Analysis of Total Petroleum Hydrocarbons in Environmental Samples Using Ultra-Fast Gas Chromatography

Application Note

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Abstract

An ultra-fast gas chromatography (UFGC) method was developed for the determination of total petroleum hydrocarbons in environmental samples. A three-minute analysis time was achieved by a using short, thin film capillary column, fast column heating ramps, and high carrier gas flows. This method was demonstrated to meet all performance criteria outlined by the ISO 16703 method. In addition to short analysis times, this UFGC method provided highly accurate and precise results. This was demonstrated by preparing and analyzing certified reference soil and river sediment samples containing two different amounts of TPH contamination.

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Introduction

Gas chromatography (GC) is the preferred technique for the quantitative analysis of total petroleum hydrocarbon (TPH) contamination in water, soil, and sediments. A number of methods have been developed to standardize this analysis within each regulatory geography. One widely used method is ISO 16703, which is designed to measure saturated, cyclic, and aromatic hydrocarbons with carbon numbers between n-decane ($C_{10}H_{22}$) and tetracontane ($C_{40}H_{82}$)[1]. This method excludes the analysis of polyclyclic aromatic hydrocarbons (PAH), which are removed from the sample using a multistep sample preparation protocol. The chromatographic analysis of the hydrocarbons does not require speciation of individual compounds or classes of compounds. Rather, the peaks are eluted from the column as an unresolved hump. This aspect makes the analysis suitable for ultra-fast gas chromatography (UFGC), where short columns are combined with fast oven programming and high carrier gas flows to reduce analysis time. UFGC is particularly attractive to contract laboratories trying to maximize sample throughput and minimize turn-around time.

The Agilent Intuvo 9000 Gas Chromatograph is designed with UFGC in mind. The unique direct column heating technology eliminates the traditional air-bath column oven, and provides 250 °C/min column heating rates from 40 °C to 350 °C. When using rapid column heating, high column flows must be precisely maintained to ensure excellent retention time repeatability from run to run. Synergy between the column heating and flow is accomplished on the Intuvo 9000 GC with the 6th generation electronic pneumatics control (EPC) inlet module. This Application Note presents an UFGC method for TPH analysis translated from ISO 16703. This UFGC approach meets the performance benchmarks set by the ISO 16703 method.

Experimental

Sample preparation

For this work, a TPH-contaminated soil sample (BAM-U021) and river sediment sample (BAM-U022) were obtained from the Bundesanstalt für Materialforschung und –prüfung in Germany. A consensus value of the TPH content for each sample is published along with an uncertainty measure for those values.

Each sample was prepared in duplicate using the extraction and cleanup procedure described in the ISO 16703 method:

- Fifteen grams of sample were ultrasonically extracted with acetone and a retention time window (RTW) standard solution (C10 and C40 dissolved in heptane).

- Sample extracts were centrifuged to remove fine particles.

- The clear extracts were washed twice with 100 mL of water.

- The organic layer was collected and dried with sodium sulfate.

- Ten milliliters of dry organic extract was cleaned with an SPE cartridge containing activated Florisil.

To facilitate the sample preparation, a kit is available from Sigma-Aldrich Company containing all components needed for the ISO 16703 procedure (p/n 56681-1KT-F)[2].

Ultra-fast gas chromatography

An Agilent Intuvo 9000 Series Gas Chromatograph was configured as follows:

- Split/splitless inlet

- Agilent Focus Liner, tapered, deactivated with glass wool (p/n 210-4022-5)

- Agilent Intuvo 9000 Guard Chip

- Single detector Intuvo Flow Technology flow path

- Agilent DB-5ht column, 5 m × 0.32 mm, 0.1 µm film

- Flame ionization detector

- Agilent 7693 Automated Liquid Sampler (ALS) with 10 µL syringe

Table 1 shows the operating conditions for the instrument.

Table 1. Instrument conditions.

