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DETERMINATION OF TOTAL PETROLEUM HYDROCARBONS IN CONTAMINATED SOIL BY FTIR AND GC-FID METHODS

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ABSTRACT. This paper presents the results obtained for total petroleum hydrocarbons (TPH) in contaminated soil by two methods: one based on conventional extraction with 1,1,2-trichloro-1,2,2-trifluroethane and determination by Fourier Transform Infrared Spectrometry (FTIR) and the other based on ultrasonic extraction with a mixture of hexane and acetone followed by determination using gas chromatography with flame ionization detection (GC-FID). In general, TPH concentrations in soil measured with FTIR were higher than those measured with GC-FID. The obtained TPH concentrations exceeded the intervention level for non-sensitive soils, according to Romanian legislation.

Keywords: *TPH, soil, GC-FID, FTIR*

INTRODUCTION

Contamination of soil with petroleum hydrocarbons is a major concern due to their potential to spread into soil and aquatic environments. Thus, the determination of hydrocarbon contaminants is one of the most frequently performed analyses in the study of contaminated sites [1, 2].

Despite the large number of hydrocarbons found in petroleum products, only a relatively small number of compounds have been characterized for toxicity [3]. The most important chemicals of concern are benzene, toluene, ethylbenzene, and polycyclic aromatic hydrocarbons (PAHs), that could pose significant cytotoxic, immunotoxic, mutagenic and/or carcinogenic risks to different organisms [4], in addition to sublethal effects which include morphological, histopathological and genetic damage [5-6], physiological and stress effects [7], endocrine disruption [8, 9] and ecological effects [10]. Certain crude oils or aromatic fractions are considered to be responsible for adverse health effects on the reproductive system in mussels, goldfish (*Carassius auratus*) and rainbow trout [11, 12].

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Due to the great number of compounds that exists in petroleum hydrocarbons (hexane, jet fuels, mineral oils, benzene, toluene, xylenes, naphthalene, fluorine), it is impossible to assess the extent of contamination by separately measuring the concentration of each hydrocarbon contaminant. To express the total concentration of non-polar petroleum hydrocarbons in soil the term total petroleum hydrocarbon (TPH), mineral oil or hydrocarbon oil index is used [13-15].

No single analytical method is capable of providing comprehensive chemical information on petroleum contaminants in soil. Non-specific methods can be used to obtain information on the type and total amount of hydrocarbons present in soil, whereas specific methods are required to give detailed information on individual contaminants [16]. There are many analytical techniques available that measure TPH concentrations in soil, with different extraction, clean up and detection methods, each technique measuring slightly different subsets of the petroleum-derived hydrocarbons present in the sample. Gas chromatography and infrared spectroscopy are the most used techniques for the TPH determination but the interpretation of analytical results requires an understanding of how the determination was made.

The objective of this study was to assess the TPH contents from 12 soil samples contaminated with petroleum hydrocarbons using gas chromatography with flame ionization detection (GC-FID) and Fourier transform infrared spectrometry (FTIR) methods.

RESULTS AND DISCUSSION

The FTIR method determines the infrared absorbance of hydrocarbons present in the extracts. There are two absorbance maxima, at 2925 and 2958 cm^{-1}, the first corresponding to $–CH_2–$ and the second to $–CH_3$. The -CH- absorbance bands corresponding to the aromatic groups located at wave numbers higher than 3030 cm^{-1} are absent from the samples due to retention on Florisil used in the clean-up process (Figure 1). The 1,1,2-trichloro-1,2,2-trifluroethane (CFE) is the preferred extraction solvent for the FTIR determinations because it is nonflammable, relatively nontoxic and is transparent in the infrared region of interest, but in accordance with the Montreal Protocol on Substances That Deplete the Ozone Layer, Class I chlorofluorocarbons, which include CFE are phased out [17].

TPH determination by FTIR is a non specific method that estimates the contents of TPH but does not provide information on the composition of the hydrocarbon mixture. Other limitations of FTIR method are the loss of highly volatile compounds during analysis, the incomplete extraction of heavy hydrocarbon molecules and can give false positive results in the presence of organic matter.

