Total Petroleum Hydrocarbons By Gas Chromatography in Colombian Waters and Soils

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ABSTRACT

Total Petroleum Hydrocarbons (TPHs) were required by the Colombian Environmental Authorities. However, the great diversity of hydrocarbon sources, in addition to the variety of available techniques and analytical methods had created confusion among the users of the data in regards to the appropriate methodologies. This study presents the results obtained in the method validation for the determination of TPHs in waters and soils/sediments using the HRGC/FID technique and its application in the Colombian Exploration and Production (E&P) industry. HRGC coupled to FID Detector (HRGC/FID) was used to determine individual alkane hydrocarbon in the Gasoline Range (GRO) and Diesel Range (DRO). The limit of detection was established in 0.020 $\mu g \ mL^{-1}$ for waters and 2.30 $\mu g \ g^{-1}$ for soils and sediments. The recovery percentage of water samples were 101 and 98%, while for soils was 99 and 97% for both, low and high levels of n-alkane hydrocarbons, respectively. This method is an economical, fast and accurate way to determinate TPHs and individual alkane hydrocarbons in water and soil samples. The method provides the robustness, limit of detection and percentage of recovery enough to comply with Colombian environmental regulations.

Keywords: Total Petroleum Hydrocarbons (TPHs), Gasoline Range Organic (GRO), Limit of Detection (LOD), Flame Ionization Detector (HRGC/FID), Hexane Extractable Material (HEM), Unresolved Complex Mixture (UCM)

1. INTRODUCTION

The term TPHs has been used to describe a wide variety of chemical compounds derived from crude oil and its by-products. The TPHs are a complex mixture of compounds with different polarities extracted from crude oil using organic solvents (Gustafson, 2007). The physicochemical characteristic of the individual alkane hydrocarbons present in water and soil/sediment samples will depend on the source of contamination (gasoline, diesel, kerosene, fuel oil, mineral oil or asphaltic material) spilled or widespread in the environmental matrices.

For the last decade, TPHs in water, soil and air samples have been required by the Colombian Environmental authorities (MS, 1984; MAVDT, 2010a; 2010b; 2010c). The numerous sources of hydrocarbons combined with the variety of available techniques and analytical methods have created confusion among the

end users of the data in regards to the appropriate methodologies. Users, government laboratories and private laboratories disagree on the scope, range of application and quality of information obtained from using different methods.

There are several methods for determining TPHs in environmental samples, however due to their specificity; most are only applied to designated petroleum fractions (Saddler and Connen, 2003). The methods, based on the determination of grease and oil (G and A) by EPA 413.1 (halogenated solvent extraction and gravimetry) and 413.2 (halogenated solvent extraction and infrared) and EPA 418.1 (EPA, 1993), which permits the extraction of the TPHs with Freon or CCl_4 and IR analysis in the C-H stretch (3240 cm^{-1}), are particularly sensitive to mineral oils and diesel, but do not yield the desired results when a sample contains products with high aromaticity such as gasoline and reforms. G and A and TPH by IR do not

consistently indicate contamination in petroleum. For example, a water or soil sample with a high concentration of humic or fulvic acids (non-petrogenic organic compounds) would give a false positive due to the strong absorbance of those compounds in the IR range (AWWA, 1998).

Recently, the U.S. EPA has removed methods that use Freon-113 as an extraction solvent and, as an alternative, recommended the use of the method EPA-1664: n-Hexane Extractable Material (HEM; Oil and Grease) and silica gel treated with n-hexane extractable material (SGT-HEM; Nonpolar Material) by extraction and gravimetry (EPA, 1999)

In the late 90's, the U.S. EPA published the SW-846 methods for solid waste, which included the EPA-8015 method for TPH determination using the GC technique. However, this method was originally designed for solvent evaluation rather than petroleum hydrocarbons. The EPA SW-846, III revision included the new 8015D method called "Non-halogenated volatile organic compounds using GC/FID", which included a guide to determine hydrocarbons in the Gasoline (GRO) and Diesel (DRO) range.

