Journal of Chromatography A, 1216 (2009) 5504–5510

Contents lists available at ScienceDirect

Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

Dispersive solid-phase extraction followed by dispersive liquid–liquid microextraction for the determination of some sulfonylurea herbicides in soil by high-performance liquid chromatography

Qiuhua Wu[a], Chun Wang[a], Zhimei Liu[b], Chunxia Wu[a], Xin Zeng[b], Jialin Wen[c], Zhi Wang[a,*]

[a] Key Laboratory of Bioinorganic Chemistry, College of Science, Agricultural University of Hebei, Baoding 071001, Hebei, China
[b] College of Food Science and Technology, Agricultural University of Hebei, Baoding 071001, Hebei, China
[c] School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, Jiangsu, China

ARTICLE INFO

Article history:
Received 19 February 2009
Received in revised form 11 May 2009
Accepted 25 May 2009
Available online 3 June 2009

Keywords:
Sulfonylurea herbicides
High-performance liquid chromatography
Dispersive solid-phase extraction
Dispersive liquid–liquid microextraction
Soil samples

ABSTRACT

Dispersive solid-phase extraction (DSPE) combined with dispersive liquid–liquid microextraction (DLLME) has been developed as a new approach for the extraction of four sulfonylurea herbicides (metsulfuron-methyl, chlorsulfuron, bensulfuron-methyl and chlorimuron-ethyl) in soil prior to high-performance liquid chromatography with diode array detection (HPLC-DAD). In the DSPE-DLLME, sulfonylurea herbicides were first extracted from soil sample into acetone–0.15 mol L^{-1} $NaHCO_3$ (2:8, v/v). The clean-up of the extract by DSPE was carried out by directly adding C_{18} sorbent into the extract solution, followed by shaking and filtration. After the pH of the filtrate was adjusted to 2.0 with 2 mol L^{-1} HCl, 60.0 μL chlorobenzene (as extraction solvent) was added into 5.0 mL of it for DLLME procedure (the acetone contained in the solution also acted as dispersive solvent). Under the optimum conditions, the enrichment factors for the compounds were in the range between 102 and 216. The linearity of the method was in the range from 5.0 to 200 ng g^{-1} with the correlation coefficients (r) ranging from 0.9967 to 0.9987. The method detection limits were 0.5–1.2 ng g^{-1}. The relative standard deviations varied from 5.2% to 7.2% (n = 5). The relative recoveries of the four sulfonylurea herbicides from soil samples at spiking levels of 6.0, 20.0 and 60.0 ng g^{-1} were in the range between 76.3% and 92.5%. The proposed method has been successfully applied to the analysis of the four target sulfonylurea herbicides in soil samples, and a satisfactory result was obtained.

1. Introduction

Sulfonylurea herbicides are widely used as selective pre- and post-emergence herbicides for the control of most broad-leaved weeds and annual grasses in many agricultural crops due to their low application rates (in the range of 10–100 g ha^{-1}), low toxicity to mammals and unprecedented herbicidal activity. However, the remaining low concentration residues of these compounds in soil can still affect the growth of susceptible plants [1]. So, sensitive and selective analytical methods are desirable for the determination of sulfonylurea herbicide residues in soil in order to control carry-over from one growing season to the next.

Sample preparation is one of the most important and crucial steps in the whole analytical process. For the determination of sulfonylurea herbicides, several sample preparation methods have been developed, including solid-phase extraction (SPE) [2–4], supercritical fluid extraction (SFE) [5], microwave-assisted solvent extraction (MASE) [6] and molecularly imprinted SPE [7].

