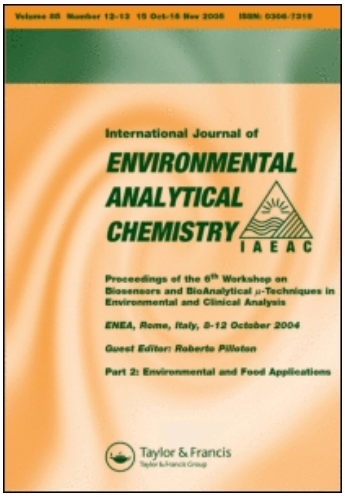

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Švábenský, Radim , Oravec, Michal and Šimek, Zdeněk(2009) 'Determination of polycyclic aromatic nitrogen heterocycles in soil using liquid chromatography/tandem mass spectrometry', International Journal of Environmental Analytical Chemistry, 89: 3, 167 — 181
To link to this Article: DOI: 10.1080/03067310802499423
URL: http://dx.doi.org/10.1080/03067310802499423

Intern. J. Environ. Anal. Chem.
Vol. 89, No. 3, 15 March 2009, 167–181

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Determination of polycyclic aromatic nitrogen heterocycles in soil using liquid chromatography/tandem mass spectrometry

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(*Received 4 June 2008; final version received 22 September 2008*)

Development of LC/MS/MS method for analysing polycyclic aromatic nitrogen heterocycles (PANHs) in soil samples is presented. Optimisation of individual chromatographic/mass spectrometric conditions was made in order to obtain a method for the determination of 15 PANHs content in an organic extract from the soil. Detection limits (LOD) in the range of 0.3–15 pg per injection were obtained for individual PANHs. LC/MS/MS method has a lower LOD value compared to LC/DAD/FLD methods in general. Developed LC/MS/MS method was used for determination of PANHs content in soil samples collected in contaminated areas of the southeast region of the Czech Republic. Highest concentrations of PANHs have been found in the samples collected in the immediate vicinity of the industrial basin. Concentrations of the contaminants in samples collected in surrounding villages were higher compared to the sample collected in clean area of the Czech Republic.

Keywords: polycyclic aromatic nitrogen heterocycles; PANHs; soil; LC-ESI/MS/MS

1. Introduction

One of the most important groups of pollutants often monitored and investigated in the environment is a group of polycyclic aromatic hydrocarbons (PAHs). However many other related compounds are being investigated intensively. A very important group of related compounds is a group of polycyclic aromatic nitrogen heterocycles (PANHs) derived from PAHs having one or more carbon atoms replaced by a nitrogen heteroatom. This change gives PANHs different physico-chemical properties compared to the analogous PAH. It can be seen especially for the PANHs with low molecular weight. Generally, the difference between PANHs and analogous PAH decreases with increasing molecular weight. For example the solubility of quinoline in water is 6110 mg L^{-1} but for the analogous PAHs naphthalene it is 31 mg L^{-1}. As can be seen, PANHs may be up to 2000 times more soluble than PAH. On the other hand, the difference in solubility of polycyclic aromatic compounds with high molecular weight such as dibenz[*a,h*]acridine (0.16 mg L^{-1}) and dibenz[*a,h*]anthracene (insoluble) in water is small [1–3]. Thanks to the higher ionisability and lower lipophylity, PANHs are more soluble in a water environment than PAHs which gives them higher environmental mobility. PANHs can be easily

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802499423
http://www.informaworld.com

transported into different parts of the environment [2,4,5]. Long-term toxicity of PANHs confirmed by many tests (Ames test, MUTATOX test, etc.) is often higher compared to their analogues of PAHs [1].

Sources of the PANHs are similar to their analogues of PAHs. The majority of the sources can be divided into two main groups. One of them is connected with the exposure of different organic materials to high temperatures; the other one is connected with the burning of fossil fuels. One of the sources of the first group is different ways of food preparation [6–8]. Exhaust fumes from cars are a good example of the second type of source. Cars emit about $6\,ng\,m^{-3}$ of the PANHs in their exhaust fumes into the air. This part of PANHs can be transported into different parts of the environment [2,5]. Other PANHs sources can also be found; wood preservation, cigarette smoke, oil processing. [9–11]. Living organisms can be exposed to PANHs in different ways. One of the ways is direct exposure to contaminated air by inhalation or in the event of smokers by deliberate inhalation of cigarette smoke [12]. Another one is contamination through food which has been contaminated during production. For example, PANHs can be adsorbed on the surface of leaves or other parts of plants directly from contaminated air or rain. The other way of plant contamination is transport of pollutants from contaminated soil. Soil organisms (earthworms, etc.) can be exposed to PANHs directly.

Two main ways have to be taken into account when considering the possible ways of PANHs transport into the soil environment. One is deposition of PANHs from the air which would contain significant amount of azaarenes in airborne particles and vapour phases [13,14]. The other way is contamination of the soil, when sewage sediments are used for the fertilising of fields. High concentrations up to $50\,ng\,g^{-1}$ of individual azaarenes have been found in sediments [15,16]. Significant amount of PANHs in the soil have been detected in areas with high industry as well [2,5,17]. For example concentration of benzo[*h*]quinoline in the air in Upper Silesia (Poland) reached $3.7\,ng\,m^{-3}$ [18]. High amounts of 2-methylquinoline ($13.3\,\mu g\,g^{-1}$) and carbazole ($34.8\,\mu g\,g^{-1}$) have been found in the area of Spotsylvania where the soil was contaminated by creosote [19].

