Application Note

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Ultrafast Total Petroleum Hydrocarbon Analysis by the Agilent 8850 GC with FID

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Abstract

In this work, an Agilent 8850 GC with a flame ionization detector (FID) was used for the ultrafast screening of total petroleum hydrocarbons (TPHs) in soil and water samples. This high-speed analysis was carried out on a 5 m Agilent J&W DB-5ht analytical column under a rapid oven ramp rate, which managed to elute *n*-tetracontane (*n*-C_{40}) within 2.5 minutes using either helium (He) or hydrogen (H_2) as the carrier gas. The system's performance in terms of (A) inlet discrimination for effective analysis of compounds with high boiling points, (B) retention time and response precision, and (C) linearity was evaluated based on HJ 1021-2019, HJ 894-2017, and ISO 16703 standards, yielding satisfactory results. One of the smart features of the 8850 GC – peak evaluation – was also showcased for its automatic monitoring of inlet liner performance, which can enhance lab productivity when the 8850 GC is used for TPH screening in real-life samples.

Introduction

TPHs refer to a broad family of hydrocarbons found in crude oil or its refined products such as gasoline, diesel, and lubricating oils. Petroleum hydrocarbons are present in the environment due to industrial activities, spills, or natural occurrences. Soil and drinking water can become contaminated with TPHs, with soil contamination reducing the usability of land development. TPH analysis can be used to analyze the hydrocarbons in soil, water, and sediment samples. This testing is an essential component of risk assessment and management when the soil and water resource needs development.

Gas chromatography (GC) is the most common technique for the quantitative analysis of TPH in water, soil, and sediment. ISO 16703[1] and China HJ 1021-2019[2] standard methods describe the measurement of TPH in soil and sediment using GC with FID (GC-FID). HJ 894-2017[3] describes TPH analysis in water samples by GC-FID. In these methods, the 10 to 30 m columns coated with nonpolar stationary phases such as Agilent J&W DB-1, DB-5, and HP-5 are often recommended for separation. The typical oven ramp rate used is 20 to 40 °C/min, and the column flow rate is between 1.5 and 3 mL/min. The GC separation takes 15 to 40 minutes to complete. The quantitation of TPHs is performed by integrating the area between the *n*-decane (*n*-C_{10}) and *n*-tetracontane (*n*-C_{40}) peaks, then calculating the corresponding TPH concentration based on the external calibration curve developed from *n*-alkanes calibration standards (HJ methods) or mineral oil calibration standards (ISO 16703). In HJ 1021 and HJ 894 methods, the integration retention time (RT) window of TPH extracts starts right before the *n*-C_{10} peak and ends after the *n*-C_{40} peak, by referring to their corresponding RTs obtained from the *n*-alkanes calibration standard. In the ISO 16703 method, the calibration standards are mineral oils of known concentrations instead of *n*-alkanes. The *n*-C_{10} and *n*-C_{40} should be added to mineral oil calibrants and TPH extracts as RT window indicators for integration. The *n*-C_{10} and *n*-C_{40} are not included in the TPH integration.

The TPH extracts usually give a hump-shaped signal across the chromatogram. The quantitation based on the hump-shaped chromatogram determines whether the TPH amount exceeds the regulation limit. In some testing labs, a screening test is performed to quickly identify samples that clearly exhibit a TPH response that exceeds the regulatory limit. These samples are then subjected to a second, more comprehensive analysis to confirm the amount of TPH present. The reason for this operation is because the purification of TPH extract takes more than one hour, so screening the unpurified sample can save time on the sample preparation. A quick screening test can further increase lab productivity by improving the daily sample throughput and saving more time for analysis of the contaminated samples.

To achieve rapid screening, a typical approach includes using a short analytical column, increasing the column flow rate, and expediting the oven heating rate. Of these, the most challenging aspect to implement is the rapid heating speed. The 8850 GC addresses this issue with its compact air-bath oven design, which can accommodate one capillary column and works under a ramping rate as high as 300 °C/min (200 to 240 V power option). Meanwhile, even under such a high ramping rate, the 8850 GC power consumption is still only 50 to 70% of that used by most air-bath oven GCs on the market.

For test labs that consistently handle a high sample throughput, the 8850 GC can help significantly reduce electricity and gas consumption as it can analyze more samples in a fixed time. Even in cases where the sample number is not as high, completing an analysis in a shorter time with reduced power usage improves lab sustainability.

Similar to the flagship Agilent 8890 GC, the 8850 GC includes GC intelligence. This includes self-guided maintenance, detector and peak evaluation capability, onboard help, and more. These intelligent features can notify users of the degradation of instrument performance quickly and assist them in maintaining instrument performance for extended uptime. One notable application of the intelligent features is the use of peak evaluation for monitoring inlet performance.

As required by the ISO 16703 method, a suitability test should be run to verify system performance before analyzing a real sample. The method requires the response ratio of *n*-C_{40} versus *n*-C_{20}, under the same concentration, to be no less than 0.8. Usually, this verification is conducted manually by the analysts. The 8850 GC peak evaluation function can automatically conduct this assessment using a preset method, and generates the result upon completion of the separation. This ensures the analysis is conducted on a GC with reliable performance, thereby enhancing efficiency and reliability.

In this application note, a fast TPH analysis method was implemented and verified on the 8850 GC. System performance was assessed according to ISO 16703, HJ 1021-2019, and HJ 894-2017 requirements. It also demonstrates the use of peak evaluation to automatically evaluate *n*-C_{40} recovery rate.

Experimental

An Agilent 8850 GC was configured with an Agilent 7650A autosampler, a split/splitless (S/SL) inlet, and an FID. The instrument configuration, analytical parameters, and consumables for the fast methods can be found in Table 1.

The calibration standards for ISO 16703 were a mixture of mineral oil A (4,000 mg/L), mineral oil B (4,000 mg/L), *n*-C_{40} (30 mg/L), and *n*-C_{10} (0.03 mg/L) in *n*-heptane, from Anpel Inc. The calibration standard for HJ 1021-2019 and HJ 894-2017 was a mixture of *n*-alkanes in *n*-hexane (from *n*-C_{10} to *n*-C_{40}, 31 components, 1,000 mg/L for each alkane). The calibration standards for ISO and HJ methods were prepared to the concentrations shown in Table 2. The 30 and 10 mg/L (for each alkane) *n*-alkanes calibrants were used for system suitability and precision tests, respectively.

The TPH extracts from real water and soil samples were provided by a collaboration lab. The TPH extraction procedure followed the procedures recommended by HJ 894-2017 and HJ 1021-2019. Data acquisition and analysis were conducted using Agilent OpenLab CDS software, version 2.8.

Table 1. Agilent 8850 GC instrument conditions and consumables.

