

OPTIMIZATION OF ULTRASONIC EXTRACTION FOR DETERMINATION OF 16 POLYCYCLIC AROMATIC HYDROCARBONS IN AIR PARTICLE

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Received: 20 January 2018; Accepted for publication: 6 April 2018

Abstract. The aim of this study is to develop a quick ultrasonic extraction procedure for determination of 16 typical polycyclic aromatic hydrocarbons (PAHs) in air particles. The determination and quantification of PAHs in air particles samples were performed using gas chromatography coupled to mass spectrometry (GC-MS) with the aid of deuterated PAH internal standards. One μg mixture of PAHs was spiked to a quarter of quartz fiber filter and extracted with four different solvents/solvent mixtures (methanol:dichloromethane, acetone:dichloromethane; acetone:hexane; dichloromethane). Ultrasonic extraction was carried out in dark at uncontrolled and controlled ultrasonic temperature (25-28 °C). The unique extraction time (20 min) was applied for all experiments. The results showed that high recovery rate of PAHs (82-108 %) were obtained with dichloromethane (as extraction solvent) in dark at ultrasonic temperature of 25 to 28 °C, while generally low recovery rate of PAHs, especially naphthalene (57 %) was obtained with methanol:dichloromethane (1:1). The ultrasonic extraction method with dichloromethane showed good reproductivity and repeatability with relative standard deviation of 16 PAHs below 6.14 %, confirming that samples analyses were precise. Analytical results of PAHs in air particles collected in Hanoi using the developed ultrasonic extraction procedure showed that 15 out of 16 PAHs were detected, in which high molecular weight (MW) PAHs (>5 rings) were abundant compared to low molecular weight PAHs (< 3 rings). This developed ultrasonic extraction method is quick, easy and sufficient for determination of PAHs in air particle.

Keywords: air particle, GCMS, PAH, extraction, analytical method.

Classification numbers: 3.2.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are included in the European Union and US Environmental Protection Agency (USEPA) priority pollutant lists because PAHs represent the

largest group of compounds that are mutagenic, carcinogenic, and teratogenic [1, 2]. Particle-associated PAHs may reach and deposit in the lungs causing a negative effect on human health. USEPA listed 16 main PAHs, where some are considered probably human carcinogens (IACR) in recent monograph [3] classified benzo[a]pyrene as human carcinogens (Group 1), benz[a]anthracene as probable human carcinogens (Group 2A) and chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene) as possible human carcinogens (Group 2B).

PAHs are formed during incomplete combustion of wood or coal burning, combustion of fuels in engines, forest fires incidence, etc. These compounds consist only of carbon and hydrogen in two or more fused aromatic rings [4]. In the atmosphere, these compounds can be present in the vapor phase (low molecular weight PAHs, 2-3 rings) and associated with the particle phase (higher molecular weight PAHs, more than 4 rings) [4].

Recently, the proliferation of motor transport, rather than industrial activities, is advanced in political and/or commercial cities, it provides the main contribution to growing levels of pollution such as PAHs. Numerous studies of atmospheric PAHs conducted in Europe, North America, and Northeast Asia have found that automobiles were the major contributor to PAHs in the urban atmosphere [5, 6]. On the other hand, motorbikes are the most popular vehicle in many Asian countries such as Taiwan, Malaysia, Thailand, Cambodia, Vietnam, Indonesia, and the Philippines owing to its convenience and cheaper expense, which suggests that motorbikes might be major contributors to the atmospheric PAHs burden in urban areas of Asian countries. According to the results of the Center for Environmental Monitoring (VEA) for environmental air quality monitoring in 2016 which showed that concentration of PM_{2.5} in Hanoi was over 3 times higher than the limitation value of the national standard for ambient air quality (QCVN 05: 2013/ BTNMT) and 7 times higher than those recommended by the World Health Organization. Previously, MONRE has reported that elevated concentration of air particles was seen at high density populated areas (e.g Hanoi and Ho Chi Minh City), particularly in the road side at the rush hours due to the increasing the number of vehicles [7]. The high concentration of particles in the atmosphere, especially fine particles (PM_{2.5}), affects to human health. Fine particles with micro size are usually acidic that persist and easily spread in the atmosphere. Therefore, it has a significant effect on human health [8].