PANHs were found not only in soil samples collected in contaminated areas, but also the natural water reservoirs may contain significant amounts of PANHs in their sediments. It was reported by Motohashi that concentrations of PANHs in sediment of Lake Lucern can be $0.8\,ng\,g^{-1}$. Far more alarming concentrations were found by the same author in the sediment of Lake Zurich. The concentration reached $50\,ng\,g^{-1}$ [15]. Total amount of PANHs in river sediment up to $2.5\,\mu g\,g^{-1}$ of PANHs can be found in rivers running through industrial areas [4].

Methods of PANHs determination described in several papers often use liquid–solid column chromatography fractionation for isolation of the PANHs group. Acid–base partitioning methods, solid phase extraction, ion exchange chromatography or thin layer chromatography has been published. As an example, extraction published by Warzecha *et al*. can be taken [18]. The extract of solid samples is divided in 2-step liquid–solid column chromatography on Al_2O_3–silicic acid into four fractions. The first fraction contains hydrocarbons, the second one carbazoles, the next aminoarenes and the last PANHs. N-hexane, dichloromethane, methanol, ammonium acetate and aqueous ammonia are used as solvents. The fractions containing PANHs are subsequently analysed using mainly HPLC with diode area detection (DAD) or fluorescence detection (FLD) [8,18,20].

Generally gas chromatography in combination with mass spectrometry or liquid chromatography with DAD/fluorescence detection is used for final analyses.

The advantage of the HPLC/DAD system is the possibility to use an organic extract from different matrices, water extract or liquid samples of the environment. The highest disadvantage of DAD detection is relatively high detection limits on nanograms level for selected PANHs [18]. Lower detection limits can be reached by using fluorescence detection.

Advantages of the GC/MS system are usually lower detection limits at 0.01 ng per injection level which are often more than a 100 times lower compared to the HPLC/DAD (5 ng per injection) and comparable to HPLC with fluorescence detection [2,18]. Detection limits in the range of 0.02–0.05 ng per injection calculated as three times the standard deviation of a blank were reached for a set of PANHs using the GC/MS method in SIM mode developed for determination of PANHs in water samples [21]. The LOD on 0.2 ng per injection were reached by Brumley using the GC/MS in scan mode for analysis of PANHs in soil samples [19]. The disadvantage of the GC/MS system is a significant sensitivity to the sample type. Due to the necessity of evaporation of the sample, samples containing solvents and compounds with higher boiling point (water, big organic compounds) are difficult to analyse. Development in the field of GC columns, where nowadays cross-linked polymeric phases are available, allows analyses of polycyclic aromatic compounds with higher molecular weights [2,15].

HPLC/MS/MS can be used to analyse not only organic extract of samples, but also samples which have water as a matrix and contain organic compounds with lower volatility. Generally it can reach very low detection limits up to 100 fg levels for selected organic compounds. Commonly used columns for determination of this group of compounds are C18 columns where the surface of silicagel is modified by octadecyl groups.

Our study is focused on the development and use of the LC-MS/MS method for analysis of the PANHs in soil samples, on low detection limits, with a reduced number of pre-separation or fractionation steps of the extract of soil sample. The samples of soil used in our study have been taken in regularly monitored selected areas around Valašské Meziříčí. The sampling area is in the north-east part of the Czech Republic. This area was known in the past as a locality of factories producing different organic compounds.

2. Experimental

2.1 *Chemicals*

PANHs used in our study were chosen on the basis of structural similarity with a group of frequently investigated PAHs. Structures containing from two to five aromatic rings and one or two nitrogen atoms were present in the group. Stock solutions of standard analytes were prepared in acetonitrile using standard substances of PANHs obtained from Sigma-Aldrich (USA) and from Dr. Ehrenstorfer GmbH (Germany) – quinoline, phthalazine, quinazoline, 2-methylquinoline, 6-methylquinoline, 8-methylquinoline, acridine, benzo[*h*]-quinoline 1,7-phenanthroline, 4,7-phenanthroline, phenazine, benz[*a*]acridine, benz[*c*]acridine, dibenz[*a,j*]acridine, dibenz[*c,h*]acridine – purity $\geq$98%. Concentration of individual PANHs in acetonitrile stock solutions was 50–100 $\mu g\,mL^{-1}$. These standard solutions have been used for preparing working solutions used not only for the optimisation of the chromatographic/mass spectrometric conditions but also for construction of the calibration curves.

Water used in the laboratory was prepared using Simplicity 185 equipment (MILLIPORE, France). Electric resistance of the prepared water was greater than

17.4 MΩ cm^{-1}. Acetonitrile used as an organic modifier of mobile phase and solvent for standard preparation was Ultra Gradient HPLC Grade (Mallinckrodt Baker B.V., Holland)

2.2 *HPLC–MS system*

HPLC system Agilent 1200 (Agilent Technologies, Inc., Palo Alto, CA, USA) coupled with the 6410 Triple Quad (Agilent Technologies, Inc., Palo Alto, CA, USA) LC-MS/MS has been used for the method development and sample analyses. Separation of PANHs was performed on Ace 5 C18, 250 × 4.6 mm i.d., 5 μm, column (Advanced Chromatography Technologies, Scotland).

