Determination of petroleum hydrocarbons and polycyclic aromatic hydrocarbons in sludge from wastewater treatment basins

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Received 20th August 2002, Accepted 16th January 2003
First published as an Advance Article on the web 13th February 2003

Screening by gas chromatography with flame ionization detection and gas chromatography-mass spectrometry has been carried out on sludge extracts of wastewater treatment basins. Soxhlet extraction with trichlorotrifluoroethane was applied. The yields for petroleum hydrocarbons and PAH recovery were high, usually in excess of 90%. The proposed investigations permit a quick assessment of petroleum pollutants in the environment.

Introduction

The petroleum industry generates a high amount of oily wastes during storage, refining and processing operations. Over several decades, petroleum products have become very common pollutants in the environment as considerable amounts of petroleum compounds are discharged into the environment through industrial effluents.

Petroleum-derived compounds, such as saturated hydrocarbons are major constituents of petroleum. Generally they are not of toxicological concern, but identification and quantification of these analytes would be valuable to serve the following purposes: tracer of the presence of petroleum products, indicator of the fate of the petroleum samples and the changes in chemical composition, *etc.*[1] Polycyclic aromatic hydrocarbons (PAHs) are relatively stable constituents of petroleum, and from the environmental aspect, they are probably the most important analytes because many of these compounds are potential or proven carcinogens.[2] Unfortunately their low aqueous solubility, limited volatility, and recalcitrance towards degradation allows PAHs to accumulate to levels at which they may exert toxic effects upon the environment.

The analysis of saturated hydrocarbons, PAHs at the trace level in complex mixtures such as sludge is a challenge for the analytical chemist, who has to select, adapt and develop the appropriate methods for sampling, storage, extraction, clean-up and isolation, and sophisticated techniques are needed for identification and quantification. Many authors[3–10] have described methods for trace analyses and discussed problems associated with performing them. Sludge acts as a trap for petroleum-derived compounds originating from the different sources, and is often regarded as one of the worst environmental matrices to extract as it can contain a large variety of pollutants as well as the analytes of interest. A number of analytical procedures[3,4] involving ambient temperature extraction in separating funnels or vessels, or extraction under reflux with different solvents have been developed for the recovery of PAHs from sludge. Traditional methods of sample preparation including Soxhlet extraction with solvents are used in German and American standard methods.[5,6] An ultrasonic extraction procedure has also enjoyed much success for the extraction of PAHs from sediments as it combines effectiveness with simplicity and speed, but information regarding sonication extraction of PAHs from sludge is still limited.[3]

Many workers[2,4,7] have found that different methods give complementary information for the analysis of petroleum-derived compounds in the environment. Analytical methods for petroleum pollution studies are of two basic types: spectroscopic and chromatographic methods. First type of methods covers infrared (IR) absorption, ultraviolet (UV) absorption and UV-fluorescence spectrometry techniques. Each technique has advantages and disadvantages. For example, UV-absorption and UV-fluorescence are the most attractive since they focus on the main hazardous hydrocarbons, the aromatic petroleum compounds. UV spectrometries are selective and very sensitive to PAHs, but results may be influenced by the presence of many other compounds (*e.g.* lipids) in high concentrations in the sludge. IR spectrometry is poorly selective. IR determinations require a short preparation and analytical time and are less expensive to used. However, a general feature of these spectroscopic methods is that a clean-up procedure must be carried out preliminarily with great care to avoid contamination.[7] In recent years, capillary gas chromatography with flame ionization detector (GC-FID) has been widely used in petroleum analyses and its application to the proposed task is quite easy. HPLC screening with fluorescence detection has been employed to screen petroleum-related aromatic compounds in sediments and sludges.[3,7,8] However, the more expensive and time consuming GC-MS technique must be used for identification and to provide structural information for the individual petroleum compounds present in environmental samples.[8,9]

The operating processes in Lukoil-Neftochim-Bourgas use water as an auxiliary factor for cooling, washing, transportation and others. Depending on the degree of contamination, those waters were subject to treatment in the purifying systems. After purification the waters fall into wastewater treatment basins.