In 2006, a novel microextraction technique named dispersive liquid–liquid microextraction (DLLME) was developed by Assadi and co-workers [8]. DLLME is a miniaturized liquid–liquid extraction (LLE) that uses microliter volumes of the extraction solvent. For DLLME, water-immiscible extraction solvent dissolved in a water-miscible dispersive solvent is rapidly injected into an aqueous solution by syringe. A cloudy solution containing fine droplets of extraction solvent dispered entirely in the aqueous phase is formed. The analytes in the sample are extracted into the fine droplets, which are further separated by centrifugation, and the enriched analytes in the sedimented phase are determined by either chromatographic or spectrometric methods. The advantages of the DLLME method are short extraction time, low cost, simplicity of operation and high enrichment factor. DLLME has been applied for the analysis of a variety of trace organic pollutants and metal ions in environmental samples [9–17].

The objective of the sample preparation is often not only to isolate the target analytes from the samples and concentrate the analytes, but also simultaneously to reduce or even eliminate the

* Corresponding author. Tel.: +86 312 7521513; fax: +86 312 7521513.
E-mail address: wangzhi@hebau.edu.cn (Z. Wang).

0021-9673/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2009.05.062

interferences originally present in the sample to facilitate their determinations at low levels. The main disadvantage of the DLLME is that it is not a selective extraction method. On the other hand, the interferences from matrix co-extractives are often present, especially for the determination of trace analytes in a complex matrix sample such as soil sample. This is the main reason that the most reported applications of DLLME have been focused on simple water samples. Therefore, the exploration of the potential applications of the DLLME technique in more complex matrix samples is desirable. SPE is widely used as a sample clean-up and concentration technique in sample preparations. Assadi and co-workers have reported the combination of SPE with DLLME for the selective determination of chlorophenols in aqueous samples with various matrices [18]. One of the advantages of such a combination is that it can be used for complex matrix samples. The combination of DLLME with in-syringe back extraction as a selective extraction method for ionizable compounds has also been reported by Melwanki and Fuh [19].

Dispersive solid-phase extraction (DSPE) was first introduced by Anastassiades et al. in 2003 [20]. As a clean-up step, the crude extract is cleaned up by addition of a small amount of SPE sorbent material to an aliquot of the extract to remove the matrix co-extractives [21–23]. DSPE is based on the SPE methodology, but the sorbent is directly added into the extract without conditioning. The clean-up is easily carried out by just shaking and centrifugation. The method was described as QuEChERS, which is the abbreviation of quick, easy, cheap, effective, rugged and safe. The commonly used sorbents include primary secondary amine, C_{18} (octadecylsilane), and graphitized carbon black [20–23]. Carbon nanotube, a novel nanomaterial, could be an effective SPE sorbent material because of its large specific surface area [24]. However, its potential application in DSPE has not been exploited until now.

In continuation to our previous endeavors in the exploration of novel sample pretreatment techniques [9,10,25–27], the aim of this work was to combine the DSPE with DLLME in the sample preparation, thus to enhance the selectivity of the DLLME and to extend its application to more complex matrix samples. In this work, the applicability of the combination of DSPE with DLLME (DSPE-DLLME) for the extraction of some sulfonylurea herbicides in soil samples prior to their analysis by HPLC was explored, and the four most widely used sulfonylurea herbicides (metsulfuron-methyl (MSM), chlorsulfuron (CS), bensulfuron-methyl (BSM) and chlorimuron-ethyl (CME)) in local area were chosen as target analytical compouds. As a result, the selectivity of the analysis was much improved and satisfactory analytical results were achieved.

2. Experimental

2.1. Reagents and materials

MSM, CS, BSM and CME were purchased from Agricultural Environmental Protection Institution (Tianjin, China). Chloroform ($CHCl_3$), dichloroethane ($C_2H_4Cl_2$), dichloromethane (CH_2Cl_2), tetrachloride ethylene (C_2Cl_4), carbon tetrachloride (CCl_4) and chlorobenzene (C_6H_5Cl) were purchased from Beijing Chemical Reagents Company (Beijing, China). Acetone, acetonitrile, tetrahydrofuran (THF), sodium bicarbonate ($NaHCO_3$), sodium chloride (NaCl), hydrochloric acid (HCl), ethanol and methanol were from Sinopharm Chemcial Reagent Co. (Beijing, China). C_{18} was obtained from Sigma–Aldrich (Steinheim, Germany). Multi-walled carbon-nanotubes (MWCNTs) with diameters at 40–60 nm were purchased from Shenzhen Nanotech Port Co. (Shenzhen, China). Double-distilled water was used for the preparation of aqueous solutions.

