



Application Note

No. 019/2009

Total Petroleum Hydrocarbons in Soil, Sediment, and Waste Samples

SpeedExtractor E-916:

Determination of Total Petroleum Hydrocarbons in Soil, Sediment, and Waste Samples using the SpeedExtractor E-916.



1. Introduction

Total petroleum hydrocarbons (TPH) is the general term used to describe a family of several hundred chemical compounds that are originally from crude oil. TPHs are released from industry, commercial or personal use. They can be found in soil and water. Exposure to TPHs such as gasoline and diesel fuel can affect human health. Therefore, many laboratories around the world are monitoring TPH levels in the environment.

Soxhlet and sonication are the classical techniques for the extraction of TPH from environmental matrices. But they require large volumes of solvent and they are time consuming. Pressurized solvent extraction (PSE), also known as pressurized fluid extraction (PFE), combines elevated pressure and high temperature. The use of higher temperatures increases the capacity of the solvents to solubilize analytes. Elevated pressures increase the penetration of the solvent in the matrix and temperatures above the boiling point of the extraction solvent can be used. As a result, PSE requires smaller amounts of solvent and it is much faster than sonication or Soxhlet extraction.

PSE has been validated by the U.S. EPA Method 3545A for a large range of organic compounds [1]. The included analytes are the semi-volatiles, organophosphorous and organochlorine pesticides, chlorinated herbicides, polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins and furans (PCDDs/PCDFs) and diesel range organics (DRO).

This application note reports the pressurized solvent extraction of TPH from soil, sediment and waste samples using the SpeedExtractor E-916. The quantification of TPH was performed by GC-FID. TPH were taken as the sum of hydrocarbons in the range C₁₀-C₄₀. This application meets the requirements of the U.S. EPA Method 3545A and the ISO 16703 and EN 14039 Standards [1,2].

2. Equipment

SpeedExtractor E-916, with 40 mL cells
Analytical balance ± 0.1 mg (Mettler AE 200)
Micropipette 10-100 μ L, Socorex (Acura 825)
Micropipette 100-1000 μ L, Socorex (Acura 825)
Vacuum manifold
Separatory funnel
Thermo Trace GC Ultra 2130, GC-FID, with Autosampler AS3000

3. Chemicals and Materials

n-Hexane, analytical grade, Merck (1.04367)
Acetone, analytical grade, Merck (1.00012)
n-Heptane, analytical grade, Merck (1.04379)
Diatomaceous earth, BUCHI (53201)
Tetracontane (C₄₀), Fluka (87086)
Decane (C₁₀), Fluka (30540)
Standard diesel, BAM (K008, 0.936 g/g)
Sodium sulphate, Sigma-Aldrich (23,859-7)
Filter papers, Whatman (1441 125)
LCTech Florisil-Sodium Sulphate Column: 2 g florisil, 2 g sodium sulphate, Elufix (9370)
GC Column: Ultra Fast Column Module Silicosteel, phase: PH M-1, length 4m, 0.25 mm ID, 0.25 μ m film thickness. (P/N: UFM00001060704)

Samples:

- 1 pre-extracted soil sample, spiked with a standard diesel to 1'800 mg/kg
- 3 certified reference materials (CRM) samples:
 - Clay loam, 0.6% water content (R.T. Corporation CRM 558-100)
 - Sediment, particle size $\leq 125 \mu\text{m}$, water content 5.7% (CRM ERM CC015a)
 - Mineral oil contaminated waste material, particle size $\leq 500 \mu\text{m}$, water content 3.9% (CRM ERM CC016)



Figure 1: Pre-extracted soil (1), clay loam (2), sediment (3), and waste material (4) samples

4. Procedure

The extraction and analysis of TPH in soil, sediment, and waste samples includes the following steps:

- Preparation of the surrogate solutions
- Preparation of sample
- Preparation of cells
- Extraction with the Speed Extractor E-916
- Clean-up
- Quantification by GC-FID

