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Member of CTi Group

WHITEPAPER

April 2024

With the introduction of the Maritime and Port Authority of Singapore's (MPA's) newly issued Port Marine Circular No 3 of 2024 for enhanced testing parameters (mandatory from 1 June 2024) for marine fuel oil batches (in addition to the existing quality assurance measures), CTI-Maritec shares insights and recommendations on the testing of COCs, TAN & SAN for bunker supply in Singapore and Polymers testing in the case of problem cases.

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1. Introduction

In the year 2022, in what can be described as one of the most significant fuel supply scandals in recent history, approximately 200 vessels were supplied with contaminated bunker fuel in the Port of Singapore. Arising from this bunker contamination incident in Singapore, an Industry Expert Group (IEG) co-chaired by the Maritime and Port Authority of Singapore (MPA) and Singapore Shipping Association (SSA) conducted thorough investigations, which revealed that the affected fuel was a blended product of High Sulphur Fuel Oil (HSFO) that contained high concentration levels of Chlorinated Organic Compounds (COC), mainly constituting 1,2-Dichloroethane, Tetrachloroethylene and other chlorinated organic compounds.

Ships that received this HSFO reported various ruinous damage, such as failure of main engines, auxiliary engines, fuel pumps, plunger barrel and injection equipment.

To help mitigate future incidents, on 8 February 2024 the MPA issued a Port Marine Circular No 3 of 2024 regarding the implementation of enhanced testing parameters for marine fuel batches intended to be delivered as bunkers in the Port of Singapore in addition to the existing quality assurance measures.

In accordance with the MPA's Port Marine Circular No 3 of 2024, from 1 June 2024, bunker suppliers in the Port of Singapore must ensure that:

- Residual & bio-residual bunker fuel do not contain Chlorinated Organic Compounds (COC) above 50mg/kg and are free from inorganic acids.
- COC must be tested using the EN 14077 accredited test method and shall be reported in the "Certificate of Quality" (COQ) provided to receiving vessels.
- Inorganic acids must use the ASTM D664 accredited test method as prescribed in ISO 8217 and the Strong Acid Number (SAN) (in addition to the Total Acid Number (TAN) shall be reported in the COQ (i.e. SAN = 0) provided to receiving vessels. For distillate / bio-distillate bunker marine fuel batches, SAN must be tested as per ASTM D664 test method and reported in the COQ.
- Residual marine fuels are free from polystyrene, polypropylene & polymethacrylate. These can be tested by filtration, microscopic examination, & Fourier-Transform Infrared spectroscopy analysis.

In view of the above, CTI-Maritec shares the following insights and recommendations related to the testing of COCs, TAN and SAN for all bunker supply in Singapore, and our recommendations for testing Polymers for reported problem cases.

2. Chlorinated Organic Compounds (COCs)

2.1 Effects of COCs in Marine Fuels & Regulatory Requirements

Organic Chlorides (COCs) are not known to be naturally present in crude oils and are usually present as a result of cleaning operations at production sites, pipelines, or tanks. They are insoluble in water but miscible with organic solvents. They dissolve fats, oil, waxes, rubber and many resins. COCs are used as solvents and as degreasing agents in dry-cleaning of fabricated metal parts, semiconductor manufacturing, insulating fluids and

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cooling gases in electrical transformers and as solvents with various applications, as extractants in pharmaceuticals, and as pesticide intermediates.

Due to COCs chemical properties and characteristics as a good solvent, the COCs present in bunker fuels can effortlessly pick up sediments and dirt from the fuel tanks/systems, which later get deposited/collected in the filters, thus resulting in severe filter clogging and separator sludging (the accumulation of impurities, sediment, or solid particles within centrifugal purifiers or separators).

Furthermore, COCs usually react adversely under the conditions faced during engine use. Some organic chlorides possess the characteristic to harden metallic surfaces making them prone to erosion, possibly due to lower boiling points of these volatile organic compounds, they could vaporize off within a fuel service system and remove the lubrication on metallic surfaces, causing scuffing and cavitation, leading to reduced engine performance and, in the worst case, total loss of power. Likewise, the high temperatures and pressures present during the engine functions combined with the shear forces applied in the engine fuel of the fuel system components result in rapid corrosive damage.

In this light, the International Council on Combustion Engines (CIMAC) working group assessed the situation around the organic chloride contamination cases in Singapore recommended that the de-minimis levels of COCs concentration do not exceed 50 mg/kg of marine fuels.

Additionally, ISO8217:2023, (currently in draft stage) clearly states in clause 6.17 that, “A fuel shall be considered to be free from organic chlorides (chlorinated hydrocarbons) when the total organic halogen content as chlorine is not exceeding 50 ppm when tested in accordance with EN 14077”.

2.2 CTI-Maritec Insights & Recommendations on Testing Approach

In dispute cases, both the CIMAC and ISO 2024 recommends using the EN 14077 test method to quantify total organic chlorides in marine fuel. However, it has been agreed that the presence of organic chlorides (COCs) can also be efficiently evaluated by other techniques such as Gas Chromatography Mass Spectrometry (GCMS) with required test precision data.

