



Determination of pesticide residues in globe artichoke leaves and fruits by GC–MS and LC–MS/MS using the same QuEChERS procedure



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ARTICLE INFO

Article history:

Received 9 September 2016

Received in revised form 13 December 2016

Accepted 6 January 2017

Available online 7 January 2017

Keywords:

Globe artichoke

Pesticide residues

Multiresidue dispersive methods

GC–MS

LC–MS/MS

ABSTRACT

Aiming to select the most suitable sample preparation for the multiresidue analysis of pesticides in globe artichoke (*Cynara cardunculus* L.), a modified QuEChERS, a matrix solid phase dispersion and a dispersive ethyl acetate extraction were compared. Trueness and precision were determined at 0.2 mg kg^{−1} for the three methods. The modified QuEChERS showed the best performance. The scope of the method was enlarged to 35 GC and 63 LC amenable pesticides, its overall performance was evaluated and validated to artichoke leaves and fruits according to DG-SANTE Guidelines. Different matrix effects were observed for most of the pesticides which were higher for leaves than fruits. Difenoconazole and flutriafol suffered signal suppression in leaves extracts but showed positive matrix effects in fruits. All pesticides were analyzed at or below their Maximum Residue Levels fixed for globe artichoke by the European Union. The method was successfully applied for the analysis of commercial samples.

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1. Introduction

The use of pesticides in agriculture has brought many benefits to the society, but the inappropriate use of agrochemicals can result in high levels of pesticide residues in the commodities, that may endanger the health of consumers. Even when applying the pesticides in accordance with Good Agriculture Practices (GAP), residues can remain on the crops (Stepán, Tichá, Hajslová, Kovalczuk, & Kocourek, 2005). For this reason, many countries have established monitoring programs and legal regulations to control the use of pesticides on edible crops. Pesticides residues must comply with the Maximum Residue Levels (MRLs) established by national and international regulations.

Globe artichoke (*Cynara cardunculus* L. subsp. *Cardunculus*) is a native plant from the Mediterranean region, and the fruit is consumed in many countries all over the world as a healthy food. The leaves that are usually discarded are employed in herbal medicinal products to relieve indigestion and as a hepatoprotective agent. The leaves are commonly used in infusions (teas) for liver

and digestive conditions (Pistón et al., 2014). Also other pharmacological activities have been associated to globe artichoke fruits and leaves in the literature, such as antioxidant, anticarcinogenic, hypocholesterolemic, antibacterial and anti-HIV. The biological properties of this plant have been associated to the presence of phenolic compounds including mono- and di-isomers of caffeoylquinic acid and flavonoids O-glycosides (Gouveia & Castilho, 2012). As globe artichoke is widely used, it is of interest to have analytical methods that can rapidly and accurately determine the level of contaminants in the crop, particularly of pesticide residues, and to determine compliance with regulatory MRLs, depending on the final use of the product (European Commission, 2005).

The only report of a multi residue method (MRMs) for pesticide residues determination in artichoke fruits in literature is from 1996, where Viana et al. described the determination of nine pesticides by gas chromatography-electron capture detection (GC-ECD) and confirmed by gas chromatography-electron impact-mass spectrometry (GC-(EI)-MS) in the selected ion monitoring mode (Viana, Moltó, & Font, 1996).

New analytical methodologies are continuously exploring more effective sample treatments, especially when it comes about complex matrices, to prevent interferences and improve the sensitivity (Neill, Pareja, Geis Asteggianti, Cesio, & Heinzen, 2010; Pérez Parada et al., 2016).

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There is a need of more accurate, faster and sensitive analytical methodologies for pesticide residues analysis in food. Modern techniques seek for miniaturization and rapid as well as cost-effective sample preparation procedures. Special attention has been given to versatile MRMs such as the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) method or the MSPD (Matrix Solid Phase Dispersion) which are suitable for large scale residue analysis in a great variety of matrices (Pérez-Parada et al., 2011). The aim is to cover as many compounds as possible, but the pesticides have different chemical structures, with different physico-chemical properties that have to be considered when developing a MRM. In this work a simple, fast and cheap method, involving a modification of the QuEChERS sample preparation with CaCl_2 in the clean up step, that can be employed to analyze 98 pesticide residues in both artichoke fruits and leaves, is presented (Anastassiades, Lehotay, Stajnbaher, & Schenck, 2003; Lehotay, Mastovská, & Lightfield, 2005; Lozano et al., 2012; Payá et al., 2007; Rajski et al., 2013). The validate method is a useful tool for the food safety assurance of this increasingly used raw material.

2. Materials and methods

2.1. Reagents

Acetonitrile (MeCN) and ethyl acetate (EtOAc) LC-grade were purchased from Pharmco (Brookfield, CT, USA). Magnesium Sulphate (MgSO_4), sodium chloride (NaCl), trisodium citrate dehydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), disodium hydrogencitrate sesquihydrate ($\text{C}_6\text{H}_6\text{Na}_2\text{O}_7 \cdot 1.5\text{H}_2\text{O}$) and sodium sulphate (Na_2SO_4) were from J.T. Mallinckrodt Baker, Inc. (Phillipsburg, NJ, USA). Calcium chloride (CaCl_2), primary secondary amine (PSA) and graphitized carbon black (GCB) were provided by SUPELCO (Bellefonte, PA, USA).

Except for LC grade MeCN and EtOAc used in the instrumental determination; all other reagents were of analytical grade.

Ultrapure water of 18.2 M Ω cm resistivity (ASTM Type I) was obtained from a Millipore (São Paulo, Brazil) Simplicity 185 purifier.

