Ultra-Fast Total Petroleum Hydrocarbons (TPH) Analysis with Agilent Low Thermal Mass (LTM) GC and Simultaneous Dual-Tower Injection

Application Note

Environmental

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Abstract

This application note is targeted for ultra-high productivity of total petroleum hydrocarbons (TPH) analysis in environmental laboratories. Agilent's Low Thermal Mass (LTM) technology is employed here to perform ultra-fast gas chromatographic (GC) separations. The LTM technology uses a column module combining a fused silica capillary column with heating and temperature-sensing components wound around it, which can be heated and cooled very efficiently. In this application note, the speed of analysis for the hydrocarbon group eluting between C_{10} and C_{44} can be dramatically increased to about 13 times faster than a conventional method. In addition, the ultra-fast cooling function of an LTM module can reduce the total GC cycle time to 5.1 minutes. The simultaneous dual-tower injection from Agilent is used to further double productivity. The final result for TPH analysis productivity is 5.1 minutes per two samples.

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Introduction

Total petroleum hydrocarbons (TPH) is a term used to describe a large family of several hundred chemical compounds that originally came from crude oil. Many environmental laboratories in the world are analyzing the total amount of TPH at a site to evaluate the water or soil contamination by TPH, such as oil, gasoline, diesel fuel, etc.

The Agilent Low Thermal Mass (LTM) system (except for an external power supply) is built into a replacement GC oven door, which is mounted as an add-on to an Agilent 7890A GC. A version is also available for the Agilent 6890 GC. The key component of LTM system is the LTM column module combining a fused silica capillary column with heating and temperature-sensing components wound around it. The LTM system can heat and cool the column very efficiently for significantly shorter analytical cycle times as compared to conventional air bath GC oven techniques involving much higher thermal mass.

The GC method translation software from Agilent is a calculator used to scale a method between different column dimensions with equal or increased speed. In this application note, a 40-minute separation with a 30-meter column is translated into a 20-minute separation with a 15-meter column at first, without LTM technology. Then the method is further translated for LTM use with a 5-meter column within 3.1 minutes.

As a base for the LTM system, the Agilent 7890A can provide dual complete analysis channels. With a configuration of dual injection towers, single sample tray, dual split/splitless inlets, and dual detectors, the simultaneous TPH analysis can be accomplished to double lab productivity, in addition to the speed gains realized with LTM.

Experimental

Standard Preparation

The custom alkanes mix (cus-908) from Ultra Scientific (North Kingstown, Rhode Island, U.S.) contains n-alkanes from n-decane (C_{10}) to n-tetratetracontane (C_{44}) in hexane at the concentration listed in Table 1. Dilutions in dichloromethane are made up at 1.0, 5.0, 10.0, 50.0, and 100.0 µg/mL concentrations.

Table 1. Custom Alkanes Mix

Component	Concentration, mg/mL	Component	Concentration, mg/mL
n-decane	0.2	n-tetracosane	0.1
n-dodecane	0.1	n-hexacosane	0.1
n-tetradecane	0.2	n-octacosane	0.1
n-hexadecane	0.1	n-triacontane	0.1
n-octadecane	0.1	n-dotriacontane	0.1
n-eicosane	0.1	n-hexatriacontane	0.1
n-docosane	0.1	n-tetracontane	0.1
n-tricosane	0.2	n-tetratetracontane	0.1

Sample Preparation

Soil samples are mixed with sodium sulfate to remove excess moisture and then sonicated with 60-mL aliquots of dichloromethane, three times. Water samples are placed in a 2-L separate funnel. A 100-mL aliquot of dichloromethane is added and the mixture is shaken automatically for about 2 minutes. The liquid-liquid extraction is repeated two more times. For both matrices, the extract is concentrated on a steam bath to either 5 mL for a soil sample or 1 mL for a water sample. The extracts are not routinely treated with silica gel, unless specified.

