*Journal of Chromatography*, 439 (1988) 151–157
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 20 235

# EFFECT OF SUPPRESSION EFFICIENCY ON SENSITIVITY IN ION CHROMATOGRAPHY

Z. W. TIAN*, R. Z. HU, H. S. LIN and W. L. HU
*Department of Chemistry, Xiamen University, Xiamen (China)*

---

## SUMMARY

The ionization equilibrium is calculated for a suppressor effluent containing remnant ions, *e.g.*, $Na^+$ in the case of anion analysis, due to imperfect suppression. It is shown that: (1) The remnant ion not only affects the background specific conductivity but also seriously depresses the peak height of samples of low concentration. The practical peak height may be much less than the ideal peak height. For $pK_{HA} > 11$, the practical peak height may be negative. (2) The sensitivity, linearity and reproducibility of conductivity detection for low concentration samples are seriously affected by the remnant ion, *i.e.*, by the conversion efficiency of the suppressor. (3) The ionization of the weak acid derived from the eluent is depressed by the common ion effect of the strong acid derived from the sample. The peak height depression depends on the ionization constant, $K_{HA}$. However, in the case of $C_{Na} > 0$, the buffer effect of HA compensates the effect of remnant $Na^+$. Therefore it is appropriate to use an eluent with $pK_{HA}$ in the range 6–8.

---

## INTRODUCTION

In ion chromatography the signal-to-noise ratio can be increased as follows: first, the baseline and the noise level can be drastically lowered by the use of a slightly ionized electrolyte as the eluent; secondly the signal can be increased several times by converting the sample species into a strongly ionized and highly conductive electrolyte[1]. This "suppression" can be ideal if the following requirements are fulfilled: (1) the conversion efficiency is perfect, for example, the remnant sodium ion concentration, $C_{Na}$, is zero when a sodium salt is used as the eluent; (2) the eluent is converted into an electrolyte with very low conductivity.

Since the above mentioned requirements cannot be fulfilled in practice, the reduction in sensitivity may be very serious. This problem will be illustrated and discussed in this paper. For convenience, the following system is taken as an example: (1) the anion to be determined is chloride or another anion of a strong acid, the mobility of which equals that of chloride; (2) the eluent is an aqueous solution of NaA, where the mobility of the anion A equals that of bicarbonate ion.

0021-9673/88/$03.50

## IONIZATION EQUILLIBRIUM IN THE SUPPRESSOR EFFLUENT

For the suppressor effluent, the following equations can be formulated

$$C_H C_A / C_{HA} = K_{HA} \tag{1}$$

$$C_H C_{OH} = K_W \tag{2}$$

$$C_H + C_{Na} - C_A - C_{OH} - C_S = 0 \tag{3}$$

$$C_{HA} + C_A = C_e - C_S \tag{4}$$

where $K$ is the ionization constant, $C$ is the concentration and the subscripts H, A, Na, OH, HA, S, W and e refer to $H^+$, $A^-$, $Na^+$, $OH^-$, HA, sample, water and eluent respectively.

For given values of the parameters $K_{HA}$, $K_W$, $C_e$, $C_S$ and $C_{Na}$, the unknown functions $C_H$, $C_A$, $C_{OH}$ and $C_{HA}$ can be determined from the above simultaneous equations. Thus, a cubic equation can be obtained for $C_H$:

$$C_H^3 + C_H^2(K_{HA} + C_{Na} - C_S) - C_H(K_{HA}C_e - K_{HA}C_{Na} + K_W) - K_W K_{HA} = 0 \tag{5}$$

Since the coefficient of the first term is positive and those of the third and fourth terms are negative, there should be one, and only one, positive root for this cubic equation. Hence, $C_H$ can be determined analyticaly or numerically.

In turn, $C_A$, $C_{OH}$ and $C_{HA}$ can be calculated using the following equations:

$$C_A = K_{HA}(C_e - C_S)/(C_H + K_{HA}) \tag{6}$$

$$C_{OH} = K_W / C_H \tag{7}$$

$$C_{HA} = C_e - C_S - C_A \tag{8}$$

The specific conductivity can be calculated as follows

$$k = (\lambda_H C_H + \lambda_{OH} C_{OH} + \lambda_{Na} C_{Na} + \lambda_S C_S + \lambda_A C_A)/1000 \tag{9}$$

where $\lambda$ is the limiting equivalent ionic conductance of the ion.

The numerical calculations were carried out by a computer program.

