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Application News

Gas Chromatography

Ultra-fast Total Petroleum Hydrocarbons (TPH) analysis using the Nexis GC-2030

No. SCA_180_038

Abstract

Shimadzu's Nexis GC-2030 can analyse nearly 250 samples in a single day, thanks to a highly optimised method that has an injection-to-injection time of less than 6 minutes per sample.

Despite the speed, this method can resolve benzene and toluene from the solvent (pentane) as well as fully elute compounds up to tetratetracontane (C_{44}). This allows it to be applied to almost all TPH applications.

Introduction

During the production and use of petroleum hydrocarbon products, the environment, including waters and soils, is repeatedly contaminated.

These products do not biodegrade readily and some pose risks to health, meaning the control of contamination is very important. The analysis of petroleum products in waters and soils is commonly referred to as TPH (Total Petroleum Hydrocarbon), which covers a range of standardised method variants.

Since some classes of petroleum products pose greater risks than others, simply reporting the total concentration of TPH does not provide a robust basis for evaluating the potential risks to the environment and human health.

For this reason, the content is divided into bands. Chromatographic separation resolves the analytes based on effective carbon (EC) numbers, whilst solid phase extraction (SPE) is typically employed to separate aromatic and aliphatic fractions.

Aromatics	Aliphatics
EC_5 – $EC_{7\ (Benzene)}$	EC_5 – EC_6
$EC_{>7}$ – $EC_{8\ (Toluene)}$	$EC_{>6}$ – EC_8
$EC_{>8}$ – EC_{10}	$EC_{>8}$ – EC_{10}
$EC_{>10}$ – EC_{12}	$EC_{>10}$ – EC_{12}
$EC_{>12}$ – EC_{16}	$EC_{>12}$ – EC_{16}
$EC_{>16}$ – EC_{21}	$EC_{>16}$ – EC_{35}
EC_{21} – EC_{35}	

Table 1: Common TPH bandings

Sample Introduction

The analysis of volatile components, below EC_8 is typically performed using Headspace or Purge & Trap techniques, as these are often difficult to resolve from the solvent. The remaining compounds are analysed using liquid injection.

Most testing laboratories analyse samlples up to EC_{40}, or even EC_{44}, meaning the petroleum hydrocarbons cover a wide boiling point range. Conventionally this would require an on-column injector (OCI) to ensure non-discriminatory sample introduction, however a recent application note (SCA_180_021) demonstrated that Shimadzu's split/splitless inlet (SPL-2030) has very little discrimination, giving a ratio of C_{40}/C_{20} >0.96.

Optimisation of method speed

Traditionally, TPH columns have been chosen with a thinner film thickness to improve elution times of the high-boiling components, but this impacts the resolution of volatile components from the solvent, which is often pentane (C_5). This means the starting temperature is typically low (30-35 °C), resulting in extremely long cool-down times and greatly impacting sample throughput.

An Rxi-1ms column from Restek, with non-conventional dimensions (Table 2), was selected to optimise sample throughput. This enables separation of the volatile components from the solvent at a higher starting temperature, whilst minimising retention of the high-boiling hydrocarbons, up to C_{44} (Figure 1).

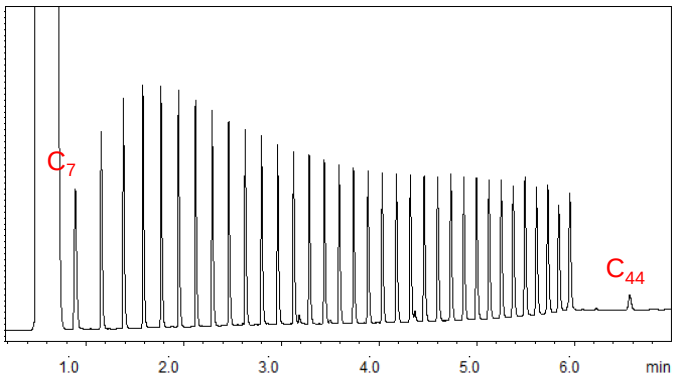

Figure 1: n-Alkane mix from C_7-C_{44} in C_5/C_6

The use of hydrogen as carrier gas also makes it possible to realise fast analysis whilst maintaining high chromatographic resolution. Thus, analysis times can be significantly reduced. Furthermore, the recent inflation in helium prices make hydrogen carrier gas methods increasingly more popular and commercially viable.

The throughput can be further optimised by utilising the ability to inject two samples at once using Shimadzu's Nexis GC-2030 with AOC-20 Plus liquid autosampler system.

SPL temperature	280 °C
Flow rate	1 mL/min ramped to 4 mL/min
Column	Rxi-1ms (Restek) 12 m x 0.2 mm x 0.33 µm
Column oven program	60 °C, 0.8 min, then maximum ramp rate to 350 °C, 1.13 min.
FID temperature	320 °C

Table 2: Method parameters for ultra-fast GC

▪ Results

A series of seven calibration standards were acquired using the optimised method parameters (Table 2). The standards were made using a 50:50 mix of diesel oil and heavy lube oil standards, from 40-4000 ppm (total hydrocarbon content).

Calibration curves were acquired for $EC_{>8} – EC_{10}$, $EC_{>10} – EC_{12}$, $EC_{>12} – EC_{16}$, $EC_{>16} – EC_{21}$, $EC_{>21} – EC_{35}$, $EC_{>35} – EC_{40}$, $EC_{>40} – EC_{44}$ and a combined group for $EC_{>8} – EC_{40}$.

