Nanofiber-based enrichment device
for sampling organic contaminants in vacuum environment

Yan Yan[1]   Deng Jianjun[1]   Deng Siwei[1]   Wang Yu[1]   Wang Feng[1]   Xiao Mei[3]   Kang Xuejun[1,2]

([1]Key Laboratory of Child Development and Learning Science of Ministry of Education, Southeast University, Nanjing 210096, China)
([2]Suzhou Key Laboratory of Environment and Biosafety, Southeast University, Suzhou 215123, China)
([3]School of Electronic Science and Engineering, Southeast University, Nanjing 210096, China)

Abstract: A novel method for sampling and enriching organic volatile contaminants in the vacuum environment combined with qualitative analysis based on the vacuum simulation test is proposed. A nanofiber is used as absorbent to collect the organic volatile contaminants in the vacuum environment and then eluted by methanol. The eluent is analyzed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS) to identify the composition of the organic contaminants. The nanofiber is composed of polystyrene and it is prepared by electrospinning. Before being used, the nanofiber is processed by ultrasound in ethanol for 15 min to remove some impurities and dried in an oven at 60 ℃, and then 10 mg of the nanofiber is wrapped in a thermoplastic polyester fabric pocket. The vacuum pump oil and di-iso-decyl phthalate (DIDP) are chosen as absorbates to test the absorbent performance of the nanofiber in the vacuum environment. Experiments are performed under the pressure of 10^{-4} and 10^3 Pa, respectively. It is shown that the nanofiber-based enrichment device can be used to adsorb the organic contaminants in the vacuum simulation environment.
Key words: nanofiber; sampling; vacuum environment; organic contaminants
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With the rapid development of electronics and in the defense industries, vacuum devices are widely used in vacuum coating, ion beam etching and space environment simulation etc. The impacts of vacuum and atmospheric environments on materials are quite different during aircraft running. With the decrease in the pres-

sure, there is a spontaneous evolution of gas from the materials of vacuum devices, and most of these gases are composed of volatile organic compounds such as phthalates, butyl tropolone, alkane, etc. These organic contaminants will cause material degradation, instrument failure, and destruction of the vacuum chamber. For example, they may deposit on the surfaces of sensors of vacuum devices[1–2]. In addition, it is reported that phthalate and siloxane are identified as the main contaminants in satellite thermal vacuum tests and solar array thermal vacuum tests[3]. Molecular organic contaminants, such as halogens, sulphur compounds, ammonia and soluble amines and hydrocarbons (C_6 to C_{16})[4], also have been detected in a high power laser vacuum facility. Therefore, the sampling, enriching and detecting of these volatile organic contaminants in vacuum environments are very important.

The organic contaminants in vacuum environments have been studied by some research institutes. In 1997, NASA developed a simulation chamber and several contamination measurements during vacuum tests. Non volatile residue (NVR) qualitative and quantitative analyses are conducted for monitoring molecular contamination, including DOP (di-2-ethylhexyl phthalate), silicones such as tetracosa methyl cyclododecan siloxane. The Fourier transform infrared spectrometry (FTIR) and the GC/MS are adopted for qualitative analysis, and gravimetry for quantitative analysis, respectively[5]. It is reported that swab is used to collect the contaminants on the sensor surfaces of vacuum devices, and then contaminants are eluted with acetone and analyzed by the GC-MS[6]. It is also reported that the direct simulation Monte Carlo (DSMC) analysis code, as released by NASA, is a general purpose, gas dynamic, transport analysis suite of codes. These codes can help to model the diffusion of contaminants through solid surfaces[7].

Because of the low concentration of the contaminants in the vacuum environment, pre-concentration and pre-treatment of the sample play a crucial role during the detection. The pre-concentration step is often combined with the sampling step. A widely used sampling technique is based on solid adsorption for substances in various envi-

ronments. The analytes can be desorbed either by using a solvent or by thermal means[8]. It is reported that passive sampling is a rapid, effective and low-cost method in monitoring chemical pollutants in various environments. The Radiello passive sampler is introduced to the market, which can enable effective sampling of organic pollutants, for example, benzene-toluene-xylenes (BTX), volatile organic compounds (VOCs), nitrogen dioxide (NO_2) and many other contaminants for industrial, indoor, outdoor and personal exposure applications[9]. The graphitized carbon blacks, Carbotrap X and Carbograph 5, can adsorb some low-boiling oxygenated compounds in gaseous samples[10]. However, these sampling methods are seldom used in the pre-concentration of contaminants in the vacuum environment.

