

## Hydrocarbons Analysis for Risk Assessment in Polluted Soils

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Policies for contaminated site management in Europe are evolving from total concentration-based of pollutants policies to risk-assessment policies. Leakages of petroleum products are usually composed of many different substances, usually grouped into the parameter Total Petroleum Hydrocarbons (TPH). However, to carry out a suitable risk assessment TPH must be divided into different fractions, according to their physicochemical properties. The purpose of this work is to develop an analytical method for the characterization of TPH fractions taking soils from a high populated area of a Spanish medium size city. Results allow determining which product was released depending on each fraction percentage and it can be compared to the regulation to determine the actions that must be performed. If the action is the risk assessment, TPH fractions are suitable for this task, enabling a detailed study of TPH risks for human health and the environment.

### 1. Introduction

Soil has become a receptor of a huge amount of pollutants among which stand out petroleum products, such as gasoline, diesel or lubricants (Cioni and Petarca, 2011). Those substances can be released and spread out to soil, causing risk to human and environmental receptors (Park and Park, 2011). The leakage is usually composed of many different substances, therefore it results more effective to group them into the parameter Total Petroleum Hydrocarbons (TPH) in terms of risk management.

TPH concentration has been used as a common approach to establish target soil cleanup levels implemented by different regulatory agencies (TPHCWG, 1998). However, policies for contaminated site management are changing from total concentration-based approaches to risk-assessment approaches, involving risk specific site analysis for humans and environment (COM, 2006). TPH concentration is not a suitable parameter for risk assessment since it includes compounds with very different physicochemical and toxicological properties. TPH should be divided into fractions according to their physicochemical and toxicity properties to carry out a suitable risk assessment. Fractionation has been sorted in terms of aliphatic and aromatic compounds and also according to their Equivalent Carbon Number (EC). However, there is no European protocol approved to carry out TPH fractionation, and even in the U.S. there are some methodologies, but not a harmonized one.

The purpose of this work is to develop an analytical method for the characterization of TPH fractions taking as case study a reference soil and soils from the surroundings of a petrol station located at a high populated area of a Spanish medium size city (Santander, 182000 inhabitants).

## 2. Methodology

### 2.1 Scenario evaluated

The case of study is focused in the surroundings of a petrol station located on a high populated area of a Spanish medium size city (Santander). Located in the city centre there is a petrol station next to the park “JardinesPereda”, considered as a green area and which includes a playground for children.

A systematic grid sampling was performed, based on the manual proposed by the Spanish Public Company IHOBE S.A. (IHOBE, 2002), adapted to the site location problems for sampling (paved areas in the park) and limited to a preliminary analysis with a low number of sampling points. Ten sampling points were selected as representative ensuring that different routes of exposure and potential receptors were studied. Figure 1 depicts petrol station location as well as the location of the different sampling points.

