TYPICAL PROFILE IDENTIFICATION OF POLLUTION SOURCES BY POLYCYCLIC AROMATIC SULFUR HETEROCYCLES

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Abstract

A semi-quantitative method has been developed for the determination of typical profiles of PASHs to identify the main sources of soil pollution. PASHs compounds selected in this study were 2,3-dimethylbenzothiophene, 6,7-dimethylbenzothiophene, naphto[1,2-b]thiophene, phenanthro[3,4-b]thiophene, 3-phenylbenzothiophene and 3-(naphthyl)benzothiophene. Extraction of soil samples was carried out by ultrasonication using a mixture of n-hexane and dichloromethane. Final analysis was performed by gas chromatography using a non-polar capillary column TR-5ms (60 m, 0.25 mm, 0.25 µm) and the detection by high resolution mass spectrometer with magnetic and electric sector using electronic impact ionization. The linear range of the standard curve prepared from contaminated soil was from 1.0 to 8.0 ngKg^{-1} (R^2>0.97). Limits of detection ranged from 0.13 ngKg^{-1} to 2.50 ngKg^{-1}. The developed analytical method was successfully applied to study the soil profiling polluted by mobile and fixed sources.

Keywords: PASH, soil, pollution sources, profiles

Introduction

Environmental pollution always has a possible source. Generally the pollution source is suspected, based on the geographical position of the nearest possible sources or by the history of the area. A new approach leads the investigation of pollution source identification to a new level due to legal regulations that require more sensitive analytical methods. Identifying the main pollutants it is not always the answer that leads to the pollution source. This new approach had succeed to identify all the pollution sources, by measuring each contribution. The main impediment of this theory is to identify, analyze and quantify the right markers which may lead to a successful study. This markers are mainly pollutants that are resistant to biodegradation and can be identified and quantified after a long period of time /1,2/. The studies of urban pollution start from flow and dispersion models of pollutants by monitoring the air quality in different stationary points. This type of monitoring provides a cumulative package of information in a short period of time. To have a clear imagine of an areal pollution, the air monitoring has to be performed in a sufficient period of time. Generally, the main markers for the identification of petrogenic and pyrogenic source are the PAH compounds, that have been intensely studied and have a strong literature support mainly due to the legal regulations all over the world /4-8/. The PAH compounds can be easier biodegraded; this fact led to another markers, from the same sources but with a higher level of biodegradation resistance /5/. These compounds are the PASH – the sulfur analogs compounds of PAH. Few PASH compounds had been studied for the identification of pollution sources /1,6,7,8/. To realize a profile of a polluted site, only two PASH compounds had been used: dibenzothiophene (DBT) and benzo[b]fenanthro[2,1]thiophene (BPh21T). The relative response of this compounds and the relative response of PAH compounds such chrysene, anthracene and phenanthrene, has been used to calculate a specific ratio that will led to a pollution profile. These ratios can be used only when the pollution is relatively recent due to the biodegradation of PAH compounds /8,9,10/.

PASH compounds	CAS number	Molecular formula	Molecular mass (g/mol)
Benzothiophene	11095-43-5	C_8H_6S	134
3-Methylbenzothiophene	1455-18-1	C_9H_8S	148
3-Phenylthiophene	2404-87-7	$C_{10}H_8S$	160
2,3-Dimethylbenzothiophene	4923-91-5	$C_{10}H_{10}S$	162
6,7-Dimethylbenzothiophene	37610-98-3	$C_{10}H_{10}S$	162
2,3,5-Trimethylbenzothiophene	28540-46-7	$C_{11}H_{12}S$	176
Naphto[1,2-b]thiophene	233-02-3	$C_{12}H_8S$	184
4-Methyldibenzothiophene	7372-88-5	$C_{13}H_{10}S$	198
1,4-Dimethyldibenzothiophene	21339-65-1	$C_{14}H_{12}S$	212
Acenaphto[1,2-b]thiophene	1969 - 60 - 4	$C_{14}H_8S$	208
2,4,6-Trimethyldibenzothiophene	185393-79-7	$C_{15}H_{14}S$	226
Benzo[b]nafto[2,3-d]thiophene	239-35-0	$C_{16}H_{10}S$	234
Phenanthro[3,4-b]thiophene	195-52-8	$C_{16}H_{10}S$	234
3-(1-Naftil)benzothiophene	55712-59-9	$C_{18}H_{12}S$	260
Benzo[b]phenanthro[2,1-d]thiophene	239-35-0	$C_{20}H_{12}S$	284
Diacenaphtothiophene	203-42-9	$C_{24}H_{12}S$	332