The ideal peak height is proportional to the concentration of the sample, $C_S$, and can be simply calculated by the following equation:

$$h_{ideal} = (\lambda_H + \lambda_S)C_S/1000 \tag{10}$$

The practical peak height, $(k)_{C_S} - (k)_{C_S=0}$, (see eqn. 9) is less than the ideal peak height. A parameter, the peak height coefficient $H_C$, is introduced and defined as follows:

$$H_C = [(k)_{C_S} - (k)_{C_S=0}]/h_{ideal} \tag{11}$$

The deviation of $H_C$ from 1 is a measure of the effect of $C_{Na}$ and $K_{HA}$ on ion chromatography sensitivity.

## EFFECT OF WEAK ACID IONIZATION (ASSUMING $C_{Na} = 0$)

The dependencies of the peak height and height coefficient on the sample concentration for different values of p$K$ are shown in Fig. 1a and b. For greater p$K$ values, *e.g.* 10 or 12, the height coefficients are almost equal to 1, the peak heights, approach their ideal values and the linearity of peak height *vs.* sample concentration is good. However, for p$K$ values less than 8, the values and the linearity deviate from the ideal case, especially for low sample concentrations. The reason is that the background conductivity is proportional to the extent of ionization of the weak acid HA and this ionization is suppressed by the common hydrogen ion effect of the strong acid derived from the sample. The smaller the p$K_{HA}$ value, the greater is the common ion effect on the extent of ionization.

## EFFECT OF REMNANT $Na^+$ FOR p$K_{HA}$ VALUES GREATER THAN 9

Peak height *vs.* sample concentration curves for different values of remnant sodium ion concentrations are shown in Fig. 2a and b. In the case of $C_S > C_{Na}$, the slopes approach the ideal values, but when $C_S < C_{Na}$ the slopes are much smaller and the peak height coefficients are less than 0.07 for p$K_{HA} = 10$. This means that the sensitivity for samples of low concentrations is seriously reduced to 1/14 of that of the ideal case if the concentration of remnant $Na^+$ exceeds that of the sample. For p$K_{HA} = 12$, the deviation is still greater, and the peak heights and height coefficients are both negative (see Fig. 3). The presence of remnant $Na^+$ can be considered as the addition of sodium hydroxide to the perfectly suppressed system HA. Since the p$K_{HA}$ value is high, the hydrolysis of NaA will take place and the concentration ratio NaA: NaOH equals $K_{HA}C_e/K_W$. The curves in Figs. 2a and 3a are similar to the titration curve of the above-mentioned system with strong acid, *e.g.*, hydrochloric acid.

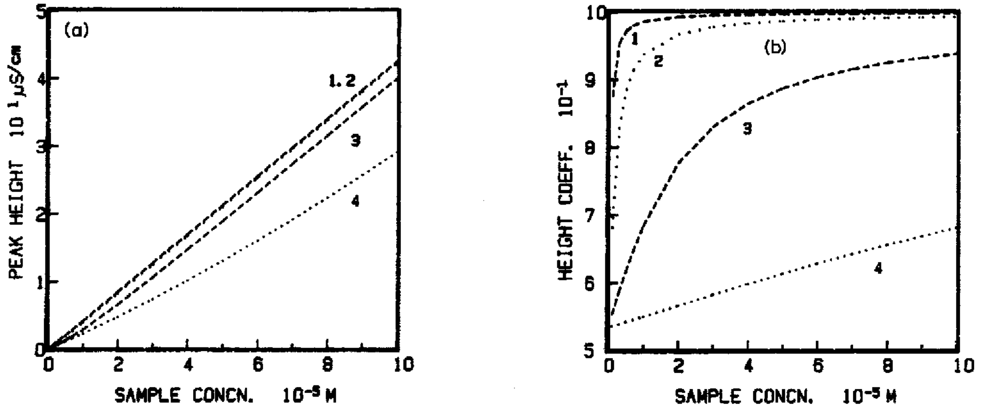


Fig. 1. Dependences of the peak height (a) and the height coefficient (b) on the sample concentration for $C_{Na} = 0$. Values of p$K_{HA}$: (1) 12; (2) 10; (3) 8; (4) 6.