Instrumentation and Conditions

Agilent 7890A GC with LTM system, consisting of:

G3440A	7890A Series GC system
#112	Split/splitless inlet with EPC (2)
#211	Capillary FID with EPC (2)
	Autoinjector modules (2)
	Autosampler tray module
G6579A	LTM system bundle for 2-channel LTM operation, for use with standard size LTM column modules (100–2000LTM DB-5 5 M × 0.32 mm id, 1.0 µm standard 5-inch LTM column module)

ChemStation 32-bit version B.04.01

Table 2. Gas Chromatograph Conditions

	Original 1X Method	2X Method	LTM Method
GC			
Agilent Technologies 7890A			
Inlet	EPC split/splitless	EPC split/splitless	EPC split/splitless
Mode	Constant pressure	Constant pressure	Ramp pressure
Injection type	Split	Split	Split
Injection volume (µL)	1.0	1.0	1.0
Inlet temp (°C)	300	300	300
Pressure, nominal (psig)	30	14.319	13.1 (0.1 min), 11.27 psi/min to 30 (1.5 min)
Liner	Helix liner, open ended, deactivated (p/n 5188-5396)	Helix liner, open ended, deactivated (p/n 5188-5396)	Helix liner, open ended, deactivated (p/n 5188-5396)
Split ratio	2:1	2:1	2:1
Gas saver	20 mL/min after 2 min	20 mL/min after 2 min	20 mL/min after 2 min
Gas type	Helium	Helium	Helium
Sample overlap	2 min after end of GC run	2 min after end of GC run	2 min after end of GC run
Oven	GC Oven	GC Oven	LTM module (p/n G6579A) with GC oven 300 °C for 3.1 min
Initial oven temp (°C)	40	40	40
Initial oven hold (min)	1	0.5	0.1
Ramp rate (°C/min)	10	20	200
Final temp (°C)	320	320	340
Final hold (min)	11	6.5	1.5
Run time (min)	40	21	3.1
Cooldown time (min)	5.4	5.4	2
Cycle time (min)	45.4	25.4	5
Column			
Type	DB-5 (p/n 123-5032)	DB-5 (p/n 123-5012)	DB-5 (p/n*)
Length (m)	30	15	5
Diameter (mm)	0.32	0.32	0.32
Film thickness (um)	0.25	0.25	1.0
FID			
Telperature (°C)	300	300	300
H_2 flow (mL/min)	30	30	30
Air flow (mL/min)	400	400	400
Makeup flow (mL/min)	25	25	25
Sampling rate (Hz)	50	50	50

*100–2000LTM DB-5 5M x 0.32 mm id, 1.0 µm standard 5-inch LTM column module

Results and Discussion

Ultra-Fast Separation of n-alkanes Mixture with LTM System and Scale-Up Using the GC Method Translator

The application is started with the analysis of a standard mixture of n-alkanes, containing n-C_{10}, n-C_{12}, up to n-C_{44}. Figure 1 compares the chromatogram of the standard mixture using three different methods in the same time scale. With the LTM system, the GC run time can be more than 10 times faster than conventional methods. In terms of cooling down, the classical GC oven such as 7890 fast oven will take about 5.4 minutes from 320 to 40 °C. Relatively, the LTM system has a much lower thermal mass, which can perform ultra-fast cooling. In this case, the LTM system will take about 2 minutes from 340 to 40 °C, for dual parallel LTM modules. In addition, sample overlap of the 7890 sample tray can prepare the sample after the end of the last GC run parallel with GC oven cooldown. The resulting cycle time for LTM is 5.1 minutes, which means about nine times faster than the conventional method.

Resolution is also a concern with fast analysis. Figure 2 is the expanded view of Figure 1 with the nominal time scale, which demonstrates that all the peaks of n-alkanes are baseline separated, even with the nine-times-faster LTM method (speed calculated by total cycle time). The result is calculated by total amount of TPH, not by the individual peak amount; peak-grouping of ChemStation is employed here. The calibration is checked by injecting the standard mixture in different concentration levels, ranging from 1 to 100 µg/mL. The calibration curve of the LTM method is displayed in Figure 3, with average n-alkanes response factor by peak-grouping.