All bands gave a regression coefficient greater than 0.999 (Fig. 2).

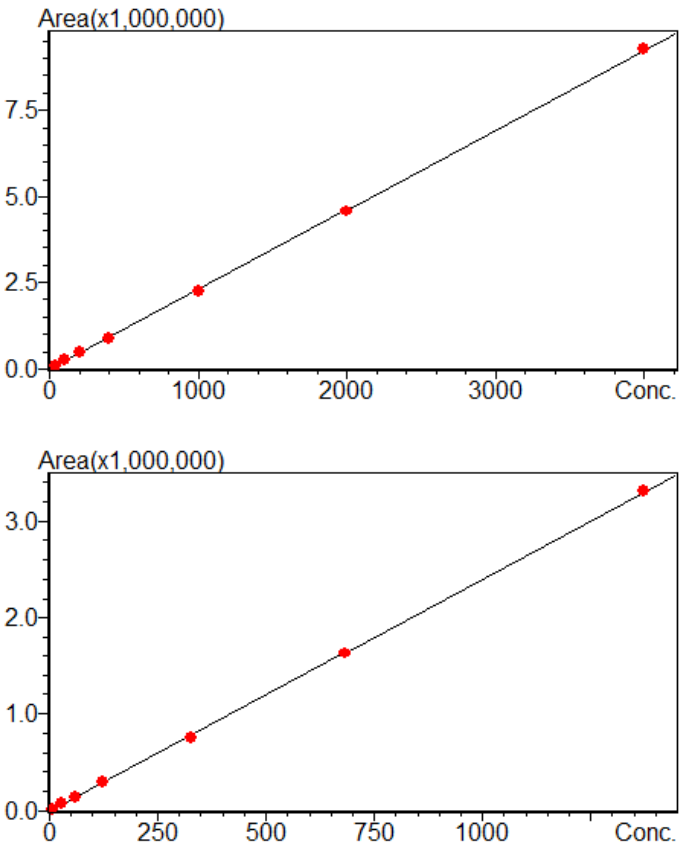

Figure 2: Calibration curve for the total TPH group ($EC_{>8} – EC_{40}$) [R^2 = 0.9999], top, and $EC_{>21} – EC_{35}$ [R^2 = 0.9999], bottom

The GC oven program was set to 7 minutes to allow for any heavy components >EC_{44} (retention time = 6.6 min) to elute. With a single line system, this gives an injection-to-injection time of 12 minutes.

Real samples from various matrices, including water, leachate and sand, were measured. The sample chromatograms (Figure 3) showed varying degrees of TPH contamination.

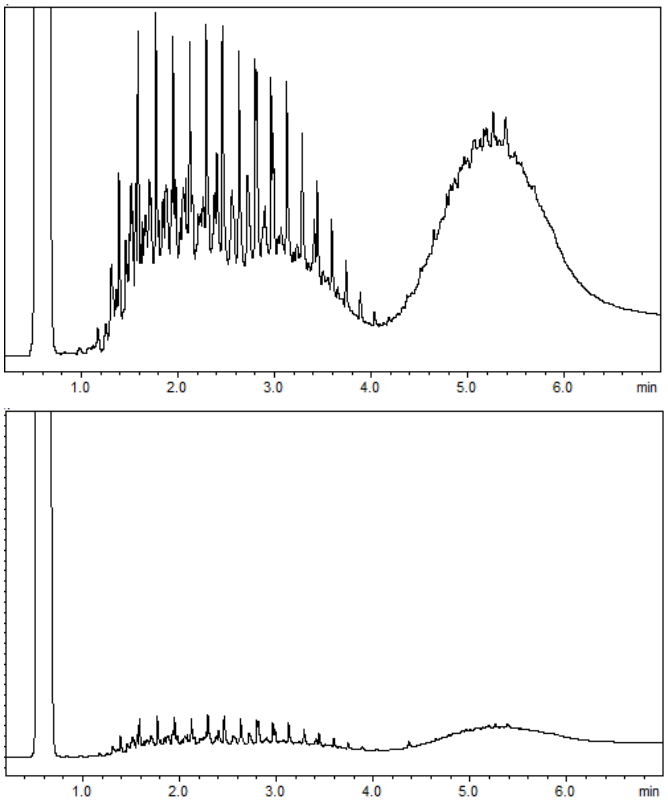

Figure 3: Chromatograms of a heavily contaminated sand sample (top) and a less contaminated water sample (bottom)

▪ Conclusion

Shimadzu‘s GC-2030 with SPL and FID offers an ideal solution for TPH and TPHCWG analysis across the widest boiling point range.

Alongside the GC-2030‘s high-powered oven, the use of hydrogen carrier gas facilitates a very short run time. The combination of this, with a dual line configuration, results in injection-to-injection run times of below 6 minutes per sample, thanks to the dual injection technology.

Over a 24-hour period, a single GC-2030 instrument is able to analyse nearly 250 samples.

The LabSolutions software platform further facilitates high-throughput analysis by offering automated reporting and simple transfer of results to LIMS.

The software‘s highly flexibile integration parameters allow various baselines and bandings to be performed, without any user intervention, offering easy conversion from an existing CDS.

▪ Acknowledgements

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