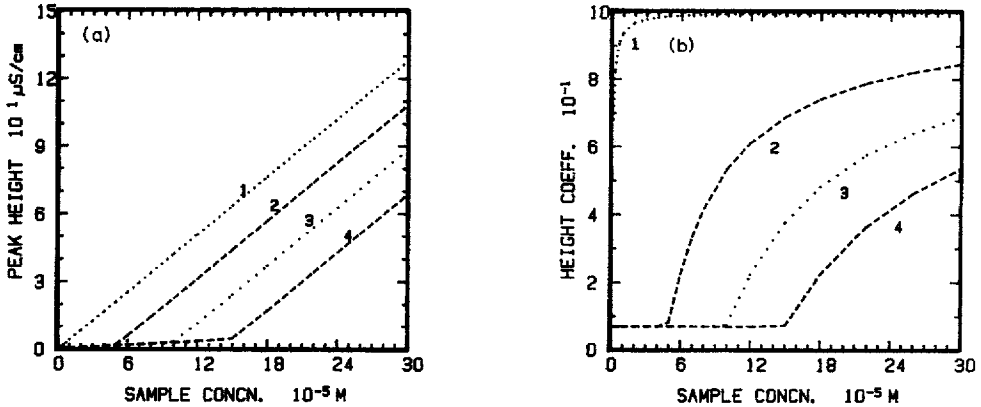


Fig. 2. Dependences as in Fig. 1, but at $pK_{HA}$ = 10 and $C_{Na}/\mu M$ = (1) 0; (2) 50, (3) 100 and (4) 150.

## EFFECT OF REMNANT $Na^+$ FOR $pK_{HA}$ VALUES LESS THAN 8

Since carbonate solution is an useful eluent, the $pK_{HA}$ value of carbonic acid (6.36) is taken as an example for calculation. The results for $pK = 6.36$ are shown in Figs. 4–6. Since the ionization of HA cannot be neglected in the case of $pK_{HA} < 8$, the relationships are more complicated than those for $pK_{HA} > 9$. It is of interest in Fig. 5a that on increasing the sodium ion concentration the conductivities exhibit minima. These curves are similar to the titration curve of HA + HCl or of pure HA solution with sodium hydroxide. The conductivity decreases due to the neutralization of hydrochloric acid (if any) by sodium hydroxide. Then the neutralization of the weak acid HA occurs and the conductivity exhibits a minimum at the equivalence point of neutralization. Therefore, the baseline conductivity cannot always be taken as a criterion of suppression efficiency. On the other hand, the peak heights and height coefficients decrease monotonously with increasing sodium ion concentration (see Fig. 5b).

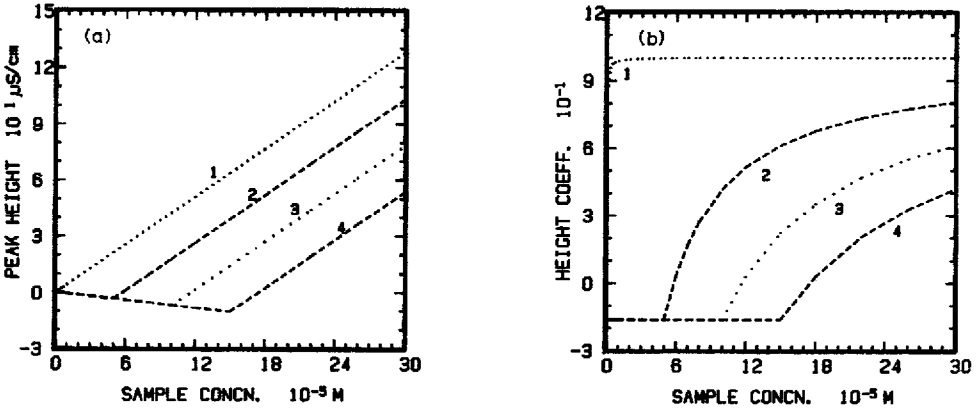


Fig. 3. Dependences as in Fig. 1, but at $pK_{HA}$ = 12 and $C_{Na}/\mu M$ = (1) 0, (2) 50, (3) 100 and (4) 150.

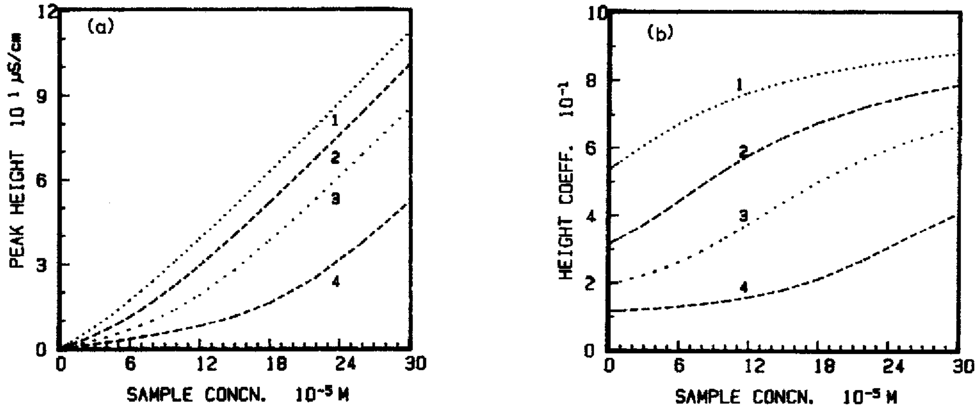


Fig. 4. Dependences as in Fig. 1, but at $pK_{HA}$ = 6.36 and $C_{Na}/\mu M$ = (1) 0, (2) 50, (3) 100 and (4) 150 in (a), (1) 0, (2) 50, (3) 100 and (4) 200 in (b).