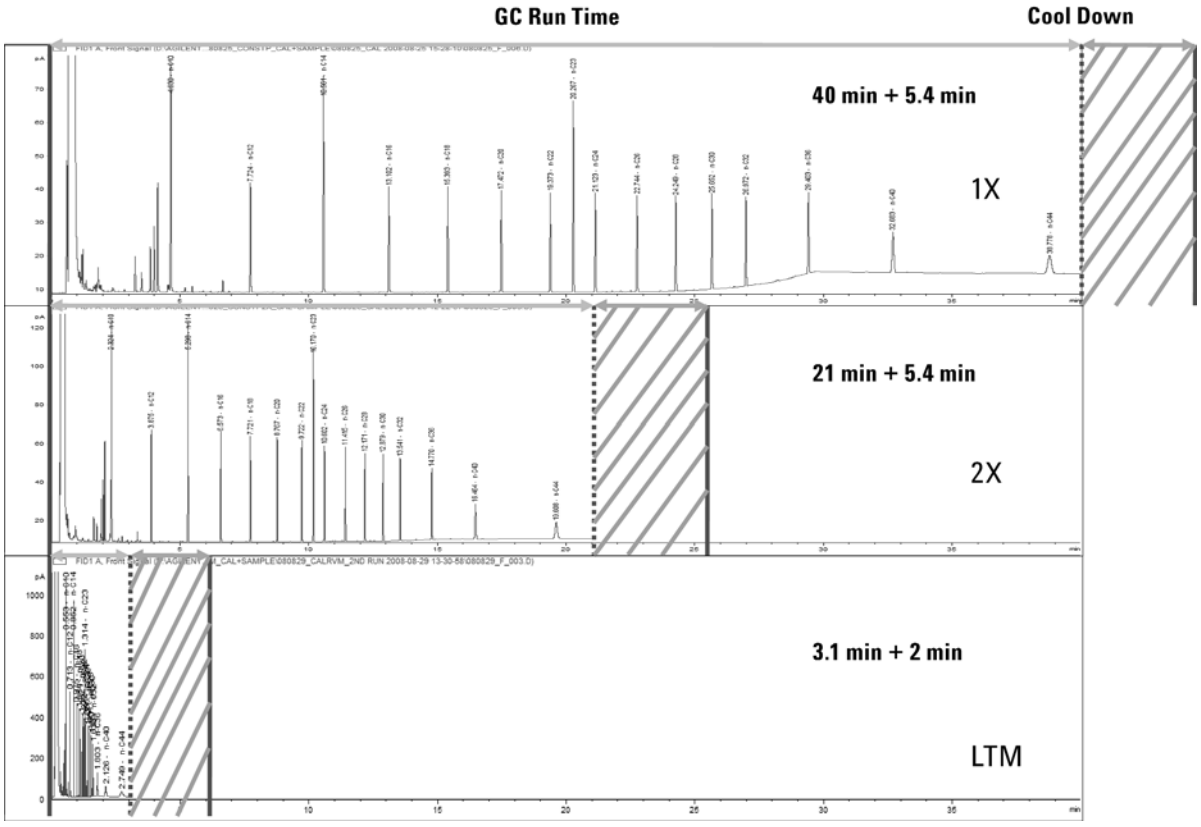

Figure 1. Comparison of conventional method and LTM method.

