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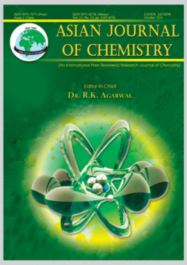

Gas Flowing-Liquid Phase Enrichment of Organic Micro Pollutants from Atmosphere

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The enrichment effects of organic micro pollutants from atmosphere by gas flowing-liquid phase and compared with XAD resin enrichment method were investigated. For optimization of the enrichment conditions, the experiment variables such as gas flow rate, temperature and different solvents were investigated. The chemical composition of the polycyclic aromatic hydrocarbons was analyzed by GC-MS. The laboratory result shows the enrichment rate was 90 ± 10 % in a certain conditions (adsorbent of dichloromethane, cryohydrate bath and 3000 mL/min of carrier gas flow). To real sampling analysis, 8 polycyclic aromatic hydrocarbons were determined and satisfactory results were obtained comparing with XAD technology. The new method of gas flowing-liquid phase is simpler and economically cheaper, especially the after treatment method is simpler than XAD and enrichment efficiency is similar with the XAD technology.

Key Words: Enrichment, Gas flowing-liquid phase, Organic micro pollutants, Polycyclic aromatic hydrocarbons, Atmosphere.

INTRODUCTION

Most organic compounds are obtained from coal, oil and natural gas, so industrial organic waste gas are major products that using these three fuels. Among these organically gas, many species are hazardous, toxic and accumulate. In the high density of these exhaust gas, people may be poisoned acutely, or even to dead. Some organic waste gas induce dermatitis and some induce carcinomatosis such as chlorethene, poly(vinyl chloride) (PVC) and fused ring compounds for example benzo(a)pyrene[1]. So it is highly significant for the health of people to enrich and detect organic micro pollutants from atmosphere. Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the atmosphere among semi-volatile organic compounds (SVOCs)[2]. Polycyclic aromatic hydrocarbons are formed mainly by the incomplete combustion of organic materials[3,4]. Some polycyclic aromatic hydrocarbons show carcinogenicity[5-8] and endocrine disruption[9]. Recently, Europe and WHO have enacted and proposed the regulations of polycyclic aromatic hydrocarbons[10-12].

In the atmosphere, polycyclic aromatic hydrocarbons exist in the particle and the gas phase[13,14]. The most polycyclic aromatic hydrocarbons with two or three aromatic rings, are mainly released in the gas phase, others are generally associated with the particle phase. The partition of polycyclic aromatic hydrocarbons in the gas and in the particle is related to many different variables like the vapour pressure, the ambient temperature the particulate size and chemical composition of the particulate[15]. At present, most researchers use high-volume sampler to collect polycyclic aromatic hydrocarbons in the atmosphere. The particle phase is trapped on a quartz or glass filter and the gas phase is collected by solid sorbet such as polyurethane foam (PUF), Tenax (EPA method TO13) or amberlite XAD resin[16]. These methods were not adequate to solve problems of the limitations of the adsorbent, such as preparing filter paper, pressure pump, adsorption column, equipments and instruments[17]. Now, some new technologies of sampling were developed, such as cascade impactor/solid sorbet[18-20], electrostatic precipitator (ESP) / solid sorbet[18] and denuder systems[21-31]. But these techniques only developed the structure of sampling device, not to change the adsorbent materials of solid adsorbent. So it is of great significance to develop a technology that have simple structure and easy after treatment process. The new technology should have perfect effect of enrich polycyclic aromatic hydrocarbons and other organic micro pollutants from atmosphere.

Among semi-volatile organic compounds, polycyclic aromatic hydrocarbons are ubiquitous and partition between the particle phase and the gas phase in atmosphere. For enhanced the enrichment efficiency of organic micro pollutants, the gas flowing-liquid phase were used. A total of 6-polycyclic aromatic hydrocarbons were selected for studying the technology and use this technology to monitoring the field experiment. To take into account the variation of the enrichment technology applied to collect gas polycyclic aromatic hydrocarbons during the different experimental conditions, the section focus on studying several experimental parameters on the influence of polycyclic aromatic hydrocarbons absorption in the technology. These usual parameters include temperature, organic absorption solvent and carrier gas flow rate.

