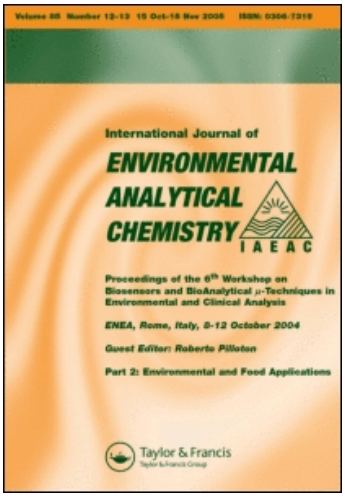


International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Analysis of Amines in the Industrial Environment

Gudjon Audunsson[a]; Marianne Dalene[a]; Jan Åke Jönsson[a]; Per Lövkvist[a]; Lennart Mathiasson[a]; Gunnar Skarping[b]

[a] Department of Analytical Chemistry, University of Lund, Lund, Sweden [b] Department of Technical Analytical Chemistry, Lund Institute of Technology, Lund, Sweden

To cite this Article Audunsson, Gudjon , Dalene, Marianne , Jönsson, Jan Åke , Lövkvist, Per , Mathiasson, Lennart and Skarping, Gunnar(1985) 'Analysis of Amines in the Industrial Environment', International Journal of Environmental Analytical Chemistry, 20: 1, 85 — 100

To link to this Article: DOI: 10.1080/03067318508077048

URL: http://dx.doi.org/10.1080/03067318508077048

Intern. J. Environ. Anal. Chem., 1985, Vol. 20, pp. 85–100
0306-7319/85/2002-0085 $18.50/0

Printed in Great Britain

Analysis of Amines in the Industrial Environment†

GUDJON AUDUNSSON, MARIANNE DALENE, JAN ÅKE JÖNSSON, PER LÖVKVIST and LENNART MATHIASSON

Department of Analytical Chemistry, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden

and

GUNNAR SKARPING

Department of Technical Analytical Chemistry, Lund Institute of Technology, P.O. Box 124, S-221 00 Lund, Sweden

(*Received November 23, 1984*)

Different methods for gas chromatographic trace analysis of a wide variety of amines are described. Both packed columns and glass capillary columns are used. The advantages of a nitrogen selective detector and a nitrogen-free stationary phase are demonstrated. Special concern is devoted to direct analysis of free amines on packed columns in organic solvents as well as in alkaline aqueous solutions with varying salt concentrations. Determination limits below 0.1 ppm are usually obtained and the precision at the 1 ppm level is generally about 2–3%. A permethylation procedure applicable to aqueous solutions has been developed for polyamines.

Air sampling in acidic absorption solutions as well as on a solid adsorbent (Chromosorb 103) combined with thermal desorption is discussed. Applications from various industries and from the building sector are presented.

KEY WORDS: Amines, gas chromatography, permethylation procedure, industrial environment, air sampling.

---

†Presented at the 14th Annual Symposium on the Analytical Chemistry of Pollutants. Barcelona, November 21–23, 1984.

INTRODUCTION

Amines frequently occur in the workplace atmosphere, for example in the polymer production industry, in cattle feed-yards and in fish industries. Earlier, the amines were considered as unpleasant but relatively harmless substances. Also, the lack of suitable trace analytical methods for amines in air has obstructed medical research in the field. Growing concern about the health hazards based on some early investigations[1,2] has lead to more research in this field[3–5] and resulted in low hygienic threshold values for amines in many industrial countries. Also, the possibility of nitrosamine formation[6] from amine and various nitrosating agents deserves attention.

For the determination of traces of volatile organic compounds in air, gas chromatography is the generally preferred method, due to its combined features of separation power, selectivity and sensitivity. Gas chromatography of amines is not without problems due to their marked tendency to adsorb in the chromatographic system, syringes, sample containers, etc. These problems can be partly solved by suitable derivatization procedures. However, a direct analysis is often advantageous, as it is less time-consuming, prevents contamination and the formation of artifacts, and reduces sample losses.

During several years, we have worked with different aspects of trace analysis and sampling of amines in the industrial environment.[7–17] This paper summarizes our present and previous work in this field.

GAS CHROMATOGRAPHIC TECHNIQUES FOR TRACE ANALYSIS OF FREE AMINES

Several types of column packings intended for separation of free amines have been available for some time. The most promising of these packings show a considerable bleeding at relatively low temperatures, seriously limiting their usefulness for trace analysis. The development of a new generation of nitrogen-selective detectors offers new possibilities, as the response from the column bleeding is supressed, provided, of course, that the stationary phase contains no nitrogen. The combination of a nitrogen selective detector and a suitable stationary phase has provided a basis of successful trace analysis of free amines.

