, coupled with tighter environmental legislation, potential for blending contamination plus more complex operational handling of fuels, has given rise to increasing fuel quality issues creating greater demand for assessment and understanding of pre-burn fuel quality, as well as employing certain fuel analysis for post-burn forensic investigation.

To this end, VPS has used its many years of experience and expertise to offer a range of GCMS-related services to help safeguard the vessel, crew and the environment as part of our fuel quality testing programmes.

GCMS offers opportunities to utilise the technique’s analytical capabilities from qualitative assessment to quantitative measurements. In whichever form employed, GCMS is a highly sophisticated analytical tool for the separation and specific identification of numerous components within a sample matrix. This technology is capable of measuring multiple chemical species from percent level to part-per-billion (ppb), or lower, with extreme accuracy.

“Pre-Burn” Chemical Screening by GCMS-Headspace Analysis

(Prevention is always less painful than cure)

As the pioneer of marine fuel quality testing, VPS has led the way in improving the value of pre-burn analysis of fuels, which can help protect valuable marine assets, safeguard the environment, reduce down-time and ultimately save money.

In order to ensure Ship Owners and Operators receive additional protection regarding chemical contamination of fuel in accordance with Section 5 of ISO8217, VPS provides a rapid turn-around “Chemical Screening” service utilising GCMS Headspace Analysis. This service can be run as a routine analysis in conjunction with standard ISO8217 testing, ensuring Ship Owners & Operators receive tangible evidence to highlight and counter any potential damage due to the presence of chemical contaminants, plus support any claim regarding fuel quality.

The GCMS Headspace technique screens fuel samples for volatile and semi-volatile organic compounds such as chlorinated hydrocarbons, monomers, phenols, acids, etc, via the following process:

1. The sample is pre-heated in a gas-tight vial to a specified temperature
2. Chemical compounds within the sample with boiling points within or moderately above the heating temperature vapourise and the headspace vapour is drawn and injected into the GCMS instrument.

Examples of Chemical Contamination of Fuels

- Sludging
- Blocked Filter
The injected sample is separated into individual compounds due to their varying retention times on the GC-column, prior to ionisation, detection and identification using the Mass Spectrometer.

A mass spectrum is produced of the chemicals identified and present, referenced against the spectral library.

The chemical contamination status of the fuel, is then given within the standard VPS ISO8217 test report.

**“Post-Burn” GCMS Forensic Investigation**

It is possible for marine fuels to achieve the ISO8217 quality specifications, yet a vessel still witness operational issues, engine damage or breakdown, upon burning the fuel, (potentially more so if chemical screening was not undertaken prior to burning the fuel). In such cases, VPS is often called upon to undertake a detailed forensic investigation on behalf of the Ship Owner or Operator to identify the cause.

One of the key tools utilised as part of such investigations is GCMS. Here, GCMS can be used in:

Headspace-mode, employing a higher operating temperature for a more detailed and longer methodology than the low-volatile-screen method, or “Direct-injection” mode, which can involve a more complex sample preparation process, prior to an extended analysis process by the GCMS instrumentation.

Such methodologies provide key information on lower volatile and higher boiling point compounds and contaminants, where the additional data provided by such comprehensive analysis can uncover the true source of the fuel quality problem.

**CASE STUDY**

A vessel bunkered 2250MT of RMG380 CST fuel oil, with a sample being taken by continuous drip and dispatched to VPS for routine analysis against ISO8217:2005 specifications. The analysis showed the fuel met specification, although the Total Sediment Potential (TSP) was slightly elevated, (0.08 versus 0.10 specification).

Seven weeks after bunkering, the vessel reported experiencing sticking of injector needles and fuel pump plungers plus clogging of fuel heaters. The vessel witnessed matting / greyish effect on fuel valve nozzles, fuel pump plungers and barrel surfaces as in the pictures below:

VPS advised the heater clogging and pump plungers/injectors sticking could be due to the elevated TSP and that Fuel System Check (FSC) samples (Before and after purifiers, plus a sample taken before the Main Engine ) should be analysed. In addition, it was advised to check the acid number and carry out the basic GC/MS analysis on a Vacuum Distillate of the bunker sample on which the original Fuel Quality Testing had been carried out.

