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Determination of volatile aliphatic amines in air by solid-phase microextraction coupled with gas chromatography with flame ionization detection

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Abstract

Practical aspects of the application of solid-phase microextraction (SPME) to the determination of volatile aliphatic amines in air are described. Analytes included methylamine (MA), ethylamine (EA), dimethylamine (DMA), diethylamine (DEA), trimethylamine (TMA) and triethylamine (TEA). New SPME stationary phases were examined. The effects of relative humidity and temperature on analytes uptake were taken into account in analysis. Gas chromatography (GC) with flame ionization detector (FID) was used for the final analysis.

Keywords: Air analysis; Solid-phase microextraction; Amines; Volatile organic compounds

1. Introduction

Amines can be found in many different matrices, from environmental samples to industrial raw materials, products and wastes. Determination of amines in these matrices is a challenging task because of the polar character of these compounds. Both their isolation from the matrix and their final chromatographic determination are usually very difficult.

Low-molecular weight aliphatic amines are widely used industrial chemicals. They find application as raw materials or intermediate products in the manufacturing of other chemicals, pharmaceuticals, polymers, pesticides, rubber, dyes, adhesives, solvents and corrosion inhibitors. They are used as surfactants, emulsifying agents and components of depilatory creams. Other uses include electroplating, textile manufacturing, vulcanization accelerators, fuel additives, rocket fuels, etc. [1–7].

Short-chain aliphatic amines are emitted to the atmosphere from numerous anthropogenic sources, including waste incineration, sewage treatment, cattle farms and industry. They are also emitted with vehicle exhaust gases and tobacco smoke. Production of some amines in Western Europe exceeds 100,000 t per year. Natural sources of amines in the environment include biodegradation of organic matter containing proteins, amino acids or other nitrogen-bearing compounds [8]. Natural aliphatic amines background

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concentration can be estimated based on emissions from animal waste and microbial activity [9].

The ever-growing interest in the state of the natural environment and ecotoxicological issues prompts the development of new methods for the determination of low levels of amines in various environmental compartments. This is particularly important in the case of air. For example, Audunsson and Mathiasson [10] described dangerous health effects of exposure to low levels of amines. Volatile amines have very low odor threshold levels (as low as 0.002 ppm for trimethylamine (TMA)), and their maximum allowable concentrations in air are also very low in most countries. All these factors make the determination of trace levels of amines in air a very important task, especially in industrial hygiene. Occupational exposure to amines is monitored among others in polymer plants, fish processing plants and industrial animal farms. Amines are also often determined in liquid samples, including physiological fluids, drinks and mineral oils, as well as in solid samples such as food and also in microbiological examination of algae and plants [10].

Preconcentration of amines from air is usually carried out by absorption in water [11] or sorption on solid sorbents [12–14]. Analyte derivatization is often included in the analytical procedure [15–18]. Preconcentration makes it possible to lower the detection limits of amines to 0.01–0.1 ppm. Unfortunately, other matrix components are also concentrated together with the amines, which may lead to errors [19]. Methods employing direct derivatization of amines in the aqueous phase are usually characterized by relatively poor sensitivity and selectivity. Much more popular is the use of derivatizing agents on solid supports, including silica, alumina and cross-linked polystyrene [19]. Unfortunately, most derivatization methods are time consuming and may lead to side effects that can make the final determination difficult. For example, when high-molecular weight derivatizing agents are used, the relative differences between the molecular weights of the derivatives may be significantly smaller than for the amines themselves, which can make their separation difficult. This is often the case when both methylamine (MA) and ethylamine (EA) are determined in a sample. Their derivatives are hard to separate.

Gas chromatography (GC) is widely used in the analysis of amines owing to its simplicity, high resolving power, good sensitivity, short analysis time and relatively low cost. In some cases, determination of amines can be carried out by direct injection of a sample into the precolumn. In general, amines are separated using strongly basic stationary phases. Packed columns deactivated with potassium chloride, trimethylchlorosilane and ammonia were used for the determination of free amines at levels exceeding single ppm. Detection limit can be improved by analyte preconcentration or by the use of more sensitive and selective detectors. Typical GC detectors used in amine determination include nitrogen–phosphorus detector (NPD), flame ionization detector (FID) and mass spectrometric detector (MSD).

