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Clean-Up of the Solid Liquid Extraction Using Certified Reference Material for Soil TPH by GC-FID

Abstract

Accurate measurement of total petroleum hydrocarbon (TPH) is needed for contamination quantitation, risk assessment and site remediation. However, the analysis of petroleum in complex matrices such as soil involves extracting the hydrocarbons, not just of petrogenic (petroleum) origin but also of biogenic (biological) sources. Thus, a clean-up step is required after the solid liquid extraction of contaminated soil to remove matrix interferences. In this study, the clean-up efficiency and petroleum hydrocarbon recoveries were evaluated for dispersive solid phase extraction (dSPE) and traditional column SPE (cSPE) using a certified reference material for soil TPH. To determine petroleum hydrocarbons in the resulting extracts, gas chromatography-flame ionization detection was used. The results of the evaluation indicated that both cSPE and dSPE using silica or florisil as adsorbent provided optimal clean-up with good recovery of targeted hydrocarbons in the three commonly regulated fractions: > C10 – C16, > C16 – C34, > C34 – C40. This clean-up step is important as this will affect subsequent sample preparation steps to separate TPH into its different fractions and individual components for assessing the level of contamination and the effectiveness of remediation for decision making based on risk assessment.

Keywords: Total petroleum hydrocarbon; Solid phase extraction; Soil; Gas chromatography-flame ionization detection

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Introduction

The growing demand for the production of petroleum and the consumption of petroleum products have raised concerns about their release into the environment and potential harm to humans, wildlife animals, and aquatic species [1]. The use of petroleum-based products, such as gasoline, kerosene, fuel oil, mineral oil, and asphalt mainly for transportation, heating and power-generation, is indispensable in modern life. However, as the number of facilities and processes is diverse, petroleum contamination of the environment continues to be a widespread global concern. Petroleum can enter the environment through leaks from underground storage tanks and spills from industrial and domestic activities. Once released into the environment, petroleum is transported in the earth's biosphere: land, water, and air [2]. This dispersal is due to the process called weathering which includes adsorption to soil particles, dissolution in water, and volatilization into the atmosphere [3,4]. Chemical transformation, including biodegradation, produces countless oxygen-containing intermediates known as polar metabolites of petroleum such as alcohols, phenols and acids. Petroleum hydrocarbons will inevitably make their way in the entire biosphere. This necessitates a rapid and accurate detection of total petroleum hydrocarbon (TPH) in a variety of environmental matrices. Accurate measurement of certain target petroleum hydrocarbons is vital for contamination quantitation, risk assessment and site remediation.

Sample preparation is an integral step before instrumental analysis [5]. Analytical separation of various sample constituents is a crucial mass transfer methodology. This operation will allow isolation of target chemicals from a complex sample matrix such as soil, sediment or living things. Further separation and purification of the target chemicals from co-extracted non-target chemicals can be attained. Analytical separation techniques include filtration, extraction, and evaporation. Petroleum in contaminated soil is easily extracted into a non-polar solvent such as dichloromethane, hexane, and pentane. Analysis for the target hydrocarbons is usually done by gas chromatography (GC) on a non-polar capillary column with a flame ionization detector (FID) [6-12].

Petroleum is composed of thousands of hydrocarbons with varying physical-chemical properties [13]. Globally and traditionally, petroleum analysis is reported as total petroleum hydrocarbon (TPH) to describe this large family of heterogeneous compounds that are found in crude oil and whose main chemical constituents are carbon and hydrogen atoms. As petroleum hydrocarbons exist as a mixture of so many different compounds, it is impossible to identify each and every individual component. Thus, it is more practical to quantify petroleum hydrocarbons in environmental samples as a group of congeners rather than as separate compounds. TPH is a sum parameter of all the components, not the sum of all individual components. To allow the separation of TPH into discrete bands, fractionation by GC analysis was based on the boiling point distribution. The retention times from C10 to C40 were reported for the three commonly regulated fractions: > C10 to C16, > C16 to C34, > C34 to C40 [14]. However, the problem

in quantitative analysis is that the method does take into account not only the hydrocarbons eluting between C10 and C40, but also other compounds present in the sample. These compounds could be the biogenic organic compounds (BOCs) and the polar metabolites produced by weathering [15,16]. These polar compounds are revealed as a hump in the GC chromatogram, generally known as the unresolved complex mixture (UCM). Therefore, to make the analysis specific for TPH, a clean-up step is necessary to remove the non-petroleum hydrocarbons and the petroleum-derived metabolites.

