APPLICATION NOTE

Total Petroleum Hydrocarbon (TPH) Analysis in Water by GC-FID Using Hydrogen as a Carrier Gas

AN172v1; March 2024, SCION Instruments

Introduction

Total petroleum hydrocarbons (TPH) describes a several hundred chemical compounds that originate from crude oil – they can range from heavy fuel oil to light gaseous compounds which have the potential to harm the environment. Some TPHs have been known to cause headaches, dizziness and numbness in the extremities.[1] They are also capable of affecting the blood, immune system, respiratory system and skin. TPH exposure may also affect organ function.[1] Understandably, this means that TPH testing of our drinking water is important in order to ensure that only safe levels of these compounds are present.

TPHs can enter the environment by accidents, industrial release, and as byproducts from commercial or private uses. TPHs may contaminate water directly through spillage and leaks. Depending on the fraction the TPHs may float on top of the water and form surface films or they may sink to the bottom of sediments.[2]

Helium has long been the standard carrier gas for GC applications however, due to recent global shortages many companies are keen to find alternatives.[3] The application described in this note has been performed using an alternative carrier gas, hydrogen. This can be produced with generators using renewable energy sources and so is a cleaner, greener option as well as avoiding the current issues over helium supply.[3]

This application can be performed on either the SCION Instruments 8300 GC or 8500 GC platforms equipped with an 8400 Pro Autosampler, S/SL injector, and FID detector.

Experimental

The tap water and contaminated puddle samples were extracted by adding 100 mL of each sample to a Duran flask with 20 mL of hexane. The solution was then stirred for 15 minutes. 10 mL of hexane was extracted from each sample and the samples were blown to dryness under nitrogen gas. Each sample was then reconstituted in 0.5 mL of hexane before being submitted for analysis.

A reference oil sample was also prepared by adding 0.5 mL of diesel fuel no. 2 to a Duran flask containing 100 mL of tap water and 20 mL of hexane. The solution was then extracted as above.

Linearity samples were prepared in hexane at 6 concentrations, 100, 60, 30, 10, 5 and 1 µg/mL. The Linearity samples were made from a 500 µg/mL stock solution which was prepared with a TPH mix standard.

5 instrument precision samples were also prepared at concentration level of 30 µg/mL.

Instrument parameters can be found in Table 1.

Table 1 Instrument parameters

Part	Settings
Autosampler	SCION 8400 PRO
Injector	275°C Split ratio 20:1
Injection Volume	1 µL
Column	SCION-5 30 m x 0.32 mm x 0.25 µmm SC30233
Carrier Gas	Hydrogen 1.5 mL/min
Oven Program	80°C (hold 0.1 min), 20°C/min to 325°C (hold 6.65 min)
Detector	FID (ceramic jet) 350°C, Air : 300 mL/min, Hydrogen : 30 mL/min, Make up (N_2): 25 mL/min
Run Time	19 min
Software	Compass CDS

Results and Discussion

The instrument method stated in Table 1 gave excellent specificity. Figure 1 shows an example chromatogram of the highest concentration linearity sample.

This chromatogram clearly demonstrates the specificity of the method, showing excellent resolution between all components as well as good peak shapes of all straight chain carbon compounds.