EXPERIMENTAL

In this study, six kinds of polycyclic aromatic hydrocarbons such as 2-ring acenapthene (Ace), fluorene (Flu), 3-ring phenanthrene (Phe), 4-ring pyrene (Pyr), 5-ring benzo(a)pyrene [B(a)Pyr] and 6-ring benzo(ghi)perylene [B(ghi)Pery] were used. Six kinds of polycyclic aromatic hydrocarbons, acenaphthene-d_{10}, phenanthrene-d_{10} and the standard polycyclic aromatic hydrocarbons in the field experiments were all purchased from Supelco (Bellefonte, PA, USA). Purities of standards were higher than 99 %. Six kinds of polycyclic aromatic hydrocarbons [Ace, Flu, Phe, Pyr, B(a)Pyr, B(ghi)Pery] were prepared in hexane as 2.0 mg/L (the same concentration of each polycyclic aromatic hydrocarbon), then the mixture of 6-polycyclic aromatic hydrocarbons solution is as the standard solution of the experiment. A 10 mg/L hexane solution of acenaphthene-d_{10} (Ace-d_{10}) was used as surrogate internal standard and the same concentration of hexane solution of phenanthrene-d_{10} (Phe-d_{10}) was used as instrument internal standards. Regent: HPLC-grade hexane, dichloromethane (DCM), trichloromethane (TCM) and methanol (MeOH) were bought from Caledon (Georgetown, Ont., Canada). Amberlite XAD-2 resin (Surface area: 300 m^2/g, Porosity: 1-56 Å, diameter: 680 μm) was bought from Shanghai Quandao Technical Company. The purity of nitrogen gas was higher than 99.99 % and was bought from Changchun Oxygen (Changchun China).

To test the feasibility of simulation sampling technology, we designed experiment apparatus as Fig. 1. The apparatus includes four sections *i.e.*, (1) The gas flow meter that control the gas flow rate and record the volume of carrier gas; (2) Gas absorber is used to add the 6-polycyclic aromatic hydrocarbons standard solution and adsorbent solvent; (3) Container of condensate water or ice or salt; (4) Bottle of tail gas have not real usefulness in this study.

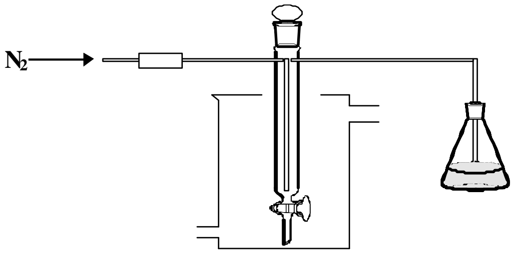

Fig. 1. Diagram of apparatus, (1. Flow meter; 2. Gas absorber; 3. Container of condensate water or ice or salt; 4. Bottle of tail gas)

Initially, 2 mL of 6-polycyclic aromatic hydrocarbons standard solution (2.0 mg/L) and 30 mL organic solvent were added to gas absorber. Then N_2 started to flow in the apparatus and the gas flow meter controlled its flow rate. As the carrier gas flowing, the volume of the solvent in the gas absorber reduced. To keep the volume of the solvent invariable, organic solvent was replenished in the gas absorber. For testing the influences of temperature to the 6-polycyclic aromatic hydrocarbons adsorption, we used the condensate water or the ice and salt to change the temperature of the absorber. Every experiment carried on 24 h. The sample in gas absorber was concentrated and detected by GC/MS (Shimadzu QP-2010). Original and rest content of each polycyclic aromatic hydrocarbon was and respectively. So remnant rate of each polycyclic aromatic hydrocarbon was calculated according to the following equation:

$$\text{Remnant } \% = \frac{Q_{SAM}}{Q_{STD}} \times 100\,\% \tag{1}$$

Gas flowing-liquid phase enrichment apparatus: To test the recovery of gas phase polycyclic aromatic hydrocarbons by enrichment apparatus, we designed simulation enrichment apparatus as Fig. 2. Compare with Fig. 1, it only increased the part of gas generator.

