WIDE-SCOPE TARGET SCREENING OF 2327 EMERGING POLLUTANTS DURING WASTEWATER TREATMENT BY RP-LC-QTOF-HR-MS/MS WITH AN ACCURATE-MASS DATABASE

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High resolution mass spectrometry has dramatically improved the possibilities of environmental analysis [1-4]. An analytical method, based on reversed phase liquid chromatography quadrupole-time-of-flight mass spectrometry (RP-LC-QToF-MS) was developed for the determination of 2327 target contaminants of emerging concern (CECs) and transformation products (TPs) in wastewater, including, among others, pharmaceuticals, illicit drugs, personal care products, pesticides, industrial chemicals and sweeteners. The method was applied to 24h-flow proportional composite influent and effluent wastewater samples from a wastewater treatment plant (WWTP) in Athens, collected in March 2014.

An in-house mass spectral database was built, containing information on the retention time, precursor ions and adducts, as well as fragment ions and their ion ratios. The analytical method, as well as the data evaluation, was optimized and validated. Analytes were extracted from wastewater samples by mixed mode solid-phase extraction, and data were acquired through broad-band Collision Induced Dissociation (bbCID) mode, providing MS and MS/MS spectra simultaneously, in both positive and negative ionization mode (two separate runs). The raw data were analyzed with Bruker's DataAnalysis 4.1 and TargetAnalysis 1.3 software.

A system of identification points (IPs) was introduced to communicate confidence in the identification of the analytes. The retention time, the accurate mass of the precursor ions, the isotopic fit score, as well as the fragment ions and their ion ratio were taken into account.
The processing method was optimized to provide a successful identification rate above 95 %, keeping the false positive results at the lowest possible level. Performance criteria for a quantitative HRMS screening method were calculated for a representative group of compounds, including linearity, repeatability, recovery rates, matrix effect factors, screening detection limits (SDL) and decision limits (CCβ).

This target screening method proved useful to study a wide number of anaytes, furthermore allowing the possibility of retrospective analysis. 344 compounds were detected in the influent wastewaters and 310 in the effluents. For each compound, IPs were attributed, according to the aforementioned IP system. For 294 compounds, quantitation was also performed using the standard additions method.

Keywords: target screening, emerging pollutants, HR-MS, identification points, screening detection limit, validation

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REFERENCES

1. Schymanski EL, Singer HP, Longree P, Loos M, Ruff M, Stravs MA, Ripolles Vidal C, Hollender J (2014), Strategies to Characterize Polar Organic Contamination in Wastewater: Exploring the Capability of High Resolution Mass Spectrometry. Environmental Science & Technology 48 (3):1811-1819. doi:10.1021/es4044374.
2. Wode F, van Baar P, Dünnbier U, Hecht F, Taute T, Jekel M, Reemtsma T (2015), Search for over 2000 current and legacy micropollutants on a wastewater infiltration site with a UPLC-high resolution MS target screening method. Water Research 69: 274-283. doi:10.1016/j.watres.2014.11.034.
3. Robles-Molina J, Lara-Ortega FJ, Gilbert-López B, García-Reyes JF, Molina-Díaz A (2014), Multi-residue method for the determination of over 400 priority and emerging pollutants in water and wastewater by solid-phase extraction and liquid chromatography-time-of-flight mass spectrometry. Journal of Chromatography A, 1350: 30-43. doi:10.1016/j.chroma.2014.05.003.
4. Hernández F, Ibáñez M, Portolés T, Cervera MI, Sancho JV, López FJ (2015), Advancing towards universal screening for organic pollutants in waters. Journal of Hazardous Materials, 282: 86-95. doi: 10.1016/j.jhazmat.2014.08.006.