Parameter	Value
Agilent 8850 GC	
Injection Volume	0.5 µL
Inlet	Splitless at 310 °C
Purge Flow	60 mL/min at 0.3 min
Carrier Gas	He
Column	Agilent J&W DB-5ht, 5 m × 0.32 mm, 0.1 µm (p/n 100-2000, custom 5-inch column)
Column Flow	6.0 mL/min, constant flow; 5.5 mL/min for H_2
Oven Program	40 °C (for 0.5 min), 250 °C/min to 120 °C, 150 °C/min to 250 °C, 100 °C/min to 320 °C (hold 0.7 min)
Detector	340 °C
Data Rate	100 Hz
Consumables	
Inlet Septa	Agilent inlet septa, high temperature, low bleed, nonstick (p/n 5183-4757)
Inlet Liner	Agilent inlet liner, Ultra Inert, low pressure drop, split, glass wool (p/n 5190-2295)
Autosampler (ALS) Syringe	Agilent ALS syringe, Gold Standard, 23 to 26 s tapered needle (p/n 5181-1273)

Table 2. Calibration standards.

Calibration Level	Total Concentration (mg/L)	
	Mineral Oil Mixture with *n*-C_{10} and *n*-C_{40} for ISO 16703	*n*-Alkanes Mixture for HJ 894-2017 and HJ 1021-2019
1	100	31
2	500	93
3	1,000	310
4	2,000	930
5	4,000	3,100
6	8,000	9,300

Results and discussion

Ultrafast TPH analysis using helium carrier gas

An ultrafast TPH analysis method using He carrier gas was implemented on the 8850 GC based on a previous application note[4], and the oven program was optimized for the 8850 GC. The 8850 GC performance was evaluated and demonstrated based on the following metrics:

- System suitability
- Analysis speed
- Response and RT precision
- Linearity
- Carryover

System suitability test

The ISO 16703 method requires an instrument suitability test be performed to evaluate the *n*-alkanes resolution and detector response. A 30 mg/L *n*-alkanes calibrant was used for this test. As shown in the chromatogram in Figure 1, all peaks demonstrate baseline separation, and *n*-C_{10} was well separated from the *n*-C_6 solvent. The response of *n*-tetracosane (*n*-C_{40}) was 96% of the *n*-eicosane (*n*-C_{20}) response, which exceeded the ISO 16703 method limit of 80%, demonstrating excellent inlet performance in terms of boiling point discrimination.

Analysis speed

Ultrafast analysis using the 8850 GC is possible due to its compact GC oven with low thermal mass, optimized oven fan, and air duct. These features help shorten oven heating and cooldown time, effectively increasing the separation speed. The oven temperature ramp rate used in this work can be achieved on the 8850 GC (200 to 240 V) fast oven option. A single analytical cycle takes approximately 8.5 minutes, including 1 minute of oven initial equilibrium, 3 minutes of separation (*n*-C_{40} eluted within 2.5 minutes), 2 minutes of post-run to remove the sample matrix from the column, and 2.5 minutes of oven cooldown (22 °C ambient). Among them, the post-run time can be adjusted according to sample matrix complexity.

For the 8850 GC 120 V option, the oven ramp rates are slower than the 200 to 240 V option. The chromatogram of *n*-alkanes separation using the 120 V fast oven ramp rate is shown in the Appendix. The retention time of *n*-C_{40} increased from 2.4 to 3.0 minutes, which is still fast and enables an analysis cycle of approximately 9 minutes.

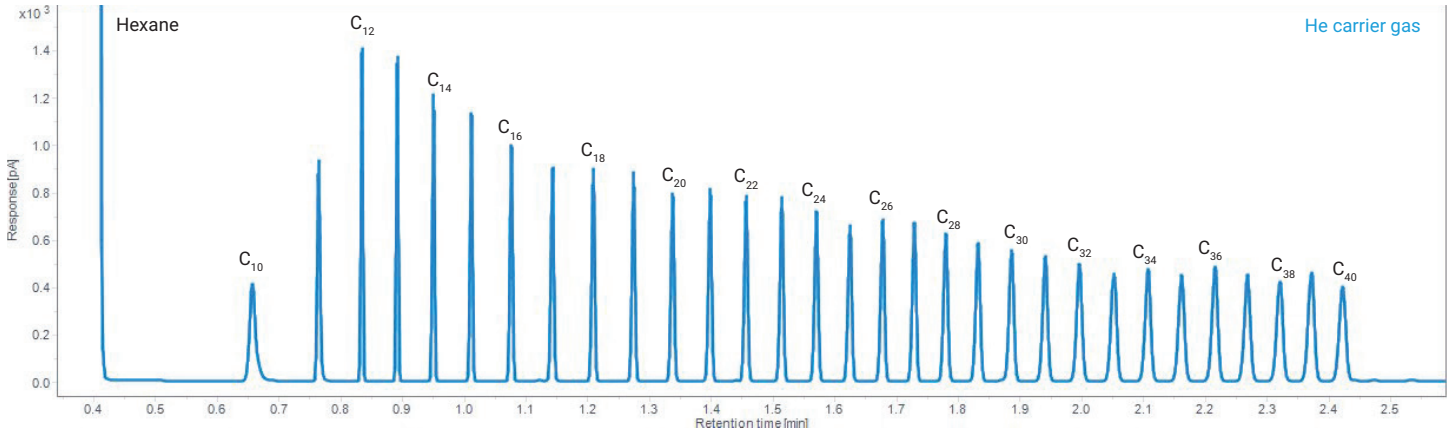

Figure 1. Chromatogram of 30 mg/L *n*-alkanes standard using the fast He method.

Precision

The system precision was tested by running six consecutive injections of 10 mg/L *n*-alkanes calibrant and 1,000 mg/L mineral oil mixtures (Figure 2). In ISO 16703, HJ 894-2017, and 1021-2019 methods, the *n*-C_{10} and *n*-C_{40} peaks are used as RT indicators for TPH integration. The high RT precision is important for accurate and repeatable measurement of TPH area. The RT range of *n*-C_{10} and *n*-C_{40} peaks in six runs of 1,000 mg/L mineral oil standard was 0.0003 and 0.005 minutes, respectively. The RT range of *n*-C_{10} and *n*-C_{40} peaks in six runs of 10 mg/L *n*-alkanes standard was 0.0008 and 0.0042 minutes. The RT statistical results of the two marker compounds in mineral oil mixture are shown in the table in Figure 2. Considering the fast separation, which eluted *n*-C_{40} within 2.5 minutes, the RT precision was good. Precise and repeatable oven thermal control and inlet pneumatic control contributed to the high RT precision performance.

The response relative standard deviation (%RSD) of each *n*-alkane was from 0.599 to 0.911%, as depicted in Figure 3. The response %RSD for integration starting from *n*-C_{10} and ending after *n*-C_{40} was 0.685% (integration required by HJ methods). The response %RSD of 1,000 mg/L mineral oil (starting after *n*-C_{10} and ending before *n*-C_{40}) was 0.322%. The repeatability results exceed the requirement of 5% in ISO 16703 method.

