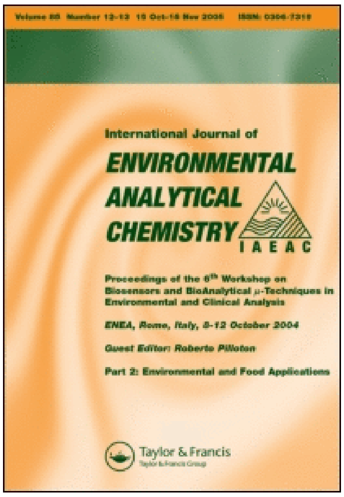

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Pressurised solvent extraction of nitrated derivatives of polycyclic aromatic hydrocarbons from roadside dust

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An analytical method based upon the pressurised solvent extraction and gas chromatography and mass spectrometry (GC-MS) for analysis of nitrated derivatives of polycyclic aromatic hydrocarbons (nitro-PAHs) in roadside dust has been developed. Five nitro-PAHs (1-nitronaphthalene, 1-nitropyrene, 9-nitroanthracene, 2-nitrofluorene, 6-nitrochrysene) were chosen for this study because of their variable physical properties and effect on human health. Experiments with spiked inert matrix were used for the best extraction conditions finding. Different extraction conditions (temperature, pressure, solvents and duration of extraction cycle) were examined. The highest recoveries were observed at the extraction pressure of 14 MPa, temperature of 100°C and two cycles of 5 min extraction time, when dichloromethane was used as an extraction solvent. These conditions were applied to the extraction of nitro-PAHs from roadside dust. After extraction the nitro-PAHs fraction was isolated by the silica gel column chromatography. The GC-MS detector was used for analyses of the extracts. Recoveries of nitro-PAHs after extraction from roadside dust ranged from 60% for 9-nitroanthracene to 108% for 6-nitrochrysene.

Keywords: Nitro-PAHs; Pressurised solvent extraction; Roadside dust; Silica gel; Clean-up

1. Introduction

Nitrated derivatives of polycyclic aromatic hydrocarbons (nitro-PAHs) environmental pollutants that are widespread. They originate from the combustion of petrochemical fuel and other organic matter or are formed in the atmosphere as a result of photochemical reaction of polycyclic aromatic hydrocarbons with hydroxyl radicals and NO_2 or

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with NO_3^- [1–5]. So far, these compounds have been found in fly ash, exhaust emissions from waste incineration plants, cigarette smoke, waste water, sediments and other environmental matrixes [6–15].

About 30 years ago, many researchers have pointed out that organic extracts of the atmospheric particulate matter and extracts of the diesel exhaust, which contains nitro-PAHs, exhibit strong direct mutagenicity when the extracts were tested on animals [16] or by Ames assay [17, 18].

In accordance with the International Agency for Research on Cancer (IARC), some nitro-PAHs are classified as possibly carcinogenic to humans [19]. For this reason, considerable effort has been spent in the last two decades to find out sources, to study their chemical, physical and toxicological properties and to develop new analytical methods for the determination of nitro-PAHs in the environment.

Several efficient extraction techniques have been developed and commonly used for isolation of analytes from solid matrix. Soxhlet extraction is still mostly used in laboratory practice as a part of many analysis protocols because of its high extraction efficiency, but this method is time- and solvent-consuming [7, 11, 15]. Other frequently employed extraction methods include sonication, supercritical fluid extraction, microwave extraction and pressurised solvent extraction (PSE) [4, 6, 9, 11, 13, 20].

In 1995 PSE was included into the standard methods by the US-EPA [21] due to its good efficiency, short extraction time, small solvent consumption, easy operation and automation.

The extraction efficiency of PSE, for selected nitro-PAHs from inert matrix, was investigated in this work. The best extraction conditions were used for the extraction of these analytes from roadside dust. Quantification of nitro-PAHs was performed using gas chromatography and mass spectrometry (GC-MS).

