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Magnetic "one-step" quick, easy, cheap, effective, rugged and safe method for the fast determination of pesticide residues in freshly squeezed juice

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ABSTRACT

A "one-step" quick, easy, cheap, effective, rugged and safe (QuEChERS) method was proposed for pesticide residue analysis in freshly squeezed juice of fruits and vegetables. In this method, a new magnetic adsorbent prepared by simple physical blending was adopt, which could endow the sample mixture with magnetic separability. To achieve the best performance of the modified QuEChERS towards target analytes, the amounts of adsorbents were investigated. Under the optimized conditions, a simple, rapid and sensitive method for the determination of 11 pesticide residues in freshly squeezed juice was established by coupling modified QuEChERS to gas chromatography/mass spectrometry analysis. The limits of quantification of the proposed method for 11 pesticides ranged from 2.0 to 49.6 ng/g. Good linearities (*R* value $\geq$0.9993) were achieved at different concentration ranges, and acceptable method reproducibility was obtained by evaluating intra- and inter-day precisions with the relative standard deviations being less than 8.5% and 13.5%, respectively. The recoveries were in the range of 70.3–114.1% at different concentrations for real samples. Compared with the traditional QuEChERS methods, extraction/partitioning and purification were integrated into one step in the proposed method, which thus was time-saving (within 3.5 min) with keeping good clean-up performance.

1. Introduction

Quick, Easy, Cheap, Effective, Rugged, and Safe (QuEChERS) is a type of sample preparation method which developed in 2003 by Anastassiades et al. [1]. Due to its advantages such as high recovery, high reproducibility and less cost [1], QuEChERS has already been proven to be useful in pesticide residue analysis, and adopted by many governments and organization laboratories [2–4] as a standard method. Typically, QuEChERS method involves two steps. The first step can be named as "extraction/partitioning". In this step, the sample is weighed in a centrifuge tube while acetonitrile is added at 1/1 (w/v) ratio for promoting the extraction of pesticide residues; after shaking, water removal agents (e.g. anhydrous magnesium sulfate and sodium chloride) are then added and the mixture is shaken again to promote the water partition from the organic phase. The extract is collected after centrifugation. The second step can be named as "purification". In this step, the obtained extract is cleaned up by proper adsorbents through dispersive solid phase extraction (DSPE) process. After shaking and centrifugation, the supernatant is directly amenable to determinative analysis via various analytical instruments, such as liquid chromatography (LC) and/or gas chromatography (GC) coupled to mass spectrometry (MS) [5,6].

In conventional QuEChERS methods, although centrifugation could help to achieve phase separation in both two steps, it took extra time and was not suitable for the detection of a large number of samples. More recently, a magnetic adsorbent was synthesized in our laboratory by "co-mixing" method to ease the purification step. When graphitized carbon black (GCB), primary secondary amine (PSA) and Fe_3O_4 magnetite nanoparticles (MNPs) are dispersed evenly together in acetonitrile (ACN), MNPs would be wrapped into PSA and GCB, along with the aggregation of PSA and GCB. The prepared adsorbent can be dispersed in the extract obtained in "extraction/partitioning" step; after adsorbing matrix

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components, it can be rapidly retrieved from the solution by applying an external magnetic field without centrifugation [7]. Due to its advantages of simple, rapid and effective, other researchers extended the application of this improved QuEChERS method [8]. However, it is notable that centrifugation was still indispensable and applied in extraction/partitioning step, therefore the existing method need to be improved.

In the current study, we proposed a new strategy to overcome the above-mentioned shortage by integrating "extraction/partitioning" and "purification" procedures into one step magnetic solid-phase extraction. To this end, a new magnetic adsorbent was prepared by simple physical blending five components (i.e. anhydrous magnesium sulfate, sodium chloride, GCB, PSA and MNPs) which provided various properties for the magnetic adsorbent. As a commonly used reagent in QuEChERS method, anhydrous magnesium sulfate ($MgSO_4$) is used to bind large amounts of water and thus significantly reduce the water phase [1]. Furthermore, in our protocol, $MgSO_4$ acted as "adhesive" and caked magnetic adsorbents and pomace together, which thus can be separated from the extract rapidly and conveniently by external magnetic field. Sodium chloride (NaCl) is an effective supplementary of $MgSO_4$. In previous studies, it was proved that the combination of $MgSO_4$ and NaCl worked very well, and the phase separation became more completely and less water remained in the ACN phase when NaCl was added to the system [1]. As a weakly polar or non-polar adsorbent, graphitized carbon black (GCB) is mainly used to remove hydrophobic compounds such as hydrophobic pigments [9]. Primary secondary amine (PSA) is a weak anion exchanger, and it could remove various polar organic acids, polar pigments, some sugars and fatty acids [2,5,10,11]. The combination of GCB and PSA were applied in many QuEChERS methods [7,8,12–15], and were found to provide satisfactory clean-up performance of total matrix components. MNPs prepared by solvothermal method are superparamagnetic [16]. These particles are very sensitive to external magnetic field; therefore they can be used to endow the adsorbents with manipulative convenience. Eleven representative pesticides (including organophosphorus, organochlorines and pyrethroids) were selected as model analytes to verify the feasibility of the modified method. It is believed that larger number of pesticides would be desirable by the proposed method. By coupling with gas chromatography–mass spectrometry (GC–MS), a time-saving and simple QuEChERS method for the analysis of pesticide residues in vegetable samples was established in the current study.

