VĚDECKÉ SPISY VYSOKÉHO UČENÍ TECHNICKÉHO V BRNĚ

Edice PhD Thesis, sv. 460

ISSN 1213-4198

Ing. Jiří Pryček

Selected Derivatives of Polycyclic Aromatic Hydrocarbons in the Environment

Brno University of Technology
Faculty of Chemistry
Institute of Chemistry and Technology of Environmental Protection

Ing. Jiří Pryček

SELECTED DERIVATIVES OF POLYCYCLIC AROMATIC HYDROCARBONS IN THE ENVIRONMENT

VYBRANÉ DERIVÁTY POLYCYKLICKÝCH AROMATICKÝCH UHLOVODÍKŮ VE SLOŽKÁCH ŽIVOTNÍHO PROSTŘEDÍ

SHORT VERSION OF Ph.D. THESIS

Study filed: Chemistry and Technology of Environmental Protection
Supervisors: assoc. prof. Zdeněk Šimek, CSc.
RNDr. Miroslav Ciganek, Ph.D.
Opponents: Ing. Zbyněk Večeřa, CSc.
assoc. prof. Jan Poustka, Ph.D.
Ing. Josef Čáslavský, CSc.
Presentation date: 12. 12. 2007

KEY WORDS

pressurised solvent extraction, polycyclic aromatic hydrocarbons, derivatives, nitro-PAH, dust, soil, fractionation

KLÍČOVÁ SLOVA

tlaková extrakce rozpouštědlem, polycyklické aromatické uhlovodíky, deriváty, nitro-PAU, prach, půda, frakcionace

Place of storage: Local library FCH BUT, 118 Purkynova, Brno

ISBN 978-80-214-3644-2
ISSN 1213-4198

TABLE OF CONTENTS

1 CURRENT KNOWLEDGE IN THIS FIELD 5

1.1 Occurrence and properties of target compounds 5
1.2 Analytical methods 6

2 MOTIVATION AND PURPOSE 8

3 EXPERIMENTAL 9

3.1 Target compounds 9
3.2 Pressurised solvent extraction 9
3.3 Roadside dust and soil sampling and sample preparation 11
3.4 Extract fractionations 11
3.5 GC-MS 11

4 THE MAIN RESULTS 12

4.1 Pressurised solvent extraction 12
4.1.1 Extraction of nitro-PAH from inert matrix 12
4.1.2 Roadside dust extraction 13
4.2 Extract fractionation 13
4.2.1 Influence of a nature of solvent 13
4.2.2 Solvent optimalization 15
4.2.3 Nitro-PAH analysis in the roadside dust and soil 20

5 SUMMARY AND MAJOR CONCLUSIONS 21

6 LIST OF ABBREVIATIONS 22

7 REFERENCES 23

8 CURRICULUM VITAE 26

9 APPENDIX 28

1 CURRENT KNOWLEDGE IN THIS FIELD

1.1 OCCURRENCE AND PROPERTIES OF TARGET COMPOUNDS

Polycyclic aromatic hydrocarbons (PAH), their derivatives and polycyclic heterocyclic aromatic hydrocarbons, called hetero-PAH, form the complex mixture of compounds occurring in the environment. Derivatives of PAH can be divided into groups according to the substituent or substituents bonded with the aromatic ring of parent PAH. From these groups – nitrated derivatives (nitro-PAH), alkyled derivatives (alkyl-PAH) and halogened derivatives are the most studied compounds. PAH containing oxygen in a sidegroup are also studied. Nitrogen (PANH), sulphur (PASH) or oxygen (PAOH) are usually incorporated in the aromatic ring of PAH. One, two or sometimes more heteroatoms can be built into the ring. By the reason of various and complicated ways of formation there exist derivatives containing different substituents bonded with aromatic ring.

Even though the parent PAH are nonpolar compounds, substituent can change compound's polarity. Therefore wide group of compounds with different properties is formed. Heteroatom incorporated into the aromatic ring slightly increase polarity [1].

PAH and their derivatives are toxicologically significant. Acute toxicity of these compounds is not as big problem as mutagenicity or carcinogenicity. Generally it is not possible to affirm, if certain PAH show mutagenic activity. This depends not only on the number of aromatic rings, but mainly on theirs position. The sidegroups also have influence on the toxicity. Carcinogenic and mutagenic effects of these compounds were being studied on some microorganisms or human cells [2-4]. International Agency for Research on Cancer (IARC) distinguishes five compound's groups according to their ability to induce cancer. The most dangerous to human race are compounds and mixtures from the first group (4-aminobiphenyl, 2-aminonaphthalene, tabacco smoke), these are classified as carcinogenic to humans [5].

Nitro-PAH are widespread environmental pollutants. They originate during the combustion of petrochemical fuel and other organic matter and/or they are formed in the atmosphere during the photochemical reactions of PAH with hydroxyl radicals and NO_2 or with NO_3^- [6]. So far, these compounds have been found in fly ash, exhaust emissions from waste incineration plants, cigarette smoke, wastewater, sediments and other environmental matrixes [7].

Alkyl-PAH mainly occur in crude oil and its products. They can originate from parent PAH or organic matter during combustion or pyrolysing processes [8,9]. They are more stabile than nitro-PAH. Hetero-PAH occur as well as alkyl-PAH in crude oil and its products [10,11].

All compounds from these groups can be metabolised by microorganisms. These processes as well as photochemical decay of these compounds lead to formation more polar compounds [12-15].

1.2 ANALYTICAL METHODS

As written above, derivatives of PAH and hetero-PAH occur in low concentrations in all environmental compartments. Usually they are present in complex matrixes. Optimal analytical procedure depends on the matrix nature. The whole procedure covers several steps – sample collection, extraction of analytes from matrix, extract fractionation (clean-up), analysis of specific fractions or clean extracts. This work is mainly focused on the analysis of solid matrixes (soils, road dusts).

Samples can be collected by special sampling equipment or brushes. All parts should be made of materials with improved inertness. After that, dust samples are dried and sieved to obtain fraction with particle size we needed. If next step does not immediately follow, the sample is stored closed in low temperature to prevent analytes from volatilisation.

Extraction is a step necessary for the isolation of analytes from solid matrix. Several efficient extraction techniques have been developed (Soxhlet extraction, automated Soxhlet extraction, ultrasonic assisted extraction, supercritical fluid extraction – SFE, accelerated solvent extraction – ASE or pressurised solvent extraction – PSE, microwave assisted extraction – MWAE, shaking samples with solvent [16].

Dichloromethane (DCM), diethylether, trichloromethane or toluene and/or its mixture with polar solvents – methanol (MeOH) or acetone are used as extraction solvents. In case the extraction procedure is too long the unstable analytes could be decomposed.

Soxhlet extraction and automated Soxhlet extraction are still the most used in laboratory practice as a part of many analysis protocols by the reason of its high extraction efficiency and not so high technical level of equipment. However this method is time consuming (6 – 48 hours) and solvent volumes are relatively large (100 – 250 ml) [3,7,17-20].

Ultrasonic assisted extraction is the second most used extraction technique. It is technically slightly demanding than Soxhlet extraction. The usual extraction time is shorter than 1 hour and solvent consumption is the same as in the case of using Soxhlet extraction [6,7,11,21].

PSE is used in laboratories less than previous techniques. It utilises solvents above their atmospheric pressure boiling point, which are still in liquid state. It is reached by affecting of higher pressure in extractor. The access of solvent's molecules to the matrix particles is better at higher temperature and extraction efficiency is the same at shorter extraction time. The time of extraction is reduced to a few minutes and solvent consumption in about one-tenth in comparison to Soxhlet extraction. These are the main advantages of using it. The main disadvantage of this technique is high technical level of equipment, high price and necessity of well-trained operators. By the reason of using smaller amount of solvents and shorter

extraction time this technique should be, as well from environmental protection point of view, more widespread in the laboratories [22-24].

Other methods are much less used for extraction because of their lower extraction efficiency or higher prices of equipment.

Extract can be filtered through the membrane filter after extraction, in case it contains solid particles. After that the volume of extract can be reduced. Evaporation of the lower pressure, drying at nitrogen stream or Kuderna-Danish concentrator are the most used methods [25].

The next step of analytical procedure is extract fractionation. This step is used for separation of analytes from remaining matrix in extract or separation from compounds that can interfere with final instrumental determination of analytes. Removing of this interference causes a decrease in limits of determination. Therefore it is possible to determine lower concentrations of analytes in the samples. Fractionation is based on difference in chemical or physical properties of compounds. The first group of clean-up technique utilises different acid-base behaviour of compounds in the solution and it is nowadays less used [26]. Disadvantage of this technique is higher solvent consumption and emulsion formation. The second group of clean-up techniques utilises several chromatographic techniques – liquid chromatography (open column or high performance – HPLC) and solid phase extraction (SPE).

The principle of open column liquid chromatography, HPLC and SPE in the target compounds separation are the same – adsorption and partition chromatography on slightly polar or polar sorbents [27]. The most polar compounds are the most retained in this system. HPLC has higher separation efficiency, but it is more expensive. On the other side open column chromatography is sufficient for separation of group of compounds with similar physical properties and it is cheaper.

Silica gel and aluminium oxide are the most used sorbents for chromatographic fractionation. Solvents or its mixture in order of increasing polarity are used for elution of compounds or group of compounds. Nonpolar fraction (alkanes) is eluted by nonpolar solvent (pentane, hexane or petrolether), aromatic fraction (PAH) is eluted by mixture of hexane and DCM, slightly polar fraction (nitro-PAH, dinitro-PAH) is eluted by DCM and polar fraction (oxy-PAH, alcohols, phthalates) is eluted by mixture of DCM with polar solvents (MeOH) or only by polar solvent [3,7,22,28-31].

Several instrumental analytical techniques are used for analysis of fractions or cleaned extracts, but two of them are used in the large scale – high resolution gas chromatography called now gas chromatography (GC) and high performance liquid chromatography (HPLC). Although the final determination follows the clean-up steps, the resultant mixture of compound is still too complex. This complexity makes demands on the high separation efficiency and low detection limits of system, especially in the case of trace analyses. Only the two techniques mentioned before

fill these requirements. Their on-line combination – HPLC-GC is sometimes used too and nowadays two-dimensional GC or HPLC are also employed [32,33].

GC shows about 10 times higher separation efficiency then HPLC, but its usage is limited to analysis of volatile and semivolatile thermostabile compounds. It is widely used for analysis of PAH consisted of less than 7 aromatic rings. Capillary GC with nonpolar or slightly polar stationary phases are used for extract analysis by the reason of its better separation efficiency than packed column GC. Mass spectrometry (MS) is the most used detector connected with GC which is used for detection of target compounds. Flame ionisation detector or electron capture detector are less used [7, 19,21,34,35].

