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TRACE ANALYSIS OF FREE AMINES BY GAS–LIQUID CHROMATOGRAPHY

MARIANNE DALENE, LENNART MATHIASSON* and JAN ÅKE JÖNSSON

Department of Analytical Chemistry, University of Lund, P.O.B. 740, S-220 07 Lund (Sweden)

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SUMMARY

Amines with chain lengths between one and fifteen carbon atoms were determined accurately at sub ppm levels by direct sample injection into a gas chromatograph. The amines were dissolved in different solvents including water. The prerequisite for success was a suitable column (28% Pennwalt 223 with 4% KOH on Gas-Chrom R, 60–230°C), the use of a nitrogen-sensitive detector (Varian TSD) and the addition of ammonia to all solutions prior to analysis. The ability of ammonia to suppress adsorption of amines on glass surfaces and on the column packing was demonstrated. The influence of solvent, column temperature and sample size on the chromatograms was studied. The decomposition of the packing when aqueous samples were injected was shown to cause interference at some column temperatures.

INTRODUCTION

Interest in the determination of amines has grown rapidly during the last few years, owing to their importance, for example, in the transformation into nitrosamines[1], in allergic reactions[2] and in the determination of isocyanates at low concentrations[3].

The most important limitation in using gas chromatography (GC) for analysis of free amines has been their adsorption on the column, resulting in severe tailing and low reproducibility. The literature on the subject was reviewed by Casselman and Bannard[4]. Most of the investigations were made at high concentrations. Amine separation by capillary GC has also been limited to the high concentration range. Schomburg *et al.*[5] recently reported considerable improvements in the analysis of amines on fused silica columns.

There have been very few papers on trace analysis of free amines. Dunn *et al.*[6] developed a method for separating dimethylamine from trimethylamine in biological samples at the ppm level. Di Corcia *et al.*[7] determined low-boiling aliphatic amines in aqueous solutions at a level of 3 ppm on a modified Carbopack B column. In most other cases, *e.g.*, in refs. 8–10, it was found to be necessary to resort to derivatization prior to analysis.

EXPERIMENTAL

A Varian 3700 gas chromatograph was equipped with an automatic flow controller for the carrier gas, a flame ionization detector (FID) and a thermionic specific detector (TSD) for nitrogen and phosphorus. A small capillary was inserted in the hydrogen line leading to the TSD. The resulting pressure drop was measured by a precision manometer. A calibration was made so that the hydrogen flow-rate could be obtained from the readings on the manometer.

The TSD response was optimized with a mixture of 2 ppm octylamine and 2000 ppm n-nonane in n-hexane (sample size 2 μl). The hydrogen flow-rate was varied between 3.3 and 5.9 ml/min and the bias voltage between −4 and −10 V. The bead current was kept to 2.95 scale divisions as recommended in the manual. The selectivity for octylamine over n-nonane was 4000 at a hydrogen flow-rate of 4.6 ml/min and a bias voltage of −10 V. The signal-to-noise ratio for octylamine was then 70. The hydrogen flow-rate was approximately the same as that recommended in the manual, but the bias voltage was considerably lower than recommended (−4 V). The air flow-rate to the detector was 175 ml/min.

Some other experiments were made on a Finnegan 4021 gas chromatograph–mass spectrometer.

The column packing was 28 % Pennwalt 223 and 4 % KOH on Gas-Chrom R (80–100 mesh) (Alltech, Arlington Heights, IL, U.S.A.). The Pennwalt 223 stationary phase was extracted from the packing by methylene chloride and investigated by IR spectroscopy and mass spectrometry (MS). About 10 g of the packing was fífilled into a glass column (190 cm × 3 mm I.D.). The carrier gas (nitrogen) flow-rate of 20 ml/min was near the HETP minimum. The temperature was varied between 60 and 230°C.

Various aliphatic and aromatic amines were used as solutes (see Table I) in different organic solvents as well as in water. Ammonia was added to all solutions to prevent salt formation of the amines and to minimize adsorption on the glass surfaces. Stock solutions of gaseous amines were prepared by dissolving 10 ml of gas in the solvent containing ammonia. The concentration of the amines in the samples was varied between 0.03 ppm and 5 ppm and the sample sizes were 1–7 μl. The sample was injected with a syringe having a non-interchangeable needle.

