Holistic targeted and untargeted workflows in food and environmental studies - LC-TIMS-HRMS providing additional insights

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High-resolution mass spectrometry (HRMS) is considered one of the most powerful techniques to detect and further identify a wide range of analytes in both food and environmental matrices. However, despite HRMS high applicability and accuracy, separation of isomeric compounds remains an analytical challenge, as they may pose identical chromatographic and spectral profiles. In this regard, trapped ion mobility spectrometry (TIMS), combined with HRMS methodologies, provides an additional orthogonal analytical dimension increasing the depth-of-coverage and holding promise for reliable identification concerning food authenticity and environmental monitoring. Here, we highlight the application of targeted and untargeted workflows based on LC-TIMS-HRMS, in one food and one environmental case study.

TIMS combined with LC-HRMS was applied in extra virgin olive oil (EVOO) to separate and identify secoiridoids isomers, found in the phenolic fraction of olive oil. Moreover, a four-dimensional (4D) untargeted approach was implemented to evaluate EVOOs' global profile, in cases of variety and geographical origin discrimination. The proposed workflow incorporates ion mobility information along with LC-HRMS analytical evidence (i.e., mass accuracy, retention time, isotopic pattern, MS/MS fragmentation), thus enhancing the identification confidence. Finally, potential authenticity markers were successfully identified and attributed to isomeric compounds.

The objectives of the second case study, were (1) to establish a high-end analytical platform that could combine multiple dimensions of separation with HRMS, to provide extensive experimental evidence for the identification of bio-TPs isomers. (2) A "biotransformation oriented" data treatment workflow, consisted of suspect and non-target screening approaches, was developed. Overall, the aim was to highlight a holistic approach for comprehensive xeno-metabolome and toxicity assessment of aquatic organisms exposed to xenobiotics and highlight the added value provided by TIMS. More specifically, the zebrafish embryo toxicity assay was used to calculate the LC50 of BTs, as well as for phenotypic evaluation of their toxicity. A holistic analytical platform was developed combining orthogonal chromatographic modes (HILIC and RPLC), trapped ion mobility and HRMS for the analysis of parent BTs and the identification and their bio-TPs. Retention time information in two orthogonal modes and collision cross-section values provided additional evidence to the accurate mass measurements and facilitated the identification of bio-TPs isomers. Overall, 26 bio-TPs were identified through suspect and non-target screening workflows. Finally, it was demonstrated that the combination of orthogonal chromatographic modes, TIMS and HRMS constitute a powerful analytical platform providing extensive analytical evidence for the identification of unknowns.