4.1 Preparation of the surrogate solutions

1. Weigh 150 mg of tetracontane in a 25 mL volumetric flask and fill up to the mark with *n*-heptane (6'000 mg/l)
2. Weigh 250 mg of decane in a 25 mL volumetric flask and fill up to the mark with *n*-heptane (10'000 mg/l)
3. Weigh 450 mg of standard diesel in a 25 mL volumetric flask and fill up to the mark with *n*-heptane (18'000 mg/l)

Note:

- The solutions were transferred into a 25 mL vial and stored at 4°C
- Shake the solutions vigorously before use
- If tetracontane precipitates, warm the solution gently until tetracontane dissolves completely before use

4.2 Preparation of the cells

1. Add approx. 3 g of diatomaceous earth into the extraction cell
2. Weigh in approx. 10 g of sample using an analytical balance
3. Mix the sample with approx. 3 g of diatomaceous earth
4. Fill the mixture sample/diatomaceous earth into the 40 mL cells using a funnel
5. Fill up the cell with diatomaceous earth
6. Add the surrogates on top of the diatomaceous earth with a micropipette: 70 μL of the tetracontane solution and 60 μL of the decane solution

Spiked sample

1. Add approx. 3 g of diatomaceous earth into the extraction cell
2. Weigh in approx. 10 g of sample using an analytical balance
3. Mix the sample with approx. 3 g of diatomaceous earth
4. Fill the mixture sample/diatomaceous earth into the 40 mL cells using a funnel
5. Add 1000 μL of the standard diesel solution
6. Fill up the cell with diatomaceous earth

4.3 Extraction with SpeedExtractor E-916

1. Extract the sample with the parameters shown in Table 1.

This method requires approx. 70 mL of solvent. The extraction time is 30 min for 6 positions.

Parameter	Value
Temperature	100°C
Pressure	100 bar
Solvent	<i>n</i> -hexane 50%, acetone 50%
Cells	40 mL
Vials	240 mL
Cycles	2
Heat-up	1 min
Hold	5 min
Discharge	2 min
Flush with solvent	1 min
Flush with gas	2 min

4.4 Clean-up

1. Wash the extract twice in a separatory funnel mit 100 mL of distilled water
2. Collect the organic phase
3. Add sodium sulphate crystals to the organic phase until they no longer clump together
4. Filtrate the organic phase
5. Rinse the flasks and the funnel with *n*-hexane (~2 x 15 mL)
6. Measure the volume V_{hexane} thus obtained with a graduated cylinder
7. Transfer approx. 8 mL of the extract to a glass florisil-sulphate column placed on a vacuum manifold
8. Filtrate without using vacuum, let the extract diffuse along the column
9. Collect the residual extract remaining on the column using vacuum
10. Collect the eluate into a 8 mL vial
11. Transfer an aliquot into a GC vial

4.5 Quantification by GC-FID

The determination of TPH was performed by GC-FID with a Thermo Trace GC Ultra 2130 equipped with an autosampler AS3000 under the following conditions:

- Temperatures: injector 300°C, detector 350°C
- UFM temperature program: 50°C to 350°C (200°C/min)
- Carrier gas: H₂
- Programmed flow: 6 mL/min (50°C); rate 2.5 mL/min/min; final value 10 mL/min (350°C)
- Injection: 1.5 µl splitless.

4.6 Calculation

TPH content

The TPH content was calculated using equation (1):

$$W_{\text{TPH}} = C_{\text{aliquot}} \cdot \frac{V_{\text{hexane}}}{m_{\text{sample}}} \quad (1)$$

- W_{TPH} : TPH content [mg/kg]
 C_{aliquot} : concentration of TPH (C₁₀-C₄₀) in the aliquot analyzed by GC-FID) [mg/l]
 V_{hexane} : volume of hexane after treatment with water (chapter 4.4) [mL]
 m_{sample} : weight of sample [g]

Z-score

The z-score is used for interlaboratory comparison. Experimental values are validated for $z < 2$ [4].

z was calculated using equation (2):

$$z = \frac{|x - V_{CRM}|}{SD_{CRM}} \quad (2)$$

x : mean value obtained using the SpeedExtractor E-916 [mg/kg]
 V_{CRM} : certified value [mg/kg]
 SD_{CRM} : interlaboratory standard deviation of the certified reference material [mg/kg]

5. Result

Tables 2-5 list the results obtained for the spiked soil, the clay loam, the sediment, and the waste material samples. Each sample was extracted fivefold.

