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Determination of volatile amines in air by diffusive sampling, thiourea formation and high-performance liquid chromatography

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ABSTRACT

A diffusive sampling method for the determination of primary and secondary amines in air was evaluated. The sampler consists of a filter, impregnated with naphthyl isothiocyanate, in a polypropylene housing. A substituted thiourea is formed *in situ* during sampling, which is desorbed and determined by high-performance liquid chromatography. The sampler was validated for the sampling of methylamine, allylamine, isopropylamine, *n*-butylamine and dimethylamine using standard amine atmospheres, and the uptake rates for the five amines were determined. The effect on uptake rate of amine concentration, sampling time and relative humidity was investigated and found to be small. The detection limits for the amines studied are below 50 $\mu g/m^3$ for an 8-h sample.

INTRODUCTION

For the monitoring of low-molecular-mass aliphatic amines in air, several methods are available involving impingers or gas dispersion bottles, acidic solvents and gas chromatographic (GC) determination. These "wet" sampling methods have disadvantages, especially with personal sampling, and dry methods are preferred. Polar solid sorbents, such as silica gel, can be used for the sampling of amines, followed by chromatographic determination of free amines in solution, but these methods are usually not very sensitive [1]. For the sampling of more reactive primary and secondary amines, sorbents are usually not suitable unless coated with a reagent. This derivatization may enhance the sensitivity for the GC or high-performance liquid chromatographic (HPLC) analysis [2,3]. We have previously reported the use of a 1-naphthyl isothiocyanate-coated XAD-2 sorbent for the determination of ethylenediamine and gaseous polyamines and of diethylamine in air [4–6]. Primary and secondary amines react rapidly and quantitatively and form stable thiourea derivatives. This method has high sensitivity when reversed-phase HPLC and UV detection are used.

Diffusive sampling has become an important method as an efficient alternative to pumped sampling in occupational hygiene [7]. We have previously reported the development of a diffusive sampler, designed to contain a reagent-coated filter for the sampling of reactive compounds. The sampler has been validated for formaldehyde, with a 2,4-dinitrophenylhydrazine-coated filter [8], and for diethylamine, with a 1-naphthyl isothio-cyanate-impregnated filter [6]. We have now validated the sampler for determination of methylamine, isopropylamine, *n*-butylamine, allylamine and dimethylamine in air.

EXPERIMENTAL

Diffusive sampler

The diffusive sampler is shown in Fig. 1. The housing, measuring 60 × 30 × 5 mm, is made of

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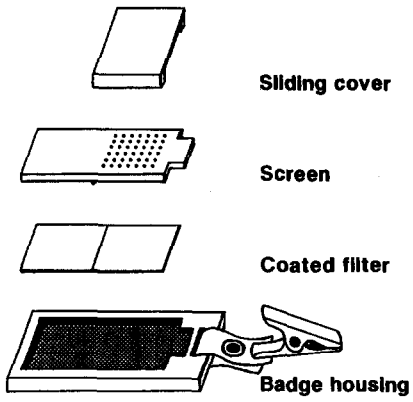

Fig. 1. Diffusive sampler for primary and secondary amines.

polypropylene. The impregnated filter, 20 × 45 mm, is placed beneath a 2.9-mm thick screen of the same size. Within an area 20 × 20 mm, the screen has 112 holes with a diameter of 1.0 mm. The filter part beneath the holes is used for sampling (sampling filter) and the other half is used to determine the filter blank (control filter). The tape is divided into the two sections by a small ridge on the back of the screen plate. A sliding cover is used to seal the holes when the sampler is not in use. The sampler is available from GMD Systems, (Hendersonville, PA, USA).

Chemicals

Solvents used for the HPLC analysis were acetonitrile (HPLC grade; Rathburn, Walkerburn, UK) and water (purified with Milli-RQ system; Millipore, MA, USA). Certified amine gas was used for the dynamic generation (methylamine 795 ± 40 ppm, isopropylamine 503 ± 25 ppm, allylamine 161 ± 5 ppm, *n*-butylamine 300 ± 15 ppm and dimethylamine 609 ± 12 ppm in nitrogen; Aga Specialgas, Lidingö, Sweden).