The most commonly used method for cleaning up the extract of petroleum compounds from environmental samples is solid phase extraction (SPE) [17,18]. The polar, oxygen or nitrogen-containing compounds and remaining traces of water are usually removed from soil extracts through SPE with silica, florisil or anhydrous sodium sulphate. As silica and florisil are polar adsorbents, all polar interferences are retained allowing the non-polar TPHs to be extracted with a non-polar solvent. SPE clean-up is performed through either dispersive SPE (dSPE) or the more traditional column SPE (cSPE) [19-21]. Initially, the soil is extracted with a non-polar solvent such as n-pentane. In dSPE, the resultant extract is then cleaned by shaking with the adsorbent in a vial. In cSPE, the extract is percolated through a column containing the adsorbent. The TPH is recovered by eluting with the original extraction solvent. After SPE, the resulting extract is quantitatively analysed by GC. Zemo and associates applied dSPE and cSPE to water samples only; thus, there is a strong need to evaluate these techniques for the solid liquid extract of soil samples.

However, the clean-up step is not required by all regulatory agencies. Routinely samples are analysed, without clean-up, for determining the full extent of petroleum contamination and evaluating potential risks. For this reason, an equivalent term called total recoverable hydrocarbons (TRH) is also commonly used to represent the biogenic (biological) and petrogenic (petroleum) hydrocarbons extracted by selected solvents [22]. These co-extracts can cause a matrix-induced chromatographic response effect which can elevate the TRH above the TPH concentration. Thus, the reliability of the analytical data is weakened by not requiring a clean-up step in the extraction method. To overcome the aforementioned limitations, this study was conducted to investigate the Zemo clean-up technique for the GC-FID analysis of TPH in contaminated soil using a certified reference material (CRM) for soil TRH. The performance of both dSPE and cSPE clean-up approaches was compared in terms of analyte recovery and matrix reduction.

Experimental

Chemicals and reagents

TPH standard mixture (Hydrocarbon Window Defining Standard) was obtained from AccuStandard, Inc. (CT, USA) and catalogue no.DRH-008S-R2. This primary stock standard solution had 33 components (n-C8 to n-C40), each at 500 µg/mL dissolved in chloroform with pristine and phytane as biomarkers. UniSolv[®] grade n-pentane was used for standard solution preparations, dilutions and blanks (PN: MER-107288,

Merck, Darmstadt, Germany). DCM was obtained from Fisher Chemicals (UK). Water used was Milli Q grade (resistivity: 18.2M Ω .cm). Anhydrous sodium sulphate (Na₂SO₄) was purchased from Merck, Darmstadt, Germany. Dichloromethane for the injector syringe wash was obtained from Fisher Chemicals (UK). Water used was Milli Q grade. The carrier gas helium was of ultra-high purity grade (99.999%). Hydrogen and nitrogen used for the detector were of ultra-high purity (99.999%) and high purity (99.99%) grade, respectively. Purified air of high purity grade was employed as the oxidant gas for the detector. Silica gel (0.075-0.250 mm, 150A^o) was from Acros, code: 419280010. Florisil (60-100 mesh) was from Acros, code: 205450010. Replacement teflon frits for the glass columns were from Sigma Aldrich (PN 504327). Prior to use, adsorbents, cartridges and sodium sulfate were dried in the oven at 130^oC for not less than 24 h. All glassware was rinsed with acetone, n-hexane and DCM, sequentially prior to use.

