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Determination of aliphatic amines using *N*-succinimidyl benzoate as a new derivatization reagent in gas chromatography combined with solid-phase microextraction

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Abstract

A simple, selective and sensitive approach was developed for the quantitation of aliphatic amines in lake water applying a new reagent (*N*-succinimidyl benzoate, SIBA), synthesized in the laboratory of the authors. Derivatization of the *n*-C_1–C_6 aliphatic monoamines and dimethylamine in aqueous solution with SIBA was followed by headspace solid-phase microextraction (SPME). Derivatives were identified by gas chromatography-mass spectrometry and determined by gas chromatography-flame ionization detection. Both derivatization and SPME conditions have been optimized. Derivatizations were performed in borate buffer (pH 8.8), at 60 °C for 22 min. SPME was carried out from saturated sodium chloride solution, at 80 °C for 60 min, desorption at 250 °C for 2 min. Detection limit of derivatized amines proved to be 0.13–7.2 nmol/l, while recovery of amines from lake water samples, in the concentration range of 100–200 μg/l, varied from 94.1 to 102.7%.

Keywords: Derivatization, GC; Amines; Succinimidyl benzoate

1. Introduction

Short-chain aliphatic primary amines and secondary amines are often present in environmental samples, biological fluids and industrial waste materials at trace level [1–3]. Besides hygienic problems due to their odorous smell, these compounds may be hazards to human health as they are sensitizers and irritants to the skin, eyes, mucous membranes and respiratory tract [4,5]. Furthermore, lower secondary amine such as dimethylamine can form carcinogenic *N*-nitroamines in the presence of nitrites or other nitrosation agents [6,7]. As a result, there is an increasing interest in the development of new analytical methods to determine these compounds.

To date, a number of approaches including gas chromatography (GC) [8–19], high-performance liquid chromatography (HPLC) [10,21–28] and capillary electrophoresis (CE) [24,29–32] have been employed to determine low-molecular-mass amines. Because of its inherent advantage of high resolution, rapid separation, low cost and easy linkage with mass spectrometry (MS) to give unequivocal identification of compounds, capillary gas chromatography is a preferred method and often used.

In GC, various derivatizing reagents have been developed and used as derivatizing reagents for aliphatic amines [8–20]. Benzensulfonyl chloride derivatives [13,18,20], imines derivatives derived from pentafluorobenzaldehyde [1,12,18,36] and alkyl chloroformate [8,9,15–18,20] derivatives are representatives. The derivatizing procedure of benzensulfonyl chloride with aliphatic amines is complicated and time-consuming. The reaction of chloroformates with aliphatic amines proceeds in organic media that cannot be used as derivatizaing reagent of aliphatic amines in water media. Although developed two-phase reaction system overcomes the drawback, excess reagent must be removed before analyses, which enhance the sampling time. Penfluorobenzaldehyde reacts only with primary amines, which limit its application. Consequently, it is of significance to develop a new derivatizing reagent to minimize and eliminate the drawbacks listed above.

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In conventional methods, liquid–liquid extraction and solid phase extraction are often used to isolate and preconcentrate aliphatic amines from aqueous phase into organic phase prior to GC analysis or derivatization. However, these methods require a large amount of organic solvent and time-consuming. Solid-phase microextraction (SPME) developed by Pawliszyn and co-workers [33–36] is a new sample preparation technique. Compared to conventional extraction methods, SPME has many advantages, such as minimized usage of toxic organic solvents, high concentrating efficiency, no transfer of organic solvents to chromatographic systems, low cost and the ability for easy on-line combination with GC.

In this paper, a new derivatizing reagent, *N*-succinimidyl benzoate (SIBA), was synthesized, characterized and used to determine methylamine, dimethylamine, ethylamine, *n*-propylamine, *n*-butylamine, *n*-pentylamine and *n*-hexylamine. A method based on the new derivatizing reagent in combination with SPME for the determination of these aliphatic amines in water by GC and GC–MS is developed.

2. Experimental

2.1. Chemicals and reagents

Methylamine (MA), dimethylamine (DMA), ethylamine (EA), *n*-propylamine (PrA), *n*-butylamine (BA), *n*-pentylamine (PA) and *n*-hexylamine (HA) were of analytical grade and purchased from Shanghai Chemicals Company in China. MA was used as hydrochloride. All other reagents such as hydrochloric acid (37%), tetrahydrofuran, boric acid as well as $Na_2B_4O_7$ were of analytical grade. De-ionized water was employed for all solution preparation.

