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Short communication

Selective determination of trimethylamine in air by liquid chromatography using solid phase extraction cartridges for sampling

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Abstract

The selective determination of trimethylamine (TMA) in air by liquid chromatography is reported. Sampling is effected by flushing air through C_{18}-packed solid-phase extraction (SPE) cartridges at a flow rate of 15 mL/min for 15 min. Next, TMA is desorbed from the cartridges and injected into the chromatographic system. The analyte is then selectively retained on a precolumn (20 mm × 2.1 mm i.d., packed with 30 μm, Hypersil C_{18} phase), and derivatized on-line by injecting 9-fluorenylmethyl chloroformate (FMOC). Finally, the TMA-FMOC derivative is transferred to the analytical column (125 mm × 4 mm i.d., LiChrospher 100 RP_{18}, 5 μm), and monitored at 262 nm. The method was applied to the measurement of TMA in air in the 0.25–2.5 μg interval (equivalent to concentrations of TMA of 1.1–11 mg/m^3), providing good linearity, reproducibility and accuracy. The mean recovery of TMA was (96 ± 7%) (n = 12), and the limit of detection was 0.05 μg. The proposed procedure allows the selective determination of TMA in the presence of other primary and secondary short-chain aliphatic amines.

Keywords: Air analysis; Solid-phase extraction; Trimethylamine

1. Introduction

Trimethylamine (TMA) is a malodorous aliphatic amine frequently identified in the gaseous emissions of several industries and wastewater treatment plants. Health effects associated with the inhalation of TMA include irritation of the respiratory tract, eyes and skin. Consequently, the sensitive determination of TMA in atmospheric and human work environments is of great interest. As most short-chain aliphatic amines, TMA is currently determined by gas chromatography (GC) [1,2] or by liquid chromatography (LC) [3]. Prior preconcentration and/or chemical derivatization of the amines is generally involved to improve the specificity and sensitivity of the analysis.

Several alternatives have been proposed for collecting airborne aliphatic amines such as the employment of sorbents (silica gel, acidic coated XAD-7) [4,5] or impringer flasks containing acidic solutions [6], but the general trend is to replace wet sampling methods by solvent-free extraction techniques. In this sense, one of the most promising approaches for sampling volatile compounds is solid phase microextraction (SPME). However, most SPME procedures described to date deal with the extraction of TMA from aqueous matrices [7]. Moreover, the formation of artefacts during the analysis of TMA in air by SPME-GC has been reported [8].

The employment of solid-phase extraction (SPE) cartridges may be a rapid and simple alternative for collecting volatile amines. This has been illustrated for a variety of primary short-chain aliphatic amines using C_{18} cartridges and *o*-phthaldialdehyde-*N*-acetyl-L-cysteine (OPA-NAC) as derivatization reagent [9]. The proposed conditions could not be used to determine TMA because OPA-NAC only reacts with primary amines. This is a limitation of LC and GC procedures involving chemical derivatization, as a vast majority of the reagents available are reactive only to primary and secondary amine groups.

We have recently proposed a LC method for the analysis of TMA in water based on its derivatization with

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9-fluorenylmethyl chloroformate (FMOC) [10]. Although FMOC is typically used as a reagent for primary and secondary amines, the employment of a solid support to effect the derivatization made possible the transformation of TMA into its FMOC derivative with a conversion yield adequate for the quantification of this compound at low ppm levels. In such study, derivatization was effected on-line into a precolumn packed with a C_{18}-based stationary phase.

In the present study, we have developed a method for the determination of TMA in air using SPE cartridges for sampling and LC. In order to attain the required sensitivity, the analyte has been subjected to derivatization with FMOC according to the procedure described in [10].

2. Experimental

2.1. Apparatus

Air sampling was done with a portable Buck-Genie VSS-5 pump (A.P. Buck Inc., Orlando, FL, USA). For flow measurements a flow-meter Multicon KS, Dräger (Lübeck, Germany) was used.

The chromatographic system consisted of a quaternary pump (Hewlett-Packard 1050 Series, Palo Alto, CA, USA), a 100 μL sample loop injector, and a UV detector (Hewlett-Packard 1046 Series). The detector was linked to a data system (Hewlett-Packard HPLC Chem Station) for data acquisition and storage. The detector operated at 262 nm.

