

ANALYSES OF PARAFFINS AND POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL WITH GC-MS

HRABOVSKI Nataša¹, ÖKRÉSZ Szilvia²,
SINADINOVIĆ-FIŠER Snežana¹

¹ DEPARTMENT OF PETROCHEMICAL ENGINEERING,
FACULTY OF TECHNOLOGY, UNIVERSITY OF NOVI SAD

² CHAIR OF ANALYTICAL CHEMISTRY, DEPARTMENT OF CHEMISTRY,
FACULTY OF NATURAL SCIENCES, UNIVERSITY OF NOVI SAD

SUMMARY

In this work the qualitative and quantitative analyses of paraffins (normal hydrocarbons C₁₀-C₄₀) and polycyclic aromatic hydrocarbons (16 EPA-PAHs) were performed. The authors have analysed soil samples in order to examine the content of paraffins and the amount of PAHs. After sampling of the soil, the paraffins were extracted with acetone/n-heptane and PAHs with a mixture of acetone/cyclohexane. Clean-up of the obtained extracts were performed on Florisil in the case of paraffins and on activated silica in the case of PAHs. The prepared samples were measured with GC-MS. For the qualitative analysis of paraffins retention time window standard solution was used. In order to perform quantitative analyses external calibration method was applied. Limits of detection and determination for the PAHs found in the sample have also been determined.

KEY WORDS:

Paraffins, PAHs, GC-MS, soil

1. INTRODUCTION

Linear paraffins i.e. aliphatic hydrocarbons of C₁₀-C₄₀ chain lengths are usually separated from kerosene or gas oil fractions of crude oil using molecular sieves. The major use is as a raw material for the production of olefins or monochloroparaffins applied to manufacture linear alkylbenzene [1]. Polycyclic aromatic hydrocarbons (PAHs) are a group of over 100 different chemicals [2] that are formed during the incomplete combustion of some organic substances such as fossil fuels, coal, oil, tobacco, etc. [3]. They are partly highly toxic and/or potentially carcinogen [4]. They are found throughout the environment - in the air, water and soil [5]. In order to examine the level of soil contamination the EPA has suggested determination of amount of 16 PAHs (naphthalene, acenaphthylene, 1,2-dihydro-acenaphthylene, fluorene, anthracene, phenanthrene,

fluoranthene, pyrene, benzo[*a*]anthracene, benzo[*b*]fluoranthene, chrysene, benzo[*k*]fluoranthene, benzo[*a*]pyrene, dibenz[*a,h*]anthracene, benzo[*g,h,i*]perylene and indeno[1,2,3-*c,d*]pyrene) in soil samples [6]. The chemical structures of the 16 EPA-PAHs are shown on Figure 1. Refineries, gas-, coking- and similar plants are well known pollutants of the environment by PAHs. Therefore it is important to track the PAH's concentration in environmental samples affected by these plants. The results of these analyses help to evaluate how a contaminated land has to be sanified.