Parameter	Value
Inlet	Splitless at 350 °C
Injection volume	0.5 µL
Constant column flow	10 mL/min helium
Column temperature program	40 °C for 0.5 minutes 250 °C/min to 350 °C 350 °C for 1.3 minutes
Intuvo flow path	Guard chip: track oven mode Bus: default (350 °C)
Detector	Flame ionization at 350 °C

Before proceeding with the calibration and analysis, a suitability test was performed by injecting a heptane solution containing 50 mg/mL of even-numbered normal alkanes from $C_{10}H_{22}$ to $C_{40}H_{82}$. This test verified the GC system's performance for resolution, recovery, and response. A six-level calibration from 0.24 mg/mL to 8.0 mg/mL was done using standards containing two different types of mineral oil. The third calibration standard (1 mg/mL mineral oil) served as the control solution for the repeatability test. After calibration, the extracts of each sample duplicate were analyzed five times to measure the precision and accuracy.

Results and Discussion

Figure 1 and Table 1 show the results of the system suitability test. The decane peak is well-separated from the heptane solvent front, and each *n*-alkane in the mixture is baseline resolved. The response of tetracontane (C40) was measured at 0.93 with respect to the eicosane (C20) response. This value exceeds the method lower limit of 0.80, indicating excellent system performance with respect to boiling point discrimination.

Figure 2 shows the calibration performance. The correlation coefficient of 0.9998 indicates a good linear fit across the full calibration range. A calibration repeatability test was done by measuring the detector response of three sequential injections of calibration standard 3 (1 mg/mL). Table 2 shows the results. The measured relative standard deviation (RSD) of 1.7 % was below the required maximum of 5 % RSD.
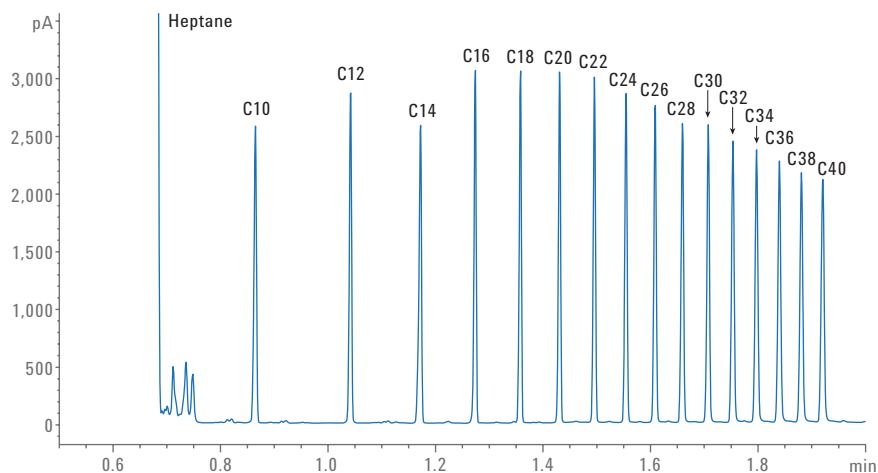

Figure 1. Separation of hydrocarbons using an Agilent Intuvo 9000 GC.

Table 1. Recovery of C10 to C40 hydrocarbons in the TPH performance mixture.

	Peak area	recovery
C10	861	0.98
C12	867	0.98
C14	877	0.99
C16	890	1.01
C18	875	0.99
C20*	882	1.00
C22	882	1.00
C24	882	1.00
C26	873	0.99
C30	867	0.98
C34	859	0.97
C36	853	0.97
C38	829	0.94
C40	817	0.93

Table 2. Results of the ISO 16703 calibration repeatability test.

