Journal of Chromatography B, 998-999 (2015) 72–79

Contents lists available at ScienceDirect

Journal of Chromatography B

journal homepage: www.elsevier.com/locate/chromb

A novel method based on MSPD for simultaneous determination of 16 pesticide residues in tea by LC–MS/MS

Yalin Cao[a,b], Hua Tang[c], Dazhou Chen[c], Lei Li[a,b,*]

[a] *State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China*
[b] *Beijing Key Laboratory of Environmentally Harmful Chemical Analysis, Beijing University of Chemical Technology, Beijing 100029, China*
[c] *Division of Metrology in Chemistry, National Institute of Metrology P.R. China, Beijing 100013, China*

ARTICLE INFO

Article history:
Received 3 December 2014
Received in revised form 9 June 2015
Accepted 15 June 2015
Available online 2 July 2015

Keywords:
Tea
Pesticides
MSPD
PVPP
LC–MS/MS

ABSTRACT

A novel method based on matrix solid phase dispersion (MSPD) coupled with liquid chromatography-tandem mass spectrometry was established for the determination and the quantification of 16 pesticides (5 carbamates, 4 organophosphorus, and 7 pyrethroids) in various tea. Matrix dispersive sorbent and further cleanup sorbent were applied to improve the efficiency of extraction and purification. PVPP, PSA and GCB were introduced as further cleanup sorbents packed at the bottom of the MSPD to remove co-eluting matrix components. Different experiment conditions, such as type of eluting solvent, its volume, matrix dispersive sorbent, sample to matrix dispersive sorbent mass ratio, and the dosage of cleanup sorbents were thoroughly studied and optimized. It was found that polyvinylpolypyrrolidone (PVPP), an inexpensive and excellent absorbent, could effectively remove polyphenols in tea, which was seldom reported before. The method showed satisfactory linearity over the range assayed 0.9986–0.9999 (1–500 ng g^{-1} for 5 carbamates and 4 organophosphorus, 2–800 ng g^{-1} for 7 pyrethroids), the limits of detections (LODs) ranged from 0.01 to 1.38 ng g^{-1}, and the limits of quantifications (LOQs) were ranging from 0.03 to 4.74 ng g^{-1}. The recoveries using this method at three spiked concentration levels (10, 100, and 500 ng g^{-1}) range from 87.7 to 99.6%. The relative standard deviation (RSD) was from 0.2 to 9.6% in all case. The proposed analytical method has been successfully applied for the analysis of 16 pesticides in commercial tea.

1. Introduction

Tea, a most widely consumed beverage throughout the world, has specific aroma and antioxidant property that is good for human health. The tea quality and safety have attracted an ever-increasing attention. Pesticide residue is one of the major chemical contaminants found in tea matrice. Carbamate, organophosphorus and pyrethroids are widely used during the cultivation of tea [1–3].These pesticides have been shown to have potentially harmful effects on the environment and human beings [2,4,5]. Therefore, some developed countries and international organizations have issued maximum residue limits (MRLs) for these pesticides in tea [6]. Due to the high risk for the consumer health, rapid and cost-effective multiple pesticide residue analysis represents an important task for both the tea producers and regulatory agencies.

To our knowledge, there is no effective standardized extraction method for analyzing pesticides in tea. In recent years, many extraction and purification methods for pesticide residues in tea have been developed, such as QuEChERS (quick, easy, cheap, effective, rugged and safe) [7–14], dispersive solid phase extraction (d-SPE) [14–17], Stir Bar Sorptive Extraction (SBSE) [18,19], sample clean-up based on magnetic multiwalled carbon nanotubes (MMWCNTs) or multiwalled carbon nanotubes (MWCNTs) [2,16,20], solid-phase microextraction (SPME) [21,22], *etc.* The most commonly employed traditional cleanup techniques comprise liquid–liquid extraction (LLE) [23], solid-phase extraction (SPE) [24–27], gel permeation chromatography (GPC) [28], and matrix solid-phase dispersion (MSPD) [29]. It is well known that these classical methods (LLE, GPC) are time costly and consume large amounts of organic solvents, SPE columns usually are expensive, and original MSPD is not suit for complicated tea matrix due to the matrix effects. These methods used in recent years (d-SPE, SBSE, MMWCNTs, MWCNTs, SPME), either are time consuming, expensive or need to synthesize a special material, the synthesis process is tedious and complicated, so they are not suited for routine detection. Although QuEChERS is