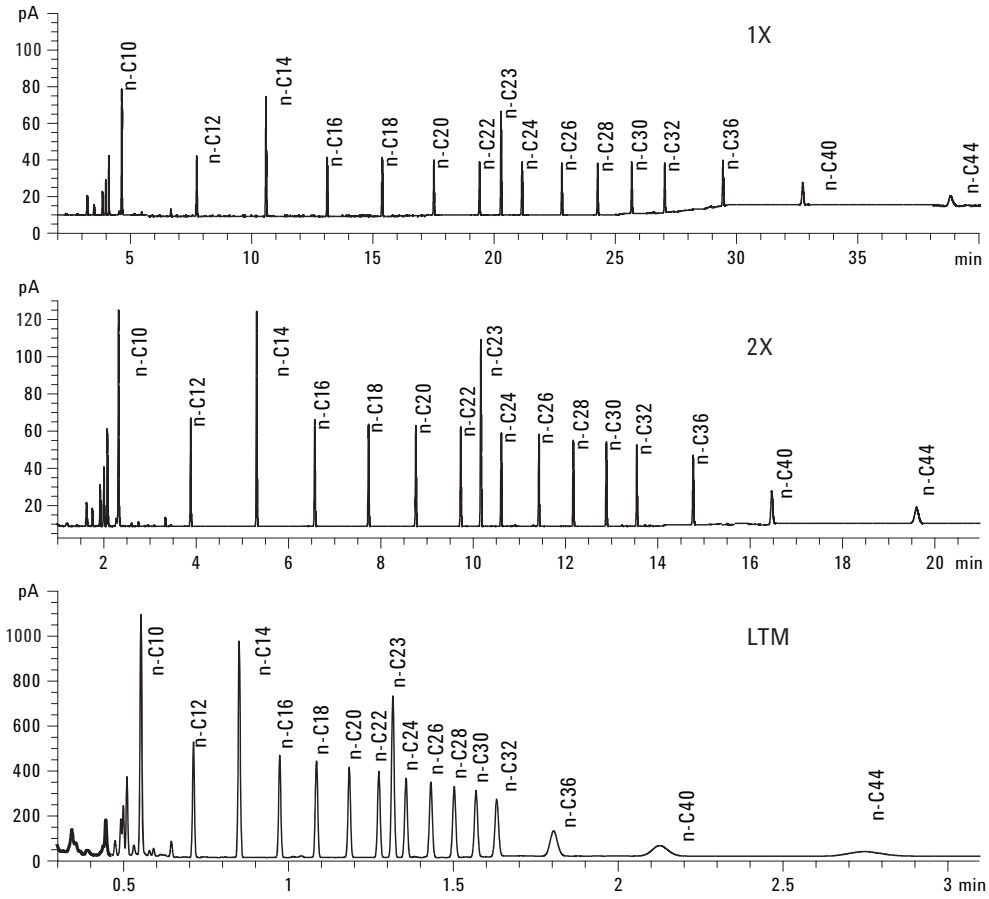

Figure 2. Expanded view of Figure 1, with the nominal time scale.

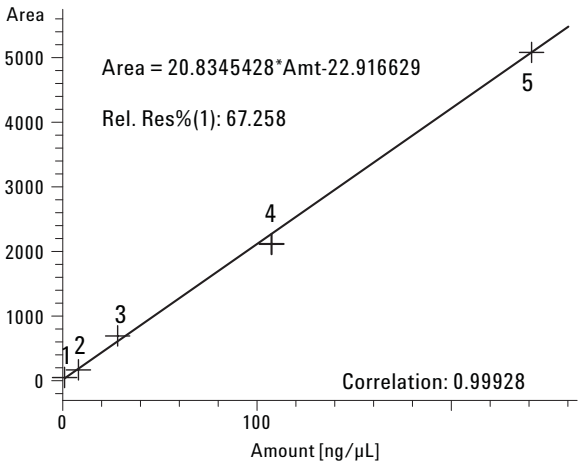

Figure 3. Calibration curve of LTM method after peak-grouping.