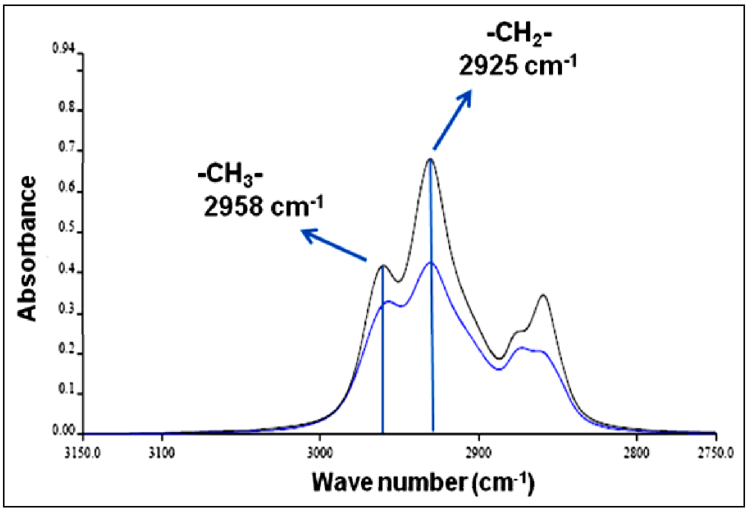

Figure 1. FTIR spectrum of TPH

Compared to FTIR method, TPH determination with GC-FID is an expensive, time consuming procedure that requires highly trained personal. The advantage of GC-FID method is that produces highly accurate results and in addition to the TPH concentration, it can also provide useful qualitative information about the type of contaminant. The disadvantages of this method are that does not determine resins, asphaltenes, and some other components with higher molecular weight that do not pass through the column, the temperatures required for the determination challenge the durability of the columns and causes column bleed, which deteriorates the analytical precision. Moreover, the lack of detailed description of the gas chromatographic settings for measuring total petroleum hydrocarbons may result in a wide range of GC operating settings that make difficult the comparisons of the results obtained by different laboratories [18].

The amount of TPH was determined as a sum parameter of resolved and unresolved components eluted from the GC capillary column between the retention times of n-decane and n-tetracontane [19, 20]. The integration window was determined using an *n*-alkanes standard solution containing C5 to C40 hydrocarbon components dissolved in carbon disulfide.

Figure 2 overlays the chromatogram of *n*-alkanes standard (red signal) with the chromatogram for TPH analysis of a soil sample extract (blue signal). The integration markers, C10 and C40, are clearly separated, thus the total area between the peak of C10 and the peak of C40 contribute to the signal, calculated after background subtraction. The integration area is presented in grey, between C10 eluted at 7.07 min and C40 eluted at 46.5 min.

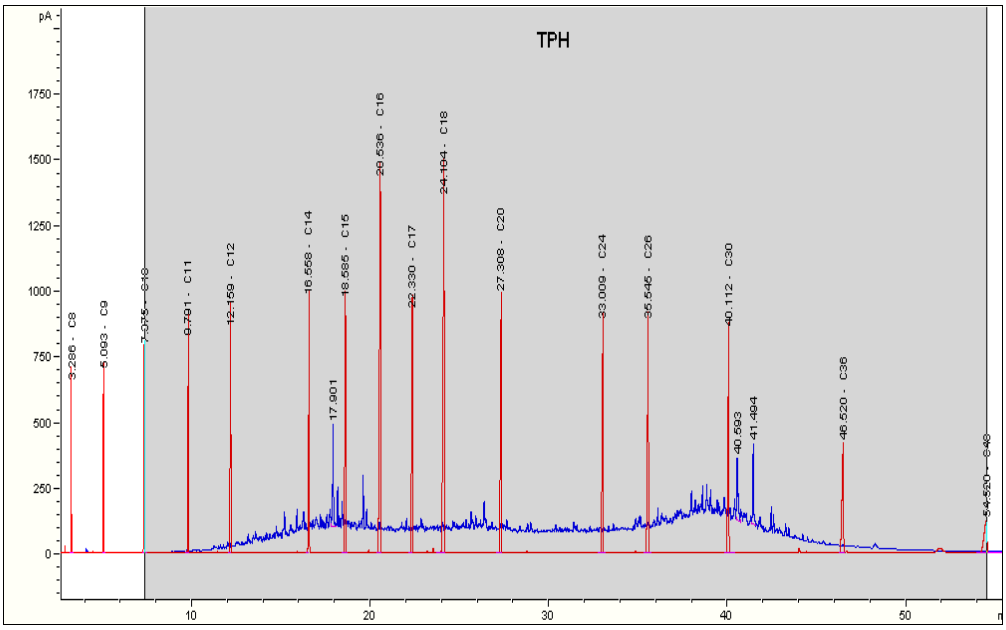

Figure 2. The chromatogram of n-alkanes standard (red signal) overlaid with the chromatogram of a soil sample extract (blue signal) in order to define the integration area (grey)