The best separation conditions were obtained by using a gradient of acetonitrile/water mobile phase combined with a change of mobile phase flow. The gradient of acetonitrile used for the elution was as follows: 0–60 min: 30–55% acetonitrile; 60–95 min: 55–90% acetonitrile. The isocratic part of the program (90% acetonitrile) followed for 25 min and finally the composition of the mobile phase was changed after 125 mins to 30% acetonitrile. The flow started at value 0.6 mL min^{-1} and decreased to 0.5 mL min^{-1} in 60 min. Column temperature was adjusted to 50°C. These conditions had been optimised on the basis of results of selectivity experiments obtained previously for mixture of PANHs and PAHs [17]. Volume of samples injected on chromatographic column was 5 μL. For optimalisation of the LC/MS/MS system concentrations 0.5 ng of individual compound per injection were used.

Positive ESI/MS mode was used for ionisation of PANHs molecules because of a higher response for all investigated compounds compared to negative ESI/MS mode (Figure 1). The flow and temperature of the drying gas were optimised to 10 mL min^{-1} and 350°C, respectively, according to technical properties of the MS instrument used. The pressure of nebuliser was set at 50 psi.

2.3 *Sampling and sample processing*

The sampling areas in Valašské Meziříčí and in selected villages in the vicinity of Valašské Meziříčí (Czech Republic) have been selected because of the potential contamination coming from chemical industries located in the town. The comparison of collected data with analytical results from a similar study using samples from these areas was another reason [17]. Two soil samples (VM1 and VM2) have been taken inside the frequented area of Valašské Meziříčí (Czech Republic) and three others in surrounding villages Juřinka, Mšenovice and Příluky. Soil samples collected from the clean area near small town Klobouky u Brna (Czech Republic) were used for comparison.

The upper 10 cm soil was taken from the sampling site by using an iron spade. Samples were packed into airtight PE bags. In the laboratory, the samples were separated from plants and stones and dried at ambient temperature (20°C) for 48 hours in a shallow layer. The drying properties were chosen to be similar to the environmental condition to protect the sample from loosing of significant part of more volatilised PANHs at high temperatures. After that, the samples were crushed in mortar and sieved through a 2 mm sieve. The sieved samples were stored in airtight PE bags in the dark at 4°C until extracted.

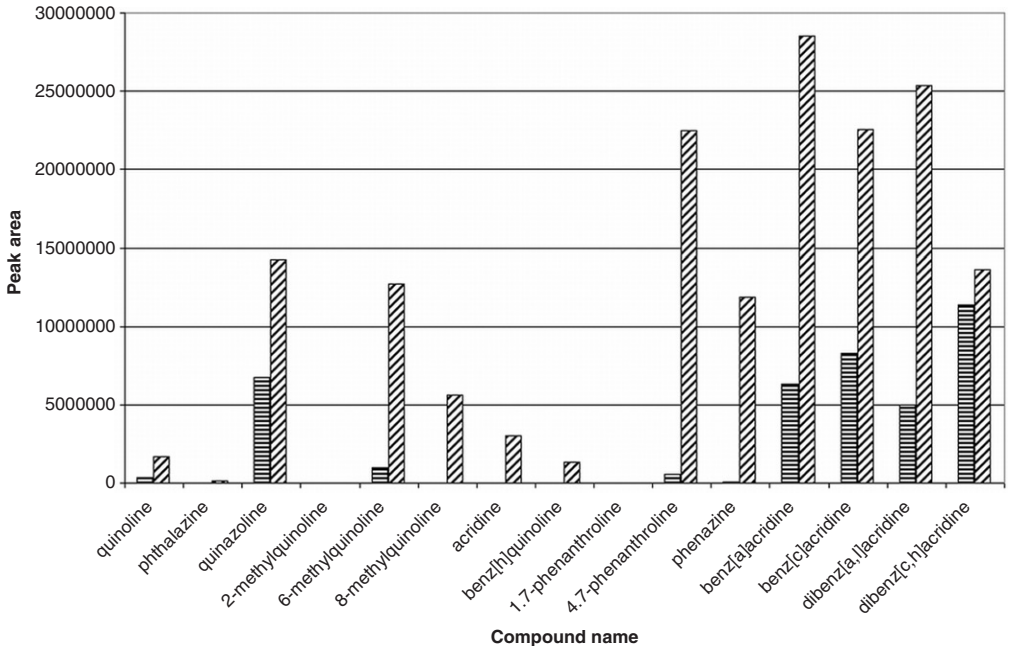

Figure 1. MS response of PANHs in ESI− and ESI+ mode. Capillary voltage 3000 V, fragmentor voltage 160 V.

An automatic BÜCHI B 811 (BÜCHI, Switzerland) extractor was used for the extraction of 5.0 g of samples. Soxhlet warm extraction using 80/20 v/v methanol/acetonitrile solvent was developed previously and extraction recoveries were 68.6%–87.4% [22]. The extract obtained by this method was concentrated exactly into 1 mL in evaporation equipment EVATERM (Labicom, Czech Republic) by using a nitrogen stream and then transferred directly into a dark HPLC vial with a PTFE stopper. This sample was directly injected into the HPLC-MS system to be analysed. Every sample was processed in triplicate. The blank samples were analysed with a set of soil samples that were extracted. These blank samples included reagents that were used in the whole analytical process. Blanks contain no analytes above the detection limit.

