Application Note SI-01381

Analysis of Mineral Oils Utilizing Temperature Programmed Large Volume Injection

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Introduction

Mineral oils are typically found in water, foods and soils. These mineral oils can be extracted using different solvents. Most popular are hexane and petroleum ether. As concentrations can be very low, some sort of sample enrichment is often used. If, however, a Large Volume Injection (LVI) technique is used, sample pretreatment becomes easier and sample throughput increases dramatically.

This application note describes the highly efficient analysis of mineral oil using the Varian 450-GC gas chromatograph equipped with a Programmable Temperature Vaporizer (PTV) Injector and the Varian Select™ Mineral Oil column. The column stationary phase was tuned for separation and stabilized for high temperature operation. The upper temperature limit of the column is 400 °C. This system is very well suited to the DIN-EN-ISO 9377-2 method that replaces DIN H53.

Instrumentation

Varian 450-GC Gas Chromatograph
Column: Varian Select Mineral Oil LVI, 15 m x 0.32 mm (pn: CP7492)
Injector: Varian 1079 PTV, full EFC control
Detection: FID, full EFC control
Autosampler: Varian CP-8400 Autosampler equipped with large solvent wash vial

Software
GC Control and Data Handling: Galaxie™ Software from Varian

Materials and Reagents

Retention Gap: 2.5 m x 0.53 mm (pn: CP8009)
Liner: Varian 1079 LVI Liner (pn: CP14988)
Reference Sample: Test Sample Mineral Oil Standard from the National Institute for Public Health and the Environment (RIVM) (CP741970)
Test Sample: Test sample alkanes for mineral oil analysis CP741971)

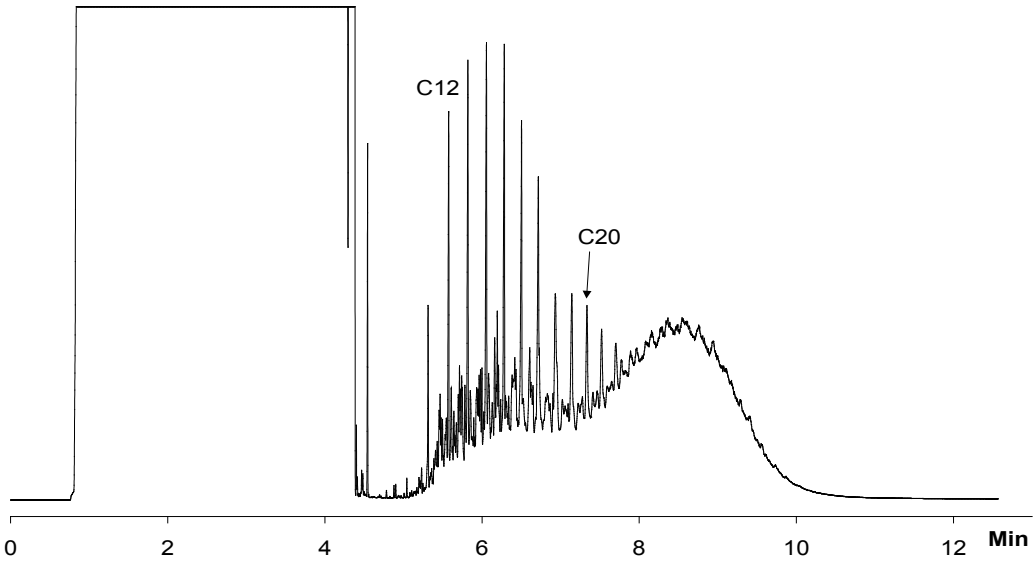

Figure 1. RIVM reference sample.

Sample Preparation

All samples were prepared by dissolving the alkanes and the reference sample in hexane.

Conditions

Sample: RIVM reference sample
Carrrier Gas: Helium, See Table 4
Injector: PTV, see Tables 1 and 2
Injection Volume: 70 µL
Oven: See Table 3
Detection: 350 °C

Table 1. PTV split event.