Determination of low-molecular weight amines by GC creates additional challenges due to their high aqueous solubility, volatility, polarity and basic character. As the molecular mass of the amine decreases, the relative effect of the amine group increases, which results in stronger sorption to polar stationary phases [20]. The amine group imparts high dipole moment on amine molecules. This dipole moment is responsible for strong interaction with silane groups and siloxane bridges, leading to strong sorption resulting in broad, asymmetrical peaks and poor sensitivity. In addition, amines tend to decompose in the GC column and to sorb to exposed parts of the equipment and instrumentation (sample vials, injector, glass wool, etc.). Primary amines have the strongest sorption tendency, followed by secondary amines and tertiary amines. MA and dimethylamine (DMA) are the most difficult to determine by GC. In general, chromatographic separation of aliphatic amines is much more difficult than separation of aromatic amines.

Liquid chromatography is also often used in the determination of alkyl amines. However, since amines have low absorptivity in the UV range, they have to be derivatized before the final determination. Even better results can be achieved by using fluorescent reagents. Typical detectors used in the determination of amines by HPLC include UV-Vis [21], coulometric detector (CD) [22], fluorescence detector (FD) [23] and chemiluminescence detector (ChD) [24].

Alkyl amines can also be separated by SFC in both packed and capillary columns at relatively high temperatures using carbon dioxide or nitrous oxide as the mobile phase [25–27]. Very good separation of trialkylamines was achieved at a temperature of 50 °C

by programming the density of CO_2. Primary aliphatic amines in the form of trifluoroacetic acid derivatives were analyzed using capillary columns and carbon dioxide as a mobile phase [28].

Capillary electrophoresis (CE) is often used when other techniques fail. Good results can be achieved in CE by proper selection of buffers and/or using modifiers. Separation time in CE is usually very short, and the sample volume can be as low as a nanolitre (nl). Very low detection limits (≅1 ppt) can be achieved with suitable detectors, such as a laser-induced fluorescence (LIF) detector [15]. In this particular case, the amines were derivatized using fluorescein isothiocyanate.

The aim of the paper is to study the possibility of the application of solid-phase microextraction (SPME) for the determination of volatile aliphatic amines in non-derivatized form in air. In the method sampling and sample preparation are combined into a single step, and sample introduction to the chromatographic column is very simple [29].

2. Experimental

2.1. Reagents and materials

Standard solutions were prepared using commercially available chromatographic grade solvents and chromatographic standards from Merck (Germany): MA (40%, w/w solution in water; density (20 °C) 0.90 g/ml); EA (70%, w/w solution in water; bp 39 °C, density (20 °C) 0.81 g/ml); DMA (40% w/w, solution in water; bp 54 °C, density (20 °C) 0.89 g/ml); diethylamine (DEA) (40%, w/w solution in water; bp 56 °C, density (20 °C) 0.71 g/ml); TMA (50%, w/w solution in water; bp 30 °C, density (20 °C) 0.85 g/ml); triethylamine (TEA) (40%, w/w solution in water; bp 88–90 °C, density (20 °C) 0.73 g/ml); HPLC-grade water.

2.2. Instrumentation

A GC 8000 Series gas chromatograph, Carlo Erba Instruments (Italy) with a FID (220 °C), was used in the study. A Stabilwax-DB/KOH megabore column (60 m × 0.53 mm × 1.5 μm) kept at 50 °C with hydrogen as a carrier gas was used for separation. The temperature of an injector, where analytes were desorbed from an SPME fiber, was 200 °C.