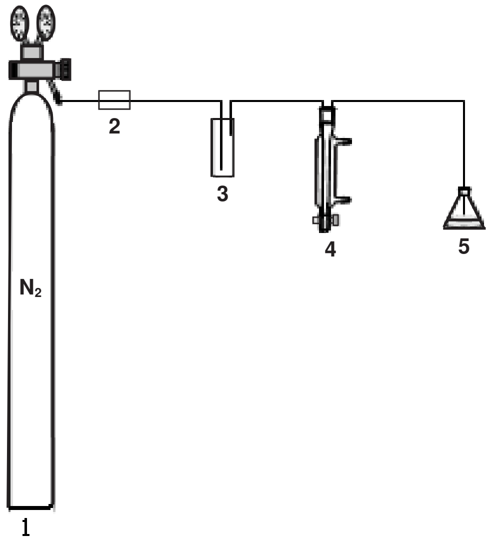

Fig. 2. Diagram of simulation enrichment apparatus, (1. Nitrogen; 2. Flow meter; 3. Gas generator; 4. Gas absorber; 5. Bottle of tail gas)

Experimental design and procedures: Initially, 2 mL (2 mg/L) of 6-polycyclic aromatic hydrocarbons standard solution was added to the gas generator and 30 mL organic solvent were added to the gas absorber. To generate 6-polycyclic aromatic hydrocarbons gas, a heating wire line was winded on the gas generator and was controlled to 200 ºC by a voltage regulator, an electrical relay and a thermometer. Then we turned on the nitrogen valve and controlled its flow rate by the gas flow meter. The heating and absorbing process kept 2 h. Then we turned off gas absorber valve and gained SAM-2. Cleaning the gas generator and the pipe between the gas generator and the gas absorber, SAM-1 was gained. Then surrogate internal standards (Ace-10) 50 mL was added in the SAM-1 and SAM-2 and concentrated them to approximately 5 mL by rotary evapourator. Finally, both samples were concentrated to 2 mL by nitrogen and added in 50 μL instrument internal standards and detected. The enrichment rate was calculated according to the following equation:

$$\text{Recovery } \% = \frac{Q_{SAM-2}}{Q_{STD} - Q_{SAM-1}} \times 100\% \tag{2}$$

where recovery % was the enrichment rate of the organic solvent, Q_{SAM-1} and Q_{SAM-2} were respectively. The content of each polycyclic aromatic hydrocarbon in the SAM-1 and the SAM-2, Q_{std} was the original content of each polycyclic aromatic hydrocarbon added in the gas generator.

XAD absorption: In order to compare with the enrichment efficiency of the gas flowing-liquid phase enrichment method and XAD enrichment method, we changed the part of the gas absorber in Fig. 2 into Fig. 3. Compare with Fig. 2, it only changed organic solvent into XAD-2 resin.

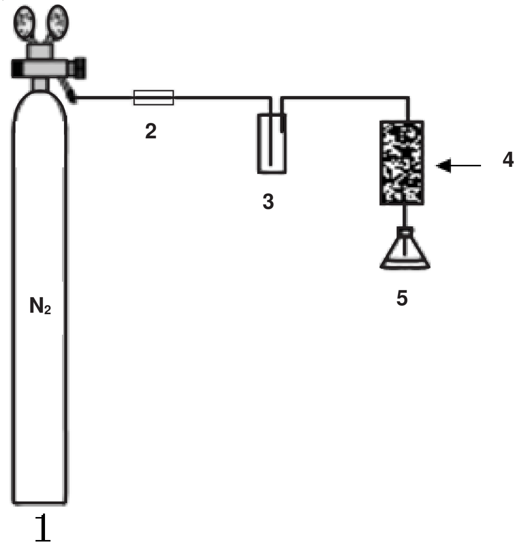

Fig. 3. Diagram of enrichment apparatus by XAD. (1. Nitrogen; 2. Flow meter; 3. Gas generator; 4. Gas absorber; 5. Bottle of tail gas)

There were some different with gas flowing -liquid phase enrichment apparatus at the adsorption material preparation and after treatment. Before each test, the XAD-2 was extracted in 8 h in dichloromethane by Soxhlet extraction. Then the XAD-2 was cooled down naturally on the tin foil paper in the dryer. In experiment, 7.5 g XAD-2 was added to a metal cylinder net (internal diameter: 1.5 cm, length: 5 cm). Then the two ports of the net were closed. The net was put into the column (part 4 in Fig. 3). After completing adsorption, the XAD-2 net was put into the Soxhlet extractor and added 50 µL of the surrogate internal standards (Ace-10). Soxhlet extraction carried on 24 h and gained SAM-2. The following process was the same as 2.3 and enrichment rate of the XAD-2 was also calculated as the equation (2), but in which, Q_{SAM-2} was the content of each polycyclic aromatic hydrocarbon in the XAD-2 adsorbent.

