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DIRECT ANALYSIS OF FREE AMINES IN SALT SOLUTIONS AT SUB-ppm LEVELS BY GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

A method is described for trace analysis of amines in salt solutions after an alkali treatment followed by direct sample injection. Different parameters that may influence the analysis have been investigated, including sample handling and storing, injector temperature, injector impregnation, pH of the solution, type of salt matrix and detector response where concentration or sample volume is varied. The determination limit is of the order of 10 ppb* for most amines where the decrease in sensitivity for high-boiling amines caused by increased peak broadening can be compensated for by the use of large sample volumes (up to 25 μl). The average precision is *ca.* 2% at an amine concentration of 4 ppm, which is roughly the same as when the amines occur in pure water or in an organic solvent. The method is now routinely used in our laboratory for analysis of amines in samples obtained from workplace atmosphere measurements, where the amines are usually collected in a dilute acidified aqueous absorbing solution.

INTRODUCTION

The need to analyse amines has recently increased. Growing concern about the quality of air, *e.g.* as reflected by a recommended value of 0.03 ppm for methylamine in the F.R.G.[1], and new evidence for health hazards consequent on exposure to amines in low concentrations[2–5], have made it desirable to analyse amines in different workplaces such as industries with polymer production, cattle feed-yards and fish industries[5–9]. The low odour-threshold for volatile amines (only 0.002 ppm for trimethylamine[10]) and the low hygienic threshold values (in the low ppm ranges) for a large number of amines in many countries make a trace method important for hygienic measurements. The same is true in other applications, *e.g.* in the determination of amines in liquid samples such as body fluids[11] and mineral oils[12] or in solid samples such as in microbiological investigations of algae[13].

The sampling procedure or sample pretreatment often leads to an acidic solution of the amines prior to analysis. Thus a trace method based on direct analysis

* Throughout the article the American billion (10^9) is meant.

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of the alkali-treated sample can be very advantageous. It saves time and minimizes the risk of sample contamination and sample losses during manipulation procedures, such as solvent extraction or derivatization steps.

In this paper we describe a method for direct trace analysis of amines by gas–liquid chromatography (GLC), which complements our previous work in this field[5,14–16].

EXPERIMENTAL

Equipment

A Varian 3700 gas chromatograph equipped with a nitrogen selective detector (Varian TSD) and a HP 3390 A integrator was used for the measurements. Typical parameter adjustments for the detector were: bias voltage, −10 V; bead current, six scale divisions; detector temperature, 250°C; air flow-rate, 180 ml/min; hydrogen flow-rate, 3 ml/min giving a selectivity of *ca.* 20000 measured as the peak-to-peak ratio for N-methylmorpholine and *n*-undecane. The injector temperature was varied between 200°C and 300°C.

The glass column (2 m × 3 mm I.D.) was packed with *ca.* 10 g of 28% Pennwalt 223 with 4% potassium hydroxide on Gas-Chrom R, 80–100 mesh (Alltech). The carrier gas was nitrogen, 25 ml/min, freed from oxygen and water vapour by use of an "Oxy-trap" (Alltech). N-type Hamilton syringes were used, and normally 2 μl were injected with a 5-μl syringe directly onto the column using PTFE-faced silicon septa (Microsep F-174N, Alltech).

Injection technique

Normally the syringe was inserted through the septum and the plunger rapidly pressed to bottom; this was followed by a constant waiting period of 4 sec before the needle was withdrawn from the injector.

Injector impregnation

Two 10-μl portions of a saturated sodium hydroxide solution were injected into the first part of the column, where *ca.* 4 cm were free from packing, at an injector temperature of 290°C. This treatment was repeated with one 20-μl portion when necessary.

Chemicals

The amines chosen as model substances (Table I) exhibited a wide variety of properties. Only aliphatic amines were considered, as aromatic mono- and diamines are usually much easier to analyse by GLC than aliphatic amines. Several of these amines occur frequently as pollutants in workplace atmospheres.

