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Study of the retention of benzotriazoles, benzothiazoles and benzenesulfonamides in mixed-mode solid-phase extraction in environmental samples☆

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ABSTRACT

In the present study, the capabilities of strong cation-exchange and strong anion-exchange sorbents for solid-phase extraction (SPE) have been evaluated for the selective retention of benzotriazoles (BTRs), benzothiazoles (BTs) and benzenesulfonamides (BSAs), which are a group of neutral analytes with interesting properties such as high polarity and the capability of delocalizing electron density. The retention of these analytes has been compared in both sorbents for the first time, using a SPE procedure specially designed to promote ionic retention of the analytes with the objective of including a washing step with an organic solvent to eliminate interferences retained by hydrophobic interactions.

As a result, ionic interactions between the analytes and both sorbents were observed, which allowed the successful introduction of a washing step using methanol in the SPE procedure even when most of the analytes were in their neutral state under SPE conditions. Consequently, a method was developed and further validated for each sorbent using liquid chromatography coupled to high-resolution mass spectrometry (LC–HRMS). Apart from the development of an improved method, special attention was paid to the discussion of the interactions present between the sorbents and each group of analytes to explain how these analytes in their neutral state might develop ionic interactions with the sorbents. At the end, the use of these sorbents helped to simplify previous developed methods where hydrophobic/hydrophilic sorbents were used, obtaining enhanced results when evaluated in river water and effluent and influent wastewaters.

1. Introduction

Mixed-mode polymeric sorbents have been developed to be applied in solid-phase extraction (SPE) to address the limitations of hydrophobic/hydrophilic sorbents. These sorbents have a polymeric backbone capable of retaining compounds through reversed-phase interactions and ionic groups capable of retaining ions with the opposite charge so both types of interactions are combined in one sorbent. The ionic groups bonded to the polymer are commonly sulfonic or carboxylic acids groups, which promote strong cation-exchange (SCX) and weak cation-exchange interactions (WCX), respectively; or quaternary amine groups for strong anion-exchange interactions (SAX); or tertiary or secondary amine groups for weak anion-exchange interactions (WAX) [1,2].

The presence of these ionic interactions allows basic or acidic compounds to be selectively extracted from complex matrices. These sorbents have been applied to extract several groups of compounds such as pharmaceuticals, drugs of abuse, herbicides, and biological compounds, among other analytes, from several biological, foodstuff and environmental matrices [1,3–9]. Generally, the methods are developed to extract the ionic analytes selectively in the elution step, which can be eluted separately from interferences that are rinsed in previous washing steps. To do so, the selection of pH values and solvents is very important and it depends on the type of sorbent and the structure of the analyte.

Benzotriazoles (BTRs), benzothiazoles (BTs) and benzenesulfonamides (BSAs) include substances containing the skeleton of benzotriazole (BTR), benzothiazole (BT) and benzenesulfonamide (BSA), respectively (Table 1), and they are considered emerging contaminants with particular chemical structures [10]. Both BTRs and BTs are heterocyclic compounds comprising two fused aromatic rings, allowing the delocalization of the electron den-

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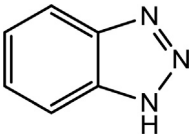
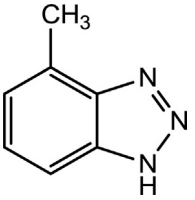
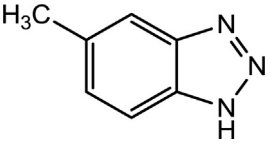
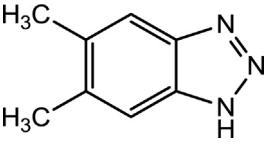
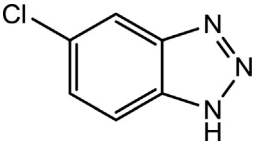
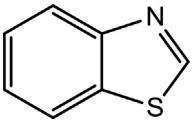
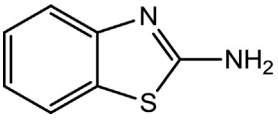
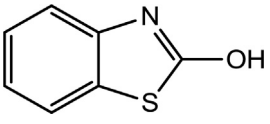
Table 1
Chemical structure, pKa, log P, and exact masses of the studied analytes.

Compound	Formula	Structure	pKa[a,b]	log P[a]	Molecular ion (m/z)	Fragment Formula (exact mass, m/z)
Benzotriazole (BTR)	$C_6H_5N_3$		8.38	1.44	$[M+H]^+$ 120.05562	$C_5H_5^+$ (65.03858) $C_6H_6N^+$ (92.04948)
4-methyl-1H-benzotriazole (4TTR)	$C_7H_7N_3$		8.74	1.82	$[M+H]^+$ 134.07127	$C_6H_7^+$ (79.05423) $C_6H_5N_2^+$ (105.04472) $C_6H_5^+$ (77.03858)
5-methyl-1H-benzotriazole (5TTR)	$C_7H_7N_3$		8.74	1.98	$[M+H]^+$ 134.07127	$C_6H_7^+$ (79.05423) $C_6H_5N_2^+$ (105.04472) $C_6H_5^+$ (77.03858)
5,6-dimethyl-1H-benzotriazole (XTR)	$C_8H_9N_3$		8.92	2.28	$[M+H]^+$ 148.08692	$C_7H_7^+$ (91.05423) $C_7H_9^+$ (93.06988) $C_6H_5N_2^+$ (105.04472)
5-chloro-1H-benzotriazole (ClBTR)	$C_6H_4ClN_3$		7.46	2.13	$[M+H]^+$ 154.01665	$C_5H_4Cl^+$ (98.99960) $C_6H_4N^+$ (90.03382) $C_5H_4{}^{37}Cl^+$ (156.01370)
Benzothiazole (BT)	C_7H_5NS		0.85	1.90	$[M+H]^+$ 136.02155	$C_6H_5S^+$ (109.01065) $C_5H_5^+$ (65.03858)
2-aminobenzothiazole (NH_2BT)	$C_7H_6N_2S$		3.94	1.88	$[M+H]^+$ 151.03244	$C_6H_5S^+$ (109.01065) $C_5H_5^+$ (65.03858) $C_6H_6SN^+$ (124.02155)
2-hydroxybenzothiazole (OHBT)	C_7H_5NOS		10.41	1.81	$[M+H]^+$ 152.01646	$C_6H_6SN^+$ (124.02155) $C_6H_6N^+$ (92.04948) $C_6H_5S^+$ (109.01065)