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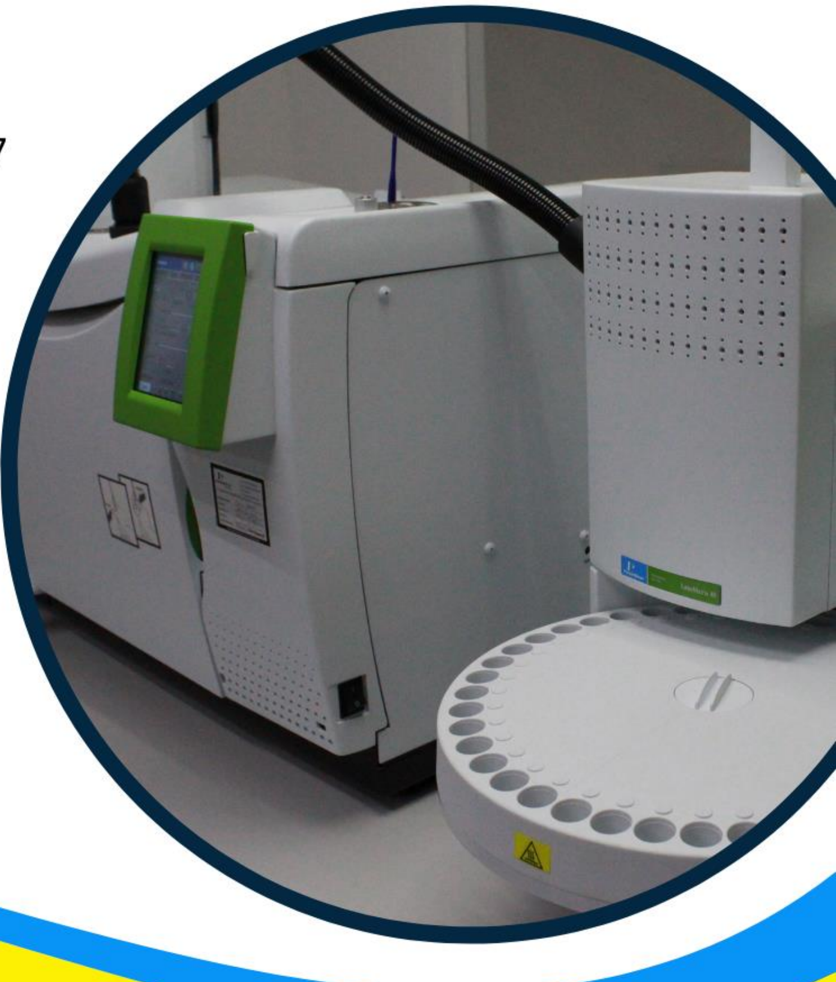
WHITEPAPER

Jan 2023

GC/MS ANALYSIS AS A COMPLEMENTARY TO ISO 8217 TABLE 1 AND TABLE 2 SPECIFICATION TESTING TO DETECT AND QUANTIFY DELETERIOUS MATERIALS WITHIN THE PURVIEW OF ISO 8217 - CLAUSE 5



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Introduction

Issue of chemical contamination had plagued the bunkering industry for years, and the risk of receiving contaminated bunker fuels is likely to persist. The importance of buying from reputable suppliers with robust quality control procedures cannot be over empathised. However, the complexity of the bunker supplier chain as well as unregulated use of cutter stocks would mean that any quality control process, no matter how robust, is likely to only minimise and not fully eliminate risk of such contaminations. It is therefore important for bunker buyers and operators have their own control measures in place.

The test scope stated in table 1 & 2 of ISO 8217 is limited and insufficient to cover the requirement for detection of deleterious materials in marine bunker fuels. Marine fuel testing laboratories had successfully addressed the limitation of ASTM D7845, the only standard GCMS test method, and is able to apply it as an effective chemical screening tool to complement the table 1 & 2 test scope. As demonstrated in the case of Chlorinated Organic Compound (COC) contamination in 2022, most fuel laboratories had successfully identified COC, using ASTM D7845 test method, as the main contaminants causing the damages. Findings had been proven to be consistent across laboratories using the same method and was well accepted by the industry and port authorities.