Sample collection: To further check the enrichment effect of organic micro pollutants from atmosphere by gas flowing-liquid phase method, we collected samples by two methods simultaneously. The sampling site was on the roof of Experimental Building about 50 above ground level, collect time was 24 h.

GC-MS analysis: Chromatographic analysis was performed on a Shimadzu GC-2010 with DB-5MS capillary column (30 m × 0.25 mm × 25 µm) and detected on a Shimadzu QPMS-2010 mass spectrometer with quadruple mass spectrometer system. Helium (> 99.99 % pure) was used as carrier gas with a flow rate of 2.22 mL/min. The injector was operating at 320 ºC with the splitless mode and the interface temperature was set at 280 ºC. For analysis of polycyclic aromatic hydrocarbons, the column temperature was maintained at 80 ºC for 4 min and then programmed to increase by 20 ºC/min to 280 ºC and then held for 16 min. The overall GC program time was 0.5 h. Six-polycyclic aromatic hydrocarbons in the standard solution and samples was qualitated by using total ion scan mode (m/z: 100-400) and quantified by using selective ion monitoring (SIM) mode. The selective ion monitoring was segmented into four sections: 9.0-11.5 min, m/z: 154, 153, 166, 165, 164; 11.5-16.5 min, m/z: 188, 178, 176, 202, 200, 101; 16.5-22.0 min, m/z: 252, 250; 22.0-27.0 min, m/z: 276, 138. The samples of field experiments was qualitated by using total ion scan mode (m/z:100-400), then quantified by using selective ion monitoring mode. The selective ion monitoring was segmented into five sections: 5.0-8.0 min, m/z: 136, 128, 142, 141; 8.0-12.2 min, m/z: 151, 152, 153, 154, 162, 164, 165; 12.2-17.2 min, m/z: 188, 178, 176, 202, 101, 200; 17.2 -24 min, m/z: 228, 226, 252, 250, 264.

RESULTS AND DISCUSSION

Feasibility of the gas flowing-liquid phase enrichment technology: In order to test the feasibility of the design of the gas flowing-liquid phase enrichment, this study firstly researched gas flow rate or temperature effect on desorption of polycyclic aromatic hydrocarbons in the liquid phase. The experimental results showed in Figs. 4 and 5.

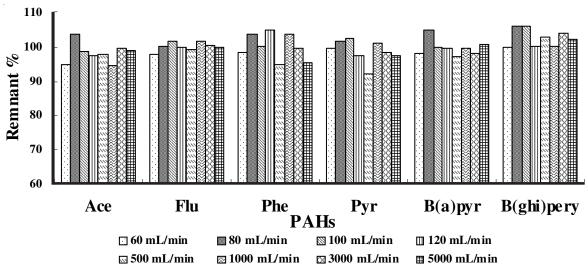

Fig. 4. Effect of the flow rate of carrier gas on the remain rate. (Room temperature, organic solvent-dichloromethane: 30 mL and experiment duration: 24 h)

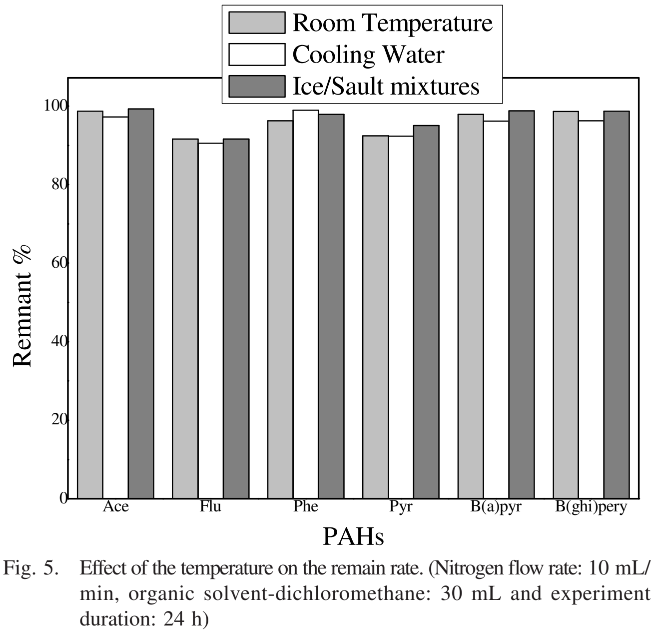

Fig. 5. Effect of the temperature on the remain rate. (Nitrogen flow rate: 10 mL/min, organic solvent-dichloromethane: 30 mL and experiment duration: 24 h)

