



Development of continuous dispersive liquid–liquid microextraction performed in home-made device for extraction and preconcentration of aryloxyphenoxy-propionate herbicides from aqueous samples followed by gas chromatography–flame ionization detection



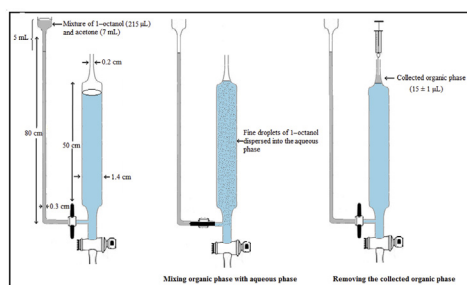
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HIGHLIGHTS

- A continuous dispersive liquid–liquid microextraction method has been developed.
- The method is applied for the analysis of herbicide residues in fruit juice and vegetable samples.
- LODs are achievable at $\mu\text{g L}^{-1}$ using GC–FID.
- EFs and ERs between 1633–2466 and 49–74% are obtained, respectively.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a rapid, simple, and efficient sample preparation method based on continuous dispersive liquid–liquid microextraction has been developed for the extraction and preconcentration of aryloxyphenoxy-propionate herbicides from aqueous samples prior to their analysis by gas chromatography–flame ionization detection. In this method, two parallel glass tubes with different diameters are connected with a teflon stopcock and used as an extraction device. A mixture of disperser and extraction solvents is transferred into one side (narrow tube) of the extraction device and an aqueous phase containing the analytes is filled into the other side (wide tube). Then the stopcock is opened and the mixture of disperser and extraction solvents mixes with the aqueous phase. By this action, the extraction solvent is dispersed continuously as fine droplets into the aqueous sample and the target analytes are extracted into the fine droplets of the extraction solvent. The fine droplets move up through the aqueous phase due to its low density compared to aqueous phase and collect on the surface of the aqueous phase as an organic layer. Finally an aliquot of the organic phase is removed and injected into the separation system for analysis. Several parameters that can affect extraction efficiency including type and volume of extraction and disperser solvents, sample pH, and ionic strength were investigated and optimized. Under the optimum extraction conditions, the extraction recoveries and enrichment factors ranged from 49 to 74% and 1633 to 2466, respectively. Relative standard deviations were in the ranges of 3–6% ($n = 6$, $C = 30 \mu\text{g L}^{-1}$) for intra-day and 4–7% ($n = 4$, $C = 30 \mu\text{g L}^{-1}$) for inter-day precisions. The limits of

Abbreviations: AOPP, Aryloxyphenoxy-propionate; DLLME, Dispersive liquid–liquid microextraction; EF, Enrichment factor; ER, Extraction recovery; FID, Flame ionization detector; GC, Gas chromatography; HPLC, High performance liquid chromatography; LLE, Liquid–liquid extraction; LOD, Limit of detection; LOQ, Limit of quantification; MRL, Maximum residue level; MS, Mass spectrometry; RSD, Relative standard deviation; SDME, Single-drop microextraction; SPE, Solid phase extraction; SPME, Solid phase microextraction.

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detection were in the range of 0.20–0.86 $\mu\text{g L}^{-1}$. Finally the proposed method was successfully applied to determine the target herbicides in fruit juice and vegetable samples.

