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Development of counter current salting-out homogenous liquid–liquid extraction for isolation and preconcentration of some pesticides from aqueous samples

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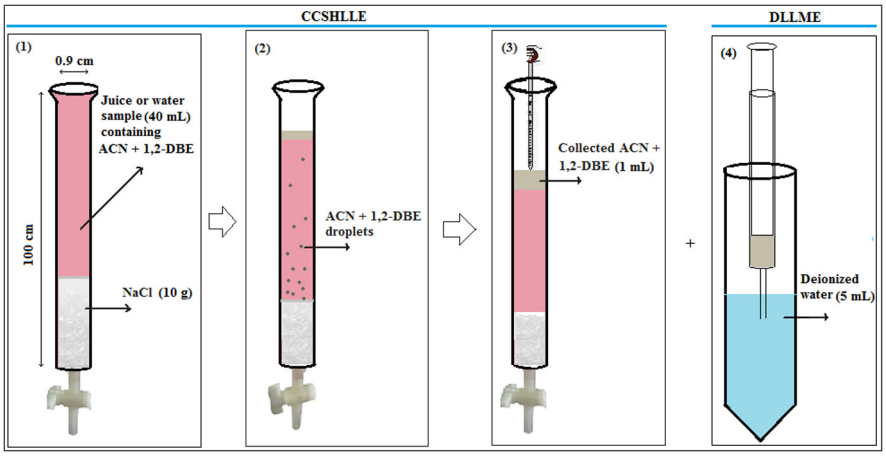
HIGHLIGHTS

- A new version of SHLLE has been developed.
- The method is applied for the analysis of pesticide residues in fruit juices.
- LODs are achievable at $\mu g\,L^{-1}$ using GC–FID.
- The method has high EFs and ERs, low LODs, and short extraction time.

GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, a new version of salting-out homogenous liquid–liquid extraction based on counter current mode combined with dispersive liquid–liquid microextraction has been developed for the extraction and preconcentration of some pesticides from aqueous samples and their determination by gas chromatography–flame ionization detection. In order to perform the method, aqueous solution of the analytes containing acetonitrile and 1,2-dibromoethane is transferred into a narrow bore tube which is filled partially with NaCl. During passing the solution through the tube, fine droplets of the organic phase are produced at the interface of solution and salt which go up through the tube and form a separated layer on the aqueous phase. The collected organic phase is removed and injected into de-ionized water for more enrichment of the analytes. Under the optimum extraction conditions, the method shows broad linear ranges for the target analytes. Enrichment factors and limits of detection for the selected pesticides are obtained in the ranges of 3480–3800 and 0.1–5 $\mu g\,L^{-1}$, respectively. Relative standard deviations are in the range of 2–7% ($n = 6$, $C = 50$ or 100 $\mu g\,L^{-1}$, each analyte). Finally, some aqueous samples were successfully analyzed using the developed method.

Abbreviations: CCSHLLE, counter current salting-out homogenous liquid–liquid extraction; DLLME, dispersive liquid–liquid microextraction; EF, enrichment factor; ER, extraction recovery; FID, flame ionization detector; GC, gas chromatography; LLE, liquid–liquid extraction; LOD, limit of detection; LOQ, limit of quantification; LPME, liquid phase microextraction; MS, mass spectrometry; RSD, relative standard deviation; SPE, solid phase extraction; SPME, solid phase microextraction.

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1. Introduction

Pesticides, such as insecticides, herbicides, fungicides and acaricides, are widely used during the cultivation and the post-harvest storage of crops. It is intended that their use to prevent the destruction of crops by controlling agricultural pests or unwanted plants and thereby improve food production [1,2]. Although the use of pesticides in agricultural applications provides a wide range of beneficial effects, their misuse can result in unacceptable high levels of the compounds in the products and also pollutes soil, air, and surface water. So, it is significant to develop a detection method with high sensitivity for evaluating food, water, and other environmental samples safety and possible risks to human health. In order to determine trace level of pesticide residues, an extraction and preconcentration step is necessary. Traditional liquid–liquid extraction (LLE) and solid phase extraction (SPE) are the most popular procedures in routine sample preparation because of their simplicity, efficiency, and wide acceptance in many standard methods [3–11]. However, LLE technique is time-consuming, requires large amounts of toxic organic solvents, and provides low enrichment of analytes. Although SPE has overcome some shortages of LLE and needs organic solvents much less than LLE, but cartridge obstruction is a problem. Another extraction procedure, namely homogeneous liquid–liquid extraction (HLLE), utilizes a phase separation phenomenon in a homogeneous solution. One version of HLLE is salting-out homogenous liquid–liquid extraction (SHLLE) which has been used for extraction and preconcentration of the selected analytes from aqueous samples [12,13]. Recent researches have been oriented towards development of efficient, economical, and miniaturized sample preparation methods. As a result, solid phase microextraction (SPME) [14,15] and liquid phase microextraction (LPME) [16,17] have been developed. Compared to LLE, SPME is a solvent-free process that includes simultaneous extraction and preconcentration of analytes from samples or headspace of the samples. However, SPME is expensive, its fiber is fragile and has a limited life time, and sample carry-over could be a problem [18]. LPME was developed as a solvent-minimized sample pretreatment procedure that is inexpensive, and since a very little solvent is used, there is minimal exposure to toxic organic solvents [19,20]. However, this method suffers from some disadvantages as follows: fast stirring tends to form air bubbles [21], extraction is time-consuming and equilibrium can not be attained after a long time in most cases [22]. To overcome these disadvantages, Rezaee et al. developed a novel liquid phase microextraction technique termed dispersive liquid–liquid microextraction (DLLME) [23], which is based on a ternary component solvent system. Some advantages of DLLME are simplicity of operation, rapidity, low sample volume, low cost and relatively high enrichment factors [24,25].