The experimental results illustrating the relationship between the peak height and remnant sodium ion concentration are shown in Fig. 6, which is in accord with Fig. 5a and b. The apparatus and procedure used has been described[2], but the electric current for supression was intentionally reduced in order to increase the remnant sodium ion concentration. The sample concentration is calibrated to the real concentration of the sample in the conductivity cell.

## DISCUSSION

The composite effects of sample concentration, remnant sodium ion concentration and $pK_{HA}$ value on the height coefficients are shown in Fig. 7. The deviation of the height coefficient from the ideal value of 1 can be explained by the shift in the following ionization equilibrium:

$$HA \rightleftarrows H^+ + A^- \tag{12}$$

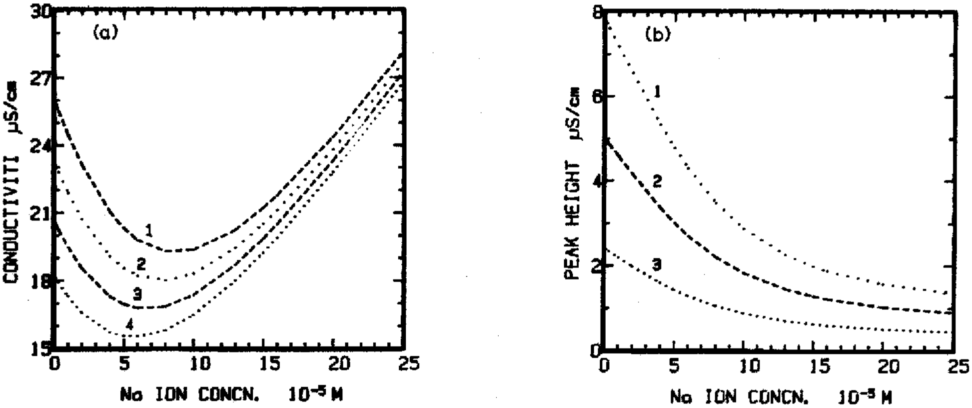
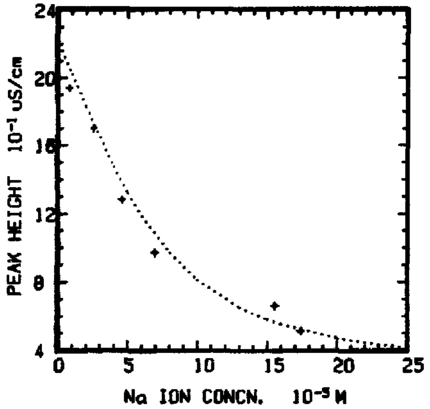


Fig. 5. Dependences of the specific conductivity (a) and peak height (b) on the sodium ion concentration for $pK_{HA}$ = 6.36 and $C_S/\mu M$ = (1) 30; (2) 20; (3) 10, and (4) 0 in (a), (1) 30, (2) 20 and (3) 10 in (b).



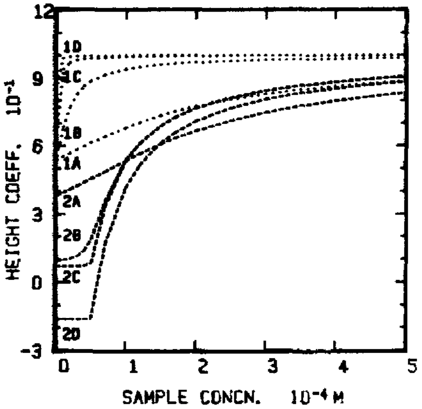


Fig. 6. A comparison of experimental results (+) with the theoretical curve of peak height *vs.* sodium ion concentration. Eluent: 0.005 *M* sodium carbonate. Sample: 9.3 $\mu M$ sodium chloride.

