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Low temperature cleanup combined with magnetic nanoparticle extraction to determine pyrethroids residue in vegetables oils

Xi Yu [a, b], Hwee Chieh Ang [a], Hongshun Yang [a, b, *], Chao Zheng [c], Yuquan Zhang [c]

[a] Food Science and Technology Programme, c/o Department of Chemistry, National University of Singapore, Singapore, 117543, Singapore
[b] National University of Singapore (Suzhou) Research Institute, 377 Lin Quan Street, Suzhou Industrial Park, Suzhou, Jiangsu, 215123, PR China
[c] Wilmar Biotechnology Research and Development Center (Shanghai) Company, Limited, 118 Gaodong Road, Pudong New District, Shanghai, 200137, PR China

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Bifenthrin (PubChem CID: 6442842)

ABSTRACT

To quantify trace pesticide residue in vegetable oil rapidly, low temperature cleanup combined with magnetic nanoparticle based solid phase extraction was developed to determine eight pyrethroids in vegetable oils, including tetramethrin, fenpropathrin, cypermethrin, decamethrin, fenvalerate, acrinathrin, permethrin and bifenthrin. Polystyrene coated magnetic nanoparticles were synthesised by a modified chemical coprecipitation combined with emulsion polymerisation method. The nanoparticles were afterwards characterised by Fourier transform-infrared spectroscopy, X-ray diffraction, transmission electron microscopy as well as vibrating sample magnetometer, and successfully employed as adsorbents for the magnetic solid phase extraction of pyrethroids which were cleaned up using low temperature approach in advance. Critical impact factors on the efficiency of the extraction method such as the mass of adsorbents used, volume and type of eluent solvent, extraction time as well as elution time were optimised subsequently. Regression analysis of the calibration curves of the eight pyrethroids yielded satisfactory correlation coefficients within the range of 0.980–0.998. Limit of detection and limit of quantification were calculated to be between 0.0290-0.0658 and 0.0890–0.1994 ng g^{-1}, respectively. Intra-day and inter-day reproducibility at different concentration levels also produced satisfactory recovery rates of 83.18–112.79% with relative standard deviations not exceeding 10.84% and 12.01%, respectively, suggesting desirable stability of the proposed method.

1. Introduction

Pyrethroids are man-made pesticides, with structures derived from naturally occurred pyrethrins found within *Chrysanthemum*

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[*] Corresponding author. Food Science and Technology Programme, c/o Department of Chemistry, National University of Singapore, Singapore, 117543, Singapore.
E-mail address: chmynghs@nus.edu.sg (H. Yang).

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cineraraefolum flowers. Pyrethroids are generally carboxylic esters and can be classified into two groups, namely Type I and Type II pyrethroids, differentiated by the absence (Type I) or presence (Type II) of a cyano group on the alcohol moiety (Blankson, Osei-Fosu, Adeendze, & Ashie, 2016). The addition of the cyano substituent greatly improves the capability of pyrethroid as an insect killer, and results in numerous uses of pyrethroids (Esteve-Turrillas, Pastor, & de la Guardia, 2005). Pyrethroids can be found in a multitude of pest control formulations commonly used in households and gardens (Yang, Dey, Buchanan, & Biswas, 2014). In addition, the much better photostability and environmental persistence of pyrethroids over its natural counterparts contribute to their huge popularity for its use in agricultural fields (Kodba & Vončina, 2007).

However, studies have revealed a link between consumption of agricultural produce such as vegetables and fruits and exposure to pyrethroid residues (Chowdhury et al., 2013; Pirsaheb, Fattahi, & Shamsipur, 2013; Yu et al., 2012b), alarming chronic exposure of pyrethroids may have some potential adverse effects on human health. Some biologists even raised concerns that exposure to pyrethroids could have undesirable effects on male reproductive system, resulting in poor quality sperms (Hayward, Wong, & Park, 2015). Other studies also discussed the harmful effects of pyrethroids on the neurological systems of humans (Yu et al., 2012b). As such, many countries have set the maximum residue limits of pyrethroid residues in various foods in order to protect the health of mass population (Yu & Yang, 2017).

Vegetable oils contain pyrethroids due to the transfer from respective oil seeds during extraction process (Lentza-Rizos, Avramides, & Visi, 2001). And since vegetable oil is an essential ingredient in the recipe of many processed food products, it is a major source of exposure to these dangerous compounds. Only trace levels of pyrethroids are deemed acceptable in vegetable oils. Considering that a mixture of pyrethroids could be present in a single oil type and the potential health hazards, developing a sensitive and efficient method of analysing trace amounts of pyrethroids multi residues in vegetable oils is essential and highly important (Wang et al., 2014a).

