

Robust and cost-effective analysis of TPH in water and soil using GC-FID

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Keywords: Total petroleum hydrocarbons, TPH, gas chromatography, flame ionization detector, FID, GC-FID, water, soil

Goal

The aim of this work is to demonstrate a simple, cost-effective analytical solution for the routine determination of total petroleum hydrocarbons in water and soil samples, for implementation at the high-throughput Welsh Water laboratory, UK, by using a Thermo Scientific™ TRACE™ 1310 Gas Chromatograph and the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS).

Introduction

Total petroleum hydrocarbons (TPH) describe a complex mixture of several hundred organic chemical compounds that originates from crude oil and range from light gas products to heavy fuel oils that can potentially contaminate the environment.

Compounds known to exist in some TPH fractions can affect blood, the immune system, liver, spleen, kidneys, developing fetus, and the lungs. Other TPH, such as some



mineral oils, are not very toxic and are used within the food industry.¹

Current sample preparation and analytical technologies used for the analysis of TPH involve methods such as Soxhlet extraction for soils and liquid-liquid extraction for water samples. These methods are time consuming and require large amounts of organic solvents, with detection using infrared spectroscopy after extraction with Freon™ 113 or tetrachloromethane, which are toxic solvents.

Various regulated methods considering the analysis of TPH are available, including ISO 16703:2011,² EN ISO 14039:2004,³ EN ISO 9377:2000,⁴ and ASTM D7678-11.⁵

The aim of this work was to develop a cost-effective, GC-FID approach for the analysis of TPH, while maintaining robustness for high-throughput analytical testing, that uses hexane as the extraction solvent, solid phase extraction (SPE) for water samples, and a sonication extraction for soil samples, followed by GC-FID analysis using hydrogen as the carrier gas.

Experimental conditions

Sample preparation

Water samples

Various water types, including tap, deionized, soft, medium, hard, and surface water, were prepared using a TPH SPE 1 g/6 mL cartridge (Biotage #752-0100-C).

A 500 mL sample with an additional 5 mL of methanol (Honeywell, >99.9%, #34860) was filtered through the SPE cartridge under vacuum. Cartridges were pre-conditioned using methanol and rinsed with deionized water (pH adjusted to 2 with HCl). After the sample passed through the cartridge, the sample bottle was rinsed with acetone (Fisher Chemical, extra pure 99%, #A/0560/17) and the acetone rinse solvent was further diluted with a small volume of DI water. Following application of the washing solution, the cartridges were left to dry under vacuum. The TPH were then eluted with 4 mL of hexane (Sigma-Aldrich #139386-500mL) and collected in test tubes. The hexane was left to soak in the cartridge for 5 min before being pulled into the test tube under gravity. Another soak step using 4 mL of hexane was carried out and eluted into the test tubes. A vacuum was applied to pull through any residual hexane left in the cartridge bed. The extracts were then concentrated to 1 mL using a TurboVap™ under a 1.5 mL/min flow of nitrogen, within a water bath held at 35 °C before being transferred into 2 mL GC-MS vials ready for analysis.

Soil samples

One gram of a certified reference TPH soil sample (Sigma-Aldrich #SQC026-100G) was well mixed before use. Then 10 mL of hexane (Sigma-Aldrich #139386-500mL) were added for the extraction, keeping the solution in an ultrasonic bath for 30 min. Other viable extraction

techniques include Accelerated Solvent Extraction (ASE) for the extraction stage, with a Thermo Scientific™ Rocket™ Evaporator for the extract concentration stages, as previously reported.⁶

To assess TPH response linearity, working calibration solvent standards were prepared with a 1:1 mix, by concentration, of diesel fuel (Restek #31235, 5000 µg/mL) and motor oil composite (Restek #31465, 50,000 µg/mL) diluted in hexane (Sigma-Aldrich #139386-500mL) ranging from 1 to 2,000 µg/mL, equivalent to 2–4,000 µg/L total TPH (C10–C40) in water samples, and 10–20,000 mg/kg in soil samples.

In addition, TPH calibration standards were prepared using an alkane mix standard (C8–C40, even carbon numbers, 500 µg/mL each, Restek #31266) ranging from 0.8 to 1600 µg/mL, equivalent to 1.6–3200 µg/L total TPH (C10–C40) in water samples, and 8–16,000 mg/kg in soil samples. Mixed C8–C40 alkane standards were also used to assign retention times for TPH group assignments.