The stock solutions of MA, DMA, EA, PrA, BA, PA and HA were prepared by dissolving each of them in 0.1 mol/l HCl (1000 μg/ml each). Working solutions were made by combining aliquots of each stock solution and diluting to appropriate concentrations with deionized and stored in a refrigerator. H_3BO_3–$Na_2B_4O_7$ buffer was prepared by mixing 0.2 mol/l H_3BO_3 and 0.05 mol/l $Na_2B_4O_7$ to the required pH value.

SIBA was synthesized in our laboratory and its 25 mg/ml solution was prepared in dried acetonitrile.

2.2. Synthesis of SIBA

Benzoic acid (0.92 g, 7.5 mmol) and *N*-hydroxysuccinimide (0.86 g, 7.5 mmol) were dissolved in a flask containing 25 ml of anhydrous tetrahydrofuran (THF). Then the flask was placed in ice-bath. To this mixture was dropped slowly the solution of 1.55 g (7.5 mmol) dicyclo-hexylcarbodimide (DCC) in 10 ml of THF. After being stirred for 12 h at 0–5 °C, the mixture was filtered to remove the white solid by-product. The filtrate was distilled under reduced-pressure and recrystallized in absolute ethanol. A 1.1 g amount of white needlish crystal was obtained. The yield is 66%. Fast atom bombardment (FAB) MS: *m*/*z* 220 $(M + H)^+$, *m*/*z* 105 (benzoyl fragment ion); IR (KBr pellet) 1820, 1788, 1734 cm^{-1} ($\nu_{C=O}$), 1208 cm^{-1} (ν_{C-N}), 1071 cm^{-1} ($\nu_{C-O)}$.

2.3. Derivatization procedure

To 1.0 ml of mixed amines solution containing primary amines and secondary amines (10 μg/ml), 2.0 ml of H_3BO_3–$Na_2B_4O_7$ buffer (0.2 mol/l, pH 8.8) and 0.6 ml of 25 mg/ml SIBA solution were added. After diluted to 15 ml, the reaction vial was sealed and heated at 60 °C for 22 min in a water bath. The vial was allowed to cool to room temperature before it was opened and was transferred to a 25 ml sample vial for SPME.

2.4. SPME procedure

The SPME fiber used was coated with polyphenylmethylsiloxane (PPMS) by sol–gel at 70 μm thickness according to the literature [37]. The length of the coated fiber is 1 cm. The fiber was conditioned at 350 °C for 2 h before use. The SIBA-amines derivatives obtained above were extracted using the SPME fiber exposed to the headspace of a 15-ml aliquot taken in a sealed 25 ml sample vial at 80 °C in a water bath for 60 min and stirred on a magnetic stir plate. After analytes are extracted, SPME fiber was subsequently injected manually into a splitless injector of the GC–MS and GC–flame ionization detection (FID) systems at 250 °C for 2 min.

2.5. GC–MS and GC–FID analyses

A Hewlett-Packard 5840A GC coupled with a VG ZAB-3F mass spectrometer (VG Analytical, Manchester, UK) was used for identification of derivatives and evaluation of the completeness of derivatization reaction. GC column was a 25 m × 0.2 mm i.d. with 0.11 μm film thickness of OV-1701. Helium was employed as the carrier gas. The oven temperature was initially 50 °C for 2 min, programmed to 220 °C at 5 °C/min, then a hold at 220 °C for 5 min. The injection port and transfer line temperatures were kept at 250 and 200 °C, respectively. The inlet pressure of helium was set to 0.04 MPa. Samples were introduced in the splitless injection mode. The electron impact (EI) source was kept at 200 °C; electron energy of 70 eV and ion accelerating voltage of 8 kV. The mass range scanned was 30–300 u.

A Hewlett-Packard 6890A GC–FID system was used for the optimization of SPME and analytical calibration. The capillary column used was a 30 m × 0.25 mm i.d. with 0.25 μm film thickness of HP-5. Samples were introduced in the splitless injection mode. The inlet pressure of nitrogen was 0.03 MPa. The flame ionization detector was kept at 260 °C and nitrogen was employed as carrier gas. The other conditions are the same as GC–MS analysis.