1-Naphthyl isothiocyanate (NIT) analytical-reagent grade; (Sigma, St Louis, MO, USA) was purified by recrystallization from absolute ethanol. The reference thiourea derivatives were synthesized from the different amines and NIT. To a solution of 500 mg of NIT a small excess of amine in 2 ml of ethanol was added dropwise at room temperature. The solution was heated for 10 min and then allowed to cool, then 7 ml of water was added, dropwise, until crystallization started. After filtration, the crystals were recrystallized from hot 50% ethanol. These thiourea derivatives were used for preparing analytical standards in acetonitrile. The solutions are stable for several months if stored in a refrigerator.

Sample analysis

The filters from the diffusive samplers were cut into two pieces for separate analysis of the sampling and control filter parts. These parts were transferred into 4-ml glass vials and shaken for 30 min with 3.0 ml of acetonitrile. The analyses were performed with a Millipore Waters (Milford, MA, USA) M-710 B automatic injector, two Millipore Waters M-6000 pumps, an M-440 absorbance detector and a computer with a Millipore Waters Maxima control and evaluation program. Volumes of 10 μl were injected and the column was a Millipore Waters Nova-Pak C_{18} (100 × 5 mm I.D., 4-μm particles). The flow-rate was 0.8 ml/min and the mobile phase was water–acetonitrile (1:1). The thiourea derivatives were detected at 254 nm with detection limits of about 0.5 ng (signal-to-noise ratio = 4:1). Chromatograms with the different amine derivatives and a blank filter are shown in Fig. 2 . The amine content of the control filter was always subtracted from that of the sampling filter when calculating air concentrations.

Laboratory validation

Standard atmospheres of amines were generated in a dynamic system by dilution of certified amine gas. The generation system and the exposure chamber were essentially the same as those used for the generation of formaldehyde [8]. The samplers were exposed six at a time, to amine levels from 0.5 to 25 mg/m^3, with sampling periods between 15 min and 8 h. The relative humidity was varied between 10% and 80%. Samplers were oriented parallel to the air stream. The air velocity was about 0.25 m/s. For confirmation of amine levels in the exposure chamber, pumped sampling with gas dispersion bottles (1 l/min) containing 15 ml of 0.02 *M* HCl was used. The solution from the gas dispersion bottles were analysed by isotachophoresis [9] or HPLC [10].

RESULTS AND DISCUSSION

To be able to meet functional criteria, a sampling

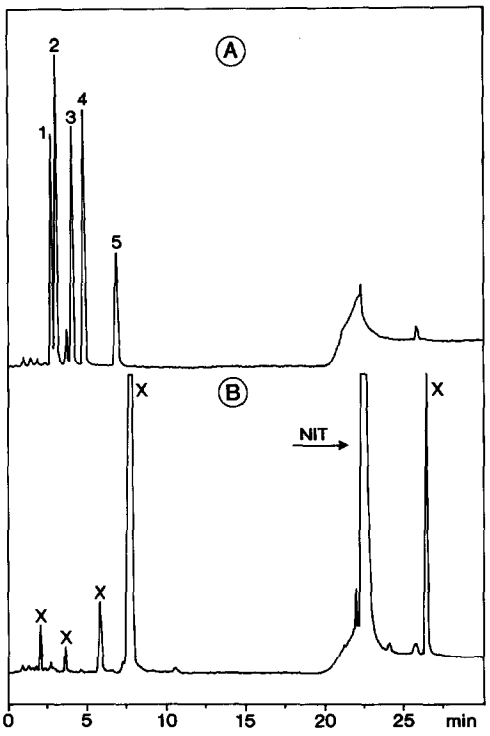

Fig. 2. HPLC of (A) amine standard solution and (B) filter blank. The urea derivatives are from (1) methylamine, (2) dimethylamine, (3) allylamine, (4) isopropylamine and (5) *n*-butylamine. The amounts of the urea derivatives are from 21 to 30 ng. X = impurities. The mobile phase was water–acetonitrile (1:1) for 15 min, then changed to acetonitrile in 0.5 min, to reduce the retention time of the unreacted naphthyl isothiocyanate (NIT), which under these conditions elutes in 23 min.