Special precautions were undertaken to obtain reproducible conditions during sample storage and injection. Samples were stored in glass test-tubes closed with Mininert Valves (Supelco), modified with PTFE caps. The samples were in contact with the membrane only when the valve was opened to insert the syringe. The membranes were grey GC septa. Some membrane types gave disturbing peaks when in contact with alkaline amine solutions. The red type of vial septa could not be used with volatile amines. Memory effects in syringes were reduced by washing first with 25 % ammonia in water, then distilled water and finally with the solvent. The syringe was rinsed with ethanol before using a solvent immiscible with water.

The use of a new very stable nitrogen-sensitive detector and the addition of ammonia to all solutions prior to analysis are important improvements in the experimental conditions compared with earlier investigations.

TABLE I

AMINES USED AS SOLUTES IN THIS INVESTIGATION

Solute	Typical column temperature (°C)
Dimethylamine	80
Ethylamine	
Isopropylamine	
Methylamine	
Trimethylamine	
Isopentylamine	120
n-Pentylamine	
Triethylamine	
Aniline	190
Benzylamine	
Cyclohexylamine	
Heptylamine	
Hexylamine	
N,N-Dimethylaniline	
Octylamine	
Piperidine	
Tripropylamine	
o-Toluidine	210
Piperazine	
Tributylamine	
Triisopentylamine	
Tripentylamine	
Isophorondiamine	230

RESULTS AND DISCUSSION

Fig. 1 shows the separation of some amines at a level of 1 ppm on a Pennwalt column with the Varian TSD. The baseline noise is low at high temperatures and the peaks are symmetrical. The importance of different parameters for the analysis will now be considered.

The packing

Pennwalt 223, Triton X-100 and Dowfax 9N9 stationary phases are often recommended for amine analysis, although Pennwalt is considered to be the best[11]. The other two stationary phases are polyoxyethers. The mass spectrum of Pennwalt 223 indicates that it is a mixture of two components. The main component consists of a polyether chain terminated by two phenyl rings, with a hydrocarbon chain on each ring. The minor component contains a methyl group instead of one of the phenyl rings. The molecular peaks occurred at m/e 554 and m/e 366. The IR spectrum of Pennwalt 223 is very similar to that of Triton X-100, except that Pennwalt 223 seems to lack free hydroxyl groups. This is favourable with respect to peak symmetry for hydrogen-bonding solutes. Elemental analysis confirms the absence of nitrogen in the molecule. Thus, column bleeding will only give compounds containing carbon, hydrogen and oxygen. The detector response to the bleeding will be low due to the high detector selectivity. In using a FID at 200°C a sensitivity of 10^{-9} A.f.s.
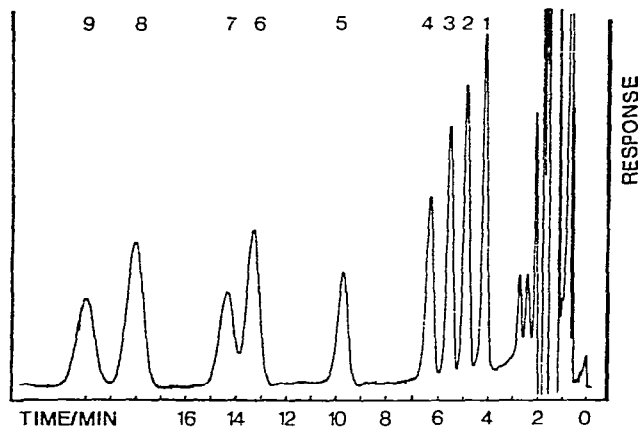
Fig. 1. Chromatogram of a mixture of amines in hexane with 500 ppm ammonia added. Injection 2 μl. Solutes (each 0.5 ppm): 1 = hexylamine; 2 = tripropylamine; 3 = cyclohexylamine; 4 = heptylamine; 5 = octylamine; 6 = aniline; 7 = tributylamine; 8 = N,N-dimethylaniline; 9 = o-toluidine. Column: 28% Pennwalt 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.

was reported[11]. This is low compared with the sensitivity found usable with TSD in this work, $4 \cdot 10^{-12}$ A.f.s.

A high liquid loading (28%) was selected in order to obtain a high column capacity, which is favourable for trace analysis. The properties of the packing were stable, as demonstrated by the fact that the relative retention of benzylamine compared with heptylamine changed less than 1% during 6 months. The decomposition of the Pennwalt 223 led to a decrease in retention times of about 6% during this time. Thus, the separation efficiency was virtually unchanged during these experiments.

