



Determination of benzotriazoles in water samples by concurrent derivatization–dispersive liquid–liquid microextraction followed by gas chromatography–mass spectrometry



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ABSTRACT

Concurrent acetylation–dispersive liquid–liquid microextraction (DLLME) combined with gas chromatography–mass spectrometry (GC–MS) has been proposed for the sensitive determination of five polar benzotriazolic compounds (1H-benzotriazole, BTri; 4 and 5-methyl-1H-benzotriazole, 4-TTri and 5-TTri; 5,6-dimethyl-1H-benzotriazole, XTri; and 5-chloro-1H-benzotriazole, 5-ClBTri) in water samples. Under optimized conditions, samples (10 mL volume) were combined with 1 mL of Na₂HPO₄ (8%, w/v) and mixed with the ternary acetylation–microextraction mixture, consisting of 100 μL of acetic anhydride, 1.5 mL of acetonitrile and 60 μL of toluene. Thus, analytes were simultaneously acetylated and transferred to the dispersed droplets of toluene. The proposed methodology achieved limits of quantification (LOQs) between 0.007 ng mL⁻¹ and 0.080 ng mL⁻¹, enrichment factors between 93 and 172 times, good reproducibility, with relative standard deviations lower than 10%, and linearity with determination coefficients above 0.9991 for all compounds in the range between LOQs and 20 ng mL⁻¹. Pseudo-external calibration, with fortified ultrapure water samples submitted to the acetylation–DLLME procedure, proved to be adequate for the accurate quantification of complex aqueous matrices such as surface or wastewater, providing recoveries comprised between 86% and 112%. BTri, 4-TTri and 5-TTri were measured in environmental samples up to a concentration of 1.9 ng mL⁻¹ for BTri in raw wastewater.

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1. Introduction

Benzotriazole derivatives are categorized as high production volume chemicals, being complexing agents widely used as anti-corrosives (e.g. in engine coolants, aircraft deicers and antifreeze liquids) and for silver protection in dish washing liquids [1,2]. Toxicological studies have demonstrated that they might be hazardous to plants [3,4], mutagenic in bacteria cell systems [4] and toxic to some microorganisms [5]. Moreover, 1H-benzotriazole (BTri) has been classified as a suspected human carcinogen by the Dutch Expert Committee on Occupational Standards [4]. In the environment, benzotriazoles are considered as emerging pollutants [1,2], with sewage treatment plants (STPs) representing one of the most important discharge sources of these compounds into the aquatic media [6–8]. Thus, they have been detected in different aquatic compartments, such as surface, ground or wastewater [1,2], sludge

[9,10] and sediments [10]. Also, benzotriazoles appear in indoor environments [11], and even in human urine [12].

Due to their polar character (log *K*_{ow} values from 1.44 to 2.25), high water solubility and low volatility, liquid chromatography (LC), usually coupled to mass spectrometry (MS), has been the preferred technique for their sensitive determination in environmental samples during last years [2]. Most water samples analysis have been carried out using triple quadrupole (QqQ) LC–MS/MS instruments, achieving methodological LOQs in the low ng L⁻¹ range [6,13–16]; furthermore, other mass analyzers, such as LTQ FT Orbitrap MS [17], HRMS [18] and QTOF MS [19], have also demonstrated their suitability for benzotriazole determination. Limited performance of gas chromatography (GC) methods for benzotriazole compounds has been overcome by the use of ionic liquid coated columns [20], derivatization processes, such as methylation [21,22] or acetylation [23], and the use of two-dimensional gas chromatography [22,24]. But for now, no simple analytical methodologies, based on the use of a routine laboratory affordable GC–single quadrupole MS instrument, have been developed, able to reach LOQs comparable to those provided by LC–MS/MS methods.

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Regarding sample preparation, solid-phase extraction (SPE), using conventional hydrophilic–lipophilic balanced polymeric materials such as OASIS HLB [6,12–14,17] or Strata X [20,22], remains as the most popular concentration technique for benzotriazoles determination in water samples. SPE is also the preferred approach to carry out multiresidue water sampling campaigns in which these emerging pollutants are often included [25–28].

Despite microextraction techniques potential advantages, such as miniaturization, low solvent consumption and high selectivity [29,30], they have just been scarcely investigated for the extraction and preconcentration of benzotriazoles. As regards solid-phase methodologies, stir-bar sorptive extraction (SBSE) has been tested for the determination of BTri in ultrapure water. Whatever the tested coating, the extraction efficiency for BTri remained below 1%, for 50 mL of ultrapure water, after 4-h sampling [31]. Benzotriazoles have also been successfully concentrated from water samples using polyethersulfone micro-sorbents [19]. However, this sample preparation method required 6 h to achieve equilibrium conditions. Slow extraction kinetics of the above methods, which are characteristic of solid-phase microextraction techniques [29], can be overcome by some liquid–liquid microextraction methodologies, such as dispersive liquid–liquid microextraction (DLLME) [32]. Following the first report by Assadi and co-workers [32] in 2006, a high number of DLLME applications have been published. Some of them, as well as the most outstanding trends in DLLME, are revised in a recent review [33]. Relevant research lines in DLLME are (1) the search for alternative extractants, displaying a lower toxicity than halogenated, high density solvents [34], and (2) the combination of DLLME with derivatization reactions [35], which permit to expand the application field of DLLME to polar and/or thermal unstable compounds, in case of GC determination, and/or improving their detectability. To the best of our knowledge, the only application of DLLME to benzotriazoles analysis considered tri-*n*-butylphosphate as extractant, with concentrated species determined by LC with fluorescence detection and LC–MS/MS [36].

