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Trace determination of low-molecular-mass substituted benzaldehydes in treated water using micro solid-phase extraction followed by liquid chromatography–mass spectrometric detection

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ABSTRACT

Aldehydes are a class of water disinfection by-products (DBPs) that are an object of special attention due to their high toxicity and carcinogenic effect. While aliphatic low-molecular-mass aldehydes (LMMAs) are often measured in waters, there is little information on the occurrence of aromatic LMMAs. This paper reports the development of a simple, rapid and sensitive method for the quantitative determination of six LMM substituted benzaldehydes (BAs) as DBPs in treated water. The method is based on the continuous *in situ* derivatisation/extraction of aldehydes on a Telos™ ENV μ-solid-phase extraction (μ-SPE) column impregnated with 2,4-dinitrophenylhydrazine (DNPH). After elution of the hydrazones with acetonitrile (ACN), the derivatives are analysed using liquid chromatography–mass spectrometry (LC–MS). Under optimum conditions, limits of detection (LODs) were obtained between 15 and 25 ng/L and the inter-day precision expressed as the relative standard deviation (RSD) ranged from 6.1% to 7.7%. Matrix effects were shown to be negligible by comparing the response factors (RFs) obtained in ultra-pure and treated waters. The proposed method is the first contribution developed for the analysis of LMM substituted BAs as DBPs in waters by LC–MS. Some of the aromatic LMMAs identified had not previously been reported for swimming pool water.

1. Introduction

The disinfection of drinking water has led to major improvements in public health in developed countries since it was introduced in the first half of the twentieth century. The highly reactive nature of oxidants (chlorine, chlorine dioxide, chloramines, ozone or their mixtures) used as disinfectants for microbial inactivation also forms a number of DBPs through reactions with naturally occurring organic and inorganic substances in the source water. Since the discovery of DBPs formation in the mid-1970s, toxicological and epidemiological studies have indicated the possible health issues posed by these harmful compounds, and hence the potential public health problem caused by water disinfection is a great concern worldwide [1–11].

Non-halogenated aldehydes are a class of organic chemicals known to be primarily formed as DBPs of drinking water ozonation [8], although both chlorine and chlorine dioxide treatment can also originate these carbonyl compounds [9–15]. Seven major aliphatic LMMAs, including formaldehyde to valeraldehyde and the dialdehydes glyoxal and methyl glyoxal have been detected and determined in treated water. However, the occurrence and analysis of aromatic LMMAs in water have scarcely been reported so far. Thus, BA has been identified in drinking water after ozone, chlorine or chlorine dioxide disinfection [10,14,16]; 2,5-dihydroxybenzaldehyde (2,5-DHBA) [11] and 2-ethylbenzaldehyde (2-EBA) [10] after ozone and chlorine dioxide treatment, respectively; and 3-hydroxybenzaldehyde (3-HBA) [17], BA and 2,5-dimethylbenzaldehyde (2,5-DMBA) [18,19] in swimming pools after chlorination.

Methods for directly determining aldehydes in water require a derivatisation step before extraction and analysis by gas chromatography (GC) or LC due to the high polarity and chemical instability of these compounds. Two well-known derivatisation reagents, recommended in the U.S. Environmental Protection Agency (EPA) Methods 556.1 [20] and 8315A [21], can be used according to the chromatographic technique involved in the separation of derivatives: *o*-2,3,4,5,6-pentafluorobenzylhydroxylamine (PFBHA), which yields non-polar oximes that can be easily extracted into an organic solvent and analysed by GC [20,22–26], and DNPH, which provides hydrazones which are LC-amenable [11,17–19,21,27–33]. EPA methods [20,21] involve an extensive work-up, consume materials, and solvents for the derivatisation and the isolation of the derivatives (liquid–liquid extraction [20] and SPE cartridges [21]) because they are formed by batch

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derivatisation. LC coupled with DNPH derivatisation is increasingly being viewed as a useful alternative to GC-PFBHA methods because it permits the analysis of highly polar compounds. These methods were essentially focused on the determination of aliphatic aldehydes [27–29,32,33] and only the analysis of BA in the presence of aliphatic LMMAs in spiked water has been the subject of two sporadic works [30,31]. Recently, we have reported two contributions with respect to the determination of LMM substituted BAs in water, namely the analysis of BA and methyl derivatives in tap, stream and swimming pool waters [18], and the determination of six LMM substituted BAs in indoor swimming pool waters after chlorination [19].

