Determination of 15 phthalate esters in air by gas-phase and particle-phase simultaneous sampling

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ABSTRACT

Based on previous research, the sampling and analysis methods for phthalate esters (PAEs) were improved by increasing the sampling flow of indoor air from 1 to 4 L/min, shortening the sampling duration from 8 to 2 hr. Meanwhile, through the optimization of chromatographic conditions, the concentrations of 9 additional PAE pollutants in indoor air were measured. The optimized chromatographic conditions required a similar amount of time for analysis as before, but gave high responsivity, the capability of simultaneously distinguishing 15 kinds of PAEs, and a high level of discrimination between individual sample peaks, as well as stable peak generation. The recovery rate of all gas-phase and particle-phase samples of the 15 kinds of PAEs ranged from 91.26% to 109.42%, meeting the quantitative analysis requirements for indoor and outdoor air sampling and analysis. For the first time, investigation of the concentration levels as well as characteristics of 15 kinds of PAEs in the indoor air from four different traffic micro-environments (private vehicles, busses, taxis and subways) was carried out, along with validation of the optimized sampling and analytical method. The results show that all the 9 additional PAEs could be detected at relatively high pollution levels in the indoor air from the four traffic micro-environments. As none of the pollution levels of the 15 kinds of PAEs in the indoor air from the 4 traffic micro-environments should be neglected, it is of great significance to increase the types of PAEs able to be detected in indoor air.

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Introduction

As a group of indoor air pollutants, phthalate esters (PAEs) have become a major concern in the present-day world. Be it in newly decorated houses (Rudel et al., 2003; Wilson et al., 2003; Kanazawa et al., 2010) or public places, such as hospitals, kindergartens, and offices (Bergh et al., 2011; Kasper-Sonnenberg et al., 2014), considerable research on the measurement of PAE concentrations as well as their pollution characteristics in indoor air has

been conducted. However, current sampling and analytical approaches are relatively complex, and lack a unified standard as well. Furthermore, both domestic and foreign sampling methods for PAEs in indoor air mainly involve either the collection of gaseous PAEs, or the PAEs in particulate matter of different particle sizes. Nonetheless, owing to the semi-volatility of PAEs, their concentration in the air is relatively low (ng/m^3–$\mu g/m^3$). Moreover, PAEs exist in both gas- and particle-phases in indoor air. At present, the measurement of particle-phase PAEs in indoor air is considered neither in domestic nor

in foreign studies, which inevitably leads to the underestimation of pollution levels of indoor PAEs.

Currently, the membrane sampling method (Wang et al., 2006; Rakkestad et al., 2007), as one type of sampling method in use, is not suitable for indoor air samples with very low pollutant concentrations, and requires relatively long sampling duration as well as having the potential for bringing secondary pollution into the sampled room; thus the solid absorption method is so far the most frequently employed as well as the most mature approach in the sampling of organics in indoor air. The key to this method is the choice of solid absorbent. For instance, Fromme et al. (2004) chose polyurethane foam (PU) to sample and analyze the PAE concentrations in the indoor air of dormitories as well as kindergartens in Berlin, with a sampling rate of 5 L/min and duration of 7 hr. Yet, this solid absorbent requires a tremendous amount of organic solvent extractant for pre-processing, resulting in waste as well as contamination of the solvent. What's worse, external pollutants may easily be introduced and the sample recovery rate is relatively low (Otake et al., 2001). Therefore, such a method is not suitable for the sampling and investigation of indoor air. Another choice is tandem activated carbon tubes, the sampling velocity and duration of which is 1 L/min and approximately 3 days, respectively. Using activated carbon for sampling has great convenience, but phthalates may be lost because of the prolonged collection and the loss of small-particle activated carbon during centrifugal separation, etc. Toda et al. (2004) proposed a method combining a Sep-Pak PS cartridge with a low-flow sampling pump to sample in residents' rooms at 2 L/min for approximately 24 hr, with a detection limit of 100 ng/m^3. Nevertheless, most Sep-Pak PS sampling kits are plastic products, which may contain PAEs that will introduce new pollutants during the measurement and result in contamination of the sampling tubes. Wang (2007) reported that the XAD-2 adsorbent has higher absorption efficiency than PU for PAEs in the gas-phase, and involves a simple pre-processing procedure and small solvent consumption, as well as economy and convenience. Thus, it has better application potential.

Apart from the study of sampling methods, a considerable number of studies on analytical approaches to measuring PAEs have been carried out globally. Methods that have been reported in early literature mainly involve spectrophotometry (Huang et al., 2012), fluorimetry (Li and Wang, 2005), chromatography (Li et al., 2004; Xiao et al., 2009), etc. As analytical technology develops, chromatography is a frequently used detection method for PAEs in the environment, mainly involving gas chromatography–mass spectrometry (GC–MS), gas chromatography-flame ionization detection (GC-FID), high performance liquid chromatography (HPLC), etc. During actual sample detection, the optimal chromatographic conditions can be chosen in accordance with the characteristics of samples. For example, Fromme et al. (2004) investigated the indoor air of urban apartments and nurseries using GC–MS, which was also utilized by Toda et al. (2004) to measure semi-volatile organics in indoor air, such as PAEs and organophosphates.

Regarding the studies of sampling and analytical methods of PAEs in indoor air, with the consideration of various indexes, involving the representativeness of samples, the cost of detection and analysis, the requirements of technology, and convenience as well as reliability, the most commonly employed and reliable approach currently used in the detection and analysis of PAEs in indoor air is solid absorbent absorption–ultrasound extraction–gas chromatographic analysis. Pei et al. (2013) carried out the simultaneous sampling of particle- and gas-phase PAEs. They also detected and analyzed the concentration levels of 6 kinds of PAEs in newly decorated homes. The total concentration levels of PAEs were relatively high and caused significant pollution. A similar method was also employed in some other studies (Song et al., 2015; Wang et al., 2015), mainly in public places, such as hospitals and offices.

