

**1. Introduction**

Marine fuel oils are heavier distillates of crude oil consisting of long chain hydrocarbons, alkanes, cycloalkanes, aromatics etc. Marine fuel oils, also termed as bunker oil, heavy fuel oil are relatively economical and are widely used as fuels in large boilers, power generators, marine vessels in large amounts. Often these fuel oil consists of relatively large amounts of chemical species which can pollute the environment during the event of accidents or due to fuel spills. Some of these compounds are shown in Figure 1. In addition to this, the presence of phenol in these fuels can cause breakdown of engine parts of the marine vessels.

The ASTM D-7845 method had listed 30 such chemical compounds which can be detected and quantified using a multi dimensional GCMS<sup>®</sup>. This method requires the use of multiple detectors namely Flame Ionization Detector (FID) and GCMS along with the use of a Programmable Temperature Vaporizing (PTV) injector, two capillary columns (a pre-column and an analytical column) and a Deans switching system.

In this experiment, a highly sensitive Shimadzu GCMS-QP2020 NX (Figure 2a) is used with some alterations from the ASTM method. With this method, it is possible to measure the listed compounds in the fuel oil according to ASTM method limits. This method provides simple and cost-effective solution in comparison with that of ASTM. Additionally, the experiment utilizes Fast Automated Scan/SIM Type (FASST) feature of the instrument which makes it possible to monitor and identify both targeted and untargeted components simultaneously.

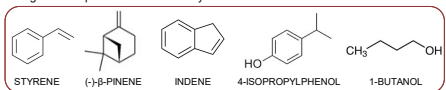


Figure 1. Structures of some of the chemical species



Figure 2a. GCMS-QP2020 NX

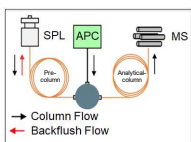


Figure 2b. System configuration

**2. Materials and methods**

**2-1. Instrument configuration and method setup**

The system configuration is detailed in Figure 2b which consists of Split/Splitless injector instead of PTV injector, two columns as recommended by the ASTM method which was connected using a T-junction connector instead of Deans Switching system and a single quadrupole MS detector. An Auxiliary Advanced Pressure Control (APC) unit which constantly supplies carrier gas through out was employed to

backflush higher boiling hydrocarbons from the pre-column. The experiment was conducted using ultra pure helium as carrier gas. The detailed instrument parameters are given in Table 1. The pre-column was used to separate the interested analytes from the high boiling hydrocarbon fraction and to pass it to the analytical column. Once the entire analytes were passed into the analytical column, the backflushing was executed. During backflush, the pre-column experiences reverse flow whereas the analytical column experiences a forward flow. This was done by decreasing the inlet pressure drastically to 14 kPa. This was facilitated using a T-junction connector mounted between the pre and the analytical column. The remaining position of the T-junction was connected to an auxiliary APC unit as shown in Figure 2b. During backflushing, the heavy components were flushed out through the vent.

Table 1. Instrument parameters

| GC inlet parameters    |             | Pre-column: SH-Rx1™, 1ms (30 m x 0.25 mm; df: 0.25 μm) [P/N: 221-75923-30] |  |
|------------------------|-------------|--|--|
| Injector Temperature   | 300 °C      | Pre-column:  | Split                                  |
| Injection mode         | Split       | Analytical column:   | Rx1™-5ms (60 m x 0.32 mm; df: 0.50 μm) |
| Injection volume       | 0.5 μL      |  |  |
| Flow Control Mode      | Pressure    |  |  |
| Pressure               | 190.6 kPa   |  |  |
| Column Flow            | 1.68 mL/min |  |  |
| Purge Flow             | 3.0 mL/min  |  |  |
| Split Ratio            | 30          |  |  |
| Auxiliary APC pressure | 104.0 kPa   |  |  |

| SPL Pressure Program |                 | Column Oven Program |                 |
|----------------------|-----------------|---------------------|-----------------|
| Rate                 | Hold Time (min) | Rate                | Hold Time (min) |
| -                    | 28.50           | -                   | 5.00            |
| -49.90               | 10.96           | 7.00                | 13.43           |

**Determination of Backflushing time:** The backflush time was measured by using hexadecane. Hexadecane was injected in the forward flushing mode and the retention time of the C16 peak was determined. Further, the same was re-injected in backflush mode by reducing the inlet pressure at an arbitrary time (backflushing time). If the C16 peak was visible in MS then multiple injections were made by reducing the backflushing time by 30 seconds until little or no C16 peak is visible. In the present experiment, the observed backflushing time was found to be 28.50 min.

