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AMMONIA AS A CARRIER GAS AND FLAME-FORMING AGENT IN GAS CHROMATOGRAPHY

V. G. BEREZKIN and L. A. SHKOLINA

A. V. Topchiev Institute for Petrochemical Synthesis, Academy of Sciences of the U.S.S.R., Leninsky pr. 29, Moscow B-71 (U.S.S.R.)

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SUMMARY

The advantage of using ammonia as a carrier gas in gas chromatography, especially in long packed capillary columns, has been studied. The use of ammonia makes it possible to decrease the pressure gradient, to reduce the HETP value and to improve other chromatographic and operating parameters.

The use of ammonia for flame formation in a flame ionization detector is proposed. It has been established that in this case the sensitivity of detecting chlorinated hydrocarbons increases compared with hydrogen flame ionization detectors (FID).

INTRODUCTION

According to Darcy's law, the pressure gradient of a flowing medium is proportional to the viscosity. Therefore, the use of carrier gases with low viscosity makes it possible to obtain high velocities using a smaller pressure gradient. This fact is of essential importance in packed capillary columns^{1,2} since their lengths and relatively low permeability call for elevated pressures (4-7 atm) at mean values of the carrier-gas linear velocity of 3-10 cm/sec.

Because of this, preference is often given to hydrogen. However, owing to its small density and, consequently, the higher molecular diffusion of the analysed compounds in it, the efficiency of a separation is reduced. Hydrogen is also extremely explosive. Investigations are being carried out on the application of ammonia as a carrier gas. Saroff *et al.*³ were the first to use a mixture of ammonia and nitrogen to convert hydrochlorides of amino acid esters into free bases directly in the flash evaporator of a chromatograph. Ilkova and Mistryukov⁴ have shown that the use of ammonia, compared with nitrogen as a carrier gas, reduces the retention time, the separation value being the same. They also observed an improvement in peak symmetry for nitrogen-containing compounds and a slight increase in the detector sensitivity. An improvement in peak symmetry by adding ammonia to carrier gas has been made by other authors⁵.

In this paper the possibility of using ammonia as a carrier gas in long packed capillary columns as well as a flame-forming agent in an FID is considered.

RESULTS AND DISCUSSION

Nitrogen, helium, and ammonia were chosen for comparison. Their physical properties are given in Table I.

It is preferable to use ammonia as a carrier gas since its viscosity is 1.8 times less than that of nitrogen and 2 times less than that of helium. The density of ammonia

TABLE I
PHYSICAL PROPERTIES OF CARRIER GASES⁶

Property	Nitrogen	Helium	Ammonia
Viscosity (10^6 P)	175	194	98
Density (g/l)	0.967	0.138	0.597

TABLE II
THE VALUES OF $H_{min.}$ AND OF THE TERM C IN PACKED CAPILLARY COLUMNS FOR VARIOUS CARRIER GASES

Column, 5.5 m \times 0.8 mm I.D.; packing, Chromaton-N (100-120 mesh) impregnated with 3% potassium hydroxide and 10% Apiezon L.

Compound	$H_{min.}$ (mm)			$C \times 10^2$ (sec)		
	Nitrogen	Ammonia	Helium	Nitrogen	Ammonia	Helium
Heptane	0.82	0.85	1.0	2.0	1.5	0.8
Octane	0.65	0.70	0.84	2.4	1.7	1.2
Toluene	0.74	0.68	0.92	1.6	1.2	0.8
<i>m</i> -Xylene	0.66	0.63	0.82	1.7	1.4	0.9

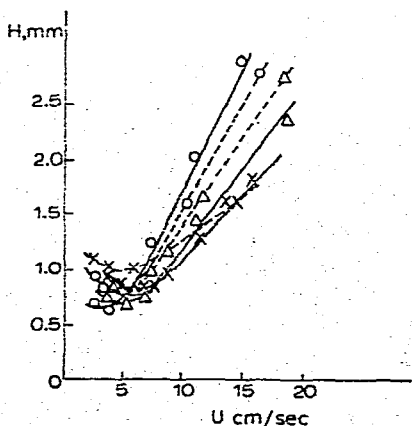


Fig. 1. H as a function of the average linear velocity (u) of the carrier gases nitrogen (O), helium (X) and ammonia (Δ). Solid line = octane; dashed line = heptane.

is intermediate between those of nitrogen and helium. Therefore, the diffusion coefficients of components are considerably higher in ammonia than in nitrogen, which must result in an increased efficiency (if the band broadening is due to mass transfer in a mobile phase).