Liquid chromatography is not unlike gas chromatography limited by volatility of compound. Target analytes are separated by reversed phase HPLC, i.e. silica gel with octadecyl or octyl side-chains as a stationary phase. Gradient elution is mainly used because of its better and faster elution of more retained molecules. Spectrophotometric – ultraviolet or fluorescence – detectors are mainly used. Mass spectrometry detector is nowadays used too, but it is not so sensitive as if it is connected with gas chromatograph [36-38].

2 MOTIVATION AND PURPOSE

This short version of Ph.D. thesis describes experiments leading to finding procedure for polycyclic aromatic hydrocarbons' derivatives analysis with special emphasis on nitrated derivatives.

These compounds are widespread semivolatile environmental pollutants. They have been found in all environmental compartments. From a chemical viewpoint nitro-PAH form group with different properties. Many PAH and their derivatives are classified as carcinogens or possibly carcinogenic to humans by IARC [5]. Nitro-PAH also constitute a group of potent direct-acting mutagens.

By these reasons we need analytical procedure for determination of these compounds in the environment. Nowadays here is a lack of knowledge about application of pressurized solvent extraction (accelerated solvent extraction) in these analytical procedures, although it is fast and solvent saving technique.

The main purposes of Ph.D. project follow:

- To do a bibliographic search regarding the analytical procedures for determination of derivatives of PAH especially in the solid samples.
- To use pressurized solvent extraction for extraction of spiked inert matrix to find out best extraction conditions and to investigate the behaviour of nitro-PAH during extraction.
- To use pressurized solvent extraction for a roadside dust extraction with special emphasis on extraction of nitro-PAH.
- To find out the best solvent system for extract clean-up when silica gel column chromatography is used.

3 EXPERIMENTAL

3.1 TARGET COMPOUNDS

Some representatives from wide group of PAH and their derivatives occurring in roadside dust were chosen due to their different properties. Alkanes belong to nonpolar compounds, 16 US EPA PAH (acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, benzo[a]pyrene, dibenzo[a,h]anthracene, fluoranthene, fluorene, chrysene, indeno[1,2,3-c,d]pyrene, naphthalene, phenanthrene, pyrene) plus 4H-cyclopenta[d,e,f]phenanthrene, dibenzofuran, 1-phenylnaphthalene, 2-methylanthracene, 5-methylchrysene, 2-methylphenanthrene, 1-methylnaphthalene, 2-methylnaphthalene, 1-methylpyrene belong to aromatic fraction,
9-nitroanthracene, 2-nitrofluorene, 6-nitrochrysene, 1-nitronaphthalene, 1-nitropyrene belong to slightly polar fraction
and anthracene-9,10-dione, 4H-cyclopenta[d,e,f]phenanthrene-4-one, dimethylanthracene-9,10-dione, methylantracene-9,10-one, 9H-fluorene-9-one belong to polar fraction.

3.2 PRESSURISED SOLVENT EXTRACTION

All PSE experiments were made by use of a pressurised solvent extractor (FASTEX, Unikovo). The stainless steel extraction vessel with an inner volume of 11 ml was used. All extraction parameters (pressure, temperature, duration and number of static extraction period, duration of solvent and gas flushing) were adjusted by means of instrument software.

Preliminary experiments were carried out with spiked inert matrix (sodium sulphate). These experiments were done to find out best extraction conditions and to investigate the behaviour (especially stability) of selected nitro-PAH during extraction process. Different extraction temperatures (60, 80, 100 °C), pressures (10, 12, 14 MPa), duration of static extraction period (5 and 10 min) and nature of solvents were tested. DCM and its mixture with methanol were examined. These solvents were selected on the basis of their frequent use as extraction solvents in environmental analyses.

Each run was performed using DCM and DCM:MeOH 1:1 v:v. About 5 g of anhydrous sodium sulphate was spiked with 100 µl of nitro-PAH spiking solution (10 $\mu g.ml^{-1}$) and filled into the extraction vessel. The top of matrix layer in the vessel was covered with a filter paper. The vessel was put into the extractor and the extractor was closed. Then extraction solvent was pumped into the vessel. The flow was stopped when one half of set extraction pressure was achieved. The vessel with solvent and matrix was preheated for 2 min to reach the selected extraction temperature. Then the solvent was pumped into the vessel to reach the set extraction pressure. Static extraction period followed. After the end of this period the extract was discharged to the 40 ml glass vial with the PTFE/silicon septa and the extraction

was repeated. To ensure that all extracted analytes reach the collection vial the vessel was rinsed with fresh solvent for 20 s at flow rate 10 ml.min^{-1}. Finally, pure nitrogen was purged through the extraction vessel for 1 min to assure that the solvent was completely transferred to the collection vial. Total extraction time was less than 30 min and total extract volume was about 25 ml per one sample extraction. Extracts were evaporated to dryness using rotary vacuum evaporator (RVE) at 30°C after filtration through anhydrous sodium sulphate. The evaporation residue was redissolved in 500 µl of methanol and analysed by GC-MS operated in SIM mode with monitored fragments M^+ and $(M-30)^+$. To exclude possible analytes losses, all these samples were analysed without any clean-up steps. The five same samples were extracted at the same extraction conditions.

The existence of potential degradation products originated during extraction was checked. The analyses of extract were performed by GC-MS, MS operated in SCAN mode.

The roadside dust extractions were carried out by the same extractor that was used in the previous experiments. DCM was used as an extraction solvent. A dust spiked with 1 µg of nitro-PAH were used in experiments, which were followed by fractionation procedures. About 2 g of dust was mixed with 3 g of anhydrous sodium sulphate and filled into 11 ml extraction vessel. Free capacity of the vessel was filled with glass beads. Two extraction cycles of 5 min at 100 °C and 14 MPa were used. Extracts were collected into 40-ml glass vials, evaporated to dryness using RVE. The evaporation residue was redissolved in 1 ml of solvent. Type of this solvent (DCM, nC6, cC6) depends on following experiments. Evaporated extracts dissolved in 500 µl of isooctane were analysed in SIM mode to find out nitro-PAH's extraction efficiency from dust.

Extracts were collected after each extraction cycle and solvent flush during the experiments investigating kinetics of extraction. Extracts were evaporated, redissolved in 500 µl of isooctane solution of HCB (0,476 µg.ml^{-1}) and analysed by GC-MS. HCB was used as an internal standard. Three extractions were carried out.

Some experiments have been aimed at the recovery investigation. To obtain quantitative data for recovery calculation, method of standard addition was used. The recovery was calculated using equation (1), where m_S is amount of compound found in spiked extract, m_N is amount of compound found in non-spiked extract, without addition of target compound, m is amount of compound added to sample before extraction

$$REC[\%] = \frac{100.(m_S - m_N)}{m} \qquad (1)$$

3.3 ROADSIDE DUST AND SOIL SAMPLING AND SAMPLE PREPARATION

A roadside dust was collected from a shoulder at the city road and highway interchange using a small brush and a trowel. A soil samples were collected at the tram stop near city road. Samples were air dried at the room temperature for one day. Dry samples were sieved to remove particles of ≥ 600 μm. Sieved samples were homogenised by mixing and kept in a 40 ml glass vials with PTFE/silicon septa wrapped with aluminium foil and stored at -18 °C in a freezer. To minimise effect of different residual water content, the samples were mixed with anhydrous sodium sulphate prior to the extraction.

3.4 EXTRACT FRACTIONATIONS

The main purpose of these part of work was to find out a suitable system using open silica gel column chromatography, that is able to separate compound's group (fractions) existing in the sample. This system should be able to separate components in the extract into at least four fractions containing compounds with similar polarity. Nonpolar fraction – alkanes and aliphatic hydrocarbons, aromatic fraction – PAH, slightly polar fraction – nitro-PAH, polar fraction – oxy-PAH.

One millilitre of extract was transferred to the top of a glass column (250 × 10 mm i.d.) filled with 5 g of fully activated silica gel capped with 1 g of anhydrous sodium sulphate. The column was rinsed with 10 ml of n-hexane before applying of a raw extract. Elution of fraction was then started using appropriate elution solvent.

Influence of a nature of solvent (nC6, cC6 and DCM), which extracts were dissolved in, has been examined. Elution was performed by 10 ml of nC6, then 15 ml of nC6:DCM 1:1 v:v, then 10 ml of DCM and then 15 ml of DCM:MeOH 1:1 v:v. Each of fractions was eluted by 1 ml of solvent except for fraction eluted by 10 ml of DCM. Fractions were evaporated at room temperature in the air atmosphere and were redissolved in 100 μl of isooctane and analysed by GC-MS operated in SCAN mode.

Cyclohexane and n-hexane have been chosen for the further experiments. Better separation of fractions in normal phase LC can be possible to get by using of higher volume of nonpolar solvent or using of solvents with lower elution strength [27]. Different volume of n-hexane and mixtures of n-hexane with DCM has been examined. Fractions of 5 or 10 ml were collected, evaporated to dryness, redissolved in 200 μl of isooctane solution of HCB (0,476 $\mu g.ml^{-1}$) and were analysed by GC-MS operated in SCAN mode.

3.5 GC-MS

All extracts and solutions were analysed by using of the gas chromatograph (GC 8060, Fisons Instruments) connected with the mass spectrometr (Trio 1000, Fisons Instruments) – GC-MS. Capillary columns – DB-5MS (Agilent – 30 m; 0,25 mm i.d.; 0,25 μm film thickness) or CP-SIL 24CB (Varian – 30 m; 0,25 mm i.d.;

0,15 μm film thickness) were installed in the gas chromatograph. The GC injection port temperature was 250°C, MS interface temperature 220°C and ion source 200°C, respectively. Helium was used as a carrier gas at the constant head pressure 150 kPa. Injections were performed in splitless mode (splitter was closed for 1 min), sample injected volume was 2 μl. The electron impact ionisation of 70 eV was used, the MS was operated in SCAN mode (40 – 305 amu) or operated in the selected ion monitoring (SIM) mode.

GC temperature programmes depend on solvent used for extract dissolving. For methanolic solutions, an initial GC oven temperature was 70 °C (1 min isothermal), then it was programmed at 25 °C.min^{-1} to 180 °C, at 10 °C.min^{-1} to 290 °C, finally it was held isothermal for 7 min. For isooctane solutions, an initial temperature was 90 °C (1 min isothermal), then it was programmed at 25 °C.min^{-1} to 180 °C, at 10 °C.min^{-1} to 290 °C, finally it was held isothermal for 25 min.