The CRM for soil TRH, NMIA MX015, was obtained from National Measurement Institute (NMI) [23]. MX015 is soil from a highly contaminated industrial site that was mixed with clean sand to give a suitable level of contamination. The certified mass fraction (w) for silica treated total recoverable hydrocarbons (TRH-silica) are given in Table 1.

Preparation of working standard solutions

Each of the calibration standard solution was prepared to a final volume of 1 mL in 2 mL GC sample vial using manual glass syringes. An intermediate standard (22 μ g/mL) was made by transferring 60 μ L of the 500 μ g/ml primary stock standard and mixing with 1300 μ L of n-pentane within a closed 2 mL GC sample vial. From the primary and intermediate standards, working calibration standard solutions were prepared in the range of 1–50 μ g/mL (for each component) for linearity using n-pentane as diluent. Considering high volatility, exact n-pentane volumes used for the dilutions were calculated based on weights in a sealed vial and converted to volume using the density value of 0.626 g/mL at 20^oC.

Instrumentation

TPH analysis was performed on an Agilent 6890N Network gas chromatograph system equipped with a flame ionization detector (FID). Chromatographic resolution was achieved with a HT-5 thin film capillary column, 12 m \times 0.22 mm ID \times 0.1 μ m film thickness (SGE part number 054631). HT-5 is a carborane modified polysiloxane with an equivalent polarity of 5% phenyl. Helium was used as carrier gas in constant flow mode at 2.0 mL/min. A deactivated fused silica retention gap column of 0.25 mm ID \times 5 m (Agilent P/N 160-2255-5) was connected to the front end of the analytical column with a fused silica connector (Agilent P/N 705-0905). The initial oven temperature was kept at 34^oC for 1.5 min, ramped to 320^oC at a heating rate of 15^oC/min and held isothermal for 3.83 min. The FID temperature was set at 320^oC. Hydrogen and air flow were 40 and 450 mL/min, respectively. Make-up gas was nitrogen with flow of 15 mL/min. Dichloromethane and n-pentane solvents were used for syringe rinses. Injection was performed using a 10 μ L syringe in an Agilent 7683B Series autosampler. The conventional split/splitless inlet temperature was kept constant at 275^oC, in pulsed

splitless mode. A 1 μ L sample is injected with a pulse pressure of 30.0 psi, which was held for 1.50 min. After the initial pressure pulse, the carrier gas flow was held constant. Liner with single taper and packed with deactivated borosilicate glass wool (Agilent part no. 5190-2293) was used. Agilent Enhanced Productivity Chemstation chromatography software (G1701EA Version E.02.02.1431) was used for data acquisition and processing.

Sample extraction procedure

Five gram of soil sample was accurately weighed and transferred into a 40 mL VOA vial. Five mL of methanol was added to this mixture as dispersing/drying solvent followed by 5 mL of extraction solvent, n-pentane. Sample was vortex mixed for 2 mins and 23 mL of saturated NaCl solution was added. Extraction was continued in an end-over shaker overnight. Sample was centrifuged for 1 hour at 4^oC and 400 rpm to enhance phase separation. Pentane extracted layer was transferred to a clean vial and stored at 4^oC prior to SPE clean-up.

Extract clean-up

For the dSPE clean-up, a known amount of Na₂SO₄ and/or adsorbent was placed in a 40-mL VOA vial. One mL of the n-pentane soil extract was added. After closing the lid, the sample was shaken. A small volume of n-pentane solvent were added and then shaken. The extract was transferred to a 25-mL volumetric flask. The process was repeated until the flask is almost full. The flask is then volumed to the mark with n-pentane; thereby diluting the original 1 mL extract to 25 mL. A 1 mL portion of the extract was transferred into a GC vial for injection. Variable amounts of Na₂SO₄ and silica and a combination of the two were tested for their effectiveness.

