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Environmental Analysis

NOVEL EXTRACTION FOR ENDOCRINE DISRUPTORS IN ATMOSPHERIC PARTICULATE MATTER

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A rapid and efficient sample preparation method, which is called microwave-assisted microsolid phase extraction, was developed for the determination of endocrine disrupting chemicals in atmospheric particulate matter. The endocrine disrupting chemicals included bisphenol A, diethyl phthalate, dibutyl phthalate, and di(2-ethylhexyl) phthalate. The endocrine disrupting chemicals were isolated by microwave-assisted extraction following adsorption by copper(II) isonicotinate using microsolid phase extraction. The endocrine disrupting chemicals were subsequently determined by high performance liquid chromatography with an ultraviolet detector. The extraction was optimized for temperature, time, desorption time, and desorption solvent. Limits of detection (in the range of 2.0–8.5 nanograms per liter), limits of quantification (in the range of 6.6–28.0 nanograms per liter), and repeatability of the procedure (less than 10 percent) were established. Diethyl phthalate, diethyl phthalate, and di(2-ethylhexyl) phthalate were determined at values from 0.57 to 68.8 nanograms per cubic meter in atmospheric particulate matter collected from an urban area, a business center, and an industrial site in Dongguan, China. The concentration of bisphenol A was below the detection limit in these samples.

Keywords: Bisphenol A; Di(2-ethylhexyl) phthalate; Dibutyl phthalate (diethyl phthalate); Diethyl phthalate; Microwave-assisted micro-solid phase extraction

INTRODUCTION

Atmospheric particulate matter, also known as particulate matter or atmospheric aerosol, are tiny pieces of solid or liquid matter suspended in the atmosphere.

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Although the amount of atmospheric particulate matter in the Earth's atmosphere is low, it may adversely affect air quality, visibility, and human health. Among the complex components of respirable suspended particles, various organic compounds are present including alkanes, alkenes, heterocycles, alkanoic acids, polycyclic aromatic hydrocarbons, ketones, and esters (Choi et al. 2012; Samy and Hays 2013). Endocrine disrupting chemicals such as bisphenol A, polychlorinated biphenyls, diethyl phthalate, dibutyl phthalate, and di (2-ethylhexyl) phthalate have been widely studied around the world due to their presence in the environment and adverse effects on wildlife and humans, including disruption to reproductive and immune systems (Mills and Chichester 2005; Tsutsumi 2005). The endocrine disrupting chemicals in atmospheric particulate matter may be directly inhaled by humans and may be toxic even at trace levels (Purdom et al. 1994; Harries et al. 1997). The concentration of each organic component is extremely low, usually in the range of 0.1–100 nanograms per cubic meter (Choi et al. 2012). Therefore, sample preparation technology plays an important role in the determination of trace endocrine disruptors in atmospheric particulate matter.

For trace analysis of particulate matter, continuous air sampling for one day by a large-volume sampler is required, followed by extraction from filters and detection by chromatography (Rushdi et al. 2014; Sousa et al. 2015). In recent years, ultrasonic extraction (Prieto-Blanco, López-Mahía, and Campíns-Falcó 2011), microwave-assisted extraction (Coscollà et al. 2009; Beser, Beltrán, and Yusà 2014), and accelerated solvent extraction (Moscoso-Pérez et al. 2008; Lintelmann et al. 2010) have been applied for organic compounds in particulate matter with improved efficiency. However, these methods require filtration, cleanup, or preconcentration, which are laborious, time-consuming, and usually involve large volumes of solvents.

A membrane protected microsolid phase extraction technique is a small device using an adsorbent within a polypropylene membrane envelope (Basheer et al. 2006). As the porous membrane afforded protection of the sorbent, no further filtration or cleanup of the extract was required, simplifying the extraction. The procedure also offers a reduced analysis time because of the small volume of organic solvent. By using different adsorbents, microsolid phase extraction has been successfully applied for determination of polycyclic aromatic hydrocarbons, polybrominated diphenyl ethers, and organophosphorus pesticides in environmental and food samples (Ge and Hian 2012; Gu et al. 2012; Huang et al. 2012; Wang et al. 2013).

In the common microsolid phase extraction procedure, the device is stirred in a hot water bath and mass transfer is achieved by traditional heating (Lee et al. 2012; Zhang, Low, and Lee 2012; Zhou et al. 2012), which was inefficient and time consuming. The microwave-assisted extraction system provides shorter extraction time and higher efficiency. More importantly, it allows selective extraction of analytes from complex matrices (Zhou, Xiao, and Li 2012; Ruan, Xiao, and Li 2014). However, microwave-assisted extraction also has drawbacks. The analyte partition between the matrix and solvent is static, such that when the equilibrium is achieved, the analyte could not move to the solvent. Hence, if there was adsorbent to remove the analyte from the extraction solution, the efficiency would be enhanced. Therefore, microwave-assisted microsolid phase extraction may combine the advantages of microwave-assisted and microsolid phase extraction and provide higher enrichment.