Fig. 7. Dependence of the height coefficient on the sample concentration for different values of $pK_{HA}$ and $C_{Na}$: (1A) $pK = 6$, $C_{Na} = 0$; (2A) $pK = 6$, $C_{Na} = 50$; (1B) $pK = 8$, $C_{Na} = 0$; (2B) $pK = 8$, $C_{Na} = 50$, (1C) $pK = 10$, $C_{Na} = 0$; (2C) $pK = 10$, $C_{Na} = 50$, (1D) $pK = 12$, $C_{Na} = 0$; (2D) $pK = 12$, $C_{Na} = 50$ $\mu M$.

(1) In the case of $C_{Na} = 0$, the deviation increases with decreasing $pK_{HA}$ value because of the common hydrogen ion effect. Since $C_{OH}$ can be neglected, eqn. 9 can be simplified as follows:

$$(k)_{C_S} = [(\lambda_H + \lambda_S)C_S + (\lambda_H + \lambda_A)C_A]/1000 \qquad (13)$$

The background specific conductivity is

$$(k)_{C_S=0} = (\lambda_H + \lambda_A)C_A^0/1000 \qquad (14)$$

where $C_A^0$ is the concentration of $A^-$ in pure HA solution without sample. The peak height is given by:

$$h = (k)_{C_S} - (k)_{C_S=0} = [(\lambda_H + \lambda_A)C_S - (\lambda_H + \lambda_A)(C_A^0 - C_A)]/1000$$

$$= h_{\text{ideal}} - (\lambda_H + \lambda_A)(C_A^0 - C_A)/1000 \qquad (15)$$

The reduction in peak height is proportional to $(C_A^0 - C_A)$, which is determined by the shift of the ionization equilibrium 12 to the left and increases with decreasing $pK_{HA}$ value.

(2) In the case of $C_{Na} > 0$, the reduction in peak height is mainly due to the replacement of $H^+$ by $Na^+$. The reduction in hydrogen ion concentration causes the ionization equilibrium 12 to shift to the right which partly compensates the reduction in hydrogen ion concentration. Therefore, the deviation of the height coefficient decreases with decreasing $pK_{HA}$ value because of this buffer effect.

(3) The deviation decreases with increasing sample concentration, because of the increase in signal.

According to the above discussion, a $pK_{HA}$ value in the range 6–8 is appropriate.

After suppression, the remnant sodium ion concentration can be determined by analyzing the eluent solution or estimated from the background specific conductivity of the eluent solution. The background specific conductivity of the sodium hydroxide eluent after passing through a commercial micromembrane suppressor has been reported[3] to be 13 $\mu S$, which is equivalent to a concentration of 52 $\mu M$. On the other hand, the lower detection limit reported, which represents the sensitivity, is generally much smaller than the remnant ion concentration. Therefore the practical peak height will be smaller than the ideal peak height for samples with low concentrations. Since the peak height coefficient decreases from 1 ($C_S \gg C_{Na}$) to a low positive value or even a negative value in the case of $C_S < C_{Na}$, the proportionality of peak height to sample concentration is invalid unless $C_S \gg C_{Na}$. The estimation of the lower detection limit by extrapolation from the experimental data at high concentration may be incorrect because of the failure of this proportionality. In addition, the experimental reproducibility may be affected by the supression efficiency, because the peak height coefficient depends notably on the remnant ion concentration which changes with conversion efficiency.

## CONCLUSIONS

(1) The conversion of an eluent into a weakly ionized electrolyte is not perfect in a suppressor, and the remnant (sodium) ion concentration in the eluent solution after passing through the commercial suppressor is too high for analysis of low concentration samples.

(2) The remnant ion not only affects the background specific conductivity but also seriously depresses the peak height of samples, of low concentration. The practical peak height may be much less than the ideal peak height. For $pK_{HA} > 11$, the practical peak height may be negative.

(3) The sensitivity, linearity and reproducibility of conductivity detection of low concentration samples are seriously affected by the remnant ion, *i.e.*, by the conversion efficiency of the suppressor.

(4) The ionization of the weak acid derived from the eluent is depressed by the common ion effect of the strong acid derived from the sample. The peak height depression depends on the ionization constant, $K_{HA}$. However, in the case of $C_{Na} > 0$, the buffer effect of HA compensates the effect of remnant $Na^+$. Therefore, it is appropriate to use an eluent with $pK_{HA}$ in the range 6–8.

(5) It is necessary to improve the conversion efficiency of the commercial suppressor so that the remnant ion concentration can be further reduced.

## REFERENCES

1 C. A. Pohl and E. L. Johnson, *J. Chromatogr. Sci.*, 18 (1980) 442.
2 Z. W. Tian, R. Z. Hu, H. S. Lin and J. T. Wu, *J. Chromatogr.*, 439 (1988) 159.
3 G. O. Franklin, *Am. Lab. (Fairfield, Conn.)*, 17 (1985) 65.