For the cSPE clean-up, the drying agent and/or adsorbent were transferred to a cartridge glass column (7.5 cm \times 1.5 cm, 6 mL bed volume capacity) with teflon frit at the bottom to support the solid material. The adsorbent was conditioned with five times the bed volume of the adsorbent using n-pentane prior to sample loading. One mL of the n-pentane extract was loaded onto the cartridge. Elution was by gravity with n-pentane as the eluent to recover the hydrocarbons. The eluates were collected in a 25-mL volumetric flask. Continuous elution was performed until the flask is almost full. The flask is then volumed to the mark with n-pentane. A 1 mL portion of the extract was transferred into a GC vial for injection.

Result

Characterization of MX015

Total carbon, nitrogen and sulfur were determined by LECO TRUMAC CNS analyser. Dissolved organic carbon was analysed by Shimadzu TOC-L Analyzer. Determination of pH was in 1 gram soil mixed with 5 mL Milli Q water. The results are shown in Table 2. MX015 has a total carbon content of 21 g/kg, based on the direct analysis of the soil sample. The reported TRH is 9.2 g/kg, which is 11.8 g/kg different from the total carbon content.

Table 1: Certified property values for silica treated TRH in CRM NMIA MX015.

NMIA MX015	> C10 – C16 (g/kg)	> C16 – C34 (g/kg)	> C34 – C40 (g/kg)	TRH (g/kg)
Certified Value	0.90 \pm 0.15	7.2 \pm 1.1	1.1 \pm 0.2	9.2 \pm 1.4

The difference of 11.8 g/kg between these two values could be related to the amount of interference that has to be removed during sample preparation.

Chromatographic separation

Initially, the separation of the hydrocarbon standard is important for the determination of the three fractions of NMIA MX015. The optimized GC method using a nonpolar column gave an analysis time of 26 mins. An injection of the TPH standard mixture verified the baseline separation of C10 from n-pentane, as shown in the chromatogram of Figure 1. The resolution of the peaks from C10 to C40 was obtained with identification using the biomarkers, pristane and phytane which co-elute with C17 and C18, respectively. The co-eluting peaks were quantified as one. Fractions were defined by the elution order of the n-alkane standards from the GC column. Quantification of peak area of TPH fraction was performed manually using forced line integration as a single group area the portion of the chromatogram, where:

> C10 – C16 Fraction of hydrocarbons measured from the end of n-C10 peak to the end of n-C16 (Fraction 1)

> C16 – C34 Fraction of hydrocarbons measured from the end of n-C16 peak to the end of n-C34 (Fraction 2)

> C34 – C40 Fraction of hydrocarbons measured from the end of n-C34 peak to the end of n-C40 (Fraction 3)

Table 2: Characterization of MX015.

Property	Value
Dissolved total carbon	0.0218%
Dissolved total organic carbon	0.0203%
Dissolved inorganic carbon	0.0015%
Carbon	2.1021%
Nitrogen	0.6191%
Sulfur	0.0429%
pH	6.17

The chromatogram of MX015 after solid liquid extraction with n-pentane is in Figure 2 which illustrates the three fractions for quantitation. The standard method for integrating the GC signal is at a level corresponding to the baseline of the solvent peak. Typically, the signal does not return to the baseline during the time window of C10-C40, depending on the nature of hydrocarbon contamination.

The response factor (RF) was determined from the calibration curve which, in turn, was used for quantification. The RF values of C14, C24 and C36 were used to calculate Fraction 1, Fraction 2 and Fraction 3, respectively. The fractions were calculated using the equation below:

Measurement Equation

$$w = (A/m) \times (V/RF)$$

w mass fraction

A peak area for fraction

m mass of sample

V volume of final extract

RF response factor

Extract without clean-up

The soil sample was extracted with n-pentane in the presence of saturated NaCl solution. After transferring the n-pentane extract into a GC vial, the extract was injected into the GC without further treatment. Figure 3 shows the amount recovered in each fraction, with the corresponding deviation from the reported value in Table 3. Fraction 1 (1.07 g/kg) is 18.6% different from the reported value of 0.9 g/kg. However, Fraction 1 is still within the upper limit of 1.1 g/kg. Fractions 2 and 3 are outside the upper limit of the certified value. The amount of 10.70 g/kg in Fraction 2 is 48.7% different from the reported value of 7.2 g/kg (with limits of 6.1–8.3 g/kg). Fraction 3 has 1.66 g/kg, which is 51.2% different from the reported value of

