Performance evaluation of electrospun nanofiber mat as samplers for the trap of trace heavy metals in atmospheric particles and its application

Guozhe Deng,*1‡ Xiaoyan Deng,*2‡ Jianjun Deng,*3 Xiaoting Lu,*4 Xuejun Kang,*1† Yuan Song*4

*1 Key Laboratory of Child Development and Learning Science of Ministry of Education of China, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, China.
*2 Geological Survey of Jiangsu Province, Nanjing 210080, China.
*3 Suzhou Dongqi Biological Technology Co., ltd, Suzhou 215123, China.
*4 Division of Child Care, Suzhou Municipal Hospital, Suzhou, Jiangsu215002, P R China.

† To whom correspondence should be addressed.
‡ These authors contributed equally to this paper.

E-mail: xjkang64@163.com
Abstract

Traditional methods for the analysis of trace heavy metals in atmosphere require collecting atmospheric particles on filter substrates, such as cellulose, quartz fiber member, etc. In this paper, we reported a different filter to capture trace heavy metals in the atmospheric particulates. Four kinds of electrospun nanofiber filters, polystyrene (PS), polystyrene-dithizone (PS-DZ), acrylic acid (AR), and acrylic acid-dithizone (AR-DZ) were produced by electrospinning and used as the filters to trap heavy metals in atmospheric particles. Based on these nanofiber filters, the digestion method and eluent were optimized. Under the optimal conditions (oscillation extraction with acetic acid - potassium acetate (HAC-KAC) buffer solution (0.1 mol·L⁻¹, pH = 4.5)), the developed method was applied successfully to determine the four particulate metal elements (As, Cd, Hg, and Pb) in air in two urban area of Suzhou, China. Furthermore, a correlation between heavy metals in air and breast milk was observed. The results confirmed that electrospun nanofiber mat could be a potential candidate for sampling of heavy metals in atmospheric particles with higher efficiency.

Keywords: electrospinning, nanofibers, adsorption performance, air pollution, human breast milk.
Introduction

Air pollution has emerged as a growing concern worldwide, and the composition of pollutants was complicated. As previously reported, various of biological (endotoxin, bacteria, virus, etc.) and chemical (heavy metals, PAHs, etc.) pollutants were attached to the particulate matter (PM).\textsuperscript{1} PM especially particles with aerodynamic diameter less than 10 μm (PM$_{10}$) and 2.5 μm (PM$_{2.5}$) in polluted air caused great attention, as long-term exposure to them (especially PM$_{2.5}$) presented discomfort and serious impacts on the health of human.\textsuperscript{2,3}

Heavy metals usually invade into the human body through diet intake,\textsuperscript{4,5} inhalation,\textsuperscript{6} and skin contact,\textsuperscript{7} then give rise to adverse effects on human health through bioaccumulation.\textsuperscript{8,9} For example, arsenic (As) is carcinogenic and can cause cancer of the skin,\textsuperscript{10} lungs,\textsuperscript{11} and liver.\textsuperscript{12} Long-term exposure to lower levels of cadmium (Cd) leads to kidney disease and lung damage,\textsuperscript{13} and lead (Pb) can damage the nervous system,\textsuperscript{14} especially children.\textsuperscript{15} Mercury was also considered as a human carcinogen\textsuperscript{1,16} and exposure to high levels can permanently damage the brain functions.\textsuperscript{17}

Therefore, to monitor the metal content in atmospheric aerosols is of great importance. However, it's a challengeable issue to capture it by filters because of the low levels of heavy metals in atmosphere, and this also needs a special sampling procedure.\textsuperscript{18-20} Cellulose acetate membrane,\textsuperscript{21} quartz film,\textsuperscript{22,23} and Teflon membrane\textsuperscript{24,25} were mostly used as sampling filters, but these traditional membrane usually suffer from various application defects, such as substantial variability in blank values, low trapping efficiency.\textsuperscript{26} Hence, the demand of a filter with high sampling efficiency and easy manipulation is increasing dramatically.

