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Static headspace analysis of aliphatic amines in aqueous samples

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Abstract

Static headspace preconcentration was developed for the gas chromatographic analysis of aliphatic amines in aqueous samples. A liquid–gas ratio of 1, an incubation temperature of 80°C (15 min), a pH of 13.7 and a mixture of salts (NaCl and K_2SO_4) at saturation concentration gave a maximal headspace amine concentration. C_1–C_4 volatile aliphatic amines were separated on a specific PoraPLOT Amines capillary column. The detection limit was 0.2 μg/l for secondary and tertiary amines using a nitrogen–phosphorus detector. Primary amines were detected at higher concentrations (from 10 μg/l to 3000 μg/l). This polar capillary column required the systematic addition of ammonia to the sample (0.05 *M* concentration) in order to obtain a good repeatability (RSD=0.6–6.4%). This technique has been applied successfully for the monitoring of amine concentration at sub-μg/m^3 level in a compost treatment plant using absorption sampling in a hydrochloric acid solution.

Keywords: Headspace analysis; Sample handling; Amines

1. Introduction

Volatile aliphatic amines are often present in environmental samples, biological fluids and industrial waste materials at ppb (v/v) (ppbv)–ppm (v/v) (ppmv) levels. Their quantification needs accurate and sensitive analytical methods. Sensitivity and selectivity can be enhanced by derivatization, preconcentration techniques and detection systems.

Sakai et al. [1] have developed a selective determination of alkylamines (I, II and III types) utilizing the thermochemical characteristics of charge transfer complexes in 1,2-dichloroethane. For aqueous samples, aliphatic and alicyclic amines are derivatizated by chloroformate and extracted by solvent [2]. Then, they can be analyzed by gas chromatography (GC) and high-performance liquid chromatography (HPLC) in a concentration range between 0.05 and 1.0 μg/l. Derivatization by pre-column or post-column connected to HPLC analytical columns has the advantage of reducing sample preparation work. A pre-column derivatization with 3,5-dinitrobenzoyl chloride has been reported for primary and secondary amine analysis by HPLC–UV detection [3].

Derivatization can also be coupled to preconcentration techniques. Solid-phase extraction cartridges with 9-fluorenylmethyl chloroformate have been developed for improved derivatization of amines before liquid chromatography analysis [4]. For aliphatic amine analysis in air and aqueous samples, direct solid-phase microextraction (SPME) is not sensitive [5]. The coupling of derivatization with SPME has lowered detection limits by two–three orders of magnitude; the tertiary amine concentration

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at the ng/l level can be detected by GC–flame ionization detection (FID) analysis. Recently, SPME and solid-phase extraction have been applied also in conjunction with capillary electrophoresis to analyze very diluted samples [6,7]. For GC analysis, headspace (HS) is a preconcentration technique particularly suitable for the sampling of volatile organic compounds in air, water and solids [8]. This technique can be 1000 times more sensitive than direct liquid injection. At the present time, few reports have been published on the use of static headspace in the analysis of free amines in aqueous samples because of the high polarity and solubility in water of these compounds. Tsukioka et al. [9] have applied the static headspace technique to tertiary alkylamines by using manual sampling and GC–MS.

Detection system performances are also essential for trace analysis. Surface ionization detection (SID) has been given considerable attention for the determination of organic compounds with low ionization potentials over the past few years [10]. A novel design for surface detection has been reported based on hyperthermal positive surface ionization. A second surface ionization detector provides a unique sensitivity for tertiary amines with detection limits down to 10^{-14} g/s [11]. The nitrogen–phosphorus detector has similar sensitivity and high selectivity for nitrogen containing compounds.

In this paper, we describe the development of a static headspace technique using a specific and selective nitrogen–phosphorus detector for the analysis of volatile aliphatic amines in aqueous samples. The main parameters of the gas–liquid equilibrium have been studied in order to increase the headspace amine concentration. The performances of a Pora-PLOT Amines capillary column have also been evaluated.