High purity pesticide standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany) and were stored in the dark at -18°C . Individual pesticide stock solutions (2000 mg L^{-1}) were prepared in MeCN and EtOAc and were stored in the dark at -18°C . Mix solutions used for calibration and spiking procedure were prepared from the stock standards at appropriate dilutions. The working standard mix solution for spiking purposes was prepared at 10 mg L^{-1} in MeCN and EtOAc. These solutions were then diluted as needed to prepare different standard solutions: 1.0, 5.0, 10.0, 50.0, 100.0 and 200.0 $\mu\text{g L}^{-1}$ in MeCN for LC–MS/MS and 10.0, 30.0, 80.0, 150.0, 400.0 and 600.0 $\mu\text{g L}^{-1}$ in EtOAc for GC–MS.

2.2. Samples

Globe artichoke leaves and fruits (approximately 2 kg) were collected in a family farm dedicated to grow the crops in Montevideo-Uruguay and used as matrix blank during method selection and validation. The fragments of leaves were identified as *Cynara cardunculus* subsp. *Cardunculus* (Voucher MVFQ 4399). Four different samples of globe artichoke leaves and fruits were also purchased in local markets in Uruguay. All samples were dried in an oven with forced air circulation (70°C), chopped and stored in the dark at 20°C . Globe artichoke fruits were analyzed as such, without further treatment.

2.3. Spiking procedure

Samples were spiked with appropriate volumes of spiking mix solution (giving 0.01, 0.02, 0.05, 0.10 mg kg^{-1} levels for LC–MS/

MS and 0.01, 0.05, 0.10, 0.20 mg kg^{-1} levels for GC–MS) and then allowed to stand at room temperature for 1 h until analysis.

2.4. Sample preparation

2.4.1. QuEChERS method

A variation of the Rajski modification of the QuEChERS citrate sample preparation procedure was employed (Rajski et al., 2013). A 2.0 g portion of chopped and homogenized artichoke (leaves or fruits) was weighed in a PP (polypropylene) conical centrifuge tube. To hydrate the sample, 4 mL of Milli-Q water were added and the suspension was vortexed for 30 s, and left to stand for 30 min. Next, 10 mL of MeCN were added and the samples were shaken by hand for 5 min. Afterwards, 4 g of MgSO_4 , 1 g of NaCl, 1 g of $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ and 0.5 g of $\text{C}_6\text{H}_6\text{Na}_2\text{O}_7 \cdot 1.5\text{H}_2\text{O}$ were added and the samples were hand shaken again for 5 min. The extract was then centrifuged (3700g) for 5 min, and 5.0 mL of the supernatant were transferred to a 15 mL PP centrifuge tube containing 150 mg of CaCl_2 and 150 mg of PSA. The extract was vortexed for 30 s and centrifuged again (3700g) for 5 min. Aliquots of 1.0 and 3.5 mL were evaporated under a gentle stream of N_2 and reconstituted to 1.0 mL with MeCN for LC analysis and with AcOEt for GC analysis respectively. Final sample concentration was 0.2 g mL^{-1} for LC and 0.7 g mL^{-1} for GC. Prior to injection, the sample was filtered through a 0.45 μm PVDF filter (Millex FG, Millipore, Milford, MA, USA). Triphenyl phosphate (TPP, internal standard, IS) was added to a final concentration of 1.0 mg L^{-1} for GC–MS analysis.

2.4.2. Ethyl acetate method

In a 50 mL PP conical centrifuge tube, 2.0g of previously chopped and homogenized sample were weighed. Then, water was added (4 mL) and the suspension was vortexed for 30 s and then left to rest for 30 min. After that, 10 mL of AcOEt were added and the mixture shaken by hand for 5 min. Immediately, 4 g of MgSO_4 and 1 g of NaCl were added and the mixture was hand shaken for 5 min. The sample was then centrifuged (3700g) for 5 min and 5.0 mL of the supernatant were transferred to a 15 mL PP centrifuge tube containing 200 mg of MgSO_4 , 200 mg of GCB and 150 mg of PSA. The extract was mixed in a vortex for 30 s and centrifuged again (3700g) for a further 5 min. Subsequently, an aliquot was evaporated under a gentle stream of N_2 and reconstituted to 1.0 mL with AcOEt for GC analysis. Final sample concentration was 0.7 g mL^{-1} . Triphenyl phosphate (TPP, IS) was added to a final concentration of 1.0 mg L^{-1} for GC–MS analysis (Lozano et al., 2012).

2.4.3. MSPD method

A glass column with a frit at the bottom was filled (from bottom to top) with the clean-up adsorbents: 0.4 g of GCB, 3.6 g of Florisil and 1.0 g of previously chopped and homogenized sample mixed with 4 g of Na_2SO_4 in a ceramic mortar with a pestle. Elution was accomplished by gravity flow using Hex/EtOAc, 4:6. The eluate was collected to 25 mL into a pear shape flask and placed in a rotary evaporator (Büchi RE 111, Switzerland) to evaporate the solvents. Finally, the MSPD extract was reconstituted to 1.0 mL with EtOAc containing Triphenyl phosphate (TPP, IS) at 1.0 mg L^{-1} for GC–MS analysis. Final sample concentration was 1 g mL^{-1} (García-Rodríguez, Cela-Torrijos, Lorenzo-Ferreira, & Carro-Díaz, 2012).

2.5. Instruments and analytical determinations

2.5.1. GC–MS analysis

A GC equipped with a MS detector (GC–MS-QP2010 Ultra) and a TR-5MS Thermo (30 m $\times$ 0.25 mm $\times$ 0.25 μm) column was used. Electron impact (EI) mass spectra were obtained at 70 eV. The MS system was programmed in the selected-ion monitoring

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