Table 1. Physical properties of PASH compounds /8,11/.

Experimental part

Reagents and materials

The PASH compounds solutions with concentration of 0.1 mg/mL, were purchased from Münster University Germany, from prof. PhD. Jan Andersson. The solvents, n-hexane and dichloromethane for trace analysis Picograde purity, were purchased from LGC Standards. Sulfuric acid 95-97% technical grade was purchased from Merck Millipore. Anhydrous sodium sulfate 99% was acquired from Chimopar, Romania. All working solutions were prepared in a mixture of 1:2 n-hexane:dichloromethane (v/v) to obtain a stock solution of 10 mg/L. A decontaminated soil was used to prepare the calibration solutions. The soil was subjected to acid treatment, conditionated at 400^0C and extracted in Soxhlet equipment with dichloromethane /12-14/. The calibration solutions were extracted from contaminated soil with the solvent mixture of n-hexane:dichloromethane 1:2 (v/v) prepared in a concentration range of 1.0 to 8.0 $ngKg^{-1}$. A vacuum filtration system with glass fiber filters of 1.6 µm was used for soil samples. Separation funnel of 1000 mL for liquid-liquid extraction was used. The extracts were concentrated with a rotative evaporator with vacuum control, Laborota 4000, from Heidolph, Germany. Ultrasonic bath PLsonic-22D, with 40KHz frequency from Multilab.

HRGC-HRMS instrumentation

The equipment used consists of a gas chromatograph Trace GC, a high resolution mass spectrometer DFS and an autosampler Triplus AS from Thermo. The separation was achieved with a non-polar capillary column TR-5ms, 60 m, 0.25 mm internal diameter and 0.25 µm stationary phase thickness, with a nominal flow of 1.0 mL/min helium. A temperature program was used to achieve the separation of PASH compounds. The temperature program start at 50^0C for 0.5 minutes and increased with 15^0C/min to 290^0C for 15 minutes. The injection port temperature was set to 260^0C. The transfer line between gas chromatograph and mass spectrometer had a temperature of 295^0C. The calibration of the mass spectrometer was performed with FC-43 compound in mass range from 50 to 600 Da. The resolution of the mass spectrometer was adjusted to 10000 (FWHM) for the mass ion of 413.977 Da.

The mass spectrometer method used MID mode to track the specific mass ions of PASH compounds.

Sample preparation

The soil samples were collected from three different pollution sources areas from Bucharest city: an animal incinerator, a solid waste incinerator and near the A2 highway. The sampling was performed at three different depths, the superficial layer, at 20 cm and 40 cm, in different month, in February, March and May. An aliquot part of aprox. 5 g of soil was weighed and subjected to acid treatment with 30 mL sulfuric acid 95-97% and 250 mL tap water, in a Erlenmeyer flask of 500 mL. The flask was ultrasonicated for 20 minutes. The soil acid solution was filtrated on a glass fiber filter and washed with 300 mL tap water. The wash water was extacted three times with 50 mL solvent mixture 1:2 (v/v) n-hexane:dichloromethane in a separation funnel of 1000 mL and dried with anhydrous sodium sulfate on a paper filter. The glass filter was dried in a vent for 24 hours. After drying, the glass filter was extracted three times with 50 mL solvent mixture 1:2 (v/v) n-hexane:dichloromethane in a ultrasonic bath for 20 minutes. The extract was dried with anhydrous sodium sulfate on a paper filter and concentrated to 0.5 mL with a rotary evaporator.

