Assessment of gaseous phase PAHs emitted from marine diesel engine using vortex-assisted dispersive liquid-liquid microextraction followed by GC/MS

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Abstract. A novel sample treatment, namely vortex-assisted dispersive liquid-liquid microextraction (VDLLME), followed by GC/MS has been developed for the determination of gaseous phase polycyclic aromatic hydrocarbons (PAHs) emitted from a marine diesel engine. The method integrates extraction, enrichment, and concentration into one step by combining sample collection and VDLLME into a much shorter and accurate procedure. We have optimized several important variables influencing the extraction efficiency including type and amount of extraction solvent, type and volume of disperser solvent, sample pH, salting-out effect, vortex and centrifugation time. Under the optimum conditions, high enrichment factors (more than 1,000) and acceptable total spiked recoveries (72.0-95.1%) were obtained using GC/MS detection. The limits of detection and quantification of the proposed method were in the ranges of 0.1-0.5 ng/L. Our total pretreatment can be competed in less than 0.5 hours so as to decreases loss of PAHs by 18.37% compared to traditional methods.

Instruction

Marine diesel engines are significant contributors to air pollution in many coastal areas. Their exhaust emissions have been found to contain numerous toxic air contaminants including the highly carcinogenic polycyclic aromatic hydrocarbons (PAHs). PAHs, compounds created during the process of incomplete combustion of the organic matter, not only have carcinogenic, teratogenic and mutagenic effects, but also can lead to the formation of other highly toxic substance (nitro-PAHs, hydroxy-PAHs) through reactions with other pollutants such as ozone, hydroxyl radicals, nitrogen, and sulfur oxides (Khamphe et al. 2013). Therefore, accurate collection and quick analysis of PAHs emissions of diesel engines is crucial to better assess health risks in coastal areas.

Rezaee suggested the dispersive liquid-liquid microextraction (DLLME), which is based on the ternary component solvent system (Rezaee et al. 2006). DLLME is simple to operate, and is an especially rapid and inexpensive extraction method with high preconcentration factors. This technique has successfully been applied to preconcentration of PAHs, drugs and pesticides (Natalia et al. 2015; Fan et al. 2015). To enhance dispersion of hydrophobic ionic liquids (extraction solvent) into the aqueous sample, vortex was introduced, this methodology, named vortex-assisted DLLME (VDLLME) offers the advantage of avoiding the possible degradation of some analytes. VDLLME has been applied for the analysis of herbicides, aflatoxin, and pesticides (Seebunrueng et al. 2014; Gure et al. 2015; Mitra et al. 2015), manly in environmental waters or fruits. However, VDLLME procedure has not been considered to date for the analysis of PAHs.

In our previous study, we reformed an instrument for fast pretreatment of PAHs and rapid sample collection (Wang et al. 2013). However, this instrument proved to be too expensive for routine use in many laboratories. In order to solve this problem, we created a more accessible sample collection method. Here we describe a pretreatment method of ACC combining with VDLLME that does not need special equipment.

Material and method

Instrument and solvent

Samples analyzed were collected and extracted from a RT-flex60c marine diesel engine (Qingdao Wartsila Corporation) according to MARPOL 73/78 annex VI. PAHs emitted from marine diesel engine were determined by GC/MS (GC/MS-QP 2010 Plus, Shimadzu, Japan) equipped with a DB-5 MS capillary column (30 m×0.25 mm×0.25 μm). The injection mode was splitless, and injection volume was 1 μL. The column flow of carrier gas (helium) was 26.2 cm/sec. The column temperature program was set at 90˚C for 1 min, and then raised by 25˚C/min to 180˚C, held for 0 min, raised by 5˚C per min to 300˚C and held for 0 min. Finally, the temperature was increased rapidly by 20˚C per min to 320˚C and kept for 5 min.

Pyridine, tetrahydrofuran, hexadecyl trimethyl ammonium bromide (CTAB), tetrachloroethylene, 1,1,2,2-tetrachloroethane, and carbon tetrachloride were purchased from Merck, Germany. Methanol, ethanol, acetonitrile (HAc), acetone, acetic acid, , and sodium chloride (NaCl) was purchursed from Kemiou Chemical, Tianjin, China. 1-hexyl-3-methylimidazolium hexafluorophosphate (HMIMPF6) were purchased from Sigma Aldrich, USA. All solvents were of analytical grade. Pure water (Millipore, Bedford, USA) was used for all the solutions and dilutions. Quantitative analysis of PAHs (2000 μg/mL, dichloromethane) was calibrated with a commercial standard mixture (Supelco EPA 610 PAH Mix, USA).