In this study, a microsolid phase device using copper(II) isonicotinate as the adsorbent was coupled with microwave-assisted extraction for simultaneously separating four endocrine disrupting chemicals from atmospheric particulate matter. The extraction time, temperature, desorption solvent, and desorption time were optimized. The extracts were determined by high-performance liquid chromatography (HPLC). The accuracy and precision of the method were evaluated and compared to traditional microwave-assisted extraction, and its suitability for the determination of trace levels of these endocrine disrupting chemicals in the particulate matter was demonstrated.

EXPERIMENTAL

Reagents and Materials

Standards of dibutyl phthalate (96.8 percent), diethyl phthalate(99.9 percent), di(2-ethylhexyl) phthalate(99.6 percent), bisphenol A(99.6 percent), acetonitrile, and methanol were purchased from J & K Scientific. The solvents used were analytical grade for synthesis of materials and HPLC grade for extraction and analysis. Ultrapure water was produced by a Heal Fore NW System (Shanghai, China). Accurel polypropylene sheet membrane (0.20 micrometer pore size) was purchased from Membrana (Wuppertal, Germany).

Preparation of Copper (II) Isonicotinate

The procedure described by Waizump et al. (1998) was modified to prepare the copper(II) isonicotinate polymer powder using copper nitrate, isonicotinic acid, and sodium hydroxide (Guangfu Fine Chemical Research Institute, Tianjin, China). A mixture of isonicotinic acid (0.1 mole) and sodium hydroxide (0.1 mole) was stirred in double distilled water, then into which the copper nitrate was added to produce a blue precipitate that was stirred for three hours. The precipitate was collected by filtration, dried in an oven at 60 degree Celsius, and ground with a mortar and pestle. The material was characterized by X-ray diffraction (**Figure** 1).

Sample Preparation

The total suspended particulate matter was collected from three places in Dongguan, China. One was collected in an urban area of Songshan Lake, the second was beside a busy street in the business center, and the third was from an industrial site. A HV-500 F high volume sampler (Sibata, Japan) was used for total suspended particulate collection on QF20 quartz fiber filters (20.3×25.4 centimeters) by using an aspiration volume of 30 cubic meters per hour over twenty-four hours. Prior to sampling, filters were preheated at 400 degree Celsius for twelve hours and then weighed after forty-eight hours of conditioning in a desiccator at constant temperature (20 ± 1 degree Celsius) and relative humidity conditions (50 ± 5 percent), according to the EN 12341 European Norm. Samples were stored at -18 degree Celsius until analysis.