Recent researches [9, 10, 11] have demonstrated that air particles absorb and carry many semi-volatile organic compounds such as polycyclic aromatic hydrocarbons (PAHs), paraffin, carbonylic compounds (n-alkanals, n-alkanones, aromatics, dicarbonylic acid, cis-pinonic acid, etc.), persistent organic pollutants, (polychlorinated biphenyl, organochlorine pesticides, dioxin like compounds, plant protection chemicals, etc.); especially, PAH is one of the major pollutants in urban areas with heavy traffic density such as Hanoi and Ho Chi Minh City. The different sources of pollution carry different components of organic pollutants therefore when we are exposed to these organic chemicals, it may cause the irritation of the eyes, nose, throat, headache, dizziness or visual disturbances; destruction of blood cells, liver cells, kidneys, dermatitis, damage to the central nervous system [12, 13, 14]. Since particles absorb many organic compounds and PAH is one of the major target pollutants in urban areas of Vietnam, moreover the reliable data of these pollutants in air particles is still limited in the country. Therefore, it is needed to study an extraction and analytical process in order to determination and quantification of PAH in air particles accurately. Various extraction and analytical processes for PAHs in airborne particles have been developed in the world, however they are mainly focused on the application of high performance liquid chromatography (HPLC) analyzers accompanied with complex extraction procedure. These methods are usually time consuming

and costly. Therefore, the objective of this study is to optimize the ultrasonic extraction process for determination of 16 PAHs in air particles with the use of gas chromatography–mass spectrometry, which is rather popularly available. This would be a rapid extraction and analytical, and cost-effective method, which is suitable with the present research condition in Vietnam. As a result, optimized ultrasonic extraction method was applied to analyze the occurrence of 16 PAHs in air particles in Hanoi. The primary results obtained will be the baseline data for the management authorities to propose appropriate solutions and countermeasures to overcome and improve air quality in Vietnam, particularly in urban areas.

2. MATERIALS AND METHODS

2.1. Reagents and materials

Sixteen mixed PAH (Table 1) stock standard solutions, 2000 $\mu\text{g mL}^{-1}$, in dichloromethane (CRM47930, QTM PAH Mix) was obtained from Supelco, Bellefonte, PA, USA. Appropriate dilutions of the standard solution with dichloromethane were made to the working solutions. Six internal standards (Table 1) were purchased from Wellington Laboratories (Ontario, Canada), Sigma–Aldrich Japan K.K. (Tokyo, Japan) and Restek (Bellefonte, PA, USA) and were used in a 10 $\mu\text{g mL}^{-1}$ hexane solution (IS).

All of solvents used (acetone, dichloromethane, methanol and n–hexane) were of pesticide residue purchased from Kanto Chemical Co. (Tokyo, Japan). Sodium sulfate (Na_2SO_4) at grade of 99% was supplied by Kanto Chemical Co. Quartz fiber filter (QR-100, 203×254 mm) was purchased from Advantec Toyo Kaisha, Ltd. Purified water generated by a Milli-Q system (Milli-Q Biocel, Millipore, USA) was washed with dichloromethane twice before used.

Table 1. PAH and internal standard compounds.

No	PAH	Internal standard
1	Naphthalene	1,4- Dichlorobenzene-d4
2	Acenaphthylene	Naphthalene -d8
3	2-Bromonaphthalene	Acenaphthene-d10
4	Acenaphthene	Anthracene-d10
5	Fluorene	Chrysense-d12
6	Phenanthrene	Perylene-d12
7	Anthracene	
8	Fluoranthene	
9	Pyrene	
10	Benzo(a)anthracene	
11	Chrysense	
12	Benzo(b)fluoranthene	
13	Bennzo(a)pyrene	
14	Ideno(1,2,3-cd)pyrene	
15	Dibenz(a,h)anthracene	
16	Benzo(g,h,i)perylene	

2.2. Preparation and extraction of sample

Half of a quartz fiber filter was cut into small species and placed in a 50 mL of brown centrifuge tube (Figure 1). Mixture of 16PAH compounds (1 ng) were spiked in to the centrifuge tube containing cut quartz filter and 20 mL of extraction solvent was added. The sample was ultrasonically agitated in the ultrasonic bath for 20 min. After that, the sample was centrifuged in 10 min (2000 rpm). The extraction solution was collected into a 50 mL evaporating flask. This extraction procedure was repeated twice with solvent volume of 15 mL each. Combined extraction solution was concentrated to approximately 1 mL using a rotary evaporator, and then 5 mL hexane was added to the extract and further concentrated to 1 mL by using gentle nitrogen stream. The concentrate was applied to a Na_2SO_4 column to remove water. After adding $1\mu\text{g}$ of internal standards to the final concentrate (about 1 mL), the 16 PAHs compounds in the samples was determined and quantified by GC/MS instrument.