Experimental Procedure

1) Aqueous-capture for collection

A stainless steel joint connecting tube (Φ5mm) was welded on the tail end of an exhaust pipe and connected with three 250 mL aqueous glass container to collect exhaust emissions without dilute with air. A fiber filter was set before the inlet of the brass pipe to protect the particular phase PAHs from the aqueous solution. The glass container included the optimized co-solvent CTAB 0.0002 mol/L, NaCl 0.01 mol/L and 5% ethanol: *n*-hexane.

2) DLLME for concentration

A volume of 5 mL of sample was placed in a 15 mL centrifuge tube with conical bottom and was then spiked with 10 μL PAHs standard solutions. After stirred 1 min, 10μL tetrachloroethylene (extraction solvent) and 1000 μL acetone (disperser solvent) and was rapidly injected into the sample solution, using 1.0 mL syringe with a blunt needle tip, in order to induce the formation of the cloudy solution consisting of fine droplets of liquid dispersed in the sample solution. Subsequently, the mixture was vortexed for 30 s at the highest speed and then centrifuged for 2 min at 9000 rpm to enhance the sedimentation of the liquid droplets. The upper phase was discarded using a 5 mL syringe. The lower layer was collected after dissolving in 500 μL of acetone, followed by vortexing for about 30 s. The solution was then transferred to a 1.5 mL vial to inject 1 μL into the GC/MS equipment.

Result and discussion

Bench test and sample collection

Marine diesel engine 7RT-flex60C was used for the sampling test (specifications were listed in Table 1). Details of optimization of the ACC method for collection of gaseous PAHs have published in a previous report (Wang et al. 2013).

Table 1   Engine specifcations of 7RT-FLEX60C

Model of engine	QMD-Wartsila 7RT-flex60C
Number of cylinder	7
Bore × stroke	600mm×2250mm
Nominal Compression ratio	18.4:1
Injection pump	Electronic controlled type
Injector number	3
Rated Power (kW) and Speed (RPM)	16520 kW × 114rpm

Maximum Fuel Rail Pressure	900 bar
Turbocharger type	ABB TPL73B12 $\times$ 2 sets
Air cooler	SAC53F $\times$ 2 sets

Optimization of the DLLME method

When selecting a suitable extraction solvent, we considered various parameters such as high density, low polarity, and the high partitioning coefficient of the PAHs in the solvent. We optimized each of these factors in pursuit of a good enrichment factor (EF) and high extraction recovery (ER). ER and EF were selected for evaluation of the extraction ability.

$$EF = C_{sed}/C_o \qquad\qquad (1)$$
$$ER = C_{sed} \times V_{sed} / C_o / V_{aq} \times 100\% \qquad\qquad (2)$$

Where C_{sed} is the concentration of analyte in seditment; C_o is the initial concentration of analyte in sample; V_{sed} is the sediment volume, and V_{aq} is the sample volume.

1)Influence of the extraction solvent

Based on the above considerations, we designed the extraction solvents to contain 100µL each of the organic solvents tetrachloroethylene, HMIMPF6, 1,1,2,2-tetrachloroethane, chloroform and carbon tetrachloride. The results showed that using tetrachloroethylene resulted in the best PAHs recovery, possibly due to its high density and low water solubility. We applied tetrachloroethylene as the extracting solvent was applied at concentrations of 2 µL, 5 µL, 10 µL, 15 µL, 20 µL and 25 µL to optimize extraction efficiency. We then reduced the polarity of the sample solution with 50% ethanol, thereby increasing the solubility of tetrachloroethylene. We found a low sediment phase volume when using 500 µL tetrachloroethylene. EF increased noticeably with increased tetrachloroethylene volume from 5 µL to 15 µL, where it reached the maximum value (Figure 1). Since using a solvent volume higher that 10µL mL considerably decreased enrichment and the preconcentration factor, we considered 10 µL tetrachloroethylene as a volume sufficient for extraction of PAHs.
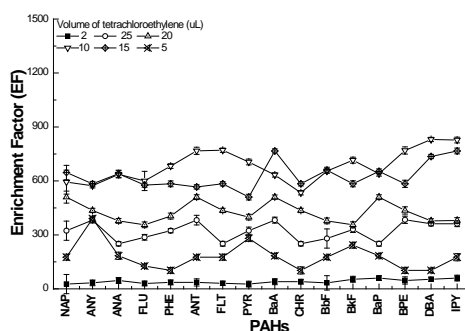