Quality assurance protocol

The method was evaluated in terms of linearity, repeatability, accuracy and sensitivity. Linearity was evaluated by constructing five point calibration curves within a wide range of concentrations from 1.0 to 8.0 $ngKg^{-1}$. Linearity was assumed if the R^2 value was higher than 97.5%, and the residuals lower than 30% for each calibration point. Precision was defined as the relative standard deviation (RSD) of a five replicates analysis contaminated soil samples spiked at $4ngKg^{-1}$ concentration. The method was considered accurate if recoveries were in the 70-120% range, and precision was satisfactory if the RSD was lower than 15%. The limit of detection (LOD) and the limit of quantification (LOQ) were estimated for each analyte from the chromatograms at the lowest analyte concentration assayed, as the concentrations giving a signal to noise ratio of 3 and 10, respectively.

Results and discussion

Method optimization

Initially, a screening method was used to identify the PASH compounds from every sample. The used method was performed using the same parameters for the gas chromatograph and the high resolution mass spectrometer was used at low resolution to scan in a range from 50 to 500 Da. The stock standard solutions of PASH compounds of 10 mg/L was used for confirmation of the identified compounds, using the retention times and the mass spectrums. The screening method identified 6 PASH compounds in the soil samples.

Table 2. Identified PASH compounds from soil samples

PASH compound	Abbreviation	Relativ retention time (min)	Specific mass ion (Da)
3-Fenilthiophene	3PhT	10.56	160
2,3-Dimethyldibenzothiophene	23DMDBT	11.70	162
6,7-Dimethyldibenzothiophene	67DMDBT	11.70	162
Naphto[1,2b]Thiophene	N12T	17.71	260
Phenanthro[3,4-b]thiophene	F34T	20.63	234
3-(1-Naphtyl)benzothiophene	31NBT	21.43	260

After screening analysis, the mass spectrometer parameters were modified to MID scanning at 10000 resolution (FWHM), to track the specific mass ions of the PASH compounds identified by screening. The calibration curves performed using the same specific mass ions of the identified PASH compounds; for 3PhT was tracked the mass ion 160.0340 Da, for 23DMDBT and 67DMDBT was tracked the mass ion 162.0500 Da, for N12T and 31NBT was tracked the mass ion 260.0660 Da and for F34T was tracked the mass ion 234.0503 Da.

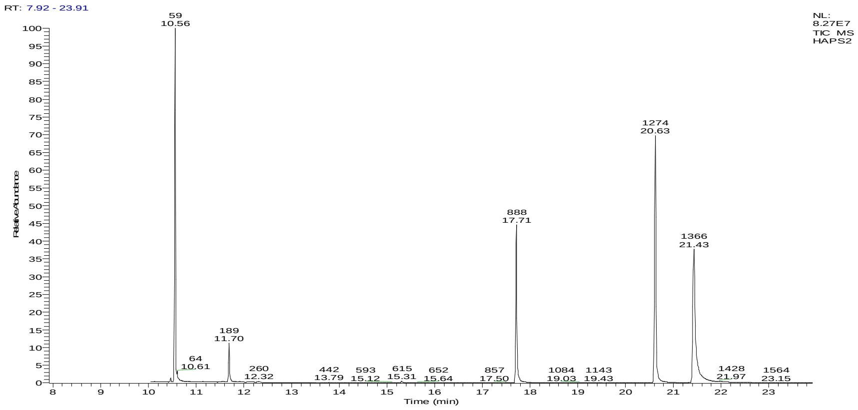
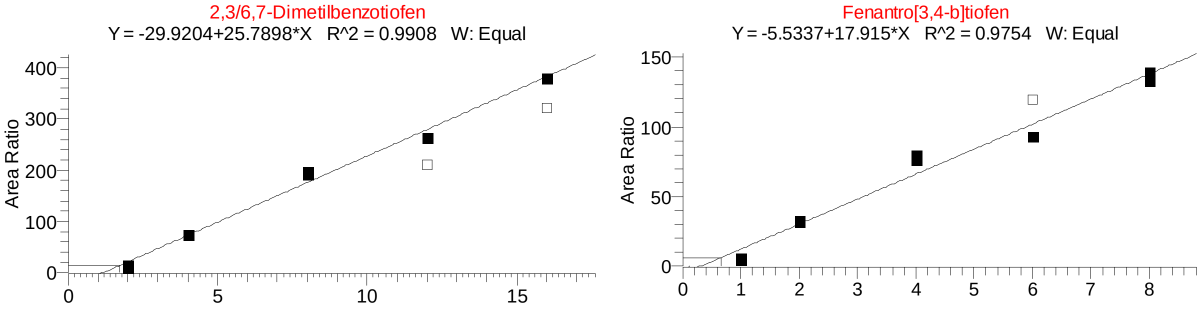