Fig. 4 shows the results obtained from the experiments carried out at some different carrier gas flow rate. From these results, it is clear that remain rate of each polycyclic aromatic hydrocarbon in dichloromethane at room temperature was high to 0.90 ± 0.10 %. In other words, desorption of the polycyclic aromatic hydrocarbons in the organic solution was a bit of and the most polycyclic aromatic hydrocarbons retained in the solution. In addition, the remnant rate was not influenced by the carrier gas flow rate, as there were no significant difference between the remnant rate at 60 mL/min-5000 mL/min of nitrogen flow rate. In the process, the volume of the polycyclic aromatic hydrocarbons and organic solution reduced with the experiment carrying out. But at the same time, the organic solvent was added, so the volume of the solution was nearly unchangeable. In effect much organic solvent was browned away while the quantity of polycyclic aromatic hydrocarbons was mostly remained.

At the same flow rate 100 mL/min, the remnant rate at different temperature showed in Fig. 5. According to the experimental results, these remnant rates were not very different at usual temperature, room temperature, condensate water or ice and salt mixture environment. Each remnant rates of polycyclic aromatic hydrocarbons in the organic solution was about 0.90. At the same flow rate, temperature had not sharply effect on the remnant rate. There were most polycyclic aromatic hydrocarbons remained in the solution at these temperature environments. So the organic solvent was almost only browned away by nitrogen.

As suggested previously, the flow rate of carrier gas and usual temperature had not sharply influenced desorption of the polycyclic aromatic hydrocarbons in the organic absorption solvent. If the polycyclic aromatic hydrocarbons gas is absorbed by the organic solvent, polycyclic aromatic hydrocarbons in the solution should not be blowed out by the carrier gas with the experiment carrying on. So the gas flowing-liquid phase enrichment technology on collecting gas polycyclic aromatic hydrocarbons is very feasible.

Influence of the temperature on absorption rate: Because different experimental conditions (temperature, organic absorption solvent and carrier gas flow rate) were suspected to influence the absorption rate, two parameters were kept constant and the third parameter varied. Fig. 6 shows that temperature had no contrasting effects on the absorption rate. In view of the results, the absorption rate of the three conditions was similar. But the temperature of polycyclic aromatic hydrocarbons gas was high, it had big different from the field sampling. So in the laboratory study, the ice/salt mixture condition was selected to reduce the temperature of the polycyclic aromatic hydrocarbons gas and the filed investigation sampled in room temperature.

But at every temperature condition, the absorption rates of these small molecular weight were higher than those large molecular weights. Obviously the absorption rate of B(a) Pyr, B(ghi)Pery were very low (< 0.50). This may be relate to the rate of the generation of each polycyclic aromatic hydrocarbons and the rate of being carried of each polycyclic aromatic hydrocarbons. At the same condition the two rates of small molecular weight polycyclic aromatic hydrocarbon were both bigger than large molecular weights polycyclic aromatic hydrocarbon. So the polycyclic aromatic hydrocarbon with high molecular weight was not timely carried by the N_2, the most of these gas remained in the space of the gas generator and the gas pipe.

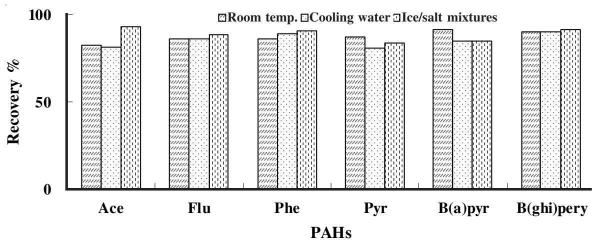

Fig. 6. Effect of the temperature on the absorption rate. (Nitrogen flow rate: 50 mL/min, organic solvent-dichloromethane: 30 mL and experiment duration: 2 h)