As a more accessible and generalised provision, CTI-Maritec has adopted a modified GCMS technique by ASTM D7845 testing method for a quick screening and detection of COCs in marine fuel. The modified ASTM D7845 testing method is accredited by SAC SINGLASS and lists nine (9) COCs (Refer to Table 1) in a basic GCMS package list.

In consideration of the above, one must note, as per the EN 14077 testing method, the total organic chlorides (COCs) can only be quantified. However, CTI-Maritec’s modified ASTM D7845 test method is capable of quantifying individual COC along with other class of organic compounds. Therefore, as a testing method EN14077 should be considered for dispute cases once organic chloride is detected by other techniques (such as GCMS) and is perhaps not ideal or a practical approach for frequent, ad hoc, or quick turnaround requirements.

CTI-Maritec strongly recommends GCMS testing for all bunker fuels should be adopted as a regular practice in the pursuit of enhanced risk management.

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Furthermore, individual COCs can also be quantified using the modified ASTM D7845 method. It is stipulated that the presence of COCs contravenes the stipulations of the Revised MARPOL Annex VI Regulation 18.3 and International Marine Fuel Standard ISO 8217 Clause 5. With this capability, data from this method can also be assessed to determine if fuel is off spec (if found to be not meeting the general requirements), which can also be used as supportive data for dispute resolution.

No.	Volatile Organic Compounds	CAS No.	Concentration (ppm)	Compound Group
1	Dichloromethane	75-09-2	xx	Chlorinated Organic Compound
2	1,1-Dichloroethane	75-34-3	xx	
3	Trichloromethane / Chloroform	67-66-3	xx	
4	1,2-Dichloroethane	107-06-2	xx	
5	Tetrachloromethane/ Carbon tetrachloride	56-23-5	xx	
6	Trichloroethylene	79-01-6	xx	
7	Tetrachloroethylene	127-18-4	xx	
8	Chlorobenzene	108-90-7	xx	
9	1,1,2,2-Tetrachloroethane	79-34-5	xx	
10	Phenol	108-95-2	xx	Phenolic Compound
11	Butanol	71-36-3	xx	Alcohol
12	Styrene	100-42-5	xx	Hydrocarbon Compound
13	Dicyclopentadiene	77-73-6	xx	
14	Dihydro-dicyclopentadiene	4488-57-7	xx	
15	Indene	95-13-6	xx	
16	Alpha-pinene	80-56-8	xx	

Table 1: Representative list of compounds (including 9 COCs) tested for in a basic GCMS package.

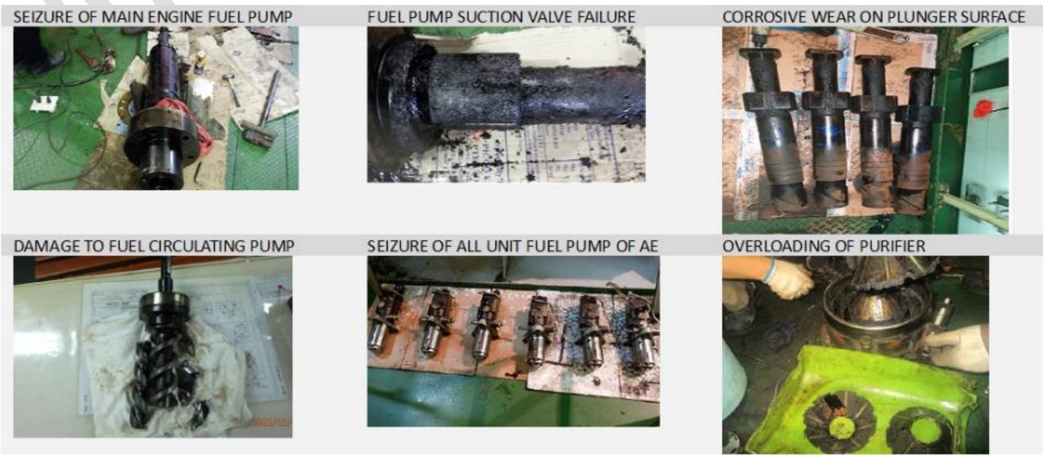
2.3 CTI-Maritec Case Study A: COCs Contamination

Challenge:

During the course of 2022, the following problems were reported from several vessels to CTI-Maritec:

- Initial purifier sludging & filter clogging
- Fuel pump damages due to wear & tear
- Leaking of ICU due to wear & tear

Additionally, below pictures were shared by vessels affected:



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Testing:

CTI-Maritec proceeded to conduct a GCMS study by modified ASTM D7845 method of reported cases, which all pointed to a correlation between elevated levels of COCs in marine fuels.

Findings:

The below Table 2 is the summary list of compounds detected in fuel samples sent-in by vessels, who reported damages.