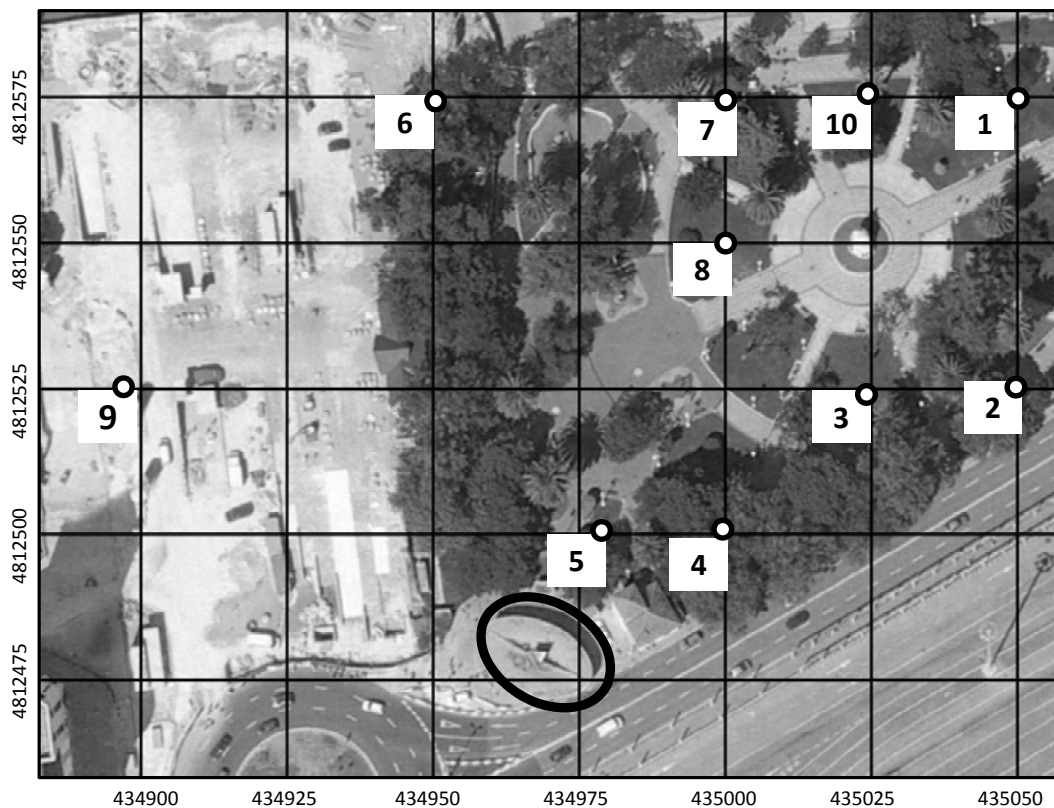


Figure 1: Santander site map showing the petrol station and the location of sampling points according to UTM coordinate system

### 2.2 Soil sample analysis using proposed method

Soil sampling methodology has been described in previous works (Pinedo et al, 2010). Figure 2 summarizes the analytical method. Soil samples pretreatment process comprises two steps: drying by lyophilization to remove all the water contained in the portion of soil to be analyzed, and sieving in order to remove stones, roots and larger soil particles, employing 600µm mesh sieves. Reference soil is CRM 355-100 (RTC) and does not need pretreatment.

Once the soil sample has been pretreated is ready for next step, the extraction. New analytical method considers that the most suitable procedure for the analysis is to carry out the extraction step based on the harmonized standard ISO 16703(2004): “Soil quality-Determination of content of hydrocarbon in the range C<sub>10</sub> to C<sub>40</sub> by gas chromatography”, and the fractionation and GC-FID analysis based on the

document "Extractable Petroleum Hydrocarbons Methodology" of the New Jersey Department of Environmental Protection (NJDEP, 2008).

For the extraction process a known amount of homogenized sample is extracted by mechanical shaking with acetone/n-heptane mixture. Thereafter, the organic layer is separated and washed twice with water and passed through anhydrous sodium sulphate (Na<sub>2</sub>SO<sub>4</sub>) for dehydration. For the whole TPH analysis, procedure for purification and analysis is also based on the standard ISO 16703(2004).

For the fractionation process a silica gel column was used to split the TPH in an aliphatic and aromatic fraction. In addition, TPH fractionation was performed according to the Equivalent Carbon Number (EC) of the compounds. The EC numbers are used because they are more closely related to environmental mobility. According to their EC, TPH fractionation method distinguishes four aliphatic fractions: EC9–12, EC12–16, EC16–22 and EC21–40; and four aromatic fractions: EC10–12, EC12–16, EC16–22 and EC21–34. Lower carbon fractions have not been considered in this TPH study because the substances included in these groups are studied separately, as their properties are quite different, and can be easily determined by Gas Chromatography-Mass Spectrometer (GC-MS).

TPH quantification has been determined by employing Gas Chromatography Flame Ionization Detector (GC-FID) for the analysis. Previously, different calibration standards at different concentrations were prepared for aliphatic and aromatic compounds, used for the determination of the retention time window as boiling point distribution markers.

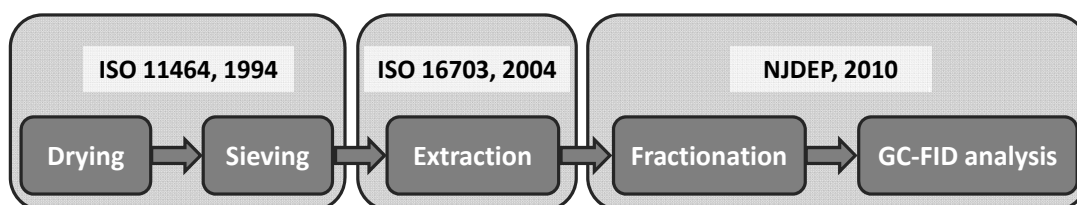


Figure 2: Schematic overview of the proposed analytical method for TPH fraction analyses

Table 1: Reference Standards employed for tuning the fractionation method.