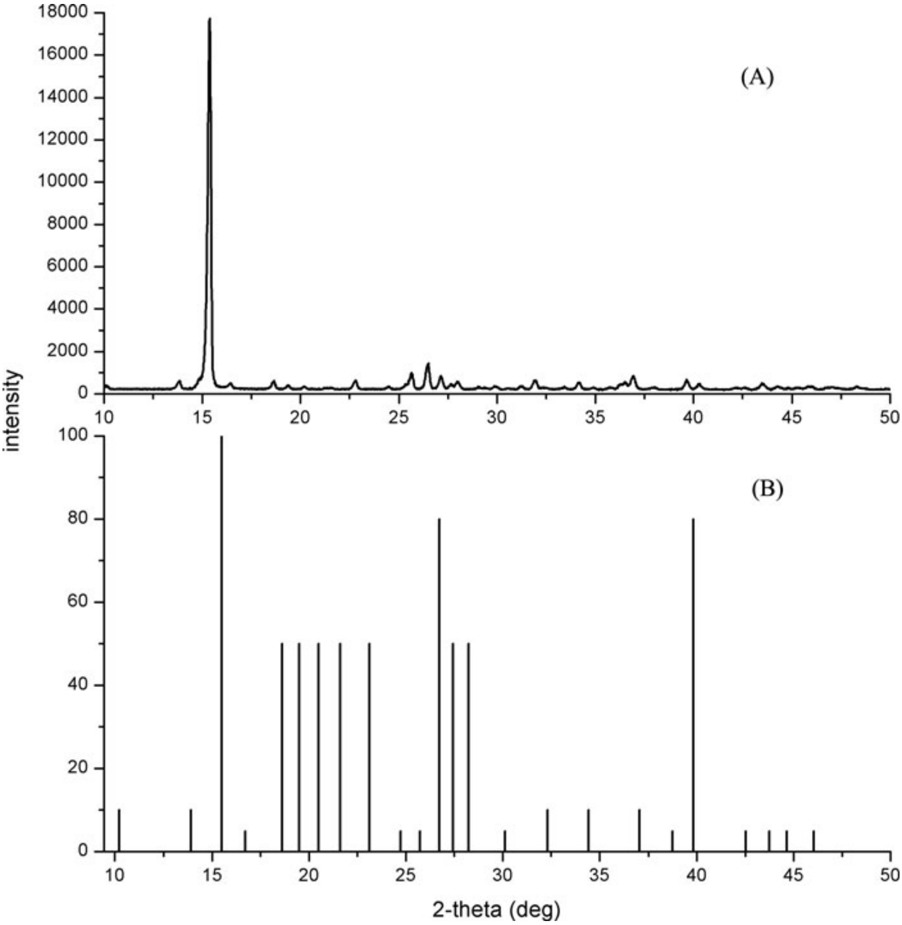

Figure 1. X-ray diffraction spectra of the metal-organic framework polymer: (A) simulated and (B) experimental.

Microwave-Assisted Microsolid Phase Extraction Procedure

A microwave extraction system (Xintuo, Shanghai, China) was used in the procedure described as follows. Filters were cut into four pieces using a scalpel, the four pieces were divided to two parts, each part contained two pieces at the diagonal direction and was extracted separately. The 10 milliliters of methanol and the microsolid phase extraction device were transferred into a microwave flask. The microsolid phase extraction device consisted of 10 milligrams copper(II) isonicotinate in an microporous polypropylene membrane envelope. The size of the microporous polypropylene membrane envelope was approximately 1.0 centimeter in length × 0.8 centimeter in width. Under a power of 400 watts of microwave irradiation, extraction was performed at 40 degree Celsius for fifteen minutes and the microsolid phase extraction devices were rinsed with hexane, and dried on filter paper. For desorbing the analytes, the microsolid phase extraction device was sonicated with 2.5 microliters of hexane for twenty-five minutes. The eluate obtained was filtered through a 0.20

micrometer membrane and evaporated to dryness under nitrogen. The residue was dissolved in 100 microliters of hexane and analyzed by HPLC.

HPLC Determination

Determination of diethyl phthalate, dibutyl phthalate, di(2-ethylhexyl) phthalate, and bisphenol A were carried out on a Summit HPLC system (Dionex). All sample solutions were passed through a 0.45 micrometer micropore filter before HPLC analysis. For bisphenol A, separation was performed on a Diamonsil C_{18} column (150 × 4.6 millimeters, i.d., 5 micrometers, J & K Chemical) with a nonlinear gradient of 75 percent methanol and 25 percent water (volume by volume) at a flow rate of 0.8 milliliter per minute followed by detection at 225 nanometers. For diethyl phthalate, dibutyl phthalate, and di(2-ethylhexyl) phthalate, the Diamonsil C_{18} column was eluted with a nonlinear gradient: 90 percent of methanol and 10 percent of water (volume by volume) at a flow rate of 1.0 milliliter per minute and detected at 225 nanometers.

RESULTS AND DISCUSSION

Microwave-Assisted Extraction and Microsolid Phase Extraction

Microwave-assisted microsolid phase extraction was performed using an improved extraction vessel. The glass extraction vessel had slender bottom region permitting a small amount of sample and a small volume of extraction solvent to be used during the procedure. The device also included a condenser, which was placed on the extraction vessel to allow the solvent to reflux upon microwave irradiation. Copper (II) isonicotinate was used as adsorbent in the microsolid phase extraction bag that was placed in the bottom of flask with the sample and extraction solvent. The analytes were transported into the extraction solvent, enhanced by microwave irradiation, and then quickly adsorbed by the copper(II) isonicotinate. Matrix interferences were prevented by the porous membrane; thus cleanup and concentration were performed in one step, which is an advantage of microsolid phase extraction.

Optimization of Extraction Time

The extraction efficiency depends on the mass transfer of analyte from the sample solution to the adsorbent. The extraction time is an important parameter to optimize microwave-assisted microsolid phase extraction and was achieved using 20 nanograms per milliliter standards of diethyl phthalate, dibutyl phthalate, di(2-ethylhexyl) phthalate, and bisphenol A. The extraction time was optimized over a range of five to thirty minutes. The results are shown in **Figure** 2. The peak areas increased up to fifteen minutes and remained constant consequently fifteen minutes was deemed to be the optimum extraction time.