No.	Sample ID	Dichloromethane (ppm), CAS No. : 75-09-2	1,2-Dichloroethane (ppm), CAS No. : 107-06-2	Tetrachloroethylene (ppm), CAS No.: 127-18-4	1,1-dichloroethane* (ppm) CAS No.: 75-34-3	Trichloromethane (ppm) CAS No.: 67-66-3	Chlorobenzene (ppm) CAS No.: 108-90-7
1	ML2208326	<10	2555	110	14	46	-
2	ML2208655	<10	1015	53	-	12	-
3	ML2205473	<10	6855	299	84	271	152
4	ML2206509	<10	3524	189	53	132	264
5	ML2205881	<10	3512	204	30	130	130
6	ML2208651	<10	4351	161	18	62	50
7	ML2208654	<10	2044	94	-	31	-
8	ML2208652	<10	1180	60	-	16	-
9	ML2208396	<10	4397	210	25	91	50
10	ML2208395	<10	4626	185	23	75	57
11	ML2208398	<10	7429	319	47	168	88
12	ML2208397	<10	2481	107	13	43	33
13	ML2208222	<10	3668	219	28	71	53
14	ML2208146	<10	5927	425	51	136	84
15	ML2206794	<10	3775	215	21	81	57
16	ML2206076	<10	3605	164	24	91	73
17	ML2206370	<10	3320	166	27	127	97
18	ML2204451	<10	6778	341	45	163	97
19	ML2205082	<10	6777	362	65	230	133
20	ML2209076	<10	1123	81	-	36	52
21	ML2209077	<10	1134	74	-	35	55
22	ML2209752	<10	2677	158	20	78	63
23	ML2210073	<10	5811	316	45	153	96
24	ML2210093	<10	5216	332	31	123	86
25	ML2210232	<10	5949	330	64	217	136

Table 2: List of compounds detected in samples sent-in by vessels, who reported damages.

The above data clearly indicates highly elevated levels of COCs, particularly in 1, 2-Dichloroethane levels (highlighted in yellow).

3. Strong Acids

3.1 Effects of Strong Acids in Marine Fuels & Regulatory Requirements

Inorganic acids are Strong Acids such as Hydrochloric, Hydrofluoric, Nitric and Sulphuric Acids. There are multiple sources/causes from where strong acids may find their way into bunker fuels, such as through hydrolysis of COCs, chemical reactions of compounds with oxygen and the sulphur content in the fuel or during the combustion process.

The presence of Strong Acids triggers corrosion in the engine parts when in contact, which can result in severe damage to fuel pumps, nozzles and injectors, as well as cause corrosion in the engines.

Strong Acid can be detected through testing for Strong Acid Number (SAN). SAN, which represents the presence of Strong Acids is covered in ISO 8217:2005, ISO 8217:2012 and ISO 8217:2017 para 5.1. which states that the "fuels shall be free from Inorganic acids...".

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3.2 CTI-Maritec Insights & Recommendations on Testing Approach

The presence of Strong Acid also lowers pH, which represents the highest potentiometric hydrogen ion concentration. The pH scale is logarithmic. Water has a pH of 7. A pH of 4 is ten times more acidic than a pH of 5 and 100 times more acidic than a pH of 6.

SAN can be detected by ASTM D664 test method, which should not be greater than zero. CTI-Maritec recommends testing SAN along with Total Acid Number (TAN) via ASTM D664 method for all bunker fuels, as an additional layer of protection towards proper maintenance of a marine vessel.

Pre-emptive testing of fuels for TAN by ASTM D664 can give indications as to the likely presence of acidic compounds. TAN can reflect naturally occurring naphthenic acids in the fuel (from the crude source) and also reflect contamination with acidic compounds, if present in the fuel. A high acid number in fuel due to naphthenic acids are common in certain parts of the world and confirmation that a fuel was manufactured from naphthenic crudes can be established by the Fourier-Transform Infrared (FT-IR) method on Solid Phase Extraction offered by CTI-Maritec.

Fuels contaminated with extraneous acidic compounds however have been linked to many operational problems in the past. ISO 8217 recognises that the presence of acids (even if within the specification limits) can cause operational problems if the acids present in fuels are not naturally occurring naphthenic acids. Further tests by Modified GCMS by ASTM D7845 and GCMS on Solid Phase Extraction can help to identify such acidic components.

Past experience has shown some of these components have been linked with severe operational problems, particularly around filters, overloading of purifiers, fuel injection pumps and fuel injectors. Such contaminants even at low levels may contravene the stipulations of Revised MARPOL Annex VI regulation 18.3 and International Marine Fuel Standard ISO 8217, Clause 5.

Testing and monitoring the TAN, can provide significant 'predictive power'. Knowing and monitoring your TAN serves as an early warning system for machinery health.

Elevated TAN levels may accelerate oil degradation and lead to equipment failure. Regular monitoring allows proactive maintenance to prevent breakdowns and extend machinery lifespan.

Therefore, CTI-Maritec recommends testing the SAN & TAN of all marine fuels as a robust 'early warning indicator' for the presence of contaminants. The test results can also be a guidance tool for clients to make informed decisions for further forensic analysis to determine presence of deleterious materials & chemical contaminants, if any.

3.3 CTI-Maritec Case Study B: TAN Levels

Challenge:

Vessel X bunkered distillate fuel and reported choking of fuel filters after using the fuel. Additionally, the below picture of the filter was shared by Vessel X.

