



The comparison of dispersive solid phase extraction and multi-plug filtration cleanup method based on multi-walled carbon nanotubes for pesticides multi-residue analysis by liquid chromatography tandem mass spectrometry



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ABSTRACT

In this study, dispersive-Solid Phase Extraction (d-SPE) cleanup and multi-plug filtration cleanup (m-PFC) methods were compared for 25 representative pesticides in six matrices (wheat, spinach, carrot, apple, citrus and peanut) by QuEChERS-LC-ESI-MS/MS detection. The type of sorbents in dispersive-SPE (d-SPE) was optimized for the above matrices. Multi-walled carbon nanotubes (MWCNTs), which mixed other materials like PSA (Primary Secondary Amines), GCB (Graphitized Carbon Black) and C18 (Octadecyl-silica), showed brilliant cleanup performance in multi residue monitoring (MRM) pesticide residue analysis. Cleanup effects with d-SPE and m-PFC methods were examined. When spiked at 3 concentration levels of 10, 100, 500 $\mu\text{g}/\text{kg}$ in above matrices, for both d-SPE and m-PFC methods, the recoveries ranged from 70 to 110% with relative standard deviations (RSDs) lower than 20%. Limits of quantification (LOQs) for both cleanup methods ranged from 1 to 25 $\mu\text{g}/\text{kg}$. Matrix-matched calibrations were performed with the coefficients of determination more than 0.99 between concentration levels of 10–1000 $\mu\text{g}/\text{kg}$. It was found that m-PFC was more convenient and effective than d-SPE with the same sorbents, due to the increased contact time and contact area between the extracts and compressed sorbents. The study demonstrated that m-PFC method could be used as a rapid, convenient and high-throughput cleanup method for analysis of pesticide residues.

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1. Introduction

The QuEChERS (quick, easy, cheap, effective, rugged and safe) method is the most used sample preparation method in pesticide analysis nowadays. It involves extraction with acetonitrile, partitioning between acetonitrile and the aqueous phase after addition of sodium chloride and magnesium sulfate, and a d-SPE cleanup procedure with a small quantity of SPE sorbents [1–3]. However, when handling difficult matrices like tea [4,5], leek [6,7] and soft drinks [8,9], the d-SPE cleanup performance was not good enough to remove interferences. So it was necessary to cleanup the extract with SPE columns, but it is more tedious and costly [10].

Carbon nanotubes (CNTs) is a type of novel and interesting carbonaceous materials first reported by Iijima in 1991 [11], which

was classified as single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) on the principle of carbon atom layers in the wall of nanotubes [12,13]. In recent years, MWCNTs have been reported to be used as effective SPE materials for the extraction of pesticides [14–16].

In our previous study, MWCNTs was being used as a type of alternative reversed-dispersive solid phase extraction materials in pesticide multi-residue analysis with QuEChERS method [17,18]. It was also being mixed with other sorbents such as PSA, GCB and C18 for dispersive cleanup of acetonitrile extracts from complex samples such as tea [19], scallion, ginger and garlic [20,21].

In the newly developed m-PFC procedure by our group, MWCNTs mixed with other sorbents and anhydrous magnesium sulfate were used as solid-phase sorbents, which packed in a short syringe cartridge. The syringe needle was kept under the surface of the extract, and then the syringe piston was pushed and pulled for several cycles. It intended to adsorb the interfering substances in the matrix, rather than the analytes, and remove water from the

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extracts with anhydrous magnesium sulfate. The m-PFC method was very rapid, which took just about tens seconds to perform without any solvent evaporation [22,23].

In this work, MWCNTs combining with other materials like PSA, C18, and GCB were used as basic d-SPE sorbents. Cleanup effects and other method performances on d-SPE and m-PFC with the same adsorbing material for the same matrix solution were compared. Six representative matrices (wheat, spinach, carrot, apple, citrus, peanut) were chosen.

Twenty-five pesticides with different Log *P* and different chemical structural catalogues were selected to validate the comparison. We selected pesticides through the following 3 steps. Firstly, the most common applied pesticides of each target matrix were chosen (<http://www.chinapesticide.gov.cn/index.html>). Secondly, maximum residue limits (MRLs) of registered pesticides on different matrices were searched (<http://www.mrlatabase.com/>). Then, some widely-used pesticides with different Log *P* were added into the selected pesticide group. Some pesticides which may have high possible residue in food commodities were also added [24,25]. Finally, we selected 25 pesticides to validate the comparison using LC-ESI-MS/MS to identify and quantify the residue levels of multi-pesticides. Analytical methods used as standard methods for these 25 pesticide analysis were LC and LC-MS according to our government guidelines (<http://www.nyhycn.com/>).

