Gas chromatographic determination of amines in aqueous solution

The gas chromatographic separation and identification of organic compounds in aqueous solution presents some problems owing to excessive tailing of the water peak. Various ways of treating the aqueous solutions before injection into the column have been described[1,2]. One method[1] proposed diluting the sample with an inert solvent followed by dehydration with Na_2SO_4. Another method[2] involved non-aqueous extraction of the solutes by organic solvents.

The use of highly polar stationary phases, which act as water retardants and thus increase the time available for chromatographic separation of low boiling compounds, was also suggested[3–6]. These methods, however, gave only qualitative results. ZAREMBO AND LYSYJ[7] found a column packing suitable for separating alcohols in aqueous solution which gave very satisfactory results.

SMITH AND RADFORD[8] suggested a column packing suitable for separation of aliphatic diamines; however, no quantitative results were reported and the method was not applied to aqueous solutions of amines.

In the present work, this column[8] was used for the quantitative separation of a variety of amines in aqueous solution.

Experimental

Equipment. An Aerograph Model A-350 Gas Chromatograph with a thermal conductivity detector was used in the present work. A Honeywell 1 mV revorder was used with the chromatograph and helium was the carrier gas. The column was a copper spiral 2½ m long, 5 mm I.D., packed with 20 % carbowax 20 M coated with 5 % KOH on Chromosorb W, 30–60 mesh (Johns Manville).

Procedure. Aqueous solutions of allyl-, propyl-, butyl-, di-*n*-butyl- and benzylamines were prepared. Five microliters of the solution were injected into the column, which was kept at 70°.

After the elution of the three lower amines, allyl-, propyl-, and butylamine (Fig. 1), programming was started and the column temperature was raised to 180° at a rate of 10 degrees per min. The other peaks were eluted in the following order: di-*n*-butylamine, water, benzylamine (Fig. 1).

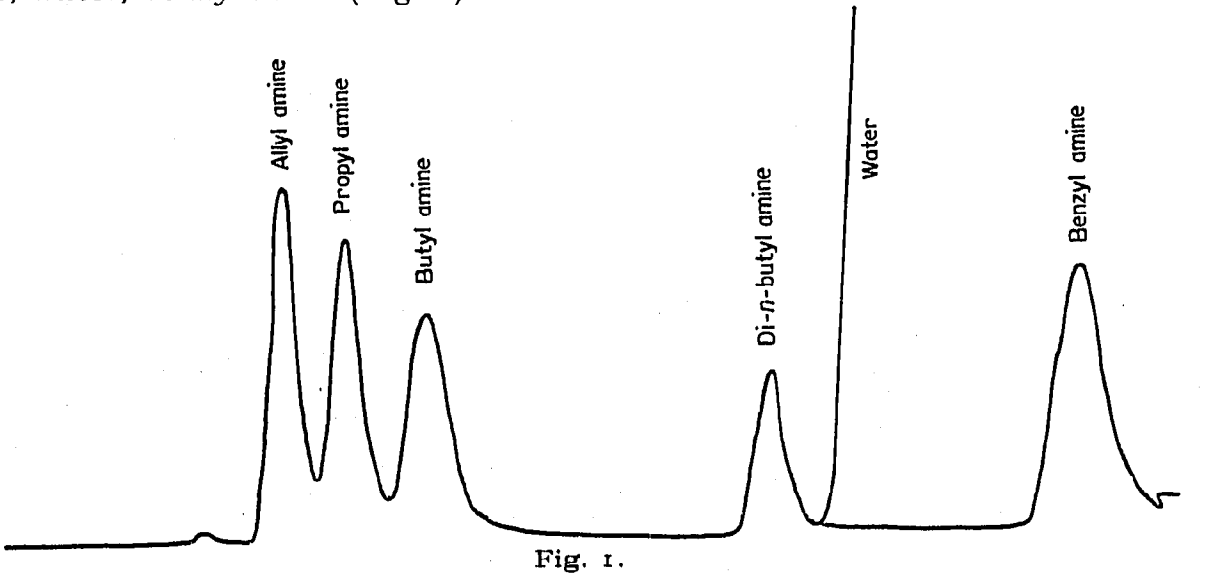

Fig. 1.

TABLE I

Run No.*	Allylamine			Propylamine			Butylamine			Di-n-butylamine			Benzylamine		
	Weight %	Area %	Deviation %	Weight %	Area %	Deviation %	Weight %	Area %	Deviation %	Weight %	Area %	Deviation %	Weight %	Area %	Deviation %
1	20.0	20.2	+1.0	20.0	19.0	—5.0	20.0	19.9	—0.5	20.0	20.4	+2.0	20.0	20.4	+2.0
2	20.0	19.6	—2.0	20.0	20.2	+1.0	20.0	20.7	+3.5	10.0	11.2	+12.0	30.0	28.2	—6.0
3	22.4	24.0	+7.1	22.4	22.0	—1.8	22.4	23.8	+6.2	5.5	5.4	—2.0	27.3	24.8	—9.1
4	15.0	15.3	+2.0	25.0	25.4	+1.6	30.0	29.7	—1.0	10.0	10.3	+3.0	20.0	19.3	—3.5
5	15.0	15.2	+1.3	15.0	14.0	—6.6	35.0	35.4	+1.1	10.0	19.9	—1.0	25.0	23.6	—5.6
6	22.2	22.7	+2.2	22.2	22.7	+2.2	22.2	22.4	+0.9	11.1	10.8	—2.7	22.2	21.6	—2.7
7	33.3	35.0	+5.1	11.1	10.8	—2.7	22.2	21.2	—4.5	11.1	11.6	+4.5	22.2	21.6	—2.7
8	10.0	10.5	+5.0	15.0	15.0	0.0	35.0	33.2	—5.1	15.0	13.3	—11.0	25.0	25.8	+3.2
9	22.2	21.7	—2.3	22.2	21.3	—4.0	33.3	33.4	+0.3	11.1	12.3	+10.8	11.1	11.3	+1.8
	Average dev.: ±2.15			Average dev.: ±1.7			Average dev.: ±0.1			Average dev.: ±1.7			Average dev.: ±2.5		

* Run No. 1: mixture of dry amines; runs 2–5: 20% amines and 80% water; runs 6–9: 90% amines and 10% water.

Results and Discussion

No attempts were made to determine quantitatively the water concentration under the described conditions. The calculation of the individual amine concentrations was made assuming the total area under the amine peaks as 100 %.

The results are presented in Table I.

It will be seen that the average error does not exceed ± 2.5 % although in some cases maximum errors of about 10 % were recorded.

Application

This method was applied to the analysis of propylamine in a complex mixture containing in addition to acrylonitrile, propionitrile, adiponitrile and potassium chloride, in acid solution. Butylamine was added as a marker.

On neutralization with NaOH, two phases appeared. The mixture was vigorously stirred with a magnetic stirrer and samples were withdrawn for chromatographic analysis during the stirring.

The determination of propylamine by the present method gave reproducible results, within the limits of ± 2.5 %.

The nitriles were determined on a separate column, as described earlier[1].

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Color detection of bile acids using thin-layer chromatography

There is common agreement that the usefulness of R_F values in thin-layer chromatography (TLC) is limited. To solve this difficulty relative mobility values are often suggested. However, use of these values, as well as of R_F, is at times unsatisfactory because of the problems of concave solvent fronts and/or incomplete separation of some acids having similar mobilities[1,2].

Recently KRITCHEVSKY, MARTAK AND ROTHBLAT[3] have demonstrated the usefulness of color detection in bile acid identification.

The present study expands on the use of color detection with particular stress