Triethylamine, piperidine and piperazine, analytical grade, and N-methylmorpholine and 1,4-diazabicyclo[2,2,2]octane (DABCO), purum grade, were otained from Fluka (Buchs, Switzerland), *n*-hexylamine, purum grade, was purchased from Aldrich (U.S.A.), dimethylamine hydrochloride (min 97.5%) from Janssen (Belgium) and *n*-propylamine, synthesis grade, from Merck-Schuchard (Hohenbrunn, Munich, F.R.G.). Hydrochloric acid, p.a. grade, and sulphuric acid, Suprapur grade, were obtained from E. Merck (Darmstadt, F.R.G.) and sodium hydroxide, puriss p.a.

TABLE I

INVESTIGATED AMINES

Dimethylamine
n-Propylamine
Triethylamine
Piperidine
N-Methylmorpholine
n-Hexylamine
Piperazine
1,4-Diazabicyclo[2,2,2]octane (DABCO)

grade, was from EKA (Bohus, Sweden). Water purified with a Milli-Q/RO-4 unit (Millipore, Bedford, MA, U.S.A.) was used for the preparation of the aqueous solutions.

Preparation of amine solutions

Stock solutions of amines were prepared in pure water (amine concentrations 1000 ppm). Samples of the stock solution were diluted with an acid (0.02–1.0 *N* of either hydrochloric or sulphuric acid) to give the desired amine concentrations (0.1–10 ppm). Throughout this investigation 1 ppm corresponds to 1 μg/ml.

Sample storing and preparation

Samples were stored in 10-ml test-tubes with PTFE-faced screw-caps. Before analysis 1 ml of the sample was transferred to a 1.5-ml test-tube with screw-cap. A small hole (1 mm) had been drilled in the screw-cap and a PTFE-faced silicon septum (Microsep F174-N, Alltech) was used as a seal. Appropriate amounts of sodium hydroxide were added by syringe through the septum prior to the GLC analysis. To minimize dilution, increasing concentrations of sodium hydroxide (2.0–8.0 *N*) were used.

Parameters investigated

To optimize the GLC system for amine analysis in alkali-treated salt solutions the following parameters were studied: injector temperature (200–300°C), injection technique, excess concentration of alkali prior to analysis, type of acid (hydrochloric or sulphuric acid), acid concentration (up to 1.0 *N*), amine concentration (0.1–10 ppm), injected sample volume, sample handling and storing.

RESULTS AND DISCUSSION

Effect of the sample solvent on the chromatogram

When we studied the effect of water on the chromatograms of the amines, we observed two ghost peaks appearing early in the chromatogram. These increased with increased injector temperature, and increased markedly as the injection volume was increased. With decreasing polarity of the solvents (*e.g.* water, methanol, ethanol, di-isopropyl ether and toluene) these peaks became smaller and in toluene they disappeared. Under normal conditions (injection volume, 2 μl; injection temperature, 290°C) they both corresponded to at most 0.5 ppm each. Similar ghost peaks have

been described by other authors[1,17], using stationary phases similar to Pennwalt 223 but with alkali-treated supports based on graphitized carbon blacks. When we repeatedly injected water samples the ghost peaks diminished, but they reappeared in undiminished size after a conditioning period of one night. The use of tap-water or water from diverse purification procedures (distillation, deionization, Milli-Q filtration) or the type of injector membrane did not noticeably affect these ghost peaks. Apparently, some degradation of the stationary phase occurs when hot and polar solvents impinge on the packing at normal injector and column temperatures. This degradation may be amplified by trace amounts of oxygen in the carrier gas. However, the ghost peaks do not usually disturb the analysis of the amines of interest.

The injection of large sample volumes (up to 15 μl) caused increased tendency of the system to show tailing and memory effects, which became severe after *ca.* 400–500 injections. However, impregnation of the injector with sodium hydroxide as described in the Experimental section, restores the system to its former performance. Under normal injection conditions the change in column performance is slow, and the system can be used for a working period of at least one month without a renewed impregnation.

The elution of the water peak does not seem to influence the quantification of amines, but some loss in sensitivity occurs when the analyte elutes simultaneously with water, diminishing with increased temperature of the detector bead. A loss of at worst 30% in sensitivity has been observed under normal operating conditions.

