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Novel multiresidue method for determination of pesticides in red wine using gas chromatography–mass spectrometry and solid phase extraction

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ABSTRACT

A new multiresidue method was developed for determination of 25 pesticide residues in red wine by gas chromatography coupled to mass spectrometry with a single run of 23.63 min. Samples were extracted from wine with solid phase extraction using Oasis HLB. Mixture of methanol and water was used for rinsing, while acetonitrile and *n*-hexane were used as elution solvents. Method was validated according to SANCO/12571/2013 criteria in wide linearity range (limit of quantification – 400 μg L^{-1}). Limits of quantification (LOQ) were well below 10 μg L^{-1} for most pesticides and recoveries at 2 × LOQ and 10 × LOQ concentration levels were in range 70–120%. Precision, expressed as a relative standard deviation, was always under 14%. The method was applied to 32 red wine samples from Croatia. Pesticides were detected in 30 samples with a total of 15 pesticides found, 7 of which were at a high concentration.

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1. Introduction

The use of agrochemicals is important part of harvest quality and food protection (Herrero-Hernández et al., 2013). Vineyards are one of the most widespread crops with inevitable usage of pesticides. Conventional cultivation of wine is characterized by significant use of number of different groups of pesticides. The most common group is fungicides, which are applied to the vine grape. Many of these products are resistant to fermentation process which results in their presence in the final product affecting the wine quality and consumer health (Jiménez, Bernal, del Nozal, Bernal, & Toribio, 2007). The European Union has set maximum residue levels (MRLs) for pesticides in vine grapes. However, MRLs for wine are still scarcely established. The approach in wine products is the same as in other processed food products. MRLs of raw products are applicable to processed food products taking into account product processing. Although technological processing of wine and fermentation result in a decrease in pesticide concentrations, in recent years a number of studies indicate wine contamination with pesticides concentration above MRLs (Economou, Botitsi, Antoniou, & Tsipi, 2009). Therefore, with growing popularity of wine and estimated worldwide wine consumption of 240 million hectoliters (OIV (International Organization of Vine, 2012), continuous monitoring of pesticide levels in wine is essential not only for consumers' health protection, but also for establishing legislations for wine contamination.

Frequent application of various pesticides simultaneously requires a determination of as many compounds as possible in a single analysis. One way to approach the problem of pesticides determination is the development of multiresidue methods (Wilkowska & Biziuk, 2011). The most common determination techniques include liquid (LC) or gas chromatography (GC) coupled to different detectors. Mass spectrometry (MS) represents powerful detection characteristics because of its sensitivity and confirmation power (Camino-Sánchez et al., 2011). GC–MS is probably the most common determination technique for multiresidue pesticides analysis in food and environmental products (Jiménez et al., 2007; Lesueur, Knittl, Gartner, Mentler, & Fuerhacker, 2008; Maštovska & Lehotay, 2004; Park et al., 2011; Soleas, Yan, Hom, & Goldberg, 2000; Wong et al., 2003; Yang et al., 2011). Recently, a number of techniques such as liquid chromatography coupled with tandem mass spectrometry (MS/MS) have been developed (Camino-Sánchez et al., 2011; Carpinteiro, Ramil, Rodríquez, & Cela, 2010; Economou et al., 2009; Fontana, Rodríquez, Ramil,

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Altamirano, & Cela, 2011a, 2011b; Pérez-Ortega, Gilbert-López, García-Reyes, Ramos-Martos, & Molina-Díaz, 2012; Sinha, Vasudev, & Vardhana Rao, 2012). Triple quadrupole (QqQ), time of flight (TOF) and hybrid quadrupole-time of flight (QTOF) represent very powerful instruments for providing accurate mass measurements and information of non-target or unknown analytes (Fontana et al., 2011a, 2011b; Portolés, Mol, Sancho, López, & Hernández, 2014; Sivaperumal, Anand, & Riddhi, 2015).

Analytical methods require constant optimization of parameters, primarily to achieve better sensitivity and selectivity as well as lower limits of detection and quantification. However, the development of such methods is a challenge due to the high complexity of the wine matrix. Namely, the presence of matrix interferences can significantly affect pesticide identification and quantification. Therefore, sample preparation is one of the most important parts of analytical procedure. Ideally, sample preparation should be fast, accurate, precise and economic (Núñez, Gallart-Ayala, Martins, & Lucci, 2012). Today, the most common sample preparation techniques are; liquid–liquid extraction (LLE) using organic solvents (Navarro, Barba, Navarro, & Oliva, 2000), solid-phase extraction (SPE) (Duca, Salquebre, Hardy, & Appenzeller, 2014; Economou et al., 2009; Fontana et al., 2011a, 2011b; He et al., 2015; Shi et al., 2014; Yang et al., 2011) and more recently QuEChERS (Lesueur et al., 2008; Sinha et al., 2012). However, SPE is often a method of choice due to its rapidity, clean-up efficiency and robustness (Fontana et al., 2011a, 2011b; He, Wang, & Wei, 2016; Kubica, Garraud, Szpunar, & Lobinski, 2015; Triñanes, Casais, Mejuto, & Cela, 2015). The most common solvents used for pesticide extraction include ethyl acetate, methanol and acetonitrile due to their suitability for a wide polarity range of pesticides (Economou et al., 2009).