2.6. Sample analyses

To 100 ml of lake water was added 0.5 ml of 37% hydrochloric acid. The sample was filtered through a 0.22 μm membrane filter. Then a 15 ml aliquot was derivatized with SIBA and extracted by SPME using the same procedure for the standard amines solutions. The recoveries analysis in lake water was thus determined by spiking standards.

3. Results and discussion

SIBA is specific to aliphatic primary and secondary amines under mild conditions and cannot react with aromatic amines, hydroxyl, thiol and phenol group. The reaction of SIBA with aliphatic amines is demonstrated in Fig. 1.

3.1. Optimization of derivatization conditions

The amount of reagent used is an important factor affecting the yields of derivatization. Because the succinimidyl esters in basic solution can hydrolyze, it is necessary to use excess reagent in derivatization reaction. The effect of concentration of reagent on the derivatization of amines (10 μg/ml each) was examined. The experimental results indicate that 800–1300 μg/ml of SIBA made derivatization yields highest and almost unchangeable. Higher concentration did not produce higher yields, while resulted in the increase of background due to a large tailing peak of solvent. In this procedure, 1000 μg/ml SIBA was selected the most appropriate.

Basic medium can catalyze reaction of succinimidyl esters with amines. In the meanwhile, it can accelerate the hydrolysis of reagent. Therefore, it is critical for derivatization reaction to optimize pH of medium. In this study, H_3BO_3–$Na_2B_4O_7$ was used to facilitate the reaction. It was found that peak areas of all SIBA-amine derivatives reach the most at pH 8.5–9.0. The effect of concentration of buffer solution on derivatization reaction was further studied within the range of 13.0–46.0 mmol/l. When the concentration of buffer ranged from 20.0 to 40.0 mmol/l, the peak areas reached the maximum and unchangeable. As a result, the buffer of pH 8.8 and at concentration of 25 mmol/l was used.

As shown in Fig. 2, the peak area of derivatives increases when the reaction temperature rises. When the temperature is higher than 70 °C, the peak area decreases. Therefore, the derivatization reaction was performed at 60 °C.

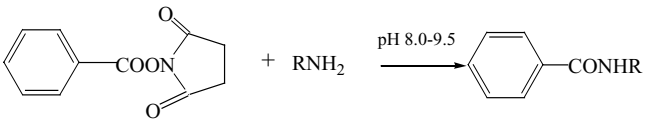

Fig. 1. The reaction of SIBA with aliphatic amines.

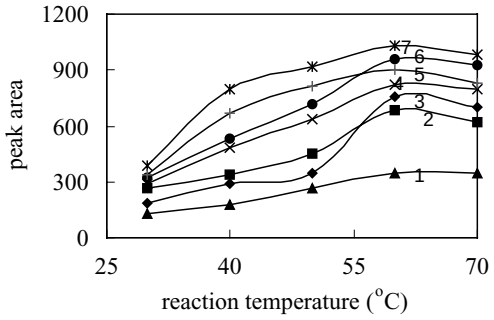

Fig. 2. The effect of reaction temperature on the peak area of SIBA-amines derivatives. 1: Ethylamine; 2: methylamine; 3: dimethylamine; 4: *n*-propylamine; 5: *n*-pentylamine; 6: *n*-hexylamine; 7: *n*-butylamine.

At 60 °C, the effect of reaction time on the peak areas was tested. The results showed the derivatization reaction reached equilibrium for all other amines excluding dimethylamine after 10 min. The peak area of SIBA-dimethylamine derivative kept constant after 20 min. To get highest yields for all SIBA-amine derivatives, 22 min was chosen as the optimal reaction time.

3.2. Identification of derivatives

The mass spectra obtained from SIBA derivatives of MA, DMA, EA, PrA, BA, PA and HA exhibited molecular ions at *m*/*z* 135, 149, 149, 163, 177, 191 and 205, respectively. A mass spectrum of SIBA-propylamine derivatives is shown in Fig. 3. Based on the molecular ions, only one hydrogen bonded amino group was replaced by SIBA.