In organic solvents a negative peak is seen when the solvent elutes, making a part of the chromatogram unusable for analysis. Ghost peaks also appear in some organic solvents, *e.g.* in alcohols, where they may even be larger and more numerous than in water.

Provided the ghost peaks in the chromatograms of aqueous samples do not interfere with the analysis of an amine, it is usually more advantageous to use water as solvent, although one has to consider the possibility of a somewhat more rapid degradation of the packing.

Optimization of the GC system

Throughout this investigation we injected aqueous samples containing widely different concentrations of ionic species and very low concentrations of amines. Difficulties encountered in this type of work predominantly depend on the injection process since, as the sample is on the column, the elution will not offer any serious problems[14,15].

Injector characteristics

As far as we know, no thorough study of the injection characteristics of strongly basic compounds has been undertaken, and this is certainly true for amines in alkali-treated salt solutions. In general, we have found[16] that impregnating the first part of the column with sodium hydroxide and using a flash-vaporization technique directly onto the column considerasbly improves the performance of the system. Recently, Kuwata *et al.*[18] have used a similar impregnation technique. Impregnation with strong alkali also results in a column that will be unaffected by a large number of injections of salt solutions, as the amount of salt deposited by the impregnation is much larger than the amount deposited in each injection of sample.

pH-dependence

In this experiment sodium hydroxide was added to aqueous amine solutions of different acid concentrations (1 ppm in each amine). The pH of the solutions was calculated from the excess of alkali added. With an increasing excess of alkali the peak area increases until a plateau is reached.

For low acid concentrations a higher relative excess of alkali is needed to reach this plateau than for higher concentrations, but an excess of *ca.* 5% of the initial acid concentration is always sufficient to get a stable measurement. We found no difference in behaviour for the two different acids studied.

Fig. 1 shows how the critical pH value necessary to reach the plateau varies with initial acid concentration. Each point in this figure is an average value of all eight amines in their salt solutions (both acids included). A pH value higher than 12.5 is sufficient in all measurements at an injectror temperature of 290°C.

Influence of injector temperature and injection techniques

The influence of injector temperature on normalized peak area (per injected volume unit) is shown in Fig. 2a for two types of injection technique. For curve A the normal technique as described in the Experimental section was used, whereas curve B resulted when the needle was drawn out immediately after injection. The curves in Fig. 2a represent piperidine at 1 ppm in pure water. Curves of similar shapes were obtained for the other amines in pure water as well as in salt solutions.

With increasing temperature the rate of evaporation increases, peak tailing decreases and a higher peak area is normally registered. However, a minimum occurs in curve A where the signal may be reduced by as much as 25% compared with the maximum. One reason may be the evaporation of sample from the hot syringe needle before the remaining volume could be read. Another reason may be a slow evaporation of the sample portion in the needle during the injection phase, resulting in a delayed portion of the sample being only partially registered in the peak area. At still higher temperatures the whole sample, including the part in the needle, is injected when using the injection procedure represented by curve A. The relation between

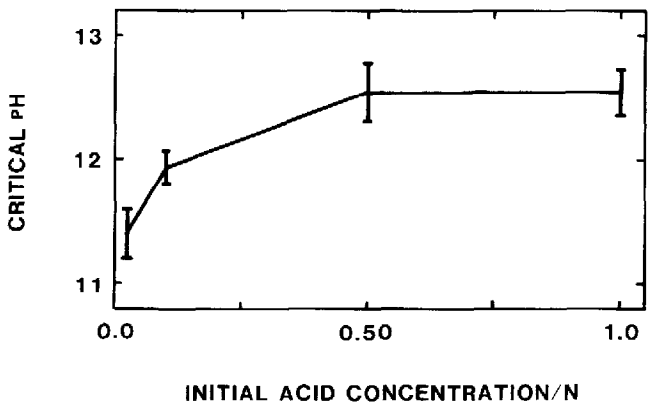

Fig. 1. Variation of critical pH with initial concentration of acid. At higher pH values than the critical one the peak area is stable. Each point is an average of all eight amines investigated and both acids. The points are given with their 95% confidence interval. The amine concentrations in this experiment were 1 ppm. The injector temperature was 290°C.

