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Comparative study of the determination of trimethylamine in water and air by combining liquid chromatography and solid-phase microextraction with on-fiber derivatization

C. Cháfer-Pericás, P. Campíns-Falcó *, R. Herráez-Hernández

Department of Analytical Chemistry, University of Valencia, Dr. Moliner 50, 46100 Burjassot, Valencia, Spain

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Abstract

This work describes a new approach for the determination of trimethylamine (TMA) in water and air by liquid chromatography (LC). The assay is based on the employment of a solid-phase microextraction (SPME) fiber for sampling and for derivatization of the analyte with the fluorogenic reagent 9-fluorenylmethyl chloroformate (FMOC). The fiber, with a Carbowax-templated resin −50 μm coating, was first immersed into a solution of the reagent. Once loaded with the reagent, the fiber was immersed into the water samples or exposed to the air samples in order to extract and to derivatize the analyte. Finally, the fiber was placed into a HPLC–SPME interface to desorb and transfer the TMA–FMOC derivative to the LC equipment. A comparative study of the analytical characteristics of the procedure in water and air samples was carried out. Under optimized conditions, the proposed approach permits the quantification of TMA in solution within the 1.0–10.0 μg/ml interval and in air within the 25–200 mg/m^3 interval. The limits of detection were 0.25 μg/ml and 12 mg/m^3 (25 °C, 1.013×10^{-5} Pa) in water and air, respectively. The utility of the proposed method for determining TMA in different kind of samples is discussed.

Keywords: Solid-phase microextraction; Trimethylamine; Liquid chromatography; Water; Air

1. Introduction

Short-chain aliphatic amines can be found in many different matrices such as natural and waste waters, industrial raw materials, or gaseous emissions from waste incineration and sewage treatment plants. They are currently determined by gas chromatography (GC) [1,2] or by liquid chromatography (LC) [3,4]. However, the quantification of these amines, particularly at trace levels, is a complex task for a number of reasons. Firstly, their isolation and preconcentration are problematic because of their physicochemical characteristics, i.e. high polarity, water solubility, volatility and basic character. Moreover, this kind of amines often shows poor chromatographic properties [5]. Another difficulty encountered in LC assays is that these compounds are rather insensitive towards UV, fluorescence and electrochemical detectors.

To overcome such problems most LC assays incorporate a chemical derivatization before the chromatographic step [3,4]. Derivatization is usually carried out in the solution mode, that is, aqueous samples are directly mixed with a solution of the reagent to form derivatives more amenable for isolation and preconcentration, resolution and detection. The quantification of aliphatic amines in air typically entails the employment of solid sorbents, impinger flasks or bubbled through an acidic solution for sampling. After sampling, the analytes are dissolved in a medium adequate for derivatization with the selected reagent [6–8]. However, most of the reagents available for amines are not reactive towards tertiary amino groups and, therefore, tertiary short-chain aliphatic amines are not included in a vast majority of the reported assays [9–11]. This is the case of trimethylamine (TMA) in spite of the fact that there is an increasing demand of methods for monitoring this amine in the environmental and industrial hygiene fields.

In a previous study we demonstrated that 9-fluorenylmethylchloroformate (FMOC), a reagent widely used in LC for primary and secondary amines, also reacts in solution with ter-

* Corresponding author. Tel.: +34 96 3543002; fax: +34 94 3544436.
E-mail address: pilar.campins@uv.es (P. Campíns-Falcó).

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tiary amines under mild conditions. This was illustrated first for the tertiary amphetamine *N*-methylephedrine [12]. However, the reaction yields were substantially lower than those observed for analogous primary and secondary ephedrines [13].

One of the approaches for increasing the analyte conversion yields and thus the sensitivity with respect to those obtained in solution derivatization is the so-called solid-support assisted derivatization technique [14]. This approach is based on retaining the analyte into a solid support, typically the packing of a solid-phase extraction (SPE) cartridge, which is then flushed with an aliquot of the derivatization reagent solution. After the reaction time the excess of reagent is eliminated by flushing the cartridge with the proper solvent and the derivative formed is desorbed and collected for subsequent analysis. Derivatization can be also performed into a precolumn connected on-line to the analytical column [15]. The later option has been used for the sensitive determination of TMA in water using FMOC as derivatization reagent [16]. This methodology was also adopted for the measurement of TMA in air using C_{18}-based SPE cartridges for sampling [17].

