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Short communication

## Ammonia as carrier gas in capillary gas–liquid chromatography

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### Abstract

Influence of helium and ammonia as carrier gases on retention of neutral solutes on polyethylene glycol has been studied theoretically and experimentally. It was shown that the influence of ammonia on the retention varied significantly depending on the solute's nature. For example, the influence is great for  $C_{22}$  *n*-alkane and it is small for phenol. Taking into account the results obtained by various researchers it makes sense to express an opinion on the expediency of development of gas chromatography operated under the conditions of acidic–basic chromatography. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Carrier gas; Ammonia

### 1. Introduction

Chemical factor has been successfully used in gas chromatography for a long time (see, e.g., Ref. [1]). It allows realization of highly selective separation. Hence, the development of this direction is of great interest. Recently we suggested acidic–basic chromatography [2,3]. Acidic–basic chromatography is a variant of gas chromatography where acidic (e.g.,  $CO_2$ ) or basic (e.g.,  $NH_3$ ) gases are used as mobile phases. As a result, partition constants for iogenic solutes (e.g., acids or bases) change in the system (stationary phase)–(gas phase). It stands to reason that small variations in retention are observed for basic solutes with acidic carrier gas (e.g.,  $CO_2$ ) or for acidic solutes with basic carrier gas (for example,  $NH_3$ ). Theoretical approach and experimental data are in good agreement.

But in analytical practice, neutral solutes are analyzed along with acidic or basic solutes. Hence, the purpose of the present short communication was to consider the influence of basic humid carrier gas ( $NH_3$ ) on the retention of neutral solutes on a capillary column coated with polar stationary liquid phase (polyethylene glycol).

The chromatographic variant allows operation of the separation process by changing carrier gas (or its composition). Thus, the role of the mobile phase in the discussed variant of gas chromatography is similar to that in liquid chromatography, although the effects observed for mobile phase in gas chromatography are much smaller.

### 2. Experimental

Experiments were made on a modified LKhM-8MD gas chromatograph (model 5, Khromatograf, Moscow, Russia) equipped with a flame ionization

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Table 1  
Some physical properties of carrier gases [5–7]

Carrier gas	Boiling point (°C)	Diffusion coefficient, relative to nitrogen (0.1 MPa, 20°C)	Viscosity, relative to nitrogen (0.1 MPa, 20°C)
Hydrogen	–252.9	7.53	0.498
Helium	–268.9	9.53	1.097
Nitrogen	–195.8	1.00	1.000
Ammonia	–33.4	1.15	0.560

detector (FID). The chromatographic separations were performed on a fused-silica capillary column 30 m length  $\times$  0.25 mm I.D. coated with polyethylene glycol, film thickness 0.25  $\mu$ m; other capillary columns used are listed in the next section. Carrier gases were: pure helium, pure ammonia and helium contained water vapors. The split ratio was 1:20–1:100. Note that ammonia used contained 0.6% H<sub>2</sub>O. Note also that the column we used with ammonia was stable for not less than 3–4 months. The sorbate retention time was measured using a modified I-02 integrator (factory ‘Mikroprovod’, Kishinev) with a resolution of 0.1 s. The same accuracy of measurements was demonstrated in Ref. [4].

Retention of CH<sub>4</sub> was considered as a hold-up time. Taking into account the high operation temperature (185°C), the sorption effects of CH<sub>4</sub> can be neglected.

Each retention value was defined as the mean from

five experiments. In this case the mean-square error did not exceed 0.2–05%.

### 3. Results and discussion

Note, that ammonia is characterized by a number of advantages in comparison with other carrier gases (see Table 1). When considering the data presented in Table 1 the following considerations of ammonia can be formulated: (1) ammonia has a lower viscosity than helium; (2) the capacity of a cylinder of liquid ammonia is much greater than that with helium; (3) ammonia can be considered to be both carrier gas and a source for the nitrogen–hydrogen mixture for flame ionization detection, since on a catalyst NH<sub>3</sub> decomposes quantitatively for H<sub>2</sub> and N<sub>2</sub> at relatively low temperatures (see Ref. [8]).

Note that most studies with ammonia as carrier gas were performed using flame ionization detection. There was no evidence of the negative influence of ammonia on the detection of this type.

