



Simultaneous determination of organophosphorus pesticides in fruits and vegetables using atmospheric pressure gas chromatography quadrupole-time-of-flight mass spectrometry



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ABSTRACT

This paper describes the application of atmospheric pressure gas chromatography quadrupole-time-of-flight mass spectrometry for the simultaneous determination of organophosphorus pesticides in apple, pear, tomato, cucumber and cabbage. Soft ionization with atmospheric pressure ionization source was compared with traditional electron impact ionization (EI). The sensitivity of GC coupled to atmospheric pressure ionization (APGC) for all the analytes was enhanced by 1.0–8.2 times. The ionization modes with atmospheric pressure ionization source was studied by comparing the charge-transfer and proton-transfer conditions. The optimized QuEChERS method was used to pretreat the samples. The calibration curves were found linear from 10 to 1000 µg/L, obtaining correlation coefficients higher than 0.9845. Satisfactory mean recovery values, in the range of 70.0–115.9%, and satisfactory precision, with all RSD_r <19.7% and all RSD_R values <19.5% at the three fortified concentration levels for all the fifteen OPPs. The results demonstrate the potential of APGC-QTOF-MS for routine quantitative analysis of organophosphorus pesticide in fruits and vegetables.

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1. Introduction

To increase the productivity of the harvest, organophosphorus pesticides (OPPs) have been widely used in fruits and vegetables to control pests. This often results in the presence of trace pesticide residue in fruits and vegetables, which are harmful to human health because of their potential mutagenicity properties (Karalliedde, Wheeler, Maclehorse, & Murray, 2000; Wang, Qiao, Ma, Zhao, & Xu, 2013; Wu et al., 2015). Therefore, there is an increasing demand to develop an accurate and sensitive analytical method for simultaneous determination of trace levels of OPPs to facilitate the risk assessment.

Due to the low concentration of the analytes and the complex matrix of the samples, a preliminary sample preconcentration

and separation technique are required. Thus, different extraction and cleanup processes for pesticides analysis such as solid phase extraction method (SPE) (Yang, Luo, Li, & Liu, 2016), dynamic microwave-assisted extraction (DMAE) (Wu et al., 2016), optimized QuEChERS (quick, easy, cheap, effective, rugged and safe) extraction method (Rizzetti et al., 2016; Zhao, Hu, Wang, Zhao, & Yang, 2015) have been used for preparation in fruits and vegetables. The outstanding QuEChERS method have been widely used for monitoring pesticides (Jia et al., 2012; Kretschmann, Cedergreen, & Christensen, 2016; Wei et al., 2015; Zhong, Wang, Dong, & Hu, 2015), synthetic musk (Saraiva, Cavalheiro, Lancelour, & Monperrus, 2016), veterinary drug (Leon, Pastor, & Yusa, 2016; Martínez-Domínguez, Romero-González, & Frenich, 2016; Stubbings & Bigwood, 2009; Wei et al., 2015; Zhang et al., 2016), and organic contaminants (Baduel, Mueller, Tsai, & Ramos, 2015; Chatterjee et al., 2016; Morrison, Sieve, Ratajczak, Bringolf, & Belden, 2016; Vavrouš et al., 2016). After sample preparation, the determination of OPPs in different sample matrices was usually carried out by using gas chromatography mass spectrometry (GC-MS) (Chen et al., 2016; Shamsipur, Yazdanfar, & Ghambarian, 2016), gas chromatography flame photometric detector (GC-FPD) (Du, Ren, & Beckett, 2004) and gas chromatography

Abbreviations: APGC-QTOF-MS, atmospheric pressure gas chromatography quadrupole-time-of-flight mass spectrometry; OPPs, organophosphorus pesticides; C18, octadecylsilane; PSA, primary secondary amine; GCB, graphitized carbon black; ME, matrix effects; SSE, signal suppression/enhancement.

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coupled to electron capture (GC-ECD) (Jardim, Mello, Goes, Frota, & Caldas, 2014). However, determination of pesticide residues by these techniques which often leads to false positives can be complicated by the interference of matrix components co-eluted with the analytes of interest and the unwanted matrix effect obtained by these techniques typically causes a loss of accuracy and sensitivity.

APGC is a soft ionization technique which generates high relative and absolute abundance molecular ions and protonated molecules resulting in less fragmentation of the analytes than conventional electron ionization (EI), thus, enhancing sensitivity and selectivity (Cheng et al., 2016; Hernando, Agüera, Fernández-Alba, Piedra, & Contreras, 2001; Sales et al., 2016). The technique can produce highly abundant precursor ions that can reduce matrix interferences effectively. The molecular ion, protonated molecular ion or mixed ions are usually present under charge-transfer or proton-transfer conditions. The capability of APGC has been demonstrated in some fields including food analysis (Organtini et al., 2015) and environmental pollutants (Domeno, Canellas, Alfaro, Rodríguez-Lafuente, & Nerin, 2012; Organtini et al., 2015; van Bavel et al., 2015). However, there are few performance evaluation reports for determination of OPPs by using APGC-QTOF-MS (Pintado-Herrera, González-Mazo, & Lara-Martín, 2014). Therefore, it is necessary to make more effort to dig the potential characteristic of APGC for the simultaneous determination of OPPs in fruits and vegetables.

The main objective of this study was to evaluate the performance of APGC-QTOF-MS by comparing the difference between EI and APGC ionization mode and to evaluate sample preparation based on QuEChERS method. An efficient and effective method for the simultaneous determination of fifteen frequently-used OPPs in fruits and vegetables using APGC-QTOF-MS was developed and the fitness of the method was validated by the analysis of some authentic environmental samples for pesticides residues.