The most abundant ion for all SIBA-amine derivatives appears at *m*/*z* 105, which means a primary cleavage occurs at amide bond. Further fragmentation of ion at *m*/*z* 105 gives fragments of *m*/*z* 77 and 51. In addition, α-cleavage of nitrogen is observed, which leads to fragment ions of (*M*–1)

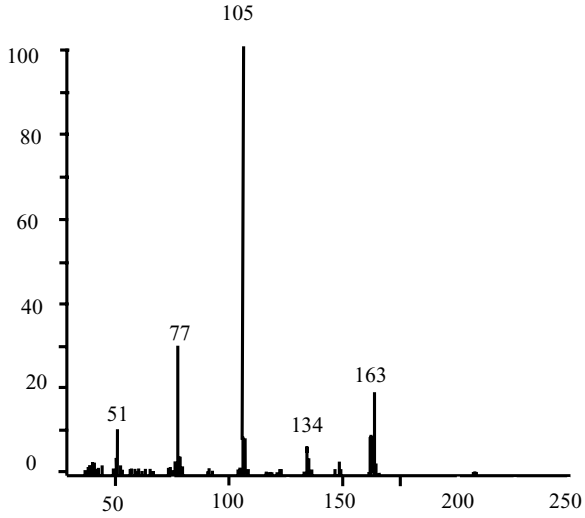

Fig. 3. The mass spectrum of SIBA-*n*-propylamine derivative.

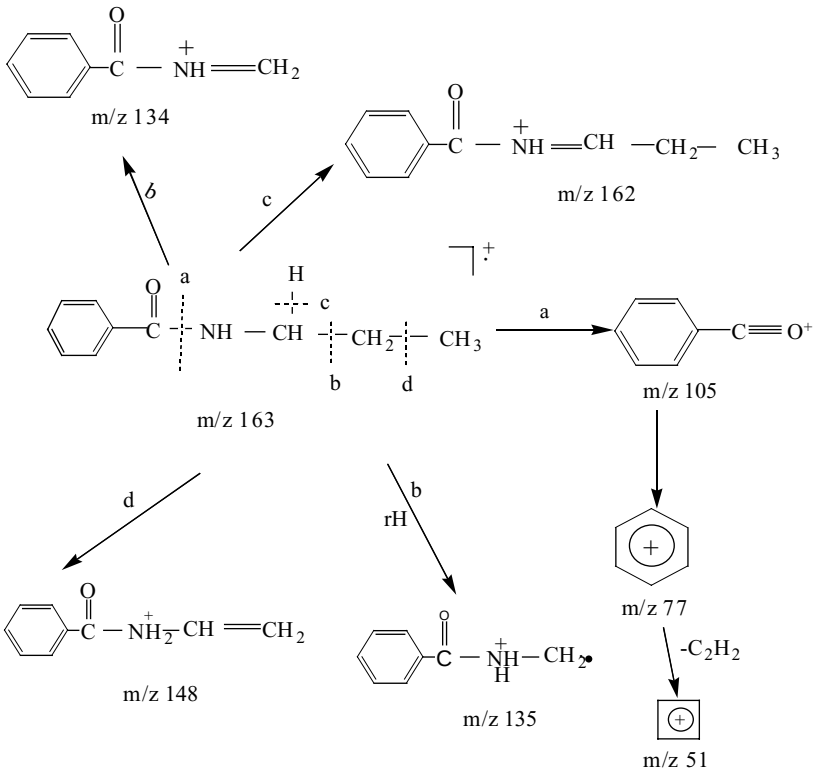

Fig. 4. The fragmental mechanism of SIBA-*n*-propylamine derivative.

with loss of hydrogen for SIBA derivatives of MA, DMA, EA at *m*/*z* 134, 148 and 162, respectively. In case of PrA, BA, PA and HA, α-cleavage of nitrogen gives fragments of $(M-1)$ with loss of hydrogen, ion at *m*/*z* 134 (without hydrogen migration) and *m*/*z* 135 (with hydrogen migration) with loss of alkyl group. As the *n*-propylamine for example, Fig. 4 shows the possible fragment pathway.

Based on the characteristic patterns, the resulting MS data support the assumption that SIBA derivatives of MA, DMA, EA, PrA, BA, PA and HA are *N*-methylbenzoylamide, *N*-dimethylbenzoylamide, *N*-ethylbenzoylamide, *N*-propylbenzoylamide, *N*-butylbenzoylamide, *N*-pentylbenzoylamide and *N*-hexylbenzoylamide, respectively.

3.3. Optimization of SPME conditions

The SPME efficiency was affected by the extraction time, temperature, ion strength, desorption time, temperature and derivatization.