The current study improved the sampling conditions based on the method employed by Pei et al. (2013) for simultaneous collection of particle-phase and gas-phase PAEs by increasing the sampling rate from 1 to 4 L/min so that the efficiency was improved, and the scientific validity of the approaches was compared. Meanwhile, the chromatographic conditions were optimized compared to the method employed by Pei et al. (2013), so that 9 additional PAEs along with the original 6 PAEs were collected and analyzed. The recovery rate ranged from 91.26% to 109.42%. In addition, the optimized method was utilized for measurement in practical environments. This study chose air samples from traffic micro-environments as experimental subjects because the determination of PAEs in indoor air from these environments required a more high-speed sampling method and also because of the complexity and closed nature of traffic micro-environments. Measurements were carried out for the first time in traffic micro-environments for the 15 kinds of PAEs, and all were detected. The degree of discrimination and responsivity of individual sample peaks were relatively high. In addition, the generation of peaks was very stable. Thus, a fundamental method has been established for the identification of types of PAE pollution and the measurement of PAEs concentration in future indoor air investigations.

1. Materials and methods

1.1. Chemicals and materials

HPLC grade chemicals and solvents were used for all extraction and GC analysis. Standard mixtures of M-8061 phthalates, including dimethyl phthalate (DMP), diethyl phthalate (DEP), diisobutyl phthalate (DIBP), dibutyl phthalate (DBP), bis(2-methoxyethyl)phthalate (DMEP), bis(4-methyl-2-pentyl)phthalate (DMPP), bis(2-ethoxyethyl)phthalate (DEEP), dipentyl phthalate (DPP), dihexyl phthalate (DHP), benzyl butyl phthalate (BBP), bis(2-n-butoxyethyl)phthalate (DBEP), dicyclohexyl phthalate (DCHP), bis(2-ethylhexyl)phthalate (DEHP), di-n-octyl phthalate (DNOP), and dinonyl phthalate (DNP) (Table 1), were purchased (AccuStandard, New Haven, CT, USA) as stock solutions in isooctane; all had concentrations of 1.0 mg/mL for each phthalate.

1.2. Sample analysis

1.2.1. Preparation of the standard solution

A standard mixture of phthalates was measured accurately and diluted with methanol to 50 mL in a volumetric flask to make a 10 mg/L mixed standard stock solution of phthalates. Then the 10 mg/L mixed standard stock solution was diluted to prepare

Table 1 – Mixed standard solution contents and properties of PAEs.

Pollutant (abbreviation)	CAS	Molecular formula	Molecular weight	Boiling point (°C)	Density (g/mL)	Peak sequence
Dimethyl phthalate (DMP)	131-11-3	$C_{10}H_{10}O_4$	194.18	283.7	1.19	1
Diethyl phthalate (DEP)	84-66-2	$C_{12}H_{14}O_4$	222.24	295–299	1.12	2
Diisobutyl phthalate (DIBP)	84-69-5	$C_{16}H_{22}O_4$	278.34	327	1.039	3
Dibutyl phthalate (DBP)	84-74-2	$C_{16}H_{22}O_4$	278.34	340	1.043	4
Bis(2-methoxyethyl)phthalate (DMEP)	117-82-8	$C_{14}H_{18}O_6$	282.29	230	1.173	5
Bis(4-methyl-2-pentyl)phthalate (DMPP)	146-50-9	$C_{20}H_{30}O_4$	334.45	–	–	6
Bis(2-Ethoxyethyl)phthalate (DEEP)	605-54-9	$C_{16}H_{22}O_4$	310.34	–	–	7
Dipentyl phthalate (DPP)	131-18-0	$C_{18}H_{26}O_4$	306.4	342	1.025	8
Dihexyl phthalate (DHP)	84-75-3	$C_{20}H_{30}O_4$	334.45	185–187	1.01	9
Benzyl butyl phthalate (BBP)	85-68-7	$C_{19}H_{20}O_4$	312.36	370	1.1	10
Bis(2-n-butoxyethyl)phthalate (DBEP)	117-83-9	$C_{20}H_{30}O_6$	366.45	270	1.06	11
Dicyclohexyl phthalate (DCHP)	84-61-7	$C_{20}H_{26}O_4$	330.42	200–235	1.2	12
Bis(2-ethylhexyl)phthalate (DEHP)	117-81-7	$C_{24}H_{38}O_4$	390.56	386	0.985	13
Di-n-octyl phthalate (DNOP)	117-84-0	$C_{24}H_{38}O_4$	390.56	380	0.980	14
Dinonyl phthalate (DNP)	84-76-4	$C_{26}H_{42}O_4$	418.61	279–287	0.98	15

PAEs: phthalate esters.
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0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 8.0 and 10.0 mg/L solutions, which were used to construct the standard curves for the different phthalates.

1.2.2. Sample collection

Before sampling, all the sampling tubes and the glass fiber filters were baked at 400°C in a muffle furnace (KS60-6.5-12G, Shanghai Y-feng Electrical Furnace Co., China) to remove any previously adsorbed organic compounds, and these instruments were then stored wrapped in aluminum foil. Indoor air samples were collected from four different kinds of traffic micro-environments. The number of air samples collected from busses, subways, taxis and private cars was 105, 40, 30, 60, respectively.

During collection, the samples were collected into a plexiglass sampling head with a glass fiber filter (37 mm in diameter, pore size of 0.45 μm (1820-037, Staplex, USA)) and subsequently a glass tube packed with 2 g XAD-2 adsorbent (1-0357, Sigma-Aldrich, St. Louis, MO,USA), using an electronically controlled air sampler (APEX). The sampling device was set 1.5 m above the floor, with a sampling time of 2 hr, and sampling flow of 4.0 L/min (air pump changes before and after sampling were less than ~5%). When sampling was completed, both ends of the sampling device remained sealed, and samples were returned to the laboratory for immediate processing. Temperature, humidity, and air pressure were recorded using an electronic temperature and humidity instrument (HTC-1, Zhengzhou Beyond Instrument Co., China) and digital air pressure gauge (BY-2003P, Suzhou Taishi Electronic Co., China).