The analytical column was a LiChrospher 100 RP_{18}, 5 μm, 125 mm × 4 mm i.d. column (Merck, Darmstadt, Germany). A precolumn 20 mm × 2.1 mm i.d., dry packed with a Hypersil ODS-C_{18}, 30 μm, stationary phase (Merck) was placed between the injector and the analytical column. The precolumn and the analytical column were connected by means of an automatic six-port switching valve (Helwett-Packard).

2.2. Reagents and solutions

All the reagents were of analytical grade. Methanol and acetonitrile were of HPLC grade (Scharlau, Barcelona, Spain). Trimethylamine, methylamine, ethylamine, propylamine, *n*-butylamine, *n*-pentylamine, dimethylamine and diethylamine were obtained from Sigma (St. Louis, MO, USA), and 9-fluorenylmethyl chloroformate was purchased from Aldrich (Steinheim, Germany). Sodium hydroxide, phosphoric acid and boric acid were obtained from Panreac (Barcelona, Spain).

Stock standard solutions of TMA and the other amines (1.0 g/L) were prepared in water. Working solutions of these compounds were prepared by dilution of the stock solutions with water. Water was deionized and filtered through 0.45 μm nylon membranes (Teknokroma, Barcelona, Spain). All solutions were stored in the dark at 2 °C.

2.3. Derivatization and chromatography

On-line solid support assisted derivatization was accomplished according to the procedure described in [10]. Briefly, the precolumn and the analytical column were connected and equilibrated with 60:40 acetonitrile–water (v/v) before each run. At the beginning of the assay the gradient elution program was started and the switching valve was rotated, so the eluent emerging from the precolumn was sent to waste. At 2.5 min 25 μL of the sample were injected into the precolumn; the FMOC reagent (50 μL) was injected at 3.0 min. The analyte and the reagent were left to react inside the column for 0.5 min. At min 3.5, the switching valve was rotated and the TMA-FMOC derivative was transferred to the analytical column for chromatography. Meanwhile, the eluent composition was changed to from 60:40 acetonitrile–water (v/v) at min zero to 60:40 acetonitrile-0.05 M borate buffer (pH 9.0) at 1.5 min, and then to 60:40 acetonitrile–water at 3.5 min. The acetonitrile content was then increased from 60 to 70% at min 10, and to 100 at 15 min. The mobile-phase flow rate was 1 mL/min.

The 0.05 M borate buffer was prepared by dissolving boric acid in water; then the pH was adjusted to the appropriate value by adding 0.5 M sodium hydroxide. All solvents were filtered through 0.45 μm nylon membranes (Teknokroma, Barcelona, Spain) and degassed with helium before use.

2.4. Air sampling for standards

For air sampling, 1 mL Bond Elut C_{18} cartridges containing 100 mg of packing (Varian, Harbor City, CA, USA) were used. The cartridges were conditioned with 1 mL of methanol followed by 1 mL of 0.05M borate buffer of pH 9.0. Air was drawn through the cartridges for 15 min at a flow rate was 15 mL/min (unless otherwise stated). The flow rate was controlled with the flow-meter at the beginning and at the end of each assay. After sampling the retained TMA was desorbed from the cartridges with 0.5 mL of 0.1 M phosphoric acid. The pH of the extracts was made basic by adding 100 μL of 0.5 M sodium hydroxide. Finally, 25 μL of the resulting mixture were injected into the chromatographic system for derivatization and chromatography. Each sample was processed in triplicate, and all assays were carried out at ambient temperature.

2.5. Analysis of TMA in air

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 the chamber, and after a variable period of time sampling was carried out.

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

3. Results and discussion

3.1. Sampling procedure

In order to optimize the sampling conditions, 50 μL of 50.0 μg/mL TMA were placed in a plastic tube which acted as a volatilization chamber [9]. The outlet of the cartridges were connected to the air pump, whereas the inlet was connected the volatilization chamber. An aliquot of 50 μL of 0.5 M NaOH was added to the solution of TMA to volatilize the amine just before starting the sampling process. Several assays were carried out under different sampling times and flow-rates. Sampling efficiency was established by comparing peak areas obtained for the analyte with those obtained from the direct injection of an standard solution of TMA containing an equivalent amount of the analyte (2.08 μg/mL).