Different column packings suggested in the literature have been compared with respect to their usefulness for trace analysis of free amines.[8] It was found that Pennwalt 223 with KOH on Gas-Chrom R was the best packing for general use, especially for aqueous samples, although some of the other packings showed advantages in certain cases.

The combination of a Pennwalt column packing, a nitrogen selective detector and strict sample handling has allowed the analysis of a wide variety of amines at sub-ppm levels in organic solvents as well as in pure water.[7] In Figures 1 and 2 representative chromatograms of test mixtures are shown. It was found that the addition of ammonia minimizes adsorption in syringes and glassware. Ammonia also reduces adsorption in the column, especially for volatile amines.

When water is used as the solvent, ghost peaks may appear.[15] However, these peaks are small and don't usually disturb the analysis, compared to an organic solvent, where a substantial part of

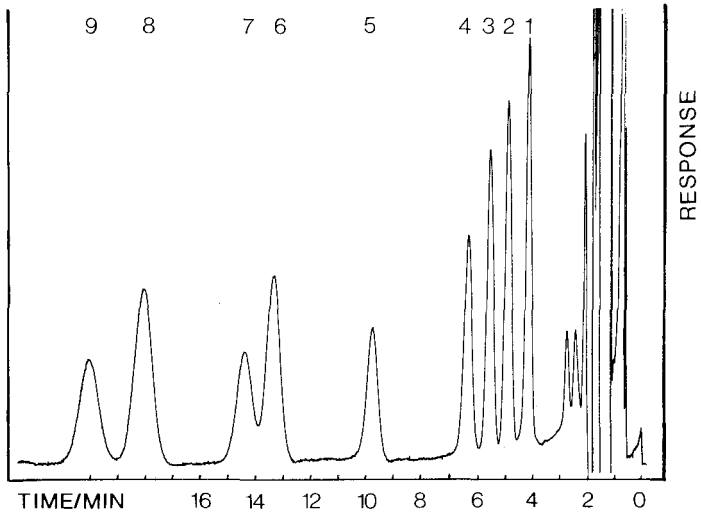


FIGURE 1 Chromatogram of a mixture of amines in hexane with 500 ppm ammonia added. Injection 2 μg. Solutes (each 0.5 ppm): 1 = hexylamine; 2 = tripropylamine; 3 = cyclohexylamine; 4 = heptylamine; 5 = octylamine; 6 = aniline; 7 = tributylamine; 8 = N, N-dimethylaniline; 9 = *o*-toluidine. Column: 28% Pennwalt 223 and 4% KOH on Gas-Chrom R (80–100 mesh). Carrier gas: nitrogen, flow-rate 20 ml/min. Detector: TSD with a bias voltage of -10 V, a bead current of 2.95 divisions, a hydrogen flow-rate of 4.6 ml/min and an air flow-rate of 175 ml/min. Temperature: 190°C. Attenuation $4 \cdot 10^{-12}$ A.f.s. From ref. 7, with permission of the publisher.

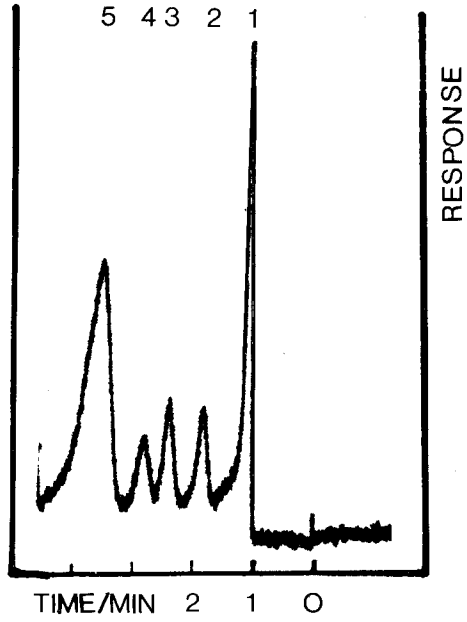


FIGURE 2 Chromatogram of volatile amines in ethanol with 500 ppm ammonia added. Solute concentrations: 1–3, about 0.03 ppm; 4, about 0.15 ppm. Sample size 1.8 μl. Solutes: 1 = ammonia; 2 = methylamine; 3 = dimethylamine; 4 = ethylamine; 5 = isopropylamine. Temperature: 5 min at 80°C, programmed from 80 to 120°C at 20°C/min, then 5 min at 120°C. Attenuation: $1 \cdot 10^{-12}$ A.f.s. Other conditions as in Figure 1. From ref. 7, with permission of the publisher.

the chromatogram is occupied by the solvent peak which may pose more serious restrictions on the analysis. The ghost peaks arise from degradation of the packing close to the injection port.

