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COMPARISON OF COLUMN PACKINGS FOR TRACE ANALYSIS OF FREE AMINES BY GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

Different packings have been compared with respect to their usefulness for trace analysis of free amines. It was found that 28% Pennwalt 223 with 4% KOH on Gas-Chrom R was the best all-round packing, especially for aqueous samples. The separation efficiency was best on Carbopack B with 4% Carbowax 20M and 0.8% KOH, and the most symmetrical peaks were obtained on Chromosorb 103. The results indicate that the choice of a nitrogen sensitive detector and the addition of ammonia to the sample solution is more important for a successful analysis than the choice of packing.

INTRODUCTION

Recently we described a method for analysis of free amines at the sub-ppm level[1]. The prerequisite for success was the use of a nitrogen sensitive detector, the addition of ammonia to all solutions prior to analysis and a suitable column (28% Pennwalt 223 with 4% KOH on Gas-Chrom R, 80–100 mesh). In this paper the importance of the choice of packing is further outlined. Column packings other than Pennwalt 223 have been used for amine analysis, but usually only at high concentrations, *e.g.*, in refs. 2 and 3. However, Di Corcia and Samperi[4] have analyzed low-boiling free aliphatic amines at a level of 1–2 ppm in water solutions using Carbopack A and B. Recently, Kuwata *et al.*[5] used silanized Chromosorb 102 modified with KOH for the same purpose, with good results at the sub-ppm level using a nitrogen sensitive detector.

The investigated packings are given in Table I. Packings 1–4 are regularly used for amine analysis and are commercially available. Packing 5 is a modification made in our laboratory. Chromosorb 103 has been chosen as representative of porous polymers. Dave[2] found this packing to be the best porous polymer for analysis of free amines at high concentrations. The use of stationary phases containing nitrogen has been avoided since it would obscure one of the great advantages of the nitrogen sensitive detector, namely a selective suppression of the baseline noise emanating from bleeding of the stationary phase.

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TABLE I

COLUMN PACKINGS

No.	*Packing*	*Amount in column (g)*
1	28% Pennwalt 223 with 4% KOH on Gas-Chrom R (80–100 mesh)	9.5
2	Carbopack B with 4% Carbowax 20M and 0.8% KOH	3.0
3	Chromosorb 103	6.3
4	10% Carbowax 20M and 2% KOH on Chromosorb W AW (80–100 mesh)	6.5
5	10% Carbowax 20M and 2% KOH on Superpak 20 M	4.2

EXPERIMENTAL

The measurements were performed with a Varian 3700 gas chromatograph provided with an automatic flow controller for the carrier gas (N_2) and a nitrogen sensitive detector (Varian TSD). The detector was operated under the same conditions as in ref. 1 with hydrogen flow-rate 4.6 ml/min, bias voltage −10 V and a bead current at 2.95 scale divisions. Both low- and high-boiling primary, secondary and tertiary amines were used as solutes. The sample size was 2–3 μl with amine concentrations below 1 ppm. Glass columns (1.70–1.90 m × ≈3 mm I.D. for packings 1, 3, 4 and ≈2 mm I.D. for packings 2, 5) were used.

RESULTS AND DISCUSSION

Attention was focused on the detection limit, peak shape, separation efficiency and the possibility of using water as a solvent. Some illustrative chromatograms are presented in Figs. 1 and 2. Other figures showing the behaviour of Pennwalt 223 in more detail can be seen in ref. 1.

Detection limit

This is similar for the different packings. Because of the long retention times on Chromosorb 103 for amines with more than 5–6 carbon atoms this packing is less suitable for trace analysis of long-chain amines. Increasing the temperature to obtain shorter retention times and sharper peaks is possible up to about 250°C when column bleeding becomes too high to allow trace analysis. The Pennwalt 223 column has a higher sample capacity than the other columns, thus somewhat lowering the detection limit.

Peak shape

Long-chain amines exhibit almost symmetrical peaks on all packings, those of the tertiary amines being the most symmetrical as expected. However, low-boiling amines such as methylamine and ethylamine give some tailing. Generally, Chromosorb 103 results in the most symmetrical peaks, followed by Pennwalt 223.

