

## M-07

## APPLICATION OF UNKNOWN AND SUSPECT SCREENING ANALYSIS FOR THE IDENTIFICATION OF VOLATILE CO-FORMULANTS IN DIFFERENT PLANT PROTECTION PRODUCTS BY GAS CHROMATOGRAPHY – HIGH RESOLUTION MASS ACCURACY SPECTROMETRY

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Plant protection products (PPPs) are widely used technical formulations containing one or more pesticides (active substances), in addition to several co-formulants responsible for improving the properties of the mixture. In spite of the current analytical focus on active substances, the importance of co-formulants is often overlooked, as these compounds are usually undisclosed, even though they have been proved to enhance pesticide toxicity.<sup>1</sup> Thus, co-formulants in PPPs need to be characterised so that they can be monitored in samples to ensure food safety.

In the present study, 11 difenoconazole and 3 chlorantraniliprole-based PPPs comprising several types of formulations, such as emulsifiable concentrates (EC), suspension concentrates (SC), dispersible concentrates (DC) and ZC, which is a mixture of capsule suspension (CS) in SC, were analysed. The selected analytical technique was gas chromatography coupled to Q-Orbitrap high resolution mass spectrometry (GC-Q-Orbitrap-MS), providing efficient separation and detection of all identified compounds. Unknown analysis was performed by NIST database, whereas suspect screening was carried out by literature review, with several criteria including a matching fragmentation pattern and a mass error lower than 5 ppm. The combination of high resolution mass spectrometry and mass accuracy conferred a high degree of reliability in the identification of co-formulants, which would have not been attained in low resolution mass spectrometry.

Finally, 42 benzene and naphthalene derivative compounds were tentatively identified, and 12 of them (3 suspect and 9 unknown) were confirmed and quantified using available analytical standards. Confirmed compounds were: 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 2-methylbiphenyl, 3-methylbiphenyl, 4-ethyltoluene, biphenyl, ethylbenzene, isopropylbenzene, naphthalene, n-propylbenzene, pentamethylbenzene and tert-butylbenzene. Results showed that the applied methodology was able to detect these co-formulants at concentrations as low as 0.03 g/L (tert-butylbenzene), encompassing a wide of range of concentrations, up to 9.63 g/L (pentamethylbenzene). Pentamethylbenzene was the only compound detected in all studied samples. Overall, EC formulations showed the greatest number of confirmed co-formulants, with a mean value of 8 co-formulants per sample.

**Keywords:** Plant protection products, GC-Q-Orbitrap, unknown analysis, suspect screening

**References:** 1. K. Nagy *et al.* Systematic Review of Comparative Studies Assessing the Toxicity of Pesticide Active Ingredients and Their Product Formulations, *Environ. Res.* 181 (2019) pp 18926.

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