It is the aim of this investigation to shed some light on those compounds that are present in the sludge from the wastewater treatment basins of Lukoil-Neftochim-Bourgas JSC. These investigations could be used to evaluate the possible input of contaminants from the wastewater treatment basins into the environment. Since the present study mainly presents the results of several sludge samples, the preliminary character of these investigations should be taken into account.

DOI: 10.1039/b208157c

Experimental

Reagents and materials

Trichlorotrifluoroethane (1,1,2-trichloro-1,2,2-trifluoroethane) was obtained from Merck (Germany) and was used for the extraction of petroleum compounds from sludges. Standard reference material containing 16 EPA priority pollutants, PAHs in methanol : methylene chloride (50 : 50) (Supelco, USA) was used as the calibration sample. Certified concentrations of PAHs in the methanol : methylene chloride ranged from 100 to 2000 μg mL^{-1}. Diesel fuel from Lukoil-Neftochim-Bourgas was used to prepare spiked samples with different concentrations of contaminants. n-Hexadecane, isooctane and benzene, all Merck (Germany) were used to prepare calibration samples for Fourier transform-infrared (FT-IR) spectrometer. Silica gel 60 (0.063–0.200 mm) Merck (Germany) was used for the clean-up procedure. Magnesium sulfate heptahydrate from Merck (Germany) was used as the drying agent. Soxhlet extraction apparatus and medium cellulose thimbles (Supelco, USA) were used for the Soxhlet extraction procedure.

Samples

Sludge samples were collected from the selected sites of the wastewater treatment basins of Lukoil-Neftochim-Bourgas. Before analysis the samples were centrifuged. The samples were stored in 250 mL pre-cleaned dark glass bottles with Teflon caps at a maximum temperature of +4 °C. Moisture determinations were made according to ASTM D 3976.[11] The concentrations of petroleum hydrocarbons and PAHs were calculated on dry weight basis.

Soxhlet extraction procedure

Soxhlet extraction was performed using an 8 g portion of sludge that was added to 10 g of magnesium sulfate heptahydrate and mixed well. The mixture was transferred into a medium cellulose thimble. The thimble was covered with a loose plug of cotton wool (pre-extracted with trichlorotrifluoroethane) and inserted into a Soxhlet assembly fitted into a 250 mL flask. A 120 mL portion of trichlorotrifluoroethane was added and the whole assembly heated for 4 h. The extract was then concentrated in a rotary evaporator to 1 mL.

Clean-up of sludge extract for FT-IR analysis

Silica gel 60 used to remove the polar organic compounds. Before use, 10 g of silica gel was rinsed with 50 mL of trichlorotrifluoroethane and left in a fume hood for 4 h. Then silica gel was activated at 140 °C for 3 h. The column (900 mm × 50 mm id) was packed with 0.5 g of activated silica gel. Then, the column was conditioned with 3 mL of trichlorotrifluoroethane. The concentrated extract was quantitatively transferred to a preconditioned silica gel. Five mL of trichlorotrifluoroethane was used to elute the petroleum hydrocarbons. The clean-up extract was used for FR-IR analysis.

Sample spiking procedure

Contaminated sludge samples were used in the extractability study of petroleum hydrocarbons and PAHs from matrices with trichlorotrifluoroethane. After sampling, the sludge was dried at a temperature of 105 °C. A cellulose thimble containing dried sludge was placed into the Soxhlet extraction unit. Duplicate extractions were performed with trichlorotrifluoroethane. The next step was ultrasonic extraction with trichlorotrifluoroethane followed by drying at 150 °C to ensure that the prepared matrix no contains pollutants (Fig. 1). The fine powdered sludge was then stored in an airtight container and was analyzed to check for contaminations and interferences. Portions of 8–10 g each were weighed into an aluminium bottle for the sludge sample spiking; diesel fuel (1 to 10 μL) was added by means of a syringe.

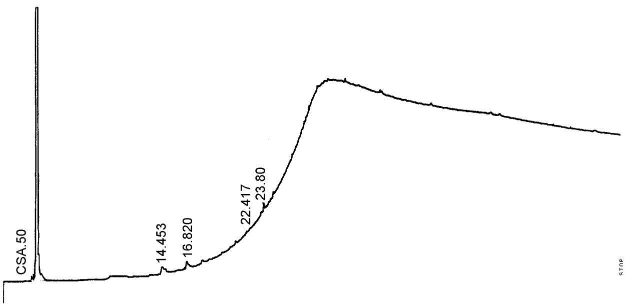

Fig. 1 Gas chromatogram (GC-FID) of sludge sample analyzed after duplicate Soxhlet extractions and ultrasonic extraction. GC conditions as described in the Apparatus section.

