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Development of fast, efficient and ecological method employing vortex-assisted dispersive liquid–liquid microextraction combined with fast gas chromatography–mass spectrometry for pesticide residues analysis in alcohol-content samples

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ABSTRACT

A fast, ecological, and efficient method employing vortex-assisted dispersive liquid–liquid microextraction (DLLME) method for isolation and preconcentration of selected endocrine disrupting pesticides from beverages containing some degree of alcohol was developed. The effect of several extraction parameters, such as selection of extractive solvent, its volume and extraction time, the salt addition was investigated. Four different extractive solvents (chloroform, tetrachloroethane, tetrachloromethane and toluene) and their combinations were evaluated for DLLME. Under the following conditions: 1 mL of fortified sample, 80 μL of tetrachloroethane, 1.5 mL of water, vortex assistance for 3 min at the speed of 1800 rpm, and no salt addition, the method was validated. Linearity was studied in the concentration range of 0.01–250 μg/L with coefficient of correlation ranging between 0.9940 and 1.0000, limits of detection and quantification ranging between 0.02–1.4 μg/L and 0.07–4.7 μg/L, respectively. Recoveries were satisfactory in the range of 70–120%, with the exception of diphenyl, alachlor and fenarimol at the lowest concentration level and *p,p*-DDE at concentration level of 100 and 250 μg/L. The applicability of the developed and validated method was proved by the analysis of real samples.

1. Introduction

Nowadays, pesticides are inevitably used in agriculture to maximize yield of high quality food products. The topic of pesticide residues in food products becomes increasingly a hot topic with the new information, that pesticides may result in endocrine and immune system disruption at lower concentrations than it was expected [1,2]. Therefore, it is necessary to investigate pesticides in these products in order to identify the residues and quantify their levels. In this context, there is a growing need for fast and more efficient methods for the analysis of pesticide residues in food as the demand for residue-free foodstuffs.

The most common way for investigation of pesticide residues in food samples is the application of multiresidue methods that allow screening for multiple pesticides in a single analytical procedure. For this purpose, either gas chromatography (GC) or liquid chromatography (HPLC) hyphenated preferably with mass spectrometry (MS) are employed [3]. Nowadays, fast GC can be performed on commercial gas chromatographs with standard equipment for high-speed injection, electronic pressure control, rapid oven heating/cooling and fast detection. Fast GC analysis provides unquestionable benefits compared with conventional GC – higher laboratory throughput, reduced GC operating costs, and better analytical precision through replicate analyses [4].

Sample preparation is a crucial step in chemical analysis. Despite the many efforts carried out during the last two to three decades to improve the techniques used for sample preparation, the sample treatment procedures in use in many application areas are still tedious multistep protocols [5]. Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are two commonly used conventional techniques for isolation and preconcentration. However, these traditional pretreatment methods require large amounts of organic solvents, long extraction time periods and they are labor-intensive. The efforts made in the field of sample preparation in the past recent years have led to the adaptation of the existing methods and development of new techniques to save time and chemicals, and improve

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overall performance [6]. Besides that, to meet requirements of Green Analytical Chemistry [7], low waste production is another key requirement. Modern analytical methods promoting procedural simplicity and miniaturization has encouraged the development of microextraction based on solvent, which is a promising way to overcome the mentioned shortcomings. So, called methods of liquid phase microextraction (LPME) has been a key factor in designing integrated analytical systems to provide low solvent consumption, low waste generation and higher sample throughput [8].

Dispersive liquid–liquid microextraction (DLLME), as one of LPME sub-techniques, was first reported by Rezaee and co-workers in 2006 [9]. The extraction by DLLME is based on the ternary component solvent system (aqueous sample, dispersive and extractive solvent). The appropriate mixture of extractive solvent (organic solvent) and dispersive solvent (water-organic miscible solvent) is rapidly injected into the aqueous sample by syringe. Thereby, a cloudy solution is formed. Target compounds immediately partition from the aqueous phase to the organic phase. After centrifugation, the analytes are separated into the organic phase (extractive solvent). The latest developments, advances and applications in DLLME were summarized in large number very recent reviews [10–15]. DLLME is commonly used for extraction of various pesticides in water [16–19] and fruit/vegetables [17,20,21] or juices [22,23]. Organic solvents that have a density higher than water are preferably employed as extractants, and they can be easily separated and deposited after centrifugation. Unfortunately, only a few solvents, which are usually highly toxic chlorinated solvents such as chloroform, chlorobenzene, carbon tetrachloride, and tetrachloroethane, can be used with this technique because of its specific requirements [24].