Nanomaterial shows different properties compared with conventional materials, so it
can greatly improve the trapping efficiency of atmospheric particles.\textsuperscript{27,28} Electrospinning is an easy method to prepare nanofiber,\textsuperscript{29} and varieties of organic/inorganic materials can be used to produce nanofibers. For example, polymers,\textsuperscript{30} ceramics,\textsuperscript{31} proteins,\textsuperscript{32,33} and their mixtures.\textsuperscript{34} Electrospun fibers usually possess some remarkable properties including special three-dimensional morphology, large specific surface area, convenient and easy preparation. These properties make them promising in applications of different fields, such as membrane distillation,\textsuperscript{35} photocatalysis,\textsuperscript{36} additive for battery,\textsuperscript{37} and air filtration media.\textsuperscript{38,39} However, as far as we know, no reports had been presented on the use of electrospun nanofiber as a sampling filter for atmospheric particles matter in multiple trace metal analysis.

In this study, the probability for using electrospun nanofiber filters to trap multiple heavy metals (Pb, As, Hg, and Cd) was explored. Four kinds of electrospun nanofiber filters produced by electrospinning of polystyrene (PS), polystyrene-dithizone (PS-DZ), acrylic acid (AR), and acrylic acid-dithizone (AR-DZ) were prepared and used as the filters to trap heavy metals in atmospheric particles. The properties of the as-spun nanofiber, including morphology, structure, wettability, and trapping performance were studied systematically. Inductively coupled plasma Mass spectrometry (ICP-MS) was used to measure the concentrations of four trace heavy metals (Pb, As, Hg, and Cd) for evaluating the performance of the homemade filters. Conditions for sample digestion were optimized, and a new method was established and applied in the monitoring of heavy metals in air, then a correlation analysis between levels of heavy metals in air and mother's breast milk was also studied.

**Experimental**
Reagents and chemicals

Polystyrene (PS, average MW: 192,000), poly (acrylic acid) (AR, average MW: 450,000), Tetrahydrofuran (THF), and N, N-Dimethylformamide (DMF) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China), all other chemicals were of analytical grade without purification.

Cellulose acetate membrane (CAm) was obtained from Whatman, ultrapure water (18.2 MΩ·cm) was obtained from a Millipore Milli-Q Plus system. All glassware used were cleaned with 5 % (v/v) nitric acid aqueous solution and rinsed with distilled water.

0.1 mol·L⁻¹ acetic acid - potassium acetate (HAC-KAC) buffer solution (pH = 4.5) was prepared by dissolving 3.86 g acetic acid and 2.93 g sodium acetate in 1000 mL distilled water.

Apparatus

ICP-MS 7700 (Agilent Technologies) was used to analyze the metal ions, a high-voltage power supply (DW-P403-1AC, Tianjin, China) and a syringe pump were used for the electrospinning. Field emission scanning electron microscope (FESEM, Zeiss Ultra Plus) was utilized to investigate the morphology and structure of the prepared nanofiber mats. X-ray powder diffraction (XRD) pattern was obtained by X-ray diffractometer (X’ Pert PRO MRD, PANalytical, Netherlands). Video Optical Contact Angle Measuring Instrument (OCA 15 plus, Dataphysics, Germany) was used to measure the contact angle of nanofiber for water and oil. The surface area was determined by nitrogen adsorption/desorption using the Brunauer-Emmett-Teller method (BEL SORP-mini BEL Japan Inc., Japan). A regulated power supply (DW-P403-1AC, Tianjin, China) was used as electrostatic spinning high DC voltage power to perform electrospinning work. A portable gaseous particles sampler (SFC-3BT, Nanjing, China) was used for air sampling.
**Preparation of standard solutions**

Standard stock solutions (1.0 mg·mL⁻¹) of metal elements (Pb, As, Hg, and Cd) were prepared in 2% nitric acid (Guaranteed reagent) aqueous solution. Working standard solutions were prepared by daily diluting the stock solution.