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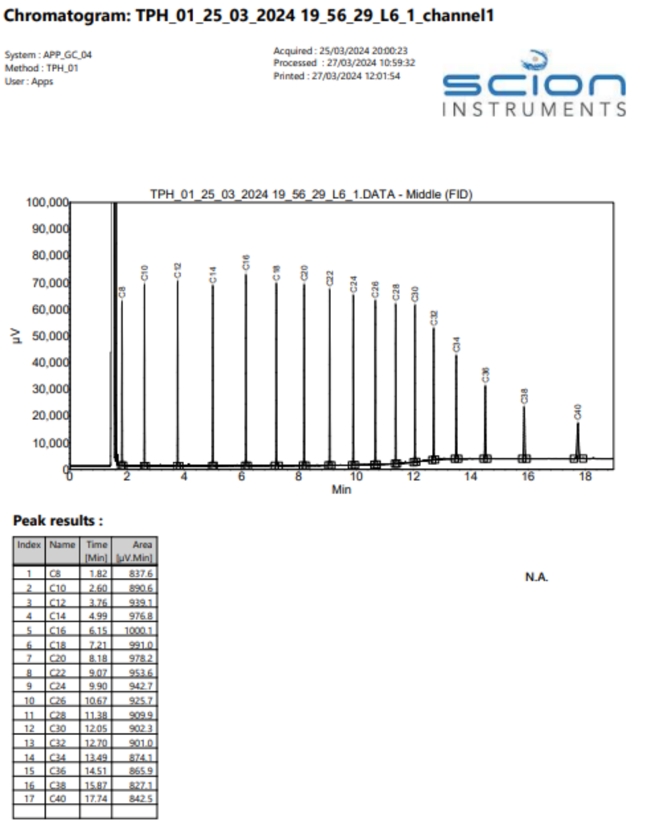


Index	Name	Time [Min]	Area [µV.Min]
1	C8	1.82	837.6
2	C10	2.60	890.6
3	C12	3.76	939.1
4	C14	4.99	976.8
5	C16	6.15	1000.1
6	C18	7.21	991.0
7	C20	8.18	978.2
8	C22	9.07	953.6
9	C24	9.90	942.7
10	C26	10.67	925.7
11	C28	11.38	909.9
12	C30	12.05	902.3
13	C32	12.70	901.0
14	C34	13.49	874.1
15	C36	14.51	865.9
16	C38	15.87	827.1
17	C40	17.74	842.5

Figure 1 Example chromatogram of highest concentration linearity sample

Table 2 shows the correlation coefficient and system precision (n=5) results for all compounds present within the TPH mix.

The r^2 values of all compounds demonstrate excellent linearity. Many regulations only require an r^2 value of ≥0.98.

System precision values of all compounds demonstrate good repeatability with all results well below the 2% which is generally considered acceptable for method validation.

Figures 2-4 show example chromatograms of a contaminated puddle sample, blank tap water sample and a reference oil sample respectively.

Results were calculated using the average response factors from the mixed hydrocarbon standard linearity samples. The reference oil gave a recovery of 91.55% showing good working of the method. The reference oil was shown to consist of C8-C24.

Table 2 Correlation coefficient and system precision results for all compounds

Compound	RSD (%)	Correlation Coefficient (r^2)
C8	0.76	0.9997
C10	0.78	0.9997
C12	0.56	0.9996
C14	0.54	0.9996
C16	0.51	0.9995
C18	0.23	0.9995
C20	0.40	0.9992
C22	0.23	0.9989
C24	0.46	0.9988
C26	0.43	0.9987
C28	0.37	0.9988
C30	0.41	0.9987
C32	0.67	0.9982
C34	0.32	0.9982
C36	0.39	0.9985
C38	0.53	0.9985
C40	0.60	0.9987

The extracted blank was shown to have no TPH present as expected.

The contaminated puddle was shown to contain C10-C26 with a total concentration of 6507.58 µg/mL.

Results for both the reference oil and extracted sample (contaminated puddle) can be seen in Table 3.

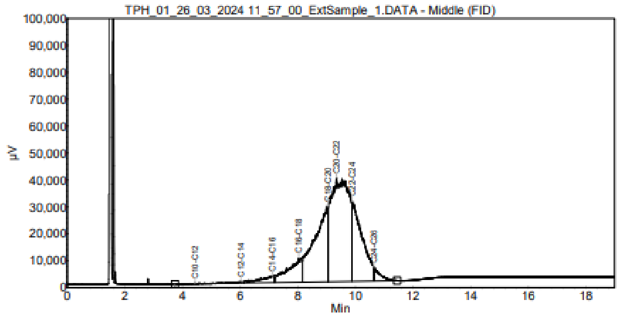
Table 3 TPH results for the Reference Oil and extracted sample (contaminated puddle)