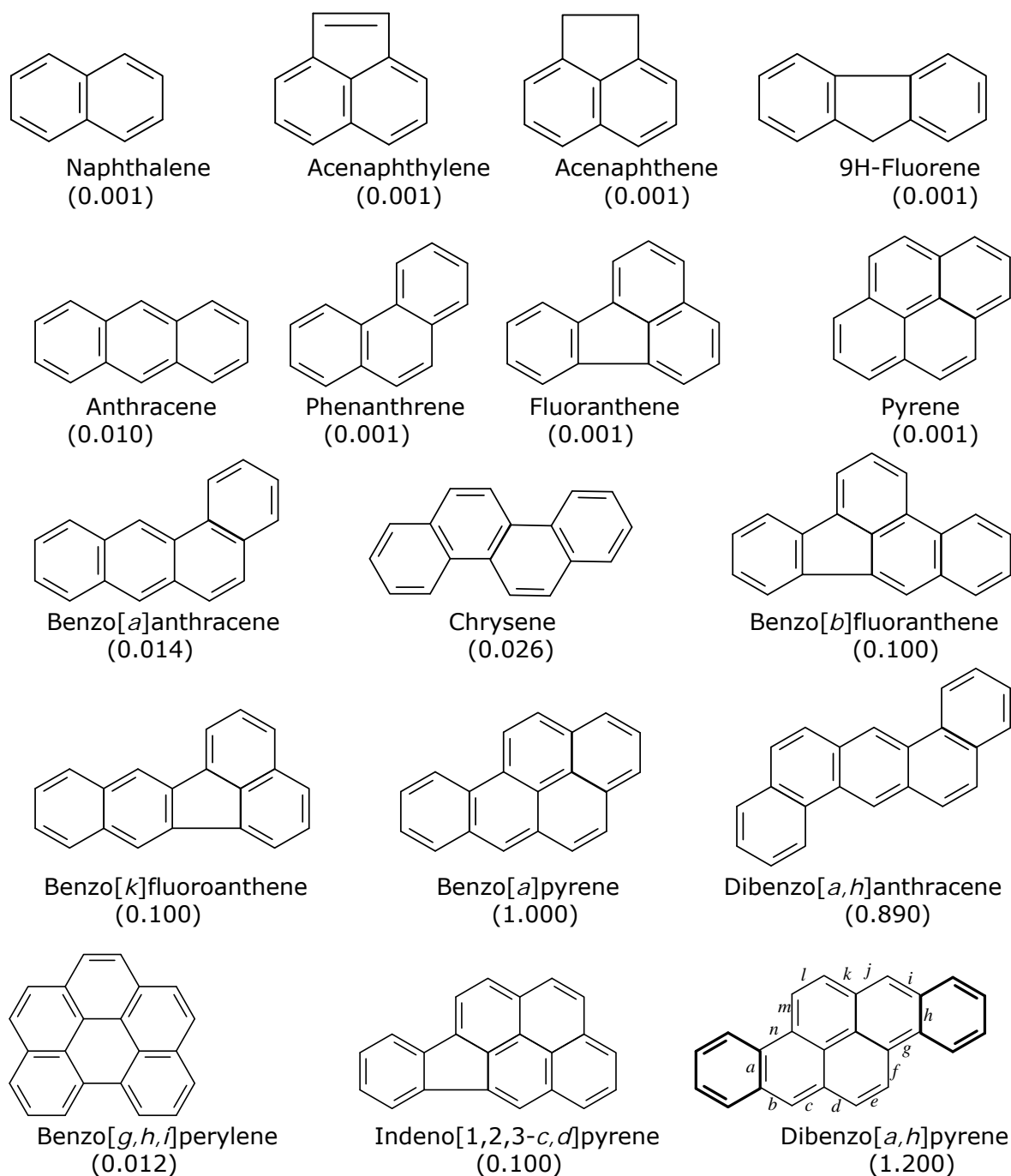


FIGURE 1. CHEMICAL STRUCTURES OF THE 16 EPA-PAHS AND DIBENZO[*A,H*]PYRENE AND THEIR RELATIVE CANCEROGENIC POTENCY VALUES (RCP)

The objectives of this work were qualitative and quantitative analyses of paraffins (normal hydrocarbons C_{10} - C_{40}) and polycyclic aromatic hydrocarbons (16 EPA-PAHs) in soil samples by GC-MS. Limits of detection and determination for the PAHs found in the sample have also been determined.

2. EXPERIMENTAL

After sampling, the soil samples are treated with a solvent to extract the contaminants. The extractions are followed by clean-up procedures. The purified extracts are analysed by GC-MS.

All GC-MS analyses are performed by using a Trace GC, Thermo Finnigan, coupled with a mass selective detector (MSD) (Trace MS plus, Thermo Finnigan). GC-MS is controlled with a computer workstation through the "Excalibur" program.

The system is equipped with a PS 255 capillary column (L 30 m; I.D. 0.25 mm; film 0.25 μ m) and an automatic sampler (AS 2000). The injector is PTV (Programmed Temperature Vaporiser). The carrier gas is helium (5.0) at 1.5 mL/min constant flow.