In the last years, SPME with polymeric coated fused-silica fibers has emerged as a valuable tool for sample preparation, as it integrates sampling, purification, preconcentration and sample introduction in a single process [18]. The solid-support assisted derivatization concept can be extended to the solid-phase microextraction (SPME) methodology. In fact, a chemical derivatization can be effected by treating the fiber with the proper reagent before or after the extraction of the analyte (on-fiber derivatization). In such a way, the entire analysis can be substantially simplified. According to the literature, FMOC is a reagent adequate for on-fiber derivatization of different amino compounds [19,20]. In the environmental field, the utility of this approach has been recently demonstrated in the LC analysis of methylamine [21] and dimethylamine [22] in water using Carbowax-templated resin coated fibers. In the present work, we have evaluated the possibility of simplifying the analysis of TMA by combining SPME and chemical derivatization with FMOC. The differences of the procedure for two matrices, water and air, are discussed. The advantages and disadvantages with respect to the solid-phase procedure previously proposed [16,17] have been outlined. The described conditions have been applied to measure TMA in air and water samples.

2. Experimental

2.1. Reagents

All the reagents were of analytical grade. Trimethylamine (TMA), methylamine, ethylamine, *n*-butilamine, *n*-pentilamine, propylamine, dimethylamine and diethylamine were obtained from Sigma (St. Louis, MO, USA), 9-fluorenylmethyl chloroformate and 3,5-dinitrobenzoyl chloride were purchased from Aldrich (Steinheim, Germany). Acetonitrile and methanol were of HPLC grade (Scharlau, Barcelona, Spain). Sodium hydroxide, 85% phosphoric acid and boric acid were obtained from Panreac (Barcelona, Spain).

Stock standard solutions of TMA and the other aliphatic amines (1.0 g/l, unless otherwise stated) were prepared in water. Working solutions of the analyte were prepared by dilution of the stock solutions with water. The pH of the samples was adjusted to 10.0 by adding 0.5 mol/l sodium hydroxide. Water was deionized and filtered through 0.45 μm nylon membranes (Teknokroma, Barcelona, Spain). All solutions were stored in the dark at 2 °C.

2.2. Apparatus

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 excitation and emission wavelengths were 264 and 313 nm, respectively. A UV detector (Hewlett-Packard 1046 Series) was also employed. The signal was monitored at 262 nm. The detectors were coupled to a data system (Hewlett-Packard, HPLC Chem Station) for data acquisition and calculation. A SPME assembly with replaceable extraction fibers coated with Carbowax-templated resin (CW-TR, 50 μm, Supelco) was used for extraction and/or derivatization.

2.3. Chromatographic conditions

A LiChrospher 100 RP_{18}, 125 mm × 4 mm i.d. column (Merck, Darmstadt, Germany) was the analytical column. The mobile phase was a mixture of acetonitrile–water in gradient elution mode, and the flow rate was 1 ml/min. According to the results presented in [21] a precolumn and a high-pressure six-port valve (Hewlett-Packard) were inserted between the SPME–HPLC interface and the analytical column to effect peak compression. The precolumn (20 mm × 2.1 mm i.d.) was dry-packed with a Hypersil C_{18}, 30 μm, stationary phase. Initially, the precolumn and the analytical column were connected and equilibrated with water. During the desorption of the analytes in the SPME–HPLC interface filled with acetonitrile, the switching valve was rotated, so the eluent emerging from the precolumn (water) was sent to waste. The chromatographic run was started when the SPME–HPLC interface was activated to send the TMA–FMOC derivative to the precolumn. At 0.5 min the six-port valve was again rotated so precolumn and the analytical column were connected again. Meanwhile, the acetonitrile content in the mobile phase was linearly increased from 0 to 60% at 2.5 min; the mobile phase composition was kept constant until 3.5 min, and then the percentage of acetonitrile was increased to 70% at 10 min, and to 100% at 15 min (in such a way both the precolumn and the analytical column were cleaned at the end of each assay). All solvents were filtered through 0.45 μm nylon membranes (Teknokroma, Barcelona, Spain) and degassed with the vacuum unit of the Hewlett-Packard pump before use.