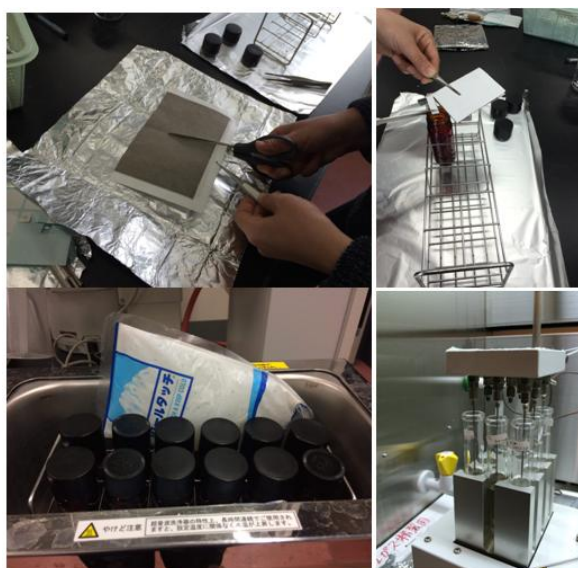


Figure 1. Preparation and extraction of air particle sample.

2.3. Selection of solvent for the extraction

Different solvents: dichloromethane; acetone: dichloromethane (1:1); acetone: hexane (1:1); methanol: dichloromethane (1:1) were monitored to select a solvent/ solvent mixture for the extraction of the 16 PAHs from the air particles. The procedure of the extraction was almost the same as described previously.

2.4. Selection of extraction condition

When using ultrasonic extraction, the temperature of sonication bath gradually increases in proportion with extraction time. Some PAHs are usually decomposed by light and temperature during extraction processes, especially for the PAHs with low molecular weight (less than 4 rings). Therefore, in order to prevent the effects of light during extraction, the sample is placed in a brown centrifuge tube and extracted under the dark conditions. The temperature of sonication bath was monitored at two conditions: (1) extraction at normal temperature and (2) extraction at controlled temperature of 25-28 °C.

2.5. Chromatographic conditions

1 μl of the extract was injected onto the GCMS, utilizing the sample injector. Capillary column DB5-MS was used for the separation of 16 PAHs with selected ion monitoring (SIM). Measurement condition of GCMS was shown in Table 2. A calibration curve for 16 PAHs was made with concentration points of each compound of: 1000, 500, 100, 50, 25, 10, 5, 0.5 and 0.1 ng mL^{-1} . All calibration curves of 16 PAHs have good linearity with correlation coefficient values of over 0.9999.

Table 2. Measurement condition of GC-MS.

GC-MS	Shimadzu GCMS-QP 2010 Plus
Column	J&W DB-5 ms (5% phenyl-95% methylsilicone) fused silica capillary column, 30 m X 0.25 mm i.d., 0.25 μm film
Column temperature	2 min at 40°C, 8°C/min to 310°C, 5 min at 310°C
Injector	250°C
Transfer line	300°C
Ion source	200°C
Injection method	splitless, 1 min for purge-off time
Carrier gas	He
Linear velocity	40 cm/s, constant flow mode
Ionization method	EI
Tuning method	target tuning for US EPA method 625
Measurement method	SIM/Scan
Scan range	45 amu to 600 amu
Scan rate	0.3 s/scan

2.6. Statistical analysis

Statistical analysis was performed using Microsoft Excel 2007 (Microsoft Japan, Tokyo, Japan).

3. RESULTS AND DISCUSSION

3.1. Extraction efficiency of PAHs using different solvents

Recoveries of 16 PAHs using different extraction solvents were showed in Table 3. Analytical results of 16 PAHs using mixture of methanol and dichloromethane (1:1) showed that high recovery rate (> 80 %) was seen for 8 PAH, while remaining 7 PAHs in the range 72-78 %. Especially naphthalene had low recovery rate (57 %), which probably due to its low molecular weight, therefore it is easily decomposed during extraction process.