4 THE MAIN RESULTS

4.1 PRESSURISED SOLVENT EXTRACTION

4.1.1 Extraction of nitro-PAH from inert matrix

The extraction temperature of PSE cartridge was held constant at 60 °C and 100 °C respectively. The pressure was varied from 10 to 14 MPa. The recoveries of target compounds obtained at the extraction temperature 60 °C with DCM as an extraction solvent ranged between 44 and 75 %. The recoveries of target compounds obtained at the same extraction temperature with DCM:MeOH 1:1 v:v as an extraction solvent ranged between 46 and 92 %. The recoveries at this extraction temperature were not significantly dependent on the extraction pressure at tested range. Relative standard deviations (RSD) of five extractions were in the range from 3 to 23 %. By the reason of low extraction recoveries, the temperature 60 °C seems to be too low to extract all amounts of analytes from matrix. No degradation products were found, when extracts were analysed at SCAN mode.

The recoveries of nitro-PAH obtained at the extraction temperature 100 °C were similar when DCM or its mixture with MeOH were used and ranged between 33 and 116 %. These recoveries increase with increasing extraction pressure. The relative standard deviations of five extractions were in the range from 6 to 30 %. The highest recoveries were obtained at 14 MPa with RSD in the range from 6 to 18 %.

Two extraction cycles at 5 and 10 min were tested. Extraction pressure was 10 MPa and extraction temperature was 100 °C. Recoveries ranged between 31 and 94 %. The prolongation of an extraction time had no effect on the increasing of recoveries. The recoveries decreased on the contrary. This could be caused by lower stability and thermolability on nitro-PAH.

Nitro-PAH with lower molecular weight (1-nitronaphthalene, 2-nitrofluorene) seem to be partially lost during evaporating of extracts. DCM was chosen for next experiments because of its better evaporability from extracts.

4.1.2 Roadside dust extraction

Amounts of compounds extracted in each cycle were measured and they are shown in the Table 1. In this table the total amounts of compounds extracted during the whole extraction are summed to 100 %. 3 parallel extraction at the same conditions were carried out.

Table 1 - Extraction kinetics, average amounts of compounds

Group	cycle 1	cycle 2	Solvent flush
	%	%	%
Alkanes	95,2	3,4	1,3
PAH	98,4	1,5	0,1
Nitro-PAH	100,0	0,0	0,0
Oxy-PAH	99,7	0,3	0,0

The biggest amount of compounds was extracted during the first cycle (5 min). Only small amount of alkanes and PAH was not completely removed from the dust, it is caused by their higher contents in the dust. The second reason is that DCM is not suitable solvent for nonpolar compounds. Extraction with usage of n-hexane should be better in case of alkanes and nonpolar compounds analyses. Polar compounds (oxidised products of PAH, phthalates) should be better to extract by mixture with some more polar solvent (MeOH, acetone).

The extraction recoveries of investigated nitro-PAH from roadside dust are shown in the Table 2. These recoveries are slightly higher than recoveries obtained in experiment with inert matrix and the RSD are similar to previous experiment. DCM was used as a extraction solvent. 3 parallel extraction at the same conditions were carried out.

Table 2 – Nitro-PAH's extraction recoveries from roadside dust

Compound	Recovery	RSD
	%	%
1-nitronaphtalene	73	14
2-nitrofluorene	70	20
9-nitroanthracene	83	15
1-nitropyrene	92	18
6-nitrochrysene	117	9

4.2 EXTRACT FRACTIONATION

4.2.1 Influence of a nature of solvent

Several different solvents (nC6, cC6 and DCM) were tested as potentially suitable solvents for redissolving of residues after evaporation of extraction solvent prior to its applying on silica gel fractionation column. Systems of the elution solvents were

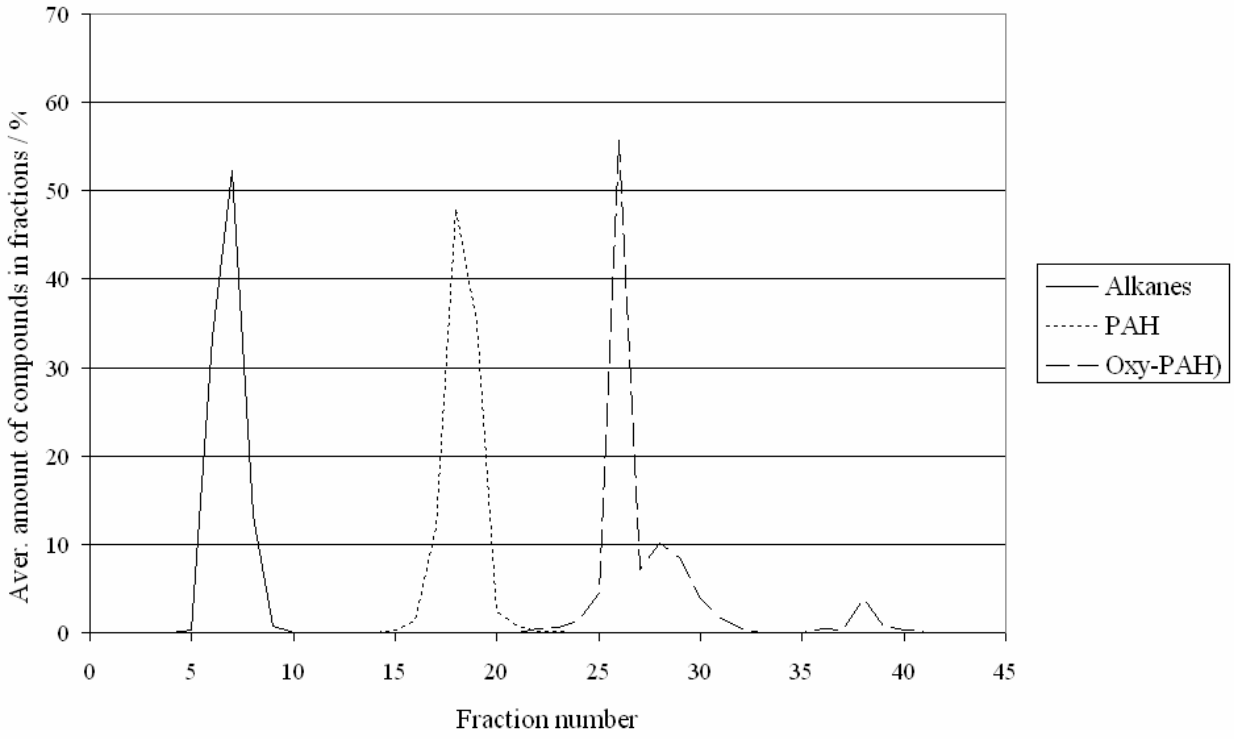

Fig. 1. Separation of fractions by silica gel column chromatography when the extract is dissolved in n-hexane.

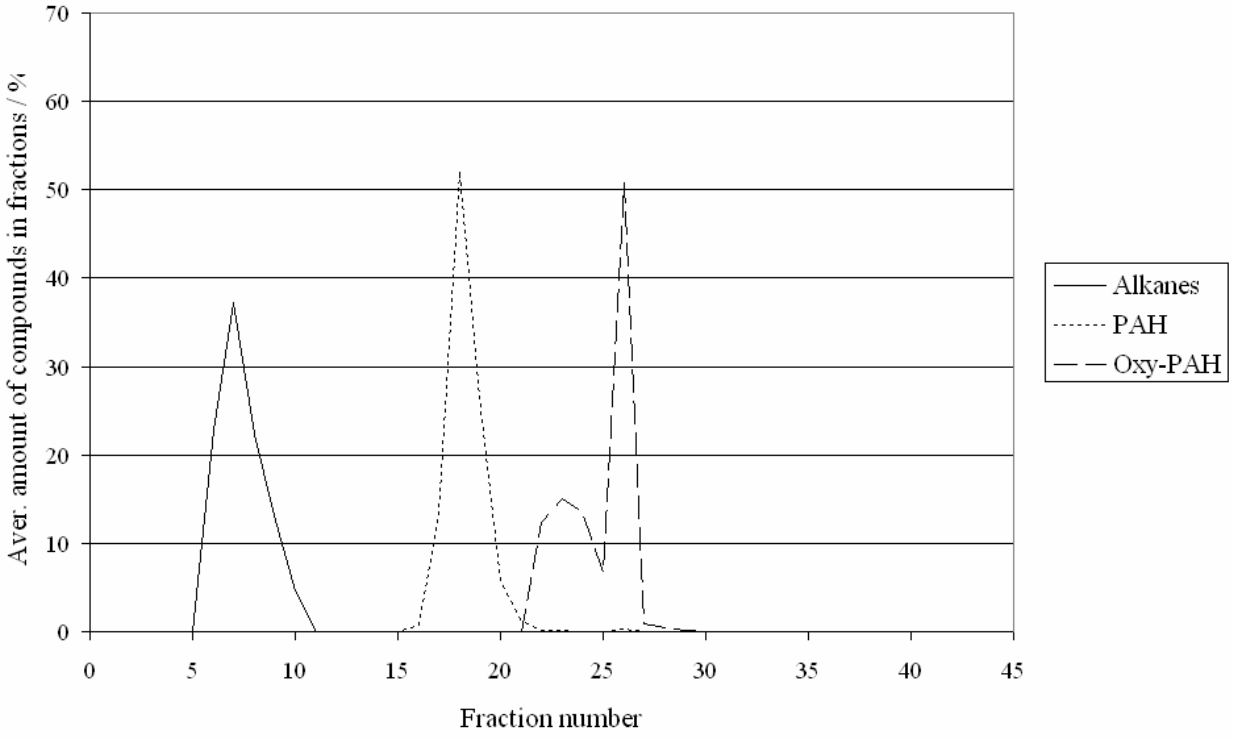

Fig. 2. Separation of the fractions by silica gel column chromatography when the extract is dissolved in cyclohexane.