Instrument and method setup

A Thermo Scientific™ TRACE™ 1310 Gas Chromatograph configured with a Thermo Scientific™ Instant Connect Programmed Temperature Vaporization (PTV) injector and an Instant Connect Flame Ionization Detector (FID) and equipped with a Thermo Scientific™ TriPlus™ RSH autosampler was used for all experiments.

Compound separation was achieved on a Thermo Scientific™ TG-Mineral Oil, 15 m × 0.32 mm i.d. × 0.15 µm film capillary column (P/N 26069-5230).

Additional details on instrument parameters are listed in Table 1 (next page).

Data processing

Data were acquired, processed, and reported using Chromeleon CDS, version 7.3. Chromeleon CDS allows the analyst to set up acquisition, processing, and reporting methods with easy data reviewing and flexible data reporting.

Table 1. GC operative conditions

TRACE 1310 GC system parameters					
Inlet module and mode	PTV, splitless				
Injection volume	1 μ L				
Liner	Baffled PTV liner, 2.0 mm \times 2.75 mm \times 120 mm (P/N 453T2845-UI)				
Inlet temperature ($^{\circ}$ C)	50				
Carrier gas	Hydrogen				
Carrier gas flow (mL/min) and mode	3.2, constant flow				
Split flow (mL/min)	50				
Splitless time (min)	0.5				
Septum purge flow (mL/min)	5				
Column	TG-Mineral Oil, 15 m \times 0.32 mm i.d. \times 0.15 μ m film capillary column (P/N 26069-5230)				
PTV parameters	Pressure (kPa)	Rate ($^{\circ}$ C/s)	Temperature ($^{\circ}$ C)	Time (min)	Flow (mL/min)
Injection	30.0	-	-	0.10	-
Transfer	-	14.5	350	0.50	-
Cleaning	-	-	350	5.00	50.0
Oven temperature program	RT (min)	Rate ($^{\circ}$ C /min)	Target temperature ($^{\circ}$ C)	Hold time (min)	
Initial	0	-	40	0.5	
Final	0.5	80	350	1.6	
Run Time	6.0	-	-	-	
FID parameters					
Detector temperature ($^{\circ}$ C)	300				
FID air flow (mL/min)	350				
FID H ₂ flow (mL/min)	35				
FID make up N ₂ flow (mL/min)	40				
FID acquisition rate (Hz)	25				

Results and discussion

The object of this study was to evaluate a cost-effective and robust GC-FID method for the quantification of TPH in water and soil samples to increase sample throughput and laboratory productivity. The analytical method was tested by considering various analytical parameters, including chromatographic resolution, carrier gas, linearity, repeatability, and robustness in matrix.

Chromatography

Good chromatographic separation for both mixed alkane standards (C10–C40, even) (Figure 1A) and diesel/motor oil composite standard (Figure 1B) in under 6 minutes was obtained using the GC conditions described in Table 1.

To determine a cost-effective method, the choice of GC carrier gas was considered. Hydrogen with its diffusivity and higher optimum linear velocity was compared to helium to evaluate shorter run time with no loss of chromatographic separation, as shown in Figure 2. The use of hydrogen as a carrier gas also allowed for a cost-effective method for the laboratory.

Linearity of response

To assess TPH linearity response, 11 working calibration solvent standards were prepared using a 1:1 mix, by concentration, of diesel fuel and motor oil composite diluted in hexane ranging from 1 to 2,000 μ g/mL. Total hydrocarbons over the range C10–C40 were quantified using an external solvent standard calibration, equivalent to a total TPH (C10–C40) concentration range of 2–4,000 μ g/L in water samples, and 10–20,000 mg/kg in soil samples, using a 1/ \times weighting factor.

