

Application of high-performance liquid chromatography-time-of-flight mass spectrometry for determination of neonicotinoid lethal bee intoxicants

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Abstract

The use of uncontrolled toxic concentrations of systemic insecticides belonging to the class of neonicotinoids in agriculture has a negative impact on the life of honeybees. The situation is aggravated by the fact that compared to other pesticides, neonicotinoids have acute toxicity to bees, contributing to their death. This paper presents a developed multimethod for qualitative and quantitative determination of certain lethal bee intoxicants of a number of neonicotinoids: thiamethoxam, clothianidin, Imidacloprid and acetamiprid by high-performance liquid chromatography-quadrupole-time-of-flight tandem mass spectrometry (HPLC-MS/MS). Sample preparation for HPLC-MS/MS was carried out using a modified QuEChERS method, followed by post-treatment of samples by dispersion solid-phase extraction (TFE). Chromatographic separation was performed by gradient reverse-phase HPLC, detecting neonicotinoids in the multiple reaction monitoring (MRM) mode. The assessment and verification of the completeness of the degree of recovery of neonicotinoids by the modified version of QuEChERS, based on the results of HPLC-MS/MS definitions, indicate that a high degree of their recovery has been achieved.

Under the proposed conditions of chromatographic separation, the analytical signals of the determined neonicotinoids are characterized by correlation coefficients (r^2) equal to 0.999. The limits of detection ($3 \cdot Sa/b$) of neonicotinoids detected under HPLC-MS/MS conditions are established, which are: $1.6 \cdot 10^{-3}$ mg/kg of thiamethoxam and Imidacloprid; $1.8 \cdot 10^{-3}$ mg/kg of acetamiprid and $1.9 \cdot 10^{-3}$ mg/kg of clothianidine. The developed HPLC-MS/MS multimethod is used for screening the material of dead bees for neonicotinoids, which are their lethal intoxicants.

References

- [1] N. Simon-Delso, V. Amaral-Rogers, L.P. Belzunces, J.M. Bonmatin, M. Chagnon, C. Downs, et al. Systemic insecticides (neonicotinoids and fipronil): trends, uses, mode of action and metabolites. *Environ Sci Pollut Res Int.* **2015**. Vol.22. P.5-34.
- [2] P. Jeschke, R. Nauen, M. Schindler, A. Elbert. Overview of the status and global strategy for neonicotinoids. *J Agric Food Chem.* **2011**. Vol.59. P.2897-2908.
- [3] State catalogue of pesticides and agrochemicals of the Russian Federation, **2018**. [Electronic resource]. URL: <http://www.mcx.ru>. (accessed 05.09.2020)
- [4] State register of medicinal products for veterinary use, 2014. [Electronic resource]. URL: https://irena.vetrif.ru/irena/operatorui?_action=clearRegListMedicine. (accessed 05.09.2020)
- [5] A. Friedli, G.R. Williams, S. Bruckner, P. Neumann, L. Straub. The weakest link: Haploid honey bees are more susceptible to neonicotinoid insecticides. *Chemosphere.* **2019**. Vol.242. P.1-10.
- [6] J. Fitzgerald. Laboratory bioassays and field evaluation of insecticides for the control of *Anthonomus rubi*, *Lygus rugulipennis* and *Chaetosiphon fragaefolii*, and effects on beneficial species, in UK strawberry production. *Crop Protection.* **2004**. Vol.23. No.9. P.801-809.
- [7] T.R. Kuhar, L.J. Stivers-Young, M.P. Hoffmann, A.G. Taylor. Control of corn flea beetle and Stewart's wilt in sweet corn with imidacloprid and thiamethoxam seed treatments. *Crop Prot.* **2002**. Vol.21. P.25-31.