SPME is a dynamic partitioning process of the SIBA-amine derivatives between the fiber and the sample solution. Equilibrium time is an important parameter for the optimization of the SPME procedure. With stirring at 60 °C, varying extraction time from 0 to 70 min, the effect of the extraction time on the amount of SIBA-amine derivatives headspace extracted from water by adding saturated sodium chloride with PPMS-coated fiber was tested. It was found that for C_1–C_4-amine derivatives of SIBA, equilibrium could be reached within 50 min; for C_5–C_6-amine derivatives of SIBA, the equilibrium time was 60 min. To get highest extraction efficiency for all SIBA-amine derivatives under investigation, 60 min was considered as the optimal time for the subsequent evaluation.

The effect of extraction temperature on the extraction efficiency is dual. On one hand, an increase in temperature could enhance the diffusion coefficiency of SIBA-amine derivatives to fiber. On the other hand, the absorption of the fiber coating will decrease with the increase in temperature, which will result in the decrease of partition coefficiency. Consequently, the optimization of temperature is critical. When the extraction time was 60 min, the dependence of the extracted amount of SIBA-amine derivatives in the PPMS-coated fiber was determined in 40–90 °C range of extraction temperature.

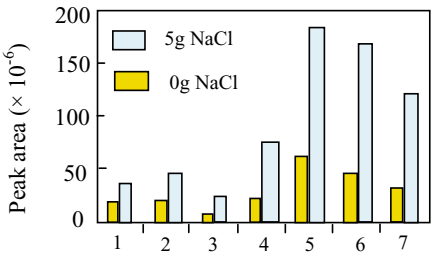

Fig. 5. The effect of the ion strength on the peak area of SIBA-amine derivatives. 1: dimethylamine; 2: methylamine; 3: ethylamine; 4: *n*-propylamine; 5: *n*-butylamine; 6: *n*-pentylamine; 7: *n*-hexylamine.

Table 1
Linear calibration range, regression equations and detection limits of SIBA derivatives of aliphatic amines[a]

Amines	Calibration range (ng/ml, FID)	Regression equation	r^2	RSD (%, $n = 6$)	Detection limit[a] (mol/l, FID)
Dimethylamine	5–1000	$y = 4.68 \times 10^4 x + 1.0 \times 10^6$	0.9970	2.6	4.27×10^{-9}
Methylamine	10–1000	$y = 1.28 \times 10^5 x + 1.0 \times 10^7$	0.9918	1.6	7.15×10^{-9}
Ethylamine	10–1000	$y = 2.44 \times 10^4 x + 3.42 \times 10^5$	0.9874	1.2	7.19×10^{-9}
n-Propylamine	1–1000	$y = 1.72 \times 10^5 x + 7.0 \times 10^6$	0.9920	2.4	2.83×10^{-10}
n-Butylamine	1–1000	$y = 4.57 \times 10^5 x + 2.0 \times 10^7$	0.9938	1.1	1.75×10^{-10}
n-Pentylamine	1–1000	$y = 4.24 \times 10^5 x + 2.0 \times 10^6$	0.9956	1.3	1.88×10^{-10}
n-Hexylamine	1–1000	$y = 3.96 \times 10^5 x + 1.0 \times 10^7$	0.9978	0.6	1.30×10^{-10}

[a] S/N: 3.

Table 2
The comparison of the detection limits of the reagents reported for aliphatic amines

Separation method	Derivatization reagent	Detection	Detection limit (mol/l)	References
GC	2,4-BSC[a]	MS	2.0×10^{-8}	[13]
	2,4-DNFB[b]	MS	1.0×10^{-8}	[13]
	SIBA	FID	1.3×10^{-10}	This work
HPLC	FMOC[c]	Fluorescence	4×10^{-7}	[26]
	2-NPO[d]	Chemiluminescence	5×10^{-7}	[27]
	ITDT[e]	Fluorescence	5×10^{-8}	[28]
	NPA-Osu[f]	Fluorescence	1.2×10^{-9}	[21]
CE	FITC[g]	Laser-induced fluorescence	1×10^{-9}	[31]

[a] Benzenesulfonyl chloride.
[b] 2,4-Dinitrofluorobenzene.
[c] 9-Fluorenylmethyl chlorformate.
[d] Bis(2-nitrophenyl)oxalate.
[e] 5-Isothiocyanato-1,3-dioxo-2-*p*-tolyl-2,3-dihydro-1*H*-benz[*de*]isoquinoline.
[f] *N*-Succinimidyl 4:3-2′-naphthapyrone-4-acetate.
[g] Fluorescein isothiocyanate.

