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Simultaneous determination of trace benzotriazoles and benzothiazoles in water by large-volume injection/gas chromatography–mass spectrometry

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ABSTRACT

Benzotriazole (BTR) and benzothiazole (BTH) derivatives have been acknowledged as emerging pollutants due to their widespread contamination in the environment and their adverse effects on aquatic organisms. A rapid and reliable analytical method, based on solid phase extraction (SPE) and large-volume injection, derivatized with *N-tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA), and analyzed by gas chromatography–mass spectrometry (GC–MS), was developed for the determination of six 1,2,3-benzotriazoles and six 1,3-benzothiazoles in aquatic matrices. It was demonstrated that MTBSTFA had a better overall performance compared with *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA) and *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). The method detection limits in tap water, river water and effluent samples were 0.050–1.3 ng L^{-1}, 0.057–1.8 ng L^{-1} and 0.10–4.0 ng L^{-1}, respectively. Mean recoveries of the target analytes at different aquatic matrices, ranged from 43% to 131% with relative standard deviations (RSDs) below 17%. The method was successfully employed to river water and effluent sewage samples collected from a sewage treatment plant in Germany. Seven target compounds were detected with the maximum concentration up to 2.9 μg L^{-1} for 4-Me-BTR in the effluent sample.

1. Introduction

Benzothiazoles (BTH, substances containing the 1,3-benzothiazole skeleton) and benzotriazoles (BTR, substances containing the 1,2,3-benzotriazole skeleton) are two kinds of high-production-volume chemicals and are widely used in a variety of industrial and consumer products [1–3]. For example, the annual production of BTRs in the U.S. was over 9000 tons in 1999 and a much greater production worldwide is expected [4]. As organic corrosion inhibitors, they play a significant role in the protection of materials from deteriorating. BTR derivatives can "slow-down" the corrosion of metal surfaces by forming metal-BTR complexes [5]. Further, they are often used in rubber production as vulcanization accelerator and as corrosion inhibitors in dishwashing agents [6,7]. BTH are most commonly used as vulcanization accelerators in rubber production and as biocides in paper manufacturing [8].

Owing to their wide application and resistance to biodegradation, both classes of compounds have been detected in raw and treated wastewater at μg L^{-1} concentration levels and in surface and ground water at ng L^{-1} concentration levels [9–14]. They have been classified as emerging pollutants due to their potential adverse effects on aquatic organisms, microbial communities and mammals even at low concentrations [15–17]. Several BTH and BTR, such as benzothiazole (BTH) and 5-methyl-1H-benzotriazole (5-Me-BTR) have been proven to be toxic to luminescent bacteria, plants and aquatic animals [18–20]. 1H-BTR was found to be mutagenic in bacteria cell systems (*Salmonella*, *Escherichia coli*) and is classified as a suspected human carcinogen [18]. A number of studies indicated that BTH and BTR could possess estrogenic effects in laboratory animals [21,22].

Liquid chromatography combined with mass spectrometry (MS) or tandem mass spectrometry (MS–MS) is often used for their determination due to the fact that most BTH and BTR are rather polar compounds [8,23,24]. Recently, gas chromatography–mass (GC–MS) or tandem mass spectrometry has increasingly been applied in the determination of BTH and BTR due to some of their advantages, such as high selectivity, good isomer separation, and reduced matrix effects [11,25–27]. However, both techniques

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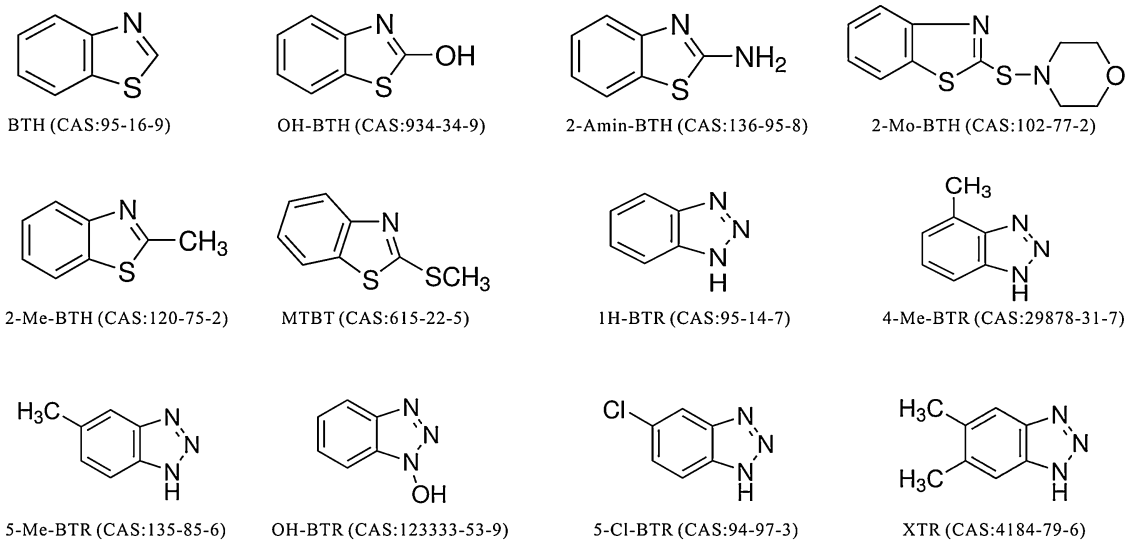