This study presents the results obtained in the analytical validation carried out in the Antek S.A. Environmental and Geochemical Laboratory- for the determination of petroleum hydrocarbons in waters and soils/sediments using the HRGC/FID technique and a Colombian gasoline/diesel mixture as a reference standard. Once validated, the method was used to determine TPHs and individual n-alkanes in water and soil matrices (freshwater, petroleum wastewater, groundwater, formation waters and soil/sediments from petroleum treatment pits) in the Colombian Exploration and Production (E&P) industry.

2. MATERIALS AND METHODS

2.1. Monitoring, Preservation and Sample Treatment
2.2. Solid and Water Samples

The holding time for solid and water samples was 14 days from collection to GC analysis. Samples were refrigerated at <4°C until its organic extraction. Aqueous samples were collected in 40 mL amber vials with a whole cap and a Teflon septum. Samples were preserved at pH<2.0 with sodium bisulfite, HCl or H_2SO_4. 10 mL of the sample were removed and discarded through the septum with glass syringe. 3 mL of n-pentane were then injected through the septum with a 5 mL syringe. The sample was extracted for 2 m in a vortex apparatus. The vial was then opened and 1.5 mL of the organic extract were placed into the vial and sent for the GC analysis.

The solid samples were collected in 20 mL vials with a solid cap and a Teflon septum. 10 g of soil or sediment were extracted with 20 mL of n-pentane. Analytical field and laboratory blanks and duplicated and spiked samples were treated the same as the water and soil/sediment samples. After adding the n-pentane, the samples were shaken for 15 m by the ultrasonic apparatus and allowed to settle for 30-60 m at room temperature. Two additional extractions, each with 20 mL of n-pentane, were performed in the same manner. 1.0 mL of the organic extract was then transferred into a vial and analyzed by GC/FID.

2.3. Chromatography Conditions

GC/FID analysis of the TPHs and PHs was made on a Hewlett Packard 5890 Series II-Plus gas chromatograph equipped with an HP 7673 Autosampler and FID detector coupled with a 30×0.32 mm DB-5 (95 metil-5%-fenilpolisiloxane) fused silica capillary column. The oven temperature was programmed from 40°C (3 min.) to 300 at 15°C/min. Samples were injected in splitless mode, with the relay open at 20 sec. Injector and detector temperatures were 250 and 320°C, respectively. Helium was used as the carrier gas at a linear velocity of 38 cm sec^{-1} (15 psig). Data handling was done with Agilent Chemstation chromatography software (version 10).

3. RESULTS

3.1. Calibration

Fresh standards were prepared in n-pentane. To build the calibration curve, a 10000 µg mL^{-1} standard stock was prepared with commercial unleaded gasoline and diesel #2 (1:1) acquired in a commercial gasoline station in Bogotá, Colombia. Additionally, an analytical standard containing 200 µg mL^{-1} of n-C10 to n-C28 of alkane hydrocarbons mix was used for identification purposes. Initial calibration curves were prepared with a range of 50-1000 µg mL^{-1} from the standard stock.

For quantification purposes, the peak area for TPHs was determined using forced line integration with Agilent Chemstation software between n-hexane (n-C6) through n-pentatriacontane (n-C35) or until the last peak eluted in the chromatographic profile. For individual PHs the area of each peak was calculated using the baseline-baseline mode and external response factor quantization. According to TNRCC-1005, the correlation for calibration curves must be≥0. 990 and the relative standard deviation of the response factors for each of calibration levels must be less than 25% of the overall calibration range (**Table 2**) (TNRCC, 2001). **Figure 1** shows the chromatographic profile of

the standard mix containing 1000 µg mL^{-1} of TPHs prepared from the standard stock of 10000 µg mL^{-1} of the gasoline: diesel mix.

3.2. Validation Results

The Limit of Detection (LOD) was determined by injecting a standard of 20 µg mL^{-1} of alkane hydrocarbons 5 times according to CFR 40 part. 136 U.S. EPA, 2012. The LOD in the aqueous matrix was established in 0.020-30 mL of water extracted, while for the solid matrix (soil/sediments) was calculated at 2.30 µg g^{-1} per 10 g of sample extracted.