3. Results and discussion

To find out the best acquisition conditions for LC/MS/MS analysis of selected PANHs, optimisation of basic instrumental parameters (capillary voltage, fragmentor voltage and collision cell energy) was made. The precursor ion masses of all the analysed compounds were determined from the full scan MS data of each analysed PANHs. In all cases the highest response was obtained for $[M+H]^+$ ions selected as precursor ions for MS/MS experiment. This is in compliance with the results published previously [23]. No significant response of adduct ions was identified. The defined precursor m/z value for PANHs used in the study can be seen in Table 1. Capillary voltage was set to 3000 V as the result of dependence of signal intensity of $[M+H]^+$ ions of individual PANHs in SIM mode (Figure 2).

Table 1. Properties of LC/MS/MS determination of PANHs.

	Quinoline	Phthalazine	Quinazoline	2-Methylquinoline	6-Methylquinoline	8-Methylquinoline	Acridine	Benzo[h]quinoline	1.7-Phenanthroline	4.7-Phenanthroline	Phenazine	Benz[*a*]acridine	Benz[*c*]acridine	Dibenz[*a*,*j*]acridine	Dibenz[*c*, *h*]acridine
Number of *N*	1	2	2	1	1	1	1	1	2	2	2	1	1	1	1
Retention order	4	1	2	6	7	9	10	11	5	3	8	12	14	13	15
Relative mass weight	129.1	130.1	130.1	143.2	143.2	143.2	179.2	179.2	180.2	180.2	180.2	229.3	229.3	279.3	279.3
Precursor ion	130.1	131.1	131.1	144.1	144.1	144.1	180.1	180.1	181.1	181.1	181.0	230.1	230.1	280.1	280.1
Product ion	77.1	77.2	77.1	77.1	115.1	77.1	152.1	152.1	127.1	127.1	77.1	202.1	202.1	252.1	252.1
Qualifier ion	103.2	104.1	103.9	128.0	91.1	127.2	128.0	127.0	154.1	154.1	127.0	214.0	213.8	264.1	265.0
Collision energy (V)	25	30	25	40	35	35	40	40	40	40	35	50	50	50	50

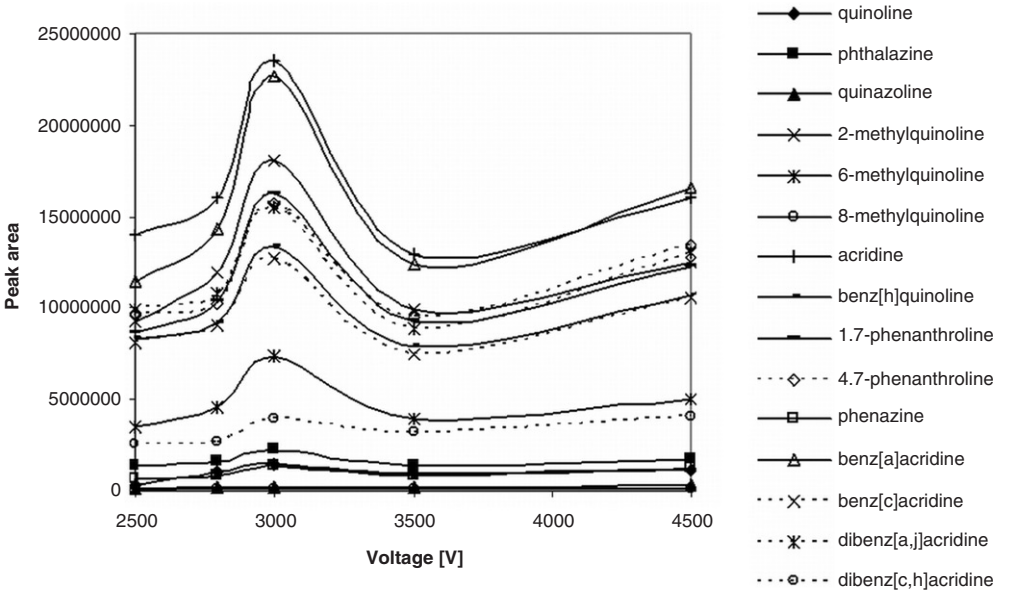

Figure 2. Mass spectrometer of PANHs $[M+H]^+$ ions at various capillary voltages. Fragmentor voltage 160 V.

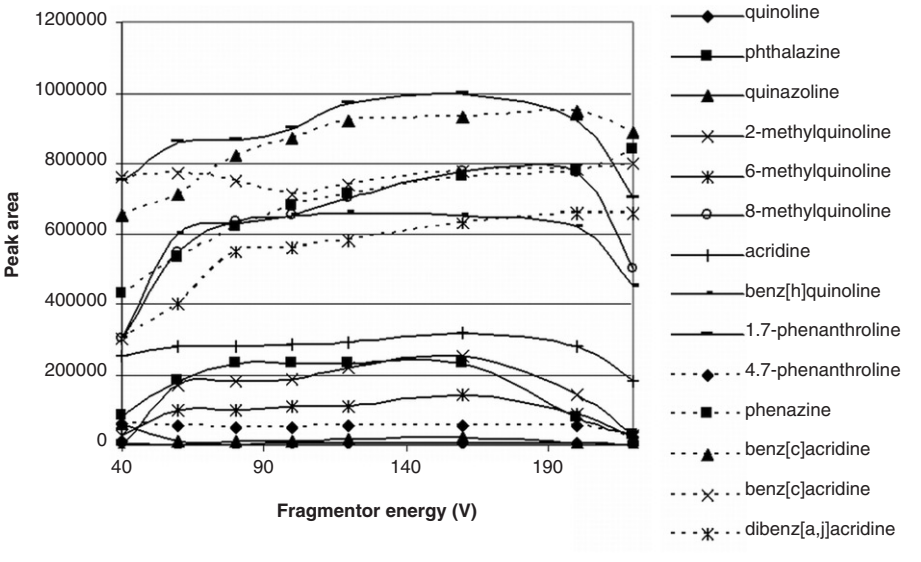

Figure 3. Effect of fragmentor voltage.