Optimization of Extraction Temperature

The extraction temperature is important for extraction because mass transfer increases with temperature. In this study, the extraction efficiency increased when the temperature increased from 30 to 40 degree Celsius. However, above 40 degree

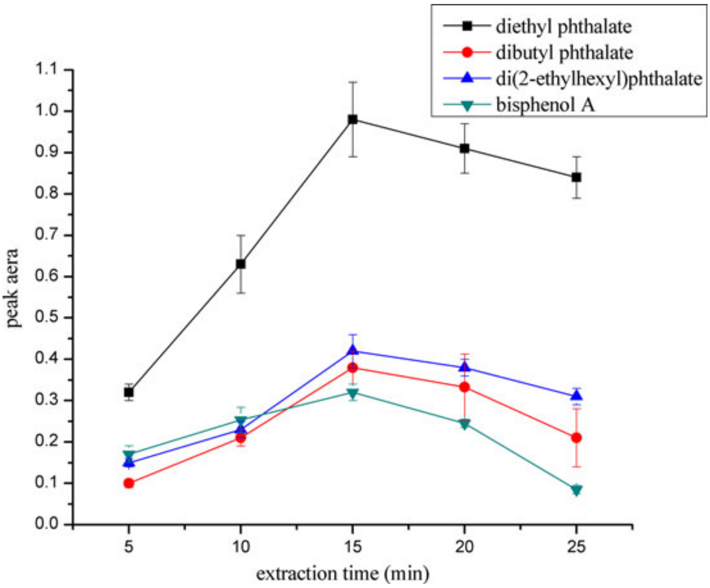

Figure 2. Optimization of extraction time profile. The conditions are described in the text.

Celsius, desorption of the analytes from the adsorbent occurred. Consequently, 40 degree Celsius was chosen to be the optimum extraction temperature (**Figure** 3).

Optimization of Desorption Solvent

After extraction, the analytes were desorbed from the microwave-assisted micro-solid phase extraction device by sonication in a suitable organic solvent.

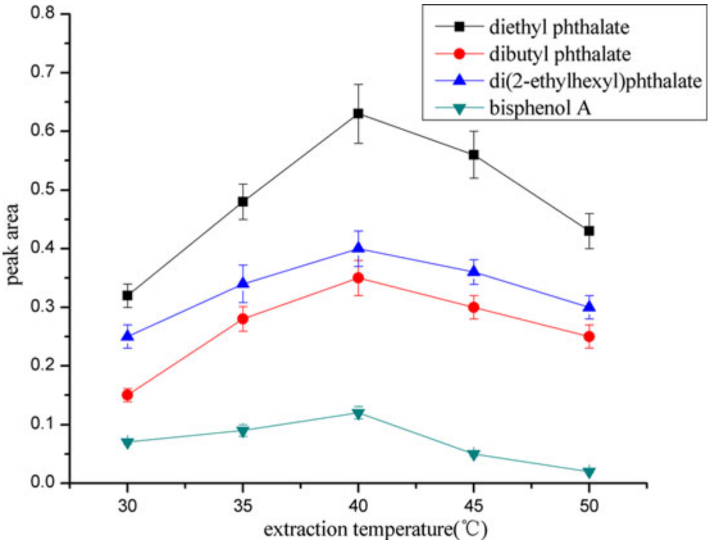

Figure 3. Optimization of extraction temperature. The conditions are described in the text.

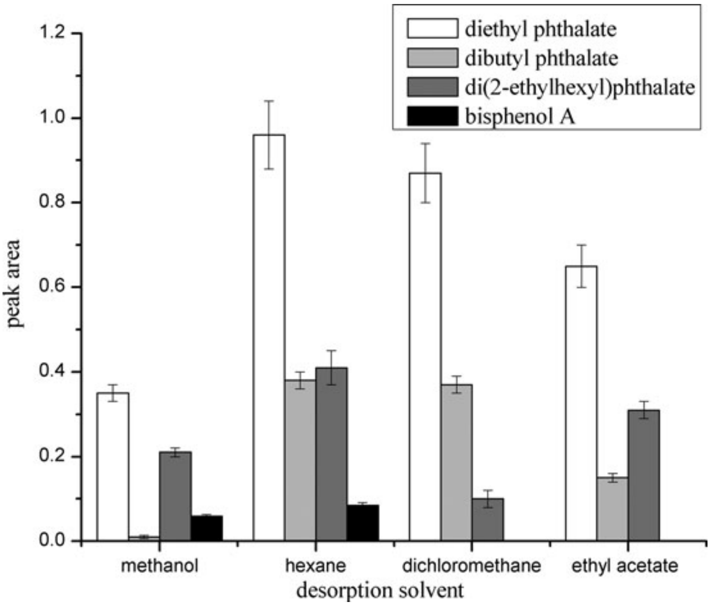

Figure 4. Optimization of desorption solvent. The conditions are described in the text.