**Collection of breast milk**

Twenty-six volunteers were recruited from Suzhou Municipal Hospital, Jiangsu, China, and breast milks were collected respectively. Ten breast milks were from Suzhou National New & Hi-Tech Industrial Development Zone (NHIDZ), and sixteen breast milks were from Suzhou Industrial Park (IP). Ethical approval for the study was obtained from the Ethnic Committee of South East University prior to the collection and analysis of these biological samples. The collected samples were stored at -20 °C immediately.

**Preparation of electrospun nanofiber mat**

A certain amount of PS was dissolved in a mixture of DMF/THF (v/v, 4/6) by vigorous magnetic stirring until it was completely dissolved, forming a 12 % (w/v) solution. PS-DZ solution was obtained by dissolving dithizone into the previous PS solution thoroughly, and finally a mixed solution contained 5 % (w/v) dithizone was formed. 10 % (w/v) AR spinning solution was obtained by dissolving AR in a mixture of Ethanol/DMF (8/2, v/v), and AR-DZ solution which contained 5 % (w/v) dithizone was formed by adding dithizone to the former solution. Prepared solutions were then electrospun using home-made electrospinning machine (Fig. 1) at the feeding rate of 1 mL·h⁻¹ under applied voltage of 20 kV. Nanofiber was collected on an aluminum foil screen at 20 cm distance from the feeding needles. Constant temperature (25 ± 2 °C) and the relative humidity (45 ± 5%) were maintained throughout the fabrication process. Due to the weakness of nanofibers filters in mechanical strength, a piece of
polypropylene nonwoven fabric (120 g·m⁻², Φ=47mm) was adhered to the aluminum foil to collect the nanofibers, the resultant nanofiber filters (Fig. 2) were dried under vacuum at 45 °C overnight, and then cut along the circular polypropylene nonwoven fabric.

Atmospheric sampling

Sampling sites were selected according to the Specifications and Test Procedures for PM10 and PM2.5 (HJ 93-2013, Environmental Protection Law of the People's Republic of China). The nanofiber filter was fixed to the sampling holder which connected with the atmospheric particle sampler. Sampling lasted for 24 h with a constant flow rate of 20 ml·min⁻¹. After sampling, the filter was stored in a sealed container at room temperature prior to be analyzing, and another filter without sampling was used as the blank.

Treatment and determination of the sample

The nanofiber filters were stored in sealed container at 4 °C for less than one week or -80 °C for long time before analysis. The filters were immersed in a closed polytetrafluoroethylene digestion tank containing 20 mL 0.1 mol·L⁻¹ HAC-KAC buffer solution completely, and then oscillated for 30 min to digest the metals adsorbed on the filter. All samples were analyzed with ICP-MS. The instrument parameters were set as follows: sample uptake phase was 15 s; peristaltic pump 0.3 rps; stable phase 20 s, peristaltic pump 0.1 rps; the data collection phase was 15 s, peristaltic pump 0.1 rps; a single scan time for general elements was 0.1 s, the flow rate of the carrier gas was 0.78 L·min⁻¹, and the auxiliary gas 0.35 L·min⁻¹.

1 ml methanol and 1 ml 50% (v/v) trichloroacetic acid aqueous solution was added to 2 ml breast milk, ultrasonic mixing for 5 min, being centrifugated at 12000 rpm for 10 min, then the supernatant was filtered with 0.45 μm membrane before loading to
ICP-MS.\textsuperscript{40}

Results and Discussion

Characterization of electrospun nanofiber filter

FESEM was utilized to investigate the morphological characteristics of nanofibrous filter mats. Fig. 3 showed SEM images of the prepared nanofiber filters and the CAm before and after sampling. The fiber diameter was estimated by Image J software and listed in Table 1. From the FESEM images, it can be seen that all the nanofiber filters were with high porosity and three-dimensional network structure, which was formed by random accumulation of the nanofibers. It can also be seen from the FESEM images that after sampling some particles were trapped on the nanofiber filters, but no particle was obviously observed in CAm mat. It may be due to the narrow horizon of FESEM which could not capture the particles.

