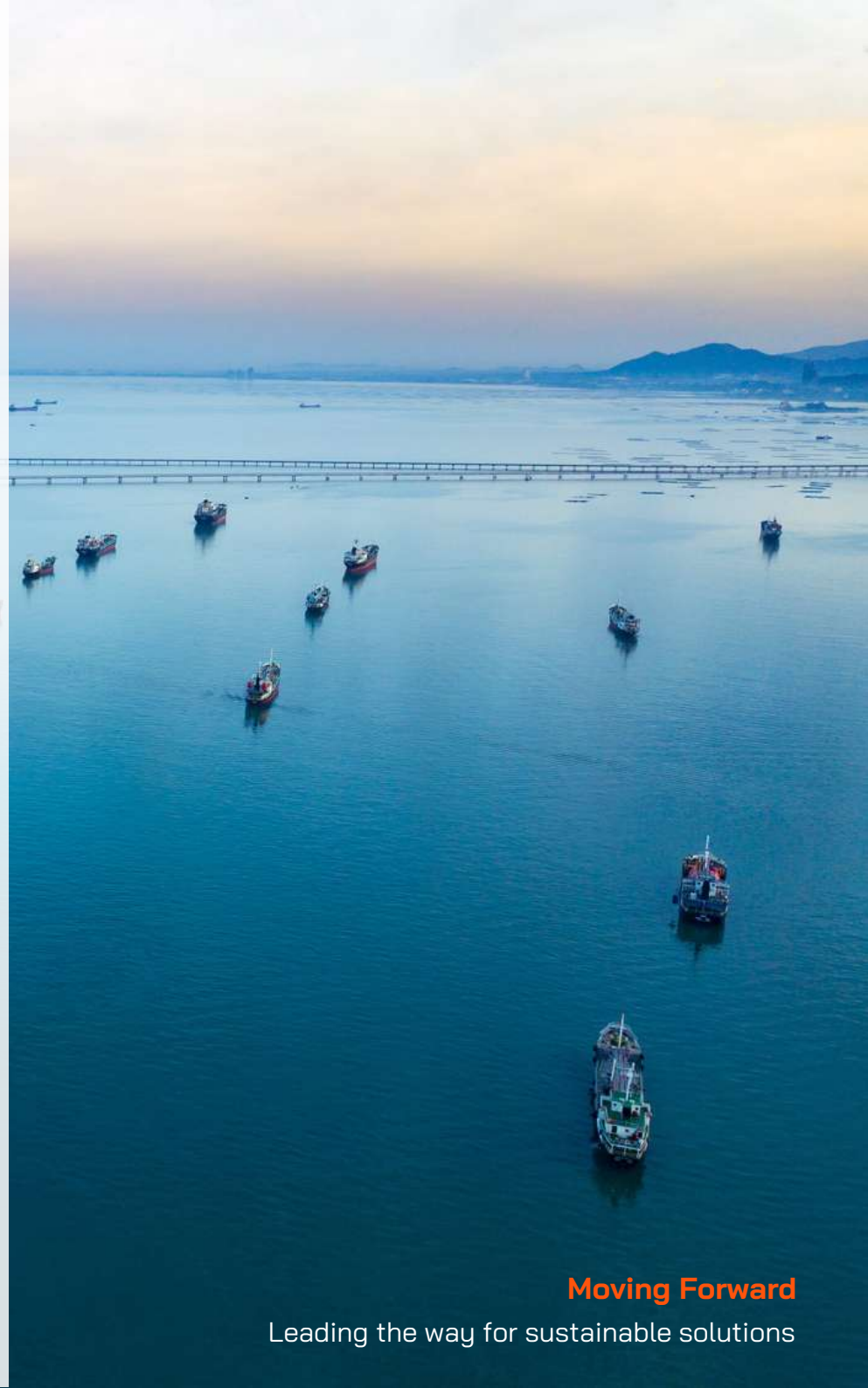
Detecting Chemical Contamination in Fuel

Safeguarding Your Vessel

Welcome to the forefront of fuel quality assurance. VPS, with decades of experience, safeguards against chemical contamination in marine fuels using Gas Chromatography-Mass Spectrometry (GCMS) technology, proactively detecting contaminants and mitigating the risk of vessel failures.As vessels face an expanding range of fuel complexities and environmental regulations, VPS stands as a reliable partner, offering a variety of GCMS-related services, from pre-burn chemical screening to in-depth forensic analysis.