Solvent desorption was evaluated using ethyl acetate, hexane, dichloromethane, and methanol. All analytes were better desorbed by hexane than the other solvents (**Figure** 4). Hence, hexane was chosen as the desorption solvent.

Optimization of Desorption Time

In the micro-solid phase extraction procedure, the adsorption and desorption are both significant. In order to achieve complete desorption of endocrine disrupting chemicals, the time for desorption was investigated in the range of five to thirty minutes. **Figure** 5 shows the optimum desorption occurred after twenty-five minutes which was employed in subsequent experiments (**Figure** 5).

Method Validation

The linearity of the HPLC system for determination of diethyl phthalate, dibutyl phthalate, di(2-ethylhexyl) phthalate, and bisphenol A was evaluated using standard solutions with diphenyl phthalate as the internal standard. The linear regression analysis of the concentration and the response (analyte peak area/internal standard peak area) are shown in **Table** 1. Limits of detection (LOD) and limits of quantification (LOQ), which were calculated at three and ten times the standard deviation above the blank sample extract were from 2.0 to 8.5 nanograms per liter and from 6.6 to 28.0 nanograms per liter, respectively. The limits of detection and quantification for bisphenol A were higher than dibutyl phthalate, diethyl phthalate, and di(2-ethylhexyl) phthalate, while lower than in a previous report (Dai et al. 2014).

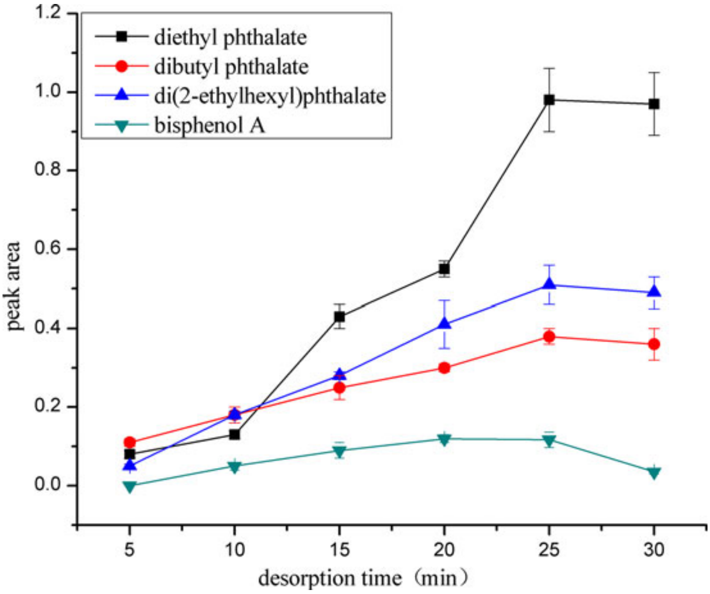

Figure 5. Optimization of desorption time. The conditions are described in the text.

In order to validate the precision and accuracy of the method, the samples were fortified with 0.05, 0.50, and 1.0 microgram per milliliter of analytes in blank filters and analyzed with five replicates. The mean recoveries of diethyl phthalate, dibutyl phthalate, di(2-ethylhexyl) phthalate, and bisphenol A in the samples were 81.7–119 percent in the fortified samples. The relative standard deviations (RSD) were less than 10 percent (**Table** 2). In summary, the method was validated with good reproducibility and satisfactory accuracy for the determination of phthalate esters and bisphenol A in atmospheric particulate matter.

The microwave-assisted extraction approach was applied for the extraction of endocrine disruptors in particulate matter. The results between microwave-assisted microsolid phase extraction and microwave-assisted extraction were compared. First, the former was faster and allowed preconcentration and cleanup in one step (Coscollà et al. 2009; Beser, Beltrán, and Yusà 2014). Second, the recoveries of endocrine disrupting chemicals were comparable between the microwave-assisted extraction microsolid phase extraction and the microwave-assisted extraction methods,

Table 1. Analytical figures of merit for endocrine disrupting chemicals in atmospheric particulate matter

Analyte	Regression equation	Linear dynamic range micrograms per milliliter	Correlation coefficient r^2	Limit of detection (nanograms per liter)	Limit of quantification (nanograms per liter)
Diethyl phthalate	$y = 0.5549x - 0.0729$	0.005–10	0.9992	2.0	6.6
Dibutyl phthalate	$y = 0.8144x - 0.0807$	0.005–10	0.9991	3.1	10.2
Di(2-ethylhexyl) phthalate	$y = 0.1653x - 0.0079$	0.005–10	0.9996	5.7	18.8
Bisphenol A	$y = 1.4484x - 0.0328$	0.01–1.0	0.9990	8.5	28.0