The SPME device was supplied by Supelco (Bellefonte, PA). Two types of fiber coatings were used in the study:

(a) Commercially available 65 μm polydimethylsiloxane/divinylbenzene (PDMS/DVB) coating (Supelco).
(b) Coatings custom-made by the team of Prof. Buszewski at the Faculty of Chemistry, Nicolaus Copernicus University (Toruñ, Poland), including ethoxy polydimethylsiloxane (PDES, ∼10 μm), polyurethane acrylate (PUA, ∼40 μm) and 50% phenyl/polydimethylsiloxane (PDMS/Ph, ∼10 μm). The procedure used to produce the custom fibers was described previously [30].

Standard gas mixtures were produced using a generator developed at the Department of Analytical Chemistry, Gdańsk University of Technology [31]. The main components of the generator included commercial amine permeation tubes (Vici Metronics, Inc.), hygrostatic humidity stabilizers and thermostated sampling chambers The tubes were characterized by permeation coefficients of 65, 140, 22, 82, 75 and 4 ng/(min cm) and length of 2, 1, 6, 1, 1 and 6 cm for MA, EA, DMA, DEA, TMA and TEA, respectively. The mixture generating set allowed the control of the relative humidity of the standard mixture at several levels: 20, 47, 66, 79 and 92%.

2.3. Procedure

2.3.1. Model investigations

The SPME–GC–FID system was calibrated using standard gas mixtures of the analytes. Analyte concentrations in the standard gas mixtures were controlled by changing the flow rate of the diluting gas. Extraction time profiles of the analytes were determined by plotting analyte peak areas vs. time of fiber exposure to the mixture (1–20 min). This was followed by the determination of the effect of standard gas mixture temperature (15–35 °C), relative humidity (0–92%) and flow rate (0–150 ml/min) on the amount of analyte extracted at equilibrium. Amines extraction by the custom fibers coated with PUA and PDES was compared to extraction by the commercial PDMS/DVB fiber.

Table 1
Characteristics of the sampling sites and sampling conditions

Site code	Site characteristics	Sampling conditions
A	*Production area* of a pharmaceutical plant	$T = 18\,^{\circ}C$, RH = 62%
B	*Chemical storeroom* consisting of a ventilated room	$T = 19\,^{\circ}C$, RH = 59%
C	*Car paint shop*, freshly renovated staff lounge	$T = 21\,^{\circ}C$, RH = 54%
D	*City market* (samples collected on a market day, ca. 2 m from a cluster of fish stands)	$T = 24\,^{\circ}C$, RH = 77%
E	*City market* (samples collected within a 20 m radius of the fish stands)	$T = 24\,^{\circ}C$, RH = 77%

2.3.2. Real samples

Indoor air, atmospheric air and workplace air were analyzed for the presence of the amines using the procedure developed. Prior to the measurements, the fibers were cleaned by thermal desorption at temperatures recommended by manufactures (commercial fibers: 250 °C, custom-made fibers: 200 °C). For transport and storage of the fibers with the amines sorbed, the needles of the fiber assemblies were sealed with silicone septa and placed on dry ice. The time between sampling and analyses was not longer than 15 min. Model experiments indicated that losses of the amines stored under the above conditions (time ≤15 min, septum sealing, dry ice) were lower than experimental errors. Sampling was carried out for 20 min. Temperature and relative humidity of the air sampled were measured. The fibers were transported to the laboratory and analysis performed according to the procedure developed in the model investigations.

Table 1 summarizes the characteristics of the outdoor air sampling sites and the sampling conditions. Samples of indoor air were collected in the central parts of the objects, at the height of the breathing zone [32]. Two or three indoor air samples were collected in parallel, depending on the number of fiber assemblies available. Both commercial and custom-made fibers were used in the measurements. During sampling, the SPME device was held ca. 50 cm away from the person performing the measurements. The fiber was exposed to sample for 20 min.

