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Evaluation of membrane filtration for cleanup in multi-residue pesticide analysis of spinach

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ABSTRACT

This study reports a new membrane filtration-based cleanup method for the analysis of pesticides. Recovery and cleanup by membrane filtration using 11 different membranes, classified by their molecular weight cut-off, pore size, and material, were examined. Three different eluent mixtures were also examined. The results indicated that membranes with a 0.1-μm pore size were the most effective among those tested. In particular, hydrophobic polyvinylidene difluoride and hydrophobic polytetrafluoroethylene gave better recoveries and cleanup than other membranes. Results from GC chromatograms and matrix effects showed that membrane filtration afforded better cleanup than the modified QuEChERS method. Furthermore, over 90% of the 89 pesticides tested had acceptable recoveries using these two membranes, according to an acceptable recovery range of 70–120%. Therefore, this technique has potential as an effective cleanup method.

1. Introduction

Currently, hundreds of pesticides are in widespread use in agricultural fields globally. Residues of these pesticides affect agricultural products, especially fruits and vegetables. Due to consumer awareness of potentially hazardous pesticide residues in agricultural products, international trade issues, regulatory requirements, and other factors, agricultural products are monitored for pesticide residues. To meet the demands of consumers, farmers, regulators, and others, analytical methods for pesticide residues in complex matrices are continually being improved. “Quick, easy, cheap, effective, rugged, and safe” (QuEChERS) methods have evolved from the original version into multi-laboratory validated methods using acetate buffering (AOAC Official Method 2007.01) or citrate buffering (CEN Standard Method EN 15662) (Koesukwiwat, Lehotay, & Leepipatpiboon, 2010). These and other versions of QuEChERS have been adopted worldwide because of their beneficial features (Anastassiades, Lehotay, Štajnbaher, & Schenck, 2003; Anastassiades, Maštovská, & Lehotay, 2003; Nguyen, Yu, Lee, & Lee, 2008; Hernández-Borges, Cabrera Cabrera, Rodríguez-Delgado, Hernández-Suárez, & Galán Saúco, 2009; Hůšková, Matisová, Hrouzková, & Švorc, 2009; Słowik-Borowiec, Szpyrka, & Walorczyk, 2015). In routine analytical applications, sample throughput is an important issue to consider when selecting an analytical method. Recently, multi-class and multi-residue pesticides analysis methods in fruits, vegetables, and other commodities have been commonly applied worldwide to the regulation of agricultural product safety, international trade, toxicological risk assessment, research investigations, and a lot of other purposes. Among them, the QuEChERS approach to pesticide analysis in agricultural products provides rapid sample preparation (high sample throughput) (Lehotay, Koesukwiwat, van der Kamp, Mol, & Leepipatpiboon, 2011). Despite the many advantages and demonstrated feasibility of QuEChERS, the major challenge encountered in the analysis of pesticide residues in agricultural products is the presence of pigments, lipids, and fatty acid compounds that might be co-extracted with the pesticides. These compounds can create massive GC interference and become a burden to the GC column and detector (Kwon, Lehotay, & Geis-Asteggiante, 2012). In addition, they can also co-elute with pesticides and cause inconsistent pesticide recoveries (Chai & Elie, 2013).

Membrane filtration is an efficient method for the removal of interference materials (Acero, Benitez, Real, & Garcia, 2009), and is widely used in separation, cleanup, and concentration (Ahn et al., 1999; Wang & Chung, 2005; Yang, F. J., Yang, D. L., Zhang, & Jian, 1993). The removal of pesticides by membranes has been

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reported (Acero et al., 2009). Although studies have investigated the analysis of pesticides using membranes (Han, Sapozhnikova, & Lehotay, 2014; Hatkeyama et al., 2006; Hong et al., 2016; Plakas, Karabelas, Wintgens, & Melin, 2006), there are few reports of the removal of interference materials by membrane filtration during pesticide analysis using GC/MS. In this study, we investigated the application of membrane filtration as an enhanced cleanup method in pesticide analysis. In this experiment, the recovery and cleanup by membrane filtration in pesticide analysis were examined. We used 11 different types of membrane, classified by molecular weight cut-off (MWCO), pore size, and material. Spinach was used in this study as a representative agricultural product because it is a typical leafy vegetable with a highly pigmented matrix.

2. Materials and methods

2.1. Chemicals and reagents

All pesticide standards were of high purity. Pesticide standard solution 31 (for GC analysis) including 85 representative of pesticides was obtained from Kanto Chemical (Tokyo, Japan). Pesticide standard solution 31, which is name of the product, contains pesticides among the product of pesticide standard solution for GC analysis. It also contains various properties of pesticides such as log K_{ow} (from −0.22–6.01), hydrophilic, hydrophobic, low MW, high MW, carbamate, organophosphate, organochloride and so on. An internal standard solution (containing phenanthrene-d_{10}, anthracene-d_{10} and 9-bromoanthracene) was obtained from Wako Pure Chemical Industries (Tokyo, Japan). They were stored at −20 °C. The standards were diluted by acetone for experiment and stock standard solutions were stored at 4 °C. All organic solvents were pesticide grade and obtained from Wako (Tokyo, Japan). InertSep GC/NH2 (500 mg/500 mg/6 mL) cartridges which composed of graphitized carbon black (GCB) and aminopropyl (NH2) sorbent were obtained from GL Sciences (Tokyo, Japan). Trisodium citrate dihydrate, disodium hydrogen citrate sesquihydrate, sodium chloride, and magnesium sulfate were obtained from Kanto Chemical (Tokyo, Japan).

