Ultrasonic wave extraction and simultaneous analysis of polycyclic aromatic hydrocarbons (PAHs) and phthalic esters in soil

ZHANG Yong-tao[1], ZHAO Guo-xing[1], LIU Jing-shang[2], ZHANG Li[1*], LI Xiao-ya[1], GUI Jian-ye[1], ZHANG Chen-ling[1]

[1]Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, 050061 Shijiazhuang, China.
[2]Shijiazhuang Geological Brigade, 050085 Shijiazhuang, China.

Abstract: A method is developed for detection of polycyclic aromatic hydrocarbons (PAHs) and Phthalic Acid Esters (PAEs) in soil samples. Ultrasonic Wave Extraction under airtight circumstances is adopted to extract the analytes in soil samples with n-hexane–acetone (V:V=1:1) as extraction solvent. This method has several advantages, including high extraction efficiency, short time, convenience and simplicity. It can be used to detect polycyclic aromatic hydrocarbons (PAHs) and Phthalic Acid Esters (PAEs) in soil.

Keywords: Polycyclic aromatic hydrocarbons; Phthalic Acid Esters; Ultrasonic assistant extraction technique

Introduction

As persistent organic pollutants, polycyclic aromatic hydrocarbons (PAHs) have teratogenicity, carcinogenicity, mutagenecity, and genotoxicity effects on organisms (ZHAO Wen-chang and CHENG Jin-ping, 2006; NIE Jing and QIAN Yan, 2009) and potential hazardous effects on human bodies (ZHENG Tian-ling and LUO Yuan-rong, 2006). The United States Environmental Protection Agency (US EPA) has blacklisted 16 polycyclic aromatic hydrocarbons (PAHs) (CAI Q Y *et al.* 2008). As vital plasticizers, phthalic Acid Esters (PAEs) possess toxicity, teratogenicity, mutagenecity and even carcinogenic effects. Studies show that PAEs are environmental estrogens. Long-time exposure to PAEs may lead to decrease of sperm quantity and quality in male bodies, and increase in incidence of female breast cancer. It may also have bad effects on the reproductive system of male fetus in parent matrix. Soil is an important media for the exchange of various substances, it is a compilation place and transfer station for PAHs in environment. PAHs pollution in soil becomes increasingly serious. PAHs concentration in soil (especially in urban areas) continues to rise. With the wide use of plastic bags, agricultural film and wide construction of plastic sheds, Phthalic Acid Esters volatile into the air slowly from plastic products, and then migrate into soil directly or indirectly, which leads to common pollution.

The pretreatment methods of polycyclic aromatic hydrocarbons and Phthalic Acid Esters in soil include Soxhlet extraction (DONG Xin-yan and YANG Yi-wei, 2005), ultrasonic extraction, accelerated solvent extraction (LI Xian-guo and YAN Guo-fang, 2009; WANG Xu-dong and LI Nan, 2010), supercritical fluid extraction and so on (Berruetal A *et al.* 1995; Martinez E *et al.* 2004). Developed in recent years, ultrasonic assistant extraction technique (UE) is a sample pretreatment method. This method makes use of ultrasonic cavitation generated from solvent and sample in process of transferring. It promotes the formation, growth, blasting and compression of solvent bubbles, disperses solid sample, expands the contact area of sample and extraction solvent, and accelerates the transfer rate of mass from solid to liquid phase. It has advantages such as shorter

*Corresponding author. E-mail: zhangli@163.com

extraction time, less impurity, and higher efficiency compared to other methods. This method extracts polycyclic aromatic hydrocarbons and Phthalic Acid Esters from soils in relatively obdurate space with ultrasound assisted extraction technique, which avoids the interference of polycyclic aromatic hydrocarbons and Phthalic Acid Esters in the traditionally open air system. Therefore it can effectively lower system blank level in laboratory. In addition, this pretreatment method is more environment-friendly (Mohammad R and Yaghoub A, 2006) and thus worth recommending to other circumstances.

1 Experiment

1.1 Chemicals and materials

Chemicals: TRACEDSQ Ⅱ gas chromatography mass spectrometry (U.S. Company Thermo Fisher), solid phase extraction element (Tianjin Heng'ao Company), nitrogen evaporator (Tianjin Automatic Science Instrument Co., LTD), constant temperature water bath apparatus. Centrifuge, Ultrasonic unit.