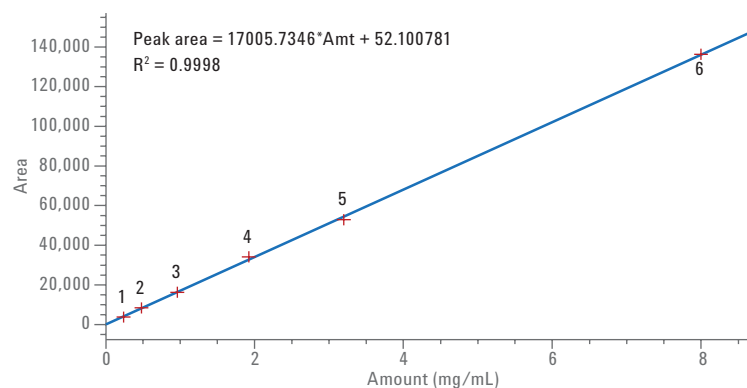| Run	Standard 3 peak area
1	18,044
2	17,644
3	18,236
Mean	17,975
Std dev	301.9
RSD	1.7 %

Figure 2. A six-level linear calibration from 0.24 mg/mL to 8 mg/mL TPH.

3

Figure 3 shows a chromatographic overlay from five injections of each BAM-U021 soil duplicate (10 injections total). The GC analysis for a single sample run was completed in about 3 minutes using ultra-fast GC conditions. The C10 and C44 peaks were added to the sample to serve as integration markers for the total TPH sample response, as shown by the dashed baseline. For these sample duplicates, each run has nearly identical chromatographic response and retention times. The two inset chromatograms offer detailed views of the C10 and C40 marker peaks. The C10 peak had a retention time range of only 0.003 minutes, while the C40 peak retention time range was even lower, at 0.001 minutes. The statistical analysis for each peak's retention time is shown in the inset table in Figure 3. It is important that these two marker peaks exhibit high retention time precision since they set the integration start and end times for determining TPH response. The analysis of the BAM-U022 river sediment sample is shown in Figure 4. This sample contains a larger amount of TPH compared to the soil sample.

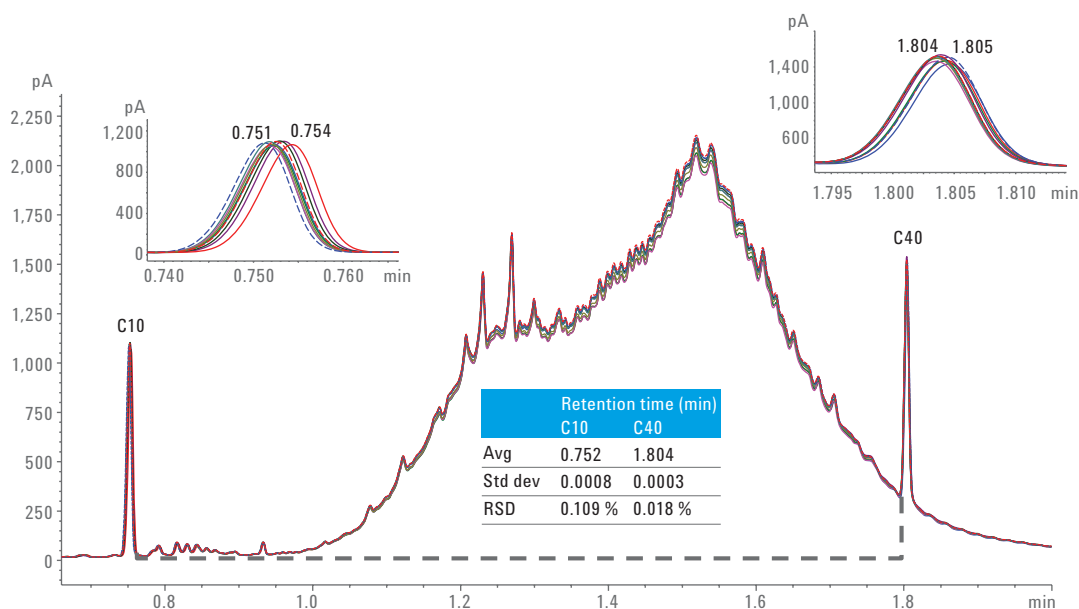| Retention time (min)		
	C10	C40
Avg	0.752	1.804
Std dev	0.0008	0.0003
RSD	0.109 %	0.018 %