Over the years, GC/MS analysis has proven to be a practical technique to employ for detection and quantification of deleterious materials, or chemical contaminants present in bunker fuels. This technique been widely used and accepted across the marine industry for marine fuel forensic testing. Chemical screening of bunker fuel is a critical element of successful onboard fuel management, and GC/MS analysis can be employed as a complement to the routine test scope, specifically to cover the detection and quantification of deleterious materials which otherwise cannot be detected by the table 1 and 2 parameters.

The Supply Chain

The bunker Supply chain consists of a complex network of different stakeholders including refineries, traders, and physical suppliers operating their own barges, with some performing their own fuel blending operation. Each stakeholder controls a different part of the supply chain, with varying extend of influence. A product moving through the supply chain, be it in the form of cutter stocks or finished grades, may have been blended numerous times with materials from different sources as it changes hands. This complexity makes it extremely difficult to ensure traceability and to prevent any forms of contamination.

The Specification

A supplier may claim that the fuel is on specification when test results fall within the ISO 8217 table 1 or table 2 requirement. However, the specification requirement is not only limited to the two tables. The fuel must conform to the characteristics and limits given in Table 1 and 2, and at the same time must also be free from any material that renders the fuel unacceptable for use in marine applications. Meeting table 1 or 2 requirement alone does not necessarily mean the fuel has meet the full specification requirement.

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Clause 5 and Annex B of ISO 8217 address the issue of deleterious materials in bunker fuels. As wide range of materials from different sources can enter the marine supply chain, from production, handling and transport systems, the responsibility of quality assurance and management to ensure deleterious materials are excluded lies on all stakeholders within the supply chain. Suppliers may already have in place, different levels of due diligence and quality control measures, however experience of the various contamination cases in past decades have shown that reliance on such status quo is inadequate to effectively address the risk of chemical contamination.

Clause 5 stipulates that the fuel delivered shall be free from any material at a concentration that causes the fuel to be unacceptable for use. However, what chemicals species and at what concentration would it renders the fuel with unacceptable for use remains highly disputed. Some chemicals species are known to be present in petroleum feedstock and are often detected bunker fuel, while some other such as organic chlorides are known to be undesirable and not usually found in petroleum sources. Linking operational issues to a specific or a combination of chemical species, as well as determination of their safe limits can prove difficult. This can be further complicated by inadequate evidence collection when operational problems are experienced onboard. As the marine industry needs time to build on its understanding of the impact specific chemical species, operators need to have their own measures in place to manage this risk and safeguard their interest.

Gas Chromatography–Mass Spectrometry (GCMS) Analysis

CTI-Maritec practices GC/MS techniques using ASTM D7845, covering low boiling point to medium boiling point chemical species, as well as GC/MS by SPE (Solid Phase Extraction) that covers high boiling point & polar chemical species. Both test methods are accredited.

GCMS and Pre-Treatment

The GCMS analysis consists of two main components, the gas chromatograph, and the mass spectrometer. The sample is injected with a carrier gas into gas chromatograph (GC) that utilizes a capillary column to separate the individual components. This allows the Mass spectrometer (MS) downstream to identify each separated component. The spectrum produced by a given chemical compound is constant and is used as "fingerprint" for the molecule, allowing the compound to be identified.

Before the GCMS testing process, samples need to be prepared and pre-treated. Pre-treatment processes may include dilution and/or Solid Phase Extraction.

GCMS by ASTM D7845

GC-MS by ASTM D7845 is an international standard test method, and currently the only standard that is developed to quantify chemical species at low levels in marine fuels oils and cutter stocks.