---

[*] Corresponding author. Fax: +86 10 64434898.
E-mail address: lilei@mail.buct.edu.cn (L. Li).

http://dx.doi.org/10.1016/j.jchromb.2015.06.013
1570-0232/

more simple and sensitive, it also needs many operation steps, such as repetitious shaking, centrifugation and transfer.

The aim of this research was to develop a rapid, cost-effective, one-step method based on matrix solid-phase dispersion (MSPD) to simultaneously determine 16 pesticides (5 carbamates, 4 organophosphorus and 7 pyrethroids) in tea by LC–MS/MS. Due to the fact that tea is a much complicated matrix, which contains many pigments, alkaloids and polyphenols, *etc.* [12,15], which can severely interfere with pesticide analysis, multiple sorbents are applied for extraction and purification. Florisil/C18 (1:1, w/w) served as matrix dispersive sorbent to facilitate the extraction process. PVPP, PSA, GCB served as further clean-up sorbents to remove polyphenols, caffeine, pigments, alkaloids, *etc.* The extraction system and further purification system were both prepared in a column, thus extraction and purification achieved by one step when collecting the eluent. It has been reported that polyvinylpolypyrrolidone (PVPP) is usually used as antioxidant and stabilizer in drinks like beer, wine [32–34]. However, PVPP can interact with many materials, especially aromatic compounds containing phenyl, due to its special molecular structure. As we all known, polyphenols are aromatic compounds, which can be absorbed by PVPP. Therefore, in this paper, PVPP was selected as sorbent to cleanup tea matrix, which was seldom reported before. Acetonitrile (ACN) was served as elution solvent to reduce co-extracting matrix interferences. The results showed that the established method was suitable for routine analysis of 16 pesticides in real tea, its sensitivity and accuracy were in line with EU standards.

2. Experimental

2.1. Apparatus and reagents

The instruments used in the experiment include: a TSQ Vantage triple quadrupole mass spectrometer (Thermo Fisher, USA) equipped with an electrospray ionization (ESI) interface, UMX5 high precision electronic balance (Max = 5.1 g, d = 0.1 mg, METTLER TOLEDO Co.), XS205 electronic balance (Max = 8.1 g, d = 0.01 mg, METTLER TOLEDO Co.), KQ3200E ultrasonic cleaners (Kunming ultrasonic instrument Co., Ltd.), nitrogen evaporator (V-EVAPTM111, Organomation Associate, Jnc.) and Gradient A10 water purification System (Milli-Q Co. USA). HPLC-grade acetonitrile (99.9%) and methanol (99.9%) were purchased from Sigma, (Germany). Dichloromethane (99.9%) was provided by Fisher Scientific Inc. (Geel, Belgium, UK). Ammonium acetate (analytical reagent grade) and formic acid (96% purity, HPLC-grade) were purchased from Merck KGaA, (TEDIA, USA). YMC*GEL ODS-A (C18, 12 nm S-50 μm). Florisil (60-100mesh ASTM) were obtained from Wz.der Floridin Company, USA. PSA (particle size 40 mm) and GCB were obtained from Supelco (Sigma–Aldrich Corp., USA). Sea sand (60–100 mesh) was purchased from Sinopharm Chemical Reagent Co., Ltd. The Florisil was calcined at 500 °C for 5 h in a muffle furnace to be actived. Polyvinylpolypyrrolidone (PVPP) was of analytical grade. Pesticide standards, Carbaryl, Pirimicarb, Propoxur, Carbosulfan were purchased from Sigma–Aldrich, Accustandard, (USA) and Dr Ehrenstorfer, (Germany). The purity of the pesticides standards were from 98.5% to 99.9%. Pesticide standard solutions, Methomyl, Dimethoate, Malathion, Chlorpyrifos, Fenitrothion (consistency 1000 $\mu g\,g^{-1}$), Kresoxim-methyl, Bifenthrin, Fenpropathrin, Lambda-cyhalothrin, Cypermethrin, Deltamethrin, Fenvalerate (consistency 100 $\mu g\,g^{-1}$), were obtained from the National Standard Material Research Center of the People's Republic of China. Internal standards (ISs), Triphenylphosphate (TPP), D_6-dimethoate, D_{10}-chlorpyrifos (purity > 98.5%) and D_6-*trans*-cypermethrin (100.000 mg/L in acetone, Purity > 98.5%) were purchased from Dr Ehrenstorfer, (Germany). Carbamate and the internal standard substance were weighed 1 mg (accurate to 0.1 mg) and a 200 $\mu g\,g^{-1}$ solution in methanol was prepared and stored under refrigerator conditions (−18 °C) protected from light. Standard working solutions of various concentrations were prepared daily by appropriate dilution of aliquots of the stock in initial mobile phase.

