



# Application Note

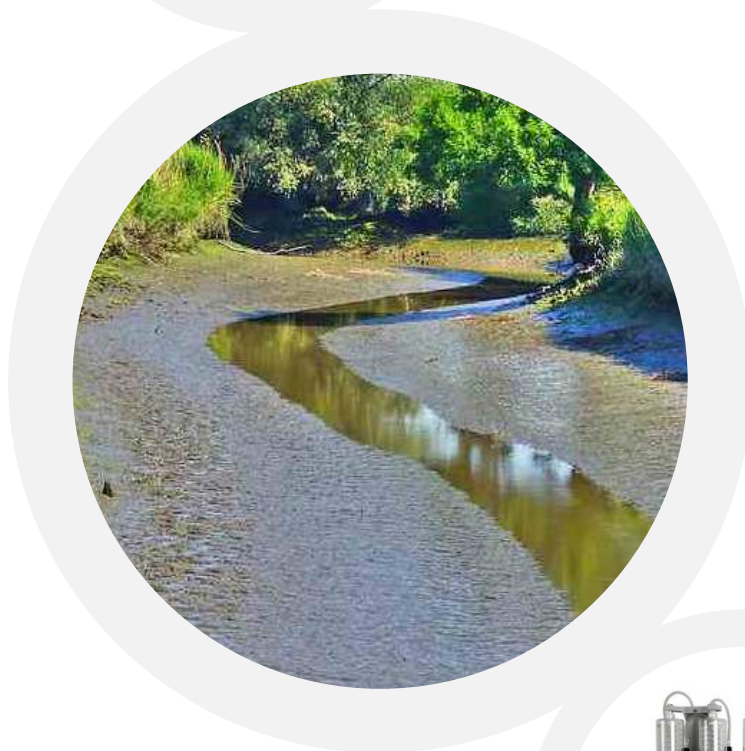
## No. 032/2010

### Total Petroleum Hydrocarbons in Soil and Sediment Samples

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Extraction System B-811:

Determination of Total Petroleum Hydrocarbons in Soil and Sediment Samples using Extraction System B-811.



## 1. Introduction

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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.

This application note reports the automated Soxhlet extraction of TPH from soil, and sediment samples using the Extraction System B-811. The quantification of TPH was performed by GC-FID. TPH was taken as the sum of hydrocarbons in the range C<sub>10</sub>-C<sub>40</sub>. This application note meets the requirements of the U.S. EPA Methods 3541 and 8015B and the DIN ISO 16703 / EN 14039 Standards [1-3].

## 2. Equipment

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- Extraction System B-811
- Analytical balance ± 0.1 mg, Mettler (AE 200)
- Micropipette 10-100 µl, Socorex (Acura 825)
- Micropipette 100-1000 µl, Socorex (Acura 825)
- Vacuum manifold
- Separatory funnel
- Thermo Trace GC Ultra 2130, GC-FID, with Autosampler AS3000

## 3. Chemicals and Materials

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- *n*-Hexane, analytical grade, Merck (1.04367)
- Acetone, analytical grade, Merck (1.00012)
- *n*-Hexane, analytical grade, Merck (1.04379)
- Diatomaceous earth, Büchi (53201)
- Thimbles 25 x 100 mm, Büchi (41882)
- Glas wool
- Tetracontane (C<sub>40</sub>), Fluka (87086)
- Decane (C<sub>10</sub>), 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 µm film thickness. (P/N: UFM00001060704)

Samples:

Three samples were used for this application (Figure 1):

- pre-extracted soil sample (1), spiked with a standard diesel to 1'800 mg/kg
- certified reference materials (CRM) samples:
  - Clay loam (2), 0.6% water content (R.T. Corporation CRM 558-100)
  - Sediment (3), particle size  $\leq 125 \mu\text{m}$ , 5.7% water content (CRM ERMCC015a)



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

## 4. Procedure

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

- Preparation of the surrogate solutions
- Preparation of the extraction thimbles
- Extraction with the Extraction System B-811
- Clean-up
- Quantification by GC-FID

### 4.1 Preparation of the surrogate solutions

1. Weigh-in 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-in 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-in 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 extraction thimbles

#### Clay loam, Sediment

1. Add approx. 3 g of diatomaceous earth into the extraction thimble
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 extraction thimble
5. Add the surrogate solutions on top of the sample with a micropipette: 70  $\mu\text{l}$  of the tetracontane solution and 60  $\mu\text{l}$  of the decane solution
6. Add glass wool onto the top of the thimble

### Spiked sample

1. Add approx. 3 g of diatomaceous earth into the extraction thimble
2. Weigh in approx. 10 g of pre-extracted soil using an analytical balance
3. Mix the sample with approx. 3 g of diatomaceous earth
4. Fill the mixture sample/diatomaceous earth into the extraction thimble
5. Add the surrogate solutions on top of the sample with a micropipette: 70  $\mu$ L of the tetracontane solution and 60  $\mu$ L of the decane solution
6. Add 1000  $\mu$ L of the standard diesel solution
7. Add glass wool onto the top of the thimble

### 4.3 Extraction with the Extraction System B-811

1. Extract the samples in the “Soxhlet Warm” extraction mode according to the parameters shown in Table 1
2. Fill-in 120 mL of solvent into the solvent beakers

The extraction time is approx. 150 min for 4 positions.