The process involves adding suitable internal standard, ethylbenzene d-10, to the sample before it is introduced into a gas chromatograph equipped with two columns configured with a splitting device. The sample first passes through the pre-column that separates the light hydrocarbon fraction and eliminates the high boiling hydrocarbon fraction to vent. The

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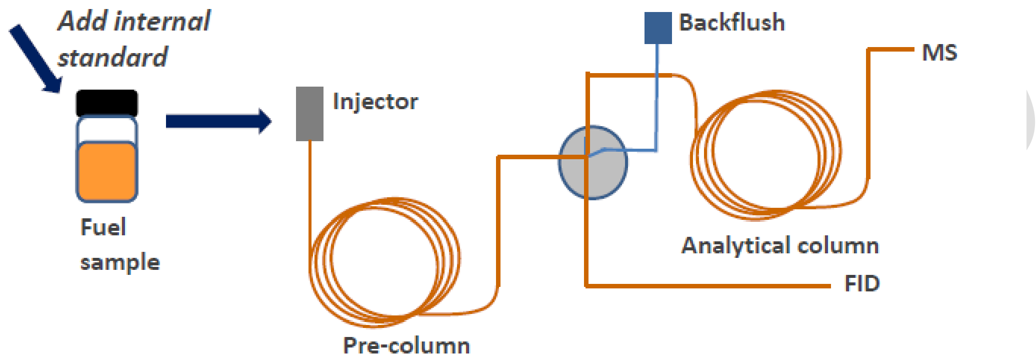
compound of interest and internal standard are then transferred to the high-resolution analytical column for chromatographic separation. The resulting chromatogram is then processed by mass spectral analysis based on selected ion monitoring.

ASTM D7845 currently provides standardized analytical methods to identify 29 specifics aromatics and oxygenated compounds. With extensive research and data collected over the years, CTI-Maritec had extended the scope of this method to include fatty acids methyl esters (FAMEs), 4-cumylphenol, phenolic compounds, chlorinated organic compounds and other low and mid-range boiling chemical species.



Deans Switching Backflush, Configuration B

Summary of Method

- Sample first passes through a pre-column which separates the light hydrocarbons and eliminates the high boiling hydrocarbons to vent (backflush).
- The compounds of interest and internal standard are transferred to the analytical column for chromatographic separation.

GCMS by SPE (Solid Phase Extraction)

This in-house test method is developed to detect and quantify polar and high boiling point chemical species, including Fatty acids, Monoglycerides, Rosin acids, Bisphenol A and Bisphenol Tars. Sample of a known weight is diluted, and polar species is isolated using a solid phase extraction (SPE) cartridge. The SPE extract was then derivatized to convert any polar components present to their trimethyl silyl esters for GC/MS analysis.

Findings

CTI-Maritec had been applying both GC/MS by ASTM D7845 & SPE to screen for a comprehensive range of chemical species, and successfully detected chemical components from a wide variety of sources. Both methods can be employed as part of routine pre-emptive testing regime, as well as means for investigation testing.

We have so far identified presence of Estonian shale oil, tall oil, cashew nutshell liquids, and other by-products from bio-based, chemical, and petrochemical industries in the bunker samples tested. These components are very likely be introduced as a cutter stock.

Non-hydrocarbon chemical species have also been detected in some cases. These chemicals may have been inadvertently included into bunker fuels during production, storage, transportation, or from bunker deliveries facilities, as the products changed hands through the bunker supply chain. In addition, some of the non-hydrocarbon chemical species detected may have originated from intermediate processing chemicals used to

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produce or process petroleum products in refineries (such as solvents or reagents). These chemicals may have not been fully removed after the processing stage and enter the bunker streams unintentionally.

Empirical data suggest that the problems encountered onboard ship can be attributed to the presence of a combination of non-hydrocarbon and polar chemical species. Based on profiles of chemical contaminants detected and the frequency of occurrence, common source of contaminant can be generally categorized into four main groups as shown in the tables below.