1.2.3. Sample pre-treatment and analysis

Samples were extracted from the XAD-2 adsorbent and glass fiber filters using an ultrasonic cleaner (SK250HP, Shanghai Kudos Ultrasonic Equipment Co., China) for 30 and 25 min, respectively, with a 10 mL mixture of dichloromethane/acetone (1:1, V/V) as the extraction solvent. Then 5 mL of supernatant was transferred into a cuvette with addition of 30 μL dimethylsulfoxide into the solution before evaporation by a high purity nitrogen concentrator (MTN-2800W, Tianjin Automatic Science Instrument Co., China); then, 970 μL methyl

alcohol was added into the cuvette. The solution was filtered with a 0.22 μm organic filter, and transferred into a 1 mL glass vial. The sample was analyzed using a gas chromatograph (FULI9790, Zhejiang Fuli Analytical Instrument Co., China) with a 30 m × 0.25 mm (inner diameter) × 0.25 μm capillary column (DB-5, Agilent Technology Inc., USA). The analysis was performed using the pulsed splitless mode with an injection volume of 2 μL. High purity nitrogen was used as the carrier gas. The column temperature was held at 60°C for 2 min, rose to 240°C with a rate of 15°C/min, then rose to 270°C with a rate of 2°C/min, followed by an increase to 310°C at a rate of 5°C/min and held for 10 min.

2. Results and discussion

2.1. Optimization and verification of sampling conditions

This study optimized the sampling conditions using 4 L/min samplers. In order to test the sampling efficiency of the 4 L/min samplers, a penetration experiment was designed. A penetration experiment is carried out to determine whether the amount of analytes collected by the penetration tubes exceeds a certain percentage (typically 5%) during air sampling.

2.1.1. Testing method

Sampling efficiency was measured by a tandem sampling penetration experiment, which joined two groups of sampling devices together (Table 2). The first group were sampling devices, whereas the second group were testing devices. First, a 30 μg PAE mixed standard solution, with three times the maximum concentration of the mixed standard solutions used for calibration, was added into the sampling device, which was subjected to a collection rate of 4 L/min for 2 hr. In this way, 480 L clean air was transferred through the tandem devices. According to the pre-processing and analysis methods described above, the concentration of PAEs in both groups of sampling devices was measured respectively. The measurement results revealed that none of the PAEs was discovered in the testing devices, implying that the 30 μg PAEs

Table 2 – Sampling efficiency of the 2 different samplers (unit: ng/m^3).

Sampling rate	DMP		DEP		DBP		BBP		DEHP	
	Gas	Particle	Gas	Particle	Gas	Particle	Gas	Particle	Gas	Particle
1 L/min	891.31	262.81	944.08	419.95	1800.7	829.64	1491.57	663.75	2050.29	1110.07
4 L/min	879.09	248.17	939.60	403.46	1788.61	813.13	1468.79	655.72	2018.44	1096.73

(62.5 μg/m^3 air sample) were completely absorbed by the sampling tubes during sample collection. Hence, the sampling efficiency was relatively high.

At the meantime, two different samplers (1 and 4 L/min) were used for repeated sampling at the same location, with results showing that the final analytical outcomes of both devices were not significantly different. Table 3 shows the results of concentration of 6 kinds of PAEs using different samplers. Compared to the other units, the 4 L/min sampler had higher efficiency due to the shorter sampling time, less noise, and was a better size for carrying.

2.2. Optimization and verification of chromatographic conditions

The boiling points of the 15 kinds of PAEs are between 185 and 386°C. Therefore, tests were conducted with reference to the recommended chromatographic conditions of M-8061-R1, so as to optimize the chromatographic conditions. Under the optimized chromatographic conditions, peaks of 15 kinds of PAEs were generated with high responsivity. In addition, individual sample peaks were well discriminated (Fig. 1). The following are the details of detection conditions: detection instrument: gas chromatography-flame ionization detector (GC-FID); chromatographic column: DB-5 (30 m × 0.25 mm i.d. × 0.25 μm); column temperature program: the initial temperature of 60°C was maintained for 2 min, and then rose to 240°C at 15°C/min. Afterwards, 270°C was reached with a rate of 2°C/min. Finally, the temperature achieved 310°C at 5°C/min and was maintained for 10 min. The temperatures of the injector and the detector were 280 and 310°C, respectively. Sample size: 2 μL, split-flow at 8 mL/min; carrier gas N$_2$: 30 mL/min; fuel gas H$_2$: 30 mL/min; combustion air: 300 mL/min.

Table 3 – Calibration curves of phthalates.

Peak sequence	PAEs	Standard curve	R^2	Retention time (min)
1	DMP	y = 2995× − 178.56	0.999939	11.498
2	DEP	y = 3631× − 387.66	0.999945	12.773
3	DIBP	y = 4479.2× − 58.476	0.999875	15.098
4	DBP	y = 4849.9× − 268.92	0.999913	15.965
5	DMEP	y = 2906× − 516.84	0.999702	16.338
6	DMPP	y = 5035.8× − 367.08	0.999900	17.165
7	DEEP	y = 2965.4× − 348.04	0.999761	17.548
8	DPP	y = 4506.1× − 317.62	0.999719	18.007
9	DHP	y = 4580.3× − 256.72	0.999877	20.665
10	BBP	y = 4433× − 590.93	0.999784	20.948
11	DBEP	y = 2850.9× − 560.54	0.999787	22.893
12	DCHP	y = 4538.6× − 310.35	0.999921	24.107
13	DEHP	y = 4610.2× − 447.61	0.999865	24.29
14	DNOP	y = 4019.4× − 679.5	0.999784	28.373
15	DNP	y = 3745× − 667.99	0.999798	32.732

2.2.1. Quality assurance and quality control

A 0.5 mL aliquot of the newly prepared 1000 μg/mL standard mixture of PAEs was accurately transferred to a 50 mL bottle for dilution with methanol. After shaking until the mixture was evenly blended, a mixed standard stock solution of phthalates with a concentration of 10 mg/L was produced. Then the 10 mg/L mixed standard stock solution was diluted to prepare 0.2, 0.4, 0.6, 0.8, 1.0, 2.0, 4.0, 8.0 and 10.0 mg/L solutions, which were used to construct the standard curves the phthalates.