In the present study, a new version of salting-out homogenous liquid–liquid extraction named counter current salting-out homogenous liquid–liquid extraction (CCSHLLE) followed by DLLME is developed to achieve high extraction recovery (ER) and enrichment factor (EF). In this method, initially the selected analytes are extracted into fine droplets of a mixture of 1,2-dibromoethane and acetonitrile during CCSHLLE from relatively high volume of aqueous sample. It was found that there is no need to pass whole of sample through the narrow bore tube filled with NaCl making this step is fast. To more enrichment of the analytes, a DLLME step is performed on the organic phase obtained from the previous step. Effect of various experimental parameters such as kind and volume of extraction and disperser solvents, flow rate, salt addition, and pH will be studied and optimized. The optimized method is applied to determine some pesticide residues in well water, river water, and apple, sour cherry, and grape juices to evaluate performance of the proposed method in real samples.

2. Materials and methods

2.1. Reagents and solutions

Diazinon, chlorpyrifos, phosalone, ametryn, propazine, and simazine were purchased from Dr. Ehrenstorfer (Agsburg, Germany). Penconazole, hexaconazole, diniconazole, difenoconazole, and tebuconazole were kindly provided by GYAH Corporation (Karadj, Iran). The structures, classes, and properties of the selected pesticides are summarized in Table 1. Acetonitrile (ACN), dimethyl formamide (DMF), acetone, 1,2-dibromoethane (1,2-DBE), and 1,1,2-trichloroethane (1,1,2-TCE) were obtained from Merck (Darmstadt, Germany). Sodium chloride, hydrochloric acid, and sodium hydroxide were also from Merck. 1,2-Dichloroethane (1,2-DCE) and 1,1,2,2-tetrachloroethane (1,1,2,2-TCE) (Janssen, Beerse, Belgium) and isopropyl alcohol (Caledon, Canada) were other used solvents. De-ionized water was obtained from Ghazi Company (Tabriz, Iran). A stock mixture solution of the studied pesticides was prepared by dissolving appropriate amounts of the analytes in ACN at a concentration of 1000 mg L^{-1} of each pesticide. Working standard solutions were prepared daily by diluting the stock solution with de-ionized water. Another mixture standard solution (1000 mg L^{-1} of each pesticide) in 1,2-DBE (extraction solvent) was prepared and directly injected into the separation system each day (three times) in order to evaluate the instrumental system quality and to calculate EFs and ERs of the analytes.

2.2. Samples

Apple, grape, and sour cherry juices with different brands were obtained from local supermarkets (Tabriz, Iran). Well water was collected from a garden well (Khoy, West Azerbaijan Province, Iran). River water was collected from a seasonal river (Khoy, East Azerbaijan Province, Iran).

2.3. Instrumentation

Quantitative analysis of the selected pesticides was performed on a Shimadzu 2014 gas chromatograph (Kyoto, Japan) equipped with a split/splitless injector operated at 300 °C in a splitless/split mode (sampling time, 1 min, and split ratio of 1:5) and a flame ionization detector (FID). Helium (99.999%) (Gulf Cryo, United Arab Emirates) was used as the carrier gas at a linear velocity of 30 cm s^{-1} and make up gas at a flow rate of 30 mL min^{-1}. Chromatographic separation was achieved on a CP-Sil 8CB capillary column (30 m × 0.25 mm i.d., and film thickness 0.25 μm) [poly(5% diphenyl–95% dimethylsiloxane)] (Chrompack, Milan, Italy). Column oven temperature was initially held at 60 °C for 2 min, then raised to 300 °C at a rate of 12 °C min^{-1}, and held at 300 °C for 7 min. FID temperature was maintained at 300 °C. For FID hydrogen gas was generated with a hydrogen generator (OPGU-1500S, Shimadzu, Japan) at a flow rate of 40 mL min^{-1}. The flow rate of air for FID was 300 mL min^{-1}. Gas chromatography–mass spectrometry (GC–MS) analysis was carried out on an Agilent 7890A–5975C instrument (Agilent Technologies, CA, USA). MS operational conditions were: ionic source, electron impact (EI) at 70 eV; ionic source temperature, 250 °C; transfer line temperature, 260 °C; mass range, m/z 55–350; acquisition rate, 20 Hz; and detector voltage, −1700 V. Library searching was performed using the commercial NIST library. Separation in GC–MS was performed on an HP-5 MS capillary column (30 m × 0.25 mm i.d., and film thickness of 0.25 μm). The carrier gas was helium at a flow rate of 1.0 mL min^{-1}. The column oven temperature programming was the same as used in GC–FID analysis mentioned above.