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Presence of Organic Chlorides in Bunker Fuel

Fuels - Conventional Fuels

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ABSTRACT

Presence of Organic Chlorides in bunker fuels have been known to cause serious problems to machinery even at low levels. Maritime and Port Authority of Singapore (MPA) reported that 200 ships have received the high sulfur fuel oils with high levels of organic chlorides between mid of February to early April of 2022. Out of the 200, about 80 ships reported machinery problems after use of these fuels.

These fuels were found to have the following types of organic chlorides; Tetrachloroethylene, 1,2-Dichloroethane, Chloroform, Carbon Tetrachloride, Trichlorethylene, 1,1,2- Trichloroethane and Chlorobenzene.

The organic chloride contamination crisis during this period was only noted in High Sulfur Fuels (HSFO). Most of the vessels have reported serious damages to Main Engine and Auxiliary Engine fuel pumps (Wear and Seizure), damage to filter candles, and higher levels of sludge generation. In some serious cases, the vessels had to be towed to the port due to extensive damages to ships' fuel systems.

Organic chlorides in the presence of high temperature tend to convert to Hydrogen Chloride (in the form of gas) which in turn converts to hydrochloric acid in the presence of water. This is the main reason for the corrosion related effects reported when using these contaminated fuels. Hydrochloric acid is a strong acid and can easily eat through the lubrication film between a fuel pump plunger and barrel, also the fuel needle valve and guide. This will result in extensive damages over a very short amount of time.

The focus of this paper is to determine the limit for the presence of organic chlorides in HSFO and VLSFOs in order to avoid machinery problems and failures. Additionally, by simulating the fuel pump condition in the laboratory, we will investigate whether organic chlorides that cause issues in heavy fuel oils would pose similar problems in Very low Sulfur Fuels (VLSFOs).

1 INTRODUCTION

An Organic chloride is an organic compound containing at least one covalently bonded atom of chlorine. Thus, organic chlorides encompass a wide variety of compounds with different structures and divergent chemical properties with a broad range of names and applications.

These organic molecules generally consist of a C-Cl bond, for example, chloroform (CH_3-Cl) or vinyl chloride (C_2H_3Cl).

Organic chlorides are generally not naturally occurring and are sourced externally to the petroleum industry. They are extensively used in the oil field as wax dissolvers & degreasers. They are generally banned on environmental grounds. Organic chlorides are generally not present in crude oils and are usually derived from cleaning operations at production sites/pipelines or tanks or external to the petroleum industry as has been found in dry cleaning chemicals.

Some organic chlorides and their common uses include:

- Carbon tetrachloride (CCl_4): Chlorinated rubber manufacture, semiconductor manufacture, metal recovery, cleaning electrical contacts.
- Tetrachloroethylene ($Cl_2C=CCl_2$): Dry Cleaning, degreasing, textile, printing, soap, paint removal
- Dichlorethane ($C_2H_4Cl_2$): Banned chemical used in degreaser, paint removers
- Vinyl chloride (C_2H_3Cl): Monomer for PVC
- Chlorobenzene (C_6H_5Cl): Degreasers, refrigerants
- Chloroprene ($CH_2=CClCH=CH_2$): Monomer for polychloroprene used as wire and cable cover, gaskets, and automotive components
- Dichloromethane (CH_2Cl_2): Paint and varnish removers (being phased out)
- Trichloroethylene ($CHCl=CCl_2$): Industrial cleaner, the solvent in paint and glue manufacture [1-2].

Due to their extensive corrosive damaging potential to various metallic components, petroleum refineries are very particular about the presence of organic chlorides. Refineries reject crude oils with more than 1 ppm of organic chlorides. Some notable references to this are below;

Crude Oil having measurable organic chlorides SHALL NOT be introduced into the Capline System. Measurable is defined as not exceeding 1 (one) ppm in the whole crude and 5 (five) ppm in the 400ºF End Point naphtha cut [3].

Chevron pipeline company outlined a 1.3 ppm limit for the organic Chlorides that can be present in the crude oil after facing problems with the presence of organic chlorides [4].

According to GOST R51858, the organic chloride content in the naphtha fraction of crude oil, up to a temperature of 400 F (204 C), should not exceed 10 ppm [5].

Paragraph 5 and Annex on deleterious substances in ISO 8217 limit the presence of chemical contaminants in bunker fuels. When fuel is found to have chemical contaminants, it is a direct violation of the ISO 8217 standard.

