



Thermally stable ionic liquid-based sol–gel coating for ultrasonic extraction–solid-phase microextraction–gas chromatography determination of phthalate esters in agricultural plastic films

Xin Zhou^{a,b}, Xiao Shao^a, Jian-jun Shu^a, Ming-ming Liu^{a,*}, Han-lan Liu^c, Xiong-han Feng^a, Fan Liu^a

^a College of Resources and Environment, Huazhong Agricultural University, Wuhan 430070, China

^b Center of Energy and Control, Chengde Iron and Steel Group Co. Ltd., Hebei Iron and Steel Group Co. Ltd., Chengde, Hebei 067102, China

^c College of Science, Huazhong Agricultural University, Wuhan 430070, China

ARTICLE INFO

Article history:

Received 24 June 2011

Received in revised form

25 November 2011

Accepted 1 December 2011

Available online 8 December 2011

Keywords:

Ionic liquid

Solid-phase microextraction

Ultrasonic extraction

Phthalate esters

Agricultural plastic film

ABSTRACT

A novel sol–gel-coated ionic liquid-based ([AMIM][N(SO₂CF₃)₂]-OH-TSO) fiber was successfully applied for the determination of phthalate esters (PAEs) in agricultural plastic films by ultrasonic extraction (UE) combined with solid phase microextraction–gas chromatography (SPME–GC) due to its high thermal stability, specific selectivity and extraction efficiency. The extractant for UE and the adsorption time for SPME were optimized to achieve higher extraction efficiency. The desorption temperature and time were also optimized to avoid the carryover effect of previous extraction, and ultimately improve the precision and accuracy of the method. The [AMIM][N(SO₂CF₃)₂]-OH-TSO fiber showed comparable, or even higher response to most of the investigated PAEs than the commercial PDMS, PDMS–DVB and PA fibers. The carryover problem, often encountered when using commercial fibers, had been eliminated when desorption was performed at 360 °C for 8 min. The proposed SPME–GC method showed good linearity over three to four orders of magnitude, and low limits of detection ranged from 0.003 to 0.063 μg L⁻¹. The relative standard deviation values obtained were below 10%, and the recoveries were in the ranges of 90.2–111.4%. Some of the PAEs studied were detected at very high concentration in these agricultural plastic film samples, resulting in a potential risk of crop damage, environmental contamination and human health exposure.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Plastic films were widely used in agriculture and particularly in protected horticulture to conserve water and fertilizer, to

provide a better microenvironment for the plants, and to protect against adverse climatic conditions over the last decades [1]. They have played an important and irreplaceable role in improving the agricultural productivity and developing the agricultural economy. Unfortunately, the extensive and expanding use of plastics in agriculture will result in increased accumulation of plastic wastes in farming circumstance, which will lead to soil compaction, and thus retarded crop growth [2]. Furthermore, phthalate esters (PAEs)—the commonly used plasticizers in plastic films, will be easily and continuously leached from the plastic wastes into the environment [3]. This ubiquitous presence of PAEs in agricultural soils will bring about potential contamination of crops, vegetables and food chains, and thus result in direct or indirect human exposure [4]. Nowadays, the US Environmental Protection Agency (EPA) and its counterparts in several other countries have classified PAEs as priority pollutants and endocrine disrupting compounds [5].

Analysis of PAEs in agricultural plastic films and their polluted soils is a difficult task, because of the high complexities of

Abbreviations: [AMIM][N(SO₂CF₃)₂], 1-Allyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide; OH-TSO, Hydroxy-terminated silicone oil; KH-570, γ-Methacryloxypropyltrimethoxysilane; PMHS, Poly(methylhydrosiloxane); TEOS, Tetraethoxysilane; TFA, Trifluoroacetic acid; PAEs, Phthalate esters; UE, Ultrasonic extraction; SPME, Solid phase microextraction; EPA, Environmental Protection Agency; DMP, Dimethyl phthalate; DEP, Diethyl phthalate; DBP, Dibutyl phthalate; DAP, Diamyl phthalate; DiOP, Diisooctyl phthalate; DnOP, Di-n-octyl phthalate; DNP, Dinonyl phthalate; DDP, Didecyl phthalate; PP, Polypropylene; PE, Polyethylene.