The precision was determined using water and soil samples containing three different levels 0.02, 1.0 and 5.0 mg L^{-1} for waters and 12000 µg g^{-1} of TPHs, respectively.

4. DISCUSSION

Comparison of typical calibration curves for TPHs between different operators showed an average correlation of 0.9996, which indicated an excellent linearity in the range evaluated and consequently guaranty that any PHs concentration present in aqueous and solid samples could be determinate with reliable precision and accuracy in such range.

Table 1 shows that the standard deviation of the concentrations (precision) was ±3 µg mL^{-1} for water samples and ±2025 µg g^{-1} for soil samples. The relative standard deviation was 6 and 2% for each matrix, respectively.

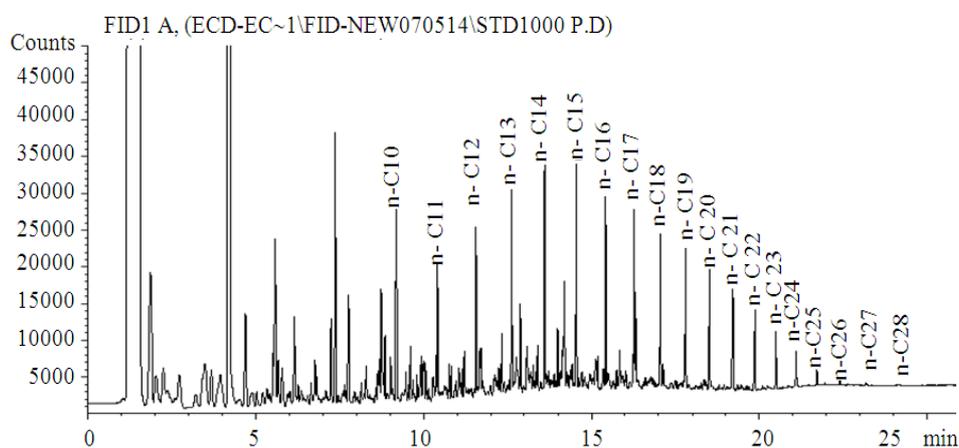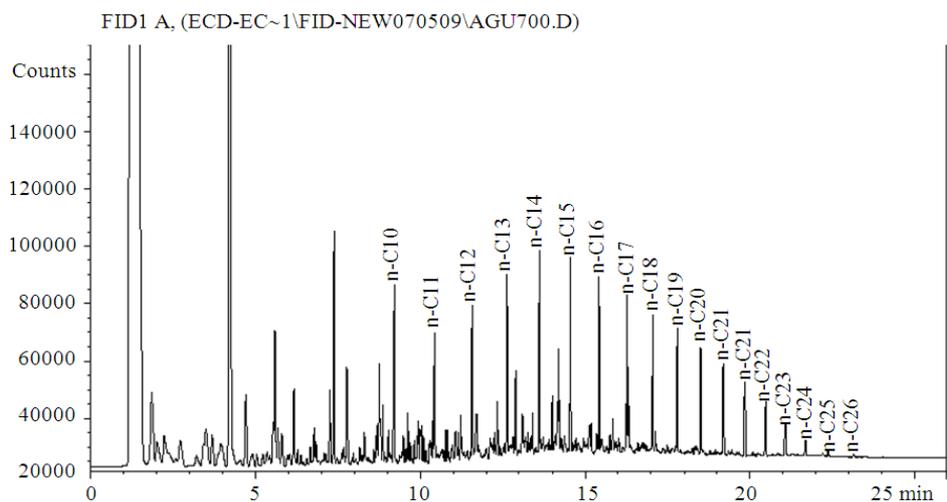**Fig. 1.** Chromatographic profile of Colombian gasoline: diesel (1:1) standard of 1000 µg mL^{-1}