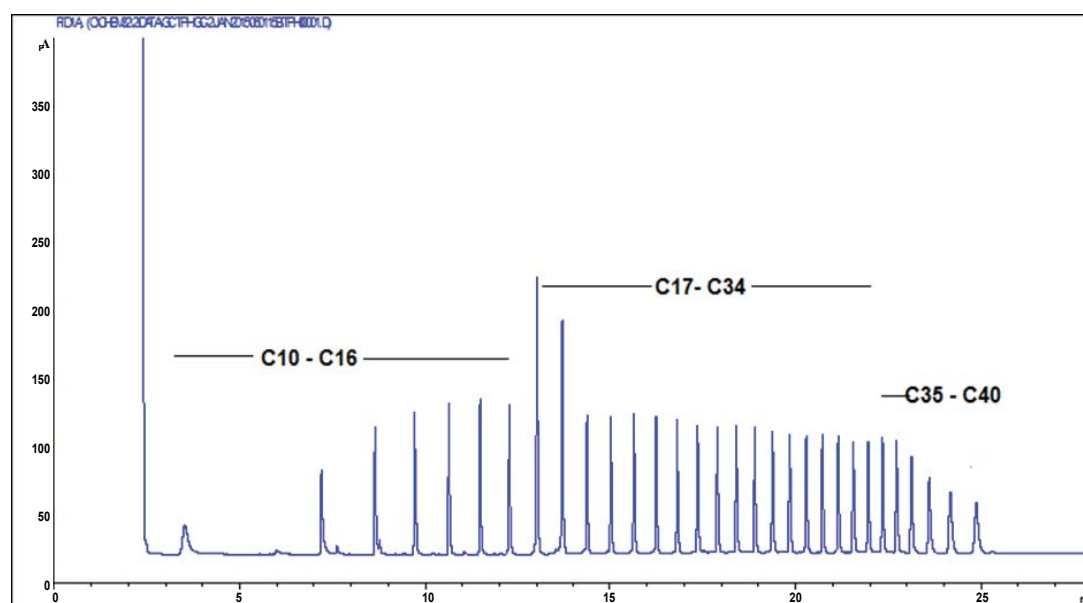


Figure 1: A typical chromatogram of a TPH standard solution at 10 ppm showed good resolution of all the alkane peaks from C10 to C40 with C10 completely resolved from the solvent front.

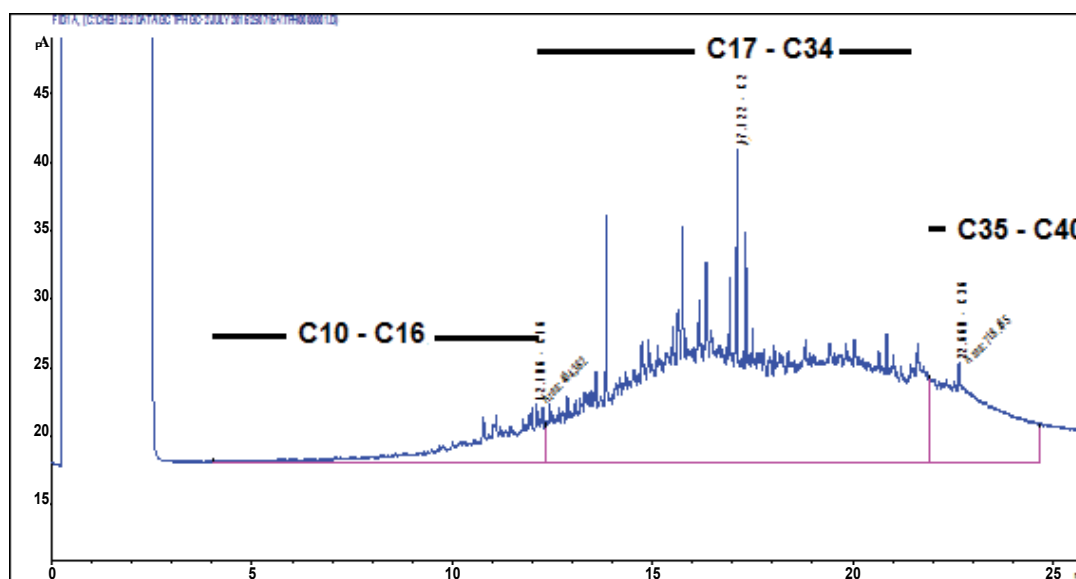


Figure 2: Chromatogram of the n-pentane extract of MX015.

