GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS) AND FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR) ANALYSIS TECHNIQUES FOR DETECTION OF CHEMICAL SPECIES IN BUNKER FUELS

Techniques

One year on following the IMO 2020 sulphur cap implementation, the global fleet have switched over from HFO to VLSFO predominantly. This issue reviews the use of VLSFO blends in relation to ISO 8217:2017 clause 5.1 where fuel composition was expanded to include hydrocarbons from petroleum and non-petroleum source. The general requirement on clause 5 deals with the preclusion of potential deleterious constituents which are non-hydrocarbon compounds finding its way into the bunker to reduce the sulphur content.

Examples on Non-Petroleum Cutter Stocks	Production Routes	Main Non-hydrocarbon Constituents
Estonian shale oil	Estonian shale oil is an oily liquid produced from retorting of Estonian oil shale.	Alkylresorcinols.
Biodiesel	To produce biodiesel, the vegetable oil or animal fat is subjected to a chemical reaction termed transesterification.	Fatty acid methyl esters (FAMEs), for some low grade biodiesels, fatty acids, monoglycerides, partial glycerides and glycerol are sometimes present as minor contaminants.
Coal (liquid fraction)	Coal is converted into liquid fractions by a process called coal liquefaction.	Phenol, phenolic compounds, styrene, naphthalenols and others.
By-products from chemical industry	Waste streams from 4-cumylphenol and bisphenols production.	Example: 4-Cumylphenol, bisphenol F compounds and bisphenol A Compound

The clause 5 of ISO 8217 does not permit the presence of added substance or chemical waste or any material at a concentration that causes the fuel to be unacceptable for use (i.e. material not at a concentration that is harmful to personnel, jeopardizes the safety of the ship, or adversely affects the performance of the machinery).

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Have there been recurring episode of Houston Bunker Saga? The speculation is an on-going concern apart from the pronounced quality issues of VLSFO reviewed thus far.

Appropriate test techniques and effect on engine component are essential knowledge in managing fuel quality issues which cannot be detected by the basic test package under ISO 8217 Table 1 and 2. Determination of chemical waste in bunker fuel can only be carried out using gas chromatography-mass spectrometry (GC-MS) and Fourier Transform Infrared Spectroscopy (FTIR) analysis techniques.

Maritec lab equips with GC-MS and FTIR facilities to detect and quantify chemical waste/chemical contaminant in bunker fuels. Maritec proprietary GC-MS and FTIR methods have attained accreditation under ISO 17025 accreditation scheme by professional certification body. The accredited GC-MS methods have undergone method validation to validate repeatability and accuracy and to establish the detection limit, quantification limit and linearity. The GC-MS quantification are achieved by calibration using both external and internal standards techniques.

No.	Accredited GC-MS and FTIR Techniques	Chemical Constituents / Chemical Contaminants Detection
1	Headspace GC-MS Analysis	Volatile organic compounds: Chlorinated compounds, butanol, indene, styrene, dicyclopentadiene, dihydro-dicyclopentadiene and others.
2	Direct Liquid Injection GC-MS Analysis	Medium range boiling point compounds: Fatty acid methyl esters (FAMEs) and others.
3	ASTM D7845 GC-MS Analysis	29 compounds as stipulated in ASTM D7845 with extra fatty acids methyl esters (FAMEs), 4-cumylphenol, phenolic compounds and others.
4	GC-MS & FTIR 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.

About Maritec

Maritec Pte Ltd, a member of CTI Group, is a leading marine fuel and lubricant testing, bunker quantity surveying and consultancy service provider, headquartered in Singapore.

Maritec has been integrated into the CTI Group's Marine Division. We will be able to provide existing (and new) clients with an augmented and wide-ranging set of inspection, testing, certification and consultancy services in the maritime industry. Combined the fuel and lubricant testing laboratory of CTI Group based in Tianjin, Shanghai, this new state-of-the-art facility will help deliver more efficient and effective fuel testing capabilities to our clients with operations in Chinese ports.

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Some cases detected from Dec-2019 to Dec-2020 by Maritec on the VLSFO

Appendix 1:

No	Chemical Contaminants	Non-petroleum Cutter Stock	Number of Cases	Range of Concentration, ppm	Vessel reported machinery problems	Photos of the Damaged Machinery	GC-MS Techniques
1	Alkylresorcinols (or alkyl 1,3-benzenediol derivatives, with a benzenediol distribution characteristic of Estonian-type shale oil)	Estonian-type shale oil	9	1565ppm to 14,078ppm of alkylresorcinols	Purifier and filter clogging		GC-MS by Solid Phase Extraction
2	Fatty acid methyl esters (FAMEs), fatty acids, monoglycerides and glycerol	Biodiesel	3	4998ppm to 12,450ppm of FAMEs; 535ppm to 2231ppm of fatty acids; 1796ppm to 7443ppm of monoglycerides; 45ppm to 198ppm of glycerol	Fuel pump damage		GC-MS by Solid Phase Extraction & ASTM D7845 GC-MS
3	Phenol, phenolic compounds and naphthalenols	Coal (Liquid Fraction)	2	644ppm to 2003ppm of phenol; 6100ppm to 8740ppm of phenolic compounds; 27ppm to 130ppm of naphthalenols	Purifier sludging		ASTM D7845 GC-MS
4	4-Cumylphenol and Bisphenol Compounds	By-product from chemical industries	2	2343ppm to 2940ppm of 4-Cumylphenol; 136ppm to 282ppm of Bisphenol F compounds; 316ppm to 1405ppm of phenol; 31ppm of Bisphenol A detected in one of the samples	Filter clogging and Fuel injection pumps damaged		GC-MS by Solid Phase Extraction & ASTM D7845 GC-MS