Gas Chromatography under the Column Outlet Pressure Higher than Atmospheric

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The effects of column outlet pressures on the HETP *vs.* carrier gas velocity curves are discussed on the basis of KOS theory. It is shown that when a column is operated at a constant outlet pressure higher than atmospheric the minimum of H-$\bar{u}$ curve shifts towards lower HETP and $\bar{u}$ values, and on the contrary the operation at reduced outlet pressure results in the shift of the minimum towards higher HETP and $\bar{u}$ values. The separation factor and number of theoretical plates obtained by a column operated at the outlet pressure of 4.0 atm are superior by *ca.* 10% to those obtained by normal gas chromatography.

Gas chromatographic columns are almost always operated under the constant outlet pressure of atmospheric. On the one hand, Haruki[1] investigated the gas chromatography under reduced pressure and concluded that the reduced pressure operation offered no advantage over normal atmospheric pressure operation. Recently, Hatch and Parrish[2] using capillary columns reported that at the optimum flow velocity, the reduced pressure operation produced efficiencies *ca.* 30% lower than those of normal gas chromatographic operation. On the other hand, Halasz *et al.*[3] and Novak and Bocek[4] reported that the column operation under the outlet pressure higher than atmospheric resulted in an improved column efficiencies. The problems were discussed theoretically on the basis of the van Deemter equation.[5,6] However, the equation being derived from the assumption of a uniform mobile phase velocity,[7] the application of the theory to gas chromatography requires an essential revision especially with respect to the pressure drop along the column.

In our previous papers,[8,9] a new equation for HETP was derived from the kinetic viewpoint, in which the pressure dependence of the diffusion coefficient in gas phase and the non-linear carrier gas velocity distribution along the column were dealt with mathematically. The validity of KOS theory[9] was confirmed experimentally in the study of the dependencies of HETP on carrier gas flow rate[9] and column length.[10] The present work aims at obtaining a clearer understanding of the effects of column outlet pressure higher than atmospheric on the HETP. The column efficiencies of the reduced pressure gas chromatography are also discussed theoretically.

Theoretical

According to KOS theory, the HETP is given by

$$H = \frac{l}{n} = \frac{9D^*l}{2w} \times \frac{(p_i^4 - p_o^4)}{(p_i^3 - p_o^3)^2} + \frac{3wF_s^2\beta^2}{2\alpha FK^2l} \times \frac{(p_i^2 - p_o^2)^2}{(p_i^3 - p_o^3)}, \quad (1)$$

where n the number of theoretical plates of a column of length l, D^* the diffusion constant under unit pressure, w permeability coefficient, p_i and p_o the inlet and outlet pressures, F and F_s the volume fractions occupied by the mobile and stationary phases, K the distribution coefficient (the ratio of concentration in the mobile phase to that in the stationary phase), α the rate constant of dissolution and β is given by

$$\frac{1}{\beta} = \frac{t_R}{t_0} = 1 + \frac{F_s}{KF}, \quad (2)$$

where t_R is the retention time of a given component and t_0 is that of air peak. The latter corresponds to the passing time of carrier gas through the whole column, and is the function of p_i and p_o,[11] namely,

$$t_0 = \frac{4l^2(p_i^3 - p_o^3)}{3w(p_i^2 - p_o^2)^2} \quad (3)$$

The average carrier gas velocity $\bar{u}$, is given by

$$\bar{u} = \frac{l}{t_0}. \quad (4)$$

The carrier gas flow-rate v, is given by the famous Darcy equation:

$$v = qu_op_oF = \frac{wqF(p_i^2 - p_o^2)}{2l}, \quad (5)$$

where q is the proportionality factor and u_o is the outlet linear velocity.

