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Analytical Methods

Determination of THMs in soft drink by solid-phase microextraction and gas chromatography

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ABSTRACT

In this study, a simple and fast method was developed for the analysis of trihalomethanes (THMs) in soft drink samples using headspace solid-phase microextraction coupled with gas chromatography (HS-SPME–GC). The influence of factors, such as, extraction temperature, extraction time, addition of sodium chloride and agitation speed on extraction yield was studied through an univariate experimental design strategy. Satisfactory recoveries ($\geqslant$90%) and precision, calculated as the relative standard deviations (RSD $\leqslant$ 11%), were obtained. The limit of detection (LOD) between 0.22 and 0.46 μg L^{-1} was achieved for THMs along with a wide linear range of concentrations. The applicability of the proposed method was demonstrated by analysing 74 real soft-drink samples. Since no matrix effects were observed, quantification could readily be carried out by external calibration with deionized water standards.

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1. Introduction

Chlorine is applied to drinking water in order to deactivate microorganisms and/or to ensure the residual concentrations in drinking water distribution systems, thus protecting water from microorganism regrowth. A multiplicity of viral, bacterial, protozoan, and parasitic diseases can be transmitted via contaminated drinking water. Infections can range from asymptomatic to mild discomfort, debilitation and even death (Rodriguez & Serodes, 2001). In the chlorination process, chlorine can react with natural organic matter including humic and fulvic substances. The trihalomethanes (THMs) are formed in this process, and the formation of halogenated compounds depends on the type and concentration of natural organic matter, bromide ion concentration, chlorine form and dose, pH, temperature and organic nitrogen concentration (Aboul & Wells, 2006; Rodriguez, Sérodes, & Levallois, 2004). The THMs formed are chloroform ($CHCl_3$), dichlorobromomethane ($CHCl_2Br$), chlorodi-bromomethane ($CHClBr_2$) and bromoform ($CHBr_3$) (Uyak, Ozdemir, & Toroz, 2007).

In 1974, for the first time studies in the United States showed a positive correlation between water supply and cancer. There was a study conducted by EPA in 113 water treatment plants. THMs were found in all the stations that used chlorine as a disinfection process (Melnick, 1989). EPA and the European Union (EU) have set the maximum contaminant level (MCL) for THMs in drinking water at 80 and 100 μg L^{-1}, respectively (The council of the European Union, 1998; United States Environmental Protection Agency (USEPA), 2001). EPA proposes to reduce this from 80 to 40 μg L^{-1}. A similar reduction occurred in 1998, when the agency reduced levels from 100 (proposed in 1979) to 80 μg L^{-1} (Pontius, 1993; Zhao, Lao, & Xu, 2004). Some European countries have stricter laws for THMs. Germany and Switzerland have set the maximum contaminant level at 10 and 25 μg L^{-1} of total THMs in drinking water (Golfinopoulos & Nikolaou, 2005). THMs are considered carcinogenic. Studies suggest that consumption of drinking water contaminated with high concentration of these compounds increases risks of bladder, kidney, stomach and pancreatic cancers in humans and animals. Therefore, exposure to such compounds should be minimised (Tokmak, Caper, Dilek, & Yetis, 2004).

Different analytical methods based on gas chromatography have been reported for determining THMs in drinking water. Most of them consist of a previous separation step to concentrate analytes, such as liquid–liquid extraction (LLE) (EPA method 551.1, 1995), purge and trap (P&T-GC) (Nikolaou, Lekkas, Golfinopoulos, & Kostopoulou, 2002), solid-phase extraction (SPE) (Gioia et al., 2004) and headspace solid-phase microextraction (HS-SPME) (Cardinali, Ashley, Morrow, Moll, & Blount, 2004). The current trend in analytical chemistry is to take on "green chemistry" ideology and in this sense, "solvent minimised" or "solvent-free" sample preparation methods have been developed, such as microextraction techniques (Pavón, Martín, Pinto, & Cordero, 2008).

The SPME technique, developed by Belardi and Pawliszyn (1989), is free of organic solvent, is simple, sensitive (Li, Zhong, Xu, & Sun, 2006) and widely applied in the determination of organic pollutants in food samples (Cavaliere, Macchione, Sindona, & Tagarelli, 2008). The principle behind SPME is the distribution of analytes between

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the sample matrix and a polymeric coating on a fused silica fibre, as well as their subsequent desorption in the injection port of a chromatograph (San Juan, Carrillo, & Tena, 2007).

According to the maximum contaminant level for THMs in drinking water established by several agencies, it is expected that THMs exist in trace levels in soft drinks, thus an extraction/preconcentration technique is required. However, few approaches have been reported for extraction of THMs from several types of soft drink (Abdel Rahman, 1982; Campillo, Viñas, López-García, Aguinaga, & Hernández-Córdoba, 2004; Wallace, 1997).

The main goal of this study was to explore the potential of the SPME technique for quantification of THMs in several kinds of soft drink matrices commercially available in the city of Florianópolis (capital of the state of Santa Catarina, Brazil). To reach this goal, the optimisation of the parameters affecting the THM extraction using the SPME fibre was performed by univariate method. The variables were temperature and extraction time, agitation speed, addition of NaCl and headspace volume. The optimised method validation included determination of the limits of detection and quantification of the proposed method, linearity, repeatability, accuracy and linear range. To the best of our knowledge, this is the first time that the SPME technique has been used to quantify THMs in soft drinks.