2.4. SPME and derivatization procedures

2.4.1. Water standards

Unless otherwise stated, the fiber was plunged into a glass vial (2 ml) containing the derivatization solution for a defined

extraction time between 1 and 55 min. This solution consisted of 0.5 ml of 0.05 mol/l borate buffer with pH between 8.5 and 11.0 and 1.0 ml of the FMOC solution. The concentration of reagent was evaluated within the 1–25 mmol/l interval. The fiber was then removed from the vial and immersed into a glass vial containing the standard with concentration up to 10 μg/ml (25 ml). After a defined period of time, that was modified between 0.5 and 45 min, the fiber was removed from the sample vial and placed in the SPME–HPLC interface for desorption of the derivatized analyte and for chromatography. The TMA–FMOC derivative was desorbed under static mode: the fiber was soaked with 200 μl of acetonitrile for a defined desorption time that was assayed between 5 and 30 min, and then the valve of the SPME–HPLC interface was changed, so the TMA–FMOC derivative was sent to chromatographic system, and the chromatographic run was started. At the end of each run the fiber was cleaned by immersing it into a glass vial containing 10 ml of acetonitrile for 2.0 min, and then into a glass vial containing 10 ml of a solution 0.1 mol/l of phosphoric acid for other 2.0 min.

Conditions for the solution derivatization were selected according to previous works [13,15]: 0.25 ml of the samples were mixed with 0.25 ml of 0.05 mol/l borate buffer (pH 9.0), and then with 0.5 ml of 1 mmol/l FMOC inside a 2 ml glass vial; after 30 min, 100 μl of the resulting mixture were injected into the chromatographic system.

The borate buffer was prepared by dissolving the appropriate amount of boric acid in water. Then the pH was adjusted to the required value with 0.5 mol/l NaOH.

Each sample was derivatized in triplicate, and all assays were carried out at ambient temperature.

2.4.2. Air standards

Gaseous standards of TMA were generated into a 25 ml glass vial with a PVC cap having an orifice for the SPME holder. An aliquot of 50 μl of a standard solution of TMA was placed into the vial. In order to facilitate the volatilization of the analyte, 50 μl of 5 mol/l NaOH were also placed inside the vial, and the resulting mixture was stirred during the volatilization and SPME operations. The fiber, previously loaded with the reagent as described in the above section, was introduced in the vial, which was then sealed with teflon. After a defined period of time between 5 and 60 min, the fiber was removed from the vial and placed in the SPME–HPLC interface for desorption of the analytes and for chromatography. The fiber was cleaned and conditioned also as described in the previous section.

Each sample was derivatized in triplicate and all assays were carried out at ambient temperature.

2.5. Analysis of real samples

2.5.1. Water samples

The optimized conditions have been applied to the analysis of different water samples: tap water, ground water, river water and sea water. The samples were previously filtered through 0.45 μm nylon membranes (Teknokroma) in order to remove any particulate matter. The samples were spiked with TMA, and then pH was adjusted to 10.0. The final concentrations of TMA in such samples ranged from 1 to 10 μg/ml. In river and ground water samples the increment of the pH lead to the precipitation of some matrix substances. Thus, these samples were filtered again after pH adjustment. Samples were processed by the optimized SPME/derivatization method (Table 1).

Table 1
Optimized procedure for the SPME extraction/on-fiber derivatization of TMA with FMOC

Action	Conditions
Pretreatment of the fibers	Reagent solution: 10 ml of 25 mmol/l FMOC + 0.5 ml of 0.05 mol/l borate buffer of pH 9.0. Adsorption time: 5.0 min
Extraction/derivatization of TMA	Adsorption/reaction time: 30.0 min in water, 15.0 min in air
Desorption of TMA–FMOC	Desorption time: 5.0 min

A 24 h washing fish water was also analyzed. Then, the sample was filtered through 0.45 μm nylon membranes (Teknokroma) and the pH was adjusted to 10.0.

2.5.2. Air samples

Air samples were prepared by contaminating the air inside a closed PVC chamber (29 cm × 18 cm × 15.5 cm) with TMA. For this purpose an opened flask containing pure TMA was placed inside three chambers. The first chamber was sampled immediately by introducing the SPME fiber (previously treated with FMOC; see Table 1) inside it for 15 min. The second and third chambers were sampled in the same form after 5 and 15 min starting from the introduction of the pure TMA flask. Other chambers were contaminated from flasks containing aqueous solutions of TMA (0.1, 5.0 and 10.0 g/l) and sampled after 5 min for 15 min by the treated SPME fiber.