Apparatus

A Fourier transform-infrared spectrometer, model IFS 66 Bruker (Germany), scanning from 3100–2700 cm^{-1}, was used for the determination of petroleum hydrocarbons in the sludge sample extract.

Gas chromatography was performed with a Hewlett Packard (HP, Palo Alto, USA) HP 5890-II series chromatograph equipped with a flame ionization detector and a 25 m × 0.32 mm id × 0.52 μm film Ultra–2 fused silica capillary column. Hydrogen (2.0 mL min^{-1}) was used as carrier gas. The injector and detector temperatures were 290 °C and 300 °C respectively, and the column oven temperature was programmed at 6 °C min^{-1} from 90 °C to 270 °C which was held for 30 min. The injection volume was 1.5 μL.

Capillary gas chromatography-mass spectrometry was carried out using a HP 5890-II series gas chromatograph connected to a 5970 Hewlett Packard mass selective detector (HP, Palo Alto, USA). The system control and the data acquisition were controlled by a MS-DOS compatible workstation (MS ChemStation based on a Vectra XM 5/90 series 3 with HP G1701AA software). For identification of contaminants the MSD was operated in SCAN mode. The MSD was operated in the selected ion monitoring (SIM) mode for determination of PAHs. The ions monitored were: *m*/*z* 128 for the naphthalene, *m*/*z* 153 for the acenaphthene, *m*/*z* 152 for the acenaphthylene, *m*/*z* 166 and *m*/*z* 165 for the fluorene, *m*/*z* 178 for the phenanthrene and anthracene, *m*/*z* 202 for the pyrene and fluoranthene, *m*/*z* 228 for the benzo[*a*]anthracene and chrysene, and *m*/*z* 252 for the benzo[*k*]fluoranthene and benzo[*a*]pyrene.[12] A fused silica capillary column (25 m × 0.32 mm id × 0.52 μm film Ultra-2) was used for the separation of petroleum compounds in the analyzed samples. The column oven temperature program started at an initial temperature of 90 °C, was held for 0 min, ramped at a rate of 6 °C min^{-1} to 270 °C, held for 30 min. The injector temperature was set at 300 °C. The mass spectrometer transfer line was heated to 280 °C, and the electron energy and multiplier voltage were 70 eV and 1500 V respectively.

Method validation

The validity of the analytical method was verified by laboratory studies using standards and samples.[13–15] The parameters for the GC-FID method validation are shown in Table 1. The concentrations of the extractable hydrocarbons were determined by the external standard method. The instrument was calibrated using standard solutions of diesel fuel in the range 800–6000 μg mL^{-1} in trichlorotrifluoroethane.

The extractable hydrocarbon concentration was calculated by group integration (C_9–C_{30}) of the resolved and non-resolved peaks. The limit of detection (LOD) in GC analysis is generally

Table 1 Parameters of method validation

		Method precision		
Diesel fuel/mg kg^{-1}	Method accuracy (recovery) (%)	SD/mg kg^{-1}	RSD (%)	Repeatability/mg kg^{-1}
40	85	1.5	4.0	4.0
170	116	6.0	3.0	17.0
690	96	21.0	3.0	58.0
1300	91	12.0	1.0	33.0

considered to be that amount of analyte which gives a peak area response three times as great as the standard deviation (SD) of the response obtained from the lowest concentration of analyte. The LOD was calculated taking into account the extraction and the percentage recovery of analyte. The limit of quantitation (LOQ) is a quantitative result obtained with a specified degree of confidence. The value for LOQ = 10 × SD is used for calculating the limit of quantitation in our investigation.[16] The LOD and LOQ for extractable hydrocarbons from sludge with a maximum amount of sample 10 g were 10 mg kg^{-1} and 30 mg kg^{-1}, respectively.

