



Development of a dispersive liquid-liquid microextraction technique for the analysis of aryloxyphenoxy-propionate herbicides in soy-based foods



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ARTICLE INFO

Article history:

Received 3 March 2016

Received in revised form 9 June 2016

Accepted 10 June 2016

Available online 12 June 2016

Keywords:

Aryloxyphenoxy-propionate herbicides
Phosphonium based room temperature ionic liquids

Ionic liquid–dispersive liquid–liquid microextraction

Liquid chromatography

Soy sauce

Soy milk

ABSTRACT

In this work, an ionic liquid–dispersive liquid–liquid microextraction (IL–DLLME) method combined with liquid chromatography and diode–array detection (DAD) was used for the determination of four aryloxyphenoxy–propionate herbicides (fenoxaprop–*p*-ethyl, quizalofop–*p*-tefuryl, propaquizafop and haloxyfop–*p*-methyl) in two soy-based foods (soy milk and soy sauce) was used. For this purpose, the phosphonium-based room temperature ionic liquid (triethyl(tetradecyl)phosphonium bistriflamide) was used as the extractant. The effect of the experimental parameters on extraction efficiency such as type of disperser solvent, disperser solvent/ ionic liquid volumes ratio, pH, nature and concentration of salt in the aqueous phase, sample volume, and centrifugation and extraction times were investigated and optimized. Since matrix effects were detected, the standard addition method was used for quantification. Under the optimized conditions, the proposed sample preparation method coupled to high performance liquid chromatography–diode array detection (HPLC–DAD) had a satisfactory performance to determine the four herbicides in soy sauce and soy milk. The enrichment factors ranged from 18 to 43 and recovery factors from 25 to 66%. Although the recoveries were not high because of the presence of organic solvent in the sample preparation step, the inter-day reproducibility was 8.4% or less, depending on the analyte, the limits of detection ($S/N = 3$) were obtained in the range of 0.12–0.34 mg L⁻¹, the limits of quantification ($S/N = 10$) between 0.36 and 1.04 mg L⁻¹, and linear ranges from LOQs to 9.26 mg L⁻¹. Finally, the IL–DLLME methodology is inexpensive, simple, fast, and environmentally friendly for the determination of the studied herbicides in soy sauce and soy milk. This study constitutes the first application of an IL–DLLME methodology to aryloxyphenoxy–propionate herbicides analysis in commercial soy-derived foods.

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1. Introduction

The aryloxyphenoxy–propionate herbicides (AOPPs) constitute a kind of selective post-emergence herbicides [1], which were registered for controlling annual and perennial grassy weeds for many crops as soy, rice, corn or peanut. AOPPs are toxic to aquatic organisms [2], especially fish, and could be inducers of liver toxicity and injury [3]. The widespread use of those compounds contributes to their presence in ground water, soil and other environmental matrices [4,5]. Recently there have been a few reported studies on the determination of some AOPPs in water [6–11], soils [12,13], crops [12,14], fruits and vegetables [9,15]. However, any analytical methodology to determine AOPPs in processed foods, specifically in crops-derived ones such as soy-sauce or soy milk, have been developed. Therefore, more sensitive and robust methods to analyze AOPPs in those complex matrices are required.

Conventional methods for the isolation and/or enrichment of AOPPs-related chemicals from water involve liquid–liquid extraction (LLE) or solid-phase extraction (SPE) [5,16]. However, SPE is a convenient technique very recommended to pre-concentrate analytes at trace levels and requires much less amounts of organic solvents but it suffers from some drawbacks such as low recoveries and low batch-to-batch reproducibility. In recent years, a lot of less solvent-consuming microextraction techniques have been used in extraction of AOPPs in water, such as solvent microextraction (SME) [4], microextraction in packed syringe (MEPS) [11] and IL–DLLME [7]. Recently, a faster, sensitive and environmentally friendly method for determination of AOPPs in environmental water samples by coupling both the dispersive magnetic SPE (d-MSEP) with both HPLC–DAD and ultrahigh pressure liquid chromatography with triple quadrupole mass spectrometer (UHPLC–MS/MS) was developed [6].