Influence of the organic solvent on absorption rate: In order to observe the highest absorption rate during the usual organic solvent, dichloromethane, trichloromethane and MeOH were selected. Fig. 7 shows effect of organic solvent on the adsorption rate in the enrichment technology. The absorption rate with dichloromethane, trichloromethane, MeOH and dichloromethane : MeOH = 1:1 (v:v) gradually reduced. May be the absorption rate is related to the polarity of the organic solvent. The polycyclic aromatic hydrocarbons is non pollard. Because dichloromethane or trichloromethane is very little polar, MeOH or dichloromethane and MeOH is the larger polarity. So at the same condition, the absorption rate in dichloromethane or trichloromethane was higher than in MeOH or dichloromethane and MeOH and the absorption rate of small molecular weight polycyclic aromatic hydrocarbons was higher than large molecular weight polycyclic aromatic hydrocarbons.

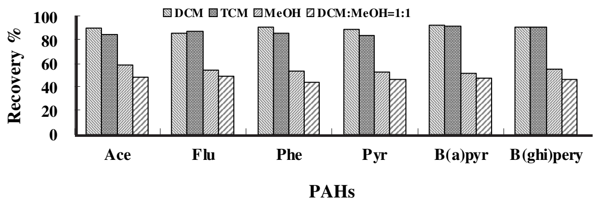

Fig. 7. Effect of the organic solvent on the absorption rate (nitrogen flow rate: 50 mL/min, organic solvent-dichloromethane (DCM): 30 mL and experiment duration: 2 h)

Influence of the carrier gas flow rate on absorption rate: The mass of polycyclic aromatic hydrocarbons gas in the generator at same temperature and during same time should be the same. The polycyclic aromatic hydrocarbons gas was carried off by the nitrogen. So the nitrogen flow rate was the key parameter to the mass carried in the organic solvent. Sixteen sets of experiments were carried out with flow rate among 50 mL/min - 5000 mL/min (Fig. 8). The adsorption rate of each polycyclic aromatic hydrocarbons increased with increasing the flow rate of N_2. But the absorption rate of small molecular weight polycyclic aromatic hydrocarbons was high at low flow rate, such as the absorption rate of Ace and Flu were more than 0.90 at 200 mL/min. But at 200 mL/min, the absorption rates of high molecular weight of Phe, Pyr, B(a)Pyr, B(ghi)Pery were respectively 0.76, 0.42, 0.12 and 0.12. With the gas flow rate increasing to 3000 mL/min, the absorption rate of each polycyclic aromatic hydrocarbons reached about 0.90. And at 4000 mL/min, 5000 mL/min, all the absorption rate of 6-polycyclic aromatic hydrocarbons were about 0.90 too. The volume of generator was small and the internal diameter of gas pipe was thin, so this study researched the 5000 mL/min as the largest flow rate. And we could infer that the same perfect adsorption rate would attain with the flow rate increasing. The consumption rate of dichloromethane increased with the gas flow rate increasing. The consumption rate of dichloromethane was 100 mL/h at 5000 mL/min of the flow rate, while the consumption rate was 54 mL/h at 3000 mL/min. So, 3000 mL/min was the better gas flow rate as the sampling. And the flow velocity was satisfied with the field sampling[16,32].

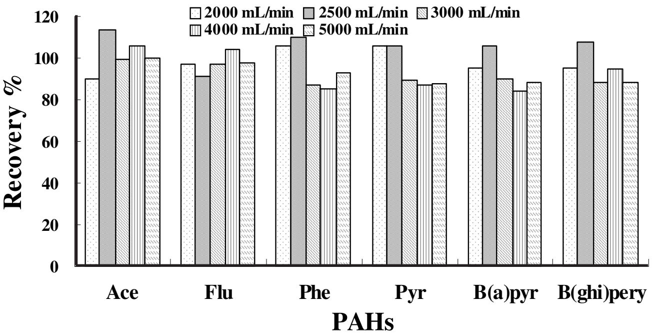

Fig. 8. Effect of nitrogen flow rate on the absorption rate. (Ice/salt mixture, organic solvent-dichloromethane: 30 mL and experiment duration: 2 h)

Comparison with XAD-2: At the same experiment conditions (nitrogen flow rate: 3000 mL/min, experiment duration: 2 h, but dichloromethane in ice/salt environment), there were only adsorbent or absorbent different and the results of the two sampling methods showed as Table-1. By comparing the two sampling method, that could check the effect of the gas flowing- liquid phase enrichment. Table-1 shows that the adsorption rate of 6-polycyclic aromatic hydrocarbons in XAD-2 and in dichloromethane both got close to 1.0, RSD % < 5 %. But the enrichment efficiency of organic solvent was slightly better than XAD-2. May be the process of treatment of XAD-2 sample was complicated and there may be more loss of polycyclic aromatic hydrocarbons in the process.