Soil samples were collected from the plough layer of the soybean field at Xixiaozhuang and Wumazhuang (Baoding, China), which were dried at room temperature, pulverized and passed through 250-μm sieve. All the solvents and soil sample extraction solutions were filtered through a 0.45-μm membrane to eliminate particulate matter before analysis.

A mixture stock solution containing MSM, CS, BSM, and CME at 10.0 μg mL^{-1} was prepared in methanol. A series of standard solutions were prepared by mixing an appropriate amount of the stock solution with double-distilled water in a 10-mL volumetric flask. All the standard solutions were stored at 4 °C in the dark.

2.2. Instruments

The HPLC system, assembled from modular components (Waters, Milford, MA, USA), consisted of an in-line degasser, a 600E pump, and a diode array detection (DAD) system. A Millennium^{32} workstation (Waters) was utilized to control the system and for the acquisition and analysis of the data. The injection loop volume is 20.0 μL. A Centurysil C_{18} column (250 mm × 4.6 mm I.D., 5.0 μm) from Dalian Johnsson Separation Science Technology Corporation (Dalian, China) was used for separations. The mobile phase was a mixture of acetonitrile–water (50:50, v/v), the pH of which was adjusted to 3.0 with 1 mol L^{-1} HCl, at a flow rate of 1.0 mL min^{-1}. The DAD monitoring wavelengths for quantification were chosen at 225 nm for MSM and CS, and 240 nm for BSM and CME.

2.3. DSPE-DLLME procedure

Soil samples were air-dried at room temperature, pulverized and passed through 250-μm sieve. 10.0 g of the soil sample was accurately weighed and put into a 50 mL centrifuge tube, to which 20.0 mL acetone–0.15 mol L^{-1} $NaHCO_3$ (2:8, v/v) was added. The resultant sample mixture was first vigorously shaken on a vibrator for 30 min and then filtrated under reduced pressure. For DSPE, 0.15 g of C_{18} per 10 mL filtrate was added and shaken for 5 min. After filtration through 0.45 μm filter, the pH of the filtrate was adjusted to 2.0 with 1 mol L^{-1} HCl, and the filtrate was transferred to a 25 mL volumetric flask, to which, acetone–water (2:8, v/v) at pH 2.0 was added to complete the volume. For the DLLME, a 5.0 mL aliquot of the above sample solution (the acetone contained in the solution was also used to act as the dispersive solvent for this DLLME) was placed in a 10 mL screw cap glass tube with conical bottom, and then 60 μL of chlorobenzene (as extraction solvent) was added into it by 100 μL syringe. After vortexing for 5 s, a cloudy solution that consisted of very fine droplets of chlorobenzene dispersed into aqueous sample was formed, and the analytes were extracted into the fine droplets. After centrifugation at 3500 rpm for 5 min, the chlorobenzene phase was sedimented at the bottom of the centrifuge tube. The sedimented phase was completely transferred to another test tube with conical bottom using 100-μL HPLC syringe and then evaporated to dryness with a mild nitrogen stream. The residue was dissolved in 15.0 μL acetonitrile, and 10.0 μL was injected into the HPLC system for analysis.

3. Results and discussion

3.1. Optimization of the DSPE procedure

In this experiment, 10.0 g of soil sample, which was free of the target analytes and spiked at 50.0 ng g^{-1} each of the four sulfonylurea herbicides, was used to study the extraction performance of DSPE under different experimental conditions. All the experiments were performed in triplicate and the means of the results were used for optimization.

3.1.1. Selection of the extraction solvent for soil sample

Sulfonylurea herbicides are weak acidic compounds (pK_a values from 3.3 to 5.2) [2]. So for the extraction of sulfonylurea herbicides