Notes

CHROM. 5076

The use of ammonia as the carrier gas in gas–liquid chromatography

In the course of our work on gas chromatographic separation of some amines, it was found that ammonia is of special interest as a carrier gas not only for chromatography of amines* but for a number of other compounds as well.

Experimental

All separations were performed on a homemade all-glass capillary chromatograph with a flame ionisation detector (FID). Capillaries were of borosilicate glass (0.25 or 0.40 mm I.D., 30–80 m in length) coated with the liquid phase as described[2]. Carbowax 4000 and Soviet methyl, phenyl and β-cyanoethyl polysiloxanes were tested as liquid phases[3]. Ammonia was fed directly into the gas system from a 1-l tank with a needle valve. The inlet pressure was 0.3–1.5 atm. Excess ammonia escaping through the splitting system (split ratio, 1:50) was captured by the water pump suction.

Results and discussion

FID sensitivity. An interesting property of ammonia as the carrier gas is that it enhances the sensitivity of the FID to an order of magnitude almost comparable with nitrogen. The baseline, at the same time, is exellent**.

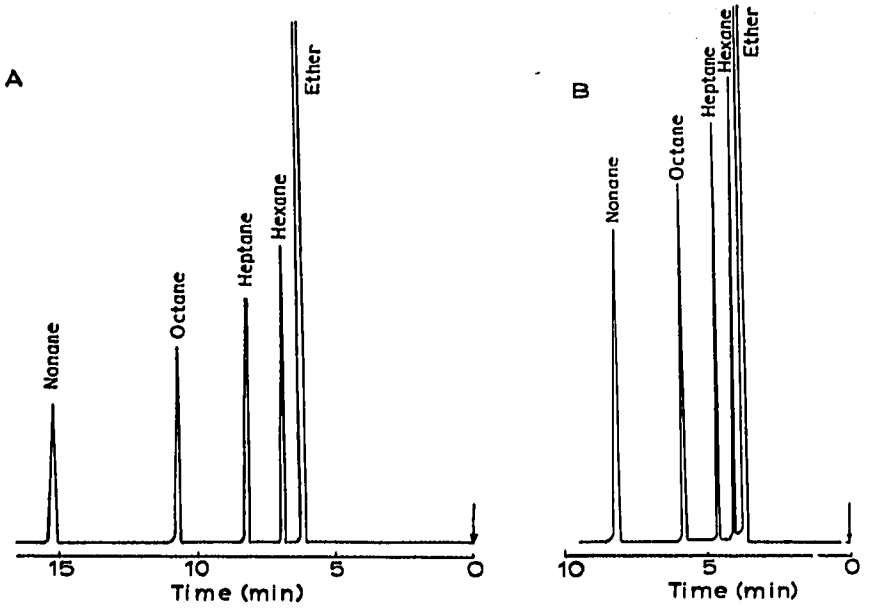

Fig. 1. Chromatogram of normal hydrocarbons. Glass capillary column (40 m, 0.25 mm I.D.). Liquid phase: phenyl polysiloxane. Temperature: 85°. Inlet pressure: 0.6 atm. (A) Carrier gas: nitrogen. (B) Carrier gas: ammonia.

* Ammonia (in a mixture with nitrogen) was recommended for converting hydrochlorides of the amino acid esters into free bases directly in the evaporator[1].