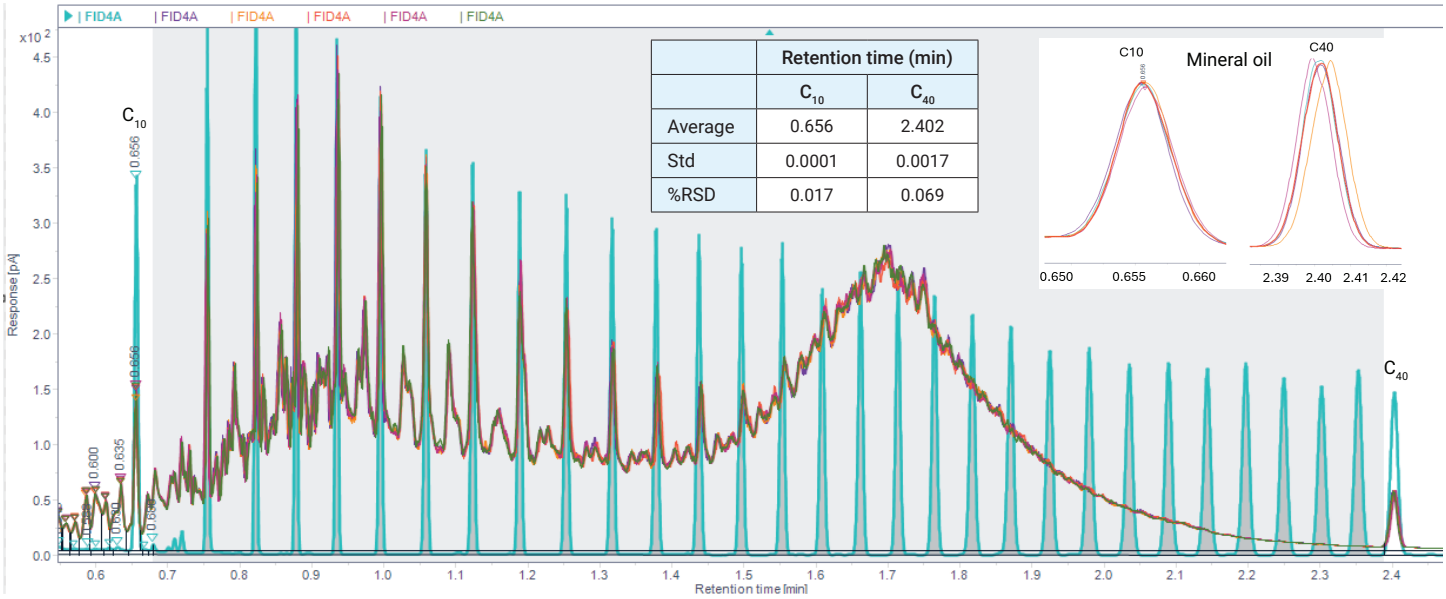

Figure 2. Chromatogram overlay of 1,000 mg/L mineral oil and 10 mg/L *n*-alkanes mixture.

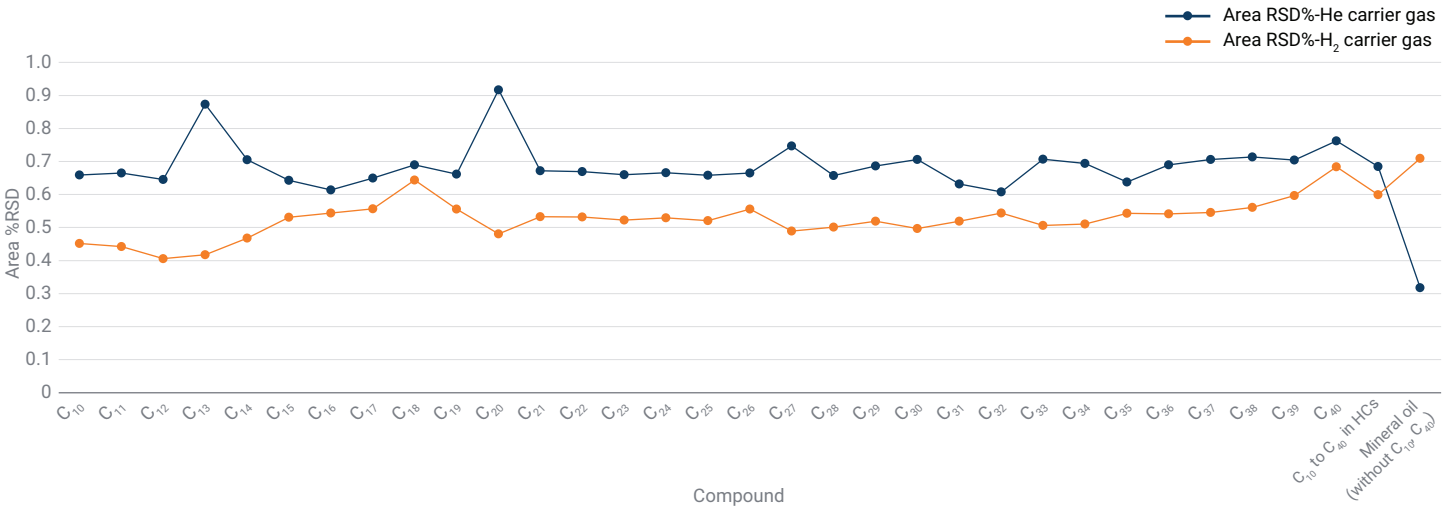

Figure 3. Area repeatability of individual *n*-alkanes, the combined peak from *n*-C_{10} to *n*-C_{40} in *n*-alkanes calibrants and the total area of mineral oil standard.

Linearity

The linearity performance is demonstrated in the two calibration curves in Figure 4. Curve 1 was developed using mineral oil standards per ISO 16703 requirement (TPH area does not include *n*-C_{10} and *n*-C_{40} peaks). Curve 2 was made using *n*-alkanes mixture following HJ 894-2017 and HJ 1021-2019 methods (TPH area includes *n*-C_{10} and *n*-C_{40} peaks). The correlation coefficient of each linearity curve was greater than 0.9998, exceeding the corresponding method requirements and indicating the FID's excellent linear response across the test concentration range.

To verify the calibration curve accuracy, two mineral oil calibrants were quantitated using the *n*-alkanes calibration curve. The alkanes linearity curve was re-established by integrating from the end point of the *n*-C_{10} peak to the beginning point of the *n*-C_{40} peak. The 500 and 4,000 mg/L mineral oil standards were measured with three injections under each concentration level. The quantitation results are shown in Table 3. The measured concentrations were 106.9 and 102.7% of the nominal values, demonstrating excellent linearity accuracy.