5.2. The fuel shall be free from any material at a concentration that causes the fuel to be unacceptable for use in accordance with Clause 1 (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).

Based on the recent paper published by CIMAC Working Group 7, fuels with a total organic chlorine content below 50 mg/kg (EN 14077) can be considered as containing de-minimis levels of organic chlorides [6].

In this paper, we will review the sources of organic chlorides in marine fuels, their effects on marine engines and the environment, and the regulations established by the IMO to limit their presence in marine fuels. Additionally, we will examine current research on determining the limit for the presence of organic chlorides in HSFOs and VLSFOs in order to avoid machinery problems and failures.

2 MATTERIAL AND METHOD

For this study, a total of twenty-three High sulfur fuel oil samples were collected with different ranges of organic chlorides from zero to 6666 ppm. The density, Viscosity, and Sulfur content of these fuels were measured as per ASTM D4052, D445 and, D4294. Table 1 shows the basic characteristics of these fuels.

Table 1. Basic characteristics of High Sulfur Fuel oils with different ranges of organic chlorides

Sample ID	Density, Kg/m3	Viscosity (50C), cSt	Sulfur %
H1	984.8	357.6	3.4
H2	972.8	317.7	3.4
H3	988.8	342.2	3.4
H4	988.4	270.2	3.5
H5	990.0	345.2	3.5
H6	988.5	334.8	3.0
H7	989.8	360.5	3.0
H8	988.8	353.7	3.0
H9	989.5	368.8	3.1
H10	990.8	375.6	3.3
H11	997.2	503.2	3.0
H12	993.0	419.0	3.0
H13	989.4	378.4	3.4
H14	990.9	374.8	3.3
H15	990.8	344.8	2.9
H16	990.7	374.6	3.0
H17	991.0	346.5	3.2
H18	991.0	386.4	2.9
H19	990.6	366.4	2.9
H20	934.4	241.1	2.1
H21	946.3	210.0	2.8
H22	950.4	160.7	3.2
H23	942.3	190.1	3.0

In addition, ten VLSFOs were selected with different ranges of organic chlorides from 5 ppm to 300 ppm. Table 2 shows the basic characteristics of the VLSFOs.

Table 2. Basic characteristics of Very Low Sulfur Fuel oils with different ranges of organic chlorides (5 ppm to 300 ppm)

VLSFOs	Density, Kg/m^3	Viscosity, cSt	Sulfur, %
V1	909.5	42.37	0.48
V2	947.9	36.22	0.46
V3	953.3	39.39	0.47
V4	952.8	127.0	0.49
V5	907.7	33.81	0.44
V6	950.9	38.74	0.44
V7	954.3	40.09	0.47
V8	931.6	82.73	0.48
V9	890.5	33.74	0.39
V10	919.3	45.95	0.47

3 RESULTS AND DISCUSSION

3.1 Mechanism of Damage in the Presence of Organic Chlorides

Organic chlorides in the presence of high temperatures tend to convert to Hydrogen Chloride which in turn converts to hydrochloric acid in the presence of water. This is the main reason for the corrosion-related effects reported when using fuels contaminated with organic chlorides. Hydrochloric acid is a strong acid and can easily eat through the lubrication film between a fuel pump plunger and barrel, also the fuel needle valve and guide. As a result, serious damage can occur in a very short amount of time.

3.2 Presence of Organic Chlorides in High Sulfur Fuels

Out of the 55 cases reported to Viswa with high organic chlorides, 11 cases reported problems. In the rest of the cases, fuel users reacted very quickly as soon as the alerts were sent by the lab. The fuel users responded by:

- Segregating the fuel and not using the fuel
- Conducting thorough checks to check for the presence of these chemicals
- Debunkering the fuels once it was confirmed that the fuel was contaminated by organic chlorides.

Problems reported after the use of these HSFOs fell into the following categories:

- Main Engine and Auxiliary Engine fuel pump (Wear and Seizure) (Figure 1a)
- Damage to filter candles (Figure 1b)
- Higher levels of sludge generation

Figure 1. a. Fuel Pump Plunger and Barrel are stuck and unable to move, b. Damaged filter cartridge

Table 3 shows the details of the 11 reported problems to Viswa Lab. Table 4 shows the ISO 8217 and additional parameters for the 11 problem samples tested by Viswa Lab. Please find the explanation related to a few problem cases on the following pages.

Table 3. Details of the problem cases reported to Viswa due to the presence of organic chlorides (all the samples are RMG 380).