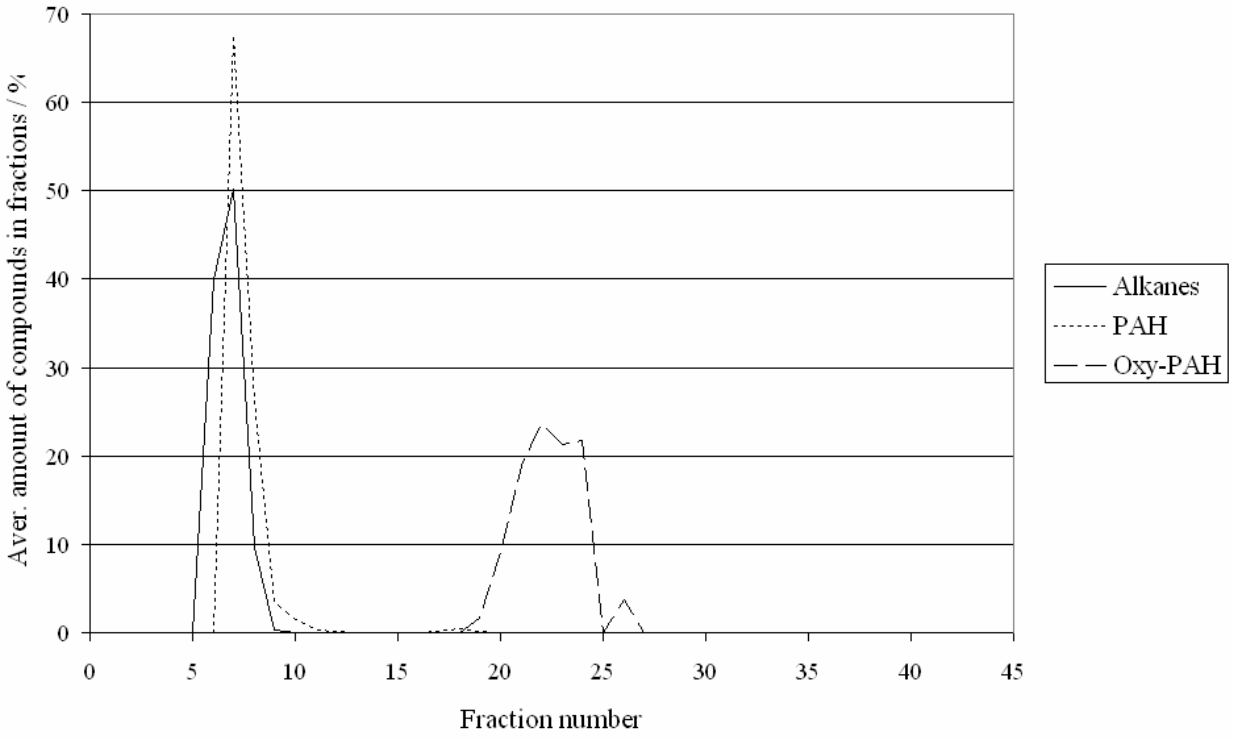

Fig. 3: Separation of the fractions by silica gel column chromatography when the extract is dissolved in dichloromethane.

the same in all these experiments and it is described in the experimental part. Resulting elution curves are shown in the figure 1 – 3. The *x*-axis represents the fraction number, the average contents of compounds in the individual fractions are displayed on the *y*-axis.

Nonpolar compounds are not retained on silica gel, so these compounds are separated from others in case of using nC6 and cC6 for extracts redissolving. Aromatic and polar fractions are also separated from each other. Volume of n-hexane or cyclohexane extract applied on the fractionation column does not affect chromatographic process because of usage of nonpolar solvent for the first fraction elution. On the other hand DCM, probably due to its higher elution strength, showed not to be suitable solvent. Nonpolar and aromatic fraction coeluted. Only polar fraction is separated and its elution is faster than in previous cases. Nonresolved organic matter (NOM) in all cases eluted together with nonpolar compounds and it decreased chemical background in other fractions.

4.2.2 Solvent optimalization

Cyclohexane and n-hexane were found as suitable solvents for redissolving of evaporation residues before their applying on silica gel column. Different volumes of nC6 used for elution have been examined for the best fraction separation. Initial volume of n-hexane has been changed from 15 to 25 ml. Obtained contents of

groups of compounds in individual fractions are shown in the Tables 3, 4, 5. The compound contents are shown in percentages.

Nonpolar compounds plus NOM were separated from the others in all experiments. Separation of aromatic, slightly polar and polar fraction from each other improved with increasing volume of nC6 on the beginning of elution. In spite of it, complete separation was not achieved. Even in this instance about 5 – 10 % of compounds' amount from each fractions were not separated from the previous eluted fraction.

Table 3 – Extract fractionation – compound's group content in each fraction in %

	Solvent	nC6		nC6/DCM			DCM		DCM/MeOH
				1 / 1					1 / 1
nC6*	Volume# / ml	10	5	5	5	5	5	5	10
	Alkanes	100	0	0	0	0	0	0	0
	PAH	0	0	32	68	0	0	0	0
	Nitro-PAH	0	0	0	73	27	0	0	0
	Oxy-PAH	0	0	0	4	6	64	26	0
cC6*									
	Alkanes	93	7	0	0	0	0	0	0
	PAH	0	0	6	92	2	0	0	0
	Nitro-PAH	0	0	0	43	56	1	0	0
	Oxy-PAH	0	0	0	2	1	43	54	1

*Extracts were applied on silica gel column dissolved in nC6 or cC6.
#Volume of individual elution step.

Table 4 – Extract fractionation – compound's group content in each fraction in %

	Solvent	nC6			nC6/DCM			DCM		DCM/MeOH
					1 / 1					1 / 1
nC6*	Volume# / ml	10	5	5	5	5	5	5	5	10
	Alkanes	100	0	0	0	0	0	0	0	0
	PAH	0	0	20	28	52	0	0	0	0
	Nitro-PAH	0	0	0	0	74	26	0	0	0
	Oxy-PAH	0	0	0	0	6	3	57	32	2
cC6*										
	Alkanes	89	11	0	0	0	0	0	0	0
	PAH	0	0	23	23	52	2	0	0	0
	Nitro-PAH	0	0	0	0	58	42	0	0	0
	Oxy-PAH	0	0	0	0	1	14	55	30	0

*Extracts were applied on silica gel column dissolved in nC6 or cC6. #Volume of individual elution step.

Table 5 – Extract fractionation – compound's group content in each fraction in %

	Solvent	nC6				nC6/DCM			DCM		DCM/MeOH
						1 / 1					1 / 1
nC6*	Volume# / ml	10	5	5	5	5	5	5	5	5	10
	Alkanes	100	0	0	0	0	0	0	0	0	0
	PAH	0	0	24	31	45	0	0	0	0	0
	Nitro-PAH	0	0	0	0	7	92	1	0	0	0
	Oxy-PAH	0	0	0	0	0	11	49	40	0	0
cC6*											
	Alkanes	92	8	0	0	0	0	0	0	0	0
	PAH	0	0	8	15	68	9	0	0	0	0
	Nitro-PAH	0	0	0	0	8	90	2	0	0	0
	Oxy-PAH	0	0	0	0	0	4	74	22	0	0

*Extracts were applied on silica gel column dissolved in nC6 or cC6. #Volume of individual elution step.

No significant differences in compound separations were found whether n-hexane or cyclohexane were used for extract applying on silica gel column. Following experiments were done with cyclohexane by the reason of its better ability to dissolve evaporation residues. Different mixture of nC6 with DCM for best fraction separation has been examined. Elution of aromatic fraction was done by mixture of nC6 with DCM in volumetric ratio 4 to 1. Obtained contents of groups of compounds in individual fractions are shown in the Tables 6 – 7.

Table 6 – Extract fractionation – compound's group content in each fraction in %

Solvent	nC6	nC6/DCM			DCM		DCM/MeOH	
		4 / 1					1 / 1	
Volume[#] / ml	10	5	5	5	5	5	10	5
Alkanes	96	4	0	0	0	0	0	0
PAH	0	0	9	90	1	0	0	0
Nitro-PAH	0	0	0	0	8	92	0	0
Oxy-PAH	0	0	0	0	0	14	86	0

Extracts were applied on silica gel column dissolved in cC6.
[#]Volume of individual elution step.

Table 7 – Extract fractionation – compound's group content in each fraction in %

Solvent	nC6		nC6/DCM			DCM		DCM/MeOH	
			4 / 1					1 / 1	
Volume[#] / ml	10	5	5	5	5	5	5	10	5
Alkanes	97	3	0	0	0	0	0	0	0
PAH	0	0	0	0	100	0	0	0	0
Nitro-PAH	0	0	0	0	0	11	89	0	0
Oxy-PAH	0	0	0	0	0	0	9	91	0

Extracts were applied on silica gel column dissolved in cC6.
[#]Volume of individual elution step.

Lower content of DCM in the mixture caused its lower elution strength. So better separation of aromatic fraction from slightly polar was achieved. But slightly polar fraction still coeluted with polar fraction. In case of nitro-PAH analysis it does not matter. Oxy-PAH are in similar concentration levels as nitro-PAH and they are separated from them on GC column. The problem caused PAH, whose concentrations were higher by several orders of magnitude. Due to their high amounts in the samples it was not possible to analyse nitro-PAH and oxy-PAH in presence of PAH and other impurities.

The final fractionation procedure chosen on the basis of previous experiments, is following:

The first fraction (fraction 1) was eluted by 10 ml of n-C6 and then by 5 ml of n-C6:DCM 4:1 v:v. Fraction 2 was eluted by 10 ml of n-C6:DCM 4:1 v:v, fraction 3

was eluted by 10 ml of DCM, fraction 4 was eluted by 10 ml of DCM:MeOH 1:1 v:v.

Table 8 shows average contents of group of compounds in each fraction obtained under the final fractionation conditions written above. Three parallel fractionation procedures were carried out.

Table 8 – Average contents of compounds' group in fractions, 3 fractionations

	Fraction 1	Fraction 2	Fraction 3	Fraction 4
	%	%	%	%
Alkanes	100	0	0	0
PAH	0	99	1	0
Nitro-PAH	0	0	100	0
Oxy-PAH	0	0	6	94

All fractions are separated from each other except fraction 3 that contains a small amount of compounds from next fraction (polar compounds). This separation is sufficient for analysis of nitro-PAH in a soil and dust samples.

Table 9 shows recoveries of target nitro-PAH and relative standard deviations obtained from an analytical procedure for their determination in roadside dust. Three determinations were carried out.

Table 9 – Nitro-PAH recoveries of analytical procedure

Compound	Recovery	RSD
	%	%
1-nitronaphtalene	65	14
2-nitrofluorene	60	18
9-nitroanthracene	79	13
1-nitropyrene	81	16
6-nitrochrysene	108	10

Examples of chromatograms of raw extract and fractions measured on DB-5MS column are listed in the appendix in the Figures 4 – 10. Some of high peaks' retention times (RT) are marked in every chromatograms, these RT are written in the table 10. Potential differences between retention times in this table and retention times in the chromatograms are caused by manual injections. Figures 4 and 5 show chromatograms of raw extract measured in SCAN mode, Figures 6 to 9 show chromatograms of fractions measured in scan mode. In the Figure 10 is shown chromatogram of fraction containing nitro-PAH. This was measured in SIM mode. If the chromatograms of measurement in SCAN mode are displayed, the chromatograms of relevant m/z for selected compounds are also displayed.

In the table 10 averages of retention times of monitored polycyclic aromatic hydrocarbons and their derivatives are written. These times were measured on DB-5MS column at the temperature program belonged to the isooctane solutions.