All the tea samples were purchased from local markets in Beijing, and analytically conformed pesticides-free tea from the National Standard Material Research Center of the People's Republic of China was used as the blank for matrix matched calibration and recovery evaluations.

2.2. Purification system preparation

The empty column and glass filter paper used in this study were reused from ISOLUTE SLE_{+} Column (25 mL capacity, Biotage, Sweden), which were ultrasoniced by alcohol for 10 min, rinsed 3 times by acetone, and evaporated to dry before used. In order to efficiently use cleanup sorbents, GCB, PVPP were dispersed by sea sand. Firstly, 50 mg GCB and 450 mg sea sand were gently blended until obtaining a homogeneous system and then transferred to the column with a glass filter paper at the bottom. Secondly, 1.0 g PSA and 1.5 g sea sand were mixed as above mentioned process and then filled into the column on the top of GCB. Lastly, 750 mg PVPP was directly added to the column on the top of PSA and then the system was covered by another filter paper. The cleanup system was prepared for the following experiments.

2.3. Extraction and cleanup

The tea was crushed and passed through a 40 mesh sieve (about 245 mm). Aliquots of 0.5 g tea was transferred to a mortar (30 mL capacity), then 100 μL 2 $\mu g\,g^{-1}$ mixed internal standard solution (TPP, D_6-dimethoate, D_{10}-chlorpyrifos and D_6-*trans*-cypermethrin) in methanol was added as a quality control for the entire procedure, after solvent evaporation (approximately one hour), gently homogenized with a pestle with 0.75 g C18 and 0.75 g FLS for 5 min to obtain a homogeneous mixture. Then the homogeneous mixture was transferred into the purification column (prepared in 2.2), successively, the column was connected to a vacuum system for solid phase extraction adjusting the flow to 0.5 mL/min. The elution step was carried out with 20 mL acetonitrile, 8 mL the first time, 10 mL for the second time. 2.0 mL additional eluent was adopted to wash the mortar and pestle, and then transferred into the column. The collected solution was evaporated under a gentle stream of nitrogen at 35 °C. Finally, the residue was dissolved in 1.0 mL initial mobile phase, and then filtered through a 0.22 μm PTFE filter for LC–MS/MS analysis.

To the matrix matched standard the residue of blank tea was dissolved in 1.0 mL spiked solution, it was used in recovery studies and matrix effect studies.

2.4. LC–MS/MS analysis

A Finnigan Surveyor HPLC system (Thermo Fisher, USA) equipped with a Finnigan Surveyor Autosampler Plus and Finnigan Surveyor MS Pump Plus was used. A ZORBAX Eclipse Plus C18 (100 mm × 2.1 mm, I.D., 3.5 mm, Agilent, USA) was used as an analytical column, fitted with a Zorbax Reliance Cartridge guard column (12.5 mm × 4 mm). The mobile phase A was water with 10 $\text{mmol}\,L^{-1}$ ammonium acetate and the mobile phase B was methanol. The flow-rate was 0.2 $\text{mL}\,\text{min}^{-1}$ and injection volume was 5 μL in each study. The temperatures of the column and sample room were set at 30 °C and 4 °C, respectively. The gradient-elution analysis program is listed in Table S1.