Case	Supply date	Problems reported
1	28-Feb-22	Vessel reported issues with fuel injection equipment.
2	18-Feb-22	Vessel has troubles with Main Engine (ME) and Auxiliary Engines (AE) after consuming the fuel oil.
3	17-Feb-22	Vessel reported issues with Aux Engine and Main Engine
4	22-Feb-22	Vessel has experiences machinery issues
5	23-Feb-22	The filter candles started to get damaged badly, M/E fuel pump worn out/damaged, A/E fuel pump seized
6	26-Feb-22	Vessel has reported issues with Aux Engine and Main Engine using the fuel
7	5-Mar-22	Vessel reported issues in fuel injection equipment.
8	19-Feb-22	Vessel has experiences machinery issues
9	22-Feb-22	Issues with Aux Engine and Main Engine
10	18-Mar-22	Vessel reported frequent clogging of filters and issues of ME and AE
11	23-Feb-22	Vessel reported sedimentation issues and frequent filter clogging issues. Vessel also reported total of 9 sets of fuel oil injectors got stuck and, in addition, a set of fuel oil heaters got clogged as well.

Table 4. ISO8217 parameters of 11 problem samples with high amounts of organic chlorides (Bunker date Feb – March 2022)

SERIAL	Unit	S1	S2	S3	S4	S5	S6	S7	S8	S9	S10	S11
DENSITY (15C)	Kg/m3	991.3	988.9	990.4	990.9	991	990.4	990.1	991.5	990.7	990	990.8
VISCOSITY (50C)	cSt	391.9	356.2	359.9	370	346.5	345.5	358.2	367.6	374.6	345.2	351.2
UPER POUR POINT	C	6	9	0	3	12	12	12	12	12	12	-
WATER	Vol%	0.24	0.35	0.5	0.5	0.5	0.6	0.5	0.5	0.5	0.45	0.4
MICRO CARBON RESIDUE	Mass%	17.2	15.5	15.5	16.0	15.4	15.6	14.7	16.3	15.6	14.1	-
SULFUR	Mass%	3.2	3.1	3.0	3.1	3.2	3.2	3.2	3.1	3.0	3.5	3.0
TOTAL SEDIMENT POTENTIAL	Mass%	0.05	0.05	0.05	0.07	0.08	0.08	0.08	0.07	0.05	0.04	-
ASH	Mass%	0.057	0.048	0.049	0.05	0.05	0.053	0.043	0.045	0.047	0.048	-
ALUMINUM		12	9	11	9	10	11	9	10	11	32	-
VANADIUM		184	160	159	161	156	169	137	155	149	98	-
SODIUM		34	26	29	28	33	32	27	27	25	42	-
SILICON		9	9	9	8	9	10	8	9	10	24	-
MAGNESIUM		3	3	3	3	3	3	2	3	3	3	-
CALCIUM		15	8	8	9	9	9	8	12	10	13	-

PHOSPHORUS	mg/Kg	<1	1	1	0	1	1	1	1	1	1	-
IRON		35	25	28	29	29	28	23	18	28	21	-
LEAD		<1	<1	<1	<1	<1	<1	<1	<1	<1	<1	-
NICKEL		30	27	32	36	35	32	26	15	34	25	-
ZINC		2	2	2	2	2	2	1	1	2	1	-
POTASSIUM		1	2	1	2	3	2	1	1	1	2	-
CALORIFIC VALUE	MJ/Kg	40.06	40.07	40	39.97	39.93	39.9	39.96	39.97	40	39.9	-
CCAI		851	850	851	852	852	852	851	852	851	851	-
ACID NUMBER	mg KOH/g	0.45	0.3	0.2	0.2	0.2	0.4	0.3	0.3	0.3	0.1	0.3
pH		5.1	5.6	5.1	5.2	5.1	5.3	5.1	5.2	4.9	7.1	5.1
RSN		7.9	13.0	12.8	12.7	12.0	12.8		11.7	13.8	11.4	12.3
Organic Chloride	mg/Kg	6024	6591	6846	6541	6666	7811	7040	5440	6418	607	6473

Details of a few cases that caused operational issues onboard:

Case 1. Issues with Auxiliary and main engine units fuel pumps

Date of Supply: February 26th, 2022

Fuel Grade: RMG 380

Report of problems from the vessel and attempts to fix: The vessel has experienced issues with the auxiliary engine and main engine fuel pump; the plunger and barrel got polished and there was an increase in clearances.

Findings from Quality Control Tests Conducted on the Fuel Oil Sample

- All parameters of the ISO 8217:2017 table 2 were found to be normal except the water content which was 0.6%.

