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Review

Analytical approaches for the determination of pesticide residues in nutraceutical products and related matrices by chromatographic techniques coupled to mass spectrometry

Gerardo Martínez-Domínguez, Patricia Plaza-Bolaños, Roberto Romero-González, Antonia Garrido-Frenich *

Research Group "Analytical Chemistry of Contaminants", Department of Chemistry and Physics, Research Centre for Agricultural and Food Biotechnology (BITAL), University of Almería, Agrifood Campus of International Excellence, ceiA3, E-04120 Almería, Spain

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ABSTRACT

A review of sample preparation and analytical techniques currently used to analyze pesticides in nutraceutical products is shown. Different sample treatments are commented, and the QuEChERS method is the most used (quick, easy, cheap, effective, rugged and safe). For the chromatographic determination, gas chromatography (GC) and liquid chromatography (LC) are evaluated. Different detection modes are discussed, and simple quadrupole mass spectrometry (Q-MS) and triple quadrupole tandem mass spectrometry (QqQ-MS/MS) are the most used. Finally, a review of the occurrence of pesticides (from the revised literature) in real samples is presented, evaluating several matrices, such as nutraceuticals, dietary supplements, medicinal plants, and fish oil. The occurrence of several pesticides was reported: γ-HCH (lindane), endosulfan, procymidone, azoxystrobin, *p,p′*-DDE, metalaxyl, quintozene, tolclofos-methyl, chlorpyrifos and hexachlorobenzene.

Contents

* Corresponding author. Tel.: +34 950015985; fax: +34 950015008.
E-mail address: agarrido@ual.es (A. Garrido-Frenich).

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1. Introduction

In the last years, a number of diseases are becoming increasingly prevalent in the industrialized countries. Arthritis, diabetes and heart diseases are becoming more common because of the increase of unhealthy habits in modern society. When pharmaceutical products are not completely effective against this problem, people usually self-medicate with other kind of products like nutraceuticals, considering that they will be more effective on preventing or treating diseases [1]. Many consumers believe that nutraceutical products will improve their health, and they also think that these "natural" remedies are both effective and free from the side effects that may occur with other medications [2]. The consumption of this type of products is increasing: the nutraceutical industry has grown since 2000, getting to $22 billion in the United States (US) [3] and reaching $12 billion on the Asiatic market [3]. The US National Institute of Standards and Technology (NIST) reported that approximately 75% of the US population takes dietary supplements, including vitamins and mineral supplements [2]. The explosive growth of the US and Japanese markets has created similar expectations for the European market. Thus, the nutraceutical products market in Europe is currently valued at $31.6 billion [3].

Nutraceuticals legislation is sometimes ambiguous because there is not a common definition for this kind of products. Several definitions can be found in bibliography, and Lockwood discusses them, defining "nutraceutical" as "a term used to describe a medicinal or nutritional component that includes a food, plant or naturally occurring material, which may have been purified or concentrated, and that is used for the improvement of health, by preventing or treating a disease" [1]. Unlike foods, dietary supplements are allowed to use "nutritional support statements", and they can be marketed without any study looking for substances that can bring along a risk for human health [1]. The Dietary Supplement Health and Education Act (DSHEA) is the US law that establishes regulations and limits label claims on dietary supplements [4]. DSHEA defines "nutraceutical" as "a dietary supplement that may contain an herb or other botanical, or a concentrate, metabolite, constituent, extract or combination of any ingredient from the other categories" [5]. In Europe, the legislation covers food supplements (Directive 2002/46/EC) [6] and herbal medicinal products (Directive 2004/27/EC) [7], but there is no formal legislation regulating nutraceutical products across the European Union (EU) [5].