The solvent

Organic solvents. n-Hexane, n-nonane, diethyl ether and ethanol, as well as mixtures of alkanes and ethanol, were used as solvents. All are suitable for trace analysis of volatile amines with the Varian TSD detector, if the amines are eluted later than the solvent. However, they cannot be used for trace analysis with the FID due to the tailing of the solvents. Even for such a highly volatile solvent as diethyl ether there are difficulties in analysing concentrations of 50 ppm octylamine with the FID. On the other hand, 0.1 ppm octylamine can easily be determined using the TSD. The only way of increasing the sensitivity in organic solvents, when using the FID and Pennwalt packing, seems to be to use solvents which are eluted after the sample components. For this purpose we tested the solvents squalane, diisobutyl phthalate, diisooctyl phthalate, 1,10-dodecanedinitrile and 3,3′-oxydipropionitrile. Diisobutyl phthalate was found to be the best, permitting determinations of a mixture of octylamine and benzylamine at a level of about 10 ppm.

One of the long chain solvents, 3,3′-oxydipropionitrile (ODPN), decomposed on the column at the temperatures investigated (above 160°C). This was confirmed by MS. Direct inlet MS showed the molecular peak of ODPN, while injection of 2 μl

ODPN on the column gave fragments characteristic of propenenitrile. ODPN has a good thermal stability as a GLC stationary phase. It has been analysed as a solute without degradation on high temperature stationary phases such as SF 96[12]. The basic character of the packing might be responsible for the decomposition. A water molecule and two propenenitrile molecules appear as reaction products. We note that another solvent, 1,10-dodecanedinitrile, similar to ODPN, was eluted after about 2 h at 180°C.

    It can be concluded that amines having between 5 and 15 carbon atoms can be analysed at a level of about 0.1 ppm with the TSD by using a solvent such as n-hexane or ethanol which are both eluted before the sample components (Fig. 2). For volatile amines it is preferable to use an alkane or an alcohol which is eluted after the sample components. The sensitivity for volatile amines is then better than 0.03 ppm (Fig. 3). By making full use of the column capacity, concentrations even less than 0.01 ppm can be determined with a sample size of 5 μl. Ethylamine and trimethylamine were only partially separated on this column. An optimization of the resolution was outside the scope of this paper.
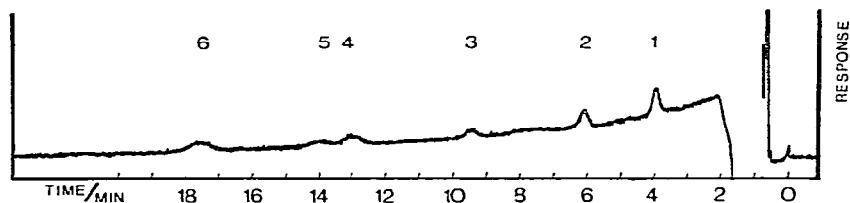

Fig. 2. Chromatogram of a mixture of amines in ethanol with 500 ppm ammonia added. Injection 3 μl. Solutes (each 0.1 ppm): 1 = hexylamine; 2 = heptylamine; 3 = octylamine; 4 = benzylamine; 5 = tributylamine; 6 = N,N-dimethylaniline. Attenuation: $2 \cdot 10^{-12}$ A.f.s. Other conditions as in Fig. 1.
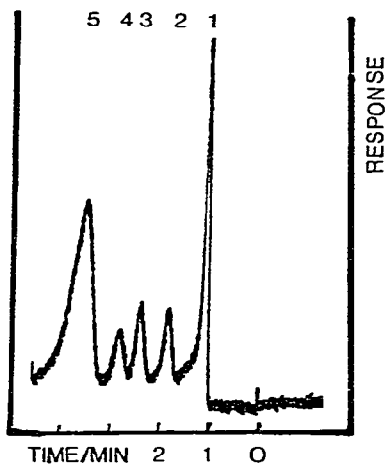

Fig. 3. Chromatogram of volatile amines in ethanol with 500 ppm ammonia added. Solute concentrations: 1–3, about 0.03 ppm; 4, about 0.15 ppm. Sample size 1.8 μl. Solutes: 1 = ammonia; 2 = methylamine; 3 = dimethylamine; 4 = ethylamine; 5 = isopropylamine. Temperature: 5 min at 80°C, programmed from 80 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 Fig. 1.