Best results were obtained at a sampling rate of 15 mL/min. At higher values poor reproducibility was observed because the pump did not deliver a constant flow rate, which can be explained by the variations in the porosity of the SPE cartridges between assays (data not shown). At a flow rate of 15 mL/min, the volatilization of the analyte was nearly complete in less than 15 min. The mean recovery of TMA was found to be (95 ± 6%), $n = 3$. Consequently, sampling at 15 mL/min for 15 min (equivalent to a sample volume of 225 mL) were the conditions selected for further work.

As an illustrative example, in Fig. 1 are the chromatograms obtained for TMA in air and for a blank under the proposed conditions.

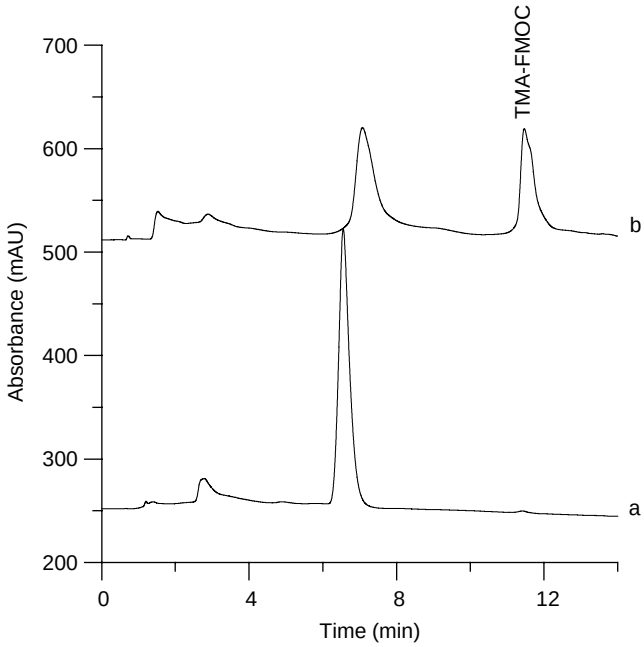

Fig. 1. (a) Chromatograms obtained for blank air, and (b) for air containing 11.1 mg/m^3 of TMA. For other details, see text. Peak at around 7.8 min (unreacted peak) decreases in samples containing TMA due to reagent consumption.

3.2. Analytical performance data

The reliability of the described method was evaluated by processing samples containing the analyte in the 1.1–11 mg/m^3 concentration range (equivalent to amounts of TMA of 10.4–104 ng). For this purpose, aqueous standard solutions of TMA within the range 5.0–50.0 μg/mL were placed in the volatilization chamber, and processed as described in the above section. The results of this study are summarised in Table 1.

As observed, good linearity was obtained over the studied range. The calibration equation was comparable to that obtained for aqueous standard solutions of TMA containing the same amounts of the analyte and injected directly into the chromatographic system, which was $y = (36900 \pm 1671)x + (642 \pm 235)$, ($r^2 = 0.98$, $n = 12$). The recovery of TMA in air samples, calculated from the ratio of the slopes of calibrations was 95%,

Table 1
Analytical performance data obtained in for TMA in air

Linearity ($y = ax + b$)	Recovery (%) ($n = 12$)	Reproducibility C.V. (%)[a]		LOD	Accuracy		
		Intra-day ($n = 3$)	Inter-day ($n = 6$)		Concentration added (mg/m^3)	Concentration determined (mg/m^3)	Er (%)
$a \pm S_a = 35131 \pm 2011$	(96 ± 7)	7	15	0.05 μg	5.56	5.33	−4
$b \pm S_b = 652 \pm 125$					11.1	11.2	+1
$r^2 = 0.990$					5.56 + a mixture of other aliphatic amines[b] (5.56 mg/m^3 each)	5.91	+6
					11.1 + a mixture of other aliphatic amines[b] (11.1 mg/m^3 each)	11.9	+9

[a] Determined at 1.25 μg of TMA.
[b] Methylamine, ethylamine, propylamine, butylamine, *n*-pentylamine, dimethylamine and diethylamine.

