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Determination of benzothiazoles and benzotriazoles by using ionic liquid stationary phases in gas chromatography mass spectrometry. Application to their characterization in wastewaters

Carmen Domínguez, Carolina Reyes-Contreras, Josep M. Bayona*

Department of Environmental Chemistry, IDAEA–CSIC, Jordi Girona 18-26, E-08034 Barcelona, Spain

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ABSTRACT

Benzothiazoles (BTHs) and benzotriazoles (BTRs) belong to a high production volume chemicals widely used in both industrial and household applications. Since they are recalcitrant to biodegradation, they are widespread in the environment. However, the BTHs and BTRs determination in environmental matrices is hindered by the coelution with coextracted organic matter and the poor selectivity in mass spectrometry due to the low mass of their diagnostic ions. Accordingly, this study examines the selectivity and suitability of new commercially available ionic liquid (IL) stationary phases for GC–MS and their application to the determination of BTHs and BTRs in wastewater samples. Five different IL columns were tested and the best results in terms of resolution, peak symmetry and analysis time were obtained with the SLB-IL59.

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1. Introduction

Benzothiazoles (BTHs) and benzotriazoles (BTRs) belong to high production volume chemicals that find broad application in various industrial processes and household products [1]. BTHs are used as biocides in paper and leather manufacturing, as vulcanization accelerator in rubber production [2] and as corrosion inhibitors [3]. BTRs are commonly used as a corrosion inhibitor in dishwasher detergents and de-icing/anti-icing fluids, an ultraviolet light stabilizer in plastics, and an antifogging agent in photography [4].

BTHs and BTRs are water soluble, resistant to biodegradation and only partially removed in wastewater treatment [5,6]. In fact, BTHs and BTRs are typical examples of polar and poorly degradable trace organic pollutants. Owing to their widespread application, several BTHs and BTRs are widely distributed in wastewater both industrial and domestic [7–10] and surface water (i.e. river and lake) [8,11–13] at concentration levels from 0.1 to 6 μg/L. BTRs have been classified as emergent pollutants [14] because even at low concentrations, they elicit negative effects to aquatic organisms [13,15].

The BTHs and BTRs determination by gas chromatography coupled to mass spectrometry (GC–MS) in the electron impact (EI) from complex matrices suffers from interferences, even in the selective ion monitoring mode because of the low mass of the diagnostic ions. On the other hand, liquid chromatography coupled to mass spectrometry (LC–MS) [6,16] or mass spectrometry in tandem (LC–MS/MS) [7,11] is usually used for their determination in environmental matrices. However, these techniques suffer from some disadvantages like the ionic suppression or enhancement in the electrospray ion sources due to the charge competition with organic matter coextracted [17]. Recently, Jover et al. [8] described the application of comprehensive two-dimensional GC coupled to time-of-flight mass spectrometry (GC×GC-TOF MS) technique as an alternative method for the determination of these compounds in aqueous matrices taking advantage of the highest resolution of two dimensional GC separation.

Over the last decade, the interest of ionic liquids (ILs) increased enormously in different areas of analytical chemistry [18,19] because their unique physicochemical properties and are considered as environmental friendly solvents [20–22]. In this regard, IL as GC stationary phases have been introduced [23] and different IL stationary phases have been previously used to separate mixtures of a series of fatty acid methyl esters [24], polycyclic aromatic hydrocarbons and chlorinated pesticides [25], essential oils [26] and flavors and fragrances [27].

Room-temperature ionic liquids (RTILs), also known as organic liquids, molten or fused salts, are a class of nonmolecular ionic solvents with low melting points [28]. However, as ILs, it is often applied to any compound that has a melting point <100 °C [19]. Most common RTIL are composed of asymmetrically substituted

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* Corresponding author. Tel.: +34 934006119; fax: +34 932045904.
E-mail address: jbtqam@cid.csic.es (J.M. Bayona).

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organic cations containing nitrogen (e.g. imidazole, pyrrolidine, pyridine) with inorganic anions (e.g. Cl^-, PF^{6-}, $BF_4{}^-$).

The interest of using IL as GC stationary phases arise from its desirable properties. In fact, the unique properties of IL including wide liquid phase range, low volatility (negligible vapour pressure), high viscosity, good thermal stability and variable polarities, make them ideal for that purpose [29]. Moreover, ILs display unusual dual-nature retention behavior, separating both nonpolar and polar compounds [30]. IL-based column performed as a nonpolar column when retaining relatively nonpolar analytes. However, they behaved significantly different when retaining highly polar and proton-donor analytes [29]. One important feature of ILs is that varying the cation or anion might significantly affect their physical and chemical properties. Therefore, in order to obtain columns with unique selectivity, many modifications are possible (i.e. anion or cation or pendant groups to anion and cation) [19]. Moreover, IL stationary phase offer greater thermal stability compared to cyanopropyl substituted polysiloxanes or polyethylene glycols with lower column bleed. They exhibit a lower background in MS applications [31] and do not generate the typical ions obtained with polar conventional stationary phase degradation.

To the best of our knowledge, there are not many studies using IL as stationary phases in environmental applications. In this study, commercially available polar IL stationary phases with different polarity and chemical properties were evaluated as GC stationary phases for the GC–MS determination of BTHs and BTRs. Five IL columns were evaluated in order to obtain the best separation between the various target analytes as well as the highest peak symmetry. The optimum stationary phase was used for the detection and quantification of BTHs and BTRs by GC–MS. In this work, the application of IL stationary phases for the determination of polar analytes occurring in complex environmental matrices such wastewater is reported for the first time.