The column performance is slowly impaired, which can be seen as an increased adsorption tendency. The column can be restored to initial conditions by the injection of 10–20 μl concentrated NaOH solution. A similar impregnation should be made when a new column is installed, to minimize adsorption in the injector end.

In many instances, there is a need for analysis of amines in salt solutions. One important reason is that the most reliable air sampling technique for amines is to use impingers or fritted glass bubblers (see below) with acidic absorption solution. Also, the extraction of amines from various samples matrices by dilute acidic solutions is more or less a standard procedure.[18,19] Before analysis,

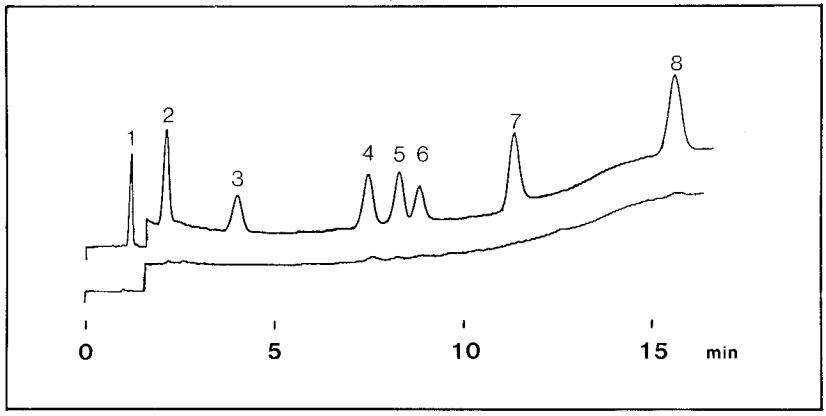


FIGURE 3 Chromatogram of some amines found in industrial environments. Peaks: 1 = dimethylamine; 2 = *n*-propylamine; 3 = triethylamine; 4 = piperidine; 5 = N-methylmorpholine; 6 = *n*-hexylamine; 7 = piperazine; 8 = DABCO. All amine concentrations are 0.3 ppm except for piperazine and DABCO (0.5 ppm) and dimethylamine (3 ppm). Sample matrix, alkali-treated 1.0 N H_2SO_4; blank injection after the analysis is shown below the chromatogram; injection volume 2 μl: detector, TSD; packing: 28% Pennwalt 223 with 4% KOH: column, glass (2 m × 3 mm I.D.) 10 g of packing; attenuation, $64 \cdot 10^{-12}$ A.f.s. for the first 1.5 min then $4 \cdot 10^{-12}$ A.f.s. Temperatures: injector, 290°C; detector, 250°C; column, 130°C (3 min) to 220°C at 10°C/min. Carrier gas: nitrogen, 25 ml/min. From ref. 15, with permission of the publisher.

alkali is added to the acidic solution, giving salt solutions containing free amines. Analysis of amines under these conditions has recently been treated in detail.[15] It was shown that with proper optimization of the gas chromatographic system, the precision is approximately the same (ca 2%) as when amines are analyzed in organic solvents and in pure water. Furthermore, losses due to adsorption in syringes and glassware are suppressed by the high ionic strength of these solutions. Figure 3 shows the analysis of a mixture of amines in alkalized 1N H_2SO_4. The amines in this mixture occur as pollutants in various working atmospheres.

The chromatographic difficulties increase with the number of amine groups in the molecule. Analysis of di- and polyamines, except for the smallest diamine, ethylenediamine, cannot be performed at sub-ppm levels. To meet the requirements for trace analysis, a permethylation procedure has recently been developed.[17] The primary and secondary amine groups are methylated, resulting in tertiary amines, greatly improving the chromatographic properties.