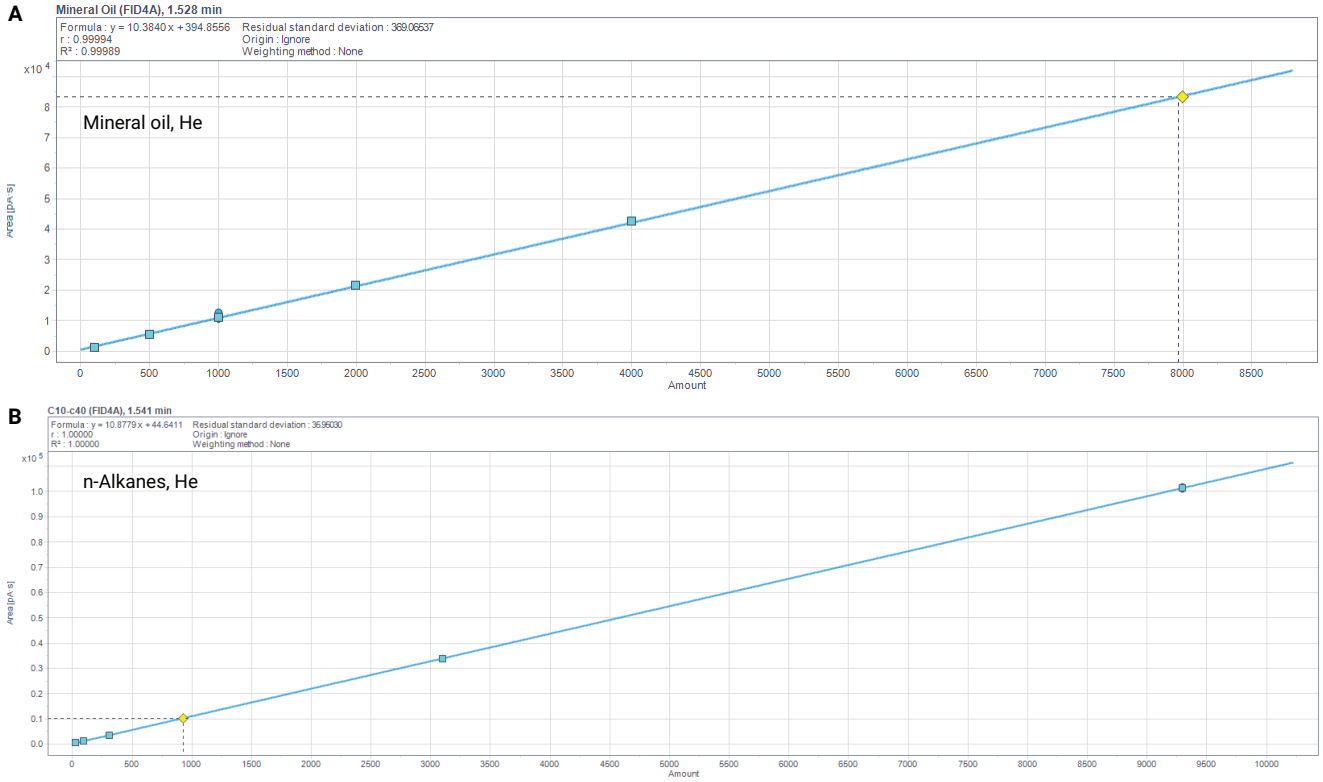

Figure 4. Calibration curve using mineral oil (A) and *n*-alkane (B) calibrants (He method).

Table 3. Calibration accuracy verification: Mineral oil standards quantitation using *n*-alkanes calibration curve.

	Mineral Oil Standard	
	500 mg/L	4,000 mg/L
Injection 1	539.4	4,099.2
Injection 2	535.6	4,120.9
Injection 3	528.4	4,105.2
Mean	534.5	4,108.4
SD	2.69	15.34
%RSD	0.50%	0.37%
Accuracy	106.9%	102.7%

Carryover performance

The system carryover performance was evaluated by comparing the chromatograms of 9,300 mg/L *n*-alkanes (blue) and the following solvent blank (aqua), as shown in Figure 5. The area covering the *n*-C_{10} to *n*-C_{40} RT window in two injections was compared, and the ratio ($Area_{blank}/Area_{sample}$) was 0.05%. This excellent carryover performance was based on a clean standard sample.

For real sample extracts, the system blank is impacted mainly by the sample matrix. To achieve a sufficiently clean system blank, proper sample purification, and timely maintenance of GC inlet and column is necessary. The 8850 GC has the intelligent capability of tracking the use of GC consumables to guide the maintenance process, which can help extend instrument uptime.

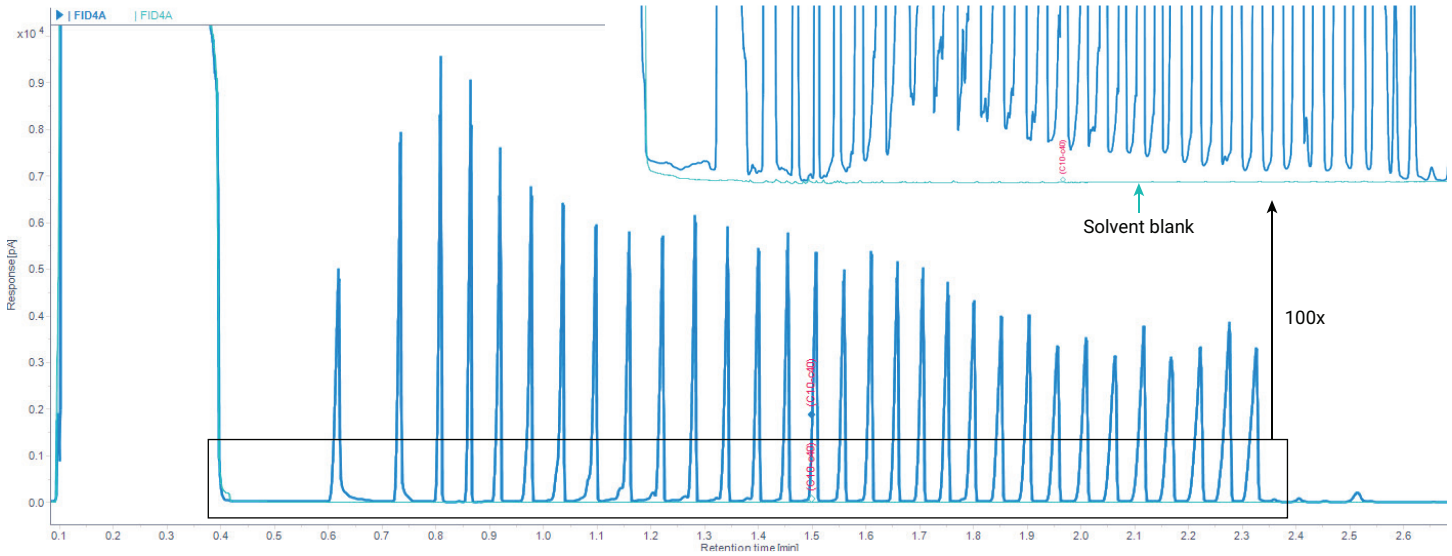

Figure 5. Solvent blank after 9,300 mg/L *n*-alkanes standard analysis.