The parameters of the GC-MS method validation are described elsewhere.[12]

The FT-IR spectrometer was calibrated using calibrating standards of n-hexadecane, isooctane and benzene. The standard mixture for the determination of petroleum hydrocarbons was prepared as follows: pipette 15 mL n-hexadecane, 15 mL isooctane, and 10 mL benzene into a 50 mL glass-stoppered flask. Pipette 0.5 mL of this mixture into a 100 mL, weighed to the nearest milligram, and dilute to volume with trichlorotrifluoroethane. Pipette appropriate volumes of this stock standard solution into 100 mL volumetric flasks and dilute to volume with trichlorotrifluoroethane to make calibration standards in range 10–500 μg mL^{-1}. A calibration plot is generated (absorbance at the aliphatic C–H stretch wavelength, range 3052 and 2783 cm^{-1}, *vs.* concentration of the petroleum hydrocarbons) using a series of standard solutions. The unknown petroleum hydrocarbons concentration in the 10 mm cell is then determined by comparing the absorbance of the extract with the calibration plot. With a maximum amount of sludge sample of 10 g the limits of detection and quantitation of petroleum hydrocarbons were 20 and 25 mg kg^{-1}, respectively.

Results and discussion

Initially the trichlorotrifluoroethane extracts of sludge samples were analyzed by GC-FID for the determination of extractable hydrocarbons. The obtained results for extractable hydrocarbons show the presence of a very complex mixture. Generally more than 200 different compounds can be observed in the extract obtained (Fig. 2). Identification of pollutants in sludge has frequently been difficult, especially if the pollutant concentrations have been low. The chromatograms for the different sludge extracts were seldom identical. The following explanation can be offered: the composition of sludge samples can be altered as results of selective sorption in the solid matrix and migration of the more soluble petroleum fractions. Under such circumstances the manner of sampling, the amounts of sludge, water content in the sludge samples *etc.* affect the results.

Identification of the some compounds was performed by comparison of the GC-retention time and the mass spectrometric fragmentation with reference substances. In this case, the name of the identified compounds is given. In many case, reference substances were not available for definite identification. Structures most compatible with the mass spectrometric data are proposed in these cases. The identification of compounds is based on the mass spectral data using MS Library Wiley. The identification of the compounds from sludge extract sample is presented in Table 2.