BET surface area was used as a common index for the assessment of nanomaterials, Table 1 showed the BET surface area, diameter, and contact angle of different nanofiber filters, as well as total amount of heavy metals (As, Cd, Hg, and Pb) trapped on the filters. As we all know, chelators have many functional groups and are widely researched for their interaction with metal ions in liquid phase. In this research, dithizone was introduced into the electrospun nanofiber filters for the trial of heavy metals trapping. After functionalized with dithizone, nanofiber filters displayed greater improvement in metal capturing performance (Table 1). Combined with this trial, it seemed that functional groups of materials rather than the parameters of surface morphology were the main factors which affect the adsorption of metals onto the nanofibers.
**X-Ray diffraction**

The XRD pattern of the synthesized nanofibers were measured and shown in Fig. 4. The broad peaks were observed for nearly all the fibers, and the intensity decreased as the angle increases, which indicated an amorphous structure. The noncrystalline structures with loosely aggregations of these polymer organic matters might benefit to the adhesion of some targets in air, which was suitable for trapping of particles matter containing metals.

**Hydrophilicity and hydrophobicity**

The hydrophilicity and hydrophobicity of filter materials are important for its application,\(^1\)\(^,\)\(^2\) hydrophilic filters are suitable for the extraction of polar compounds from aqueous medium,\(^3\)\(^,\)\(^4\) while hydrophobic filters are mostly used for gas filtration.\(^5\) Table 1 showed the hydrophilicity and hydrophobicity of the materials, PS and AR nanofiber filters were all hydrophobic according to the measurement of contact angle. After modification with dithizone, their contact angles were not obviously changed, but the total amount of metals captured by the filters were significantly increased, this may be attributed to the incorporation of functional group to PS and AR nanofibers.

**Optimization of digestion method for sample**

Sample preparation techniques such as hot plate and microwave digestion have been used widely for the dissolution of target elemental analytes for their subsequent analytical determination, and have become established standard methods for elemental extraction prior to instrumental analysis. Nevertheless, digestion procedure employed is time-consuming step in the overall analysis. Hence other strategies, such as ultrasonic extraction and sequential extraction for the treatment of solid samples have been tried in efforts to shorten the sample preparation step.\(^6\)\(^,\)\(^7\) In this research, three methods were compared for the digestion of the four metals captured by the filter mat, and the detailed
procedures were as follows.

Method 1. Ultrasonic

The filter mat was put into 20 mL 0.1 moL·L⁻¹ acetic acid-potassium acetate buffer solution (pH = 4.5) and sonicated for 30 minutes, then the solution was filtered through a 0.25 μm needle filter before determination and a blank filter mat was treated at the same time.

Method 2. Oscillation

The filter mat was put into a centrifuge tube containing 20 mL 0.1 moL·L⁻¹ acetic acid-potassium acetate buffer solution (pH = 4.5) and oscillated for 30 minutes, then the solution was filtered through a 0.25 μm needle filter before determination, and a blank filter mat was treated at the same time.

Method 3. Digestion

The filter mat was put into a polystyrene vessel with 20 mL of nitric acid-hydrogen peroxide (v/v, 1/1) for heating digestion. After the solution mixture evaporated completely, 5 mL 10 % nitric acid aqueous solution was added into the beaker to dissolve the residue, and diluted to 20 ml with water, a blank filter mat was treated at the same time.

The total amount of heavy metals (As, Cd, Hg, and Pb) in the three methods mentioned above were compared, results were expressed as the ratio of ultrasonic and oscillation to that of heating digestion and shown in Fig.5. Though heating digestion is a conventional and standard method, the desorption efficiencies of the four heavy metals from the nanofiber mat filters were relatively low, which may be attributed to the thermal shrinkage of PS nanofibers at high temperature, hindering the leaching of heavy metals from the filters. Compared with heating digestion method, ultrasonic leaching method obtained less of heavy metals. Hence, oscillation treatment was chosen for the
leaching of As, Cd, Hg, and Pb from the filters.