Discover the transformative power of GCMS in ensuring fuel quality, protecting vessels, and avoiding the costly consequences of chemical contamination.

EXPERIENCE ▶ INNOVATION ▶ SUSTAINABILITY



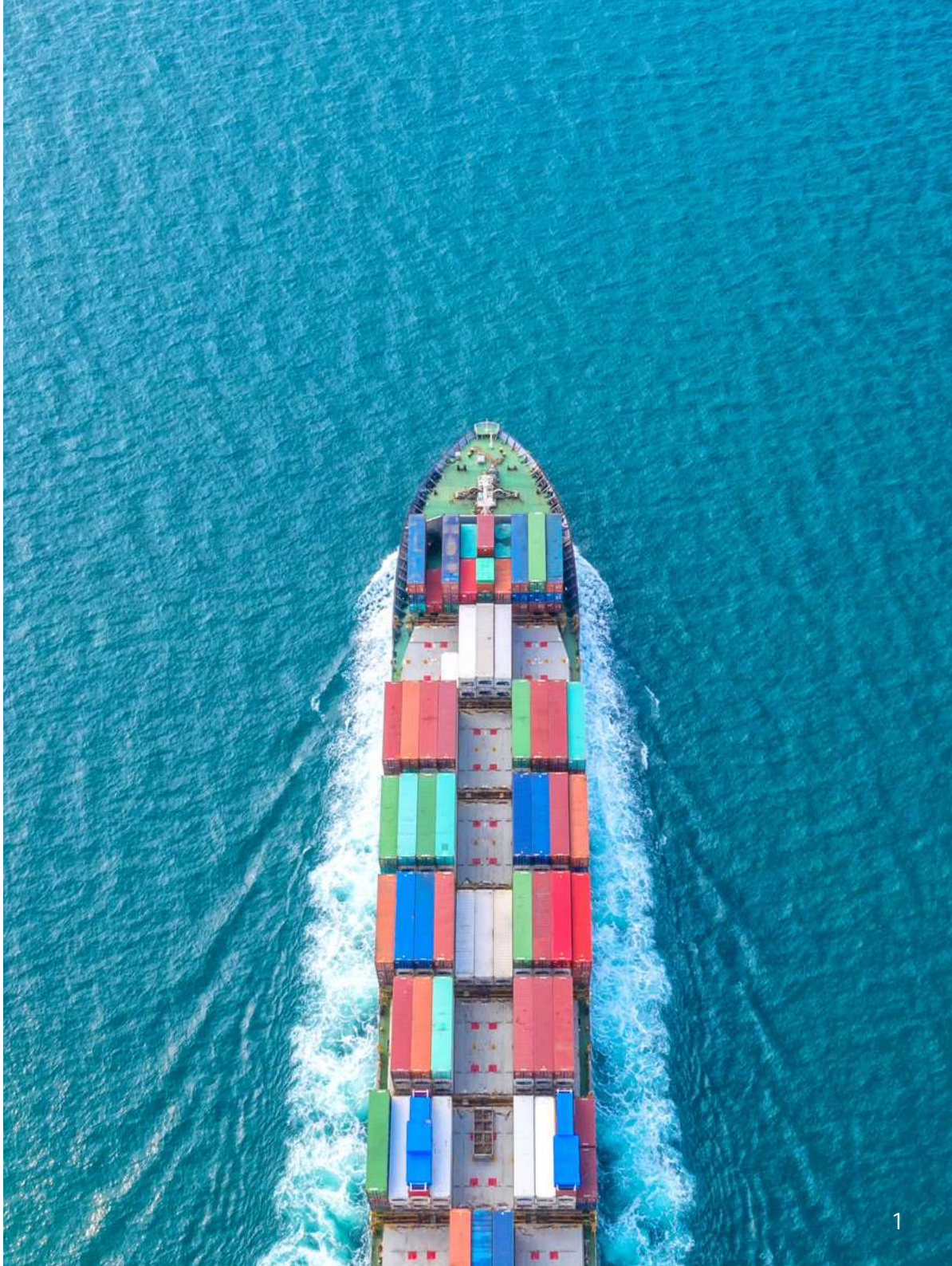
Moving Forward

Leading the way for sustainable solutions

Introduction

Whilst the International Marine Fuel Standard, ISO8217, provides good levels of vessel, crew and environmental protection as a commercial standard for bunker fuels, it cannot cover all potential eventualities. However, ISO8217 and MARPOL Annex VI states, “Marine fuels should not include any substance or chemical waste which jeopardises 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 materials would contravene Regulation 18 of Annex VI and Section 5 of ISO8217.

As far back as 1999, when organic acids were detected in fuels bunkered in Rotterdam, chemical contamination of fuels has been a frequent issue. Over the years, hundreds of vessels have experienced costly engine damages, including high number of vessels affected in major contamination events in Houston (2018 and 2023), Europe (2022) and also in Singapore (2022). In addition to these highly publicised contamination events, there have been many single cases of vessel damage across the world due to the presence of chemical contaminants within fuel. All of these cases, large or small, have shown numerous different chemical contaminants, or combinations of contaminants, which have been identified as being responsible for these damages.



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 more widely used within other transportation modes and now marine. 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 asphaltenic 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.

