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Analytical Methods

Vortex-assisted magnetic dispersive solid-phase microextraction for rapid screening and recognition of dicofol residues in tea products

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ABSTRACT

A simple and rapid vortex-assisted magnetic dispersive solid-phase microextraction (VAMDSME) method coupled with gas chromatography-electronic capture detection was developed for rapid screening and selective recognition of dicofol in tea products. The magnetic molecularly imprinted microspheres (mag-MIMs) synthesised by aqueous suspension polymerisation using dichlorodiphenyltrichloroethane (DDT) as a dummy template showed high selectivity and affinity to dicofol in aqueous solution and were successfully applied as special adsorbents of VAMDSME for rapid isolation of dicofol from complex tea matrix. Good linearity was obtained in a range of 0.2–160 ng g^{-1} and the limit of detection based on a signal to noise ratio of 3 was 0.05 ng g^{-1}. The recoveries at three spiked levels ranged from 83.6% to 94.5% with the related standard deviations (RSD) $\leqslant$ 5.0%. The VAMDSME-GC protocol, which took advantages of the selective adsorption of molecularly imprinted microspheres and rapid magnetic phase separation, as well as the short equilibrium time by vortex-assisted, could avoid the time-consuming procedures related to other traditional extraction methods.

1. Introduction

Dicofol [1,1-bis(4′-chlorophenyl)2,2,2-trichloroethanol, Kelthane] is an organochlorine pesticide used widely as a pre-harvest acaricide on cotton, fruits, vegetables, teas and field crops, and a substitute for organochlorine pesticides such as dichlorodiphenyltrichloroethane (DDT) (Li et al., 2009). Since dicofol has a similar structure to DDT, it is associated with similar concerns to DDT such as its persistence, bioaccumulation, residual period, acute toxicity, and neurological damage in humans and animals (Fujii et al., 2011). Thereby, the residues of dicofol in a wide variety of crops including teas are strictly limited by many countries (Wang, Yan, Qiu, Qiao, & Yang, 2011). Since dicofol is acutely toxic to humans and thought to be a human carcinogen, it is important to develop a simple, accurate, rapid and sensitive analytical method for determination of dicofol in tea products.

Due to the complexity of sample matrices and the trace levels of dicofol in samples, pre-treatment is usually necessary before instrumental analysis. Recently, liquid–liquid extraction (LLE), solid-phase extraction (SPE), matrix solid-phase dispersion (MSPD), single-drop microextraction (SDME), and microwave-assisted steam distillation (MASD) have been used in sample preparation for the extraction of dicofol from environmental water (Wang, Weston, Ding, & Lydy, 2010), vegetables (Zhang et al., 2008), fish (Chen et al., 2009), soil (Rissato, Galhiang, Apon, & Arruda, 2005), and apple samples (Singh et al., 2009). However, solvent extraction generally requires large volumes of organic solvents and multiple steps, and conventional SPE sorbents (C_{18}, silica, florisil, etc.) usually co-extract compounds that interfere with analysis due to non-specific interface interactions. Thus, the development of new sorbents with high affinity, specific recognition, and high stability is desirable.

Molecularly imprinted polymers (MIPs), as an artificial template recognising materials with high affinity and selectivity, have attracted considerable attention since their inception by Wulff and Sarhan (Wulff & Sarhan, 1972; Wulff, 2002) and Vlatakis et al. (Liu et al., 2011; Vlatakis, Andersson, Muller, & Mosbach, 1993). These polymers have many outstanding advantages, such as high selectivity and affinity to target molecule, high mechanical strength, chemical stability, and reusability (Chang, Chen, & Li, 2012). These properties open up wide opportunities for the use of MIPs in many fields, such as SPE (Qiao et al., 2011), chromatographic separation (Xia, Guo, Song, Zhang, & Zhang, 2006), membrane separation (Zhu, Zheng, Xie, & Wang, 2012), sensors (Qiu, Luo, Sun, Lu, & Li,

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2012), drug release (Abeouss, Asad, Azodi-Deilami, Beik-mohammadi, & Aslanzadeh, 2011), and catalysts (Resmini, 2012), etc. However, the template leakage of MIPs in real applications often affects the results of quantitative analysis (Yan, Liu, Gao, & Sun, 2013). Moreover, the small MIPs particle size makes separation from aqueous samples difficult, which restricts their application (Chang et al., 2012).

As known, magnetic materials as sorbents have several advantages in comparison with traditional sorbents (Li et al., 2010, 2011; Xu et al., 2011; Zhang, Tan, Hu, & Li, 2012). The separation process can be performed directly in sample solution containing solid sorbent, and the magnetic nanoparticles (MNPs) can be collected and separated from liquid phase using a magnetic field, which avoids the tedious filtration or centrifugation procedure (Meng, Bu, Deng, & Zhang, 2011; Wu, Zhao, Feng, Wang, & Wang, 2011). Therefore, when MNPs are coated with MIPs, these suspended magnetic dummy molecularly imprinted microspheres (mag-MIMs) can not only selectively recognise analytes in the sample solution, but also can be easily isolated from the sample using a magnetic field (Jing et al., 2011). Moreover, the mag-MIMs adsorbents exhibit strong recognition of MIPs, super-paramagnetism, and greater surface area of magnetic composite materials (Lin et al., 2012).