Optimization of the eluent

To desorb metals adsorbed on the air filter membrane is a crucial step before determination. Nitric acid and hydrochloric acid were the mostly used leaching solution, but these strong acids are dangerous and harmful to experimental operators. To select a suitable leaching solution, 0.2 mol·L\(^{-1}\) tartaric acid, 0.2 mol·L\(^{-1}\) citric acid, 5 % nitric acid, and HAC-KAC buffer solution (0.1 mol·L\(^{-1}\), pH = 4.5) were studied in oscillation extraction of the four heavy metals collected on the filters. The data of total amount of heavy metals (As, Cd, Hg, and Pb) normalized to that in HAC-KAC buffer solution was shown in Fig. 6. It was clearly that the release efficiencies of As, Cd, Hg, and Pb in HAC-KAC buffer solution were significantly higher than that in the other two solutions. This result was also consistent with other reports. Therefore, HAC-KAC buffer solution was selected as the digestion solution.

Trapping efficiency

Four fabricated nanofiber filter and the commercial cellulose acetate membrane were compared for the trapping efficiencies of heavy metals (As, Cd, Hg, and Pb) in atmospheric particles. Samples were digested by oscillation with HAC-KAC buffer solution (0.1 moL·L\(^{-1}\), pH = 4.5), and determined by ICP-MS. The results were shown in Fig. 7, it indicated that all the nanofiber filters showed better trapping performance for total amount of heavy metals compared with CAM, this can be attributed to the different capture mechanism of the prepared nanofiber filters and CAM. CAM filter is micro size and it capture PM particles mainly by thick physical barrier and adhesion, but nanofiber filters are with nano size and they capture PM particles by strong surface adhesion and also allow air penetrate the filters easily, so nanofiber filters can capture the smaller PM particles. The results also showed that functionalized nanofiber filters
trapped more heavy metals than unfunctionalized nanofiber filters. PS-DZ nanofiber filter show better trapping efficiency for the total metals, while AR-DZ only show higher trapping efficiency for As and Cd compared with AR.

**Method performance**

Repeated spike tests (n = 3) of four metals standard solution (0, 0.5, 1, 2, 5, 10, 20 μg·L⁻¹) on PS-DZ blank filters were used to evaluate method performance. The quantitative analytical parameters of the developed nanofiber based method were evaluated and summarized in Table 2. Only the result for Hg is difference from others which was not good as expected. It might be the characteristic of low concentration and the diverse morphological distribution of mercury in atmosphere that caused the instability of results.

**Analysis of heavy metals in atmospheric particles and biological samples**

To verify the feasibility of this established method, it was applied to the monitoring of heavy metals from atmospheric particles in different urban areas of Suzhou, China. A correlation analysis between levels of heavy metals in air and mother's milk was carried out, and the results were shown in Table 3. It was clear that the level of the four metals in air were overall higher in IP than that in NHIDZ, and it was no surprise to find that the level of three metals (As, Cd, Pb) were overall higher in breast milk from women living in IP than that in NHIDZ. While no significant differences were observed for Hg in breast milk, which indicated that maybe mercury is an element with a different absorption and distribution style. It was demonstrated again that the four typical toxic metals can be frequently ingested into human body through diet and drinking water, of course, also through inhalation.