Another sample was obtained by contaminating the air inside the chamber with a fish maintained inside for 4 h. Moreover, the air of a fish supermarket was sampled and the laboratory air was analyzed too. The on-line derivatization method [17] was applied to these three air samples in order to compare the results obtained by SPME. In this method, the sampling was dynamic using an air pump. By this method TMA was selectively determined.

Each sample was processed in triplicate, and all assays were carried out at ambient temperature.

3. Results and discussion

3.1. Optimization of the SPME extraction/derivatization procedure in aqueous standards

Among the commercially available fiber coatings, CW-TR retained less unwanted products when using FMOC as derivatization reagent [21], and therefore, this was the fiber coating selected for the present study. SPME extraction of the reagent followed by the extraction/derivatization of the analyte was selected according to a previous study [22]. The results were compared with those obtained by derivatizing TMA in solution.

Initially, the effect of the concentration of reagent was evaluated. The adsorption time for the reagent was 5 min, whereas

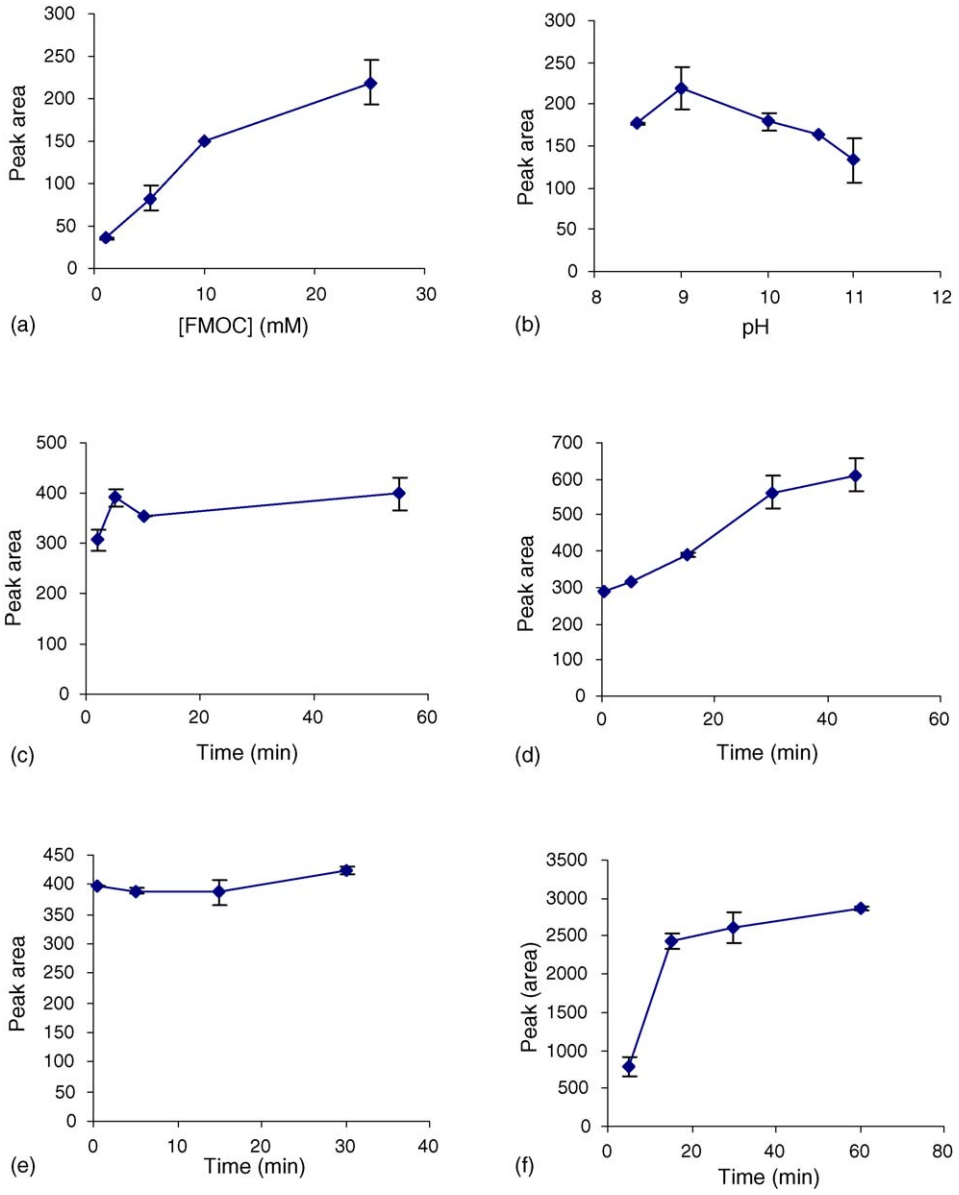

Fig. 1. Effect of experimental variables on TMA–FMOC responses (error bars signify ±1S.D. from the mean of $n = 3$): (a) concentration of FMOC, (b) pH, (c) adsorption time for FMOC, (d) adsorption time for the TMA, (e) desorption time, and (f) volatilization time. For other experimental details, see text.