Simultaneous Dual-Channel Analysis with Agilent Dual-Tower Injection

Agilent 7890A and 6890 GCs make dual-channel analysis possible, with the configuration of a single sample tray and dual injection towers, inlets, columns, and detectors. Typically, a dual-channel configuration is used to identify target compounds in one GC run, using different retention time in columns of different polarity. The purpose here is to double lab productivity using dual identical channels at a much lower cost compared to two single-channel instruments. ChemStation can provide different choices for final data file generation. Figure 4 shows one option of detection signal setting for separating the dual-tower injection into two individual data files. Figure 5 is the chromatogram of two real samples with simultaneous dual-tower injection.

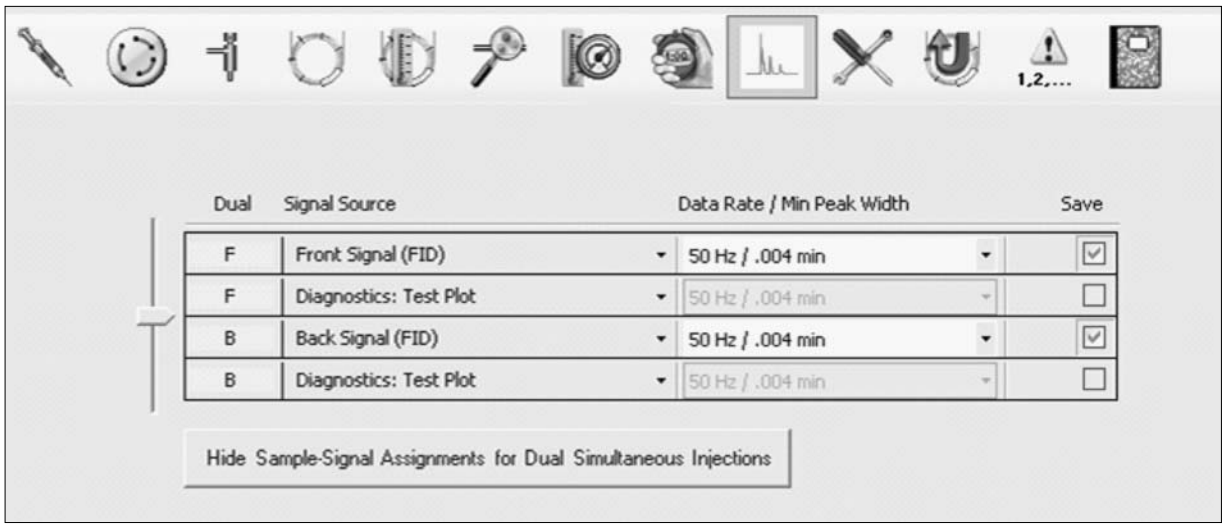

Figure 4. Signal setting for dual-tower injection to generate two individual data files.