2. Theory

The development of static headspace analysis consists of the determination of the best parameters in order to increase the headspace concentration of solute *i* symbolized by $C_{i,G}$. The expression of $C_{i,G}$ is $C_{i,G} = C_{i,L0}/(K + \beta)$ with the initial liquid concentration of solute *i* $C_{i,L0}$, the partition coefficient $K = C_{iL}/C_{iG}$ ($C_{i,L}$ and C_{iG} respectively liquid and gas concentrations of solute *i* at the equilibrium) and the ratio $\beta = V_G/V_L$ (V_L and V_G respectively liquid and gas volumes in the vial). *K* depends on temperature *T*, pH and ionic strength (salt concentration) [12]. Sensitivity of the headspace technique symbolized by *S* can be defined by $S = f(V_{g,inj}/(K + \beta)$ where *f* is the detector sensitivity factor and $V_{g,inj}$ the injected gas volume. The headspace technique can be compared with liquid direct injection by α, the sensitivity gain, calculated by $\alpha = (V_{g,inj}/V_{l,inj})/(K + \beta)$ with the injected liquid volume being $V_{l,inj}$. So, the sample preparation and the analytical instrument performances determine the sensitivity and accuracy of the headspace technique.

3. Experimental

3.1. Chemicals

Primary amines (methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, tertiobutylamine), secondary amines (dimethyl, diethyl, ethylmethyl, diisopropylamine) and tertiary amines (trimethyl, dimethylethyl, triethyl, diethylmethylamine) were obtained from Aldrich France and pyridine, ammonia (20% purity in water), hydrochloric acid (37% purity in water), sodium chloride, potassium sulfate and sodium hydroxide from Prolabo France. Methyl and ethyl alcohol, methyl ketone, formaldehyde and acetaldehyde were also obtained from Prolabo France. Deionized water was used to prepare all solutions.

3.2. Standard solutions

Stock standards of nitrogenous compounds were prepared by dissolving the pure analytes in 0.12 *M* hydrochloric acid aqueous solution in a range from 10^{-2} *M* to 10^{-4} *M*. These solutions were then diluted in 0.12 *M* hydrochloric acid aqueous solution by factors from 0.5 to 10^4 to prepare the working solutions. Sodium hydroxide was dissolved in deionized water to obtain a 8.1–8.2 *M* NaOH solution. A standard of alcohols, ketone and aldehydes at a concentration of 10^{-2} *M* was prepared in deionized water.

3.3. Sample preparation

In a Chromacol headspace vial of 22.7±0.3 ml, they were added in this following order:

(i) a mass, *M*, of a salt or a salt mixture (3, 4 and 5 g of NaCl; 3.2 g/1.0 g of the mixtures of NaCl/K_2SO_4),

(ii) a volume, V_{Sample}, of diluted standard (1, 2, 5, 7 and 10 ml),

(iii) only with HS–GC–nitrogen–phosphorus detection (NPD) analysis, a volume, V_{NH3}, of ammonia (20% purity in water) using a syringe of 100 μl capacity (20, 50, 100 μl),

(iv) a volume, V_{NaOH}, of a 8.1 *M* sodium hydroxide solution using a syringe of 500 μl capacity (165, 230, 500, and 1000 μl).

When ammonia and the sodium hydroxide solution were added, it was very important to introduce the syringe needle via the vial bottom in order to keep the acidic surface of amine solution and avoid some amine losses. Next, the vial was sealed with a PTFE-lined septum. This operation did not damage the septum before the headspace sampling. The vial was stirred manually for 2 min before static headspace analysis.

3.4. Instruments and static headspace analysis

The Serie 8000 Fisons Instruments gas chromatograph was equipped with a split/splitless injector, a flame ionization detector, a nitrogen–phosphorus detector and a Fisons Instruments HS 850 headspace autosampler (Fisons Instruments, France). This autosampler utilized a glass syringe at controlled temperature (2.5 ml capacity) and standard vial sizes of 10 or 20 ml volume. The vial temperature was regulated by an incubator equipped with an automatic mixing system by micro-vibration. Samples were kept at chosen temperatures (60°C, 80°C and 95°C) for 15 min and 30 min. Vials were pressurized by increasing the incubator temperature or by injecting a nitrogen volume equal to the sample volume after sample incubation. In every case, the vial pressure after sampling was higher than atmospheric pressure. The carrier gas was nitrogen from Air Liquide France.

The first time, HS parameters were determined by HS–GC–FID analysis. The column was a 15 m× 0.32 mm I.D. bonded Rtx-1 of 3 μm film thickness (Restek, France). The respective injector and detector temperatures were 200°C and 250°C. Two analytical programs were used:

Program P1: carrier gas flow-rate: 2.22 ml/min; injected gas volume: 2.0 ml; split ratio: 7.9; oven temperature program: 60°C for 3 min, followed by an increase to 120°C at 10°C/min and a final 3 min hold at 120°C.

