Development and application of a novel accurate mass based suspect screening methodology for the analysis of pharmaceutical residues in surface water by time-of-flight mass spectrometry

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The growing interest in analytical methods for multi-residue screening and target quantification of potential harmful micropollutants such as pharmaceuticals in the environment requests full-spectrum high-resolution mass spectrometry (HRMS). Instruments such as time-of-flight (TOF) MS have shown the potential to analyze and identify based on accurate mass a virtually unlimited number of analytes simultaneously and offer the ability for both suspect screening and target quantification [1-3]. In suspect screening using full-spectrum HRMS, there is no a priori need for standards because the acquired chromatograms are searched for the exact ion masses of a predefined list of suspect compounds within a certain mass tolerance. In a next stage, confirmation of the found suspects with analytical standards is possible, and a target quantification can be performed through validation of only the limited set of confirmed compounds. The challenge for such suspect screening and also the focus of the presented work is to define the optimum mass error tolerance and to develop a strategy that minimizes the false negative rate (5%) without detecting numerous false positives.

In a first step, different algorithms for the determination of the accurate mass were investigated. We showed that optimal mass accuracy was obtained after centroiding the spectra. Subsequently, a new suspect screening strategy was developed using large-volume injection ultra performance liquid chromatography coupled to TOF-MS aiming the detection of 69 pharmaceuticals in surface water. As a novel approach, the screening takes into account the signal intensity-dependent accurate mass error, which assured the detection of 95% of pharmaceuticals present in surface water. Application on five Belgian river water samples showed that 2/3 of the found peaks was finally confirmed by retention time of analytical standards.

The data obtained for the five Belgian river water samples revealed the occurrence of 30 pharmaceuticals belonging to different classes. Through full validation of the method, target quantification was performed and the applicability of the newly developed suspect screening method is discussed.

References

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