3. Results and discussion

3.1. Results of model investigations

3.1.1. Exposure time

Exposure time is one of the most important parameters in analysis by SPME. It is advantageous to allow the analytes to reach equilibrium with the coating. Equilibration was studied by determining analyte peak areas as a function of time the fiber was exposed to the standard gas mixture. The time was varied between 1 and 20 min. Examples of the exposure time profiles obtained in the study are shown in Fig. 1. In general, the profiles for all the analytes looked similar. The equilibration time depended, to some extent, on the analyte, temperature and relative humidity of the standard mixture. For example, an increase in relative humidity from 0 to 92% and a simultaneous increase in temperature by 20 °C made the equilibration times longer by 7 min for MA, DMA, TMA and EA, and 4 min for DEA and TEA. In general, the equilibration times for the analytes ranged from 8 min for TEA through 10 min for DEA and 15 min for the remaining analytes. Based on this, it was decided that in the analysis of real samples, the exposure time should be at least 15 min.

3.1.2. Desorption time and temperature

Recovery of the analytes sorbed by the SPME fiber depends on the time and temperature of thermal desorption. A temperature of 200 °C was selected for desorption, which is the upper desorption temperature proposed by Buszewski and coworkers [30] for the custom-made fibers. At lower temperatures (desorption time: 120 s) desorption was quantitative for some amines only. Time desorption profiles at 200 °C were determining by measuring peak areas for desorption times in the range of 20–180 s, increased in 20 s intervals.

The results indicate that though the minimum time for quantitative transfer of the analytes from the SPME fiber to the GC column depends on an amine it is never longer than 120 s for all the amines studied at a temperature of 200 °C.

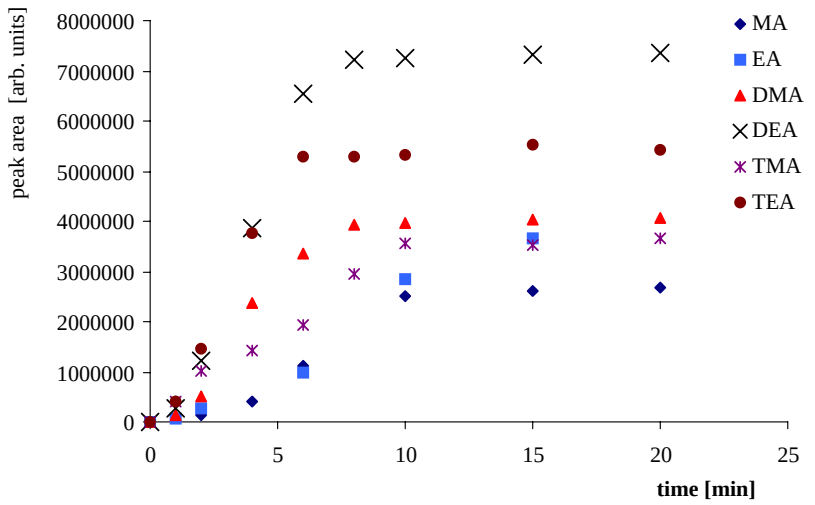

Fig. 1. Exposure time profiles for the PDMS/DVB fiber coating. Standard gas mixture flow rate 15 ml/min (the concentration of analytes in standard gaseous mixture: MA = 8.67 mg/m^3, DMA = 8.80 mg/m^3, TMA = 5.0 mg/m^3, EA = 9.33 mg/m^3, DEA = 5.47 mg/m^3, TEA = 0.53 mg/m^3), RH 47%, temperature 15 °C.

3.1.3. Evaluation of the sorption properties of the custom-made fibers

The properties of the custom-made fibers were compared to those of the commercially available PDMS/DVB fiber. Preliminary evaluation of the affinity of the amines to the different coatings was carried out by exposing the fibers for 20 min (time longer than equilibration time for any amine studied), to a standard gas mixture of the amines at RH = 0%, V = 15 ml/min and T = 15 °C. Since the thicknesses of the coatings were different, the affinity could not be evaluated by direct comparison of the analyte peak areas obtained for the different fibers under the same conditions. Analytes partition coefficients between the sample and the coating were determined instead [29]. Table 2 lists the partition coefficient determined. The results indicate that only one of the new coatings, i.e. PUA, was characterized by higher values of the partition coefficients (10% for MA and 20.5% for DMA) than the commercial PDMS/DVB coating.