Figure 3. An overlay of 10 chromatograms obtained from duplicate analyses of the BAM-U021 soil sample. The inset chromatograms and the table show the retention time precisions for the C10 and C40 marker peaks.
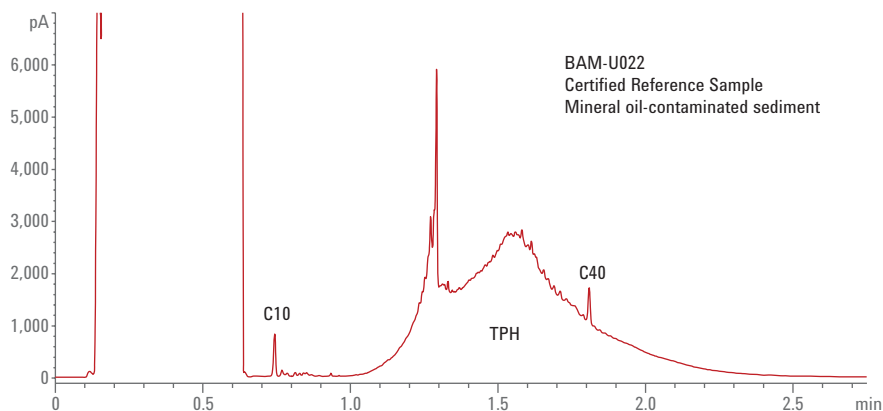
BAM-U022
Certified Reference Sample
Mineral oil-contaminated sediment

Figure 4. Ultrafast GC analysis of TPH in a contaminated river sediment sample.

4

Table 3 shows the quantitative results for each sample. Three analysis performance measures are demonstrated using this data. First, the method accuracy is shown by comparing the measured TPH contents to the certified values published by BAM. The amount of TPH measured in each sample's duplicate analysis agrees with the certified value, well within the accepted errors. Next, overall instrument precision is shown using the calculated RSDs from the analyses results. Five runs of each sample's duplicates were shown to have RSDs of less than 1 %. Finally, overall method precision is measured from the duplicate analysis results using the single lab repeatability (r) test described in the ISO 16703 method. For the BAM-U021 soil sample, the experimental repeatability of 59 mg/kg is well below the required maximum value of 139 mg/kg. Likewise, the repeatability test for the BAM-U022 river sediment sample is 126 mg/kg, well below the maximum value of 337 mg/kg required by the method.

Table 3. Calibration repeatability results obtained from three sequential injections of standard 3 (1 mg/mL).

Run	U021 A (mg/kg)	U021 B (mg/kg)	U022 A (mg/kg)	U022 B (mg/kg)
1	3,462	3,480	8,701	8,630
2	3,487	3,485	8,724	8,658
3	3,502	3,482	8,656	8,610
4	3,513	3,479	8,736	8,732
5	3,538	3,492	8,728	8,606
Mean	3,500	3,484	8,709	8,647
Cert. value	3,560 ± 260		8,270 ± 550	
Std dev	28.547	5.234	32.319	51.704
RSD	0.82 %	0.15 %	1.37 %	0.60 %
r (exp)	59		126	
r* (ref)	136		337	

Conclusion

An ultra-fast GC method was developed for the analysis of TPH in environmental samples.

- The UFGC method completes a TPH sample run in 3 minutes using short columns, fast oven programming, and high carrier gas flows.

- The Agilent Intuvo 9000 GC direct column heating and 6th generation EPC delivers a fast GC analysis with characteristically high retention time precision, eliminating the need for line-up manipulation of the data.

- The UFGC method meets the ISO 16703 benchmarks for selectivity, resolution, discrimination, and calibration.

- Quantitative results for certified reference samples shows extremely good accuracy.

- Quantitative results exceed the repeatability requirements of the ISO 16703 method.

References

1. Soil Quality-Determination of content of hydrocarbon in the range C10 to C40 by gas chromatography. ISO 16703:2004(E). Geneva, Switzerland: ISO

2. http://www.sigmaaldrich.com/technical-service-home/product-catalog.html

www.agilent.com/chem

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