The use of Room Temperature Ionic Liquids (RTILs) in different areas of Analytical Chemistry has increased considerably in recent years due to their advantages over conventional organic solvents such as low toxicity, flammability and volatility [17]. As a counterpart, due to the typical high viscosities of the RTILs, a dilution with solvents such as methanol or

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acetonitrile can be necessary before injection into the HPLC column, which decreases the enrichment factor [18].

Although phosphonium-based RTILs (PB-RTILs) have been known and synthesized for years, they have been more or less neglected in the literature, mainly in LLE, as compared to their imidazolium- or pyrrolidinium-based counterparts [19,20]. PB-RTILs are made of tetraalkylphosphonium cations with different anions and have some additional advantages compared to the nitrogen-based RTILs (NB-RTILs), such as very high thermal and chemical stability, higher solvation properties and they are cheaper [18]. There are about 20 different types of PB-RTILs commercially available. Cytec Industries Inc. sells phosphonium salts under the Cyphos® trade name [21].

The (IL-DLLME) has been developed as an efficient sample preparation and preconcentration method. The advantages of IL-DLLME are the use of a small volume of ionic liquid, ease of operation, rapidity, low cost, high recovery for several compounds, high enrichment factors and environmentally friendly nature [22,23]. The extraction by IL-DLLME is based on a ternary solvent system: the aqueous sample, the dispersive solvent and the extraction solvent. An appropriate mixture of the extraction solvent (an organic solvent or an ionic liquid) and the dispersive solvent (a water-organic miscible solvent) is rapidly injected into the aqueous sample with a syringe and a cloudy solution is formed. After centrifugation, the analytes are collected into the small volume (a single drop) of the extraction solvent while the dispersive solvent remains in the initial aqueous solution [22]. There has been a large number of works that use nitrogen-based RTILs (NB-RTILs) as the solvent extraction in LLE, especially those with the cation dialkylimidazolium, while the use of phosphonium-based RTILs (PB-RTILs) is very scarce. Recently, a flow injection system for online IL-DLLME using the less dense than water IL tetradecyl(triethyl)phosphonium chloride (Cyphos 101) for preconcentration of cobalt (Co) was presented [24]. Also, the use of tetradecyl(triethyl)phosphonium bis-2,4,4-trimethylpentylphosphinate (Cyphos 104) as an effective extractant of lactic acid (LA) in aqueous systems by LLE have been measured [25].

In this study a simple and sensitive analytical method to determine aryloxyphenoxy-propionate herbicide residues (AOPPs) in soy sauce and soy milk was developed. The IL-DLLME methodology using a PB-RTIL as extractant and final analysis by HPLC-DAD were used. Special attention to the optimization of IL-DLLME parameters to maximize the extraction efficiency and to assure ruggedness has been given. The most important figures of merit of the analytical methodology were obtained.

This work represents the first proposal to determine aryloxyphenoxy-propionate herbicides residues in soy sauce and soy milk.