Real sample analysis

TPH extracts from water and soil samples (both chromatograms are shown in Figure 6) were analyzed using the ultrafast method. The TPH in water sample was measured at 703 mg/L (corresponding to 70.3 mg/kg in the real sample). The TPH in soil extract was estimated to be 21,575.6 mg/L (approximately 2,157.5 mg/kg), which exceeded the calibration range. Under normal circumstances, a dilution for re-analysis or re-extraction on a lower amount of sample would be needed if an accurate quantitation is required for a highly contaminated sample. However, in this study, reanalysis was not performed; instead, the repeatability of the test results was demonstrated at different concentrations. As shown in Table 4, the quantitation precision of real samples (quantitation followed HJ methods) was consistent with the above-mentioned precision performance based on the *n*-alkanes and mineral oil standards.

Table 4. Quantitation precision of water and soil samples.

	Water Sample (mg/L)	Soil Sample (mg/L)
Run1	696.835	21,613.108
Run2	710.080	21,538.217
Run3	706.085	21,734.649
Mean	703.457	21,575.663
SD	6.794	99.135
%RSD	0.965	0.459

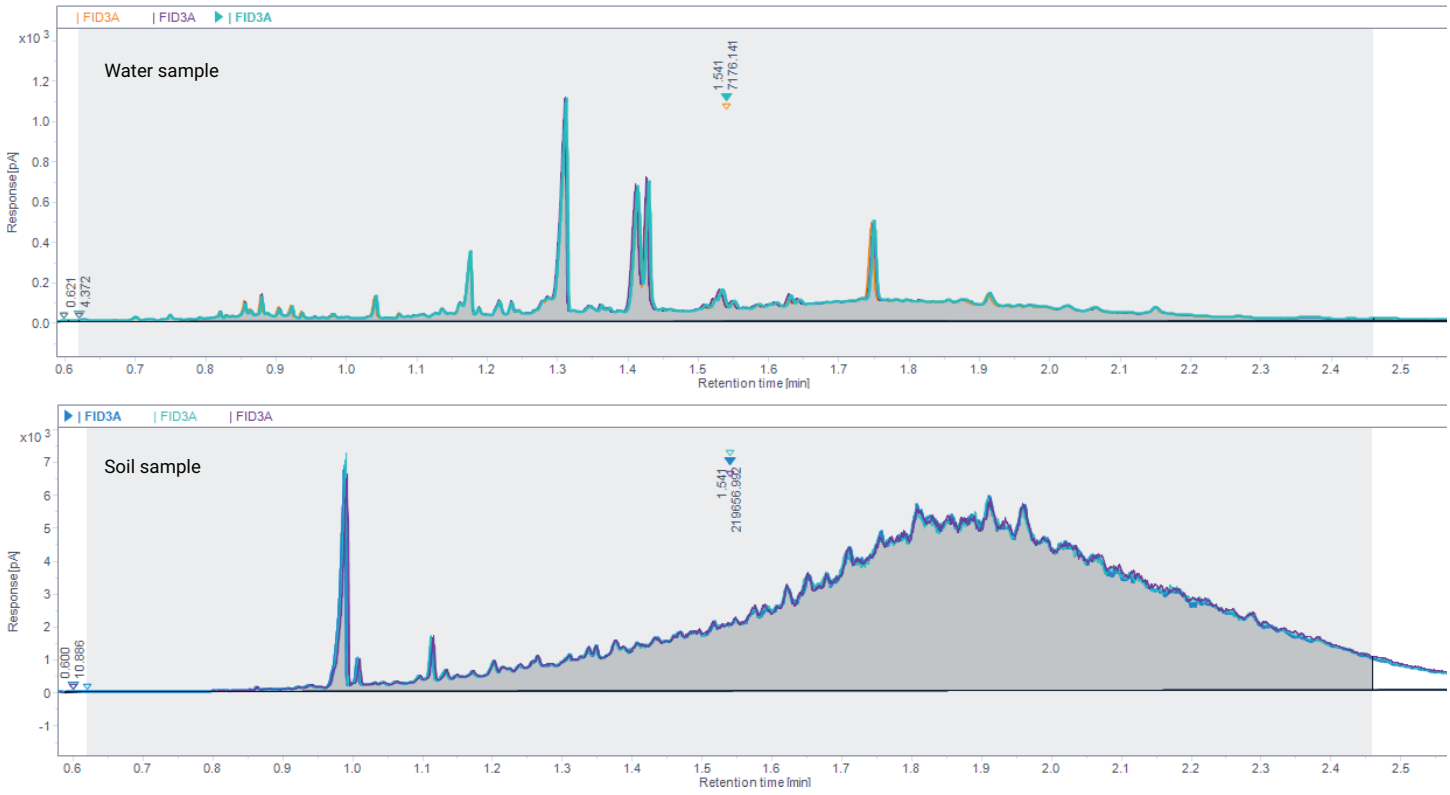

Figure 6. Chromatograms of TPH extracts from water and soil samples using the He method.

Ultrafast TPH analysis using hydrogen carrier gas

To handle the He shortage issue, more labs are transferring their GC methods from He to H_2 carrier gas. In this work, the TPH analysis using H_2 carrier gas was evaluated in case such a method transition is needed in some test labs.

The parameters in H_2 method were translated from the He method using the Agilent Method Translator tool in OpenLab CDS software. When translating the method, the speed gain was selected as 1.0, thus the oven ramp program was unchanged and the resulting column flow rate was translated to 5.5 mL/min. The chromatograms using H_2 and He carrier gas are shown in Figure 7. The RTs of each *n*-alkane in two methods are very close to each other because the speed gain was chosen as 1.0. The peak shape using H_2 carrier gas was slightly better than that obtained by the He method because H_2 has a low plate height and flatter Golay curve at high linear velocities compared to He.

