



Simultaneous determination of benzothiazoles, benzotriazoles and benzosulfonamides by solid phase microextraction-gas chromatography-triple quadrupole mass spectrometry in environmental aqueous matrices and human urine



Attilio Naccarato, Emanuela Gionfriddo, Giovanni Sindona, Antonio Tagarelli*

Dipartimento di Chimica e Tecnologie Chimiche, Università della Calabria, Via P. Bucci Cubo 12/C, I-87030 Arcavacata di Rende (CS), Italy

ARTICLE INFO

Article history:

Received 9 January 2014

Received in revised form 24 February 2014

Accepted 25 February 2014

Available online 12 March 2014

Keywords:

Benzothiazoles

Benzotriazoles

Benzosulfonamides

Solid-phase microextraction

Human urine

Gas chromatography

ABSTRACT

This work proposes a new approach for the simultaneous determination of benzothiazoles, benzotriazoles and benzosulfonamides in different environmental matrices and human urine, using solid-phase microextraction coupled with gas-chromatography-triple quadrupole mass spectrometry (SPME-GC-QqQMS). The analytes object of this investigation have been classified as toxic to aquatic organisms and their presence in human urine was reported to occur as result of human exposure to contaminated environment. In this work many of the challenges related to the chemical diversity and polarity of the analytes selected were overcome conducting a multivariate optimization of the working conditions by using the approach of "Experimental design". Tests performed to assess the performances of five SPME coatings in direct immersion mode revealed the polyacrylate coating to be the most suitable for the extraction of the probe analytes. A central composite design (CCD) was employed to determine the optimal conditions for four factors affecting the solid-phase microextraction process: extraction time, extraction temperature, pH and percentage of sodium chloride. The optimal working condition determined by using Derringer's desirability function were 40 min as extraction time, pH 7.1 and 6.0% of NaCl. Since the extraction temperature do not significantly affects the responses for all the analytes considered, analyses were performed at room temperature. A careful evaluation of the matrix effect for all the matrices tested was carried out. The results obtained showed that the proposed method did not significantly influenced by matrix effects in most of the cases tested, and thus allows the use of simplified calibration procedure. Satisfactory values of accuracy and precision were also obtained for all the matrices considered.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Benzotriazoles (BTRs) and benzothiazoles (BTHs) are extensively employed in various industrial and household applications and BTRs have already been classified as toxic contaminants to aquatic organisms, causing long-term adverse effects [1–5]. The main representative compounds of BTRs are 1*H*-benzotriazole and tolyltriazole i.e. a mixture of 4-methylbenzotriazole and 5-methylbenzotriazole. BTRs are widely used as additives in different processes, principally as corrosion inhibitors, UV stabilizer for plastics and in photography, antifreeze liquids and industrial cooling system [6–8]. BTHs also are used as corrosion inhibitors and as

biocides in paper, lumber and leather industry. Moreover, BTHs are added to antifreezes and cooling liquids and are employed as vulcanizations accelerators and in the production of azo dyes [9–12]. Benzosulfonamides have widespread applications as plasticizers, fungicides and intermediates in the synthesis of pesticides, drugs, sweeteners and dyes [13–15].

Many studies have been reported for the determination of BTRs and BTHs in different waters such as drinking water, rivers, lakes, ground water and wastewaters [7–12,16–30]. The majority of these methods are based on high-performance liquid chromatography (HPLC) coupled to mass spectrometry (MS) [7,9,16,28] or mass spectrometry in tandem acquisition mode (LC-MS/MS) [17,18,23–27,30] and in fewer cases on gas chromatography (GC)-MS [8,10,11,20–22,29]. Recently, Ying et al. described the determination of BTRs in environmental waters and biosolid samples by GC-MS/MS analysis following a preliminary solid phase

* Corresponding author. Tel.: +39 0984493332; fax: +39 0984493307.
E-mail address: a.tagarelli@unical.it (A. Tagarelli).

extraction (SPE) and pressurized liquid extraction (PLE) step for liquid and solid samples, respectively [31]. Moreover, recently an LC–MS/MS method was developed and applied for the quantification of BTRs and BTHs in human urine for the first time [32]. Very few studies have been published about the quantification of benzosulfonamides in waters [21,33–35] and, in particular, only one of them is based on gas chromatography technique [21]. Generally, the determination of BTRs and BTHs by liquid chromatography coupled to electrospray mass spectrometry suffers from some drawbacks. This is because ion suppression or enhancement in electrospray ion sources can occur due to the organic matter co-extracted in complex aqueous matrices. Indeed, in most of these methods quantification requires use of standard addition procedure. With regards to GC–MS, some disadvantages can be related to interfering species in single ion monitoring because of low mass of the diagnostic ions. The triple quadrupole analyzer (QqQ) allows quantitative analysis by operating in multiple reaction monitoring (MRM) acquisition i.e. by selecting a parent-daughter ion couples for each target compounds [36,37]. GC is more widely used in pollutants analysis due to its ease of operation and high separation efficiency and then this chromatographic technique in conjunction with triple quadrupole mass spectrometry (GC–QqQ–MS) represents a reliable analytical tool since very satisfactory sensitivity and specificity can be achieved.