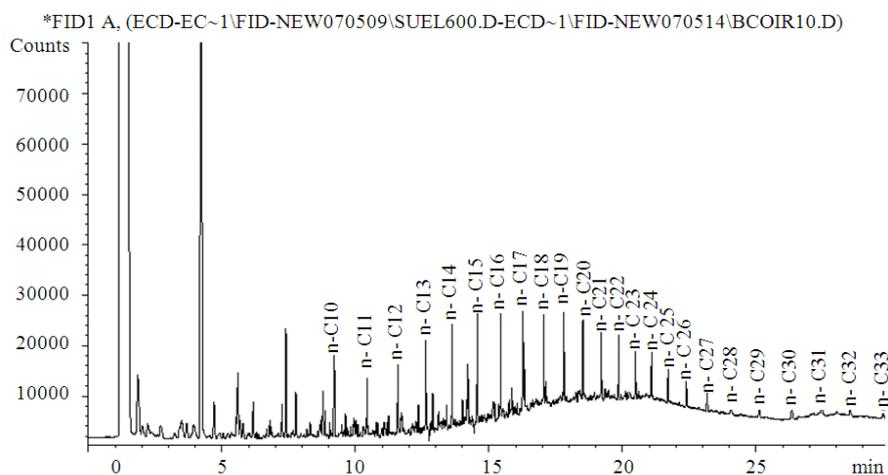**Fig. 2.** Chromatographic profile of spiked water sample spiked with 233 µg mL^{-1} of PHs

Fig. 3. Chromatographic profile of spiked soil sample spiked with 3000 µg g^{-1} PHs
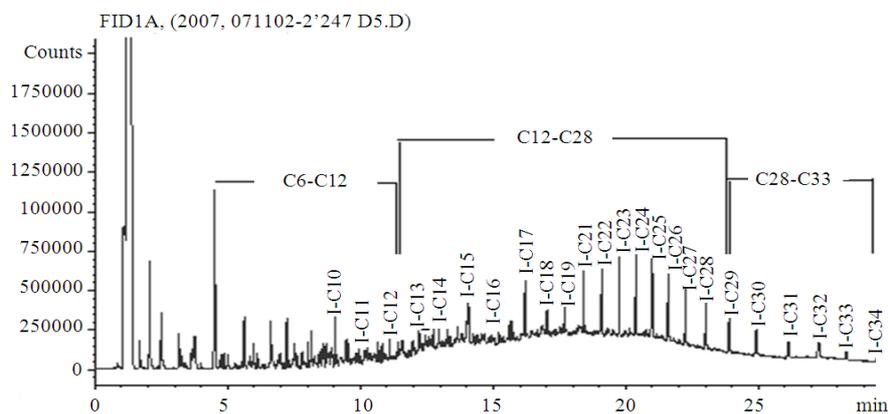

Fig. 4. GC/FID profile of a waste water sample (Antek-24705) from a petroleum treatment mud pit showing the individual n-alkane distribution
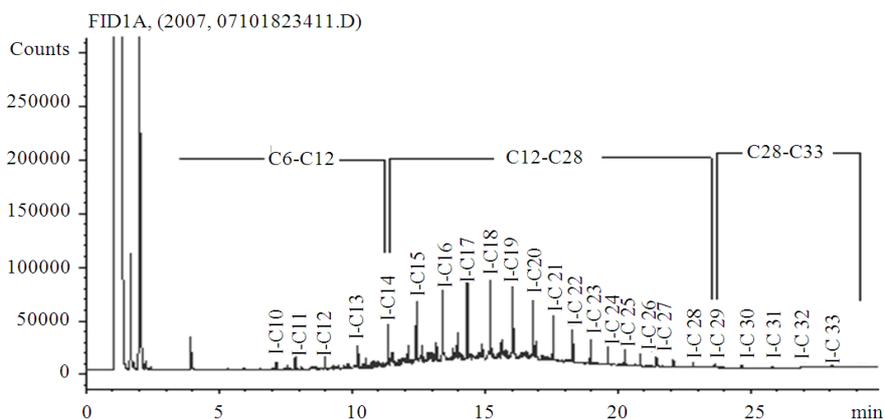

Fig. 5. GC/FID chromatogram of a contaminated soil (Antek-23411) from a treatment petroleum mud pit showing the individual n-alkane distribution