2. Experimental

2.1 *Reagents and chemicals*

Dichloromethane (DCM), methanol (MeOH), *n*-hexane, isooctane (all HPLC gradient grade, Merck, Darmstadt, Germany), cyclohexane (p.a., Merck, Darmstadt, Germany, purified by rectification before use). Nitro-PAHs – see figure 1 – 1-nitronaphthalene (1-NNa, 99%), 1-nitropyrene (1-NPy, 98%), 9-nitroanthracene (9-NAnt, 97%), 2-nitrofluorene (2-NFlu, 98%), 6-nitrochrysene (6-NChr, 95%) were supplied by Sigma-Aldrich, St. Louis, MO, USA. Silica gel 60 (70–230 mesh, Fluka, St. Louis, MO, USA, activated 4 h at 180°C). Anhydrous sodium sulphate (p.a., ONEX, Roznov pod Radhostem, CZ, dried 1 h at 650°C), helium (99.999%, Messer Technogas, Krefeld, Germany), nitrogen (99.99%, Linde, Höllriegelskreuth, Germany). Nitro-PAHs solution ($10\,\mu g\,mL^{-1}$) in methanol was used for spiking of inert matrix to optimise the PSE conditions. Nitro-PAHs solution ($100\,\mu g\,mL^{-1}$) in isooctane was used for calibration of the solutions preparation. All nitro-PAHs reagents and solutions were stored refrigerated in the dark.

2.2 *Analytical instrumentation*

All extracts were analysed on a gas chromatograph GC 8060 connected to a mass-spectrometer detector Trio 1000 (Fisons, Manchester, UK). A DB-5MS column

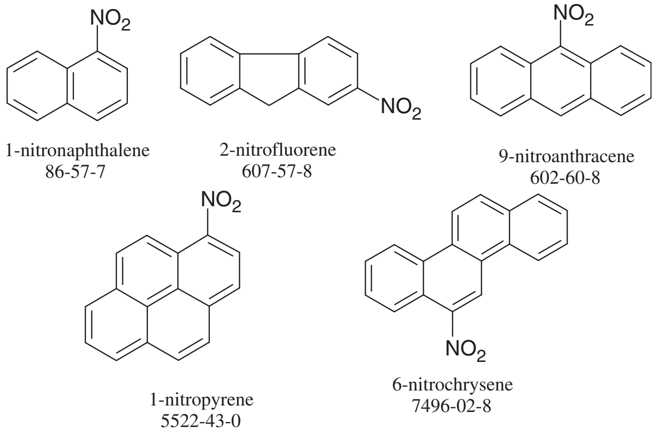

Figure 1. Nitro-PAHs chosen for experiments – structures and CAS numbers.

(30 m × 0.25 mm i.d., 0.25 μm phase thickness) (J&W Scientific, Palo Alto, CA, USA) was used. The GC injection port temperature was 250°C, MS detector interface temperature 220°C and ion source temperature 200°C, respectively. Helium was used as a carrier gas at a constant head pressure of 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 and the MS detector was operated in selected ion monitoring (SIM) mode. Monitored ions were M^+ and $M\text{-}30^+$. For analysis of inert matrix extracts, the initial GC oven temperature was 70°C (1 min isothermal), and then it was programmed at $25°C\,min^{-1}$ to 180°C and at $10°C\,min^{-1}$ to 290°C, then it was held isothermal for 6 min. For the roadside dust extract, the initial GC oven temperature was 90°C (1 min isothermal), and then it was programmed at $25°C\,min^{-1}$ to 180°C and at $10°C\,min^{-1}$ to 290°C, then it was held isothermal for 6 min. Different initial temperatures were used because different solvents were used for dissolving the extracts.

2.3 *Optimisation of PSE conditions*

All PSE experiments were made by the use of a pressurised solvent extractor (FASTEX, Unikovo, Brno, CZ). A 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. Different extraction temperatures (60, 80, 100°C), pressures (10, 12, 14 MPa), duration of static extraction period (5 and 10 min) and nature of solvent were tested. In this study, 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. Sodium sulphate was used in the experiments to find out the extraction efficiency and to investigate the behavior (especially stability) of these compounds during the extraction process. Sodium sulphate has a small active surface and processes on this surface do not affect the behavior of these compounds during extraction. The samples were extracted under the conditions given by the experimental design listed in table 1.