Water as solvent. Water was injected (2 μl), when the detector was operated at high sensitivity ($1 \cdot 10^{-12}$ A.f.s. with the TSD and $4 \cdot 10^{-11}$ A.f.s. with the FID). Typical chromatograms are shown in Figs. 4 and 5. From these chromatograms it can be seen that either water or some degradation products are eluted from the column and interfere with the detection. Chromatograms obtained with the FID show that determinations above 100°C would be irreproducible. With the TSD, the ghost peak from the water injection prevents determinations of amines in part of the chromatogram, if the temperature is above 80°C. The baseline is restored much faster than with FID.
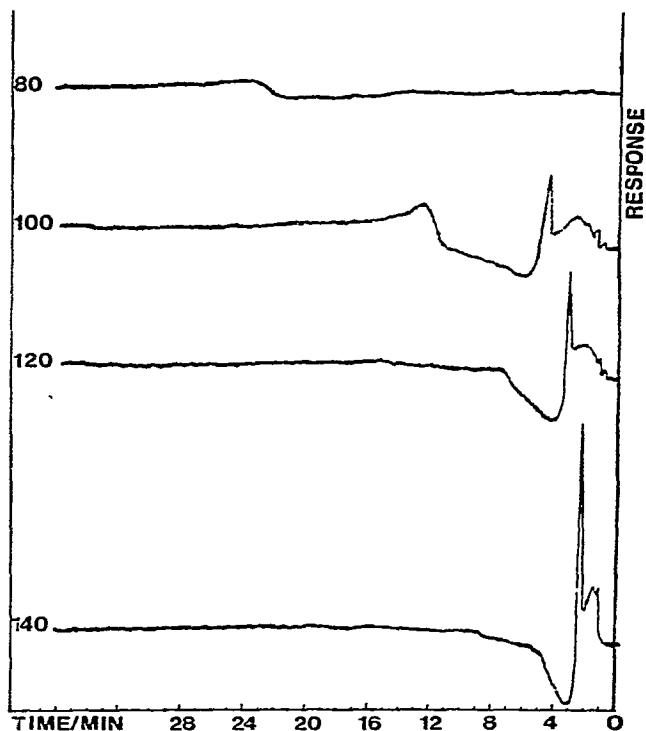

Fig. 4. Chromatograms from injections of 2 μl of water at various temperatures (80–140°C) with TSD. Attenuation: $1 \cdot 10^{-12}$ A.f.s. Other conditions as in Fig. 1.

The problem of interfering peaks when injecting aqueous solutions of amines is well known. Ghost peaks have been obtained on different column packings[13,14]. Onuska[15] reported that the Pennwalt packing is stable at 134°C. It is also stated in a technical bulletin[11] that one of the merits of the Pennwalt 223 packing is that it adsorbs water completely up to 160°C. The earlier investigations were performed at much lower detector sensitivity than used here. The effects shown in Fig. 5 were probably too small to be observed in the previous studies.

The influence of water on the Pennwalt 223 packing was also studied by MS. The baseline spectrum was subtracted from spectra taken during elution of the ghost
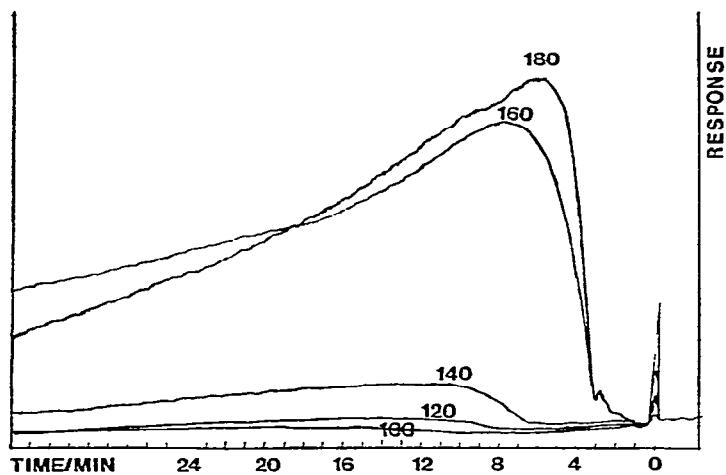
Fig. 5. Chromatogram from injections of 2 μl of water at various temperatures (100–180°C) with FID. Attenuation: $4 \cdot 10^{-11}$ A.f.s. Other conditions as in Fig. 1.

peak. The results showed that the peak was completely or almost completely due to water. On the other hand, it is unlikely that the FID detector would give such a large peak for water. Therefore it seems more probable that small amounts of decomposition products are eluted simultaneously with water. This is also consistent with the results in Fig. 4. The chromatograms, obtained with the TSD, show one sharp positive peak followed by a dip in the baseline. The conditions were chosen so that hydrocarbons gave a small but positive signal. The peak is probably due to hydrolysis products and the dip is caused by a decrease in sensitivity when the ceramic bead is cooled by the eluting water.