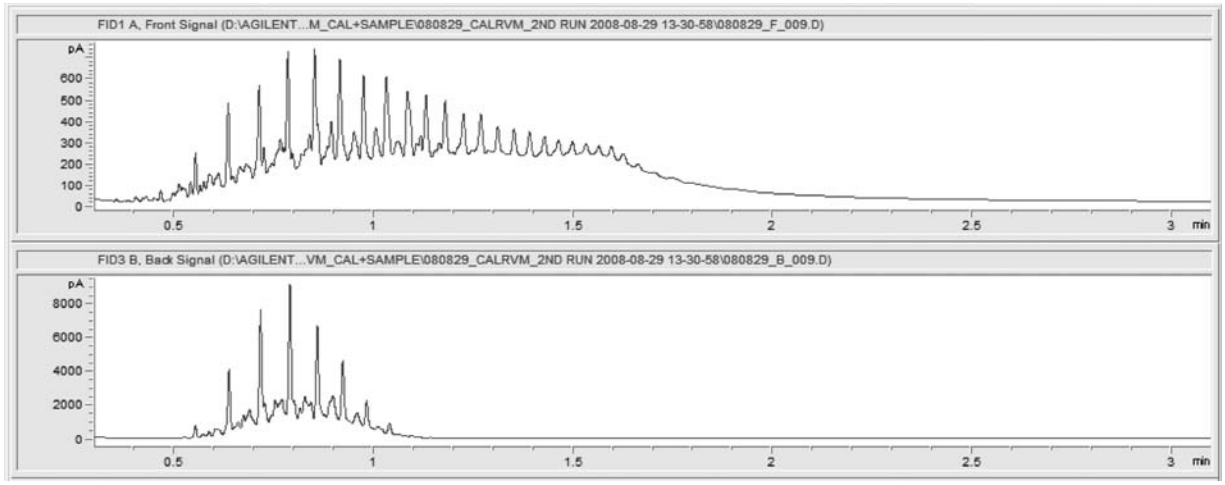

Figure 5. Chromatogram of two real samples with simultaneous dual-tower injection.

Quantitative Analysis of TPH with Peak-Grouping and Peak-Summing

Peak-grouping is used to average each n-alkane response factor. With this average response factor, the nominal calibration curve can be used for quantitation of each peak, including unidentified peaks eluting between n-C_{10} and n-C_{44}. In this case, the compound peak-grouping details and unidentified peak calibration settings can be seen in Figure 6.

Another requirement for TPH analysis is quantitation across the whole eluting time range between n-C_{10} and n-C_{44} to calculate all petroleum hydrocarbons not only n-alkanes. Baseline-holding and peak-summing in the ChemStation integration events table are necessary to meet this requirement; the related setting can be seen in Figure 7. For example, the integration result of real sample is shown in Figure 8.

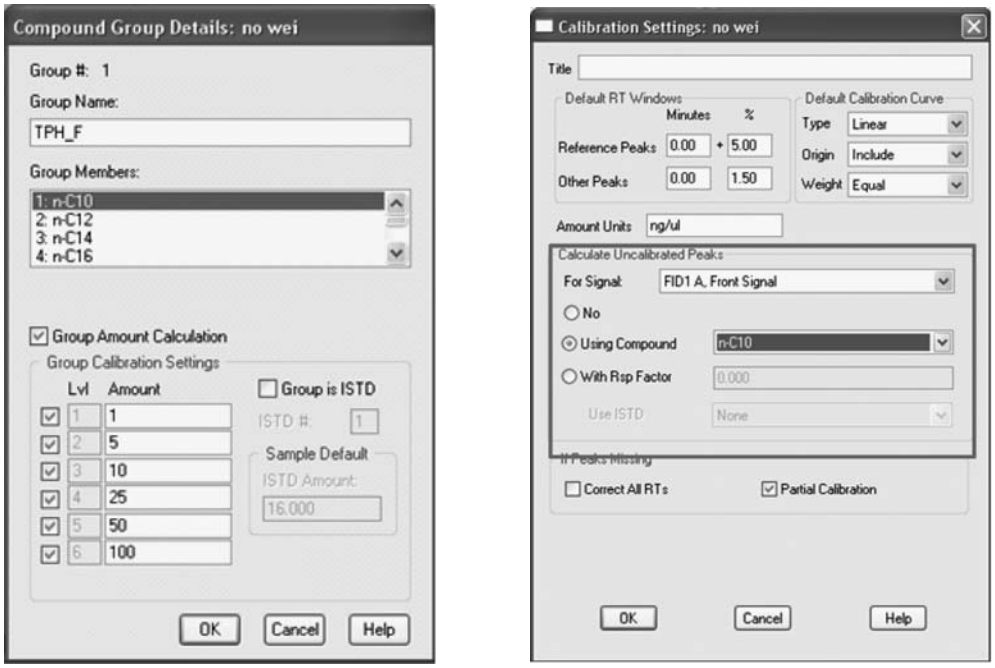

Figure 6. Peak-grouping (left) and unidentified peak calibration setting (right) in ChemStation.