Earlier we suggested simultaneous use of ammonia as carrier gas and a source of hydrogen for flame formation in flame ionization detection [8]; in that case, ammonia was passed through a small reactor filled with a catalyst for ammonia synthesis at 450–550°C. The reactor was placed directly before the detector. The mixture (N<sub>2</sub>+3H<sub>2</sub>O) was formed as a result of ammonia decomposition and it caused the formation of flame in FID.

Table 2 presents the data on relative retention

Table 2  
Influence of carrier gas on relative retention of solutes<sup>a</sup>

Solute	Helium		Ammonia	
	Retention factor, <i>k</i>	Relative retention, $\alpha$	Retention factor, <i>k</i>	Relative retention, $\alpha$
<i>n</i> -C <sub>20</sub>	1.257	0.887	1.206	0.863
Butylbenzoate	1.257	0.887	1.212	0.864
Benzyl alcohol (standard)	1.417	1.000	1.396	1.000
<i>n</i> -C <sub>21</sub>	1.746	1.232	1.672	1.197
Diphenyl ether	2.074	1.464	1.992	1.436
Phenol	2.139	1.508	2.131	1.524
<i>n</i> -C <sub>22</sub>	2.421	1.708	2.324	1.663

<sup>a</sup> Experimental conditions: column 30 m  $\times$  0.25 mm I.D. coated with polyethylene glycol (*d<sub>f</sub>* = 0.5  $\mu$ m), oven temperature 195°C.

(retention factor and relative retention time) for neutral solutes with two carrier gases (helium and ammonia). As follows from Table 2, when helium is changed for ammonia the variation of retention factor is not great, but it is pronounced for all compounds except phenol.

A diagram of  $\Delta k = k(\text{He}) - k(\text{NH}_3)$  dependence on the nature of compounds to be analyzed is shown in Fig. 1. When helium replaced ammonia, the least variation in retention factor (see Table 2) was observed for phenol:  $\Delta k = 0.008$  (0.37%). Then, following in the order of increasing benzyl alcohol,  $\Delta k = 0.21$  (1.5%), and with the most variation,  $\Delta k = 0.097$  (6.9%) was obtained for *n*-C<sub>22</sub> alkane. The question arises whether the observed variations in retention factor are significant or they should be considered to be negligible. To answer the question we compared variation in retention times  $t_R$  (value to be measured) but not in retention factor  $k$  (value to be calculated), because the former values are measured at the experiments. With the above-mentioned  $\Delta k$  values we calculated retention times  $t_R$  at a carrier gas velocity of 30 cm/s (hold up time  $t_m$ , 100 s). With the known expression  $t_R = t_m(k + 1)$  (see, e.g., Ref. [9]), the following equation for retention times with different carrier gases can be obtained:  $\Delta t_R = t_m \Delta k$ . The following variation in retention times can be obtained (when helium is replaced for ammonia): for phenol  $\Delta t_R = 0.8$  s, for benzyl alcohol  $\Delta t_R = 2.1$  s, for *n*-C<sub>22</sub>  $\Delta t_R = 9.7$ . Since the solute

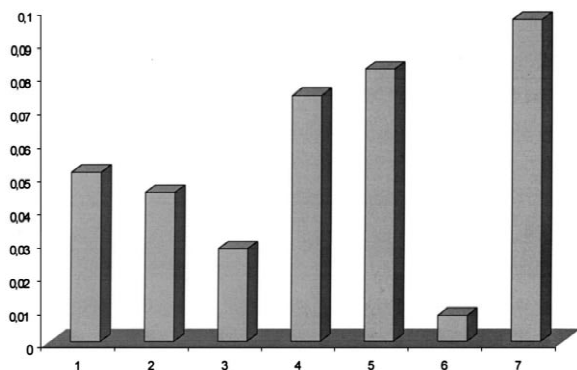


Fig. 1. Diagram of retention factor variation  $\Delta k = k(\text{He}) - k(\text{NH}_3)$  for organic compounds to be analyzed. Solutes: (1) *n*-C<sub>20</sub>; (2) butylbenzoate; (3) benzyl alcohol; (4) *n*-C<sub>21</sub>; (5) diphenyl ether; (6) phenol, (7) *n*-C<sub>22</sub>.

retention time was measured with a resolution of 0.1 s, the variation in retention times for all compounds due to the replacement of carrier gas is significant, and for six compounds (out of the seven compounds under investigation) it is in 20–90 times greater than experimental error. This allowed us consider  $\Delta k$  to be significant.