- From GCMS Comprehensive analysis test Viswa has identified a total presence of organic chlorides at 7811 ppm.

- In addition, this fuel also had poor reserve stability (RSN at 12.8), a very high xylene equivalence number (55.5). This indicates the fuel has a poor stability reserve. This could cause a higher level of sludge generation, deposition, filtration issues, and sludging in the purifiers.

- While the total acid number is within the ISO8217 limit, pH shows that the sample is acidic.

Table 5. Additional test finding summary (Case 1)

Test parameters	Result	Comments
GCMS CRA	Organic chlorides 7811 ppm	High levels of organic chlorides can cause damage to marine machinery
RSN	12.8	When RSN is more than 10 it indicates the fuel has low reserve stability indicating the asphaltene will flocculate or already started flocculating.
pH	5.29	Acidic (Normal fuel pH is normal around 7.5)
TAN (mg KOH/g)	0.41	Normal
SAN (mg KOH/g	0	Strong acid is absent
Xylene equivalent	55.5	XE is high (Normal 30). When XE is more than 30 the fuel may have poor stability reserve.
Toluene Insoluble	0.5	Normal

Case 2. Fuel pumps are worn out, filter damaged, and issues with the Main engine.

Date of Supply: February 23-2022

Fuel Grade: RMG 380

Report of problems from the vessel and attempts to fix them: The Vessel bunkered 423MT of high sulfur fuel (RMG 380) on 23rd February 2022. Based on the report from Chief Engineer, the fuel was in use since the 26th of February and the machinery problem started after 6 days of use between the 2nd of March and of 5th March. The vessel had to return to Singapore to take on new bunkers. The following problems were reported:

- M/E fuel pump worn out/damaged

- A/E fuel pump seized
- Pitting marks (corrosion) were noted on the damaged plungers
- The filter candles started to get damaged

A few pictures of the affected machinery parts as received from the vessel are shown in Figures 4 & 5 & 6.

Figure 2. a. Damaged Filter cartridge, b. Damaged main engine fuel pump barrel, C. Damaged fuel pump plunger

Findings from quality control tests conducted on the fuel oil sample:

• ISO 8217:2017 table 2, all parameters were found to be normal.

• From the GCMS CRA test, we noted the presence of a significant level of organic chlorides. Total organic chlorides were found to be 6667 ppm.

• From additional test analysis, we have noted this fuel has poor reserve stability (RSN at 12), and a very high xylene equivalence number (55.5). This indicates the fuel has a poor stability reserve and contains high levels of sediment. This could cause a higher level of sludge generation, deposition, filtration issues, and sludge in the purifiers.

• While the total acid number is within the ISO8217 limit, pH shows that the sample is acidic. The standard test did not detect the presence of any strong acid and the total acid number is also normal. However, find the pH of the oil is acidic (5.5) as compared with that of a standard fuel oil around 7.5.

• The pH of the oil in the engine system could be much more acidic as the oil is at higher temperatures and pressure in a closed-loop fuel circulation system. Viswa heated the fuel to 70C and then measured the pH again and noted that it dropped from 5.5 to 4.9. Severe acidic corrosion could explain the issue of the filter cartridge material failing as well as wear and rust formation on the fuel plunger/barrel.

Table 6. Additional test finding summary (Case 2)

Test parameters	Result	Comments
GCMS CRA	Organic chlorides 6667 ppm	High levels of organic chlorides can cause damage to marine machinery
RSN	12	When RSN is more than 10 it indicates the fuel has low reserve stability indicating the asphaltene will flocculate or already started flocculating.
pH	5.5	Acidic (Normal fuel pH is normal around 7.5)
TAN (mg KOH/g)	0.25	Normal
SAN (mg KOH/g)	0	A strong acid is absent
Xylene equivalent	55.5	XE is high (Normal 30). When XE is more than 30 the fuel may have poor stability reserve.
Toluene Insoluble	1.1	Normal

Case 3. Main engine and Auxiliary engine filter clogging

Date of Supply: March-18-2022

Fuel Grade: RMG 380

Report of problems from the vessel and attempts to fix them: The Vessel bunkered 1198.19 MT of high Sulphur fuel (RMG 380) on 18 March 2022. The vessel had used this fuel for 2 days and reported frequent clogging of the ME and AE HSFO backflush filters.

Findings from Quality Control Tests Conducted on the Fuel Oil Sample

• ISO 8217:2017 table 2 parameters were found to be normal.

