

A method for the determination of dimethylamine in air by collection on solid support sorbent with subsequent derivatization and spectrophotometric analysis

Y. Moliner-Martínez, P. Campíns-Falcó*, R. Herráez-Hernández

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

Received 23 June 2004; received in revised form 4 October 2004; accepted 8 October 2004

Abstract

A new method for dimethylamine determination in air is reported. The proposed assay is based on the employment of C₁₈-packed solid phase extraction cartridges for sampling. The retained amine is then derivatized inside the cartridges with the reagent 1,2-naphthoquinone-4-sulfonate. By observing the coloured area of the cartridge, a semiquantitative estimation of the amine can be made. It was also possible to distinguish between primary and secondary amines by visual inspection. Quantitative tests entailed desorption from the cartridges of the derivatives formed, and measurement of the absorbance of the collected extracts. The selected conditions were applied to quantify dimethylamine up to 100 µg, the quantification and detection limits being 6.7 and 2 µg, respectively. Satisfactory linearity and precision were obtained. Possible interferences by ammonia, primary amines and diethylamine were tested. The applicability of the procedure was demonstrated by estimating the concentration of dimethylamine in generated and real air samples. The procedure was useful for short-term exposure limit and threshold limit value estimations.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Air; Dimethylamine; In situ; Visual assay; C₁₈ support

1. Introduction

Some volatile aliphatic amines are of environmental interest due to their odorous and toxic characteristics and because of their role in nitrogen cycling, nutrient transfer and atmospheric acidity. These highly reactive compounds undergo atmospheric reactions to form a variety of products [1], among them nitrosamines, which are potentially carcinogenic substances [2]. Owing to their widespread industrial use and natural sources, there is an increasing interest in the development of reliable, rapid-response and easy-to-operate methods for their determination in air, preferably well-suited for on-site analysis.

Sampling and derivatization play a significant role in the analysis of short-chain aliphatic amines in air. For sampling,

several procedures based on the employment of impinger flasks containing acidic solutions [3] or sorbents as silica gel [4], the most usual, have been proposed. To avoid possible sample instability on silica gel, OSHA developed a method (OSHA 34), which employs XAD-7 coated with 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole [5]. In the last years, different methods based on solid phase microextraction (SPME) have also been proposed [6–8].

In recent studies, this research group has demonstrated the possibility of using conventional solid phase extraction (SPE) cartridges for sampling [9,10]. Air samples are flushed through C₁₈-based SPE cartridge to retain the analytes. After sampling, the cartridges are flushed with an aliquot of reagent, so that the analytes are derivatized inside the cartridges (solid support-assisted derivatization procedure developed by the research group since 1996) [11–13]. After a given reaction time, the excess of reagent is eliminated (if required) by drawing a volume of the proper solvent. Finally, the deriva-

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

tives formed are desorbed from the cartridges and collected for measurement. In the field of air analysis, this approach has been successfully applied in the fluorimetric determination of some primary aliphatic amines using the reagent *o*-phthalaldehyde (OPA) for derivatization [9]. More recently, this methodology has been used in combination with the reagent 9-fluorenylmethyl chloroformate (FMOC) to determine trimethylamine by liquid chromatography and UV detection [10]. In both studies, standards of the gaseous amines were generated from aqueous standard solutions of the analytes. Aliquots of the aqueous solutions were placed into an opened tube that acted as a volatilization chamber, and the volatilized amines were pulled into the SPE cartridges during the sampling step. Similar analytical results were obtained for both, gaseous and aqueous amine standards.

In the present work, we have evaluated the possibility of extending the solid support assisted approach to the analysis of dimethylamine in air. Unbiased UV–vis or fluorimetric methods could be used as methods of samples screening in order to reduce costs and saving time in the environmental laboratory or for in situ determinations. This is important when a high number of samples must be processed. This work investigates such a rapid, low-cost and on site screening procedure.

The reagent 1,2-naphthoquinone-4-sulfonate (NQS) has been selected for derivatization because it forms coloured derivatives [14]. Therefore, information could be obtained by colorimetry after desorption from the cartridges of the derivatives formed or/and also by visual inspection of the cartridges. They can be used as detector supports for in situ estimation. NQS is also a non-hazard reagent (Directive 67/548/CEE). Sampling conditions have been optimized for C₁₈-packed SPE cartridges. So far only a few measurements of aliphatic amines have been reported [1], we have included in the present study the most usual primary and secondary amines tested. This work proposes an assay for dimethylamine, which is in the list of priority pollutants in Europe and its presence is documented in vulcanization fumes (0.1 mg m⁻³) [2], polymer plants, fish processing plants, fish stands of city markets (140.1 and 79.2 mg m⁻³) and industrial animal farms atmospheres [1,8]. Short-term exposure limit (STEL) and threshold limit value (TLV) are legislated, being 9.4 and 3.8 mg m⁻³ of air at 20 °C and 1.013 × 10⁵ Pa, respectively [15].