Effect of the value of the fragmentor voltage on signal intensity of $[M+H]^+$ ions had been investigated in a wide range from 40 to 220V in SIM mode using selected precursor ion masses of individual PANHs. The best results of the highest responses were obtained for fragmentation voltage equal to 160V in most cases (Figure 3).

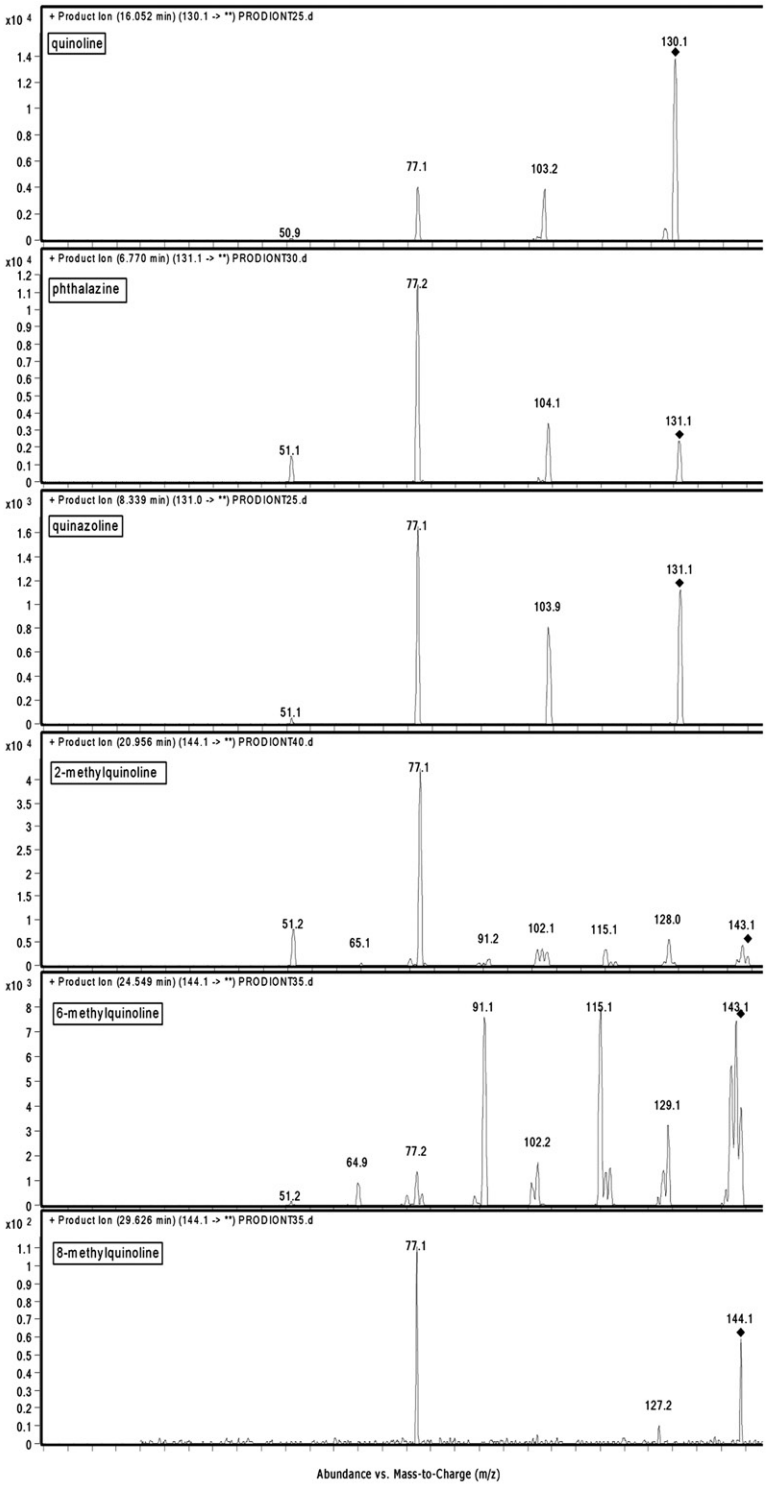

Figure 4. Spectra of PANHs products ions.

