



Full length article

## Comparison of micellar extraction combined with ionic liquid based vortex-assisted liquid–liquid microextraction and modified quick, easy, cheap, effective, rugged, and safe method for the determination of difenoconazole in cowpea



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## ABSTRACT

Two simple sample pretreatment for the determination of difenoconazole in cowpea was developed including micellar extraction combined with ionic liquid based vortex-assisted liquid–liquid microextraction (ME-IL-VALLME) prior to high performance liquid chromatography (HPLC), and modified quick, easy, cheap, effective, rugged, and safe method (QuEChERS) coupled with HPLC–MS/MS. In ME-IL-VALLME method, the target analyte was extracted by surfactant Tween 20 micellar solution, then the supernatant was diluted with 3 mL water to decrease the solubility of micellar solution. Subsequently, the vortex-assisted liquid–liquid microextraction (VALLME) procedure was performed in the diluted extraction solution by using the ionic liquid of 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM]PF<sub>6</sub>) as the extraction solvent and Tween 20 as an emulsifier to enhance the dispersion of the water-immiscible ionic liquid into the aqueous phase. Parameters that affect the extraction have been investigated in both methods. Under the optimum conditions, the limits of quantitation were 0.10 and 0.05 mg kg<sup>-1</sup>, respectively. And good linearity was achieved with the correlation coefficient higher than 0.9941. The relative recoveries ranged from 78.6 to 94.8% and 92.0 to 118.0% with the relative standard deviations (RSD) of 7.9–9.6% and 1.2–3.2%, respectively. Both methods were quick, simple and inexpensive. However, the ME-IL-VALLME method provides higher enrichment factor compared with conventional QuEChERS method. The ME-IL-VALLME method has a strong potential for the determination of difenoconazole in complex vegetable matrices with HPLC.

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## 1. Introduction

Cowpea (*Vigna unguiculata* L. Walp) is rich in vitamins, dietary fibre, antioxidants and minerals. It is an economically important vegetable commodity in China with a total planting area of 330,000 ha [1,2]. Large scale commercial cultivation of this crop is significantly affected by several diseases and insect pests such as anthracnose and botrytis cinerea [3]. Thus, pesticides are widely used to ensure high crop yields, while the pesticide residue is regarded as significant risk to the health of human beings [4]. The pesticide difenoconazole is used to control anthracnose in cowpea plant and the difenoconazole residue is detected at a high frequency on cowpea [5]. The maximum residue limit (MRL) for

difenoconazole in cowpea commodity is 0.7 mg kg<sup>-1</sup> by the Codex Alimentarius Commission (CAC) [6].

In the analytical method of difenoconazole residue, many extraction methods were reported, such as solid-phase extraction (SPE) [7,8], liquid–liquid extraction (LLE) [9] and quick, easy, cheap, effective, rugged, and safe (QuEChERS) method [10]. QuEChERS method attracted the attention of experts on pesticide residue analysis since it was first developed [11]. This method was particularly popular for the determination of polar, middle polar and non-polar pesticide residues in various food matrices [12]. However, the amount of acetonitrile used to extract analytes was usually larger than that of samples, an additional time-consuming concentration procedure or a highly sensitive instrument for analysis was needed. To increase the sensitivity of the method, based on the traditional sample pretreatment techniques, several method modifications were developed such as dispersive liquid–liquid microextraction (DLLME) [13,14] or QuEChERS combine with DLLME [15]. DLLME

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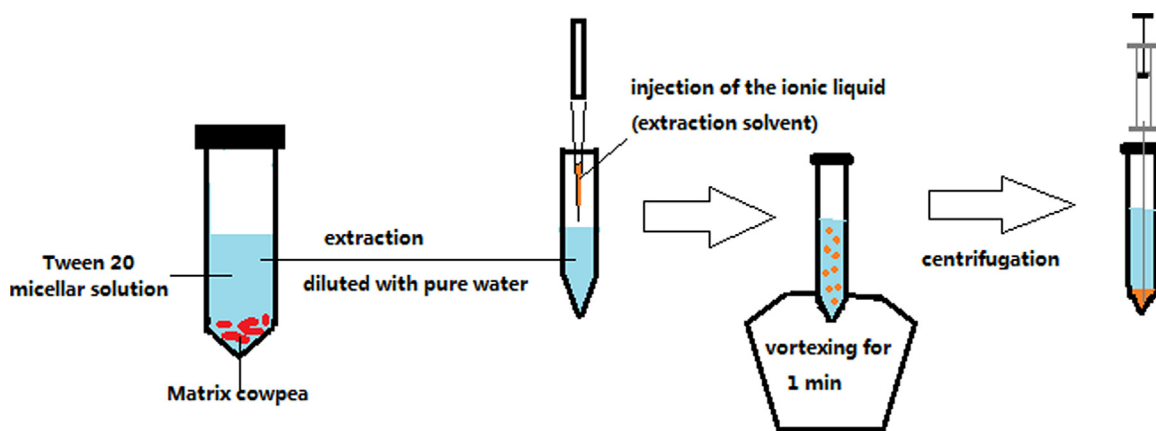