The recovery rate was quite high in the range of 80-112 % for 15 out of 16 PAHs when using acetone:dichloromethane (1:1) as the extraction solvent. Slightly low recovery rate (71 %) was observed for naphthalene. Another experiment was carried out using acetone: hexane (1:1) for extraction of 16 PAHs in air particles, it showed that 8 PAHs had recovery rates in the range of 73-99 %, while 6 PAHs had values in the range of 72-78 %, however naphthalene and fluorene showed low recovery rate of 65 % and 69 %, respectively. The good recovery rate (82-108 %) was observed for 16 PAHs when using dichloromethane as an extraction solvent.

Table 3. Recoveries of 16 PAHs using different extraction solvents.

No	Compound	Recovery of PAH, %			
		DCM	Ace: DCM (1:1)	Ace: Hex (1:1)	MeOH:DCM (1:1)
1	Naphthalene	82.7	71.0	64.9	57.3
2	Acenaphthylene	94.8	98.0	85.5	97.8
3	2-Bromonaphthalene	85.3	83.1	77.3	76.3
4	Acenaphthene	90.8	80.9	74.0	75.5
5	Fluorene	85.8	82.1	69.3	76.1
6	Phenanthrene	85.0	86.0	73.8	78.0
7	Anthracene	92.0	93.2	79.7	82.3
8	Fluoranthene	100	101	83.4	93.3
9	Pyrene	81.6	81.0	73.4	71.5
10	Benzo(a)anthracene	104	104	93.7	94.7
11	Chrysense	86.9	86.4	79.4	78.4
12	Benzo(b)fluoranthene	108	112	93.6	98.7
13	Bennzo(a)pyrene	98.0	97.0	87.9	79.9
14	Ideno(11,2,3-cd)pyrene	84.4	84.7	83.0	81.2
15	Dibenz(a,h)anthracene	86.4	85.5	79.6	82.4
16	Benzo(g,h,i)perylene	90.1	80.1	78.2	76.6

DCM: Dichloromethane; Ace: acetone; Hex: Hexane; MeOH: methanol.

Table 4. Recoveries of 16 PAHs at normal and controlled temperature.

No	Compound	Recovery PAH, %	
		24-28 °C	Normal temperature
1	Naphthalene	84	77
2	Acenaphthylene	96	88
3	2-Bromonaphthalene	90	84
4	Acenaphthene	90	80
5	Fluorene	87	85
6	Phenanthrene	86	85
7	Anthracene	94	88
8	Fluoranthene	93	93
9	Pyrene	91	86
10	Benzo(a)anthracene	98	89
11	Chrysense	85	84
12	Benzo(b)fluoranthene	109	97
13	Bennzo(a)pyrene	95	97
14	Ideno(11,2,3-cd)pyrene	89	84
15	Dibenz(a,h)anthracene	89	85
16	Benzo(g,h,i)perylene	92	89

In overall comparing the recovery rate of 16 PAHs using different solvents/ solvent mixture (Figure 2) showed that dichloromethane appeared at good recovery (82-108 %) for all 16 PAHs studied. Therefore dichloromethane is a suitable solvent for extraction of PAHs in air particle samples using ultrasonic extraction.

3.2. Extraction efficiency of PAHs at different extraction condition

The investigated sample was placed in a brown centrifuge tube and extracted under the dark conditions. Extraction efficiency of 16 PAHs was monitored at normal condition and at controlled temperature of 25-28 °C. The results (Table 4) showed that, recoveries of PAHs were not significantly different in the two monitored conditions, although the PAH results were slightly higher when temperature was adjusted at 25-28 °C. The recovery of naphthalene at normal condition was 77 %, i.e. lower than the controlled temperature (84 %). Therefore, maintaining the sonication bath at a temperature in the range of 25-28 °C is the best for ultrasonic extraction of PAHs in air particles.

3.3. Examination of accuracy and reproductivity of optimization ultrasonic extraction method

Table 5. Analytical results of blank samples and spiked air particle samples.