The variation in retention is also observed for other retention values (for example, for retention index). The variation of retention index for some compounds is more pronounced. For example,  $\Delta I = I(\text{He}) - I(\text{NH}_3)$  is  $\Delta I = -8.32$  for benzyl alcohol, but that for phenol is  $\Delta I = -11.56$ . Note that according to Ref. [8], reproducibility of retention index is rather great (mean standard deviation  $S = 0.03$  iu, with the confidence interval  $\pm 0.07$  iu). Let us assume that in routine measurements this value is not more than 0.3 iu (i.e., 10 times as great as was established in Ref. [4]). Even at such overestimation of measurement error, the established variations in retention index  $\Delta I$  for the two mentioned neutral compounds are 28–39 times greater than the error. Hence, when one carrier gas is changed for another the obtained variation in retention values is of practical importance, e.g., for separation of critical pairs.

Note that minimum HETP value with ammonia is less than that with helium. Thus, in some cases ammonia as a carrier gas is preferable to helium (e.g., when analytical determination is in target).

The obtained result can be predicted theoretically. As known (see, for example, Ref. [9]), the dependence of height equivalent to a theoretical plate (HETP,  $H$ ) on carrier gas velocity ( $u$ ) is described by the Golay's equation:

$$H = B/u + (C_g + C_L)u \quad (1)$$

where  $B = 2D_g$  is the longitudinal diffusion term;  $C_g$  and  $C_L$  are the coefficients of the resistance to mass transfer in the mobile and stationary phases, respectively.

For a column coated with a thick film of SLP, the coefficient of the resistance to mass transfer in the stationary phase is greater than that in the gas phase, i.e.:

$$C_g \ll C_L \quad (2)$$

Table 3  
Influence of ammonia as a carrier gas on the retention of acidic, basic and neutral solutes (in comparison with helium)

N	Solutes	The changes in retention when helium is changed for ammonia	Positive effect
1	Acidic compounds (e.g., organic acids)	Retention values for acids are increased considerably [2,3].	Selectivity improves essentially. This is an additional characteristic which is useful for identification and group separation.
2	Basic compounds (e.g., primary amines)	Retention values for amines are decreased considerably, chromatographic zones are more symmetric (even with acidic centers in chromatographic system) [10–13]	It is possible to separate basic solutes with conventional capillary columns.
3	Neutral solutes	Retention values are not changed considerably, but in capillary chromatography the changes in selectivity (and efficiency) can be significant	It is possible to improve the separation of neutral compounds.

In this case the following expression is valid:

$$H_{\min} = 2\sqrt{B \cdot C_L} \quad (3)$$

Hence,

$$\lambda = \frac{H_{\min}(\text{He})}{H_{\min}(\text{NH}_3)} = \sqrt{\frac{B(\text{He})}{B(\text{NH}_3)}} = \sqrt{\frac{D_g(\text{He})}{D_g(\text{NH}_3)}} \quad (4)$$

The data on diffusion of volatile compounds in He and  $\text{NH}_3$  show that  $D_g(\text{He}) > D_g(\text{NH}_3)$ . With this ratio  $\lambda > 1$ , i.e., minimum HETP values for solutes with  $\text{NH}_3$  are smaller than those with He.

The results obtained allow estimation of organic solutes of general groups of the compounds to be analyzed (see Table 3). The practical recommendations listed in Table 3 allow conclusion on significant variation in retention (and, therefore, in selectivity). Taking into account the studies by Abdel-Rehim and co-workers [10–13] and our studies [2,3] it makes sense to use acidic–basic chromatography more widely and develop a special gas chromatograph with ammonia as carrier gas as to make practical application of ammonia and some non-standard carrier gases more simple for chromatographers.

#### 4. Conclusion

The performed theoretical and experimental

studies count in favor of the wider application of ammonia as a carrier gas in practical chromatography.

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