Determination of Total Petroleum Hydrocarbons in Rubble and Soils by Accelerated Solvent Extraction and GC-FID

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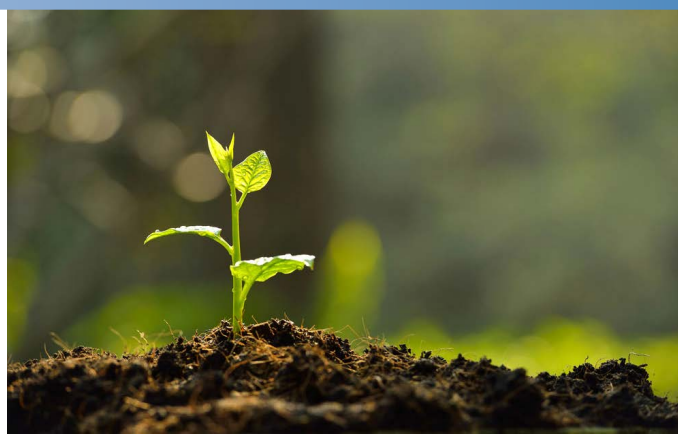
Key Words
Pressurized Fluid Extraction, UNI EN 14039:2005, Hydrocarbons >C_{12}, Hydrocarbons C_{10}-C_{40}, In-Line Clean-Up, Rocket Evaporator, Gas Chromatography, Flame Ionization Detection

Goal
To demonstrate an accelerated solvent extraction and GC-FID procedure for total petroleum hydrocarbons (TPH) in contaminated soils and rubble.



Introduction
The hydrocarbon contamination of soil that occurs through the spillage or leakage of petrol, diesel, or lubricants is one of the most common forms of environmental pollution. Hydrocarbons have been routinely determined by infrared spectroscopy after extraction with halogenated solvents such as 1,1,2-trichloro-1,2,2-trifluoroethane (Freon® 113) or tetrachloromethane. Because of ozone depletion concerns, the use of chlorofluorocarbons has been banned or severely limited in many countries. Alternative methods like Soxhlet extraction (United States Environmental Protection Agency (U.S. EPA) Method 3540) and ultrasonic extraction (U.S. EPA Method 3550) are presently used for the extraction of hydrocarbons from soils prior to their analytical determination. Those techniques are very labor intensive and suffer from high solvent consumption, often requiring 18 hours and 500 mL of solvent per sample.

Accelerated Solvent Extraction was developed to reduce the amount of solvent and time required for extraction of organic contaminants from solid samples. With Accelerated Solvent Extraction, extractions can be completed in as little as 20 minutes and use less than 50 mL of solvent per sample. Accelerated Solvent Extraction uses elevated temperature to improve the extraction efficiency of organic contaminants from solid samples. This technique also uses elevated pressure to keep solvents in a liquid state above their boiling point in order to achieve rapid and reproducible extractions. Due to the use of elevated temperature, interferences may be extracted along with desired analytes during those conventional extraction processes. These unwanted co-extractables may interfere with analyte detection or decrease instrument performance. Traditionally, chromatographic techniques such as gel-permeation chromatography (GPC) or a glass column packed with specific adsorbents are used to clean sample extracts prior to separation and analysis. For example, the determination of the hydrocarbon content in solid waste according to the UNI EN 14039:2005 requires a post-extraction clean-up in a glass column with Florisil®.

Recent advances using Accelerated Solvent Extraction systems, as described in several publications,[1-18] include procedures for selective removal of interferences during sample extraction, thus combining extraction and purification into a single step. This advance eliminates the need to perform offline sample clean up procedures and reduces the amount of time spent on sample preparation prior to analysis with GC.

The method reported here is applicable to soils with a hydrocarbon content (>C_{12}) between 25 and 4000 mg/kg and waste with a hydrocarbon content (C_{10}-C_{40}) between 50 and 8000 mg/kg expressed on a dry matter basis. All hydrocarbons with a boiling range of approximately 175 °C to 525 °C, e.g. *n*-alkanes from $C_{10}H_{22}$ to $C_{40}H_{82}$, isoalkanes, cycloalkanes, alkyl benzenes, alkyl naphthalenes, and polycyclic aromatic compounds are determined as total petroleum hydrocarbons (TPH).

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Experimental

Equipment

An ED53 oven from Binder™ was used for drying the samples. A Sartorius™ analytical balance was used for weighing the dry soil samples and the standards. A Fritsch™ Pulverisette™ planetary ball mill was used to grind the samples. The extractions were carried out with the Thermo Scientific™ Dionex™ ASE™ 350 Accelerated Solvent Extractor (P/N 083114, 120 V, or P/N 083146, 240 V) (Figure 1) equipped with 34 mL stainless steel extraction cells (P/N 068089). The extracts were collected in 60 mL double-ended Thermo Scientific™ Rocket™ Flip-Flop tubes (P/N 076360) (Figure 2) and directly concentrated in a 2 mL autosampler glass vial (Thermo Scientific™ Chromacol™ VAGK ISP: GC 2-SVW + 9-SCK(B)-ST1) with the Thermo Scientific Rocket Evaporator (P/N 075904, 120 V or 082766, 240 V) (Figure 3).

