BEYOND MEASURE

SCION INSTRUMENTS

Analysis of Total Petroleum Hydrocarbons using Temperature Programmed Large Volume Injection

Application Note AN0010

INTRODUCTION

Mineral oils are typically found in water, foods and soils. These mineral oils can be extracted using different solvent; most popular are hexane and petroleum ether. As concentrations can be very low, some sort of sample enrichment is often used, e.g. rotary evaporation. If, however, a Large Volume Injection (LVI) technique is used, sample pretreatment becomes easier and sample throughput can be increased significantly.

This application note describes the analysis of mineral oils (or Total Petroleum Hydrocarbons / TPH) using the Scion 456-GC gas chromatograph equipped with a Programmable Temperature Vaporizer (PTV) Injector and the Select™ Mineral Oil column. The column stationary phase was tuned for separation and stabilised for high temperature operation. The upper temperature limit of the column is 400 °C. This system is suited to the DIN-EN-ISO 9377-2 method that replaced DIN H53.

EXPERIMENTAL

The SCION 456-GC holds a PTV inlet with a packed LVI inlet liner, a Column selected for this analysis (15m*0.32mm *0.5 µm, part number CP492), and FID. Samples are injected by a CP-8400 autosampler for best precision. With the LVI liner packing typically having capacity for more than 100 µl solvent, the injections are performed in “at-once” mode.

A n-alkane standard was prepared by dissolving C10-C44 n-alkanes mix CP741971 into n-Hexane. A Reference Sample Mineral Oil Standard from the National Institute for Public Health and the Environment (RIVM) (CP741970) was diluted in n-Hexane for use as a Quality Control sample. This material elutes fully before n-C44, it is well characterized, stable, widely used & available.

Samples are prepared by extraction of soil or water with n-Hexane (with ‘in vial extraction’ being a viable option).

Table 1. Analytical Conditions

Conditions	
Injector	PTV with LVI Liner 45°C (0.45 min), 350° (200°/min), hold 8 min) Split 1:75 (0.45 min hold), Splitless until 3.0 mins. Split 1:150, after 3 mins.
Column	Scion Select Mineral Oil LVI 15 m x 0.32 mm
Oven	35° (4), 60 (150°/min), 250°(50°/min, 350 (30°/min, hold 1.5 min). Total Runtime 12.25 mins
Carrier Gas	Helium, 99.999% @ 7psi, (Pressure Pulse 15 PSI when split closed)
FID	350°C,
Injection Vol.	70 µL (in n-Hexane)

RESULTS

The sample was introduced in the PTV at temperatures equal to the boiling point of the solvent. Initially, the split was open allowing the majority of the solvent to evaporate from the vent. After a short time (0.17 min), the split vent was closed and the temperature increased. This caused the evaporation and injection of the sample into the column. To check the system suitability, the ratios C_{10}/C_{20} peak area and C_{40}/C_{20} 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.

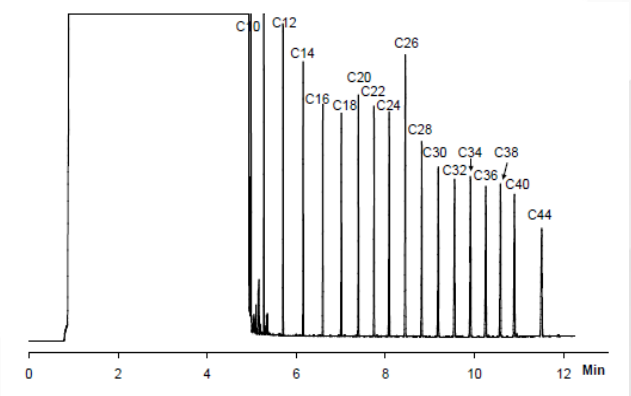

Fig 1. n-Alkanes calibration in Hexane (70 µL injection)

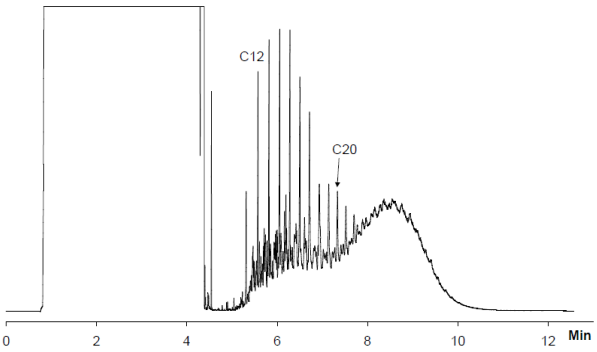

Fig 2. Reference Sample in Hexane (70 µL injection)

From Figure 3, 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 optimised settings, a RIVM reference sample was analyzed (Figure 2). This sample was also analyzed many times in a repeatability study (Figure 3 and Table 2). The repeatability data in Table 2 clearly show that the system functions very well. RSD % on area is about 0.7%.

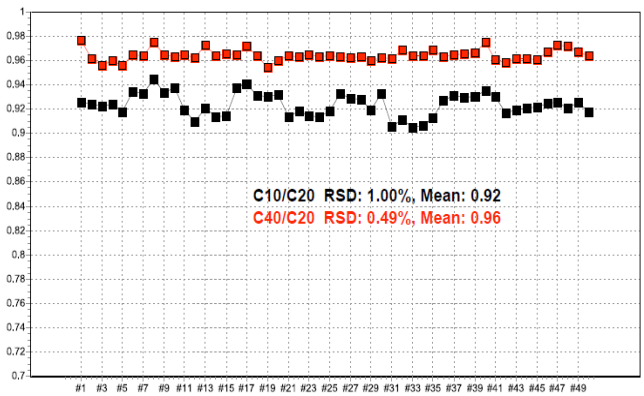

Fig 3. C10/C20 and C40/C20 discrimination check (must be between 0.85 and 1.2), n=50

Table 2. Repeatability of RIVM Reference Sample (n=8)

Run#	C10-C20 Area	C20-C40 Area
1	1201945	1860482
2	1208160	1867572
3	1205740	1846200
4	1212652	1826600
5	1194517	1850616
6	1190459	1854375
7	1189986	1851459
8	1193781	1852083
RSD (%)	**0.72%**	**0.64%**

Conclusion

The system setup for this application was carefully optimised. Scion's 456-GC Gas Chromatograph equipped with a PTV injector with packed liner, specific column and high temperature FID all play a crucial role in this application. With this optimised method the results are good. Without doing elaborate steps in sample preparation (eliminating the evaporation step), results be obtained in 12 minutes with excellent precision. Repeatability for area by fraction is <1 % RSD. Longevity and linear response over Carbon Number have been demonstrated.

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