The results from GC-MS analysis confirm the presence of the

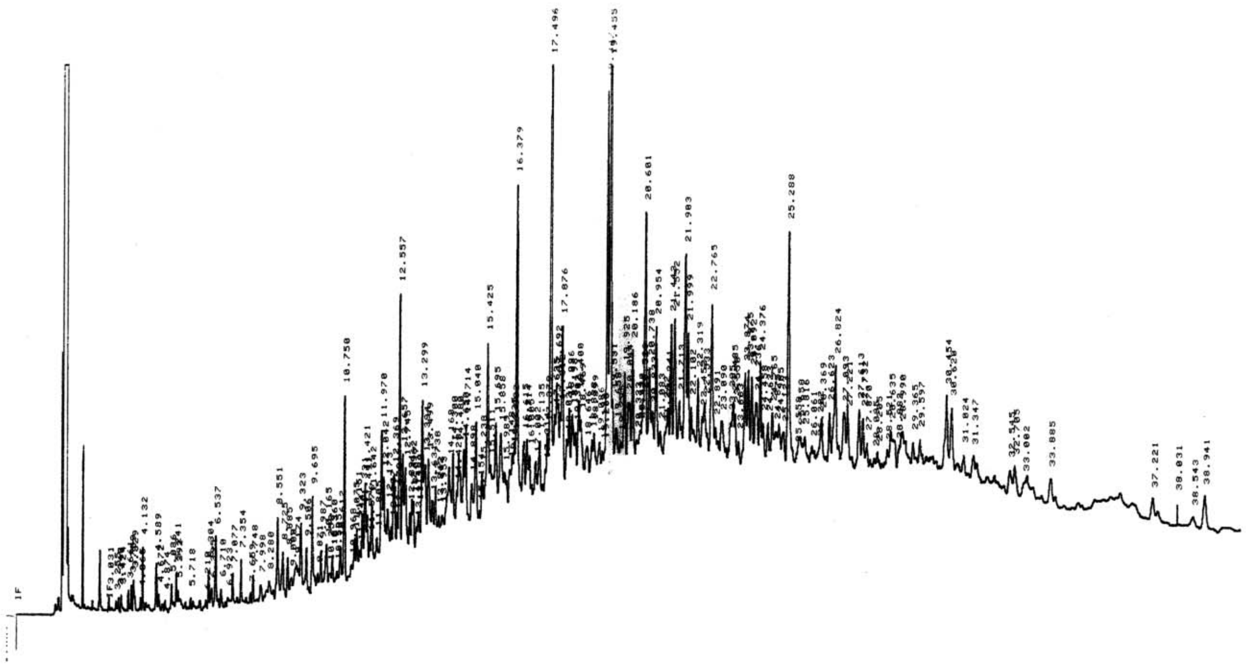

Fig. 2 Chromatogram of the extract from the sludge sample. Column, 25 m × 0.32 mm id fused silica capillary with Ultra-2 bonded phase. The identified components are listed in Table 2.

Table 2 Identification of compounds in sludge sample

RT/min	Compound
4.132	C_6-benzene
4.672	C_6-benzene
5.241	2-Methyl-dodecane
8.551	C_{13}-isoalkane
9.323	2-Methyl-naphthalene
9.506	C_{13}-isoalkane
9.695	1-Methyl-naphthalene
10.750	2,6,10-Trimethyldodecane
11.151	Biphenyl
11.331	C_2-naphthalene
11.421	C_2-naphthalene
11.451	C_2-naphthalene
11.642	C_2-naphthalene
11.970	C_2-naphthalene
12.042	C_2-naphthalene
12.369	C_2-naphthalene
12.465	2,6,10-trimethyltridecane
13.299	Methyl-biphenyl
14.300	C_3-naphthalene
17.714	C_3-naphthalene
14.898	C_3-naphthalene
15.040	C_3-naphthalene
15.425	Fluorene
16.379	Norpristane
17.496	2,6,10,14-Tetramethyl-pentadecane (pristane)
17.692	C_1-fluorene
17.876	C_1-fluorene
19.342	Phenanthrene
19.455	2,6,10,14-Teramethyl-hexadecane (phytane)
20.601	Butyl phthalate
20.954	C_{20}-isoalkane
21.443	C_1-phenanthrene
21.552	C_1-phenanthrene + C_{20}-isoalkane
21.903	C_1-phenanthrene
21.999	C_1-phenanthrene
22.765	C_3-fluorene + unknown
22.874	C_2-phenanthrene
24.092	C_2-phenanthrene
24.376	Fluoranthene
25.288	Pyrene
26.369	C_1-fluoranthene + C_{21}-isoalkane
26.824	C_1-fluoranthene + C_{21}-isoalkane
27.613	C_1-fluoranthene + unknown
27.732	C_1-fluoranthene + unknown
28.635	C_1-fluoranthene + unknown
28.990	C_2-fluoranthene + unknown
30.454	Benzo[*a*]anthracene
30.620	Chrysene
32.545	C_1-benzo[*a*]anthracene + unknown
32.705	C_1-chrysene + unknown
33.885	C_1-benzo[*a*]anthracene + unknown

isoprenoids (2,6,10-trimethyldodecane, 2,6,10-trimethyltridecane, norpristane, pristane and phytane), n-alkanes, unresolved complex mixture of aliphatics originating from degraded oil, PAHs (naphthalene, acenaphthalene, phenanthrene, fluorene, pyrene, benzo[*a*]anthracene, chrysene) and small quantities of oxygen containing compounds (phthalates, aldehydes, ketones, aromatic acids in any samples).

Global quantification method for the petroleum hydrocarbons using IR spectrometry is applied. This method is well-suited to rapid screening for petroleum pollution in widespread and extended environmental studies.[17,18] It is simple and quickly set up and gives immediate results, however this method does not give direct information on the structure of compounds in the samples.

In addition the GC-FID method was compared with the Soxhlet-IR method. The extractable hydrocarbon and petroleum hydrocarbon concentrations were measured. The data from analysis of the eluent from extracting four sludge samples are listed in Table 3. The results indicate reasonable agreement between the extractable hydrocarbons obtained by GC-FID method and petroleum hydrocarbons determined by IR method.