**Conclusions**
The four nanofiber filters made from different polymer materials with or without dithizone had been fabricated. A comparative study for the trap of four metal elements (As, Cd, Hg, and Pb) in atmospheric aerosols by different filters was carried out. The oscillation extraction using acetic acid - potassium acetate buffer solution was proved to extract the four metals effectively from the nanofiber filters. Nanofiber filters incorporated with dithizone presented significantly higher trapping efficiencies for the metals compared with conventional CAM. Furthermore, we observed that there were associations between the concentrations of the four toxic metals (As, Cd, Hg, and Pb) in atmospheric particles and in mother's milk using a controlled concurrent study involving healthy volunteers living in two urban area with different levels of air pollution. Potential applications of nanofiber filters in sampling of metal elements in atmospheric particles matters were especially appealing, since several benefits offered by them: significantly higher sampling efficiency, shorter sample preparation times, simplicity, and enhanced safety compared to traditional wet digestion. The results showed that using nanofiber filters to sample metal elements in atmospheric aerosols maybe an effective and preferable method for the determination of trace elements in airborne particles, and the method possesses the potential application in research of air pollution and human health.

Acknowledgements

This work was supported by the National Key Research and Development Plan [No. 2018YFF0215204]; the National Natural Science Foundation of China [No. 81673230]; and the National Instrumental Research Program [No. 2014YQ06077303].
References

1. F. J. Kelly, and J. C. Fussell, *Atmospheric Environment.*, 2012, 60, 504.

2. D. Y. H. Pui, S. C. Chen, and Z. Zuo, *Particuogy.*, 2014, 13, 1.

3. R. M. Harrison, and J. Yin, *Sci. Total Environ.*, 2000, 249, 1.

4. A. Singh, R. K. Sharma, M. Agrawal, and F. M. Marshall, *Food and Chemical Toxicology.*, 2010, 48, 611.

5. T. Roychowdhury, H. Tokunaga, and M. Ando, *The Science of the Total Environment.*, 2003, 308, 15.

6. M. Kampa, and E. Castanas, *Environmental Pollution.*, 2008, 151, 362.

7. J. Rovira, M. Nadal, M. Schuhmacher, and J. L. Domingo, *Environmental Research.*, 2015, 140, 308.

8. M. Zabochnicka-Świątek, M. Krzywonos, *Pol. J. Environ. Stud.*, 2014, 23, 551.

9. L. T. Krupskaya, and V. P. Zverev, *Russian Journal of General Chemistry.*, 2014, 84, 2542.

10. H. S. Yu, W. T. Liao, and C. Y. Chai, *Journal of Biomedical Science.*, 2006, 13, 657.

11. I. Celi, L. Gallicchio, K. Boyd, T. K. Lam, G. Matanoski, X. Tao, M. Shiels, E. Hammond, L. Chen, K. A. Robinson, L. E. Caulfield, J. G. Herman, E. Guallar, and A. J. Alberg, *Environmental Research.*, 2008, 108, 48.

12. J. Liu, and M. P. Waalkes, *Toxicol Sci.*, 105 (2008, 105, 24.

13. S. Satarug, *Toxics.*, 2018, 6, 15.

14. T. Sanders, Y. Liu, V. Buchner, and P. B. Tchounwou, *Rev. Environ Health.*, 2009, 24, 15.

15. Y. Finkelstein, M. E. Markowitz, and J. F. Rosen, *Brain Research Reviews.*, 1998, 27, 168.

16. P. Koedrith, Y. R. Seo, *Int J Mol Sci.*, 2011, 12, 9576.

17. P. Grandjean, *Reproductive Toxicology.*, 2007, 23, 414.

18. B. J. Majestic, J.J. Schauer, M.M. Shafer, P.M. Fine, M. Singh, and C. Sioutas, *J. Environ. Eng. Sci.*, 2008, 7, 289.

19. C. Migon, B. Gentili, and B. Journel, *Oceanologica Acta.*, 1999, 23, 37.

20. B. Chen, A.F. Stein, P.G. Maldonado, A.M. Sanchez, Y.G. Castanedo, and N. Castell, *Atmospheric Environment.*, 2013, 71, 234.