The TPH concentration in the soil samples varied between 3400-48000 mg/kg determined by FTIR method and between 3100-45000 mg/kg determined by GC-FID method (Figure 3). In the 1-6 samples a high level of contamination with crude oil was noticeable visually and olfactory.

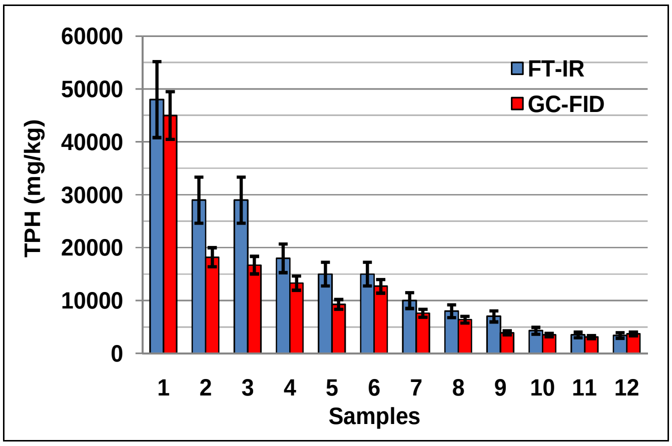

Figure 3. TPH concentrations in soil determined by GC-FID and FTIR methods

Both methods revealed significant amounts of TPH in all samples that exceeded the intervention level for non-sensitive soils (2000 mg/kg) according to Romanian legislation [21].

The TPH results obtained by the two methods are difficult to compare due to differences in analytical procedures, natural organic matter interferences, and different extraction and/or clean-up procedures.

The accuracy and precision in the studied methods was checked by the determination of TPH in two certified reference materials. No significant differences were found between the obtained results (mean value±standard deviation of three replicates) and the certified values (Table 1).

Table 1. The determined and certified values for the TPH concentration in CRM 358-100 and CRM PR 9583, expressed as mean value ± standard deviation (n=3)

CRM	**Reference value**	**Confidence Interval (95%)**	**Prediction Interval (95%)**	**Determined value**
	mg/kg			
CRM 358-100				
GC-FID	3650±1160	2790-4510	1070-6230	4190±1510
FTIR	3650±1160	2790-4510	1070-6230	3580±1190
CRM PR 9583				
GC-FID	9510±2155	8858-10162	5237-13783	9340±1978
FTIR	6721±1462	6036-7406	3584-9857	6250±1400

CONCLUSIONS

The obtained results showed that the TPH concentrations in all samples exceeded the intervention level for non-sensitive soils, according to Romanian legislation, indicating a highly contaminated area and a potential environmental and health risk. Therefore, the use of decontamination methods to decrease the risks by reducing the TPH concentration in the site is mandatory.

Both analytical methods used were found to be effective for the determination of TPH concentration in contaminated soil samples, although the obtained results are dependent on the analytical method. Despite the fact that TPH determination by FTIR method is simple, quick and inexpensive, its use is currently decreasing due to the worldwide ban of CFE production. In contrast to FTIR method, GC-FID method for TPH determination in soil supports green chemistry principles, by the use of non-halogenated solvents.

EXPERIMENTAL SECTION

Reagents and Samples

All reagents were purchased form Merck (Darmstadt, Germany) or Supelco (Bellafonte, USA) and were at least p.a. quality. Chromatographic grade n-hexane and acetone and IR grade 1,1,2-trichloro-1,2,2-trifluroethane (CFE) were used for extraction. Anhydrous sodium sulfate was used for drying, while Florisil® (60–100 mesh) was used for purifying the extracts. Calibration solutions were prepared using a mixture of 1:1 (m/m) additive-free diesel oil/motor oil.