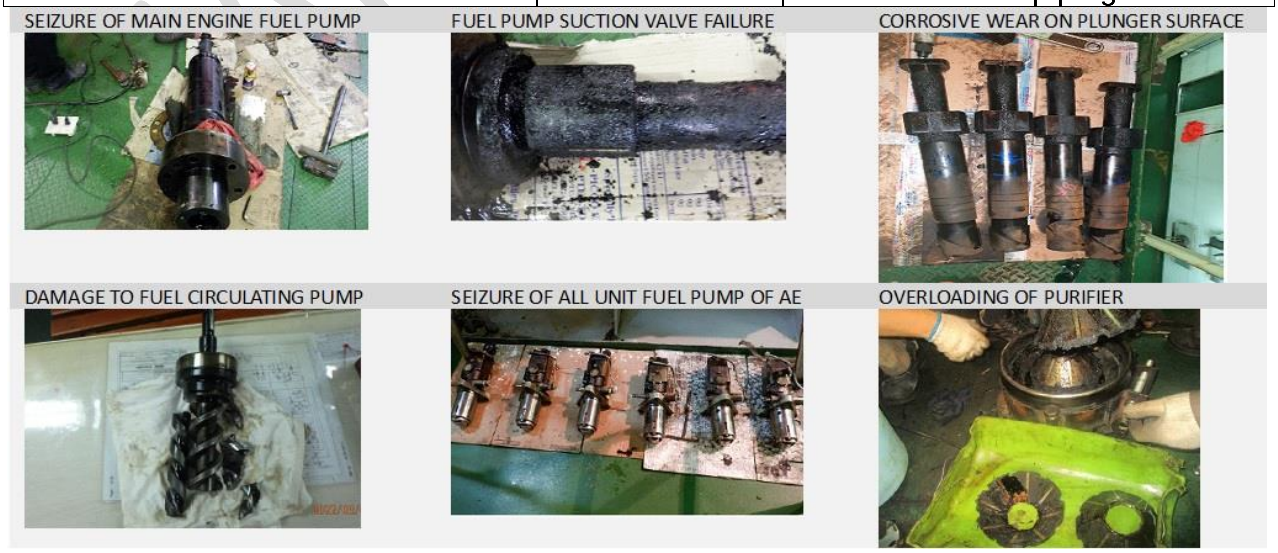
It is noted that most of the groups tend to have certain low boiling point phenolic compounds (Phenol) or chlorinated organic compounds included in the blend, and this may be one of the indicators to ascertain the presence of further potential higher boiling point deleterious materials.

Chlorinated Organic Compounds

These are compounds containing a carbon-chlorine bond. They are widely used in the oil field as a wax dissolver and are usually derived from cleaning operations at production sites, pipelines, and tanks. For refineries theses compound are undesired contamination in crude oils as they can transform into hydrochloric acid during the refining process and cause intense corrosion. Most refineries allow no more than 1 ppm organic chlorides in the crude charge.

In 2022, approximately 200 ships were affected by fuel contaminated with Chlorinated Organic Compound (COC), of which about 80 ships reported various issues with their fuel pumps and engines, the concentration detected was up to 7000ppm. CIMAC issued a recommendation to limit COC in marine fuel of 50ppm following a cause-and-effect evaluation of the 2022 incident.

Chemical Contaminants or Chemical Constituents	GC/MS Techniques	Common Machinery issue reported
▶ Chlorinated organic compounds (consists of 1,2-dichloroethane, tetrachloroethylene and others)	ASTM D7845 GC/MS	Damage to fuel injection equipment and sludging of fuel system components. Minor corrosion in fuel piping internals.



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By-Product or Processed Product Derived from Bio-based or Plant-based Sources and By-Product from Chemical Industry

Fatty acids, rosin acids, butanol, phenolic compounds are common components found in by-product derived from bio or plant-based source. 4-cumylphenol is used for production of phenolic resins and bisphenol F is used in manufacture of plastics and epoxy resins, both are from chemical industry.

Presence of these components have been detected, together with FAME components in fuels bunkered in 2022 from the ARA region. Vessels had reported damage to fuel injection pumps when the fuel is consumed. The detected concentration of phenol was up to 3500ppm, phenolic compounds up to 10,500ppm, fatty acids up to 600ppm, phenethyl alcohols up to 7600ppm, bisphenol F isomers was up to 120ppm and 4-cumylphenol up to 6500ppm.