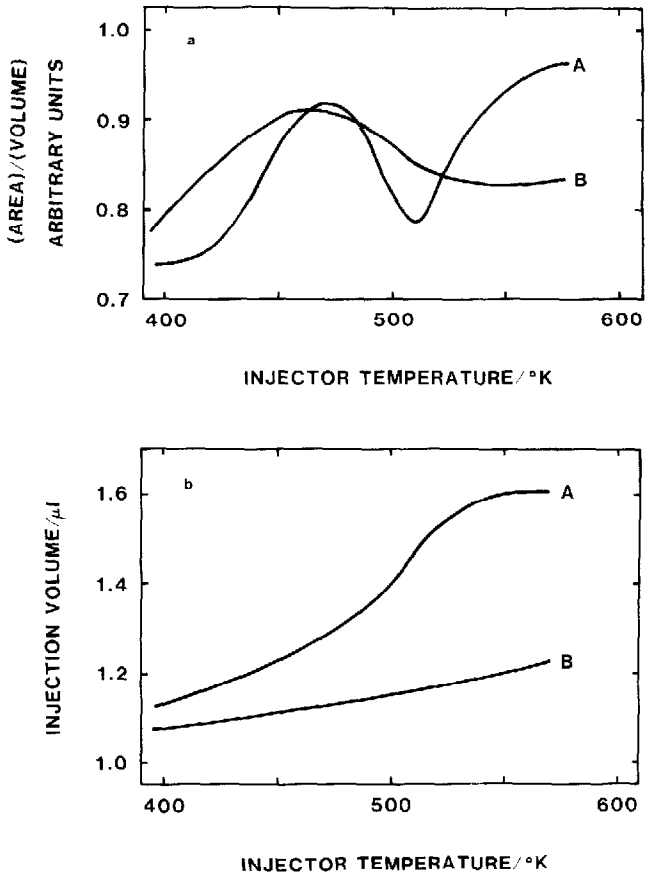

Fig. 2. (a) Variation of peak area per unit injection volume with injector temperature. These curves represent piperidine at 1 ppm in pure water. In curve A the normal injection procedure was used (injection followed by a waiting period of 4 sec) whereas curve B resulted when the needle was drawn out immediately after injection. (b) Influence of injector temperature on the volume of injected sample. Curves A and B correspond to same injection techniques represented in a.

injected volume and injector temperature is shown in Fig. 2b for the amines in pure water.

The minimum of curve A moves to slightly lower temperatures with increasing ionic strength of the sample solution, owing to enhanced vapour pressure of the amines above the solution. However, for a chosen salt concentration all the amines studied showed a minimum at approximately the same injector temperature, indicating that the injection process is determined almost solely by the solvent and much less by the amines considered here.

A relatively high injector temperature is thus desirable to avoid working close to any minima where sensitivity is reduced. The injection procedure corresponding to curve A has a standard deviation roughly three times smaller than the one corresponding to curve B.

Carrier gas flow-rate and column temperatures

We have found it advantageous to use carrier gas flow-rates considerably higher than those corresponding to the minimum of the Van Deemter curve (determined with the relatively well-behaved triethylamine). One reason for better chromatographic behaviour may be a more rapid transfer of solute to the column at higher flow-rates.

An increase in column temperature generally leads to less adsorption, resulting in better chromatographic performance and somewhat higher sensitivity. However, at high temperatures the elution of some amines of interest may be very close to the maximum of the water peak, leading to impaired sensitivity. In choosing parameters for a temperature programme one may have to consider the influence of both these features on the analysis.

Fig. 3 shows a chromatographic run of the amines in Table I after proper optimization of the chromatographic system.