2. Experimental

2.1. Apparatus

All the spectrophotometric measurements were done on a Hewlett–Packard 8453 diode-array spectrophotometer (Avondale, PA, USA) furnished with a 1-cm pathlength quartz cell. The vacuum station IST VacMaster or a syringe for manual operation was used for transferring solutions to the cartridges.

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. A gas detector pump Accuro (Dräger, Lübeck, Germany) was used for air sampling in amine test colorimetric tubes (Dräger, Lübeck, Germany). A water bath equipped with a thermostat (Clifton, New Abbot, Devon, UK) was also used.

2.2. Chemicals

All the chemicals were of analytical grade. Ammonium chloride, methylamine, ethylamine, propylamine, butylamine, pentylamine, dimethylamine, diethylamine and 1,2-naphthoquinone-4-sulfonate acid were obtained from Sigma (St. Louis, MO, USA). Methanol and diethyl ether were obtained from Scharlau (Barcelona, Spain). Sodium carbonate and *n*-hexane were purchased from Merck (Darmstadt, Germany), and sodium hydroxide and acetonitrile were obtained from Baker (Deventer, Holland). Sodium hydrogen-carbonate (Probus, Badalona, Spain) and hydrochloric acid (Panreac, Barcelona, Spain) were also used. Ultrapure water was obtained from a Nanopure II system (Sybron, MS, USA).

Bond Elut C₁₈200 mg extraction columns were from Varian (Habor City, CA).

2.3. Stock aqueous standard solutions

Unless otherwise stated, stock standard solutions of ammonium and amines (1000 or 10,000 mg L⁻¹) were prepared in water; working standard solution of the amines was prepared by dilution of stock standard solutions with water.

2.4. Air standards

An open volatilization chamber described in [9] for primary amines was tested for generating air standards of dimethylamine (see Fig. 1). The vaporization chamber was made with a plastic tube of 11.5 or 6.0 cm length. An aliquot of the solution of the amines (50 µL) was placed at the end of the tube, whereas the other extreme was connected to the inlet of the SPE cartridge by means of a polyvinyl chloride (PVC) tube (40 mm × 6 mm, i.d.). Next, the pump was activated at 30 mL/min and 50 µL of NaOH was immediately added to the samples (forming a 100 µL drop). After a defined sampling time, the pump was stopped, the cartridges were removed,



Fig. 1. Schematic diagram of the volatilization chamber: 1-C₁₈ cartridge and 2-PVC tube. For other details, see text.

and the retained amines were subjected to derivatization as established below. Before each assay, the cartridges were conditioned with 1 mL of methanol and 1 mL of carbonate buffer 1% (see the next section). The residue of the amine standard drop placed in the volatilization camera was collected in water and measured by the above derivatization procedure in order to estimate if the volatilization was quantitative.

A factorial design 2^3 was used to evaluate the effect of the length of the air path, concentration of NaOH and switching on the pump before or after the addition of the NaOH solution to the dimethylamine standards, on the efficiency of dimethylamine volatilization. Two lengths (11.5 and 6.0 cm) and two NaOH concentrations (0.5 and 1 M) were assayed.

The influence of the NaOH concentration added to the standard drop was also studied by the univariate optimization method between 0.5 and 10 M by using an air path of 11.5 cm and a sampling time of 15 min. The possibility of heating the NaOH solution before adding it to the amine was also evaluated.

The volatilization time was varied between 5 and 120 min employing an air path of 11.5 cm and NaOH 10 M at 85 °C.

All assays were carried out at ambient temperature, and each sample was assayed in triplicate.

2.5. Derivatization

Conditions for the derivatization of the amines into the SPE cartridges (corresponding to either volatilized samples or the aqueous samples) were selected according to the results presented in [14]: cartridges with the retained amine were flushed with 0.5 mL of carbonate buffer (8%, m/m) of pH 10.5, and then with 0.5 mL of 1.83×10^{-2} M NQS. After 15 min (reaction time), the cartridges were cleaned with 2 mL of carbonate buffer 1% followed by 3 mL of water, in order to remove the unreacted NQS. The derivatives formed were desorbed by flushing with 2 mL of a mixture of water-acetonitrile (1:1, v/v) and collected into a quartz cell.

Carbonate buffer (1%, m/m) of pH 10.5 was prepared by dissolving the adequate amount of sodium hydrogencarbonate in water, and then, by adjusting the pH with 1 M NaOH. Carbonate buffer (8%, m/m) of pH 10.5 was prepared by dissolving sodium carbonate and then, by adjusting the pH with 1 M HCl. The derivatizing reagent NQS was prepared by dissolving the pure compound in water.