Compound	Ref Oil (µg/mL)	Ext Sample (µg/mL)
C8-C10	105.556	N/A
C10-C12	1350.134	0.103
C12-C14	1136.876	20.877
C14-C16	926.277	138.566
C16-C18	590.280	505.694
C18-C20	292.990	1560.508
C20-C22	121.024	2881.451
C22-C24	54.277	1275.247
C24-C26	0.46	125.140
C26-C40	N/A	N/A
Total	**4577.41**	**6507.58**

Chromatogram: TPH_01_26_03_2024 11_57_00_ExtSample_1_channel1

System : APP_GC_04
Method : TPH_01
User : Apps

Acquired : 26/03/2024 12:01:00
Processed : 27/03/2024 09:25:44
Printed : 27/03/2024 11:54:36



Peak results :

Index	Name	Time [Min]	Area [µV.Min]
1	C10-C12	4.43	1.0
2	C12-C14	6.02	203.4
3	C14-C16	7.11	1350.0
4	C16-C18	8.03	4926.8
5	C18-C20	9.05	15203.5
6	C20-C22	9.34	28073.0
7	C22-C24	9.88	12424.3
8	C24-C26	10.64	1219.2
Total			63401.1

N.A.

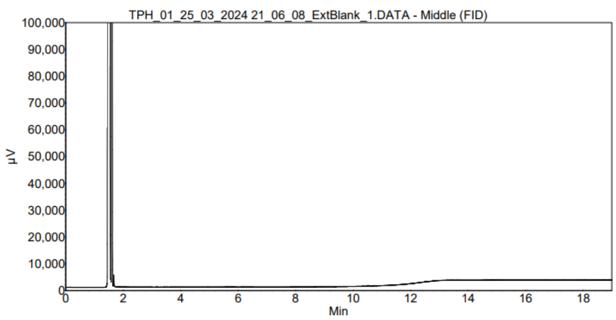
Figure 2 Example chromatogram of an extracted sample

Figures 5-6 show overlayed chromatograms of both the reference oil and extracted sample (contaminated puddle) overlayed with the highest level linearity sample of the mixed hydrocarbon standard.

Chromatogram: TPH_01_25_03_2024 21_06_08_ExtBlank_1_channel1

System : APP_GC_04
Method : TPH_01
User : Apps

Acquired : 25/03/2024 21:10:02
Processed : 27/03/2024 11:10:08
Printed : 27/03/2024 12:03:03



Peak results :

Index	Name	Time [Min]	Area [µV.Min]
Total			0.0

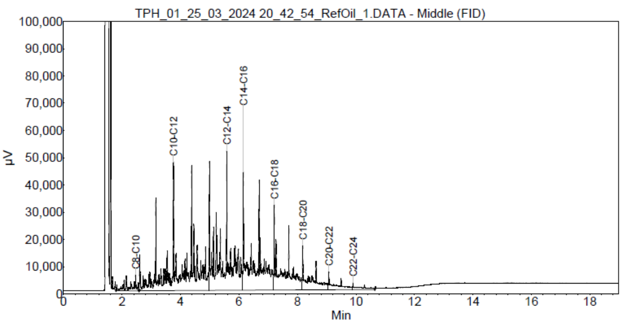
N.A.

Figure 3 Example chromatogram of a tap water sample

Chromatogram: TPH_01_25_03_2024 20_42_54_RefOil_1_channel1

System : APP_GC_04
Method : TPH_01
User : User1

Acquired : 25/03/2024 20:46:49
Processed : 01/04/2024 09:40:10
Printed : 01/04/2024 10:12:52



Peak results :

Index	Name	Time [Min]	Area [µV.Min]
8	C8-C10	2.46	1028.4
1	C10-C12	3.76	13153.9
2	C12-C14	5.58	11076.2
3	C14-C16	6.15	9024.4
4	C16-C18	7.21	5750.9
5	C18-C20	8.18	2854.5
6	C20-C22	9.07	1179.1
7	C22-C24	9.90	528.8
Total			44596.1

N.A.