Regarding sample preparation methods involved in the analysis of LMMAs in water by LC, a minor number of studies have dealt with the use of microextraction techniques [27,30,31] as an alternative to the classical SPE approach [17,21]. This trend can be ascribed to the incompatibility of extracting solvents with LC mobile phases, which requires an extra step of solvent exchange and reconstitution of extracts. Head-space single drop [31], salt-assisted liquid–liquid microextraction with water-miscible organic solvents [30] and μ-SPE [27] have been used for the determination of carbonyl compounds in spiked water and aliphatic LMMAs in rainwater after derivatisation with DNPH and analysis by LC with UV detection.

The aim of this work was the development of a sensitive analytical method for the quantification of six LMM substituted BAs in treated water, especially in swimming pools. In previous papers [18,19,28,29] a novel DNPH derivatisation procedure using a μ-SPE unit was successfully developed for the analysis of aldehydes in water. When compared with classical SPE, this μ-SPE approach reduces the consumption of time, materials and solvents for the derivatisation and isolation of the hydrazones as well as increases the sensitivity because higher pre-concentration factors can be achieved. The present work describes the development of a Telos™ ENV μ-SPE unit for the continuous *in situ* derivatisation/extraction of LMM substituted BAs from treated water, followed by LC–MS. It is noteworthy that the proposed method is the first report on the determination of aromatic LMMAs in waters by LC–MS using DNPH as the derivatising reagent.

2. Materials and methods

2.1. Standards and solutions

All the chemicals and solvents used were of analytical grade. BA (≥99.0%), 3-methylbenzaldehyde (3-MBA, ≥97.0%), 2-EBA (≥88.0%), 2,5-DMBA (≥99.0%), 3-HBA (≥97.0%) and 2,5-DHBA (98.0%) were supplied by Aldrich (Sigma–Aldrich Química, Madrid, Spain). Acetaldehyde (C2, ≥99.5%) was supplied by Sigma (Sigma–Aldrich Química) whereas propionaldehyde (C3, ≥96.0%), butyraldehyde (C4, ≥99.0%) and valeraldehyde (C5, ≥97.0%) were acquired from Fluka (Sigma–Aldrich Química). Each aldehyde stock solution (4.0 mg/mL) was prepared in methanol (Romil Chemicals, Cambridge, UK) and stored at 4 °C. Standard mixtures of the analytes were prepared daily by appropriate dilution of stock solutions in LC–MS ultra-grade water (Chromasolv, Fluka). DNPH was of analytical reagent grade (≥99%) and purchased from Fluka. A 60 mM stock solution was prepared by dissolving 594.4 mg of the chemical in 50 mL of a solution containing 12 M hydrochloric acid, ultra-pure water and acetonitrile (2:5:1, v/v/v) and then stored in a freezer. Successive diluted solutions were prepared in LC–MS ultra-grade water. RP-C18, a silica sorbent with octadecyl functional groups (particle size 50 μm, surface area 600 m^2/g), was acquired in Sigma; Dowex 50WX8 hydrogen form, a strongly-cation exchange polymeric resin (particle size 20–50 mesh, capacity 1.1 meq/mL by wetted bed volume), was supplied by Fluka; LiChrolut EN (particle size 40–120 μm, surface area ~1200 m^2/g) was provided by Merck (Darmstadt, Germany); while Telos™ ENV (mean particle size 80 μm, surface area ~900 m^2/g) was kindly supplied by Kinesis Inc. (Vidrafoc S.A. Madrid, Spain).