According to our experimental results, the quantity of the extracted SIBA-amine derivatives increased at temperature up to 80 °C and decreased at higher temperature. Therefore, 80 °C was chosen as extraction temperature.

By adding an inorganic salt to the aqueous samples, the ion strength of water can be enhanced, thereby increasing the partition of organic compounds into the polymer coating. In the study, a saturated solution was made by adding 5 g of sodium chloride to 15 ml of sample solution with magnetic agitation. As can be seen in Fig. 5, the amount extracted by the fiber was greatly enhanced with the addition of sodium chloride. It was also found that extracted SIBA-amine derivatives were completely desorbed for 2 min at 250 °C.

The gas chromatograms of SIBA-amine derivatives under the optimized derivatization and SPME extraction are shown in Fig. 6. The separation of derivatives was completed within 28 min. The resulting peaks of all SIBA-amine derivatives under investigation are very sharp and symmetry.

3.4. Analytical calibration

The quantitative applicability of the method for the determination of amines established was evaluated at five different amounts of analytes taken for derivatization over the range 1–1000 ng/ml. The calibration graphs were established

Table 3
Analytical results of lake water sample

Samples	Added (ng/ml)	Found[a] (ng/ml)	RSD (%, $n = 6$)	Recovery (%)
Dimethylamine	0	246.5	2.8	
	100	337.4	1.3	95.9
	200	430.3	2.2	96.9
Methylamine	0	20.32	1.6	
	100	106.4	2.9	94.1
	200	192.9	1.2	96.3
Ethylamine	0	0		
	100	87.5	1.1	94.5
	200	170.6	1.9	95.3
n-Propylamine	0	21.83	2.7	
	100	118.6	3.1	96.8
	200	220.3	1.2	101.2
n-Butylamine	0	36.35	2.2	
	100	134.1	2.3	97.8
	200	231.9	1.9	97.2
n-Pentylamine	0	40.69	2.1	
	100	139.4	1.4	102.7
	200	237.9	1.2	98.6
n-Hexylamine	0	0	0	
	100	96.8	0.8	96.8
	200	195.4	1.2	99.7

[a] Average ($n = 6$).

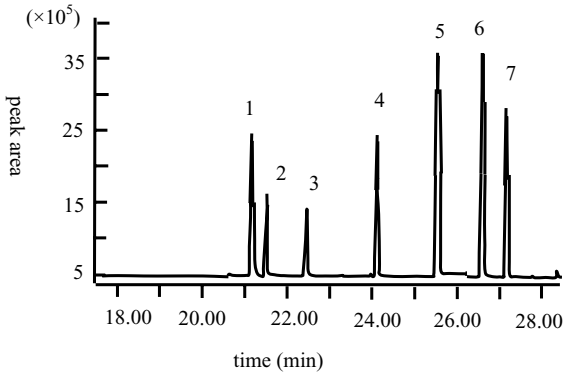

Fig. 6. The gas chromatograms of aliphatic amines derivatized with SIBA by SPME. Chromatographic conditions: column: HP-5 (30 m × 0.32 mm, 0.25 μm), oven temperature: 50 °C initially, kept 5 min at 50 °C, programmed to 220 °C at 5 °C/min, then hold 5 min at 220 °C. Detector temperature: 260 °C; carrier gas: nitrogen; column pressure: 0.03 MPa; injector temperature: 250 °C; injection: splitless; fiber: PPMS. Peaks: 1: dimethylamine; 2: methylamine; 3: ethylamine; 4: *n*-propylamine; 5: *n*-butylamine; 6: *n*-pentylamine; 7: *n*-hexylamine.

with the peak areas. The linear regression equations, correlation coefficients, relative standard deviations (RSDs) and detection limits are shown in Table 1. The experimental results showed the method was reproducible. The proposed method provides equivalent or better sensitivity than those reported (see Table 2).