Figure 1. Dionex ASE™ 350 Accelerated Solvent Extractor.

Figure 2. Rocket Flip-Flop Vial.

Figure 3. Rocket Evaporator.

The samples were analyzed with a Thermo Scientific™ FOCUS™ GC Gas Chromatograph equipped with a split/splitless injector, a Thermo Scientific™ TRACE™ TR-5 GC column (30 m × 0.25 mm × 0.25 µm, P/N 260E142P), and a flame ionization detector (FID).

Solvents and Standards

Pesticide-grade hexane (Fluka™, P/N 34484) was the extraction solvent for ASE. Thermo Scientific™ Dionex™ ASE™ Prep Diatomaceous Earth (DE) (P/N 062819) was used. Silica gel (70-230 mesh for column chromatography, P/N 453337) was purchased from Carlo Erba Reagents™. *n*-decane (P/N D901), *n*-dodecane (P/N D221104) and *n*-tetracontane (P/N 87087) were purchased from Sigma-Aldrich®. *n*-octadecanoic acid octadecyl ester (P/N 46408) was purchased from Fluka. Diesel standard (without additives, DIN H53, P/N CA03009000) and mineral oil standard (without additives, DIN H53, P/N CA03009010) were purchased from Dr. Ehrenstorfer GmbH. Mineral Oil Standard Mixture Type A and B at a concentration of ~8000 mg/mL in heptane (P/N 69246, exact content on the label) was purchased from Fluka. Sodium sulfate (P/N 31481) was purchased from Sigma-Aldrich.

Standard solutions with concentrations of 4000.0, 2000.0, 1000.0, 500.0, 200.0, and 100.0 mg/L were prepared from an 8000 mg/L stock solution of both diesel and mineral oil standards. The silica gel was activated by heating at 550 °C for at least 4 h. The test solution of *n*-octadecanoic acid octadecyl ester ($C_{36}H_{72}O_2$) was prepared by dissolving 100 mg of *n*-octadecanoic acid octadecyl ester in 100 mL *n*-hexane. The clean-up efficiency of each batch of silica gel was checked by adding 10 mL of the test solution to a clean-up column filled with 2.0 g of silica gel and 2 g of sodium sulfate. After chromatographic analysis of the eluate the percent recovery of the *n*-octadecanoic acid octadecyl ester should not exceed 5%. The retention time window (RTW) standard solution for C_{10}-C_{40} was prepared by weighing 30 mg of *n*-tetracontane into a 1 L volumetric flask, followed by the addition of *n*-hexane and 30 µL (about 21 mg) of *n*-decane. The retention time window (RTW1) standard solution for >C_{12} was prepared by weighing 30 mg of *n*-tetracontane into a 1 L volumetric flask, followed by the addition of *n*-hexane and 35 µL (about 26 mg) of *n*-dodecane.

Extraction, Concentration, and Measurement

A cellulose filter (Thermo Scientific, P/N 056780) was placed in the bottom of a 34 mL extraction cell, followed by 5 g of activated silica gel and another cellulose filter. Four gram samples of soil from residential areas, 2 g of soil from industrial areas, or 2 g of rubble were mixed in a glass beaker with a sufficient amount of Dionex ASE Prep DE and the resulting mixture carefully poured into the extraction cell. Any empty volume was filled with Dionex ASE Prep DE. The Accelerated Solvent Extractor system was programmed according to the conditions reported in Table 1.

Table 1. Conditions for Accelerated Solvent Extraction.

Solvent	*n*-Hexane
Temperature	100 °C
Static Cycles	1
Extraction Time	5 min
Rinse Volume	60%
Purge Time	90 s
Total Extraction Time per Sample	20 min
Total Solvent Volume per Sample	40 mL

The extracts were directly collected into Flip-Flop vials and evaporated on the Rocket Evaporator using the preprogrammed Low Boiling Point Method until nearly dry. The leftover was reconstituted with 1 mL of the RTW or RTW1 solution according to the type of analysis requested and injected in the GC. The GC conditions are summarized in Table 2.

Table 2. Gas chromatograph conditions.

