

ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS IN SETTLED DUST: DEVELOPMENT OF A SIMPLE SAMPLE PREPARATION METHOD

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TÓM TẮT

PHÁT TRIỂN PHƯƠNG PHÁP XỬ LÝ MẪU ĐƠN GIẢN CHO PHÂN TÍCH HYDROCARBON THƠM ĐA VÒNG TRONG MẪU BỤI LẮNG

Hydrocarbon thơm đa vòng (PAHs) là một nhóm chất ô nhiễm hữu cơ điển hình với những đặc điểm chung như tồn tại phổ biến trong môi trường, bền vững, có khả năng tích lũy sinh học và có độc tính. Quy trình phân tích PAHs trong mẫu môi trường nhìn chung tương đối phức tạp và đòi hỏi nhiều công đoạn xử lý mẫu như tách chiết và làm sạch dịch chiết. Trong nghiên cứu này, một số kỹ thuật chiết và làm sạch dịch chiết cho phân tích PAHs trong mẫu bụi lắng được khảo sát để đề xuất một phương pháp xử lý mẫu đơn giản, hiệu quả. PAHs (16 chất ưu tiên nghiên cứu theo US EPA) được phân tích trên hệ thống sắc ký khí khối phổ (GC/MS). Quá trình rửa giải PAHs cũng được khảo sát cho 2 loại cột hấp phụ chứa silica gel và Florisil. Cột silica gel được lựa chọn vì khả năng hấp phụ phù hợp biểu hiện qua thể tích dung môi rửa giải nhỏ hơn so với cột Florisil. Dịch chiết mẫu được đưa lên cột thủy tinh nhỏ chứa 1 g silica gel và 2 lớp sodium sulfate khan với 4 mL hexane, sau đó PAHs được rửa giải với 6 mL hỗn hợp dung môi dichloromethane/hexane (1:3, v/v). Các kỹ thuật chiết siêu âm sử dụng đầu dò phát siêu âm và bể rung siêu âm được so sánh, cho thấy hiệu quả chiết tương đương. Tuy nhiên, bể rung siêu âm được khuyến cáo sử dụng với các ưu điểm như có thể chiết đồng thời nhiều mẫu và hạn chế sự nhiễm bẩn giữa các mẫu. Mẫu bụi (khoảng 0,2 g) được chiết lần lượt với 2 mL acetone và 2 mL hỗn hợp acetone/hexane (1:1, v/v). Độ thu hồi của PAHs trong toàn bộ quy trình phân tích được xác định trên mẫu bụi thêm chuẩn, dao động từ 60% đến 120% (với RSD < 20%). Giới hạn phát hiện của phương pháp đối với các PAHs dao động từ 0,20 đến 2,0 ng/g. So với các kỹ thuật cổ điển cho phân tích PAHs như chiết Soxhlet và làm sạch trên cột hấp phụ lớn, quy trình phân tích này có ưu điểm vượt trội về thời gian xử lý mẫu ngắn và tốn ít dung môi, hóa chất.

Từ khóa: PAHs, settled dust, ultrasonic extraction, gas chromatography, mass spectrometry.

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are a diverse group of organic pollutants of global concern due to their widespread occurrence, bioaccumulation potentials, and toxicity [1]. PAHs are semivolatile and hydrophobic

contaminants, resulting in their high adsorptivity on particle surface (i.e., settled dust) [5]. Therefore, many studies have determined PAH concentrations in dust with implications for environmental pollution monitoring and human exposure assessment. These studies usually focused on 16 compounds assigned as priority

pollutants by the US Environmental Protection Agency (US EPA), including naphthalene (Nap), acenaphthylene (Acy), acenaphthene (Ace), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flt), pyrene (Pyr), benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenz[a,h]anthracene (DA), indeno[1,2,3-cd]pyrene (IP), and benzo[ghi]perylene (BP) [2].

