



Development of a sensitive thermal desorption method for the determination of trihalomethanes in humid ambient and alveolar air

J. Caro, M. Gallego*

Department of Analytical Chemistry, Campus of Rabanales, University of Córdoba, E-14071 Córdoba, Spain

ARTICLE INFO

Article history:

Received 22 January 2008

Received in revised form 14 April 2008

Accepted 16 April 2008

Available online 26 April 2008

Keywords:

Thermal desorption

Sorbent tubes

Trihalomethanes (THMs)

Swimming pools

Ambient and alveolar air

ABSTRACT

A sensitive and reliable method has been developed for the determination of trihalomethanes (THMs) in air samples through adsorption in sorbent tubes and thermal desorption (TD) of the compounds, followed by gas chromatography (GC)–mass spectrometry (MS) analysis. Three commercial sorbent materials were compared in terms of adsorption efficiency and breakthrough volume, finding Chromosorb 102 to be the most appropriate adsorbent for air sampling. The method allows us to reach detection limits of 0.03 ng (0.01 $\mu\text{g m}^{-3}$ for 3 l of air), linear ranges from 0.1 to 2000 ng and specific uncertainties of ca. 5.0 ± 0.2 ng for all THMs. Several salts were tested to reduce water retention (from the humid air of an indoor swimming pool) at the sampling stage, Na_2SO_4 being the one that provides optimum efficiency. The method was validated by a new recovery study in which several tubes with and without adsorbent were spiked with THMs and analyzed by TD-GC/MS, recoveries ranging from 92% to 97% for all the compounds. Finally, the performance of the method was evaluated through the analysis of ambient air samples from an indoor swimming pool and alveolar air samples from swimmers to assess their THM uptake. THMs were found to be stable in the sorbent tubes for at least 1 month when stored at 4 °C.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Trihalomethanes (THMs), including chloroform, bromodichloromethane, dibromochloromethane and bromoform, are one of two major groups of organic disinfection by-products (DBPs) identified in chlorinated water in the 1970s [1]. Because of their carcinogenic risks, THMs were first regulated by the US Environmental Protection Agency (EPA) under the THM regulation in 1979 with a maximum contaminant level at 100 $\mu\text{g l}^{-1}$, which was lowered to 80 $\mu\text{g l}^{-1}$ in 1998 [2,3]. Public pools are usually disinfected by gaseous chlorine or sodium hypochlorite and cartridge filters in the United States and Europe [4,5]. These methods produce a variety of DBPs such as THMs, as reported since 1980 [6]. Human exposure studies have shown that THMs can be found in the blood, plasma and exhaled breath [7–9] and urine [10] of swimmers and even of non-swimmers within an indoor pool setting. Inhalation and dermal exposure are likely to be important routes of human exposure to THMs in swimming pools, with ingestion from accidental swallowing of water being a minor route.

Volatile halogenated compounds are usually extracted from air onto sorbent columns, and after carrying out a solvent or thermal

desorption (TD) step, the target compounds are transferred into a gas chromatograph (GC) [11]. Along with GC separation, electron capture detection (ECD) and electron impact mass spectrometry (MS) are the most frequent detectors used; recent integration of other detectors has been reviewed [11,12]. Infrared spectroscopic methods have also been proposed due to their simplicity and rapidity in detecting gas samples containing volatile organic compounds (VOCs) [13]. The performance of a short-path TD method for 77 VOCs using a dual sorbent system (Tenax GR and Carbosieve SIII) provided excellent performance except for very low concentrations or large samples of highly humid air [14]. Automated monitoring of volatile halogenated compounds is currently an issue in ambient air analysis; the combination of adsorbent traps with Peltier cooling and with selective MS allowed good analyte recovery and rapid desorption without the need for post-desorption cryofocussing [15]. A type of multi-walled carbon nanotubes (MWCNTs) has been evaluated as an adsorbent for trapping VOCs (chloroform included). The breakthrough volume of chloroform (using gas injection into a GC/FID) is two orders larger with MWCNTs than on Carbo-pack B [16]. Novel trends in sample preparation have recently been summarized for the determination of VOCs in air [17].

THM concentrations in the air of swimming pools have been determined by collecting 10 l of air on activated carbon adsorbents, desorption with 3-phenoxybenzylalcohol at 110 °C for 30 min in a vial, and manual injection of the extract into a GC/ECD [18]. Air and breath samples from people exposed to household water-use

* Corresponding author. Tel.: +34 957 218 614; fax: +34 957 218 614.

E-mail address: qa1gafem@uco.es (M. Gallego).

activities have been collected directly into canisters to determine THMs by automated GC/MS using a modified version of US EPA Method TO-14 [19]. Aggazzotti et al. have published several articles about the determination of THMs in water, blood and air as indicators of exposure in indoor swimming pools. Ambient air and breath samples were analyzed by direct injection of samples into a gas chromatograph with ECD using a gas-tight syringe [7]. More recently, air samples were collected in tedlar bags and breath on glass tubes with two valves (at the end of expiration the valves were closed) [9]. Both air samples were analyzed as described above [7]. Water interference is a special issue in order to avoid chromatographic problems and detector damage. Several options to reduce the amount of water that is brought into the GC system via the sorbent materials are found in the literature [20]. Therefore, water removal remains an important issue in the analysis of volatile halogenated compounds [11].