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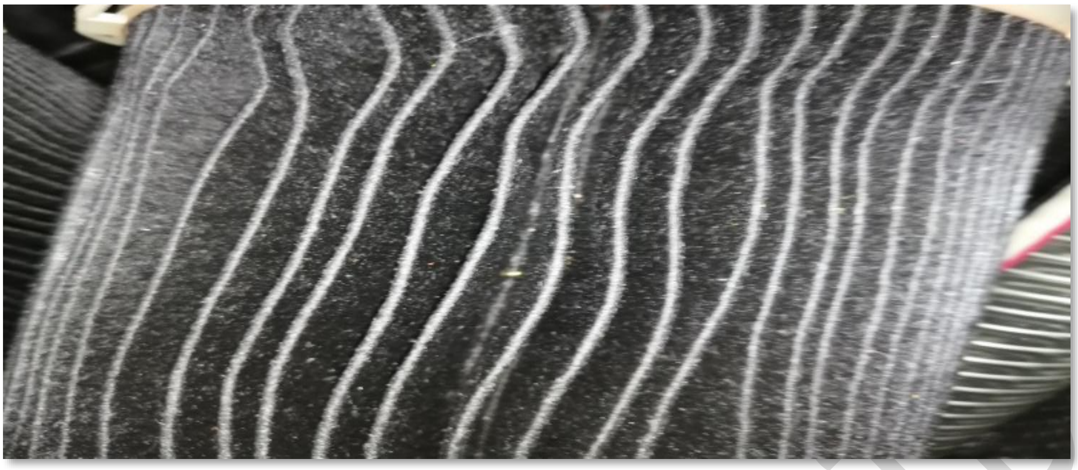

Testing & Findings:

Regular ISO 8217 full testing did not indicate any issues related to the fuel. Therefore, CTI-Maritec carried out a thorough investigation using our in-house testing methods and below were the Key Findings concluded as the root cause of the reported problem.

- Total Acid Number (TAN): 0.60 mg KOH/g.
- Strong Acid Number (SAN): NIL
- pH: 6.2.
- Total organic Fatty acids by GCMS SPE 983 PPM ranging from C14 to C18 Acids.

While unable to fully confirm, one can assume the source of these elevated levels of acids could be from waste biodiesel, TOFA (Tall Oil Fatty Acids), Seed oil Fatty Acids, etc.

4. Polymers

4.1 Effects of Polymers in Marine Fuels & Regulatory Requirements

Polypropylene (PP), Polystyrene (PS), Polyethylene (PE), Polyethylene Terephthalate (PET), or Polyvinylchloride (PVC) and Polymethacrylate (PMMA) are polymeric compounds, which are mainly thermoplastics and plastic waste. The presence of these compounds in marine fuel can cause several machinery issues like fuel pump damage, issues with fuel injectors, filter chocking, etc. The presence of these compounds contravenes Clause 5 of the International Marine Fuel Standard ISO 8217.

4.2 CTI-Maritec Insights & Recommendations on Testing Approach (recommended in cases of reported problems)

CTI-Maritec has developed and recommends the testing protocol for polymers in the case of problem cases by Filtration, microscopic examination, & Fourier-Transform Infrared (FT-IR) Spectroscopy analysis. This in-house method was accredited by SAC-SINGLASS.

FT-IR Spectroscopy is a powerful analytical technique used to investigate the chemical composition of fuel oils. FT-IR Spectroscopy measures the interaction of infrared light with a fuel sample and when infrared light passes through a sample, certain frequencies are absorbed by the sample’s molecules.

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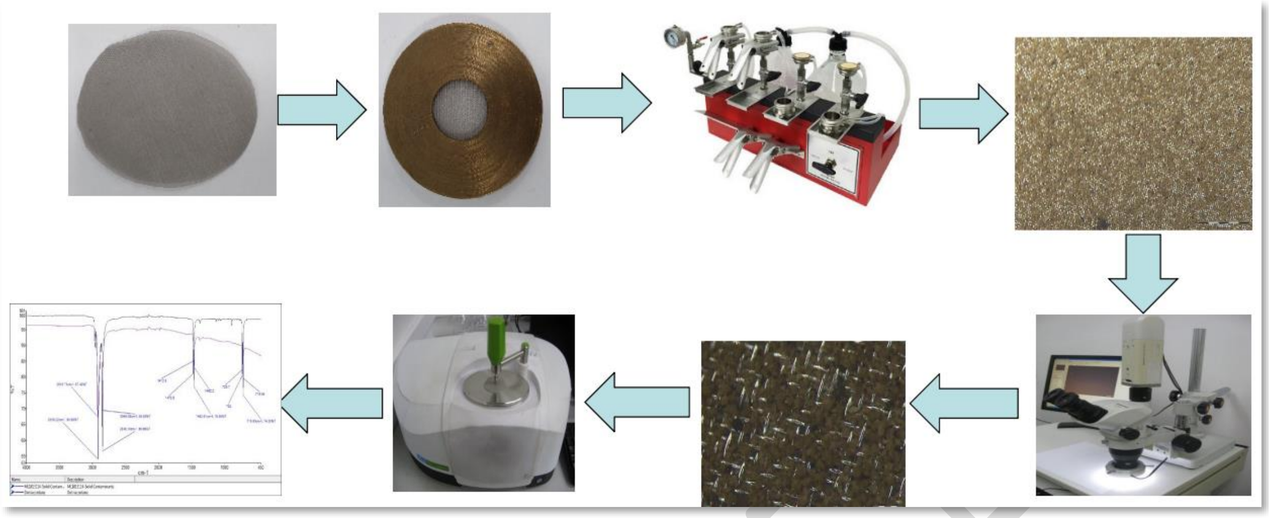
The resulting infrared spectrum provides information about the functional groups present in the material, allowing for any polymer compounds to be clearly identified.



