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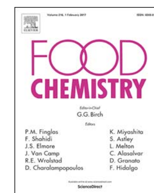

Analytical Methods

Analysis of pesticide residues in tuber crops using pressurised liquid extraction and gas chromatography-tandem mass spectrometry

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ABSTRACT

Tuber crops substantially contribute to the food security in the developing countries. Often, their cultivation involves unregulated applications of pesticides, leading to MRL non-compliances. Despite their rising currency in international trade, there exist scarcely any methods for pesticide residue analysis in these matrices. Therefore, we developed a multi-residue method for simultaneous analysis of a diverse range of pesticides in tuber crops, based on pressurized liquid extraction by ethyl acetate, followed by selective identification and quantification of the residues using GC–MS selected reaction monitoring. The method was evaluated for 150 pesticides. Results showed that their limits of quantification were 0.1–10 ng/g, with recoveries of 70–120%. When compared to the conventional analytical techniques, such as QuEChERS and buffered ethyl acetate extraction, this method provided superior performance in terms of precision, and recovery of the spiked and incurred residues with similar productivity. The method holds promise for commercial and regulatory residue analysis.

1. Introduction

In the developing countries, the principal tropical root crops, namely yam (*Dioscorea alata*), taro (*Colocasia esculenta*), and sweet potato (*Ipomoea batatas L.*) are largely known to contribute to the food security (FAO, 2010; Chandrasekara & Josheph Kumar, 2016; Scott, Rosegrant, & Ringler, 2000a; Shajeela, Mohan, Jesudas, & Soris, 2011; Campus & State, 2014). Despite their high annual global production and rising share in the global trade (Scott, Rosegrant, & Ringler, 2000b), good agricultural practices (GAP)-based recommendations for the safe use of pesticides are meagerly available for these crops. Often, their cultivation involves unregulated applications of pesticides, thereby leading to non-compliance issues related to trade, and potential health hazards to consumers (Campus & State, 2014; Olufade, Sosan, & Oyekunle, 2014; Cervera et al., 2010; Frenich, Fernández, Moreno, Vidal, & López-Gutiérrez, 2012; Gushit, Ekanem, Harami, & Chindo, 2013). According to a report provided by the United States – Food and Drug Administration, every year around 10% of the imported tuber crop samples fail to comply with the MRLs (U.S. FDA, 2013). In 2014, the European Union placed a temporary prohibition on the import of taro from India on account of food safety issues (EFSA, 2010). Despite these concerns, there exist scarcely any validated methods for the analysis of pesticide residues in these matrices. Given this gap of knowledge, we endeavored to develop an effective sample preparation method for multiresidue analysis of pesticides, particularly in yam, taro, and sweet potato.

In the field of pesticide residue analysis, pressurized liquid extraction (PLE) is a well-known technique that involves the extraction of residues from solid or semi-solid samples (Verma, 2010) at elevated temperatures and pressures, providing superior recoveries (Kettle, 2013; Beyer & Biziuk, 2008; Picó, 2017; Vazquez-Roig & Picó, 2015).

Because of its importance, the PLE has been adopted by many researchers for the extraction of pesticides from various agricultural and food matrices (Chiesa et al., 2016; Kostik, 2014; Pang et al., 2006; Frenich, Salvador, Vidal, & López-López, 2005; Nemoto & Lehotay, 1998; Ridgway, Lalljie, & Smith, 2007). Higher recoveries of pesticides had been reported by the PLE in comparison to the supercritical fluid extraction (SFE) (Lehotay & Lee, 1997). Similarly, PLE was found to be superior over the soxhlet extraction (Suchan, Pulkrabová, Hajšlová, & Kocourek, 2004). Kostik, 2014 and Pang et al., 2006 used the solid phase extraction (SPE) as a clean-up approach after extraction of pesticides by the PLE. Fairly recent, a PLE method with “in-cell” clean-up has been reported for the detection of contaminants in honey in which the sample was cleaned by florisil for removing the co-extractives (Chiesa et al., 2016).

Despite various studies conducted so far, there is hardly any report

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that focuses on the use of PLE for pesticide residue analysis in tuber matrices. Therefore, the aim of this study was to evaluate the applicability of a method based on the PLE and GC–MS/MS for the multi-residue analysis of pesticides in the aforementioned tuber matrices. Our findings highlight the advantages of this method over the conventional extraction techniques based on the QuEChERS (Lehotay, Maštovská, & Lightfield, 2005) technique, and also a similar kind of extraction technique that utilizes ethyl acetate (Banerjee et al., 2007; Jadhav, Oulkar, Shabeer, & Banerjee, 2015). The originality of this research is demonstrated through the application of the PLE technique in developing a semi-automated sample preparation method without any clean-up to perform a highly selective, sensitive, and targeted residue analysis.

2. Experimental

2.1. Selection of pesticides and tuber matrices

In this study, a total of 150 GC amenable compounds (excluding isomers), which are either commercially used, banned, or have restricted usage in Indian agriculture (www.cibrc.nic.in), was included. The PLE method was initially optimized and validated in yam, and subsequently, extended in taro, and sweet potato. The organically grown pesticide residue-free tuber crop matrices were obtained from the ICAR-Central Tuber Crops Research Institute, Thiruvananthapuram, India.

2.2. Reagents and preparation of standard solution

Certified pesticide reference standards (> 98% pure) were purchased from Ehrenstorfer GmbH (Augsburg, Germany). Pesticide residue grade ethyl acetate, acetonitrile, and other reagents were procured from Sigma Aldrich (Bangalore, India). The stock solutions of the pesticide standards were prepared by dissolving 10 mg of each analyte in 9 g ethyl acetate (10 mL weighs 9 g). An intermediate standard of 10 mg/L was prepared by mixing appropriate quantities of the individual stock solutions, followed by the requisite volume make-up. The calibration standards (range: 5–250 ng/mL) were subsequently prepared by serial dilution.