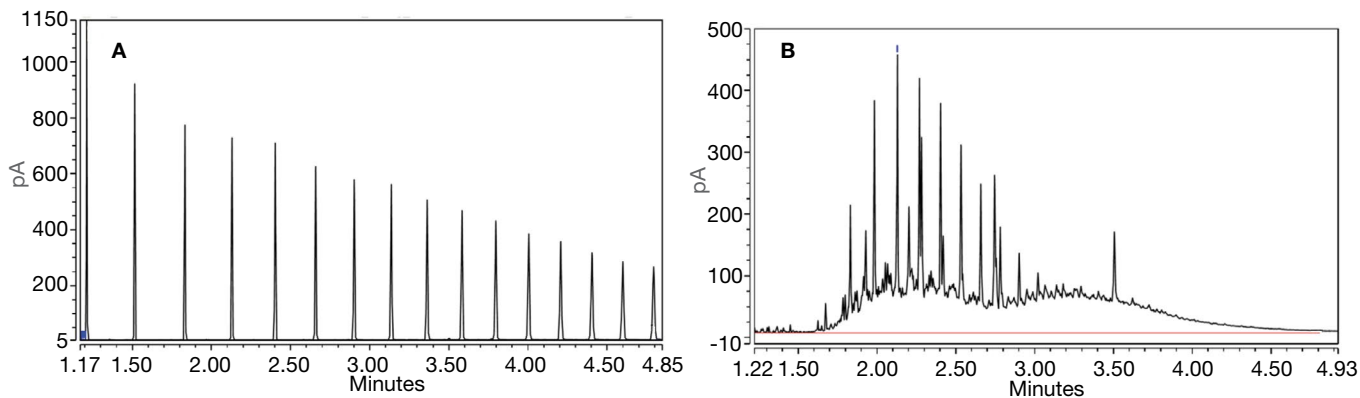


Figure 1. Example of chromatographic separation of TPH. (A) Mixed alkane standards (total concentration C10–C40 = 400 µg/mL) and (B) diesel/motor oil composite mixed standard (total concentration C10–C40 = 1000 µg/mL). Carrier gas: H₂, 3.2 mL/min constant flow, column: TG-Mineral Oil, 15 m × 0.32 mm i.d. × 0.15 µm film capillary column.