In order to confirm the above assumptions, the relationship between the column efficiency and the nature of the carrier gas has been investigated. Experiments were run in a glass spiral column (5.5 m × 0.8 mm I.D.) packed with Chromaton-N, 160–200 mesh, (Lachema, Brno, Czechoslovakia) treated with 3% potassium hydroxide and impregnated with 10% Apiezon L. The dependence of H (the height equivalent to a theoretical plate) on the average linear velocity of the carrier gases, e.g., at 97° for hydrocarbons is shown in Fig. 1. It follows from Fig. 1 and Table II, that the value of $H_{min.}$ for aliphatic hydrocarbons is slightly higher (1.05 times) with ammonia as carrier gas than with nitrogen and 1.2 times lower compared to the values obtained with helium. For aromatic hydrocarbons, the value of $H_{min.}$, obtained when ammonia is used, is 1.07 times lower than that obtained with hydrogen as carrier gas and 1.3 times lower than that obtained with helium.

For every compound studied, the C value (the C term in the Van Deemter equation), obtained with ammonia as carrier gas, is intermediate between the C values obtained with nitrogen and helium as carrier gases. The replacement of nitrogen with ammonia reduces the value of C by a factor of approximately 1.3.

Thus, the experimental results indicate that, without increasing the value of $H_{min.}$, the use of ammonia, compared with nitrogen as a carrier gas, reduces the resistance to mass transfer. In comparison with helium, ammonia considerably increases the efficiency. Hence, the use of ammonia as a carrier gas in packed capillary columns is well justified when one bears in mind the main advantage, namely the small pressure gradient. Thus, for the column used in these experiments the inlet pressure for ammonia as carrier gas (3.8 atm) is 1.5 times lower than that for nitrogen (5.9 atm) and 1.6 times lower than that for helium (6.2 atm).

The benefits of using ammonia as carrier gas to speed up an analysis are illustrated by the separation of alkylcyclohexanol. (The analysis was carried out at 160° on a column (14.8 m × 0.8 mm I.D.) packed with Chromosorb W and 5% Carbowax 20M. 32 peaks were registered on the chromatogram). The results presented in Table III show that the use of ammonia instead of nitrogen reduces the analysis

TABLE III

RESULTS OF ALKYL CYCLOHEXANOL SEPARATION USING DIFFERENT CARRIER GASES

Column, 14.8 mm × 0.8 mm I.D.; temperature, 160°; packing, Chromosorb W impregnated with 5% Carbowax 20M.

Carrier gas	Inlet pressure (atm.)	Average linear carrier gas velocity (cm/sec)	Run time (min)
Nitrogen	8.5	4.0	130
Ammonia	5.0	4.0	125
Ammonia	7.5	6.2	82

TABLE IV

SENSITIVITY OF AMMONIA AND HYDROGEN FLAME IONIZATION DETECTOR TOWARDS SOME ORGANIC COMPOUNDS

Column, 1 m \times 2 mm I.D.; temperature, 80°; packing, Chromosorb W impregnated with 3% potassium hydroxide and 10% Apiezon L. Hydrogen and air flow-rates 20 and 200 ml/min, respectively; ammonia and oxygen flow-rates 30 and 200 ml/min, respectively.

Compound analyses	Ratio of sensitivity of ammonia detector to that of hydrogen detector	Relative correction factor	
		Ammonia detector	Hydrogen detector
Hexane	2.4	0.98	0.77
Octane	1.9	1.00	1.00
Benzene	1.9	1.00	1.00
Ethanol	2.3	0.48	0.34
Butylamine	2.1	0.64	0.57
Hexamethylenimine	2.0	0.74	0.68
Chloroform	5.2	0.28	0.11
Carbon tetrachloride	10.3	0.39	0.07

time by a factor of 1.6 without the separation deteriorating. When the run time is the same, the resolution is better, the inlet pressure being 1.7 times lower.