The main objective of this work was development of a new multiresidue method for simultaneous determination of 25 pesticides in wine samples by GC–MS. Pesticides were selected based on their frequency of application and recent literature on residues in Mediterranean wines. The focus of the study has been set on red wines due to increasing knowledge of its benefits in prevention of cardiovascular diseases (Minuti, Pellegrino, & Tesei, 2006) and rising worldwide trend of its production and consumption. The additional specific goal of investigation was to present and optimize SPE methodology in order to achieve maximum efficiency for the target pesticides by reducing the influence of complex matrix, especially the significant anthocyanin interference. Proposed methodology has been evaluated in terms of limits of detection (LOD) and quantification (LOQ), linearity, precision and accuracy. Also, the influence of complex matrix on identification and quantification of target pesticides under proposed analytical method has been investigated and the quality of selected sample preparation method has been evaluated in terms of extraction efficiency. Under final conditions, analytical procedure has been applied to 32 Croatian wine samples of different varieties in order to provide the first insight into pesticide residue levels, application and distribution in Croatia.

2. Materials and methods

2.1. Solutions and reagents

Certified pesticide standards used in this work were purchased from Sigma–Aldrich (Steinheim, Germany) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). Solvents (HPLC grade) used for pesticide extraction were acetone, acetonitrile, methanol, water and *n*-hexane purchased from J. T. Baker (Deventer, Netherlands). Cartridges used for SPE were Oasis HLB (60 mg/3 mL) from Waters (Miliford, Massachusetts, USA). Cellulose acetate membrane filters (0.22 μm pore size) were purchased form Millipore (Bedford, Massachusetts, USA).

Individual standard pesticide stock solutions were prepared in acetone (500 mg L^{-1}). The standard working mixtures were prepared from stock solutions by appropriate dilution with acetone. Standard and stock solutions were stored at 4 °C in the dark.

2.2. Sample preparation

Red wine without the presence of target pesticide (*Babić*) was used for method development. Wine was filtered through cellulose acetate membrane filters and processed within 48 h. SPE was performed using Oasis HLB and vacuum manifold (Supelco, Bellefonte, Pennsylvania, USA) at flow rate of 5 mL min^{-1}. 10 mL of the wine sample was diluted to a final volume of 20 mL with ultra-pure water, spiked with target pesticides and passed through cartridges previously conditioned with 3 mL of acetonitrile and 3 mL of water. After the concentration step, cartridges were rinsed with 3 mL of mixture methanol/water (50/50% v/v) and vacuum dried for 15 min. Finally, analytes were eluted with 10 mL of the elution solvent, first with 1×2 mL of *n*–hexane following 4×2 mL of acetonitrile. The eluent was evaporated to dryness by vacuum rotary evaporator (EZ-2 Plus, Genevac, Ipswich, UK) and diluted with 1 mL of acetone before GC–MS analysis.

2.3. GC–MS analysis

The pesticides were determined using a 6890N gas chromatograph with the mass spectrometer 5975 inert and 7863B autosampler (Agilent, Santa Clara, California, USA). Chromatographic separation was performed on HP-5MS capillary column, 30 m × 0.25 mm, i.d. × 0.25 μm film thickness, (Agilent J&W Scientific Products, Santa Clara, California, USA). The oven temperature program was as follows: initial temperature 120 °C, held for 1 min; 30 °C per minute to 190 °C, held for 1 min; 5 °C per minute to 205 °C, held for 1 min; 2 °C per minute to 217 °C, with no held; 6 °C per minute to 232 °C, held for 1 min; 10 °C per minute to 240 °C, with no held; 40 °C per minute to 320 °C, held for 3 min. Total run was 23.63 min with solvent delay 4.5 min. Injections were performed in a pulsed splitless mode with an injection temperature of 250 °C. Injection volume was 5 μL. Temperature of ion source was 230 °C, transfer line temperature was 280 °C and MS quad temperature was 150 °C. Electron impact ionization was set to 70 eV. Carrier gas was helium (Messer, purity 6.0, Zagreb, Croatia) with the flow rate of 1.0 mL min^{-1}. The analysis was performed in a single ion monitoring (SIM) mode.

2.4. Method performance: sample quantification, validation and matrix effect

2.4.1. Sample quantification

The developed analytical procedure was applied to commercial wine samples. Since a matrix effect was expected (and established as described in Section 3.4.) candidates for quantification approach were techniques that account for the matrix effect. Matrix-matched calibration was considered, as a frequently used method for minimization of matrix effect (Araujo, 2009). In matrix-matched calibration, blank matrix of similar characteristics as real sample is needed for construction of appropriate calibration curve (SANCO/12571/2013, 2013). Red wine chemistry is diverse (Bakker & Clarke, 2012) and red wine matrices can vary between different grape variety, wine regions and technological processing of wine. Variations in chemical composition of red wine matrices may even exceed the point where selected blank wine matrix cannot be considered similar enough to the real wine sample. Furthermore, pesticide application is widespread, so it is reasonable to assume that

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