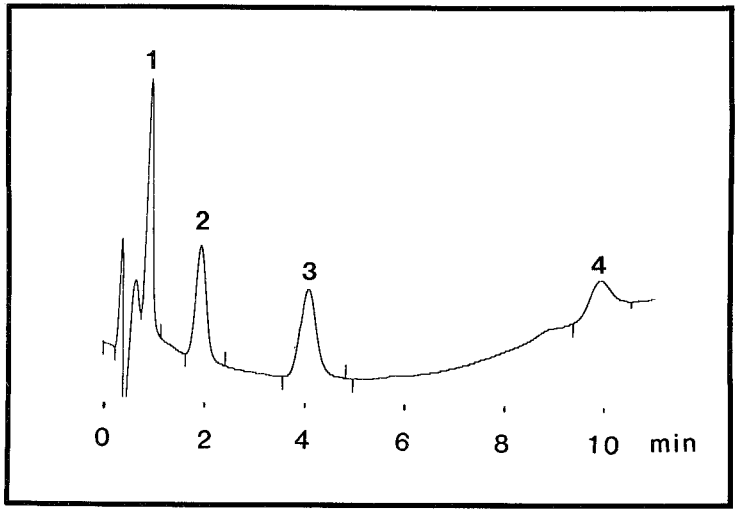


FIGURE 4 Chromatogram of permethylated ethylenediamine (1), 1.4-butanediamine (2), diethylenetriamine (3) and triethylenetetraamine (4). Injection of 2 μl of a 1 ppm solution. Column as in Fig. 3. Detector: TSD with bead heating current, 5.5 scale division, bias voltage -10 V, 250°C; hydrogen flow-rate, 4 ml/min, air flow-rate 180 ml/min. Temperature program: 170°C to 225°C at 10°C/min. From Ref. 17 with permission of the publisher.

Solutions of polyamines down to about 0.1 ppm could be accurately analyzed. A typical chromatogram is shown in Figure 4.

In some instances, the composition of the working atmosphere may be so complex that the chromatographic resolution obtainable with a packed column is insufficient. Thus, methods based on capillary gas chromatography may be required. However, the capillary columns presently available do not allow trace analysis of free amines except in special cases. The choice of sample solvent is more restricted; water is detrimental to the columns. Long-chained tertiary amines as well as aromatic amines were successfully analyzed as can be seen in Figure 5.[16] In other cases, a derivatization is necessary; one example is to use perfluorofatty acid anhydrides.[14] The structures of the amide derivatives were confirmed by mass spectrometry. For highest sensitivity an electron capture detector can be used, while a nitrogen selective detector offers higher selectivity in real samples.[12] This is illustrated in Figure 6.

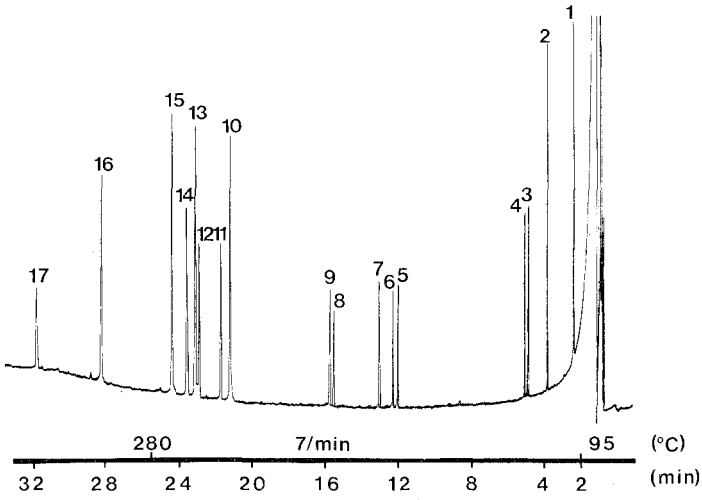
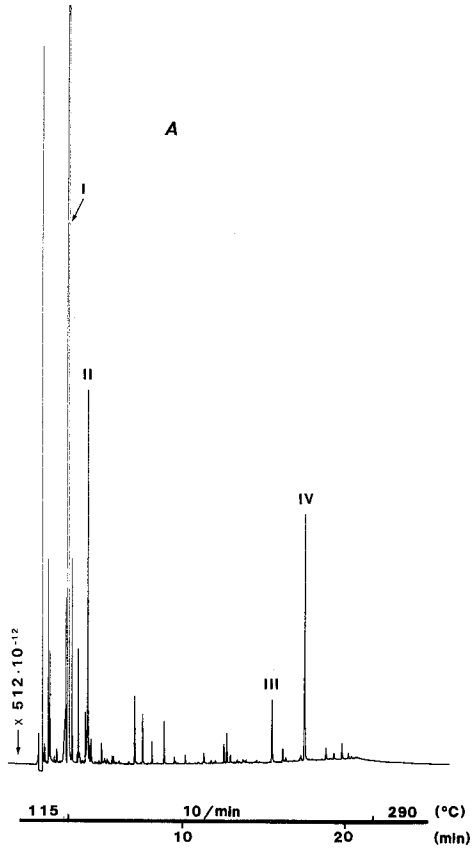


FIGURE 5 Chromatogram of some aromatic and tertiary aliphatic amines of interest in the rubber industry. 0.5 pmole of each substance was injected. Column 20 m × 0.32 mm ID Duran 50 glass capillary column with OV-73 stationary phase, film thickness 0.4 μm. Carrier gas: helium at 0.5 kp/cm^2. Temperature programming as shown. Peaks: 1 = aniline, 2 = N, N-dimethylaniline, 5 = α-naphtylamine, 6 = β-naphtylamine, 9 = 4-aminobiphenyl, 17 = trioctylamine.