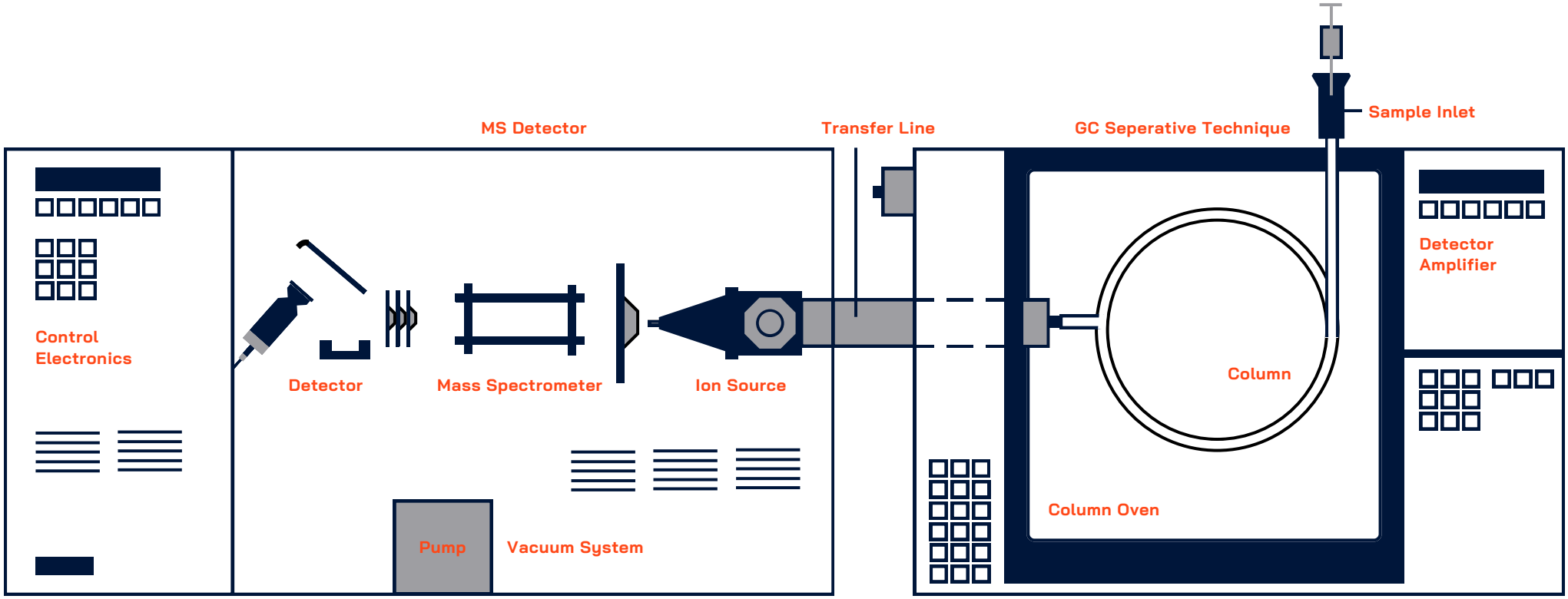


Figure 1: Gas Chromatography Mass Spectrometry Instrument

Examples of chemical contamination effects

Chemical Contaminants	Impact
Dimethyl Esters of Butanoic, Pentanoic and Hexanoic Acids (Dimethyl Adipate = Methyl Hexanoic Acid)	Mechanical failure – filter clogging, sticking fuel pumps, plunger & barrels leading to failure of fuel pumps, injectors and fuel handling components
1,2-Dichloroethane & 1,1,2-Trichloroethane & Naphthalene	Sludging at purifier, sticking of fuel pumps, cavitation, complete blackout, vessel towed
Styrene, ethylbenzene, alphamethylbenzenemethanol, phenyl-ethanone, Benzeneethanol, Phenolic compounds	Failures to injection pumps and nozzles. Injection pumps stuck quickly with hard black lacquer coating – same condition with fuel plungers and bushings
Alpha-pinene, Phenolic compounds (mainly 4-(-1-methylethyl)- phenol	Main engine and auxiliary engines pumps seized and purifier (sludging filters and centrifuge)
Terpenes (mainly Pinene), Phenolic compound – mainly 4-(1-methylethyl)-phenol	Main engine and auxiliary engine pumps and purifier seized (sludging at filters and centrifuge)
Range of cyclic dienes (cyclohexadiene, acetylene) and Styrene	Significant drop in power, Continuous drop for some days
Monoterpenes (mainly pinene) & Phenolic compounds – mainly 4-(1-methylethyl)-phenol	Filter problems and fuel pump damage. Vessel switched over to distillate
Monophenols, Di-Phenols (resorcinols), Alkenes. These 3 groups of compounds are found at high levels in Shale Oil, suggesting this has been used as part of the blend stock for this fuel oil	Purifier stopped and the inner housing around the drum and sludge channel were full of sludge containing hard asphalt sediments
Styrene, Cyclohexanol, Butanol, Butyl ester of propenoic acid (Butyl acrylate), Phenylethylalcohol, methylethylphenol	Sticky hard film which stops the valve rods in open position.
Hexadecanoic acid (palmitic acid) & octadecanoic acid (linoleic acid)	Both main engine and auxiliary engine fuel plungers were badly affected
C16-C18 carboxylic acids	Auxiliary engine plungers damaged
Various Phenol isomers (e.g. methyl, ethyl, etc.)	Sticking of fuel pumps (lacquering)

Pre-Burn Chemical Screening by GCMS-Head Space

A proactive approach to protecting sea-going vessels must always be the best and most cost-effective. Therefore, VPS utilise a GCMS-Head Space technique to provide a pre-burn chemical screening service to detect the presence of contaminants within marine fuel.

GCMS Headspace uses the fact that the chemicals of interest are volatile in nature and therefore by simply heating the sample in a gas-tight vial, forces the volatile chemicals into the gaseous headspace of that vial, which can then be sampled and injected directly into the GCMS instrument. Therefore, this technique detects such volatile components as, chlorinated hydrocarbons, styrene, dicyclopentadiene (DCPD), indene, dienes, napthas, etc.