Program P2: carrier gas flow-rate: 1.87 ml/min; injected gas volume: 2.0 ml; split ratio: 15.4; oven temperature program: 80°C for 1 min, followed by an increase to 160°C at 20°C/min and a final 4 min hold at 160°C.

Trimethyl, propyl, (or isopropyl), diethyl, butylamine and pyridine were chosen for a good separation on a short apolar capillary column and a fast analysis. Response factors symbolized by *F* were calculated as integrator area units per initial amine concentration in liquid phase before sample preparation (area units per nmol/L). The *F* values of these six compounds could be compared in order to evaluate their ability to be extracted from aqueous liquid matrix because their response to the flame ionization detector was similar.

The second time a nitrogen–phosphorus detector and another capillary column were used to improve analytical performances (HS–GC–NPD analysis, program P3).

Program P3: PoraPLOT Amines capillary column; 10 μm film thickness (Chrompack, France); dimensions of 27.5 m (with 2.5 m particle trap)×0.32 mm I.D; carrier gas flow-rate (N_2): 2.3 ml/min; injected gas volume: 2.0 ml; split ratio: 20; injector temperature: 250°C; detector temperature: 300°C; oven temperature program: 130°C for 6 min, followed by an increase to 220°C at 10°C/min and a final 20 min hold at 220°C.

4. Results and discussion

4.1. Static headspace parameters

The static headspace parameters (β, pH, *T* and ionic strength) have been studied in order to evaluate their separated and combined effects on headspace amine concentration and determine the ability of

each aliphatic amine type (primary, secondary and tertiary amines) to be extracted from aqueous matrix. The amine response factor F was defined by area unit per initial liquid amine concentration.

The best value of β (V_G/V_L) was 1 for a vial of 22.7 ml capacity (Fig. 1). The β influence on the trimethylamine response factor was the highest because the trimethylamine partition coefficient K is the lowest. So the β value gets important for the calculation of headspace concentration. Liquid volumes higher than 10 ml could not be tested because the vial pressure was lower than the atmospheric pressure after headspace phase sampling.

A basic pH is necessary to extract amines from the aqueous solution. From pH 11.4 to 13.7, response factors were multiplied by an average of 2.1 (Fig. 2). For a volume of 8.2 M NaOH solution higher than 1000 μl, the pH was not modified significantly. Tsukioka et al. [9] indicated that the tertiary amine response factors decreased drastically when the NaOH concentration in the sample exceeded values of 3–4 M. The NaOH solution volume of 1000 μl was chosen to obtain a pH of 13.7 and limited the sample dilution (0.6 M NaOH concentration in the sample).

The vial temperature is limited by the sample matrix boiling point (about 100°C). At a vial temperature of 95°C, there were some water problems (peak broadening, memory effect, increased bleeding...) if the analytical program P1 was applied. These problems were solved by adopting the program P2 (split ratio and initial oven temperature were increased). The sensitivity was improved by adding NaCl to the sample. The vial temperature enhanced a lot response factors when the temperature attained the zone of compound boiling point (propyl and butylamine) (Fig. 3). The incubation times of 15 and 30 min did not modify headspace concentration. A temperature of 80°C was chosen in order to limit water vapor injection on the column.

NaCl was selected to increase the ionic strength due to the high solubility of this salt (39.12 g NaCl/100 ml of saturated solution at 100°C or 6.7 mol/L) and the chemical inertia. A basic salt could not be used because some amine losses could occur when the salt was added to the sample. The ionic strength of NaCl solution can be considered equivalent to the dissolved NaCl molar concentration. From 0 to 300 g/l NaCl, response factors were multiplied by an average of 5.2 (Fig. 4). When the NaCl

