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Analytical Methods

Magnetic effervescent tablets containing ionic liquids as a non-conventional extraction and dispersive agent for determination of pyrethroids in milk

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ABSTRACT

Conventional magnetic effervescent tablet has many drawbacks, such as not practicable for field processing, rapid moisture absorption, and poor tablet storage characteristics. Herein, we developed a novel magnetic effervescent tablet containing ionic liquid microextraction (MET-ILM) for determination of pyrethroids in dairy milk. It contains only Na_2CO_3 as an alkali source (no acidic source) in the Fe_3O_4 magnetic tablet; the CO_2-forming reaction is initiated in the acidic solution containing the analytes, and thus the prepared tablet can be stored for long time periods without deterioration. The combined action of extractant and sorbent vastly increase the extraction efficiency. The optimized procedure consisted of an effervescent tablet, 2:1 HCl:Na_2CO_3, and 60 μL $[C_6MIM]PF_6$ as extraction solvent. The LODs for five pyrethroids were 0.024–0.075 μg kg^{-1} with recoveries of 78.3–101.8%. The RSDs were < 4.8% and < 6.3% for intra- and inter-day precisions. Overall, the method is very feasible for use in the field.

1. Introduction

Pyrethroids are synthetic pesticides which are widely applied as insecticides in stored grain, crops and indoor environments. The increasingly widespread use of pyrethroids in our daily lives has contributed to an increased hazard for pyrethroids residue transfer to food-producing animals, which may be acutely toxic and dangerous for human health (Chen et al., 2014; Stanislaw et al., 2013). Humans show somewhat unspecific symptoms after occupational exposure to pyrethroids. Male reproduction and development are primary concerns and children are especially regarded as being highly susceptible to risk from long-term exposure to pyrethroids (Saillenfait, Ndiaye & Sabaté, 2015).

As a result of widespread use, pyrethroid residues are known to migrate to foods, such as vegetable oil, eggs, fruits, vegetables, fish, and milk (Ciscato, Gebara & Spinosa, 2014; Daniela, et al., 2014; Meneghini et al., 2014; Pirsaheb, Fattahi & Shamsipur, 2013; Yu, Ang, Yang, Zheng & Zhang, 2017; Yu & Yang, 2017; Zhang, Wang, Lin, Fang & Wang, 2012). Milk and milk products are consumed regularly in our daily lives on account of their nutritional value and characteristic flavor. However, the presence of pyrethroid residues in milk gives rise to public health concerns because of pyrethroid accumulation from inhaled air, veterinary treatment and contaminated cattle feed (Bushra, Samina & Shafiqur, 2014; Dallegrave, Pizzolato, Barreto, Eljarrat, and Barceló, 2016; Hamid, Wan, Mohd, and Hassan, 2016). Therefore, it is critical to monitor pyrethroid contents in milk due to its importance as a food source resulting in a growing demand to develop simple and efficient methods to analyze trace-level pyrethroids in milk samples.

Because direct determination of pyrethroids is not possible in complex milk samples, effective sample pretreatment and cleanup are required prior to instrumental analysis. Reported pretreatment methods include on-site dispersive liquid–liquid microextraction (DLLME) based on solidification of switchable solvents (Hu, Wang, Qian, Liu, et al., 2016), in-syringe low-density ionic liquid DLLME (Hu, Wang, Qian, Wang, et al., 2016), QuEChERS (quick, easy, cheap, effective, rugged and safe) (Luiz, Bolaños, González, Vidal & Frenich, 2011), membrane protected micro-solid-phase (Sajid, Basheer & Mansha, 2016), and directly suspended droplet microextraction (DSDME) (Liu & Min, 2012). These methods provide adequate efficiency, but have several limitations such as use of organic solvents, long processing time and simultaneous extraction of numerous interference compounds (Wang, Shu, Li, Yang & Qiu, 2016; Zainudin, Salleh, Mohamed, Yap & Muhamad, 2015).

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In recent years, researchers have attempted to develop simple methods that use “green solvents” (e.g., ionic liquids and switchable solvents) to replace traditional volatile organic solvents to separate and concentrate pyrethroids (Chen et al., 2015). For example, the application of magnetic materials and effervescence reactions has recently gained much attention (Yang et al., 2016; Yu & Yang, 2017). A ternary solvent system is composed of target analytes, extraction agent and dispersive agent, and the magnetic sorbent is recovered using a simple magnet. The centrifugation or vortex step can be eliminated by using an external magnetic field. These methods can simplify experimental processing and vastly improve extraction efficiency. However, the effervescence step is often slow and not suitable for field use. In addition, the magnetic effervescent tablets have poor storage characteristics as the acid and alkaline salts in the magnetic effervescent tablets react during storage and absorb moisture.

In conventional microextraction methods, extraction and dispersive solvents are used to concentrate target analytes. Most of these methods employ organic solvents, which are potentially harmful to the environment and may lead to low analyte recovery as the disperser can dissolve the target analytes. Therefore, ionic liquids (ILs) were used in our new method as a “non-conventional extraction and dispersing agent”. ILs are regarded as green solvents due to their special properties, such as thermal stability, low vapor pressure, environmentally benign and good solubility for target compounds (Lu et al., 2011).

To address the limitations of traditional effervescence microextraction techniques, we developed a novel, environmentally-friendly and rapid method for determination of pyrethroids in milk samples. The method employs IL-mediated and effervescence-assisted microextraction for sample pretreatment. First, effervescent tablets were prepared with Fe_3O_4 magnetic nanoparticles, $[C_nMIM][PF_6]$ and sodium carbonate. Next, the magnetic effervescent tablet was placed in the acidified sample solution containing the analytes and the extraction agent was dispersed into the solution as a result of effervescence. Finally, the analytes sorbed to the magnetic nanoparticles were recovered using a magnet. Because this method does not rely on complex and environmentally sensitive devices or instrumentation, it can easily be performed in the field. The magnetic effervescent tablets are stable in storage because the acid and alkaline salts are not in contact with other in the effervescent tablets, and the Fe_3O_4 magnetic nanoparticles can be recovered and recycled. The newly developed method was optimized and applied to pyrethroid detection in dairy milks with different fat contents. The method is simple, rapid, environmentally benign and low cost making it an attractive technique for detection of trace pesticides in food and environmental samples.