the time for extraction/reaction of the amine was 15 min. The pH of the derivatization solution was 9.0, and the desorption time for the TMA–FMOC derivative was 5 min. As observed in Fig. 1a, the response obtained for the TMA–FMOC derivative increased as the concentration of reagent was increased. However, concentrations higher than 25 mmol/l could not be used because the peak at 5.8 min, corresponding to the reagent, overlapped with the peak of the TMA–FMOC derivative. Therefore, a concentration of 25 mmol/l was selected for further work. The pH optimum was 9.0 (Fig. 1b).

Another parameter studied was the adsorption time for the reagent. This parameter was modified between 1 and 55 min (Fig. 1c) while keeping the other parameters constant, but no significant improvement was observed by using times longer than 5 min.

As regards the extraction time for the analyte, which can be also considered the reaction time, it was evaluated between 0.5 and 45 min using an adsorption time for the reagent of 5 min. The other conditions were kept constant. The results obtained (Fig. 1d) indicated that the maximum extraction/conversion yields were reached for times longer than 30.0 min. Finally, different desorption times in the 5–30 min were assayed but not significant improvement was found (Fig. 1e).

On the basis of the above results, the conditions selected for the determination of TMA were those summarized in Table 1. In Fig. 2 are depicted the chromatograms obtained for a blank (water) and for a standard solution of TMA processed under optimized conditions.

The SPME mediated derivatization lead responses for TMA–FMOC higher than those achieved by the solution deriva-

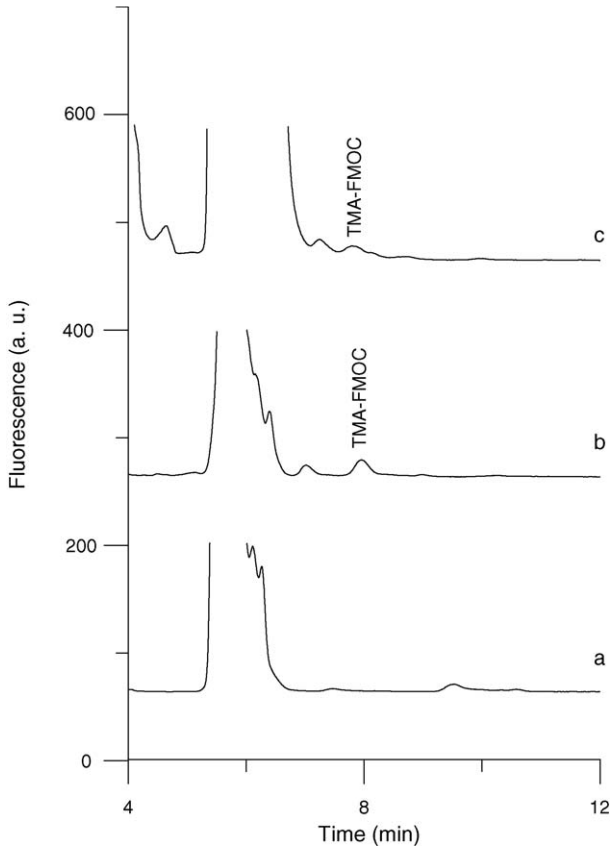

Fig. 2. Chromatograms obtained for: (a) blank (water) sample under optimized conditions, (b) chromatogram obtained for an standard solution of TMA (5 μg/ml) under optimized conditions, and (c) chromatogram obtained for TMA (7.5 μg/ml) by the solution derivatization method. For other experimental details see text.

tization approach (see Fig. 2). Moreover, more unwanted peaks (corresponding to condensation or degradation products of FMOC) were observed when using solution derivatization.