Carrier Gas	Helium
Flow Rate	2.0 mL/min, constant flow
Oven Temperature	45 °C (hold 1 min), 25 °C/min to 340 °C (hold 2 min)
Injector Temperature (SSL)	300 °C
Injection Mode	Splitless
Splitless Time	0.80 min
Splitflow	50 mL/min
Detector Temperature (FID)	340 °C
Injected Volume	2 µL

Results and Discussion

Soils are an extremely complex matrix to analyze, particularly when they originate from contaminated sites. The nature and composition of the soil has a significant impact on the extraction efficiency and the sensitivity of the method. The typical soil consists of approximately 45% mineral, 5% organic matter, 20–30% water, and 20–30% air. In particular, the organic matter contains high molecular weight, non-volatile material that can remain in the GC system thus leading to poor analytical performance. Many analysts use extensive sample preparation techniques to extract and concentrate the compounds of interest from this unwanted nonvolatile material. These extraction and concentration techniques can however become time consuming and costly. Construction and demolition rubble samples are also of concern because of their possible contamination with hydrocarbons and other compounds like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs).

According to the UNI EN 14039:2005, the soil sample is extracted with an acetone - *n*-heptane mixture. Acetone is then removed from the extract with water. The resulting organic phase is subjected to solid phase extraction with Florisil to remove the organic matter such as humus and humic compounds, and the eluate is analyzed by GC-FID. The same norm also mentions Accelerated Solvent Extraction as an alternative extraction procedure; however, it is still followed by a manual clean-up with Florisil. Several recent publications describe procedures for selective removal of interferences during Accelerated Solvent Extraction, thus combining extraction and purification into a single step.

Due to the compositional complexity of petroleum products, it is impossible to assess the extent of petroleum hydrocarbon contamination by separately measuring the concentration of each hydrocarbon contaminant. One parameter that is currently widely used for expressing the total concentration of nonpolar petroleum hydrocarbons in soil is termed TPH. It is a non-specific, method-defined parameter that is determined by GC-FID. The total peak area of resolved and unresolved components in the chromatogram range delimited by the retention times of *n*-decane and *n*-tetracontane is integrated (Figure 4). Only semi- and non-volatile hydrocarbons are therefore included in the TPH parameter.

The first extractions were done using spiked soils that were previously heated for 4 h at 800 °C in order to completely remove the organic matter. The TPH spike levels were 25, 50, and 750 mg/kg. Twenty samples were extracted for the fraction >C_{12}, and twenty samples for the fraction C_{10}-C_{40}. The test results showed that spike recovery rates were between 84.0% and 101% for >C_{12} and 79.0% and 96.6% for C_{10}-C_{40}. The UNI EN 14039:2005 additionally prescribes a maximum RSD of 9.14% for a low contaminated soil and 8.13% for a highly contaminated soil (corresponding to 697 mg/kg and 1818 mg/kg, respectively). For rubble, the maximum RSD is 6.05%, corresponding to 7841 mg/kg. With a maximum RSD of 5.7% for >C_{12} and 5.5% for C_{10}-C_{40}, both parameters were in full compliance with the requirements of the European norm. A typical chromatogram for a 750 mg/kg spiked sample is showed in Figure 4. All the results are summarized in Tables 3 and 4.

The concentration of the contaminated soil was around 4000 mg/kg as shown in Figure 5. The sample was processed according to the procedure described in the Extraction, Concentration, and Measurement section. The diesel oil fraction, corresponding approximately to C_{11}-C_{18}, can be clearly recognized as the main pollutant in this sample.

Table 3. Average recovery and RSD for >C_{12}.

Concentration mg/kg		
25	50	750
88.9	105.0	99.3
81.8	106.8	101.3
84.4	105.0	100.5
87.6	99.1	101.2
90.8	99.8	99.4
85.2	94.7	102.2
81.9	101.6	97.8
79.9	107.2	99.4
87.8	95.5	103.7
78.1	106.2	102.2
76.1	101.2	100.0
90.1	98.4	100.0
89.8	89.7	101.6
81.5	103.3	100.0
90.8	102.1	104.7
75.4	91.3	103.6
84.2	92.7	99.8
85.9	95.2	95.8
79.0	109.3	100.4
80.9	95.9	98.2
Average Recovery %		
84.0	100.0	100.5
RSD		
5.8	5.7	2.1

Table 4. Average recovery and RSD for C_{10}-C_{40}.