Thus, the use of ammonia as a carrier gas has the following advantages: (1) lower pressure gradient owing to smaller viscosity, which is very important for long packed capillary columns; (2) the value of H_{min} in the case of ammonia is approximately the same as for nitrogen and considerably lower than for helium; (3) the symmetry of chromatographic bands sometimes improves owing to adsorption of ammonia on active sites of solid support; (4) the capacity of cylinders filled with ammonia is greater than those filled with permanent gases which makes it possible to replace the cylinders less often and to employ small cylinders for portable chromatographs.

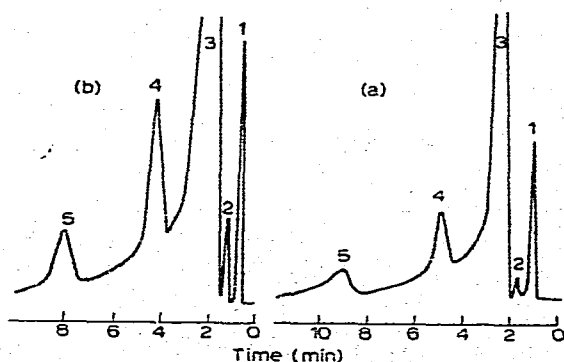


Fig. 2. Chromatograms of artificial mixture (85.6% benzene, 3.7% ethanol, 3.7% chloroform, 3.5% octane, 3.5% hexamethylenimine); (a) Hydrogen FID; (b) ammonia FID. Experimental conditions: column, 1 m \times 2 mm I.D.; adsorbent, 10% Apiezon L and 3% potassium hydroxide on Chromosorb W; temperature, 80°. Hydrogen and air flow-rates, 20 and 200 ml/min, respectively. Ammonia and oxygen flow-rates, 30 and 160 ml/min, respectively. 1 = Ethanol; 2 = chloroform; 3 = benzene; 4 = octane; 5 = hexamethylenimine.

TABLE V

RESPONSE OF AMMONIA FLAME IONIZATION DETECTOR AS A FUNCTION OF AMMONIA AND OXYGEN FLOW-RATES

Flow-rate (ml/min)		Response of the detector (conventional units)				
NH ₃	O ₂	CHCl ₃	CCl ₄	C ₈ H ₁₈	C ₆ H ₁₁ NH	C ₂ H ₅ OH
25	210	3.9	—	45	29.2	12.2
25	300	4.4	—	45	29	13.6
30	150	7.3	—	30	23.8	13.0
30	180	9.9	—	44	37.5	16.0
30	200	17.0	23	60	43.0	28.0
30	250	13.6	20	67	—	—
40	130	524.0	685	—	—	—
40	300	45.0	—	69	78.0	—
40	330	129.0	—	80	60.0	28.0

Since ammonia burns in oxygen, it was of interest to consider its possible application as a flame-forming agent in a flame ionization detector. For this purpose, without changing the design of the FID used in the Tsvett 1-65 chromatograph, ammonia was fed from the column into the burner nozzle when ammonia was used as carrier gas, and through the channel for hydrogen supply when other gases were used as carriers. In this case oxygen was fed through the air channel. The flow-rates of ammonia and oxygen were 25–40 and 150–330 ml/min, respectively. The sensitivity of an ammonia flame ionization detector towards alkanes, aromatic hydrocarbons, alcohols, and amines is approximately twice that of the hydrogen flame detector⁷ (see Table IV). The sensitivity towards chlorinated hydrocarbons increases by a factor of 5–10 (see Fig. 2), being twice as sensitive to carbon tetrachloride as to chloroform. The relative sensitivity (octane as standard) rises by a factor of 2.6 and chloroform. The relative sensitivity of chloroform and carbon tetrachloride (octane