3.2. SPME extraction/derivatization procedure in gaseous standards

The SPME fiber was loaded with FMOC as described in Table 1 and exposed to the TMA vapours inside a vial for different times within the 5–60 min interval. Times longer than 15 min did not substantially improved the signal obtained for TMA–FMOC, as it can see in Fig. 1f. Consequently, the time

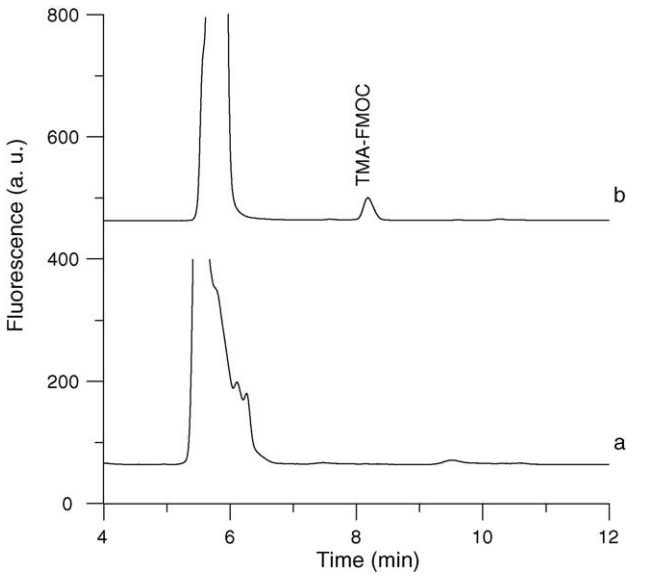

Fig. 3. Chromatograms obtained for: (a) blank air and (b) air containing 200 mg/m^3 of TMA. For other experimental details, see text.

used for extraction/derivatization of the analyte in next experiments was 15.0 min because at this time the equilibrium was reached. After this time, the fiber was removed from the vial and inserted into the HPLC–SPME interface.

In Fig. 3 are shown the chromatograms obtained for blank air and for air containing TMA under the proposed conditions.

3.3. Analytical performance

3.3.1. Water samples

The results of Table 2 indicated that the method provided adequate linearity within the tested concentration interval. The intra-day and inter-day coefficients of variation were established at three concentration levels within the tested interval. The values obtained (see Table 2) were suitable. The limit of detection (LOD), established for a signal-to-noise ratio of 3, was 0.25 μg/ml. It is interesting to note that these values are of about five times greater than the values obtained by the solid-support assisted derivatization method using a precolumn [16]. This is due to the fact that, owing to the small dimensions of commercially available fibers, the amounts of TMA and FMOC that can be extracted to the fibers, and thus the amounts of TMA–FMOC

Table 2
Analytical data for the determination of TMA

Sample type	Interval	Linearity $y = a + bx$ ($n = 10$)	Precision			LOD
			Concentration/ amount	Intra-day R.S.D. (%) ($n = 3$)	Inter-day R.S.D. (%) ($n = 6$)	
Water	1.0–10.0 μg/ml	$a \pm s_a$: 37.3 ± 1.4	1.0 μg/ml	23	23	0.25 μg/ml
		$b \pm s_b$: 47 ± 9	5.0 μg/ml	16	12	
		r^2: 0.98	10.0 μg/ml	7	16	
Air	25–200 mg/m^3 (25 °C, 1.013 × 10^{-5} Pa)	$a \pm s_a$: 98 ± 12	25 mg/m^3	10	9	12 mg/m^3
		$b \pm s_b$: 1.672 ± 0.102	100 mg/m^3	17	14	
		r^2: 0.97	200 mg/m^3	16	14	

Table 3
Accuracy for the determination of TMA in different type of samples

Sample type	Added TMA	Determined TMA
Standard solution	5.0 μg/ml	6 ± 1 μg/ml
Standard solution containing a mixture of TMA and other aliphatic amines	1.0 μg/ml[a], 5.0 μg/ml[b]	1.2 ± 0.4 μg/ml, 4 ± 1 μg/ml
Tap water	5.0 μg/ml	4.7 ± 0.9 μg/ml
Ground water	5.0 μg/ml	6 ± 1 μg/ml
River water	1.0 μg/ml	0.84 ± 0.15 μg/ml
Air	25 mg/m^3	32 ± 8 mg/m^3
	100 mg/m^3	90 ± 20 mg/m^3

[a] A mixture containing 1.0 μg/ml in each amine of methylamine, ethylamine, *n*-butilamine, *n*-pentilamine and diethylamine. For other details see text.
[b] A mixture containing 5.0 μg/ml in each amine of methylamine, ethylamine, *n*-butilamine, *n*-pentilamine and diethylamine. For other details see text.

that can be formed, are lower than those extracted/formed in a precolumn. Nevertheless, the sensitivity would be adequate for the determination of TMA in waste water [23]. The experimental effort by using the SPME procedure is reduced in relation to that necessary for the precolumn method. Also, it is remarkable that the SPME method is a non-destructive sampling procedure. The limit of quantification (LOQ), established for a signal-to-noise ratio of 10, was 1 μg/ml.