We use this technique in a qualitative approach in our screening service, where the results provided are classed as a "PASS", or as a "Caution" depending upon whether there is a volatile contaminant present or not. When a "Caution" result is raised, we then undertake a more detailed extended headspace analysis to identify the contaminant more accurately.

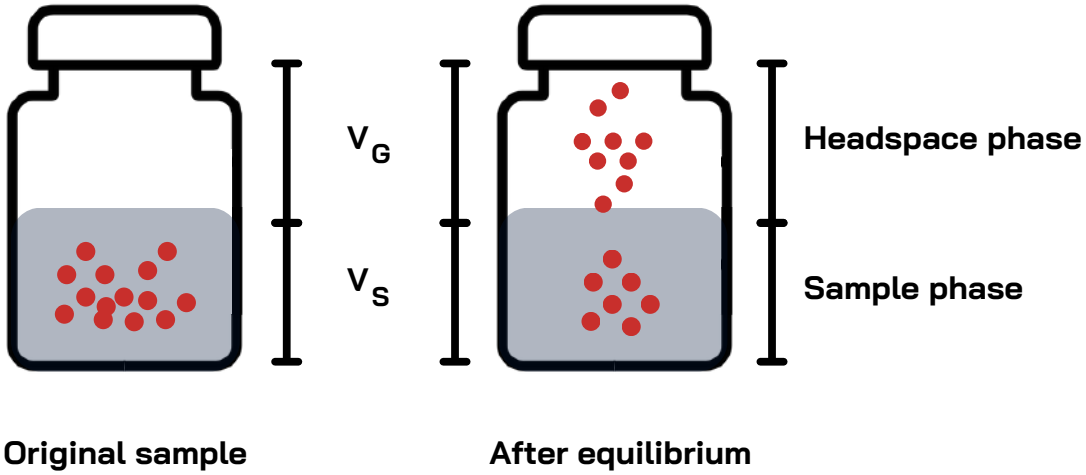


Figure 2: Head Space Sample Preparation

GCMS Vacuum Distillation is used in a more forensic approach to investigating chemical contamination of marine fuels. It provides a more detailed but lengthy sample preparation technique prior to the GCMS analysis, where we take a representative fraction of the fuel within a set boiling range. This is a more detailed analysis than Headspace and can provide quantitative results for chlorinated hydrocarbons, styrenes, alkenes, alcohols, indenes, DCPD, etc. This technique provides a very detailed GCMS analysis of the sample to very low detection levels and is used a lot in fuel claims cases.

GCMS Acid Extraction is again a more detailed and lengthy sample preparation technique prior to the GCMS analysis, but this time it is used to detect, identify and measure the presence and quantity of phenols, fatty acids, ketones, alcohols, aldehydes, ethers etc. Note these are mainly chemically different species than those which are detected by headspace, or vacuum distillation. Again, this technique can provide quantitative results, following a very lengthy sample preparation process and subsequent GCMS analysis.

The above GCMS analysis techniques are capable of detecting numerous chemical groups:

- Chlorinated Hydrocarbons
- Phenols & Alkyl Phenols
- Styrene & Alkyl Styrenes, Dicyclopentadiene, Indene
- BTX, Alcohols, Esters, Ketones

