



# An enhanced sensitivity and cleanup strategy for the nontargeted screening and targeted determination of pesticides in tea using modified dispersive solid-phase extraction and cold-induced acetonitrile aqueous two-phase systems coupled with liquid chromatography-high resolution mass spectrometry



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## ARTICLE INFO

### Chemical compounds studied in this article:

Caffeine (PubChem CID: 2519)  
 Acetamidiprid (PubChem CID: 213021)  
 Carbendazim (PubChem CID: 25429)  
 Chlorpyrifos (PubChem CID: 2730)  
 Imidacloprid (PubChem CID: 86418)  
 Thiamethoxam (PubChem CID: 5821911)  
 Fipronil (PubChem CID: 3352)  
 Difenconazole (PubChem CID: 86173)  
 Buprofezin (PubChem CID: 50367)  
 Methomyl (PubChem CID: 4109)

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 High resolution mass spectrometry

## ABSTRACT

At present, matrix interferences in tea are still a great challenge for analysis of multi-pesticide residues. Herein, a simple sample preparation method was developed based on the modified dispersive solid-phase extraction (DSPE) procedure and cold-induced acetonitrile aqueous two-phase systems (ATPS). In modified DSPE procedure, polyvinylpyrrolidone (PVPP) was selected as the matrix dispersive adsorbent to remove polyphenols from the tea with the removal rate of > 98.3%. Using cold-induced acetonitrile ATPS, caffeine of the tea extract was sharply reduced by 81.2%, and a 0.798–3.167 of enrichment factor for the representative pesticides was achieved. In liquid chromatography-high resolution mass spectrometry analysis, a full scan/data independent acquisition approach was used for the nontargeted screening and targeted determination of pesticides. In data analysis, an in-house database of pesticides was constructed, and a simple accurate mass calibration method was used to correct the accurate mass variation, which was conducive to reduce the number of false detects.

## 1. Introduction

Tea is the most popular consumed drink in the world, except the water. Due to the presence of many functional components, such as polyphenols, caffeine and amino acids, tea has extensive health benefits for humans (Carneiro, Batista, Braga, Nogueira, & Rahal, 2016; Gramza-Michalowska et al., 2016; Singh & Katiyar, 2013). In the world, pesticides are intended to control pests (including weeds) and serve as plant protection products. So, it is an inevitable use of pesticides throughout tea planting and growth to protect tea from weeds, fungi or insects. However, pesticide residues in tea can be indirectly consumed

by people, which may cause acute and delayed health effects on people exposed to excessive pesticides (Kame & Hoppin, 2004). In view of wide consumption in tea and potential toxicity of some pesticides, there is the more and more attention for pesticides control, monitoring and exposure risk assessment in tea (Cao et al., 2018; Cladiere, Delaporte, Le Roux, & Camel, 2018; Colapinto, Arbuckle, Dubois, & Fraser, 2015; Li, Wang, Gao, Song, & Lu, 2018). To protect the health of consumers, a simple, sensitive and accurate multi-pesticide residues method is urgently needed for risk monitoring and exposure assessment in tea.

A quick, easy, cheap, effective, rugged, and safe (QuEChERS) sample preparation method based on the dispersive solid-phase

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extraction (DSPE) procedure has been well-developed for analysis of multi-pesticide residues in food over a decade (Gonzalez-Curbelo et al., 2015; Ma et al., 2018; Zhan, Ma, Huang, Jian, & Zhao, 2017). Pesticides in high moisture food, such as vegetables and fruits, are often extracted using acetonitrile (MeCN), followed by salt-out assisted phase separation and DSPE cleanup. In DSPE procedure, primary secondary amine (PSA), graphitized carbon black (GCB), C18, Z-Sep+ and multi-walled carbon nanotubes (MWCNTs) are the most widely-used solid sorbents to adsorb the interferences of the extracts (Faraji, Noorbakhsh, Shafieyan, & Ramezani, 2018; Han et al., 2016; Rejczak & Tuzimski, 2017; Ucles et al., 2015). Modified QuEChERS methods were also applied to tea matrices for pesticide residues analysis (Chen et al., 2018; Chen, Yin, Wang, Jiang, & Liu, 2014; Jiao et al., 2016). For example, tea (as a dry sample) needs to be presoaked in water (H<sub>2</sub>O) before salt-out assisted phase separation, because most references have reported that the addition of water in presoaking tea was conducive to extraction of pesticides. Additionally, a new adsorbent, polyvinylpyrrolidone (PVPP), was applied in DSPE procedure to eliminate tea polyphenols (Hou et al., 2015; Jiao et al., 2016). It is well known that tea contains high content of caffeine accounting for about 3% of tea's dry weight. High content of caffeine in the tea causes serious pollution and ion signal suppression to the ESI source. With the increase of tea samples injected into analytical column, strong residue of caffeine in the background baseline would be occurred, which not only aggravate the contamination of the analytical column, but also have a certain matrix effect for the target pesticides. However, the existing methods of sample preparation were difficult to remove caffeine well. To the best of our knowledge, only a reference was available for eliminating caffeine effectively by planar solid phase extraction procedure, in which, planar thin-layer chromatography (TLC) was used to completely separate pesticides from caffeine and to focus them into a sharp zone, followed by extraction of the target zone by the TLC-MS interface (Oellig & Schwack, 2012). Nevertheless, this procedure required additional equipment and complex operation steps, and the possible drawback was that some pesticides, similar polarity to caffeine, were easily co-removed with caffeine. Some researchers had adopted another way using a dilution of the QuEChERS sample extract by a factor of 25–40, which would reduce ion suppression to less than 20% (Stahnke, Kittlaus, Kempe, & Alder, 2012). Jiao et al. reported that a dilution factor of 20 for QuEChERS sample extract could also eliminate the matrix effect of eight neonicotinoid pesticides in six types of tea (Jiao et al., 2016). However, this dilution treatment would inevitably reduce the sensitivity of quantitative analysis for multi-pesticide residues. As such, there is a need of a simple and effective sample preparation that is not only capable of removing the interferences in tea, especially for caffeine, but also applicable to satisfying the accurate and sensitive determination of multi-pesticide residues in large batch of tea sample.