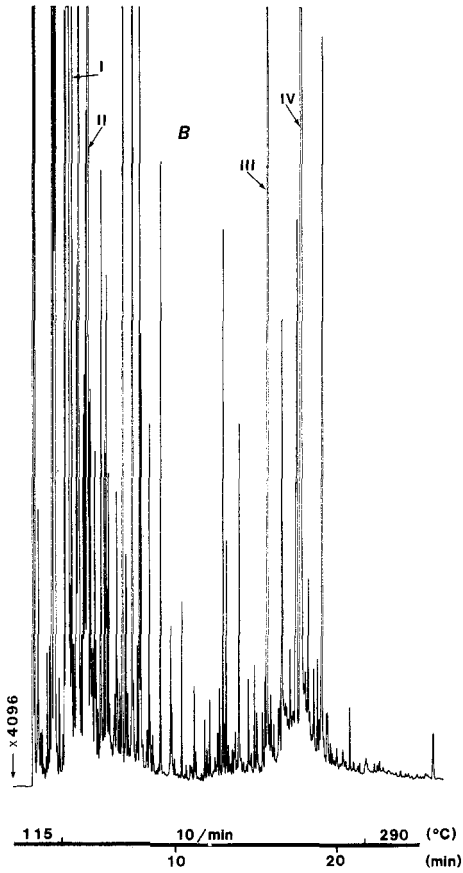
AIR SAMPLING

The most general sampling methods for amines is the liquid absorption method, whereby the air to be sampled is pumped through an acid solution. Both impingers and fritted glass bubblers are used. This technique is characterized by high capacity and results in an acidic sample solution with good long-term stability. It is a cheap and technically simple method, demanding little preliminary study to give satisfactory results. It is also applicable for sampling of aerosols.[20] Studies of sampling efficiency currently in progress have shown that the losses depend on the volume sampled (Figure 7), the flow rate and, to some extent, on the acid concentration. As an example of the flow-rate dependence, the loss after 250 l sampling of 1 ppm n-hexylamine in 20 ml 0.1 N H_2SO_4 was negligible at a flow rate of 1.0 l/min, 1% at 2.5 l/min and ca 12% at 4.0 l/min.

Solvent-free sampling of air pollutants, combined with thermal desorption directly into a gas chromatograph offers some advantages



6(a)



6(b)

FIGURE 6 Chromatograms of HFBAA-treated polyurethane pyrolysis products with (A) TSD (1 μl injected) and (B) ECD (0.2 μl injected) systems. Column: 30 × 0.32 mm ID Duran 50 glass capillary column with OV-73 stationary phase, film thickness 0.2 μm. Temperature programming as shown. Carrier gas, helium at 0.5 kp/cm^2; ECD, constant current mode; voltage, 50 V; pulse width 0.1 μsec; temperature, 300°C, make-up gas, argon-methane (95:5), flow-rate 60 ml/min; standing current, 1.9 nA. Peaks: I = aniline; II = *p*-methylaniline; III = 2,4′-MDA and iv = 4,4′-MDA. From ref. 12 with permission of the publisher.