Trace levels of PAHs in environmental samples have been analyzed by using gas chromatography/mass spectrometry (GC/MS) methods, which require massive sample preparation, labor, and time [4,6,7]. There is no standard method for the analytical procedure of PAHs in dust. The US EPA proposed Method TO-13A for determination of PAHs in ambient air using GC/MS [11]. In this method, the samples (filter or sorbent) spiked with surrogates were Soxhlet extracted with 700 mL of diethyl ether/hexane (1:9) for 18 h. The extract volume was then reduced to 1 mL in hexane by using Kuderna-Danish concentrator. The extract was purified by passing through an activated silica gel column. The column was washed by diethyl ether/hexane (1:9), pre-eluted by 40 mL pentane, sample loaded with a total of 3 mL hexane, washed with 25 mL pentane (to remove aliphatic interferences), and eluted with 25 mL diethyl ether/pentane (1:9). The eluate was concentrated and spiked with internal standards before GC/MS analysis. By using this procedure, about 6 L of solvents and 3 working days are required for a batch of 6 samples.

To reduce consumed chemicals and time, we developed a simple and rapid sample preparation procedure for PAH analysis in settled dust samples. The dust samples were extracted by using two ultrasonication techniques such as direct extraction (ultrasonic processor) and indirect extraction (ultrasonic water bath). Some extract clean-up techniques were also investigated. The proposed method was applied to analyze a representative settled road dust sample with and without native standard spiking.

2. METHODS

2.1. Sample preparation

For matrix-spike samples of extraction tests, a composite road dust sample was prepared by pooling several individual samples. The individual samples were collected on different roads in Hanoi urban area during 2016–2023 period by manual sweeping road surface with non-plastic brushes. The samples were then subsequently sieved through 1-mm and 100- μ m, and homogenized thoroughly. The dust fraction with particle size < 100 μ m was used. The composite sample was stored in a glass bottle at room temperature in dark. Recovery tests for clean-up steps (i.e., sorbent columns) were performed by using solvent-spike samples, which contain known amounts of native standards in hexane. Procedural and solvent blank samples were prepared by using sodium sulfate and hexane, respectively.

2.2. Instrumental analysis

PAHs were analyzed by using an 8890 GC system equipped with a 7010B GC/TQ detector and 7693A autosampler (Agilent Technologies). The separation column was DB-5MS UI (30 m \times 0.25 mm \times 0.25 μ m, stationary phase 5% phenyl 95% methyl polysiloxane; Agilent Technologies). Carrier gas was helium with a flow rate of 1.2 mL/min. The samples were injected to the GC/MS system at splitless mode with injection volume of 1 μ L. Temperature of injection port, interface, and ion source was 300, 310, and 230 $^{\circ}$ C, respectively. The column oven temperature program was initially set at 80 $^{\circ}$ C (hold 1 min), increased to 170 $^{\circ}$ C (20 $^{\circ}$ C/min), to 220 $^{\circ}$ C (4 $^{\circ}$ C/min), to 270 $^{\circ}$ C (3 $^{\circ}$ C/min), and finally to 310 $^{\circ}$ C (20 $^{\circ}$ C/min, hold 20 min). The MS detector was operated in electron impact ionization (EI, 70 eV) and selected ion monitoring (SIM) modes.

3. RESULTS AND DISCUSSION

3.1. Elution tests of clean-up columns

To evaluate retention behavior of PAHs on small sorbent columns, we prepared two columns, assigned as S column (containing 1 g activated silica gel, capped with two sodium sulfate layers)

and F column (containing 1 g activated Florisil, capped with two sodium sulfate layers). After dry packing, the columns were washed with 5 mL dichloromethane (DCM) and 5 mL hexane. Blank-spike samples (50 ng each native PAH in 0.5 mL hexane in a glass tube) were loaded to the columns. The tube was washed 3 times with a total of 1.5 mL hexane. This first 2-mL portions of hexane were assigned as samples S1 and F1 for silica and Florisil columns, respectively. The columns were washed by additional 4 portions of 2-mL hexane, resulting in samples S2, S3, S4, S5 (for silica) and F2, F3, F4, F5 (for Florisil). Finally, 4-mL portions of DCM/hexane (1:3) were added to columns, assigned as samples S6 (for silica) and F6 (for Florisil). Recoveries of PAHs through the two columns are shown in Fig. 1.