method must be thoroughly validated. Several procedures for the evaluation of diffusive samplers have been proposed. The latest and most important is the procedure described by the Commité Européen de Normalisation (CEN) [11]. The diffusive sampler was validated according to the protocol published by CEN. The effects of concentration, sampling time, relative humidity (RH), zero exposure and storage were investigated. The effects of wind velocity and sampler orientation were studied in connection with validation of the sampler for formaldehyde [8]. In that study the wind velocity at the sampler face was varied between 0.05 and 1.0 m/s. The uptake rate was constant within the wind velocity range studied. Most personal sampling conditions give wind velocities of about 0.1 m/s [7]. Perpendicular orientation of the sampler resulted in a slight increase in the uptake rate at high wind velocity. At wind velocities below 0.02 m/s the sampler performed well, allowing static area sampling of indoor air [8]. As wind velocity and sampler orientation effects are parameters associated with the sampler and not the analyte, these effects were not studied further.

The amine concentration in the exposure chamber was calculated from the dilution of the certified amine gas. Good agreement (within 10%) was generally obtained between the concentrations given by the reference method and the calculated concentrations.

In the validation experiments with dimethylamine, the concentrations were varied between 1.87 and 18.7 mg/m^3 (1 and 10 ppm), the sampling time between 30 and 480 min and the relative humidity between 10% and 80%. Table I gives the uptake rate of dimethylamine calculated from the different experiments.

The statistical analysis was performed with the use of multiple regression [12]. The parameters concentration, sampling time and relative humidity were scaled in the interval -1 to $+1$. The intercept of the regression curve gives the mean uptake rate and the parameter estimates give an indication of the influence on the uptake rate by the different variables. For significance the estimate has to be greater than the standard error. The results of the regression analysis of the data for diethylamine are given in Table II. As can be seen, no influence of concentration and relative humidity can be detected. The effect of time is statistically significant but small and will not significantly influence the overall uncertainty of the method. The mean uptake rate was 15.8 ml/min (R.S.D. = 6%, n = 54).

To evaluate the stability of the thiourea derivative during sampling, a zero exposure test was performed. Amine exposure for 30 min was followed by a zero concentration (clean air) exposure for 7.5 h . As shown in Table I, a small but significant decrease in uptake rate can be noted. Compared with the mean uptake rate, the decrease was only 4%. As can be seen from Table I, the derivative was stable during storage for 14 days at 18°C.

The validation experiments with *n*-butylamine were performed with various concentrations between 1.52 and 24.2 mg/m^3 (0.5 and 8 ppm), sampling times between 15 and 480 min and relative

TABLE I

UPTAKE RATE OF DIFFUSIVE SAMPLER AT VARIOUS DIMETHYLAMINE CONCENTRATIONS, RELATIVE HUMIDITIES AND SAMPLING TIMES

Face velocity = 0.3 m/s. RH = relative humidity; R.S.D. = relative standard deviation; N = number of determinations.

Concentration (mg m^{-3})	Sampling time (min)	RH (%)	Uptake rate (ml min^{-1})	R.S.D. (%)	n
18.7	30	10	15.6	3	6
18.7	30	80	17.8	2	6
1.87	480	10	15.4	6	6
1.87	480	80	14.8	2	6
18.7	480	10	15.6	1	6
18.7	480	80	15.5	5	6
18.7	240	45	15.6	3	6
1.87	240	45	16.4	3	6
9.4	120	45	15.6	2	6
18.7	30	80	15.1[a]	3	3
9.4	120	45	15.7[b]	3	6

[a] Exposure for 30 min followed by exposure to zero concentration for 7.5 h.
[b] Stored for 14 days at 18°C after exposure.

humidity between 10% and 80%. Table III shows the uptake rate of the diffusive sampler with these parameter variations. The mean uptake rate was 11.2 ml/min with an R.S.D. of 11% (n = 51). The statistical evaluation showed a small but significant influence of concentration and time. The zero exposure and the storage tests showed no instability of the n-butylamine derivative (Table III).