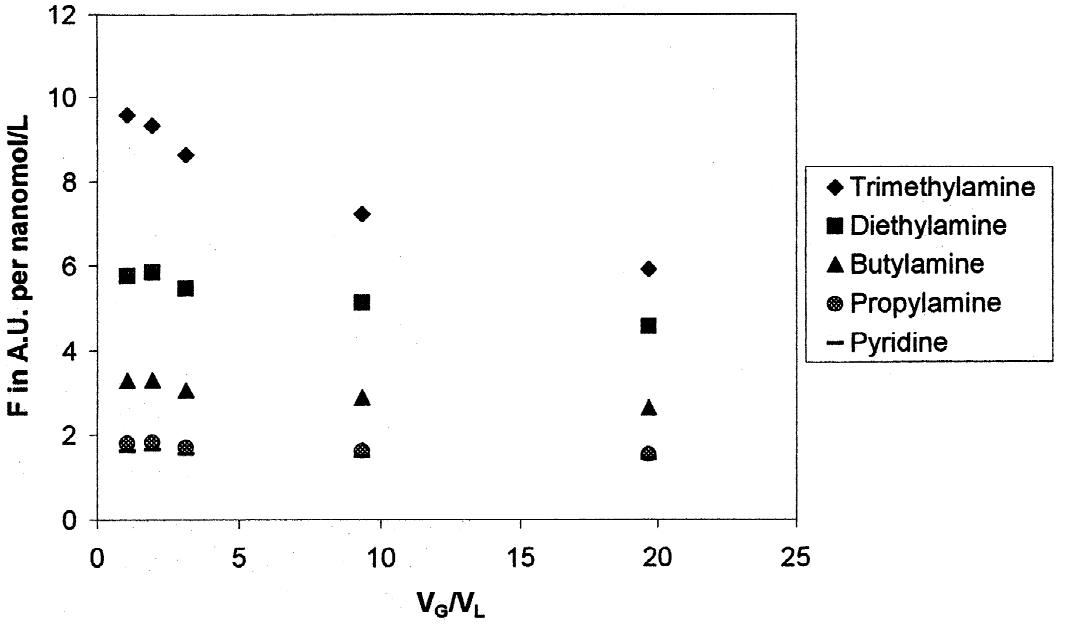

Fig. 1. β Influence on response factor ($\beta = V_G/V_L$). Conditions: $V_{NaOH} = 10\%$ of initial solution volume, $V_{vial} = 22.7$ ml, $T = 50$°C, $t = 15$ min, analytical program P1. A.U. = Area units.

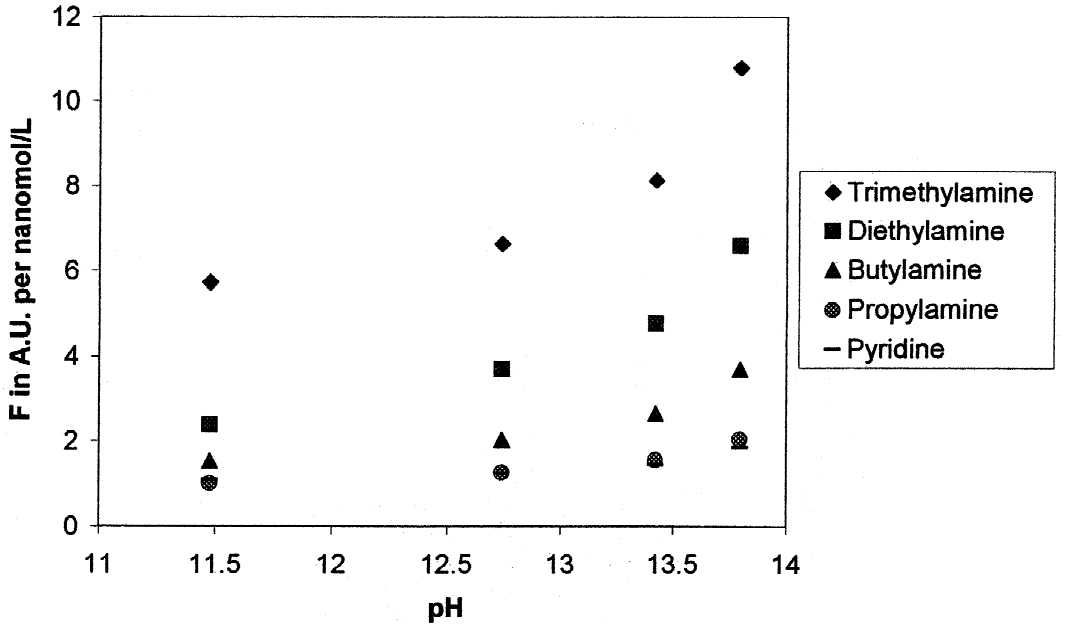

Fig. 2. pH influence on response factor. Conditions: $V_{8.1\ NaOH}$ = 165, 230, 500 and 1000 μl, V_{Sample} = 10 ml, T = 50°C, t = 15 min, analytical program P1. A.U. = Area units.