• From the GCMS CRA test we noted the presence of a significant level of organic chlorides. Total organic chlorides were found to be 607 ppm.

• From additional test analysis we have noted this fuel has poor reserve stability (RSN at 11.4), a very high xylene equivalence number (45.4). This indicates the fuel has a poor Stability reserve and contains a high level of sediment. This could cause a higher level of sludge generation, deposition, filtration issues, and sludge in the purifiers.

• While the total acid number is within the ISO8217 limit, pH shows that the sample is acidic. Severe acidic corrosion could explain the issue of the filter cartridge material failing as well as wear and rust formation on the fuel plunger/barrel.

Table 7. Additional test finding summary (Case 3)

Test parameters	Result	Comments
GCMS CRA	Organic chlorides 607 ppm	High levels of organic chlorides can cause damage to marine machinery
RSN	11.4	When RSN is more than 10 it indicates the fuel has low reserve stability indicating the asphaltene will flocculate or already started flocculating.
pH	5.1	Acidic (Normal fuel pH is normal around 7.5)
TAN(mg KOH/g)	0.11	Normal
SAN (mg KOH/g	0	Strong acid is absent
Xylene equivalent	45.5	XE is high (Normal 30). When XE is more than 30 the fuel may have poor stability reserve.
Toluene Insoluble	0.5	Normal

Figure 3. a. Fuel injector seizure, b. Fuel Pump Plunger and Barrel are sticky and unable to move, c. Damaged filter cartridge.

3.2.1 Aging study and simulating the fuel pump condition for HSFOs

In order to simulate the fuel pump condition, the HFOs were heated to the injection temperature from 2 days to 5 days. The injection temperature was calculated in a way to reach the viscosity of 15 cSt at the injection point. The acid number and pH of the samples were measured as per ASTM D664 for up to 5 days. As was explained in section 3.1 due to the conversion of organic chlorides into hydrochloric acid, the corrosion can cause extensive issues in short term. Carbon steel and low alloy steels are subject to excessive corrosion when exposed to any concentration of HCl acid solution at a pH below about 4.5 [7].

Based on the results shown in Figure 4, the pH of the samples with low organic chlorides content (less than 40 ppm) will stay greater than 4.5 even after 5 days of aging at injection temperature. Table 8 shows the list of organic chloride components that are present in samples 1 to 23. This includes samples H19 to H23 without organic chlorides. The pH of samples 19 to 23 is greater than 4.5 even after 5 days of aging at injection temperature. In addition, for samples H1 and H2 with low organic chloride content, the pH is greater or equal to 4.5 after 5 days of aging.

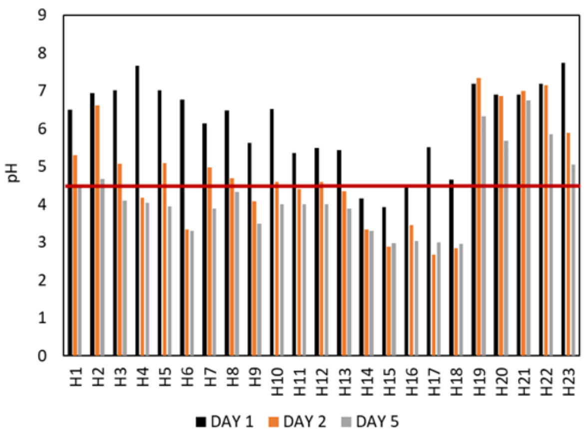

Figure 4. pH Values of HSFOs on Day 1 (Without aging), after 2 days and 5 days of aging of the samples at injection temperature

Table 8. The organic chloride content of twenty-three high-sulfur fuel oils

Sample ID	Chloroform	1,2-Dichloroethane	Carbon tetrachloride	Trichloroethylene	1,1,2-Trichloroethane	Tetrachloroethylene	Chlorobenzene	1,4-Dichlorobenzene	Total Organic Chlorides, ppm
H1	< 2	39	< 2	< 2	< 2	< 2	< 2	< 2	40
H2	< 2	12	< 2	< 2	< 2	< 2	< 2	< 2	12
H3	13	411	< 2	< 2	70	37	16	< 2	548
H4	11	233	< 2	< 2	94	27	10	< 2	375
H5	15	442	< 2	7	109	34	< 2	< 2	607
H6	36	873	5	< 2	142	53	29	< 2	1138
H7	28	839	< 2	6	197	88	24	< 2	1182
H8	29	874	< 2	6	212	87	22	< 2	1230

