Determination of Triazole Fungicides Using Hollow Fiber Liquid Phase Microextraction Prior to Gas Chromatography—Mass Spectrometry Analysis

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ABSTRACT: A two phase hollow fiber liquid phase microextraction (HF-LPME) and gas chromatography mass spectrometry (GC-MS) method for the separation and determination of triazole fungicides, namely, penconazole, hexaconazole, diclobutrazole and diniconazole, is described. The extraction conditions were optimized for the four triazole fungicides as follows: extractant solvent, toluene; extraction time, 20 min; stirring rate, 720 rpm; no salt addition; and no pH adjustment. Under the optimal extraction conditions, the method showed good linearity ($r^2 = 0.997−0.999$), acceptable reproducibility (RSD% = 6−9%), low limit of detection (0.3−0.8 μg·L$^{-1}$), and satisfactory relative recoveries. The linear range is 1−5000 μg·L$^{-1}$. The developed HF-LPME method was applied for the determination of triazole fungicides in farm, river, and tap water and also grape juice samples.

INTRODUCTION

Fungicides are used on a large scale for agricultural purposes to control plant diseases through fungal attack. The adverse effects of fungicides on both human and environmental health are a matter of public concern. Thus, both the actual state and the transition of fungicide residues in various matrices including water, soil, and agricultural products should be extensively monitored,1 because, as a result of their widespread use, they contaminate crops and natural waters. Azole fungicides used in agriculture are moderately lipophilic and fairly persistent, with typical half-lives of weeks to months.2 Conventional methods of sample preparation for fungicides determination include liquid−liquid extractions (LLE),3−6 supercritical fluid extraction (SFE),7 microwave assisted extraction (MAE),8 and solid-phase extraction (SPE).9−12 These techniques, which are easy to carry out and also provide excellent recoveries, are, however, time-consuming, tedious, and hazardous to operators’ health as a result of the large volumes of organic solvents involved.13 Considerable efforts have been made trying to develop new sample preparation techniques that save time and labor and reduce solvent consumption. Solid phase microextraction (SPME) has become popular for the analysis of organic compounds. SPME has been applied extensively to determine pesticide residues in water samples.14−21 The coated fiber is expensive and fragile, and in some cases, sample carry-over problems do exist.22 Later on, for solving some of problems mentioned in SPME, liquid phase microextraction (LPME) was developed as an alternative sample preparation method.23−26 Sarafraz-Yazdi and Amiri have published a comprehensive review on different methods of liquid phase microextraction (LPME). In LPME, extraction normally takes place into a small amount of a water-immiscible solvent (acceptor phase) from an aqueous sample containing analytes (donor phase).27 It can be divided into three main categories: single-drop microextraction (SDME), which for the first time was reported by Jeannot and Cantwell,28,29 dispersive liquid−liquid microextraction (DLLME), which was developed by Assadi,30 and hollow-fiber liquid phase microextraction (HF-LPME), which was introduced by Pedersen-Bjergaard and Rasmussen.31 In the HF-LPME method, a low polarity (water immiscible) organic solvent is immobilized as a thin supported liquid membrane (SLM) in the wall of a porous hollow fiber. The target analytes are extracted from an aqueous sample through the organic SLM and further into an acceptor solution inside the lumen of the hollow fiber.31,32 This technique reduced solvent consumption, and this system offers greater stability than the other LPME procedures such as single drop microextraction (SDME), where the hanging drop is often lost as a result of stirring during the extraction procedure.33,34 After the extraction, the acceptor solution is directly subjected to analysis. Regarding the acceptor solution, it can be an organic solvent providing a two-phase LPME system, which is directly compatible with GC35−37 or an aqueous solution providing a three-phase extraction system, compatible with HPLC or CE.38−42

In this work, a new application of HF-LPME method followed by gas chromatography−mass spectrometry was investigated for the determination of some fungicides (hexaconazole, penconazole, diclobutrazole, and diniconazole) in water and grape juice samples. The factors affecting the extraction efficiency, such as the type of extraction solvent, extraction time, addition of salt, stirring rate, and effect of pH were considered and optimized. Quality parameters and matrix effects were evaluated by analyzing spiked samples. The result reveals that the proposed method is simple, rapid, practical, and in accordance with green chemistry principles to reduce solvent consumption.

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