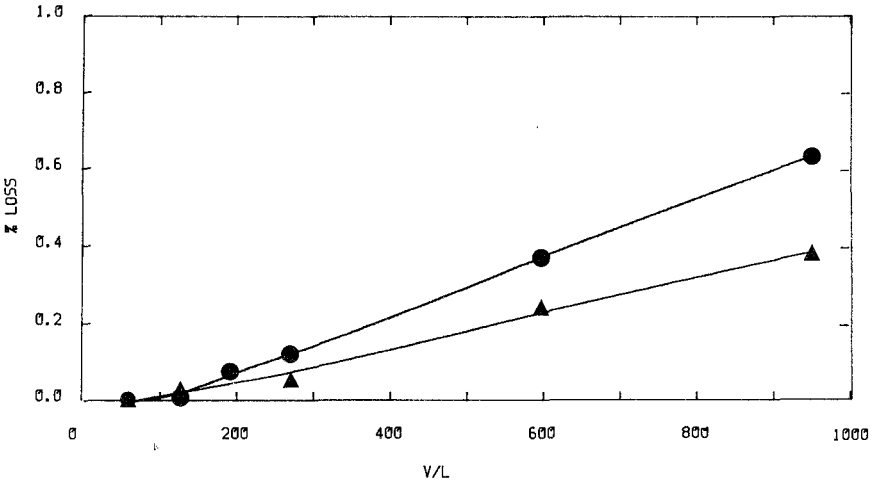


FIGURE 7 Triethylamine, 2 ppm (●) and n-propylamine, 1.5 ppm (▲), sampled in 10 ml 0.5 M H_2SO_4. The loss was determined as the amount found in a backup impinger.

over liquid absorption sampling. It is convenient in field work, as it eliminates risks of spillage and avoids the handling and transport of liquid reagent solutions. As the entire collected sample is analyzed in one chromatographic run, pollutants at very low concentrations can be determined using small sampling volumes. On the other hand, as the entire sample is consumed, duplicate analyses or derivatization steps are impossible. This type of sampling generally needs more validation work than liquid sampling.

For free amines, solvent-free sampling can be performed using the porous polymer Chromosorb 103 as an adsorbent.[13] A 100% recovery of N-methylmorpholine (0.25–7 mg/m^3) in air at flow rates of 80–90 ml/min was observed. Breakthrough was obtained after ca 100 l air per g of adsorbent. Theoretical calculations of the breakthrough capacity agree well with the experimental data, as can be seen in Figure 8.

APPLICATIONS

The analytical methods described above have been used for the determination of amines in different working places.

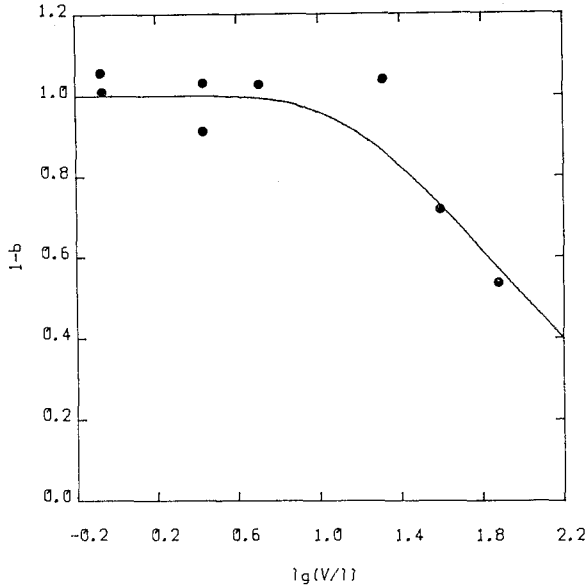


FIGURE 8 Breakthrough b (lost amount/total amount sampled) as a function of sampling volume V. Points denote experimental values,[13] the curve is theoretically predicted (P. Lövkvist and J. Å. Jönsson, to be published).

One important application has been air pollutants in the polyurethane industry, where the sampling of amines and isocyanates has been combined with a simultaneous medical investigation of exposed workers.[11]

Amine concentrations more than 1000 times higher than the total isocyanate concentration were observed. This indicates that the respiratory symptoms found among the workers may, at least partly, be attributed to amine rather than isocyanate exposition. Eye symptoms, "blue haze",[11] can also be correlated to amine exposure. This has been confirmed in further investigations at working places with similar production.

Isocyanates are hydrolyzed to the corresponding amines in the acidic sampling solution. Thus they can be determined in the same chromatographic run as the amines present in the atmosphere.[10] An extractive enrichment into toluene with a factor of ca 10 may be needed to obtain enough sensitivity for hydrolyzed isocyanates after

TABLE I

Air concentrations (ppm) of amines and isocyanates in a polyurethane factory. DABCO = 1,4-diazabicyclo-(2,2,2)octane, TDI = 2.4- and 2.6-toluene diisocyanate.