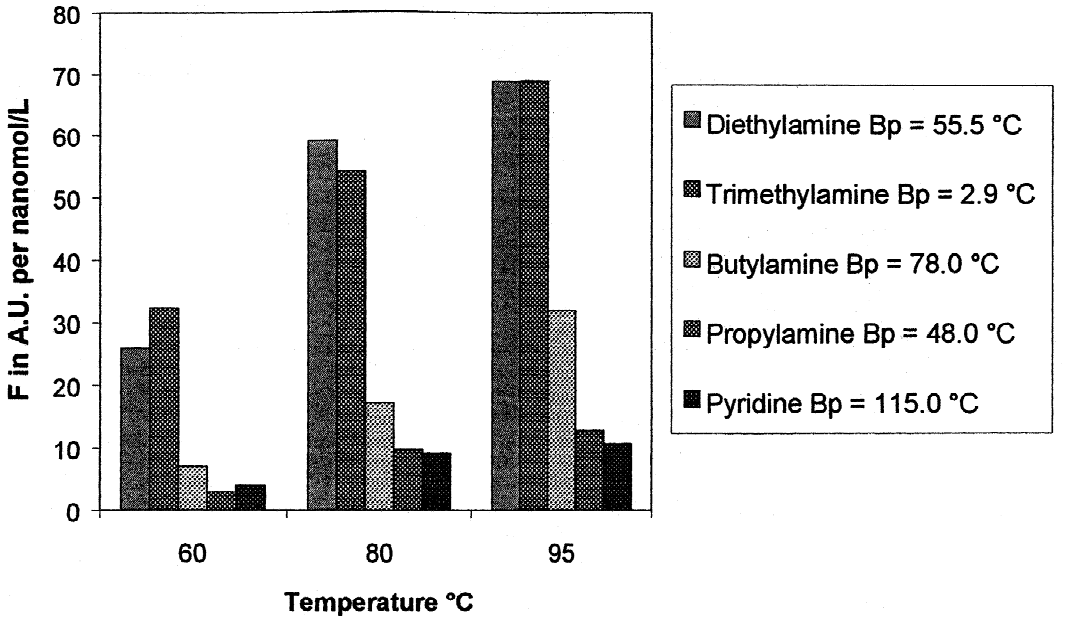

Fig. 3. Temperature influence on response factor. Conditions: $V_{8.1\ NaOH}$ = 1000 μl, V_{Sample} = 10 ml, t = 15 min, M_{NaCl} = 3 g, analytical program P2.

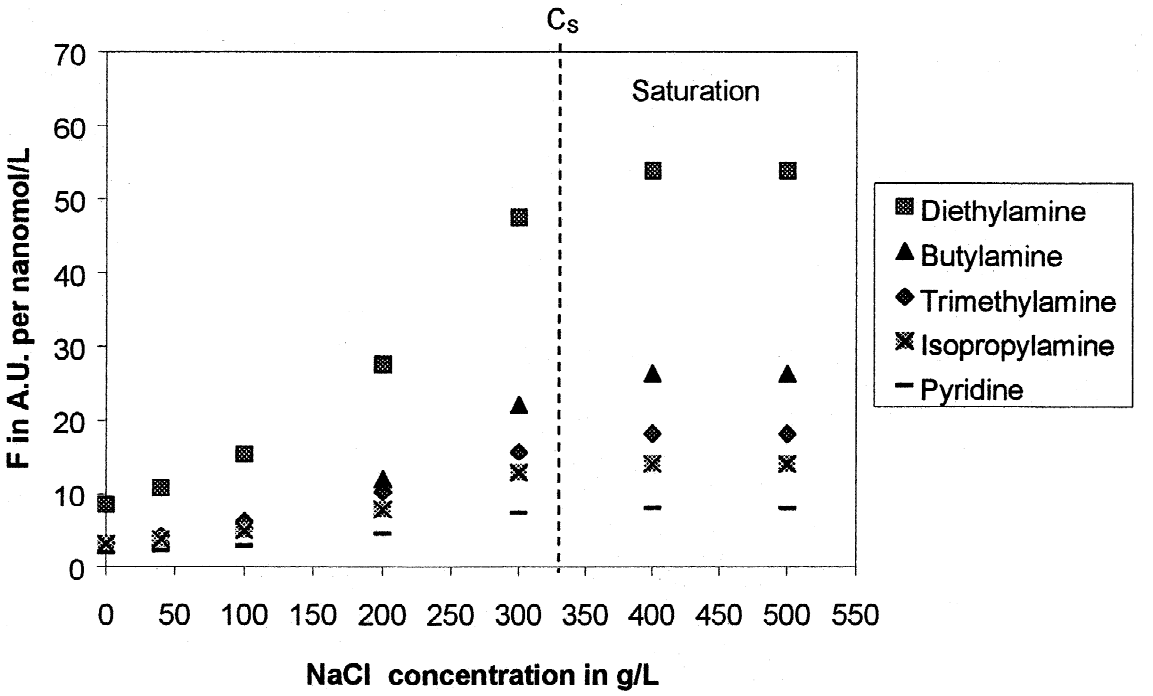

Fig. 4. NaCl concentration influence on response factor (C_S: saturation concentration). Conditions: $V_{8.1NaOH}=1000$ μl, $V_{Sample}=10$ ml, $T=80°C$, $t=15$ min, analytical program P2. A.U.=Area units.