Table 10 – Averages of retention times (RT) of monitored compounds – DB-5MS column – alphabetically listed

Compound	RT / min		Compound	RT / min
Acenaphthene	5,70		2-methylanthracene	9,29
Acenaphthylene	5,53		2-methylphenanthrene	9,19
Anthracene	8,43		5-methylchrysene	15,51
Benzo[a]anthracene	14,86		1-methylnaphthalene	4,40
Benzo[b]fluoranthene	18,10		2-methylnaphthalene	4,24
Benzo[k]fluoranthene	18,17		1-methylpyrene	12,47
Benzo[g,h,i]perylene	29,00			
Benzo[a]pyrene	19,54		9-nitroanthracene	12,16
4H-cyklopenta[d,e,f] phenanthrene	9,65		2-nitrofluorene	11,79
Dibenzo[a,h]anthracene	27,29		6-nitrochrysene	20,23
Dibenzofuran	5,86		1-nitronaphthalene	7,02
Phenanthrene	8,36		1-nitropyrene	16,87
1-phenylnaphthalene	11,65			
Fluoranthene	11,12		Anthracene-9,10-dione	10,60
Fluorene	6,41		4H-cyklopenta[d,e,f] phenanthrene-4-one	11,28
Chrysene	15,07		9H-fluorene-9-one	8,12
Indeno[1,2,3-c,d]pyrene	26,50		Methylanthracene-9,10-dione	11,71
Naphthalene	3,63		Dimethylanthracene-9,10-dione	13,02
Pyrene	11,82			

4.2.3 Nitro-PAH analysis in the roadside dust and soil

A roadside dust and soil were extracted by pressurised solvent extraction. 2 g of sample mixed with 3 g of anhydrous sodium sulphate was extracted. Spiked samples for finding recoveries were used. Two cycles at 5 min at 100 °C and 14 MPa and 20 s solvent flush were carried out. Extracts were evaporated by RVE and redissolved in 1 ml of cyclohexane. 500 µl of this solution was applied on the top of glass column filled with 5 g of fully activated silica gel. Final fractionation procedure mentioned above was used. Fractions 1, 2 and 4 were discarded and fraction 3 was evaporated and redissolved in 200 µl of isooctane solution of HCB (0,476 $\mu g.ml^{-1}$) and were analysed by GC-MS operated in SIM mode.

Only 1-nitropyrene from selected nitro-PAH was found and determined in the roadside dust. Its concentration in the roadside dust was 37 ± 6 $ng.g^{-1}$. No target

compounds were found in soil sample. Detection limits of the method ranged from 50 to 220 pg of individual nitro-PAHs injected into gas chromatograph.

5 SUMMARY AND MAJOR CONCLUSIONS

At the beginning of my Ph.D. project a bibliographic search regarding the analytical procedures (sample collection, extraction, clean-up, extract analysis) for determination of derivatives of PAH, their toxicological properties, their occurrence and behaviour in the environment with special emphasis on solid matrixes (soils, dusts) and nitrated derivatives of PAH was done. Besides this the attention was paid to the pressurised solvent extraction and its usage for extractions of investigated compounds from the environmental samples. It has been continued in this search during the time of this project to keep myself in touch with the work of others.

Inert matrix spiked with nitro-PAH was used to find out the best extraction conditions and the behaviour of nitro-PAH during extraction time. Influence of temperature, pressure, duration of static extraction period and nature of solvent has been examined. Two cycles of 5 min static extraction time was used. No significant differences were found whether dichloromethane or its mixture with methanol 1:1 v:v was used as an extraction solvent. At lower temperature (60 °C) the extraction recoveries were not significantly dependent on tested extraction pressures (10 to 14 MPa). It ranged 44 and 92 % with relative standard deviations of five extractions in the range from 3 to 23 %. This temperature seemed to be too low to extract all amounts of analytes. At temperature of 100 °C the recoveries ranged 33 and 116 % and they increased with increasing extraction pressure. The highest recoveries were obtained at the pressure of 14 MPa. The recoveries decreased with the prolongation of an extraction time. No degradation products were found after extraction. The best extraction conditions were 100 °C and 14 MPa and DCM as an extraction solvent. These conditions have been used for roadside dust extractions.

Extracts from roadside dust have been used in the next experiments. Compounds in extracts were divided into 4 groups containing compounds with similar polarity.

The recoveries of nitro-PAH extraction from a roadside dust were in the range from 70 to 117 % with RSD 9 to 20 %.

The fractionation step is required after extraction to decrease chemical background and separate minorite compounds (derivatives of PAH) from parent PAH. Silica gel column chromatography with fully activated silica gel (5 g) was chosen with this purpose.

Elution of compounds was performed by 10 ml of n-C6, 15 ml of nC6:DCM 1:1 v:v, 10 ml of DCM and 15 ml of DCM:MeOH 1:1 v:v. N-hexane and cyclohexane were found to be the best solvents for extracts applying on the column. They were able to separate compounds into three groups (nonpolar, aromatic and polar). Nitro PAH coeluted with aromatic fraction. DCM was not suitable probably due to its higher elution strenght. In this case only polar fraction was separated from each other.

Optimalization of solvents used for compounds elution was performed with the aim to find the best solvent system, that is able to separate nitro-PAH from parent PAH. It was not fulfilled by increase of nC6 volume for elution. In this instance about 5 – 10 % of compounds' amount from each fraction were not separated from the previous fraction. Another possibility how to provide better separation of fractions is the usage of solvents with lower elution strenght. Mixture of nC6:DCM 4:1 v:v was used. Better separation of aromatic fraction from slightly polar fraction was achieved. Slightly polar and polar fraction still partially coelute. However it is sufficient for analysis of nitro-PAH. The final fractionation procedure, that was chosen on the basis of previous experiments, is following:

The first fraction (fraction 1) was eluted by 10 ml of n-C6 and then by 5 ml of n-C6:DCM 4:1 v:v. Fraction 2 was eluted by 10 ml of n-C6:DCM 4:1 v:v, fraction 3 was eluted by 10 ml of DCM, fraction 4 was eluted by 10 ml of DCM:MeOH 1:1 v:v.

The recoveries of selected nitro-PAH and RSD obtained from this analytical procedure were in the range 60 to 108 % (RSD 10 to 18 %). Detection limits of the method ranged from 50 to 220 pg of individual nitro-PAHs injected into gas chromatograph.

Only 1-nitropyrene from selected nitro-PAH was determined in examined roadside dust. Its concentration in the roadside dust was 37 ± 6 ng.g^{-1}.

6 LIST OF ABBREVIATIONS

Some common abbreviations used in the short version of Ph.D. thesis are listed below in alphabetical order.

alkyl-PAH	alkyled derivatives of polycyclic aromatic hydrocarbons
amu	atomic mass unit
ASE	accelerated solvent extraction
cC6	cyclohexane
DCM	dichloromethane
GC	gas chromatography
HCB	hexachlorobenzene
HPLC	high performance liquid chromatography
IARC	Internation Agency for Research on Cancer
M	molar mass
m/z	fragment mass divided by its charge
MeOH	methanol
MS	mass spectrometry detector
MWAE	microwave assisted extraction
nC6	hexane
nitro-PAH	nitrated derivatives of polycyclic aromatic hydrocarbons
NOM	nonresolved organic matter
oxy-PAH	ketones and quinones of PAH
PAH	polycyclic aromatic hydrocarbons

PANH	polycyclic aromatic nitrogen heterocyclic hydrocarbons
PAOH	polycyclic aromatic oxygen heterocyclic hydrocarbons
PASH	polycyclic aromatic sulphur heterocyclic hydrocarbons
PSE	pressurised solvent extraction
PTFE	polytetrafluoroethylene (Teflon™)
RSD	relative standard deviation
RT	retention time
RVE	rotary vaccum evaporator
SFE	supercritical fluid extraction
SIM	selected ion monitoring mode (MS data acquisition)
SPE	solid phase extraction
US EPA	U.S. Environmental Protection Agency

7 REFERENCES

1. Yaffe, D.: Multimedia analysis of PAHs and nitro-PAH daughter products in Los Angeles basin. *Risk Analysis*, 2001, vol. 21, no. 2, pp. 275-294.
2. Lai, C.C.: Synthesis and bacterial mutagenicity of oxidised derivatives of nitro-polycyclic aromatic hydrocarbons. *Polycyclic Aromatic Compounds*, 1999, vol. 16, pp. 61-69.
3. Östby, L.: Mutagenicity testing of organic extracts of diesel exhaust particles after fractionation and recombination. *Archives of Toxicology*, 1997, vol. 71, pp. 314-319.
4. Casellas, M.: Bioassay-directed chemical analysis of genotoxic components in urban airborne particulate matter from Barcelona (Spain). *Chemosphere*, vol. 30, no. 4, pp. 725-740.
5. IARC Monographs, *Overall Evaluations of Carcinogenity to Humans, Group 1: Carcinogenic to humans*, Vol. 1-88. Last revision 7th July 2004, [cit. 2005-07-18], accessible from: <http://www-cie.iarc.fr/monoeval/crthgr01.html>.
6. Sasaki, J.: Products of the gas-phase OH and NO_3 radical-initiated reactions of naphthalene. *Environmental Science and Technology*, 1997, vol. 31, pp. 3173-3179.
7. Dušek, B.: Determination of nitrated polycyclic aromatic hydrocarbons and their precursors in biotic matrices. *Journal of Chromatography A*, 2002, vol. 982, pp. 127-143.
8. Aislabie, J.: Polycyclic aromatic hydrocarbons in fuel-oil contaminated soils, Antarctica. *Chemosphere*, 1999, vol. 39, is. 13, pp. 2201-2207.
9. Wang, S.-F.: Gas chromatographic-mass spectrometric determination of polycyclic aromatic hydrocarbons formed during pyrolysis of phenylalanine. *Journal of Chromatography A*, 2004, vol. 1025, pp. 255-261.
10. Kropp, K.G.: A review of the occurrence, toxicity and biodegradation of condensed thiophenes found in petroleum, *Canadian Journal of Microbiology*, 1998, vol. 44, pp. 605-622.
11. Wilhelm, M.: Determination of basic nitrogen-containing polynuclear aromatic hydrocarbons formed during thermal degradation of polymers by