2. Materials and methods

2.1. Chemicals and reagents

Standard solutions of parathion (100 mg/L), phosphoric acid (100 mg/L), parathion-methyl (100 mg/L), fenthion (100 mg/L), triazophos (100 mg/L), diazinon (100 mg/L), dimethoate (100 mg/L), pirimiphos-methyl (100 mg/L), fenitrothion (100 mg/L), malathion (100 mg/L), phosalone (100 mg/L), quinalphos (100 mg/L), chlorpyrifos (100 mg/L), tolclofos-methyl (100 mg/L) were obtained from Agro-Environment Protection Institute, Ministry of Agriculture (Beijing, China). Analytical grade acetone for pesticide residue analysis was purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China), acetonitrile for extraction of pesticides was obtained from Beijing chemical works (Beijing, China). Anhydrous magnesium sulfate (MgSO_4) was purchased from Xilong Chemical Co., Ltd (Beijing, China) and sodium chloride (NaCl) was obtained from Sinopharm Chemical Reagent Co., Ltd (Beijing, China). Chromatography grade hexane was obtained from Thermo Fisher Scientific Corporation (Shanghai, China). Ultra-pure water was collected from a Milli-Q system (Bedford, MA, USA). Bondesil octadecylsilane (C18, 40 μm), primary secondary amine (PSA, 40 μm) and graphitized carbon black (GCB, 40 μm) sorbents were purchased from Bonna-Agela Technologies (Tianjin, China). Nylon syringe filters (0.22 μm ; Tengda, Tianjin, China) were used to filter the concentrated extracts.

2.2. APGC-QTOF-MS instrumentation

All measurements of the fifteen OPPs were performed by an Agilent 7890A GC system (Agilent Technologies, Santa Clara, CA)

equipped with a 7693 autosampler (CTC Analytics, Zwingen, Switzerland) coupled to a Q-TOF (Xevo G2-S, Waters Corporation, Manchester, UK), combined with a APGC source. A HP-5MS (Agilent Technologies) analytical column of 30 m \times 0.250 mm inner diameter and 0.25 μm of film thickness was used. The GC oven temperature program for the gas chromatography was as follows: initial temperature of 80 $^\circ\text{C}$ held for 1 min, ramped at 20 $^\circ\text{C min}^{-1}$ to 200 $^\circ\text{C}$ and held for 1 min, then increased ramp by 10 $^\circ\text{C min}^{-1}$ to 300 $^\circ\text{C}$ and held for 2 min, resulting in a total run time of 20 min. Helium (purity > 99.999%) was used as carrier gas at 1.5 ml/min. API positive polarity and sensitivity mode were selected for MS ionization. The Xevo G2-S QTOF was operated at a scan time of 0.2 s and the mass range was considered as m/z 50–650. For mass spectrometry (MSE, where E represents collision energy which involves the rapid alternation between two conditions of energy), two acquisition functions were used in applying different collision energies: a low energy (6 eV) function and a high energy function which in the case of a collision energy ramp (20–40 eV), thus providing the accurate mass of precursor ion, in addition to accurate mass fragment ions for further confirmatory purposes. The corona voltage was 2.2 kV, the cone gas was set at 150 L/h and an ion source of 100 $^\circ\text{C}$. Perfluorotributylamine (PFTBA) was utilized for daily MS calibration. The instrument was operated at proton-transfer conditions that adding water into the ionization source as a modifier.

The oven temperature program and analytical column of GC analysis are the same with the APGC-QTOF-MS analysis. Splitless injections of 1 μL sample were carried out at 280 $^\circ\text{C}$.

2.3. Recommended sample treatment

The extraction procedure was carried out following the QuEChERS method. Approximately, 500 g of the sample matrices (apple, pear, tomato, cucumber and cabbage) were chopped and homogenized before the preliminary test. 10 g of the thoroughly homogenized samples were weighed into a 50 mL polypropylene centrifuge tube with a screw cap and 10 mL acetonitrile were added to the tube. The tube was shaken vigorously for 10 min with a vortex mixer. Next, a total of 1 g of NaCl and 4 g of anhydrous MgSO_4 were added and shaken vigorously for 5 min. The tubes were centrifuged for 5 min at a relative centrifugal force (RCF) of 2811g, then 1.5 mL upper layer solvent was transferred into a 2 mL centrifuge tube which contained an amount of cleaning agent containing 80 mg C18 and 150 mg MgSO_4 for apple and cucumber samples, 40 mg PSA and 150 mg MgSO_4 for pear and tomato samples, 40 mg C18 and 150 mg MgSO_4 for cabbage samples. Then 2 mL centrifuge tubes were vortexed for 1 min and centrifuged for 5 min at RCF 2400 \times g. Then 900 μL the upper layer solvent was transferred into a 5 mL tube and nitrogen blow to dryness by using sample concentrator. The analytes were redissolved in 900 μL hexane and filtered using a 0.22 μm Nylon syringe for APGC-QTOF-MS injection.

2.4. Method validation

To evaluate the performance of the validated method, the method was developed in terms of specificity, linearity, limits of detection (LOD), limit of quantification (LOQ) and precision, stability. Standard stock solution (5 mg L^{-1}) of the mixture of the fifteen organophosphorus pesticides was prepared in chromatography grade hexane. Five different sample matrixes with fifteen organophosphorus pesticides of the mixture were spiked at three levels (50, 100 and 500 $\mu\text{g L}^{-1}$) and analyzed together with control samples. In addition, there was no laboratory contamination in the control samples. The pure solvent calibration standards were used to evaluate the matrix effects (ME). %ME is the %difference in the

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