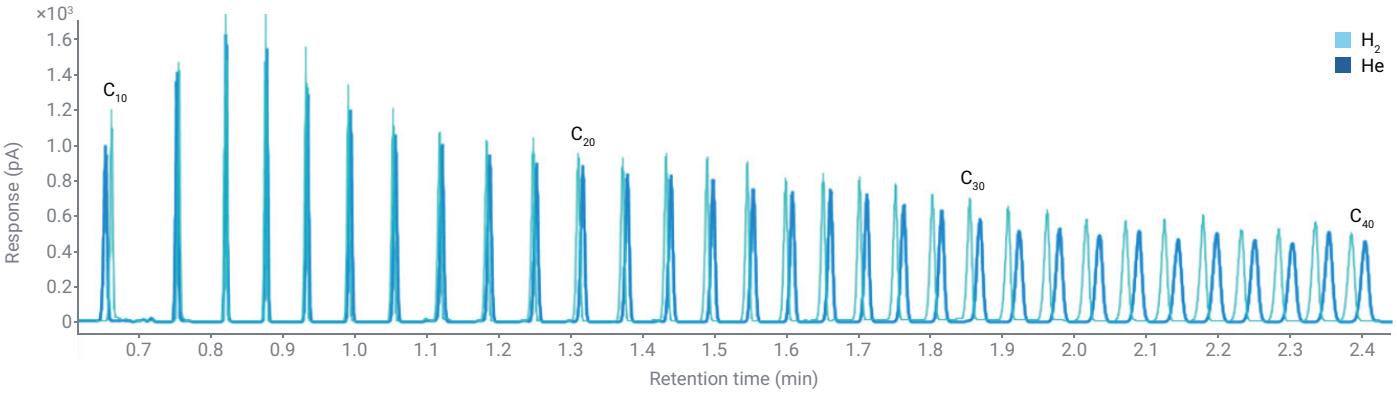

Figure 7. Separation of 30 mg/L *n*-alkanes using H_2 and He methods.

The system repeatability and linearity were evaluated based on the same approach used for the He method. The response repeatability results were comparable between the two methods, as shown in Figure 3. The linearity performance was also satisfactory, with R^2 of both calibration curves exceeding 0.999 (Figure 8).

Autonomous evaluation of suitability test results using peak evaluation

In the routine analysis of TPH samples, the *n*-alkanes standard is included in the sample batch for system suitability evaluation. The assessment of the suitability test result, particularly the response ratio of *n*-C_{40} to *n*-C_{20}, is usually conducted by analysts after the chromatograms are processed by data analysis software. If the response ratio falls below 80%, corrective action is required to restore instrument performance before analyzing real samples. With the peak evaluation feature on the Agilent 88x0 Series GCs, this suitability test result can be evaluated automatically by the GC itself. When executing a sequence that includes the suitability sample and real samples, the 8850 GC can automatically locate and integrate the *n*-C_{20} and *n*-C_{40} peak upon completion of the suitability sample acquisition. The 8850 GC can also calculate the response ratio and compare it with the preset limit in the method. If the ratio falls below 80%, the GC will generate a red warning and take action during the sequence based on the preconfigured Action on Failure settings in the peak evaluation method.

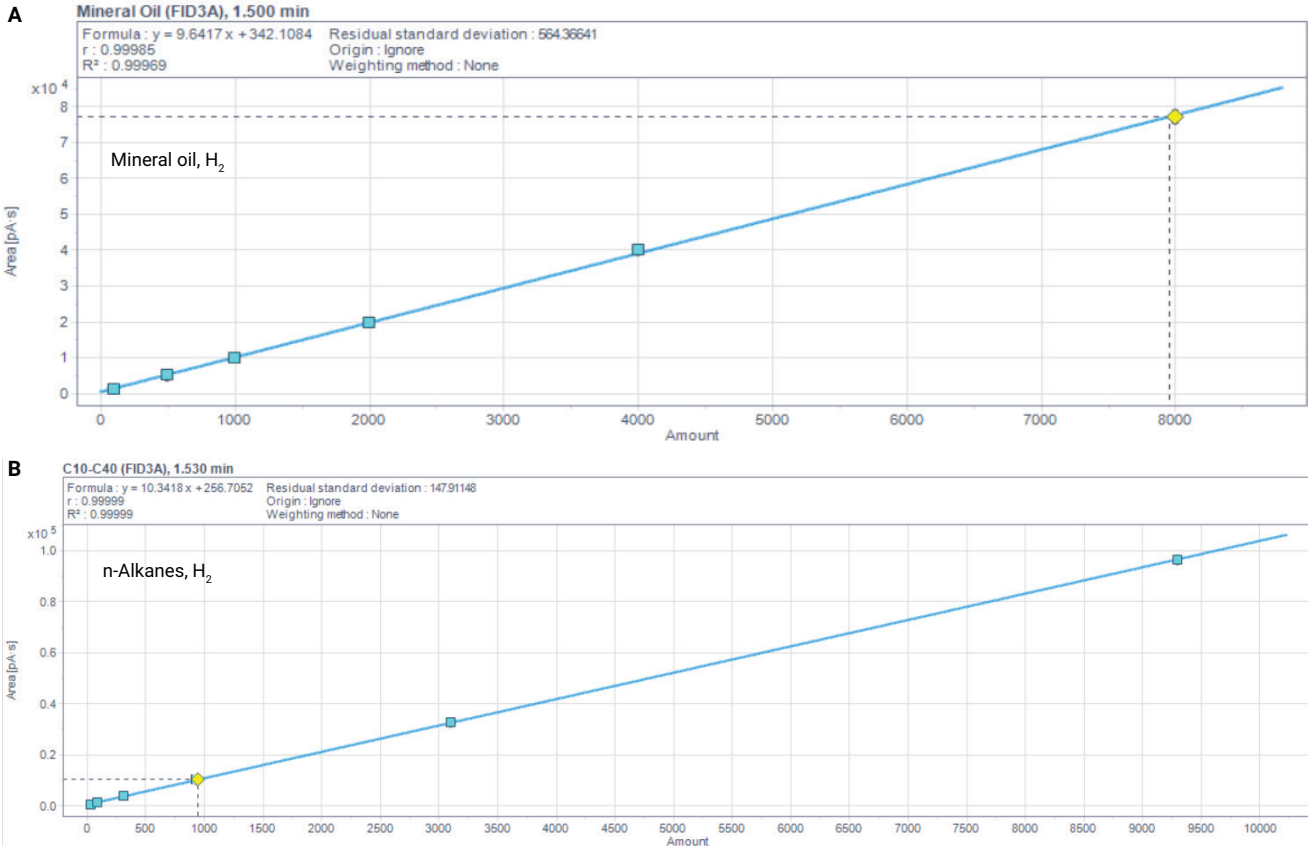

Figure 8. Calibratiaon curves of *n*-alkanes and mineral oil calibrants using H_2 carrier gas.

To conduct peak evaluation, a reference chromatogram and evaluation method needs to be set up as follows:

Step 1 – Generate a reference chromatogram: Reference chromatogram generation is performed to establish the reference point of the target evaluation. The reference chromatogram is acquired through Peak Evaluation Setup, a GC plugin tool in Openlab CDS. The acquired chromatogram can be integrated by the GC according to the settings in the Integrations Settings tab. The resulting peak list is saved in the GC for later use. Figure 9 shows the reference chromatogram and the peak list generated from the chromatogram after onboard integration by the GC.