3. PARAFFINS

Sampling and extraction.

Approximately 1 kg of soil sample was collected [7]. After sieving the moist soil, 20.08 g is being weighted. The amount of water is determined with a separate probe.

The soil is treated with 20 mL acetone. 10 mL of retention time window (RTW) standard solution is added to the sample. RTW standard solution is containing small quantities of n-decane ($C_{10}H_{22}$) and n-tetracontane ($C_{40}H_{82}$) in n-heptane. It is using to determine the total peak area between the range defining standards n-decane and n-tetracontane. Extraction of the paraffins with acetone/n-heptane is performed by sonication during 30 min.

After extraction, approximately 30 mL of distilled water is added, shortly shaken and centrifuged for 1h. The organic layer is transferred to another centrifugal tube, approximately 50 mL water is added and centrifuged once again for 20 min. Organic layer is separated again.

Clean-up.

Clean-up step of the obtained extract is needed because the polar compounds have to be removed. In order to perform the clean-up, a micro-column is being filled with 1 g of activated Florisil and 0.25 g of anhydrous sodium sulphate is added on the top. The obtained organic layer is transferred to the top of the column and purified. An aliquot of the purified extract is taken into a vial and analysed by GC-MS [8].

With each series of samples a blank determination should be carried out using all reagents in identical amounts but without a soil sample.

GC-MS analysis.

Blank and sample extracts are analysed under identical conditions as the paraffins standard solutions. The concentrations of the paraffins in the standard solutions are 0.5 g/L n-heptane and 2.0 g/L n-heptane.

GC-MS conditions are the following. Volumes of 1 µL are injected to the programmable temperature vaporization (PTV) port in splitless mode. The initial temperature is 70°C, heated up to 320°C. GC-column PS 255 is used with the temperature programme applied: 60°C for 1.7 min, 12°C/min to 300°C, 300°C held for 20 min. MSD with electron impact mode of 70 eV is operated in total ion chromatogram (TIC) mode.

4. POLYCYCLIC AROMATIC HYDROCARBONS

Sampling and extraction.

10.08 g of soil is weighted. Extraction of the 16 EPA-PAHs is performed by adding 50 mL acetone and 50 mL cyclohexane to the weighted soil sample and shaking for 2 hours on a horizontal mechanical shaker. The obtained extract is filtered and dried with anhydrous sodium sulphate, and then evaporated on the rotary vacuum evaporator (water bath temperature 40°C) to a volume of approximately 10 mL.

The solution is transferred into a graduated flask and filled with cyclohexane up to 100 mL volume.

Clean-up.

Because of many other substances present in the soil sample, namely humic substances and other hydrocarbons, which interfere the determination of the 16 EPA-PAHs, it is necessary to remove them from the sample. Therefore a clean-up step is included.

In order to prepare the clean-up column, 2 g of activated silica is suspended in 10 mL of cyclohexane and poured into a glass clean-up column. Anhydrous sodium sulphate (0.25 g) is added to the top of the column. Aliquot of 1 mL of the evaporated extract is being transferred to the column. Washing is performed with 5 mL of cyclohexane.

The PAHs are eluted with 10 mL of cyclohexane/dichloromethane mixture (1:1). This cyclohexane/ dichloromethane fraction containing the PAHs is evaporated to a volume of app. 1 mL and is totally transferred into a measured autosampler vial.

The solvent is changed to toluene by heating the sample on 40-45°C in a stream of nitrogen. The final amount of toluene in the vial is determined by weighting. In order to check the whole procedure, a blank sample is run as well.

GC-MS analysis.

The injection volume is 1 µL. PTV injection port is used, the splitless time lasts for 1.70s and is heated up to 300°C. The ion source temperature is set at 320°C. The oven temperature programme is set from 70°C for 1.0 min, to 170°C at 15°C/min, to 190°C at 8°C/min, to 230°C at 15°C/min, to 300°C at 8°C/min, and 300°C held for 10 min.