Two millilitres of amine aqueous standards containing the same total mass (μg) as the air standards were processed. The flushed volume was transferred to other cartridge in order to test the amount of amine not retained. All assays were carried out at ambient temperature, and each sample was assayed in triplicate.

2.6. Analytical performance data

The total amounts of dimethylamine in the aqueous standards subjected to volatilization, sampling and derivatiza-

tion were varied from 10 to 100 μg . Other amines were tested (methylamine, ethylamine, propylamine, butylamine, pentylamine and diethylamine) from 40 to 280 μg . Several mixtures were also processed (see Table 3 for composition). Ten blank assays were carried out. The working wavelength for measurement of the NQS derivatives formed for primary amines was 444 nm, whereas for secondary amines was 480 nm. All assays were carried out at ambient temperature.

2.7. Application to the analysis of contaminated air samples

Synthetic air samples were prepared by contaminating the air inside several closed PVC chambers (29 cm \times 18 cm \times 15.5 cm) with dimethylamine and with a mixture of dimethylamine and methylamine. For this purpose, an opened flask containing the pure amine was placed inside three chambers for 17 h, next the time sampling were 15, 60 and 75 min at 30 mL min^{-1} (20 °C and 1.023×10^5 Pa). Two replicates were done in the same day. The atmosphere was also generated in four different days and sampled for 15 min.

Other chambers were contaminated for 10 and 20 h and sampled for 15 min (20 °C and 1.023×10^5 Pa) and for one day and sampled for 15 min (25 °C and 1.023×10^5 Pa). Chambers containing dimethyl- and methylamine contaminated also for one day, under the latter conditions, were also processed. Each sample was assayed in triplicate in all these cases.

In addition, chambers contaminated one day in the conditions above indicated were sampled with amine test colorimetric tubes. When the air samples were sucked through the tube, the colour changed to blue. Five strokes were done for air sampling (500 mL of air approximately). Calculations of the concentrations were done based on the specifications of the colorimetric tubes.

2.8. Application to the analysis of real air samples

Three workplace samples were analysed with the proposed procedure. They were collected in a closed city market at 1 m from three fish stands. Prior to the measurements, the cartridges were conditioned in situ with 1 mL of methanol and 1 mL of carbonate buffer 1%. Next, the air sampling was carried out for 15 min at 30 mL min^{-1} . Samples were collected at the height of the breathing zone. The transport and storage of the cartridges with the amines sorbed was done in hermetic plastic bags. The samples were transported to the laboratory near the city market and the analysis was performed according to the proposed procedure. Sampling temperature was 24.5 °C and relative humidity was 45%. Those values were similar to laboratory conditions. Each sample was assayed in duplicate and a standard of 10 μg of DMA was used as reference.

Table 1
Optima conditions and efficiency of the sampling and volatilization process for primary and secondary amines

Analyte	Solution of NaOH added to the aqueous standards		Sampling time (min)	Efficiency (%) $n = 6$
	Concentration (M)	Temperature		
Methylamine	1	Ambient	15	97 ± 3
Ethylamine	1	Ambient	15	84 ± 6
Propylamine	1	Ambient	15	94 ± 1
Butylamine	1	Ambient	15	105 ± 2
Pentylamine	1	Ambient	15	83 ± 9
Dimethylamine	10	85 °C	75	97 ± 4
Diethylamine	10	85 °C	75	82 ± 5

3. Results and discussion

3.1. Generation of standards with the open volatilization chamber

In the present study, we begun by using the conditions selected for volatilization of the primary amines in [9], sampling for 15 min at ambient temperature. Good results were obtained as can be seen in Table 1 for the primary amines, but the efficiency was smaller for dimethylamine. These values were calculated by comparing the absorbances measured for the gaseous standards with those obtained for aqueous standards containing an equivalent amount of amine and subjected directly to derivatization into the SPE cartridges with NQS. The retention was quantitative for aqueous standards because the blank signal was obtained in the collected fraction of the standard in a second cartridge processed in the same way.

As regards the volatilization by sampling of dimethylamine, the first variable studied was the solvent used to prepare the standard solutions of dimethylamine. No improvements on the efficiencies were observed compared with those achieved with aqueous samples (Fig. 2a), and therefore, water was always used as the solvent for preparation of the standard. From the factorial design (see Section 2) we observed that the time sequence used for placing the NaOH solution and for switching on the air pump in the manifold shown in Fig. 1 had a significant effect on analyte responses. The more relevant factor was the moment in which the air pump was activated. Much better results were found when the pump was switched on before the addition of NaOH. The best efficiencies were obtained when using a length for the air path of 11.5 cm (see Fig. 1).