Table 3 Determination of the extractable hydrocarbon concentration and petroleum hydrocarbons in sludge sample with GC method compared with IR method

	Extractable hydrocarbons/mg kg^{-1} d.w.		Petroleum hydrocarbons/ mg kg^{-1} d.w.
Sample	GC method	IR method	IR method
Sludge 1	68	100	68
Sludge 2	226	258	222
Sludge 3	57	76	66
Sludge 4	143	182	143

Solvents commonly used to extract PAHs from sludge are toluene, methanol, dichloromethane and cyclohexane. Recoveries reported range between 67 and 130% depending upon the procedure applied.[3–5] Trichlorotrifluoroethane is currently used for the extraction of petroleum hydrocarbons in standard methods for the extraction of water and wastewater.[6] We tested the efficiency of trichlorotrifluoroethane for Soxhlet extraction of PAHs from petroleum contaminated sludge samples. The results obtained are shown in Table 4. The recovery of the PAHs determined by GC-MS was generally good for all compounds and ranged from 80 to 93%. The yields of the different PAHs decrease with the number of aromatic rings. Bedding *et al.*[10] demonstrated that losses of PAHs to the walls of a glass bottle increased with increasing molecular weight.

In order to determine PAHs, the method was applied to sludge samples from the wastewater treatment basins of Lukoil-Neftochim-Bourgas. Four samples representing various levels of PAH contamination were analyzed. The results are presented in Table 5. The results show that the sample profiles as well as the concentrations of PAHs were different from area to area in the wastewater treatment basins. Different PAHs mixtures were found to be present in each sample, dependent upon the source of contamination, the environmental conditions, the contamination extent, and the degree of weathering of the samples.

Conclusion

These investigations demonstrate that the approach used for the analysis of petroleum hydrocarbons and PAHs in sludge is very useful for screening purposes. We applied a GC method to the analysis of sludge samples containing petroleum hydrocarbon concentrations in the range of 40 to 1300 mg kg^{-1}. A lower limit of detection than the comparable IR method was obtained.

The GC and IR methods are used for the determination for petroleum hydrocarbons in sludge samples and its comparability by speed and equipment accessibility is established. The methods are cheaper than GC-MS and the IR method is the

Table 4 Extraction of PAHs (μg kg^{-1}) from sludge

Compounds	Spiked concentration/μg kg^{-1}	Recovery[a] (%)
Naphthalene	38	89
Acenaphthene	30	80
Acenaphthylene	27	91
Fluorene	37	90
Phenanthrene	44	93
Anthracene	40	89
Pyrene	42	90
Benz[*a*]anthracene	50	80
Benzo[*k*]fluoranthene	50	84
Fluoranthene	60	87
Chrysene	50	80
Benzo[*a*]pyrene	100	83

[a] Means based on at least 3 replicate experiments.

Table 5 Concentrations of PAHs by GC-MSD/SIM in sludge samples

Compounds	Concentration/µg kg^{-1} d.w.			
	Sample 1	Sample 2	Sample 3	Sample 4
Naphthalene	320	11	720	<0.1
Acenaphthene	130	<0.1	<0.1	<0.1
Acenaphthalene	110	25	530	20
Fluorene	730	29	970	56
Phenanthrene	770	20	1600	51
Anthracene	180	<0.1	<0.1	<0.1
Pyrene	320	<0.2	610	24
Benz[*a*]anthracene	90	<0.2	1000	10
Benzo[*k*]fluoranthene	10	47	<0.5	<0.5
Fluoranthene	170	10	1600	<0.1
Chrysene	90	<0.2	1000	<0.2
Benzo[*a*]pyrene	10	<0.5	<0.5	<0.5

fastest. The advantage of the GC-MS method is the more thorough information about the structure of compounds present in sludge samples.

The main restriction however, is the limited identification of unknown substances when using electron impact mass spectrometry, because a great number of substances could not be identified based on their mass spectra alone. For these substances, additional information was needed *e.g.* by using high resolution MS or applying chemical ionization techniques to obtain molecular ions.

The analytical data and results obtained using these methods are important and essential in monitoring the composition of petroleum pollutants and assessing the damage of petroleum hydrocarbons and PAHs to the natural resources.

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