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Analytical Methods

Vortex-assisted ionic liquid dispersive liquid–liquid microextraction for the determination of sulfonylurea herbicides in wine samples by capillary high-performance liquid chromatography

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ABSTRACT

A new sample treatment, namely vortex-assisted ionic liquid dispersive liquid–liquid microextraction (VA-IL-DLLME), followed by capillary liquid chromatography has been developed for the determination of four sulfonylurea herbicides (SUHs): flazasulfuron (FS), prosulfuron (PS), primisulfuron-methyl (PSM) and triflusulfuron-methyl (TSM) in wine samples. The ionic liquid (IL) 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$) was used as extraction solvent and was dispersed using methanol into the sample solution, assisted by a vortex mixer. Various parameters influencing the extraction efficiency, such as type and amount of IL, type and volume of disperser solvent, sample pH, salting-out effect, vortex and centrifugation time were studied. Under the optimum conditions, the limits of detection and quantification of the proposed method were in the ranges of 3.2–6.6 and 10.8–22.0 μg kg^{-1}, respectively; lower than the maximum residue limits set by the EU for these matrices. The proposed method was successfully applied to different wine samples and satisfactory recoveries were obtained.

1. Introduction

Sulfonylurea herbicides (SUHs) are characterised by their broad-spectrum weed control at low application rates, good crop selectivity and low acute and chronic animal toxicity. They are very effective inhibitors of acetolactate synthases (ALS), a key enzyme in biosynthesis of branched-chain amino acids. This inhibition leads to termination of plant cell division and growth (Brown, 1990).

The widespread use of SUHs has created great concern among legislative bodies mainly due to the health and safety of consumers. Their intensive use has resulted in contamination of environmental waters, soils and agricultural products and subsequently they have been identified to have direct and/or indirect toxic effects on food and biological systems (Tadeo, Sánchez-Brunete, Pérez, & Fernández, 2000). As one of several consequences, grapes and their processed products, such as wine, could be contaminated by SUHs. The International Organization of Vine and Wine estimated that 244.3 Mhl of wine were consumed last year over the world (International Organization of Vine and Wine, 2012) so the control of pesticides content in wine is a matter of concern. The European Union (EU) has established maximum residue limits (MRLs) of certain pesticides in wine grapes, including SUHs, ranging from 0.01 to 5 mg kg^{-1}, depending on the particular compound being the MRL for FS, PS and TSM of 20 μg kg^{-1}. Also, a MRL of 10 μg kg^{-1} is established as a default value for matrices not included in the regulation, such as is the case with wine (Regulation (EC) No. 396/2005; Regulation (EC) No. 149/2008). Therefore, it is important to develop simple, rapid, environmentally friendly and sensitive analytical methods for the determination of trace level of SUH residues in wine samples in order to evaluate their safety and possible risk to human health.

In the monitoring of contaminants at trace levels in food analysis, the sample preparation step plays a crucial role for the selective extraction and preconcentration of the target analytes in order to obtain accurate and sensitive results. A traditional sample preparation technique such as liquid–liquid extraction (LLE) has been commonly used, despite the inherent drawbacks associated with the

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large quantities of toxic organic solvents required (Berrada, Font, & Moltó, 2003). In recent years, a number of miniaturized sample preparation techniques have emerged, being successfully applied to the monitoring of a variety of analytes at trace level in different samples. One of such methods is dispersive liquid–liquid microextraction (DLLME), introduced by Rezaee et al. (2006). This technique is based on the formation of a cloudy solution by rapidly injecting a mixture of extraction and disperser solvents into an aqueous sample containing the target analytes. A large number of reviews have summarised the development and application of DLLME (Asensio-Ramos, Ravelo-Pérez, González-Curbelo, & Hernández-Borges, 2011; Cruz-Vera, Lucena, Cárdenas, & Valcárcel, 2011; Kocúrová, Balogh, Šandrejová, & Andruch, 2012; Nuhu, Basheer, & Saad, 2011; Rezaee, Yamini, & Faraji, 2010; Yan & Wang, 2013). Besides its several merits, DLLME is still mainly using toxic organic solvents.

Recently, room temperature ionic liquids (RTILs) have received enormous consideration, as environmentally friendly extraction solvents. RTILs have unique physicochemical properties, which depend on the nature and size of their cationic and anionic constituents. They are less hazardous than organic solvents and are generally considered as green solvents. Some of their properties are: negligible vapour pressure, good thermal stability and adjustable viscosity and miscibility in aqueous samples (Rezaee et al., 2010; Trujillo-Rodriguez, Rocio-Bautista, Pino, & Afonso, 2013). The use of ILs as extraction solvents in DLLME system was first reported in 2008 (Baghdadi & Shemirani, 2008; Zhou, Bai, Xie, & Xiao, 2008a, 2008b). This new development does not use organic solvents or uses very small amounts, when combined with DLLME technique. To enhance dispersion of hydrophobic IL (extraction solvent) into the aqueous sample, various strategies, based on the assistance by temperature (Baghdadi & Shemirani, 2008; Zhou et al., 2008a, 2008b), ultrasounds (Gao, Yang, Yu, Liu, & Zhang, 2012; Sun, Shi, & Chen, 2011; Zhang & Lee, 2012; Zhang, Liang, et al., 2012; Zhou & Zhang, 2010), microwave (Mesa, Padró, & Reta, 2013; Xu et al., 2011a, 2011b) or vortex (Zhang, Chen, Liu, Chen, & Pan, 2012) have been introduced. This latter methodology, named vortex-assisted IL-DLLME offers the advantage of avoiding the possible degradation of some analytes (Andruch, Burdel, Kocurova, Šandrejova, & Balogh, 2013; Zhang, Liang, et al., 2012).