Table 1. Experimental design for nitro-PAHs extraction from inert matrix.

Experiment no.	Temperature (°C)	Pressure (MPa)	Static extraction time (min)
1	60	10	5
2	60	12	5
3	60	14	5
4	100	10	5
5	100	12	5
6	100	14	5
7	100	10	10

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-PAHs spiking solution (10 µg mL^{-1}) and filled in the extraction vessel. The top of the matrix layer in the vessel was covered with a filter paper. The vessel was put into the extractor and closed, the extraction solvent was then pumped into the vessel. The flow was stopped after one-half of the set extraction pressure was achieved. The vessel with solvent and matrix was preheated for 2 min to reach the selected extraction temperature. The solvent was then pumped into the vessel to reach the set extraction pressure. A static extraction period then 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 a flow rate of 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. The total extraction time was less than 30 min and the total extract volume was about 25 mL for each samples extraction. The extracts were evaporated to dryness using a rotary vacuum evaporator at 30°C after filtration through anhydrous sodium sulphate. The evaporation residue was redissolved in 500 µL of methanol and analysed by GC-MS. To exclude possible losses of analytes, all these samples were analysed without any clean-up steps. The same five samples were extracted under the same extraction conditions.

The occurrence of potential degradation products that originated during extraction was checked. The analyses of extract were performed by GC-MS, MS operated in SCAN mode, when m/z 40–350 were monitored.

2.4 *Roadside dust sampling and sample preparation*

Roadside dust was collected from a shoulder at the city road and highway interchange (Palackeho/Hradecka, Brno, CZ) in September 2003 after a dry weather period of 14 days using a small brush and a trowel. The dust sample was air dried at room temperature for one day. The dried sample was sieved to remove particles ≥600 µm. The sieved dust sample was homogenised by mixing and kept in 40 mL glass vials with PTFE/silicon septa wrapped with aluminium foil and stored at −18°C in a freezer. To minimise the effect of different residual water contents, the dust samples were mixed with anhydrous sodium sulphate before extraction.

2.5 *Roadside dust extraction*

Extraction of nitro-PAHs from the roadside dust were carried out by the same pressurised solvent extractor as in the previous experiments. Dichloromethane was used as the extraction solvent. About 2 g of the roadside dust was mixed with 3 g of anhydrous sodium sulphate and filled into a 11 mL extraction vessel. The free capacity of the vessel was filled with glass beads. Two extraction cycles of 5 min at 100°C and 14 MPa were used for each sample. Extracts were collected into the 40 mL glass vials, evaporated to dryness using a rotary vacuum evaporator at 30°C. The evaporation residue was redissolved in 1 mL of cyclohexane. Three samples were extracted.

The extraction recoveries of nitro-PAHs were established by a standard addition method. About 2 g of the roadside dust was mixed with 3 g of anhydrous sodium sulphate. The mixture was spiked with 50 μL of nitro-PAHs spiking solution, filled into the 11 mL extraction vessel and extracted under the same conditions as a nonspiked dust. Three samples were extracted.