high-performance liquid chromatography-fluorescence detection. *Journal of Chromatography*, 2000, vol. 878, pp. 171-181.
12. Al-Bashir, B.: Behavior of nitrogen-substituted naphthalenes in flooded soil – part I. Sorption/desorption and biodegradation. *Water Research*, 1994, vol. 28, is. 8, pp. 1817-1825.
13. Nadalig, T.: Degradation of phenanthrene, methylphenanthrenes and dibenzothiophene by a Sphingomonas strain 2mpll. *Applied Microbiology and Biotechnology*, 2002, vol. 59, pp. 79-85.
14. Andersson, J.T.: Photochemical degradation of crude oil components: 2-methyl, 3-methyl and 2,3-dimethylbenzothiophene. *Polycyclic Aromatic Compounds*, 1996, vol. 11, pp. 145-151.
15. Meade, J. D.: Aerobic co-metabolism of sulphur, nitrogen and oxygen heterocycles by three marine bacterial consortia. *Journal of Basic Microbiology*, 2002, vol. 42, is. 1, pp. 19-36.
16. US EPA method 3500C: Organic extraction and sample preparation. US EPA, 1999. 17 p.
17. Meyer, S.: Simultaneous determination of PAHs, hetero-PAHs (N, S, O), and their degradation products in creosote-contaminated soils. Method development, validation, and application to hazardous waste sites. *Analytical Chemistry*, 1999, vol. 71, pp. 4023-4029.
18. Nicol, S.: Simultaneous determination of polycyclic aromatic hydrocarbons and their nitrated derivatives in airborne particulate matter using gas chromatography – tandem mass spectrometry. *Journal of Separation Science*, 2001, vol. 24, pp. 451-456.
19. Wilson, N.K.: Concentrations and phase distributions of nitrated and oxygenated polycyclic aromatic hydrocarbons in ambient air. *Atmospheric Environment*, vol. 29, no. 19, pp. 2575-2584.
20. Leotz-Gartziandia, E.: Sampling and analysis of polycyclic aromatic hydrocarbons (PAH) and oxygenated PAH in diesel exhaust and ambient air. *Polycyclic Aromatic Compounds*, 2000, vol. 20, pp. 245-258.
21. Priego-López, E.: Ultrasound-assisted extraction of nitropolycyclic aromatic hydrocarbons from soil prior to gas chromatography-mass detection. *Journal of Chromatography A*, 2003, vol. 1018, pp. 1-6.
22. Bezabeh, D.Z.: Determination of nitrated polycyclic aromatic hydrocarbons in diesel particulate-related standard reference materials by using gas chromatography/mass spectrometry with negative chemical ionisation. *Analytical and Bioanalytical Chemistry*, 2003, vol. 375, no. 1.
23. Turrio-Baldassarri, L.: Evaluation of the efficiency of extraction of PAHs from diesel particulate matter with pressurised solvents. *Analytical and Bioanalytical Chemistry*, 2003, vol. 375, pp. 589-595.
24. Pryček, J.: Development of an analytical method for polycyclic aromatic hydrocarbons and their derivatives. *Journal of Chromatography A*, 2004, vol. 1030, pp. 103-107.

25. Popl, M.: *Analytická chemie životního prostředí*. 4th ed. Praha: Publisher VŠCHT, 1999. 218 p. ISBN 80-7080-336-3.
26. Lewtas, J.: Bioassay-direct fractionation of the organic extract of SRM 1649 urban air particulate matter, *International Journal of Environmental Analytical Chemistry*, 1990, vol. 39, pp. 245-256.
27. Churáček, J.: *Úvod do vysokoúčinné kapalinové kolonové chromatografie*. 1st ed., Publisher SNTL Praha, 1985, 192 p.
28. Carlsson, H.: Clean-up and analysis of carbazole and acridine type polycylic aromatic nitrogen heterocyclics in complex sample matrices. *Journal of Chromatography*, 1997, vol. 790, pp. 73-82.
29. Vincenti, M.: Sub-part-per-billion determination of nitro-substituted polynuclear aromatic hydrocarbons in airborne particulate matter and soil by electron capture – tandem mass spectrometry. *Journal of the American Society for Mass Spectrometry*. 1996, vol. 7, pp. 1251-1254.
30. Becker, G.: Determination of polycyclic aromatic sulphur heterocyclic compounds in airborne particulate by gas chromatography with atomic emission and mass spectrometric detection. *Journal of Chromatography A*, 1998, vol. 826, pp. 57-66.
31. Dimashki, M.: Measurement of nitro-PAH in the atmospheres of two cities. *Atmospheric Environment*, 2000, vol. 34, pp. 2459-2469.
32. Tollbäck, P.: Coupled LC-GC-NPD for determination of carbazole-type PANH and its application to personal exposure measurement. *Journal of High Resolution Chromatography*, 2000, vol. 23, is. 2, pp. 131-137.
33. Frysinger, G.S.: Resolving the unresolved complex mixture in petroleum-contaminated sediments. *Environmental Science & Technology*, 2003, vol. 37, pp. 1653-1662.
34. Tancell, P.J.: Diesel combustion of an alkyled polycyclic aromatic hydrocarbon. *Fuel*, 1996, vol. 75, no. 6, pp. 717-723.
35. Cecinato, A.: Relevant organic component in ambient particulate matter collected at Svalbard islands (Norway). *Atmospheric Environment*, 2000, vol. 34, pp. 5061-5066.
36. Schauer, Ch.: Analysis of nitrated polycylic aromatic hydrocarbons by liquid chromatography with fluorescence and mass spectrometry detection: air particulate matter, soot, and reaction product studies. *Analytical and Bioanalytical Chemistry*, 2004, vol. 378, pp. 725-736.
37. Rivera, L.: Solid-phase extraction for the selective isolation of polycyclic aromatic hydrocarbons, azaarenes and heterocyclic aromatic amines in charcoal-grilled meat. *Journal of Chromatography A*, 1996, vol. 731, pp. 85-94.
38. Murahashi, T.: A sensitive method for the determination of 6-nitrochrysene, 2-nitro-fluoranthene and 1-, 2- and 4-nitropyrenes in airborne particulates using high-performance liquid chromatography with chemiluminiscence detection. *Analytica Chimica Acta*, 1997, vol. 343, pp. 251-257.

8 CURRICULUM VITAE

Name: Jiri
Surname: Prycek
E-mail: prycek@email.cz

Education:

2000 – 2007	doctoral study programme, IChTEP, FCH BUT, Brno
1995 – 2000	master study, IChTEP, FCH BUT, Brno
1991 – 1995	Maticni secondary grammar school, Ostrava

Work experience:

2004 – present	State Phytosanitary Administration, Plant Protection Product Section – gas chromatography analyst
2001	Polymer Institute Brno – risk evaluation of chemicals

Professional knowledge:

Environmental analysis, pressurised solvent extraction, gas chromatography with mass spectrometry detection, analyses of active ingredients in plant protection products

Additional skills:

Computing	MS Office	thorough knowledge
Languages	Czech	mother tongue
	English	FCE (6/2005)

Publications resulting from Ph.D. project:

Jiri Prycek, Miroslav Ciganek, Zdenek Simek: *Clean-up of extracts for nitrated derivates of polycyclic aromatic hydrocarbons analyses prior to their gas chromatographic determination*. Journal of the Brazilian Chemical Society, 18 (6), 1125 – 1131, 2007.

Pryček J., Ciganek M., Šimek Z.: *Pressurised solvent extraction of nitrated derivatives of polycyclic aromatic hydrocarbons from a roadside dust*. International Journal of Environmental Analytical Chemistry, 86 (5), 313 – 324, 2006.

Pryček J., Ciganek M., Šimek Z.: *Development of an analytical method for PAH and their derivatives,* Journal of Chromatography A, 1030 (1– 2), 103 – 107, 2004.

The rest of publications:

Ivo Kuritka, Pavel Broza, Jiri Prycek, Frantisek Schauer: *Mass spectrometry characterization of methylphenylsilane-hydrogen RF plasmas.* Plasma Processes and Polymers, 4 (1), 53 – 61, 2007.

O. Salyk, P. Broza, N. Dokoupil, R. Herrmann, I. Kuritka, J. Prycek and M. Weiter: *Plasma polymerisation of methylphenylsilane*, Surface and Coatings Technology, 200, 486 – 489, 2005.

Contributions in collections: 12

Attended meetings:

17th International mass spectrometry conference, 27.8. – 1.9.2006, Prague, CZ.

3rd FAO/WHO Joint Meeting on Pesticide Specifications (JMPS) and 48th CIPAC Meeting, 3. – 10.6.2004, Brno, CZ.

6th Doctoral student contest, 18.9.2003, Brno, CZ.

27th Symposium on high performance liquid phase separations and related techniques, 15. – 19.6.2003, Nice, France.

5th Doctoral student contest, 17.10.2002, Brno, CZ.

2nd Meeting on Chemistry and Life, 10. – 11.9.2002, Brno, CZ.

54th Congress of the Chemical Societies, 30.6. – 4.7.2002, Brno, CZ.

Technologies and Processes for Sustainable Development and Pollution Reduction /Prevention, 14.-16.1.2002, Brno CZ.

53rd Congress of the Chemical Societies, 3. – 6.9.2001 Banska Bystrica, SK.

9 APPENDIX

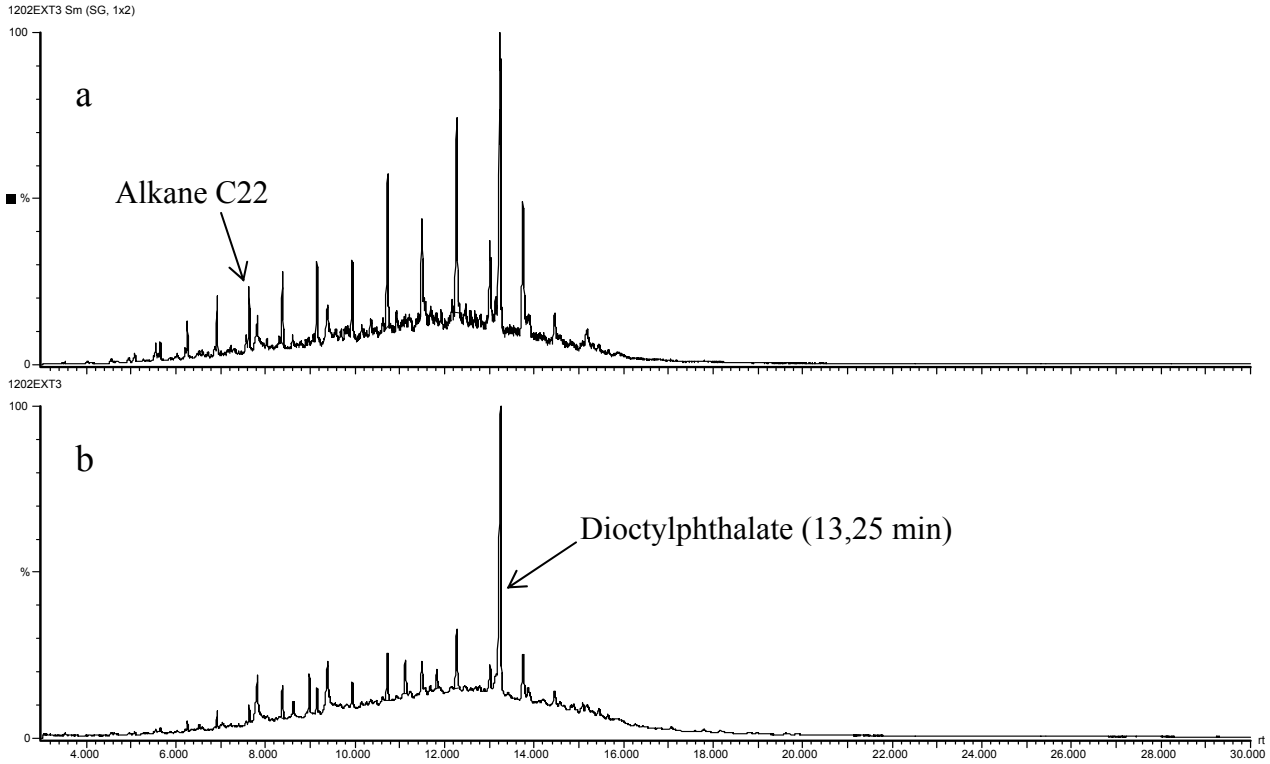

Fig. 4: Example of chromatogram of raw extract from the roadside dust measured in SCAN mode – a) selected m/z = 71 – alkanes, b) TIC.