1.1 g/kg (with limits of 0.90–1.3 g/kg). The TRH is 13.43 g/kg which is outside the reported range of 7.8–10.6 g/kg. This extraction technique does not provide sufficient background removal prior to analysis. The exceedances show that the major matrix interferences are eluting in Fractions 2 and 3. The process of removing these interferences was then investigated through different clean-up methods.

Drying of extract

The first step investigated for clean-up was the removal of residual water in the extract. The n-pentane extract was dried by shaking with anhydrous Na_2SO_4 in a 40-mL VOA vial. Different amounts of Na_2SO_4 were tested: 0.5, 1, 2 and 3 grams. The results of the drying process are shown in Figure 4. Deviations of Fractions 1, 2 and 3 from the reported values are in Table 4. The increasing amount of Na_2SO_4 decreased the deviation from the reported value; thereby, improving the recovery of Fractions 1 and 2. However, there is no trend in the effect of the amount of Na_2SO_4 for the recovery of Fraction 3. The deviation of Fraction 3 after Na_2SO_4 drying did not dropped significantly from the non-dried extract as compared to Fractions 1 and 2. This result indicates that probably Fraction 3 has other interferences that are not soluble in water which the Na_2SO_4 could not remove; thereby, this fraction requires extensive clean-up.

SPE clean-up with silica

One mL of the n-pentane extract was cleaned with Na_2SO_4 and silica using the dSPE and cSPE methods to compare efficiency. In the dSPE method, the extract was initially shaken with 1 gram Na_2SO_4 in a VOA vial. The resulting extract was transferred to another VOA vial containing 1 gram silica. This process was repeated by adding n-pentane after every transfer to ensure complete recovery. After shaking with silica, the extract was transferred to a 25-mL volumetric flask for dilution to the mark to obtain the desired concentration for GC analysis. In the cSPE method, 1 gram silica was accurately weighed and transferred to the glass column, then topped with 1 gram Na_2SO_4 . The column was conditioned with n-pentane prior to

loading of the 1 mL n-pentane extract. The elution solvent was n-pentane. The eluent was collected in a 25-mL volumetric flask for final dilution to the mark. The recovery results are in Figure 5, with percent deviation from the reported values in Table 5. Both dSPE and cSPE methods have decreased the deviation, making the recovery of each fraction closer to the reported value. Overall, the efficiency of the dSPE and cSPE in the removal of matrix interferences is comparable.

SPE clean-up with florisil

The performance of other types of adsorbent was investigated by replacing silica with florisil. One gram florisil was loaded into the glass column and then topped with 1 gram Na_2SO_4 . All other conditions were kept the same as in the silica experiment. The recovery using florisil is in Figure 6. The deviations from the reported values of the three fractions are 0.8, -1.2 and 11.1% (Table 6). The recovery of each fraction approximates that of the reported value making florisil as efficient as silica in removing matrix interferences. As florisil is more polar than silica, it is expected to remove more of the polar interferences.

Repeatability of clean-up method

The repeatability of the clean-up method using Na_2SO_4 and silica was validated by processing several aliquots of the n-pentane extract through the SPE column. The precision was evaluated by calculating the %RSD. The results of the repeatability study are in Table 7. The observed means for the > C10 – C16, > C16 – C34 and > C34 – C40 fractions are 0.9, 7.3 and 1.3 with %RSD of 6.8, 5.8 and 6.2, respectively. The extraction efficiencies based on the amount recovered are 100.7, 100.8 and 114.1 % for the three fractions, respectively.