concentration attained the saturation concentration (presence of undissolved salt in the vial sample), the response factors remained constant. The common-ion effect due to the NaOH addition reduced the NaCl solubility by about a mass percentage of 13%. The NaCl concentration increased all the more the response factor that the amine was hydrophobic (increasing of alkyl length and substitution degree of amine). The salt effect was limited for primary amines with an alkyl group lower than C_3. For pyridine, the ionic strength influence was low because this compound has a boiling point above incubator temperature (115°C) and a high hydrosolubility.

The effect of ionic strength was much higher than that of pH (response factors multiplied respectively by the averages of 5.2 and 2.1). Both parameters adjusted to the best values produced a synergistic effect on the enrichment of headspace amine concentration for the more hydrophobic compounds. The butylamine and diethylamine response factors were multiplied by an average of 13.1 by adjusting the pH at 13.7 and the NaCl concentration at 300 g/l. In order to have a maximal ionic strength, other salts which do not contain chloride and sodium ions can be added. The addition of K_2SO_4 at saturation concentration to NaCl saturated solution multiplied response factors still by an average of two.

4.2. Linearity, repeatability, detection limit

Regression gave coefficient of correlation values of 0.99915–0.99994 for two orders of magnitude. Relative standard deviations (RSDs) of 0.8% or less were attained for concentrations 100 times higher than limit detection (Table 1). The sample preparation development was very important to obtain these very good RSD values: use of an inert salt, keeping the acidic surface of the sample during the pH adjustment and salt addition up to the saturation concentration.

Table 1
Linearity, repeatability, detection limit

Analyte	Repeatability (RSD, %) $n=5$	Linearity[a] (r^2)	FID detection limit[b] (μg/l)
Trimethylamine	0.56	0.99988	4
Propylamine	0.71	0.99915	17
Diethylamine	0.74	0.99999	5
Butylamine	0.58	0.99935	8
Pyridine	0.35	0.99994	26

[a] Five levels with a dilution range of 500.

[b] Final sample preparation: V_{Sample}: 10 ml, $V_{8.1\ NaOH}=1000$ μl, $T=80$°C, $t=15$ min, $M_{NaCl}=3.2$ and $M_{K_2SO_4}=1.0$ g, analytical program P2.

4.3. Optimization of volatile aliphatic amine separation and detection.

4.3.1. Ammonia addition

Aliphatic amine analysis warrants caution because of the polar and basic properties of these compounds. Ammonia addition reduces amine adsorption and peak tailing on polar columns [13]. For C_1–C_4 aliphatic amine separation on a PoraPLOT Amines column, the ammonia addition to the sample was indispensable at a minimal concentration of 0.052 *M* in order to have a good repeatability ($0.9\% < RSD < 3.1\%$ for $n=3$). A poor repeatability was obtained by increasing the vial temperature from 80°C to 95°C because the column was overloaded by the injected water vapor ($9.1\% < RSD < 29.3\%$). The split ratio could not be reduced lower than a value of 20. The column had to be heated at a temperature of 220°C for a minimum of 20 min after each analysis in order to remove the water from the column.

4.3.2. Separation, repeatability, linearity, detection limit and selectivity

PoraPLOT Amines capillary column was specifically developed for analysis of volatile aliphatic amines in water. It can isothermally separate methyl, dimethyl, trimethyl and ethylamine at 130°C in eight min using hydrogen as carrier gas. However, the nitrogen–phosphorus detector works with this gas as combustion gas, whose flow-rate has to be controlled accurately at a fixed value. Therefore, the hydrogen carrier gas was substituted by nitrogen. The initial column temperature was fixed at 110°C in order to separate ethylamine and trimethylamine, but the retention times were twice as long. Subsequently, an initial temperature of 130°C was adopted in order to reduce analysis time (chromatogram Fig. 5). Regression gave correlation coefficients of 0.994–0.9997 for three orders of magnitude and relative standard deviations of 0.6%–6.1% for indicated concentrations in Table 2. Detection limits of 0.2–20 μg/l for secondary and tertiary amines were attained with a nitrogen–phosphorus detector. Correlation coefficients were not as good as those of Table 1 because of the adsorption phenomena on the PoraPLOT Amines column. These phenomena increased progressively after about ten thousand injections and was pronounced for C_1–C_4 primary amines which could not be quantified under 100–50 μ*M*. Chromatographic performances can be reduced with fast drops of injector pressure. Electronic pressure control use is not recommended because a electrical power cut can damage the column.

