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Analysis of Imidacloprid on Tissue Section Using SALDI-MS Imaging

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Extended Abstract

Neonicotinoid pesticides (Neonics) were banned in European Union. However, they have still been used for agricultural crops as well as other purposes such as for pet insecticides in Japan or other countries [1]. Because Neonics provide rapid and effective pest control even though Neonics impact aquatic invertebrates, non-target insects including beneficial insects such as honeybees. The trace amounts of residual Neonics and their metabolites have been detected in environmental air, river, well-water, maline sediment, and soil, *etc* [2]. It is well known that Neonics are metabolised in plants, mammals, human body, and also commensal/environmental microbiomes, the metabolites often show high toxicity to mammals compared to intact structure [3]. Despite the environmental persistent of Neonics, bio-uptake, tissue distribution, metabolism, discharges in mammals are not fully elucidated. To resolve their function, the detailed analysis of Neonics and its metabolites is indispensable.

Matrix-assisted laser desorption/ionization mass spectrometry imaging (MALDI-MSI) method is a powerful tool for the detection and distribution analyses of Neonics and their metabolites in the tissue sections derived from plants or mammals [4]. For the detection of Neonics by MALDI-MSI, organic MALDI matrices such as 2,5-dihydroxybenzoic acid or α-cyano-4-hydroxycinnamic acid are usually used. However, imidacloprid (IMI), one of the major Neonics, is easily fragmented by laser irradiation with organic MALDI matrices. Actually, IMI is detected as guanidine IMI at *m/z* 211 (protonated ion), and molecular ion of IMI is not detected in MALDI-MS spectrum [5]. The fragment ion at *m/z* 211 is also matched to the ion derived from desnitro-IMI (dn-IMI) which is the most toxic metabolite of IMI [3]. Therefore, the peaks of IMI and dn-IMI are hard to distinguish in a MALDI-MS spectrum. In addition, IMI and the metabolites show poor ionization efficiency using organic MALDI matrices, especially on plant section.

Recently, surface-assisted laser desorption/ionization (SALDI) -MSI using inorganic nanoparticles has been developed that improvement of ionization efficiency of molecules and reducing backgrounds in the low *m/z* region [6]. In this study, we applied SALDI-MSI method for the detection of IMI on a cucumber section after vapor deposition of metals. Finally, molecular ions of IMI were detected in a MS spectrum using SALDI-MSI after vapor deposition of silver, and the MS imagings of IMI distribution using molecular ions on the cucumber section were clearly obtained. Thus, SALDI-MSI after vapor deposition of silver would be a powerful tool for analysis of Neonics.

References

[1] C. Nimako, S. M. M. Nakayama, Y. B. Yohannes, Y. Ikenaka, M. Ishizuka, "Status report on neonicotinoid pollution in Japan: Emphasis on human, animal, and environmental health, ", *Environ*., *Monit., Contam., Res.,* 2023, pp. 69-91.
[2] M. J. Berens, P. D. Capel, and W. A. Arnold, "Neonicotinoid insecticides in surface water, ground water, and wastewater across land-use gradients and potential effects," *Environ., Toxicol., Chem.*, 2021, pp. 1017-1033.
[3] D. Loser, K. Grillberger, M. G. Hinojosa, J. Blum, Y. Haufe, T. Danker, Y. Johansson, C. Moller, A. Nicke, S. H. Bennekou, I. Gardner, C. Bauch, P. Walker, A. Forsby, G. F. Ecker, U. Kraushaar, M. Leist, "Acute effects of the imidacloprid metabolite desnitro-imidacloprid on human nACh receptors relevant for neuronal signalling," *Arch., Toxicol.*, 2021, pp. 3695-3716.

[4] Y. Zhang, D. Chen, M. Du, L. Ma, P. Li, R. Qin, J. Yang, Z. Yin, X. Wu, H. Xu, “Insights into the degradation and toxicity difference mechanism of neonicotinoid pesticides in honeybees by mass spectrometry imaging,” *Sci., Total Environ.*, 2021, 145170.
[5] S. Ohtsu, M. Yamaguchi, H. Nishiwaki, E, Fukusaki, S. Shimma, “Development of a visualization method for imidacloprid in *Drosophila melanogaster via* imaging mass spectrometry,” *Anal., Sci.*, 2018, pp. 991-996.
[6] S. Matsushita, T. Hasegawa, M. Hiraoka, A. Hayashi, Y. Suzuki, “TLC-based MS imaging analysis of glycosphingolipids and glycerin fatty acid esters after 1,2-dichloroethane washing,” *Anal., Sci.,* 2021, pp. 1491-1495.