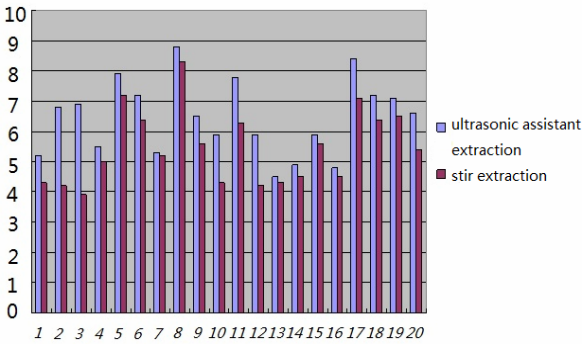
Materials: Dichloromethane (pesticide residue grade), acetone (pesticide residue grade), n-Hexane (pesticide residue grade), anhydrous sodium sulfate (excellent pure, baked at 600 ℃, 3h), quartz sand (excellent pure, bake at 600 ℃, 3h), Florisil from SUPELCO, 16 polycyclic aromatic hydrocarbons and Deuterated Compounds from Sigma- Aldrich company.

1.2 Column and instrument requirement

Column: DB-5MS quartz capillary column (30 m×0.25 mm×0.25 μm); Carrier gas: High purity helium gas (99.999%); Chromatogram temperature program: initial temperature is 40 ℃ and maintains 1 minute; temperature rises at a speed of 7 ℃ per minute to 120 ℃; 10 ℃ per min to 220 ℃; 5 ℃ per min to 300 ℃ and maintains for 5 minutes. Injection port temperature: 240 ℃; Joint lever temperature: 260 ℃; Ionsource temperature: 250 ℃; Injection pattern: Splitless injecting samples 1.0 μL; Solvent delay time: 6.0 min; Scanning system: Segment Selected Ion Monitoring.

1.3 Pretreatment of soil samples

Take accurately 5.0 g naturally dried soil sample (grinding 100 mesh), add the same weight of quartz sand, and put them into a 20 ml headspace bottle. Then add 10ml of mixed solution of acetone-n-hexane (V:V=1:1) via 20 min ultrasonic oscillation. When the extraction is finished, centrifuge and extract. Then add the extraction into the headspace bottle and mix it with 10 ml of acetone-n-hexane mixed solution (V:V=1:1). Extraction is repeated three times. The extracted liquid is mixed and dried by anhydrous sodium. After concentration, K-D is purified by Florisil Reinst column. Then add Internal Standard and use gas chromatography mass spectrometry to detect.



1-Acenaphthene, 2-Acenaphthylene, 3-Acenaphthene, 4-Fluorene, 5-Dibutyl phthalate, 6-Phenanthrene, 7-Anthracene, 8-Dibutyl phthalate, 9-Fluoranthene, 10-Pyrene, 11-Butyl benzyl phthalate, 12-Benzo (a) anthracene, 13-Chrysene, 14-Diisooctyl phthalate, 15-Benzo (b) fluoranthene, 16-Benzo (k) fluoranthene, 17-Benzo (a) pyrene, 18-Indeno (1, 2, 3-cd) pyrene, 19-Dibenz(a,h)anthracene, 20-Benzo (g, h, i) perylene

Fig. 1 Contrast between ultrasonic assistant extraction technique and stir extraction technique

2 Result and discussion

2.1 Efficiency contrast between ultrasonic assistant extraction technique and stir extraction technique

Based on ultrasonic cavitation, ultrasonic assistant extraction technique produces numerous bubbles and blasting in soil samples rapidly. The

shock wave peels off the analyte, both intra and extra particles of soil samples immersed in solvent, evaporates to upper headspace as temperature rises. With the increase of ultrasonic frequency, the number of bubbles increases and the impact decreases. Therefore, high frequency ultrasound is very suitable for cleaning small particles without destructing the work piece surface. The expansion and burst of cavitation bubbles come from high-frequency and high-strength sound wave applied on the liquid. Although magnetic-driven control rod stir is operated based on water wave flow and has effects on the surface of soil particles, it cannot produce effective impact on the interior analyte of soil particles. The paper makes a contrast between ultrasonic assistant extraction technique and stir extraction technique. The results are shown in Fig. 1. It shows clearly that ultrasonic assistant extraction technique is better than stir extraction technique in terms of efficiency.

2.2 Influence of extraction time

The paper examines the time efficiency of ultrasonic extraction. To be specific, the extraction efficiency at 5 min, 10 min, 15 min, 20 min, 30 min, 40 min, 50 min, 60 min period at 60 ℃ are examined, the results of which are shown in Table 1. Results show that efficiency increases as the extraction time increases, and basic equilibrium is achieved at 15 min. In order to ensure complete extraction of all the analytes, the experiment determines the ultrasonic extraction time to be 20 minutes.