TABLE-1
COMPARISON BETWEEN THE ENRICHMENT EFFICIENCY OF XAD-2 AND DCM to 6-PAHs

Q_{DCM}/Q_{XAD}	SAM-1	SAM-2	SAM-3	Average	RSD %
Ace	1.03	1.03	1.11	1.06	4.2
Flu	1.01	1.04	1.03	1.03	1.4
Phe	1.01	1.10	1.05	1.05	4.6
Pyr	1.01	1.03	1.06	1.03	2.6
B(a)pyr	1.06	1.09	1.21	1.12	7.3
B(ghi)pery	1.05	1.08	1.06	1.06	1.7
Mean	1.03	1.06	1.07	1.06	3.6

Field validation: To check the matrix effect of the gas flowing-liquid phase enrichment, some analyses were carried out in the atmosphere. The new and the traditional sampling methods carried out at the same time in the same environment. Eight polycyclic aromatic hydrocarbons was detected by GC/MS. Table-2 presented the results in the new sampling technology and the ratios of 8 polycyclic aromatic hydrocarbons concentrations in dichloromethane compared to in XAD-2. The ratios showed that the dichloromethane solvent collection efficiencies was mostly similar to the XAD-2. All ratios were at about 0.9-1.4, RSD % < 30 %. The reason of different may be the difference of adsorbing process between dichloromethane and XAD-2. And there were fine polycyclic aromatic hydrocarbons particles in the both collection adsorbent. But the two adsorbent were carried out in the same sampling conditions. Generally the new technology is valuable to sampling the polycyclic aromatic hydrocarbons gas phase in the atmosphere.

TABLE-2
AMBIENT GAS PHASE 8 PAHs CONCENTRATIONS IN THE GAS FLOWING – LIQUID PHASE ENRICHMENT AND THE RATIOS COMPARED TO THE 8 PAHs CONCENTRATIONS IN XAD-2

Q_{DCM}/Q_{XAD}	SAM-1	SAM-2	SAM-3	Average	RSD %
Naphthalene	1.22	1.31	1.11	1.21	8.1
2-Methnaphthalene	0.99	1.23	1.17	1.13	11.2
1-Methnaphthalene	1.00	0.85	1.27	1.04	20.3
Acenaphthylene	1.07	0.72	1.09	0.96	21.8
Acenaphthene	1.29	1.17	1.72	1.39	20.5
Fluorene	1.11	1.02	1.16	1.10	6.6
Phenanthreme	0.79	1.07	1.26	1.04	22.9
Anthracene	1.40	1.09	1.05	1.18	16.3

Conclusion

The work presents a novel gas flowing-liquid phase enrichment technology of sampling and enriching organic micro pollutants from atmosphere, as well as experimental results had proved the feasibility for the technology by simulating analysis of 6-polycyclic aromatic hydrocarbons. To simulating analysis, analysts could be absorbed and enriched into an acceptor solvent for 108 mL of dichloromethane in ice salt bath yielding 90 % enrichment at 3000 mL/min of carrier gas for 2 h. To real sampling analysis, 8 polycyclic aromatic hydrocarbons were determined and the compared ratios also showed the technology enough to evaluate the polycyclic aromatic hydrocarbons in the atmosphere. The design and its application were simple and cheap.

Forming laboratory and field investigations on the performances of a gas flowing-liquid phase enrichment technology, the results indicated that the new technology could conveniently and efficiently sample the gas phase polycyclic aromatic hydrocarbons. Due to the polycyclic aromatic hydrocarbons are the representative of organic gas pollutes, so the new technology should effectively sample the other organic gas pollutes in the atmosphere. But the new technology need further improvement, for example : design the bigger structure of the apparatus to sampling more air and do more field sampling to perfect the new technology. All the results of studies show that the technology is feasible to enrich the organic micro pollutants from atmosphere.

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