Compared to the pesticide residues in fruits and vegetables which can be analysed by newly developed nanotechnology (Ling et al., 2016; Yang et al., 2016; Yang, Lv, Yan, Wu, & Li, 2015; Zhang, Yu, Li, Mustapha, & Lin, 2015), in any analysis process of an oil sample, it is crucial that lipids are well separated from the analytes of interest since a slight amount of lipids can lead to severe interference of the analysis results (Oujji et al., 2013; Wei et al., 2012). However, fatty matrices are notorious for being difficult to clean up and remove (Oujji et al., 2014). Conventional methods include liquid-liquid extraction which usually involves multiple liquid-liquid partitioning procedures. Other methods include saponification and Soxhlet extraction (Taghvaee, Piravivanak, Rezaei, & Faraji, 2016). These methods, however, either require large amounts of solvents, rendering them environmentally unfriendly or are essentially too laborious (Farajzadeh, Khoshmaram, & Nabil, 2014). Low-temperature cleanup method, on the other hand, uses very limited amount of organic solvents and minimises the need for lengthy procedures (Chen et al., 2009). To carry out the procedure, a small amount of organic solvent is typically used to extract analytes of interest from the oil sample before the mixture is frozen at between -18 and -25 °C. The difference in melting points of the fat and the organic solvent allows the fat to be frozen out whilst the organic solvent remains in the liquid supernatant. The organic layer can then be simply decanted off for subsequent steps. A previous report introduced this method to determine multiresidues in rapeseed oil (Jiang, Li, Jiang, Li, & Pan, 2012). Later, another group applied this method to determine polycyclic aromatic hydrocarbons in edible oils successfully (Payanan, Leepipatpiboon, & Varanusupakul, 2013).

For the extraction step, traditional methods such as solid phase extraction and solid phase microextraction have their shortcomings (Wilkowska & Biziuk, 2011; Yang et al., 2015). The former is too time-consuming, tedious and requires vacuum while the latter utilises an expensive fibre that is fragile (Cao et al., 2014). Therefore, over the years, solid phase extraction (SPE) technology was much developed in order to overcome the shortcomings.

Most developments in SPE technology are directly related to the sorbent material. Efforts have been made to make the sorbent material magnetic, which led to magnetic solid phase extraction (MSPE) (Wan Ibrahim, Nodeh, Aboul-Enein, & Sanagi, 2015; Zhao et al., 2011). The magnetic properties ease the removal of the extraction medium from the sample solution by using a strong magnet (Bagheri et al., 2016; Jiang et al., 2012). Further developments incorporated nanoparticles in MSPE (Yu & Yang, 2017). Nanoparticles were shown effective due to the high surface area to volume ratio which allows for rapid adsorption of analytes (Yu et al., 2012a). Furthermore, magnetic nanoparticles can be functionalised and modified with different types of coating with affinity to specific analytes of interest (Wang et al., 2014b). For example, ferrite nanoparticles were used to extract Sudan dyes from food and water samples (Yu et al., 2012a). And polyaniline-coated magnetic particles were able to determine pyrethroids residue concentrations in tea drinks (Wang et al., 2014a). These methods could also be applied for pesticide residue in organic foods due to the trace amount of residue (Li et al., 2015; Liu, Tan, Yang, & Wang, 2017; Zhang & Yang, 2017).

In the present study, a novel approach utilising a low temperature clean-up and subsequent MSPE extraction with polystyrene-coated magnetic nanoparticles (PSt/MNPs) was developed to determine eight different pyrethroids commonly used in agricultural sector in vegetable oils, including tetramethrin, fenpropathrin, cypermethrin, decamethrin, fenvalerate, permethrin, acrinathrin and bifenthrin. The coupling of these two methods successfully removed lipid matrices and efficiently preconcentrated the targeted analytes, indicating affinity between polystyrene coatings and the analytes. The developed method was potentially excellent, efficient, economic and requiring less solvent for detecting pyrethroids residue in oil. It could aid in ensuring that vegetable oils exceeding acceptable threshold of pyrethroids residue can be quickly screened and not consumed by the public.

2. Materials and methods

2.1. Oil samples

Five different oils were purchased from local supermarkets in Singapore. These consisted of soybean oil, canola oil, sunflower oil, corn oil and virgin olive oil. The canola oil was determined to be free of pyrethroid residues using a modified standard recommended by Association of Official Analytical Chemists (AOAC) and was therefore used for the optimisation and method validation experiments (Pang, Cao, Fan, Zhang, & Li, 1998).

2.2. Chemicals and standards

Pyrethroid standards of bifenthrin (97.2%), fenvalerate (98.6%), permethrin (99.9%) and decamethrin (98.0%) were acquired from Aoke Biology Research Co. Ltd, China. Acrinathrin (99.7%), cypermethrin (94.3%), tetramethrin (98.3%) were acquired from Fluka, Sigma Aldrich Co., USA. Fenpropathrin (99.4%) was acquired from Chem Service Inc., USA. HPLC-grade acetonitrile, methanol and acetic acid were sourced from Macron Fine Chemicals, USA.