Concentration mg/kg		
25	50	750
77.9	101.6	102.0
80.3	101.3	100.7
80.9	90.2	95.9
82.7	98.6	98.0
88.8	101.5	93.5
81.1	90.6	93.7
78.6	96.6	86.8
77.6	104.5	94.9
76.5	95.3	96.3
73.5	98.9	93.4
72.7	91.8	97.9
84.2	94.9	86.7
85.6	87.1	93.9
73.1	99.0	100.3
78.8	103.5	98.6
75.5	89.0	104.3
81.4	94.1	102.0
83.4	89.1	94.1
70.2	103.3	89.3
77.3	100.8	105.0
Average Recovery %		
79.0	96.6	96.4
RSD		
6.0	5.7	5.4

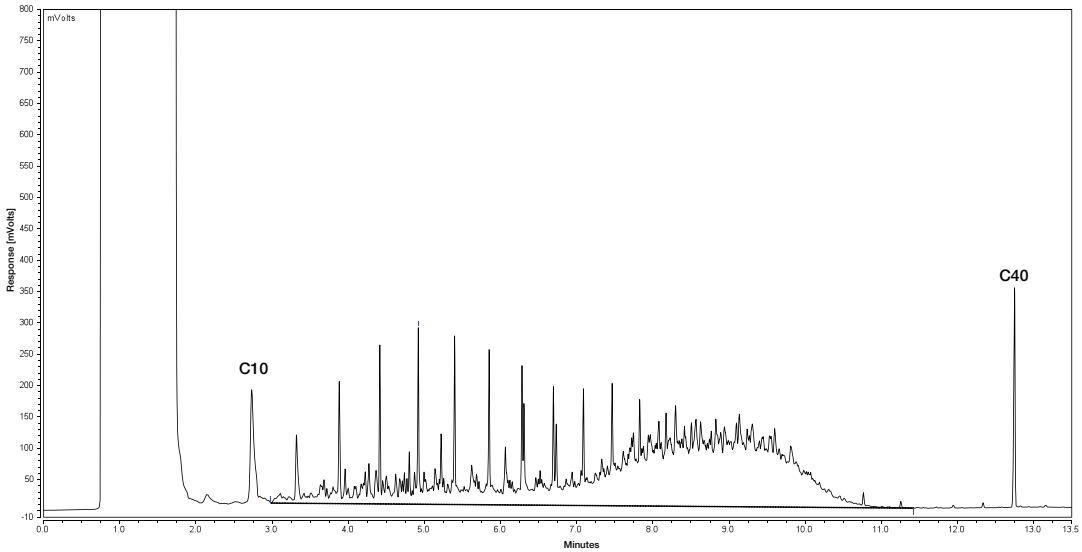

Figure 4. Chromatogram for 750 mg/kg spiked soil sample after ASE-extraction and concentration.

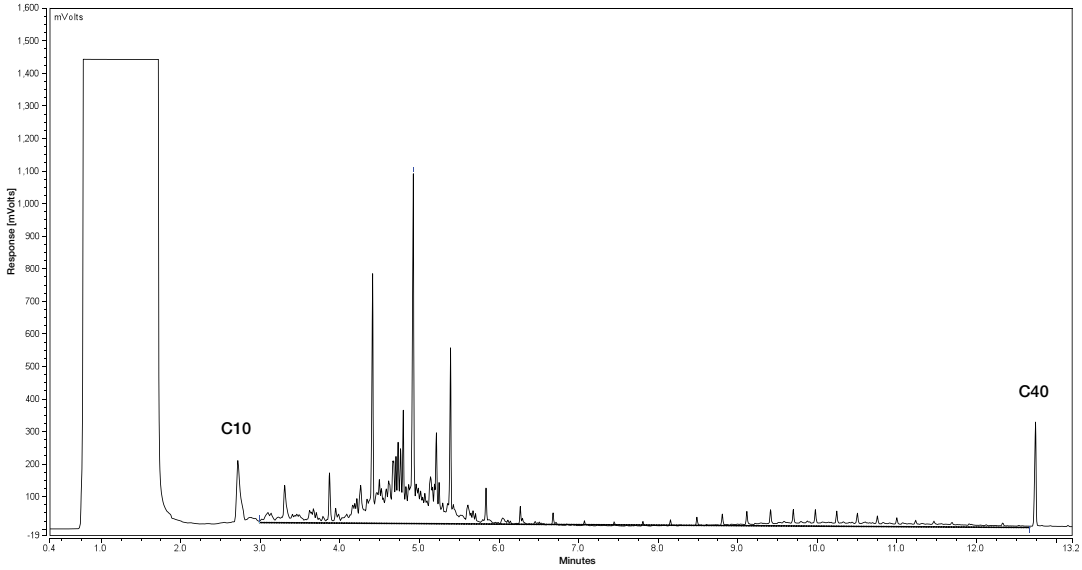

Figure 5. Chromatogram for a heavily contaminated soil sample after ASE and concentration.

Conclusion

When using Accelerated Solvent Extraction with in-cell cleanup to extract hydrocarbons from contaminated soils, the spike recovery is between 84.0% and 100.5%. The selective removal of interferences with the in-cell cleanup avoids time-consuming and costly post-extraction manual purification procedures. Processing a sample using Accelerated Solvent Extraction requires only 20 min and only 40 mL of solvent. The Rocket Evaporator eliminates the need for cumbersome nitrogen stream evaporation. By using the Flip-Flop system the samples can be concentrated directly into the GC vial.

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