The Vessel landed an additional sample taken at the transfer pump. The following analysis was carried out:

1. Standard analysis (2012 test scope) + Acid Number + basic GC/MS analysis on Vacuum Distillate on the fuel oil sample taken after transfer pump.
2. Acid Number + basic GC/MS analysis on Vacuum Distillate for the bunker sample which was originally analyzed.

**GC-MS HEAD SPACE ANALYSIS OF THE ORIGINAL BUNKER SAMPLE TESTED SHOWED THE FOLLOWING CONTAMINANTS:**

**Chlorinated Compounds** which are not normally found in fuel oils

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular formula</th>
<th>CAS No</th>
<th>Estimated concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dichloroethene, (E)</td>
<td>C₂H₄Cl₂</td>
<td>107-06-2</td>
<td>Qualitative</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>C₂H₃Cl₃</td>
<td>79-00-5</td>
<td>Qualitative</td>
</tr>
<tr>
<td>Chloro benzene</td>
<td>C₆H₅Cl</td>
<td>108-90-7</td>
<td>Qualitative</td>
</tr>
</tbody>
</table>

**GC-MS ANALYSIS ON VACUUM DISTILLATE**

GC-MS analysis was performed on the vacuum distillate <309.7°C of the sample. The results indicated the presence of the following components which are not normally found in fuel oils:

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular formula</th>
<th>CAS No</th>
<th>Estimated concentration %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dichloroethane</td>
<td>C₂H₄Cl₂</td>
<td>107-06-2</td>
<td>0.01</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>C₂H₃Cl₃</td>
<td>79-00-5</td>
<td>0.03</td>
</tr>
<tr>
<td>Chloro benzene</td>
<td>C₆H₅Cl</td>
<td>108-90-7</td>
<td>0.01</td>
</tr>
</tbody>
</table>
GC-MS ANALYSIS OF FUEL OIL SAMPLE TAKEN AFTER TRANSFER PUMP

GC-MS head space analysis was performed on the fuel oil sample. The results indicated the presence of the following components which are not normally found in fuel oils:

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular formula</th>
<th>CAS No</th>
<th>Estimated concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dichloroethene</td>
<td>C₂H₂Cl₂</td>
<td>540-59-0</td>
<td>Qualitative</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>C₃H₅Cl₂</td>
<td>79-00-5</td>
<td>Qualitative</td>
</tr>
<tr>
<td>1,1,2-Trichloropropane</td>
<td>C₄H₅Cl₂</td>
<td>598-77-6</td>
<td>Qualitative</td>
</tr>
<tr>
<td>Chloro benzene</td>
<td>C₆H₅Cl</td>
<td>108-90-7</td>
<td>Qualitative</td>
</tr>
</tbody>
</table>

GC-MS ANALYSIS ON VACUUM DISTILLATE

GC-MS analysis was performed on the vacuum distillate <2976°C of the sample. The results indicated the presence of the following components which are not normally found in fuel oils:

<table>
<thead>
<tr>
<th>Component</th>
<th>Molecular formula</th>
<th>CAS No</th>
<th>Estimated concentration %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-dichloroethane</td>
<td>C₂H₄Cl₂</td>
<td>107-06-2</td>
<td>0.02</td>
</tr>
<tr>
<td>1,1,2-Trichloroethane</td>
<td>C₂H₉Cl₃</td>
<td>79-00-5</td>
<td>0.05</td>
</tr>
<tr>
<td>Chloro benzene</td>
<td>C₆H₅Cl</td>
<td>108-90-7</td>
<td>0.01</td>
</tr>
</tbody>
</table>

GCMS CHROMATOGRAM

Clause 5.1 of the ISO 8217:2005 International Standard states that “The fuel should not include any added substance or chemical waste which jeopardizes the safety of the ship or adversely affects the performance of the machinery; or is harmful to personnel; or contributes overall to additional air pollution”.

VPS had seen previous cases where ships using fuels containing similar chlorinated contaminants had reported problems with fuel pumps and fuel valves after using the contaminated fuels. Based on the unusual components found in the fuel and the problems reported on board the vessel, it was recommended to discontinue the use of this fuel.

The use of this problem fuel was discontinued. The vessel’s losses equated to 5 hours off-hire, fuel pump spare parts/rubber O-rings and unable to use the remaining fuel.

Pre-burn Chemical Screening by GCMS Head Space Analysis of the bunker sample at the time of the initial analysis would have identified the contaminants in the fuel prior to the use of the fuel thereby avoiding damages to the engine.