The addition of organic compounds (formaldehyde, acetaldehyde, methyl ketone and methyl and ethyl alcohol diluted in water) to the amine sample at a concentration of 100 μ*M* before its preparation did not modify amine response factors. Detector selectivity avoided interference peaks.

4.4. Application on site

Emissions of compost treatment plants were characterized using absorption sampling in 0.12 *M* hydrochloric acid solution and HS–GC–NPD analysis. The sampling efficiency has been checked by Audunsson et al. [14]. C_1–C_4 volatile aliphatic amines are separated on a PoraPLOT Amines column and detected at low concentration levels with a specific and sensitive nitrogen–phosphorus detector (Fig. 6). The main detected amine was trimethylamine at 3613 μg/l concentration (865 $\mu g/m^3$ in gaseous emissions). Other amines were detected at 0.3–70 μg/l concentration levels for relative standard deviations of 21–4% (0.07–16.8 $\mu g/m^3$ in gaseous emissions). Primary amines were not detected. Compounds eluted after the triethylamine retention time could not be identified. These would be secondary or tertiary ramified aliphatic amines or C_4–C_6 cyclic nitrogen compounds.

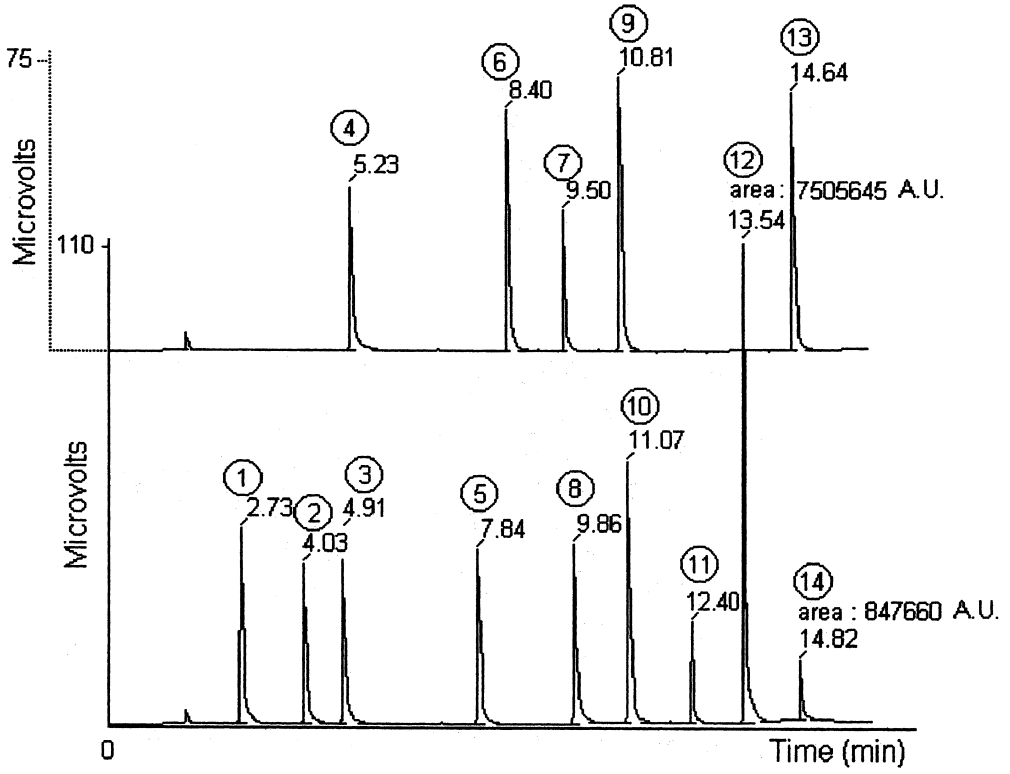

Fig. 5. Chromatogram of aliphatic amines (peak names in Table 2) separated on PoraPLOT Amines capillary column (HS–GC–NPD) analysis, analytical program P3).