Table 1. Precision of the TPHs method for Colombian water and soil samples

	Concentration (μg/g)			Concentration (μg/mL)		
	Water	Water	Water	Soil	Soil	Soil
SAMPLE	12139-1	12139-2	12139-3	11178-1	11178-2	11178-3
DAY 1	45.0	49	44	116086	118015.0	119436.0
DAY 2	38.0	46	46	114918	114611.0	116364.0
DAY 3	43.0	43	44	118792	119395.0	116974.0
Average	42.0	46	45	116599	117340.0	117591.0
Standard deviation	4.0	3	1	1987	2462.0	1626.0
Aver. Standard deviation		3			2025.0	
CV %	9.0	7	3	2	2.0	1
Average CV%	6.0				2.0	

Table 2. Response Factors for five calibration levels. Calibration curves were done on three different days by three different technicians

Calibration Level (μg/mL)	Response factor Calibration curve no 1 Day 1	Response factor calibration curve no 2 Day 2	Response factor calibration curve no 3 Day 3
50	0.000256	0.00027	0.000341
100	0.000339	0.000358	0.000351
200	0.000336	0.000348	0.000365
500	0.000333	0.000348	0.000338
1000	0.000333	0.000336	0.000340
Average	0.000319	0.000332	0.000347
Standard Dev.	0.000031	0.000031	0.000010
Relative Std Dev.	9.000000	9.000000	3.000000

Table 3. Accuracy of the method using spiked water samples

Water samples	Petroleum Hydrocarbons (PHs)					
	Experimental concentration, (μg/mL)	Theoretical concentration, (μg/mL)	Recovery, (%)	Average recovery (%)	Standard Deviation	CV %
Low 1a	53	50	106	102	7	7
Low 1b	52		104			
Low 1c	46		92			
Low 2a	55		110			
Low 2b	53		106			
Low 2c	46		92			
High 1a	237	233	102	98	3	3
High 1b	220		94			
High 1c	225		97			
High 2a	236		101			
High 2b	222		95			
High 2c	224		96			

Table 4. Determination of % recovery in spiked soil samples

Soil samples	Petrogenic Hydrocarbons					
	Experimental concentration (μg/g)	Theoretical concentration (μg/g)	Recovery (%)	Average recovery (%)	Standard deviation	CV %
Low 1a	979	989	99	99	0.1	0.1
Low 1b	982	993	99			
Low 1c	984	995	99			
High 1a	2897	3000	97	97	0.1	0.1
High 1b	2898	3000	97			
High 1c	2895	3000	97			

Table 5. Comparison of EPA 418.1 by IR and GC/FID method in the quantitative determination of PHs in samples from Colombian petroleum industry

Samples	PHs Concentration [*] Extraction and IR EPA 418.1	Extraction and GC/FID TNRCC, Texas 1005
Antek 22205-water, (μg/mL)	205764	234042
Antek 23410-water, (μg/mL)	5331	5198
Antek 23411-water, (μg/mL)	22105	22036
Antek 18371-Soil, (μg/g)	510	570
Antek 22148-Soil, (μg/g)	47369	49262

Table 2 shows the response factors for each concentration level in three calibration curves built in 3 different days. For a specific concentration, the response factor could be taken as an expression of the calibration sensitivity. In a linear calibration, the response factors were similar and followed the slope of the curve. The variation coefficients for the average response factors over the five calibration levels on three different days were 9, 9 and 3%, respectively, which comply with the TNRCC-1005 requirement for the % C.V. which must be less than 25% overall calibration range.

The accuracy was calculated measuring spiked water and soil samples in two different ranges. Water samples were analyzed six times. **Figure 2** shows the chromatographic profile for a sample of water spiked with 233 μg mL^{-1}, while the results of the accuracy study are shown in **Table 3**. The recoveries of TPHs in water samples spiked with 50 and 233 μg mL^{-1} were 102 and 98%, with relative standard deviations of 7 and 3%, respectively.