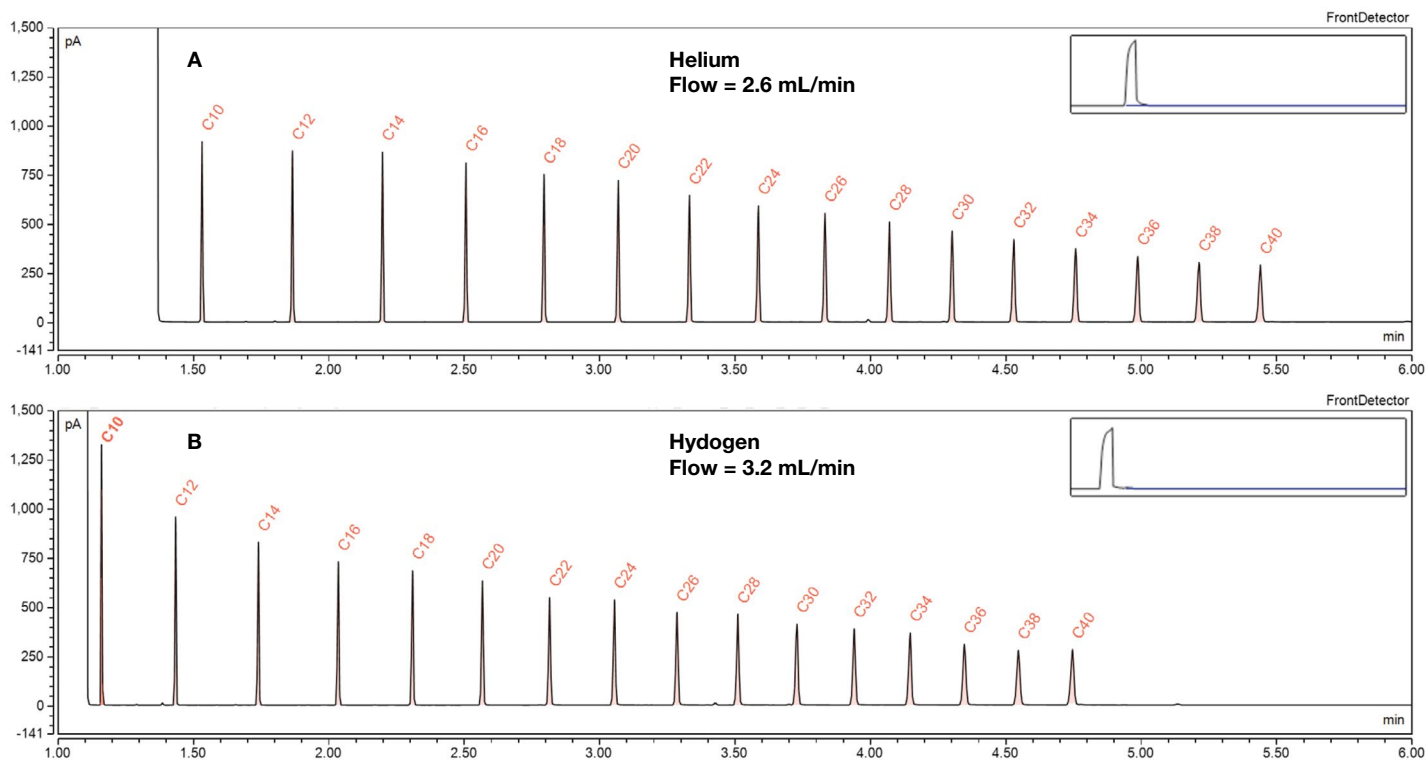


Figure 2. Example of chromatographic separation of mixed alkane standards C10–C40, each at 25 µg/mL, with carrier gas (A) helium and (B) hydrogen, with the carrier gas flow set to the optimum max for each gas when using the TG-Mineral Oil, 15 m × 0.32 mm i.d. × 0.15 µm film capillary column. The chromatograms are annotated with alkane numbers.

Excellent linearity was demonstrated for TPH, with an R^2 value of 0.9987 and an average residual %RSD (AvCF %RSD) of 5.7, as shown in Figure 3 where both the coefficient of determination (R^2) and the AvCF %RSD are annotated.

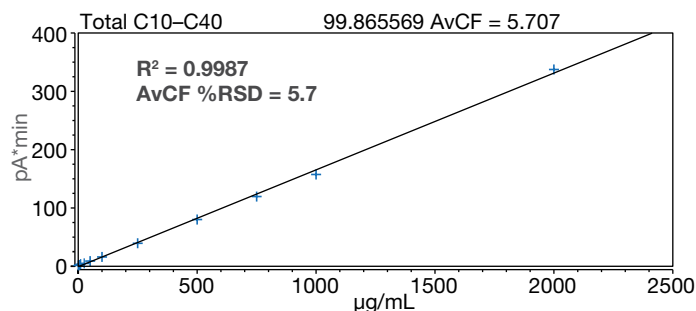


Figure 3. Calibration linearity assessment, for 1:1 mix of diesel fuel and motor oil composite, annotated with the average calibration factor (ACF) %RSD and coefficient of determination (R^2) for TPH (integrated over the range C10–C40)

In addition, an alternative calibration to assess TPH linearity, 11 calibration standards were prepared using an alkane mix standard (C10–C40, even, 500 $\mu\text{g/mL}$ each) ranging from 0.8 to 1,600 $\mu\text{g/mL}$, equivalent to 1.6–3,200 $\mu\text{g/L}$ total TPH (C10–C40 in waters samples, and 8–16,000 mg/kg in soil samples, using 1/ \times weighting factor. Mixed C10–C40 alkane standards were also used to assign retention times for TPH group processing assignments.

Excellent linearity was demonstrated for total TPH (C10–C40), with an R^2 value of 0.9993 and an average residual %RSD (AvCF %RSD) of 5.0, as shown in Figure 4.

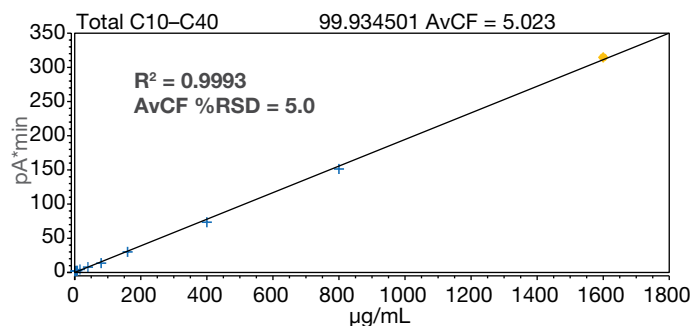


Figure 4. Calibration linearity assessment, for alkane mix standard (C10–C40, even, 400 $\mu\text{g/mL}$ total concentration), annotated with the average calibration factor (ACF) %RSD and coefficient of determination (R^2) for TPH (integrated over the range C10–C40)