Discussion

The reported values of the CRM used in this study were developed using GC-FID and soxhlet for sample preparation and SPE with Na_2SO_4 and silica for clean-up. The soxhlet extraction used dichloromethane:acetone (1:1) as solvent. A solvent exchange of the extract to toluene was performed prior to GC

analysis. In this study, the values for the CRM were also obtained using GC-FID. However, sample extraction was by mechanical end-over shaking with n-pentane as solvent. Solvent exchanged was not done in this method. This solid liquid extraction was

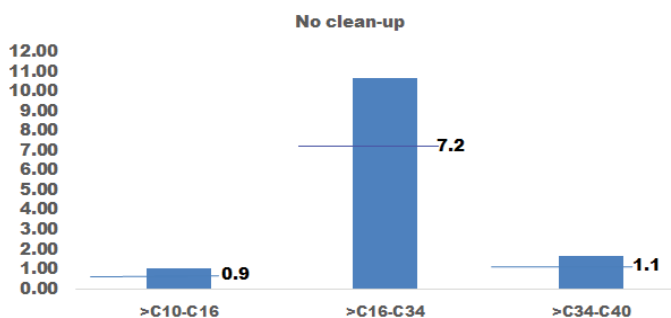


Figure 3: Amount of each fraction recovered (g/kg) without clean-up of n-pentane extract of MX015, showing deviation from the reported values.

Table 3: Fraction recovery without clean-up.

	> C10 – C16	> C16 – C34	> C34 – C40
Amount (g/kg)	1.07	10.70	1.66
Deviation from the reported value	0.17	3.50	0.56
% Deviation from the reported value	18.6	48.7	51.2

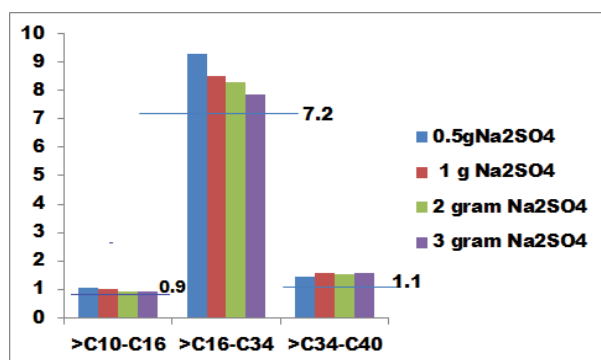


Table 5: Percent deviation of the recovery of each fraction from the reported value using dSPE and cSPE methods.

% deviation	> C10 – C16	> C16 – C34	> C34 – C40
Na ₂ SO ₄ , silica dSPE	4.4	0.3	6.5
Na ₂ SO ₄ , silica cSPE	5.4	-2.5	8.8

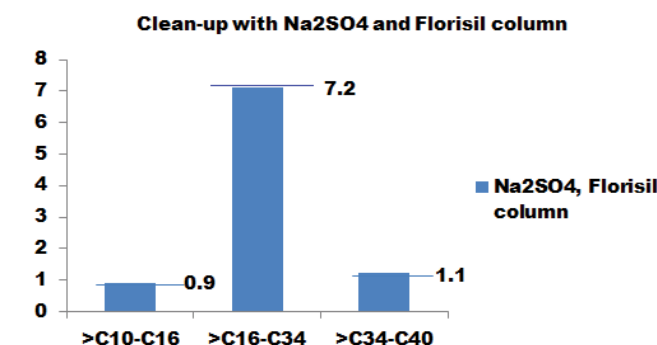


Figure 6: Recovery of MX015 obtained with florisil and Na₂SO₄.

Table 6: Percent deviation of the recovery of each fraction from the reported value using florisil adsorbent with Na₂SO₄.

% deviation	> C10 – C16	> C16 – C34	> C34 – C40
Na ₂ SO ₄ , silica dSPE	4.4	0.3	6.5
Na ₂ SO ₄ , silica cSPE	5.4	-2.5	8.8

Table 7: Repeatability of clean-up method using Na₂SO₄ and silica cSPE.