Equation 1 can be rearranged into

$$y = a + bx, \quad (6)$$

where

$$y = \frac{(p_i^3 - p_o^3)^2}{n(p_i^4 - p_o^4)} \quad (7)$$

$$x = \frac{(p_i^2 - p_o^2)(p_i^3 - p_o^3)}{(p_i^2 + p_o^2)} \quad (8)$$

$$a = \frac{9D^*}{2w} \quad (9)$$

and

$$b = \frac{3wF_s^2\beta^2}{2\alpha FK^2l^2}. \quad (10)$$

Experimental

The measurements were carried out with a Hitachi Model 063 gas chromatograph equipped with a Hitachi 056 recorder, thermal conductivity detertor being used. The sample cell outlet was connected to a pressure gauge and a needle valve, so that the column outlet pressure is controlled, the arrangement being almost the same as reported by Novak and Bocek.[4] Helium was used as carrier gas. The flow-rate was measured with a soap-film meter and corrected for the water vapor pressure. The stainless steel column of 1 m by 0.3 cm i.d. was packed with 25% dinonyl phthalate on 80—100 mesh Shimalite BT. The packed column was preconditioned for 10 h at 130 °C under an appropriate helium flow. The measurements of HETP were carried out at

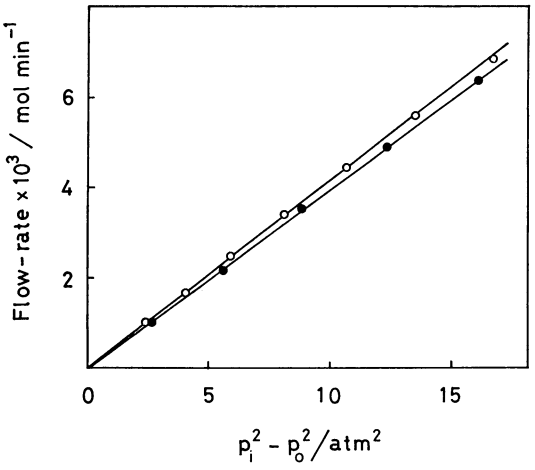

Fig. 1. Helium flow-rate plotted against ($p_i^2-p_o^2$) at the constant outlet pressures: (○) p_o 1.0 atm, p_i 1.8—4.2 atm; (●) p_o 3.0 atm, p_i 3.4—5.0 atm. Column: 1 m by 0.3 cm i.d., 25% DNP on Shimalite BT, 74.0 °C.

the column temperature of 74.0 °C, employing benzene as a solute. The sample sizes of 0.8, 0.6, 0.4, and 0.2 μl were injected twice at each level. The numbers of theoretical plates were calculated from the formula[12]

$$n = 5.55(t_R/W_{1/2})^2, \quad (11)$$

where t_R and $W_{1/2}$ designate the peak maximum distance from the start line and the peak width at the half peak height, respectively, and extraporated to zero charge of sample amount. Peak asymmetry was estimated from the skewness which is defined as the ratio of the slopes of tangents at the inflection points of both sides of the peak.[13] The mean carrier gas velocity was evaluated from the retention time of air peak. The effect of column outlet pressure on the separation of adjacent peaks 1 and 2 was estimated from the value:[12]

$$R = \frac{2(t_{R-2}-t_{R-1})}{W_1+W_2} \quad (12)$$

Results and Discussion

In Fig. 1, the carrier gas flow-rate was plotted against ($p_i^2-p_o^2$) for the column operations under atmospheric and increased outlet pressures. Both lines showed good linearity as expected from Eq. 5, only a slight difference in the slopes being found. The dependence of passing time of air peak on the pressure differences was shown in Fig. 2. The relationship between $\bar{u}$ and pressure drop given by Eqs. 3 and 4 can be now written as

$$\bar{u} = \frac{4.8(p_i^2-p_o^2)^2}{p_i^3-p_o^3}, \quad (13)$$

where $\bar{u}$ is expressed in cm s^{-1} and the coefficient 4.8 is evaluated from dividing the column length of 100 cm by the slope of plot in Fig. 2.

The effects of column outlet pressure on column efficiency were illustrated in Figs. 3 and 4. In Fig. 3, the validity of Eq. 6 was confirmed, the linear regression equation being determined as

$$y = 1.73\times10^{-3} + 2.29\times10^{-4}\,x$$

for atmospheric outlet pressure operation and

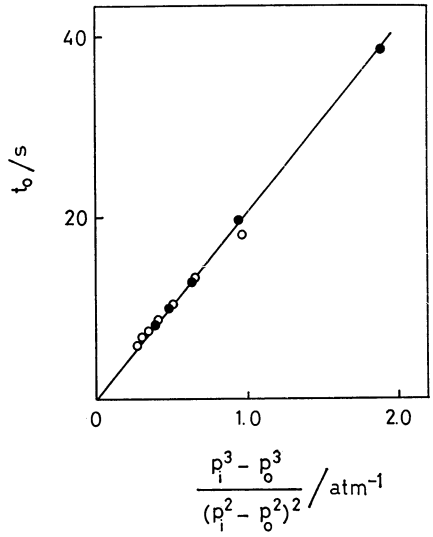

Fig. 2. Dependence of passing time of carrier gas on the inlet and outlet pressures. The open and closed circles have the same meanings as in Fig. 1.