**2-2. Standard and Sample preparations**

The ASTM method stipulates the use of 5 levels of standards with calibration performed using internal standard methodology. Ethylbenzene d-10 (500 ppm) was used as the internal standard (IS). The certified calibration standard mixture of five levels were used. Each standard vial contains 500 ppm of IS along with all the 30 analytes prepared in toluene. The concentration of all the analytes were different and it ranges from 10 to 1000 ppm. The concentration of various analytes are shown in Table 2 along with respective target ion m/z used for the quantification. The analysis was carried out by simultaneous scan and SIM which is termed as "FASST". One target ion and two reference ions were selected for each analyte.

Unknown sample was also tested in the same method conditions. 1 mL of the fuel sample was pipetted and diluted 5 times using toluene in a 10 mL glass vial. From this, 750 μL of the sample was taken in a GC vial and added 250 μL of 2000 ppm ethylbenzene d-10. The resultant concentration of IS in the final sample was 500 ppm. The content in the vial was vortexed and 0.5 μL of this solution was injected into GCMS using autosampler.

Table 2. Analyte m/z and concentration chart

| Name                   | Rt (min) | Target m/z | Concentration (ppm) |         |         |         |         | Linearity coefficient (r <sup>2</sup> ) |
|------------------------|----------|------------|---------------------|---------|---------|---------|---------|---|
|                        |          |            | Level 1             | Level 2 | Level 3 | Level 4 | Level 5 |   |
| 1-BUTANOL              | 10.445   | 56         | 10.01               | 25      | 75.1    | 150.2   | 300.4   | 0.9996                                  |
| CYCLOHEXANOL           | 18.188   | 82         | 10.03               | 25.1    | 75.3    | 150.5   | 301     | 0.9990                                  |
| ETHYLBENZENE D10       | 17.406   | 98         | 500                 | 500     | 500     | 500     | 500     | XX                                      |
| DI-BUTYL ETHER         | 18.26    | 57         | 9.95                | 24.9    | 74.8    | 149.2   | 298.4   | 0.9999                                  |
| N-BUTYLACRYLATE        | 18.461   | 55         | 9.97                | 24.9    | 74.8    | 149.5   | 299     | 0.9996                                  |
| STYRENE                | 18.513   | 104        | 9.99                | 25      | 74.9    | 149.9   | 299.7   | 0.9997                                  |
| D-LA PINENE            | 20.17    | 93         | 9.93                | 24.8    | 74.5    | 148.9   | 297.8   | 0.9998                                  |
| PHENOL                 | 21.05    | 94         | 20.05               | 40.1    | 120     | 240.6   | 481.2   | 0.9973                                  |
| α-METHYLSTYRENE        | 21.357   | 118        | 9.98                | 25      | 74.9    | 149.7   | 299.5   | 0.9995                                  |
| (-)-β-PINENE           | 21.483   | 93         | 10.03               | 25.3    | 75.2    | 150.4   | 300.9   | 0.9999                                  |
| 4-METHYLSTYRENE        | 21.747   | 118        | 10.02               | 25.1    | 75.1    | 150.3   | 300.5   | 0.9988                                  |
| TRANS-β-METHYL STYRENE | 21.806   | 117        | 9.97                | 24.9    | 74.8    | 149.5   | 299.1   | 0.9997                                  |
| 2-METHYL STYRENE       | 21.859   | 117        | 9.81                | 24.5    | 73.6    | 147.2   | 294.3   | 0.9989                                  |
| 3-METHYL STYRENE       | 22.658   | 117        | 10.01               | 25      | 75.1    | 150.2   | 300.4   | 0.9993                                  |
| RLIMONENE              | 22.882   | 88         | 10.02               | 25.1    | 75.2    | 150.3   | 300.6   | 0.9995                                  |
| DICYCLOPENTADIENE      | 23.23    | 66         | 9.9                 | 24.8    | 74.3    | 148.5   | 297.1   | 0.9996                                  |
| INDENE                 | 23.282   | 115        | 20.01               | 40      | 120     | 240.1   | 480.3   | 0.9995                                  |
| 1-PHENYLETHANOL        | 23.44    | 107        | 19.91               | 39.8    | 119     | 238.9   | 477.7   | 0.9986                                  |
| α-DIMETHYL STYRENE     | 24.412   | 117        | 19.77               | 39.5    | 119     | 237.2   | 474.5   | 0.9995                                  |
| 2,4-DIMETHYL STYRENE   | 24.641   | 117        | 19.96               | 39.9    | 120     | 239.5   | 478.9   | 0.9995                                  |
| 2,5-DIMETHYL STYRENE   | 24.761   | 117        | 20.08               | 40.2    | 121     | 241     | 481.9   | 0.9995                                  |
| 2-PHENYLETHANOL        | 24.893   | 91         | 19.99               | 40      | 120     | 239.9   | 479.8   | 0.9975                                  |
| 2-ETHYLPHENOL          | 25.393   | 107        | 49.62               | 99.2    | 248     | 496.2   | 992     | 0.9991                                  |
| 2,4-DIMETHYL PHENOL    | 25.689   | 107        | 20.03               | 40.1    | 120     | 240.3   | 480.6   | 0.9984                                  |
| 4-ETHYL PHENOL         | 26.103   | 107        | 10.03               | 20.1    | 60.1    | 120.3   | 240.6   | 0.9992                                  |
| 4-ETHYL PHENOL         | 26.144   | 107        | 10.03               | 20.1    | 60.1    | 120.3   | 240.6   | 0.9990                                  |
| 2-PHENOXY ETHANOL      | 27.516   | 94         | 50.15               | 100     | 251     | 501.5   | 1003    | 0.9982                                  |
| 4-ISOPROPYLPHENOL      | 27.624   | 121        | 50.23               | 101     | 251     | 502.3   | 1005    | 0.9990                                  |
| 2-PHENOXY PROPANOL     | 28.171   | 108        | 50.1                | 100     | 251     | 501     | 1002    | 0.9988                                  |
| 1-PHENOXY-2-PROPANOL   | 28.219   | 94         | 49.99               | 100     | 250     | 499.9   | 1000    | 0.9990                                  |
| STYRENE GLYCOL         | 29.474   | 107        | 20.01               | 40      | 120     | 240.2   | 480.3   | 0.9847                                  |

