



Fundamental study of a novel membrane filtration cleanup method for pesticide analysis in agricultural products



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ABSTRACT

The recovery and purification characteristics of membrane filtration for pesticide analysis of agricultural products were investigated. Eight different types of membranes classified by their molecular weight cut off (MWCO) and material were used. The results showed that the recovery and purification characteristics varied according to the eluting solvent used, as well as the membrane's MWCO and material. The recovery increased as the MWCO increased, and the purification increased when the eluting solvent contained water. A GK membrane with acetonitrile–water (1:1, v/v) was the most effective membrane filtration method among those tested. The pesticide analysis of spinach using the GK filtration method indicated that this method results in better purification than the modified QuEChERS method.

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1. Introduction

Agrichemicals are widely used in agriculture to prevent the destruction of food crops by pests or unwanted plants and improve plant quality (Bakirci & Hisil, 2011; Gözde, Dilek, Fatih, & Semih, 2014; Słowik-Borowiec, Szpyrka, & Walorczyk, 2015). Despite the wide range of benefits of using pesticides in agriculture, the incorrect application of these chemicals, such as the use of an inappropriate pesticide type on foodstuffs or their unwarranted use, can result in high and undesirable levels of these compounds in the products that reach consumers (Cserhádi, Forgács, Deyl, Miksik, & Eckhardt, 2004). Therefore, analyzing pesticides in agricultural products is necessary. However, more than 800 pesticides belonging to more than 100 substance classes have been registered and used globally for decades, and the chemical and physical properties of these may vary considerably. Although a multi-class, multi-residue analytical method would be the most useful for regulatory pesticide monitoring, the diverse properties of pesticides complicate the development of such a universal method (Siweon, Sooyeon, Jinyoung, MeeKyung, & Jeonghan, 2015; Urairat, Steven, & Natchanun, 2011). The most used approach for pesticide

extraction from food samples is currently QuEChERS (Zeying et al., 2015). QuEChERS, which stands for quick, easy, cheap, effective, rugged, and safe, provides satisfactory results for a wide range of pesticides. Since it was first introduced, the QuEChERS method has been widely accepted by the scientific community (Anastassiades, Mastovska, & Lehotay, 2003; Anastassiades, Lehotay, Štajnbaher, & Schenck, 2003; Daniela, Gian, Paola, Stefania, & Maria, 2012). This method and its modified variants are used primarily to analyze pesticide residues in fruits and vegetables (Raphaell et al., 2013; Słowik-Borowiec et al., 2015; Tibor, Esther, Zdenek, Ivan, & Adam, 2004). However, many agricultural product samples are known to be rich in pigments and fatty acids, and as a result, interference materials can be retained in the final extract, despite using a cleanup method. Matrix-induced signal enhancement can greatly affect analyte responses and performance by causing analyte retention and degradation. Furthermore, interference materials derived from agricultural products can become a burden to GC columns and detectors (Hyeyoung, Steven, & Lucía, 2012). To overcome this issue, we focused on developing a cleanup procedure specific to pesticide analysis. Membrane filtration is one of the efficient methods for removing interference materials (Juan, Javier, Francisco, & Carolina, 2009). The membrane's ability to control the permeation rate of a chemical species is key for the efficacy of this technique, and membranes also have additional advantages, such as flexibility, which can be combined with other separation

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processes. For these reasons, membrane filtration is widely used in separation, purification, and concentration processes (Kai Yu and Tai-Shung, 2005; Kyu-hong, Kyung-guen, Ho-young, & Ick-tae, 1999; Robert, 1995, chap. 13). In particular, it has been developed mainly for gas separation, wastewater reclamation, and drinking water processing to remove pollutants and natural organic materials (Daeyoun & Sangyong, 2011; Patrick, Tulay, & Philip, 2013; Plakas, Karabelas, Wintgens, & Melin, 2006; Yeomin, Paul, Shane, & Eric, 2006). Although some studies investigating analysis of pesticides by membranes have been reported (Eriko et al., 2006; Juan et al., 2009; Konstantinos, Anastasios, Thomas, & Thomas, 2006; Lijun, Yelena, & Steven, 2014). However, there are few reports on the removal of interference materials by membrane filtration during pesticide analysis using GC/MS. In this study, we investigated the recovery and purification achievable by membrane filtration for pesticide analysis. We used 8 different types of membranes that were classified in terms of their MWCO and material. Additionally, spinach was used as the agricultural product because it is a representative leafy vegetable with a highly pigmented matrix.