2.3. Standardization of sample preparation technique

2.3.1. Homogeneity test and sample size optimization

To obtain homogeneity, each sample type (1 kg) was spiked with the pesticide mixture at 25 ng/g. With a Robot-coupe® (Robot Coupe USA Inc., Ridgeland, MS), the samples were thoroughly crushed. At 15000 rpm, a portion (200 g) of the sample was further smoothed to a fine paste (Banerjee et al., 2007). In order to optimize the sample size, two different amounts of the homogenate (1.5 and 3 g) were mixed with diatomaceous earth (1:1, to fill about 80% of the 10 mL extraction cell), and extracted separately. Using the Student's *t*-test, the recoveries ($n = 6$) were statistically compared.

2.3.2. Partitioning with water and concentration of sample extract

After adding sodium sulphate (~10 g), the total volume of the PLE extract (27 mL) was subjected to partitioning with water (~10 mL). Since the extract got diluted by the addition of the rinse solvent, an evaporation step was introduced to ensure adequate method sensitivity. In terms of the recovery (at 1 ng/g), and LOQ (Limit of Quantification) ($n = 6$), the concentrated extract (1 g matrix/mL) was subsequently compared to another extract, which was analyzed without any evaporation, or concentration.

2.3.3. Optimization of the PLE instrument method parameters

The PLE was performed using a Dionex (Sunnyvale, CA) ASE350 (accelerated solvent extractor) instrument, equipped with stainless-steel extraction cells (10 mL), collection vials (250 mL), cellulose filter disks, and diatomaceous earth (drying agent). High-purity nitrogen was used to purge, and/or pressurize the extraction cells.

Two solvents, namely, ethyl acetate, and acetonitrile, were compared for their extraction efficiency. Conventionally, the PLE is carried out between 75 to 125 °C (http://www.dionex.com/en-us/webdocs/4736-TN208_FINAL.pdf). Four different extraction temperatures (100, 110, 120, and 130 °C) were evaluated in terms of recoveries (%), and any appreciable degradation of the target compounds. The comparative effect of various combinations of the number of static cycle (1, 2, and 3), and static time (3, 4, 5, and 6 min) was separately investigated for both the solvents in terms of recoveries.

In the final optimized PLE method, the sample homogenate (3 g), with 0.5% acetic acid, was thoroughly mixed and dispersed with diatomaceous earth (Prep DE, 1:1). The optimized conditions included extraction solvent (ethyl acetate, 100%); temperature (100 °C); pressure, (1400 psi); pre-heat time (0 min); heating time (5 min); static time (3 min); static cycles (3 in numbers); flush volume (60%); and nitrogen purge time (60 s). This amounted to a total extraction time of 20 min, along with the manual steps which added 15–18 min. After we added Na_2SO_4 (10 g) to the extract (27 mL), and passed it through a cellulose thimble, it was partitioned with water (10 mL). The supernatant was subjected to vortexing (2 min), and centrifugation (5000 rpm, 5 min). Under a gentle stream of nitrogen, 9 mL of the extract was evaporated (Rocket™ Evaporator, ThermoFisher Scientific). Following that, the residue was reconstituted in 1 mL ethyl acetate for injection into GC–MS/MS. The optimized method was then compared with the modified QuEChERS (Lehotay et al., 2005), and buffered ethyl acetate (BEA) (Jadhav et al., 2015) methods for studying the recovery and the matrix effect.

2.4. GC-MS/MS

For the quantitative analysis, we used a TSQ-8000 Evo triple quadrupole GC–MS/MS system (Thermo Scientific, Waltham, Massachusetts, USA), equipped with Triplus RSH autosampler. The injections (2 μL) were carried out in the splitless mode with a splitless straight liner at an isothermal temperature (280 °C). For the chromatographic separation, an Rxi®-5SilMS column (15 m × 0.25 mm, 0.25 μm, Restek Corporation, Bellefonte, PA, USA) was used. Helium was the carrier gas with a flow rate of 1.24 mL/min in the constant flow mode, while argon was used as the collision gas. After the injection, the purge flow to the split vent was maintained at 30 mL/minute for 1 min (splitless time).

For a fast GC–MS/MS analysis, the initial oven temperature was set at 65 °C (1 min), and then increased to 280 °C at the rate of 30 °C/minute (6 min), resulting in a total run time of 14.1 min. The transfer line and ion source temperatures were 290 and 250 °C, respectively. Based on the parameters previously optimized by our group (Nagarajan, Khan, Utture, Dasgupta, & Banerjee, 2013; Khan, Girame, Utture, Ghosh, & Banerjee, 2015), the mass spectrometer (MS) was operated in the selected reaction monitoring (SRM) mode, where 2 mass transitions per analyte were monitored with some modifications (Supplementary Table 1). The system was controlled by the Trace Finder EFS software version 3.2.

2.5. Method performance

The analytical method was validated as per the DG Sante/11945/2015 guidelines (SANTE, 2016) (https://ec.europa.eu/food/sites/food/files/plant/docs/pesticides_mrl_guidelines_wrkdoc_11945.pdf). On the basis of the solvent and matrix-matched calibrations (5–250 ng/g), the limits of detection (LOD) and quantification (LOQ) were estimated by considering the signal-to-noise ratios (S/N) of ≥3 and 10, respectively, with the recoveries of 70–120% at the LOQs. The recovery experiments were carried out by fortifying the blank matrix ($n = 6$) with the

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