2.6 *Extract fractionation and analysis*

One millilitre of the obtained extract was transferred to the top of a glass column ($250 \times 10\,\mathrm{mm}^2$ i.d., MERCI, Brno, CZ) filled with 5 g of fully activated silica gel. The adsorbent was capped with 1 g of anhydrous sodium sulphate. The column was rinsed with 10 mL of *n*-hexane before the raw extract was applied. The extract was first eluted with 10 mL of *n*-hexane and 5 mL of *n*-hexane : DCM 4 : 1 v : v to obtain fraction enriched in alkanes (fraction 1), then 10 mL of *n*-hexane : DCM 4 : 1 v : v to obtain fraction enriched in parent PAHs and alkylated derivatives of PAH (fraction 2). Nitro-PAHs were eluted with 10 mL of DCM (fraction 3) followed by a fraction containing polar compounds (oxygenated PAH, phthalates) eluted with 10 mL of DCM : MeOH 1 : 1 v : v (fraction 4). Fractions 1, 2 and 4 were discarded and fraction 3 was evaporated to dryness, redissolved in 200 μL of isooctane and kept in a 2 mL vial until further analysis. GC-MS analyses were carried out at the conditions mentioned above. Each extract was measured twice. To obtain quantitative data for recovery calculation, standard solution of nitro-PAHs with the same concentration as spiking solution were analysed before and after each extract analysis. The recovery was calculated using equation (1), where m_S is the amount of compound found in the spiked extract, m_N is the amount of compound found in the non-spiked extract, without addition of target compound, m is the amount of compound added to the sample before extraction

$$\mathrm{REC}\,[\%] = \frac{100(m_\mathrm{S} - m_\mathrm{N})}{m} \tag{1}$$

3. Results and discussion

3.1 *Optimisation of PSE conditions*

A nitro-PAHs spiked anhydrous sodium sulphate was subjected to PSE with the aim to find conditions for this extraction technique comparable in extraction efficiency with results obtained using Soxhlet extraction of selected nitro-PAHs. Extraction temperature, pressure, duration of static extraction time and constituents of extraction solvents were considered to obtain suitable conditions for extraction of nitro-PAHs from inert matrix by PSE.

The extraction temperature was held constant at 60 and 100°C, respectively. The pressure varied from 10 to 14 MPa. The recoveries of extraction of the target compounds, with DCM as an extraction solvent, are shown in figures 2 and 3. In figures 4 and 5 recoveries of the extraction obtained under the same temperature and pressure conditions with DCM : MeOH 1 : 1 v : v as an extraction solvent are shown.

The recoveries of target compounds obtained at the extraction temperature 60°C, with DCM as an extraction solvent and 10 MPa extraction pressure ranged between 44 and 77%. The relative standard deviation (RSD) of five extractions was in the range 18–23%. The recoveries obtained at the pressure 12 and 14 MPa varied from 50 to 75% with the RSD 3 to 20%. When using the mixture DCM : MeOH as an

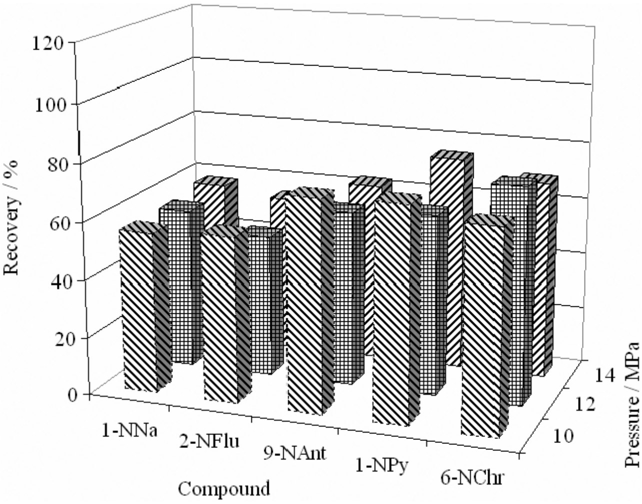

Figure 2. Recovery of nitro-PAHs extracted at 60°C and 2 cycles at 5 min static extraction time with DCM, the average recovery values of five extractions were used.