The effect of the concentration of NaOH on the efficiency of the dimethylamine volatilization are depicted in Fig. 2b. As observed, increasing the concentration of the base resulted in increased efficiency. Compared with the addition of untreated solutions, heating the NaOH solutions at 85 °C substantially increased the signals.

Finally, the effect of the volatilization time was evaluated. As observed in Fig. 2c, the time required to achieve nearly quantitative recovery of dimethylamine was 75 min. No amine was found in the residue of the volatilization chamber. In Table 1 are summarized the optimized conditions

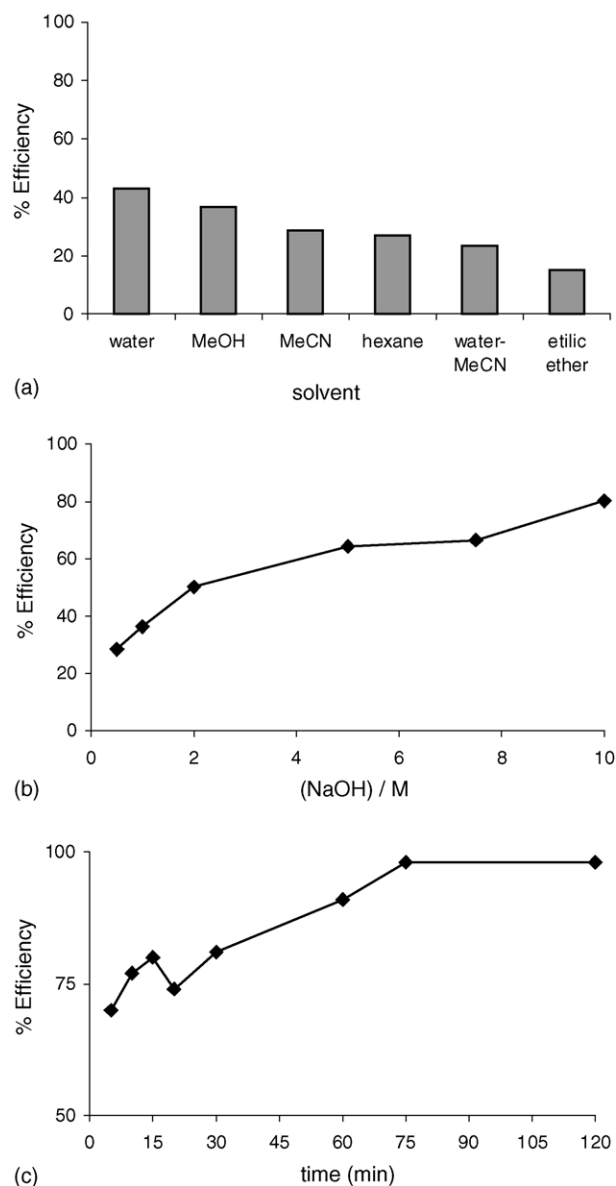


Fig. 2. Efficiencies obtained for dimethylamine (20 μg) as a function of: (a) solvent of the standards; (b) concentration of NaOH; and (c) sampling time. For other details, see text.

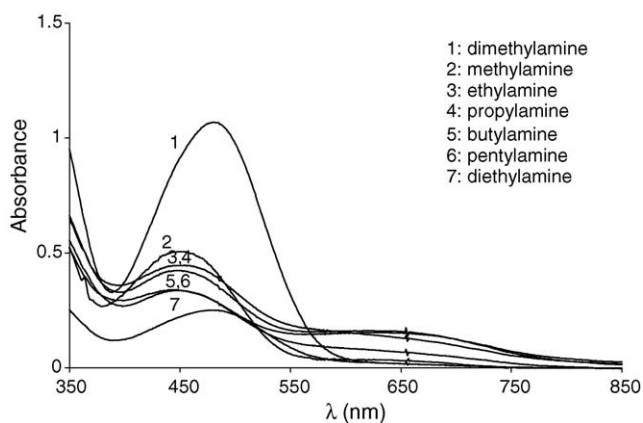


Fig. 3. Spectra for NQS derivatives of the amines. Dimethylamine 40 μg and methyl-, ethyl-, propyl-, butyl-, pentyl- and diethylamine 80 μg.

for this amine, as well as the efficiency achieved. The optimal conditions found for dimethylamine were applied to the volatilization of diethylamine.