** When switching over from nitrogen to ammonia, the detector current increases slightly (see ref. 1).

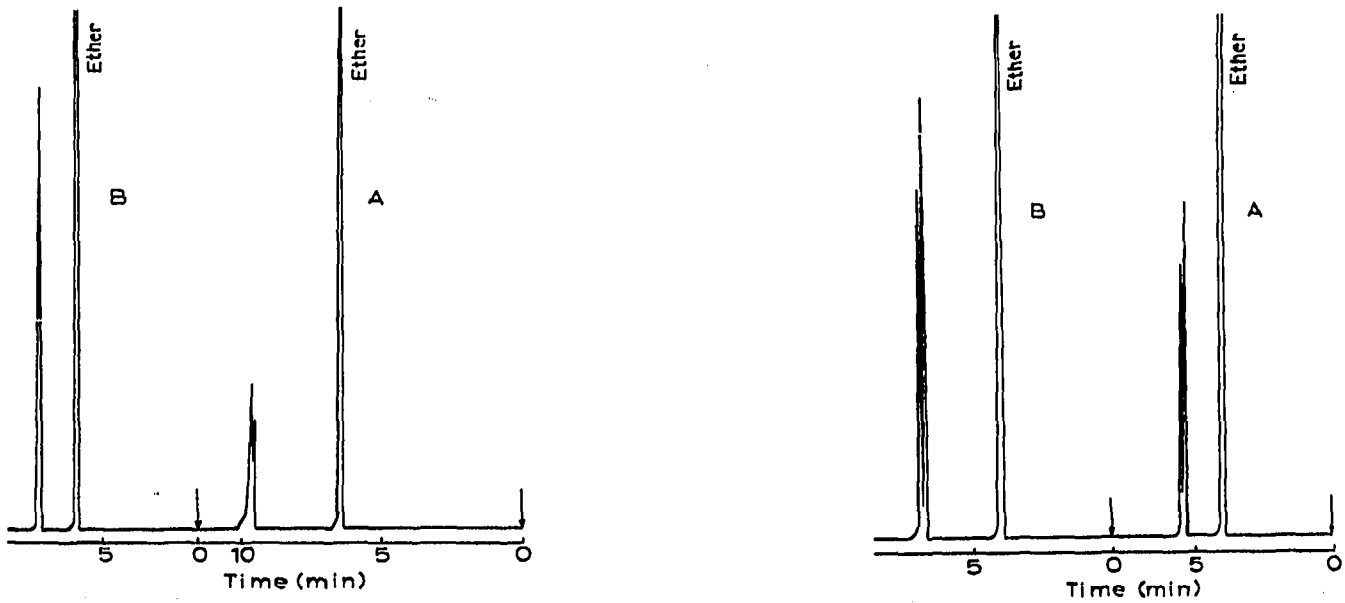

Fig. 2. Chromatogram of *cis-* and *trans*-1,3,5-trimethylpiperidines. (A) Carrier gas: nitrogen. (B) Carrier gas: ammonia. Inlet pressure: 0.6 atm. Temperature: 120°. Column: see legend to Fig. 1.

Fig. 3. Chromatogram of *cis-* and *trans*-N-methylperhydropyridine (A) and *cis-* and *trans*-N-methyldecahydroquinoline (B). Carrier gas: ammonia. Inlet pressure: 0.6 atm. Temperature: 160°. Column: see legend to Fig. 1.

Retention times. As may be seen from Fig. 1 A, B, for normal paraffins ammonia yielded almost half the retention times that nitrogen did. At the same time, the actual separation of these mixtures and the shape of their peaks do not alter when the carrier gas is changed. For other compounds (*e.g.* see Fig. 2), separation may change if the carrier gas is changed.

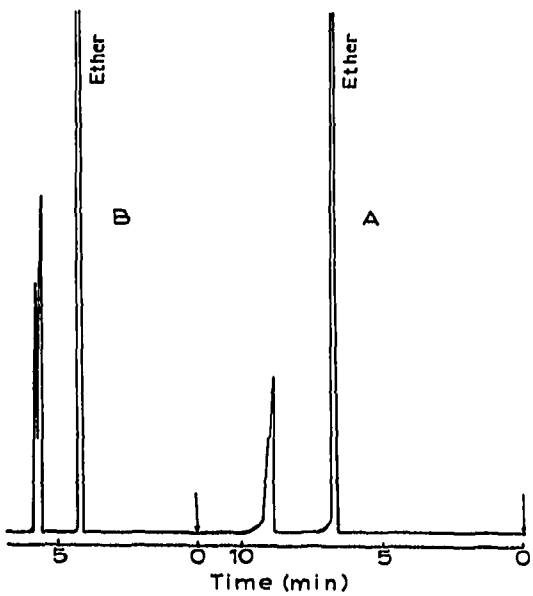

Fig. 4. Chromatogram of *cis-* and *trans*-3,5-dimethylpiperidines. (A) Carrier gas: nitrogen. (B) Carrier gas: ammonia. Inlet pressure: 0.6 atm. Temperature: 125°. Column: see legend to Fig. 1.

Thermal stability of liquid phases. With ammonia as carrier gas no excessive bleeding was noticed with the polyether and polysiloxane liquid phases studied. Some polysiloxane capillary columns were run for a long time (several months) at temperatures up to 200–250° with no signs of deterioration.

Chromatography of amines. In Figs. 3 and 4 are shown some chromatograms of amines obtained with nitrogen and ammonia as carrier gases. These chromatograms indicate the substantial reduction of tailing and, in some cases, remarkable increase in separation (see Fig. 4). Here the tail-reducing property of ammonia only on polysiloxane liquid phases deserves special comment. On polyethylene glycol*, ammonia has no obvious effect on peak shapes except for shortening the retention times. Thus, tail-reduction seems to be connected with the competitive interaction of amines and ammonia with silicone atoms of the liquid phase.

The results of this preliminary research show that ammonia as the carrier gas may be advantageously used for chromatography of amines and other compounds non-reactive towards ammonia.

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* Coated on KOH-treated glass columns.