The primary and secondary ion numbers of PAHs are determined by using the full scan mode for pure PAH standards.

The quantification of PAHs is performed by using the selective ion-monitoring (SIM) mode. The external calibration for each of the PAHs is performed with a standard solution of 16 PAH compounds (Priority pollutants PAH in Acetonitrile – Multicomponent Standard Solution SRM 1647D, LGC Promochem, Wesel, Germany) and the referred diluted solutions into toluene (0.1; 0.03; 0.01; 0.003;).

5. RESULTS AND DISCUSSION

5.1. PARAFFINS

Chromatograms of the paraffins standard solution (2.0 g paraffins/L n-heptane) and the obtained soil extract are shown on Figure 2.

Total peak area is determined on each chromatogram. Peak areas and concentrations of the standard solutions are used for the construction of the calibration curve.

The equation of the calibration curve is calculated by Excel and then used to determine the content of paraffins in the soil sample. Elution factors are also being considered.

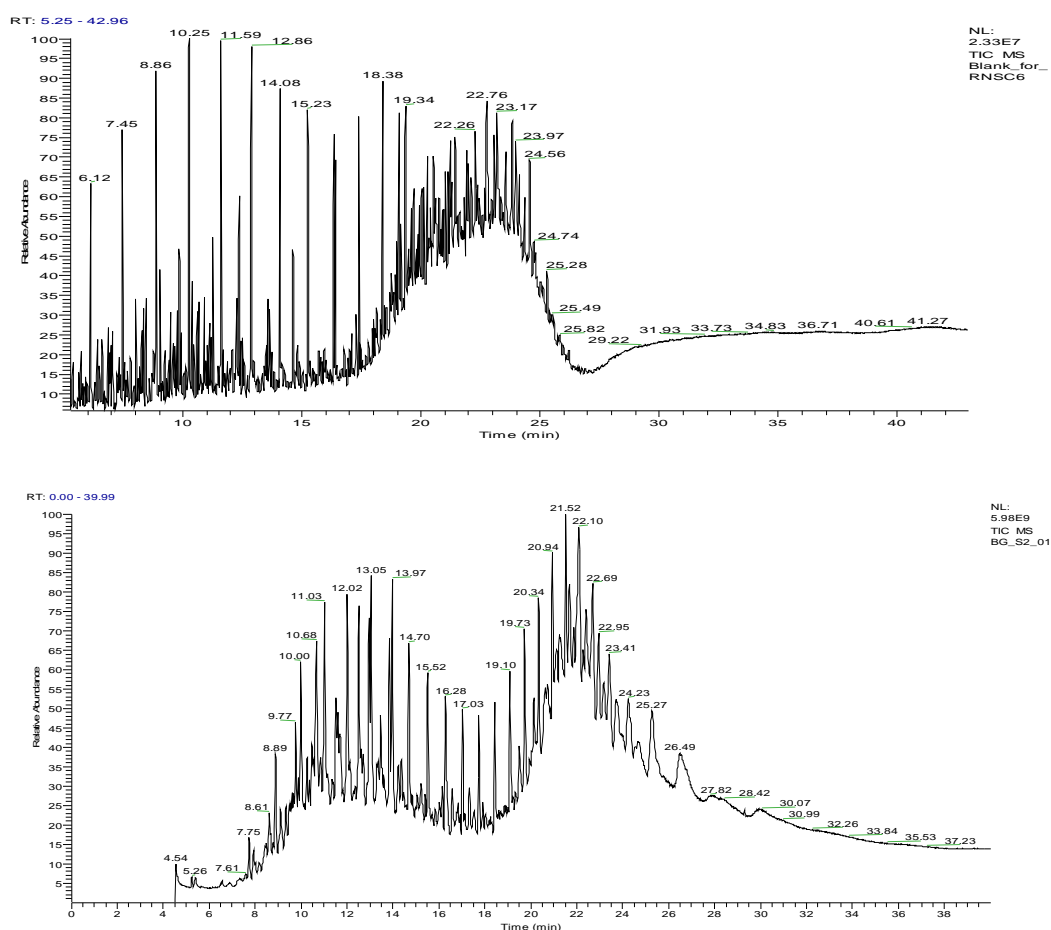


FIGURE 2. CHROMATOGRAMS OF THE PARAFFINS STANDARD SOLUTION AND THE OBTAINED SOIL EXTRACT

It is determined that the soil sample contains 9.2699g paraffins/kg of dry matter of soil. The result shows high contamination of soil with diesel and oil containing heavier hydrocarbons. The sample extract used for clean-up procedure was dark coloured and very small amount of final extract was obtained. Because of that we had to dilute our extract with factor of 5. From the chromatogram it can be seen that the peaks are very nice separated. A non-horizontal baseline at the end of the chromatogram indicates that the sample contains irresolvable high-boiling hydrocarbons.

5.2. POLYCYCLIC AROMATIC HYDROCARBONS

Chromatograms of the 16 EPA-PAHs standard solution and the obtained soil extract is shown on Figure 3.

The amounts of the PAHs are determined by external calibration. Calibration curves (concentration v.s. determined peak area of the identified PAH) are drawn with Excel for all PAHs found in the sample. In order to calculate the concentrations of the PAHs in the sample, linear regression is used. The final results are given as μg PAH/g of dry matter of soil. Limits of detection and determination for the PAHs found in the sample have also been determined, taking required signal to noise ratios equal to 3 and 10, respectively.

