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Comparative study of pyrethroids residue in fruit peels and fleshes using polystyrene-coated magnetic nanoparticles based clean-up techniques

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Chemical compounds studied in this article:
Bifenthrin (PubChem CID: 6442842)
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Decamethrin (PubChem CID: 40585)
Fenvalerate
Fenpropathrin (PubChem CID: 47326)
Permethrin (PubChem CID: 40326)

ABSTRACT

An efficient and rapid method for quantifying pyrethroids pesticide residue in fruits samples was developed in the present study. The application of lab prepared polystyrene magnetic nanoparticles based magnetic solid phase extraction technique combined with liquid-solid extraction helped clean-up the sample and preconcentrate the targeted analytes prior to HPLC quantification. The lab prepared nanoparticles were characterised with Fourier transform infrared spectroscopy, atomic force microscopy, X-ray diffraction spectroscopy, as well as vibrating sample magnetometer to study their size, morphology, crystal structure, functional groups and magnetism properties, respectively. Afterwards, optimisation of the parameters affecting extraction efficiency was carried out in order to achieve optimum conditions for extracting pyrethroids residue from fruit samples. Analytical performances were evaluated by carrying out experiments at optimum conditions. Results showed that the limit of detection and limit of quantification were below 0.1445 and 0.5116 ng g^{-1}, respectively for the six pyrethroids tested. The recovery rates were within the range of 73.6%–123.1% with intra-day and inter-day relative standard deviation being less than 16.5% and 15.4%, respectively, suggesting satisfactory reproducibility of the proposed method. Real sample analysis was performed using 6 kinds of commonly consumed fruits obtained from local supermarkets in Singapore, including apples, pears, oranges, lemons, grapes and nectarines. The peel and flesh were tested separately to study the difference of pyrethroids residue in different parts of fruits. The grape sample tested was detected with permethrin residue on its peel. There was no violation since the permethrin amount detected was way much lower than the maximum residue limit set by local government.

1. Introduction

Fruits play an inseparable part in our daily diet as they are known to contain various nutrients, which can help us lead a

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healthy and energetic life (Pertuzatti, Sganzerla, Jacques, Barcia, & Zambiazi, 2015). They are also versatile in the recipes for many popular processed food products, including flavoured soft drinks, fruit wines, puddings, cakes, pies, salads etc. Being abundant in dietary fibres, oligosaccharides, minerals as well as multiple natural antioxidants, the consumption of fruits reduces health risks such as cancer, stroke and coronary heart diseases and meanwhile slows down our ageing process and preserves the youth (Fu et al., 2015; Wang et al., 2012). Noticeably, many fruits show a greater amount of nutrients such as the dark coloured proanthocyanidins, polyphenols and flavonoids on their peels as compared to flesh and thus are recommended by nutrition specialists to be consumed as a whole rather than peeled (Cao et al., 2016).

Synthetic pesticides, such as pyrethroids, are widely used to protect the crops in modern agriculture due to their enhanced performances compared to traditional pest control approaches (Yu, Ang, Yang, Zheng, & Zhang, 2017). However, these effective chemicals in agricultural can be detrimental to our health (Liou, Nayigiziki, Kong, Mustapha, & Lin, 2017; Yu & Yang, 2017), which is one key factor that organic foods now get popular (Li et al., 2015; Liu, Tan, Yang, & Wang, 2017; Sow et al., 2017; Zhang & Yang; 2017; Zhao, Zhang, & Yang, 2017). The chemical structures of several commonly applied pyrethroids in agriculture, including bifenthrin, cypermethrin, decamethrin, fenvalerate, fenpropathrin and permethrin are shown in Fig. 1. According to existing studies, most of the pesticide residues are found on fruit peels rather than the flesh part (Yang et al., 2016; Yang et al., 2016; Yang, Zhao, Kinchla, Clark, & He, 2017). Fernández-Cruz et al. reported that 88% of the fenitrothion residue exist on kaki fruit peels (Fernández-Cruz, Villaroya, Llanos, Alonso-Prados, & García-Baudín, 2004). Li et al. found that majority of the tomato clothianidin residues are detected on their peels (Li et al., 2012). While the peeling of fruits before consumption is a common practice to reduce pyrethroid exposure, much of the nutrients are found on fruit peels, thus decreasing its nutritional value.