21. X. Zhao, B.C. Pan, W.M. Zhang, S.J. Zhang, and Q.X. Zhang, *Chemical Engineering Journal.*, 2011, 170, 381.

22. G. C. Fang, Y.S. Wu, W.J. Lee, T.Y. Chou, and I.C. Lin, *Journal of Hazardous Materials.*, 2007, 144, 492.

23. T. Kameda, A. Akiyama, A. Toriba, N. Tang, and K. Hayakawa, *Intern. J. Environ. Anal. Chem.*, 2010, 90, 976.

24. T. Spitzer, and W. Dannecker, *Anal. Chem.*, 1983, 55, 2226.

25. L. L. Ashbaugh, and R.A. Eldred, *J. Air & Waste Manage. Assoc.*, 2004, 54, 93.

26. N. Upadhyay, B. J. Majestic, P. Prapaipong, and P. Herckes, *Anal Bioanal Chem.*, 2009, 394, 255.

27. P. Kampalanonwat, and P. Supaphol, *ACS Appl. Mater. Interfaces.*, 2012, 2, 3619.

28. S. Jeong, H. Cho, S. Han, P. Won, H. Lee, and S. Hong, *Nano Lett.*, 2017, 17,
4339.
29. D. Li, and Y. Xia, Adv Mater., 2004, 16, 1151.
30. Z. M. Huang, Y. Z. Zhang, M. Kotaki, and S. Ramakrishna, Composites Science and Technology., 2003, 63, 2223.
31. D. Li, J. T. McCann, Y. Xia, and M. Marquez, J. Am. Ceram. Soc., 2006, 89, 1861.
32. D. N. Rockwood, R. C. Preda, T. Yücel, X. Wang, M. L. Lovett, and D. L. Kaplan, Nature Protocols., 2011, 6, 1612.
33. H. Souzandeh, K. S. Johnson, Y. Wang, K. Bhamidipaty, and W. H. Zhong, ACS Appl. Mater. Interfaces., 2016, 8, 20023.
34. D. Annur, Z. K. Wang, J. D. Liao, and C. Kuo, Biomacromolecules., 2015, 16, 3248.
35. L. D. Tijing, J. S. Choi, S. Lee, S. H. Kim, and H. K. Shon, J. Membr. Sci., 2014, 453, 435.
36. K. Mondal, S. Bhattacharyya, and A. Sharma, Ind. Eng. Chem. Res., 2014, 53, 18900.
37. Z. He, M. Li, Y. Li, J. Zhu, Y. Jiang, W. Meng, H. Zhou, L. Wang, and L, Dai, Electrochimica Acta., 2018, 281, 601-610.
38. A. Greiner, and J.H. Wendorff, Angew. Chem. Int. Ed., 2007, 46, 5670.
39. M. H. Wang, R.J. Qu, C.M. Sun, P. Yin, and H. Chen, Chemical Engineering Journal., 2013, 221, 264.
40. J. P. Goulle, L. Mahieu, J. Castermant, N. N. Laurent Bonneau, G. Laine, D. Bouige, and C. Lacroix, Forensic Science International., 2005, 153, 39.
41. L. Huang, J. T. Arena, S. S. Manickam, X. Jiang, B. G. Willis, and J. R. McCutcheon, Journal of Membrane Science., 2014, 460, 241.
42. P. S. Kulkarni, S. U. Patel, and G. G. Chase, Separation and Purification Technology., 2012, 85, 157.
43. C. Feng, K. C. Khulbe, T. Matsuura, S. Tabe, and A. F. Ismail, Separation and Purification Technology., 2013, 102, 118.
44. R. Asmatulu, H. Muppala, Z. Veisi, W. S. Khan, A. Asaduzzaman, and N. Nuraje, Membranes., 2013, 3, 375.
45. A. Vanangamudi, S. Hamzah, and G. Singh, Chemical Engineering Journal., 2015, 260, 801.
46. P. Cid, I. Lavilla, and C. Bendicho, Intern. J. Environ. Anal. Chem., 1999, 73, 79.
47. J. M. Matong, L. Nyaba, and P. N. Nomngongo, Chemosphere., 2016, 154, 249.
48. S. Canepari, E. Cardarelli, A. Pietrodangelo, and M. Strincone, Talanta., 2006, 69, 588.
Table 1  Materials characteristics and the total amount of four metal elements captured