Soil samples were analyzed in triplicate. **Figure 3** shows the chromatographic profile of a soil sample spiked with 3000 μg g^{-1} of PHs. The results in **Table 4** show that the recoveries for soil spiked with 990 and 3000 μg mL^{-1} yielded 99 and 97% with relative standard deviations of 0.1 and 0.1%, respectively.

4.1. Petroleum Hydrocarbons in Colombian Water and Soil Samples

Table 5 compares the results obtained by EPA 418.1 method (solvent extraction and infrared) with the method validated in this study, based on TNRCC-1005, in water and soil samples. Although the results are similar and its differences fall within the standard deviation (precision) for each method, the EPA-418 does not determine the

source and physicochemical characteristics of the contamination. The chromatographic profile shown in **Fig. 4** shows that the sample Antek-24705 has a unimodal hydrocarbon distribution between n-C$_6$ to n-C$_{33}$ with a hump between n-C$_{12}$ to n-C$_{29}$ known as an "Unresolved Complex Mixture" (UCM). The abundance of low molecular weight hydrocarbons (<n-C23) suggests that the contamination in this water sample is recent and has the characteristics of light crude oil, or that the source of the hydrocarbon mixture is a combination of crude oil and a light by-product such as gasoline, diesel, or jet fuel. The presence of a UCM indicates that the crude oil present in the sample had originally a biodegradation in progress or that such process began in the treatment pit. According to TNRCC-1005, the sample shows the presence of Gasoline Range Organic (GRO), which is between n-C6 to n-C12 and Diesel Range Organic (DRO) n-C12-n-C28.

Antek 23411 soil samples (**Fig. 5**) shows a unique fingerprint associated with a contamination of crude oil. However the absence of low molecular weight hydrocarbons (<n-C23) could indicate that this fraction has been lost by a weathering process (evaporation) in the pit. Additionally the low UCM in the sample suggests that there was no biodegradation process in progress in the original crude oil sample. In this particular case, the unimodal distribution between n-C8 to n-C33 with major peaks around n-C17 suggest that the crude oil sample was sourced in an algal-microbial pale environment, which could serve to identify source contamination when there are several sources of such contamination.

5. CONCLUSION

This study presents the analytical validation of a method to determine the TPHs and individual petroleum hydrocarbons between n-C6 to n-C35 in Colombian water and soil/sediment samples using HRGC/FID. The method was applied successfully to determine TPHs in the E and P petroleum industry.

The Limit of Detection (LOD) in an aqueous matrix was established at 0.020 per 30 mL of water extracted, while for solid matrices (soil/sediments) it was calculated at 2.30 μg g^{-1} per 10 g of sample extracted. The precision was determined using soil and water samples containing 12000, 0.02, 1.0 and 5.0 mg L^{-1} of PHs, respectively. The results obtained for the standard deviation of the sampled areas was ±3 μg mL^{-1} for water samples and ±2025 μg g^{-1} for soil samples. The relative

standard deviation was 6 and 2% for each matrix, respectively. The method was linear with a range of 50-1000 μg mL^{-1} with a correlation of 0.9996 on average for two operators working at the same operative conditions. The relative standard deviation for the average response factors over five calibration levels of three different days was 9, 9 y 3%, respectively. Those values comply with the TNRCC-1005 requirement for % C.V., which must be less than 25% of the overall calibration range.

The accuracy was calculated measuring spiked water and soil samples in two different ranges. Water samples were analyzed six times. **Figure 2** shows the chromatographic profile for a sample of water spiked with 233 μg mL^{-1}, while the results of the accuracy study are shown in **Table 3**. The recoveries of TPHs in water samples spiked with 50 and 233 μg mL^{-1} were 102 and 98%, with relative standard deviations of 7 and 3%, respectively.

The results obtained by this validated method are comparable with those obtained by the EPA 418.1 method (solvent extraction and IR). Though the results were similar, the presented method is fast, reliable and allows the source and characteristics of the contamination to be determined. This fingerprinting process allows differentiation between hydrocarbons from crude oil and gasoline by-products, diesel or lube oil.

6. ACKNOWLEDGMENT

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