Figure 1. Chromatogram of identified PASH compounds



(a)

(b)

Figure 2. Calibration curves of 23DMDBT- 67DMDBT (a) and F34T (b) by MID method tracking the specific mass ions, 162.0500 Da for 23DMDBT and 67DMDBT and 234.0503 Da for F34T

Method validation

The linearity of the MS analyser response was investigated by performing duplicate injections standard solutions. The range tested was from 1.0 to 8.0 µgkg^{-1}. A linear response was observed. Figures 2 shows the calibration curve obtained for 23DMDBT and F34T. Figure 1 shows the separation of the five from six PASH compounds. 23DMDBT and 67DMDBT couldn’t be separated. Recoveries achieved for all target compounds ranged from 68% to 83% for spiked soil samples at 1 ngKg^{-1} and 4 ngKg^{-1} . Limits of detection ranged from 0.13 ngKg^{-1} to 2.47 ngKg^{-1}. Precision of the method was studied by analysing five replicates of 1 ngKg^{-1} and 4 ngKg^{-1} standard soil sample as RSD (%). The results are shown in Table 3.

PASH compound	Rec (%) 1ngKg^{-1}	Rec (%) 4ngKg^{-1}	RSD (%) 1ngKg^{-1}	RSD (%) 4ngKg^{-1}	LOD ngKg^{-1}
3-Fenilthiophene	69.3	74.1	3.75	2.48	0.22
2,3-Dimethyldibenzothiophene	72.3	78.9	3.94	2.63	0.13
6,7-Dimethyldibenzothiophene			4.02	3.78	1.07
Naphto[1,2b]Thiophene	72.0	75.3	4.47	4.11	1.43
Phenanthro[3,4-b]thiophene	70.7	73.1	5.23	4.72	1.89
3-(1-Naphtyl)benzothiophene	68.1	72.4	6.72	5.81	2.47

Table 3. Results obtained in the validation study (n=5) for the determination of 6 PASH compounds in spiked soil samples.

Analysis of real soil samples

To identify the specific profiles of the pollution sources, three relative ion mass ratios were chosen for all six PASH compounds as shown in Table 4.

Relative mass ratios		
23/67DMDBT : F34T	N12T :2367DMDBT	3PhBT:31NBT
162.0500:234.0500	260.0660:162.0500	160.0340:260.0660

Table 4. Specific relative mass ratios chosen for the profile of the soil samples.

The results of analyzes were calculated and graphically resumed. For the soil samples from waste incinerator area was obtained a specific profile of PASH compounds as shown in Tables 5,6 and 7.

Table 5. Soil sample collected in 23 February.