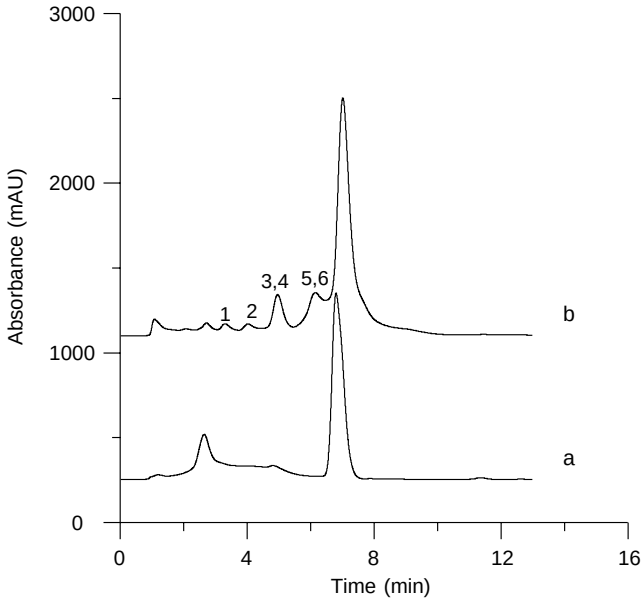

Fig. 2. (a) Chromatograms obtained for a mixture of (1) methylamine, (2) ethylamine, (3) propylamine, (4) dimethylamine, (5) butylamine, and (6) diethylamine under the proposed conditions, and (b) chromatogram obtained for the same mixture by injecting the FMOC 0.1 min after the injection of the sample. The concentration of each amine in the samples was 11.1 mg/m^3. For other details, see text.

which is consistent with the value obtained in the above section.

The method provide suitable reproducibility, with intra-day and inter-day coefficients of variation of 9 and 15%, respectively (for an amount of TMA of 1.25 μg). The limit of detection (established as the concentration required to generate a signal-to-noise ratio of 3) was 0.05 μg of TMA (equivalent to a concentration in air of 0.22 mg/m^3). This value is comparable to the limits of detection (LODs) reported by other methods proposed for the analysis of TMA in air [4,11]. However, the sample volume required in the present assay (and therefore, the sampling time) is significantly reduced.

The selectivity of the method was tested by analysing standard solutions containing mixtures of TMA and other short-chain aliphatic amines (methylamine, ethylamine, propylamine, *n*-butylamine, dimethylamine and diethylamine). None of the amines tested were detected in the chromatograms of the air samples (Fig. 2a), as they were excluded from the precolumn during the time elapsed between their injection and the injection of the reagent (0.5 min) [10]. When reducing this time interval, all amines were identified in the resulting chromatograms (Fig. 2b), which indicates that they were also retained in the SPE cartridges during sampling. However, their FMOC derivatives showed retention times lower than that of TMA-FMOC. Therefore, under the proposed conditions the assay can be considered selective for TMA. This was confirmed by determining the concentration of the TMA in samples containing mixtures of all amines tested (see Table 1).

3.3. Application

The procedure was applied to the analysis of air contaminated with TMA. The mean concentration of the analyte in this samples was established after different collecting times from the calibration curve obtained for TMA in air samples. The results obtained were (0.568 ± 0.008 mg/m^3), (0.85 ± 0.09 mg/m^3) and (1.64 ± 0.04 mg/m^3) for sampling times of 10 min, 20 min and 4 h (equilibrium), respectively ($n = 3$). Moreover, the amounts of TMA measured under equilibrium conditions on different days were rather similar, with a coefficient of variation of 9% ($n = 9$). This indicates that the proposed procedure offers suitable reproducibility.

4. Conclusions

Conventional C_{18} SPE cartridges can be used to sample TMA from air. The proposed approach avoids the use of solutions to retain the analyte and thus, is well suited for portable sampling devices. Compared with earlier described procedures, the time required for sampling is significantly reduced because the derivatization of TMA with FMOC increases the sensitivity. In fact, this is, to our knowledge, the first method proposed for the analysis of TMA in air based on its chemical derivatization. Most existing methods for the analysis of aliphatic amines in air can not be applied to TMA because they use reagents capable of reacting only with primary and secondary amines [5,12].

The sensitivity, accuracy and reproducibility achieved by the proposed method are adequate for monitoring occupational exposure of TMA [4]. Moreover, the presence of other primary and/or secondary short-chain aliphatic amines does not interfere, therefore, the method can be considered selective for TMA.

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