Estimation of instrument detection limit (IDL)

System sensitivity, defined as the instrument detection limit (IDL), was determined experimentally by performing $n=9$ replicate injections of a diluted diesel fuel and motor oil composite solvent standard (5 $\mu\text{g/mL}$). Calculations of IDLs were made using a one-tailed Student's t-test at the 99% confidence interval for the corresponding degrees of freedom and taking into account the concentration on column for TPH (C10–C40) and absolute peak area %RSD. The IDL was calculated as 0.33 μg on column for total TPH (C10–C40), which relates to an IDL for soils of <5 mg/kg and water of <1 $\mu\text{g/L}$ using the sample preparation details as given.

Peak area repeatability and robustness in matrix

Repeatability and robustness of TPH responses in matrix were assessed by carrying out repeated injections ($n=99$) of a certified reference soil, analyzed over five batches, which included full diesel/motor oil composite calibration, with check standards (mid-level) inter-dispersed during and at the end of the sequence. The five batches were analyzed over five consecutive working days, with no inlet or column maintenance performed. Excellent repeatability of both peak area and calculated concentration was obtained for all batches with %RSD of 5.7 for peak area and %RSD of 5.3 for concentration ($n=99$). Figure 5A shows the repeatability throughout the 99 injections of the five batches, while Figure 5B shows the overlay of $n=20$ GC-FID chromatograms from batch 2.

Water sample analysis

Various water types that included tap, deionized, soft, medium, hard, and surface water were prepared using a TPH SPE 1 g/6 mL cartridge as detailed. In addition, deionized and hard water samples were spiked with 1:1 mix of diesel fuel and motor oil composite to concentrations of 500 and 200 $\mu\text{g/L}$, respectively. A summary of the results achieved is shown in Figure 6; %RSD <5 for $n=3$ replicate injections was achieved.

Reporting

Chromeleon CDS simplifies the data processing and streamlines high-throughput data analysis. Intuitive results reviewing and flexible data reporting is possible for both total TPH (C10–C40) and TPH alkane group ranges. Using the mixed alkane standard C10–C40 peaks as retention time markers, integration events can be used to establish the required TPH group retention time ranges. Figure 7 illustrates the integration ranges against mixed alkane standards. A TPH custom report for the analysis of the certified reference soil is shown in Figure 8, reporting TPH alkane ranges.