2. Materials and methods

2.1. Chemicals

GC grade (Suprasolv) hexane, methanol, acetone, and ethyl acetate were obtained from Merck (Darmstadt, Germany). Benzothiazole (BT), 2-hydroxybenzothiazole (OHBT), 2-(methylthio) benzothiazole (MTBT), 1*H*-benzotriazole (BTri), 5-methyl-1*H*-benzotriazole (5-TTri), 2-mercaptobenzothiazole (MBT), 5,6-dimethylbenzotriazole (XTri) (purity of ≥96% for all analytes) and triphenylamine (TPhA) analytical grade were purchased from Sigma–Aldrich (Steinheim, Germany). Strata-X polymeric solid-phase extraction (SPE) cartridges (100 mg/6 mL) were obtained from Phenomenex (Torrance, CA, USA) and the 0.7 μm glass fiber filters with a diameter of 47 mm were purchased from Millipore (Bedford, MA, USA).

2.2. Standard solutions

Individual stock solutions of all standards were prepared at a concentration of 3 mg/mL in ethyl acetate. A mix solution, which contained all standards at a concentration of 300 μg/mL was prepared in ethyl acetate by dilution from the individual stock solution. Working standard solutions were prepared by serial dilution with ethyl acetate to reach a concentration range of 0.031–3 μg/mL. All working standard solutions were stored at −20 °C and where stable at least for three months.

2.3. Optimization of the GC–MS conditions

The GC–MS method optimization was carried out with BTHs and BTRs mix solution prepared in ethyl acetate (Table 1). Their determination was performed in a Trace GC–MS (Thermo Scientific, Dreieich, Germany) in the electron impact mode (70 eV ionization energy). Identifier and qualifier ions of BTHs and BTRs are shown in Table 1. Five commercially available ionic liquid columns of 30 m × 0.25 mm ID coated with 0.20 μm film thickness of different IL stationary phases (i.e. SLB-IL59, SLB-IL61, SLB-IL76, SLB-IL82 and SLB-IL111) were obtained from Supelco (Bellefonte, PA, USA). According to the supplementary information provided by Supelco I + D department, these stationary phases show different composition and polarity. However, only the chemical composition for SLB-IL59 is disclosed (i.e. 1,12-diamide (tripropylphosphonium) dodecane bis (trifluoromethansulphonyl) amide) [32]. A SUPELCOWAX-10 (30 m × 0.25 mm ID, 0.25 μm film thickness) also from Supelco, was selected as a reference polar column. The final temperatures were selected according to the recommended upper temperature limit (UTL) at isothermal conditions and the temperature programming rates of different evaluated columns are shown in Table 2.

A sample volume of 2 μL was injected in the splitless mode at an injector temperature of 270 °C and the purge valve activated 50 s after the injection. Helium was used as a carrier gas (99.9995% purity) at a flow rate of 1 mL/min. The transfer line and ion source were set at 280 °C and 200 °C respectively. Acquisition was performed in the full-scan mode ranging from m/z 50 to 500 amu at 2 scans/s with 6 min of solvent delay. Acquired data were processed by using the Themo Scientific X-calibur software.

The linearity range was from 0.031 to 3.0 μg/mL. The correlation coefficients (r^2) of the calibration curves were always higher than 0.993. The limit of detection (LOD) and limit of quantification (LOQ) were compound dependent in the range from 0.025 to 0.562 μg/L and from 0.060 to 0.815 μg/L respectively. These parameters were calculated as three times the standard deviation of a procedural blank, for the LOD and ten times for the standard deviation for the LOQ. Quantification and other quality control parameters have been reported elsewhere [8].

2.4. Sample extraction

The BTHs and BTRs in wastewater samples were analyzed following a filtration through a Whatman glass fiber filter with a pore size of 0.7 μm and processed as reported previously by Matamoros and et al. [33] (Fig. 1). This analytical methodology has been successfully developed for BTHs and BTRs determination in complex aqueous matrices [8] exhibiting recoveries in the range from 69 to 80% for BTHs and from 78 to 98% for BTRs in wastewater. Moreover, RSD obtained in water samples were lower than 10% for all analytes ($n = 3$). Briefly, a sample volume of 200 mL was acidified to pH = 3 with hydrochloric acid (HCl) and percolated through an activated polymeric solid-phase extraction cartridge (100 mg Strata X) from Phenomenex (Torrance, CA, USA). Loaded cartridges were eluted with 10 mL of hexane/ethyl acetate (1:1). The obtained extract was evaporated to ca. 20 μL under a gentle nitrogen stream and 186 ng of triphenylamine were added as internal standard. The vial was then reconstituted with ethyl acetate to a final volume of 300 μL. Final determination was performed on a TRACE GC–MS (Thermo Scientific, Dreieich, Germany).

2.5. Application to wastewater samples

The developed GC–MS methodology was applied to wastewater samples from a pilot wastewater treatment plant (Silvouta, NW, Spain). This treatment system consists of an upflow anaerobic sludge blanket (UASB) reactor and two constructed wetlands (CWs) operated in series. The first CW was a surface flow (SFCW) and the second a horizontal subsuperficial flow (SSFCW). Following sand and grease removal, the anaerobic reactor was fed with raw

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