Quantitative analysis

Sample handling

The concentration of some of the investigated amines in alkali-treated salt solutions decreased significantly with time, even when the sample solutions were kept in ordinary screw-capped test-tubes and opened only for analysis. This effect was studied in more detail by measuring the change in amine concentration with time in alkali-treated solutions of various salt concentrations kept in open test-tubes at room temperature. The amount of all the amines examined, except the most water-soluble or most involatile (piperidine, N-methylmorpholine, piperazine and DABCO) decreased in the samples. The decrease in amine concentration was roughly linear with time, and within precision limits of the experiment we found that the rate of escape of the amines as a function of ionic strength is the same for both alkali-treated hydrochloric and sulphuric acid samples. The loss rate from 1 ppm solutions is given

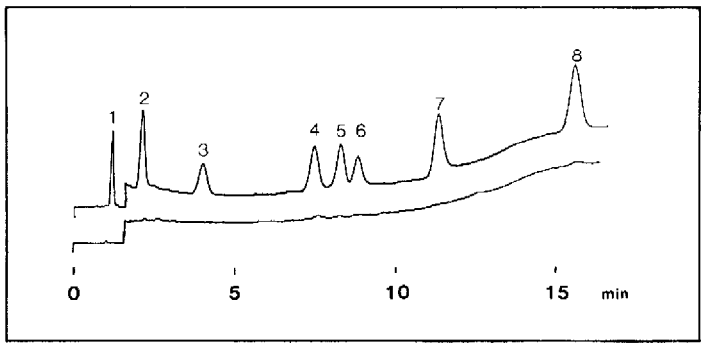

Fig. 3. Chromatogram of the investigated amines after optimization of the GC system. Peaks: 1 = dimethylamine; 2 = *n*-propylamine; 3 = triethylamine; 4 = piperidine; 5 = N-methylmorpholine; 6 = *n*-hexylamine; 7 = piperazine; 8 = DABCO. All amine concentrations are 0.3 ppm except for piperazine and 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.

TABLE II

LOSS RATE OF AMINES

Initially at 1 ppm in alkali-treated acid solutions. Rate is expressed in percentage loss/(h cm^2). Temperature, 20°C.

Solute	*Total ionic strength of salt (mM)*				
	30	*140*	*440*	*870*	*1220*
Dimethylamine	1.6	4.6	6.8	12	19
n-Propylamine	1.6	4.8	7.0	11	17
Triethylamine	36	50	56	61	63
Piperidine	0	0.4	0.9	1.9	1.9
n-Hexylamine	0	3.9	19	38	45

in Table II. A safe procedure for avoiding losses of this kind is to use tightly sealed vessels, *e.g.* those described in the Experimental section.

Calibration curves

A calibration curve can be constructed either by injecting constant volumes of standard solutions of various solute concentrations or by injecting different volumes of a single standard solution. Both types of curves are discussed below.

Peak area versus amine concentration in various matrices. Amine samples of various amine concentration (0.5–10 ppm at six concentrations) in different matrices were injected. The injection volume was constant and *ca.* 2 μl. The matrix was an alkali-treated hydrochloric or sulphuric acid of various concentrations (0.02–1.0 *N*). Linear relationships were obtained between peak area (per injected volume unit) and amine concentration, giving a pooled correlation coefficient of 0.9992. No significant difference was found in this respect between different salt concentrations, different amines or acid types at the 95% level of significance, the 95% confidence interval being 0.9988–0.9994. All the lines passed through the origin at the 95% level of significance. The statistical theory used for these and subsequent calculations is obtained from refs. 20 and 21.

TABLE III

DIFFERENCES BETWEEN CALIBRATION LINES OBTAINED IN SALT-MATRICES AND PURE WATER WITH AMINE CONCENTRATION VARIED

Figures in the table show for how many amines (of totally eight) the difference is significant at a 95% level and figures in parentheses give the number of amines for which the line in water lies significantly below the salt line.

	Initial acid concentration (N)			
	0.02	*0.10*	*0.50*	*1.00*
Alkali-treated HCl	5(4)	3(2)	3(3)	7(3)
Alkali-treated H_2SO_4	1(0)	4(2)	5(4)	6(2)
Fraction of amines showing difference (both acids)	0.4	0.4	0.5	0.8

(1) Comparison with water. The influence of the various matrices on the amine analysis was studied by comparing the calibration lines for amines in these matrices with those obtained in pure water solutions. A 95% confidence region was calculated for the regression lines of amines in different salt solutions and in pure water. Table III shows the number of amines, eight in all, for which the water line was not included in the confidence region for this amine in salt solution. Only piperazine and DABCO predominantly show a stronger signal in salt solution than in water. A higher salt concentration means an increase in vapour pressure, which facilitates vaporization in the injector. This also leads to decreased adsorption of these amines as a result of the strongly alkaline environment in test-tubes and syringes.