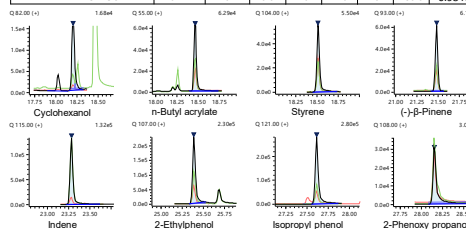


Figure 2. SIM chromatogram at level-1

**3. Results**

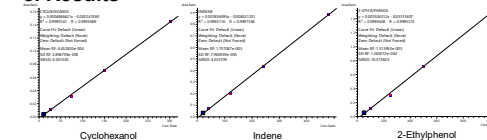


Figure 3. Calibration curves

Calibration curve was plotted for all the 30 analytes using ethylbenzene d-10 as internal standard. SIM mode was used for the quantification whereas the scan mode was used for qualitative analysis. SIM chromatograms for eight compounds are shown in Figure 2 and linearity curves for three compounds are shown in Figure 3. For various analytes, the concentrations were different at each level. ASTM recommends r<sup>2</sup> > 0.90. The linearity coefficient for all the compounds were observed to be greater than 0.98. The sample was also processed using the same calibrated method. The results of sample analysis shown noticeable concentrations of Dibutyl Ether, and the concentration calculated was 200 ppm.

The Ultra Fast Mass Spectrometry (UFMS) capability of the instrument benefits in trace level analysis with superior sensitivity. Besides this, the simultaneous scan and SIM feature (FASST) is useful in identifying the target and untargeted component, particularly in the unknown samples. The MS spectrum acquired from the sample can be used for the comparison with that of the standard and with the MS library thereby confirming the presence of compounds. This gives an additional confidence in the analysis results as demonstrated in Figure 4.

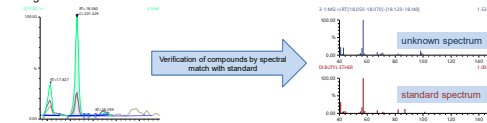


Figure 4. FASST chromatogram of Di-butyl ether in the sample along with spectral match with standard sample

**4. Conclusion**

- A GCMS method for the quantification of 30 chemical species from marine fuel oil using backflushing technique.
- This method developed without using PTV, FID and Deans switch makes it a simple, cost-effective technique.
- The FASST mode used in this experiment is useful in determining the presence of untargeted compounds or contaminants in samples.
- The superior sensitivity and robustness of Shimadzu GCMS-QP2020 NX model ensures high quality data for chemical species in marine fuel oil samples.

**5. References**

[1] ASTM D-7845-17- Standard Test Method for Determination of Chemical Species in Marine Fuel Oil by Multidimensional Gas Chromatography/Mass Spectrometry.

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