Time	Integration Events	Value
Initial	Slope Sensitivity	10
Initial	Peak Width	0.04
Initial	Area Reject	1
Initial	Height Reject	1
Initial	Shoulders	OFF
0.000	Integration	OFF
4.560	Area Sum	ON
4.560	Baseline Hold	ON
4.560	Integration	ON
39.100	Integration	OFF
39.100	Area Sum	OFF

Figure 7. Baseline-holding and peak-summing setting in the ChemStation integration events table.

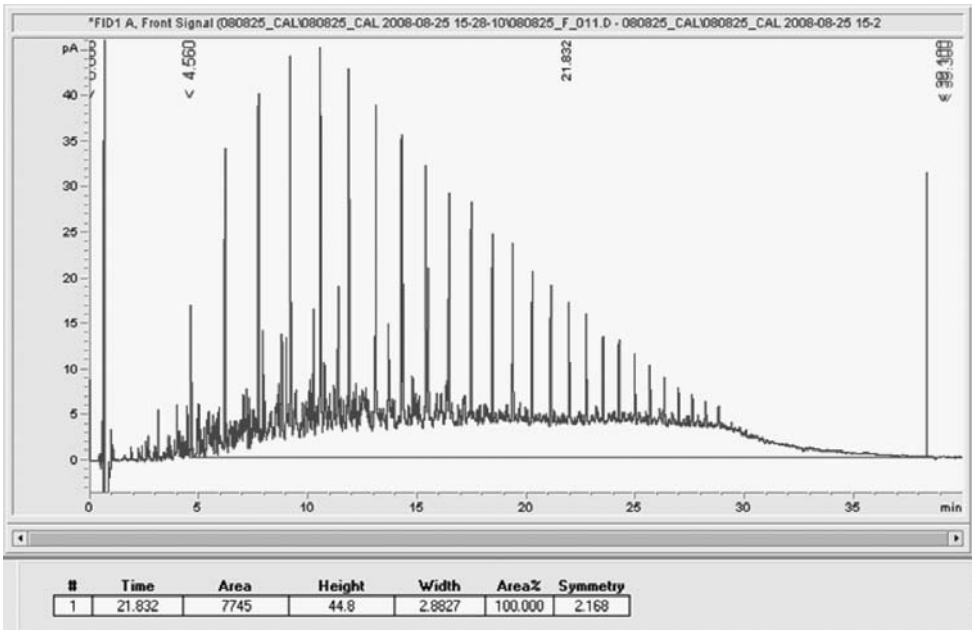

Figure 8. Integration result of real sample after baseline-holding and peak-summing.

Real Sample Analysis

After calibration by peak-grouping and integration through peak-summing, the quantitation result can be reported as the total amount of TPH in a real sample. As a comparison of quantitation results with three different acquired methods, Table 3 demonstrates that the real sample analysis result by the ultra-fast LTM method is comparable with conventional methods.

Table 3. Comparison of Quantitation Result with Three Different Acquired Methods

	TPH Concentration (µg/mL)
Original method (30 m)	1097
2X method (15 m)	920
LTM method (5 m)	909

Conclusions

The low thermal mass of the Agilent LTM system can perform very efficient column heating and cooling, and is used here to develop an ultra-fast TPH analysis to meet the requirement for high lab productivity. Dual-tower injection is also used to further double the productivity with much less cost. The final solution with the LTM system and dual-tower injection can perform TPH analyses at a rate of 5.1 minutes per two samples. The total productivity increase is 18x compared to a conventional analysis on a single-channel system.

References

1. "Agilent Low Thermal Mass (LTM) System for Gas Chromatography," Agilent Technologies publication 5989-8711EN, June 2008
2. Wei Luan, Chuanhong Tu, and Michael Woodman, "Evaluation of Total Petroleum Hydrocarbon in Soil Using LC with Fraction Collector and GC/MS," Agilent Technologies publication 5989-6012EN, April 2007

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