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A new selective method for dimethylamine in water analysis by liquid chromatography using solid-phase microextraction and two-stage derivatization with *o*-phthalaldialdehyde and 9-fluorenylmethyl chloroformate

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Abstract

A new method is presented for the determination of DMA in water as its 9-fluorenylmethyl chloroformate (FMOC) derivative using solid-phase microextraction (SPME) and liquid chromatography. The method is based on the employment of SPME fibres coated with carbowax-templated resin (CW-TR) for analyte extraction and derivatization. The fibres were successively immersed in the samples, in a solution of *o*-phthalaldialdehyde and *N*-acethyl-L-cysteine (OPA–NAC) and finally, in a solution of FMOC. OPA–NAC reacted on the fibre with possible primary aliphatic amines present in the samples, particularly with PA which is a direct interferent in the determination of DMA with FMOC. In such a way, the formation of PA–FMOC during the second stage was prevented, and thus the method was selective for DMA. The proposed procedure was applied to the determination of DMA in the 1.0–10.0 μg/mL range. The method provided suitable linearity, accuracy and reproducibility, and limits of detection and quantification of 0.3 and 1.0 μg/mL, respectively. The applicability of the method for the determination of DMA in different types of water is shown.

Keywords: Dimethylamine; Water; Solid-phase microextraction; On fibre two-stage derivatization

1. Introduction

Today, the potential of solid-phase microextraction (SPME) for sample preparation is widely recognized. SPME integrates sampling, extraction, preconcentration and sample introduction into a single process, resulting in high sample throughput. Moreover, it is a inexpensive, solvent-free and versatile technique that can by coupled to either gas chromatography (GC) or liquid chromatography (LC). SPME can also be combined with chemical derivatization to improve the extraction efficiency, or to make the analytes more amenable for chromatography and detection.

To date, derivatization has almost exclusively used in SPME-GC [1]. Two alternatives have been described to perform derivatization: addition of the reagent to the samples and subsequent extraction of the derivatives formed, and extraction of the analytes onto the fibres and subsequent derivatization of the analytes (on-fibre derivatization). Some of the applications in this area are the determination of fatty acids in aqueous or gaseous phases [2], the determination of amphetamines in urine [3], the determination of aliphatic amines in water and urine [4], and the quantification of aldehydes in water [5].

More recently, attempts have been made to combine chemical derivatization with SPME/LC. In this sense, Pawliszyn and co-workers described a procedure for the analysis of anatoxin-a in aqueous samples based on its derivatization

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on the surface of SPME fibres with the fluorogenic reagent 4-fluoro-7-nitro-2,1,3-benzoxadiazole [6]. The reagent was dropped or sprayed onto the fibre containing the extracted analyte. The fibre was then heated to 70 °C for 10 min, and finally, the fibre was inserted into the interface of the LC equipment. We have recently described a method for the analysis of methylamine in water based on its on-fibre derivatization with 9-fluorenylmethyl chloroformate (FMOC) [7]. Derivatization was accomplished by immersing the fibres with the extracted analyte into the reagent solution. The same reagent has been also used to derivatize amphetamines in an study aimed at comparing two extraction/derivatization strategies: SPME and subsequent on-fibre derivatization of the extracted amphetamines, and solution derivatization followed by SPME of the derivatives formed [8]. The latter approach was found to be the only option suitable for the analysis of urine samples. This was because the extraction of matrix components into the fibre coating prevented the extraction of the reagent. For the analysis of aqueous matrices, the SPME/on-fibre derivatization approach was preferable as the analysis did not modify sample composition.

The literature shows numerous LC assays which involve relatively complex derivatization procedures. This is the case of methods in which the analytes must be previously transformed into species capable of reacting with the selected derivatization agent. The simultaneous use of two reagents has been proposed to resolve samples containing a large number of target compounds. Other applications describe the use of an additional reaction aimed at eliminating from the reaction medium possible interferents before the derivatization of the compounds of interest.

In the present work we have evaluated the possibility of using SPME to effect two-stages derivatizations with two different reagents. The secondary amine dimethylamine (DMA) has been selected as a model compound. As many other short-chain aliphatic amines, DMA is a compound of environmental interest due to its toxicity, reactivity and likely occurrence as a result of its wide industrial use. Moreover, DMA may react with nitrosating agents giving the carcinogenic compound *N*-nitrosodimethylamine. For these reasons, there is an increasing demand of analytical methods for monitoring DMA in environmental waters.

Most LC methods specifically developed for the analysis of DMA entail derivatization with FMOC [9,10]. However, in the course of our studies on the derivatization of aliphatic amines we have observed that DMA–FMOC derivative tends to coelute with the derivative originated by propylamine (PA). This interference was not taken into consideration in previously reported methods. Overlapping of DMA and PA occurs under a variety LC conditions [11]. To overcome this problem, in the present study we propose a sequential derivatization with *o*-phtaldialdehyde and *N*-acetyl-L-cisteyne (OPA–NAC), and then with FMOC (see Fig. 1). Since OPA–NAC is only reactive towards primary amines, in the first stage PA is transformed into PA–OPA–NAC. In the second stage FMOC only reacts with DMA. Since the PA–OPA–NAC and DMA–FMOC derivatives present very different features, they can be satisfactory resolved under typical reversed phase conditions. On the basis of the results obtained a new method is presented for the selective determination of DMA in water.

2. Experimental

2.1. Apparatus and chromatographic conditions

The chromatographic system consisted of a quaternary pump (Hewlett-Packard 1050 Series, Palo Alto, CA, USA), a SPME–HPLC interface (Supelco, Bellefonte, PA, USA) and a fluorescence detector (Hewlett-Packard, 1050 series). The detector was coupled to a data system (Hewlett-Packard, HPLC Chem Station) for data acquisition and calculation. For measurement of the FMOC derivatives the excitation and emission wavelengths were 264 and 313 nm, respectively. The OPA–NAC derivatives were monitored at excitation and emission wavelengths of 330 and 440 nm, respectively.

2.2. Reagents and solutions

All the reagents were of analytical grade. Dimethylamine, methylamine, ethylamine, propylamine, *n*-butylamine, *n*-pentylamine and diethylamine were obtained from Sigma (St. Louis, MO, USA). 9-Fluorenylmethyl chloroformate (FMOC) and *N*-acetyl-L-cysteine (NAC) were purchased from Aldrich (Stenheim, Germany). *o*-Phthaldialdehyde (OPA) was obtained from Fluka (Buchs, Switzerland). Sodium hydroxide, boric acid and hydrochloric acid were purchased from Panreac (Barcelona, Spain). Acetonitrile was of HPLC grade (Scharlau, Barcelona, Spain).

Stock standard solutions of DMA and the other amines (10 000 μg/mL) were prepared in water. Working solutions of these compounds were prepared by dilution of the stock solutions with water. All solutions were stored in the dark at 2 °C.

2.3. Columns and mobile phases

A LiChrospher 100 RP18, 125 mm × 4 mm i.d. column (Merck, Darmstadt, Germany) was the analytical column. In the optimized procedure a precolumn and a high-pressure six-port valve (Hewlett-Packard) were inserted between the SPME–HPLC interface and the analytical column in order to effect peak compression [7]. The precolumn (20 mm × 2.1 mm i.d.) was dry-packed with a Hypersil C_{18}, 30 μm, stationary phase. At the beginning of each chromatographic the precolumn and the analytical column were disconnected, so the eluent (water) was sent to waste. At 0.5 min, the valve was rotated, and the percentage of acetonitrile in the mobile-phase was progressively increased,