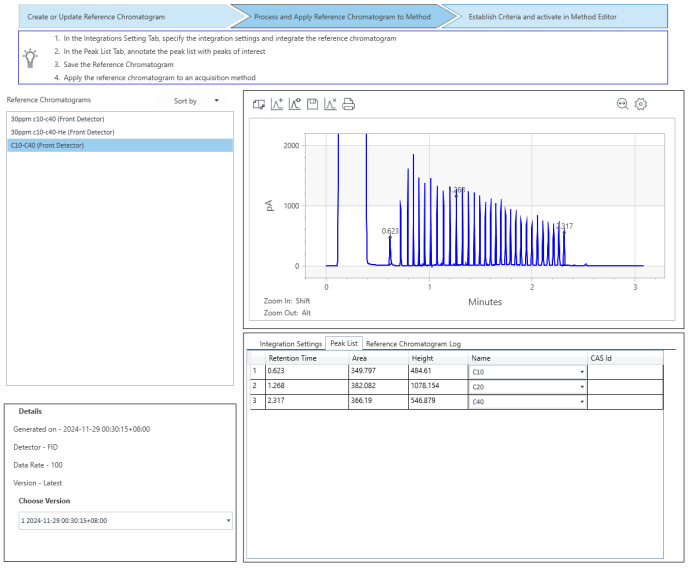

Figure 9. Reference chromatogram of 10 mg/L *n*-alkanes and its integration result according to the preset integration events.

Step 2 – Select target compounds from the peak list for evaluation: With the integration of the reference chromatogram, its peak list is generated and shown in the Peak List review table in the Peak Evaluation window of the acquisition method. The peak of interest can be selected from this table for further evaluation. Here, *n*-C_{20} and *n*-C_{40} were selected for evaluation (Figure 10).

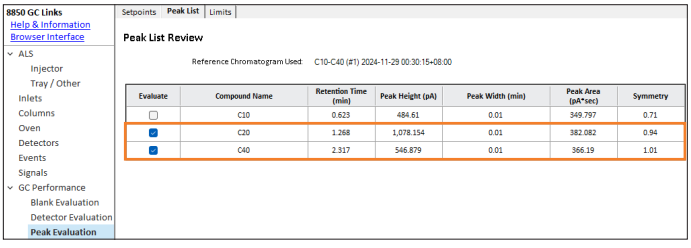

Figure 10. Probe compound peak selection from the peak list of the reference chromatogram.

Step 3 – Choose peak attributes that need evaluation, and set evaluation limits: Under the Limits tab of the Peak Evaluation window, the peak attributes and the acceptable limits can be set. As shown in Figure 11, two metrics – Retention Time and Relative Peak Area – are selected, and the corresponding limits are set for *n*-C_{40}. The GC uses the reference RT to identify the *n*-C_{40} peak in the following suitability analysis. For relative peak area computation, *n*-C_{20} was selected as the comparison compound. The low limit of their response ratio was set at 16.52% instead of 80% because the limit set point (%) is a relative value compared to what is obtained in the reference chromatogram. Here, 16.52% lower than the *n*-C_{40}/*n*-C_{20} response ratio (0.9580) in the reference chromatogram means that the absolute response ratio low limit is approximately 80% (the calculation was made according to Equation 1). The Retention Time metric of *n*-C_{20} was selected for identification of the *n*-eicosane peak.

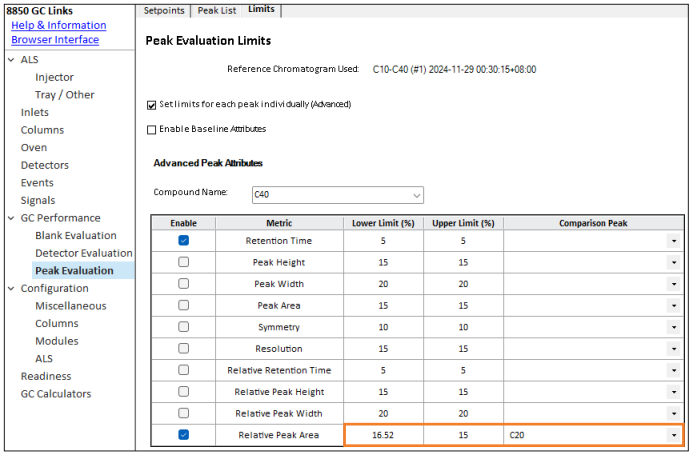

Figure 11. Peak evaluation limits for *n*-C_{40} peak.

Equation 1.

The absolute low limit of *n*-C_{40}/*n*-C_{20} response ratio = $Area_{C40}/Area_{C20}$ ratio in reference chromatogram × [1 - lower limit (%)]

Step 4 – Action on Failure setting

There are two action options triggered by the failed evaluation result: Abort and Continue. The Abort action means that the sequence will stop if the *n*-C_{40} versus *n*-C_{20} relative peak area evaluation result is less than 80%. The Continue action means the sequence will continue, but a red warning sign will be generated on the GC touch screen and software interface to indicate that the system performance needs correction action. In this work (Figure 12), **Abort** is selected.

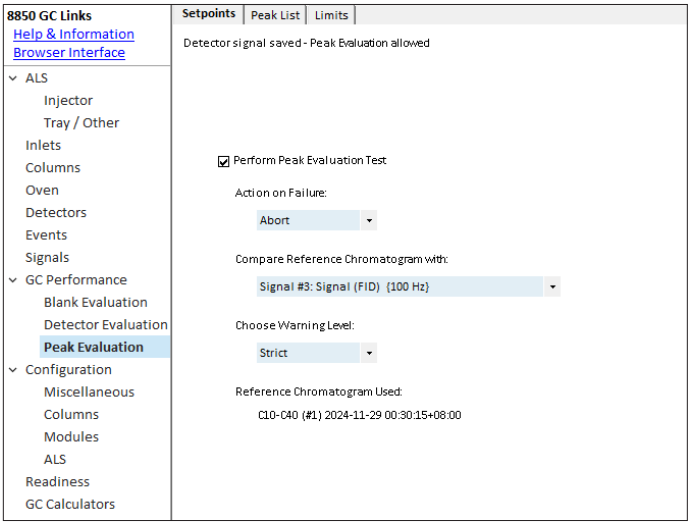

Figure 12. Peak evaluation test failure action setting.

When the above settings are completed and saved, the peak evaluation method can be applied for suitability sample test. In this work, a sequence of three solvent blanks, one suitability sample, and 10 real samples was repeated to test whether the peak evaluation function can effectively monitor inlet performance and stop the sequence as expected. During the first 30 injections of TPH extracts, the *n*-C_{40}/*n*-C_{20} response ratio decreased from 0.9423 to 0.8365, as shown in the peak evaluation reports of the first four suitability tests (Figure 13). The sequence was stopped after the fifth suitability test failed with the *n*-C_{40}/*n*-C_{20} response ratio decreasing to 0.7806. It was found that 40 samples were analyzed before the system performance deteriorated below the suitability test performance requirement.