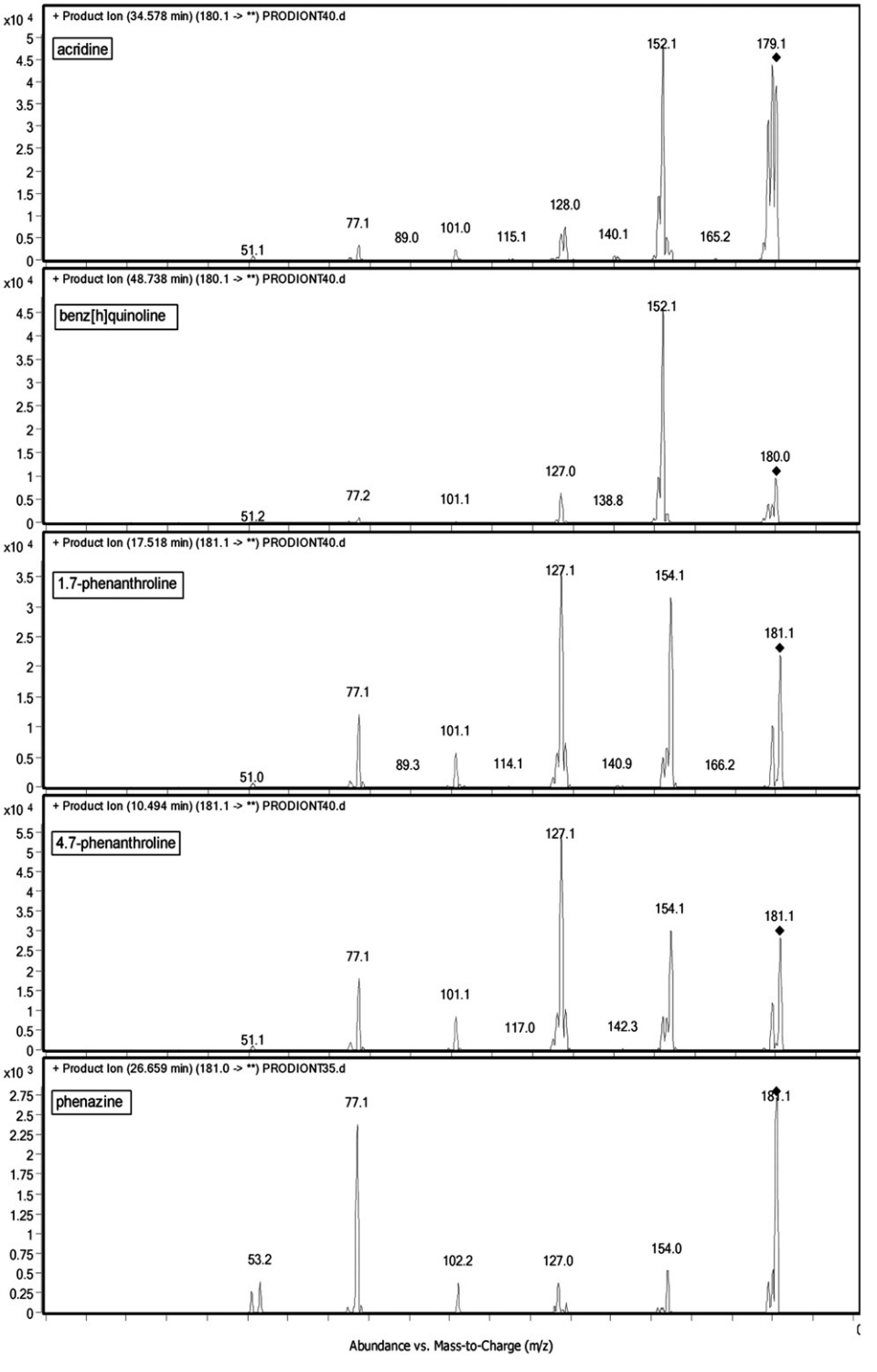

Figure 4. Continued.