No	Compound	Recovery of PAH, %						Average, RSD,	
		Blank	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	%	%
1	Naphthalene	0	88.4	82.4	81.8	82.8	81.0	83.3	3.56
2	Acenaphthylene	0	86.9	94.0	91.4	93.8	91.1	91.4	3.13
3	2-Bromonaphthalene	0	93.7	88.1	85.6	87.8	85.3	88.1	3.82
4	Acenaphthene	0	93.4	87.8	85.3	87.6	85.1	87.9	3.83
5	Fluorene	0	90.2	84.7	84.4	84.5	82.1	85.2	3.49
6	Phenanthrene	0	89.4	84.0	81.6	83.8	81.4	84.0	3.83
7	Anthracene	0	97.4	91.5	88.9	91.3	88.7	91.6	3.83
8	Fluoranthene	0	96.8	90.9	91.2	90.7	88.1	91.6	3.45
9	Pyrene	0	95.4	89.7	87.1	89.4	86.9	89.7	3.82
10	Benzo(a)anthracene	0	84.8	95.7	92.9	95.5	92.7	92.3	4.76
11	Chrysene	0	89.8	84.9	82.8	84.2	82.0	84.7	3.61
12	Benzo(b)fluoranthene	0	97.4	107	104	107	103	104	3.66
13	Benzo(a)pyrene	0	97.0	95.0	86.3	94.1	91.7	92.8	4.42
14	Ideno(1,2,3-cd)pyrene	0	91.7	89.2	86.7	88.5	86.2	88.5	2.50
15	Dibenzo(a,h)anthracene	0	99.5	89.1	86.6	88.3	86.1	89.9	6.14
16	Benzo(g,h,i)perylene	0	97.5	92.1	89.5	91.3	89.0	91.9	3.68

After selection of suitable extraction solvent (dichloromethane) and extraction condition (at the dark and at ultrasonic temperature of 25-28 °C), we have analyzed repeatability of air particle samples, which were spiked (1 ng each) with the mixture of 16 PAHs. The samples were extracted 3 times with dichloromethane (20 mL, 15 mL, and 15 mL for each extraction) in the dark and at controlled temperature of 25-28 °C. Two blank samples were extracted along with 5 air particle samples with the same procedure in order to examine the contamination during extraction processes. Analytical results were shown in Table 5.

Analytical results of blank sample showed that there is no contamination during extraction and analysis processes. Average recovery of 16 PAHs in was over 83 % with standard deviation in the range of 2.50-6.14 %. This can be concluded that this ultrasonic extraction method using dichloromethane as the extraction solvent produced a good reproductively and repetability and suitable for extraction of PAHs in the air particles.

3.4. Ultrasonic extraction procedure for 16 PAHs in the air particle

Ultrasonic extraction procedure for 16 PAHs in the air particle are showed in Figure 3. The optimized ultrasonic extraction method for extracting PAHs in air particles is quick, and cost-effective. The extraction steps were minimized therefore it avoids contamination. This method produced the high recoveries for 16 PAHs with good repeatability and reproductivity.

3.5. Results of PAHs in air particles in Hanoi using optimized ultrasonic extraction method

The optimized ultrasonic extraction method was applied to analyze the occurrence of 16 PAHs in the air particles that collected in Hanoi.

3.5.1. Preparation of quartz fiber filter

Prior to use of quartz fiber filters for air particle sampling, the filters were equilibrated in a desiccator at room temperature for 48 hours and weighted before and after sampling. Each filter was wrapped in an aluminum foil envelop and placed in a lockable polypropylene bag until extraction [15].

3.5.2. Air particle collection and extraction

Two air particle samples were collected at Pham Van Dong road at the height of 3.0 meters by Kimoto high volume air sampler system (Model-120H) on April 12th and 13th, 2017. Sampling time for each sample was 8 hours (from 9:00 to 17:00). Air flow was adjusted at the rate of 400 liters per min. Total air volume for the sample 1 and 2 was 208 and 232 m³, respectively. A half of filter after sampling was used to analyze PAHs using above optimized ultrasonic extraction method.