Due to the excellent adsorption/desorption effects, the nanofiber is often used for solid phase extraction during the sample pre-treatment[11−12]. However, it is seldom used for the enrichment of organic contaminants in vacuum environments. Experiments show that the nanofiber is a highly effective adsorbent with the advantages of reutilization and easy absorption and desorption. In this paper, the nanofiber-based enrichment device is used to sample and enrich volatile organic contaminants in the simulated vacuum environment.

1 Experimental

1.1 Instruments and reagents

The Agilent 7890A gas chromatography with DB-5 (5% diphenyl 95% dimethyl polysiloxane, 60 m × 0.32 mm × 0.25 μm) is used to separate and analyze different components.

The Agilent 6890 gas chromatography with HP-5 (5% phenyl-methyl polysiloxane, 30 m × 0.32 mm × 0.25 μm) and an MSD Agilent 5973 mass detector are used to separate and identify different components.

Vacuum pump oil is provided by the School of Electronic Science and Engineering, Southeast University and methanol (HPLC-grade) is obtained from the Shandong Yuwang Industrial Co., Ltd., Chemical Branch (Shandong, China). Phthalate (DIDP) (AR) and methanol (HPLC-grade) are also obtained from the Shandong Yuwang Industrial Co., Ltd., Chemical Branch (Shandong, China).

1.2 Preparation of nanofiber-based enrichment device

The nanofiber is composed of polystyrene and it is prepared by electrospinning[13−15]. Before being used, the nanofiber is treated by ultrasound in ethanol for 15 min to remove impurities and dried in oven at 60 ℃, and then 10 mg of the nanofiber is wrapped in a thermoplastic polyester fabric pocket. The nanofiber-based enrichment device is shown in Fig.1.
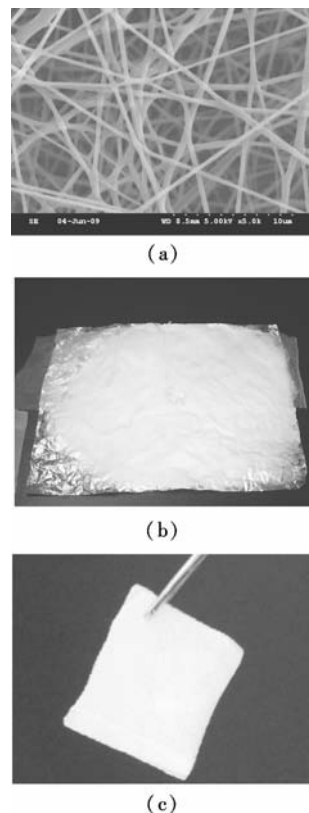
Fig.1 Nanofiber-based enrichment device. (a) Scanning electron microscope images of nanofiber; (b) Photograph of nanofiber; (c) Nanofiber-based enrichment device

1.3 Simulation vacuum device (vacuum quartz tube)

Place the vacuum pump oil or DIDP in the bottom of the quartz tube. Fire the central part of the quartz tube and make it thin enough to place the nanofiber-based enrichment device. Finally, vacuum the tube under a pressure of 10^{-4} and 10^3 Pa, respectively, and then seal it. The simulation vacuum device is shown in Fig.2.
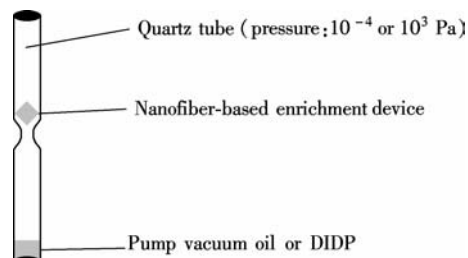
Fig.2 Schematic representation of simulation vacuum device

1.4 Sample collection and separation

One of the quartz tubes without adding any liquid sample is used as a blank control. The vacuum pump oil or DIDP is put in the bottom of the quartz tube. All the quartz tubes are vacuumed under a pressure of 10^{-4} and 10^3 Pa, respectively, and the end of each quartz tube is sealed by calcining. After that, the nanofiber-based enrichment devices are taken out of these quartz tubes. The

nanofiber is picked out from the device and eluted by 1 mL of methanol for 2 h. 1 μL of the eluted solution is injected into GC and GC-MS to identify the composition of the organic contaminants.