3.1.4. Temperature effect

The effect of temperature on the amount of amine sorbed by the SPME fibers used in this work was examined in 15–35 °C temperature range at different relative humidities and standard gas mixture flow rates. In all cases, the amount of analyte sorbed decreased with temperature. Fig. 2 presents examples of extraction time profiles of the amines studied for the PDMS/DVB coated fiber at different temperatures at RH = 0% and V = 35 ml/min. For the conditions specified for Fig. 2, the amount of analyte decreased by 10% for TEA, 23% for TMA, 31% for DEA, 47% for DMA and 62% for MA when the temperature increased from 15 to 35 °C. When the relative humidity was 66% and the standard gas mixture flow rate was 70 ml/min, temperature increase from 15 to 35 °C resulted in a decrease in the amount of analyte extracted by 17% for EA, DEA and TEA, 30% for DMA and TMA, and 49% for MA.

Table 2
Partition coefficients of selected amines for different SPME fiber coatings

Analyte	Fiber coating			
	PDES	PUA	PDMS/50% Ph	PDMS/DVB
MA	123	492	195	452
EA	110	430	125	493
DMA	35	572	215	475
DEA	45	321	132	659
TMA	49	302	141	523
TEA	113	670	270	1230

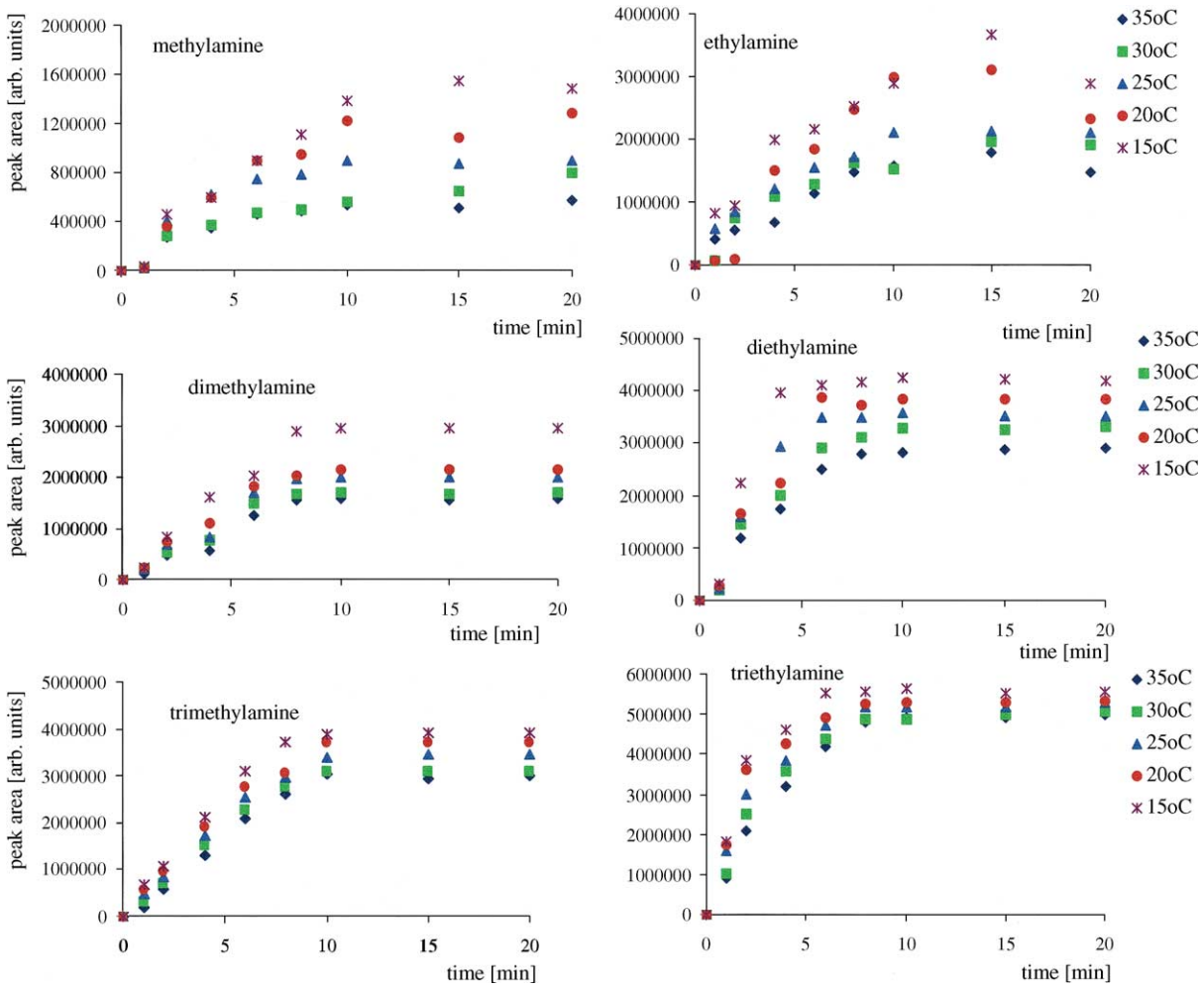

Fig. 2. The effect of temperature on the amount of analyte extracted by the SPME fiber (PDMS/DVB) at RH = 0% and $V = 35$ ml/min.

In the case of the other fibers studied the temperature effect was similar.

The results clearly indicate that temperature should always be measured or controlled when collecting real samples by SPME.

3.1.5. *The effect of relative humidity*