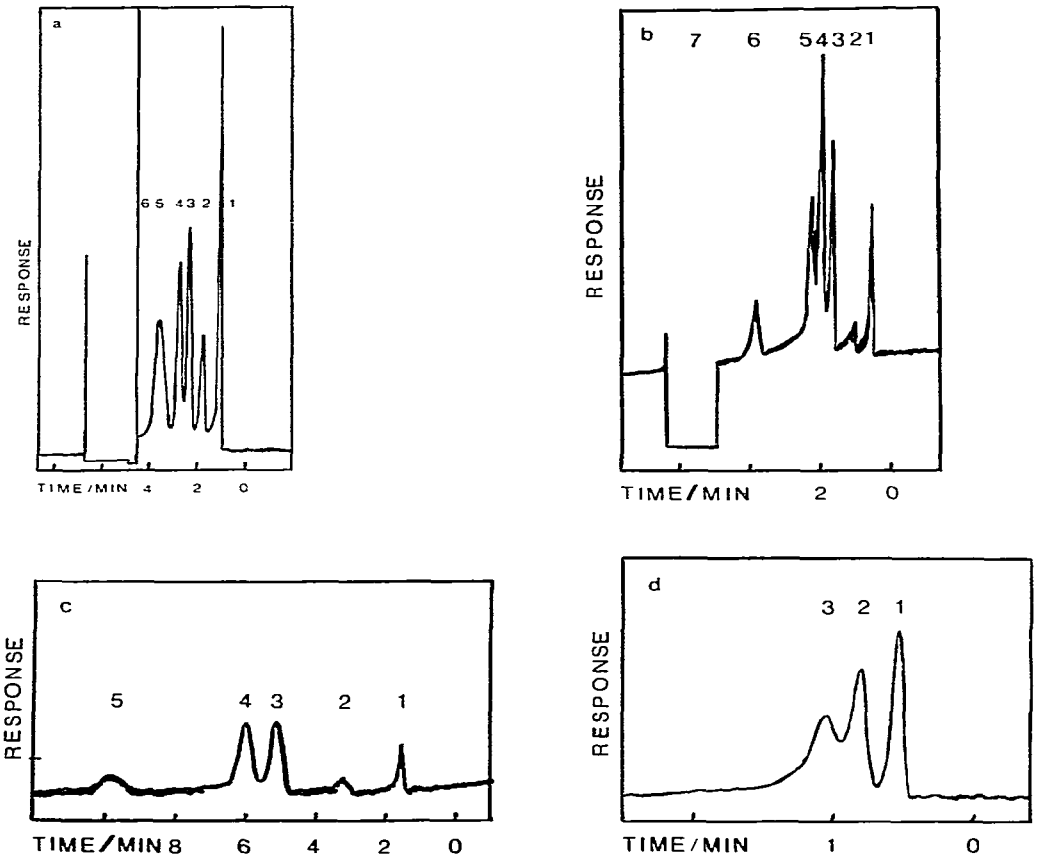

Fig. 1. Chromatograms of low-boiling amines on different columns. The packings are described in Table I. Temperatures: injector, 220°C; detector, 250°C. a, Pennwalt 223. Column temperature: 5 min at 80°C, then programmed to 120°C at 20°C/min and finally held at 120°C for 5 min. Solutes: 1 = ammonia; 2 = methylamine; 3 = dimethylamine; 4 = ethylamine; 5 = isopropylamine; 6 = hexane solvent; concentrations of about 1000 ppm of 1, 0.2 ppm of 2 and 0.5 ppm of 3–5. Sample size: 3.4 μl. Attenuation: $1 \cdot 10^{-12}$ a.u.f.s. b, Carbopack B. Column temperature: 70°C. Solutes: 1–4 as in a; 5 = trimethylamine; 6 = isopropylamine; 7 = ethanol solvent; concentrations of about 500 ppm of 1 and 0.1 ppm of 2–6. Sample size: 3.0 μl. Attenuation as in a. c, Chromosorb 103. Column temperature: 120°C. Solutes 1–5 and solvent as in a; concentrations of about 500 ppm of 1, 0.1 ppm of 2 and 0.5 ppm of 3–5. Sample size and attenuation as in a. d, Superpak 20M. Column temperature: 60°C. Solutes: 1 = trimethylamine; 2 = methylamine and dimethylamine; 3 = ethylamine; concentration 0.1 ppm each. Solvent: ethanol. Sample size: 2.4 μl. Attenuation as in a.