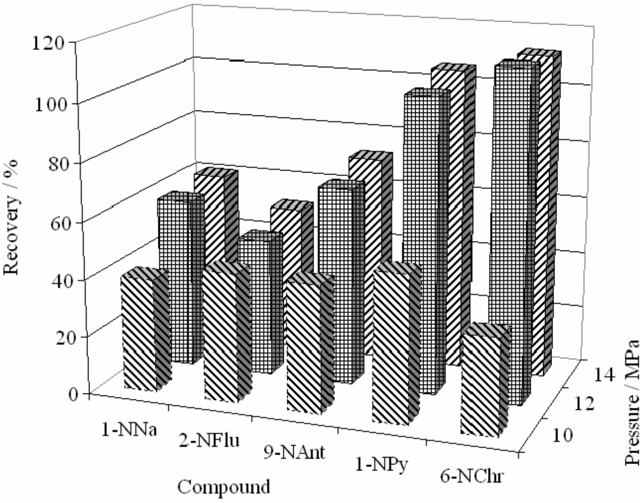

Figure 3. Recovery of nitro-PAHs extracted at 100°C and 2 cycles at 5 min static extraction time with DCM, average recovery values of five extractions were used.

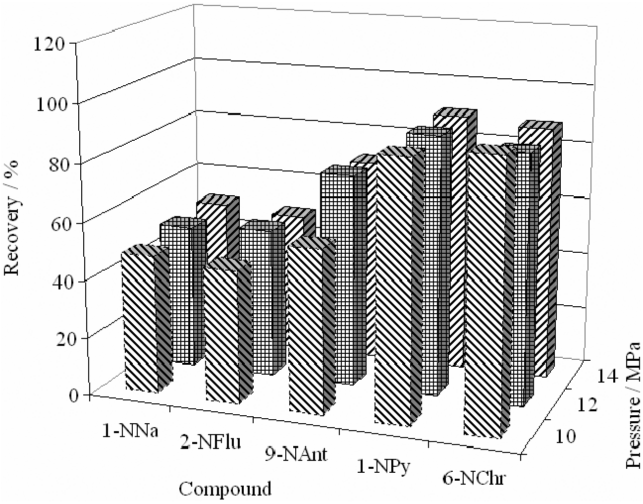

Figure 4. Recovery of nitro-PAHs extracted at 60°C and 2 cycles at 5 min static extraction time with DCM : MeOH 1 : 1 v : v, the average recovery values of five extractions were used.

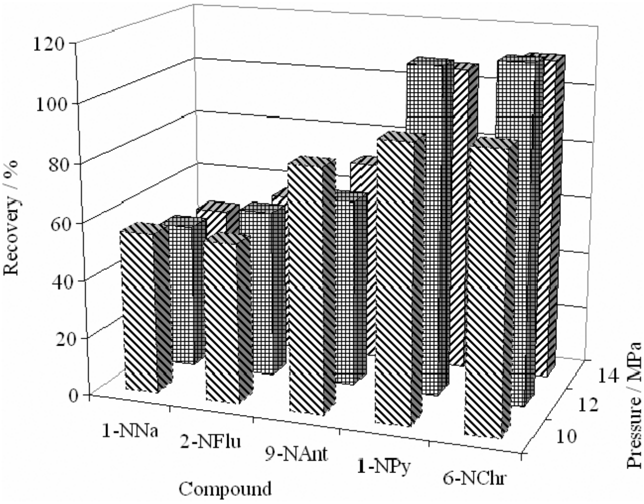

Figure 5. Recovery of nitro-PAHs extracted at 100°C and 2 cycles at 5 min static extraction time with DCM : MeOH 1 : 1 v : v, the average recovery values of five extractions were used.

extraction solvent and 10 MPa extraction pressure, the recoveries between 46 and 92% were obtained. The RSD of five extractions was in the range from 5 to 14%. At pressures 12 and 14 MPa, the recoveries varied from 49 to 90% with RSD from 8 to 17%. Because of low extraction recoveries, the temperature of 60°C seems to be too low for extraction of all amounts of analytes from this matrix. No degradation products were found when the extracts were analysed at SCAN mode.

The recoveries obtained at the extraction temperature 100°C and DCM as an extraction solvent, ranged from 33 to 51% with RSD in the range from 20 to 30% at 10 MPa extraction pressure. Extraction recoveries increased with the increasing

Table 2. Recoveries of extraction nitro-PAHs from inert matrix[a] – the effect of duration of static extraction time.