Fig. 1. Chemical structures and CAS numbers of BTR and BTH compounds analyzed.

often experience matrix effects when analyzing complex environmental matrices [28–30]. In addition, the limits of quantifications (LOQs) of most methods (generally higher than several or 10 ng L^{-1}) were not sensitive enough to determine these compounds in trace levels in surface water, groundwater or seawater, etc. In this study, we developed a method for the determination of six BTR and six BTH (Fig. 1) as *tert*-butyldimethylsilyl derivatives using GC–MS based on large-volume injection (LVI). Thus, the main objectives of the present study were to compare and select most effective silylation reagent, and to optimize operating conditions for LVI technique, silylation and SPE extraction. The developed method was applied to screen these compounds in river water and effluent samples from a sewage treatment plant (STP) in Germany.

2. Experimental

2.1. Chemicals and materials

Analytical standards (≥97%) of six BTH including benzothiazole (BTH), 2-aminobenzothiazole (2-Amin-BTH), 2-hydroxybenzothiazole (2-OH-BTH), 2-methylthiobenzothiazole (MTBT), 2-methylbenzothiazole (2-Me-BTH), 2-(morpholinothio)-benzothiazole (2-Mo-BTH) and six BTRs including 1H-benzotriazole (1H-BTR), 1H-hydroxybenzotriazole (OH-BTR), 4-methyl-1H-benzotriazole (4-Me-BTR) and 5-methyl-1H-benzotriazole (5-Me-BTR), 5,6-dimethyl-1H-benzotriazole (XTR), and 5-chloro-1H-benzotriazole (5-Cl-BTR) were purchased from Sigma–Aldrich (Germany). Silylation reagents, *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA, 97%) and two mixtures *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA, 98%) with 1% trimethylchlorosilane (TMCS) and *N*-*tert*-butyldimethylsilyl-*N*-methyltrifluoroacetamide (MTBSTFA, 99%) with 1% *tert*-butyldimethylchlorosilane (TBDMCS) were purchased from Restek Corporation (Germany). 1H-BTR-d_4 and BTH-d_4 used as surrogate and internal standard respectively were obtained from Sigma–Aldrich (Germany). GC grade *n*-hexane, cyclohexane, methanol (MeOH), acetonitrile (ACN), dichloromethane and acetone were obtained from Merck (Darmstadt, Germany). Ultra-pure water was prepared with a Milli-Q water purification system (Schwalbach, Germany). Oasis HLB cartridges (500 mg, 6 mL) were purchased from Waters. Unless noted otherwise, chemicals used in the analysis were purer than the analytical grade.

Standard stock solutions (10 mg mL^{-1}) of all analytes were prepared in MeOH. Mixed standards solution (1 μg mL^{-1}) was prepared in MeOH/H_2O (1:1, v/v) for recovery tests by spiking various concentration levels into aquatic matrices. The calibration mixed standards were prepared from stock solutions through serial dilutions with *n*-hexane. All mixed standards solution was stored at 4 °C in a refrigerator for up to 3 months.

2.2. Sample collection and preparation

Tap water from the laboratory was used for the development and optimization of the method. One grab sample of effluent was collected from a municipal STP, which was located in a city with a population of around 120,000 inhabitants. The STP consisted of a mechanical treatment for the separation of solids followed by activated sludge treatment. One river water grab sample was collected from the Göttingen section of the River Leine (Germany). The river sample was taken directly from the river bank. All water samples were stored in pre-cleaned 1 L brown glass bottles (Fisher scientific, Schwerte, Germany) and kept at 5 °C in a refrigerator. The samples were analyzed within one week. After complete precipitation, the supernatant was used for analysis instead of a filtered aliquot.

2.3. Sample extraction and derivatization

The final optimized SPE method was described as follows. The water samples (1 L for tap and river water and 100 mL for sewage water) were acidified to pH 3.0 using 3 M HCl. All blanks and samples were spiked with a known amount of surrogate before extraction. The samples were then passed through Oasis HLB cartridges at a flow rate of 5 mL min^{-1}. The cartridges had previously been conditioned using 10 mL of MeOH and 10 mL of acidified Milli-Q water (pH 3.0). Thereafter, the cartridges were washed with 10 mL of acidified Milli-Q water/MeOH (95:5, v/v) (pH 3.0) and 10 mL of Milli-Q water, respectively, and then dried under vacuum for 30 min. The analytes were eluted by 4 × 2 mL MeOH/ACN (1:1, v/v). The solvent was evaporated to dryness under a gentle stream of nitrogen, and reconstituted in 960 μL of acetone, 20 μL of internal standard (1.0 μg mL^{-1}) and 20 μL of silylation reagent. After being completely mixed, the mixtures were then transferred to a 2 mL amber glass vial. The sealed vials were incubated at 38 °C for 1 h before instrument analysis. For the determination of recoveries

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