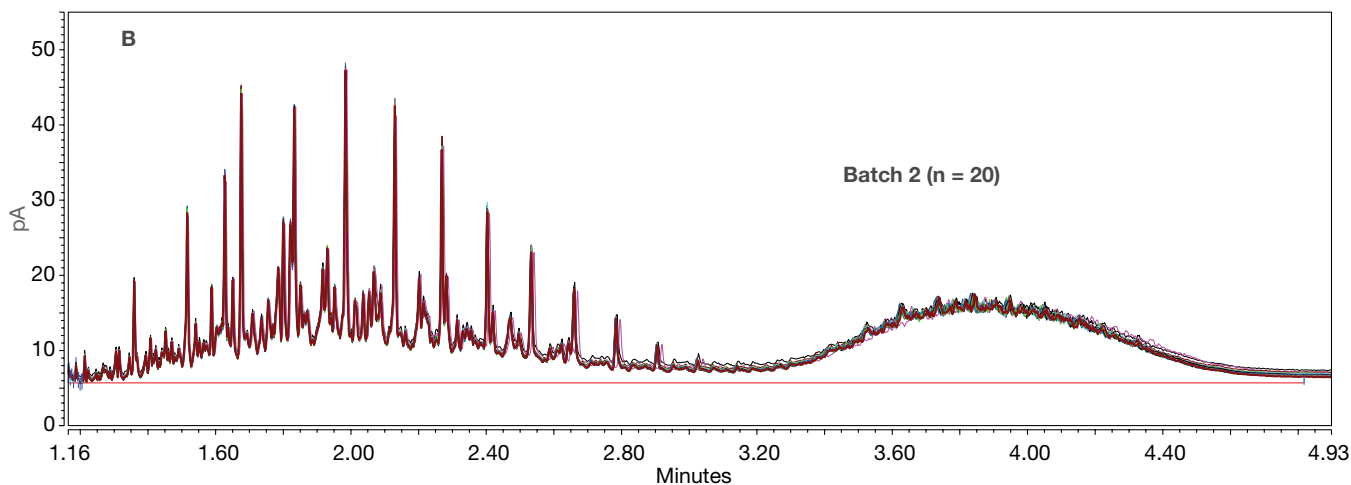
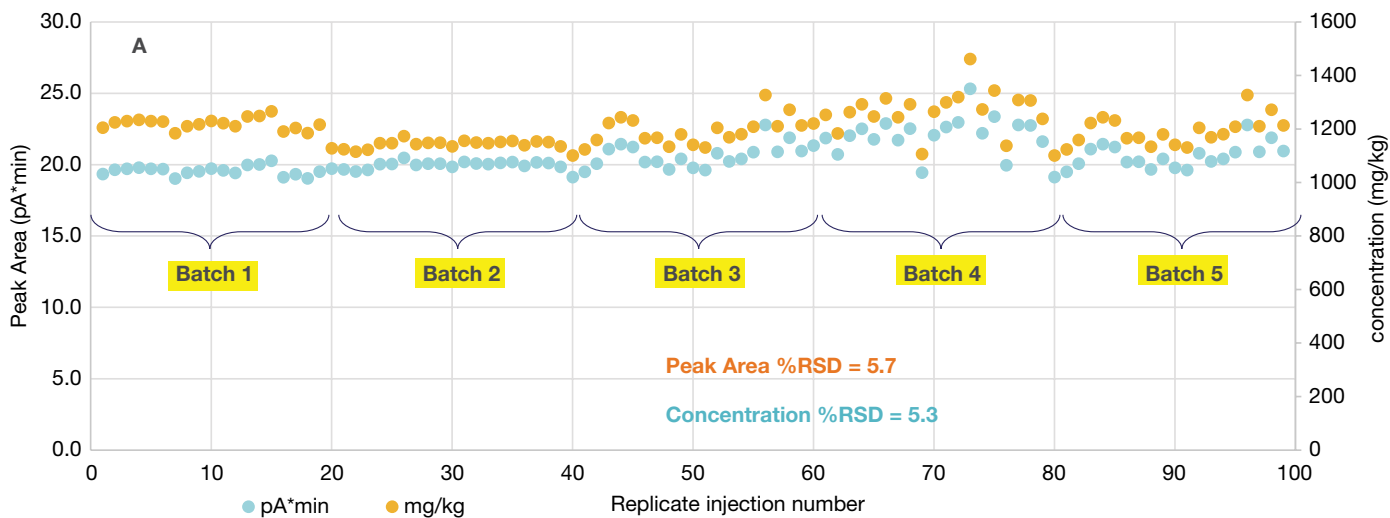


Figure 5. Peak area repeatability and robustness in matrix. (A) Repeatability and robustness illustrated with five batches over five consecutive working days of TPH soil analysis, ~20 injections per batch of the certified reference soil. Each batch included full calibration, interspersed with a check mid-level standard. (B) Overlaid GC-FID chromatograms for a certified reference soil sample in batch 2 (n=20).