Therefore, main aims of this work are (1) the development of a simple, easy, highly efficient, environmental friendly and low cost sample preparation proposal, based on a concurrent derivatization–DLLME extraction, and (2) the combination with a relatively inexpensive determination technique, such as GC–MS, for the sensitive and selective determination of trace levels of benzotriazolic compounds in complex aqueous matrices. The performance of the developed method is compared to that corresponding to previously published approaches. Although acetylation and DLLME have been previously combined for the effective extraction of environmental pollutants [37] and food off-flavors [38], this approach has not been explored for benzotriazol compounds.

2. Experimental

2.1. Standards, solvents and material

Standards of BTri (98%), 4-methyl-1H-benzotriazole (4-TTri; 100%), 5-methyl-1H-benzotriazole (5-TTri; 98%), 5,6-dimethyl-1H-benzotriazole (XTri; 99%) and 1H-benzotriazole-(ring- d_4) solution (BTri- d_4), 10 $\mu\text{g mL}^{-1}$ in acetone, used as internal surrogate (IS) through derivatization and liquid microextraction steps, were purchased from Sigma–Aldrich (Milwaukee, WI, USA). Two different standards of 5-chloro-1H-benzotriazole (5-ClBTri), with nominal purities of 98% and 99% were acquired from TCI (Zwijndrecht, Belgium) and Sigma–Aldrich, respectively. Stock solutions of the above compounds and diluted mixtures, used to spike water samples employed during optimization of extraction conditions, were prepared in acetonitrile and stored at 4 °C for a maximum of 2

weeks. A standard of 1-acetyl-1H-benzotriazole (97%) was also provided by Sigma–Aldrich.

Methanol and acetonitrile (HPLC-grade) were from Merck (Darmstadt, Germany). Acetone, toluene, chlorobenzene, carbon tetrachloride and 1,1,1-trichloroethane (trace analysis grade) were provided by Sigma–Aldrich. Ultrapure water was obtained from a Milli-Q system (Millipore, Billerica, MA, USA). Sodium acetate, sodium chloride, acetic acid, sodium bicarbonate (NaHCO_3), disodium hydrogen phosphate (Na_2HPO_4) and acetic anhydride were also obtained from Sigma–Aldrich. Cellulose acetate membrane filters (0.45 μm pore size) were purchased from Millipore (Bedford, MA, USA).

Acetylated derivatives of target compounds, used during optimization of GC–MS determination conditions, were prepared as described elsewhere for BTri [23]. In brief, 10 mL of ultrapure water, containing a 0.8% (w/v) of Na_2HPO_4 , were spiked with benzotriazole standards prepared in acetonitrile. Thereafter, 150 μL of acetic anhydride were poured into the same vessel, 5 mL of toluene were added and vials were manually shaken for 2 min. Derivatized species were concentrated in the upper organic phase (toluene), which was recovered using a Pasteur pipette before GC–MS analysis. In the particular case of BTri, the commercially available acetylated standard was also used. Concentrations of acetylated benzotriazoles in toluene, used in this study, varied from 50 to 1500 ng mL^{-1} .

2.2. Samples

Grab samples of treated wastewater were obtained from different STPs located in Galicia (Northwest Spain); moreover, time-proportional 24-h composite samples were received from the inlet stream of a STP serving a 100,000 inhabitants city, in the same region. River water was obtained from two pristine creeks and the river receiving the discharge of the above STP.

2.3. Optimization of sample preparation conditions

Optimization of acetylation and DLLME conditions was performed with spiked (0.050–20 ng mL^{-1}) aliquots of ultrapure water, adjusted at different pHs, considering also different volumes of derivatization reagent (acetic anhydride), dispersant and extractant solvents. Extractions were performed in conical bottom glass tubes (nominal volume 12 mL), provided by Afora (Barcelona, Spain), which were manually shaken during derivatization and microextraction steps. Thereafter, tubes were centrifuged and the settled drop of extractant (case of chlorinated solvents) recovered after removal of the upper aqueous phase. When using toluene as extraction solvent, the floating organic phase, together with some water, was first transferred, using a micropipette 0.2 mL tip, to a conical insert (0.3 mL volume) to improve separation between aqueous and toluene phases. Thereafter, enough volume of the toluene layer could be recovered, with a 0.1 mL gas tight glass syringe, to be handled with the autosampler of the GC–MS instrument. Sample preparation conditions were optimized using uni- and multi-variate strategies based on the use of experimental factorial designs. In the latter case, the Statgraphics software (Statpoint Technologies, Warrenton, VA, USA) was used for experimental design creation and analysis.

Under optimal conditions, samples (10 mL) were first mixed with 1 mL of Na_2HPO_4 (8%, w/v) in the DLLME tube. Acetylation and microextraction of target compounds were simultaneously carried out by addition of a ternary mixture, consisting of 100 μL of acetic anhydride, 1.5 mL of acetonitrile and 60 μL of toluene. Reaction and centrifugation (3000 rpm) times were set at 1 and 5 min,

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