

Determination of Benzotriazole and Its Derivatives in Aqueous Sample with Air-assisted Liquid-Liquid Microextraction Followed by High-performance Liquid Chromatography



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Abstract: Benzotriazole and its derivatives are persistent contaminants and ubiquitous in aquatic environments. Here, a simple, reliable method based on air-assisted liquid-liquid microextraction coupled with high-performance liquid chromatography with a UV detector for determining 1H-benzotriazole, 5-methyl-1H-benzotriazole and 5-chloro-1H-benzotriazole in aqueous samples was developed. In this procedure, the analytes quickly entered into the extraction solvent via the bolus flow formed during the movement of the plunger without disperser solvent. 1-Hexanol was used as the extractant, thus avoiding chlorinated solvents, and a narrow-neck tube with round bottom was self-made to facilitate collection of the low-density extract phase and centrifugation at high speed. Those main parameters, including sample volume, type and volume of extraction solvent, number of suction-injection cycle, salt addition, and the pH were optimized. Under the optimized conditions, the pretreatment could be completed within two minutes with a good linearity ($r > 0.9996$). Satisfactory intra-day (3.0%–4.3%, $n = 5$) and inter-day (5.9%–7.8%, $n = 5$) precisions were observed. Further, the method was applied in analysis of real samples including tap water, lake water, river water, and municipal waste water with good recoveries (73%–116%).

Key Words: Air-assisted liquid-liquid microextraction; Benzotriazoles; High-performance liquid chromatography

1 Introduction

Benzotriazole and its derivatives (BTRs) are high volume chemicals (annual production of 10000 tons in the USA) with broad applications in industry and in the home^[1]. The main BTRs compounds are 1H-benzotriazole (BTri), tolyltriazole (TTR) and chlorobenzotriazole^[2–4]. BTRs have been used as flame and corrosion inhibitors^[5], dishwashing detergents, silver protectors in dishwashing liquids^[3], ultraviolet light stabilizers for plastics, and antifreeze agents^[6–8]. Due to the relatively low octanol-water partition coefficients, BTRs are soluble in water^[4–6]. In part because of this, they are only partially removed in wastewater treatment and are resistant to

biodegradation^[7,8]. Thus, BTRs are classified as persistent and ubiquitous emerging contaminants in the aquatic environment, since they have shown significant anti-androgenic activity to zebra fish and fathead minnows *in vitro*^[9,10], and mutagenic activity to bacteria (*Salmonella*, *Escherichia coli*)^[11]. What make it worse is that 1H-benzotriazole (BTri) is also a suspected human carcinogen^[2]. The main BTRs compounds, BTri, 5-methyl-1H-benzotriazole (5-TTri) and 5-chloro-1H-benzotriazole (5-CIBTri), have been detected in human urine originating from different countries with the highest total BTRs concentration of 24.5 $\mu\text{g L}^{-1}$ found in a Chinese sample, which indicates human exposure^[12]. Now only Australia has a drinking water guideline limit (7 ng L^{-1}) for TTR^[13]. For

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evaluating their environmental and health risk roundly and deeply, an easy-accessible method for quantitative analysis of BTRs, especially the pretreatment means, is prime.

Due to the low volatility, derivatization become a necessary operation for gas chromatography to determine BTRs^[14–16], and thus liquid chromatography are mostly used and liquid chromatography coupled with mass spectrometry (LC-MS) is common in literatures because of the high sensitivity from MS^[13,17,18]. However, the expensive MS impedes spread and application of the method. In the study, one of goals is to create a protocol suitable for laboratories with only modest liquid chromatography with a UV detector (LC-UV) instrumentation^[19].