* Corresponding author at: Huazhong Agricultural University, No.1, Shizishan Street, Hongshan District, Wuhan, Hubei Province 430070, China.
Tel.: +86 27 8728 0271; fax: +86 27 8728 8618.

E-mail addresses: liumm@mail.hzau.edu.cn, liumm35@163.com (M.-m. Liu).

the sample matrixes and the low concentrations at which these compounds are usually present. It is usually necessary to carry out extensive sample pretreatment prior to instrumental analysis in order to obtain reproducible, accurate and sensitive quantitative results. Until now, various pretreatment techniques have been proposed for the extraction and concentration of PAEs from plastic, sediment, sludge, leachate and soil samples, such as ultrasonic extraction (UE) [6], microwave assisted extraction [7,8], supercritical fluid extraction [9,10], accelerated solvent extraction [11,12], soxhlet extraction/solid phase extraction [13,14], microwave assisted extraction/dispersive solid phase extraction [15], solid phase microextraction (SPME) [16] and UE/SPME [17]. However, most of these methods require large volumes of toxic organic solvents which are environmentally unfriendly, and the extraction processes are complicated, tedious and time-consuming.

SPME has broken a new path for sample pretreatment over the last two decades due to its solvent-free and miniaturization characteristics [18]. In the past few years, there have been several papers that deal with the SPME analysis of PAEs using different fibers such as calix[4]arene [17], carbowax-divinylbenzene [19], polyacrylate [20], polyaniline [21] and calix[6]arene [22]. However, some of these fibers are not so stable that they cannot tolerate too high desorption temperature [23]. For example, the recommended maximum operation temperature for PDMS (100 μm) fiber was 280 °C. This temperature is not high enough for complete desorption of PAEs from this fiber since PAEs have very high molecular masses and boiling points. Therefore, the precision was poor for some of these fibers [5,19].

Ionic liquids, as a class of non-molecular ionic solvents, have many favorable properties [24]. These unique properties have made ionic liquids desirable extraction media and selective stationary phases in SPME [25–35]. In our previous work, a chemically bonded ionic liquid-based organic–inorganic hybrid SPME fiber, 1-allyl-3-methylimidazolium bis(trifluoromethanesulphonyl)imide–hydroxy-terminated silicone oil ([AMIM][N(SO₂CF₃)₂]-OH-TSO), was prepared by sol–gel method and free radical cross-linking technology [36]. This fiber was found to be highly selective and sensitive to phenolic environmental estrogens and aromatic amines compared with commercial PDMS, PDMS–DVB and PA fibers. It also has high thermal stability with a transition temperature of 402 °C, good solvent resistance, satisfactory coating preparation repeatability and long lifetime. All these advantages make it very suitable for the analysis of PAEs in plastic films used in agriculture.

In this study, the sol–gel-coated [AMIM][N(SO₂CF₃)₂]-OH-TSO fiber was developed and employed for the determination of PAEs in several agricultural plastic films by UE combined with SPME–GC. The solvent types used for UE and the adsorption time used for SPME were optimized. To avoid carryover effect of previous extraction, the temperature and time needed for complete desorption of PAEs from this fiber was also determined.