2. Experimental

2.1. Reagents and materials

Individual standard stock solutions of chloroform (Tedia, Fairfield, USA), dichlorobromomethane, chlorodibromomethane (Sigma–Aldrich, Milwaukee, USA) and bromoform (Synth, Diadema, Brazil) were prepared in methanol (Supelco, Bellefonte, PA, USA) resulting in solutions of 4700, 2500, 2500 and 7460 mg L^{-1}, respectively. Intermediate standard solutions of 100, 10, 1 and 0.2 mg L^{-1} of each compound were prepared in methanol by the dilution of standard stock solutions with methanol. Dichloromethane (Sigma–Aldrich) and diiodomethane (Sigma–Aldrich) were used as internal standards. Stock standard solutions of 2000 mg L^{-1} of dichloromethane and diiodomethane in methanol were prepared. Intermediate standard solutions of 100 mg L^{-1} were prepared in the same way as the THMs intermediate standard solutions. All standard solutions were stored at 0 °C.

Sodium chloride (Nuclear, Diadema, SP, Brazil) was used for the modification of the ionic strength of the samples. Sodium hydroxide (Nuclear) 6 mol L^{-1} was prepared in mineral water and used to reduce the carbonic acid (pK_a 6.1) of the samples until pH 6.1. Mineral water was used since in previous assays with distiled water and ultra pure water, trace concentrations of these compounds were detected. Other authors have reported the presence of THMs, especially chloroform, in all aqueous matrices and even in the air (Zoccolilo, Amendola, Cafaro, & Insogna, 2005). For this reason, mineral water was also used to construct the external calibration curve.

The investigated fibres were polydimethylsiloxane (PDMS, 100 μm), carboxen–polydimethylsiloxane (CAR–PDMS, 75 μm), divinylbenzene–carboxen–polydimethylsiloxane (DVB–CAR–PDMS, 50/30 μm), polyacrylate (PA, 85 μm), carbowax–divinylbenzene (CW–DVB, 65 μm) and polydimethylsiloxane–divinylbenzene (PDMS-DVB, 65 μm) purchased from Supelco (Bellefonte, PA, USA).

2.2. Instruments

Chromatographic analysis was performed on a Shimadzu GC-14B gas chromatograph, equipped with split/splitless injector and electron capture detector. Chromatographic separation was carried out in an Rtx-WAX capillary column (30 m × 0.25 mm, 0.25 μm in film thickness). Ultra pure nitrogen was used as the carrier and make-up gas at 1.0 and 48 mL min^{-1}, respectively. Split ratio was 1:120. Column oven temperature was 40 °C (2 min), 8 °C min^{-1} to 80 °C, 20 °C min^{-1} to 180 °C (1 min). Injector temperature was fixed at 280 °C, except when the CW–DVB fibre was used because the manufacturer recommends a maximum temperature of 260 °C. The detector temperature was fixed at 260 °C. The total chromatographic run was 12 min.

The identity of the THMs in the samples was confirmed using a Shimadzu GC–MS-QP2010 Plus. The quadrupole mass detector was operated at 200 °C in the electron impact mode at 70 eV. The ion source temperature was set to 200 °C, and the transfer line was set to 280 °C. The column oven temperature programs were 40 °C (4 min), 5 °C min^{-1} to 80 °C, 20 °C min^{-1} to 180 °C, and splitless mode was used. The analytical column was an Rtx-5MS. Carrier gas was helium at 1 mL min^{-1}. The mass acquisition range was 35–400 *m/z*. The peaks were identified on the basis of their fragmentation patterns using the NIST Mass Spectral Search Program 05 (NIST, Washington, DC).

2.3. Sample collection

The soft drinks were collected from supermarkets in Florianópolis (SC, Brazil). In this study several brands of soft drinks, flavours and types of packaging (PET and glass bottles, and cans) were taken into consideration. All samples were stored at 0 °C.

2.4. Solid-phase microextraction procedure

SPME extraction was performed with carboxen–polidimetilsiloxano (CAR–PDMS) fibre. The fibre was conditioned at 300 °C for 1 h prior to use. Blank desorptions were periodically carried out. Samples (20 mL) were transferred into vials (40 mL, Supelco) which contained 20% (w/v) sodium chloride salt, 150 μL sodium hydroxide 6 mol L^{-1}. Internal standard at 50 and 25 μg L^{-1} of, respectively, dichloromethane and diiodomethane were used.

The incubation and extraction temperature was 30 °C. The samples were equilibrated for 8 min before the extraction step. The speed of the magnetic stirring was 1000 rpm. The fibre was immersed in the headspace of the sample for 15 min, immediately drawn back into the needle and transferred without delay (less than 5 s) into the injection port of the GC. A desorption time of 3 min at 280 °C was used in this study. All analysis was performed in triplicate.

3. Results and discussion

3.1. Effect of carbon dioxide on THM extraction

When a soft drink bottle is opened, the pressure is reduced to the atmospheric pressure, causing decomposition of the carbonic acid releasing CO_2. To avoid this problem, the addition of NaOH to the sample can significantly reduce the carbonic acid concentration due to the formation of Na_2CO_3 and $NaHCO_3$.

The effect of CO_2 on the extraction of THMs from soft drink was studied comparing the extraction efficiency of adding or not adding 150 μL of NaOH 6 mol L^{-1} to a 20 mL soft drink sample. CAR–PDMS fibre, extraction time of 10 min, extraction temperature at 20 °C and stirring magnetic speed of 500 rpm were used in this study. As can be seen from Fig. 1, the best extraction efficiency occurs with addition of NaOH 6 mol L^{-1}, except for chloroform which is the more volatile of the target analytes. The improvement of the extraction efficiency for the other THMs was up to 35%. The analytes are released from the aqueous phase to the gas phase when

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