4.3 CTI-Maritec Case Histories A – D of identifying Polymers using In-house FT-IR Spectroscopy Method

Case A: Polyester

Reported Challenges:

Vessel A reported a machinery problem and the marine fuel oil failed specs on KV 50. Furthermore, Vessel A reported that a foreign matter, which looked like sponge, was observed in the fuel (as can be seen from images shared by Vessel A below).

Testing:

CTI-Maritec conducted Overlay FT-IR Spectroscopy in-house testing method upon isolation and identification on the fuel sample to investigate and identify the presence of the foreign matter.

Findings:

Polyester/sponge materials were isolated and clearly identified. Images below show the Overlay FT-IR Spectra of the isolated sponge materials using the CTI-Maritec in-house method.

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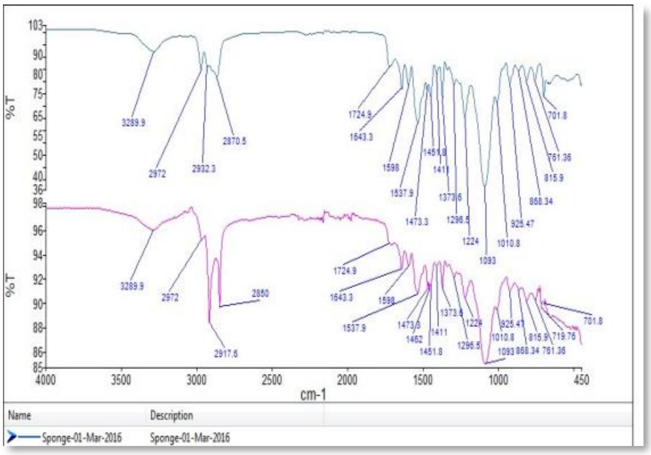
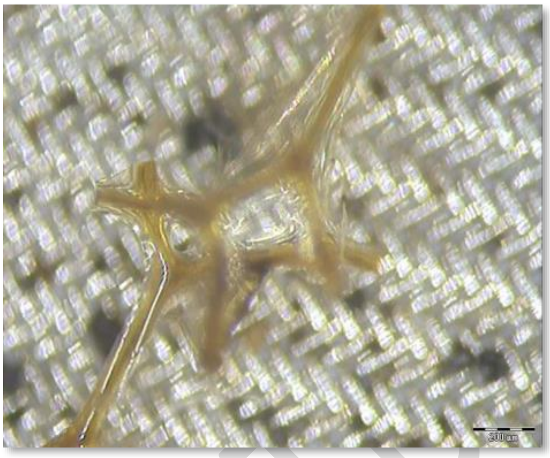
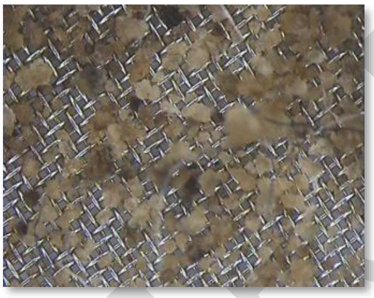


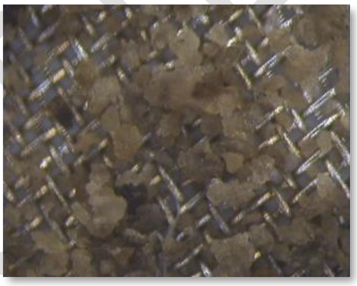


Case B: Polyethylene

Reported Challenge:

Vessel B reported machinery problems and filter clogging as seen in the images shared by Vessel B below.



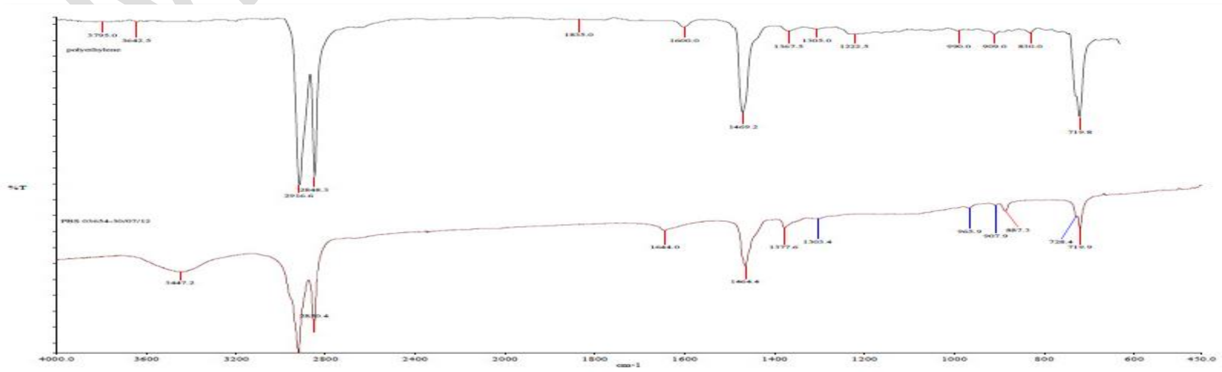


Testing:

CTI-Maritec conducted Overlay FT-IR Spectroscopy in-house testing method on the sample to investigate and identify the foreign material causing the clogging and machinery issues.