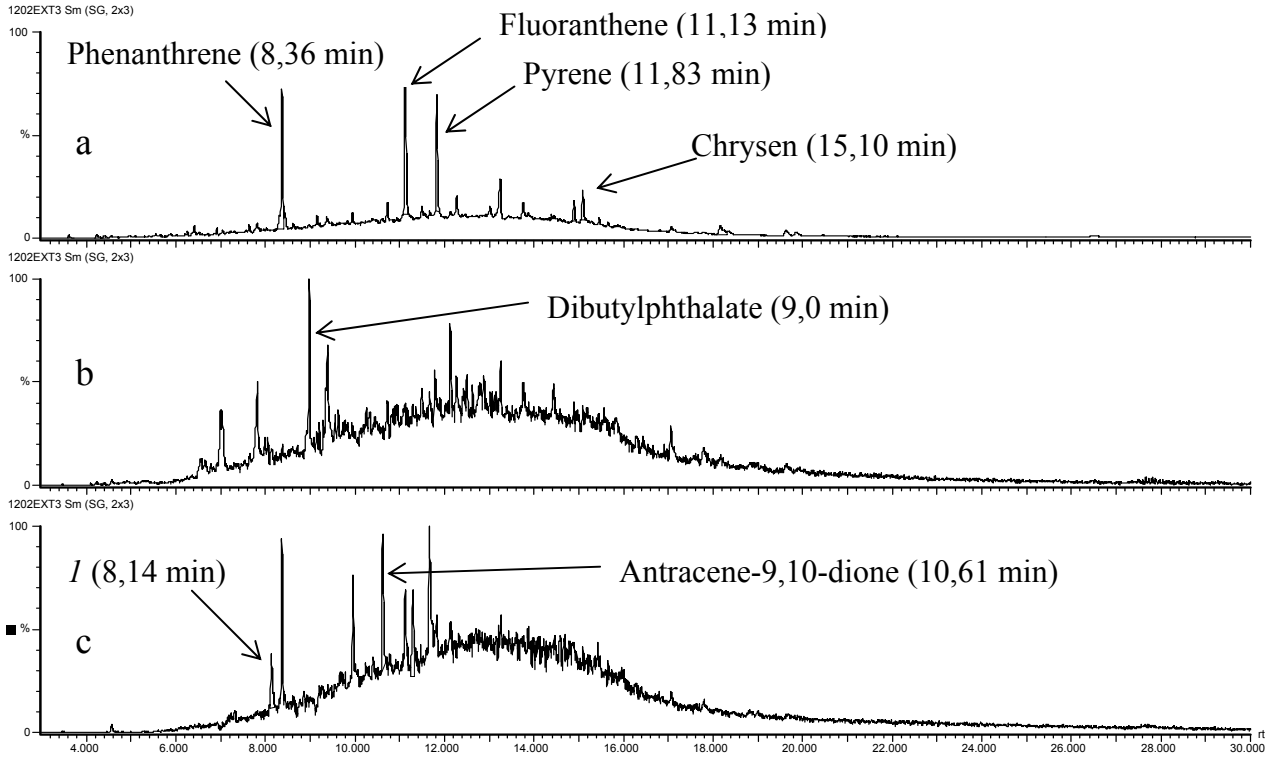

Fig. 5: Example of chromatogram of raw extract from the roadside dust measured in SCAN mode – a) selected m/z for PAH and alkyl-PAH, b) selected m/z for nitro-PAH, c) selected m/z for oxy-PAH, *1* – 9H-fluorene-9-one.

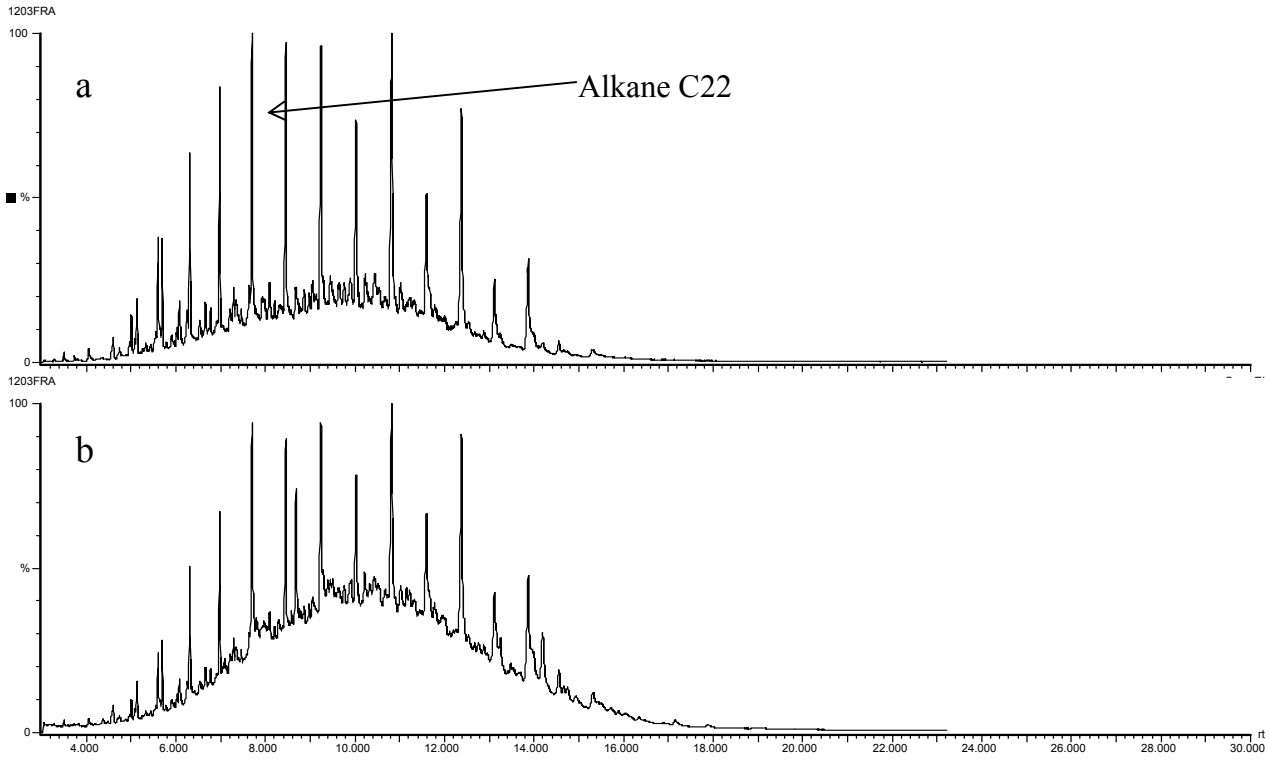

Fig. 6: Example of chromatogram of fraction 1 measured in SCAN mode – a) selected m/z = 71 – alkanes, b) TIC.

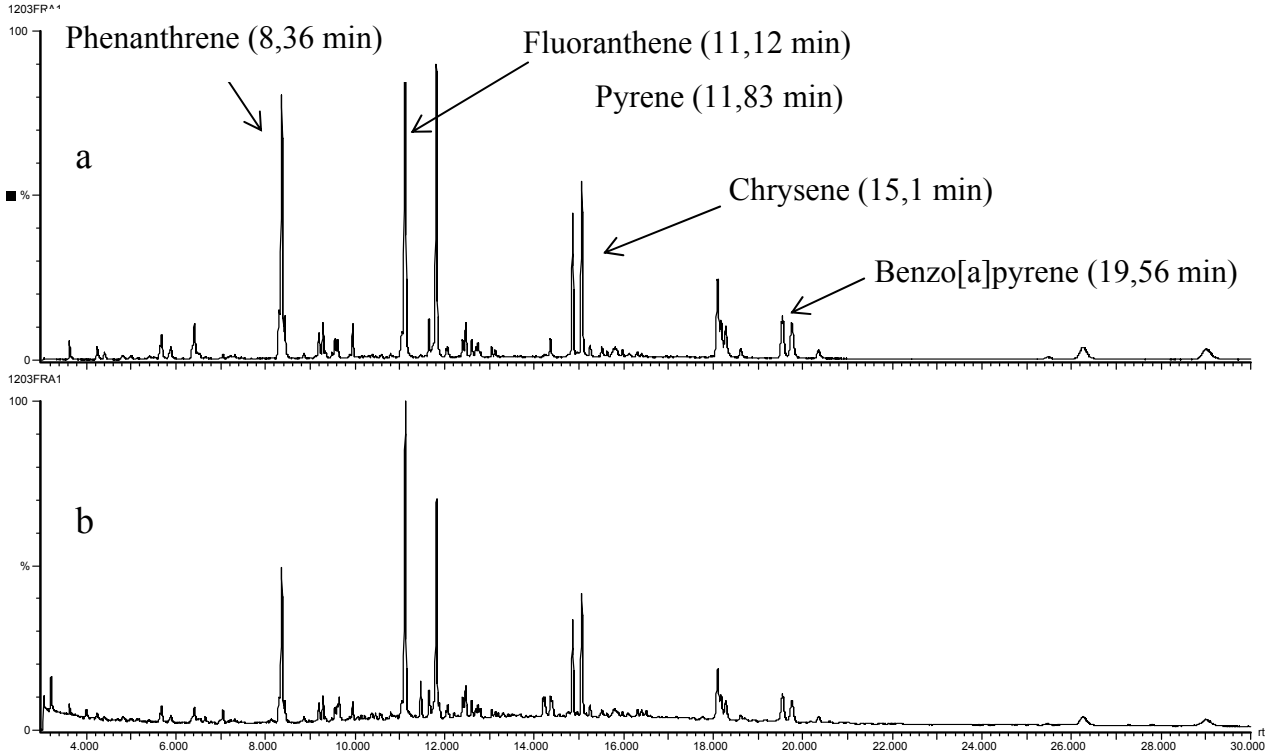

Fig. 7: Example of chromatogram of fraction 2 measured in SCAN mode – a) selected m/z for PAH and alkyl-PAH analysis, b) TIC.