Table 2
HS–GC–NPD analysis features (analytical program P3): response factor (*F*, area units per nmol/L), linearity (correlation coefficient r^2), repeatability at *C* concentration (RSD) and detection limit (*DL*)

Aliphatic amines	Peak number	Retention time min	*F* (area units per nmol/L)	Linearity, r^2	*C* (μ*M*)	RSD (%, *n*=3)	*DL* (μg/l)
Methylamine	1	2.73	12.2	0.9963	500	2.7%	1000
Dimethylamine	2	4.03	76	0.9941	100	3.6%	20
Trimethylamine	3	4.91	723	0.997	6.4	4.4%	0.2
Ethylamine	4	5.23	38.6	0.9944	500	1.8%	10
Ethylmethylamine	5	7.84	171	0.9972	10	3.8%	0.7
Isopropylamine	6	8.40	107	0.9947	250	1.9%	5
Dimethylethylamine	7	9.50	527	0.9966	6.4	1.4%	0.3
Propylamine	8	9.86	30.1	0.9985	250	6.4%	2000
tert.-Butylamine	9	10.81	184	0.9994	250	3.2%	0.8
Diethylamine	10	11.07	443	0.9972	10	6.1%	0.3
Diethylmethylamine	11	12.40	1037	0.9978	4	1.2%	0.2
Butylamine	12	13.54	25.1	0.9997	250	0.6%	3000
Diisopropylamine	13	14.64	1033	0.994	10	5.3%	0.2
Triethylamine	14	14.82	1327	0.998	4	5.1%	0.2

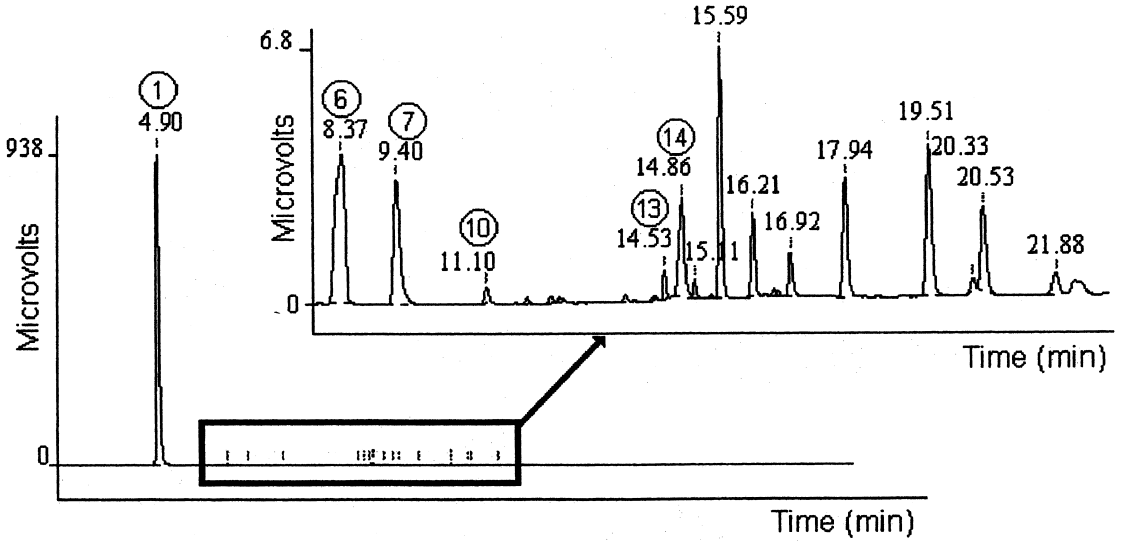

Fig. 6. Chromatogram of compost treatment plant sample (HS–GC–NPD analysis, analytical program P3, peak names in Table 2).

5. Conclusion

For aliphatic amine analysis in aqueous samples, the static headspace technique sensitivity was improved by adjusting V_G/V_L ratio at 1, pH at 13.7, by adding a mixture of NaCl and K_2SO_4 at saturation concentration and by incubating the vial at a temperature of 80°C for 15 min. The PoraPLOT Amines column required the ammonia addition to the aqueous sample at a minimal concentration of 0.052 *M* in order to obtain a good analysis repeatability. Secondary and tertiary amines can be analyzed at a μg/l concentration level by using a headspace autosampler and a specific and sensitive nitrogen–phosphorus detector.

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