Cold-induced acetonitrile aqueous two-phase systems (ATPS) was first previously used by Gu et al. in protein purification (Gu, Gu, Zheng, Wiehl, & Kopchick, 1994; Pence & Gu, 1996), and then they subsequently applied it to phase partition of some antibiotics, peptides and amino acids (Gu & Zhang, 2007). Recently, Chung et al. developed a multi-residue veterinary drugs method in milk, egg and meat based on this technique (Chung & Lam, 2015), and Shao et al. also applied this technique for phase separation of some compounds from fish matrices (Shao, Agar, & Giese, 2017). Compared with salt-out assisted acetonitrile ATPS widely employed for initial phase separation in QuEChERS method, cold-induced acetonitrile ATPS does not need to utilize any salts, which can reduce the cost of salt and avoid the addition of new impurities. Furthermore, another special merit of cold-induced acetonitrile ATPS is that different concentrations of MeCN/H<sub>2</sub>O mixture can yield different phase separation ratio (defined as a ratio of the volume of upper layer to the volume of lower layer). By this merit, we developed a new sample preparation method to complete the simultaneous sample enrichment and effective sample cleanup in this study. To the best of our knowledge, this is the first time to apply this technique for

multi-pesticide residues in complex tea matrices. In addition, a one-step simultaneous extraction and cleanup method based on the modified DSPE was also proposed in this work.

In recent years, with the development of full scan (FS) detection technique, liquid chromatography-high resolution mass spectrometry (LC-HRMS) was more and more widely used in multi-pesticide residues analysis due to its high throughput and the ability of nontargeted screening (Gomez-Ramos, Ferrer, Malato, Aguera, & Fernandez-Alba, 2013; Goon, et al., 2018; Saito-Shida, Hamasaka, Nemoto, & Akiyama, 2018). Using FS mode, a qualitative analysis by fragmentation approach often needs to be performed to reduce the number of false detects, in which, three different fragmentation approaches, including data-dependent acquisition (DDA), data independent acquisition (DIA) and all ion fragmentation (AIF) have been described and used in recent studies (Farre, Pico, & Barcelo, 2014; Goon et al., 2018; Hu et al., 2017; Jia et al., 2017; Kumar et al., 2013). The present work evaluates these three fragmentation approaches and establishes a suitable data acquisition method for nontargeted multi-pesticide residues analysis.

## 2. Materials and methods

### 2.1. Chemicals and materials

Acetonitrile (MeCN), methanol (MeOH), formic acid and ammonium formate (HPLC grade) were supplied from Fisher Scientific (Fair Lawn, NJ, USA) and Tedia (Weston, OH, USA). Polyvinylpyrrolidone (PVPP) was analytical-grade and obtained from J&K Scientific (Beijing, China). C18, PSA and NanoCarb adsorbents were purchased from Bonna-Agela Technologies (Tianjin, China). GCB powder was purchased from Shimadzu-GL Sciences (Shanghai, China), and Z-Sep+ and MWCNTs powder (> 98% carbon basis, O.D. × L: 6–13 nm × 2.5–20 μm) was obtained from Sigma-Aldrich (Shanghai, China). Deionized water (H<sub>2</sub>O, Milli-Q) was used throughout this study. Multi-pesticide standards were all obtained from Dr. Ehrenstorfer (Augsburg, Germany), and isotope internal standards (ISs, imidacloprid-d4 and chlorpyrifos-d10) were purchased from C/D/N Isotopes, Inc (Pointe-Claire, Quebec, Canada).

### 2.2. Sampling and preparation of tea samples

A total of ninety seven tea samples, including oolong, white, black, green, dark and yellow tea, were collected in local markets from Fujian and Beijing Provinces, China. A tea sample (FV-T02) with certificated values for target pesticides was obtained from the European Union Reference Laboratories (EURLs).

The tea sample extract was prepared as described in Fig. S1, Supplementary material, briefly summarized herein: (1) 1.0 g of tea sample spiked with 20 μL of mixed ISs (1 mg/L) was soaked in 2 mL of H<sub>2</sub>O for 30 min, then added with 0.4 g of PVPP, and vortexed for 1 min; (2) the sample was extracted ultrasonically for 15 min with 8 mL of MeCN and centrifuged at 7500 rpm for 5 min; (3) the supernatant (1 mL) was transferred to a 2 mL centrifuge tube, and added with 0.8 mL H<sub>2</sub>O, and vortexed for 30 s; (4) the diluted extract obtained in step (3) were frozen for 1.5 h in a –20 °C freezer, and then thawed at room temperature, where, phase separation was cold-induced; (5) the upper MeCN layer was pipetted out into another 2 mL centrifuge tube with 5 mg of NanoCarb to conduct the DSPE procedure, in which the extraction solution was vortexed for 30 s to make pigments to be adsorbed to NanoCarb adsorbent in an adsorption equilibrium, then the supernatant was obtained, and injected into the LC-HRMS for subsequent analysis.

### 2.3. Preparation of standards and calibration standard solutions

The individual pesticide standards (1.0 mg/mL) and ISs (0.1 mg/mL) stock solutions were prepared by dissolving into MeOH-MeCN (1:1,

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