1.4.1 GC condition

The GC experimental condition of analyzing the volatile part of the vacuum pump oil in the simulation vacuum environment is shown as follows. The gas chromatography is equipped with a split injector. The temperature of the injection port is 270 ℃, and the split ratio is 10∶1. 1 μL of the desorbed solution is injected for analysis. The column temperature is held at 50 ℃ for 2 min and increased to 250 ℃ at 15 ℃/min for 20 min. The flow rate of the nitrogen carrier gas is set to be a constant of 1 mL/min.

1.4.2 GC-MS condition

The GC-MS experimental condition of analyzing the volatile part of the vacuum pump oil in the simulation vacuum environment is given as follows. The gas chromatography is equipped with a split injector, and the temperature of the injection is 260 ℃. 1 μL of the desorbed solution is injected for analysis. The column temperature is held at 50 ℃ for 2 min and increased to 250 ℃ at 15 ℃/min for 30 min. The flow rate of the helium carrier gas is set to be a constant of 1 mL/min. The mass spectrometer, with the ion source temperature maintained at 200 ℃, is used in the full scan mode. The mass spectra are scanned with a mass-charge ratio (m/z) ranging from 35 to 500. The electron energy is 70 eV and the acquisition rate is 2 spectra/s.

The GC-MS experimental condition of analyzing the volatile part of DIDP in the simulation vacuum environment is shown as follows. The gas chromatography is equipped with a split injector, the temperature of the injection is 300 ℃. 1 μL of the desorbed solution is injected for analysis. The column temperature is held at 50 ℃ for 5 min and increased to 150 ℃ and 250 ℃ at 5 ℃/min for 10 min, respectively, and then to 300 ℃ at 10 ℃/min for 10 min. The flow rate of the helium carrier gas is set to be a constant of 1 mL/min. The mass spectrometer, with the ion source temperature maintained at 200 ℃, is used in the full scan mode. The mass spectra are scanned with a mass-charge ratio ranging from 35 to 500. The electron energy is 70 eV and the acquisition rate is 2 spectra/s.

2 Results and Discussion

2.1 Volatile components analysis of vacuum pump oil

The chromatogram of GC in Fig. 3 shows that the volatile parts of the vacuum pump oil are composed of multi-components compounds, and the nanofiber-based enrichment device has a good adsorption performance on various components of the vacuum pump oil in different vacuum environments.
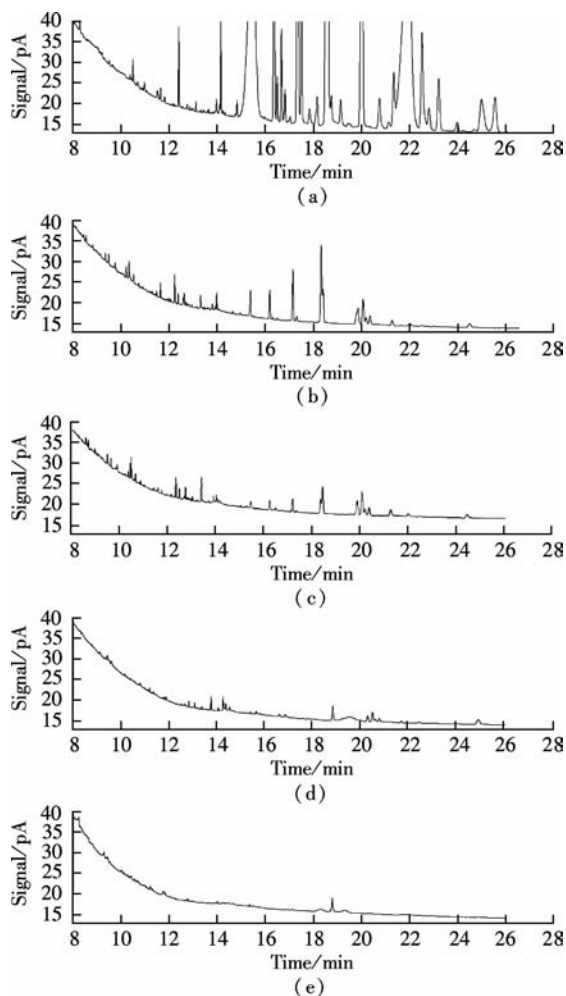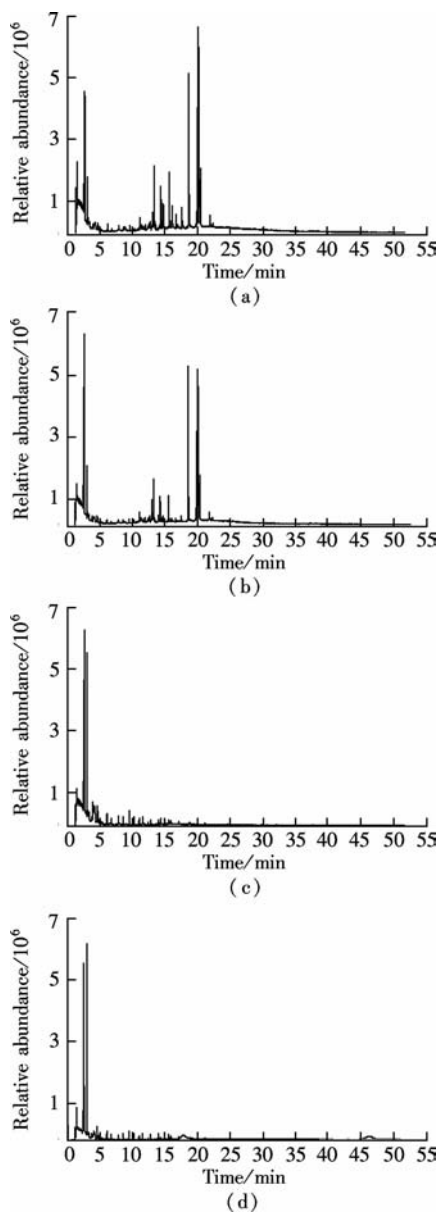