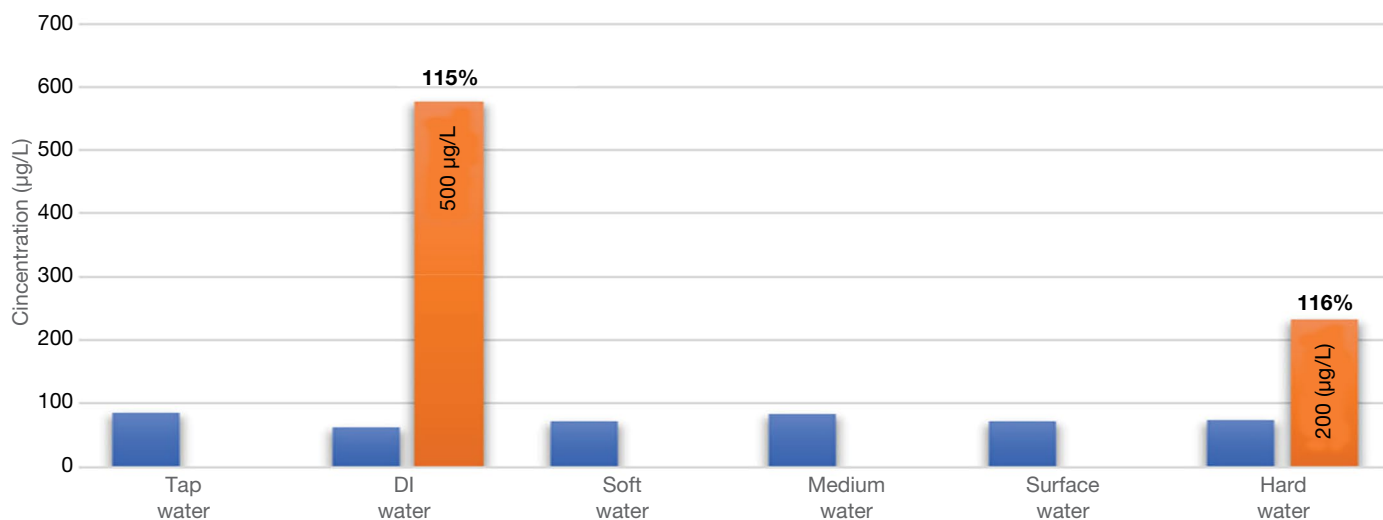


Figure 6. TPH (C10–C40) results for tap, deionized, soft, medium, hard, and surface water prepared using a TPH SPE 1 g/6 mL cartridge (n=3). Deionized and hard water samples were spiked with a 1:1 mix of diesel fuel and motor oil composite to concentrations of 500 and 200 µg/L, respectively. The spiked samples are annotated with spiked concentration and blank corrected recovery of 115% for DI water and 116% for hard water. %RSD <5 achieved for all replicate injections.

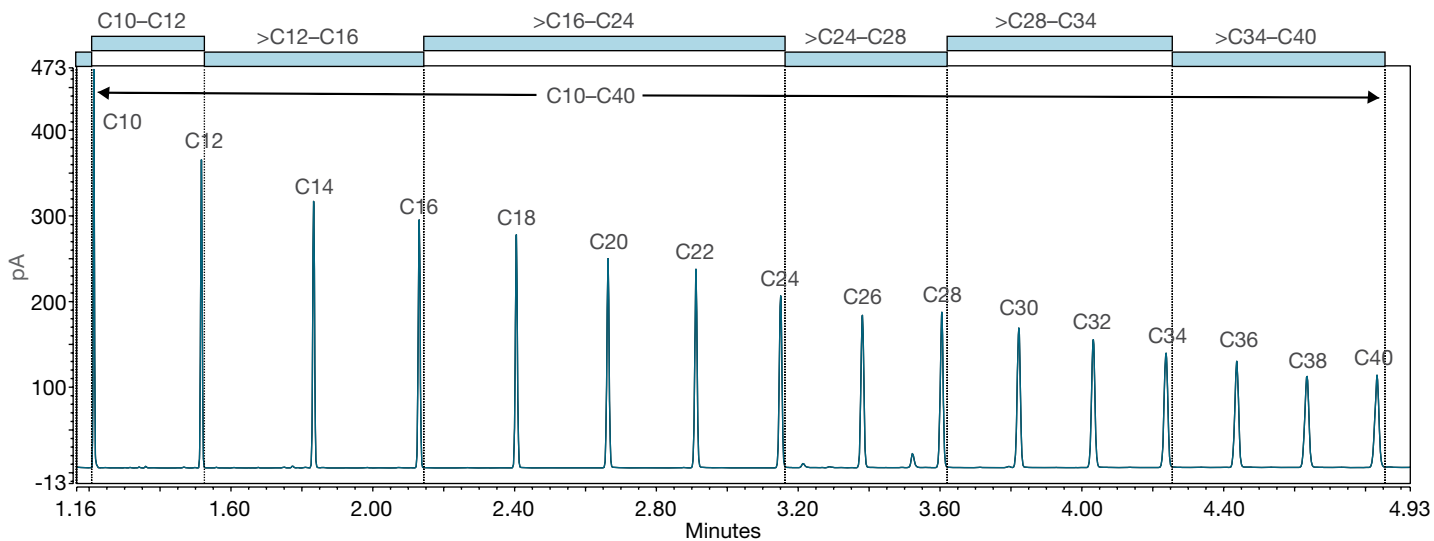
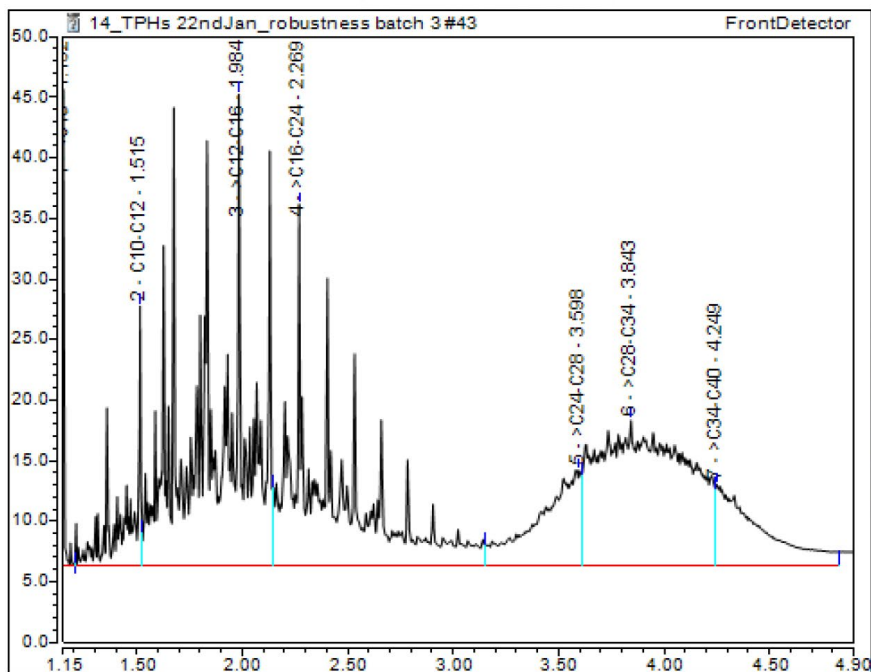