In addition to the analytical technique, sample preparation is usually the most challenging issue in measuring pollutants in environmental samples. Current analytical tools to monitor BTRs are based on solid phase extraction (SPE)^[13,20–22] or liquid-liquid extraction (LLE)^[23]. In view of the waste from large volume of organic solvent (several milliliters), the high price and disposable cartridges, and the issues from sample carry-over, SPE method had been ignored in the present study. LLE was adopted because it has been developed into liquid phase microextraction, which could save organic solvents and time, meeting the requirement of green chemistry. In 2006, Assadi and co-workers^[24] introduced a dispersive liquid-liquid microextraction (DLLME), during which extraction solvent was dispersed into an aqueous sample solution with the help of disperser solvent^[4,15]. However, several milliliters of polar disperser solvent such as methanol or acetonitrile might decrease the partition coefficient of analytes in the extraction solvent and led to lower extraction efficiency. Current work on the DLLME focuses on techniques that could reduce or completely eliminate toxic organic solvents. Thus some disperser solvent-free techniques such as dynamic liquid-phase microextraction (LPME)^[25], vortex-assisted liquid-liquid microextraction (VALLME)^[26], ultrasound-assisted emulsification microextraction (USAEME)^[27] have been developed. For the dynamic LPME, the extractant must have the lowest solubility in water and need many extraction cycles (15–20 cycles). In view of the deficiencies of dynamic LPME, air-assisted liquid-liquid microextraction (AALLME) was developed by Farajzadeh and Mogaddam^[28]. In AALLME, the extractant and aqueous solution are emulsified by rapidly forcing the mixture into and out of a glass syringe, followed by injecting air^[29] or adding chemical demulsifier^[30] or centrifuging^[31] for driving the organic and aqueous phases separation. The AALLME procedure can often be finished in two minutes, and it is a simple and efficient extraction and pre-concentration procedure for organic compounds. Farajzadeh *et al.*^[28] originally applied this technique to determine phthalate esters or triazole pesticide residues^[32] in aqueous samples. Since then, AALLME has been employed to extract fungicides^[29], phenolic^[33], organophosphorus pesticides^[34], benzoylurea insecticides^[35], antioxidants^[36],

anti-inflammatory drugs^[37]. To the best of our knowledge, the study of AALLME in the pretreatment for quantitating BTRs has not yet been reported. In this study, AALLME was introduced into sample preparation coupled with the common high-performance liquid chromatography with a UV detector (HPLC-UV) for determining BTRs. To obtain the optimal AALLME conditions for BTRs analysis, effects of various parameters including the type and volume of extraction solvent, salt addition, number of suction-injection cycle, and pH of the aqueous samples on the detection were investigated. Furthermore, the analytic performance and possible application of the method in tap water, lake water, river water, and wastewater samples were investigated.

2 Experimental

2.1 Chemicals and solutions

The chemical standards of benzotriazole derivatives including BTri (99%), 5-TTri (98%) and 5-CIBTri (99%) were purchased from J&k (Beijing, China). 1-Hexanol (99%), 1-octanol (99%), 1-undecanol (98%) and 1-dodecanol (99%) were purchased from Aladdin (Shanghai, China). *n*-Hexane, toluene, acetonitrile and methanol of HPLC-grade were obtained from Honeywell (Morristown, USA). Sodium chloride, sodium hydroxide and hydrochloric acid were obtained from Hushi (Shanghai, China). Ultra-pure water was used throughout the experiment (Beijing Purkinje system, Beijing, China).

A stock solution containing three BTRs (BTri, 5-TTri and 5-CIBTri) was prepared in methanol at a concentration of 100 $\mu\text{g mL}^{-1}$ and stored at 4 °C in dark. Working standard solutions were prepared daily by appropriate dilutions of stock solution of BTRs with ultra-pure water.

2.2 Sample collection

Tap water samples were collected from the laboratory after allowing them to flow for 5 min. River water samples were collected from the Xiangjiang River (Changsha, Hunan Province, China). Lake water samples were collected from the Houhu Lake (Changsha, Hunan Province, China). Raw wastewater (influent) and treated wastewater (effluent) samples were collected from the wastewater treatment plant situated in the east of Changsha (Hunan Province, China). Samples were filtered through a 0.45- μm polytetrafluoroethylene (PTFE) membrane and stored in the dark at 4 °C and analyzed within 48 h. pH value of samples was adjusted to 3.0–7.0 using HCl solution (0.1 M) prior to determination.

2.3 Instrumentation and chromatographic conditions

Chromatographic separations were performed on an Agilent

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