Chemical Contaminants or Chemical Constituents	GC/MS Techniques	Non-petroleum Cutter Stock	Common Machinery issue reported
▶ Fatty acids (C14 to C18)	GC/MS by Solid Phase Extraction	By-product or processed product derived from bio-based or plant-based sources.	Damage to fuel injection pumps.
▶ Fatty acids (C24 to C30)			
▶ Rosin acids			
▶ Bisphenol F isomers			
▶Butanol	ASTM D7845 GC/MS		
▶Cyclohexanol			
▶Phenol			
▶Phenolic compounds			
▶ Phenethyl alcohols			
▶Fatty acid methyl esters (FAMEs)			
▶4-Cumylphenol			
▶Slightly reactive hydrocarbons with double bond (C=C)			
▶2-Ethylhexanoic acid			
▶ Benzenediols and its derivatives			

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Cashew Nutshell Liquid

Cashew Nutshell Liquid (CNSL) is by-product of the cashew industry. This nutshell liquid is obtained from the hard cashew nutshell and contains mainly anacardic acid, cardanol and cardol. These contaminations were detected in the fuels bunkered in 2022 from the ARA region, along with Fatty acids, Monoglycerides, FAME, Phenol, 4-Cumylphenol and high level of potassium. The concentration of cardol and cardanol were each up to 17000ppm, anacardic acid up to 3500 ppm and phenol was up to 400ppm. Vessel using this fuel had reported damage to fuel injection pumps and severe blockage of fuel injectors.

Chemical Contaminants or Chemical Constituents	GC/MS Techniques /Elemental Analysis	Non-petroleum Cutter Stock	Common Machinery issue reported
▶Fatty acids	GC/MS by Solid Phase Extraction	Cashew Nutshell Liquid	Damage to fuel injection pumps and severe blockage of fuel injectors.
▶ Monoglycerides			
▶ An alkyl-phenol - C15 isomer (ginkgol, a cardanol)			
▶ An alkylresorcinol - C15 isomer or an alkyl 1,3-benzenediol -C15 isomer (bilobol C15:1, a cardol)			
▶2-Hydroxy-6-alkylbenzoic acid (an anarcardic acid)			
▶FAMEs	ASTM D7845 GC/MS		
▶Phenol			
▶4-Cumylphenol			
▶Potassium	IP 501		

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Estonian Shale Oil

Estonian shale oil is an oily liquid produced from retorting of Estonian oil shale. Shale oil is permitted as a blend component under ISO 8217:2017 specifications. However, stability of a fuel can be affected by the presence of high concentration of polar chemical species. In high concentrations, alkylresorcinols (main component of shale oil) & phenolic compounds may induce instability in fuels causing asphaltenes flocculation under certain conditions.

The concentration of alkylresorcinols detected was up to 72,000ppm and phenol was up to 2600ppm. Issues reported by vessel while using these fuels include overloading and blockage of fuel purifiers, filters, and damage to fuel injection equipment. These symptoms are in line with the effects of excessive sludge formation.

Chemical Contaminants or Chemical Constituents	GC/MS Techniques	Non-petroleum Cutter Stock	Common Machinery issue reported
▶ Alkylresorcinols (or alkyl 1,3-benzenediol derivatives, with a benzenediol distribution characteristic of Estonian-type shale oil)	GC/MS by Solid Phase Extraction	Estonian-type shale oil	Overloading and blockage of Fuel Purifiers, filters, and damage to fuel injection equipment.
▶Phenol	ASTM D7845 GC/MS		
▶ 4-Cumylphenol			
▶ 1-Naphthalenol			
▶2-Naphthalenol			
▶1-Phenylethanol			
▶2-Phenylethanol			
▶2-Ethylphehol			
▶4-Isopropylphenol			
▶Styrene			
▶ Dicyclopentadiene			
▶Indene			
▶Dihydro-dicyclopentadiene			



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GCMS Analysis as a Complementary Test Solution

Damage caused by poor quality bunkers can be costly, not only in terms of repair to ship's engines but also in terms of lost opportunity as well as lost time involved in dispute resolution and de-bunkering. CTI-Maritec is constantly evaluating the solutions that we offer to our clients. With our advanced analysis techniques, robust database of deleterious compounds and a team of expert technical advisors, we would be able to assist any client in identifying, managing, and mitigating risk of deleterious material in the bunker fuel.