Figure 4 Example Chromatogram of the reference oil sample

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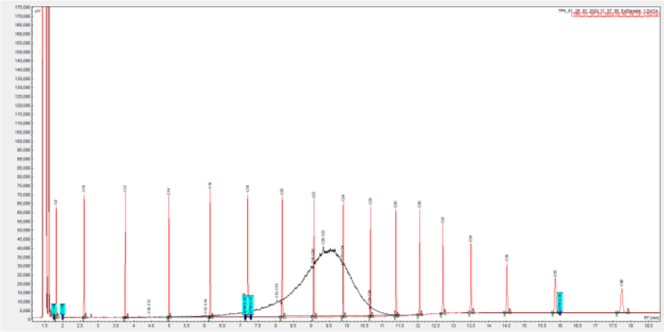

Figure 5 Overlay of highest concentration linearity sample and contaminated puddle sample

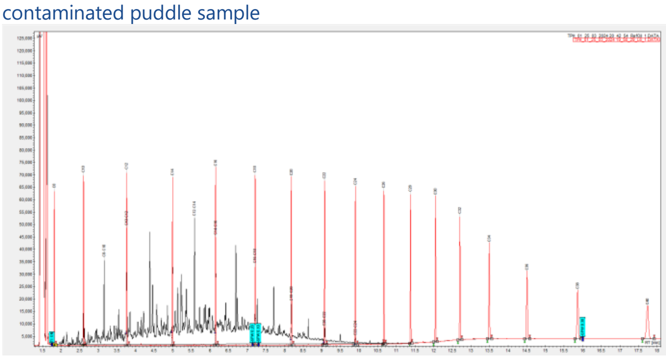

Figure 6 Overlay of highest concentration linearity sample and a reference oil sample

Conclusion

A method has been successfully developed and validated for the determination of total petroleum hydrocarbons (TPH) in water.

Samples were extracted by liquid-liquid extraction (LLE), check out the SCION knowledge centre on our website where we have multiple technical notes on sample preparation including LLE.

SCION instruments recommends checking with local regulatory authorities to ensure all testing and reporting requirements are met, or contact the SCION applications team for assistance.

For more information, please contact:

E: sales-eu@scioninstruments.com

W: www.scioninstruments.com

Ordering Information

Ordering Information for the 8300 GC	
Part	**Part Number**
8300-GC, with S/SL inlet and FID detector (120V)	839001701
8300-GC with S/SL inlet and FID detector (230V)	839001702
8400 PRO Autosampler for 8300 and 8500 GC	840000001
Suggested Consumables	
Part	**Part Number**
SCION-5 30 m x 0.32 mm x 0.25 µm	SC30233
Liner STR QW PK/5	41312100
15% Graphite/85% Vespel Ferrule 1/16" with 0.5 mm hole pk/10	41312149
BTO Septa 9 mm, pk/50	CR298713
10 µL fixed needle syringe, 5 cm, 0.47 mm OD, 26 g conical needle	41312133
Vial, 9-425 Screw Thread, 2 mL Clear Glass 12 x 32 mm Flat Base with Label, pk/100	41311000

For ordering info on the SCION 8500 GC, which offers greater functionality with the option of up to 4 detectors (including MS), please contact your local SCION sales representative

References

1. Total Petroleum Hydrocarbons (TPHs) - The Center for Health, Environment & Justice (chej.org), https://chej.org/total-petroleum-hydrocarbons-tphs, (Accessed March 2024)
2. ToxFAQs for Total Petroleum Hydrocarbons (TPH), https://wwwn.cdc.gov/TSP/ToxFAQs/ToxFAQsDetails.aspx?faqid=423&toxid=75#:~:text=TPH%20may%20enter%20the%20environment,sink%20to%20the%20bottom%20sediments., (Accessed March 2024)
3. Innovation News Network, Helium Shortage 4.0, https://www.innovationnewsnetwork.com/helium-shortage-4-0-what-caused-it-and-when-will-it-end/29255/, (accessed March 2024)