Nutraceutical products can be divided into three categories: (i) dietary supplements (vitamins, minerals, co-enzime Q, carnitine, ginseng, Ginkgo Biloba, Saint John's Wort, Saw Palmetto), (ii) functional foods (oats, bran, psyllium, lignin, prebiotics, omega-3, canola oil, stanols), and (iii) medicinal foods (transgenic cows, lactoferrin, transgenic plants, health bars) [8]. These products represent a huge food market and their quality controls should not be different from conventional food. Bearing in mind that a nutraceutical product is a concentrated form of a food or plant, it is possible to find substances utilized in plant protection, such as pesticides. The quality guide for botanical food supplements released by the European Botanical Forum specify that for botanical extracts, contaminant controls should be performed on the processed extract, whenever it has been demonstrated that certain organic chemical contaminants can be concentrated during the extraction process [9]. Moreover, there are occasional reports of inaccurate labeling, adulteration, contamination (e.g. with pesticides, heavy metals, or toxic botanicals), and drug interactions for these products [2]. Pesticide maximum residue levels (MRLs) for every food and animal feed have been defined by different organizations across the world, like the World Health Organization (WHO), the Food and Agriculture Organization of the United Nations (FAO) [10], the US-Environmental Protection Agency (US-EPA) [11] or EU [12]. However, the Regulation EC 396/2005 [13], which includes MRLs, only concerns raw materials. Therefore, MRLs should be defined in these nutraceuticals, in order to assure the safety of this type of products.

In this sense, analytical methods that allow the detection and quantification of pesticides on these products are necessary. Because of the complexity of this type of matrices, the first step in the analytical methods used for the determination of pesticide residues in nutraceutical and related products is the extraction and/or clean-up of the target compounds from the matrix. Several extraction approaches such as QuEChERS (acronym of quick, easy, cheap, effective, rugged and safe), pressurized liquid extraction (PLE) and matrix solid phase dispersion (MSPD) could be applied [14]. Then, chromatographic techniques such as gas (GC) and liquid (LC) chromatography are coupled to several detectors such as electron capture detection (ECD) [15], or diode array [16] for the determination of pesticide residues in this type of matrices. However, they have being replaced by mass spectrometry (MS) detection [17,18], considering that reliable confirmation is achieved with this detection technique.

The objective of this paper is the review of sample preparation and analytical techniques currently used to determine pesticides in nutraceutical products; special attention will be paid on GC and LC coupled to classical and advanced detectors, such as MS.

2. Sample extraction

According to the revised bibliography, most of the studies are focused on medicinal plants (raw material), and only in some cases on dietary supplements (final product) that come from medicinal plants. In other particular cases, fish oils were also evaluated. All these products are considered nutraceuticals bearing in mind the aforementioned definitions. Therefore, the different extraction techniques applied for these particular products will be discussed in this section. Table 1 shows a summary of the main procedures.

2.1. Medicinal plants and herbal infusions

For this type of matrix, a variety of sample treatments can be used, such as QuEChERS [17,19–29], PLE [30], Soxhlet extraction [31–35], solid–liquid extraction (SLE) [36–38], MSPD [15,39], solid phase micro-extraction (SPME) [40,41] and solid-phase extraction (SPE) [16,42], as it can be observed in Table 1.

The QuEChERS method has been used for the extraction of a large variety of medicinal plants, and it is currently the preferred option for the determination of pesticides in plant-based products. This extraction procedure was originally developed by Anastassiades et al. in 2003 [43] for the analysis of pesticides in vegetables and fruits. Nowadays, it represents a simple, rapid, effective and inexpensive methodology to extract pesticide residues from different matrices. The QuEChERS method basically consists of an extraction with acetonitrile followed by a clean-up stage using the dispersive solid-phase extraction (dSPE) with primary-secondary amine (PSA) [44]. A high number of studies reported the application of this methodology using either the original QuEChERS or the modified versions. The subsequent study by Lehotay et al. [45] described a modification of the original method using a buffered solvent (also known as the American QuEChERS version): this method uses acetonitrile with 1% of acetic acid (v/v), magnesium sulfate and sodium acetate to determine multiple pesticides, obtaining recoveries between 68% and 96% and precision, expressed as relative standard deviation (RSD), between 15% and 33%. It was introduced to improve the recoveries of more acidic compounds (e.g. chlortalonil, captan). Chang [20,21] also utilized