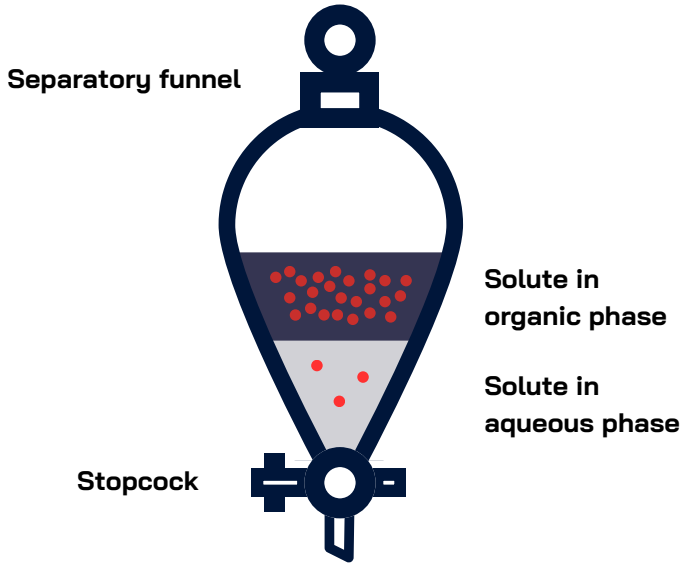


Figure 3: GCMS Acid Extraction Sample Preparation

The GCMS analysis will provide a detailed chromatograph, from which VPS expert analysts can interpret the results providing accurate determination of the chemicals present within the fuel sample.