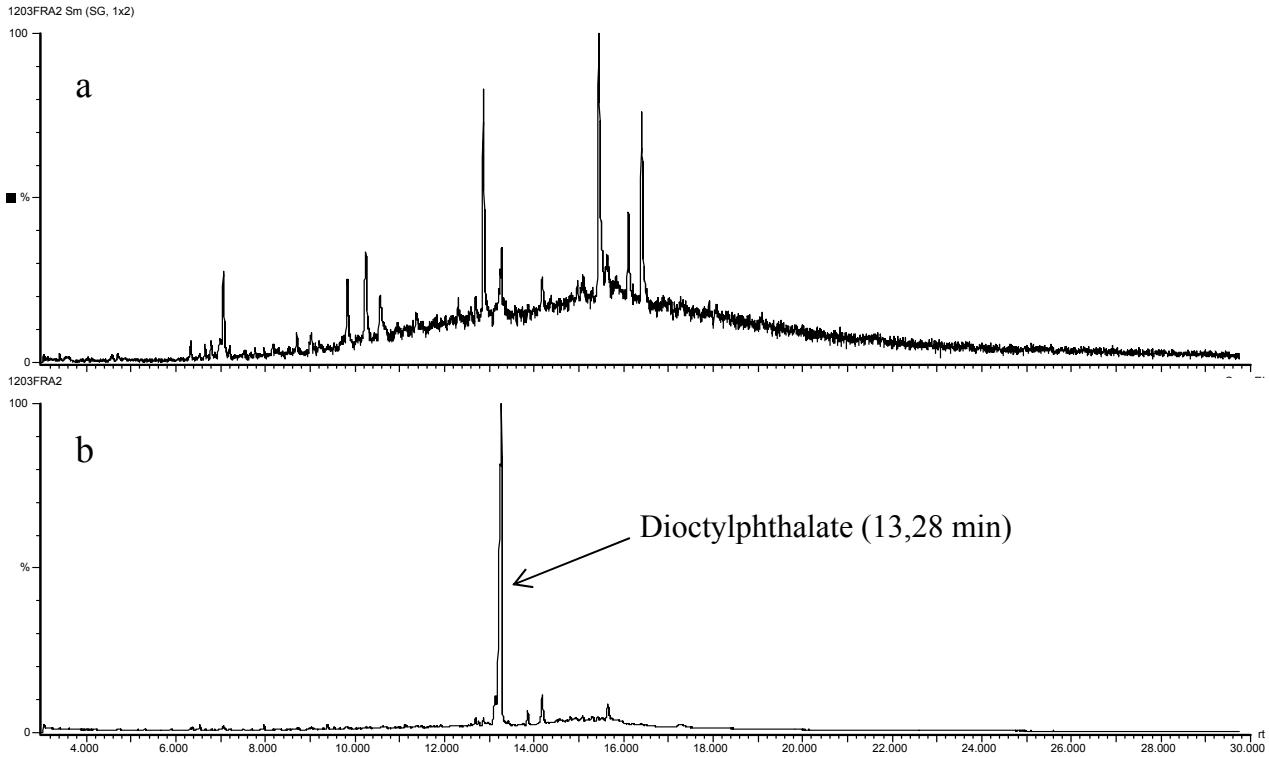

Fig. 8: Example of chromatogram of fraction 3 measured in SCAN mode – a) selected m/z for nitro-PAH analysis, b) TIC.

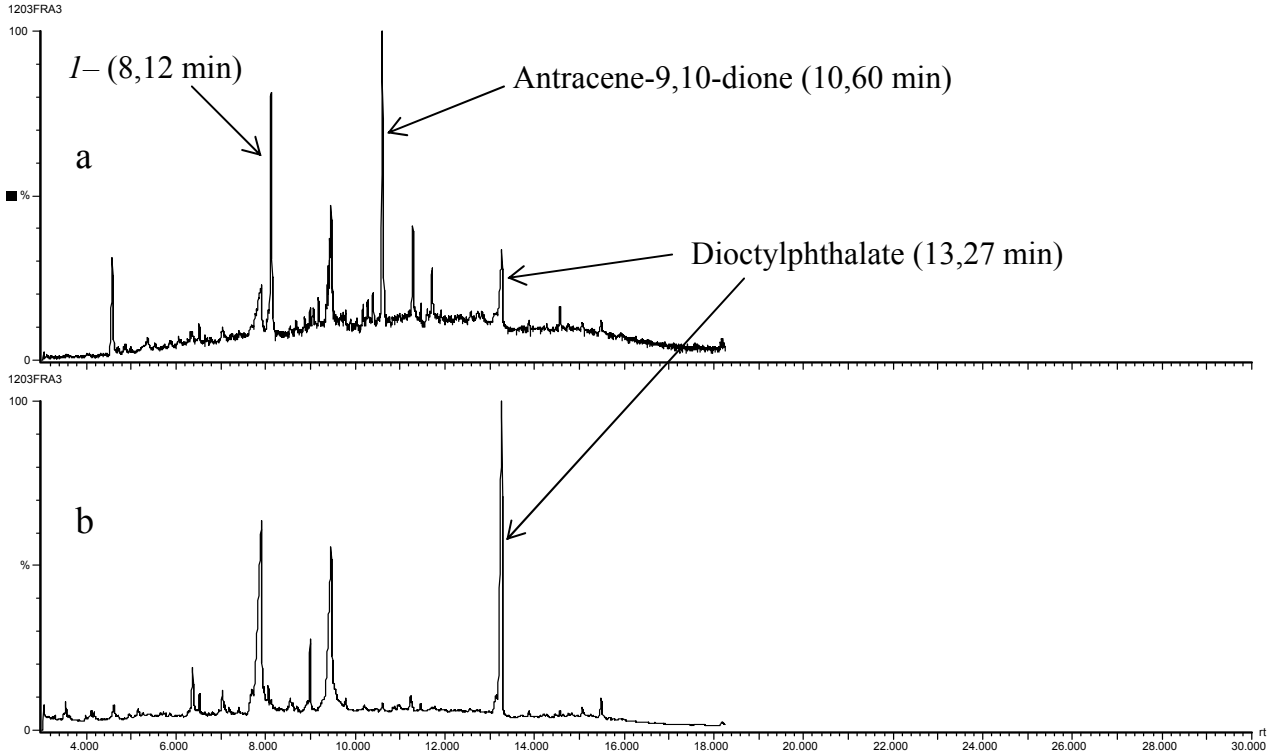

Fig. 9: Example of chromatogram of fraction 4 measured in SCAN mode – a) selected m/z for oxy-PAH analysis, b) TIC, *1* – 9H-fluorene-9-one.

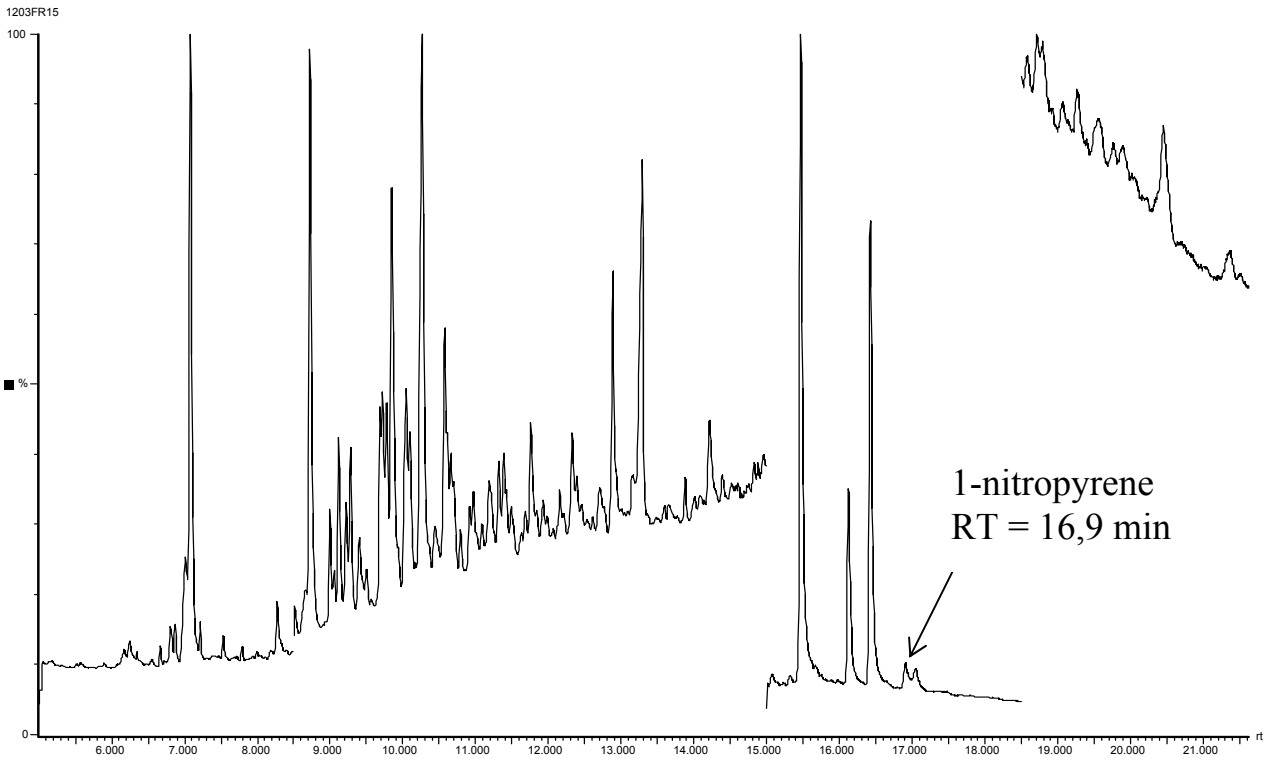

Fig. 10: Chromatogram of fraction 3 measured in SIM mode. Retention time of 1-nitropyrene is 16,9 min.