The y and x values refer to the peak area and concentration of each PAE, respectively (Table 4). Based on the standard curve of each phthalate drawn based on peak areas, the correlation coefficients were all relatively high and retention times were clear and definite.

In order to ensure the reliability of this method, rigorous quality control is required in data collection and analysis. The characteristics of the analytical method for the 15 kinds of PAEs were tested, and the recovery rate (R) of gas-phase and particle-phase PAEs, relative standard deviation (RSD), method detection limit (MDL) as well as instrument detection limit (IDL), were measured.

R and RSD of the measurement approach: 0.5 mL of the mixed standard solutions of phthalates with concentrations of 0.4, 1.0, 4.0 and 10.0 μg/mL were placed into a blank spiked tube packed with XAD-2 adsorbent and a glass fiber filter. Each concentration was repeated three times. After being stabilized for 2 hr, the solutions were then processed using the pre-processing method described above. The recovery and RSD of samples were then calculated. Detailed results are shown in Table 4.

The MDL was measured by the Environmental Protection Agency (EPA) method, whereby the detectable minimum concentration of analyte is determined at the 99% confidence level: 0.01 μg/mL mixed standard solution was added into 20 portions of blank samples. The MDL was calculated according to the standard deviation of the measured results for parallel samples by the following equation. Table 4 shows the calculated results.

$$MDL = t_{(n-1, 1-\alpha=0.99)} \times SD$$

where, n is the number of replicate samples measured; SD is the standard deviation for the test results of 20 standard addition samples; t represents the value when the degree of freedom is n-1, which is 3.143, and 1-α is the confidence level.

The IDL represented the detection limit of the chromatography system using GB/T5009.1-2003. In other words, the minimum concentration that the instrument can recognize, which is three times the instrument noise during measurements. The specific
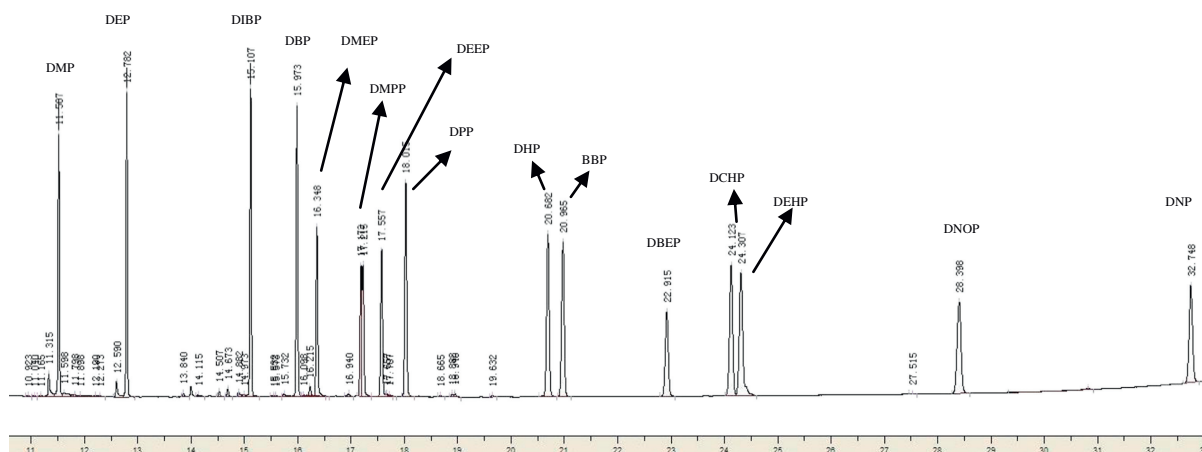
Fig. 1 – GC chromatogram of phthalates standard solution. GC: gas chromotography.

formula is shown as follows. Table 4 shows the calculated results.

$$IDL = \frac{S}{d}$$

where, S (mV·min) is three times the instrument noise, which is the minimum concentration signal that an instrument can recognize; d ((mV·min)/(ng/m^3)) is the slope of the regression equation of the standard curve.

As a result, the recovery rate of all gas-phase and particle-phase samples of the 15 kinds of PAEs ranged from 91.26% to 109.42%. The RSDs were between 2.48% and 4.76%, and were all lower than 5%. The method and IDLs ranged from 19.32 to 41.29 ng/m^3 and from 16.43 to 27.63 ng/m^3, respectively, meeting the monitoring and analysis requirements for environmental air samples.

3. Application of analysis method

3.1. Concentration levels

Table 5 shows the measured concentration levels of various PAEs in each kind of traffic micro-environment using the optimized sampling method and analytical method. As can be seen, the PAEs (both gas-phase and particle-phase) could all be collected and detected, with the number of PAEs detected approaching fifteen, indicating that the optimized method has high efficiency and precision.