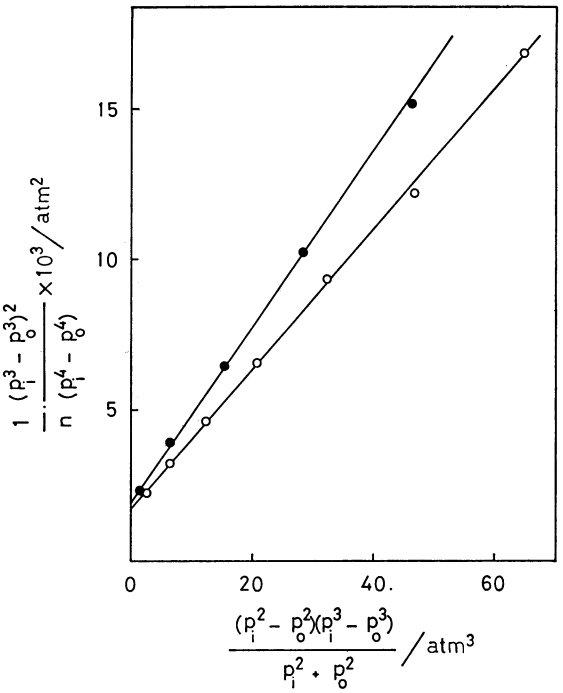

Fig. 3. Effect of column inlet and outlet pressures on HETP (*cf.* Eq. 6). The symbols on each line are the same as in Fig. 1.

$$y = 1.98\times10^{-3} + 2.88\times10^{-4}\,x$$

for the elevated outlet pressure of 3.0 atm. The 95% confidence limits of the expected value of y when $x=0$ were $(1.73\pm0.29)\times10^{-3}$ and $(1.98\pm0.22)\times10^{-3}$, respectively. No significant difference was found between the intercepts at the significance level of 5% (t-test). On the other hand, the regression coefficients with 95% confidence limits being $(2.29\pm0.08_6)\times10^{-4}$ and $(2.88\pm0.08_7)\times10^{-4}$, respectively, the difference between the slopes was highly significant. The β value and hence the K value being constant and independent of pressure drop as shown in Table 1, the variation in the slopes of lines may be due to the change

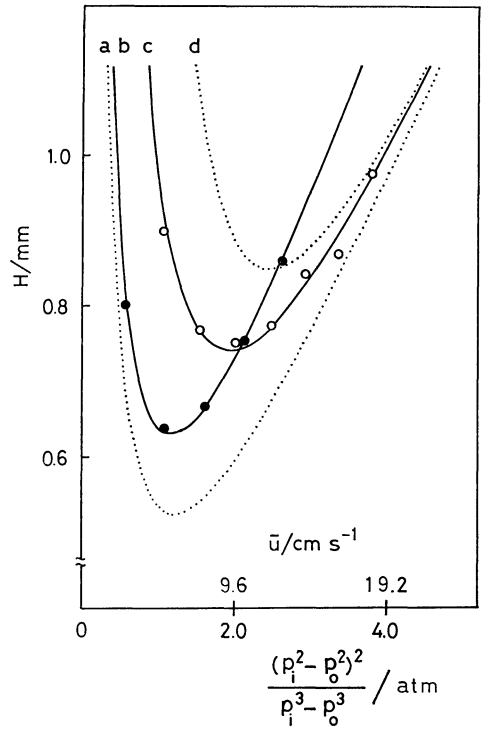

Fig. 4. Dependence of H-$\bar{u}$ curves on the column inlet and outlet pressures. Solid lines b and c are experimentally obtained H-$\bar{u}$ curves. The symbols have the same meanings as in Fig. 1. Dotted lines denote theoretically obtained H-$\bar{u}$ curves by the combination of Eqs. 13 and 14, inserting the values: (a) p_o 3.0 atm, p_i 3.3—6.6 atm; (d) p_o 0.1 atm, p_i 1.5—4.4 atm.