3.5. Application to real water sample

The proposed method was applied to the determination of aliphatic amines in lake water. The chromatograms of unspiked and spiked standard solutions are shown in Fig. 7. As can be observed, dimethylamine, methylamine, *n*-propylamine, *n*-butylamine and *n*-pentylamine were detected in the sample tested. The amounts calculated for the samples by using the calibration equations obtained for the standard samples are summarized in Tables 2 and 3. The recoveries ranged from 94.1 to 102.7% and the RSDs from 1.1 to 2.8%.

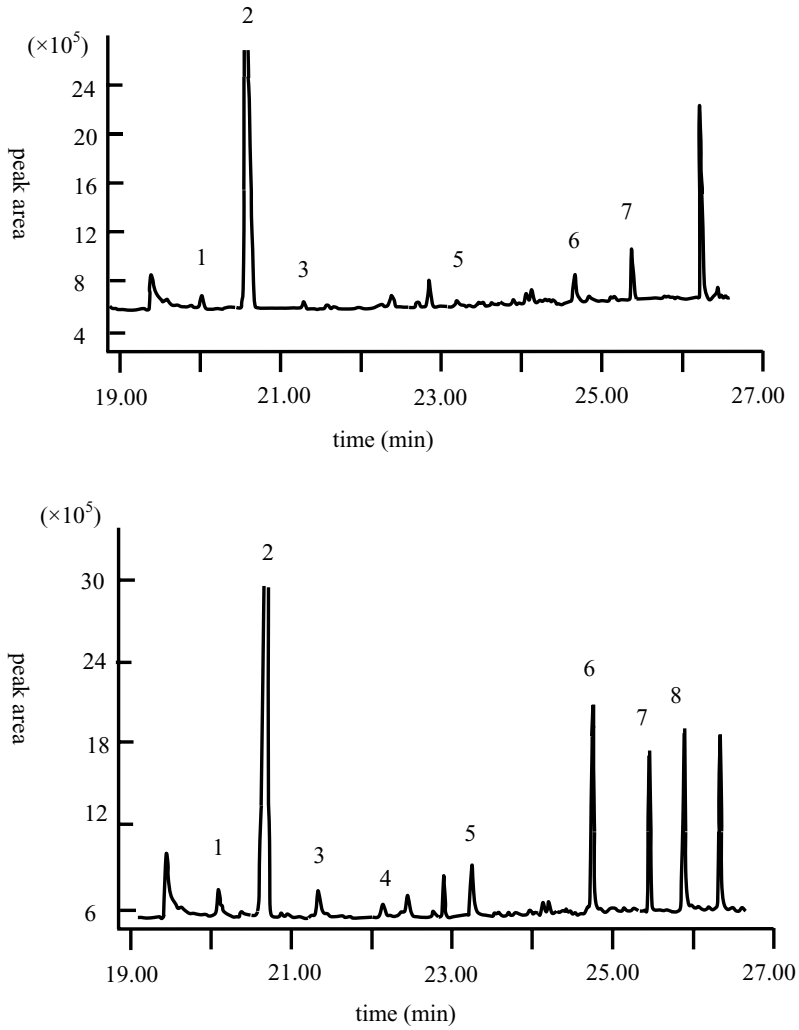

Fig. 7. Chromatograms obtained from (a) lake water sample, (b) the same sample spiked with 100 ng/ml of dimethylamine, methylamine, ethylamine, *n*-propylamine, *n*-butylamine, *n*-pentylamine and *n*-hexylamine. Chromatographic conditions as in Fig. 6. Peaks: 1: dimethylamine; 2: unknown; 3: methylamine; 4: ethylamine; 5: *n*-propylamine; 6: *n*-butylamine; 7: *n*-pentylamine; 8: *n*-hexylamine.

4. Conclusions

The described method consists of an aqueous-phase derivatization using SIBA, followed by SPME and then GC–FID and GC–MS determination. The procedure offers a simple, highly selective and sensitive way to determine aliphatic amines in lake water. The newly synthesized derivatizing reagent, SIBA, was a useful reagent with the advantages including mild reaction conditions and selectivity to amino group. The SPME also offers solvent free and highly sensitivity compared with other techniques used. The method showed good linearity over the concentration range from 1 to 1000 ng/ml for *n*-propylamine, *n*-butylamine, *n*-pentylamine, *n*-hexylamine, 5–1000 ng/ml for dimethylamine and 10–1000 ng/ml for methylamine, ethylamine. The limits of detection were in the low nmol/l range when the signal-to-noise ratio was 3. The method has been applied to real sample with satisfactory results.

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