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Analytical Methods

Dispersive liquid–liquid microextraction method based on solidification of floating organic droplet for the determination of triazine herbicides in water and sugarcane samples

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ABSTRACT

Dispersive liquid–liquid microextraction method based on solidification of floating organic droplet (DLLME-SFO) was developed for the analysis of triazines. As model compounds four selected triazine herbicides namely, simazine, atrazine, secbumeton and cyanazine were employed to estimate the extraction efficiency. The experimental conditions were comprehensively studied for the DLLME-SFO method. Under the use of 10 μL of 1-undecanol as extraction solvent, 100 μL of acetonitrile as disperser solvent and 5% (w/v) NaCl for 3 min the results demonstrated that the repeatability (RSD%) of the optimised DLLME-SFO method ranged from 0.03% to 5.1% and the linearity in the range of 0.01–100 ppb. Low limits of detection (0.037–0.008 ppb), and good enrichment factors (195–322) were obtained. The DLLME-SFO method applied in water and sugarcane samples showed excellent relative recoveries (95.7–116.9%) with RSDs <8.6% ($n = 3$) for all samples.

1. Introduction

Triazine herbicides are recognised herbicides which have been broadly used in agriculture over the recent decades. They are very important to obtain productions with high-yield, sustainable agriculture. But on the other hand due to their solubility in water and mobility in soil they are considered omnipresent environmental pollutants and by various mechanisms they can break through surface and ground water. Toxicity of triazine herbicides can be ranging from high toxicity to low toxicity. Additionally from high exposures to triazines there is anxiety from possible carcinogenicity as well as other health problems which have long term affect for example Parkinson's diseases (Costello, Cockburn, Bronstein, Zhang, & Ritz, 2009). Therefore, the range of dangerous health problems can be caused by triazine herbicides is ranging from skin rashes to death. Moreover, small amounts of these compounds in environmental cause hazardous effects on animals and humans. Furthermore, these compounds cannot be directly detected from samples, thus we need sensitive analytical methods for determining the low concentrations of triazine herbicides in environmental samples.

Sample preparation step is considered one of the most important steps in any analytical procedure. Meanwhile, most sample matrices such as, soil, food or wastewater is considered very complex. So, in order to obtain successful sample preparation methods, three main objectives have to be achieved: (1) sample matrix simplification, (2) analyte enrichment, and (3) sample cleanup (Kokosa, Przyjazny, & Jeannot, 2009). Triazine herbicides have been analysed in various environmental samples over the years by using many useful sample preparation methods. They have been widely analysed and extracted from environmental samples using conventional liquid–liquid extraction (LLE) and solid phase extraction (SPE) (Balinova, 1993; Durand, Bouvot, & Barceló, 1992). Many limitations including time-consuming, manual labour, consumption of large quantities of environmentally unfriendly organic solvent and emulsion formation problem are disadvantages in these methods. Supercritical fluid extraction method (SFE) has also been applied for the analysis and extraction triazine herbicides from different environmental matrices: soils, sediments and plants (Paplloud & Haerdi, 1995), as well as fortified and incurred eggs (Pensabene, Fiddler, & Donoghue, 2000). SFE is an alternative method for other extraction methods, using CO_2 as a replacement for hazardous organic solvents. Skillfulness, high-purity carbon dioxide and high-pressure delivery system are required which render this technique expensive.

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Microwave-assisted extraction (MAE) is a relatively new and hopeful extraction technique which heats the solvent and the sample to enhance the mass transfer rate of the analyte of interest from the sample solution into the extraction solvent by employing microwave energy. MAE technique coupled with high performance liquid chromatography (HPLC) for the determination of triazine herbicides in sheep liver and solid phase microextraction coupled with gas chromatography–mass spectrometry (GC–MS) for the determination of triazines in soil have been reported (Cheng et al., 2007; Shen & Lee, 2003).

In the recent year, because the rapid and effective isolation of analytes from a mixture by use of a small amount of solvent is the main goal of every sample preparation method, research has been directed toward efficient, accurate and miniaturized extraction and sample preparation methods. Therefore, solid phase microextraction (SPME) and solvent microextraction (SME) have been developed from SPE and LLE, respectively.

SPME is very simple, portable, easy to use and solvent- free sample preparation method, which have been extensively used for the determination of triazine herbicides from various environmental, food, and biological samples (Aguilar, Pen~alver, Pocurull, Borrull, & Marce, 1998; Barnabas, Dean, Fowlis, & Owen, 1995; Basheer & Lee, 2004; Hernandez, Beltran, Lopez, & Gaspar, 2000; Huang, Huang, & Sung, 2004; Kumazawa et al., 2000; Perreau & Einhorn, 2006; Rocha, Pappas, & Huang, 2008) by different procedures. Although SPME is relatively new and an important sample preparation method with many advantages compared to other conventional methods, yet it is suffered from many weaknesses such as the fibre being fragile, expensive and has limited lifetime e.g. adsorption temperature, sample carry-over and reduce performance with time.