3.2. Characteristics of PAEs pollution

As shown in Figs. 2 and 3, the nine new additional PAEs were DIBP, DMEP, DMPP, DEEP, DPP, DHP, DBEP, DCHP, DNP, DIBP and DMP. Within the four traffic micro-environments, PAE total concentrations (both gas-phase and particle-phase) showed the trend private car > busses > taxi > subway. When traveling in a private car, the total concentrations of DMP, DIBP, DBP, DEEP, BBP, DBEP, DNOP and DNP were higher than for the other traffic micro-environments. When traveling in a taxi, the total concentrations of DEP, DMEP as well as DMMP were higher than for other means of transportation. When travailing by bus, the total concentrations of DHP and DCHP were higher than for other means of transportation. The total gas concentration of PAEs was 1.18 and 1.09 times higher than the particle concentration in indoor air from subways and taxis, respectively, and the total particle concentration of PAEs was 1.01 and 1.25 times higher than the gas concentration in indoor air from busses and private cars, respectively, indicating that gas-phase and particle-phase make

No.	PAEs	State	R (%)	RSD (%)	MDL (ng/m^3)	IDL (ng/m^3)
Table 4 – Characteristics of the PAE analytical method.						
1	DMP	Gas	94.51	2.86	31.67	27.63
		Particle	92.59	4.32	28.11	
2	DEP	Gas	91.87	2.95	19.32	22.79
		Particle	91.26	3.87	19.37	
3	DIBP	Gas	97.28	2.74	25.86	18.47
		Particle	96.54	4.42	25.13	
4	DBP	Gas	95.41	3.01	28.85	17.06
		Particle	94.96	4.38	24.86	
5	DMEP	Gas	100.64	2.96	37.26	28.48
		Particle	99.65	3.98	36.48	
6	DMPP	Gas	101.84	2.57	29.69	16.43
		Particle	100.73	4.33	28.43	
7	DEEP	Gas	105.75	2.58	41.29	27.91
		Particle	103.28	4.01	38.67	
8	DPP	Gas	97.28	2.69	29.76	18.36
		Particle	96.49	3.85	29.43	
9	DHP	Gas	105.83	2.59	31.75	18.07
		Particle	105.29	3.95	31.49	
10	BBP	Gas	108.98	2.48	38.78	18.67
		Particle	103.79	3.19	28.85	
11	DBEP	Gas	98.63	2.75	29.47	29.03
		Particle	97.68	4.28	29.18	
12	DCHP	Gas	107.72	2.68	37.21	18.23
		Particle	103.28	4.06	29.67	
13	DEHP	Gas	109.42	2.75	37.64	17.95
		Particle	102.23	3.98	24.61	
14	DNOP	Gas	101.86	3.01	29.17	20.59
		Particle	94.12	4.27	23.47	
15	DNP	Gas	94.06	2.96	35.26	22.10
		Particle	93.51	4.76	33.42	
16	Average	Gas	100.74	2.77	32.20	21.45
		Particle	98.36	4.11	28.74	

Table 5 – Concentration levels of PAEs in indoor air from different kinds of traffic micro-environments (unit: ng/m^3).

Pollutant	State	Bus	Subway	Taxi	Private car
		Range (mean)	Range (mean)	Range (mean)	Range (mean)
DMP	Gas	1152.0–11,529 (4628.5)	1178.4–6391.6 (3005.2)	1230.6–6381.1 (3340.6)	1241.8–10,804 (5408.2)
	Particle	53.256–5155.7 (2286.4)	69.609–2872.7 (1362.7)	373.56–2850.4 (1714.6)	61.433–12,756 (3648.8)
DEP	Gas	848.22–6925.5 (3416.4)	1066.0–7394.4 (2778.3)	1161.1–6403.0 (3903.1)	1111.9–5755.7 (3535.6)
	Particle	136.73–1599.1 (1009.2)	80.441–1190.0 (775.29)	101.11–2871.7 (1461.8)	101.69–10,602 (1631.0)
DIBP	Gas	404.59–6606.3 (1508.1)	630.41–6093.1 (2069.0)	861.85–2720.4 (1535.4)	604.64–5532.2 (1641.1)
	Particle	637.84–18,546 (6319.8)	1070.6–6302.2 (3109.6)	1135.7–5435.8 (3201.3)	606.36–21,938 (10771)
DBP	Gas	454.31–1659.1 (1024.6)	542.38–1126.8 (857.52)	519.15–1295.9 (948.77)	396.06–1574.5 (1055.8)
	Particle	630.98–4426.3 (1942.1)	582.32–3455.8 (1528.4)	499.29–1964.3 (1127.9)	160.32–8202.5 (2274.8)
DMEP	Gas	1020.6–2076.1 (1437.8)	1058.7–1997.9 (1340.2)	1101.5–2034.4 (1583.4)	1051.1–2813.9 (1509.8)
	Particle	106,505–2137.8 (1375.0)	1099.3–1915.6 (1316.2)	1235.8–1604.3 (1339.1)	1108.8–1491.7 (1347.6)
DMPP	Gas	252.70–1860.1 (895.46)	541.20–1279.6 (828.45)	206.95–1544.7 (848.11)	283.35–1792.9 (906.78)
	Particle	471.54–1884.4 (712.18)	528.30–1717.4 (892.41)	480.01–1878.8 (934.47)	476.33–1800.9 (760.85)
DEEP	Gas	732.36–2077.4 (1402.6)	940.55–1794.1 (1196.3)	573.67–1890.6 (1443.8)	470.63–2680.1 (1420.1)
	Particle	686.97–1812.9 (1199.7)	461.32–1407.9 (1006.8)	928.03–1414.6 (1103.1)	615.82–4684.0 (1407.1)
DPP	Gas	509.84–163,503 (701.36)	468.61–1973.4 (967.35)	496.40–1663.8 (731.96)	518.19–1869.2 (757.84)
	Particle	447.75–2411.8 (705.36)	403.67–1460.0 (775.84)	438.17–2350.2 (674.43)	437.37–2218.1 (860.93)
DHP	Gas	589.67–2521.9 (1405.1)	431.99–2365.3 (1301.3)	540.15–2287.2 (1225.8)	554.47–3006.9 (2198.3)
	Particle	207.23–8471.4 (1031.4)	187.15–741.64 (457.19)	217.22–622.18 (467.45)	197.19–8024.3 (950.58)
BBP	Gas	751.58–3696.6 (1641.5)	517.43–2356.0 (1183.8)	906.91–2900.0 (1479.4)	499.63–3946.6 (2198.3)
	Particle	784.52–3434.8 (1645.4)	718.80–2209.5 (1313.8)	970.73–3708.7 (2237.2)	670.85–2856.9 (1906.8)
DBEP	Gas	778.46–3951.8 (1922.9)	784.65–4249.0 (1709.4)	853.10–2688.7 (1784.7)	754.73–9664.4 (1010.3)
	Particle	990.30–2287.9 (1345.4)	828.82–1451.8 (1156.2)	1099.1–1881.2 (1311.4)	968.59–7114.6 (1248.8)
DCHP	Gas	283,037–1486.3 (1097.1)	124.48–1267.4 (858.52)	279.25–1581.7 (1054.4)	176.18–1407.8 (1010.3)
	Particle	742.7–1898.6 (1239.9)	735.43–1565.5 (1141.0)	412.86–1480.3 (1083.3)	405.69–2945.3 (1248.8)
DEHP	Gas	1305.5–2494.4 (1658.9)	1186.1–7688.6 (3183.2)	1375.0–2355.2 (1746.1)	1200.3–7467.4 (2461.6)
	Particle	1054.0–17,173 (2056.8)	1382.8–9317.7 (3118.3)	1373.0–18,101 (3223.3)	1026.8–28,025 (3709.7)
DNOP	Gas	765.93–1686.0 (1163.3)	765.93–1560.1 (1276.7)	771.56–1325.5 (1129.8)	771.56–1670.3 (1236.5)
	Particle	769.51–1957.1 (1209.5)	769.51–1207.1 (1008.8)	764.14–1252.7 (1071.0)	764.16–2650.9 (1236.2)
DNP	Gas	687.81–1876.3 (1221.3)	584.86–1402.5 (1137.4)	562.72–1459.4 (1223.6)	582.82–1780.1 (1252.1)
	Particle	991.02–1647.1 (1201.9)	842.78–1211.5 (1072.0)	1010.8–1278.8 (1127.8)	967.12–3479.8 (1424.8)
Total	Gas	17,081–35,668 (25125)	16,227–29,219 (23693)	14,268–27,651 (23979)	13,145–36,754 (28550)
	Particle	16,186–37,640 (25280)	14,706–26,971 (20035)	18,856–32,560 (22078)	22,029–45,158 (34955)