Figure 7. Mixed alkane chromatograms (C10–C40, even). TPH alkane group ranges are highlighted, which are used to establish the required retention times for peak group and integration events.

TPH Soil Report

Sequene 14 TPHs 22ndJan robustness batch 3
 Injection name ref soil batch3 rep19
 Vial position 110
 Injection time 27/Jan/2021 01:41



No.	Group Name	Retention Time min	Area pA*min	Relative Area %	Concentration mg/kg
1	<C10	1.152	0.064	0.32	3.72
2	C10-C12	1.515	0.869	4.31	50.49
3	>C12-C16	1.984	5.634	27.95	327.41
4	>C16-C24	2.269	4.337	21.52	252.03
5	>C24-C28	3.598	1.803	8.94	104.75
6	>C28-C34	3.843	5.768	28.62	335.20
7	>C34-C40	4.249	1.683	8.35	97.81
Total:			20.157	100.00	1171.418

Figure 8. Chromeleon CDS custom report for the certified reference soil, reporting TPH alkane ranges

Conclusions

The results obtained demonstrate that the TRACE 1310 GC-FID in combination with the TriPlus RSH autosampler and Chromeleon CDS offer a rapid and robust solution to laboratories that analyze TPH in environmental samples.

- Good chromatographic separation, in less than 6 minutes, was achieved using a TG-Mineral Oil, 15 m × 0.32 mm i.d. × 0.15 µm film capillary column, using hydrogen as the carrier gas for cost-effective, high-throughput analysis.
- Excellent linearity was obtained for TPH (C10–C40) over a calibration range of 1 to 2,000 µg/mL using mixed diesel fuel and motor oil composite calibration standards, and 0.8 to 1,600 µg/mL using mixed alkane calibration standards.
- Excellent repeatability and robustness were achieved for the analysis of a certified reference soil (n=99) over five batches analyzed over five consecutive working days, achieving %RSD of 5.7 for peak area and %RSD of 5.3 for concentration. In addition, no inlet or column maintenance was performed during the robustness test.
- Various water types including tap, deionized, soft, medium, hard, and surface water were analyzed. Deionized and hard water samples were spiked with a 1:1 mix of diesel fuel and motor oil composite to concentrations of 500 and 200 µg/L, respectively, achieving blank corrected results of 115% and 116%. %RSD <5 for n=3 for all replicate sample and spiked sample injections was achieved.
- Chromeleon CDS simplifies the analytical workflow with user-friendly data acquisition and data processing, suitable for high-throughput laboratories. The intuitive data reviewing and flexible data reporting enables effortless reporting of TPH alkane group ranges.

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