Figure 1. Effect of the volume of extracting solvent tetrachloroethylene on enrichment factor.

2) Selection of the disperser solvent

Addition of the disperser solvent produced the emulsion necessary in DLLME for developing the cloudy phase and for the transfer of PAHs from the sample solution to the sediment phase. Six volumes of acetone, 200 µL, 500 µL, 700 µL, 1000 µL, 1500 µL and 2000 µL were applied to optimize extraction conditions. At 1000µL acetone, the cloudy phase did not form well so as to resulting in low EF. RF reached was highest at 1000 µL of acetone, and clearly decreased at 1500 µL. Therefore, we selected 1000µL as the optimal volume of disperser solvent.

3) Effect of the sample pH

In VDLLME, pH of the sample solution is very important. Adjust pH could deionized PAHs so as to reduce the solubility of PAHs. PH values were designed in the range from 1.0 to 4.0 using HCl or NaOH. The highest peak areas of PAHs were obtained at pH2 (Fig. 2). At higher pH the PAHs might not be completely transformed to their neutral form, so pH2 was chosen as the optimum.
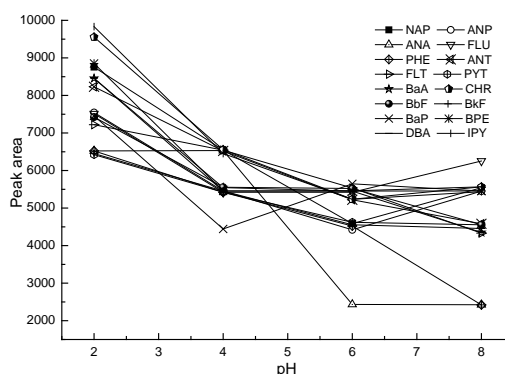
Figure 2. Effect of the sample pH.

4) Effect of the salt addition

The addition of salts generally can reduce the solubility of the PAHs in the aqueous sample and thus enhance their partitioning into the organic phase for liquid phase. The effect of salt addition was investigated by adding NaCl from 0% to 20% (m/v). As seen in Fig. 3, peak areas of the PAHs increased slightly with the amount of salt up to 5% and then decreased, which resulted in a decrease in the peak areas. Thus, 5% (w/v) NaCl was selected.
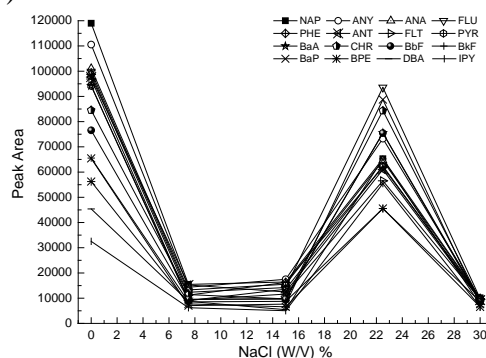

Figure 3. Effect of the salt addition.

5) Effect of vortex and extraction times

Generally, the dispersion of the extraction solvent into the sample depends on the rotational speed and vortex time. So, the vortex agitation time was varied in the range of 0-120 s. The peak areas of PAHs increased slightly till 30 s. 30 s were selected in the experiments.

Extraction time was the time between the injection of disperser (containing extraction solvents) and centrifugation for DLLME. Extraction times were designed from 1-30 minutes at the speed of 9000 rpm. It was observed that the peak areas of the PAHs slightly increased up to 1 min and then remained constant. It was suggested that the large surface area between the aqueous and organic phases increase extraction efficiency.