3.2. Analysis of the gaseous standards of amines

Gaseous standards of the amines, each one generated according to the conditions of Table 1, were processed in order to obtain relevant analytical data. For quantification purposes, the absorbances of the derivatives formed for amines were measured at their respective adsorption maximum (Fig. 3), 444 nm for primary amines-NQS derivatives and 480 nm for secondary-NQS derivatives. As shown in Table 2 linear calibration graphs were obtained over the tested concentration intervals. This table also shows the equations obtained for aqueous standards containing equivalent amounts of the analytes, and processed directly into the SPE cartridges. It can be observed that calibration curves for gaseous and aqueous samples were statistically equivalent (at a confidence level of 99%). This proves that under the proposed conditions, the amines are quantitatively volatilized and retained in the SPE cartridges. The same conclusion can be derived from the limits of detection (LODs, calculated as $3 s_{bl}/b$ where s_{bl} is the standard deviation of 10 blank assays and b is the slope of the corresponding calibration graphs) found in both kinds of samples. The values obtained were in the 2–25 μg range. Thus, it was demonstrated that aqueous standards could be used to determine these amines in air samples. This is also the case where silica gel is the adsorbent [4].

The limits of quantification (LOQs) for the amines tested can be estimated as $10 s_{bl}/b$, i.e., by multiplying the LODs given in Table 2 by the factor 10/3.

Fig. 4 compares the sensitivities at 480 nm of all the amines assayed. As can be seen in this figure dimethylamine presented the highest value, being about five times higher than those obtained by the other amines. The interference of the other amines in dimethylamine determination will be low if they are present at similar concentration level. Ammonia was not an interference because no NQS derivate

Table 2

Analytical parameters obtained for the amines tested: (1) aqueous standards directly processed in the SPE cartridges and (2) gaseous standards generated and processed under optimized conditions ($n = 3$)

Analyte	Absorbance vs. μg of amine			Absorbance vs. mol of amine			R^2	$s_{y/x}, n$	LOD (μg ⁻¹)
	$a \pm s_a$	$(b \pm s_b) \times 10^2$ (μg ⁻¹)	R^2	$a \pm s_a$	$(b \pm s_b) \times 10^{-4}$ (mol ⁻¹)	R^2			
Methylamine	1	0.07 ± 0.03	0.80 ± 0.03	0.9974	0.0400; 4	0.9974	0.0400; 4	9	
	2	0.01 ± 0.03	0.85 ± 0.03	0.9931	0.0713; 4	0.9936	0.0713; 4	9	
Ethylamine	1	0.08 ± 0.04	0.43 ± 0.03	0.9700	0.0723; 4	0.9677	0.0723; 4	17	
	2	0.09 ± 0.02	0.37 ± 0.02	0.9820	0.0509; 4	0.9820	0.0509; 4	21	
Propylamine	1	0.06 ± 0.02	0.41 ± 0.02	0.9889	0.0418; 6	0.9889	0.0418; 6	18	
	2	0.08 ± 0.03	0.40 ± 0.02	0.9811	0.0562; 6	0.9811	0.0562; 6	19	
Butylamine	1	0.05 ± 0.03	0.40 ± 0.02	0.9910	0.0448; 6	0.9910	0.0448; 6	19	
	2	0.04 ± 0.02	0.41 ± 0.01	0.9903	0.0394; 6	0.9903	0.0394; 6	19	
Pentylamine	1	0.02 ± 0.01	0.36 ± 0.01	0.9962	0.0219; 6	0.9963	0.0219; 6	20	
	2	0.030 ± 0.009	0.31 ± 0.06	0.9967	0.0169; 6	0.9967	0.0169; 6	25	
Dimethylamine	1	0.05 ± 0.01	2.56 ± 0.04	0.9987	0.0181; 4	0.9987	0.0181; 4	2	
	2	0.09 ± 0.03	2.5 ± 0.1	0.9932	0.0416; 4	0.9932	0.0416; 4	2	
Diethylamine	1	0.02 ± 0.04	0.40 ± 0.03	0.9862	0.0666; 5	0.9862	0.0666; 5	11	
	2	0.00 ± 0.05	0.39 ± 0.03	0.9832	0.0719; 5	0.9832	0.0719; 5	10	

1, aqueous standards and 2, air standards.