Findings:

Polyethylene was isolated and clearly identified. The image below shows the Overlay FT-IR Spectra of solids collected on sample & reference polyethylene using the CTI-Maritec in-house method.



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Case C: Polypropylene

Reported Challenges:

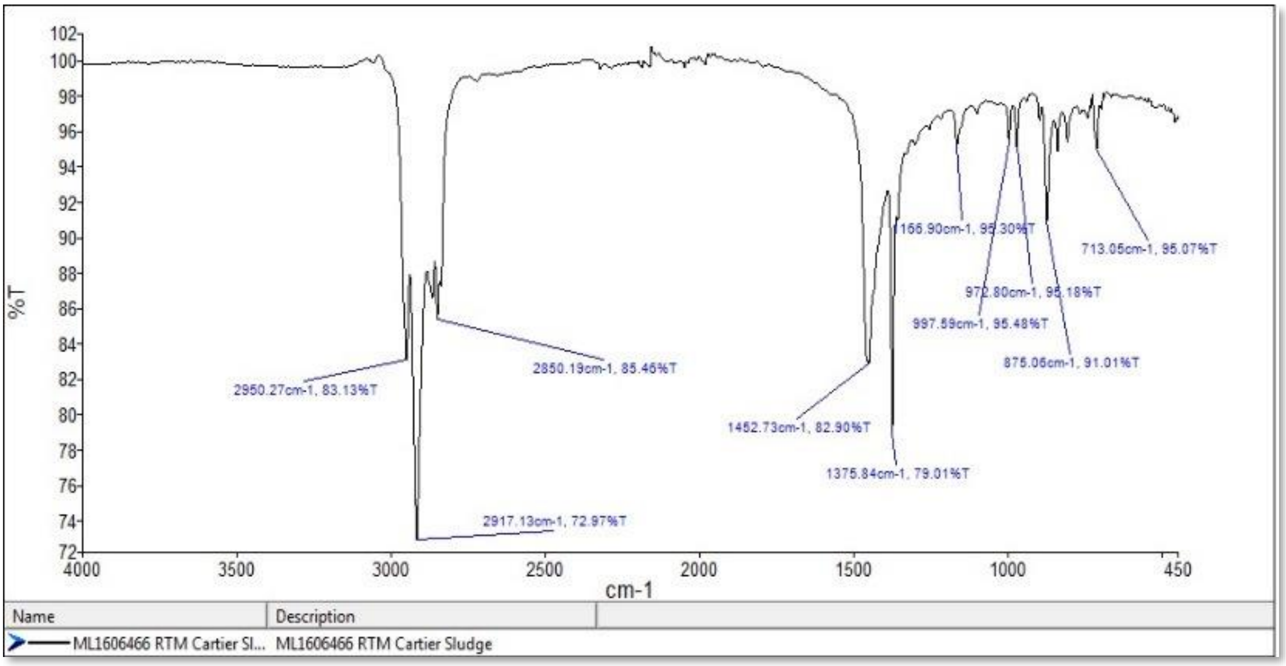
Vessel C reported machinery problems and identified sludge materials at the vessel's manifold sampling point after the bunkering process. The sludge sample consisted of plastic-like materials immersed in the fuel oil (as seen in the images shared by Vessel C below).

Testing:

CTI-Maritec conducted Overlay FT-IR Spectroscopy in-house testing method on the sample to investigate and identify the foreign materials.

Findings:

Polypropylene was isolated and clearly identified. The images below show the Overlay FT-IR Spectra of solids collected on sample.