Diffusive sampling of isopropylamine was validated with various concentrations between 1.23 and 24.5 mg/m^3 (0.5 and 10 ppm), sampling times between 30 and 480 min and relative humidities between 10% and 80%. In Table IV the uptake rate of isopropylamine in the different experiments is shown. The mean uptake rate was determined to be 10.2 ml/min with an R.S.D. of 9% (n = 60). The statistical analysis showed a small but significant influence on uptake rate from concentration and relative humidity. The zero exposure test shows a small decrease in uptake rate (8%) compared with the mean uptake rate (Table IV). The isopropylamine derivative was stable according to the storage test which is shown in Table IV.

The diffusive sampling of methylamine was validated with various concentrations from 1.29 to 25.8 mg/m^3 (1 to 20 ppm), sampling times from 30 to 480 min and relative humidity from 10% to 80%. The uptake rate of methylamine in the different measurements is shown in Table V. The mean uptake rate was determined to 17.4 ml/min and the R.S.D. was 14% (n = 54). The statistical analysis showed a small negative influence from the concentration and a larger negative influence from time. This is probably due to a reversible reaction from the thiourea derivative to methylamine and 1-naphthyl isothiocyanate. This theory is supported by the result from the zero exposure test which shows a 36% decrease in uptake rate compared with the mean uptake rate when exposed to zero concentration for 7.5 h (Table V). The diffusive sampler can still be used for exposure measurements of methyla-

TABLE II

MULTIPLE REGRESSION ANALYSIS ON THE INFLUENCE OF CONCENTRATION, SAMPLING TIME AND RELATIVE HUMIDITY ON UPTAKE RATE OF DIMETHYLAMINE

Variable	Parameter estimate (ml/min)	Standard error
Uptake rate (intercept)	15.8	0.11
Concentration	0.12	0.12
Time	−0.51	0.14
Relative humidity	0.23	0.20

TABLE III

UPTAKE RATE OF DIFFUSIVE SAMPLER AT VARIOUS n-BUTYLAMINE CONCENTRATIONS, RELATIVE HUMIDITIES AND SAMPLING TIMES

Face velocity = 0.3 m/s.

Concentration (mg m^{-3})	Sampling time (min)	RH (%)	Uptake rate (ml min^{-1})	R.S.D. (%)	n
24.2	15	10	9.7	7	5
24.2	15	80	9.4	2	5
1.52	480	10	10.5	3	6
1.52	480	80	10.6	9	6
24.2	480	10	12.7	1	5
24.2	480	80	11.5	2	6
24.2	240	45	11.4	3	6
1.52	120	45	12.9	2	6
12.9	120	45	12.1	2	6
24.2	30	80	11.4[a]	5	5
12.9	120	45	12.3[b]	2	6

[a] Exposure for 30 min followed by exposure to zero concentration for 7.5 h.
[b] Stored for 14 days at 18°C after exposure.

mine but with a higher standard deviation. The storage test shows no instability or reversible reaction, as can be seen from Table V.

In the validation experiment with allylamine, concentrations were varied between 0.47 and 9.5 mg/m^3 (0.2 and 4 ppm), sampling time between 30 and 480 min and relative humidity between 10% and 80%. Table VI gives the uptake rate of allylamine in the different measurements. The mean uptake rate was determined to 14.9 ml/min with an R.S.D. of 8% (n = 53). The statistical analysis gave a significant influence on uptake rate from concentration and relative humidity. This influence is small and can be disregarded. The zero exposure test

TABLE IV

UPTAKE RATE OF DIFFUSIVE SAMPLER AT VARIOUS ISOPROPYLAMINE CONCENTRATIONS, RELATIVE HUMIDITIES AND SAMPLING TIMES

Face velocity = 0.3 m/s.

Concentration (mg m^{-3})	Sampling time (min)	RH (%)	Uptake rate (ml min^{-1})	R.S.D. (%)	n
24.5	30	10	11.8	4	6
24.5	30	80	10.0	3	6
1.23	480	10	11.2	2	6
1.23	480	80	10.1	1	6
24.5	480	10	10.3	5	6
24.5	480	80	10.0	3	6
24.5	240	45	10.0	3	6
1.23	240	45	9.6	11	6
12.3	120	45	9.6	9	12
24.5	30	80	9.4[a]	4	3
12.3	120	45	10.3[b]	5	6

[a] Exposure for 30 min followed by exposure to zero concentration for 7.5 h.
[b] Stored for 14 days at 18°C after exposure.