2. Experimental

2.1. Apparatus

A SP-6890 capillary GC system (Shandong Lunan Ruihong Chemical Instrument Corporation, Shandong, China) equipped with a capillary split/splitless injector and a flame ionization detector was employed for the UE–SPME–GC analysis of PAEs. On-line data collection and processing was accomplished with N2000 Chromastation Software (Zhejiang University Zhida Information Engineering Co., Ltd, Hangzhou, China). The chromatography

separations were performed using a SE-54 fused silica capillary column (30 m \times 0.25 mm I.D., 0.25 μm film thickness) (Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China). The column temperature program was: 150 °C for 2 min, and then programmed at 15 °C min⁻¹ to 300 °C, held for another 20 min. The injection port temperature was maintained at 360 °C and the detector temperature was at 380 °C. Nitrogen gas was used as the carrier gas at a linear velocity of 12–15 cm s⁻¹ in the 1:20 split mode for all the analytes. An ultrasonicator model SB-3200 (Branson Ultrasonics Co., Ltd, Shanghai, China) was used for the extraction of PAEs from the agricultural plastic film samples. A magnetic stirrer DF-101B (Zhengzhou Greatwall Scientific Industrial and Trading Co., Ltd, Zhengzhou, China) was used for stirring the sample solution during extraction. The homemade SPME syringes with sol–gel-derived [AMIM][N(SO₂CF₃)₂]-OH-TSO fibers were applied to the extraction of PAEs from the methanolic extracts of the agricultural plastic film samples. The commercial PDMS (100 μm), PDMS–DVB (65 μm) and PA-coated fibers (85 μm) for comparison were purchased from Supelco (Bellefonte, PA, USA).

2.2. Reagents and materials

The fused-silica fiber (125 μm , O.D.) with protective polyimide coating was purchased from Fibrehome Telecommunication Technologies Co., Ltd. (Wuhan, China). [AMIM][N(SO₂CF₃)₂] was obtained from Chengjie Chemical Co., Ltd. (Shanghai, China). OH-TSO and poly(methylhydrosiloxane) (PMHS) were purchased from Xinli Chemical Industry Co., Ltd. (Zigong, China). Tetraethoxysilane (TEOS) and γ -methacryloxypropyltrimethoxysilane (KH-570) were obtained from the Chemical Plant of Wuhan University (Wuhan, China). Trifluoroacetic acid (TFA) and benzophenone were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), diamyl phthalate (DAP), diisooctyl phthalate (DiOP), di-n-octyl phthalate (DnOP), dinonyl phthalate (DNP), didecyl phthalate (DDP), NaCl, CH₂Cl₂, CH₃OH, and acetone were analytical-reagent grade and supplied by Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. A stock standard solution was prepared by dissolving 10 mg of each PAEs compound in 10 mL methanol in a volumetric flask to reach a concentration of 1 mg mL⁻¹. Six kinds of polypropylene (PP) and polyethylene (PE) plastic films used in agriculture were purchased from the market of agricultural machinery in Wuhan. The PP films have no specific thicknesses which can only be divided into three different categories: thin, medium and thick, and the most thickness of which is less than 0.06 mm. The thicknesses of the PE films are 0.06 mm, 0.08 mm and 0.10 mm, respectively.

2.3. Fiber preparation

The sol–gel coated [AMIM][N(SO₂CF₃)₂]-OH-TSO fiber was prepared as follows: A 50 mg of [AMIM][N(SO₂CF₃)₂] was dissolved in 300 μL of CH₂Cl₂. Then 90 mg of OH-TSO, 100 μL of TEOS, 50 μL of KH-570, 10 μL of PMHS and 8 mg of benzophenone were added and mixed thoroughly by ultrasonic agitation. A 60- μL portion of 95% TFA in water was subsequently added dropwise to the resulting solution under vigorous ultrasonic agitation. The mixture was then centrifuged at 12,000 $\times g$ for 8 min to remove the precipitate. The clear supernatant was transferred to another clean plastic tube for further use in the coating process. The treated fused-silica fiber was dipped in the sol solution for 2–3 h to facilitate the formation of IL-based organic–inorganic copolymer and its chemical bonding to the fiber substrate. After that, the fiber was drawn out from the sol solution to volatilize the solvents, and inserted vertically into the sol solution once more. A sol–gel

Download English Version:

<https://daneshyari.com/en/article/7686923>

Download Persian Version:

<https://daneshyari.com/article/7686923>

[Daneshyari.com](https://daneshyari.com)