Only *n*-hexylamine shows weaker signals in all salt concentrations than in water, probably as a result of its limited solubility, especially at higher salt concentrations. Generally there is an increase in the number of differences between water and salt solutions with increasing salt concentration.

(2) Precision. To compare the behaviour for different amines in different matrices we used the variances of the regression lines, normalized by the regression line value at the average amine concentration in the chosen interval (0.5–10 ppm).

The variances for each amine at different salt concentrations were compared using Bartlett's test, and no significant difference was generally found at the 95% level. Averaged values of relative standard deviations (R.S.D.) are given in Table IV.

Using the same test as above we found no significant difference (95% level) between the variances of the amines in a certain matrix whether we considered amine solutions in alkali-treated hydrochloric acid, alkali-treated sulphuric acid or pure water. According to Table IV, the average R.S.D. values for both acid types do not differ but the precision is generally higher in pure water than in salt solutions.

Peak area versus sample volume at constant amine concentration in various matrices. All the amines investigated (concentrations 1 ppm, in general six sample sizes), showed a linear response up to at least 5 μl. Thereafter some lines levelled off

TABLE IV

R.S.D. FOR CALIBRATION REGRESSION LINES WHEN AMINE CONCENTRATION IS VARIED

R.S.D. is given for the average amine concentration in the interval 0.5–10 ppm, (usually about 4.5 ppm). Each entry is an average of four lines (each line corresponds to one of four salt concentrations). Numbers in parentheses represent degrees of freedom.

	R.S.D. in alkali-treated HCl solution (%)	*R.S.D. in alkali-treated H_2SO_4 solution (%)*	*R.S.D. in pure water (%)*
Dimethylamine	1.8	1.7	1.5
n-Propylamine	2.3	2.2	1.3
Triethylamine	1.9	1.8	1.6
Piperidine	2.3	1.8	1.3
N-Methylmorpholine	1.5	1.8	0.94
n-Hexylamine	2.0	2.9	2.9
Piperazine	2.0	2.3	1.6
DABCO	1.9	1.4	1.4
	2.0 (113)	2.0 (122)	1.7 (251)

and in other cases split peaks appeared. With increasing retention volume the linearity was extended, and the most involatile amines (piperazine and DABCO) showed a linear response up to the highest injection volumes investigated (25 μl). This is in agreement with a theory of Hollingshead *et al.*[22], which predicts for temperature programming that the contribution to the band-broadening caused by injection is inversely proportional to the isothermal retention volume at the initial temperature.

No significant difference (95% level) was found for correlation coefficients in different salt concentrations for any of the amines. Neither were significant differences found for the two acid types, nor did the amines differ in their correlation coefficients. Thus all the lines could be pooled to give one correlation coefficient with a value of 0.9976 (95% confidence interval ranging from 0.9969 to 0.9982). Thus the correlation is noticeably poorer than in the concentration mode. The origin was always included in the 95% confidence interval for the intercept.

In general, the calibration lines in alkali-treated hydrochloric acid have a greater slope than in alkali-treated sulphuric acid, and when the differences were tested using a single-sided Student's *t*-test it turned out (Table V) that a large fraction of the lines showed significantly greater slopes for alkali-treated hydrochloric acid by a factor of 1.2–1.8.

The number of theoretical plates decreases by *ca.* 50% when the injection volume is changed from 0.5 μl to 10 μl for all amines except piperazine and DABCO. The decrease in resolution is, as expected, proportional to the square root of the decrease in theoretical plate number. However, with piperazine and DABCO, an initial increase in theoretical plate number occurs with a maximum at *ca.* 5 μl, most probably depending on a condensation effect theoretically described by Giddings[23]. This behaviour may be expected for other highly involatile amines. For different salt concentrations, including pure water, all amines show a similar variation in theoretical plate number and resolution. This means that the behaviour is mostly controlled by the solvent.