Amount (g/kg)	> C10 – C16	> C16 – C34	> C34 – C40
Trial 1	0.9486	7.0175	1.1963
Trial 2	0.9120	6.7970	1.2751
Trial 3	0.8818	7.1218	1.3777
Trial 4	0.8168	7.4678	1.2394
Trial 5	0.9741	7.8778	1.1849
Mean	0.9	7.3	1.3
SD	0.1	0.4	0.1
%RSD	6.8	5.8	6.2

Figure 4: Amount of each fraction (g/kg) recovered at different weights of Na₂SO₄.

Table 4: Percent deviation of the recovery of each fraction from the reported value using different amounts of Na₂SO₄.

% deviation	> C10 – C16	> C16 – C34	> C34 – C40
0.5 gram Na ₂ SO ₄	17.3	29.1	32.0
1 gram Na ₂ SO ₄	10.2	17.9	43.4
2 gram Na ₂ SO ₄	4.9	15.1	40.7
3 gram Na ₂ SO ₄	3.4	9.3	44.9

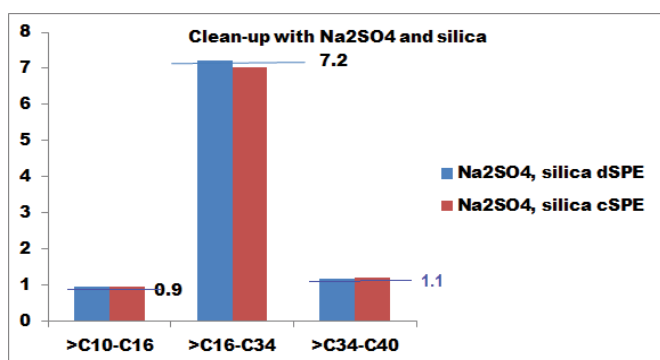


Figure 5: Comparison of dispersive SPE and column SPE on the recovery of the three fractions of MX015.

proven to be equivalent to the reference method, only if SPE clean-up was performed. It can be observed that > C10 – C16 and > C16 – C34 fractions are cleaned-up well using SPE to obtain recoveries close to the 100% reported value. For the > C34 – C40 fraction, the recovery is equal or closer to the upper limit of 1.3 g/kg, instead of the reported value of 1.1 g/kg. Polar UCMs in Fraction 3 could not be removed completely by the 1 gram Na₂SO₄ and 1 gram silica. Probably, sample loading may have exceeded the capacity of the adsorbent to remove the interferences detected in Fraction 3. The effect of increasing the amount of silica to the recoveries of the fractions could be investigated in the future.

Conclusion

The TPH analysis remains the primary tool to detect and quantify the bulk components of petroleum releases into the environment which includes the BOCs and petroleum metabolites. Extractable TPH analysis with clean-up quantifies the petroleum hydrocarbons whereas extractable TPH analysis without clean-up provides an estimate of the amount of both the petroleum hydrocarbons, BOCs and petroleum metabolites. Samples processed with and without clean-up were compared to assess the relative degree of matrix interference. Results showed

that the solid liquid extraction of petroleum from soil cannot completely remove matrix interferences. The solvent extraction of soil samples will also to some extent extract similar but unrelated chemicals which will give positive bias results; thus, necessitating the need for a clean-up step. SPE using dSPE or cSPE method with Na₂SO₄ and silica yielded a cleaner extract; thus, resulting to better recoveries of the > C10 – C16, > C16 – C34 and > C34 – C40 fractions. Florisil provided the same efficiency as the silica. In this study, the extraction and clean-up method for the CRM was proven to be equivalent to the reference method. This sample preparation technique is important as this will affect subsequent sample preparation steps to separate TPHs into its different fractions and individual components for assessing the level of contamination and for decision-making on the effectiveness of remediation based on risk assessment.

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Compliance with Ethical Standards

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Ethical approval: This article does not contain any studies with human participants or animals performed by any of the authors.

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