The effect of relative humidity of the standard gas on the amount of analyte extracted by all the SPME fibers used was studied by comparing the amounts extracted at different humidities in the amount extracted at RH = 0%. Each experiment was performed in triplicate.

Fig. 3 illustrates the effect of humidity at a temperature of 35 °C and standard mixture flow rate of 100 ml/min, when a PUA coated fiber is used.

An increase in relative humidity from 0 to 92% at 35 °C and $V = 100$ ml/min resulted in a decrease in the amount of analyte extracted by the fiber by ∼20% for TEA, TMA and DEA, ∼53% for EA and DMA and 80% for MA. In general, the amount of amines sorbed by the fiber decreased noticeably with increasing relative humidity at all temperatures and standard gas mixture flow rates for all the fibers used. This clearly indicates that relative humidity has to be recorded during measurements and humidity effect

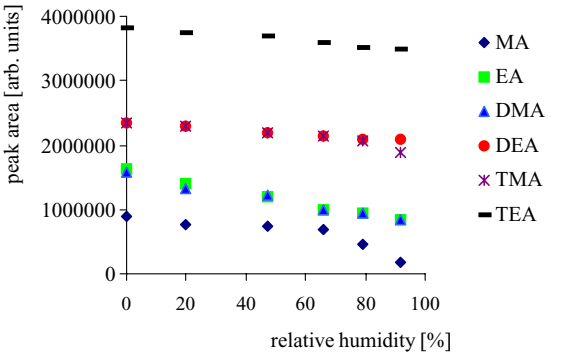

Fig. 3. The effect of relative humidity of the standard gas mixture on the amount of analyte extracted by the SPME fiber (PUA) at 35 °C and 100 ml/min.

should be taken into consideration in the process of calibration.

3.1.6. Calibration of the SPME–GC–FID system

Calibration was carried out at five different temperatures (15, 20, 25, 30 and 35 °C) and six different relative humidity levels (0, 20, 47, 66, 79.2 and 92%) for the following analyte concentration ranges: MA, 0.86–8.67 mg/m^3; EA, 0.93–9.33 mg/m^3; DMA, 0.88–8.80 mg/m^3; DEA: 0.54–5.47 mg/m^3; TMA: 0.52–5.00 mg/m^3; TEA: 0.05–0.53 mg/m^3. The SPME fiber exposure time was 15 min in each case. The calibration was performed for all the fibers used. Table 3 summarizes the parameters of the calibration curves obtained in the case of PDMS/DVB.