Table 3
Results obtained in the analysis of mixtures of amines in air ($n = 2$)

Sample composition ($\mu\text{g}/\text{sample}$)							Signal of the mixture $\sum(\text{signal of the individual solutions})$ (%)
Methylamine	Ethylamine	Propylamine	Butylamine	Pentylamine	Dimethylamine	Diethylamine	
40	40						67, 73
		40	40				125, 135
					40	40	96, 98
40					40		115, 117
				40		40	108, 114
		40	40	40			103, 84
				40	40	40	68, 67
40					40	40	71, 76

was obtained. However, in atmospheres containing diethylamine at concentrations higher than dimethylamine concentrations, the method would be biased for the latter amine. If present, the bias error introduced by primary amines at concentrations higher than that corresponding to dimethylamine could be eliminated by considering bivariate or multivariate calibration. In this work, we proposed bivariate calibration for simplicity. The measurement wavelengths were 444 and 480 nm. The procedure is outlined in the following; first the additivity of the signals was demonstrated. The proposed methodology was applied to different mixtures of the amines tested. The samples and concentrations assayed are listed in Table 3. As can be seen in this table, the signals measured for the mixtures of the amines were comparable to the values obtained by addition of the signals obtained for the samples of the individual amines. Then, the amine signals are additive.

On the other hand, the slope values expressed as mol^{-1} for all primary amines at 444 nm were similar (see Table 2), the mean value and standard deviation were 25 and 5, respectively. With these results, it was corroborated that the primary amine response in the NQS reaction was not dependent on the primary amine, and that any primary amine could be used as a representative compound by expressing the total primary amine concentration as mol or as mg L^{-1} of N. A sample containing methylamine ($1.3 \mu\text{mol}$) and

dimethylamine ($0.9 \mu\text{mol}$) was analyzed in duplicate. We selected this sample because papers dealing with the measurement of aliphatic amines [1,2,8] reported that they could be present together. By using the bivariate calibration (employing measurements at 444 and 480 nm) the concentrations of dimethylamine and methylamine were estimated, being 0.9 and $1.1 \mu\text{mol}$, respectively. These values indicate that it is possible to determine both, dimethylamine and primary amines.

3.3. Visual assay

The primary amines formed a red–brown derivative, whereas the secondary amine derivative presented an orange colour (see Fig. 5). Therefore, the employment of NQS in combination with SPE cartridges for sampling and derivatization is advantageous over previously reported methods, as it was possible to distinguish in situ if primary amines are also present together with dimethylamine by visual inspection of the cartridges after derivatization. The coloured area in the cartridges could be also used to estimate semi quantitatively the concentration of amine as can be derived by observing Fig. 5, which is a clear advantage of the proposed procedure over methods based on the employment of colourless reagents. Besides, this assay improves markedly the selec-

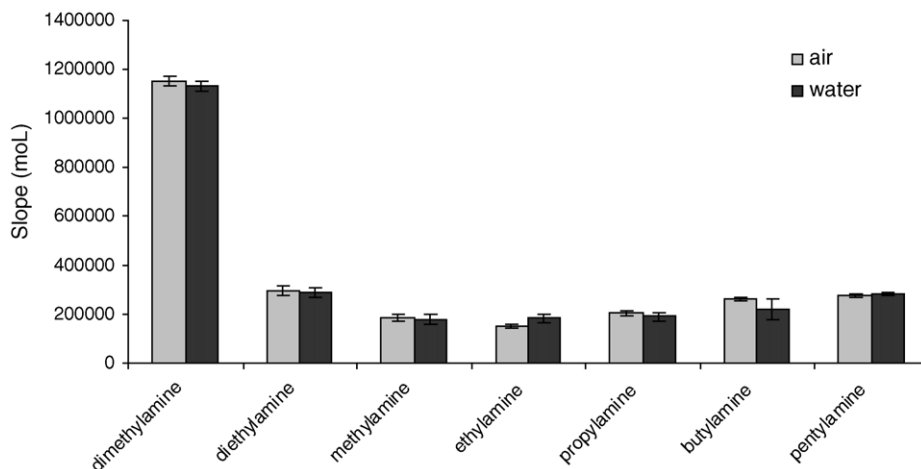


Fig. 4. Sensitivities (slopes of the linear calibration graphs) at 480 nm for the amines assayed.

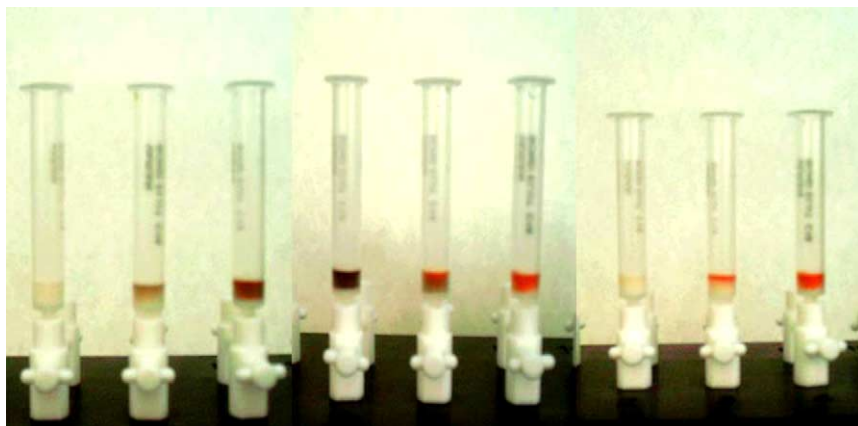


Fig. 5. Pictures of the SPE cartridges after derivatizing the amines collected from air: (a) blank (left), and methylamine 20 μg (centre) and 140 μg (right); (b) methylamine 140 μg (left), methylamine 140 μg plus dimethylamine 140 μg (centre), and dimethylamine 140 μg (right); and (c) blank (left), and dimethylamine 20 μg (centre) and 140 μg (right). For other details, see text.