For practical analysis of volatile amines with TSD the negative influence of water can easily be avoided by choosing a low column temperature. Fig. 6 shows an analysis at 60°C. The performance of the column at higher temperature can be
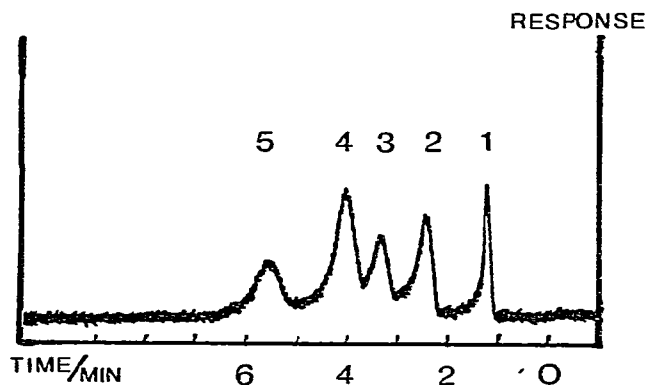

Fig. 6. Chromatogram from injection of 3 μl of a mixture of volatile amines in water. Solute concentration 0.1 ppm. Solutes: 1 = ammonia; 2 = methylamine; 3 = dimethylamine; 4 = ethylamine; 5 = isopropylamine. Temperature: 60°C. Attenuation: $1 \cdot 10^{-12}$ A.f.s. Other conditions as in Fig. 1.

improved substantially if the sample size is decreased. Aqueous amine samples (0.1 ppm, size ≤1 μl) can be determined using column temperatures in the range of 100–200°C. One obvious drawback is that the high capacity of the column cannot be utilized, which increases the determination limit for the amines.

Alkali-treated (NaOH or KOH) column packings have been used in those investigations where spurious water peaks and the negative influence of large samples have been noted. Di Corcia et al.[7] showed the favourable effect of a decrease of the loading of KOH from 0.8% to 0.3% w/w on Carbopack B. The same effect was achieved by decreasing the amount of water. Thus both these factors must be controlled to optimize the analysis.

The ammonia concentration

Injection of the five lowest boiling amines at 0.03 ppm gave increasing peak areas with ammonia concentrations up to 5000 ppm where they levelled off. The peak areas were corrected for a small amount of volatile amines present in the ammonia reagent. The increase of peak area with ammonia concentration was important only at amine concentrations below 1 ppm. However, some ammonia must be added to the test-tube in which the sample is stored. Results for methylamine and dimethylamine are shown in Fig. 7. The percentage adsorption was calculated from the change in peak areas, taking the area at 5000 ppm ammonia as a reference. For heptylamine and benzylamine (at 1 ppm) the peak area increased by only about 10% and 3% respectively when the ammonia concentration increased from 100 to 1000 ppm. The smaller increase compared with the short chain amines can be explained by their lower polarity. The difference between heptylamine and dibenzylamine is obviously due to the aromatic character of the latter.

The adsoption in test-tubes and syringes was investigated by filling the test-tube with methylamine (0.1 ppm) and ammonia (0–5000 ppm) in ethanol. The tube was emptied and filled with a solution of 5000 ppm ammonia in ethanol. A sample
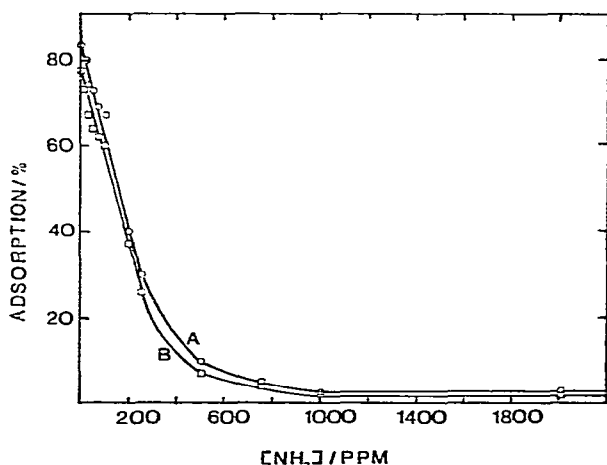