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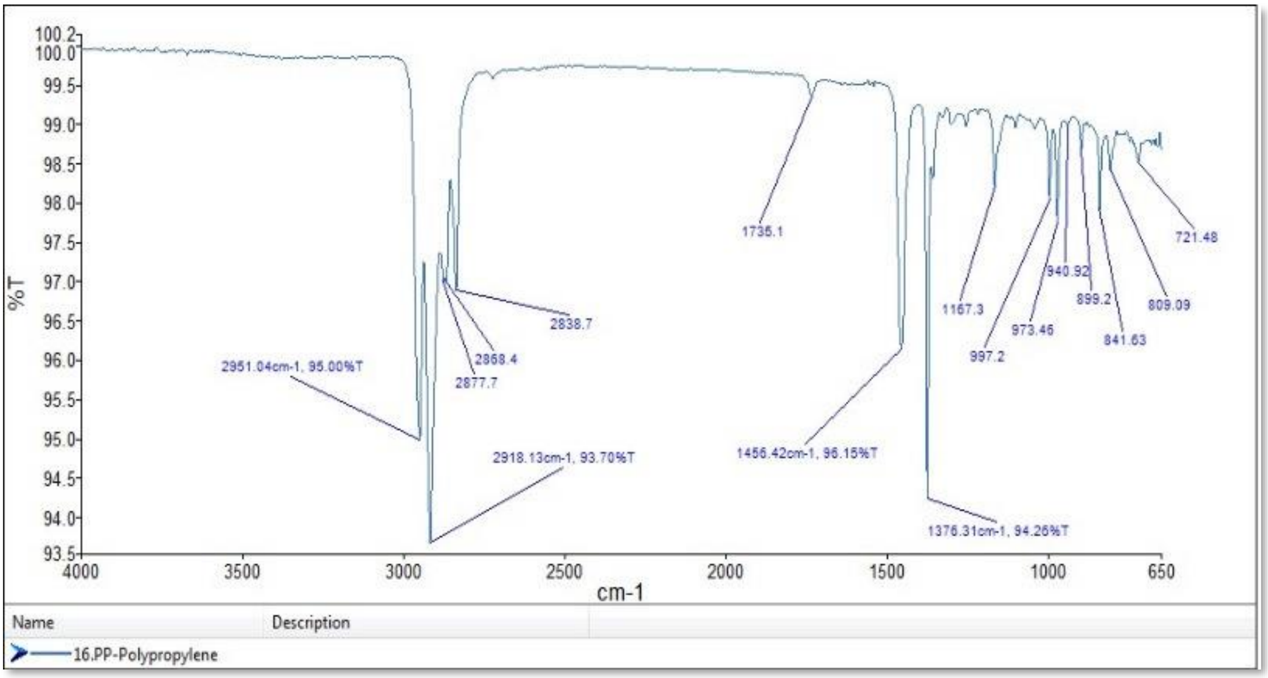
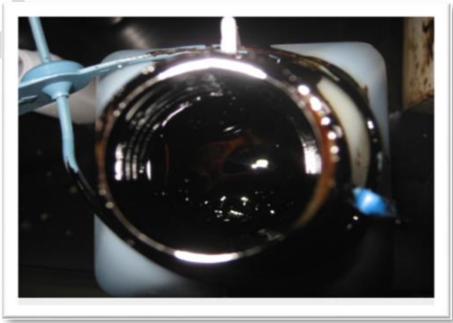


Case D: Polystyrene

Reported Challenge:

Vessel reported machinery problem and solid substances were observed in the vessel's fuel oil as can be seen in the pictures shared by Vessel D below.

Testing:

CTI-Maritec conducted Overlay FT-IR Spectroscopy in-house testing method on the sample to investigate and identify the foreign materials.

Findings:

Polystyrene was isolated and clearly identified. The images below show the Overlay FT-IR Spectra of solids collected on sample.

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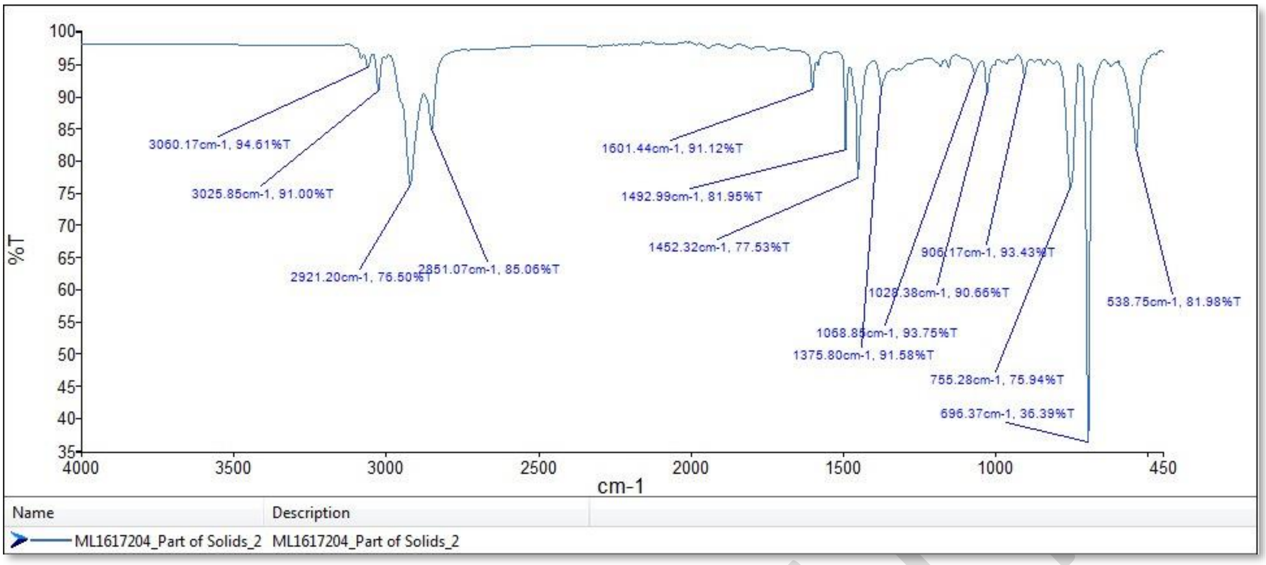