After recognising the usage of pyrethroids as a potential health threat, strict regulations have been set up around the world and maximum residue limits (MRLs) for pyrethroids residue in fruits have been drawn up by authorities such as World Health Organisation (WHO), Food and Drug Association (FDA) and the Agri-Food & Veterinary Authority of Singapore (AVA) (AVA, 2017; FDA, 2017; WHO, 2017). In Singapore, more than 90% of food products are imported as it is a country with limited natural resources and the fruits have to be tested to be within the MRLs before it can be released to the market (Isabelle et al., 2010). Although the standards may vary between different countries and regions, the MRLs for different pyrethroids in various fruits and fruit related products are usually set at part per million levels, which are trace amount, in order to safeguard our health when we consume these fruits (Radišić, Vasiljević, Dujaković, & Laušević, 2013). Unfortunately, it is hardly possible for us to make an exhaustive list for MRLs, which means that these regulations are not stringent enough and may have loopholes. Fruits and fruits related products with over amount of pyrethroids residue which might harm our health are still frequently reported (Quijano, Yusà, Font, & Pardo, 2016). And we need not only more elaborated regulation system, but also sensitive, rapid and convenient detection techniques to help us determine the actual amount of pyrethroids in fruit samples (Nguyen, Zhang, Mustapha, Li, & Lin, 2014).

Association of analytical chemists (AOAC) had come up with a series of standard analytical methods for determination of chemical hazards in food materials, which are generally acknowledged as authoritative and reliable (Zarzycki, 2017). The AOAC method for determination of pyrethroids in fruits is liquid-solid extraction combined with solid phase extraction clean-up (Zhang, Zhang, & Jiao, 2014). However, this method suffers from drawbacks such as long analysis time and high cost per test. Scientists also came up with ways to improve the method, including matrix solid-phase dispersion, molecularly imprinted polymers based solid phase extraction and ultrasonic assisted extraction techniques etc. (Gao, Piao, & Chen, 2015; Ling et al., 2016; Ma & Chen, 2014). However, each method has its respective disadvantages such as non-recyclable expensive adsorbents, tedious packing and elution procedures, low selectivity and application limitation for specific

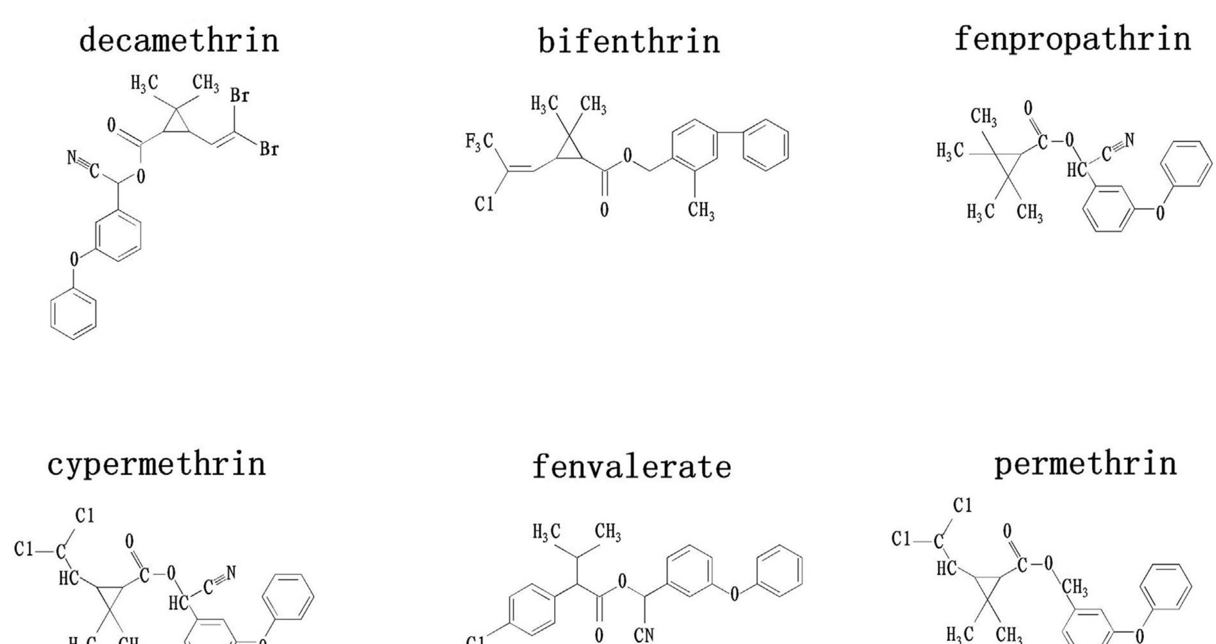

Fig. 1. Chemical structures of six kinds of commonly applied pyrethroids.