Separation efficiency

The best separation of long-chain amines was obtained on Pennwalt 223 and Carbopack B. Separation of volatile amines such as methylamine, dimethylamine, ethylamine, trimethylamine and isopropylamine is achieved only on Carbopack B. On Pennwalt 223 and Chromosorb 103 the separation between ethylamine and trimethylamine is insufficient. Determinations of volatile amines on the Carbowax 20M packing (no. 4) are inferior to those on the other packings due to low separation efficiency and very short retention times. The modified Superpak 20M packing (no. 5)

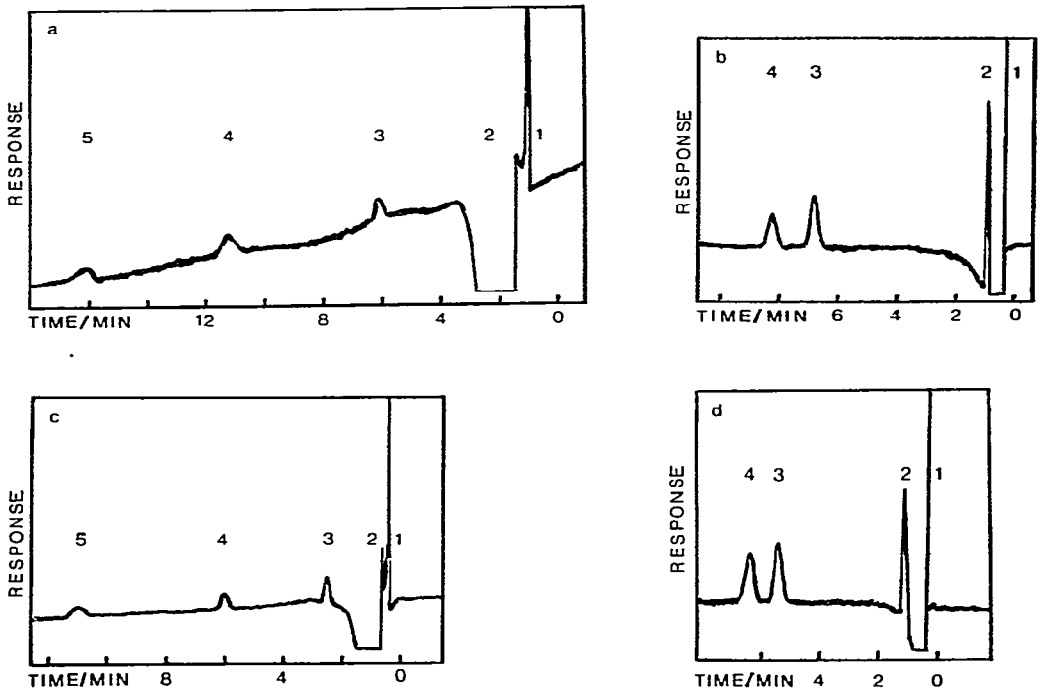

Fig. 2. Chromatograms of cyclohexylamine, aniline and *o*-toluidine on different columns. The packings are described in Table I. Temperatures: injector, 220°C; detector, 250°C. a, Chromosorb 103. Column temperature: 240°C. Solutes: 1 = ammonia; 2 = hexane solvent; 3 = cyclohexylamine; 4 = aniline; 5 = *o*-toluidine; concentrations of 500 ppm of 1 and 0.4 ppm of 3–5. Sample size: 3.4 μl. Attenuation: $1 \cdot 10^{-12}$ a.u.f.s. b, Carbowax 20M (no. 4 in Table I). Column temperature: 150°C. Solutes: 1 = hexane solvent; 2 = cyclohexylamine; 3 = aniline; 4 = *o*-toluidine; concentration 0.4 ppm each. Sample size and attenuation as in a. c, Carbopack B. Column temperature: 190°C. Solutes 1–5 as in a; concentrations of about 500 ppm of 1 and 0.1 ppm of 3–5. Sample size and attenuation as in a. d, Superpak 20M. Column temperature: 190°C. Solutes 1–4 and concentrations as in b. Sample size and attenuation as in a.

gives an interesting elution order for the most volatile amines, with trimethylamine being eluted first and well separated from the others. In combination with Pennwalt 223, this packing can be used as an alternative to Carbopack B for the analysis of volatile amines.