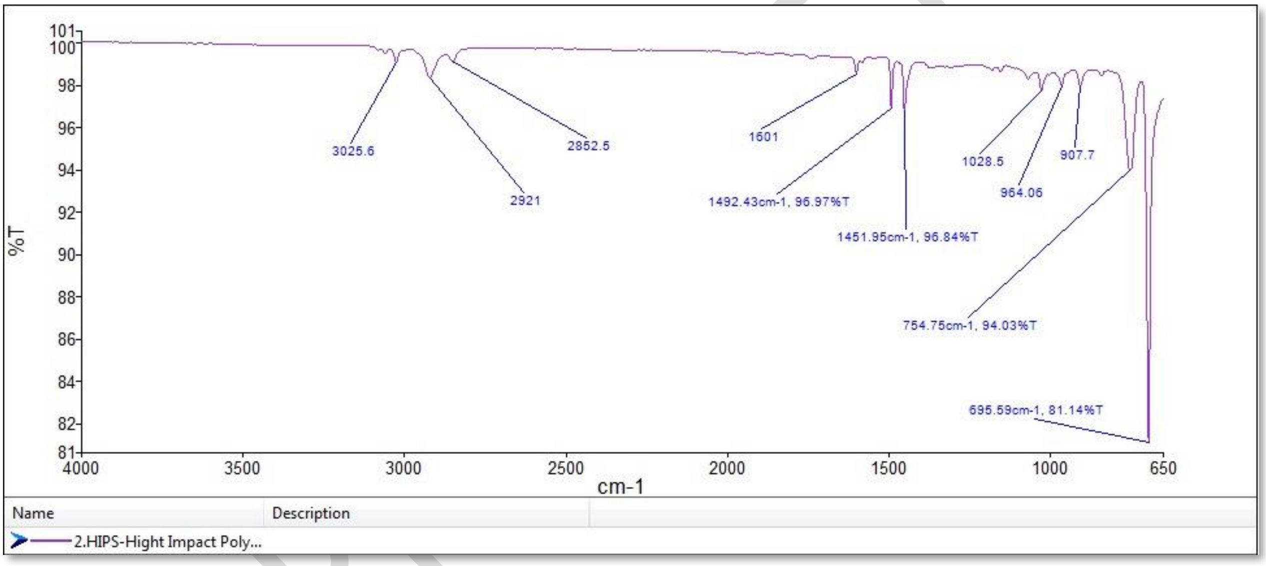

5. CTI-Maritec Extended Analysis Testing

As published in CTI-Maritec website, CTI-Maritec provides best-in-class Extended Analysis as supplementary packages to our Marine Fuel Oil Testing Programme (MFPT).

The ranges of analytical techniques include:

- GCMS by headspace, ASTM D7845 by Direct Liquid Injection & Solid Phase Extraction (SPE)
- Quantification of Total Chlorinated Organic Compounds (COCs) by EN14077 test method
- Fuel Ignition and Combustion Analyzer (FCA)
- Fuel Stability by P-value via SMS 1600
- Solid Contaminants by FT-IR
- Determination of Cat Fine Size Distribution
- Biofuel Test Package
- FOMP (Fuel Operation Management Package)

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6. Conclusion

The issue of chemical contamination has plagued the bunker industry for years, and the risk of receiving contaminated bunker fuels is likely to persist. This is mostly due to complex bunker Supply Chains, which consists of a network of different stakeholders including refineries, traders, and physical suppliers operating their own barges, with some performing their own fuel blending operation.

However, with the imminent enforcement of MPA's Port Marine Circular No 3 of 2024, the stage is set to raise the bar of the bunkering fuel quality in the Port of Singapore and further support stronger vessel health. In many ways this new requirement being enforced in Singapore could also pave the way for other international Port Authorities to implement the same requirements for their bunker suppliers. The knock-on effect could prove highly beneficial to the marine fuel oil bunkering world.

Furthermore, a key learning from the 2022 incidents is the critical need for bunkering buyers / ship owners / vessels to adopt, as a standard practice, an enhanced fuel testing approach as a pre-emptive measure in securing their vessel's health. Bunker buyers are also encouraged to consult the bunker suppliers in advance and have proper contractual agreement for the quality of fuel bunkered.

Fuel testing partners such as CTI-Maritec, possess accredited, customisable and highly experienced extended testing methods available 24x7, to help ensure our customer's interests are protected in the best means possible.

7. References

- Official MPA Port Marine Circular No 3 of 2024 with Annex B of FAQs accessible via *https://www.mpa.gov.sg/docs/mpalibraries/media-releases/pc24-03*
- CTI-Maritec Whitepaper published 15 January 2023. Viewable at *https://www.maritec.com.sg/resources/ck/files/GCMS_Whitepaper_from_Maritec_Pte_Ltd_Jan_2023.pdf*
- https://cdn.standards.iteh.ai/samples/80579/ac3799af8f0941ad985d86d76c9fed40/ISO-FDIS-8217.pdf

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