A standard mixture of normal paraffins containing n-alkanes from C5 to C40 was used to determine the retention times of n-decane (C10) and n-tetracontane (C40). CRM 358-100 TPH in soil (RTC, Laramie, USA) and CRMPR 9583 TPH in soil (RIZA Institute for Inland Water Management and Waste Water Treatment, Netherlands) certified reference materials was used for the quality control of the determinations.

Twelve soil samples from a contaminated area of NW Romania were collected from 0-20 cm depth and stored in glass jars for transport to laboratory, in the autumn of 2009 [22].

Instrumentation

An Agilent 7890N gas chromatograph with a flame ionization detector (FID) equipped with automatic liquid sampler (HP Model 7673) and HP-5 fused-silica capillary column from J&W Scientific and a Perkin Elmer Spectrum BX II Fourier Transformation Infrared Spectrometer (FTIR) equipped with DTGS detector and single beam sample compartment were used for TPH determination. The LABOSHAKE 500 LS (Gerhardt, Germany) reciprocating shaker and a SONOREX Longlife RK 103H ultrasonic bath (Bandelin, Germany) was used for the extractions. All extraction steps were carried out in a CHEMFREE 2000 (Faster, Italy) fume hood equipped with appropriate filters.

TPH determination by GC-FID following ultrasonic extraction

Approximately 10 g soil was dried with anhydrous sodium sulfate in a 100 ml glass beaker. The sample was sonicated with 20 ml of 1:1 (v/v) hexane : acetone mixture for 15 min [23, 24]. The extract was transferred into a 20 ml volumetric flask, through a glass funnel packed with Florisil to retain more polar solutes. The solvent level was brought up to the 20 ml marker with hexane/acetone mixture. A volume of 1 µl aliquot of the final solution was injected

Table 2. Instrumental configuration and experimental conditions used for GC-FID analysis of TPH

Injector	Split/Splitless
Column	HP-5 (fused-silica capillary column coated with cross-linked 5% phenyl methyl siloxane) 30 m x 320 µm x 0.25 µm
Detector	FID
Inlet temperature	290°C
Injection mode	Splitless
Injection volume	1 µl

Carrier gas	He 2,5 ml/min
Oven temperature	Initial 50°C for 2 min 6°C/min to 300°C, 16 min
Detector temperature	300°C
Detector gases	H_2:40 ml/min; Air: 450 ml/min; He make-up: 30 ml/min

in the gas chromatograph in splitless mode. The instrumental configuration and the experimental conditions are summarized in Table 2. For TPH quantification, calibration standards were prepared by contamination of clean soil with 20 g/l 1:1 (m/m) mixture of additive-free diesel oil/motor oil in hexane-acetone mixture at concentrations between 100 and 5000 mg/kg TPH.

TPH determination by FTIR following classical extraction

About 10 g of sample was weighted and chemically dried with anhydrous sodium sulfate, then shaken two times with 20 ml CFE in screw capped glass bottles for 30 minutes. Sodium sulfate was added to the extract in order to eliminate any existing moisture and filtered through Whatman glass fiber disks. To eliminate polar compounds like water, vegetable oils and animal fats a clean-up step was applied passing the extracts through a 10 cm long column packed with Florisil (60-100 mesh), and filled up to 50 ml with CFE. The extracts spectrum was recorded between 3150-2750 cm^{-1} (average of 8 scans) at 4 cm^{-1} resolution using 10 mm optical path-length quartz cells in transmittance (%). Samples with absorbance bellow 0.2 were concentrated by evaporation while samples with absorbance higher than 0.8 appropriately diluted.

The calibration was made using of 8 soil standards with TPH concentrations of 10, 50, 100, 250, 500, 1000, 1500, 2000 mg/kg soil made in laboratory by contamination of clean soil with 20 g/l 1:1 (m/m) mixture of additive-free diesel oil/motor oil in CFE. The soil standards were mixed by mechanical shaking for 48 hours and subjected to the same analysis steps as the samples. TPH concentration was calculated based on calibration dependence of the peak area measured between 3100 and 2800 cm^{-1} with the concentration of the calibration standards.

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