2.2. Membranes

Seven different polyethersulfone (PES) membranes were used in this study: 0.1-μm-pore size was obtained from AS ONE Corporation (Osaka, Japan); a pore size of 0.05 μm, and MWCOs of 150 kDa and 50 kDa were obtained from Daisen Membrane Systems (Tokyo, Japan); MWCOs of 10 kDa and 5 kDa were obtained from Koch Membrane Systems (Wilmington, USA); and an MWCO of 1 kDa was obtained from Daisen Membranes Systems (Tokyo, Japan). Five different types of membrane with a pore size of 0.1 μm were also used in this study: PES membrane was obtained from AS ONE Corporation (Osaka, Japan); two types of polyvinylidene difluoride (PVDF) membrane, one hydrophobic and one hydrophilic, were obtained from Merck Millipore (Osaka, Japan); and two types of polytetrafluoroethylene (PTFE), one hydrophobic and one hydrophilic, were obtained from Flon Industry (Tokyo, Japan). Total 11 membranes were evaluated (PES membrane was duplicated).

2.3. Instruments and GC/MS analytical conditions

HP4750 Stirred Cell obtained from Sterlitech (Kent, WA, USA) was used for membrane-filtration apparatus and a SepPak elution pump obtained from Waters (Milford, MA, USA) was used for sample elution from solid column. For centrifugation, Kubota 5922 from Kubota (Osaka, Japan) was used. GC (TRACE GC Ultra) coupled with a MS (Polaris Q) obtained from Thermo Fisher Scientific (Waltham, MA, USA) was used for pesticide measurement. Aliquots (2 μL) from 1 mL of recovery sample and 500 μL of blank sample were injected into the GC system respectively. The oven program started at 50 °C (held for 1 min), which was ramped at 30 °C min^{-1} to 125 °C, and 5 °C min^{-1} to 200 °C. Finally, the temperature was ramped at 10 °C min^{-1} to 300 °C and it was held for 11.5 min. MS detection was performed in 70 eV of electron ionization mode. Calibration standards were prepared in acetone at 50 ng mL^{-1}, 100 ng mL^{-1}, 200 ng mL^{-1}, and 400 ng mL^{-1} A 1.5 m, 0.25 mm guard column obtained from Sigma-Aldrich (St. Louis, MO, USA) was coupled the DB-5MS capillary column (30 m, 0.25 mm i.d., 0.25 μm) obtained from Agilent Technologies (Santa Clara, CA, USA).

2.4. Method performance

Calibration curves were used to determine pesticide concentrations, and were constructed for each pesticide using four different concentrations of the pesticide standard solution in the range of 50–400 ng g^{-1}. The coefficients of determination (R^2) exceeded 0.99 in all pesticides, except for allethrin, isoxathion-oxon, phenothrin, fenbuconazole, flumioxazin and tolfenpyrad, which were little low between 0.92 and 0.98. The limit of quantitation (LOQ) was calculated as ten times the standard deviation. The LOQ obtained from pesticides were in the range 3–30 ng g^{-1}.

2.5. Cleanup by membrane filtration

Pesticide-free spinach was selected in this study which obtained from a local market (Matsuyama, Ehime, Japan). We use modified QuEChERS method based on Lebotay method (Lehotay et al., 2010) for initial extraction. The procedure was as follows: (1) Weighed 10 g of each a chopped spinach sample in to a 50-mL polypropylene centrifuge tubes; (2) Added acetonitrile (MeCN, 10 mL) into the tubes and it was vigorously shaken for 1 min by hand after all tubes was sealed. Poured trisodium citrate dehydrate (1 g), disodium hydrogen citrate sesquihydrate (0.5 g), sodium chloride (1 g), and magnesium sulfate (4 g) to the tube and shaken vigorously by hand for 1 min after all tubes was sealed; (3) The mixtures were centrifuged at 3500 rpm (2330 rcf) for 10 min to separate the organic phase (MeCN) from the aqueous and solid phases; (4) Transferred 5 mL of each MeCN supernatant into three tubes and three types of mixed solvent were added to each tube, respectively; (5) For yield a total volume of 12.5 mL, three types of analyte solution was mixed with extract. The 5:5 water–MeCN (*v/v*) analyte solution was made by adding 1.25 mL of MeCN and 6.25 mL of water, the 6:4 water–MeCN (*v/v*) analyte solution was made by adding 7.5 mL of water and the 7:3 water–MeCN (*v/v*) analyte solution was made by following method: the supernatant (5 mL) was first evaporated to 2 mL, then add 1.75 mL of MeCN and 8.75 mL (6) Before membrane filtration, first of all, membrane was installed in the membrane-filtration apparatus. 20 mL of mixed solvent (5:5, 6:4, or 7:3 water–MeCN (*v/v*)) was added on the membrane by pipette for pre-washing (0.5 MPa, 30 °C, and 400 rpm). Then, 10 mL of the extract was added on the membrane for filtration. Finally, 5 mL of mixed solvent was added for rinse, total volume of filtered solution was 15 mL. At this point, cleanup effect was determined visually by the color of the extract.

2.6. Recovery with spiked standard solutions using modified QuEChERS method

Three different 12.5-mL crude standard samples (5:5, 6:4, and 7:3 water–MeCN (*v/v*)), containing 125 μL of pesticide standard solution, were used as pesticide-contaminated samples, while