2. Material and methods

2.1. Chemicals and materials

Trihexyl(tetradecyl)phosphonium bistriflamide, (Cyphos 109, [(C₆)₃C₁₄P][NTf₂]) was purchased from Cytec (New Jersey, USA). Reagents were of analytical grade or better: haloxyfop-*p*-methyl, quizalofop-*p*-tefuryl, fenoxaprop-*p*-ethyl y propaquizafop from Agrofina (Bs. As., Argentina) (Fig. 1), acetic acid anhydrous (Merck, Hohenbrunn, Germany), sodium acetate anhydrous (J.T. Baker, México), sodium chloride and potassium chloride (Anedra, Argentina), magnesium sulfate 7-hydrate (Biopack, Argentina), potassium phosphate (Merck, Hohenbrunn, Germany), isopropanol HPLC grade (Sintorgan, Bs. As., Argentina), phosphoric acid 85% (Merck, Hohenbrunn, Germany), potassium dihydrogen phosphate (Merck, Hohenbrunn, Germany), monoacid potassium phosphate (Carlo Erba, Divisione Chimica Industriale- Milano, Italy), citric acid (Panreac, Castellar del Vallès, Spain), formic acid (Anedra, Bs. As., Argentina), sodium hydroxide (Analar, Poole, United Kingdom), sodium tartrate (J. T. Baker, Estado de México, México), potassium hydrogen phthalate (Anedra, Bs. As., Argentina), *tris* (tris(hydroxymethyl)aminomethane) (Carlo Erba, Divisione Chimica Industriale- Milano, Italy), chlorhidric acid 37% (Anedra, Bs. As., Argentina), acetone (Biopack, Bs. As., Argentina), methanol and acetonitrile grade HPLC (J. T. Baker, Estado de México, México) and ethanol (Carlo Erba, Divisione Chimica Industriale- Milano, Italy). Solutions were prepared with MilliQ® water.

Conical graduated polypropylene light-blue screw-capped test tubes (17 × 120 mm, 15 mL) for the IL-DLLME experiments and sample conditioning were used. The samples were filtered through a Micro-Mate TM interchangeable syringe (Popper & Sons Inc., New Hyde Park, NY, USA) containing a 0.22 mm cellulose-nitrate membrane.

2.2. Instrumentation and chromatographic conditions

All chromatographic studies were performed on an HP 1100 liquid chromatograph (Agilent Technologies, Palo Alto, CA) equipped with vacuum degasser, binary pump, autosampler, thermostatted column device, and photodiode array detector (DAD). The column was a Symmetry C-18 (3.9 × 150 mm; 5 μm) from Waters (Milford, USA). Optimum separation was achieved with a water-methanol mobile phase at a flow rate of 1 mL min⁻¹ and temperature of 25 °C. The gradient elution program was (solvent A: water; solvent B: methanol): 70% B, 0 min; 76% B, 15 min; 100% B, 20 min; 70% B, 28 min. The sample injection volume was 20 μL. All mobile phases were filtered through 0.22-μm nylon membranes (Osmonics-Magna) for organic solvents

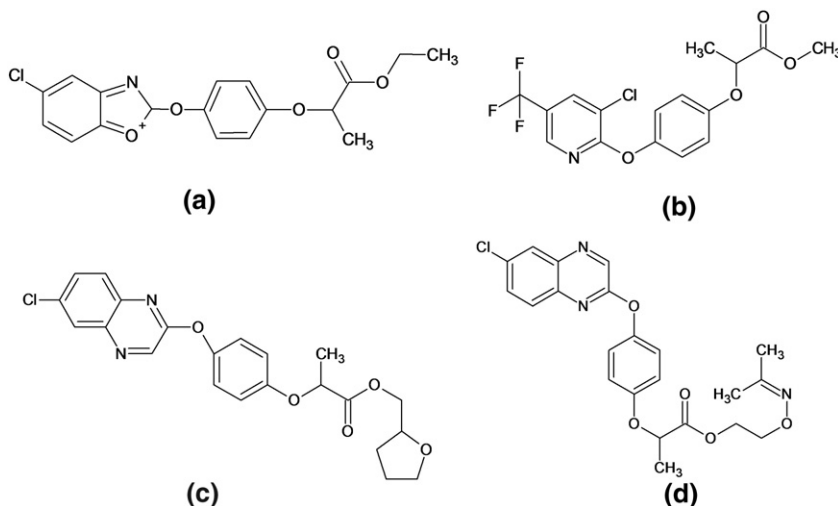


Fig. 1. Chemical structures of (a) fenoxaprop-*p*-ethyl; (b) haloxyfop-*p*-methyl; (c) quizalofop-*p*-tefuryl; (d) propaquizafop.

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