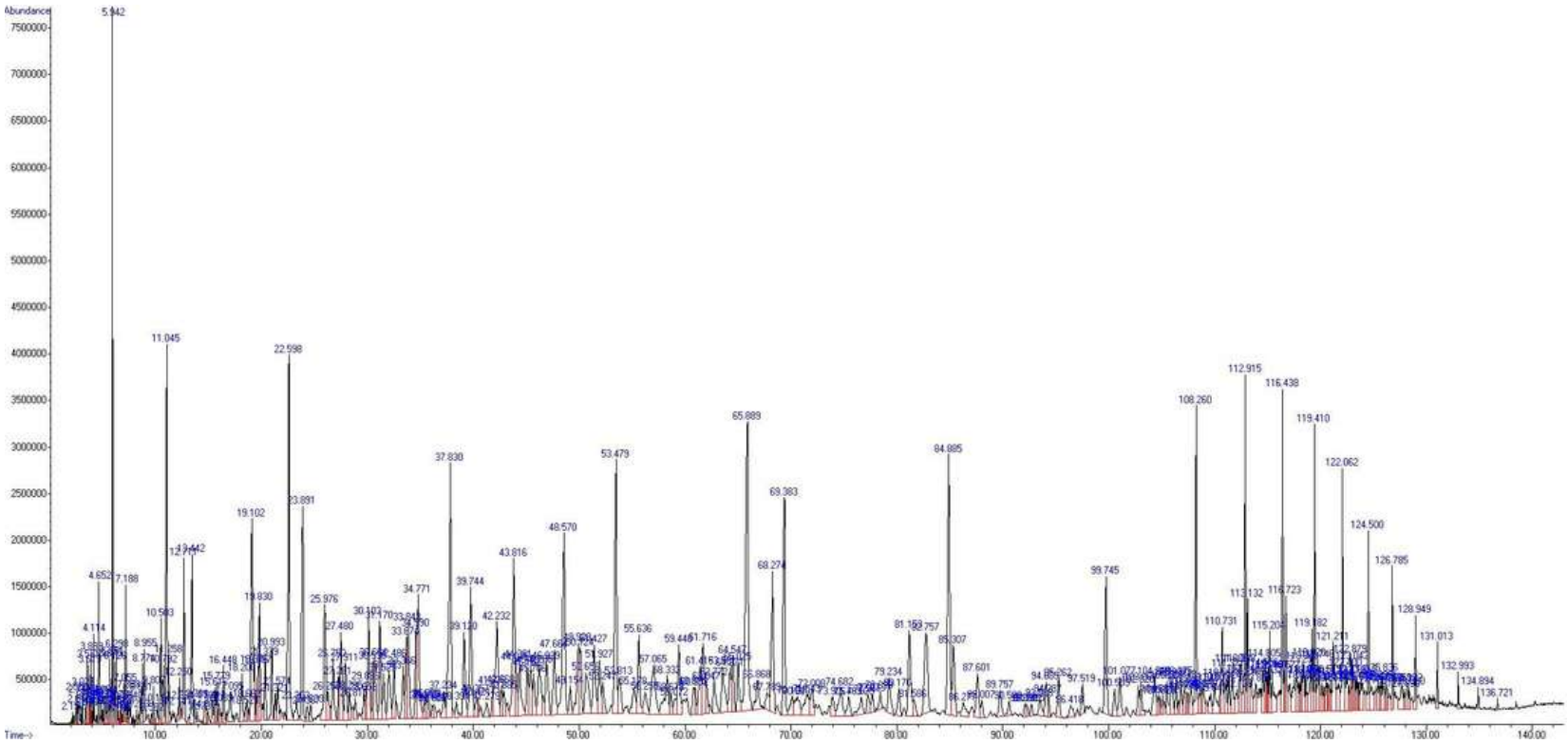


Figure 4: GCMS Chromatograph

Discover the power of proactive fuel protection | A case study

Explore the real-life repercussions of chemically contaminated marine fuel through a compelling case study that sheds light on the challenges and costs ship owners and operators may encounter when their vessels are fueled with compromised substances.

Case Overview: Singaporean-owned Chemical and Product Tanker

In April 2023, a chemical and product tanker owned by Singapore bunkered 415 m/tons of Very Low Sulphur Fuel Oil (VLSFO) in Houston. As the vessel ignited the fuel in May, it swiftly encountered a myriad of issues affecting both auxiliary and main engines. From exhaust gas temperature deviations to worn-out fuel pumps and plunger barrels, the vessel faced a cascade of problems, culminating in a complete engine stoppage en route to the next US port.

Diagnosis through Advanced Technology

Utilising cutting-edge Gas Chromatography Mass Spectrometry (GCMS) Acid Extraction methodology, VPS's forensic laboratory identified the presence of phenols and fatty acid compounds within the fuel. This crucial insight guided the necessary repairs to both auxiliary and main engine fuel pumps, incurring a total spares cost of $200,000.

Recovery and Evaluation Process

Following repairs, Class and Engine Manufacturer representatives assessed the vessel's performance. A meticulous sea trial secured US Coast Guard approval to berth and maneuver in US coastal waters. By the end of July, the contaminated fuel was successfully de-bunkered in Houston.

The Value of Proactive Protection: VPS Recommends GCMS-HS Screening

VPS advocates a proactive approach to safeguarding vessels, crew, and the environment. The GCMS-HS chemical screening service offers unparalleled benefits and value, serving as an affordable and rapid detection service before fuel combustion. In 2018, a Swedish Club report highlighted that the average cost of a single fuel-related damage case is $344,000, while a single GCMS-HS screening test costs less than 0.008% of a bunker stem. This service provides enhanced protection, mitigating the risks associated with volatile chemicals in marine fuel.

