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Original Article

Validation and assessment of matrix effect and uncertainty of a gas chromatography coupled to mass spectrometry method for pesticides in papaya and avocado samples

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ABSTRACT

In this paper a method of using the “quick, easy, cheap, effective, rugged, and safe” (QuEChERS) extraction and gas chromatography coupled to mass spectrometry detection (GC–MS) was developed for the analysis of five frequently applied pesticides in papaya and avocado. The selected pesticides, ametryn, atrazine, carbaryl, carbofuran, and methyl parathion, represent the most commonly used classes (carbamates, organophosphorous, and triazines). Optimum separation achieved the analysis of all pesticides in < 6.5 minutes. Validation using papaya and avocado samples established the proposed method as linear, accurate, and precise. In this sense, the correlation coefficients were > 0.99. The limits of detection (LOD) and quantification (LOQ) in papaya ranged from 0.03 mg/kg to 0.35 mg/kg and from 0.06 mg/kg to 0.75 mg/kg, respectively. Meanwhile for avocado, LOD values varied from 0.14 mg/kg to 0.28 mg/kg and LOQ values ranged from 0.22 mg/kg to 0.40 mg/kg. Recoveries obtained for each pesticide in both matrices ranged between 60.6% and 104.3%. The expanded uncertainty of the method was < 26% for all the pesticides in both fruits. Finally, the method was applied to other fruits.

1. Introduction

Pesticides are extensively used to control pests that cause damage to crops. In this way, the application of these compounds intends to ensure the quantity and quality of fruits and vegetables required for consumers. However, this can lead to the bioaccumulation of pesticide residues in them. For this reason and considering the negative effects of the

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pesticides on human health; such as genotoxicity, inhibition of acetyl cholinesterase activity, hepatic, and renal toxicity [1,2]; pesticide monitoring is important to ensure a minimal exposure to them.

Gas chromatography (GC), coupled with different detectors, is a very useful technique employed for the analysis of volatile pesticides such as organochlorides, organophosphates, and carbamates. Mass spectrometry detector (MS) is the most useful for pesticide residue determination in food matrices when an appropriate sample preparation and cleanup procedures are applied [3].

In this sense, GC coupled to mass spectrometry detection (GC–MS) has been successfully used for the analysis of pesticides in different fruits and vegetables including rice, orange, apple, and spinach [4]; grape [5]; pomegranate, grape, okra, tomato, and onion [6]; banana [7]; orange [8]; rice [9]; apple and tomato [10]; cantaloupe melon, broccoli, sweet potato, and lemon [11]; apple–blueberry sauce, pea, and lime [12]; mango [13]; mango and papaya [14]; turnip, green cabbage, French bean, eggplant, apple, nectarine, and grape [15]; berry fruits [16]; Brazilian melon [17]; apple, orange, carrot, and tomato [18].

Due to the complexity of fruit and vegetable matrices, different extraction procedures have been used for GC analysis of pesticide residues. Established 3500 and 3600 series Environmental Protection Agency methods are widely used for this task [19,20]. However, the current trend in pesticide analysis is to develop more efficient and environmentally friendly methods. These methods involve sample preparation techniques such as microwave assisted extraction (MAE), matrix solid-phase dispersion (MSPD), solid–liquid extraction (SLE) [5], dispersive solid phase extraction (DSPE) [6], solid-phase microextraction (SPME) [10,13,15,21], solid phase extraction (SPE) [16], and “quick, easy, cheap, effective, rugged, and safe” (QuEChERS) method [5–9,11,17,18].

QuEChERS is a procedure which has shown good performance on the difficult task of the extraction of pesticides from food matrices. This sample treatment has been applied for the extraction of a wide range of pesticides with diverse chemical properties in several types of fruits and vegetables, which have different compounds such as sugar, pigments, and high water content [5,9,22]. Owing to the widespread use of this procedure, different versions of QuEChERS method have been developed; among these are the Association Official Analytical Chemists (AOAC; acetate buffering) version and the CEN (citrate-buffering) version. The acetate buffering version had showed higher recoveries for the pH-dependent pesticides, therefore it is more frequently used [12].

Nowadays validation is considered an essential part of the method evaluation; it has the aim of determining if an analytical method is suitable and reliable for its purpose. By using the data produced from method validation the method uncertainty can be estimated. Uncertainty is an important parameter for method evaluation defined as “a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand” [23,24].

The uncertainty may originate from many possible sources, which are related to the different stages of the analytical method. Potential uncertainty sources are sampling, matrix effects, uncertainties of masses and volumetric equipment, reference values, approximations and assumptions incorporated in the measurement method and procedure, and random variation [23,25].

Each uncertainty source should be treated independently to obtain its contribution to the overall uncertainty of an analytical method. In this sense, the contributions of all the uncertainty sources are considered to estimate the combined uncertainty of the method. From the combined uncertainty, an expanded uncertainty is determined. This last term represents an interval within which an analytical result is believed to lie with a high level of confidence [17,23].

In this paper a method using QuEChERS extraction and GC–MS was developed for the analysis of five frequently applied pesticides in papaya and avocado. The studied pesticides were representative of three of the most commonly used classes, which are: triazines (ametryn and atrazine), carbamates (carbaryl and carbofuran), and organophosphorous (methyl parathion). The proposed method was validated according to European guidelines. In addition, the expanded uncertainty was evaluated taking into account the different sources of uncertainty that affect the process.

2. Methods

2.1. Materials and reagents

Standards of the pesticides carbofuran (CF), carbaryl (CAR), atrazine (ATZ), ametryn (AME), and methyl parathion (MeP), all with purity > 98%, acetic acid, acetonitrile, and methanol, all HPLC grade, were obtained from Sigma-Aldrich (St. Louis, MO, USA). Helium (99.999% purity) was supplied by Praxair (Colima, México). A methanol stock solution of each pesticide at 50 mg/L was weekly prepared. Methanolic working solutions were prepared daily by mixing pesticide stock solutions. These solutions were stored in the dark at 4°C. Working solutions were used for GC–MS method optimization and spiking fruit matrices used for method validation. Other chemicals used in this work were analytical reagent grade.

DisQuE Dispersive Sample Preparation kit containing extraction and clean-up tubes from Waters (Milford, MA, USA) and nylon filters (0.45 μm pore size) from Phenomenex (Torrance, CA, USA) were used for sample preparation.

2.2. Instruments

A Varian 3900 GC coupled to a Saturn-2100T mass spectrometry detector and equipped with a CombiPAL autosampler and MS Workstation version 6.9 software from Varian (Palo Alto, CA, USA) were used for chromatographic analysis. The analytical column Zebron ZB-5MS Crossbond (5% phenyl–95% dimethyl-polysiloxane; 30 m, 0.25 mm internal diameter, 0.25 μm film thickness) from Phenomenex (Torrance, CA, USA) was used in this study.

An NB-101B food processor (Homeland Houseware, Los Angeles, CA, USA), an analytical balance model CX220 (Citizen Scale, Metuchen, NJ, USA), a Vortex-Genie 2 mixer (Scientific Industries, Bohemia, NY, USA), a Sorvall Biofuge Primo R centrifuge (Thermo Electron Corp., Schwerte, Germany), and a