Fig. 1. Experimental design of ME-IL-VALLME procedure in this study.

consists in the formation of a cloudy solution promoted by vortex oscillation energy or other microwave energy, and then the analytes are jointed in the sediments phase by centrifugation [16]. DLLME was widely applied as the alternative extraction or preconcentration method in aqueous samples for its outstanding merits of quickness, high enrichment factor, and operation simplicity [17–19]. It also could be used in solid samples such as maize, tomato, apple and pear matrix by using an extra acetonitrile extraction procedure [16,20,21]. In the combination of QuEChERS and DLLME, the acetonitrile used as dispersive solvent in DLLME was obtained from QuEChERS. Compared to conventional DLLME, it consumed relatively large volume of acetonitrile [22,23].

In recent years, extensive attempts were made to develop new sample preparation techniques allowing good accuracy and precision in the extraction of pesticide from vegetables with less organic solvents usage such as supercritical fluid extraction (SFE) [24] and cloud point extraction (CPE) [25]. The CPE was a type of micelle-mediated phase separation technique. Micelle-mediated phase separation is based on the cloud point phenomenon of surfactant and micellar solution solubilization, the hydrophobic and hydrophilic compound will be separate by changing the experiment parameters [26,27]. Micelle-mediated extractions consisted three steps: (i) solubilization of solutes in aqueous micelles; (ii) separation of a surfactant-rich phase from the aqueous bulk induced by proper conditions (temperature, pH, or adding ionic salt solution or an organic solvent); and, (iii) recovery of the surfactant-rich phase for analysis. CPE has been successfully applied for the determination of trace pesticide residues in different matrices including apple, pear, apple juice and pear juice [28,29]. However, it was limited by the separation of the surfactant-rich phase, the separation conditions were difficult to control, resulting in low extraction efficiency and time-consuming operation, and the high viscosity of the surfactant-rich phase also restricted its application. To solve these problems, micelle-mediated extractions combined with liquid phase microextraction to concentrate analyte from the micellar solution could be simplify the separation procedure of the surfactant-rich phase.

In the present work, for the determination of difenoconazole in cowpea samples, two approaches were developed based on modified QuEChERS prior to HPLC–MS/MS and micellar extraction combined with ionic liquid based vortex-assisted liquid–liquid microextraction (ME-IL-VALLME) prior to HPLC. In the novel ME-IL-VALLME method, a more environment-friendly separation process was studied to reduce the use of organic solvent. Micellar solution was used to extract the difenoconazole from cowpea sample and to emulsify water-immiscible ionic liquid into the diluted micellar solution. The effects of various experimental parameters

in ME-IL-VALLME were optimized including type and concentration of the micellar solution, volume of ionic liquid and vortex time. The performance of the ME-IL-VALLME method was evaluated by comparing the results with those obtained from the modified QuEChERS. The advantages and disadvantages of both methods were discussed. The recommended methods were successfully applied for the determination difenoconazole in cowpea sample.

## 2. Materials and methods

### 2.1. Reagents and materials

Difenoconazole (97.5% purity) was purchased from J&K Scientific LTD. (Beijing, China).

Surfactants (Triton X-114, Triton X-100, Tween 80 and Tween 20) were purchased from Beijing Chemical Reagents Company (Beijing, China). Ionic liquid of 1-hexyl-3-methylimidazolium hexafluorophosphate ([HMIM]PF<sub>6</sub>) was obtained from Shanghai Chengjie Chemical Regent Company (Shanghai, China). Chromatographic pure solvents (acetonitrile, methanol) were purchased from Dikma (USA). Primary secondary amine (PSA), Ostadecylsilane (C<sub>18</sub>), Graphitized carbon black (GCB) and multi-walled carbon nanotubes (MWNTs) were obtained from Agela Technologies (Tianjin, China). Ultra-pure water was purified on a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Individual stock solutions of difenoconazole (1000 mg L<sup>-1</sup>) was prepared in acetonitrile and stored at –20 °C. Working standard solutions were prepared daily by appropriate serial dilutions in ultra-pure water.

### 2.2. Sample preparation

#### 2.2.1. ME-IL-VALLME procedure

As shown in Fig. 1. In micellar extraction, 4 g of homogenized cowpea sample was placed in a 50-mL centrifuge tube. A total of 20 mL of Tween 20 micellar solution (concentration of Tween 20 was 10 mmol L<sup>-1</sup>) was added and the mixture was shaken for 5 min. After that, the solution was centrifuged at 3800 rpm for 5 min to separate the fine solid particles of cowpea from the solution.

In IL-VALLME, 3 mL of the supernatant was transferred into a 15-mL screw cap plastic tube with conical bottom, then diluted with 3 mL of pure water, 30 μL of ionic liquid was added as an extraction solvent. The tube was vigorously shaken on a vortex mixer immediately for 1 min. After centrifuging at 3800 rpm for 5 min, the ionic liquid phase was collected by a microsyringe then diluted with 30 μL methanol prior to HPLC analysis.

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