Special category of samples are liquid samples containing some degree of alcohol, such as brandy, liqueurs, wine, herbal potions etc. DLLME was used for the determination of various toxic compounds as selection of pesticides and mycotoxins in alcohol-containing samples, mainly in wines. It can be also combined with other techniques such as SPE to improve the selectivity of the sample preparation [25]. The number of analytes extracted by DLLME is limited usually to a few individuals from the same chemical group. Gure et al. [26] determined sulfonylurea herbicides in wines. The ionic liquid 1-hexyl-3-methylimidazolium hexafluorophosphate ([C6MIM][PF6]) was used as the extraction solvent and was dispersed using methanol. The addition of dispersion agent was necessary, because for lower volumes than 700 μL of dispersant, the cloudy suspension could not be formed. Lai et al. [27] determined ochratoxin A in rice wine. Rice wine samples were first diluted to 18% alcohol with water, DLLME procedure was followed that included ionic liquid (IL) ([HMIM][PF_6]) as the extraction solvent and additional ethanol was used as dispersive solvents. Ten fungicide residues in red and white wine were extracted by a binary mixture of acetone and 1-undecanol from diluted (1:1) wine samples [28]. Seven neonicotinoids were determined in honey liqueur using dichloromethane and acetonitrile as extractant and dispersant, respectively [29].

Generating homogeneous and fine drops in DLLME is an important step. There are more possibilities to improve generation of cloudy system without dispersive solvents. Ultrasound-assisted emulsification was applied by Liang et al. [16] for extraction with ILs for determination of four fungicides in environmental water samples, and by Rogueiro et al. [30] for emergent contaminants and pesticide in environmental water. You et al. [31] applied ultrasound-assisted surfactant-enhanced emulsification for determination of six fungicide residues in juices and red wine, where 1-dodecanol was used as an extraction solvent with low density and proper melting point near room temperature. The extractant droplet was collected by solidifying it at a low temperature. The surfactant, Tween 80, was used as an emulsifier to enhance the dispersion of the water-immiscible extraction solvent into an aqueous phase. Chu et al. [32] used no dispersive solvent, but used up-and-down-shaker-assisted DLLME the determination of 6 fungicides in wine.

The aim of this study was to develop a dispersive liquid–liquid microextraction method for isolation and preconcentration of selected pesticides of different chemical groups from samples with higher degree of alcohol (40%). Special attention was devoted to the careful evaluation and selection of DLLME parameters. Ethanol naturally present as a sample component served in the function of dispersant. Thereafter, the performance of the overall method (DLLME followed by fast GC–MS) was characterized, with special attention focused on accuracy evaluation. To the best of our knowledge, such combination of microextraction benefitting from the presence of dispersive agent directly in the high-alcohol content sample (plum brandy) was not applied.

2. Materials and methods

2.1. Chemicals

Twenty-seven individual pesticide standards from various chemical groups (organophosphorous, organochlorine, chloroacetamide, triazole, azole, pyrethroid, dicarboximide, pyrimidine and carbamate pesticides) were obtained from various vendors (Dr. Ehrensdorfer, Augsburg, Germany; Bayer, Leverkusen, Germany; Chromservis SK, Slovakia) with high purity above 96%.

The stock solution of pesticide standards at a concentration of 1 mg/mL was prepared in ethanol, acetonitrile (MeCN), or toluene (all Suprasolv grade, Merck KGaA, Darmstadt, Germany). Composite solution of all pesticides was prepared at a concentration of 0.02 mg/mL. The next solvents were used: tetrachloromethane (Merck KGaA, Darmstadt, Germany); tetrachloroethane, chloroform, purified water (all from Sigma Aldrich, Steinheim, Germany), hexane (Stillorgan Industrial park, Dublin, Ireland). The solvents used were preferably of pesticide residue grade or reagent grade purity. Triphenylphosphate (1 mg/mL) and heptachlor (1 mg/mL) served as internal standards (I.S.) and were prepared in toluene. The working pesticide solutions with internal standards were prepared by an appropriate dilution of a mixture of stock solutions in MeCN or ethanol (Merck KGaA, Darmstadt, Germany).

Stock solutions were kept frozen at −18 °C; diluted working solutions were prepared daily and stored at +4 °C.

Real sample, plum brandy with ethanol content of 40%, was obtained from Slovak producers.

Sodium chloride (NaCl), per analysis grade, was from Lachema (Lachema a.s., Brno, Czech Republic); it was baked at 600 °C for 6 h and stored in reagent flask until usage.

2.2. Instrumental equipment and conditions

An Agilent 6890N gas chromatograph (Agilent Technologies, Little Falls, DE, USA) hyphenated with an Agilent 5975 mass-selective detector was used. For injection, an Agilent 7683B autosampler and a programmable temperature vaporization injector (PTV) were used. A volume of 2 μL of solutions were injected in solvent vent injection mode under temperature programmed conditions as follows: 80 °C (hold 0.20 min), 400 °C/min to 300 °C (hold 2.00 min), and 400 °C/min–350 °C (hold 5.00 min). Gas chromatographic column CP-Sil 8 CB (Agilent Technologies, The Netherlands) with chemically bonded 5% diphenyl 95% dimethylsiloxane stationary phase and dimensions 15 m × 0.15 mm I.D. × 0.15 μm film thickness was connected to a non-polar deactivated pre-column (1 m × 0.32 mm I.D.) and it was used for separation under the following temperature programmed conditions: 100 °C held for 1.75 min,