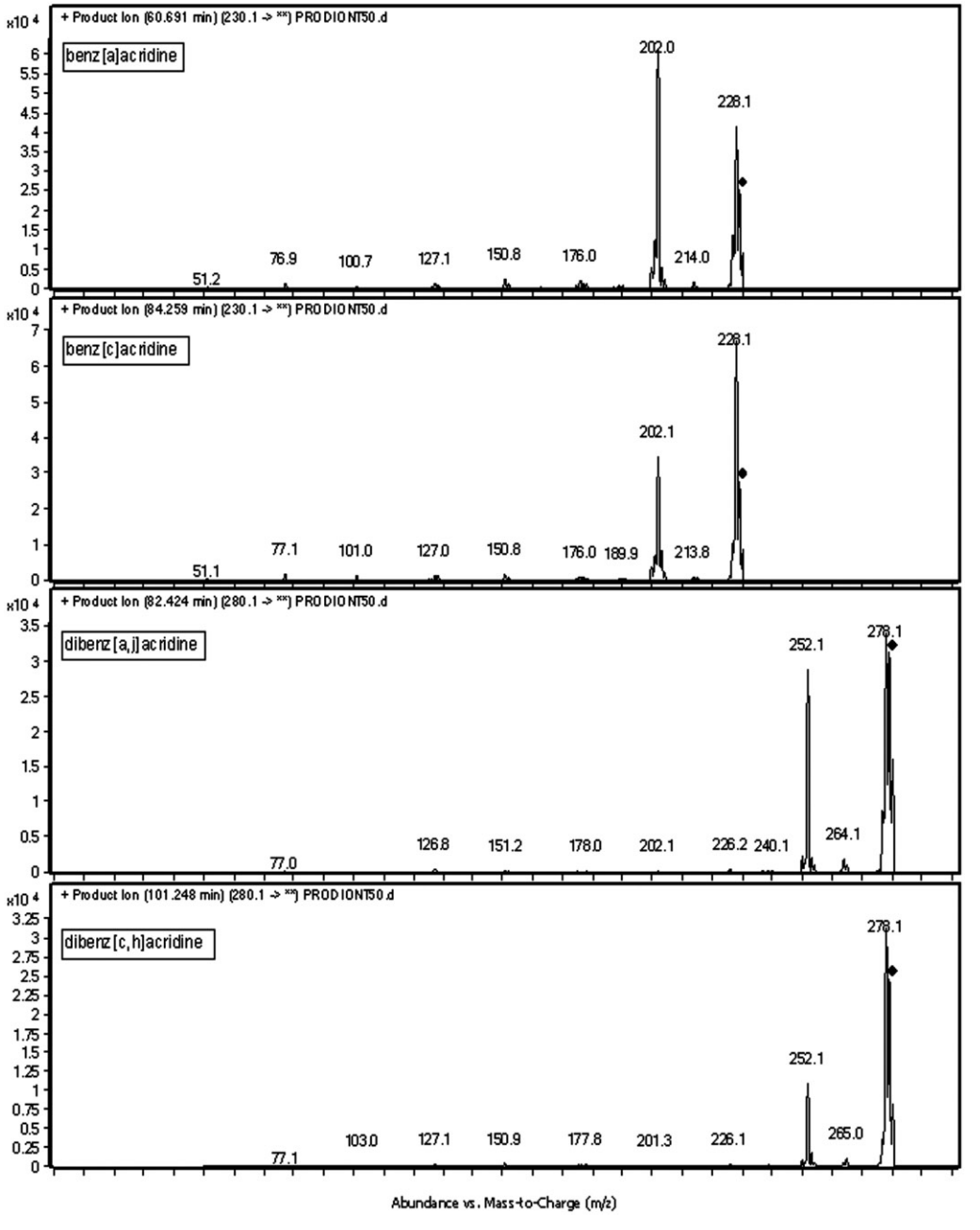

Figure 4. Continued.

Capillary voltage 3000 V, fragmentor voltage 160 V and selected m/z values of precursor ions (Table 1) were used in the step of identification of product ions suitable as quantification and validation ions. The most suitable ions selected for individual PANHs from product ion spectra (Figure 4) at optimum collision energy are summarised

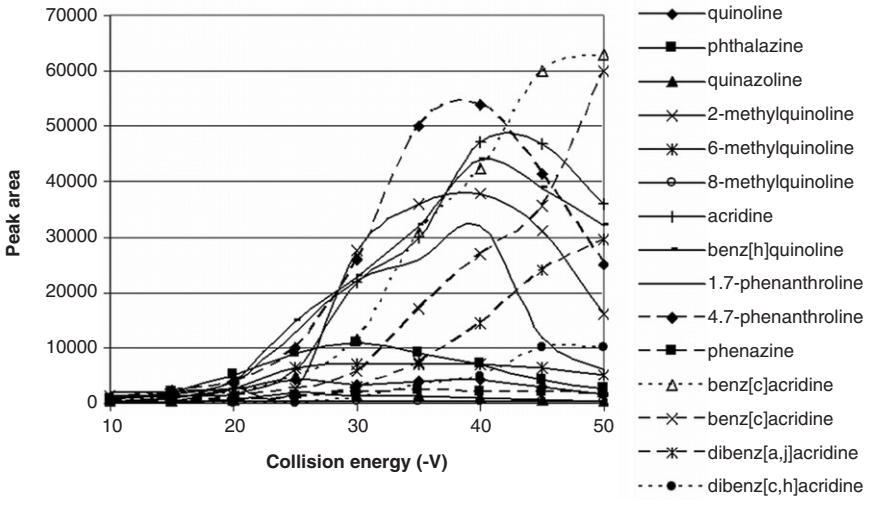

Figure 5. Effect of collision cell energy.

in Table 1. Effect of collision cell energy on intensity of fragment ions available for selected reaction monitoring analytical mode was studied in the range of 10–50 V limited by technical parameters of the mass spectrometer used (Figure 5).

The optimal collision energy used for generation of the most intensive quantitative product ions was −25 V or −35 V for PANHs with two condensed rings, except of 2-methylquinoline. The optimal collision energy in the case of PANHs with 3 condensed rings was −35 V or −40 V. Instrumentally maximum available collision energy −50 V was used for compounds with 4 and 5 condensed rings to obtain maximum response for product ions which was used for quantitative determination of the compound in all cases.

Only limited information concerning fragmentation patterns of PANHs in LC-MS/MS systems are available in a literature. Therefore standards are frequently used for identification of PANHs comparing published spectra [2,12]. The aim of our study was not to rigorously identify the structure of product ions. However the probable fragment structure can be proposed on the basis of knowledge of GC-EI/MS fragmentation of polycyclic aromatic compounds or azaarenes [24]. Although some selected quantitative ions would be assigned to typical fragments of aromatic compounds such as ions with m/z 77.1 to $[C_6H_5]^+$ ion or m/z 51 to $[C_4H_3]^+$ ion, rigorous confirmation of fragmentation pathways of PANHs in various LC-MS/MS properties will be the subject of further study.

Lower detection limits have been reached compared to HPLC/DAD/FLD using properties of the LC/MS/MS method described in Table 1 [17]. For detection limits comparison of individual detection methods see Table 2. Detection limits were determined either as three times of standard deviation of a blank or calculated from linear type of calibration curves made in the concentration range from 0.1 to 1.0 ng μL by the Graham method [25]. The father offered lower values compared to that found in a literature. The reason would be a significantly decreased magnitude of instrumental noise of the LC/MS/MS experimental setup using a triple quadruple mass spectrometer.

Relatively broad range of PANHs concentration was determined in soil samples (Table 3). The main source of soil contamination in the Valašské Meziříčí can be stipulated as the industrial production basin for the processing of crude oil based on the fact that

Table 2. Detection limits comparison (pg of PANH per injection on LC column).

