A novel methodology for the identification of co-formulants in plant protection products based on chromatographic techniques coupled to high resolution mass spectrometry

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Plant protection products (PPPs) are essential agricultural tools used for pest control. They are composed of at least an active substance (pesticide) and several other components (co-formulants), which comprise a great part of their composition, and include solvents, preservatives, surfactants, emulsifiers, etc. Whereas active substances are completely characterised, information regarding co-formulants is still notably insufficient, since manufacturers are not enforced to disclose them, even though some of them have been proved to trigger negative effects on health.1 Thus, there is a need of analytical methodologies capable of dealing with the identification of these compounds.

The proposed analytical methodology involves a workflow featuring sample treatment, sample analysis, method validation, and quantification. Cutting-edge techniques covering a wide range of polarity and volatility are proposed; liquid chromatography (LC) and gas chromatography (GC), coupled to Q-Orbitrap high resolution mass accuracy spectrometry (Q-Orbitrap-HRMAS). This methodology also addresses different acquisition methods, such as full scan MS or data independent acquisition (DIA).

Regarding data treatment, a combination of suspect screening, based on previous literature research, and most importantly, unknown analysis, is discussed, which can make a huge difference in the results, as opposed to other traditional methodologies relying just on suspect screening. Additionally, different, but complementary, strategies and software for unknown analysis are presented to ensure a reliable tentative identification of co-formulants.

This communication aims at proposing a novel methodology for the elucidation of co-formulants present in PPPs. The methodology is supported by a real case of study based on our findings and experience in the study of co-formulants PPPs, in which 15 PPPs were studied and 120 co-formulants were tentatively identified and 21 were confirmed with analytical standards, including for example, benzene and naphthalene derivatives, alkyl ethoxylates and sodium alkyl benzene sulfonates. The proposed methodology is also highly applicable to other analytical problems focused on the characterisation of samples.

In all, this methodology intends to contribute to the state of the art of the analysis PPPs, as well as to be a resource for further studies concerning PPPs.

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