IL-DLLME has been applied for the analysis of pesticide residues including organophosphorus (He et al., 2009; He, Luo, Jiang, & Qu, 2010; Zhang, Chen, et al., 2012; Zhou et al., 2008b), benzoylureas (Zhou & Zhang, 2010), triazine and phenylurea herbicides (Wang, Ren, Liu, Ge, & Liu, 2010; Zhang, Liang, et al., 2012), multiclass pesticides (Asensio-Ramos, Hernández-Borges, Borges-Miquel, & Rodríguez-Delgado, 2011; Ravelo-Pérez, Hernández-Borges, Herrera-Herrera, & Rodríguez-Delgado, 2009; Ravelo-Pérez, Hernández-Borges, Asensio-Ramos, & Rodríguez-Delgado, 2009) and pyrethroids (Zhou et al., 2008a), manly in environmental waters or fruits. However, IL-DLLME procedure has not been considered to date for the analysis of SUHs.

In this paper, vortex-assisted IL-DLLME (VA-IL-DLLME) procedure combined with capillary HPLC-DAD is proposed for the trace level determination of four SUHs: flazasulfuron (FS), prosulfuron (PS), primisulfuron-methyl (PSM) and triflusulfuron-methyl (TSM) in wine samples. The utilization of capillary HPLC has also provided additional advantages such as better resolution, lower detection limits and lower solvent consumption compared to conventional HPLC, as has been previously reported by the authors (Gure, Lara, Megersa, García-Campaña, & del Olmo-Iruela, 2013). The effect of various parameters on the extraction performance of the target analytes were studied and optimized. Furthermore, the applicability of the method was demonstrated by a selective extraction and quantitative determination of the target SUHs from different wine samples.

2. Experimental section

2.1. Chemicals and reagents

All chemicals and reagents used in this study were of analytical grade, while the solvents were of HPLC grade. Methanol, acetonitrile, ethanol and acetone were supplied by VWR BDH Prolabo (West Chester, PA, USA); sodium hydroxide (NaOH), acetic acid (HOAc), hydrochloric acid (HCl) and sodium chloride (NaCl) were purchased from Panreac-Química (Madrid, Spain). Citric acid monohydrate ($C_6H_8O_7{\cdot}H_2O$), 1-Butyl-3-methylimidazolium hexafluorophosphate, $[C_4MIM][PF_6]$, ($\geqslant$97.0%) and 1-Hexyl-3-methylimidazolium hexafluorophosphate, $[C_6MIM][PF_6]$, ($\geqslant$97.0%) were obtained from Sigma Aldrich (St. Louis, MO, USA). Ultrapure water, purified with a Milli-Q Plus system (Millipore Bedford, MA, USA), was used throughout the experimental work. Mobile phase solvents were filtered under vacuum through nylon 66 membranes, 0.2 μm × 47 mm (Supelco, Bellefonte, PA, USA). Nylon syringe filters, 0.22 μm × 13 mm (Agela technologies, New York) were used for filtration of the sample extracts prior to injection into the capillary HPLC system.

Analytical standards of PSM (99.9%), PS (97.9%) and TSM (99.5%) were obtained from Sigma Aldrich (St. Louis, MO, USA). FS (99.3%) was purchased from ChemService Inc (West Chester, USA). Stock standard solutions containing 1000 mg L^{-1} of each compound were prepared by dissolving accurately weighed amounts of each standard in 10 mL of acetonitrile and stored in the dark at 4 °C. An intermediate working solution containing 20 mg L^{-1} of PS, PSM and TSM as well as 30 mg L^{-1} of FS were also prepared in acetonitrile.

A 0.2 M citrate buffer was used to adjust sample pH. It was prepared by dissolving accurately weighed amount of $C_6H_8O_7{\cdot}H_2O$ in ultrapure water. The pH was adjusted to the required value using sodium hydroxide and hydrochloric acid.

2.2. Instrumentation and equipment

The determination of SUHs was performed using an HP-1200 series capillary HPLC (Agilent Technologies, Germany) equipped with a capillary pump (maximum flow rate: 20 μL min^{-1}), online degasser and autosampler (8 μL loop), column thermostat and a diode array detector (DAD). Chromatographic separations were achieved at a temperature of 25 °C on a Luna C_{18} column (150 mm × 0.3 mm I.D., 5 μm particle size) from Phenomenex (Micron, Madrid, Spain). Data acquisition and processing were accomplished using ChemStation software, (Rev. A.10.02, Agilent Technologies, Germany).

A pH-meter (Crison model pH 2000, Barcelona, Spain), was used for pH measurements. A centrifuge, model universal 320R (Hettich, Tuttlingen, Germany); an evaporator with nitrogen (SystemEVA-EC, VLMGmbH, Bielefeld, Germany); 1 mL, 2 mL and 5 mL syringes (Tuttlingen, Germany) with a blunt needle and a vortex (Genie 2 model from Scientific industries, Bohemia, USA) were used for sample preparation.

2.3. Chromatographic conditions

The reversed phase separation of the four SUHs was performed on a Luna C_{18} column. A binary mobile phase consisting of eluent A (water) and eluent B (acetonitrile), both containing 0.01% HOAc (*v*/*v*), with a gradient program of 32% B (2 min), 32–95% B (18 min) and 95% B (14 min) was used throughout the analysis. Prior to the subsequent injection, the capillary HPLC column was re-equilibrated with the initial composition of the mobile phase for 10 min. Analysis were performed with a flow rate