Since FMOC is also reactive towards primary and secondary short-chain aliphatic amines potentially present in the samples, the effect of these compounds was evaluated. The compounds assayed were methylamine, ethylamine, *n*-butilamine, *n*-pentilamine and diethylamine. Indeed, all the above amines were extracted and derivatized under the proposed conditions but their respective FMOC derivatives presented retention times different that that of TMA–FMOC. In order to test whether these amines would interfere with the determination of TMA due to the consumption of FMOC, different samples containing the analyte and a mixture of the other amines were assayed. The results obtained (Table 3) demonstrated that TMA was determined with suitable accuracy at the concentration levels assayed.

Dimethylamine (DMA) and propylamine (PA) are considered interferences because they elute at the same retention time as the TMA, also DMA forms the same derivative as the TMA [22]. So, different procedures were evaluated, in order to eliminate the DMA and PA present in samples. In instance, after loading the sample, the clean-up step was affected by solid-phase extraction passing through the C_{18} cartridge different volumes of acetic acid 0.1 M and acetate buffer 0.1 M (pH 4). Different reagents for primary and secondary amines were evaluated, dinitrobenzoil chloride (DNB) and dansylchloride, then the sample derivatized was flushed through the solid-phase cartridge, and the derivatives were eliminated with the minimum volume of acetonitrile. The best procedure to eliminate these interferences was to derivatize 5 ml of sample with DNB 40 mmol/l, then the derivatives were retained into a solid-phase extraction C_{18} cartridge, after that they were eliminated by flushing 0.5 ml of acetonitrile. Having done that, the TMA was desorbed by flushing 5 ml of phosphoric acid 0.1 mol/l, then the extracts were basified. Finally, it was effected the SPME. The tolerance levels for DMA and PA were evaluated. They were 0.25 and 0.5 μg/ml, respectively. For these tolerance values of concentration no chromatographic peaks were obtained by processing the samples by the clean-up procedure. The recovery obtained for TMA in presence of DMA and PA at tolerance levels was 100 ($s = 5$, $n = 4$). If real samples contain levels of DMA and PA higher than the tolerance ones, it was necessary to effect the derivatization in a precolumn connected on-line to the analytical column [16]. Because this procedure is selective to the TMA determination, and PA and DMA eluted at different retention times. By the SPME method it was determined the PA, DMA and TMA together.

The accuracy of the method was evaluated by analyzing standard solutions containing different concentrations of TMA within the tested concentration range. The results of this study are summarized in Table 3. As observed, the concentrations obtained were close to the real concentrations in all samples assayed.

Several samples were fortified with TMA and subjected to the proposed procedure. The fortified concentrations of TMA in these samples were calculated from the calibration equation obtained with standard solutions of TMA (Table 2). The values obtained in this study are listed in Table 3. Expanded uncertainties using a coverage factor of 2 are given in Table 3. The estimate is compliant with EURACHEM/CITACGuide [24] and is a full estimate based on in-house method validation. The overall run to run variation (precision) of the analytical procedure was the main contribution to the uncertainty. Comparable precision values were obtained by processing aqueous standards and samples. As for the standard samples, the proposed method provided values close to the fortified concentrations, except in sea water. In such sample, the responses obtained were significantly lower than those corresponding to standard samples. The peak areas observed in sea water were of about 38% of those observed for standard samples containing the same concentrations of amine. When processing an aqueous standard solution containing 5.0 μg/ml of TMA and 35 g/l of NaCl, the mean area obtained for TMA–FMOC was 41% ($s = 3$, $n = 3$) of those obtained for aqueous standard solution. Therefore, the employment or standards spiked with NaCl to construct the calibration curve would be required in the quantification of TMA in sea water.

3.3.2. Air samples

The results showed in Table 2 indicated that the method provided adequate linearity. The coefficients of variation were obtained at different concentration levels within the tested inter-

val. As we can see in Table 2, the precision can be considered suitable for this kind of analysis.