Relative mass ratios	Superficial layer	20 cm	40 cm
23/67DMDBT-F34T	0.075	0.052	0.038
N12T23-67DMDBT	1.12	1.07	0.87
3PhBT-31NBT	0.045	0.022	0.01

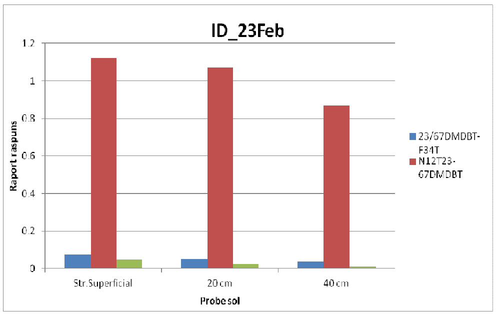


Table 6. Soil sample collected in 17 March

Relative mass ratios	Superficial layer	20 cm	40 cm
23/67DMDBT-F34T	1.32	0.9152	0.6688
N12T23-67DMDBT	19.712	18.832	15.312
3PhBT-31NBT	0.792	0.3872	0.176

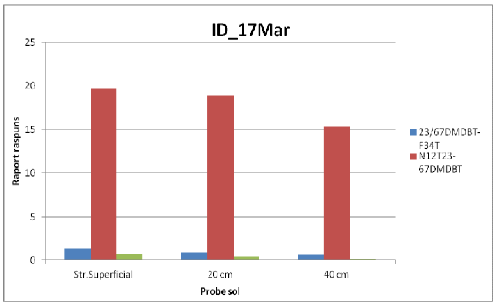
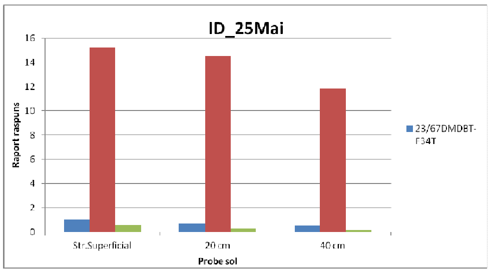


Table 7. Soil sample collected in 25 May

Relative mass ratios	Superficial layer	20 cm	40 cm
23/67DMDBT-F34T	1.02	0.7072	0.5168
N12T23-67DMDBT	15.232	14.552	11.832
3PhBT-31NBT	0.612	0.2992	0.136



For the animal incinerator area soil samples were obtained a specific profile of PASH compounds as shown in table 8,9 and 10.

Table 8. Soil sample collected in 23 February.

Relative mass ratios	Superficial layer	20 cm	40 cm
23/67DMDBT-F34T	0.69	0.51	0.42
N12T23-67DMDBT	0.07	0.062	0.03
3PhBT-31NBT	0.25	0.21	0.12

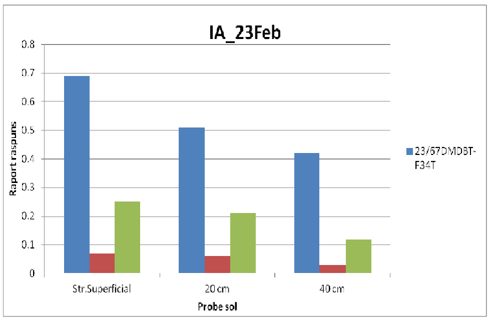


Table 9. Soil sample collected in 17 March.

Relative mass ratios	Superficial layer	20 cm	40 cm
23/67DMDBT-F34T	0.62	0.458	0.377
N12T23-67DMDBT	0.062	0.055	0.026
3PhBT-31NBT	0.224638	0.188	0.107

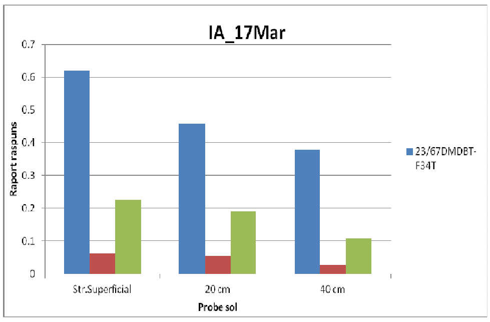
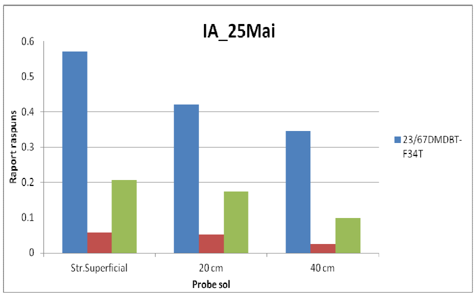


Table 10. Soil sample collected in 25 May.