Table 2. Recovery and precision in atmospheric particulate matter

Sample site	Analyte	Concentration	Mean recovery (percent)	Relative standard deviation (percent)
Collected at business center	diethyl phthalate	6.1 nanograms per cubic meter	81.7	6.8
	dibutyl phthalate	4.5 nanograms per cubic meter	84.2	4.5
	di(2-ethylhexyl)phthalate	11.9 nanograms per cubic meter	81.2	3.6
	bisphenol A	Not detected	100.7	8.5
Collected at industrial site	diethyl phthalate	19.2 nanograms per cubic meter	95.5	8.8
	dibutyl phthalate	23.5 nanograms per cubic meter	86.5	5. 7
	di(2-ethylhexyl)phthalate	68.8 nanograms per cubic meter	110.4	9.2
	bisphenol A	Not detected	92.3	5.5
Collected at urban area in Dongguan	diethyl phthalate	0.65 nanogram per cubic meter	95.2	6.2
	dibutyl phthalate	0.57 nanogram per cubic meter	83.7	7.9
	di(2-ethylhexyl)phthalate	5.56 nanograms per cubic meter	85.4	9.4
	bisphenol A	Not detected	119.2	8.1

which were all between 80 and 120 percent. Third, the detection limits of 2.0–8.5 nanograms per liter for endocrine disrupting chemicals of the novel method were lower using microwave-assisted extraction (10–50 nanograms per liter). Fourth, the microsolid phase extraction method showed better selectivity for endocrine disrupting chemicals than microwave-assisted extraction because the porous propylene envelope acted as a filter to exclude soluble components. Therefore, the microwave-assisted micro-solid phase extraction may provide better selectivity than microwave-assisted extraction for endocrine disrupting chemicals. The microsolid phase extraction method also uses less organic solvent than the microwave-assisted extraction approach. In summary, microwave-assisted microsolid phase extraction is comparable or even better than the well-established microwave-assisted extraction in terms of the accuracy, sensitivity, selectivity, and reduced use of organic solvents for the determination of endocrine disrupting chemicals in atmospheric particulate matter.

Analysis of Atmospheric Particulate Matter

The developed method was further applied to atmospheric particulate matter collected from three sites (**Figure** 6). The results showed that diethyl phthalate, dibutyl phthalate, and di(2-ethylhexyl) phthalate were present from 0.57 to 5.56 nanograms per cubic meter in atmospheric particulate matter from the urban area, 4.5–11.9 nanograms per cubic meter from the business center, and 19.2–68.8 nanograms per cubic meter from the industrial site. Bisphenol A was below the detection limit in all samples.

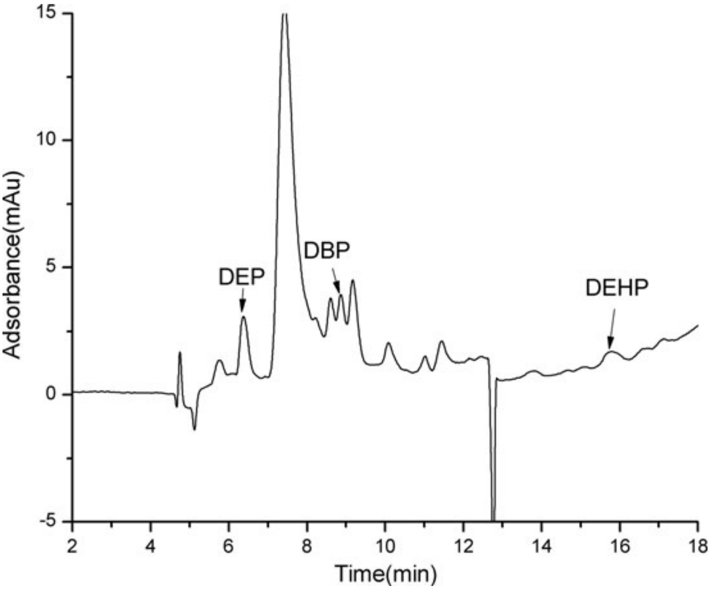

Figure 6. High-performance liquid chromatogram of atmospheric particulate matter from an urban area. DEP = diethyl phthalate, DBP = dibutyl phthalate, DEHP = di(2-ethylhexyl)phthalate.