Extended Services for Comprehensive Analysis

For cases requiring further analysis, VPS offers Extended Head-Space, Vacuum Distillation, and/or Acid Extraction GCMS analysis. Coupled with expert analytical experience, these services support our commitment to ensuring the utmost protection for our customers.

Conclusion

The maritime industry is current working to reduce emissions to meet the IMO target of net-zero on or around 2050. There have been lots of measures adopted over the last few years to improve fuel efficiency and reduce emissions. This has included slow steaming, vessel design, air lubrication etc. However, all of these methods still involve the use of fossil fuels. So, the next step is to start using alternative fuels with significantly reduced or even zero carbon footprints. This has started with many new builds and some retrofits on vessel with dual fuel engines allowing the use of alternative fuels such as methanol.

In the future we will also start to see other fuels being used, such as methanol and hydrogen, and there is a lot of current research ongoing around the use of ammonia as a zero-carbon fuel and also some consideration around the use of nuclear energy to power vessels.

Join us on this journey

Join us in the journey towards a greener, more sustainable maritime industry. At VPS, we are committed to accelerating the shift towards a low-carbon future, and we invite you to be part of this transformative change.

Are you a vessel owner or a stakeholder in the maritime industry? Let's collaborate to reduce your carbon footprint and make your operations more eco-friendly. With VPS, you will gain access to data-driven solutions, expert advice, and digital tools that guide you along the path to sustainability. Together, we can create a more environmentally responsible and economically efficient maritime sector.

Contact us today and let's pave the way to a cleaner, greener future for the maritime industry.

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