different contributions to the total concentration of PAEs in indoor air from these four traffic micro-environments.

As demonstrated in Fig. 3, within the four traffic micro-environments, the concentrations of gas-phase PAEs showed the trend private car > busses > taxis > subway. When traveling in a private vehicle, the gas-phase concentrations of DMP, DBP, DMPP, BBP, DBEP and DNP were higher than for other transportation modes. When traveling in a taxi, the gas-phase concentrations of DEP, DMEP as well as DEEP were higher than for other means of transportation. When traveling by bus, the gas-phase concentrations of DHP and DCHP were higher than other transportation modes.

As demonstrated in Figs. 3 and 4, within the four traffic micro-environments, the concentrations of particle PAEs followed the trend, private car > busses > taxi > subway. When traveling in a private vehicle, the particle-phase concentrations of DMP, DEP, DIBP, DBP, DEEP, DPP, DBEP, DEHP, DNOP and DNP in PAEs were higher than for other transportation modes. When traveling in a taxi, the particle-phase concentrations of DMPP and BBP were higher than other modes. When traveling by bus, the particle-phase concentrations of DMEP, DHP and DCHP were higher than other modes.

As shown in Fig. 3, in the indoor air of busses, DMP, DEP and DBEP were the three PAE pollutants that had the highest gas concentrations, accounting for 39.6% of the total PAEs in the gas-phase. Moreover, DIBP, DEHP and DMP were the three

PAE pollutants that had the highest particle level, accounting for 42% of the total particle state. In addition, DIBP, DMP and DEP were the three PAEs pollutants with the highest total concentrations in busses, accounting for 38%.

In the indoor air of subways, DEHP, DMP and DEP were the three PAE pollutants with the highest gas-phase concentrations, accounting for 38% of total gas-state PAEs. Moreover, DEHP, DIBP and DBP were the three PAE pollutants with the
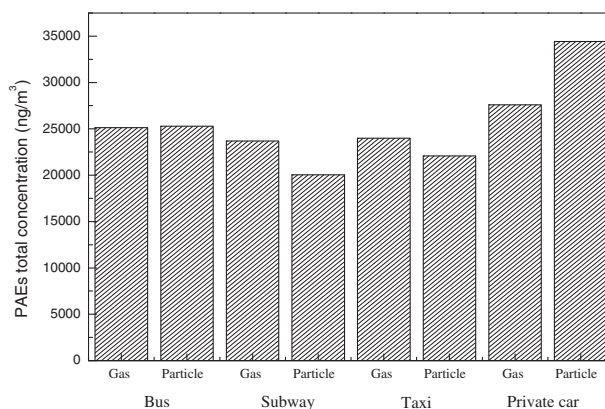

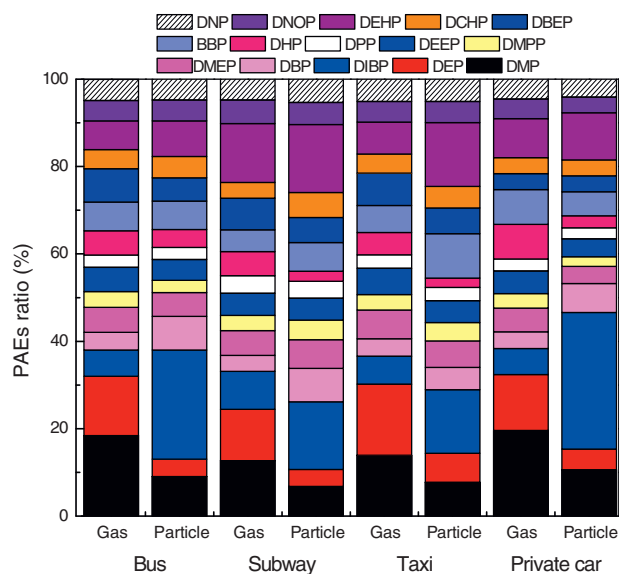**Fig. 2 – Total concentration of PAEs in different phases from four kinds of traffic micro-environment.**

Fig. 3 – Concentration of phthalates in indoor air from different kinds of traffic micro-environment.