Liquid phase microextraction (LPME) method has been developed and many reports have been carried out in order to extract and determined triazine herbicides such as single drop microextraction (SDME) (Ye, Zhou, & Wang, 2007), hollow fibre-protected microextraction (HF-LPME) (Rasmussen & Pedersen-Bjergaard, 2004; Shen & Lee, 2002) and dispersive liquid–liquid microextraction (DLLME) (Nagaraju & Huang, 2007). However, there are some drawbacks in these methods e.g. fast stirring speed lead to break up of the organic drop in SDME, air bubble could be formed on the surface of hollow fibre and poor reproducibility due to manual cutting of the membrane in the laboratory in HF-LLME and use of toxic organic solvents in DLLME (Zgoła-Grześkowiak & Grześkowiak, 2011). To overcome some of these drawbacks, new mode namely dispersive liquid–liquid microextraction based on solidification of floating organic droplet (DLLME-SFO) has been introduced. Numerous works have been reported on the use of DLLME-SFO for the analysis of organic and inorganic compounds in various environmental samples such as steroid hormones, polychlorinated biphenyl (PCB), organochlorine pesticide (OCP), pyrethroid pesticides and heavy metals. (Chang & Huang, 2010; Matsadiq et al., 2011; Mirzaei, Behzadi, Abadi, & Beizaei, 2011), but to the best of our knowledge, the use of DLLME-SFO for the analysis of triazine herbicides in aqueous samples have not yet been reported.

In this work dispersive liquid–liquid microextraction method based on solidification of floating organic droplet was used as new application for the determination of triazine herbicides in water and sugarcane samples. Sugarcane is one of the most important agricultural plants in most countries of the world, where it is considered economic wealth used as a food source. The importance of choosing it as a sample for analysis is emanating from dangerous environmental and human health problems that can emerge in sugarcane production, due to the use of triazine herbicides indiscriminately during the cultivation of sugarcane in order to control pests and diseases.

2. Experimental

2.1. Chemicals and reagents

All triazine herbicides used (atrazine, simazine, cyanazine and secbumeton) had purity of >98% these were purchased from Riedel-dehaën (Seelze, Germany). Extraction solvents (1-dodecanol, 1-undecanol and *n*-hexadecane) were obtained from Merck (Hohenbuunn, Germany). Acetone and methanol (grade AR) were obtained from QRëC-Brightchem (Penang, Malaysia). Acetonitrile (HPLC grade) was obtained from J.T. Baker (USA). Sodium chloride (GR for analysis) was obtained from Merck KGaA (Germany). Double-distilled deionized water of at least 18 MΩ was purified by NanoUltra-pure water system (Barnstead, USA).

2.2. Instrumentations

Analysis of triazines was performed by injecting 2 μL aliquot of the extract into Agilent Technologies, 6890 N gas chromatograph equipped with Agilent Technologies, 5973 inert MS detector. Isothermal GC separations were carried out on a HP Ultra 2 capillary column (25 × 0.2 mm i.d. and 0.33 μm film thicknesses). Helium gas was used as carrier gas at a flow rate of 1.0 mL min^{-1} and data were interpreted using MSD Chem-Station. The oven temperature programme employed for separation of triazine herbicides is as follows: 150 °C for 0 min; increased at 5 °C min^{-1} to 220 °C held for 0 min. The GC oven temperature and the injection port temperature were maintained at 250 °C and all injections were made in the split mode. The mass detector was used in the full scan mode and scanned over the range m/z 1.6–800 to confirm the retention times of the analytes. Selective ion monitoring (*SIM*) mode was used for the determination of triazine herbicides. For identify, confirmation of triazines were made by selecting the most abundant characteristic ions of each triazine, and two characteristic fragment ions were monitored in addition to the molecular ion. The m/z selected for SIM detection mode was as follows: simazine (201, 186, and 173), atrazine (215, 200, and 173), secbumeton (225, 210, and 196), and cyanazine (240, 225, and 172). A centrifuge model 2420 was from KUBOTA Corporation (Japan) was used for centrifuging.

2.3. Sampling and pre-treatment of samples

Stations for the collection of farm, tap and lake water samples included UTM farm water near agriculture research farm for research, Collage Pardana inside UTM, Skudai, Johor Malaysia and lake inside UTM, respectively. Sugarcane peel and sugarcane juice samples were collected from local store in Skudai, Johor Malaysia. The sugarcane juice sample was centrifuged for 15 min at 3500 rpm. After the centrifugation, 5 mL of the juice was diluted with distilled water for the DLLME. Meanwhile, the peel of sugarcane sample was washed using distilled water and the wash water was collected for analysis. The five samples i.e. farm water, tap water, lake water sugarcane juice and wash water of sugarcane peel, were then filtered using 0.45 μm pore-size membrane filters (NALG, Belgium) for further analysis.

2.4. Dispersive liquid–liquid microextraction based on solidification of floating organic droplet procedure

The experimental steps for DLLME-SFO are illustrated in Fig. 1A 5 mL portion of deionized water was placed in 10 mL screw cap glass test tube with conical bottom and spiked with each triazine herbicides at concentration of 0.01 ppm. Extraction solvent with low density than water and disperser solvent were mixed to gather and rapidly injected by a syringe into the sample solution by using