HILIC-QTOF-HR-MS/MS FOR WIDE-SCOPE SCREENING OF POLAR MICROPOLLUTANTS IN ENVIRONMENTAL SAMPLES

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Hydrophilic interaction liquid chromatography (HILIC) has been a valuable complementary, orthogonal approach to reverse phase (RP) chromatography [1-3]. Hyphenated to high resolution mass spectrometry it can provide additional information and selectivity for the target screening of polar micropollutants in the environment, by allowing the detection of additional polar analytes or giving more confidence to the identification of polar analytes detected in RP methods, due to the enhanced sensitivity for polar compounds.

In this study, a HILIC-QToF-MS/MS method was developed, optimized and validated for the determination of 902 polar and semi-polar micropollutants in wastewater samples. Identification parameters for every analyte were recorded in a constantly-growing in-house database, containing information on the retention time, precursor ions and adducts, as well as fragment ions and ion ratios.

Various HILIC stationary phases were compared, including diol-, amide-, bare silica and zwitterionic chemistries. The ACQUITY BEH Amide column proved to be the best option overall, covering a wide range of compounds with satisfactory elution profiles and retention. Optimization of the mobile phase composition, the composition of the solvents in the vial and the ESI parameters was also performed to yield 601 out of 902 compounds being well-retained with k'>1. The analysis was carried out in both positive and negative ionization mode, through broad-band Collision Induced Dissociation (bbCID) mode, providing MS and MS/MS spectra simultaneously. The method was applied on influent and effluent wastewater samples from the wastewater treatment plant (WWTP) in Athens. Sample preparation consisted of a mixed mode solid-phase extraction (SPE) step and reconstitution of the dried extract in the optimum conditions for HILIC analysis.

Validation of the method was carried out for a representative group of 70 compounds and performance criteria were calculated, such as linearity, recoveries, repeatability, matrix effect, screening detection limits (SDL) and limits of identification (LOI).

Screening analysis of the wastewater samples revealed the presence of 178 compounds in influent and 149 compounds in effluent samples. Comparison of the results with those identified from the RPLC-HRMS/MS method revealed higher sensitivity for the polar compounds by HILIC, as well as the detection of some compounds that were not detected in the RP mode, like amphetamine and some amphetamine derivatives (MDA).

The HILIC-HR-MS/MS method constitutes a valuable alternative approach for the determination of polar compounds in environmental samples. Moreover, it can be an excellent supplementary, orthogonal technique to RP-HRMS screening methods, by giving additional confidence for the identification of suspect compounds.

Keywords: HILIC, emerging pollutants, wastewaters, orthogonal selectivity

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REFERENCES

1. Van Nuijs ALN, Tarcomnicu I, Covaci A (2011), Review, Application of hydrophilic interaction chromatography for the analysis of polar contaminants in food and environmental samples. Journal of Chromatography A, 1218: 5964-5974. doi:10.1016/j.chroma.2011.01.075.
2. Jandera P (2011), Stationary and mobile phases in hydrophilic interaction chromatography: a review. Analytica Chimica Acta 692: 1-25. doi:10.1016/j.aca.2011.02.047.
3. Schuhmacher R, Sulyok M, Krska R (2008), Recent developments in the application of liquid chromatography–tandem mass spectrometry for the determination of organic residues and contaminants. Analytical Bioanalytical Chemistry 390: 253-256. doi: 10.1007/s00216-007-1674-4.