(1) Precision. The effect of salt concentration on calibration line precision for each amine was tested in the same way as in the concentration mode. Here, however, it turned out that four of the eight amines differed in variance (95% level) considering matrices of different salt concentrations, prepared by alkali treatment of hydrochloric acid solutions. For sulphuric acid, two amines showed such a difference. The vari-

TABLE V

DIFFERENCES BETWEEN ALKALI-TREATED HCl AND H_2SO_4 SOLUTIONS AS MATRICES FOR AMINES WHEN SAMPLE VOLUME IS VARIED

Each entry show the number of amines (out of eight) having significantly larger calibration slopes in alkali-treated HCl than in alkali-treated H_2SO_4 solutions. Amine concentration was 1.0 ppm and volume varied between 0.5 and 10 μl.

Significance level (%)	*Initial concentration of acid (N)*			
	0.02	*0.10*	*0.50*	*1.0*
95	6	8	8	6
97.5	5	8	8	5
99.5	5	8	8	4

TABLE VI

DIFFERENCES IN VARIANCES OF CALIBRATION LINES WHEN CALIBRATING AGAINST SAMPLE VOLUME OR CONCENTRATION

Figures in the table show the number of amines (out of eight) having significantly higher variances when sample volume is varied than when amine concentration is varied. The tests are based on variance averages from four calibration lines for each amine, where each line corresponds to one of four different salt concentrations.

	Level of significance (%)		
	95	*97.5*	*99.5*
Alkali-treated HCl	8	7	6
Alkali-treated H_2SO_4	5	4	4
Fraction of amines showing difference (both acids)	0.8	0.7	0.6

ances also differed significantly between the amines in a given matrix. However, the composition of the matrix (acid type and salt concentrations) did not significantly influence these differences at the 95% level. Thus the discrepancies here may mainly be ascribed to the properties of the solutes. A percentage R.S.D. of *ca.* 3.5% at 4 ppm was found for most of the amines, compared with 2% in the concentration mode.

Comparison between concentration and volume variation. The linear working range for the concentration dependence is generally at least two orders of magnitude higher than when the sample size is varied. Another factor to consider is that the increased sample volume means a faster degradation of the packing necessitating a more frequent injector impregnation. Still another factor, which may be very important, is the loss of separation efficiency when the sample volume is increased.

As stated above, there is no significant difference in precision at the 95% level when different acid matrices are compared, either in the case of concentration or volume variation. As shown in Table VI, the use of the concentration mode is markedly advantageous. In our opinion the expansion of the solvent, the rate of which is dependent on the sample size, and its influence on the packing performance is the major course of this difference.

The sensitivity in a given system is favoured by a high slope of the calibration line. Because there is a difference in slopes for the two types of acid when the sample volume is varied, the lines for hydrochloric and sulphuric acids have been treated separately. The comparison has been performed according to Appendix I below, where comparable response factors have been obtained using water solutions as reference. Notice that in the alkali-treated sulphuric acid matrix the response factor is always higher in concentration mode. With hydrochloric acid, the response factors are higher in some cases and lower in others than in the concentration mode. No trend could be observed either with respect to amine type or salt concentration. It is important to note that this means that in the sample size mode the quantification of amines may be severely influenced by the composition of the matrix.

Considering all the results discussed above it is clear that use of the concen-

tration mode is preferable in all instances. Only for the case of trace analysis, when the sensitivity may be insufficient, the sample size mode may be attempted in connection with temperature programming.

Choice of matrix

In many applications there is a choice of matrix. For example, in environmental air sampling of amines, acidified aqueous solutions are preferably used as absorbing medium which gives a free choice between acid type and concentration. Ordinary solvent extraction[6,16] or stripping procedures[24] can be used for enrichment and at the same time for matrix modification to get higher sensitivity or to minimize the influence of interfering substances in the original matrix.