The concentrations of phthalate esters in atmospheric particulate matter from the industrial area were much higher than the other two sites due to the industrial pollution. The levels were also higher in the business center compared to the urban area. The results varied with season, climate, and even sampling time in the same day. This preliminary study showed favorable extraction efficiency, low detection limits, and good repeatability, suggesting this method is promising for monitoring air quality.

CONCLUSIONS

An extraction device termed microwave-assisted microsolid phase extraction was developed and applied for the determination of endocrine disrupting chemicals in atmospheric particulate matter. By coupling to HPLC with an ultraviolet detector, good reproducibility (relative standard deviations less than 10 percent) and low detection limits (from 2.0 to 8.5 nanograms per liter) were demonstrated. Compared with the well-developed microwave-assisted extraction method, this method offers advantages in terms of reduced organic solvent consumption, high sensitivity, and good selectivity for endocrine disrupting chemicals. This approach is a promising alternative microextraction technique in environmental samples or other samples with complicated matrices.

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REFERENCES

Basheer, C., A. A. Alnedhary, B. S. M. Rao, S. Valliyaveettil, and H. K. Lee. 2006. Development and application of porous membrane-protected carbon nanotube micro-solid-phase extraction combined with gas chromatography/mass spectrometry. *Analytical Chemistry* 78: 2853–58. doi:10.1021/ac060240i

Beser, M. I., J. Beltrán, and V. Yusà. 2014. Design of experiment approach for the optimization of polybrominated diphenyl ethers determination in fine airborne particulate matter by microwave-assisted extraction and gas chromatography coupled to tandem mass spectrometry. *Journal of Chromatography A* 1323: 1–10. doi:10.1016/j.chroma.2013.10.081

Choi, J.-K., J.-B. Heo, S.-J. Ban, S.-M. Yi, and K.-D. Zoh. 2012. Chemical characteristics of PM2.5 aerosol in Incheon, Korea. *Atmospheric Environment* 60: 583–92. doi:10.1016/j.atmosenv.2012.06.078

Coscollà, C., V. Yusà, M. I. Beser, and A. Pastor. 2009. Multi-residue analysis of 30 currently used pesticides in fine airborne particulate matter (PM 2.5) by microwave-assisted extraction and liquid chromatography–tandem mass spectrometry. *Journal of Chromatography A* 1216: 8817–27. doi:10.1016/j.chroma.2009.10.040

Dai, X. L., D. Li, L. Z. Zhang, S. J. Jiang, Y. J. Yu, Y. J. Wang, and L. J. Dong. 2014. Determination of phthalate esters in particle matter (PM2.5) by microwave-assisted extraction and gas chromatography-mass spectrometry. *J. Instrumental Anal.* 33: 349–53.

Ge, D., and K. L. Hian. 2012. Zeolite imidazolate frameworks 8 as sorbent and its application to sonication-assisted emulsification microextraction combined with vortex-assisted porous membrane-protected micro-solid-phase extraction for fast analysis of acidic drugs in environmental water samples. *Journal of Chromatography A* 1257: 19–24. doi:10.1016/j.chroma.2012.08.032

Gu, Z.-Y., C.-X. Yang, N. Chang, and X.-P. Yan. 2012. Metal–organic frameworks for analytical chemistry: from sample collection to chromatographic separation. *Accounts of Chemical Research* 45: 734–45. doi:10.1021/ar2002599

Harries, J. E., D. A. Sheahan, S. Jobling, P. Matthiessen, P. Neall, J. P. Sumpter, T. Tylor, and N. Zaman. 1997. Estrogenic activity in five United Kingdom rivers detected by measurement of vitellogenesis in caged male trout. *Environmental Toxicology and Chemistry* 16: 534–42. doi:10.1002/etc.5620160320

Huang, J., J. Liu, C. Zhang, J. Wei, L. Mei, S. Yu, G. Li, and L. Xu. 2012. Determination of sulfonamides in food samples by membrane-protected micro-solid phase extraction coupled with high performance liquid chromatography. *Journal of Chromatography A* 1219: 66–74. doi:10.1016/j.chroma.2011.11.026

Lee, T. P., B. Saad, E. P. Ng, and B. Salleh. 2012. Zeolite linde type L as micro-solid phase extraction sorbent for the high performance liquid chromatography determination of ochratoxin A in coffee and cereal. *Journal of Chromatography A* 1237: 46–54. doi:10.1016/j.chroma.2012.03.031

Lintelmann, J., M. H. França, E. Hübner, and G. Matuschek. 2010. A liquid chromatography–atmospheric pressure photoionization tandem mass spectrometric method for the determination of azaarenes in atmospheric particulate matter. *Journal of Chromatography A* 1217: 1636–46. doi:10.1016/j.chroma.2010.01.029