Standard	Number of components	Provider
NJDEP EPH 10/08 Rev.02 Aliphatics Calibration Standard	20	Restek
NJDEP EPH 10/08 Rev.02 Aromatics Calibration Standard	18	Restek
NJDEP EPH 10/08 Rev.02 Aliphatics Fractionation Check Mix	18	Restek
NJDEP EPH 10/08 Rev.02 Aromatics Fractionation Check Mix	16	Restek
MA EPH Surrogate Spike Mix	2	Restek
MA Fractionation Surrogate Spike Mix	2	Restek

Table 1 summarizes the different reference standards employed for tuning the fractionation analysis method. Calibration standards are used to obtain the calibration curve for each fraction. Fractionation Check Mixes are employed to calculate recovery rates in order to validate the method. The Surrogate Spike Mix is used to monitor the whole process, including extraction and fractionation efficiency. The MA Fractionation Surrogate Spike Mix is used to monitor the fractionation efficiency of the silica gel cartridge and establish the optimum hexane volume required to efficiently elute the aliphatic fraction without significant aromatic breakthrough.

### 3. Results and discussion

#### 3.1 Validation of TPH fractionation analysis

As a first step, aliphatic and aromatic check mix standards were prepared for the validation of the proposed fractionation method with a concentration of 100 µg/mL each component. Results from the chromatographic quantification are shown in Table 2. Recoveries in the interval 40-140% are accepted

by NJDEP (2010). According to the data shown in Table 2 recovery of aliphatic components are in the interval 60-107% while aromatic components presents recovery value in the interval 84-119 % except for 1,2,3-trimethylbenzene with a recovery of 32%. An acceptable relative standard deviation (RSD) is reached in all cases.

Table 2: Recovery and relative standard deviation (RSD) for the quantification of different aliphatic and aromatic check mix standards by means of GC-FID.

Component	Aliphatic		Aromatic	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
C9	62	12	32	4
C10	71	11	-	-
C12	75	12	-	-
C14	78	12	84	19
C16	87	14	85	14
C18	97	14	98	11
C20	96	13	107	10
C21	97	14	109	11
C22	98	13	112	10
C24	97	13	109	10
C26	97	13	113	10
C28	96	13	110	11
C30	96	13	116	10
C32	97	13	116	11
C34	94	13	108	11
C36	98	13	119	10
C38	103	13		
C40	107	12	97	12

In a second step the extraction and fractionation phases have been evaluated by means of the solid reference material CRM 355-100 with a TPH concentration of 7040 ±2740 mg/kg. Recovery of the fractionation method process is monitored by the fractionation surrogate spike mix, which contains the components: 2-Bromonaphthalene for monitoring aliphatic fractionation, and 2-Fluorobiphenyl for monitoring aromatic fractionation. Recoveries obtained for 2-Bromonaphthalene and 2-Fluorobiphenyl are 97 and 101% respectively. The surrogates' recoveries have been used to adjust the recovery obtained in the reference material CRM 355-100. Table 3 depicts concentrations obtained for each aliphatic and aromatic fraction for both two samples.

Table 3: Concentrations for each TPH fraction for the solid reference material CRM 355-100.

	EC9-C12	EC12-C16	EC16-C21	EC21-C40	Aliphatic sum
Aliphatic (mg/kg)	124	843	686	3288	4941
	EC10-C12	EC12-C16	EC16-C21	EC21-C34	Aromatic sum
Aromatic (mg/kg)	45	321	447	142	955

The sum of the different fractions gives a TPH value of 5896 mg/kg, with a percentage recovery about 84% for TPH. These values are within the range proposed by NJDEP (2010) (40-140%). This process enables us to verify that the method is ready for the fractionation of real solid samples.