Table 6 – Concentration levels of phthalates in indoor air from private cars (unit: ng/m³).

Pollutant	State	Min	Max	Mean
DMP	Gas	811.4	1413.2	1101.6
	Particle	–	–	–
DEP	Gas	545.6	1855.6	1303.2
	Particle	94.2	543.4	275.0
DBP	Gas	226.7	2103.8	986.6
	Particle	404.6	2027.5	893.9
BBP	Gas	605.4	1355.5	841.8
	Particle	372.0	2504.7	1792.8
DEHP	Gas	509.2	2267.9	1324.7
	Particle	523.8	29,789.8	6934.5
DNOP	Gas	–	–	–
	Particle	–	–	–
$\sum$PAEs		4092.9	43,861.4	15,454.1

–: non-detected

highest particle-phase concentrations, accounting for 39% of total particle-state PAEs. In addition, DEHP, DIBP and DMP were the three PAE pollutants with the highest total concentrations in subways, accounting for 36%.

In the indoor air of taxis, DEP, DMP and DBEP were the three PAE pollutants with the highest gas-phase concentrations, accounting for 38% of total gas-state PAEs. Moreover, DEHP, DIBP and BBP were the three PAE pollutants with the highest particle-phase concentrations, accounting for 39% of total particle-state PAEs. In addition, DEP, DMP and DEHP were the three PAE pollutants with the highest total concentrations, accounting for 33%.

In the indoor air of private cars, DMP, DEP and DBEP were the three PAE pollutants with the highest gas concentrations, accounting for 42% of total gas-state PAEs. Moreover, DIBP, DEHP and DMP were the three PAE pollutants with the highest particle-phase concentrations, accounting 52% of total particle-state PAEs. In addition, DIBP, DMP and DEHP were the three PAE

pollutants with the highest total concentrations, accounting for 44%.

In conclusion, the 9 newly added PAEs accounted for a relatively large proportion of the total concentration of PAEs. In particular, DIBP and DBEP contributed large fractions of the PAE pollution in indoor air from various traffic micro-environments. Therefore, the concentration levels of these 9 PAEs significantly influence the PAE pollution in indoor air from traffic micro-environments, and should not be neglected.

3.3. Comparison of two methods

We chose a private car that had serious PAE pollution in its indoor air as a reference and used the method of Pei et al. (2013) to measure the pollution level of 6 kinds of PAEs in the indoor air from the private car (Table 6), then compared the results to those measured by the method developed in this study.

As can be seen, the total mean concentration (both gas- and particle-phase) of PAEs was 15,454.1 ng/m³, and the range was 4092.9–43,861.4 ng/m³. DEHP and BBP, as the main pollutants, accounted for 53.44% and 17.05% in the total mean concentration of PAEs, respectively.
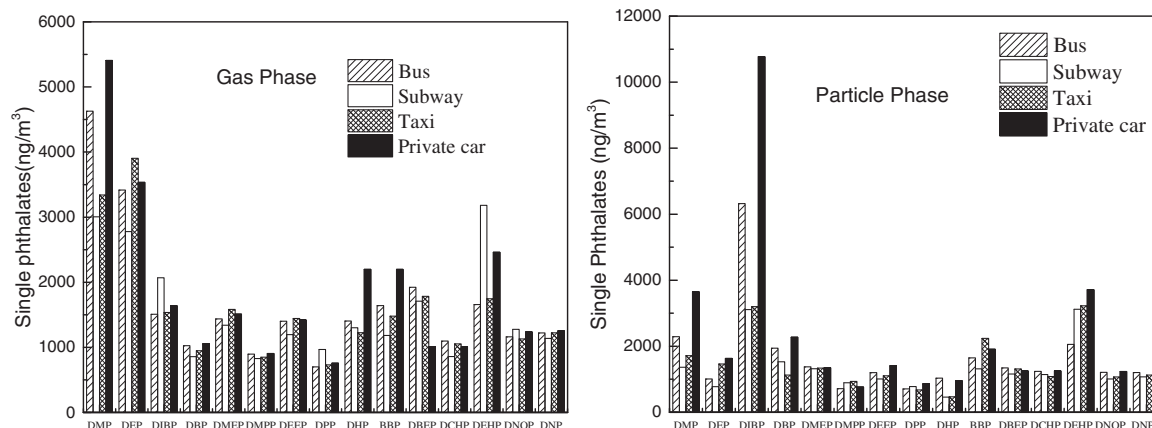

Fig. 4 – Mean contribution of single phthalates to the total content in indoor air of four traffic micro-environment.

By comparing the concentration levels of different kinds of PAEs in indoor air from a private car using the two kinds of sampling and analytical methods as shown in Fig. 5, we found differences between the contribution rates of various kinds of PAEs. Using the optimized sampling and analytical method able to detect 15 kinds of PAEs, we found that DMP contributed the highest proportion among gas-phase PAE pollution levels, DIBP contributed the highest proportion among particle-phase PAE pollution levels and the 15 kinds of PAEs in the gas-phase and particle-phase could all be detected. The detection rate of indoor air PAEs in this investigation, both in the gas-phase and particle-phase, was 100%. Using the sampling and analytical method able to detect 6 kinds of PAEs, we found that DEHP contributed the highest proportion among gas-phase PAE pollution levels, with DNOP non-detected. The detection rate of indoor air PAEs in this investigation in the gas-phase was 83.3%. We also discovered that DEBP contributed the highest proportion among particle-phase PAE pollution level, with DMP and DNOP non-detected. The detection rate of

indoor air PAEs in this investigation in the particle-phase was 66.7%.