This paper describes the development and evaluation of a TD-GC/MS method for the determination of THMs in the ambient air of a swimming pool and in the alveolar air of people exposed (swimmers). In this sense multisorbent tubes (usually employed to date for mixtures of VOCs) are not necessary and only tubes filled with the best adsorbent for these compounds (low water retention, high breakthrough volumes, no generation of artefacts, etc.) were used. Furthermore, the present work is the first of its kind to include a rigorous study of several salts packed into a tube placed in front of the sorbent tube in order to eliminate the water present in the ambient air of the indoor swimming pool. The inclusion of a drying tube is mandatory, taking into account the high levels of humidity in the swimming pool (60–80% relative humidity), as the water can reach the chromatographic column as well as the mass spectrometer in addition to a decrease in the retention of analytes in the sorbent material. On the other hand, the methods proposed for the sampling of breath are neither robust nor reliable [7–9]; in this method a Bio-VOC sampler for alveolar air was used. Finally, a new recovery experiment was proposed using TD-GC/MS in all instances, since it is normally carried out in the VOC literature by comparing the analysis of a spiked tube by TD-GC/MS versus the response obtained by direct injection of the same amount by GC/MS [14,21].

2. Experimental

2.1. Chemicals and materials

Chloroform (CHCl_3), bromodichloromethane (CHBrCl_2), dibromochloromethane (CHBr_2Cl) and bromoform (CHBr_3), all of them with a purity $\geq 99\%$, were purchased from Sigma–Aldrich (Madrid, Spain). Methanol, calcium chloride, potassium carbonate and sodium sulphate were supplied by Panreac (Barcelona, Spain). Three commercial sorbent materials, including two porous polymers (Tenax TA and Chromosorb 102 with a surface area of 35 and $350 \text{ m}^2 \text{ g}^{-1}$, respectively) and a graphitized carbon black (Carbopack B, surface area $100 \text{ m}^2 \text{ g}^{-1}$), all of them with 60/80 mesh, and unsilanized glass wool were supplied by Supelco (Madrid, Spain).

2.2. Sorbent tubes

Stainless steel thermal desorption tubes (6 mm O.D. \times 90 mm long, 5 mm I.D., Markes International Limited, Pontyclun, UK) were used in this study. The tubes were cleaned in ultrasonic shaker with methanol for 2 h and dried in an oven at 100°C for 1 h. Clean tubes were then packed with 200 mg of Tenax TA, Chromosorb 102 or Carbopack B and plugged at both ends with a sorbent retain-

ing gauze. A TC-20 tube conditioning system (Markes International Limited) was used to clean up to 20 tubes simultaneously. According to the commercial conditions recommended for each sorbent material, tubes were conditioned at variable temperatures heating at 220, 250 and 300°C for 120 min and then at 230, 300 and 400°C for 30 min, for Chromosorb 102, Tenax TA and Carbopack B, respectively; in all cases a flow rate of nitrogen (5.0 grade, Air Liquid, Seville, Spain) at 100 ml min^{-1} was applied. After conditioning, background chromatograms of the sorbent tubes were investigated and these conditioning parameters were found to be effective for cleaning the tubes. Moreover, in blank experiments, the tubes were found to be stable for at least 30 days since no background levels of the target compounds were found. Therefore, after conditioning, the sorbent tubes were immediately capped with brass long-term storage caps and stored in sealed glass jars at 4°C for up to 1 month.

Calibration solutions containing the four THMs at concentrations between $10 \mu\text{g l}^{-1}$ and 200 mg l^{-1} were prepared fortnightly in methanol by serial dilution of the stock standard solutions of each THM in methanol (1 mg ml^{-1}), which were stored in amber glass bottles at 4°C . A calibration solution loading rig (CSLR) system was used for the introduction of liquid calibration standards into the sorbent tubes. The CSLR system consisted of an unheated injector with a controlled carrier gas supply (nitrogen) and a sorbent tube connection point. The sampling end of the sorbent tube was connected to the CSLR system and the carrier gas flow rate was set at 90 ml min^{-1} , which was swept via the injector through the sorbent tube to vent. $10 \mu\text{l}$ aliquots of the calibration solutions were introduced through the injector septum using a standard GC syringe. A tube loading time of 10 min was used to ensure that methanol was eliminated being the target analytes quantitatively retained. Then the sorbent tubes containing known amounts of THMs (from 0.1 ng to $2 \mu\text{g}$) were analyzed immediately by TD-GC/MS.

2.3. Air samples

The study was carried out in an indoor swimming pool located in the Rabanales University Campus in Córdoba (Spain). Ambient air samples were taken in the sorbent tubes using a SKC Sidekick pump (Markes International Limited), with a pump flow calibrated by a rotameter at 200 ml min^{-1} , passing through the tubes an air stream during 15 min to obtain air volumes of 3 l. The relative standard deviation of the flow rate was less than 2%. The samples were collected at a height of 50 cm at the edge of the pool, being the tubes immediately capped after collection with the storage caps to avoid losses. During each sampling session (1 h), three spot samples of ambient air were collected. To reduce/avoid the water (that is brought into the GC system via the sorbent materials) retention at the sampling stage from the ambient air of the swimming pool installation, a drying tube was placed in front of the sampling tube. For this purpose, a glass tube (6 mm O.D. \times 90 mm long, 4 mm I.D., Markes International Limited) was filled with 400 mg of Na_2SO_4 , fixed with unsilanized glass wool plugs, and then capped with the storage caps. The drying and the sorbent tubes were connected by using specific stainless steel unions fitted with PTFE ferrules (Markes International Limited) before the sampling stage. To check that the pump flow does not undergo changes after sampling due to the retention of water in the drying tube, the flow rate passing through both tubes was again measured. No significant difference between the flow rates before and after sampling was obtained.

Alveolar air samples were kindly supplied by swimmers at the indoor swimming pool. During the time in which the study was carried out, all subjects consumed only mineral water, free from THMs. These samples were collected approximately 5 min before and after the bath activity in the sorbent tubes using Bio-VOC sam-

Download English Version:

<https://daneshyari.com/en/article/1243390>

Download Persian Version:

<https://daneshyari.com/article/1243390>

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