We have shown that in aqueous solutions the choice of acid or acid concentration is of minor importance. The precisions in the amine determinations are roughly the same and so are the detection limits. It is well known that the stability of amines is enhanced by storage in acidified media[19]. Over a period of 6 months we found no significant change in amine concentration in either case. However, after alkali treatment, it is preferable to use low ionic strength to minimize losses due to increased vapour pressure and to avoid salting-out effects of the analyte. In pure water the precision is somewhat higher than in salt solutions, but the influence of salts on detection limits of amines is negligible.

For repeated injections the precision in the chromatographic procedure is the same for salt solutions, pure water and organic solvents, resulting in 1–2% R.S.D. (three injections, 1 ppm solutions of amines). The overall precision for an analysis of amines in salt solutions is 3% R.S.D. and in pure water and in organic solvents it is 2.5% R.S.D. (4 ppm solutions). In salt solutions the precision is the sum of the uncertainty in the calibration line and the uncertainty due to alkali addition to the solution prior to analysis, the last procedure being an additional moment compared with pure water and organic solutions. Further addition of *ca.* 5% to the deviation results, when the extraction procedure precedes the analysis in organic solvents.

Determination limit

The determination limits for the most involatile amines are *ca.* 0.03 ppm with the usual 2-μl injection. For the most volatile amines this limit is an order of magnitude lower. However, as discussed above, the injection volume for highly involatile amines may be increased at least 10 times to give roughly the same determination limit for all amines in this investigation. The precision decreases when analyses are performed at these low levels. However, calibration curves for piperazine and DABCO, based on four different concentrations and two repeated injections, gave both a correlation coefficient as good as 0.98 in the concentration intervals 25–300 ppb and 10–130 ppb respectively. The chromatographic behaviour when picogram amounts of these amines are analysed is illustrated in Fig. 4.

Applications

The method described in this paper is now routinely used in our laboratory for analysing amines in samples obtained from working place atmosphere. The air samples are normally obtained by midget impingers containing acidified aqueous solutions, generally 0.1 *N* in sulphuric acid. An extractive enrichment procedure for

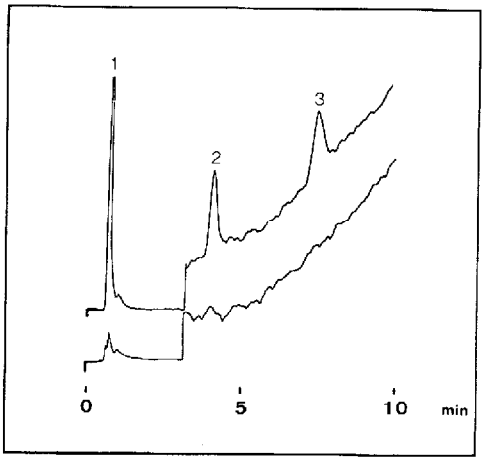

Fig. 4. Chromatogram of (1) NH_3 (1000 ppm), (2) piperazine (30 ppb) and (3) DABCO (10 ppb). Blank injection after the analysis is shown below the chromatogram. Injection volume, 3 μl; attenuations, $256 \cdot 10^{-12}$ A f.s. for the first 3 min then $1 \cdot 10^{-12}$ A f.s.; column temperatures, 220°C (1 min) to 235°C at 2°C/min. Other parameters as in Fig. 3.

amine analysis has been described before[16], and a derivatization procedure for polyamines[25] has recently been developed at our laboratory. Together with the method described in this paper, a general method for analysis of most amines occurring in workplace atmospheres using the same chromatographic system is now available.

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APPENDIX I

Comparison between calibration slopes in concentration mode and sample size mode

To get a true comparison for the mass-dependent TSD detector between the slopes in the concentration mode and the sample size mode, the peak area was divided by the sample volume when the concentration was varied and by the solute concentration when the sample size was varied.

A comparison of this kind, which involves a great number of runs, is time-consuming. Thus the decrease in detector sensitivity with time must be accounted for. To do this a matrix of pure water containing the amine investigated was used as a reference. After each run of the amine in different matrices a water reference solution was always chromatographed. The quotient between the slope in salt solutions and water solutions was calculated for both the concentration mode and the sample size mode. Finally, the two quotients were compared by statistical means.

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