Table 4
Detection and quantitation limits determined from calibration curves

Compounds	Quantitation limits (mg/m^3)	Detection limits (mg/m^3)
TEA	0.86	0.30
DEA	0.57	0.21
EA	1.06	0.38
MA	1.03	0.31
DMA	1.88	0.67
TMA	0.55	0.19

In all cases, it was found that the values of the linear correlation coefficients r were greater than the critical value $r_{cr} = 0.88$ for the number of measurements $n = 5$ and the probability level $P = 95\%$ ($f = n-2$), which indicates that the correlation was significant. Consequently, a linear relationship between the concentration of the analyte in the standard gas mixture and the peak area was assumed.

Detection and quantitation limits determined from calibration curves using the PDMS/DVB fiber are given in Table 4.

3.1.7. A comparison of SPME amines sampling under static and dynamic conditions

The standard gas mixture generator made it possible to perform SPME sampling under dynamic or static conditions. In the dynamic sampling mode, the fiber was exposed to a standard gas mixture flowing continuously through the thermostated sampling

Table 3
Parameters of the calibration curves ($y = ax + b$) for the SPME–GC–FID system

Conditions	Analyte	$a \times 10^6$ ($S_a \times 10^5$) (arbitrary units mg/m^3)	$b \times 10^6$ ($S_b \times 10^5$) (arbitrary units)	r^2
$T = 35$ °C, RH = 0%	MA	0.13 (0.05)	0.05 (0.22)	0.9955
	EA	0.36 (0.15)	0.12 (0.69)	0.9948
	DMA	0.36 (0.26)	0.16 (1.14)	0.9851
	DEA	1.01 (0.32)	0.38 (0.87)	0.9971
	TMA	1.11 (0.39)	0.53 (0.99)	0.9961
	TEA	10.12 (7.87)	2.79 (2.09)	0.9823
$T = 25$ °C, RH = 20%	DEA	11.14 (7.25)	0.70 (1.95)	0.9874
$T = 30$ °C, RH = 47%	TEA	11.44 (17.81)	1.60 (4.77)	0.9321
$T = 25$ °C, RH = 66%	EA	0.32 (0.38)	0.38 (0.18)	0.9591
$T = 15$ °C, RH = 79.2%	DMA	0.36 (0.34)	0.01 (0.15)	0.9743
$T = 20$ °C, RH = 92%	MA	0.09 (0.04)	0.01 (0.16)	0.9942
$T = 35$ °C, RH = 20%	TMA	0.71 (0.90)	0.78 (2.26)	0.9540

S_i: standard deviation of i.

chamber, which simulated the conditions during sampling of flowing gas streams. In the static mode, the fiber was exposed to a constant volume of the mixture enclosed inside the sampling chamber. The chamber was first flushed with the mixture, following which its flow was stopped by switching appropriate valves and sampling commenced. The chamber was flushed with the standard gas mixture after each sampling session. This sampling mode was designed to mimic the conditions during sampling of indoor or atmospheric air The sampling temperatures were 15 °C for dry mixture (RH = 0%) and 20 °C for a relative humidity of 47%. Dynamic sampling was performed at a velocity of 0.087 cm/s. The volume of a sampling chamber was ca. 120 cm^3 (31 cm^2 × 4 cm i.d.).

The results obtained in the two sampling modes were compared using statistical tests: precision using Snedecor's *F*-test and differences between the mean by means of Student's *t*-test (the probability level of 95%, for $f = (n_A + n_B - 2) = 10$ d.f.).

At the 95% probability level precision and differences between the averages values of the two approaches did not differ significantly. This indicates that the static sampling and dynamic sampling at a velocity of up to 0.087 cm/s have similar analytical characteristics.