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1. Introduction

Herbicides, including the substances with high toxic effects and persistence in the environment, are extensively used in agriculture activities all over the world in order to combat weeds and diseases. Although the use of herbicides in agricultural applications provides a wide range of beneficial effects, the extensive use of them can be a problem because of their potential harm to the environment and known or suspected toxic effects in humans, such as neuro developmental impairment, acute neurological toxicity, possible dysfunction of the reproductive, endocrine and immune systems, chronic kidney diseases, cancer and other potential diseases [1–4]. One of the most important herbicides is aryloxyphenoxy-propionate (AOPP) herbicides. AOPPs are a kind of selective post-emergence herbicides, which are used in controlling annual and perennial grassy weeds in many agriculture products like cotton, tomato, potato, onion and garlic [5]. They interfere with production of fatty acids needed for plant growth by inhibition of acetyl Co-enzyme A carboxylase [6]. In most cases AOPPs can be rapidly deesterificated to their acidic forms by plants or soil, which increases their polarity and solubility but does not influence their bioactivities [7–9]. Increasing public concern about the health risks from herbicides residues in the diet has led to strict regulation of the maximum residue levels (MRL) and total dietary intake of herbicides residues in foodstuffs [10]. So the demand to develop selective and sensitive analytical techniques (sample preparation step as well as detection system) for the determination of herbicide residues which are usually present in trace amounts was increased. A perfect sample preparation method should be able to extract the analytes from sample matrix as well as perform preconcentration of them. Solid phase extraction (SPE) [11,12] and liquid–liquid extraction (LLE) [13] are extensively used as the sample preparation methods before chromatographic techniques such as gas chromatography (GC) [14,15], and high-performance liquid chromatography (HPLC) [16–19]. However, in LLE, a large volume of organic solvents is required, and in SPE, cartridges are usually expensive and are susceptible to block. Moreover, these methods are time-consuming. In recent years, some other sample pretreatment methods such as solid-phase microextraction (SPME) [20] and single-drop microextraction (SDME) [21] have been used in order to simplification, miniaturization, and minimization of organic solvents. Although these microextraction methods eliminate some problems of the above-mentioned extraction methods but they suffer some problems too. SPME fibers are relatively expensive, generally fragile and have a limited lifetime. In addition, SPME has been reported to suffer from sample carry over problems [22]. SDME has some problems like solvent drop instability and limited extraction surface area [23]. In 2006, dispersive liquid–liquid microextraction (DLLME) was presented by Assadi et al. [24] as a consequence of the demand for low-cost, rapid, and environmentally friendly sample pretreatment method. In DLLME, a mixture of a water-immiscible extraction solvent and a water-miscible disperser solvent is injected into the aqueous solution of analytes. By this action, the disperser solvent disperses the extraction solvent into the aqueous phase as fine droplets and results a cloudy solution. In this step, the target analytes are extracted into the fine droplets of extraction solvent which is then separated by

centrifuging. Simplicity, rapidity, minimal use of harmful solvents, low cost, and achieve to high enrichment factors (EFs) are the major advantages of method. DLLME, as a powerful sample preparation and preconcentration technique, has attracted great attention among the various research groups all over the world due to its wide range of applications to organic and inorganic compounds in different matrices [25–31]. Unfortunately most DLLME methods use 5 mL as the aqueous phase volume in which EFs higher than 500 (by assumption 10 μL for the final volume of the organic phase) are not achievable.

The goal of this study was to develop a new version of DLLME performed in a home-made device for the extraction and preconcentration of some herbicides from high volume of fruit juice and vegetable samples to reach very high EFs. AOPP herbicides were selected as model compounds in this work. In this method, two glass tubes connected with teflon stopcock are used as an extraction device. In the extraction device the mixture of an extraction solvent and a disperser solvent is entered continuously into the aqueous phase through the stopcock and the extraction solvent is dispersed into the aqueous phase by dissolving the disperser solvent. Simplicity in operation, rapidity, environmentally friendly, and high EFs are some advantages of the proposed method.

2. Experimental

2.1. Reagents and solutions

Four AOPP herbicides used in this study, including clodinafop-propargyl, diclofop-methyl, fenoxaprop-*P*-ethyl, and haloxyfop-*R*-methyl were kindly provided by GYAH Corporation (Karadj, Iran). Acetone, dimethyl formamide (DMF), acetonitrile (ACN), toluene, 1-octanol, *n*-hexane, *tri*-butylamine, and dimethyl sulfoxide (DMSO) were obtained from Merck (Darmstadt, Germany). Sodium chloride, magnesium sulfate, sodium sulfate, hydrochloric acid, and sodium hydroxide were also supplied from Merck. Deionized water (Ghazi Co., Tabriz, Iran) was used in all experiments for preparation of aqueous solutions. A mixture stock solution of the selected herbicides was prepared in acetone with a concentration of 1000 mg L^{-1} (each herbicide) and stored in a refrigerator at 4 °C. Working standard solutions were prepared daily by diluting the stock solution with deionized water. A mixture standard solution of the analytes (1000 mg L^{-1} of each herbicide) in 1-octanol (extraction solvent) was prepared and directly injected into the separation system each day (three times) in order to investigate the instrumental system quality and to calculate EFs and extraction recoveries (ERs) of the analytes.

2.2. Samples

Packaged fruit juice samples including apple, grape, and peach juices with different brands were purchased from local stores (Tabriz, Iran). All juices were centrifuged at 1968 $\times g$ for 5 min before applying the method on them. The obtained supernatants were diluted at a ratio of 1:2 with deionized water and exposed to the proposed microextraction method. Vegetable samples including garlic, onion, lettuce, carrot, cucumber, and tomato were

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