Table 1: Extraction method of the Extraction System B-811

Step	Heating level	Time (Cycles)
1 (Extraction)	Upper level 5 Lower level 10	25 cycles
2 (Rinse)	Lower level 10	5 minutes
3 (Drying) → not necessary	0	0
Extraction solvent	<i>n</i> -hexane 50%, acetone 50%, (v/v)	
Volume of solvent	120mL	

### 4.4 Clean-up

1. Wash the extract in a separatory funnel with 100 mL of distilled water twice
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 20 mL)
6. Measure the volume  $V_{\text{hexane}}$  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 using 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: H<sub>2</sub> : program-med flow: 6 mL/min (50 °C); rate 2.5 mL/min; final value 10 mL/min (350 °C)
- Injection: 1.5  $\mu$ l splitless

## 4.6 Calculation

### TPH content

Calculate the TPH content using equation (1):

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

$W_{\text{TPH}}$  : TPH content [mg/kg]  
 $C_{\text{aliquot}}$  : concentration of TPH (C<sub>10</sub>-C<sub>40</sub>) in the aliquot analyzed by GC-FID [mg/L]  
 $V_{\text{hexane}}$  : volume of hexane after treatment with water (chapter 4.4) [mL]  
 $m_{\text{sample}}$  : sample weight [g]

### z-score

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

Calculate z using equation (2):

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

$x$  : mean value obtained using the Extraction System B-811 [mg/kg]  
 $V_{\text{CRM}}$  : certified value [mg/kg]  
 $SD_{\text{CRM}}$  : interlaboratory standard deviation of the certified reference material [mg/kg]

## 5. Results

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Tables 2-4 show the results obtained for the spiked soil, the clay loam and the sediment samples. Each sample was extracted fourfold.

The results of the spiked sample are displayed in Table 2. The Extraction System B-811 provided a good recovery of 92% with an rsd of 0.8%, which meets the acceptance criteria of U.S. EPA 8015B (80-120%) [2].

Table 2: Results for spiked soil

### **Spiked Soil**

	$m_{\text{sample}}$ [g]	$C_{\text{aliquot}}$ [mg/l]	$V_{\text{hexane}}$ [mL]	$W_{\text{TPH}}$ [mg/kg]
Sample 1	10.0232	152	110	1668
Sample 2	10.0048	156	105	1637
Sample 3	10.0500	157	105	1648
Sample 4	10.0590	152	110	1662
<b>Mean value</b>				<b>1654</b>
<b>sd</b>				<b>14</b>
<b>rds [%]</b>				<b>0.8</b>
<b>Theoretical value</b>				<b>1800</b>
<b>Recovery [%]</b>				<b>92</b>

Tables 3 and 4 display the results obtained for the two certified samples. The TPH content  $w_{\text{TPH}}$  was calculated according to equation (1).

Table 3: Results for clay loam

**Clay Loam (CRM 558-100)**

	$m_{\text{sample}}$ [g]	Caliquot [mg/l]	$V_{\text{hexane}}$ [mL]	$w_{\text{TPH}}$ [mg/kg]
Sample 1	10.0013	66.3	90	597
Sample 2	10.0157	46.9	113	529
Sample 3	10.0461	57.5	102	584
Sample 4	10.0119	52.3	115	601
<b>Mean value</b>				<b>578</b>
<b>sd</b>				<b>33.1</b>
<b>rds [%]</b>				<b>5.7</b>
<b><math>V_{\text{CRM}}</math> (<math>SD_{\text{CRM}}</math>)</b>				<b>661 (132)</b>
<b>z</b>				<b>0.6</b>

Table 4: Results for sediment

**Sediment (CRM ERM CC015a)**

	$m_{\text{sample}}$ [g]	Caliquot [mg/l]	$V_{\text{hexane}}$ [mL]	$w_{\text{TPH}}$ [mg/kg]
Sample 1	10.0098	251	91	2282
Sample 2	10.0635	233	90	2084
Sample 3	10.0516	253	90	2265
Sample 4	10.0470	242	92	2216
<b>Mean value</b>				<b>2212</b>
<b>sd</b>				<b>89.8</b>
<b>rds [%]</b>				<b>4.1</b>
<b><math>V_{\text{CRM}}</math> (<math>SD_{\text{CRM}}</math>)</b>				<b>1820 (192)</b>
<b>z</b>				<b>2.0</b>

The z-score was calculated for both certified reference material samples. In each case, the z-score was within  $z \leq 2$ , which means that the mean value does not differ significantly from the certified value [4]. The method described is comparable to the methods used by the laboratories participating in the interlaboratory tests which the certified values are based on.

## 6. Conclusion

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The results show that the Extraction System B-811 provided good recoveries and reliable results for the extraction of TPH from solid matrices. Approx. 120 mL of solvent were consumed per sample and the extraction time was approx. 150 min for 4 samples.

## 7. Acknowledgements

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

## 8. References

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- [1] US EPA 3541 "Automated Soxhlet Extraction"
- [2] US EPA 8015B "Total Petroleum Hydrocarbons (TPH) as Gasoline and Diesel"
- [3] DIN ISO 16703 / EN 14039 "Determination of content of hydrocarbon in the range C<sub>10</sub> to C<sub>40</sub> by gas chromatography"
- [4] SO/IEC 43-1: 1997 "Proficiency testing by interlaboratory comparisons".
- [5] Operation Manual Extraction System B-811