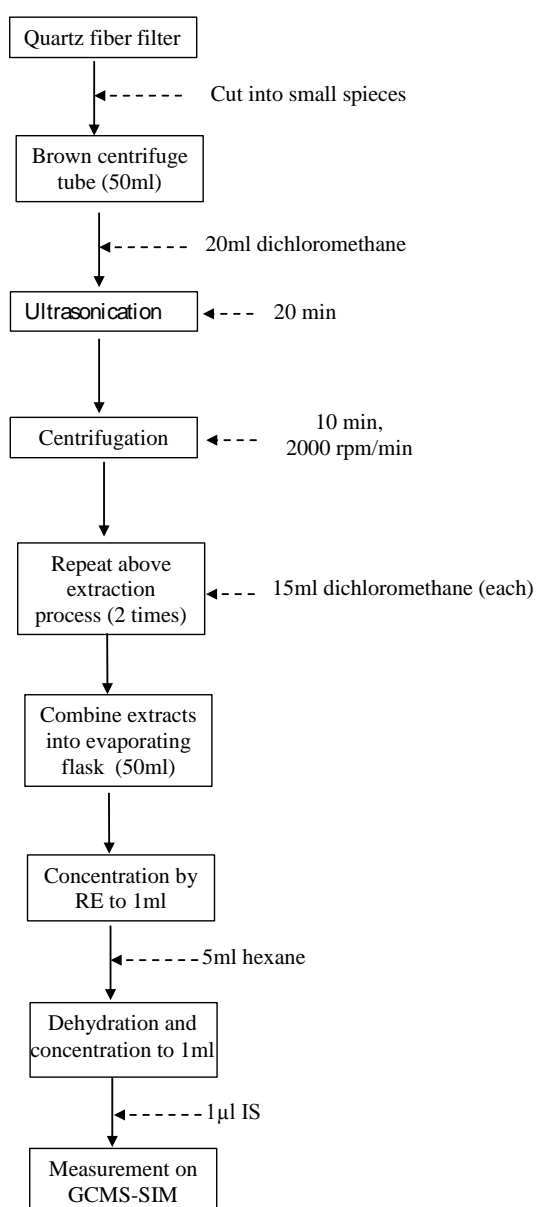


Figure 2. Ultrasonic extraction procedure for 16 PAHs in the air particle.

3.5.3. Analytical results of air particle samples

Analytical results of two air particle samples (Table 6, Figure 4-5) showed that 15 out of 16 pahs were detected. Pahs with high molecular weight (> 5 rings) such as benzo(b)fluoranthene, bennzo(a)pyrene, ideno(11,2,3-cd)pyrene, benzo(g,h,i)perylene were detected at high concentration, especially benzo(b)fluoranthene was seen at elevated value of 3.22 ng m^{-3} and 2.08 ng m^{-3} . Ideno(11,2,3-cd)pyrene and benzo(g,h,i)perylene were also detected at concentration of over ng m^{-3} . However, low molecular pahs (< 3 rings) were detected at slightly low concentration (< 0.1 ng m^{-3}), while PAH 4 rings was detected at concentration in the range of $0.12\text{-}0.59 \text{ ng m}^{-3}$. 2-Bromonaphthalene was not detected in investigated air particle samples.

Table 6. Analytical results of two air particle samples.

No	PAH	Sample 1	Sample 2	Sample 1	Sample 2
		ng		ng/m ³	
1	Naphthalene	7.26	7.74	0.07	0.07
2	Acenaphthylene	4.85	8.22	0.05	0.07
3	2-Bromonaphthalene	0	0	0	0
4	Acenaphthene	0.29	1.21	0.003	0.01
5	Fluorene	1.64	5.65	0.016	0.05
6	Phenanthrene	25.2	38.4	0.24	0.33
7	Anthracene	5.66	13.8	0.05	0.12
8	Fluoranthene	51.9	56.8	0.50	0.49
9	Pyrene	61.3	68.8	0.59	0.59
10	Benzo(a)anthracene	41.2	36.7	0.39	0.32
11	Chrysene	61.8	62.8	0.59	0.54
12	Benzo(b)fluoranthene	335	241	3.22	2.08
13	Benzo(a)pyrene	139	88.1	1.34	0.76
14	Indeno(1,2,3-cd)pyrene	234	208	2.25	1.79
15	Dibenz(a,h)anthracene	20.4	83.7	0.19	0.72
16	Benzo(g,h,i)perylene	299	213	2.88	1.84

4. CONCLUSIONS

The ultrasonic extraction procedure for determination of 16 typical polycyclic aromatic hydrocarbons (PAHs) in air particles was optimized. This method is quick, simple and cost-effective. The extraction steps were minimized therefore it avoids contamination. Moreover, the method produced the high recovery rates for 16 PAHs with good repeatability and reproductivity.

In addition, this method was successfully applied to analyze PAHs in two air particle samples collected at Pham Van Dong road in Hanoi. The preliminary results showed that high molecular weight PAHs (> 5 rings) were detected at high concentrations while opposite trend was seen for low molecular weight PAHs (about 10 times lower). Accordingly, the elevated vehicle density (especially motorcycle) was considered to be the main contributor to PAH inputs in the air particles in Hanoi.