tivity achieved with colorimetric tubes based on acid–base reactions, which respond to all the basic amino groups.

3.4. Analysis of air samples

Fig. 6 shows the results obtained after 17 h of chamber contamination. Similar values for the atmosphere were obtained sampling between 15 and 75 min, the mean value was $3.0 \pm 0.5 \text{ mg m}^{-3}$. The procedure could be used to estimate both STEL and TLV limits. For the first limit the sampling time recommended is 15 min and for the second one the European norm establishes to sample a percentage of 25% of the time of exposition (8 h) if the atmosphere is uniform. If the sampling time is 15 min, eight samples are needed. If the sampling time is 1 h, only two samples are required. The limit of detections expressed as mg m^{-3} (20 °C, $1.023 \times 10^5 \text{ Pa}$) considering 15 or 60 min as sampling time at 30 mL min^{-1} were 3.2 and 1.1, respectively. Those values indicated that the procedure is adequate for estimating STEL and TLV limits.

The atmosphere with 17 h of contamination was generated in four different days and a mean value of 3.2 mg m^{-3} was obtained sampling 15 min with a relative standard deviation of 8%.

For the two atmospheres with 10 and 20 h of contamination, the concentration of amine was calculated from the calibration equations obtained from both gaseous stan-

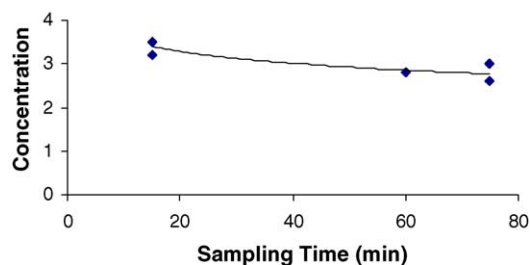


Fig. 6. Dimethylamine concentration (mg m^{-3}) in an air synthetic sample generated after 17 h of contamination as function of the sampling time.

dard samples and aqueous solutions directly processed into the cartridges (Table 2). The concentrations measured were 1.05 ± 0.03 and $3.82 \pm 0.03 \text{ mg m}^{-3}$, after 10 and 20 h, respectively. The values calculated from the calibration equations obtained by derivatizing the aqueous standards were 1.08 ± 0.03 and $3.81 \pm 0.01 \text{ mg m}^{-3}$. This confirms that aqueous standards instead of air standards can be utilised in the analysis of air samples [9].

A comparative study between the proposed method and the amine test colorimetric tubes (Dräger) was carried out from the chambers contaminated one day. The results obtained are shown in Table 4. As can be seen comparable results were obtained for dimethylamine in presence or absence of methylamine when the proposed procedure is applied.

The colorimetric tubes provide a semiquantitative estimation of dimethylamine (Table 4). The mean value obtained for the chambers with dimethylamine alone was 35% higher than that calculated with the proposed procedure. This percentage is consistent with the specifications of the tube manufacturer. The values obtained for the chamber contaminated also with methylamine are not comparable with those obtained by the proposed method because the colorimetric tubes respond to

Table 4
Results obtained in the analysis of one day contaminated chambers

Samples	Found concentration ($\mu\text{g} \pm \text{s}$)	
	NQS	Colorimetric tube
Chamber one-day contaminated with dimethylamine	6.8 ± 0.6	9.5 ± 1.5
Chamber one-day contaminated with dimethylamine and methylamine	$7.0 \pm 0.4 (11 \pm 1)^{\text{a}}$	12 ± 2
City market, stand 1	$7^{\text{b}} \pm 1^{\text{c}}$	
City market, stand 2	$9^{\text{b}} \pm 2^{\text{c}}$	
City market, stand 3	$11^{\text{b}} \pm 2^{\text{c}}$	

^a Found methylamine (μg).

^b Concentrations expressed as mg m^{-3} .

^c Expanded uncertainty.

all amines. As can be derived from the results of Table 4 the precision obtained with the colorimetric tubes is worse than that achieved by the NQS procedure.