Sample	N-methyl morpholine	DABCO	TDI (HPLC)	TDI (GLC)
1	3.7	0.017	0.0028	0.0026
2	7.6	0.046	0.0013	0.0017
3	7.6	0.110	0.0013	<0.0014

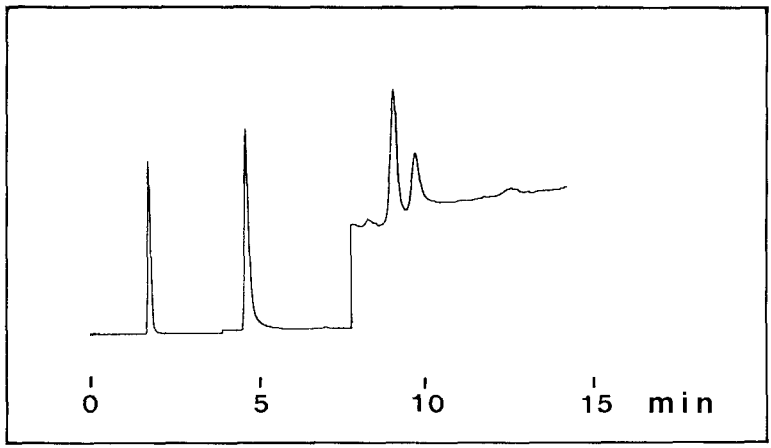


FIGURE 9 Chromatogram from a working atmosphere containing N-methylmorpholine (1.75 min, 2600 ng/μl). DABCO (4.7 min, 22 ng/μl), 2,6-TDA (9.2 min, 1.2 ng/μl) and 2,4-TDA (9.9 min, 1.4 ng/μl). Injection volume: 1.5 μl. Attentuation: $2^{8} \cdot 10^{-10}$ $-2^{-4} \cdot 10^{-10}$ A.f.s. Column temperature: 80 to 210°C at 21°C/min. Detection: TSD. Packing: 10% Pennwalt 223 with 4% KOH. Column: glass (1 m × 2 mm ID), 1.5 g of packing. Carrier gas: nitrogen, 20 ml/min. From ref. 10 with permission of the publisher.

sampling of 5–10 l of air. Table I shows some results obtained in a typical polyurethane factory, and gives a comparison with a well-established liquid chromatographic method for isocyanate analysis.[21] A typical chromatogram is shown in Figure 9.[10]

Futher work on these matters is in progress in cooperation with the Occupational Allergy Unit, Sahlgren's Hospital, Gothenburg.

TABLE II

Concentrations ($\mu g/m^3$) of dicyclohexylammonium nitrite (DICHAN) in workplace air (packing of metal parts). Air sample volume ca. 0.5 m^3. The measured amounts of dicyclohexylamine is assumed to originate from DICHAN.

Sample	Total dust	DICHAN in dust	DICHAN vapour	DICHAN total
1	625	20	1.1	21
2	500	5.1	0.8	5.9
3	285	2.1	1.3	3.4
4	465	2.7	1.5	4.2
5	530	4.8	1.1	5.9
6	150	7.2	1.6	8.8

Dicyclohexylamine as its nitrite salt (DICHAN) is used for impregnation of paper to prevent corrosion of metal parts wrapped therein. There is a decided risk that carcinogenic nitrosamines are formed in workplaces where this paper is handled. In such a work place dust was collected with a cellulose acetate filter connected before and in series with a liquid absorption sampler. DICHAN was determined in the dust and in the absorption solution as the dicyclohexylamine. The filters were extracted with water from which the amine was subsequently extracted into toluene after alkalization. This procedure was used to ascertain a homogenous solution as the water solubility of the free dicyclohexylamine is poor. Results are shown in Table II and a typical chromatogram is shown in Figure 10.

Indoor air quality has been investigated with respect to amines and ammonia. The background is that some types of self-levelling screed used to smooth out irregularities in floors contained casein and other proteins as additives. With a concrete matrix of high humidity and high pH-value, unpleasant odours have arisen in a large number of new buildings in Sweden and people working in these buildings complained about respiratory problems and eye irritations. Ammonia and short-chained amines were suspected to cause some of these problems and were accordingly determined.

Table III shows the results from a private house, representative for a group of houses with these problems. Analysis was performed as

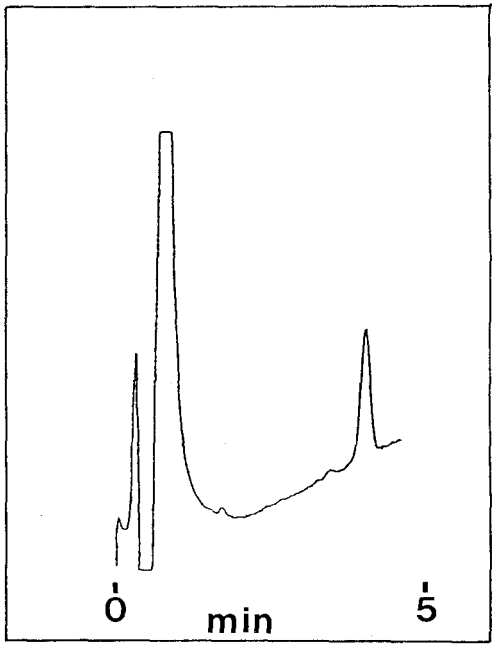


FIGURE 10 *Chromatogram of dicyclohexylamine, 0.4 ppm in toluene. 10% Pennwalt 223 column. Temperature program 175°C (1 min)–210°C (3 min), 25°C/min.*