Mills, L. J., and C. Chichester. 2005. Review of evidence: are endocrine-disrupting chemicals in the aquatic environment impacting fish populations? *Science of the Total Environment* 343: 1–34. doi:10.1016/j.scitotenv.2004.12.070

Moscoso-Pérez, C., J. Moreda-Piñeiro, P. López-Mahía, S. Muniategui-Lorenzo, E. Fernández-Fernández, and D. Prada-Rodríguez. 2008. Pressurized liquid extraction followed by high performance liquid chromatography coupled to hydride generation atomic fluorescence spectrometry for arsenic and selenium speciation in atmospheric particulate matter. *Journal of Chromatography A* 1215: 15–20. doi:10.1016/j.chroma.2008.10.100

Prieto-Blanco, M. C., P. López-Mahía, and P. Campíns-Falcó. 2011. On-line analysis of carbonyl compounds with derivatization in aqueous extracts of atmospheric particulate PM10 by in-tube solid-phase microextraction coupled to capillary liquid chromatography. *Journal of Chromatography A* 1218: 4834–39. doi:10.1016/j.chroma.2011.05.093

Purdom, C. E., P. A. Hardiman, V. V. J. Bye, N. C. Eno, C. R. Tyler, and J. P. Sumpter. 1994. Estrogenic effects of effluents from sewage treatment works. *Chemistry and Ecology* 8: 275–85. doi:10.1080/02757549408038554

Ruan, C., X.-H. Xiao, and G.-K. Li. 2014. Microwave-assisted extraction coupled with countercurrent chromatography for the rapid preparation of flavonoids from *Scutellaria barbata* D. Don. *Journal of Separation Science* 37: 1364–69. doi:10.1002/jssc.201400168

Rushdi, A. I., A. H. El-Mubarak, L. Lijotra, M. T. Al-Otaibi, M. A. Qurban, K. F. Al-Mutlaq, and B. R. T. Simoneit. 2014. Characteristics of organic compounds in aerosol particulate matter from Dhahran city, Saudi Arabia. *Arabian Journal of Chemistry*. doi:10.1016/j.arabjc.2014.03.001

Samy, S., and M. D. Hays. 2013. Quantitative LC–MS for water-soluble heterocyclic amines in fine aerosols (PM2.5) at Duke Forest, USA. *Atmospheric Environment* 72: 77–80. doi:10.1016/j.atmosenv.2013.02.032

Sousa, E. T., M. P. Cardoso, L. A. Silva, and J. B. de Andrade. 2015. Direct determination of quinones in fine atmospheric particulate matter by GC–MS. *Microchemical Journal* 118: 26–31. doi:10.1016/j.microc.2014.07.013

Tsutsumi, O. 2005. Assessment of human contamination of estrogenic endocrine-disrupting chemicals and their risk for human reproduction. *The Journal of Steroid Biochemistry and Molecular Biology* 93: 325–30. doi:10.1016/j.jsbmb.2004.12.008

Waizump, K., M. Takuno, N. Fukushima, and H. Masuda. 1998. Structures of pyridine carboxylate complexes of cobalt(II) and copper(II). *Journal of Coordination Chemistry* 44: 269–79. doi:10.1080/00958979808023079

Wang, Z., X. Zhao, X. Xu, L. Wu, R. Su, Y. Zhao, C. Jiang, et al. 2013. An absorbing microwave micro-solid-phase extraction device used in non-polar solvent microwave-assisted extraction for the determination of organophosphorus pesticides. *Analytica Chimica Acta* 760: 60–68. doi:10.1016/j.aca.2012.11.031

Zhang H., W. P. Low, and H. K. Lee. 2012. Evaluation of sulfonated graphene sheets as sorbent for micro-solid-phase extraction combined with gas chromatography–mass spectrometry. *Journal of Chromatography A* 1233: 16–21. doi:10.1016/j.chroma.2012.02.020

Zhou, T., X. Xiao, and G. K. Li. 2012. Microwave accelerated selective soxhlet extraction for the determination of organophosphorus and carbamate pesticides in ginseng with gas chromatography/mass spectrometry. *Analytical Chemistry* 84: 5816–22. doi:10.1021/ac301274r

Zhou, Y. Y., C. Y. Zhang, Z. G. Yan, K. J. Li, L. Wang, Y. B. Xie, F. S. Li, Z. Liu, and J. Yang. 2012. The use of copper (II) isonicotinate-based micro-solid-phase extraction for the analysis of polybrominated diphenyl ethers in soils. *Analytica Chimica Acta* 747: 36–41. doi:10.1016/j.aca.2012.08.023