Consequently, it can be stated that SPME can be used for repeatable sampling of amines both under static conditions, including indoor, atmospheric and workplace air analysis, and under dynamic conditions (up to the velocity of 0.087 cm/s applied in studies).

3.2. Determination of the levels of volatile aliphatic amines in air

The method developed was applied to determine aliphatic amines in the air from the sites where the presence of volatile amines can be expected. To account for the effect of relative humidity on the amount of analyte extracted by the SPME fiber coated with PDMS/DVB, determination of aliphatic amine concentration in real air samples was based on bracketing. Before the collection of real air samples, the SPME device was calibrated using standard gas mixtures of 47% relative humidity. After the field measurements, two-point calibration (bracketing) was completed by exposing the SPME device to standard mixtures of an appropriate concentration and higher or lower relative humidity, depending on the humidity level recorded during the field measurements. Temperature of the standard mixtures was kept the same as during field sampling. In this way, the effect of temperature, relative humidity and analyte concentration level on extraction efficiency were all accounted for.

Table 5
Concentrations of selected aliphatic amines in the air (mg/m^3) at the sampling sites examined (PDMS/DVB)

Analyte	Sampling site (Table 1)					Limiting values	
	A	B	C	D	E	STEL[a]	TLV[b]
MA	n.d.	n.d.	n.d.	112.4	21.1	15	5
EA	16.3	5.1	4.3	n.d.	n.d.	15	5
DMA	n.d.	n.d.	n.d.	140.1	79.2	18	9
DEA	83.2	6.3	n.d.	n.d.	n.d.	75	30
TMA	n.d.	n.d.	n.d.	24.3	2.2	24	12
TEA	148.2	2.5	n.d.	n.d.	n.d.	n.s.	n.s.

n.d.: not detected; n.s.: not specified.

[a] STEL: mean short-term exposure or maximum concentration of a substances which a worker may be exposed to for a continuous 30 min period, with a low probability of adverse health effects for the worker and his/her future generations [33].

[b] TLV: maximum permissible 8 h time-weighted average concentration of a material which a worker may be exposed to with a low probability of adverse health effects for the worker and his/her future generations when working 42 h per week [33].

Table 5 presents the concentration levels of aliphatic amines found in the air of the sampling sites examined. In order to compare the pollution with permissible levels, STEL specified in the regulations of the Polish Ministry of Employment and Social Policy [33] and TLV values are also given in this table.

The presence of aliphatic amines in the air of the sites examined was expected due to the nature of these sites. However, the fact that in several cases the amine concentrations found exceeded the allowable levels indicates that employees at these sites worked under hazardous conditions.

SPME allows a rapid evaluation of air quality, which can be particularly useful in site screening. Once elevated concentrations of the analytes are found in the air, time-weighted average concentrations should be determined using other methods, more labor- and time-intensive. The use of SPME makes it possible to reduce the number of such measurements to the necessary minimum, resulting in time and cost savings. At the same time, preliminary information about air quality can be gained in a short time, hence actions

aiming at the reduction of the levels of hazardous substances in air can be initiated faster than when using conventional methods.

4. Conclusions

SPME can be used for the isolation and preconcentration of volatile aliphatic amines from air without the need for derivatization. Temperature and humidity of the air both affect the amount of analyte extracted from a sample, therefore have to be controlled and/or measured during sampling. On the other hand, no significant effect of the standard gas mixture flow rate in the range studied (velocity up to 0.087 cm/s) on extraction efficiency was found, which means that SPME can be used equally efficiently for the determination of amines in stagnant air (e.g. atmospheric air, workplace air, etc.), and in slowly flowing gas streams. Sampling by SPME is very straightforward. It obviates the need for complicated instrumentation used for sample collection and determination of the sample volume. The entire analysis can be completed in a relatively short time. Selectivity of the extraction process can be affected by the nature of the SPME coating. For example, the partition coefficients determined for the custom-made PUA coating were greater by 10% for MA and 20.5% for DMA compared to the commercial PDMS/DVB coating.

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