Fig. 3 Chromatogram of sample tube (containing vacuum pump oil) and blank tube. (a) Methanol solution of vacuum pump oil; (b) Sample vacuum quartz tube (10^{-4} Pa); (c) Sample vacuum quartz tube (10^3 Pa); (d) Blank vacuum quartz tube (10^{-4} Pa); (e) Blank methanol solution

The pre-treatment of the sample is the same as the operation in Section 1.4. To further identify the components of the vacuum pump oil, 1 μL of the methanol leaching solution is injected into the GC-MS for analysis. The results are given in Fig. 4, and the relevant substances are given in Tab. 1.

2.2 Volatile components analysis of DIDP

As a common organic contaminant, DIDP is placed in the vacuum quartz tube to investigate the adsorption properties of the nanofiber-based enrichment device. The pre-treatment of the sample is the same as the operation in Section 1.4. 1 μL of the methanol leaching solution is injected into the GC-MS for analysis. The retention time of DIDP is 40 min. Selection ions are obtained at a mass-charge ratio of 149 and 307, respectively, as the qualitative ion fragment peaks of DIDP (see Fig. 5). It is shown that the nanofiber-based enrichment device performs a good adsorption effect on DIDP in the vacuum environment. The results are given in Fig. 6.
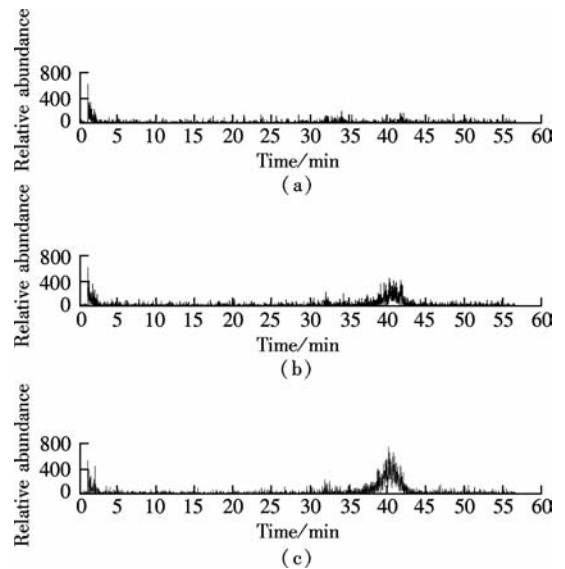
Fig. 4 Mass spectra of sample tube (containing vacuum pump oil) and blank tube. (a) Sample vacuum quartz tube (10^{-4} Pa) ; (b) Sample vacuum quartz tube (10^3 Pa) ; (c) Blank vacuum quartz tube (10^{-4} Pa) ; (d) Blank methanol solution