Fig. 7. Percentage adsorption of methylamine (A) and dimethylamine (B) at various concentrations of ammonia and with ethanol as solvent. Solute concentration 0.03 ppm. Column temperature 80°C. Attenuation: $1 \cdot 10^{-12}$ A.f.s. Other conditions as in Fig. 1.

was injected into the gas chromatograph. For this sample, the change in peak area due to adsorption on the columns can be neglected (see Fig. 7). The results are shown in Fig. 8. The percentage adsorption was calculated by taking the peak area from the original test-tube solution, containing 5000 ppm ammonia, as reference. The adsorption decreases rapidly with increasing ammonia concentration, and becomes negligible at 100 ppm. Hexylamine, heptylamine, octylamine and N,N-dimethylaniline were also investigated in the same way. An ammonia concentration of 100 ppm prevented adsorption on glass surfaces even at amine concentrations of 1 ppm.
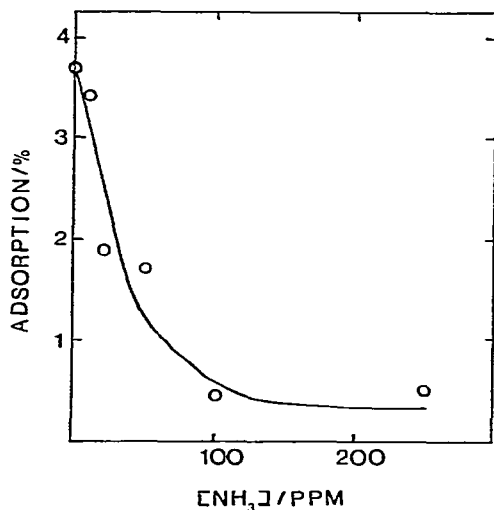

Fig. 8. Adsorption of methylamine on glass surfaces from an ethanolic solution containing various concentrations of ammonia. Concentration of methylamine 0.1 ppm. Temperature: 22°C.

The adsorption in test-tubes and syringes is small compared with the adsorption effects on the column (see Figs. 7 and 8). An ammonia concentration of about 500 ppm is sufficient to obtain a good reproducibility. At this concentration the losses due to adsorption level off, making unimportant small variations in ammonia concentration. The peak shapes of amines at low concentrations, especially for methylamine, are improved after addition of ammonia. The tailing is reduced and the peaks become higher, but the retention times are virtually unchanged. The same behaviour was observed by Dunn et al.[6], who used traces of ammonia in the carrier gas stream.

It should be mentioned that, although a nitrogen-selective detector is used, the detector response ratio of ammonia to amines is only $1:10^4$, i.e., large amounts of ammonia can be present with little effect on the baseline.

Reproducibility and linearity

The reproducibility and linearity were tested by using amine samples containing 500 ppm ammonia. The samples were stored in closed vials. Repetitive injection of 2-μl samples gave a standard deviation of 2–4% (five injections) in different solvents (ethanol, n-hexane and water). The concentration of volatile amines (chain length up to three carbon atoms) was 0.2 ppm and 0.4 ppm for the others. The reproducibility

is equal to that expected when considering the high detector sensitivity and that the peak area was determined by triangulation. The calibration curves were linear in the range 0.1–5 ppm for the solutes given in Table I. Higher concentrations were not investigated.

The variation of peak area with sample size was investigated up to 7 μl and found to be linear. The high liquid loading (28%) gives high column capacity.

CONCLUSIONS

With knowledge of the characteristics of the Pennwalt packing, the solvent effects and the influence of ammonia, it is possible to obtain reproducible analyses of amines down to 0.03 ppm for short chain amines and to 0.1 ppm for other amines. The column performance was satisfactory. With organic solvents it was possible to inject samples larger than 7 μl thus decreasing the determination level. Volatile amines can also be determined at low concentrations in water by keeping the column temperature below 80°C. The sensitivity can be increased by another factor of 5–10 by increasing the temperature of the ceramic bead. However, this reduces the lifetime of the bead and decreases the selectivity towards hydrocarbons. The stability of the column packing and the detector mean that the system is well suited for routine analysis of trace amounts of amines. Many of the precautions reported in earlier investigations have not been necessary here, probably because of the addition of ammonia and the use of a selective detector.

ACKNOWLEDGEMENT

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