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- [8] M. Henry, M. Beguin, F. Requier. O. Rollin. A common pesticide decreases foraging success and survival in honey bees. *Science*. **2012**. Vol.336. No.6079. P.348-350.
- [9] A. Decourtye, J. Devillers. Comparative sublethal toxicity of nine pesticides on olfactory learning performances of the honeybee *Apis mellifera*. *Archives of environmental contamination and toxicology*. **2005**. Vol.48. No.2. P.242-250.
- [10] D. Laurino, A. Manino, A. Patetta, M. Porporato. Toxicity of neonicotinoid insecticides on different honey bee genotypes. *J. Bull. Insect*. **2013**. Vol.66. No.1. P.119-126.
- [11] I.M. Fitsev, O.V. Shlyamina, A.Z. Mukharlyamova, S.L. Mokhtarova, E.R. Rakhmetova, A.G. Mukhammetshina, and Zh.R. Nasybullina. Gas chromatography-mass spectrometry screening persistent organic pollutant in environmental monitoring of vital activity objects. *Butlerov Communications*. **2020**. Vol.62. No.6. P.89-99. DOI: 10.37952/ROI-jbc-01/20-62-6-89
- [12] N. Mantzos, A. Karakitsou, I. Zioris, E. Leneti, I. Konstantinou. QuEChERS and solid phase extraction methods for the determination of energy crop pesticides in soil, plant and run off water matrices. *Int. J. Environ. Anal. Chem*. **2013**. Vol.93. P.1566-1584.
- [13] M.F. Abdel-Ghany, L.A.Hussein, N.F. El Azab, A.H. El-Khatib, M.W. Linscheid. Simultaneous determination of eight neonicotinoid insecticide residues and two primary metabolites in cucumbers and soil by liquid chromatography-tandem mass spectrometry coupled with QuEChERS. *J. Chromatogr. B*. **2016**. Vol.1031. P.15-28.
- [14] I.M. Fitsev, O.V. Shlyamina, A.M. Sayfutdinov, A.R. Makaeva. Quechers sample preparation for the determination of pesticides by chromatomass spectrometry. *Collection of materials of the International conference "Fundamental scientific research as a factor of ensuring the competitiveness of society and the state"*. April 10, **2020**. Belgorod, Russia.
- [15] S.H. Abd-Alrahman. Residue and dissipation kinetics of thiamethoxam in a vegetable-field ecosystem using QuEChERS methodology combined with HPLC-DAD. *Food Chem*. **2014**. Vol.159. P.1-5.
- [16] G. Tanner, C. Czerwenka. LC-MS/MS analysis of neonicotinoid insecticides in honey: methodology and residue findings in Austrian honeys. *J. Agricult. Food Chem*. **2011**. Vol.59. P.12271-12277.
- [17] S. Zheng, H. Wu, Z. Li, J. Wang, H. Zhang, M. Qian. Ultrasound/microwave assisted solid-liquid- solid dispersive extraction with high-performance liquid chromatography coupled to tandem mass spectrometry for the determination of neonicotinoid insecticides in *Dendrobium officinale*. *J. Sep. Sci*. **2015**. Vol.38. P.121-127.
- [18] P. Fidente, S. Seccia, F. Vanni, P. Morrica. Analysis of nicotinoid insecticides residues in honey by solid matrix partition clean-up and liquid chromatography–electrospray mass spectrometry. *J. Chrom. A*. **2005**. Vol.1094. No.1-2. P.175-178.
- [19] Z. Xiao, X. Li, X. Wang, J. Shen, S. Ding. Determination of neonicotinoid insecticides residues in bovine tissues by pressurized solvent extraction and liquid chromatography–tandem mass spectrometry. *J. Chrom. B. Analytical Technologies in the Biomedical and Life Sciences*. **2011**. Vol.879. No.1. P.117-122.
- [20] I.M. Fitsev, O.V. Shlyamina, A.R. Makaeva, G.R. Nasybullina, A.M. Saifutdinov. Detection of Cypermethrin Residues in Toxicological Control Objects using Gas Chromatography – Mass Spectrometry with Solid-Phase Extraction. *Int. J. of Mechanical and Production Engineering Research and Development*. **2020**. Vol.10. No.3. P.5563-5570.
- [21] I. Machado, N. Gerez, M. Piston, H. Heinzen, M. Cesio. Determination of pesticide residues in globe artichoke leaves and fruits by GC-MS and LC-MS/MS using the same QuEChERS procedure. *Food Chem*. **2017**. Vol.227. P.227-236.
- [22] Z. Khan, et al. Analysys of pesticide residues in tuber crops using pressurized liquid extraction and gas chromatography-tandem mass spectrometry. *Food Chem*. **2018**. Vol.241. P.250-257.