Tab. 1 Potential volatile components in vacuum pump oil

Components	Molecular weight	Retention time/min
C_3H_7NO	73	3.864
$C_7H_{14}O_2$	130	6.427
$C_9H_{18}O_2$	158	7.580
$C_{10}H_{20}O_2$	172	8.604
$C_{16}H_{18}$	210	14.628
$C_{15}H_{22}O$	218	15.932
$C_4H_{10}Cl_2Si$	157	16.678
$C_{15}H_{19}N$	213	17.578
$C_{15}H_{20}Si_2$	256	20.000
$C_{18}H_{31}NO$	277	27.131
$C_2H_6Cl_2Si$	128	30.754
$C_7H_{11}NS$	141	35.463
$C_4H_5N_3O_2$	127	41.497
$C_{13}H_{26}O_3$	230	48.856
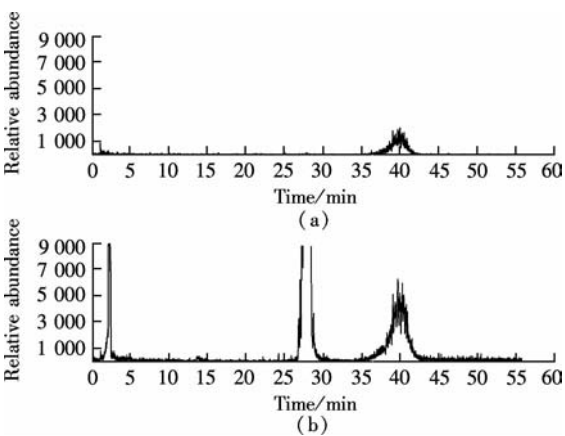
Fig. 5 The mass spectra of DIDP standard. (a) $m/z = 307$; (b) $m/z = 149$

Fig. 6 Mass spectra of sample tube (containing DIDP) and blank tube. (a) Blank vacuum quartz tube (10^{-4} Pa) ; (b) Sample vacuum quartz tube (10^3 Pa) ; (c) Sample vacuum quartz tube (10^{-4} Pa)

3　Conclusion

In this paper, a nanofiber-based enrichment device is used for sampling and enriching volatile organic contaminants from the vacuum pump oil and DIDP in different simulated vacuum environments. From the results of GC and GC-MS for identifying the components of the volatile organic contaminants, it can be seen that the nanofiber-based enrichment device has a good adsorption effect on the vacuum pump oil and DIDP in different vacuum environments.

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真空环境下基于纳米纤维富集器的污染物采集

晏　嫣[1]　邓剑军[1]　邓思维[1]　王　羽[1]　王　丰[1]　肖　梅[3]　康学军[1,2]

([1] 东南大学儿童发展与学习科学教育部重点实验室,南京210096)
([2] 东南大学苏州研究院苏州环境与生物安全重点实验室,苏州215123)
([3] 东南大学电子科学与工程学院,南京210096)

摘要:建立了在真空条件下检测有机污染物挥发组分的新方法.在模拟的真空环境中进行有机污染物的采样、富集.利用纳米纤维作为吸附剂采集真空中的有机污染物,并且用甲醇洗脱.甲醇洗脱液中的组分利用气相色谱(GC)和气质联用(GC-MS)进行检测.纳米纤维由静电纺丝法制成,其材料为聚苯乙烯.实验前,纳米纤维在乙醇溶液中超声15分钟以去除杂质,后将其移入60 ℃的烘箱烘干,最后将10 mg处理好的纳米纤维装入热塑性聚酯布袋中制成富集器.选择真空泵油和邻苯二甲酸二异癸酯(DIDP)作为目标物测试吸附剂,在真空环境中研究其采集效果.实验分别在压力为 10^{-4} 和 10^3 Pa 的环境中进行.实验结果表明,基于纳米纤维的富集器在模拟的真空环境中对有机物具有采样和富集效果.

关键词:纳米纤维;采样;真空环境;有机污染物

中图分类号:O659.1