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ARTICLE

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LC-MS/MS Analysis of Neonicotinoid Insecticides in Honey: Methodology and Residue Findings in Austrian Honeys

Gina Tanner[†] and Christoph Czerwenka*

Competence Center for Residue Analysis, Austrian Agency for Health and Food Safety, Spargelfeldstrasse 191, 1220 Wien, Austria

ABSTRACT: An analytical method for the simultaneous determination of residues of eight neonicotinoid insecticides and two metabolites in honey using LC-MS/MS was developed and validated. Two approaches of sample preparation were investigated, with the final method involving acetonitrile extraction and subsequent cleanup by dispersive solid-phase extraction (QuEChERS type). Validation was based on quintuplicate analysis at three fortification levels and showed satisfactory recoveries (60−114%) and high precision (RSDs between 2.7 and 12.8%). Low limits of detection and quantification could be achieved for all analytes ranging from 0.6 to 5 μg/kg and from 2 to 10 μg/kg, respectively. Investigations of Austrian honey samples revealed the presence of acetamiprid, thiacloprid, and thiamethoxam residues in honey; however, no sample exceeded the maximum residue limits. On average, flower honey samples contained neonicotinoid residues in higher quantities compared to forest honey samples.

KEYWORDS: neonicotinoid insecticides, pesticide residues, honey, QuEChERS, LC-MS/MS

■ INTRODUCTION

The relatively new group of neonicotinoids constitutes a class of highly potent insecticides, which were developed in a series of syntheses from nitro-substituted ketene aminales.[1] The so-called first-generation neonicotinoids (acetamiprid, imidacloprid, nitenpyram, and thiacloprid) are characterized by a 6-chloro-3-pyridyle heterocycle, the second-generation compounds (clothianidin and thiamethoxam) contain a 2-chloro-5-thiazolyl moiety, whereas dinotefuran belongs to the third generation and features a 3-tetrahydrofuranyl group (Figure 1).[1] Additionally, flonicamid, which is characterized by a 4-trifluoromethyl-3-pyridyl group, is frequently assigned to the neonicotinoid group. New neonicotinoids are continuing to be developed to date.[2] Neonicotinoids act in a very specific way as agonists on the postsynaptic nicotinic acetylcholine receptor of the insect's central nervous system, causing a blockage of signal transmission. Distinct advantages of neonicotinoids are their high efficacy, selectivity, and plant systemicity as well as long-lasting effect and versatile application.[3] A further crucial factor for the success of neonicotinoids is the absence of a cross-resistance to longer-established insecticide classes such as carbamates, organophosphates, or synthetic pyrethroids, against which many pests have developed resistances over the years.[4,5] The versatile application of neonicotinoid insecticides covers many crops ranging from cereals and vegetables to various fruit cultures.

Upon the use of neonicotinoids as a measure of pest management, beneficial insects such as honeybees may also be affected. Depending on the application form of neonicotinoid insecticides, different routes of exposure of honeybees to these pesticides can be envisaged. The application of neonicotinoids as chemical sprays can contaminate the blossoms of plants on and beside agricultural fields as well as foraging honeybees during their flight. The same ways of exposure can also occur upon abrasion and environmental drift of neonicotinoids contained in seed dressings during the sowing process. Additionally, neonicotinoids applied in seed dressings are distributed in the plants, and honeybees might come into contact with them through their presence in pollen or nectar. When honeybees come into contact with neonicotinoids, the insecticides may be taken along into the beehive, and residues may finally be found in bee products such as honey. For different neonicotinoid residues maximum residue limits in honey have been set by the European Union (EU) ranging from 10 to 200 μg/kg (Table 1). The residue definitions of acetamiprid, flonicamid, and thiamethoxam also include one metabolite each (Table 1).

Due to the widespread application of neonicotinoid insecticides, appropriate analytical methods for the detection and quantification of their residues in honey are required. In recent years several publications have reported analytical methods for the analysis of pesticide residues in honey. A review of chromatographic methods[6] provided an overview of the approaches employed for the extraction of pesticide residues from honey as well as the chromatographic methods used to measure them. In terms of neonicotinoids, most of the reported multiresidue methods included one or more substances from this group of insecticides. With regard to methods focusing on the analysis of residues of the neonicotinoid group, papers have been published dealing with fruits and vegetables[7−10] as well as foodstuffs of animal origin.[9] Only a small number of publications have specifically targeted the analysis of neonicotinoid residues in honey.[11−13] Whereas the methods by Schöning and Schmuck[11] and Kamel[13] focused only on imidacloprid and its metabolites, Fidente et al.[12] included acetamiprid, imidacloprid, thiacloprid, and thiamethoxam in their method. In terms of sample preparation, different approaches were employed in these studies. Whereas Kamel[13] utilized a modified QuEChERS method[14] supplemented by subsequent solid phase extraction using a C_{18}

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