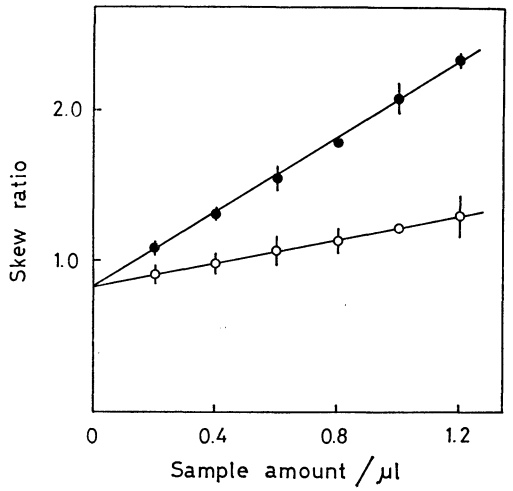

Fig. 5. Effects of pressure drop and sample amount on the skew ratio of benzene peak. The column inlet and outlet pressures are: (○) p_o 1.0 atm, p_i 2.4 atm; (●) p_o 4.0 atm, p_i 4.8 atm. Other conditions are the same as in Fig. 1. The vertical line on each plot denotes 95% confidence limits.

Table 1. Constancy of β value

Pressure/atm	$1/\beta = t_R/t_0 = 1 + F_s/KF$
$p_o = 1.0$	
$p_i = 1.8-4.2$	$17.0_8 \pm 0.1_2$ $(n=7)$
$p_o = 3.0$	
$p_i = 3.4-5.0$	$16.9_7 \pm 0.3_8$ $(n=5)$

in the rate constant α of dissolution caused by the pressure change.

Inserting the numerical values obtained from the atmospheric outlet pressure operation into Eq. 1, the column length being 1000 mm, one derives

$$H/\text{mm} = \frac{1.73(p_i^4 - p_o^4)}{(p_i^3 - p_o^3)^2} + \frac{0.23(p_i^2 - p_o^2)^2}{p_i^3 - p_o^3}. \quad (14)$$

The so-called H-$\bar{u}$ curves were shown in Fig. 4, in which the solid lines on the plots were obtained from the regression equations. The dotted lines were illustrated by combining the calculated values of Eqs. 13 and 14. When Eq. 14 holds for the operation at column outlet pressure of 3 atm, curve a in Fig. 4 is given. The shift of the minimum towards lower $\bar{u}$ and H values is obviously found in the theoretically predicted H-$\bar{u}$ curve and experimentally obtained one, although the curves do not coincide completely each other as discussed previously. On the other hand, in the case of gas chromatography under the reduced column outlet pressure of 0.1 atm, the shift of the minimum towards higher $\bar{u}$ and H values is predicted as shown by curve d in Fig. 4. This tendency was already experimentally observed by Hatch and Parrish.[2]

The column operation under the increased pressure resulted in peaks with leading shape, the skewness decreasing with decreasing sample amount as shown in Fig. 5. It is interesting to compare the results with that reported by Haruki,[1] who observed that the gas chromatography under the reduced pressure gave the peaks with trailing shape with decreasing inlet and outlet pressures.

An attempt was made to find the effect of the increased column pressure on the resolution. A 0.6 μl portion of a mixture containing 0.3 μl benzene, 0.1 μl ethylbenzene, 0.1 μl of *m*- and *o*-xylenes was chromatographed at 94.4 °C under the various outlet and inlet pressures, namely, one combination is $p_o = 1.0$ and $p_i = 1.8—3.6$ atm and the other is $p_o = 4.0$ and $p_i = 4.4—4.5$ atm. The resolution of ethylbenzene from *m*-xylene and the number of theoretical plates for *o*-xylene were calculated. At the optimum flow-rate, the elevated pressure operation resulting in the peaks with longer retention time produced both the column efficiency and the resolution *ca.* 10% higher than those of normal operation.

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