The air calibration equation $y = (98 \pm 12) + (67 \pm 4)x$ (μg), was compared to that obtained for aqueous standard solutions of TMA $y = (47 \pm 9) + (1.49 \pm 0.06)x$ (μg). From the ratio of the slopes of calibration equations expressing the concentration in absolute values (μg), we obtained that the signals corresponding to the air standards are of about 50 times greater than the signals obtained for aqueous standards. This fact can be due to greater facility of TMA molecules in gaseous phase to get to the porous fiber phase than the molecules in aqueous phase. Therefore, to quantify TMA in air samples cannot be used aqueous standards against to the dynamic sampling method proposed previously [17].

The long-time exposition level by the OSHA is 12 mg/m^3 [6] and the short-time exposition level (STEL) is 24 mg/m^3. The LOD, established for a signal-to-noise ratio of 3, was 12 mg/m^3 and the LOQ, established for a signal-to-noise ratio of 10, was 20 mg/m^3. Therefore, the method would be adequate for monitoring short-time exposure. It is interesting to note that the LOD is of about 55 times greater than the value obtained by the dynamic sampling method using a solid-phase extraction cartridge and derivatizing in a precolumn connected on-line to the analytical column [17]. This is due to the small dimensions of the fiber compared with the SPE cartridge dimensions and also by the passive sampling affected by the SPME procedure. However, as in the case of water analysis, the SPME-based method optimized the experimental effort. It is also remarkable that passive sampling methods do not require maintenance, while active sampling methods need to control and maintain a pump. The accuracy of the method was evaluated by generating air standards containing two different concentrations of TMA within the tested concentration range. As we can see in Table 3, the concentrations obtained were close to the real concentrations. Comparable precision values were obtained by processing aqueous or gaseous standards. The uncertainties were calculated as outlined above for water samples.

4. Application to real samples

The fish washing water sample was analyzed. The results indicated the absence of DMA and PA. The found TMA expressed as mean value ± expanded uncertainty using a coverage factor of 2 was 2.48 ± 0.13 μg/ml. In the following found concentrations are done as indicated here. This result was compared with that obtained with the procedure based on on-line derivatization in a precolumn connected to the analytical column [16] that was 2.5 ± 0.3 μg/ml of TMA. Both results are statistically similar.

Finally, the proposed procedure was applied to air samples contaminated with the analytes in order to evaluate STEL values (see Section 2). For this purpose, the air inside a close chamber was contaminated with pure TMA. The mean concentrations found were 170 ± 40 and 190 ± 20 mg/m^3 after contaminating the chamber for 5 and 15.0 min, respectively. In another set of experiments different solutions of TMA were placed into the chamber for 5 min, and then sampling/derivatization was affected. The amount of TMA found were 64 ± 13, 104 ± 5 and 137 ± 2 mg/m^3 when using solutions containing 0.1, 5.0 and 10.0 g/l of TMA, respectively.

Other air samples were laboratory air, fish supermarket air and the air of a chamber 4 h after placing a fish inside. They were sampled and analyzed by the two procedures (dynamic and static). The found concentrations were below the STEL legislated value.

5. Conclusions

The present paper describes the utility of SPME for the isolation and derivatization of TMA with FMOC prior to LC. Best results are obtained by loading the fibers with the reagent first and then, by extracting the analyte which is simultaneously derivatized on the fiber. It should be noted that the conventional (solution) derivatization method is not suitable because as the analyte is a tertiary amine low conversion yields are obtained under mild reaction conditions.

The proposed approach can be used to quantify TMA in waste water. The levels of tolerance for propylamine and dimethylamine in water samples were 0.5 and 0.25 μg/ml. These interferences can be eliminated by means the solution derivatization with DNB and then with the clean-up step through SPE cartridge.

The method can be also used to quantify TMA in air. The sensitivity attainable is adequate for estimating short-term exposure limits in occupational atmospheres. This is particularly important in the analysis of TMA in air because SPME proposed procedure is a passive sampling method.

The advantages of using SPME technique in comparison with previous assays based on liquid–liquid or solid-phase extraction for both, water and air samples, are that the experimental effort and sample manipulation were reduced significantly. Also, it is remarkable that the proposed procedure is a non-destructive sampling method. Moreover, the selectivity was improved, because the most polar compounds of water were not extracted with the coated fiber.

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