The results corresponding to the spiked sample are displayed in Table 2. The SpeedExtractor E-916 gave a good recovery of 90.8% with an rsd of 3.3%, which meets the acceptance criteria of U.S. EPA 8015B (80-120%) [3].

Table 2: Results for spiked soil

Spiked Soil

	m_{sample} [g]	Caliquot [mg/l]	V_{hexane} [mL]	W_{TPH} [mg/kg]
Sample 1	10.0020	228	70	1596
Sample 2	10.0000	241	71	1711
Sample 3	10.0150	226	71	1671
Sample 4	10.0133	239	70	1590
Sample 5	10.0014	224	71	1590
Mean value				1634
rds [%]				3.3
Theoretical value				1800
Recovery [%]				90.8

Tables 3-5 display the results obtained for the three certified samples. The TPH content w was calculated according to equation (1).

Table 3: Results for clay loam

Clay Loam (CRM 558-100)

	m_{sample} [g]	Caliquot [mg/l]	V_{hexane} [mL]	W_{TPH} [mg/kg]
Sample 1	10.0397	66.5	77	510
Sample 2	10.0655	64.3	78	498
Sample 3	10.0140	67	75	502
Sample 4	10.0380	78.2	76	592
Sample 5	10.0418	66.5	77	510
Mean value				522
rds [%]				7.5
V_{CRM} (SD_{CRM})				661 (132)
z				1.05

Table 4: Results for sediment

Sediment (CRM ERM CC015a)

	m _{sample} [g]	Caliquot [mg/l]	V _{hexane} [mL]	W _{TPH} [mg/kg]
Sample 1	10.0354	339	66	2230
Sample 2	10.0108	338	66	2228
Sample 3	10.0181	349	65	2264
Sample 4	10.0188	335	65	2173
Sample 5	10.0200	311	65	2017
Mean value				2182
rds [%]				4.4
V_{CRM} (SD_{CRM})				1820 (192)
z				1.88

Table 5: Results for waste material

Waste Material (CRM ERM CC016)

	m _{sample} [g]	Caliquot [mg/l]	V _{hexane} [mL]	W _{TPH} [mg/kg]
Sample 1	10.0127	390	72	2804
Sample 2	10.0311	396	70	2763
Sample 3	10.0120	415	70	2902
Sample 4	10.0043	391	70	2736
Sample 5	10.0115	409	70	2860
Mean value				2813
rds [%]				2.4
V_{CRM} (SD_{CRM})				3010 (342)
z				0.58

The z-score was calculated for each sample. In each case, $z < 2$, which means that the mean value does not differ significantly from the certified value. The method described here is therefore comparable to the methods used by the laboratories who participated to the interlaboratory tests on which the certified values are based.

6. Conclusion

The results show that the SpeedExtractor E-916 provided good recoveries and reliable results for the extraction of TPH from solid matrices. Moreover, the SpeedExtractor E-916 only uses 70 mL of solvent per sample and the extraction time is only 30 min for 6 positions.

7. Acknowledgements

We sincerely thank Urs Maier and his analytical team from Bachema AG, Schlieren, Switzerland, for the analytical work.

8. References

- [1] US EPA 3545A "Pressurized Fluid Extraction (PFE)"
- [2] ISO 16703 / EN 14039 "Determination of content of hydrocarbon in the range C10 to C40 by gas chromatography"
- [3] US EPA 8015B "Total Petroleum Hydrocarbons (TPH) as Gasoline and Diesel"
- [4] ISO/IEC 43-1: 1997 "Proficiency testing by interlaboratory comparisons"