	DCM		DCM/MeOH	
	Time (min)		Time (min)	
	5	10	5	10
Compound	Recovery (%)	Recovery (%)	Recovery (%)	Recovery (%)
1-NNa	40 ± 4	32 ± 4	56 ± 9	50 ± 6
2-NFlu	45 ± 5	40 ± 8	55 ± 7	52 ± 8
9-NAnt	44 ± 8	31 ± 8	84 ± 7	63 ± 13
1-NPy	51 ± 4	61 ± 14	94 ± 14	70 ± 13
6-NChr	33 ± 5	49 ± 11	94 ± 14	59 ± 13

[a] Average recovery and standard deviation values of five extractions. The extraction pressure was 10 MPa, and the extraction temperature 100°C.

extraction pressure. The highest recoveries were obtained at 14 MPa (51–112%) with RSD in the range from 6 to 18%. When using DCM : MeOH mixture as an extraction solvent, recoveries between 48 and 116% were obtained. The RSD varied from 5 to 20%.

Recoveries obtained with increasing duration of static extraction time are shown in table 2. The prolongation of 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 of nitro-PAHs.

No significant differences in recoveries of extraction were found at the extraction pressure 14 MPa and temperature 100°C when using dichloromethane or its mixture with methanol. Nitro-PAHs with lower molecular weight (1-nitronaphthalene, 2-nitrofluorene) seem to be partially lost during evaporation of extracts. Dichloromethane was chosen because of its better evaporability from the extracts of roadside dust.

3.2 *Roadside dust analysis*

A spiked and nonspiked dust were extracted and fractionated under conditions mentioned above. The chromatogram of raw extract measured in SCAN mode is shown in figure 6. High chemical background made analysis of nitro-PAHs impossible. Chromatograms of fraction 3 that contains nitro-PAHs are shown in figures 7 and 8. Fractionated extracts were measured in SCAN and SIM modes. The SCAN mode showed low sensitivity to detect nitro-PAHs in extract (figure 7). Consequently measurements in SIM mode were used for nitro-PAHs quantification in extracts (figure 8).

Only 1-nitropyrene from selected nitro-PAHs was detected in these samples. Owing to the absence of other nitro-PAHs in the sample, their recovery could be directly calculated from the response of spiked samples and standard solution. The recoveries after extractions and standard deviations of target nitro-PAHs are as follows: 1-nitronaphthalene (65 ± 9)%, 2-nitrofluorene (60 ± 11)%, 9-nitroanthracene (79 ± 10)%, 1-nitropyrene (81 ± 13)%, 6-nitrochrysene (108 ± 11)%. The concentration of 1-nitropyrene compound in the roadside dust was $37 \pm 6\,\mathrm{ng\,g^{-1}}$. The nitro-PAHs were extracted at least efficiently as by Soxhlet extraction, which was used for comparison.