Accredited GC/MS Test Package and Associated Detections

No.	Accredited GC/MS Techniques	Chemical Contaminants / Chemical Constituents Detection
1	Basic Chemical Species by ASTM D7845 GC/MS Analysis	10 Basic Chemical Species: Dichloromethane;1,2-Dichloroethane; Tetrachloroethylene; Phenol; Butanol; Alpha-pinene; Styrene; Indene; Dicyclopentadiene; Dihydro-dicyclopentadiene
2	ASTM D7845 GC/MS Analysis	29 compounds as stipulated in ASTM D7845 with extra fatty acids methyl esters (FAMEs), 4-cumylphenol, phenolic compounds, chlorinated organic compounds) and others. Chlorinated organic compounds include the followings: a) Dichloromethane; b) 1,2-Dichloroethane; c) Tetrachloroethylene; d) 1,1-Dichloroethane; e) Trichloromethane/ Chloroform; f) Trichloroethylene; g) Chlorobenzene; h) 1,1,2,2-Tetrachloroethane; i) 1,1,2-Trichloroethane; j) Tetrachloromethane/ Carbon tetrachloride
3	GC/MS Analysis by Solid Phase Extraction (SPE)	Polar and high boiling point chemical species: Fatty acids, rosin acids, monoglycerides, Estonian shale oil (alkyl 1,3-benzendiols), bisphenol F, bisphenol A; bisphenol tars & others. Fatty acids include the followings: Caprylic acid; Capric acid; Lauric acid; Myristic acid; Palmitic acid; Linoleic acid; Oleic acid, Stearic acid and others. Monoglycerides include the followings: Monocaprylin, Monocaprin, Monolaurin, Monomyristin, Monopalmitin, Monoolein, Monostearin and others.

A basic chemical species screening test can be done by using the ASTM D7845 method. This low cost and time saving option is designed to screen for a specific group of 10

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chemical species. This test can be incorporated as a routine, complementing to a standard table 1 and table 2 test package meant for bunker delivery samples. When required, the full range of testing covering 29 compounds, as well as FAMEs, 4-cumylphenol, phenolic compounds, chlorinated organic compounds and other low and mid-range boiling chemical species can be undertaken to ascertain the risk to vessel machinery and arrive at suitable mitigation actions.

For a routine pre-emptive as well as investigation testing, both GC/MS by ASTM D7845 & GC/MS by SPE can be conducted concurrently to cover a comprehensive range of chemical species.

In an unfortunate event when the fuel fails the specifications and/or to detection of deleterious materials, it would be prudent for operators to put the supplier/charterer on notice based on Clause 5 general requirements. If use to the fuel is unavoidable and the crew experience treatment or combustion difficulty, or when engine damage may occur, it is important to ensure all events are well documented, including dates and times of first occurrences, when the fuels were first used, duration of usage and the tanks which the fuel has been stored. Any damaged or affected components such as filters, separators or fuel pumps must preserved and retained onboard for further inspections. Photographic or video evidence should also be taken for records. As the burden of proof is on the vessel to establish links between the bunker quality and the damage sustained onboard, the quality of the evidence and the decisions taken when a fuel related problem arises is crucial to a party's success in prosecuting or defending a claim at a later stage.

Moving Forward

With the implementation of IMO GHG policy in the coming years, biofuels are expected to be a widely adopted drop in transition fuel to meet the carbon emission requirements. The extent of contamination from deleterious materials derived as a by-products or impurities from the production of biofuels have yet to be seen, but such related contaminants may eventually find their way into bunker supply chain.

The variety of chemical species that will be detected in marine fuels is expected to change as components used in bunker is likely to be more diverse. This would also result in extra pressure on any supplier 's product quality control system. It is therefore crucial for bunker buyer and operators to have their own comprehensive testing regime in place, to safeguard their interest. GCMS analysis as a complementary to the standard table 1 and 2 test, would be essential moving forward.