2. Materials and methods

2.1. Chemicals and reagents

All pesticide standards were high purity. Pesticide standard solution 31 (for GC analysis, containing 85 types of pesticides) was obtained from Kanto chemical (Tokyo, Japan) and used as the standard solution. It contains various types of pesticides such as hydrophilic, hydrophobic, low MW, high MW, carbamate, organophosphate, organochloride and so on. An internal standard solution (containing phenanthrene-d₁₀, anthracene-d₁₀, 9-bromoanthracene) was obtained from Wako Pure chemical Industries (Tokyo, Japan) and used as a syringe spike which was added to the sample at the same concentration as used in the calibration for verifying validity of sample. Stock standard solutions of 200 ng μL^{-1} were prepared in acetone and stored in the dark at 4 °C. All organic solvents were pesticide analysis grade and were obtained from Wako (Tokyo, Japan). InertSep PSA (500 mg/6 mL) and InertSep GC/NH₂ (500 mg/500 mg/6 mL) cartridges 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

Polyamide membranes (NFG with MWCO of 600–800 Da, NFW with MWCO of 300–500 Da, and NFX with MWCO of 150–300 Da) were obtained from Synder Filtration (CA, USA). A polyethersulfone membrane (NP030 with MWCO of 400–600 Da) was obtained from Daicel Membrane Systems (Tokyo, Japan). A polypiperazine amide membrane (XN45 with MWCO of 500 Da) was obtained from TriSep (Goleta, CA, USA). A composite polyethersulfone membrane (MPF-36 with MWCO of 1000 Da) was obtained from Koch Membrane Systems (Wilmington, MA, USA), and thin-film composite membranes (GK with MWCO of 3000 Da and GH with MWCO of 2000 Da) were obtained from Lenntech (Rotterdam, Netherlands).

2.3. Instruments and GC/MS analytical conditions

We used HP4750 Stirred Cell obtained from Sterlitech (Kent, WA, USA) as the membrane-filtering apparatus and a SepPak elution pump obtained from Waters (Millford, MA, USA) for the cleanup process. Model 5922 instrument was obtained from Kubota (Osaka, Japan) and used for centrifugation. The pesticides

were identified and quantified with GC (TRACE GC Ultra) coupled with MS (Polaris Q) obtained from Thermo Fisher Scientific (Waltham, MA, USA). Aliquots (2 μL) of the final extracts were injected into the GC system. The oven temperature program started at 50 °C (hold for 1 min) and then increased at a rate of 30 °C min^{-1} to 125 °C and at a rate of 5 °C min^{-1} to 200 °C. Finally, the temperature was increased at a rate of 10 °C min^{-1} to 300 °C (hold for 11.5 min). Calibration standards in acetone were prepared at 50 ng mL^{-1} , 100 ng mL^{-1} , 200 ng mL^{-1} , and 400 ng mL^{-1} for GC/MS measurement. Mass spectrometric detection was performed in electron ionization mode (EI, 70 eV). A DB-5MS capillary column (30 m \times 0.25 mm i.d., 0.25 μm) was obtained from Agilent Technologies (Santa Clara, CA, USA) and used. An untreated, non-polar fused silica capillary column (1.5 m \times 0.25 mm) from Sigma–Aldrich (Saint Louis, MO, USA) was used as the guard column.

2.4. Method performance

We used the calibration curve for determining the concentration of pesticides. The calibration curve was constructed for each pesticide using four different concentrations of the pesticide standard solution in acetone. The method linearity was in the range of 50–400 ng g^{-1} . The resulting coefficients of regression (R^2 value) exceeded 0.99 in all cases. The LOD was calculated three times of standard deviation, whereas the LOQ was equal to ten times of standard deviation. The LODs obtained for most of the pesticides were in the range of 1–10 ng g^{-1} .

2.5. Determination of the purification by visual extract observation

In this study, pesticide-free spinach obtained from a local market (Matsuyama, Ehime, Japan) was used. Sample preparation was based on a QuEChERS method (Steven et al., 2010). A chopped sample (10 g) was added to a 50-mL polypropylene centrifuge tube. Then, 10 mL of acetonitrile (MeCN) was added, the tubes were vigorously shaken for 1 min by hand. Subsequently, 1 g of trisodium citrate dihydrate, 0.5 g of disodium hydrogen citrate sesquihydrate, 1 g of sodium chloride, and 4 g of magnesium sulfate were added and shaken vigorously by hand for 1 min. The mixture was centrifuged at 3500 rpm for 10 min to separate the organic phase (MeCN) from the aqueous and solid phases. After 5 mL of supernatants were transferred to tubes, three types of mixed solvent were added each tubes respectively to yield a total volume of 12.5 mL to generate three types of the analyte solutions. In case of the methanol (MeOH) analyte solution, the MeCN was evaporated, and then, 12.5 mL of MeOH was added, in case of the MeCN analyte solution, 7.5 mL of MeCN was added and in case of the MeCN-water (1:1, v/v) analyte solution, 1.25 mL of MeCN and 6.25 mL of water were added. Before membrane filtration, 20 mL of mixed solvent (MeOH, MeCN, or MeCN-water (1:1, v/v)) was added to the membrane which was placed in the membrane-filtering apparatus for pre-washing (0.5 MPa, 30 °C, and 400 rpm). Then, 10 mL of the analyte solution was added to the membrane-filtering apparatus for filtration. Finally, 5 mL of mixed solvent was added to rinse the membrane, and the total filtered solution reached a volume of 15 mL. At this point, the purification was determined visually according to the color of the extract.

2.6. Determination of the recovery using spiked standard solutions

Three types of 12.5 mL crude standard samples (MeOH, MeCN, and MeCN-water (1:1, v/v)) including 125 μL of pesticide standard solution were used as the pesticide-contaminated samples, and three types of 12.5 mL crude reference samples (MeOH, MeCN, and MeCN-water (1:1, v/v)) including 125 μL of acetone without

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