TABLE III

Air concentrations (ppm) of ammonia and some amines in a private house. Sampling volume 0.65 m^3 in a liquid volume of 10 ml.

Place	Ammonia	Dimethyl amine	Diethyl amine
Kitchen	0.25	0.010	0.002
Sleeping room	0.20	0.013	0.002
Living room	0.25	0.003	0.0002

described above. The response from ammonia of the nitrogen selective detector is at least two orders of magnitude lower than from amines, but still sufficient for these measurements.

The concentrations of amines found in this investigation is somewhat higher than those found in public buildings, probably due to less effective ventilation. The general pattern, however, was always the same with short-chained aliphatic amines dominating.

CONCLUSION

Atmospheres with a complex amine composition can now be analyzed at trace level, using the methodology presented in this paper. Nearly all amines present in the industrial environment can be subjected to these techniques which are routinely used by several laboratories working in the field of occupational hygiene in Sweden.

This provides the basis for an extension of trace amine analysis to more complicated matrices. Work is in progress concerning biological monitoring of amines in urine samples. The demands of clean-up procedures and the requirement of high sample throughput are met by development of an automated flow system based on membrane techniques.

Acknowledgement

This work was supported by various grants from the Swedish Work Environment Fund.

References

1. N. Ito, Y. Hiasa, Y. Konishi and M. Marugami, *Cancer Research* **29,** 1137 (1969).
2. J. Peyps, C. A. C. Pickering and W. G. London, *Clin. Allergy* **2,** (1972).
3. R. E. Brubaker, H. J. Muranko, D. B. Smith and G. J. Beck, *J. Occup. Med.* **21,** 688 (1979).
4. E. K. Weisburger, A. B. Russfield, F. Homburger, H. J. Weisburger, E. Boger, C. van Dongen and K. C. Chu, *J. Environ. Pathol. Toxicol.* **2,** 325 (1978).
5. L. Hagmar, T. Bellander, B. Bergöö, and B. G. Simonsson, *J. Occup. Med.* **24,** 193 (1982).
6. *Environmental Carcinogens—Selected Methods of Analysis,—N-Nitroso Compounds* (IARC, Lyon, 1983), Vol. 6.

7. M. Dalene, L. Mathiasson and J. Å. Jönsson, *J. Chromatogr.* **207,** 37 (1981).
8. L. Mathiasson and P. Lövkvist, *J. Chromatogr.* **217,** 177 (1981).
9. A. M. Olsson and J. Å. Jönsson, *Advances in Chromatography 1981* (ed. A. Zlatkis), Houston (1981), pp. 149–155.
10. G. Audunsson and L. Mathiasson, *J. Chromatogr.* **261,** 253 (1983).
11. L. Belin, U. Wass, G. Audunsson and L. Mathiasson, *Br. J. Ind. Med.* **40,** 251 (1983).
12. G. Skarping, L. Renman and M. Dalene, *J. Chromatogr.* **270,** 207 (1983).
13. P. Lövkvist and J. Å. Jönsson, *J. Chromatogr.* **286,** 279 (1984).
14. G. Skarping, B. E. F. Smith and M. Dalene, *J. Chromatogr.* **303,** 89 (1984).
15. G. Audunsson and L. Mathiasson, *J. Chromatogr.* **315,** 299 (1984).
16. M. Dalene and G. Skarping, *J. Chromatogr.* (submitted).
17. M. Dalene, T. Lundh and L. Mathiasson, *J. Chromatogr.* **322,** 169 (1985).
18. P. Burchill, A. A. Herod and E. Pritchard, *J. Chromatogr.* **246,** 271 (1982).
19. T. Kremmer, L. Holczinger, M. Boldizsar, L. Edweci and S. Bardocz, *J. Chromatogr.* **286,** 371 (1984).
20. W. A. Heitbrink and L. J. Doemeny, *Am. Ind. Hyg. Assoc. J.* **40,** 354 (1979).
21. C. Sangö and E. Zimerson, *J. Liq. Chromatogr.* **3,** 971 (1980).