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Pesticides in honey: A review on chromatographic analytical methods

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ABSTRACT

Honey is a product of high consumption due to its nutritional and antimicrobial properties. However, residues of pesticides, used in plagues' treatment in the hive or in crop fields in the neighborhoods, can compromise its quality. Therefore, determination of these contaminants in honey is essential, since the use of pesticides has increased significantly in recent decades because of the growing demand for food production. Furthermore, pesticides in honey can be an indicator of environmental contamination. As the concentration of these compounds in honey is usually at trace levels and several pesticides can be found simultaneously, the use of highly sensitive and selective techniques is required. In this context, miniaturized sample preparation approaches and liquid or gas chromatography coupled to mass spectrometry became the most important analytical techniques. In this review we present and discuss recent studies dealing with pesticide determination in honey, focusing on sample preparation and separation/detection methods as well as application of the developed methods worldwide. Furthermore, trends and future perspectives are presented.

Contents

Abbreviations: AED, Atomic electron detector; APCI, Atmospheric pressure chemical ionization; ASE, Accelerated solvent extraction; CME-UABE, Coacervative microextraction ultrasound-assisted back-extraction; DD, Double derivatization; DLLME, Dispersive liquid liquid microextraction; dSPE, Dispersive solid phase extraction; ECD, Electron capture detector; ESI, Electrospray ionization; ET, Elevated temperature; Fl, Spectrofluorimetric detector; FPD, Flame photometric detector; GC, Gas chromatography; HPLC, High performance liquid chromatography; HRMS, High resolution mass spectrometry; HS-SPME, Headspace solid phase microextraction; IL, Ionic liquid; IT, Ion trap; IT/MS, Ion trap mass spectrometry; LC/DD/Fl, Liquid chromatography double derivatization coupled with spectrofluorimetric detector; LLE, Liquid liquid extraction; LOD, Limit of detection; LOQ, Limit of quantification; LTP, Low temperature purification; MEPS, Microextraction by packed sorbent; MRL, Maximum residue level; MS, Mass spectrometry; MS/MS, Tandem mass spectrometry; MSPE, Magnetic solid phase extraction; Nd, Not detected; nf, Not found; NPD, nitrogen phosphorus detector; PSA, Primary secondary amine; QuEChERS, Quick, easy, cheap, effective, ruged and safe; SBSE, Stir bar sorptive extraction; SDME, Single drop microextraction; SLE, Solid supported liquid liquid extraction; SPE, Solid phase extraction; SPME, Solid phase microextraction; ToF, time of flight; UA, Ultrasound assisted; UHPLC, Ultra high performance liquid chromatography; UV, Ultraviolet

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1. Introduction

The use of pesticides has increased significantly during the last decades [1–3]. Although the use of these compounds brings benefits to agriculture, many of them reach a distinct destination than the target species and could contaminate soil, water and food. Since some pesticides are carcinogenic and some can cause dysfunctions in the nervous and reproductive systems, even at low concentrations, they can be extremely harmful to human health [1,2,4]. Thus, the risks to food safety due to the use of these compounds are constant motives to concern worldwide [5,6].

The monitoring of pesticides in honey is necessary to warrant consumers' safety. Furthermore, the control of pesticides in honey can provide information about the use of pesticides in crop fields and in the neighborhoods [7]. According to Rissato et al. [7] bees and honey can be used as biomarkers for monitoring environmental contamination. Thus, analytical methods for the routine determination of pesticides in honey are needed. Today's analytical challenge is the use of multiresidue methods capable of analyzing several pesticides simultaneously; with high sensitivity and specificity; with minimal use and disposal of solvents which can be detrimental to human and environmental health; and fast [8,9].

The determination of pesticide in food requires sample preparation, separation and quantification. Furthermore, the performance of the method must be investigated to demonstrate its fitness for the purpose. Due to the low concentration of pesticides in food samples, the distinct chemical properties and the matrices complexity, sample extraction, purification and concentration are needed [10]. Most of the sample preparation procedures are carried out by conventional techniques, such as liquid liquid extraction (LLE); however, they have the disadvantages of being expensive and using large amounts of organic solvents, which are generally toxic for the technician and can contaminate the environment. These limitations have led to the development of new techniques which are convenient, consume less organic solvents and have the ability to detect analytes in very low concentrations. In recent years, efforts in the field of analytical chemistry focused on the miniaturization of sample preparation associated with increased selectivity and sensitivity [11].

However, most of these efforts are far from being ideal. Miniaturized extraction techniques, developed recently, have been applied and optimized for the extraction of pesticides from honey, in order to solve the problems associated with conventional methods [12–14]. However, they still have limitations on application, quickness, sensitivity and reliability of the results.

Besides the extraction and purification procedures, the choice of the separation/detection approach is of fundamental importance. Technological advances in mass spectrometry have achieved the need for sensitivity and selectivity [15]. Liquid chromatography coupled with tandem mass spectrometric detection (LC-MS/MS) and gas chromatography coupled with tandem mass spectrometric detection (GC–MS/MS) have shown great success in multiresidue analysis of antibiotics and pesticides in honey [16–19]. These techniques provide information regarding the retention time of each compound and allows gathering of two or more transitions to quantify and confirm identity of the analyte. They also present high sensitivity, consistent with the Maximum Residue Levels (MRLs) established by international legislation [20].

In 2007, Rial-Otero et al. [21] published a review on methods employed for pesticide analysis in honey. They also presented the trends they expected to become reality in the following years. Afterwards several innovative techniques of sample preparation, separation and detection were developed and employed for determination of pesticides in honey. In this context, this review aims to present and discuss the studies published in the period between 2008 and 2015 dealing with pesticide determination in honey. Special focus was given on sample preparation and separation/detection methods as well as application of the developed methods worldwide.

2. Honey

The Codex Alimentarius defines honey as the natural sweet substance produced by honey bees from the nectar of plants or from secretions of living parts of plants or excretions of plant sucking insects on the living parts of plants, which the bees collect, transform by combining with specific substances of their own, deposit, dehydrate, store and leave in the honey comb to ripen and mature [22].

Honey is composed of a mixture of sugars [23], mainly fructose (~38.5%) and glucose (~31.0%) but also maltose, sucrose and other complex carbohydrates [24]. However, the percentage of sugars varies depending on the raw material used for its production [25]. It also contains other components in minor proportions, such as minerals (calcium, copper, iron, magnesium, phosphorus, and potassium), proteins, amino acids, vitamins, flavonoids, pigments, several organic acids, and compounds with antioxidant properties including chrysin, pinobanksin, vitamin C, catalase and pinocembrine [24,t26–29]. The physicochemical evaluation of honey is important for its characterization and to ensure the quality of the product in the market [23,30].

Besides being appreciated for the characteristic flavor and nutritional value [31], humans have also used honey due to its antimicrobial and antiseptic properties, and as a preservative in fruit and grains [29,32]. The healing properties of honey have been known in medicine since ancient times. During the last century, honey was subjected to numerous clinical and laboratorial investigations, which confirmed their medical benefits as antimicrobial, especially against *Staphylococcus* strains which are resistant to methicillin among other bacteria [33,34].

2.1. Pesticides in honey

The constant growth of the world's population has demanded increased food production. However, annual losses due to plagues on agriculture are about 1 billion ton around the world, with a production decrease of 20–30% [35]. Therefore, to overcome this problem, the chemical industries are looking for new substances with activity against plagues and other biological threats [36]. Currently, there are more than 100 pesticides registered in the European Union's market [37].

Pesticides (herbicides, fungicides, insecticides or acaricides)