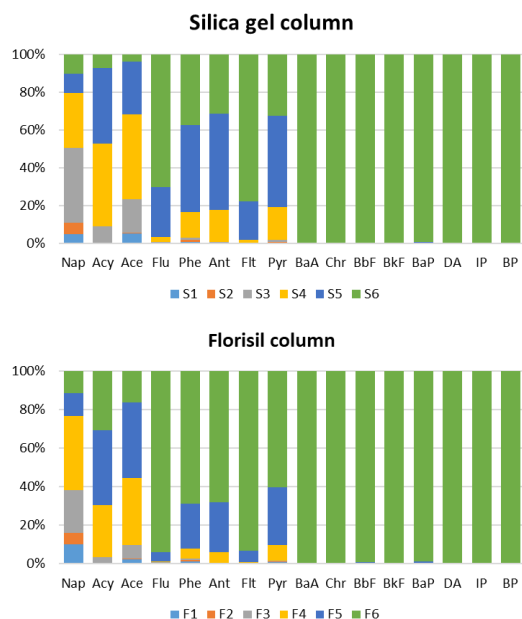


Fig. 1: Recovery of PAHs after column clean-up
Elution patterns of PAHs through the silica gel and Florisil columns are relatively similar. Fractions 1 and 2 elute minor amounts of most PAHs (except for 10–18% of Nap). Considerable proportions of several lighter compounds (e.g., Nap to Pyr) were associated with fractions 3, 4, 5. Meanwhile, the remaining compounds (BaA to BP) were mainly eluted with final fraction of DCM/hexane (1:3). These results are in accordance with those reported by Titaley et al. (2016), which indicated PAHs can be eluted from silica columns by 20% DCM in hexane [10]. The

first 4-mL portions can be discarded because they contain aliphatic interferences. Except for some compounds (e.g., Acy, Ace, Ant, Phe, Pyr) showing higher peak intensity from Florisil column, the remaining compounds were easily eluted from silica gel column. To reduce solvent amounts and time for solvent evaporation, we selected silica gel columns for further experiments. To compensate elution related to fractions 3, 4, 5 (6 mL hexane), after sample loading with a total of 4 mL hexane (fraction 1 and 2), we increased volume of elution solvent (DCM/hexane, 1:3) to 6 mL. This elution volume is also suitable with our column capacity.

3.2. Comparison of extraction techniques

Two dust samples (0.2 g each) were transferred to 10-mL tubes and spiked with surrogates (20 ng each). One sample was extracted with the ultrasonic processor (VCX 130; Sonic & Materials, Inc., US) by 2 mL acetone and 2 mL acetone/hexane (1:1), each time in 10 min (sample P). The other sample was extracted with ultrasonic water bath (WUC-32; Jiayuada, China) by similar solvents, each time in 15 min (sample W). After extraction, the extract fractions were combined and reconstituted in 0.5 mL hexane. The extract was then applied to a silica gel column with 4 mL hexane (discarded) and eluted by 6 mL DCM/hexane (1:3). The eluate was concentrated, spiked with internal standard (chrysene-d12), and conditioned in 200 μ L hexane before GC/MS analysis. The results are shown in Fig. 2.

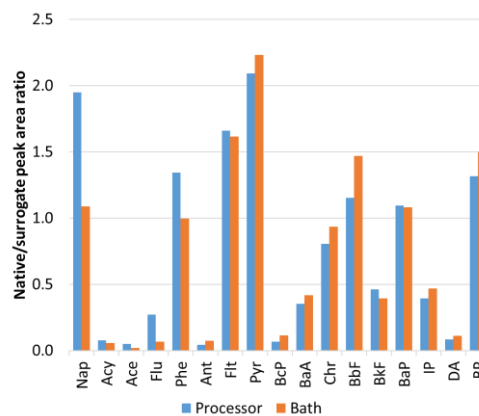


Fig. 2: Extraction efficiency of PAHs from dust obtained by two ultrasonic extraction techniques

Except for Nap and Flu, extraction efficiencies of ultrasonic processor and water bath were relatively comparable for most PAHs. Although ultrasonic processor showed higher signals of Nap and Flu, the use of water bath exhibited advantages on simple operation for multiple samples at the same time without cross contamination risk. Moreover, water bath can provide better yields of some compounds such as Chr, BbF, and BP. One ultrasonic processor can be used for single sample at a time, and requires careful cleaning after each extraction. Therefore, both ultrasonic processor and water bath can be used with consideration of their own advantages and disadvantages. However, the use of ultrasonic water bath is recommended to simultaneously extract several samples with low cross contamination risk.