2. Materials and methods

2.1. Chemicals and reagents

Standards for the five pyrethroid insecticides (bifenthrin, fenpropathrin, permethrin (mixed isomers), deltamethrin (mixed isomers) and fenvalerate (mixed isomers)) and chromatographic-grade isooctane were purchased from Aladdin Reagent Co. (Shanghai, China). The chemical structures of the five pyrethroid insecticides are shown in Supplementary Fig. 1. Sodium chloride (NaCl), sodium carbonate (Na_2CO_3), acetone and hydrochloric acid (HCl, analytical grade) were supplied by Zhejiang Zhongxing Chemical Reagent Co. (Hangzhou, China). Magnetic Fe_3O_4 nanoparticles were purchased from Shanghai Mclean Biochemical Sci. & Technol. Co. (Shanghai, China). Three ionic liquids (purity > 99.0%) were gratis supplied by Shanghai Chengjie Chemical Co. (Shanghai, China): 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4MIM][PF_6]$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6MIM][PF_6]$), and 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8MIM][PF_6]$). Ultrapure water was prepared using a Milli-Q system (Millipore, Bedford, MA, USA).

Mixed standard solutions of pyrethroid insecticides were prepared in isooctane at a concentration of 1000 μg L^{-1}. A HCl solution (1.47 mol L^{-1}) was used to adjust sample pH. Six dairy milk samples were purchased from Wenzhou Baixin Supermarket (Wenzhou, China): full-fat milk (high calcium milk; Yili brand, Inner Mongolia, China), pure milk (6% fat content; Yili brand), half-skimmed milk (high calcium low fat milk; Yili brand), yogurt (2% fat content; Yili brand), skimmed milk (Shuangwaiwai brand; Wahaha, Hangzhou, China), and skimmed milk (zero fat content; Yili brand). Milk samples were stored in a 4 °C refrigerator for 10 min, centrifuged at 3000 rmp for 5 min, filtered, and stored at 4 °C before further analysis.

2.2. GC analysis

The five pyrethroids were analyzed using an Agilent 7890 GC (Agilent Technologies, Wilmington, DE, USA) equipped with an electron capture detector (ECD), a splitless injector and an Agilent HP-5 fused-silica capillary column (30 m × 0.32 mm i.d. and 0.25 μm film thickness). The injection and detector temperatures were set at 260 and 300 °C, respectively. Oven temperature was initially held at 80 °C for 3 min, increased to 200 °C for 3 min at 15 °C min^{-1}, increased to 250 °C for 2 min at 5 °C min^{-1}, increased to 280 °C for 2 min at 8 °C min^{-1}, followed by a 10 °C min^{-1} ramp to 300 °C, and held at 300 °C for 2 min. Nitrogen (purity 99.999%) was used as carrier gas at a flow rate of 2 mL min^{-1}.

2.3. Preparation of magnetic effervescent tablets

For 10 tablets, a mixture of Na_2CO_3 (3.392 g), Fe_3O_4 nanoparticles (100 mg) and $[C_nMIM][PF_6]$ (60 μL) was ground into a fine and homogeneous powder. An aliquot (0.1866 g) of the above mixture was compressed into a magnetic effervescent tablet (8-mm diameter × 2-mm thickness) using a T5 Single Punch Press (Shanghai Pharmaceutical Equipment Co., Shanghai, China) and dried at 60 °C for 1 h in a drying oven.

2.4. MET-ILM procedures

Fig. 1 shows the schematic diagram of the proposed MET-ILM procedure incorporating a non-conventional extraction and dispersive agent. An appropriate volume of standard solution (1.0 mg L^{-1}), 1.95 mL of 1.47 mol L^{-1} HCl and 2.0% (w/v) NaCl was homogeneously mixed in 8 mL pretreated milk samples in a centrifuge tube (Fig. 2a). Subsequently, a magnetic effervescent tablet was slowly placed in the centrifuge tube (Fig. 2b). This resulted in a large amount of bubble formation with the effervescence occurring from bottom to top in a 60 °C water-bath (Fig. 2c). The effervescence procedure lasted for ca. 2 min and the extraction solvent, i.e., ionic liquid, was effectively dispersed by the release of CO_2 (Fig. 2d). Then, a magnet was placed at the bottom of the centrifuge tube, which attracted and isolated the ionic liquid-coated magnetic nanoparticles containing the sorbed analytes. The magnetic nanoparticles were gently settled until they were completely sedimented (Fig. 2e). The supernatant was discarded and 500 μL acetone was added to dissolve the analytes from the magnetic nanoparticles. The organic solvent was passed through a 0.22 μm filter, dried with a gentle nitrogen gas flow and dissolved in isooctane. Finally, 1.0 μL of the extraction solvent was injected into the GC-ECD for pyrethroid quantification.

2.5. Statistical analysis

Experimental data were reported as mean ± SD (standard deviation, n = 3). Post-hoc Tukey test was used for multiple mean comparisons among different treatments (Fig. 3a). Dunnett test was applied for two mean comparisons among different treatments (Fig. 3d and f). All statistical analyses were conducted with SPSS 18.0 (SPSS, Chicago, USA) using a $*p < 0.05$, $**p < 0.01$, or $***p < 0.001$