Relative mass ratios	Superficial layer	20 cm	40 cm
23/67DMDBT-F34T	0.57	0.421	0.346
N12T23-67DMDBT	0.057	0.051	0.024
3PhBT-31NBT	0.206	0.173	0.099



For the highway area soil samples were obtained a specific profile of PASH compounds as shown in table 11,12 and 13.

Table 11. Soil sample collected in 23 February.

Relative mass ratios	Superficial layer	20 cm	40 cm
23/67DMDBT-F34T	4.78	2.45	2.01
N12T23-67DMDBT	1.83	1.62	1.45
3PhBT-31NBT	3.87	3.72	3.61

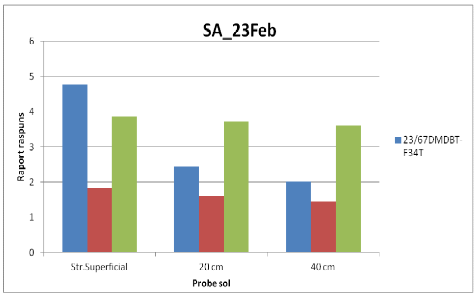


Table 12. Soil sample collected in 17 March.

Relative mass ratios	Superficial layer	20 cm	40 cm
23/67DMDBT-F34T	3.12	2.7	1.1
N12T23-67DMDBT	4.12	3.565	1.452
3PhBT-31NBT	3.3	2.855	1.163

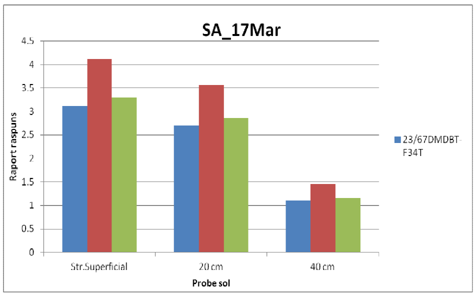
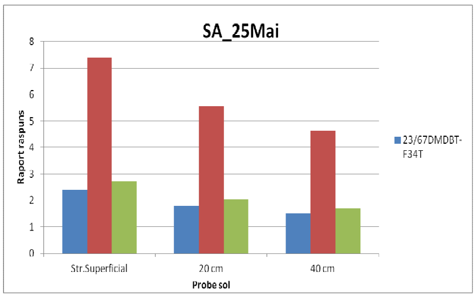


Table 13. Soil sample collected in 25 May.

Relative mass ratios	Superficial layer	20 cm	40 cm
23/67DMDBT-F34T	2.4	1.8	1.5
N12T23-67DMDBT	7.39	5.542	4.618
3PhBT-31NBT	2.72	2.04	1.7



Conclusions

An analytical method was developed to identify the corresponding pollution profiles of different sources. The method provides sufficient sensitivity and separation capacity to identify and quantify six PASH compounds used for determination of specific profiles of different pollution sources. The limit of detection and recovery satisfy the needs for the study purpose. Analysis of incinerator area soils shows distinctive profiles, while the highway area soil presents different profiles in each collecting period. The different profiles of the highway area soils could be explained by the auto traffic on the highway. The highway A2 is extensively used to travel from Bucharest to Constanta. In the cold season very few personal automobiles travel to Constanta and the highway it is mostly used by tucks. The trucks use diesel engines leading to the specific profile of PASH compounds from February. In March, it is an increasing of gasoline engines due to the personal automobiles that run to Constanta. Due to the short holiday in May, the number of gasoline engines on the highway increased and that leads to the specific profile obtained for the soil collected in May. The obtained profiles demonstrated that the developed method is optimal to identify the pollution sources from the various city areas.

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