In the present work, a simple and rapid vortex-assisted magnetic dispersive solid-phase microextraction (VAMDSME) technique using mag-MIMs adsorbents was developed for the first time to rapidly extract dicofol in tea products. The mag-MIMs synthesised by aqueous suspension polymerisation using DDT as dummy template showed high selectivity and affinity to dicofol and were successfully applied as selective adsorbents of VAMDSME for the isolation of dicofol from complex tea matrix. Moreover, vortex-mixing as a mild microextraction shorten the time for equilibrium adsorption whilst increasing extraction efficiency.

2. Experimental

2.1. Chemicals

Dicofol and DDT were obtained from Dacheng Pesticide Co. Ltd. (Shandong, China) and their molecular structures are shown in Fig. 1. Dichloromethane (DCM), toluene, acetone, and hexane were obtained from Huadong Chemical Co. (Tianjin, China). Methanol (MeOH), acetonitrile (ACN), acetic acid (AA), methacryclic acid (MAA), oleic acid (OA), aqueous ammonia, *n*-hexane, and 2,2-azobisisobutyronitrile (AIBN) were purchased from Kermel Chemical Co. Ltd. (Tianjin, China). Iron trichloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and iron dichloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) were purchased from Fuchen Chemical Co. Ltd. (Tianjin, China), and ethylene glycoldimethacrylate (EGDMA) was obtained from Sigma–Aldrich (St. Louis, MO, USA). Double deionized water was filtered with 0.45 μm filter membrane before use.

2.2. Instrumentation and conditions

The chromatographic analysis was carried out on a Shimadzu GC-2014 system equipped with a split/splitless injector and ECD-2014 detection (Shimadzu, Japan). High purity nitrogen (99.999%) was used as carrier gas with flow rate of 5.0 mL/min and split ratio of 5. The DB-5 capillary column (5% phenyl-methylpolysiloxane, 30 m × 0.53 mm × 1 μm) was obtained from Agilent Co. (Wilmington, DE, USA). An N-2000 data workstation (Zheda Zhineng Co. Ltd., Hangzhou, China) was used as the data acquisition system. The temperature-programmed mode was as follows: the oven temperature was 210 °C and held for 20 min. The temperature of injection port and detection were set at 230 °C, and 280 °C, respectively. A Vortex-5 oscillator (Qilin Medical Instrument, Jiangsu, China) was used to assist the analyte extraction from the tea solution. The properties of mag-MIMs were observed by a scanning electron microscopy (KYKY-2800B, operating at 25 kV), Fourier-transform infrared spectroscopy (Shimadu, Japan), and a vibration sample magnetometer (LakeShore 7307, at 300 K).

2.3. Preparation of Fe_3O_4 with hydrophobic shell

The Fe_3O_4 magnetites were prepared by co-precipitation method (Deng, Wang, Hu, Yang, & Fu, 2005) as follows: 0.02 mol $FeCl_2{\cdot}4H_2O$ and 0.03 mol $FeCl_3{\cdot}6H_2O$ were dissolved into 100 mL of deaerated water, and 2 mL of oleic acid was added to the mixture. The mixture was subjected to ultrasound for 20 min and stirred (600 rpm) under nitrogen whilst ammonium hydroxide (15 mL) was added drop-by-drop and the temperature increased to 60 °C. After 30 min, another 2 mL of oleic acid was added dropwise to the mixture, which was stirred at 600 rpm and then left to react for 1 h at 80 °C. After that, the magnetic precipitates were isolated from the solution using a magnet, and washed with water and ethanol in sequence before being dried at 50 °C in vacuum for 24 h.

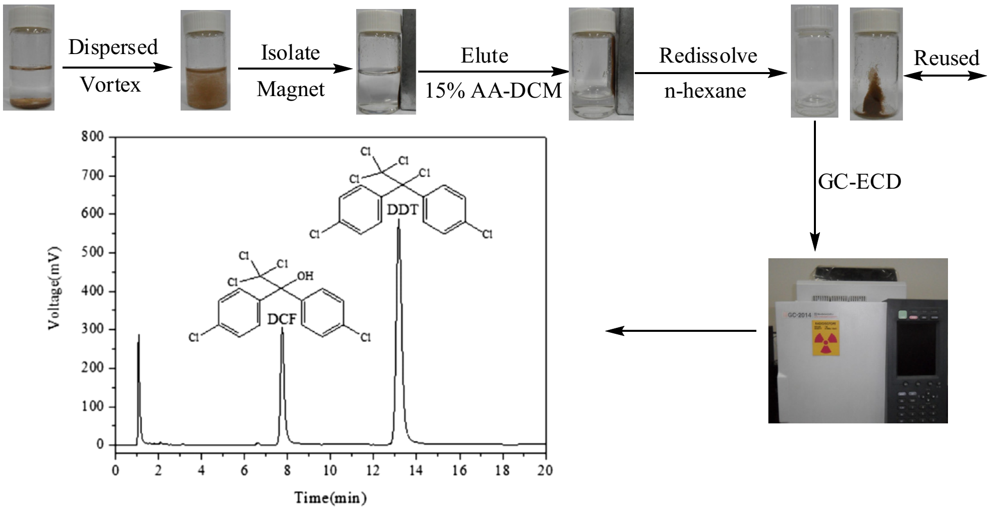

Fig. 1. The schematic diagram of VAMDSME-GC method.