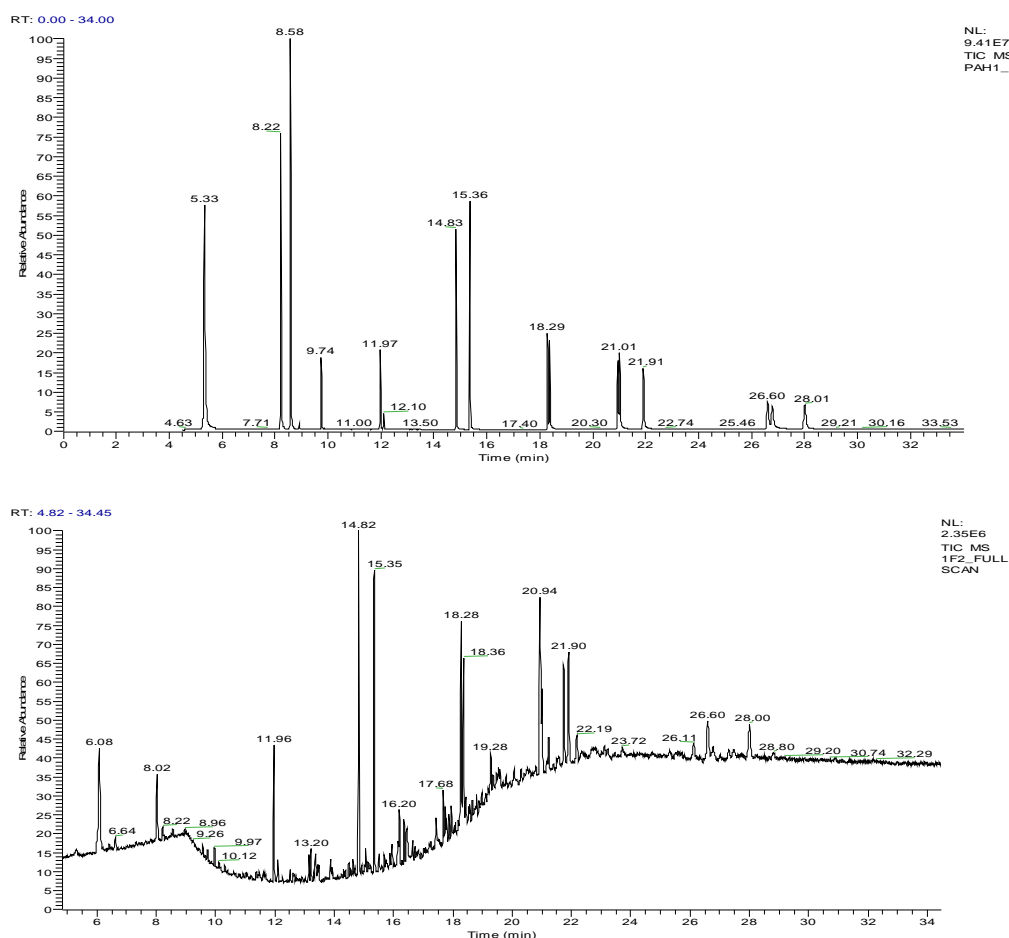


FIGURE 3. CHROMATOGRAMS OF THE 16 EPA-PAHs STANDARD SOLUTION AND THE OBTAINED SOIL EXTRACT

Results are given in Table 1.

Since benzo(a)anthracene and chrysene, as well as benzo(b)fluoranthene and benzo(k)fluoranthene co-eluate under the applied conditions, these compounds are determinable only as the summe of two. The result for 1,2-dihydro-acenaphthylene is a negative value, because the amount found in the sample is below LOQ, therefore not considerable. Naphthalene and anthracene were not found in the sample.

TABLE 1. CONCENTRATIONS OF THE PAHS FOUND IN THE SAMPLE AND THEIR LOD AND LOQ VALUES

PAH	[µg/kg]	LOD [µg/l]	LOQ [µg/l]
Naphthalene	-	-	-
Acenaphthylene	133	0,15	0,49
1,2-Dihydro- acenaphthylene	-177	0,36	1,20
Fluorene	1	0,18	0,63
Anthracene	-	-	-
Phenanthrene	198	0,22	0,73
Fluoranthene	285	0,28	0,95
Pyrene	268	0,33	1,13
Benzo[a]anthracene+ Chrysene	407	0,43	1,45
Benzo[b]fluoranthene+Benzo[k]fluoranthene	474	0,56	1,88
Benzo[a]pyrene	256	1,08	3,60
Dibenz[a,h]anthracene	66	0,55	1,83
Benzo[ghi]perylene	132	0,49	1,63
Indeno[1,2,3-cd]pyrene	168	0,45	1,51
Σ PAH concentration		2388	

ACKNOWLEDGEMENTS