2. Experimental

2.1. Chemicals and materials

All the 25 standard compounds (as in Table S1 in supplementary materials) were purchased from the Institute of the Control of Agrochemicals, Ministry of Agriculture, Peoples' Republic of China. The purities of the standard pesticides were more than 95%. Stock solutions of 10 mg/L of mixture pesticides were prepared in acetonitrile and stored at -20°C . The working solutions were diluted from the stock solutions daily. HPLC-grade acetonitrile was obtained from Fisher Chemicals (Fair Lawn, New Jersey, USA). Analytical reagent grade anhydrous sodium chloride (NaCl), anhydrous magnesium sulfate (MgSO_4) and absolute ethyl alcohol were obtained from Sinopharm Chemical Reagent (Beijing, China). The water used was purified with a Milli-Q water purification system from Millipore, USA. MWCNTs with average outer diameters of 10–20 nm, PSA, C18 and GCB were provided by Tianjin Bonna-Agela (Tianjin, China). MWCNTs were dried for 1 h at 100°C to remove the adsorbed water and kept in desiccators for storage. SPE columns, sieve plates for

assembling m-PFC columns were provided by Tianjin Bonna-Agela (Tianjin, China).

2.2. Assembling m-PFC columns

Schematic diagram of the m-PFC column was shown in Fig. 1. In order to simplify the equipment, we modified the original m-PFC columns. The new column contained 5 parts: a SPE column, a piston, two sieve plates, the sorbents and a syringe needle. The sorbents were packed between two sieve plates in the SPE column. Before application, the sieve plates were soaked in absolute ethyl alcohol for 1 h. One sieve plate was placed tightly into the column's bottom. After that, sorbents were loaded in the column, and then another sieve plate was placed into the column in order to compress the sorbents. At last, the piston and the syringe needle were assembled.

2.3. Apparatus

Centrifugation was performed in two different instruments: an Anke TDL-40B centrifuge equipped with a bucket rotor ($8 \times 100\text{ mL}$) (Shanghai, China) and a SIGMA 3K15 microcentrifuge equipped with angular rotor ($24 \times 2.0\text{ mL}$) (BMH Instruments Co., Ltd., China), and a TARGIN VX-III Multi-Tube Vortexer was used for preparing the samples.

2.4. LC-MS/MS conditions

The chromatographic system was an Agilent 1200 series HPLC system which consisted of a vacuum degasser, autosampler, column heater, a quaternary solvent delivery system and a binary pump. The separations were performed using a $50 \times 2.1\text{ mm} \times 3.5\ \mu\text{m}$ Eclipse plus C18 analytical column from Agilent technologies (USA). Separation of the analytes from the C18 column was performed at a flow rate of 0.2 mL/min . The column was kept at 30°C . The injected sample volume was $5\ \mu\text{L}$. Gradient elution was performed with acetonitrile as mobile phase A and 0.1% formic acid in ultrapure water as mobile phase B. The gradient elution was 0–3 min, linear gradient 30–60% A; 3–6 min, linear gradient 60–70% A; 6–15 min, linear gradient 70–99% A; finally, 15–16 min, linear gradient return to the initial composition 30%A, holding 9 min. The total running time was 25 min. Separation of the 25 analytes was achieved in 15 min. Analysis of these compounds was carried out on an Agilent 6410 Triple Quad detector (USA) using the MRM mode and positive ESI mode. Table S1 in supplementary materials showed optimized MRM data acquisitions.

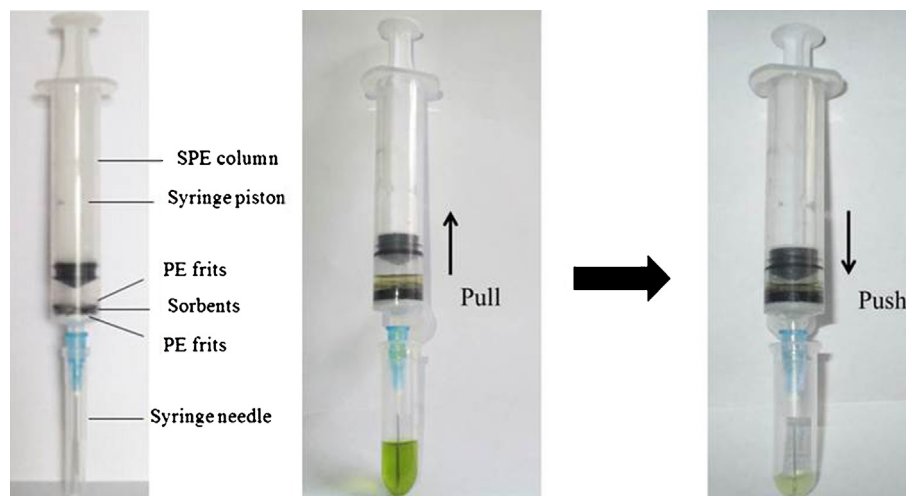


Fig. 1. Schematic diagram of m-PFC.

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