Table 1 Influence of extraction time

Analyte	5 min/%	10 min/%	15 min/%	20 min/%	30 min/%	40 min/%	50 min/%
Acenaphthene	101.1	82.8	108.5	104.5	100.1	101.9	92.2
Acenaphthylene	81.4	84.4	98.7	99.3	95.8	93.3	94.2
Acenaphthene	84.3	89.8	89.9	91.3	90.5	90.7	90.6
Fluorene	81.0	82.8	97.5	95.6	92.7	94.5	91.6
Dibutyl phthalate	87.6	81.0	93.8	94.5	93.8	94.4	90.2
Phenanthrene	91.3	89.5	93.0	92.2	91.5	90.9	92.1
Anthracene	73.7	80.9	94.8	96.1	90.2	94.7	94.4
Dibutyl phthalate	82.9	102.1	103.8	102.8	102.7	101.9	94.9
Fluoranthene	91.4	98.4	107.9	106.5	102.3	92.2	102.6
Pyrene	95.5	84.4	97.7	96.5	94.7	90.7	91.3
Butyl benzyl phthalate	76.2	80.1	92.4	94.8	91.76	92.3	92.9
Benzo (a) anthracene	79.9	81.5	87.8	90.2	90.1	90.0	90.0
Chrysene	74.1	87.2	93.4	91.7	90.7	90.8	90.4
Diisooctyl phthalate	87.6	83.3	101.7	98.3	92.1	97.3	96.4
Benzo (b) fluoranthene	95.04	80.8	105.3	104.6	92.6	95.6	93.3
Benzo (k) fluoranthene	74.6	82.9	87.9	90.7	90.0	90.0	90.6
Benzo (a) pyrene	70.6	87.2	90.8	89.9	89.9	89.9	89.91
Indeno (1,2,3-cd) pyrene	77.2	85.7	96.7	95.8	94.1	94.5	95.7
Dibenz (a,h) anthracene	72.2	83.1	87.3	86.5	86.8	87.0	87.5
Benzo (g,h,i) perylene	75.8	83.5	89.7	91.2	90.7	90.0	90.7

2.3 Choice of extraction solvent

In order to identify the best solvent, the experiment chooses 5 different solvents including hexane-acetone (V:V=1:1), methylene dichloride, acetone, N-hexane, dichloromethane-acetone (V:V=1:1) to inspect the recovery effect of different solvents on the analyte. Each experiment is done 7 times and results are shown in Table 2. It shows that hexane–acetone (V:V=1:1) gets the best recovery result. Therefore, hexane–acetone (V:V=1:1) is determined to be the best extraction solvent.

2.4 Analysis of real samples

The method is used to analyze soil samples in different matrix, and the results are shown in

Table3. Most polycyclic aromatic hydrocarbon sand Phthalic Acid Esters are detected at different degrees. It is found that the rate of PAHs detection was higher in industrially developed areas and areas with large flow of vehicles. The same result is shown in wheat fields.

Table 2 Extraction efficiency of extraction solvent

Analyte	n-hexane-acetone	Dichloromethane-acetone	Dichloromethane	Acetone	n-hexane
Acenaphthene	104.5	83.3	72.5	70.9	79.0
Acenaphthylene	99.3	75.0	73.4	76.7	74.9
Acenaphthene	91.3	88.5	76.4	75.2	61.4
Fluorene	95.6	80.3	74.5	77.0	73.4
Dibutyl phthalate	94.5	82.9	70.4	79.5	78.7
Phenanthrene	92.2	85.9	77.8	76.1	68.1
Anthracene	96.1	85.2	69.6	76.6	60.0
Dibutyl phthalate	102.8	77.8	75.8	77.0	66.1
Fluoranthene	106.5	91.0	69.5	72.3	77.6
Pyrene	96.5	75.0	75.1	84.7	61.1
Butyl benzyl phthalate	94.8	80.2	76.6	72.4	81.6
Benzo (a) anthracene	90.2	77.9	76.6	77.8	74.6
Chrysene	91.7	79.5	66.4	73.2	71.8
Diisooctyl phthalate	98.3	73.7	75.0	72.8	79.8
Benzo (b) fluoranthene	104.6	90.3	70.8	74.4	79.1
Benzo (k) fluoranthene	90.7	75.1	70.5	79.0	71.4
Benzo (a) pyrene	89.9	84.0	67.1	85.0	71.5
Indeno (1,2,3-cd) pyrene	95.8	77.4	69.8	72.5	79.0
Dibenz (a,h) anthracene	86.5	82.0	68.7	76.2	67.3
Benzo (g,h,i) perylene	104.5	74.6	66.4	74.1	76.2