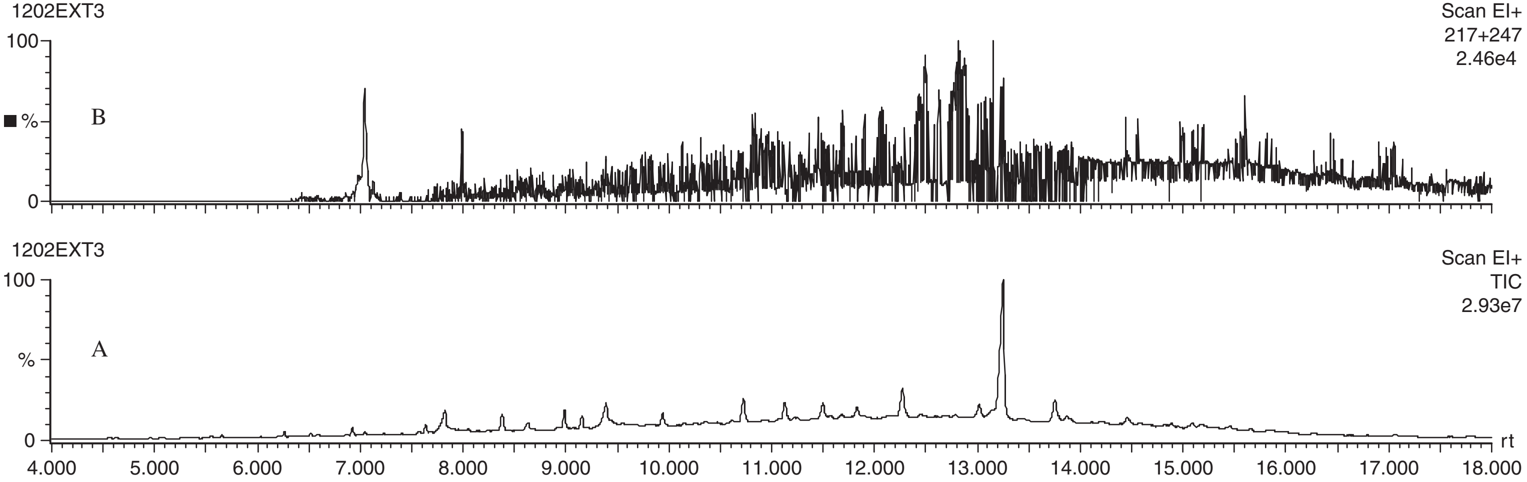

Figure 6. Chromatogram of raw extract. A – total ion current (TIC), B – extracted masses for measurement of 1-nitropyrene (m/z 217 and 247). Y-axes are scaled to the highest peak.

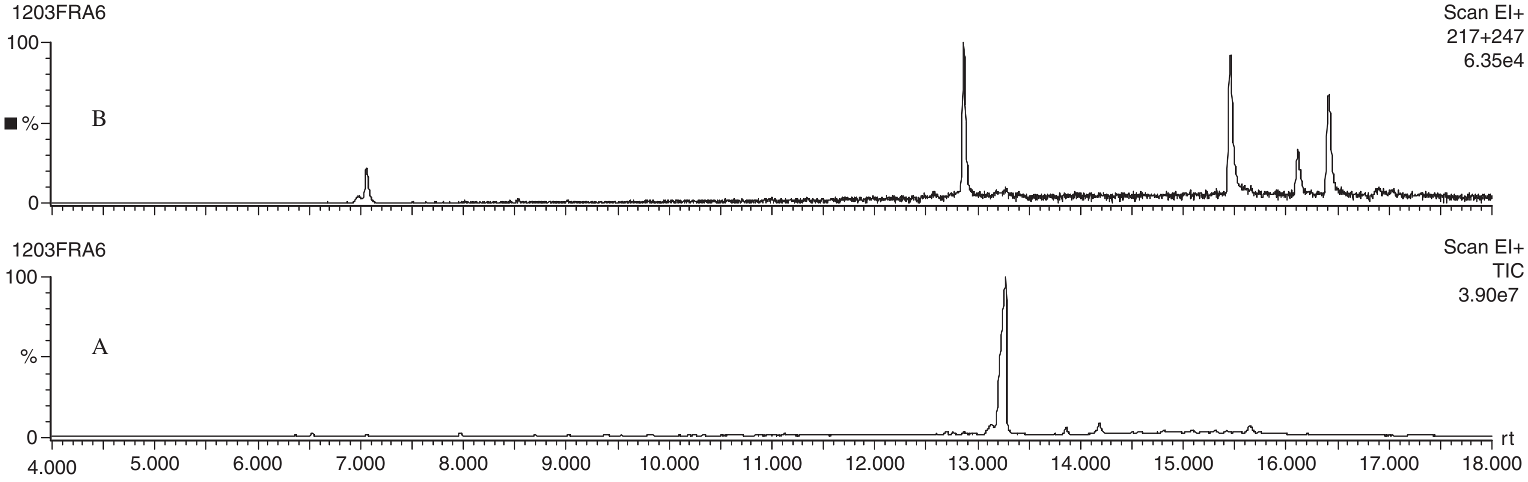

Figure 7. Chromatogram of fraction containing nitro-PAHs (fraction 3), measured in SCAN mode. A – total ion current (TIC), B – extracted masses for measurement of 1-nitropyrene (m/z 217 and 247). Y-axes are scaled to the highest peak.