Method	Quinoline	Phthalazine	Quinazoline	2-Methylquinoline	6-Methylquinoline	8-Methylquinoline	Acridine	Benzo[h]quinoline	1.7-Phenanthroline	4.7-Phenanthroline	Phenazine	Benz[a]acridine	Benz[c]acridine	Dibenz[a,j]acridine	Dibenz[c, h]acridine
[a]LC/MS/MS	7.9	2.6	15	0.8	4.4	2.6	1.0	0.4	0.9	0.3	9.1	0.5	0.7	0.6	1.6
[b]LC/MS/MS	24	42	18	15	12	22	74	56	69	11	69	38	49	25	32
[b]LC/DAD	2140	4000	2290	5080	2080	2100	1130	1110	5000	2260	2030	943	1170	973	950
[b]LC/FLD	12700	No FL.	3970	1520	2980	1040	7.4	39	69	25	298000	7.6	6.0	2.1	111

Notes:[a]3 × S/N method.
[b]Graham method.

Table 3. Results of soil sample analyses (ng g^{-1} of dry soil).

Site	Quinoline	Phthalazine	Quinazoline	2-Methylquinoline	6-Methylquinoline	8-Methylquinoline	Acridine	Benzo[*h*]quinoline	1.7-Phenanthroline	4.7-Phenanthroline	Phenazine	Benz[*a*]acridine	Benz[c]acridine	Dibenz[*a*, *j*]acridine	Dibenz[*c*, *h*]acridine
Klobouky	ND	ND	ND	0.83	ND	ND	0.71	1.00	0.86	0.05	ND	1.06	0.82	0.80	0.79
Juřinka	1.82	ND	ND	0.88	0.98	ND	1.64	1.14	1.20	1.24	0.93	6.39	4.83	1.80	0.83
Mšenovice	1.85	1.14	ND	0.91	1.00	ND	4.84	1.73	0.95	0.13	ND	19.9	28.6	4.95	1.35
Přiluky	1.91	ND	ND	0.87	0.95	ND	4.31	1.24	0.87	0.04	ND	6.16	5.87	2.29	0.88
VM1	10.3	ND	ND	4.28	4.40	ND	114	13.1	4.29	0.79	7.30	196	226	51.4	9.05
VM2	15.3	ND	ND	5.03	6.05	ND	182	17.3	3.57	0.93	6.34	111	270	64.0	13.0

ND: Not detected.

most of the contaminants are present in the samples in much higher concentrations (sum of determined azaarenes is 640.9–694.1 ng g^{-1}) compared to the reference area of Klobouky u Brna where the sum of all determined azaarenes is only 6.9 ng g^{-1}.

Phenazine is well known as a product of microbial colonies in the soil and therefore the contamination of the sample from Mšenovice by this compound could be caused not only by human activity [26].

From the results it can be seen that contamination of the soil is caused more by PANHs with higher molecular weight compared to the PANHs with lower molecular weight. This may by caused due to the fact that PANHs with lower molecular weight are more volatile compared to those with higher molecular weight and have a lower affinity to soil. The average coefficient of variation of determination of azaarenes in soil samples (including sampling preparation, extraction and analytical determination) was 16.4%.

4. Conclusion

The possibility to use LC/MS/MS for determination of selected PANHs in soil samples was described in this study. The successful and sensitive ionisation of PANHs with one and/or two nitrogens in basic polycyclic aromatic structure, as well as their selected methyl derivatives allow to identify and quantify this compound in soil samples collected in potentially contaminated areas. It has been shown in our work that, thanks to significantly lower detection limits for the LC/MS/MS analytical method, concentrations of PANHs in the soil samples taken in the selected areas in the Czech Republic can be measured at environmentally relevant concentration levels without the need of pre-separation of investigated PANH and PAH and significant pre-concentration steps. Compared to the HPLC/DAD/FLD method, the LC/MS/MS method provides much lower detection limits. Because of the properties of LC/MS/MS used in our study which do not allow the ionisation of PAH and their detection in MS/MS mode, no interference of PANHs and PAH in LC/MS/MS analysis can occur. Retention properties can therefore be adjusted with regard to PANHs separation and final determination.

Concentrations of PANHs which have been found in the samples used in our study are in accordance with data presented in various papers. The most polluted area was Valašské Meziříčí city with sum of azaarenes 640.9–694.1 ng g^{-1}. Also in the villages near this city the concentrations of pollutants are higher (Juřinka 23.7 ng g^{-1}, Mšenovice 67.3 ng g^{-1}, Příluky 25.4 ng g^{-1}) compared to Klobouky u Brna where the sum of all detected azaarenes was only 6.9 ng g^{-1}. Although concentration of PANHs determined by Brumley in soil samples from Spotsylvania (USA) was in some cases much higher the direct contamination of analysed samples with creosote would be the reason [19].

Because of the very similar mass spectra of individual PANHs and possible fragmentation pathways the only mass information application for identification of individual PANHs in the mixture may have limited use. Combination with precision retention characteristics, FLD detection and/or UV spectra will improve the credibility of PANHs identification. LC-ESI/MS/MS has a high potential for determination of a broader group of PANHs in the presence of PAHs and their derivatives.

Acknowledgement

This work was supported by the project of Ministry of Education, Youth and Sports Czech Republic MSM 0021622412.

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