The majority of the cited LC and GC approaches available in literature provide a solid phase extraction (SPE) step as sample preparation procedure. Since the use of more efficient and environmental friendly extraction methods is increasingly required, in the last years, several microextraction techniques were applied to the determination of different pollutants. Despite this, in only one study microextraction approach (dispersive liquid–liquid microextraction, DLLME) was used to extract BTRs and BTHs from water samples [26]. Solid phase microextraction (SPME) is a microextraction technique which allows the simultaneous extraction and pre-concentration of organic compounds. Since its introduction, SPME has gained popularity as a simple, solvent-free, reliable and flexible tool the sampling of several analytes in various matrices. Moreover, SPME enhances enrichment factors in the concentration of a variety of volatile and semi-volatile compounds, with minimal sample volume needed compared to solid phase extraction or liquid–liquid extraction. The combined use of SPME and a GC–QqQ–MS system has allowed the development of simple and very sensitive methods for the assay of pollutants, biomarkers and trace food components in aqueous matrices [38–43]. Recently, a headspace SPME followed by GC–ion trap MS method was developed for the determination of benzotriazole UV stabilizers in water samples [44].

The main objective of the present work was to develop a rapid and versatile method for simultaneous analysis of BTRs, BTHs and benzosulfonamides by SPME–GC–QqQ–MS in environmental waters and human urine. The reason that supports the selection of human urine matrix together with the other aqueous matrices is the possible contamination of humans as recently demonstrated by Asimakopoulos et al. as result of exposure to contaminated environment [32]. The combination of SPME and tandem mass spectrometric technique in multiple reaction monitoring (MRM) acquisition mode was evaluated and optimized to achieve a very simple automated method without the need for time consuming step and use of toxic solvents prior to instrumental analysis. Furthermore, tandem mass spectrometry was used to obtain a high specific protocol capable of unequivocal analytes assay. Five commercially available SPME fibers were tested and the variables affecting the SPME process were optimized by the multivariate approach of “Experiment design”. To the best of our knowledge, there has been no report on the determination of BTRs, BTHs and benzosulfonamides using SPME and, furthermore, GC–MS/MS

approach has never been applied to the analysis of BTHs and benzosulfonamides in any matrix.

2. Experimental

2.1. Materials

All analytes [Benzothiazole (BTH), 2-methylbenzothiazole (2-MeBTH), 2-(methylthio)benzothiazole (2-MeSBTH), 2-aminobenzothiazole (2-NH₂BTH), 2-hydroxybenzothiazole (2-OHBTH), 2-mercaptobenzothiazole (2-SHBTH), benzotriazole (BTR), 4-methyl-1H-benzotriazole (4-MeBTR), 5-methyl-1H-benzotriazole (5-MeBTR), 5-chlorobenzotriazole (5-ClBTR), 5,6-dimethyl-1H-benzotriazole (5,6-MeMeBTR), benzenesulfonamide (BSA), p-toluenesulfonamide (p-TSA) and N-ethyl p-toluenesulfonamide (N-Et-p-TSA)] and sodium chloride were purchased from Sigma–Aldrich (Milan, Italy). Benzotriazole-d4 (BTR-d4) and p-toluenesulfonamide-d4 (p-TSA-d4), used as internal standards, were bought from Sigma–Aldrich and C/D/N Isotopes (Pointe-Claire, Quebec, Canada), respectively. The tested solid phase microextraction fibers (polyacrylate 85 μm (PA), carboxen/polydimethylsiloxane 85 μm (Car/PDMS), divinylbenzene/carboxen/polydimethylsiloxane 50/30 μm (DVB/Car/PDMS), polydimethylsiloxane/divinylbenzene 65 μm (PDMS/DVB) and polydimethylsiloxane 100 μm (PDMS)) were purchased from Supelco (Bellefonte, PA, USA) and conditioned as recommended by the manufacturer. Aqueous solutions were prepared using ultrapure water obtained from a Milli-Q plus system (Millipore, Bedford, MA). The certified reference material “Wastewater” was bought from RTC International (Laramie, WY, USA). 0.45 μm micropore filters were supplied by Millipore (Bedford, MA). Synthetic urine (negative urine control) was obtained from Cerilliant (Round Rock, TE, USA).

2.2. Instrumentation and apparatus

GC–MS analyses were performed using a TSQ Quantum GC (Thermo Fischer Scientific) system constituted by a triple quadrupole mass spectrometer (QqQ) Quantum and a TRACE GC Ultra equipped with a TriPlus autosampler for fully automated SPME analysis. The capillary column was 30 m × 0.25 mm i.d., 0.25 μm film thickness Thermo TR-5MS (95% polydimethylsiloxane, 5% polydiphenylsiloxane). The GC oven temperature was initially held at 65 °C for 1 min, then ramped at 10 °C min⁻¹ to 240 °C, then ramped at 50 °C min⁻¹ to 290 °C and held at this temperature for 3 min. The carrier gas was helium at 1 ml min⁻¹ of purity 99.999% and argon at a pressure of 1.0 mTorr was used as collision gas. For SPME analyses, a Thermo PTV straight Liner 0.75 mm × 2.75 mm × 105 mm was used as GC inlet liner. Analyses were performed in splitless mode and by setting the injector temperature at 290 °C. The QqQ mass spectrometer was operated in electron ionization (EI) in multiple reaction monitoring (MRM) mode. The transfer line and ionization source temperatures were set at 280 and 250 °C, respectively. The emission current was set at 25 μA. The scan width was set at 1.2 m/z for all segments. Peak width of Q1 and Q3 was fixed at 0.7 amu. All signals were acquired in “Profile” mode. Instrumental parameters used in EI–MS/MS acquisition are shown in Table 1.

2.3. Samples

Five tap water samples were collected from public water supply of Rende (CS, Italy) after allowing the tap to flow for 5 min. Surface water samples were collected at three local rivers sited in Cosenza's City great urban area (CS, Italy) in July 2013. In particular, Campagnano, Crati and Busento were considered. Glass amber bottles

Download English Version:

<https://daneshyari.com/en/article/7613444>

Download Persian Version:

<https://daneshyari.com/article/7613444>

[Daneshyari.com](https://daneshyari.com)