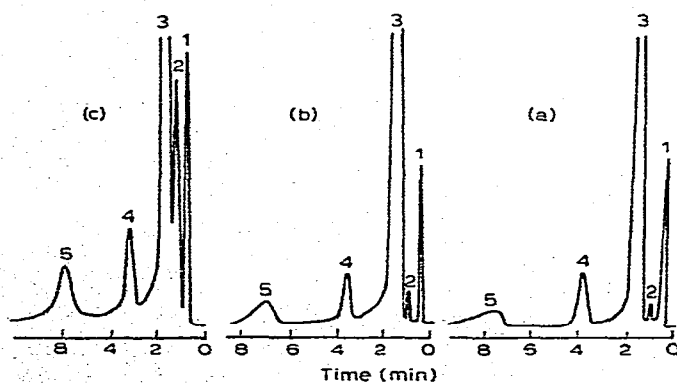


Fig. 3. Chromatograms of artificial mixture (83.4% benzene, 4.1% chloroform, 2.9% octane, 5.5% ethanol, 4.1% hexamethylenimine). (a) Hydrogen FID; hydrogen flow-rate, 20 ml/min; air flow-rate, 200 ml/min; (b) ammonia FID; ammonia flow-rate, 30 ml/min; oxygen flow-rate, 180 ml/min; (c) ammonia FID; ammonia flow-rate, 40 ml/min; oxygen flow-rate, 220 ml/min. 1 = Ethanol; 2 = chloroform; 3 = benzene; 4 = octane; 5 = hexamethylenimine. For experimental conditions see Fig. 2.

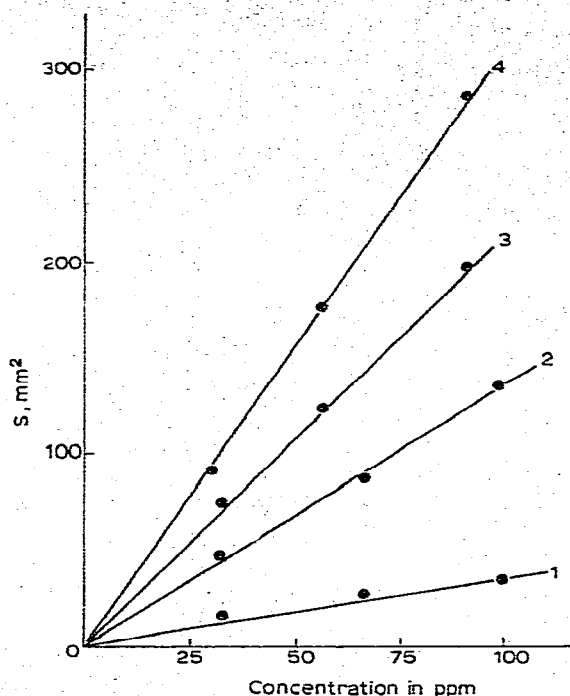


Fig. 4. Response of ammonia FID on component concentration. 1 = Chloroform; 2 = ethanol; 3 = hexamethylenimine, 4 = octane. Ammonia and oxygen flow-rates are 30 and 200 ml/min, respectively.

as standard) rises by a factor of 2.6 and 5.5, respectively, when the hydrogen flame is replaced by ammonia flame (see Table IV). It is known⁸ that the sensitivity of a hydrogen flame ionization detector towards chlorinated hydrocarbons is low and inversely proportional to the number of chlorine atoms in the molecule. The sensitivity towards chlorinated hydrocarbons in an ammonia flame ionization detector rises, evidently, in direct proportion to the number of chlorine atoms in the molecule.

We have also shown that an even higher sensitivity towards all compounds investigated (see Table V) and especially towards chlorinated hydrocarbon (see Fig. 3) can be obtained by changing the ratio between ammonia and oxygen flow-rates. Thus, when the flow-rates of ammonia and oxygen change from 30 to 40 and 250 to 130 ml/min, respectively, the sensitivity towards carbon tetrachloride increases approximately 40-fold. However, under these conditions the detector behaves in a non-linear manner. At ammonia flow-rates up to 30 ml/min the detector operates linearly (see Fig. 4). The main advantages of the proposed detector over a hydrogen one are as follows: (1) noticeable increase in sensitivity towards the organic compounds in question; (2) selective rise in sensitivity towards chlorinated hydrocarbons (5–10-fold); (3) a sharp increase in sensitivity towards chlorinated hydrocarbons, namely by a factor of ten or more in a non-linear region of detection used at present for a qualitative determination of small amounts of these compounds.

An increased background current and corrosive products formed in the flame are the only disadvantages of this detector.

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