Acknowledgements. This study was supported by Vietnam Academy of Science and Technology; project Number VAST.ĐLT 10/17-18. The authors wish to thank Professor Kiwao Kadokami (Faculty of Environmental Engineering, The University of Kitakyushu, Japan) for his great supports, useful comments, and constructive suggestions on this manuscript.

REFERENCES

1. Sverdrup L. E., Nielsen T., Krogh P. H. - Soil ecotoxicity of polycyclic aromatic hydrocarbons in relation to soil sorption, lipophilicity, and water solubility, Environ. Sci. Technol. **36** (2002) 2429-2435.

2. Qiao M., Wang C., Huang S., Wang D., Wang Z. - Composition, sources, and potential toxicological significance of PAHs in the surface sediments of the Meiliang Bay, Taihu Lake, China. *Environ. Int.* **32** (2006) 28-33.
3. International Agency for Research on Cancer (IARC) - Agents Classified by the IARC Monographs, Lyon, France. <http://monographs.iarc.fr/ENG/Cassification/index.php> (assessed January 2018).
4. Ravindra K., Sokhia R., Van Grieken R. - Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation, *Atmos. Environ.* **42** (2008) 2895-2921.
5. Chang K. F., Fang G. C., Chen J. C., Wu Y. S. - Atmospheric Polycyclic Aromatic Hydrocarbons (PAHs) in Asia: A Review from 1999 to 2004, *Environ. Pollut.* **142** (2006) 388-396.
6. Albinet A., Leoz-Garziandia E., Budzinski H., Villenave E. - Polycyclic Aromatic Hydrocarbons (PAHs), Nitrated PAHs and Oxygenated PAHs in Ambient Air of the Marseilles Area (South of France): Concentrations and Sources, *Sci. Total. Environ.* **384** (2007) 280-292.
7. Ministry of Natural Resources and Environment of the Socialist Republic of Viet Nam, Vietnam National Environmental Report 2013 - Air environment. <http://vea.gov.vn/vn/hientrangmoitruong/baocaomtquocgia/Documents/Bao%20cao%20moi%20truong%20quoc%20gia%202013.pdf> (assessed January 2018).
8. National Environmental Report www.iges.or.jp/files/network/PDF/IIASA/20150310/S1B-3_Nguyen.pdf (assessed January 2018).
9. Fontal M., van Drooge B. L., López J. F, Fernández P., Grimalt J. O. - Broad spectrum analysis of polar and apolar organic compounds in submicron atmospheric particles, *J. Chromatogr. A.* **1404** (2015) 28-38.
10. Mesquita S. R., van Drooge B. L., Oliveira E., Grimalt J. O., Barata C., Vieira N., Guimarães L., Piña B. - Differential embryotoxicity of the organic pollutants in rural and urban air particles, *Environ. Pollut.* **206** (2015) 535-542.
11. Růžičková J., Raclavská H., Raclavský K., Juchelková D. Phthalates in PM_{2.5} airborne particles in the Moravian-Silesian Region, Czech Republic. *Perspectives in Science.* **7** (2015) 178-183.
12. Pope C.A., Burnett R.T., Thun M.J., Calle E.E., Krewski D., Ito K., Thurston G. D. - Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution, *J. Am. Med. Assoc.* **287** (2002) 1132-1141.
13. Raaschou-Nielsen O., Andersen Z. J., Hvidberg M., Jensen S. S., Ketzel M., Sørensen M., Loft S., Overvad K., Tjønneland A. - Lung cancer incidence and long-term exposure to air pollution from traffic, *Environ. Health Perspect.* **119** (2011) 860-865.
14. Topinka J., Rossner P. Jr., Milcová A., Schmučerová J., Pěnčíková K., Rossnerová A., Ambrož A., Štolcpartová J., Bendl J., Hovorka J., Machala M. - Day-to-day variability of toxic events induced by organic compounds bound to size segregated atmospheric aerosol, *Environ. Pollut.* **202** (2015)135-145.
15. Hien T. T., Thanh L.T., Kameda T., Takenaka N., Bandow H. - Distribution characteristics of polycyclic aromatic hydrocarbons with particle size in urban aerosols at the roadside in Ho Chi Minh City, Vietnam. *Atmos. Environ.* **41** (2007) 1575-1586.