Journal of Chromatography, 170 (1979) 325–329

CHROM. 11,535

IMPROVEMENTS IN THE GAS CHROMATOGRAPHIC DETERMINATION OF TRACE AMOUNTS OF ALIPHATIC AMINES IN AQUEOUS SOLUTION

ANTONIO DI CORCIA, ROBERTO SAMPERI and CLAUDIO SEVERINI
Istituto di Chimica Analitica, Università di Roma, 00185 Rome (Italy)
(Received October 24th, 1978)

SUMMARY

The analysis of aliphatic amines at the parts per million level in aqueous solution has been improved with respect to a previously reported chromatographic method which made use of Carbopack B modified with 0.8% potassium hydroxide and 4% PEG 20M by altering these concentrations to 0.3% and 4.8%, respectively, by using a modified coating procedure. By this means, difficulties in duplicating from batch to batch the chromatographic characteristics of the column packing have been eliminated, and the instability of the retention times of amines on prolonged use of the column, the intolerance of the packing to injections of water and overlapping of tailed peaks for alcohols with the amine peaks no longer affect the trace determination of amines.

INTRODUCTION

Erratic or irreproducible results are often obtained when the quantitative determination of very dilute aqueous solutions of low-boiling aliphatic amines by gas chromatography is attempted. In recent years, very few papers have suggested effective improvements to the trace determination of free aliphatic amines. Dunn *et al.*[1] developed a method for separating trace amounts of free dimethylamine from trimethylamine contained in biological samples with over 85% resolution and very little tailing. However, methylamine in the sample interfered.

Graphitized carbon black (Carbopack B) deactivated with potassium hydroxide and partially covered with either polyethylene glycol (PEG) (Carbowax) 20M[2] or polyethyleneimine (PEI) 40M[3] permitted the determination of C_1–C_4 aliphatic amines in aqueous solution at the parts per million level.

The long-term use of Carbopack B modified with 4% PEG 20M and 0.8% potassium hydroxide has revealed certain deficiencies with this packing. First, it has been found difficult to reproduce its selectivity characteristics routinely. In some instances, only a partial separation of dimethylamine and ethylamine is obtained. Secondly, when the column is in continuous use a slight but uninterrupted decrease in the retention times of the amines is observed. Thirdly, the peaks for methylamine and ethylamine occasionally exhibit some tailing. Fourthly, a baseline disturbance

is caused by the injection of the aqueous sample, which can interfere in the determination of ethyl-, trimethyl- and propylamine. Finally, it has been found that when alcohols are present in large amounts in a sample, their peaks, especially that of methanol, tail severely and obscure the amine peaks. This effect is probably due to anomalous interactions between the alcoholic eluates and potassium hydroxide.

The object of this paper is to show that a modified procedure for coating the Carbopack surface improves both the batch-to-batch reproducibility of this packing and the symmetry of the peaks of primary amines. Moreover, it has been found that if the concentration of potassium hydroxide is decreased to 0.3%, untailed peaks for both amines and alcohols are obtained. In particular, the simultaneous determination of C_1–C_4 aliphatic amines, C_1–C_3 alcohols and acetone at the parts per million level can be accomplished by modifying Carbopack B with 0.3% potassium hydroxide and 4.8% PEG 20M. When this column packing is used, the chromatographic profile is not affected by water and changes in elution times during continuous use of the packing are eliminated.

EXPERIMENTAL

Carbopack B, which is a graphitized carbon black with a surface area of about 100 m^2/g, was supplied in the 60–80 mesh range by Supelco (Bellefonte, Pa., U.S.A.). It was ground and sieved to 100–120 mesh.

The coating of the Carbopack surface is critical and must be carried out correctly in order for good and reproducible results to be obtained. The column packing was prepared by dissolving a weighed sample of potassium hydroxide in methanol and adding the solution to a known weight of Carbopack B in a flat dish. The total amount of solvent must be such that its level is no more than few millimetres above the level of the adsorbing solid particles. The bulk of the solvent was evaporated so that the Carbopack particles became a slush-like mass, which was then stirred thoroughly with a spatula until the material became dry. By this means, a regular distribution of potassium hydroxide on the Carbopack surface was achieved. If stirring of the Carbopack particles was not carried out, we found that the deposition of potassium hydroxide from methanol occurred mainly on the Carbopack particles in the upper layers of the bed. The extent of this effect depends on the rate of evaporation of the methanol.