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About Maritec

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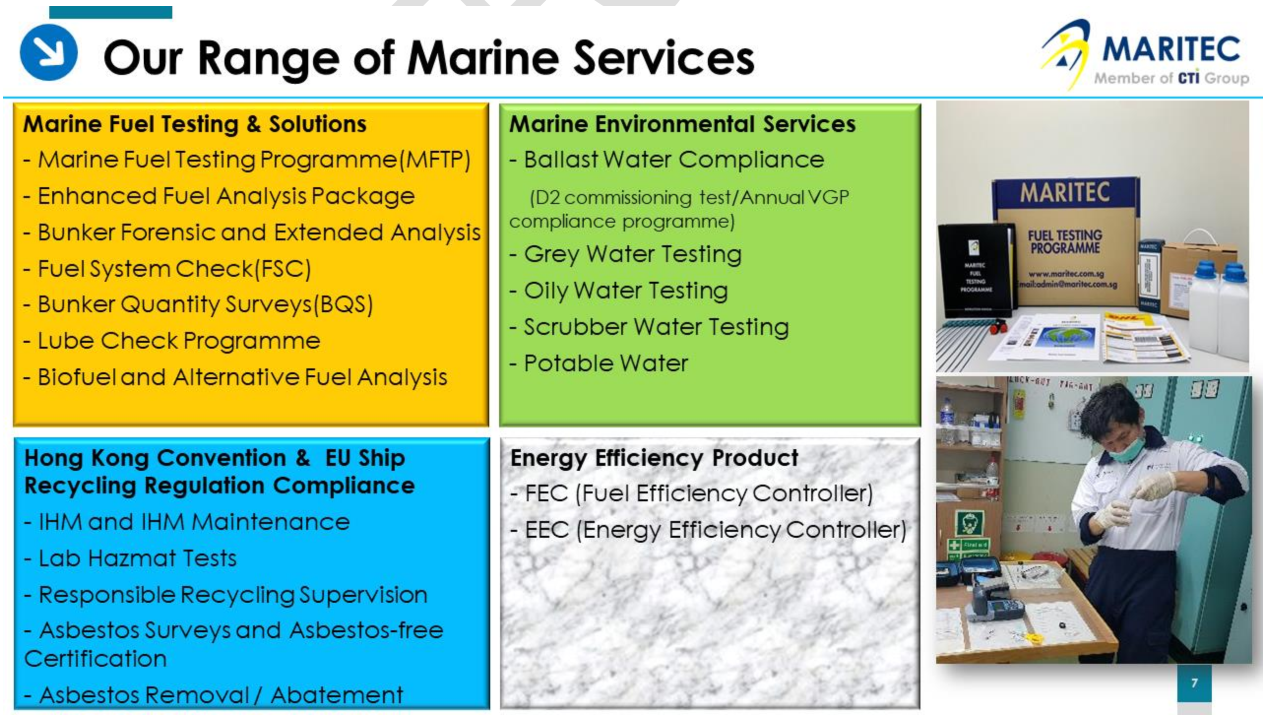
Maritec was incorporated in 1999 as a marine fuel laboratory in Singapore providing analysis results and technical advice to a portfolio of international shipping companies.

In June 2020, Maritec was acquired by Centre Testing International Group (CTI Group). Within a few months, the Marine Services Division of CTI Group has been fully integrated with Maritec. As the result of the acquisition and integration, Maritec is the only organization who is able to provide comprehensive inspection, testing, certification and consultancy services for Marine fuel quality & quantity, water quality and prevention of hazardous material in ships since then.

Leverage on the resources and strength of CTI Group, Maritec's operation team consists of hundreds of professionals in the fields of Marine Engineer, Petroleum Engineer, Environment Specialist, Mechanical Engineer, Electronic Engineer, Chemical Engineer, Legal Specialist and Information Technology Specialist to deliver first-class services to the marine customers.



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