One of the main reasons for *n*-C_{40} recovery failure is inlet liner contamination. When the liner was replaced, the *n*-C_{40}/*n*-C_{20} response ratio was recovered to 0.9652. The TPH extracts used here are from heavily contaminated soil samples (the actual TPH concentration was 5 to 20 times the calibration maximum limit), which is why only 40 injections degenerated the liner's performance to an unsuitable level. If the sample matrices are cleaner, the liner can endure more injections. In fact, it is difficult for test labs to know the sample matrix complexity and predict how many injections can be made before changing the liner/septum. Usually, test labs define the frequency of liner/septum maintenance, which is often established based on previous experience, as part of an analysis SOP.

The peak evaluation tool can track liner performance and give a more precise estimation on when to perform inlet maintenance in this case. In addition, for the sequences run overnight, with the peak evaluation action set as Abort, the sequence will stop if the evaluation result shows "failed". The saved samples can be analyzed after the system performance is recovered by inlet maintenance.

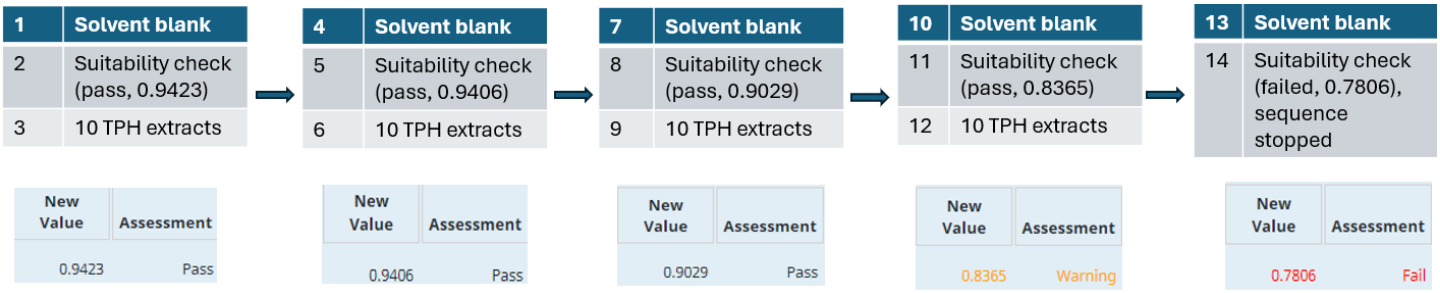

Figure 13. Peak evaluation used in suitability test to monitor liner performance.

Conclusion

This application note demonstrates an ultrafast TPH analysis on an Agilent 8850 GC. The system performance using He carrier gas was verified according to ISO 16703, HJ 1021-2019, and HJ 894-2017 methods, including resolution, system suitability, repeatability, linearity and carryover. The system demonstrated excellent performance in all of these areas.

Also demonstrated is an ultrafast analysis using H_2 carrier gas. The H_2 method showed equivalent performance in terms of *n*-C_{40}/*n*-C_{20} recovery, linearity range, and RT/response precision.

The peak evaluation function of the 8850 GC is demonstrated in the application of autonomous system suitability verification, which can help effectively track GC inlet performance and indicate when maintenance is needed.

Overall, this application note demonstrates that an Agilent 8850 GC can generate reliable TPH analysis results and significantly improve lab productivity in an intelligent way.

References

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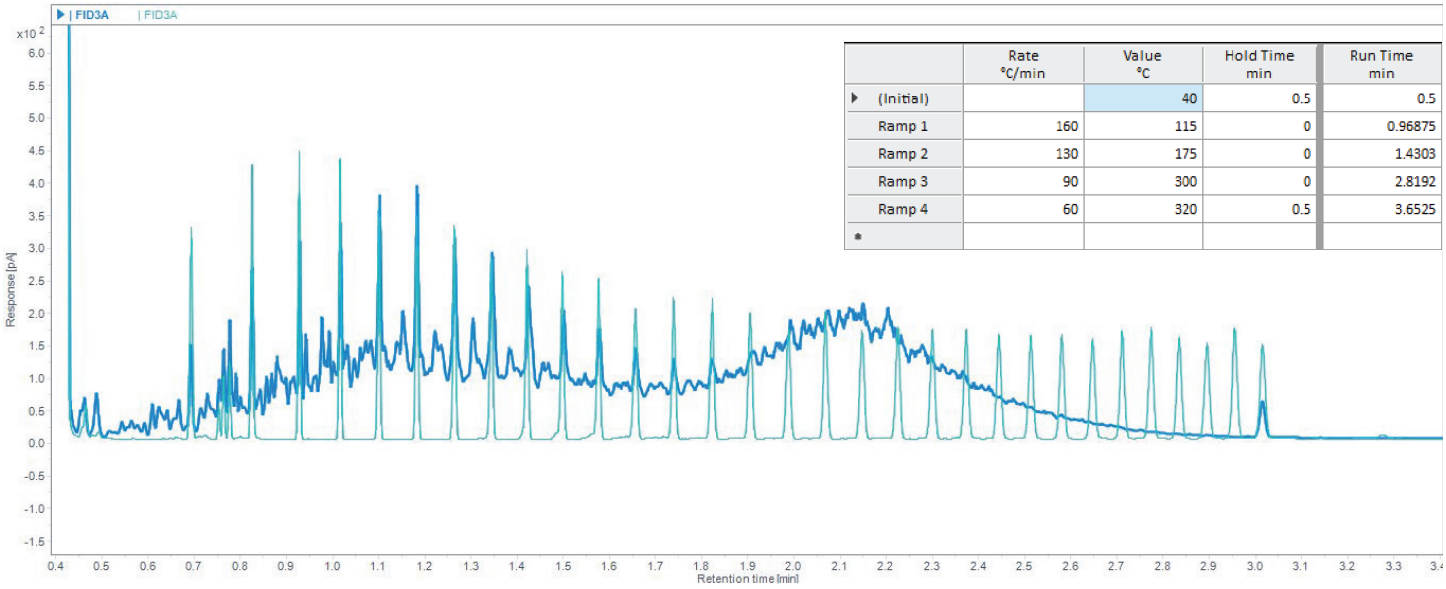
2. Soil and sediment- Determination of Petroleum hydrocarbons (C10-C40)-Gas Chromatography. HJ 1021-2019.
3. Water quality -Determination of Extractable Petroleum Hydrocarbons (C10-C40)-Gas Chromatography. HJ 894-2017.
4. McCurry, J. D. Analysis of Total Petroleum Hydrocarbons in Environmental Samples Using Ultrafast Gas Chromatography, *Agilent Technologies application note*, publication number 5991-7367EN, **2018**.

Appendix

Ultrafast TPH analysis on an Agilent 8850 GC using maximum 120 V fast oven ramp rates



	Rate °C/min	Value °C	Hold Time min	Run Time min
(Initial)		40	0.5	0.5
Ramp 1	160	115	0	0.96875
Ramp 2	130	175	0	1.4303
Ramp 3	90	300	0	2.8192
Ramp 4	60	320	0.5	3.6525

Figure A1. *n*-Alkanes separation using a 120 V fast oven ramp rate.

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