2. Experimental

2.1. Chemicals and reagents

Anhydrous magnesium sulfate ($MgSO_4$), ethylene glycol (EG), ethylene diamine (ED), ferric trichloride hexahydrate ($FeCl_3 \cdot 6H_2O$), sodium chloride (NaCl), and sodium acetate (NaAc) were purchased from Sinopharm Chemical Reagent (Shanghai, China). All these chemicals were used directly without further purification. High performance liquid chromatography (HPLC) grade acetonitrile (ACN), acetone and methanol were purchased from Fisher Scientific Company (Fair Lawn, NJ, USA). C_{18}, PSA and GCB were purchased from Weltech Co., Ltd (Wuhan, China). Purified water was obtained with a Millipore Milli-Q apparatus (Bedford, MA, USA).

The standard solution of 11 pesticides, including organophosphorus, organochlorines and pyrethroids (Table 1) was provided by the Agro-Environmental Protection Institute, Ministry of Agriculture (Tianjin, China). Triphenyl phosphate (TPP, 99%) was used as an internal standard (I.S.) supplied by J&K Chemical Ltd. (Tianjin, China). D-Sorbitol (≥99.5%, HPLC grade) employed as an analyte protectant was supplied by Aladdin (Shanghai, China). The working solution of pesticides and the I.S. working solution were prepared with acetone at a concentration of 1.0 μg/mL and stored at −20 °C in darkness. With the working solution, the sample solution was spiked to the desired concentration for the following experiments. The analyte protectant stock solution was prepared in methanol/water (97/3, v/v) with a concentration of 10 mg/mL, and was directly added to pesticide extracts yielding final concentrations of 1.0 mg/mL.

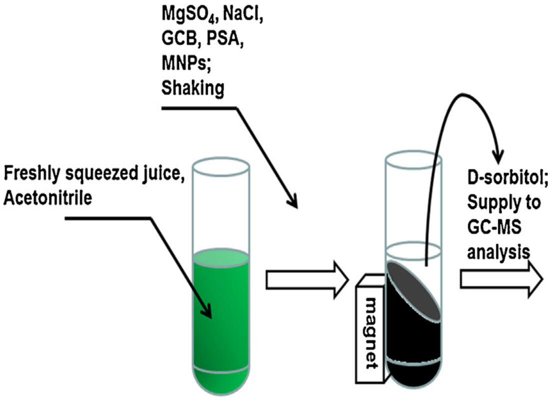

Fig. 1. Schematic of magnetic "one-step" QuEChERS.

2.2. Preparation of magnetic adsorbents

MNPs were synthesized via a solvothermal process according to our previously reported method [17,18]. Briefly, $FeCl_3 \cdot 6H_2O$ (5.0 g) was dissolved in EG (100 mL). NaAc (15.0 g) and ED (50 mL) were then added to the solution. After being vigorously stirred for 30 min, the homogeneous mixture was sealed in a teflon-lined stainless-steel autoclave (200 mL). The autoclave was heated to 200 °C and maintained for 8 h, and then allowed to cool to room temperature. The product was magnetically collected, and washed with water/ethanol for several times. The washed product was then vacuum-dried at 60 °C for 6 h.

Magnetic adsorbents were prepared by simple physical blending. Briefly, GCB (240 mg), PSA (1080 mg), $MgSO_4$ (7200 mg), NaCl (1800 mg) and MNPs (720 mg) were added to a mortar and ground into homogeneous fine powder. The powder was obtained for further use in magnetic "one-step" QuEChERS method.

2.3. Sample preparation

A schematic representation of developed sample preparation based on magnetic "one-step" QuEChERS method is shown in Fig. 1. Fruit and vegetables (cucumbers, tomatoes, grapes and pears) were cut into small pieces and comminuted with an electric grinder to make squeezed juice. Then the freshly squeezed juice with pomace (2.0 g) was weighted into a plastic centrifuge tube (10-mL). Pesticide standards were spiked at a known concentration (100 ng/g) to study the performance of the proposed method under different conditions. One of the cucumber samples was checked to be free of any analytes and used as blank sample for calibration and validation purposes. The pesticide standards were directly spiked into a 2.0 g cucumber sample over a range of 2–500 ng/g. Triphenyl phosphate was added as internal standard (I.S.) at a level of 100 ng/g. Acetonitrile (2.0 mL) was added and the tube was shaken vigorously for 1 min to ensure that the solvent interacted well with the entire sample. As-prepared magnetic adsorbent (1840 mg) were added to the mixture and the shaking step was repeated for 1 min. The supernatant was separated from magnetic conglomerates by a magnet (Supplementary data 2). Then 0.8 mL supernatant was transferred