The determination of trimethylamine in low concentrations is complicated by its insufficient separation from ammonia, which is eluted shortly before trimethylamine. However, it is still possible to analyse trimethylamine by keeping the ammonia concentration low and using the high selectivity, in the order of 10^4:1 for trimethylamine over ammonia. Trimethylamine, being a tertiary amine, is not as strongly adsorbed as primary and secondary amines. A concentration of 15–25 ppm ammonia is sufficient to control the reproducibility. This would allow determination of trimethylamine at a level of 0.01 ppm.

Water as solvent

Pennwalt 223 can be used with water as a solvent, although some problems still

exist, see ref. 1. Recent investigations indicate a slight decrease in detector sensitivity when the water is eluted. In practice, this is only a problem when analyzing short-chain volatile amines. The water is eluted before a long-chain amine and the detector sensitivity is restored when the amine reaches the detector. Volatile amines, preferably analysed at about 60–80°C, are eluted before the water peak. To restore the detector sensitivity before the next analysis, the temperature can be increased to about 120–140°C for some minutes. The total analysis time will be about twice the elution time for the last volatile amine peak in the chromatogram.

On Carbopack B water causes strong interference with ghost peaks and baseline drift. A decrease in the sample size to less than 1 μl somewhat improves this situation. However, Di Corcia *et al.*[6] have described a modification of the Carbopack B packing with only 0.3% KOH which further improves the column behaviour. The favourable effect of decreasing the percentage of KOH from 0.8 to 0.3% is in accordance with recent findings on packings with Carbowax 20M, KOH and Chromosorb W AW[7]. It was found that 1–2% KOH is sufficient to markedly decrease the adsorption of amines. This fact, together with a high percentage of Carbowax 20M, results in a high contribution of partition to the retention mechanism, which improves the separation efficiency.

The ratio of the percentage of KOH and Carbowax (about 1:10) suggested in this investigation is of the same magnitude as that used by Di Corcia *et al.*[6]. Injection of 2 μl water on Chromosorb 103 gives an interfering peak in the analysis of low-boiling amines. The restoration of the baseline level after the water is eluted is slow, which makes this packing a poor choice also for the analysis of long-chain amines in water solutions.

Carbowax 20M (no. 4) can be used for analysis of amines in water solution but the separation efficiency for volatile amines is poor and the reproducibility of peak areas is not as good as on Pennwalt 223. The last observation is true also for the modified Superpak 20M packing (no. 5).

In conclusion, we have found that Pennwalt 223 seems to be the best all-round packing. However, when using non-aqueous solvents, Carbopack B (no. 2) and Chromosorb 103 (no. 3) are almost equally as good. One disadvantage of Chromosorb 103 is the longer time necessary to obtain a steady baseline, after a change in column temperature, compared with the other packings. It should be noted that the results indicate that the choice of a nitrogen selective detector and the addition of ammonia is in many cases more important than the choice of column packing.

REFERENCES

1 M. Dalene, L. Mathiasson and J. Å. Jönsson, *J. Chromatogr.*, 207 (1981) 37.
2 S. B. Dave, *J. Chromatogr. Sci.*, 7 (1969) 389.
3 R. E. Poulson, *J. Chromatogr. Sci.*, 7 (1969) 152.
4 A. Di Corcia and R. Samperi, *Anal. Chem.*, 46 (1974) 977.
5 K. Kuwata, Y. Yamazaki and M. Uebori, *Anal. Chem.*, 52 (1980) 1980.
6 A. Di Corcia, R. Samperi and C. Severini, *J. Chromatogr.*, 170 (1979) 325.
7 A. M. Olsson and J. Å. Jönsson, in A. Zlatkis (Editor), *Advances in Chromatography 1981*, Chromatography Symposium, Houston, TX, 1981, p. 149.