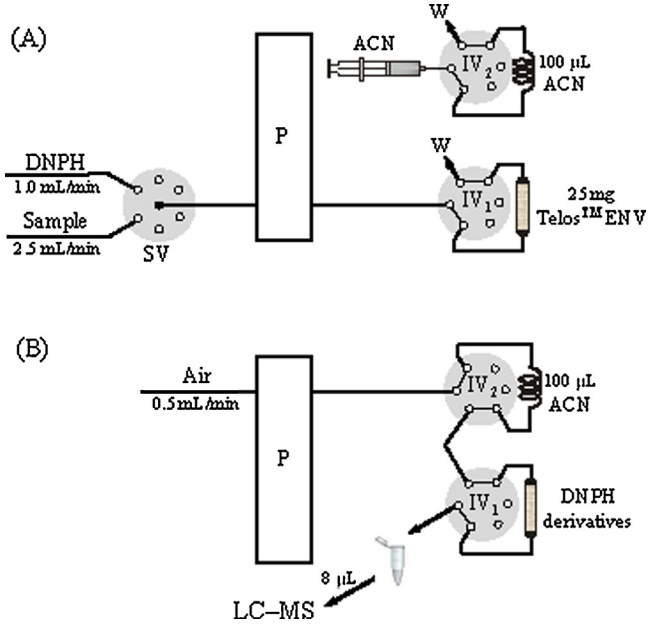

Fig. 1. Continuous-flow μ-SPE system developed for the derivatisation/extraction of LMMAs in treated water samples. (A) Loading DNPH and ACN. Derivatisation/extraction of aldehydes, and (B) elution of hydrazones. P, peristaltic pump; SV, selecting valve; W, waste.

2.2. Derivatisation and extraction of aldehydes with the μ-SPE system

A scheme of the μ-SPE system used for derivatisation/extraction of LMMAs is depicted in Fig. 1. It consisted of a Minipuls-3 peristaltic pump from Gilson (Middleton, WI, USA) fitted with poly(vinylchloride) tubes and two model 5041 injection valves (IV) from Rheodyne (Cotati, CA, USA). The μ-SPE columns were made from PTFE capillaries of 3 mm I.D. and 1 cm long and packed with 25 mg of different sorbent materials. The μ-columns were sealed at both ends with small plugs of glass wool to prevent material losses and their ends were capped by fitting 30 mm × 0.5 mm I.D. PTFE tubing into a 10 mm × 1 mm I.D. PTFE tube to facilitate its insertion into the flow system. The μ-columns were conditioned with different solutions according to the sorbent used: 1 mL of methanol and 1 mL of ultra-pure water for RP-C18, 1 mL of 1.0 M hydrochloric acid and 5 mL of ultra-pure water for Dowex 50WX8, 0.5 mL of ACN and 1 mL of ultra-pure water for LiChrolut EN and 1 mL of ACN and 2 mL of ultra-pure water for Telos™ ENV. All solutions were delivered at a flow rate of 0.5 mL/min.

After conditioning, the μ-SPE column (Telos™ ENV, 25 mg, 1 cm long) was impregnated with 2.0 mL of a 2.5 mM DNPH solution (1.0 mg of DNPH) at 1.0 mL/min. Then volumes up to 100 mL of treated water or standard solution in 2.0 M hydrochloric acid containing between 5 and 250 ng of aldehydes were aspirated at 2.5 mL/min through the μ-SPE column. The aldehydes were *in situ* derivatised with DNPH on the Telos™ ENV μ-column, located in the loop of IV_1, the sample matrix being sent to waste. Simultaneously, the loop of IV_2 was filled by hand with the eluent (ACN) by means of a syringe. Prior to elution, by switching IV_1, any residual aqueous solution remaining inside the μ-column and the connectors was flushed by passing an air stream at 0.5 mL/min for 2 min.