Time (min)	Split state	Split ratio
Initial	ON	75
0.45	OFF	100
3.00	ON	150

Table 2. PTV temperature program.

Rate (°C/min)	Step (°C)	Time (min)
Initial	45.0	0.45
200.0	350.0	8.00
	Total Time	9.97

Table 3. Oven program.

Rate (°C/min)	Step (°C)	Time (min)
Initial	35.0	4.00
60.0	150.0	0.00
50.0	250.0	0.00
30.0	350.0	1.50
	Total Time	12.25

Table 4. Carrier gas pressure program.

Rate (psi/min)	Step (psi)	Time (min)
Initial	7.0	1.25
400.0	15.0	1.72
400.0	7.0	0.98
2.0	10.9	0.00
1.7	14.3	0.00
1.7	17.8	1.11
	Total Time	12.24

Results and Discussion

The sample was introduced in the PTV at temperatures equal to the boiling point of the solvent. Initially, the split was open allowing much of the solvent to evaporate from the vent. After a short time (0.17 min), the split vent was closed and the temperature rose. This caused the evaporation and injection of the sample into the column. To check the system suitability, the ratios C10/C20 peak area and C40/C20 peak area were measured. Both values must be between 0.8 and 1.2. Figure 2 shows a chromatogram of the reference sample when using a regular liner.

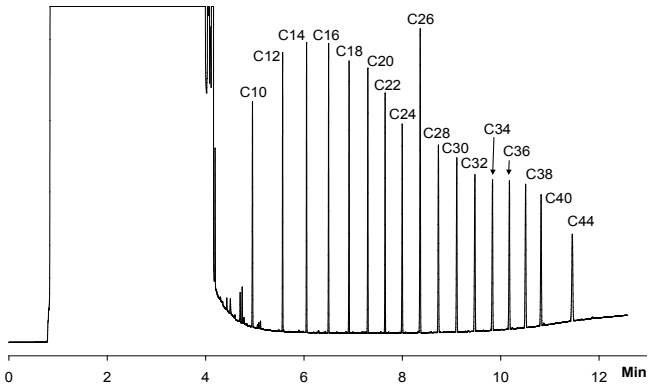

Figure 2. Calibration sample with regular liner.

The C10/C20 and C40/C20 values are plotted in Figure 3.

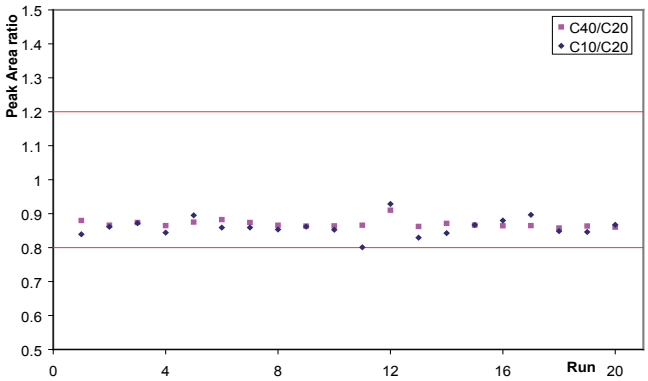

Figure 3. Repeatability chart showing C10/C20 and C20/C40 performance.

All values, although low, are within the specified range. If, however, a specially designed packed liner is used the chromatogram illustrated in Figure 4 is obtained.

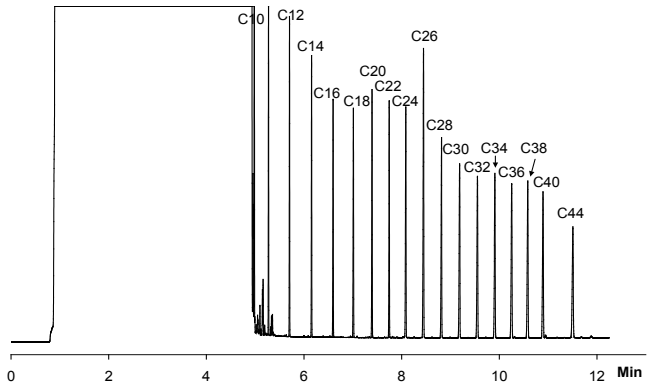

Figure 4. Chromatogram of a calibration sample with the Varian Mineral Oil liner.