3.3. Method recovery test

Based on the above investigations, we proposed two analytical procedures for PAHs in dust samples by using ultrasonic processor and ultrasonic water bath. These two procedures were applied to analyze dust samples spiked with both 16 native PAH standards and 7 deuterated surrogates (20 ng each). About 0.2 g dust with spiked standards was extracted subsequently with 2 mL acetone (10 min) and 2 mL acetone/hexane (10 min) by using two different extraction techniques (ultrasonic processor and water bath). After extraction, the extract portions were combined, concentrated, and constituted in 0.5 mL hexane. The clean-up steps were similar for the two procedures. The silica column was washed by 5 mL dichloromethane, 5 mL hexane, loaded with 0.5 mL extract and 3.5 mL hexane, and eluted with 6 mL dichloromethane/hexane (1:3). The eluate was concentrated, spiked with internal standard, and constituted in 0.2 mL hexane before GC/MS analysis.

Chromatograms of spiked dust samples obtained by two procedures are presented in Fig. 3. All peaks can be identified and the background signals are relatively low and stable. There is no significant difference in recoveries of both native and surrogate compounds between the processor and water bath extraction techniques. The recoveries ranged from 60% to 120%, which are within the acceptable levels reported by previous studies on PAHs in dust [3,8,10].

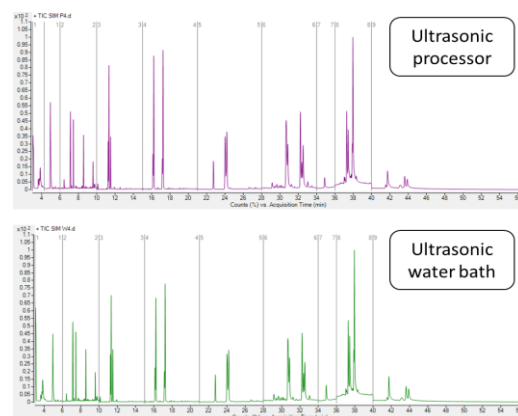


Fig. 3: Chromatograms of PAHs in spiked dust samples obtained by ultrasonic processor and ultrasonic water bath extraction

3.4. Method detection limits and repeatability

To estimate method detection limits (MDLs), we repeatedly analyzed blank samples (sodium sulfate) with and without spiking PAH standards at low levels (5 ng/g). The MDLs of compounds detected in blank samples were estimated as average blank levels plus three standard deviations. The MDLs of compounds not detected in blank samples were calculated as three standard deviations of measured levels in spiked blank samples. MDLs of PAHs ranged from 0.20 to 2.0 ng/g (Table 2), providing good detection efficiency of the method for trace levels of these compounds in dust samples.

Table 2: Repeatability and method detection limits of PAHs in dust samples

Compound	RSD (5 ng/g)	RSD (200 ng/g)	MDL (ng/g)
Nap	8%	5%	2.0
Acy	10%	6%	0.40
Ace	10%	8%	0.40
Flu	6%	5%	0.30
Phe	6%	4%	0.60
Ant	12%	10%	0.70
Flt	8%	6%	0.70
Pyr	16%	12%	0.60
BaA	10%	8%	0.40
Chr	5%	5%	0.80
BbF	5%	6%	0.90
BkF	15%	10%	1.0
BaP	10%	12%	0.20
DA	8%	6%	0.20
BP	12%	10%	0.70
IP	9%	11%	0.30

The repeatability of the analytical procedure was also estimated by triplicate analysis of dust samples spiked with PAH standards at two levels (5 ng/g and 200 ng/g). Relative standard deviations (RSD) of PAHs at spiking levels of 5 ng/g and 200 ng/g ranged from 6% to 16%, and from 4% to 12%, respectively. RSD values lower than 20% of our method were generally acceptable for repeatability criteria of PAHs at ppb levels.

4. CONCLUSIONS

In this study, a simple and rapid sample preparation method was developed for the determination of 16 PAHs in settled dust samples. Two ultrasonic extraction techniques (ultrasonic processor and water bath) were compared, showing generally comparable efficiency. Clean-up techniques were also tested. Clean-up on activated silica gel column with loading and washing solvent as hexane, and eluting solvent as dichloromethane/hexane (1:3) showed acceptable recovery, purification efficiency, and reasonable solvent amount. PAH elution from Florisil columns is somewhat difficult compared to silica columns, which probably requires larger solvent volume and/or polarity. The methods were applied to measure dust-spiked samples, exhibiting recoveries from 60% to 120%. Our results indicate that ultrasonic extraction coupled with small clean-up column can be utilized as an efficient method for the determination of PAHs in dust.

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