Table 4 also gives the results obtained by the proposed method for the real samples processed. Although only the cartridge conditioning is carried out in the field due to its proximity to the laboratory, it could be possible making all the assay in the field, even the absorbance measurement if a transportable colorimeter is available.

Expanded uncertainties using a coverage factor of 2 are given in Table 4 for the city market samples. The estimate is compliant with EURACHEM/CITAC Guide [16] and is a full estimate based on in-house method validation. The mass concentration in the final sample is given by $m_o = m_{\text{ref}} (A_o/A_{\text{ref}})$, where m_{ref} is the mass concentration of the reference standard in μg and, A_o and A_{ref} are the absorbances corresponding to the sample and standard, respectively. The estimate of the level of DMA in the atmosphere (in mg m^{-3}) is given by $C_o = m_{\text{ref}} (A_o/A_{\text{ref}})/Q \cdot t$, where Q is the pump flow rate and t is the sampling time. 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 or gaseous standards (around R.S.D. 8%), chamber samples (see Table 4) and real city market samples. For these real samples the precision was estimated by considering the standard deviation of the normalised difference data (the difference of the two replicates for each sample divided by the mean) and divided by $\sqrt{2}$, which also provides a measure of the overall run to run variability. The contributions to the uncertainty introduced by the purity of the reference standard and the sampling time are so small (compared to the precision estimate) that it is clearly safe to neglect this contribution. The precision of the pump is 3% considering manufacturer's specification. The relative combined standard uncertainty was 0.1.

4. Conclusions

This work shows a simple, low-cost and rapid method for the determination of dimethylamine in air, based on the employment of C_{18} -based SPE cartridges for sampling and derivatization with NQS. It has also been confirmed that the employment of an opened volatilization chamber is a good option for the generation of gaseous standards of amines. The assay combines SFE and colorimetric or visual measurements and could be made in the field.

An additional advantage over methods using colourless reagents is that a visual inspection of the coloured area in the SPE after derivatizing the analytes allows the differentiation between primary and secondary amines, as well as the semiquantitative estimation of the total amount of amine. In terms of selectivity and precision, the visual assay is better than that based on colorimetric tubes.

The proposed solid support assisted procedure permits to estimate STEL and TLV limits established by the legislation for dimethylamine measuring absorbance of the NQS-derivates after desorption from the cartridges.

Acknowledgements

The authors would like to thank the Ministerio de Ciencia y Tecnología of Spain for financial support received for the Project BQU2003-06138. Y. Moliner Martínez expresses her grateful to Ministerio de Educación, Cultura y Deporte of Spain for her pre-doctoral grant.

References

- [1] I.-H. Chang, C.-G. Lee, D.S. Lee, *Anal. Chem.* 75 (2003) 6141.
- [2] P. Simon, C. Lemacon, *Anal. Chem.* 59 (1987) 480.
- [3] L. Groenberg, P. Loevkvist, J.A. Joensson, *Chemosphere* 24 (1992) 1533.
- [4] NIOSH Manual of Analytical Methods (NMAM), fourth ed., 8/15/94, USA.
- [5] OSHA Manual of Analytical Methods, 1991, USA.
- [6] J. Koziel, M. Jia, A. Khaled, J. Noah, J. Pawliszyn, *Anal. Chim. Acta.* 400 (1999) 153.
- [7] J. Koziel, M. Jia, J. Pawliszyn, *Anal. Chem.* 72 (2000) 5178.
- [8] J. Namiesnik, A. Jastrzebska, B. Zygmunt, *J. Chromatogr. A* 1016 (2003) 1.
- [9] Y. Martínez-Moliner, P. Campíns-Falcó, R. Herráez-Hernández, J. Verdú-Andrés, *Anal. Chim. Acta* 502 (2004) 235.
- [10] C. Cháfer-Pericás, R. Herráez-Hernández, P. Campíns-Falcó, *J. Chromatogr. A* 1042 (2004) 291.
- [11] R. Herráez-Hernández, P. Campíns-Falcó, A. Sevillano-Cabeza, *Anal. Chem.* 68 (1996) 734.
- [12] J. Verdú-Andrés, P. Campíns-Falcó, R. Herráez-Hernández, *Analyst* 126 (2001) 1683.
- [13] S. Meseguer-Lloret, C. Molins-Legua, P. Campíns-Falcó, *J. Chromatogr. A* 978 (2002) 59.
- [14] P. Campíns-Falcó, C. Molins-Legua, A. Sevillano-Cabeza, R. Porras-Serrano, *Analyst* 122 (1997) 673.
- [15] European Directive 2000/39/CE, Brussels, 6/8/2000.
- [16] EURACHEM/CITAC (1995), Guide Quantifying Uncertainty in Analytical Measurement, second ed. 2000.