The same procedure was followed when PEG 20M dissolved in methylene chloride was added to potassium hydroxide-modified Carbopack B.

The dried material was re-sieved to maintain the required mesh range and was packed into a 1.8 m × 0.15 cm I.D. glass column by a procedure described elsewhere[4].

The column packed with Carbopack B modified with 0.3% potassium hydroxide + 4.8% PEG 20M was conditioned at 220° for 15 h. Before using this column, 5-μl volumes of water were injected 30 times in rapid succession at the conditioning temperature. After about 10 min, the column was cooled to the operating temperature. Injections of water at 220° must also be made when the column has not been used for a long time.

A gas chromatograph (Model GI, Carlo Erba, Milan, Italy) equipped with a flame-ionization detector was used.

Hydrogen containing less than 2 ppm of both oxygen and water was used. To dilute it and to optimize the sensitivity of the detector, nitrogen was added at the column outlet with a flow rate 1.5–1.7 times that of hydrogen.

RESULTS AND DISCUSSION

Fig. 1 shows the chromatogram of an aqueous mixture containing about 3 ppm of low-boiling aliphatic amines and alcohols obtained on Carbopack B modified with 0.3% potassium hydroxide and 4.8% PEG 20M.

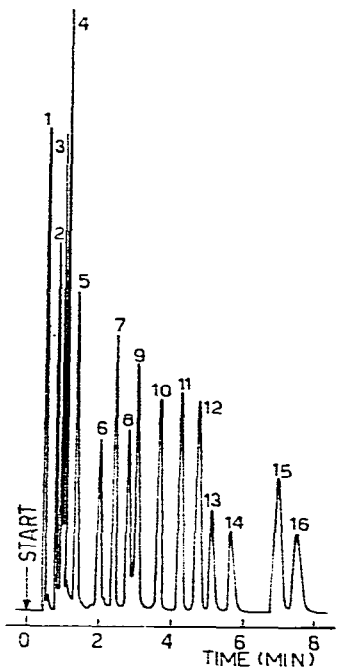

Fig. 1. Chromatogram showing the separation of C_1–C_4 aliphatic amines, C_1–C_3 alcohols and acetone. Column, 1.8 m × 1.5 mm I.D., Carbopack (100–120 mesh) + 0.3% potassium hydroxide and 4.8% PEG 20 M. Concentration, about 3 ppm of each individual component; sample size, 1.5 μl; column temperature, 76°; injection port temperature, 200°; carrier gas, hydrogen; dead time, 15.8 sec; make-up gas, nitrogen at a flow-rate 1.5–1.7 times than that of hydrogen. Peaks: 1 = methylamine; 2 = dimethylamine; 3 = ethylamine; 4 = trimethylamine; 5 = methanol; 6 = isopropylamine; 7 = acetone; 8 = *n*-propylamine; 9 = ethanol; 10 = *tert.*-butylamine; 11 = diethylamine; 12 = isopropanol; 13 = *sec.*-butylamine; 14 = isobutylamine; 15 = *n*-propanol; 16 = *n*-butylamine.

It can be seen that peaks without tails were obtained for a few nanograms of primary aliphatic amines. Similar peak symmetry can be obtained by coating the Carbopack surface with 0.8% potassium hydroxide and 4% PEG 20M[2], provided that the same coating procedure is followed. In contrast, when both column packings were prepared as reported elsewhere[2], some tailing of the amine peaks invariably occurred. This demonstrates that the previous coating procedure[2] results in non-homogeneous deposition of potassium hydroxide, which causes insufficient deactivation of some active centres of the Carbopack surface.

Difficulties found in the past in duplicating the column packing for amine

analysis can also be ascribed to insufficiently controlled deposition of PEG 20M during evaporation of the solvent. We prepared many batches of Carbopack B modified both with 0.3% potassium hydroxide + 4.8% PEG 20M and 0.8% potassium hydroxide + 4% PEG 20M by modifying the coating procedure as reported above. In no instance did we note batch-to-batch variations of the retention times for amines (within ±1%).