TABLE V

UPTAKE RATE OF DIFFUSIVE SAMPLER AT VARIOUS METHYLAMINE CONCENTRATIONS, RELATIVE HUMIDITIES AND SAMPLING TIMES

Face velocity = 0.3 m/s.

Concentration (mg m^{-3})	Sampling time (min)	RH (%)	Uptake rate (ml min^{-1})	R.S.D.	n
25.8	30	10	20.3	5	6
25.8	30	80	20.4	2	6
1.29	480	10	18.7	3	6
1.29	480	80	16.5	7	6
25.8	480	10	14.3	3	6
25.8	480	80	14.1	1	6
25.8	240	45	16.0	2	6
1.29	240	45	17.5	9	6
6.25	120	45	19.0	4	6
25.8	30	80	15.7[a]	1	3
12.3	120	45	20.6[b]	2	5

[a] Exposure for 30 min followed by exposure to zero concentration for 7.5 h.
[b] Stored for 14 days at 18°C after exposure.

gives a decrease in uptake rate of 25% compared with the mean uptake rate (Table VI). This is probably the same effect as can be seen with methylamine, *i.e.*, a reversible reaction of the thiourea derivative. However, this effect for allylamine is smaller and cannot be seen from the other experiments. No instability of the derivative was evidenced by the storage experiments, as can be seen in Table VI.

CONCLUSIONS

The present diffusive sampler is meant to be used for sampling of reactive compounds. It was specially designed for use with reagent-coated filter tape. With the use of 1-naphthyl isothiocyanate as reagent the sampler can be used for sampling of primary and secondary amines in air. The uptake rates

TABLE VI

UPTAKE RATE OF DIFFUSIVE SAMPLER AT VARIOUS ALLYLAMINE CONCENTRATIONS, RELATIVE HUMIDITIES AND SAMPLING TIMES

Face velocity = 0.3 m/s.

Concentration (mg m^{-3})	Sampling time (min)	RH (%)	Uptake rate (ml min^{-1})	R.S.D. (%)	n
9.5	30	10	14.0	2	6
9.5	30	80	15.5	9	5
0.47	480	10	15.7	4	6
0.47	480	80	15.2	7	6
9.5	480	10	14.6	2	6
9.5	480	80	14.0	2	6
9.5	240	45	14.1	2	6
0.47	240	45	14.5	3	6
4.7	120	45	16.7	7	6
9.5	30	80	11.1[a]	14	3
4.7	240	45	13.4[b]	3	3

[a] Exposure for 30 min followed by exposure to zero concentration for 7.5 h.
[b] Stored for 14 days at 18°C after exposure.

TABLE VII

UPTAKE RATES AND DETECTION LIMITS FOR THE DIFFERENT AMINES

Amine	Uptake rate (ml/min)	R.S.D. (%)	n	Detection limit (mg/m^3)[a]
Methylamine	17.4	14	54	0.4
Isopropylamine	10.2	9	60	0.7
n-Butylamine	11.2	11	51	0.3
Allylamine	14.9	8	53	0.2
Dimethylamine	15.8	6	54	0.4
Diethylamine[b]	12.0	6	35	0.5

[a] Corresponding to 30-min diffusive sampling.
[b] From Ref. 6.

for the different amines studied are summarized in Table VII. The influence on uptake rates of concentration, sampling time and relative humidity was generally not detectable or small. The only exception was methylamine, where a probable reverse reaction from the thiourea occurred, which resulted in a larger negative influence of the sampling time. However, the effect was small enough not to reduce significantly the utility of the method.

The chromatographic determination of the thiourea derivatives is highly sensitive and specific. Short-time sampling is possible with detection limits below 1 mg/m^3, as can be seen from Table VII. After proper validation, the sampler may also be used for other primary and secondary amines. Previously, the sampler has been shown to perform well at very low wind velocities. Overall, the sampler is suitable for both static and personal monitoring of low levels of primary and secondary amines in air.

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