This work was supported in part by German Academic Exchange Service (DAAD) and the Institute of Environmental Research (INFU), Dortmund, FRG. Prof. Dr Michael Spittler and Dr Joern Sickerling provided assistance in GC-MS analyses.

REFERENCES

- [1.] Suresh, B., Gubler, R., Sasano, T., CEH Report, Normal Paraffins, 2001. [online]
<http://ceh.sric.com/Public/Reports/683.5000>
- [2.] Air Quality Guidelines – Second Edition, Polycyclic aromatic hydrocarbons (PAHs) WHO Regional Office for Europe, Copenhagen, Denmark, 2000, pp. 4,15. [online]
www.who.dk/document/aiq/5_9pah.pdf
- [3.] De P. Pereira, P.A., de Andrade, J.B., Miguel, A.H., *Analytical Sciences* 17 (2001) 1229-1231.

- [4.] ATSDR – Public Health Statement: Polycyclic Aromatic Hydrocarbons (PAHs) [online]
www.atsdr.cdc.gov/toxprofiles/tp69.html
- [5.] Blankenhorn, I., Meijer, D., van Delft, R.J., *Fres. J. Anal. Chem.* 343 (1992) 497-504.
- [6.] EPA Introduction to PAHs [online]
www.epa.nsw.gov.au/air/dopahhm/pahintroduction.htm
- [7.] ISO DIS 10381-1, Soil quality – Sampling – Part 1: Guidance on the design of sampling programmes
- [8.] PrEN 14039:2000, Characterisation of waste-Determination of hydrocarbon content in the range of C₁₀-C₄₀ by gas chromatography