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Method development for the quantitative analysis of bisphenols and screening of phthalates in aqueous matrices using liquid chromatography coupled to high-resolution mass spectrometry

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Bisphenol A (BPA) and phthalates are used worldwide as plasticizers in the production of plastic products. Bisphenol A and some phthalates, like di(2-ethylhexyl) phthalate (DEHP), are known to be endocrine disruptors and are therefore regulated and banned in certain products. Bisphenol analogues, like bisphenol S (BPS) and bisphenol F (BPF), and new phthalates are introduced as alternatives because of their similar chemical structures and properties. For BPA, the European Food Safety Authority (EFSA) re-evaluated the tolerable daily intake (TDI) and lowered it to 0.2 ng/kg/bw/day, a 20,000-fold lower value than the previously established value from 2015. Based on this new TDI, monitoring of BPA and its alternatives in drinking water at concentration levels < 1 ng/L is expected to be necessary. For phthalates, a screening method for this group of chemicals and their monoester is needed to identify new, potentially toxic, phthalates.

This research aimed to develop a single analytical method that quantifies bisphenols at a concentration level below 1 ng/L and screens for phthalates (monoester) in drinking water and wastewater treatment plant effluent water. Several parameters of a solid phase extraction (SPE) and liquid chromatography coupled with high-resolution Orbitrap mass spectrometry (LC-HRMS) method were optimized for 22 bisphenols, 10 phthalates, and 11 phthalate monoesters.

The screening method for the phthalates (monoesters) was not fully developed because of observed retention time shifts with the column and mobile phase chosen. The quantitative method for the 22 bisphenols includes a sample preparation method with a glass HLB SPE column that concentrates drinking and effluent water by a factor of 100. The method is followed by a 20-minute gradient on a C18 reversed-phase column with ultrapure water and methanol, both with 1 mM ammoniumfluoride (NH4F). This resulted in a SPE-LC-HRMS method that quantifies 22 bisphenols in drinking water and WWTP effluent water below 2.0 ng/L and 5.5 ng/L, respectively. Five drinking water samples and three WWTP effluent locations were measured to test the method on real samples.

Keywords: phthalates, bisphenols, liquid chromatography, high-resolution mass spectrometry