Table 3 Analysis of real samples

Analyte	Sample 1 (ug/Kg)	Sample 2 (ug/Kg)	Sample 3 (ug/Kg)	Sample 4 (ug/Kg)
Acenaphthene	6.9	23.6	15.6	12.3
Acenaphthylene	63.8	86.7	-	-
Acenaphthene	-	109.6	32.6	-
Fluorene	56.3	10.9	26.3	7.8
Dibutyl phthalate	75.3	208.4	225.9	-
Phenanthrene	132.6	168.4	47.8	18.5
Anthracene	214.6	325.6	29.6	6.3
Dibutyl phthalate	96.5	98.8	105.8	16.0
Fluoranthene	260.8	290.4	44.6	19.6
Pyrene	68.4	66.5	14.3	5.7
Butyl benzyl phthalate	94.9	80.9	196.6	7.4
Benzo (a) anthracene	326.7	276.9	5..9	18.6
Chrysene	86.4	283.9	6.5	-
Diisooctyl phthalate	68.3	73.7	15.1	2.8
Benzo (b) fluoranthene	18.9	166.7	5.7	7.6
Benzo (k) fluoranthene	23.8	236.9	4.3	-
Benzo (a) pyrene	23.4	189.4	10.9	5.6
Indeno (1,2,3-cd) pyrene	-	19.5	-	-
Dibenz (a,h) anthracene	34.2	-	3.2	-
Benzo (g,h,i) perylene	15.4	29.8	-	-

-:not detected. sample 1: (Soil near national highway); sample 2: (Soil in parterre of industrial areas); sample 3: (Wheat field soil); sample 4: (Scenic spot soil).

3 Conclusions

The paper adopts ultrasonic assistant extraction technique (UE) to assist the extraction of plasticizer and polycyclic aromatic hydrocarbons in soil samples. It identifies the extraction time and the amount of solvent and electrolyte, and experiments on the influence of extraction time on efficiency. The experiment shows that the method can realize simultaneous extraction and analysis of polycyclic aromatic hydrocarbons and plasticizer compounds in soil. Simple and convenient, the method can be popularized in soil pollutant detection.

Acknowledgements

Our special thanks goes to the corresponding author ZHANG Li for her support to the research and ZHANG Gui-qin from Weichai Power Ltd. for paper translation and polishing. The article receives support from the Fundamental Research Funds for the Institute of Hydrogeology and Environmental Geology, the Chinese Academy of Geological Sciences (SK201204).

References

Berruetal A, Gallo B, Vicence F. 1995. A review of solid phase extraction: Basic principle and new developments. Chromatographia, 40(7/8): 474-478.

CAI Q Y, MO C H, WU Q T. 2008. The status of soil contamination by semivolatile organic chemicals (SVOCs) in China: A review. Science of the Total Environment, 389(2-3): 209-224.

DONG Xin-yan, YANG Yi-wei. 2005. Progress in the determination of trace polycyclic aromatic hydrocarbons in complex matrices. Chinese Journal of Chromatography, 23(6): 609-615.

LI Xian-guo, YAN Guo-fang. 2009. Determination of polycyclic aromatic hydrocarbons in seawater using solid phase extraction-high performance liquid chromatography with fluorescent detection. Pe Riodical of Ocean University of China, 39(5):1087-1092.

Martinez E, Gros M, Lacorte S. 2004. Simplified procedures for the analysis of polycyclic aromatic hydrocarbons in water, sediments and mussels. J Chromatogr A, 1047(2):181-188.

Mohammad R, Yaghoub A. 2006. Determination of organic compounds in water using dispersive liquid-liquid microextraction. Journal of Chromatography A, 1116(1): 1-9.

NIE Jing, QIAN Yan. 2009. The health hazards of polycyclic aromatic hydrocarbons in food pollution and its prevention measures. Environment and Sustainable Development, (4): 38-41.

WANG Xu-dong, LI Nan. 2010. Determination of trace polycyclic aromatic hydrocarbons in water by solid phase extraction and GC/MS. China Academic Journal Electronic Publishing House, 32(4):25-27.

ZHAO Wen-chang, CHENG Jin-ping. 2006. PAHs: Sources, pathway and their monitoring. Environmental Science and Technology and Analysis, 29(3): 105-107.

ZHENG Tian-ling, LUO Yuan-rong. 2006. Advances in research of microbial degradation of high molecular weight polycyclic aromatic Hydrocarbons-Benzo (a) pyrene. Chin J Appl Environ Biol, 12(6): 884-890.