Alcohols, especially methanol, are eluted as tailed peaks on Carbopack B modified with 0.8% potassium hydroxide + 4% PEG 20M. When alcohols were present in large amounts in the sample, we found that the determination of amines was not possible because the alcohol peaks obscured the amine peaks. Moreover, the extent of the peak broadening for an alcohol was found to be dependent on the amount of potassium hydroxide deposited on the Carbopack surface. This effect is probably due to anomalous interactions which can take place between compounds that contain hydroxyl groups and potassium hydroxide when the latter is present in too large amounts. This drawback was eliminated simply by decreasing the concentration of potassium hydroxide to 0.3%. At this concentration, as can be seen, amines are still eluted without peak tailing and no anomalous interactions occur between the alcohols and the potassium hydroxide-modified Carbopack.

A concentration of PEG 20M of 4.8% was found to be effective in avoiding overlapping of amine and alcohol peaks.

A serious deficiency of the previous column packing for amines (Carbopack B coated with 0.8% potassium hydroxide and 4% PEG 20M) is that retention times and separation factors change during the use of the column at the operating temperature. In order to evaluate the stability of the column packing over a prolonged period of use, two sets of experiments were carried out by using two columns, one packed with the previous column packing and the other with Carbopack B modified with 0.3% potassium hydroxide + 4.8% PEG 20M.

The two columns were conditioned at 220° for 15 h and then 30 injections of 5-μl volumes of water into both columns were made. After 10 min, the columns were cooled to 76°. At this temperature, 1.5-μl volumes of an aqueous solution of amines were injected five times into both two columns and the mean retention times of the amines were measured. The same operation was repeated after continuous use of the columns for 24 h. A decrease in the retention times (8.3% for *n*-butylamine) was measured for the column packed with Carbopack B coated with 0.8% potassium hydroxide + 4% PEG 20M, whereas the other column did not show variations in the retention times. Experiments were carried out with Carbopack B modified with 0.3% potassium hydroxide + 4.8% PEG 20M for a further 4 days by injecting each day 1.5 μl of an aqueous solution of amines. Even in this instance we did not observe any variation in the chromatographic characteristics of the column packing. The column was then capped and stored for 25 days, then operated again at 76°. In this instance we noted an inexplicable decrease of 21% in the retention times of amines. The column temperature was subsequently increased to 220° and, after several hours, water was injected by following the procedure described above. The column packing was regenerated as the retention times of the amines and separation factors at 76° returned to those obtained 1 month earlier. The regenerated column was again kept in use for 5 days at 76° and no variations in the chromatographic characteristics were observed.

The different behaviour of the two column packings examined may be accounted for by a slow reaction between potassium hydroxide and the terminal hydroxyl groups of the PEG 20M, provided that the surface concentration of the basic deactivating agent on Carbopack is relatively large. In this hypothesis, during the use of the column packing the slow but continuous decrease in the retention times of polar compounds is caused by the slow decrease in the polarity of the stationary phase.

As can be seen, Carbopack B modified with 0.3% potassium hydroxide + 4.8% PEG 20M was not affected by injections of water. When the column packing is used for the first time, an interferring peak due to water appears initially between the methanol and isopropanol peaks, but this becomes negligible after five or six injections of water at the operating temperature. The same is not true when Carbopack B modified with 0.8% potassium hydroxide and 4% PEG 20M is used. In this instance, the water interferes in the analysis of amines in aqueous solution at the parts per million level. This effect can be explained by a decrease in the chemical inertness of PEG 20M towards water as the basicity of the substrate increases.

REFERENCES

1 S. Dunn, M. Simenhoff and L. Wesson, *Anal. Chem.*, 48 (1976) 41.
2 A. Di Corcia and R. Samperi, *Anal. Chem.*, 46 (1974) 977.
3 A. Di Corcia, A. Liberti and R. Samperi, *J. Chromatogr. Sci.*, 12 (1974) 710.
4 A. Di Corcia, A. Liberti and R. Samperi, *J. Chromatogr.*, 122 (1976) 459.