|        | Diameter (nm) | Surface area (m²/g) | Contact angle | Total metal (μg)b |
|--------|--------------|---------------------|--------------|------------------|
| CAM    | —            | —                   | Nd³          | 0.0033           |
| PS     | 407.6±118.7  | 2.16                | 126.6        | 0.0055           |
| AR     | 1222.8±269.2 | 3.53                | 123.0        | 0.0057           |
| PS-DZ  | 289.4±72.3   | 4.11                | 141.0        | 0.1562           |
| AR-DZ  | 518.2±176.7  | 7.42                | 138.6        | 0.0541           |

a. No data available.

b. The data of this column are presented as the mean of three replicates.
Table 2  Analytical performance of the established method

| Analytes | R²  | RSD (%) | LOD (μg/m³) | LOQ (μg/m³) | Recovery (%)  |
|----------|-----|---------|-------------|-------------|---------------|
| As       | 0.9992 | 4.4     | 0.0035      | 0.0117      | 94 ± 1.2      |
| Cd       | 0.9988 | 15.7    | 0.0022      | 0.0072      | 76 ± 2.3      |
| Hg       | 0.9989 | 34.9    | 0.0084      | 0.0281      | 74 ± 2.6      |
| Pb       | 0.9965 | 5.3     | 0.0175      | 0.0584      | 91 ± 1.5      |
Table 3  The amount of heavy metals in atmospheric particles and mother's breast milk in different area

| Element | Level of metals in air | Level of metals in mother's breast milk |
|---------|------------------------|-----------------------------------------|
|         | NHIDZ                  | IP                                      |
|         | (ng/m³)                | (ng/m³)                                 |
| As      | 171.53                 | 218.75                                  |
| Cd      | 88.89                  | 63.54                                   |
| Hg      | 79.17                  | 184.72                                  |
| Pb      | 393.75                 | 415.97                                  |
|         | NHIDZ                  | IP                                      |
|         | (ng/mL, n=10)         | (ng/mL, n=16)                           |
| As      | 6.46 ± 5.93            | 27.87 ± 16.59                           |
| Cd      | 12.40 ± 2.60           | 13.37 ± 4.1                             |
| Hg      | 3.03 ± 1.52            | 2.76 ± 1.33                             |
| Pb      | 212.58 ± 37.80         | 305.80 ± 56.42                          |
**Figure Captions**

Fig. 1  Schematic diagram of home-made electrospinning device.

Fig. 2  Samplers made from different materials: (A) PS; (B) AR; (C) PS-DZ; (D) AR-DZ.

Fig. 3  FESEM image (before sampling, a: PS; d: PS-DZ; g: AR; j: AR-DZ; m: CAm. after sampling, b: PS; e: PS-DZ; h: AR; k: AR-DZ; n: CAm.) and diameter distribution (c: PS; f: PS-DZ; i: AR; l: AR-DZ) of different nanofiber filters.

Fig. 4  XRD pattern of obtained nanofibers.

Fig. 5  Normalized data of total amount of heavy metals (As, Cd, Hg, and Pb) obtained with ultrasonic and oscillation to that of heating digestion.

Fig. 6  Normalized data of total amount of heavy metals (As, Cd, Hg, and Pb) desorbed in the three acids to that of in HAC-KAC.

Fig. 7  Comparison of four metals captured by different filters.
Fig. 1
Fig. 2
Fig. 3
Fig. 4
Data of total amount of heavy metals (As, Cd, Hg, and Pb) desorbed by ultrasonic and oscillation were normalized to that by heating digestion.

Fig. 5
* Data of total amount of heavy metals (As, Cd, Hg, and Pb) digested by the other three acids was normalized to that by HAC-KAC.

Fig. 6
*TAM: Total amount of four heavy metals (As, Cd, Hg, and Pb).

Fig. 7
Graphical Index