4. Conclusions

The sampling method for PAEs was optimized by improving the sampling efficiency, and shortened the sampling duration from 8 to 2 hr. while maintaining the same or even higher sample recovery rates. The analysis method for PAEs in indoor air was also improved by empirical testing and practical application based on previous research. The 9 additional PAEs were taken into account, and quality control was carried out through testing based on 5 indexes. Accordingly, the optimized analysis method is capable of effectively detecting 15 kinds of PAEs pollutants, indicating its high efficiency and scientific validity. Thus, a fundamental method has been established for the identification of types of PAE pollution and the measurement of PAE concentrations in future indoor air investigations.
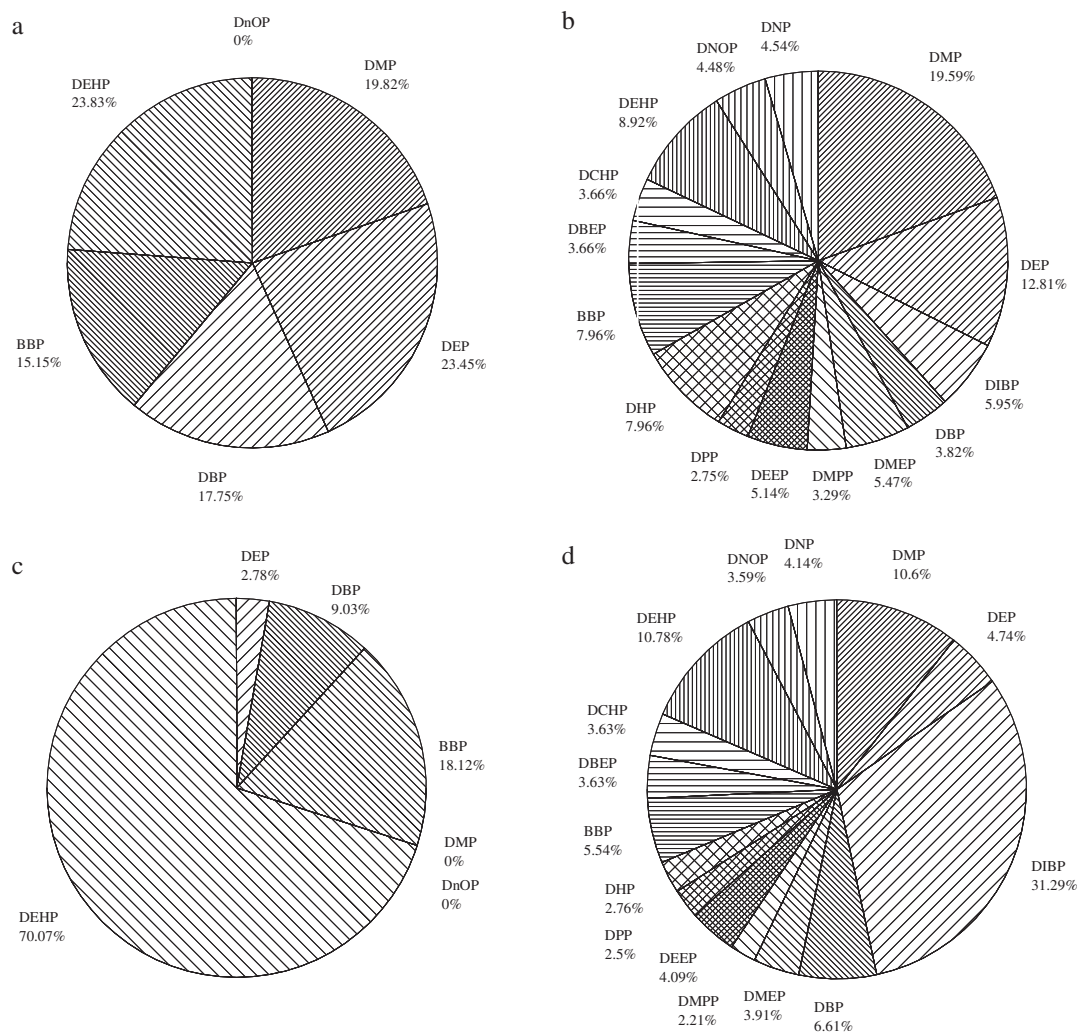

Fig. 5 – The comparison of mean proportion of PAEs (gas- and particle-phase) in indoor air from private cars using different methods. (a, c) mean proportion of 6 PAEs in gas- and particle-phase, respectively. (b, d) mean proportion of 15 PAEs in gas- and particle-phase, respectively.

The optimized method was applied in measurements on air samples in four traffic micro-environments, including subways, busses, taxis and private cars. Optimized sampling and analysis methods were employed for the measurement of concentrations of PAEs (both gas-phase and particle-phase) in the above 4 traffic micro-environments along with the exploration of pollution characteristics. All the 9 additional PAEs could be detected at relatively high pollution levels in the indoor air from the traffic micro-environments. What's more, they made a remarkable contribution to the total concentration of the 15 kinds of PAEs as well. Among them, DMP and DIBP were found to be the most highly concentrated gas-phase and particle-phase PAEs in the 4 traffic micro-environments, respectively. As none of the pollution levels of the 15 kinds of PAEs in the indoor air of the 4 traffic micro-environments should be neglected, it is of great significance to increase the types of PAEs being detected in indoor air.

Acknowledgments

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