### 3.2 TPH fractionation analysis

Spanish regulation includes a set of preliminary triggers for requiring a formal and site-specific risk assessment. 50 mg/kg for TPH is the maximum concentration limit approved by Spanish regulation on contaminated soils (Presidency Ministry, 2005). Higher concentration will require a site-specific risk assessment. Figure 3 represent TPH values for the sampling points corresponding to the site under study. As observed in Figure 3, eight of the ten values exceed the Spanish maximum regulation limit of 50 mg/kg. According to Spanish regulation, site-specific risk assessment must be performed in sites where TPH values exceed the maximum limit, in order to determine whether these concentrations induce an acceptable or unacceptable risk.

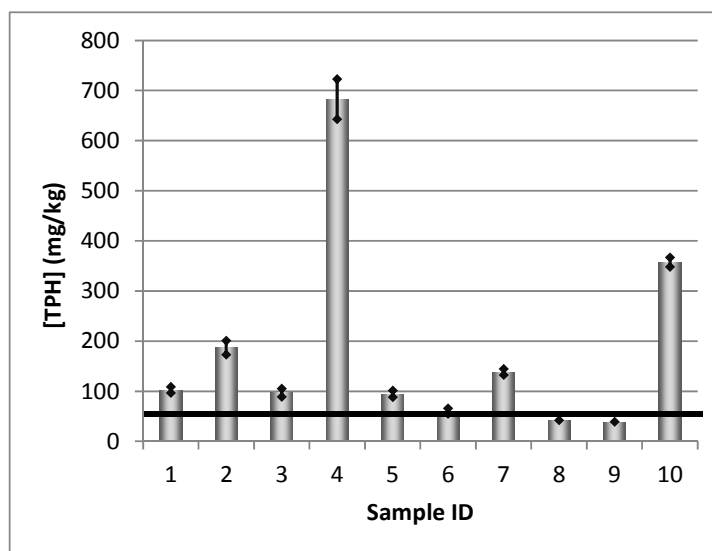


Figure 3: TPH concentrations obtained at each sampling point, and the maximum regulation limit in Spain (Presidency Ministry, 2005) represented by the red line.

The fractionation analysis has been carried out for the sample that presented the highest TPH values. The soil sample N° 4, with a TPH concentration of 683 ±40 mg/kg has been selected for this purpose. The results are exposed in Table 4, obtaining that the sum of the different fractions gives a TPH value of 569 mg/kg, and recovery is about 83% for TPH. These values are within the range proposed by NJDEP 2010 (40-140%). However, further assays must be carried out in order to reduce the variability from the different processes of the procedure. Fraction analysis indicates that aromatic EC21-34 is the most abundant fraction. Nevertheless, lighter fractions have not been found. This may correspond to weathered diesel and mineral oil leakages.

Table 4: Concentrations for each TPH fraction for Soil sample N° 4.

	EC9-C12	EC12-C16	EC16-C21	EC21-C40	Total
Aliphatic (mg/kg)	ND	35	65	81	181
	EC10-C12	EC12-C16	EC16-C21	EC21-C34	Total
Aromatic (mg/kg)	ND	26	85	277	388

## 4. Conclusions

In this study, an analytical method for the characterization of TPH fractions has been developed and evaluated. Analysis of TPH in the surroundings of a petrol station located at a high populated area of a Spanish medium size city (Santander, 182000 inhabitants) demonstrated that TPH concentration were

above Spanish maximum limit. Therefore, a site-specific risk assessment must be performed in order to determine whether these concentrations induce an acceptable or unacceptable risk.

The proposed method can be summarised in the following steps: i) pre-treatment, ii) extraction, following ISO 16703(2004), iii) fractionation in four aliphatic fractions: EC9–12, EC12–16, EC16–22 and EC21–40; and four aromatic fractions: EC10–12, EC12–16, EC16–22 and EC21–34 following NJDEP (2010) and iv) quantification by means of GC-FID.

TPH recoveries from soil are above 80%, an acceptable range according to NJDEP (2010). Nevertheless, extraction process must be performed in order to increase percentage recoveries. Aromatic EC21-34 is the most abundant fraction in the soil sample, which may correspond to weathered diesel and mineral oil leakages. The obtaining of TPH fractions, according to their physicochemical and toxicity properties, will allow, in a next step, a suitable risk assessment for the considered site.

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