Methodology validation

Our results in establishing our method are summarized in Table 2. Using this method, we found good linear relationships between peak area and concentration of PAHs in the range of 5-20 ng/L ($R^2 > 0.9990$). The limits of detection (LOD) of our proposed method for the targeted PAHs were in the range of 0.1-0.5 ng/L (S/N = 3). The limit of quantitative (LOQ) was in the range of 0.2-1.0 ng/L. The blank recovery yields ranged from 74.7% to 94.3%. The result showed that GC/MS in SIM mode after ACC-DLLME was an efficient and accurate method for monitoring PAHs at very low concentration in exhaust samples.

Table 2   Method validation of capture and analysis

PAHs	R^2	LOD (ng/L)	LOQ (ng/L)	SR	RSD (%)
NAP	0.9991	0.2	0.2	72.0	5.34
ANY	0.9995	0.5	0.2	76.3	2.13
ANA	0.9990	0.1	0.3	84.3	1.19
FLU	0.9990	0.1	0.5	79.3	6.75
PHE	0.9994	0.2	0.5	81.2	1.24

ANT	0.9992	0.2	0.5	80.5	2.81
FLT	0.9998	0.2	0.50	95.1	6.53
PYR	0.9997	0.1	0.50	88.2	1.43
BaA	0.9994	0.1	0.5	80.6	8.64
CHR	0.9991	0.1	0.5	84.4	1.56
BbF	0.9995	0.1	0.4	82.6	9.27
BkF	0.9994	0.2	0.2	80.3	6.68
BaP	0.9998	0.2	0.50	78.5	7.94
BPE	0.9997	0.5	1.00	83.3	3.52
DBA	0.9995	0.5	1.00	76.7	9.98
IPY	0.9995	0.5	1.00	72.1	9.36

PAHs and abrreviations: Naphthalene (NAP); Acenaphthylene (ANY); Acenaphthene (ANA); Fluorene (FLU); Phenanthrene (PHE); Anthracene (ANT); Fluoranthene (FLT); Pyrene (PYR); Benz(a)anthracene (BaA); Chrysene (CHR); Benzo(b)fluoranthene (BbF); Benzo(k)fluoranthene (BkF); Benzo(a)pyrene (BaP); Benzo(g,h,i)perylene (BPE); Dibenz(a,h)anthracene (DBA): Indeno(1,2,3-cd)pyrene (IPY)

Evaluation in real applications

Spiked samples were tested to further validate the applicability of the ACC-DLLME-GC/MS method. The spiked recoveries were in the range of 72.0-95.1% and the relative standard deviation (RSD) was 1.19-9.98% (Table 1). All target PAHs dissolved in the aqueous solution, regardless of size, resulting in a total PAH volume of 60.75 µg/m^3. To evaluate the variability of the method, the experiments were carried out for three days and subjected to three parallel tests. The average values and standard deviations were then calculated. PAHs were quantitatively captured in aqueous solution, but had great deviations in capture volumes of the semi-volatile PAHs, NAP, ANY, ANA and FLU.

Comparison with traditional process

In order to compare the result of our proposed method with traditional methods, we used a traditional method for collection and extraction of PAHs. It used a PUF method for collection (8 hours), and Soxhlet method for extraction (8 hours), KD evaporator, and GC/MS for detection resulting in a total volume of extracted PAHs of 49.59 µg/m^3. This result suggests a loss of 18.37% PAHs through traditional process of collection compared to our proposed method (60.75 µg/m^3). The proposed method was also compared with some reported method (Table 2). Since our protocol calls for a collection and pretreatment time less than 0.5 hours, our method could be completed in 1/10 of the time required for traditional methods.

Conclusion

In order to evaluate gaseous phase PAHs emitted from the diesel engine, we improved a pretreatment process that coupled ACC with VDLLME. Our proposed method does not require special equipment, and could integrate the extraction, enrichment, and concentration processes into one step. Quantitative analysis of PAHs was considerably shortened compared to traditional methods and required less than 30 minutes from the sample collection to detection. Furthermore, the detection limits reached to *ng* grade, which illustrated the high precision our method. Finally, our proposed collection and extraction method can be accomplished in 10% of the time required when using traditional methods and retain more of the volatile compounds. Therefore, we present our protocol as a more efficient method of accurate collection and extraction of PAHs from exhaust.

Acknowledgements

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