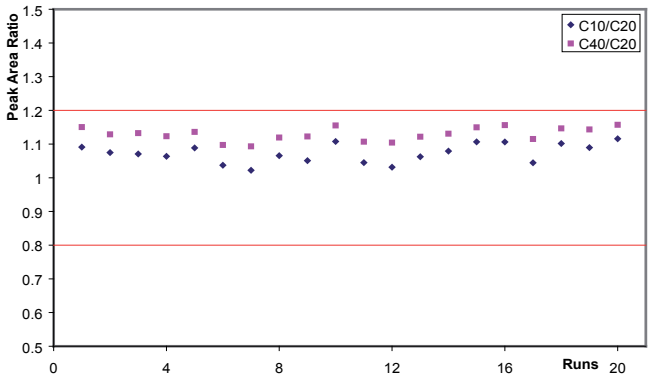

Figure 5. Repeatability data on C10/C20 and C20/C40 with a packed liner.

From Figure 5, it can be concluded that the ratios are much higher. This indicates an improved recovery of the sample components and thus less discrimination. The optimized liner contains a packing that retains the sample components for a slightly longer duration. Therefore, more solvent can be vented off compared to a regular liner. Settings, however, must be chosen carefully. If too much packing is present, mineral oil components are retained for too long resulting in discrimination. With these optimized settings, a RIVM reference sample was analyzed (Figure 1). This sample was was also analyzed many times in a repeatability study (Figure 6 and Table 5).

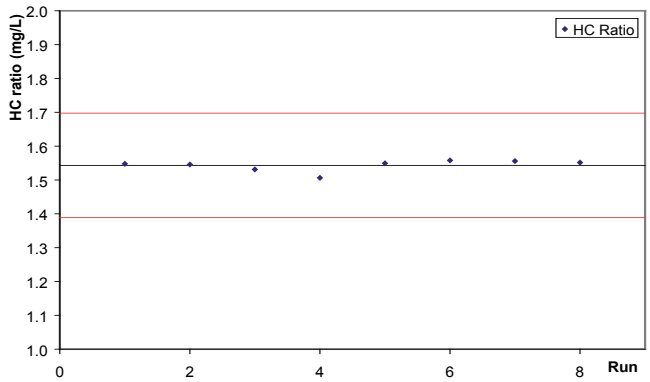

Figure 6. Repeatability of the hydrocarbon ratio of the RIVM reference.

Table 5. Repeatability data of RIVM reference sample.

Run	Area/C10-C20 fraction	Area/C20-C40 fraction	HC Ratio
1	1201944.7	1860482.4	1.548
2	1208160.4	1867571.7	1.546
3	1205740	1846199.5	1.531
4	1212651.5	1826599.8	1.506
5	1194517	1850616.1	1.549
6	1190457.6	1854374.9	1.558
7	1189986	1851458.5	1.556
8	1193781.4	1852083.6	1.551
Average	1199654.825	1851173.313	1.543
St. dev.	8640	11926	0.0170
RSD (%)	0.720	0.644	1.098

The repeatability data in Table 5 clearly show that the system functions very well. RSD % on area is about 0.7. For the hydrocarbon ratio this value is 1.1 %.

Conclusion

The system setup for this application is carefully optimized. The Varian liner, the Varian Select Mineral Oil LVI column and the Varian 450-GC Gas Chromatograph equipped with a PTV injector and high temperature FID all play a crucial role in this application. With this optimized system configuration the results are very good. Hydrocarbon ratio analysis is 1.1 % RSD where the method reports 3.0 % to 14.1 %, depending on the sample in the precision section.

References

ISO 9377-2:2000. Water quality – Determination of hydrocarbon oil index – Part 2: Method using solvent extraction and gas chromatography. International Organization for Standardization, Geneva, Switzerland.

These data represent typical results.
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