H9	74	1760	< 2	11	231	127	57	2	2262
H10	40	2259	< 2	8	256	197	49	4	2814
H11	79	2323	< 2	18	371	157	56	4	3008
H12	17	1620	< 2	5	392	232	36	< 2	2302
H13	51	2206	< 2	< 2	464	226	52	5	3002
H14	23	4003	15	6	539	287	109	4	4987
H15	72	4204	< 2	26	770	326	96	6	5501
H16	113	5068	3	18	886	219	104	7	6418
H17	92	5120	53	25	944	309	116	8	6666
H18	89	3839	4	21	826	481	93	10	5363
H19	-	-	-	-	-	-	-	-	0
H20	-	-	-	-	-	-	-	-	0
H21	-	-	-	-	-	-	-	-	0
H22	-	-	-	-	-	-	-	-	0
H23	-	-	-	-	-	-	-	-	0

3.3 Presence of Organic chlorides in Very Low Sulfur Fuels

Ten VLSFOs with different ranges of organic chloride content from 5 ppm to 300 ppm were heated and aged at the injection temperature (shown in Table 9) for 2 and 5 days. The TAN and pH of the samples were measured as per ASTM D664. pH results showed that the pH of the VLSFO samples even with 300 ppm of organic chlorides will be greater than 4.5 after 5 days of aging of the samples at injection temperature. In addition, for the VLSFOs, we do not see significant changes in acid number value even after 2 and 5 days of aging of the samples at 100°C. Subjecting organic chlorides to the high temperature in the presence of water can convert them to hydrochloric acids. Since VLSFOs have lower viscosity in comparison to HSFOs, they are heated to lower temperatures. As a result, the conversion of organic chloride compounds to Hydrogen Chloride may take a longer time. As a result, any fuel with the presence of organic chlorides in the fuel can result in detrimental effects over a period of time and hence should be treated with caution.

Table 9. The organic chloride content of ten very low sulfur fuel oils

VLSFOs	Organic Chlorides, ppm	1,2-Dichloroethane	Tetrachloroethylene	Dichlorotoluenes
V1	22	<2	8	14
V2	11	<2	11	<2
V3	11	<2	11	<2
V4	5	<2	5	<2
V5	180	167	13	<2
V6	13	<2	13	<2
V7	10	<2	10	<2
V8	10	<2	10	<2
V9	299	275	24	<2
V10	51	40	11	<2

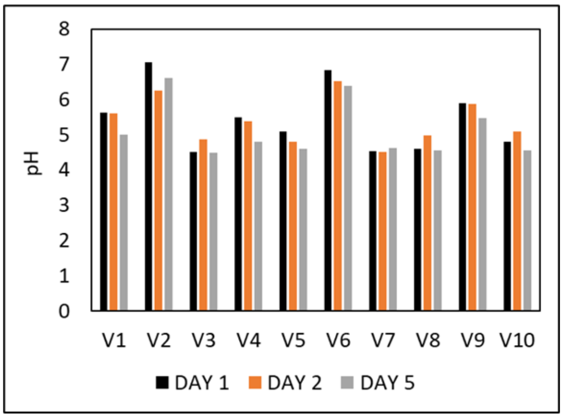

Figure 5. pH Values of VLSFOs on Day 1 (Without aging), after 2 days and 5 days of aging of the samples at injection temperature

4 CONCLUSION

Contamination of bunker fuel with organic chlorides has become a source of major concern for fuel users and suppliers. Organic chlorides in the presence of high temperatures tend to convert to Hydrogen Chloride which in turn converts to hydrochloric acid in the presence of water. The presence of hydrochloric acid (a strong acid) in the fuel system even at low levels will result in extensive corrosion and severe damage to the machinery. According to Chevron and Capline documents, organic chloride content shall not exceed 1.3 or 1 ppm respectively in the refineries.

ISO8217 does not include the GCMS test in the fuel analysis. However, paragraph 5 and Annex on deleterious substances in ISO 8217 limit the presence of chemical contaminants in bunker fuels. Viswa Labs recommends GCMS test analysis in order to determine the level of the organic chlorides in fuel and fit for use.

Based on this study to avoid corrosion, the concentration of organic chlorides in marine fuel should be less than 40 mg/L.

Although if the fuel is being heated to a lower temperature it will take a longer time for organic chlorides to get converted to hydrochloric acid, it is not recommended that the level of organic chlorides exceeded 40 ppm even in low viscosity fuels.

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