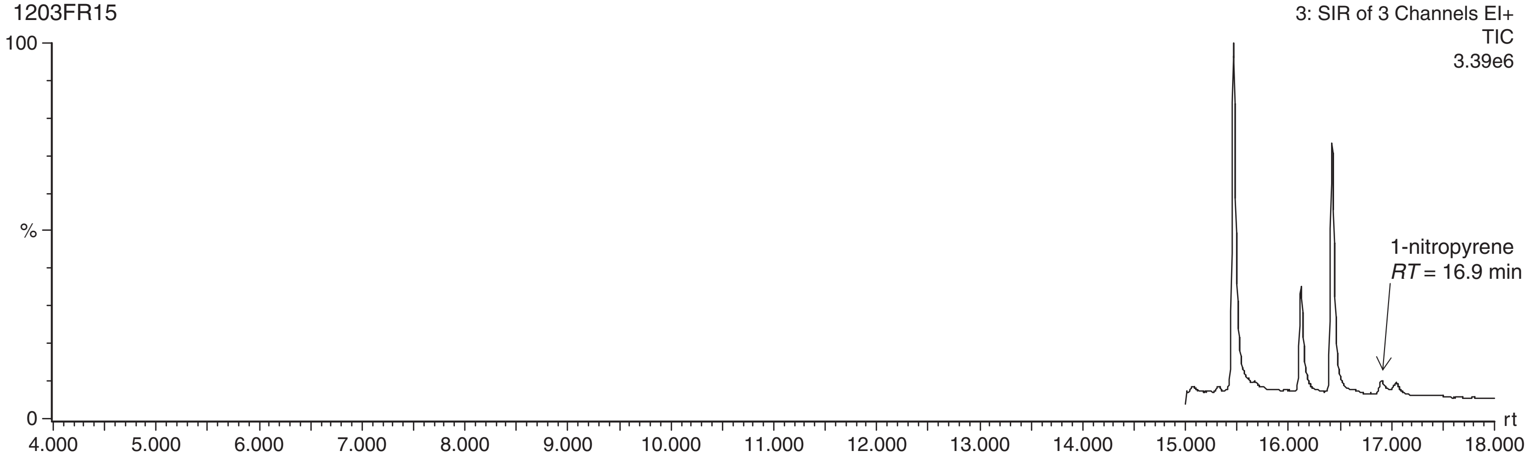

Figure 8. Chromatogram of fraction containing nitro-PAHs (fraction 3), measured in SIM mode. Retention window with total ion current (TIC) of masses for measurement of 1-nitropyrene (m/z 217 and 247). Y-axes is scaled to the highest peak. Retention time of 1-nitropyrene is 16.9 min.

These results were compared with the results obtained by Soxhlet extraction applied to the samples of atmospheric particles. The recoveries in the range of 53% for 1-nitronaphthalene to 73% for 1-nitropyrene (RSD 21–33%) were observed [7]. In [22] Soxhlet extraction was applied to the soil samples. The recoveries ranged from 91 to 109%.

4. Conclusions

This work showed possibilities of using the pressurised solvent extraction for extraction of nitro-PAHs from solid samples. The highest recoveries were obtained at the extraction temperature of 100°C, pressure of 14 MPa and two cycles of 5 min, if spiked inert matrix was used for the experiments. These conditions were applied to extraction of nitro-PAHs from roadside dust. The results showed that PSE is an efficient technique for extracting nitro-PAHs from contaminated solid samples comparable with results obtained with Soxhlet extraction.

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