

Abstract

Benzotriazolic compounds (BZ) are recognized as contaminants of emerging concern. The polar compounds are used as additives in mechanical fluids and dishwasher detergents, while the non-polar compounds act as UV stabilizers in plastics and personal care products. They have harmful effects on aquatic organisms and are possibly carcinogenic, some can also bioaccumulate. Due to their poor removal in wastewater treatment plants, they easily enter the environment and were determined in groundwater, surface and wastewater samples, in sediments, soil, dust and biological samples in low concentrations (ng/l – µg/l).

For their determination, sensitive instrumental techniques (e.g. LC-MS/MS) are usually used in concert with extraction methods for their pre-concentration. The most often used extraction technique is the solid-phase extraction (SPE), but in recent years it is becoming increasingly replaced with microextraction techniques, which require less solvents and sorbents. Two of these techniques, dispersive liquid-liquid microextraction (DLLME) and hollow-fiber microextraction (HFME), were the focus of this work. The parameters, optimized for their highest enrichment factors, included sample volume, pH and ionic strength, mixing speed, extraction time and parameters, specific for each method (e.g. solvent volumes, fiber length).

LC-DAD and LC-MS/MS methods were developed for the evaluation of extracts, using gradient elution with acetonitrile and 0.1% methanoic acid in water. The instrumental limits of detection for polar BZ with LC-MS/MS ranged 1.6–12.9 µg/l.

Two different DLLME methods were developed, one for a mixture of polar and non-polar BZ and the other only for polar BZ. In the first case, a mixture of CHCl₃ and CCl₄ was used as the extraction solvent, while in the second case only CHCl₃ was used. In both cases acetonitrile was used as the dispersive solvent. The final enrichment factors (EF) ranged 10–29 for both groups of compounds and 10–85 for only the polar BZ. The DLLME method for polar BZ was compared to the methods found in literature and also tested as a clean-up step for the extraction of a dust sample.

An HFME method was developed for polar BZ, where 1-octanol was used as the membrane solvent and 0.1 M NaOH as the acceptor solution. The enrichment factors were 38–162 in pure water, but similar values in river water were achieved only after the addition of EDTA to the sample.

The SPE method with highest EF for polar BZ was chosen from literature and compared to the microextraction methods for extraction of river water samples, in regards to EFs, matrix effects, repeatability, extraction time, solvent volumes, and ease of handling. From the analytical standpoint, comparable results were obtained with SPE and DLLME, a bit worse with HFME, but both microextraction methods successfully reduced the use of solvents in regards to SPE.

Samples of groundwater, river water, and wastewater were analysed with the use of matrix-matched calibration. Some of the analytes were found in influent and effluent wastewater, but none were detected in river and groundwater samples.

Keywords: benzotriazoles; microextraction; dispersive liquid-liquid microextraction (DLLME); hollow-fibre microextraction (HFME); environmental samples